Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
DOI: 10.1002/zaac.202000405
ARTICLE

A General Synthetic Route to NHC-Phosphinidenes: NHC-mediated Dehydrogenation of Primary Phosphines

Luis Werner,[a] Günther Horrer,[a] Michael Philipp,[a] Katharina Lubitz,[a] Maximilian W. Kuntze-Fechner,[a] and Udo Radius*[a]

Dedicated to Professor Dr. Peter Klüfers on the Occasion of his 70th Birthday

The dehydrocoupling of primary phosphines with *N*-heterocyclic carbenes (NHCs) to yield NHC-phosphinidenes is reported. The reaction of two equivalents of the NHCs Me_2Im (1,3-dimethylimidazolin-2-ylidene), Me_4Im (1,3,4,5-tetramethylimidazolin-2-ylidene), iPr_2Im (1,3-di-*iso*-propylimidazolin-2-ylidene) and Mes_2Im (2,4,6-trimethylphenylimidazolin-2-ylidene) with $PhPH_2$ and $MesPH_2$ led to the NHC stabilized phosphinidenes (NHC)PAr: (iPr_2Im)PPh (**1**), (Mes_2Im)PPh (**2**), (Me_4Im)PPh (**3**), (Mes_2Im)PMes (**4**), (Me_2Im)PMes (**5**), (Me_4Im)PMes (**6**) and (iPr_2Im)PMes (**7**). The reaction of $tBuPH_2$ with two equivalents of the NHCs afforded the corresponding NHC stabilized parent phosphinidenes (NHC)PH: (iPr_2Im)PH (**8**), (Mes_2Im)PH (**9**) and (Me_4Im)PH (**10**). Reaction of **1** with oxygen and sulfur led to isolation of iPr_2Im-$P(O)_2Ph$ (**11**) and iPr_2Im-$P(S)_2Ph$ (**12**), whereas the reaction with elemental selenium and tellurium gave (NHC)PPh cleavage with formation of (iPr_2Im)Se (**13**), iPr_2ImTe (**14**) and different *cyclo*-oligophosphines. Furthermore, the complexes [{(iPr_2Im)PPh}$W(CO)_5$] (**15**), [$Co(CO)_2$(NO){(iPr_2Im)PPh}] (**16**) and [(η^5-C_5Me_5)Co(η^2-C_2H_4){(iPr_2Im)PPh}] (**17**) have been prepared starting from **1** and a suitable transition metal complex precursor. The complexes **16** and **17** decompose in solution upon heating to *ca.* 80 °C to yield the NHC complexes [Co(iPr_2Im)$(CO)_2$(NO)] and [(η^5-C_5Me_5)Co(iPr_2Im)(η^2-C_2H_4)] with formation of *cyclo*-oligophosphines. The reaction of **1** with [$Ni(COD)_2$] afforded the diphosphene complex [Ni(iPr_2Im)$_2$(*trans*-PhP=PPh)] **18**.

Introduction

Phosphinidenes[1] represent a group of highly reactive, low-valent, six electron species, which can be made manageable by terminal coordination on either transition metal complexes or *Lewis*-bases.[2,3] In the early 1980s 7-phosphinonorbornadienes were found to be promising starting materials for the preparation of phosphinidenes in solution, yet their isolation turned out to be difficult. Coordination to [$M(CO)_5$] (M = group VI metal) complexes made 7-phosphino-norbornadienes isolable and moreover led to the discovery of the electrophilic terminal transition metal phosphinidene complex [$(OC)_5W$=PPh] by Matthey *et al.* These complexes with the general formula [$(OC)_5M$=PPh] are not isolable, but can be generated *in situ* for further reactions.[2a,4] All literature known metal carbonyl phosphinidene-complexes of the general formula [$(OC)_nM(PR)$] are unstable at room temperature except of [{($Dipp_2Im^{H/Me}$)C(Ph)}P]$Fe(CO)_4$ (Dipp = 2,6-di-*iso*-propylphenyl) published recently by Ghadwal and coworkers.[4c] First examples of nucleophilic transition metal phosphinidene complexes, the bent metallocene complexes [(η^5-$C_5H_5)_2$M=PMes*] (Mes* = 2,4,6-*t*BuC_6H_2; M = Mo, W) were presented by Lappert *et al.* in 1987.[5] These 18-electron phosphinidene complexes were synthesized using salt metathesis of lithium metallocene hydrides [{(η^5-$C_5H_5)_2$MHLi}$_4$] with dichlorophosphine Mes*PCl_2 under elimination of LiCl. Salt metathesis is the most common route to synthesize nucleophilic phosphinidene complexes, which resulted in variations of bent metallocene phosphinidene complexes including early-transition-metal complexes [(η^5-$C_5H_5)_2$M-(Me_3P)(=PMes*)]; (M = Zr, Hf),[6,7] as well as the uranium complex [[(η^5-$C_5Me_5)_2$U(Me_3PO)(=PMes*)].[8] Lammertsma *et al.* demonstrated that this synthetic route is also feasible for late transition metals, e.g. by treating the dichloro complexes [(η^5-C_5H_5)Ir(L)Cl_2)] (L=PPh_3, iPr_2Im^{Me}) with LiPHMes* to give [(η^5-C_5H_5)Ir(L)(=PMes*)].[9]

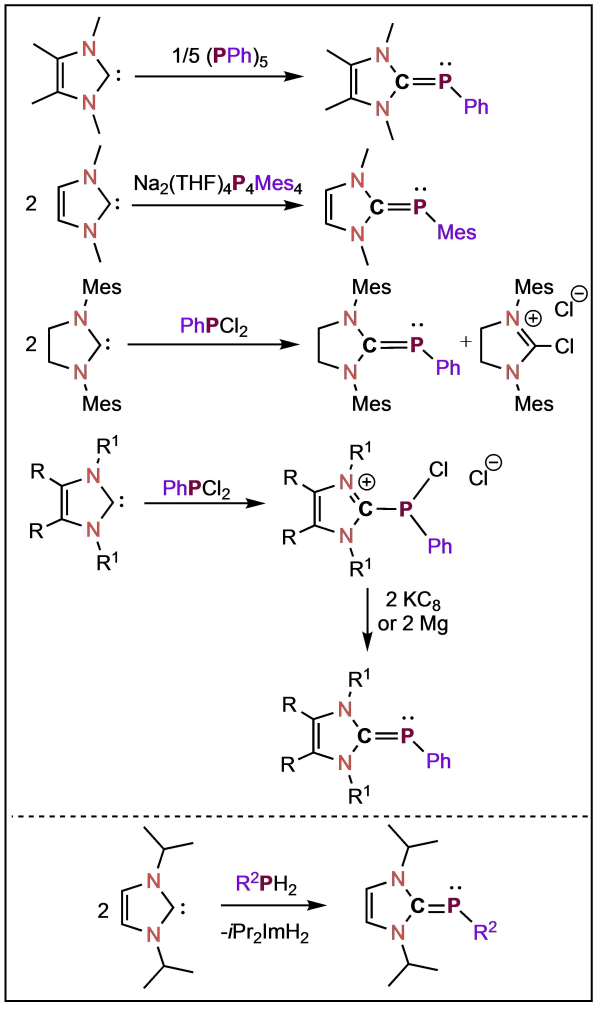
The stabilization of metal-free phosphinidenes was introduced with an early example by Schmidpeter *et al.* in 1980 with a report on the isolation of cyanophosphinidene-substituted heterocycles.[10] Arduengo *et al.* reported in 1997 the synthesis and isolation of the NHC pnictinidene adducts Mes_2Im=PnR (Mes_2Im = 1,3-dimesitylimidazolin-2-ylidene; Pn = P, As; R = C_6H_5, CF_3, C_6F_5) and related compounds such as (Me_4Im)PPh (NHC = *N*-heterocyclic carbene, Me_4Im = 1,3,4,5-tetramethyl-imidazolin-2-ylidene), and provided thus the first example that NHCs are suitable molecules for the stabilization of reactive

[a] *L. Werner, G. Horrer, M. Philipp, Dr. K. Lubitz, Dr. M. W. Kuntze-Fechner, Prof. Dr. U. Radius*
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg, Germany
E-mail: u.radius@uni-wuerzburg.de
Homepage: http://www.ak-radius.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/zaac.202000405

phosphinidenes.[11] Since then, synthesis and application of NHC-phosphinidenes gained more and more importance.[3]

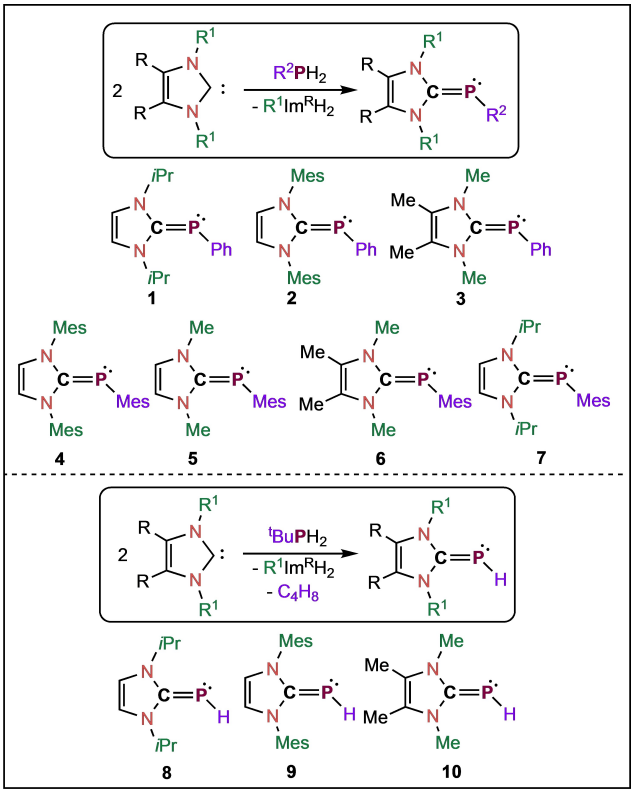
Several synthetic routes have been developed for the preparation of NHC phosphinidene adducts since then (Scheme 1).[3] The aforementioned first 'bottleable' NHC-phosphinidenes such as (Me_4Im)PPh were obtained by reaction of Me_4Im and pentaphenyl-*cyclo*-pentaphosphine $(PPh)_5$.[11] Several NHC-phosphinidenes such as (Mes_2Im)PPh or (Mes_2Im)PCF_3, have been synthesized from $(PPh)_5$ or similar compounds such as $(PCF_3)_4$ following this methodology (Scheme 1).[3,11] However the scope of this procedure is strongly dependent on the availability of the *cyclo*-phosphine used. The synthesis of NHC-phosphinidenes is also feasible *via* the reaction of two equivalents of free carbene with dichlorophosphines, which in selected cases leads to the NHC-phosphinidene and $[NHC–Cl]^+Cl^-$.[11a] Instead of using NHC as the chlorine acceptor, Bertrand *et al.* presented a reductive pathway, i.e. the reaction of the NHC with dichlorophosphines and subsequent two electron reduction with potassium graphite or magnesium powder, which leads to the desired NHC-phosphinidenes (Scheme 1).[12] The formation of NHC-phosphinidenes is also known from a



Scheme 1. Major synthetic routes to NHC-phosphinidenes.

variety of other NHC and phosphinidene precursors aside from the commonly applied routes starting from chloro-,[11a,12] and *cyclo*-polyphosphines.[11] For example, (Me_4Im)P(Rind) was synthesized from the reaction of diphosphenes (Rind)P=P(Rind) (Rind = 1,1,3,3,5,5,7,7-octa-R-substituted s-hydrindacen-4-yl; R = Et, Me) and two equivalents of the free carbene Me_4Im.[13] The reaction of $P(SiMe_3)_3$ with *N,N'*-1,3-bis(2,6-di-*iso*-propylphenyl)-2,2-difluoroimidazoline led to ($Dipp_2$Im)P($SiMe_3$) and subsequently to ($Dipp_2$Im)PH upon addition of methanol.[14] Another efficient route to NHC-phosphinidenes was established by Grützmacher and Gudat *et al.* by using the phosphaethynolate anion OCP^- as phosphorus transfer reagent in the reaction with *N*-arylated imidazolium salts.[15] Na(OCP) is also a useful reagent for the preparation of tetrel-substituted phosphaketenes (e.g. $Ph_3E(PCO)$, E = Sn, Ge), which afforded NHC-phosphinidene adducts upon coordination to NHCs and subsequent thermolysis.[16] An interesting example of an intramolecular carbene-stabilized phosphinidene was provided by Hahn *et al.*, which was synthesized from the reaction of the phosphaalkyne iPr_2NCP with Me_4Im. The bicyclic azaphospholene product of this reaction is formed by unusual C–H activation at the nitrogen substituent of the NHC.[17] Similar to polyphosphines, other polyphosphorus compounds such as Na_3P_7 or $(Me_3Si)_3P_7$ also provide access to NHC-phosphinidenes of NHCs of varying steric demand by reaction with dihydroimidazolium chlorides, as reported by Grützmacher and Gudat *et al.*[15] Moreover Hey-Hawkins and co-workers demonstrated that $Na_2(THF)_4P_4Mes_4$ is a suitable precursor for (Me_2Im)PMes, if reacted with Me_2Im or $[Me_2Im–H]^+I^-$.[18]

We recently explored the reactivity of NHCs and related molecules with group 13 to 15 main group element hydrides[19] and other main group element compounds.[20] We demonstrated that the reaction of iPr_2Im (1,3-di-*iso*-propylimidazolin-2-ylidene) with substrates such as hydrostannanes[19d] or primary and secondary phosphines[19b] leads to dehydrogenative element element coupling. P–P coupling was exemplified by the stoichiometric reaction of iPr_2Im with secondary phosphines, e.g. Ph_2PH, which afforded the dihydroaminal iPr_2ImH_2 and the P–P coupled product Ph_4P_2 in 89% yield. A similar reaction protocol with primary phosphines $ArPH_2$ (Ar = Ph, *p*Tol) leads to the P–P coupled rings P_4Ph_4, P_5Ph_5 and P_6Ph_6. In contrast, using primary phosphines in sub-stoichiometric amounts, i.e. a 1:2 ratio regarding to iPr_2Im, yields the dihydroaminal iPr_2ImH_2 and the NHC-phosphinidene (iPr_2Im)PAr (Ar = Ph, *p*Tol) quantitatively as judged from NMR spectroscopy. In this reaction, the ambiphilic character of the NHC is exploited i) as an activator of the primary phosphine P–H bond and ii) as a hydrogen acceptor. Thus, we considered the NHC mediated dehydrogenation of phosphines as a very interesting approach for the selective synthesis of NHC-phosphinidenes (Scheme 1, bottom) and we report herein on primary phosphine dehydrocoupling using different NHCs as a general and convenient synthetic approach to prepare NHC-phosphinidenes in moderate to high isolated yields (up to 71%). Furthermore, we also report a novel synthesis to different parent NHC-phosphinidenes (NHC)PH and preliminary investigations concerning the reactivity of (iPr_2Im)



Scheme 2. Dehydrogenative synthesis of NHC-phosphinidenes (NHC)PAr (**1**–**7**, top) and (NHC)PH (**8**--**10**, bottom).

PPh towards chalcogenides and selected transition metal complexes.

Results and Discussion

Our previous work demonstrated that the reaction of the primary aryl-substituted phosphines $PhPH_2$ and *p*-TolPH_2 with iPr_2Im in a stoichiometric ratio NHC:phosphine = 2:1 led selectively to the formation of the NHC-phosphinidene adduct (iPr_2Im)PPh (**1**) and (iPr_2Im)PTol in good isolated yield. One equivalent of the NHC serves as a hydrogen acceptor leading to the dihydroaminal iPr_2ImH_2 and the other equivalent is needed to stabilize the phosphinidene generated.[19b] As this approach represents a convenient way to access NHC-phosphinidenes we were interested to explore this preparative route in more detail. Thus, we reacted two equivalents of different NHCs with $PhPH_2$ to probe their ability to act as hydrogen-acceptor as well as different primary phosphines, i.e. $PhPH_2$, $MesPH_2$ and *t*BuPH_2 with different NHCs to probe different phosphines (Scheme 2).

Thus, we applied the same reaction protocol on the primary phosphines $PhPH_2$, $MesPH_2$ and *t*BuPH_2 in combination with iPr_2Im, Mes_2Im, Me_2Im and the backbone methylated NHC, Me_4Im. The reaction of two equivalents Mes_2Im and Me_4Im with one equivalent phenyl phosphine in xylene or toluene at 135 °C and 110 °C, respectively, was monitored *via* ^{31}P NMR spectroscopy. During the reactions new species were detected in the ^{31}P NMR spectra, the corresponding ^{31}P resonances were significantly downfield shifted in comparison to phenyl phosphine (*c.f.* −124.2 ppm). The signals at −23.7 ppm ((Mes_2Im)PPh (**2**)) and −52.9 ppm ((Me_4Im)PPh (**3**)) were assigned accordingly to the corresponding NHC-phosphinidenes and are in good agreement with those reported earlier by Arduengo *et al.* and by Layfield and coworkers (Table 1).[11,21] For the reaction of Mes_2Im with $PhPH_2$ no NMR signals for corresponding P–P coupling products were observed. After the reaction reached quantitative conversion without any side products formed, as judged from ^{31}P NMR spectroscopy, the solvent was evaporated, and the residue suspended in *n*-hexane. Subsequent filtration and washing with portions of *n*-hexane to remove the residual dihydroaminal $NHCH_2$ led to the isolation of (Mes_2Im)PPh (**2**) as a bright yellow solid in good yield (61 %). The reaction of two equivalents Me_4Im with $PhPH_2$, however, afforded aside from the product (Me_4Im)PPh (**3**) *cyclo*-oligophosphines P_4Ph_4, P_5Ph_5 and P_6Ph_6 as major side products, even in presence of an excess of NHC (i.e. 2.1 equivalents). Thus, (Me_4Im)PPh (**3**) was also formed using this procedure, but only in low yields of approximately 14 % judged from the integration of the ^{31}P NMR signals of the isolated yellow solid, which contained a mixture of (Me_4Im)PPh (**3**) and different oligophosphines. We did not try to separate the *cyclo*-oligophospines from (Me_4Im)PPh (**3**).

As the primary aryl phosphines seem to be suitable sources for the dehydrogenative route to NHC-phosphinidenes, we also investigated the reaction of mesityl phosphine $MesPH_2$ towards NHCs. $MesPH_2$ was reacted in a 1:2 ratio with the four different NHCs at higher temperatures. After the phosphine was completely consumed (judged on ^{31}P NMR spectroscopy) and

Table 1. Important ^{31}P and $^{13}C\{^1H\}$ chemical shifts (P=C_{NHC}) and $^1J_{CP}$ coupling constants recorded in C_6D_6 and isolated yields of compounds **1**–**7**.

Compound	δ_{NCN} $^{13}C\{^1H\}$ [ppm]	δ ^{31}P [ppm]	$^1J_{CP}$ [Hz]	yield [%]
(iPr_2Im)PPh (**1**)	168.2	−59.9	104	88
(Mes_2Im)PPh (**2**)	169.8	−23.7	103	61
(Me_4Im)PPh (**3**)	168.9	−52.9	97	14
(Mes_2Im)PMes (**4**)	170.3	−59.0	103	33
(Me_2Im)PMes (**5**)	170.4	−73.5	101	53
(Me_4Im)PMes (**6**)	169.5	−74.8	100	47
(iPr_2Im)PMes (**7**)	168.4	−79.5	105	–

subsequent work up, the literature known NHC-phosphinidenes (Mes_2Im)PMes (**4**), (Me_2Im)PMes (**5**) and (Me_4Im)PMes (**6**) were isolated in moderate to fair yields (**4**: 33%, **5**: 53%, **6**: 47%). Layfield and coworkers reported an iron- and cobalt-catalyzed synthesis for the NHC-phosphinidenes (Mes_2Im)PMes (**4**) and (Me_4Im)PMes (**6**).[21] Layfield *et al.* also reacted Mes_2Im directly with $MesPH_2$ to exclude formation of the NHC-phosphinidene without any catalyst under otherwise catalytic conditions. Upon heating Mes_2Im and $Dipp_2Im$ with $MesPH_2$ at 80 °C in deuterobenzene for several days, these authors observe no reaction, whereas ^1H and ^{31}P NMR spectra of the combination Me_4Im/$MesPH_2$ showed that $MesPH_2$, MesP(H)Me, and (Me_4Im)PMes are present in an approximate ratio of 7:1:1 and the mixture is thus dominated by starting materials.[21] However, using more elevated temperatures up to 110 °C or higher, dehydrocoupling is feasible even without the need for a catalyst with formation of (Mes_2Im)PMes (**4**), (Me_2Im)PMes (**5**), (Me_4Im)PMes (**6**) and (iPr_2Im)PMes (**7**).[19a] For (Me_4Im)PMes (**6**), the direct reaction of two equivalents of Me_4Im with one equivalent of $MesPH_2$ results in the complete consumption of starting materials after 10 days at 110 °C. This simple, yet efficient synthetic route represents an alternative, even though long reaction times are required. It is remarkable that these simple reactions are in some cases, for example for (Me_4Im)PMes (**6**), high in yield compared to the catalyzed analogues.[21] Due to limited rotations around the C–P bond some signals in the ^1H NMR spectrum of (Me_4Im)PMes (**6**) are significantly broadened at room temperature, which was also observed by Layfield et al.[21] Hence, temperature dependent NMR spectra in THF-d_8 were recorded which show splitting into sharp signals at 248 K (see Figure S11 in the SI). This is in good agreement to the data reported before.[21] In a similar fashion, the hitherto unknown (iPr_2Im)PMes (**7**) was synthesized and isolated as a sticky oil. The formation of (iPr_2Im)PMes (**7**) was unambiguously verified by ^1H, $^{13}C\{^1H\}$ and ^{31}P NMR spectroscopy. (iPr_2Im)PMes (**7**) shows a single resonance at −81.0 ppm in the ^{31}P NMR spectrum, similar to other (NHC)PMes species such as (Mes_2Im)PMes (**4**) (-50.0 ppm), (Me_2Im)PMes (**5**) (−73.5 ppm) and (Me_4Im)PMes (**6**) (−74.8 ppm) (see Table 1). However, the NMR spectra of the isolated yellow oil show small amounts of different, unassigned side products, which could not be separated. A doublet resonance for the NHC carbene carbon atom of (iPr_2Im)PMes (**7**) in the $^{13}C\{^1H\}$ NMR spectrum at a chemical shift of 168.4 ppm with a $^1J_{CP}$ coupling constant of 105.0 Hz to the adjacent phosphorus atom verifies the formation of the NHC-phosphinidene. Compared to the free NHC, this resonance is noticeably shifted to higher field and is also in perfect agreement to the $^{13}C\{^1H\}$ NMR spectroscopic data for the carbene carbon atom of (iPr_2Im)PPh (**1**) at 168.2 ppm (Table 1).

In addition to the characterization by NMR spectroscopy and high-resolution mass spectrometry, the NHC-phosphinidene (Me_4Im)PMes (**6**) was also structurally characterized. Single-crystals of **6** suitable for X-ray diffraction were obtained by storing a saturated solution of this compound in *n*-pentane at room temperature for several days (see Figure 1).

(Me_4Im)PMes (**6**) crystallizes in the space group Cc with one molecule in the asymmetric unit. The P–C distance of 1.791(2) Å

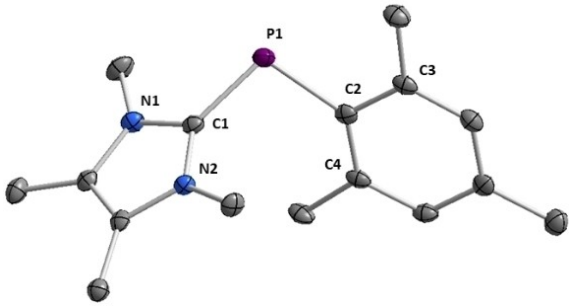
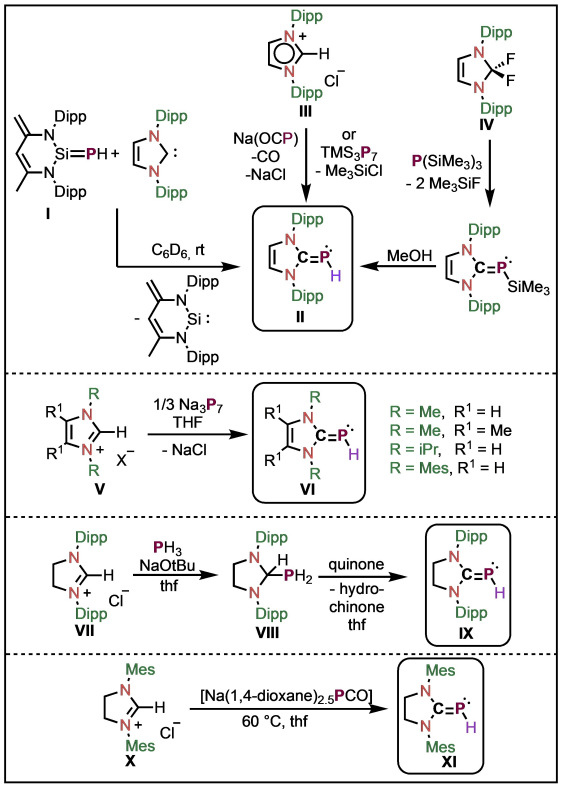


Figure 1. Molecular structure of (Me_4Im)PMes (**6**) in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **6**: P1-C1 1.791(2), C1-N1 1.363(3), C1-N2 1.358(3), P1-C2 1.842(2), C2-C3 1.425(3), C2-C4 1.409(3); C2-P1-C1 102.3(1), N1-C1-N2 104.8(2); N–C–P–C 67.4(2).

is similar to those of $P-C_{Carbene}$ bonds observed in the molecular structures of other NHC-phosphinidenes (Me_4Im)PR reported earlier, which lie in a range of 1.77 to 1.79 Å for a variety of substituents at the P atom with different steric bulk ((Me_4Im)PH 1.7721(14) Å, (Me_4Im)PPh 1.794(3) Å, (Me_4Im)P(Dmp) 1.786(4) Å).[3a] The angle C1-P1-C2 of 102.3(1)° for (Me_4Im)PMes (**6**) matches the C–P–C angle of (Me_4Im)PPh (102.34(14)°),[3a] whereas the torsion angle N–C–P–C of **6** of 67.4(2)° is widened compared to (Me_4Im)PPh (51.0(3)°) and (Me_4Im)P(Dmp) (55.5(4)°).[3a]

In comparison to aryl phosphinidenes, there are far less examples for alkyl substituted NHC-phosphinidenes and unsubstituted, i.e. parent NHC-phosphinidenes. One example for a CF_3 substituted species was presented by Arduengo *et al.*,[11a] while NHC adducts of the parent phosphinidene (:PH) include examples of NHCs with different steric properties as well as saturated and unsaturated NHC backbones. The first synthesis of such a compound was reported by Driess *et al.* in 2013. These authors obtained ($Dipp_2Im$)PH (**II**) (Scheme 3) by treating phospasilene **I** with the carbene $Dipp_2Im$, which results in a room temperature transfer of the PH moiety.[22] The synthesis of ($Dipp_2Im$)PH (**II**) is also feasible starting from the [HCl] salt of the carbene (**III**) by reaction with phosphaethynolate, Na(OCP), or TMS_3P_7 as "P" transfer reagent as described by Grützmacher *et al.*[23] Another synthetic route presented by Tamm *et al.* uses *N,N'*-1,3-bis(2,6-di-*iso*-propylphenyl)-2,2-difluoroimidazoline (**IV**) and $P(SiMe_3)_3$ which forms the (NHC)$PSiMe_3$ adduct. Subsequent treatment of (NHC)$PSiMe_3$ with methanol furnishes **II** in good yield (Scheme 3).[14]

Grützmacher and Gudat and coworkers reported an alternative synthesis for NHC=PH compounds mainly of sterically less demanding NHCs in 2016. Whereas the reaction of the imidazolium salts **V** with P_4 and KO*t*Bu only led to unselective product formation and polyphosphorous side products, the reaction of **V** with Na_3P_7 in THF afforded the NHC-phosphinidenes (**VI**) selectively.[24] For the synthesis of ($sDipp_2Im$)PH (**IX**) ($sDipp_2Im$ = 1,3-Bis-(2,6-di-*iso*-propylphenyl)-imidazolidin-2-ylidene) either PH_3 or $\{[Na(OtBu)]_{2.5}[Na(PH_2)]\}$ can be used as



Scheme 3. Synthetic routes to NHC-phosphinidenes (NHC)PH.

phosphinidene source, and treatment with the [HCl]-salt (**VII**) and dehydrocoupling of the intermediate **VIII** with quinone afforded the desired compound. Dehydrogenation to the phosphinidene-carbene adduct **VIII** was achieved using an *ortho*-quinone as hydrogen acceptor.[25] Recently von Hänisch *et al.* reported a synthesis for (*s*Mes$_2$Im)PH (**XI**) (*s*Mes$_2$Im = 1,3-dimesityl-imidazolidin-2-ylidene) applying a slightly modified reaction protocol based on the synthesis for (Dipp$_2$Im)PH (**II**) developed by Grützmacher (Scheme 3).[23,26]

Treating *t*BuPH$_2$ with two equivalents of *i*Pr$_2$Im in xylene at 125 °C for 5 days resulted in complete consumption of the primary phosphine. After workup, a pale-yellow solid was isolated and ^{31}P and ^{31}P{^{1}H} spectroscopy revealed a resonance at −149.9 ppm with a $^1J_{PH}$ coupling constant of 166 Hz, which is consistent with the existence of a phosphorous bound hydrogen atom. These data obtained match perfectly with the data reported earlier by Grützmacher and Gudat and coworkers for (*i*Pr$_2$Im)PH (**8**) (Table 2).[24] Thus, the reaction did not afford the expected *tert*-butyl substituted NHC-phosphinidene, but the parent NHC phsophinidene (*i*Pr$_2$Im)PH (**8**) was isolated in 28% yield instead. To gain a better insight into the course of the transformation we repeated the reaction in a temperature range between −78 °C and 0 °C, but only starting material in form of *t*BuPH$_2$ was detected by means of ^{31}P NMR spectroscopy. However, a ^{31}P NMR resonance of (*i*Pr$_2$Im)PH (**8**) was already observed when heating the 2:1 mixture of *i*Pr$_2$Im and *t*BuPH$_2$ to 50 °C, and an intermediate *tert*-butyl substituted phosphinidene species was never isolated or observed for this reaction spectroscopically.

Also (Mes$_2$Im)PH (**9**) and (Me$_4$Im)PH (**10**) can be synthesized from the reaction of *t*BuPH$_2$ and two equivalents NHC (Mes$_2$Im: 135 °C in xylene, Me$_4$Im: 110 °C in toluene). The primary phosphine *t*BuPH$_2$ was completely consumed after five days and the NHC-phosphinindenes (Mes$_2$Im)PH (**9**) (δ ^{31}P = −147.2 ppm) and (Me$_4$Im)PH (**10**) (δ ^{31}P = −149.9 ppm) were isolated as off-white and colorless solids in yields of 71% and 51%, respectively (Table 2). Formation of the H substituted species was also supported by the observation of the corresponding P–H vibrations in the IR spectra of the compounds **8**–**10** (**8**: 2302 cm^{-1}, **9**: 2269 cm^{-1}, **10**: 2293 cm^{-1}, Table 2). Compared to other established synthetic routes for (Mes$_2$Im)PH (**9**) and (Me$_4$Im)PH (**10**), these reactions are remarkably high yielding using a standard primary phosphine,[24] but also limited in the NHC used. As an example, we have found that the reaction of Me$_2$Im with *t*BuPH$_2$ in a 2:1 ratio in toluene at 115 °C leads to (Me$_2$Im)PH (**11**) only in traces even after 10 days and the mixture is dominated by starting material (according to ^{31}P NMR spectroscopy).

Single crystals of (*i*Pr$_2$Im)PH (**8**) suitable for X-Ray diffraction analysis were obtained by storing a saturated solution of the compound in *n*-hexane at room temperature (see Figure 2). NHC-phosphinidene **8** crystallizes in the space group $P2_12_12_1$ with one molecule in the asymmetric unit. The P–C distance of 1.7788(4) Å observed for **8** is similar to that of the Me$_4$Im analogue (Me$_4$Im)PH (1.7721(14) Å) reported previously.[3a] The angle C–P–H of 92.886(9)° and the torsion angle H–P–C–N of 2.612° reveal an almost ideal eclipsed conformation between the phosphinidene moiety and the NHC ligand.

The dehydrocoupling route presented here allows the synthesis and isolation of (*i*Pr$_2$Im)PPh (**1**) on a multigram (here: 4 g) scale with an excellent yield of 88%. With this NHC-phosphinidene at hand we were interested in first reactivity studies. To probe oxygen sensitivity, we initially reacted the NHC-phosphinidene (*i*Pr$_2$Im)PPh (**1**) with dry oxygen (0.5 bar) in toluene (Scheme 4). Directly after addition of oxygen, the

Table 2. Important ^{31}P, ^{1}H and ^{13}C{^{1}H} chemical shifts (P=C$_{NHC}$) and coupling constants recorded in C$_6$D$_6$, IR data and isolated yields of compounds **8**–**10**.

Compound	δNCN ^{13}C{^{1}H} [ppm]	δ ^{31}P [ppm]	δPH ^{1}H [ppm]	^{1}JPH [Hz]	^{1}JCP [Hz]	ṽPH [cm^{-1}]	yield [%]
(*i*Pr$_2$Im)PH (**8**)	173.7	−149.9	2.64	166	93	2302	28
(Mes$_2$Im)PH (**9**)	176.3	−147.2	2.07	164	85	2269	71
(Me$_4$Im)PH (**10**)	174.6	−149.9	2.49	165	88	2293	51

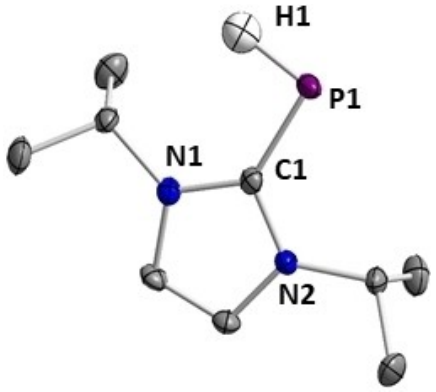
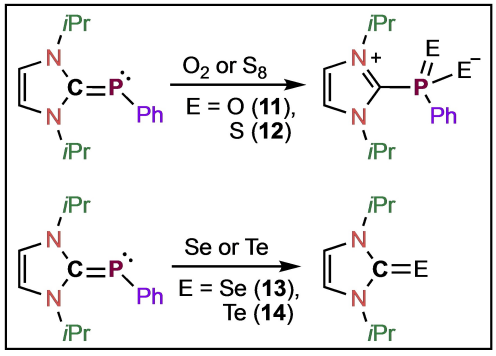


Figure 2. Molecular structure of (*i*Pr$_2$Im)PH (**8**) in the solid state. Hydrogen atoms are omitted for clarity with exception of H1. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **8**: P1-H1 1.3504(4), P1-C1 1.7788(4), C1-N1 1.3636(3), C1-N2 1.3613(3); H1-P1-C1 92.886(9), N1-C1-N2 105.278(16); H1-P1-C1-N1) 2.612.



Scheme 4. Reactions of NHC-phosphinidene **1** with chalcogenids.

reaction mixture changes its color from orange to colorless with formation of a colorless precipitate. After workup, compound *i*Pr$_2$Im-P(O)$_2$Ph (**11**) was isolated as a colorless solid in 55% yield. NMR spectroscopic investigations revealed a significant downfield shift of the ^{31}P NMR resonance at −0.8 ppm in CD_3CN compared to the NHC-phosphinidene **1**, similar as observed for the NHC adducts of phenyldioxophosphorane presented previously by Tamm *et al.* (Me$_4$Im–P(O)$_2$Ph: −1.0 ppm, Mes$_2$Im–P(O)$_2$Ph: −23.0 ppm, Dipp$_2$Im–P(O)$_2$Ph: −18.9 ppm).[27] Further, the doublet resonance for the NHC carbene carbon atom is noticeably shifted in the ^{13}C{^{1}H} NMR spectrum, i.e. *i*Pr$_2$Im-P(O)$_2$Ph (**11**) gives rise to a signal at 147.9 ppm ($^1J_{CP}$ = 94.5 Hz), whereas the resonance for (*i*Pr$_2$Im)PPh (**1**) is located at 168.2 ppm ($^1J_{CP}$ = 104 Hz).

Similarly, the reaction between equimolar amounts of (*i*Pr$_2$Im)PPh (**1**) and elemental sulfur (S_8) in THF afforded the NHC adduct of phenyldithiophosphorane *i*Pr$_2$Im-P(S)$_2$Ph (**12**) (Scheme 4), which gives rise to a ^{31}P NMR resonance at 54.1 ppm in $CDCl_3$. This compound is well soluble and sufficiently stable in acetonitrile and chloroform which allows full characterization by NMR spectroscopy. A doublet for the NHC carbene carbon atom was detected in the ^{13}C{^{1}H} NMR spectrum at 147.2 ppm with a coupling constant $^1J_{PC}$ of 40.4 Hz, which is much smaller than $^1J_{PC}$ coupling observed for *i*Pr$_2$Im-P(O)$_2$Ph (**11**) ($^1J_{PC(NHC)}$ = 94.5 Hz). Similarly, the $^1J_{PC}$ coupling constant of the ^{13}C{^{1}H} NMR resonance at 142.3 ppm for the phenyl C_{ipso} attached to phosphorous of 91.0 Hz is much smaller compared to **11** ($^1J_{PC(Ph)}$ = 145.6 Hz). Furthermore, the compound *i*Pr$_2$Im-P(S)$_2$Ph (**12**) was also characterized by X-ray diffraction (see Figure 3).

*i*Pr$_2$Im-P(S)$_2$Ph (**12**) crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The molecular structure of **12** reveals a distorted tetrahedral geometry at phosphorus with a large S-P–S angle of 119.29(2)°. The P–$C_{Carbene}$ bond length of 1.8732(14) Å is significantly longer than the P–C_{Phenyl} bond of 1.8247(14) Å and the C=P bond observed in NHC-phosphinidenes (*vide supra*). However, the bond lengths and angles obtained for **12** are in good agreement with the data reported by Tamm *et al.* for Me$_4$Im-P(S)$_2$Ph previously.[27]

The reaction of **1** with elemental (grey) selenium and tellurium did not lead to the selenium and tellurium analogues of **11** and **12**, but yielded (NHC)PPh cleavage with formation of the isolated compounds (*i*Pr$_2$Im)Se (**13**) and (*i*Pr$_2$Im)Te (**14**) and different *cyclo*-oligophospines, according to NMR spectroscopy (^{31}P–NMR: P_4Ph_4 −48.2, P_6Ph_6 −22.0, P_5Ph_5 −3.6 to −2.7 ppm). The NMR data of **13** are in good agreement to those reported by Ganter *et al.*,[28] most characteristic is the ^{13}C{^{1}H} NMR resonance of the NHC carbene carbon atom at 153.5 ppm and a singlet at −19.7 ppm in the ^{77}Se{^{1}H} NMR spectrum. Tamm and coworkers reported the isolation of Me$_4$Im substituted diselenophosphorane from the analogous reaction of (Me$_4$Im)PPh with grey selenium in THF at room temperature.[27] The compound (*i*Pr$_2$Im)Te (**14**) shows a characteristic resonance at −184.6 ppm in the ^{123}Te{^{1}H} NMR spectrum which is in agreement with the ^{123}Te NMR spectrum reported for closely related *i*Pr$_2$Im^{Me}=Te at −167.8 ppm as reported by Kuhn and Henkel *et al.*[29]

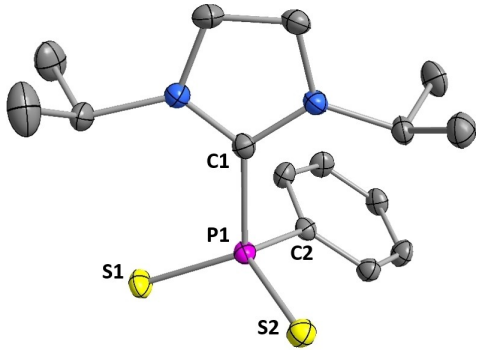


Figure 3. Molecular structure of *i*Pr$_2$Im-P(S)$_2$Ph (**12**) in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **12**: P1-C1 1.8732(14), P1-S1 1.9739(5), P1-S2 1.9626(5), P1-C2 1.8247(14); C1-P1-S1 107.17(5), C1-P1-S2 104.29(4); C1-P1-C2 99.33(6), S1-P1-S2 119.29(2), S2-P1-C2 112.45(4), S1-P1-C2 107.17(5).

(iPr$_2$Im)Te (**14**) crystallizes in the triclinic space group P1 with two molecules in the asymmetric unit (Figure 4). The molecular structure shows as expected a Te atom bonded to the NHC iPr$_2$Im. The bond length C1-Te1 of 2.092(4) Å is identical within standard deviation to the closely related C–Te distance reported for (iPr$_2$Im^{Me})Te.[29b]

The developed synthetic protocol for NHC-phosphinidenes of the general formula (NHC)PR (Scheme 2) paired with the observation of (NHC)PPh cleavage by treatment of (iPr$_2$Im)PPh (**1**) with elemental selenium and tellurium to yield (iPr$_2$Im)Se (**13**) and (iPr$_2$Im)Te (**14**) (Scheme 4) is particularly useful to determine the electronic properties of NHCs by ^{31}P and ^{77}Se NMR spectroscopy as demonstrated by Bertrand and Ghadwal recently.[12,30]

Several transition metal complexes of NHC-phosphinidenes have been reported so far in the literature. Larocque and Lavoie provided an early example in 2014 and reported the reaction of a first-generation ruthenium benzylidene Grubbs complex with (Mes$_2$Im)PPh. Ligand exchange of one PPh$_3$ ligand occurred and led to the formation of a ruthenium NHC-phosphinidene complex, maintaining the NHC-phosphinidene.[31] Tamm *et al.* reported the synthesis of NHC-phosphinidene coinage metal complexes from the reaction of the NHC-phosphinidene (Dipp$_2$Im)PPh with MCl (M = Cu, Ag, Au)[32] and a series of tungsten and molybdenum pentacarbonyl complexes of NHC-phosphinidenes.[33] Different complexes [{(Dipp$_2$Im)PR}M(CO)$_5$] (R = H, Ph, Mes, M = Mo, W) of NHC-phosphinidenes of the sterically demanding Dipp$_2$Im have been synthesized and it has been demonstrated that NHC phospinidenes are good donor ligands. For example, the CO band for the CO stretch in the IR spectrum of [{(Dipp$_2$Im)PPh}Rh(CO)$_2$Cl] at 2006 cm^{-1} lies much lower compared to those of other important ligand classes in complexes [(L)Rh(CO)$_2$Cl], e.g. phosphines (PPh$_3$: 2052 cm^{-1}) or NHCs (Mes$_2$Im: 2038 cm^{-1}, Dipp$_2$Im: 2037 cm^{-1}).[33] These results encouraged us to study the ligation properties of the sterically less demanding NHC-phosphinidene (iPr$_2$Im)PPh (**1**) with respect to selected transition metal complexes (Scheme 5). The tetrahydrofuran adduct [W(CO)$_5$(thf)], which was *in situ* generated by photolysis of [W(CO)$_6$] in THF, was reacted with (iPr$_2$Im)PPh (**1**) and yielded [{(iPr$_2$Im)PPh}W(CO)$_5$] **15** in quantitative yield according to ^{31}P NMR spectroscopy. This complex was isolated as a yellow solid in 54% yield. The ^{31}P NMR resonance of the NHC-phosphinidene tungsten complex was observed at −81.1 ppm, significantly shifted from −60.1 ppm for (iPr$_2$Im)PPh (**1**), and coupling of the phosphorus nucleus with the tungsten center with a coupling constant of $^1J_{PW}$ = 112.3 Hz was observed. Tamm *et al.* reported a wide range of ^{31}P NMR chemical shifts for similar compounds, e.g. −57.7 ppm in THF-d$_8$ for [{(Dipp$_2$Im)PPh}W(CO)$_5$] with a coupling constant of $^1J_{PW}$ = 120 Hz, close to our data.[33]

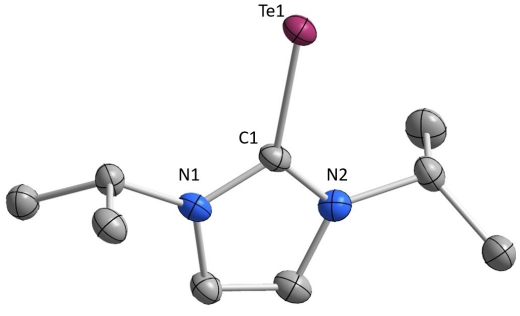
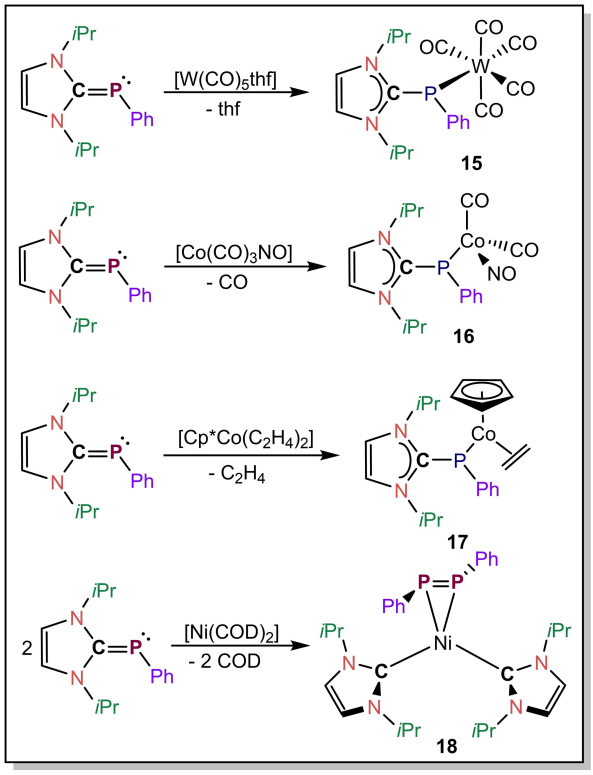


Figure 4. Molecular structure of (iPr$_2$Im)Te (**14**) in the solid state. Hydrogen atoms are omitted for clarity. Atomic displacement ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (°) for **14**: C1-Te1 2.092(4), N1-C1 1.340(6), C1-N2 1.355(6).

We recently reported the reaction of [Co(CO)$_3$(NO)][34] with different NHCs, which leads to replacement of carbonyl ligands and to formation of either [Co(NHC)(CO)$_2$(NO)] or [Co(NHC)$_2$(CO)(NO)] in overall good yields.[35] The use of the sterically demanding NHCs Dipp$_2$Im, Mes$_2$Im and the cyclic (alkyl)(amino)carbene ^{Me}cAAC selectively led to complexes of the type [Co(NHC)(CO)$_2$(NO)], even if an excess of NHC was provided. Similarly, NHC phosphine complexes [Co(iPr$_2$Im)(PR$_3$)(CO)(NO)] (PR$_3$ = PMe$_3$, PEt$_3$, PHiPr$_2$) and [Co(NHC)(PMe$_3$)(CO)(NO)] (NHC = Me$_4$Im, MeiPrIm, MetBuIm, iPr$_2$Im^{Me}) are available from the reaction of [Co(NHC)(CO)$_2$(NO)] and phosphines.[35b] Therefore, [Co(CO)$_3$(NO)] might be a suitable precursor for either a cobalt NHC-phosphinidene complex [Co{(NHC)PR}(CO)$_2$(NO)] or a NHC-stabilized cobalt phosphinidene complex [Co(NHC)(PR)(CO)(NO)] or [Co(NHC)(PR)(CO)$_2$].[35] However, the reaction of (iPr$_2$Im)PPh (**1**)with [Co(CO)$_3$NO] resulted with CO release in the formation of the red complex [Co{(iPr$_2$Im)PPh}(CO)$_2$(NO)] (**16**) in 42% yield. Complex **16** reveals significantly shifted ^{1}H NMR data as compared to the analogous NHC complex [Co(CO)$_2$(NO)(iPr$_2$Im)] (**XII**),[35] i.e. a doublet at 0.82 ppm (**XII**: 0.92 ppm) for the methyl protons and a doublet of septets at 5.02 ppm (**XII**: 4.60 ppm) for the methine protons of the iPr substituent as well as a broad doublet at 6.07 ppm (**XII**: 6.40 ppm) for the NHC-backbone protons. The resonances of the NHC carbene carbon atom in the ^{13}C{^{1}H} NMR spectrum of **16** at 163.7 ppm (**XII**: 219.8 ppm) reveals a $^1J_{CP}$ coupling constant to the phosphorus atom of 91.2 Hz, which is in accordance with an intact NHC-phosphinidene unit and thus confirms the formation of the NHC-phosphinidene ligated complex **16**. The large quadrupole moment of ^{59}Co affects the NHC carbene carbon and the carbonyl carbon resonance in the ^{13}C{^{1}H} NMR spectrum, the latter was not observed, but also the ^{31}P NMR resonance, which appears as a broadened signal at −45.5 ppm. This resonance is also in good agreement with other reported NHC-phosphinidene carbonyl complexes, which show ^{31}P resonances typically in the range between −25 to −164 ppm.[33] In addition, an intense NO (1694 cm^{-1}) and two CO (1925 cm^{-1} and 1992 cm^{-1}) stretching modes were observed in the IR spectrum of **16**, which indicate a high electron density at the cobalt atom. However, heating of **16** in solution led to decomposition of this complex with formation of [Co(iPr$_2$Im)(CO)$_2$(NO)] and *cyclo*-oligophosphines and not to the formation of an NHC-stabilized cobalt phosphinidene complex, as might expected.

Various group 8 and 9 half sandwich phosphinidene complexes of the type [(η^6-C$_6$R$_6$)M(L)(=PAr)] (M = Ru, Os; L = PR$_3$, NHC)[37] or [(η^5-C$_5$R$_5$)M(L)(=PAr)] (Co,[38a] Rh,[38a] Ir;[9a,2b] L = PR$_3$,



Scheme 5. Reaction of (iPr$_2$Im)PPh (**1**) with selected transition metal complexes.

NHC) as well as related NHC-phosphinidene metal complexes are known.[38] Therefore, we envisioned the synthesis of NHC-stabilized phosphinidene complexes [(η^5-C_5R_5)Co(NHC)(=PAr)] starting from (iPr$_2$Im)PPh (**1**) and [(C_5R_5)Co]-synthons such as [(C_5R_5)Co(η^2-C_2H_4)$_2$]. We have reported previously different complexes with the [(η_5-C_5R_5)Co(NHC)] complex moiety on several occasions.[36] The reaction of [(C_5Me_5)Co(η^2-C_2H_4)$_2$] with (iPr$_2$Im)PPh (**1**) afforded the NHC-phosphinidene cobalt complex [(η^5-C_5Me_5)Co{(iPr$_2$Im)PPh}(η^2-C_2H_4)] (**17**) (Scheme 5). Complexes **17** and [(η^5-C_5Me_5)Co(iPr$_2$Im)(η^2-C_2H_4)] (**XIII**) reported previously[36a] can be easily distinguished by NMR spectroscopy. The ^{1}H NMR spectrum of **17**, for example, reveals a resonance at 1.93 ppm (**XIII**: 1.78 ppm) characteristic for C_5Me_5 protons and the *iso*-propyl methine protons give rise to a broadened doublet of septets at 4.57 ppm (**XIII**: one septet at 6.20 ppm). The NHC carbene carbon atom resonance at 163.7 ppm (**XIII**: 193.8 ppm) in the ^{13}C{^{1}H} NMR spectrum shows $^1J_{CP}$ coupling of 98.7 Hz, and ^{31}P NMR resonance at +25.8 ppm is shifted compared to the NMR resonance of **1** at −60.1 ppm.

Similar as observed for **16**, complex **17** decomposes upon heating in solution. At room temperature, both NHC-phosphinidene complexes are stable in solution for a prolonged period of time. However, after gradually heating both complexes up to 80 °C the NHC complex [(η^5-C_5Me_5)Co(iPr$_2$Im)(η^2-C_2H_4)] was formed together with *cyclo*-oligophosphines.

To support these experimental observations, additional quantum-mechanical DFT calculations on the BP86/def2-TZVP level of theory were performed. According to these calculations the decomposition of [Co{(iPr$_2$Im)PPh}(CO)$_2$(NO)] **16** to yield [Co(iPr$_2$Im)(CO)$_2$(NO)] and *cyclo*-P_5Ph_5 is exergonic by $\Delta G^{298} = -37.46$ kJ·mol, whereas the formation of [Co(iPr$_2$Im)(PPh)(CO)(NO)] (and CO) is endergonic by $\Delta G^{298} = +129.43$ kJ·mol (Figure 5). Thus, the calculations clearly predict [PPh] cleavage from **16** and oligophosphine formation, a transfer to the cobalt atom with substitution of a CO ligand seems not to be feasible.

Over the past years we investigated the chemistry of different NHC-stabilized nickel complexes in stochiometric and catalytic reactions in some detail.[39] As NHC-phosphinidenes have not been used as ligands in any nickel complex so far, we became interested to use (iPr$_2$Im)PPh (**1**) in nickel chemistry. Wolf and Goicoechea reported the reaction of the paramagnetic nickel(I) NHC complex [(η-C_5H_5)Ni(Mes$_2$Im)] with [Na(dioxane)$_{1.8}$][PCO] which led to the isolation of carbene-

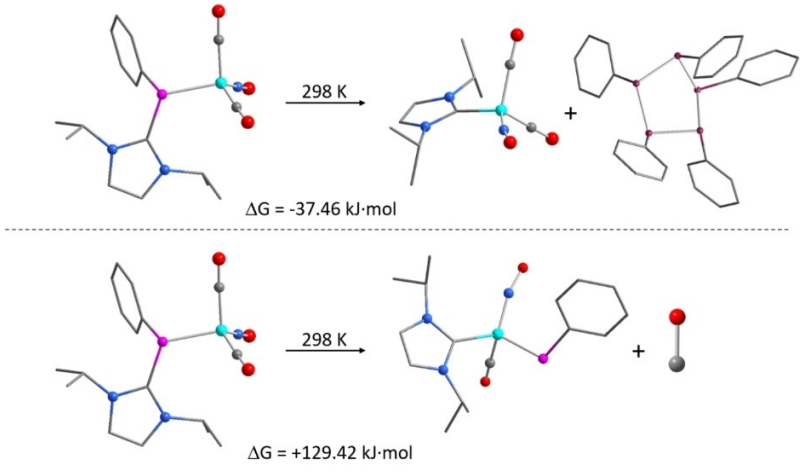


Figure 5. Free reaction enthalpies (ΔG^{298}, at 298 K) calculated at the def2-TZVP/BP86-level of theory for the formation of [Co(iPr$_2$Im)(CO)$_2$(NO)] **II** and *cyclo*-P_5Ph_5 (top) or [Co(iPr$_2$Im)(PPh)(CO)(NO)] (bottom) starting from [Co(CO)$_2$(NO){(iPr$_2$Im)PPh}] (**16**).

phosphinidenyl-bridged dimer (μ^2-CO)[μ^2-P(Mes$_2$Im)]Ni$_2$(Mes$_2$Im)Cp.[40]

The reaction of (*i*Pr$_2$Im)PPh (**1**) with the nickel(0) precursor [Ni(COD)$_2$] in a 2:1 molar ratio in toluene at room temperature led to isolation of a diphosphene complex [Ni(*i*Pr$_2$Im)$_2$(*trans*-PhP=PPh)] (**18**) (Scheme 5), which was characterized using NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. In contrast to the transition metal complexes of **1** with tungsten and cobalt reported here, no η^1-coordination of (*i*Pr$_2$Im)PPh (**1**) was observed but direct coordination of *i*Pr$_2$Im to the nickel center with coupling of the phoshinidene units occurred instead. Thus, complex **18** is formed by formal NHC-phosphinidene cleavage and phosphinidene coupling in the coordination sphere of nickel with coordination of the NHC and the diphosphene to the nickel atom. However, independent on the stoichiometry and temperature we were using, we could not detect any intermediate for this reaction. For **18**, a single resonance in the ^{31}P NMR spectrum was detected at −40.9 ppm in C_6D_6 and −42.9 ppm in toluene-d$_8$, which lies in a similar region as observed for the palladium and platinum derivatives [Pd(dppe)(*trans*-PhP=PPh)] ($\delta = -34$ ppm) and [Pt(dppe)(*trans*-PhP=PPh)] ($\delta = -24$ ppm) reported previousely.[41] The resonance of the NHC carbene carbon atoms in the ^{13}C{^{1}H} NMR spectrum of **18** appear as a triplet at 193.9 ppm, in the typical range for this kind of NHC nickel complexes,[39] with a $^2J_{CP}$ coupling constant of 8.3 Hz, which is much smaller than the $^1J_{CP}$ coupling constant typically observed for NHC-phosphinidene complexes (typically *ca.* 90 Hz, *vide supra*). The ^{1}H NMR resonances of the NHC ligands in **18** are broadened at room temperature, consistent with a hindered rotation of the ArP=PAr ligand around the Ni-(PP)$_{centroid}$ vector and/or of the NHC ligands around the Ni–C bonds. Cooling to −50 °C resolved the spectra into four *i*Pr methyl and two *i*Pr methine resonances, as typically found for a pseudo-C_{2v} type structure in solution. At 90 °C, two *i*Pr methyl resonances and a single *i*Pr methine signal were observed, which were still broadened (see Figure S66 of the SI).

Conclusion

The dehydrocoupling of primary phosphines with NHCs to yield NHC-phosphinidenes was investigated and we demonstrate here that dehydrocoupling of primary phosphine using NHCs is a general and convenient synthetic approach to prepare NHC-phosphinidenes in moderate to high isolated yields. The reaction of primary phosphines ArPH$_2$ (Ar = Ph, *p*Tol, Mes) with NHCs led to addition of hydrogen to the NHC carbene carbon atom with formation of the dihydroaminal NHCH$_2$ and the NHC-phosphinidene (NHC)PAr. The NHC phosphinidenes (*i*Pr$_2$Im)PPh (**1**), (Mes$_2$Im)PPh (**2**), (Me$_4$Im)PPh (**3**), (Mes$_2$Im)PMes (**4**), (Me$_2$Im)PMes (**5**), (Me$_4$Im)PMes (**6**) and (*i*Pr$_2$Im)PMes (**7**) have been synthesized using this approach. If *t*BuPH$_2$ is used as the phosphine source, the parent NHC-phosphinidenes (NHC)PH were obtained, as exemplified by the preparation of (*i*Pr$_2$Im)PH (**8**), (Mes$_2$Im)PH (**9**) and (Me$_4$Im)PH (**10**). The NHC-phosphinidene (*i*Pr$_2$Im)PPh (**1**) is oxygen-sensitive, as the reaction of **1** with oxygen led to the isolation of *i*Pr$_2$Im-P(O)$_2$Ph (**11**). The reaction with elemental sulfur afforded *i*Pr$_2$Im-P(S)$_2$Ph (**12**). Treatment of **1** with elemental selenium and tellurium did not lead to the selenium and tellurium analogues of **11** and **12**, but to (NHC)PPh cleavage with formation of (*i*Pr$_2$Im)Se (**13**) and (*i*Pr$_2$Im)Te (**14**) and different *cyclo*-oligophospines. Furthermore, several transition metal complexes of the NHC-phosphinidene **1** were synthesized. *In situ* prepared [W(CO)$_5$(thf)] reacts with **1** quantitatively to yield [{(*i*Pr$_2$Im)PPh}W(CO)$_5$] (**15**), the reaction of **1** with [Co(CO)$_3$NO] results with CO release in the formation of [Co{(*i*Pr$_2$Im)PPh}(CO)$_2$(NO)] (**16**) and the reaction of [(C$_5$Me$_5$)Co(η^2-C$_2$H$_4$)$_2$] with **1** afforded [(η^5-C$_5$Me$_5$)Co{*i*Pr$_2$Im)PPh}(η^2-C$_2$H$_4$)] (**17**). Both cobalt complexes, [Co{(*i*Pr$_2$Im)PPh}(CO)$_2$(NO)] (**16**) and [(η^5-C$_5$Me$_5$)Co{*i*Pr$_2$Im)PPh}(η^2-C$_2$H$_4$)] (**17**) are stable in the solid state and in solution at room temperature, but decompose to the NHC complexes [Co(*i*Pr$_2$Im)(CO)$_2$(NO)] and [(η^5-C$_5$Me$_5$)Co(*i*Pr$_2$Im)(η^2-C$_2$H$_4$)], respectively, and *cyclo*-oligophosphines upon heating to 80 °C in solution. A different behavior was observed for the reaction of (*i*Pr$_2$Im)PPh (**1**) with the common nickel(0) precursor [Ni(COD)$_2$], which afforded the diphosphene complex [Ni(*i*Pr$_2$Im)$_2$(*trans*-PhP=PPh)] (**18**). This complex was formed by formal NHC-phosphinidene cleavage, NHC coordination to nickel and phosphinidene coupling in the coordination sphere of the nickel atom.

Experimental Section

General considerations

All reactions and subsequent manipulations involving organometallic reagents were performed under argon atmosphere by using standard Schlenk techniques or in a Glovebox (Innovative Technology Inc. and MBraun Uni Lab) as reported previously.[39] All reactions were carried out in oven-dried glassware. Toluene, *n*-hexane and THF were obtained from a solvent purification station (Innovative Technology) by previous purification through alumina columns. The deuterated benzene solvent was purchased from Sigma-Aldrich and dried thoroughly over molecular sieves. The carbene ligands *i*Pr$_2$Im, Me$_2$Im, Me$_4$Im[42] and Mes$_2$Im[43] were prepared according to published procedures. Elemental analyses were performed in the microanalytical laboratory of the University of Würzburg with an Elementar vario micro cube. Infrared spectra were recorded on a Bruker alpha spectrometer as solids by using an ATR unit. NMR spectra were recorded at 298 K using Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz, ^{31}P, 162.0 MHz) and Bruker Avance 500 (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz, ^{31}P, 202.5 MHz) spectrometers. ^{1}H NMR chemical shifts are listed in parts per million (ppm) and reported relative to TMS and were referenced via residual proton resonances of the deuterated solvent (C_6D_5H: 7.16 ppm (C_6D_6); C_7D_7H: 2.08, 6.97, 7.01, 7.09 ppm (tol-d$_8$); C_4D_7HO: 1.72, 3.58 ppm (thf-d$_8$); CD_2HCN: 1.94 (CD_3CN); $CHCl_3$: 7.26 ($CDCl_3$)) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (C_6D_6: 128.06 ppm; tol-d$_8$: 20.43, 125.13, 127.96, 128.87, 137.48 ppm; thf-d$_8$: 25.31, 67.21; CD_3CN: 1.92, 118.26; $CDCl_3$: 77.16).[44]

Synthesis of (*i*Pr$_2$Im)PPh (1): Phenyl phosphine (2.00 g, 18.2 mmol) was added at room temperature to a solution of *i*Pr$_2$Im (5.80 g, 36.3 mmol) in 20 mL of toluene and the clear solution was heated to 105 °C for 3 h. All volatiles were removed *in vacuo* and a light orange residue was suspended in 20 mL of *n*-hexane. After

filtration, the yellow solid was washed with *n*-hexane (3×10 mL) and dried *in vacuo* to afford 4.15 g (15.9 mmol; 88%) of a yellow solid. **^{1}H NMR (400.1 MHz, C_6D_6, 298 K)**: δ = 0.90 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H*$_3$), 5.06 (dsept, 2H, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 4.0 Hz, *i*Pr-C*H*), 6.19 (s, 2H, C*H*C*H*), 6.91, 7.07, 7.64 (m, 5 H, aryl-*H*). **^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K)**: δ = 21.8 (s, *i*Pr-CH$_3$), 49.9 (d, $^3J_{CP}$ = 10 Hz, *i*Pr-CH), 115.4 (d, $^1J_{CC}$ = 3 Hz, C*H*C*H*), 122.2, 128.1 (aryl-C*H*), 132.1 (d, $^2J_{CP}$ = 19 Hz, aryl-C*H*$_{ortho}$), 150.3 (d, $^1J_{CP}$ = 50 Hz, aryl-C*H*$_{ipso}$), 168.2 (d, $^1J_{CP}$ = 104 Hz, NCN). **^{31}P NMR (162.0 MHz, C_6D_6, 298 K)**: δ = −59.9 (s, P). $C_{15}H_{21}N_2P$ (260.32 g/mol): calcd.: 69.21, H 8.13, N 10.76; found: C 69.80, H 7.91, N 10.60 **HRMS LIFDI** (m/z): calculated for $C_{15}H_{21}N_2P$ [M$^+$]: 260.1437; found: 260.1429. **IR** (ATR[cm^{-1}]): 458 (m), 493 (m), 583 (w), 658 (w), 676 (s), 693 (vs, δ$_{CH}$), 738 (vs, δ$_{CHoop}$), 878 (w), 1021 (w, δ$_{PAroop}$), 1070 (m), 1198 (s), 1300 (m), 1370 (m, δ$_{CH}$), 1406 (m, δ$_{CH}$), 1466 (m, δ$_{CH}$), 1574 (m, ν$_{CC}$), 2010 (vw), 2183 (vw), 2970 (vw, ν$_{CH}$), 3050 (vw, ν$_{CH}$).

Synthesis of (Mes_2Im)PPh (2): Phenyl phosphine (150 mg, 1.36 mmol) was added at room temperature to a solution of Mes_2Im (871 mg, 2.86 mmol) in 12 mL of xylene and the clear solution was heated to 135 °C for 3 d. All volatiles were removed *in vacuo* and the pale-yellow residue was suspended in 11 mL of *n*-hexane. After filtration, the yellow solid was washed with 8 mL of *n*-hexane and dried *in vacuo* to afford 340 mg (824 μmol; 61%) of a yellow solid. **^{1}H NMR (400.1 MHz, C_6D_6, 298 K)**: δ = 2.03 (s, 6H, mesityl-C*H*$_{3para}$), 2.24 (s, 12H, mesityl-C*H*$_{3ortho}$), 5.83 (s, 2H, C*H*C*H*), 6.57 (s, 4H, mesityl-C*H*$_{meta}$), 6.68, 6.75 (m, 3H, aryl-*H*), 7.45 (m, 2H, aryl-*H*). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 18.5 (d, $^5J_{CP}$ = 2.88 Hz, mesityl-CH$_{3ortho}$), 21.0 (s, mesityl-C*H*$_{3para}$), 118.6 (d, $^3J_{CP}$ = 3.5 Hz, C*H*C*H*), 124.8 (s, Ph-C$_{para}$), 126.5 (d, $^3J_{CP}$ = 3.8 Hz, Ph-C$_{meta}$), 129.4 (s, Mes-C$_{meta}$), 134.4 (s, Mes-C$_{ipso}$), 135.9 (d, $^4J_{CP}$ = 1.9 Hz, Mes-C$_{ortho}$), 137.5 (d, $^2J_{CP}$ = 14.3 Hz, Ph-C$_{ortho}$), 138.4 (s, Mes-C$_{para}$), 139.4 (d, $^1J_{CP}$ = 42.0 Hz, Ph-C$_{ipso}$), 169.8 (d, $^1J_{CP}$ = 102.5 Hz, N*C*N). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −23.7 (s, *P*). $C_{27}H_{29}N_2P$ (412.52 g/mol): calcd.: 78.61, H 7.09, N 6.79; found: C 78.11, H 7.05, N 6.59. **HRMS LIFDI** (m/z): calculated for $C_{27}H_{29}N_2P$ [M$^+$]: 412.2063; found: 412.2051. **IR** (ATR[cm^{-1}]): 405 (w), 466 (m), 485 (m), 517 (w), 566 (m), 577 (s), 668 (m, ν$_{PC}$), 699 (vs, δ$_{CHoop}$), 738 (m, δ$_{CHoop}$), 850 (s, δ$_{CHoop}$), 921 (m, δ$_{CHoop}$), 1031 (w), 1038 (w), 1117 (vw, ν$_{PAr}$), 1217 (m), 1264 (w), 1290 (m), 1327 (vs), 1394 (m, δ$_{CH}$), 1437 (m, δ$_{CH}$), 1482 (s, δ$_{CH}$), 1590 (m, ν$_{CC}$), 1604 (m, ν$_{CC}$), 1990 (vw), 2151 (vw), 2206 (w), 2907 (vw, ν$_{CH}$), 2942 (vw, ν$_{CH}$), 2999 (vw, ν$_{CH}$), 3136 (w, ν$_{CH}$).

Synthesis of (Me_4Im)PPh (3): Phenyl phosphine (50 mg, 454 μmol) was added at room temperature to a solution of Me_4Im (119 mg, 954 μmol) in 10 mL of toluene and the clear solution was heated to 110 °C for 7 d. All volatiles were removed *in vacuo* and the residue was suspended in 12 mL of *n*-pentane. After filtration, the yellow solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 88 mg (379 μmol; 14%, P_nPh_n impurities) of a yellow solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 1.25 (s, 6H, C*H*$_3$), 3.02 (s, 6H, NC*H*$_3$), 6.95, 7.13 (m, 3H, aryl-*H*), 7.63 (m, 2H, aryl-*H*). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 8.4 (s, *C*H$_3$), 33.5 (d, $^3J_{CP}$ = 10.4 Hz, NCH$_3$), 122.1 (s, aryl-CH), 122.4 (d, $^1J_{CC}$ = 3.2 Hz, *C*=*C*), 127.9 (d, J_{CP} = 5.6 Hz, aryl-CH), 132.5 (d, J_{CP} = 19.0 Hz, aryl-CH), 149.6 (d, J_{CP} = 48.7 Hz, aryl-CH), 168.9 (d, $^1J_{CP}$ = 97.3 Hz, NCN). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −52.9 (s, *P*). **HRMS LIFDI** (m/z): calculated for CHNP [M$^+$]: 232.1124; found: 232.1121. **IR** (ATR[cm^{-1}]): 413 (w), 448 (m), 481 (s), 546 (w), 621 (vw), 662 (m), 695 (vs, δ$_{CH}$), 734 (vs, ν$_{PC}$), 856 (m), 990 (w), 1021 (m, ν$_{CH}$), 1064 (s), 1094 (m, ν$_{PAr}$), 1170 (m), 1209 (wδ$_{CH}$), 1364 (s, δ$_{CH}$), 1425 (m, δ$_{CH}$), 1470 (m, δ$_{CH}$), 1576 (s, ν$_{CC}$), 1651 (m, ν$_{CC}$), 1981 (w, ν$_{CC}$), 2008 (w, ν$_{CC}$), 2151 (m, ν$_{CC}$), 3048 (vw, ν$_{CH}$).

Synthesis of (Mes_2Im)PMes (4): Mesityl phosphine (50 mg, 329 μmol) was added at room temperature to a solution of Mes_2Im (210 mg, 690 μmol) in 10 mL of xylene and the clear solution was heated to 135 °C for 12 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane. After filtration, the orange solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 50 mg (110 μmol; 33%) of an orange solid. **^{1}H NMR** (400.1 MHz, THF-d_8, 298 K): δ = 2.03 (s, 6H, mesityl-C*H*$_{3para}$), 2.08 (s, 6H, mesityl-C*H*$_{3ortho}$), 2.13 (s$_{br}$, 3H, mesityl-C*H*$_{3para}$), 2.29 (s, 12H, mesityl-C*H*$_{3ortho}$), 6.34 (s, 2H, mesityl-C*H*$_{meta}$), 6.48 (s$_{br}$, 2H, mesityl-C*H*$_{meta}$), 6.66 (s, 1H, CHC*H*), 6.98 (s, 1H, CHC*H*), 7.02 (s, 2H, mesityl-C*H*$_{meta}$). **^{1}H NMR** (500.1 MHz, THF-d_8, 248 K): δ = 2.04 (s, 3H, mesityl-C*H*$_{3para}$), 2.10 (s, 6H, mesityl-C*H*$_{3ortho}$), 2.13 (s, 3H, mesityl-C*H*$_{3para}$), 2.28 (s, 12H, mesityl-C*H*$_{3ortho}$), 2.32 (s, mesityl-C*H*$_{3para}$), 6.35 (s, 2H, mesityl-C*H*$_{meta}$), 6.48 (s, 2H, mesityl-C*H*$_{meta}$), 6.72 (s, 1H, CHC*H*), 6.85 (s, 1H, CHC*H*), 7.01 (s, 2H, mesityl-C*H*$_{meta}$). **^{13}C{^{1}H} NMR** (100.6 MHz, THF-d_8, 298 K): δ = 17.7 (d, mesityl-C*H*$_{3ortho,}$ $^3J_{CP}$ = 48.5 Hz), 18.9 (s, mesityl-C*H*$_{3para}$), 21.1 (s, mesityl-CH$_{3para}$), 25.7 (s, mesityl-CH$_{3ortho}$), 124.0 (s, C*H*CH), 127.7 (s, mesityl-CH$_{meta}$), 129.5 (s, *C*HCH), 129.9 (s, mesityl-*C*H$_{meta}$), 134.8 (s$_{br}$, mesityl-C$_{para}$), 136.1 (d, $^1J_{CP}$ = 43.0 Hz, mesityl-C$_{ipso}$), 144.4 (d, *J* = 8.9 Hz, mesityl-C$_{ortho}$), 170.5 (d, $^1J_{CP}$ = 103.2 Hz, NCN). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −59.0 (s, *P*). **^{31}P NMR** (202.5 MHz, THF-d_8, 298 K): δ = −60.6 (s, *P*). **^{31}P NMR** (202.5 MHz, THF-d_8, 248 K): δ = −63.2 (s, *P*). $C_{30}H_{35}N_2P$ (454.60 g/mol): calcd.: 79.26, H 7.76, N 6.16; found: C 76.84, H 8.27, N 6.57. **HRMS LIFDI** (m/z): calculated for $C_{30}H_{35}N_2P$ [M$^+$]: 454.2532; found: 454.2519. **IR** (ATR[cm^{-1}]): 481 (s), 577 (m), 654 (m, ν$_{PC}$), 703 (vs, δ$_{CHoop}$), 805 (m), 842 (s), 919 (m), 1078 (s, ν$_{PAr}$), 1113 (s, ν$_{PAr}$), 1213 (w), 1264 (m), 1288 (s), 1321 (vs), 1390 (m, δ$_{CH}$), 1482 (m, δ$_{CH}$), 1606 (vw, ν$_{CC}$), 2004 (m), 2061 (w), 2126 (vw), 2222 (vw), 2911 (w), 3129 (w, ν$_{CH}$).

Synthesis of (Me_2Im)PMes (5): Mesityl phosphine (50 mg, 329 μmol) was added at room temperature to a solution of Me_2Im (66 mg, 690 μmol) in 10 mL of toluene and the clear solution was heated to 115 °C for 7 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane. After filtration, the yellow solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 43 mg (175 μmol; 53%) of a yellow solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 2.24 (s, 3H, mesityl-C*H*$_{3para}$), 2.67 (d, 6H, NC*H*$_3$), 2.67 (s, 6H, mesityl-C*H*$_{3ortho}$), 5.57 (s, 2H, C*H*C*H*), 6.95 (s, 2H, mesityl-C*H*$_{meta}$). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 21.2 (s, mesityl-CH$_{3para}$), 25.0 (d, $^3J_{CP}$ = 12.0 Hz, mesityl-CH$_{3ortho}$), 35.6 (d, $^3J_{CP}$ = 10.6 Hz, NCH$_3$), 118.1 (d, $^3J_{CP}$ = 3.3 Hz, *C*HCH), 134.3 (s, Mes-C$_{para}$), 138.7 (d, $^1J_{CP}$ = 44.8 Hz, Mes-C$_{ipso}$), 143.3 (d, $^2J_{CP}$ = 10.0 Hz, Mes-C$_{ortho}$), 170.4 (d, $^1J_{CP}$ = 101.2 Hz, NCN). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −73.5 (s, *P*). $C_{14}H_{19}N_2P$ (246.29 g/mol): calcd.: 68.27, H 7.78, N 11.37; found: C 62.37, H 7.57, N 14.05. **HRMS LIFDI** (m/z): calculated for $C_{14}H_{19}N_2P$ [M$^+$]: 246.12870; found: 246.1275. **IR** (ATR[cm^{-1}]): 460 (w), 475 (m), 503 (vs), 552 (m), 570 (vs), 634 (vs), 723 (s, δ$_{CH}$), 752 (m, δ$_{CHoop}$), 846 (m, δ$_{CHoop}$), 1048 (m), 1097 (s, ν$_{PAr}$), 1147 (m), 1186 (w), 1233 (m), 1329 (m, δ$_{CH}$), 1382 (m, δ$_{CH}$), 1457 (m, ν$_{CC}$), 1568 (w, ν$_{CC}$), 1602 (w, ν$_{CC}$), 1924 (vw), 1963 (vw), 2169 (w).

Synthesis of (Me_4Im)PMes (6): Mesityl phosphine (50 mg, 329 μmol) was added at room temperature to a solution of Me_4Im (86 mg, 690 μmol) in 10 mL of toluene and the clear solution was heated to 110 °C for 10 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane. After filtration, the solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 42 mg (153 μmol; 47%) of a pale yellow solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 1.25 (s, 6H, CC*H*$_3$), 2.28 (s, 3H, mesityl-C*H*$_{3para}$), 2.71 (s, 6H, mesityl-C*H*$_{3ortho}$), 2.81 (d, 6H, $^2J_{HN}$ = 0.8 Hz, NC*H*$_3$), 7.00 (m, 2H, mesityl-C*H*$_{meta}$). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 8.4 (s, *C*H$_3$), 21.3 (s, mesityl-CH$_{3para}$), 25.1 (d, $^3J_{CP}$ = 12.5 Hz, mesityl-CH$_{3ortho}$), 32.3 (d, $^3J_{CP}$ = 11.6 Hz, NCH$_3$), 120.9 (d,$^1J_{CC}$ = 3.4 Hz, CHCH), 133.6 (s, mesityl-CH), 140.5 (d, J_{CP} = 47.8 Hz, mesityl-CH), 142.6 (d, J_{CP} = 10.2 Hz, mesityl-CH), 169.5 (d, $^1J_{CP}$ = 99.6 Hz, NCN). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −74.8 (s, *P*). **IR** (ATR[cm^{-1}]): 403 (w), 450 (vs), 479 (vs), 517 (w), 564 (m), 617 (m), 636 (w, ν$_{PC}$), 699 (m, ν$_{CH}$), 725 (m, ν$_{CH}$), 829 (w, δ$_{CHoop}$), 850 (s, δ$_{CHoop}$), 1046 (s, ν$_{CH}$), 1092 (vs, ν$_{PAr}$), 1194 (vs), 1384 (m, δ$_{CH}$), 1449 (m, δ$_{CH}$), 1574 (s, ν$_{CC}$), 1651

(w), 1994 (m), 2049 (m), 2141 (s, ν_{CC}), 2194 (m, ν_{CC}), 2208 (m, ν_{CC}), 2518 (w), 2840 (w, ν_{CH}), 2875 (w, ν_{CH}), 3615 (w).

Synthesis of (*i*Pr$_2$Im)PMes (7): Mesityl phosphine (200 mg, 1.31 mmol) was added at room temperature to a solution of *i*Pr$_2$Im (420 mg, 2.76 mmol) in 10 mL of xylene and the clear solution was heated to 135 °C for 5 d. All volatiles were removed *in vacuo* and the sticky residue was washed with *n*-hexane (3×10 ml) and dried *in vacuo* to afford a sticky orange oil. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 0.90 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H*$_3$), 2.24 (s, 3H, mesityl-C*H*$_{3para}$), 2.72 (s, 6H, mesityl-C*H*$_{3ortho}$) 4.69 (dsept, 2H, $^3J_{HH}$ = 4.1 Hz, $^4J_{PH}$ = 2.6 Hz, *i*Pr-C*H*), 6.12 (s, 2H, C*H*C*H*), 6.97 (s, 2H, mesityl-C*H*$_{meta}$). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): 21.2 (s, mesityl-*C*H$_{3para}$), 21.6 (s, *i*Pr-*C*H$_3$), 25.0 (d, $^3J_{CP}$ = 12.2 Hz, mesityl-*C*H$_{3ortho}$), 49.0 (d, $^3J_{CP}$ = 11.1 Hz, *i*Pr-*C*H), 114.3 (d, $^1J_{CC}$ = 3.6 Hz, *C*HCH), 128.5 (s, mesityl-*C*H$_{meta}$), 133.7 (s, mesityl-*C*$_{para}$), 140.4 (d, $^1J_{CP}$ = 48.4 Hz, mesityl-*C*$_{ipso}$), 142.6 (d, $^2J_{CP}$ = 10.4 Hz, mesityl-*C*$_{meta}$), 168.4 (d, $^1J_{CP}$ = 105.0 Hz, *N*CN). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −79.5 (s, *P*).

Synthesis of (*i*Pr$_2$Im)PH (8): *tert*-Butyl phosphine (169 mg, 1.88 mmol) was added at room temperature to a solution of *i*Pr$_2$Im (600 mg, 3.94 mmol) in 10 mL of xylene and the clear solution was heated to 125 °C for 5 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration, the solid was washed with 8 mL of *n*-hexane and dried *in vacuo* to afford 97 mg (530 μmol; 28%) of a pale yellow solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 0.95 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H*$_3$), 2.64 (d, 1H, $^1J_{PH}$ = 166.1 Hz, P*H*), 4.49 (dsept, 2H, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 2.7 Hz, *i*Pr-C*H*), 6.09 (s, 2H, C*H*C*H*). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 21.1 (s, *i*Pr-*C*H$_3$), 48.8 (d, $^3J_{CP}$ = 7.9 Hz, *i*Pr-*C*H), 113.1 (d, $^3J_{CP}$ = 3.0 Hz, *C*HCH), 173.7 (d, $^1J_{CP}$ = 92.9 Hz, *N*CN). **^{31}P{^{1}H} NMR** (162.0 MHz, C_6D_6, 298 K): δ = −149.9 (s, *P*). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −149.9 (d, $^1J_{PH}$ = 166.1 Hz, *P*H). $C_9H_{17}N_2P$ (184.22 g/mol): calcd.: 58.68, H 9.30, N 15.21; found: C 58.67, H 9.30, N 15.02. **HRMS LIFDI** (m/z): calculated for $C_9H_{17}N_2P$ [M$^+$]: 184.1124; found: 184.1122. **IR** (ATR[cm^{-1}]): 460 (vs), 638 (s, ν_{PC}), 670 (m, δ_{CHoop}), 736 (s, δ_{CHoop}), 884 (s, ν_{PH}), 1066 (s), 1131 (m), 1174 (m), 1217 (s), 1329 (m, δ_{CH}), 1364 (s, δ_{CH}), 1408 (vs, δ_{CH}), 1464 (w), 1566 (w), 2179 (vw), 2302 (m, ν_{PH}), 2968 (m, ν_{CH}), 3070 (m, ν_{CH}).

Synthesis of (Mes$_2$Im)PH (9): *tert*-Butyl phosphine (50 mg, 555 μmol) was added at room temperature to a solution of Mes$_2$Im (355 mg, 1.17 mmol) in 10 mL of xylene and the clear solution was heated to 135 °C for 5 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration, the off-white solid was washed with 8 mL of *n*-hexane and dried *in vacuo* to afford 132 mg (392 μmol; 71%) of an off-white solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 2.07 (d, 1H, $^1J_{PH}$ = 164 Hz, P*H*), 2.09 (s, 6H, mesityl-C*H*$_{3para}$), 2.21 (s, 12H, mesityl-C*H*$_{3ortho}$), 5.92 (s, 2H, C*H*C*H*), 6.76 (s, 4H, mesityl-C*H*$_{meta}$). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 18.2 (d, $^5J_{CP}$ = 1.9 Hz, mesityl-*C*H$_{3ortho}$), 21.1 (s, mesityl-*C*H$_{3para}$), 117.7 (d, mesityl-*C*H, J_{CP} = 2.9 Hz), 129.8 (s, mesityl-*C*H$_{meta}$), 134.7 (s, mesityl-*C*H), 136.5 (s, *C*HCH), 138.9 (s, mesityl-*C*H), 176.3 (d, *N*CN, $^1J_{CP}$ = 85.4 Hz). **^{31}P{^{1}H} NMR** (162.0 MHz, C_6D_6, 298 K): δ = −147.2 (s, *P*). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −147.2 (d, $^1J_{PH}$ = 164 Hz, P*H*). $C_{21}H_{25}N_2P$ (336.42 g/mol): calcd.: 74.98, H 7.49, N 8.33; found: C 71.47, H 7.17, N 7.65. **HRMS LIFDI** (m/z): calculated for $C_{21}H_{25}N_2P$ [M$^+$]: 336.1750; found: 336.1738. **IR** (ATR[cm^{-1}]):477 (m), 501 (m), 572 (s), 603 (m), 666 (s, ν_{PC}), 697 (vs, δ_{CHoop}), 762 (m, δ_{CHoop}), 852 (vs), 872 (s), 929 (w, ν_{PH}), 1033 (m), 1099 (m), 1143 (w), 1225 (vs), 1339 (vs, δ_{CH}), 1355 (vs, δ_{CH}), 1398 (m, δ_{CH}), 1437 (m, δ_{CH}), 1484 (s, δ_{CH}), 1588 (m, ν_{CC}), 2269 (m, ν_{PH}), 2913 (vw, ν_{CH}), 2944 (vw, ν_{CH}), 3021 (vw, ν_{CH}), 3138 (vw).

Synthesis of (Me$_4$Im)PH (10): *tert*-Butylphosphine (50 mg, 555 μmol) was added at room temperature to a solution of Me$_4$Im (145 mg, 1.17 mmol) in 10 mL of toluene and was heated to 110 °C for 5 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane. After filtration, the solid was washed with 8 mL of *n*-pentane and dried *in vacuo* to afford 44 mg (282 μmol; 51%) of a colorless solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 1.26 (s, 6H, C*H*$_3$), 2.49 (d, 1H, $^1J_{PH}$ = 165 Hz, P*H*), 2.84 (s, 6H, NC*H*$_3$). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 8.4 (s, *C*H$_3$), 31.6 (d, $^3J_{CP}$ = 7.8 Hz, NCH$_3$), 120.2 (d, $^1J_{CC}$ = 3.1 Hz, *C*HCH), 174.6 (d, $^1J_{PC}$ = 88.0 Hz, *N*CN). **^{31}P{^{1}H} NMR** (162.0 MHz, C_6D_6, 298 K): δ = −149.9 (s, *P*). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −149.9 (d, $^1J_{PH}$ = 165 Hz, P*H*). $C_7H_{13}N_2P$ (156.17 g/mol): calcd.: 53.84, H 8.39, N 17.94; found: C 51.22, H 7.98, N 16.64. **HRMS LIFDI** (m/z): calculated for $C_7H_{13}N_2P$ [M$^+$]: 156.0811; found: 156.0809. **IR** (ATR[cm^{-1}]): 436 (s), 481 (m), 621 (w), 833 (w, δ_{CHoop}), 921 (m, δ_{PHoop}), 1064 (m, ν_{CH}), 1099 (s, ν_{CC}), 1164 (m), 1209 (m, δ_{CH}), 1260 (vw, δ_{CH}), 1345 (m, δ_{CH}), 1384 (vs, δ_{CH}), 1433 (m), 1457 (m), 1576 (m, ν_{CC}), 1663 (w, ν_{CC}), 2014 (vw), 2155 (vw, ν_{CC}), 2208 (vw, ν_{CC}), 2293 (m, ν_{PH}), 3019 (vw, ν_{CH}).

Synthesis of *i*Pr$_2$Im-P(O)$_2$Ph (11): A solution of (*i*Pr$_2$Im)PPh (**1**) (100 mg, 384 μmol, 1.0 eq.) in 5 mL toluene was thoroughly stirred under an atmosphere of 0.5 bar O_2 at room temperature for 1 h. The resulting solid was filtered off, washed with *n*-hexane (3×5 mL) and dried *in vacuo*. **Yield** : 61.2 mg (209 μmol, 55%) of a colorless solid. **^{1}H NMR (500.1 MHz, CD$_3$CN, 298 K)**: δ = 1.31 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 6.28 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 7.43 (d, 2H, $^4J_{HP}$ = 1.2 Hz, C*H*CH), 7.38–7.43 (m, 3H, aryl-*H*), 7.71–7.77 (m, 2H, aryl-*H*) ppm. **^{13}C{^{1}H} NMR (125.8 MHz, CD$_3$CN, 298 K)**: δ = 23.3 (*i*Pr-*C*H$_3$), 51.5 (*i*Pr-*C*H), 120.3 (d, $^3J_{CP}$ = 3.6 Hz, *C*HCH), 129.2 (d, $^2J_{CP}$ = 12.7 Hz, aryl-*C*H), 131.6 (d, $^4J_{CP}$ = 2.8 Hz, aryl-*C*H), 132,2 (d, $^3J_{CP}$ = 9.8 Hz, aryl-*C*H), 140.8 (d, $^1J_{CP}$ = 145.6 Hz, aryl-*C*P), 147.9 (d, $^1J_{CP}$ = 94.5 Hz, *N*CN) ppm. **^{31}P{^{1}H} NMR (202.5 MHz, CD$_3$CN, 298 K)**: δ = −0.8 (s) ppm. **^{31}P NMR (202.5 MHz, CD$_3$CN, 298 K)**: δ = −0.8 (t, $^3J_{PH}$ = 12.3 Hz, *P*) ppm. $C_{15}H_{21}N_2PO_2$ (292.32 g/mol): calcd.: 61.63, H 7.24, N 9.58; found: C 61.09, H 7.23, N 9.17. **HRMS LIFDI** (m/z): calculated for $C_{15}H_{21}N_2PO_2$: 292.3188; found [M+H$^+$]: 293.1413. **IR** (ATR[cm^{-1}]): 436 (m), 447 (w), 494 (m), 555 (s), 579 (s), 614 (w), 630 (w), 673 (vs), 699 (s), 743 (w), 765 (w), 787 (vw), 881 (vw), 995 (vw), 1024 (vw), 1071 (vw), 1092 (w), 1136 (w), 1158 (vw), 1173 (vw), 1201 (m), 1305 (vw), 1373 (vw), 1399 (vw), 1419 (vw), 1436 (w), 1462 (vw), 1562 (vw), 2297 (vw), 2929 (vw), 2980 (vw), 3045 (vw), 3078 (vw), 3100 (vw), 3139 (vw), 3182 (vw).

Synthesis of *i*Pr$_2$Im-P(S)$_2$Ph (12): A solution of (*i*Pr$_2$Im)PPh (**1**) (100 mg, 384 μmol) and S_8 (14.0 mg, 436 μmol) in 5 mL THF was heated for 24 h at 65 °C. The precipitate was filtered off and washed with THF (3×5 mL) and *n*-hexane (1x 5 mL). The product was dried *in vacuo* to afford 41.2 mg (126 μmol, 33%) of a light yellow solid.**^{1}H NMR (500.1 MHz, CDCl$_3$, 298 K)**: δ = 1.28 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 6.08 (sept, 2H, $^3J_{HH}$ = 6.6 Hz, *i*Pr-C*H*), 7.16 (d, 2H, $^4J_{PH}$ = 1.1 Hz, C*H*CH), 7.41–7.48 (m, 3H, aryl-*H*), 8.19–8.27 (m, 2H, aryl-*H*) ppm.**^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$, 298 K)**: δ = 23.0 (s, *i*Pr-*C*H$_3$), 51.2 (d, $^3J_{CP}$ = 1,0 Hz, *i*Pr-*C*H), 118.5 (d, $^3J_{CP}$ = 1.2 Hz, *C*HCH), 128.4 (d, $^2J_{CP}$ = 13.6 Hz, aryl-*C*H), 131.0 (d, $^4J_{CP}$ = 3.4 Hz, aryl-*C*H), 131.1 (d, $^3J_{CP}$ = 12.0 Hz, aryl-*C*H), 142.3 (d, $^1J_{CP}$ = 91.0 Hz, aryl-*C*P), 146.9 (d, $^1J_{CP}$ = 38.9 Hz, *N*CN) ppm. **^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$, 298 K)**: δ = 53.9 (s) ppm. **^{31}P NMR (202.5 MHz, CDCl$_3$, 298 K)**: δ = 53.9 (t, $^3J_{PH}$ = 14.7 Hz, *P*) ppm. $C_{15}H_{21}N_2PS_2$ (324.44 g/mol): calcd.: 55.53, H 6.52, N 8.63; found: C 55.25, H 6.72, N 8.55. **HRMS LIFDI** (m/z): calculated for $C_{15}H_{21}N_2PS_2$ [M$^+$]: 324.0884; found: 324.0878. **IR** (ATR [cm^{-1}]): 410 (vw),432 (vw), 461 (w), 524 (vs), 548 (vs), 589 (vw), 669 (vw), 702 (s), 722 (vw), 754 (w), 803 (w), 885 (m), 907 (vw), 940 (vw), 979 (vw), 1003 (vw), 1024 (vw), 1050 (m), 1067 (m), 1081 (w), 1132 (m), 1150 (vw), 1179 (w), 1213 (w), 1252 (s), 1350 (w), 1373 (vw), 1393 (vw), 1417 (vw), 1434 (vw).

Synthesis of (*i*Pr$_2$Im)Se (13): A suspension of (*i*Pr$_2$Im)PPh (**1**) (100 mg, 384 μmol) and black selenium (30.3 mg, 384 μmol) in 5 mL toluene was heated for 24 h at 85 °C. The resulting Solution was filtered off and all volatiles were removed *in vacuo*. The remaining residue was suspended in 5 mL *n*-hexane. The suspension was

filtered off, washed *n*-hexane (2×5 mL) and dried *in vacuo* to afford 38.3 mg (165 µmol, 43%) of a colorless solid. **^{1}H NMR (500.1 MHz, $CDCl_3$, 298 K)**: δ = 1.39 (d, 12H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 5.30 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-*CH*), 6.92 (s, 2H, *CHCH*) ppm.**^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 298 K)**: δ = 22.2 (s, *i*Pr-CH_3), 50.7 (s, *i*Pr-*CH*), 115.4 (s, *CHCH*), 153.5 (s, *NCN*) ppm. **^{77}Se{^{1}H} NMR (95.4 MHz, $CDCl_3$, 298 K)**: δ = −19.7 (s) ppm. $C_9H_{16}N_2Se$ (231.21 g/mol): calcd.: 46.75, H 6.98, N 12.12; found: C 49.97, H 6.16, N 8.26. **HRMS LIFDI** (m/z): calculated for $C_{15}H_{21}N_2Se$ [M$^+$]: 232.0479 found: 232.0474.

Synthesis of (*i*Pr$_2$Im)Te (14): A suspension of (*i*Pr$_2$Im)PPh (**1**) (100 mg, 384 µmol) and amorphous tellurium (75.0 mg, 588 µmol) in 5 mL toluene was heated for 24 h at 85 °C. The resulting solution was filtered and all volatiles of the filtrate were removed *in vacuo*. The remaining residue was suspended in 5 mL hexane, filtered and washed with *n*-hexane (2×5 mL) and dried *in vacuo* to afford 27.4 mg (98.0 µmol, 26%) of an off-white solid. **^{1}H NMR (500.1 MHz, C_6D_6, 298 K)**: δ = 0.93 (d, 12H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 5.45 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-*CH*), 6.26 (s, 2H, *CHCH*) ppm. **^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K)**: δ = 21.8 (s, *i*Pr-CH_3), 54.0 (s, *i*Pr-*CH*), 116.7 (s, *CHCH*), 131.5 (s, *NCN*) ppm. **^{123}Te{^{1}H} NMR (130.9 MHz, C_6D_6, 298 K)**: δ = −184.6 (s, *Te*) ppm. $C_9H_{16}N_2Te$ (279.84 g/mol): calcd.: 38.63, H 5.76, N 10.01; found: C 40.62, H 6.16, N 8.26. **HRMS LIFDI** (m/z): calculated for $C_{15}H_{21}N_2Te$ [M$^+$]: 282.0376; found: 282.03693.

Synthesis of [(W(CO)$_5$){(*i*Pr$_2$Im)PPh}] (15): $W(CO)_6$ (135 mg, 384 µmol) was suspended in THF (7 mL) and irradiated with UV light for 16 h. To this solution, (*i*Pr$_2$Im)PPh (**1**) (100 mg, 384 µmol) dissolved in THF (5 mL) was added. The reaction mixture stirred at room temperature overnight. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane. After filtration, the solid was washed with *n*-pentane (2×6 mL) and dried *in vacuo* to afford 122 mg (208 µmol; 54%) of a yellow solid. **^{1}H NMR** (400.1 MHz, C_6D_6, 298 K): δ = 0.80 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-CH_3), 4.98 (dsept, 2H, *i*Pr-*CH*), 6.00 (s, 2H, *CHCH*), 7.02 (m, 3H, aryl-*H*), 7.63 (m, 2H, aryl-*H*). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 22.2 (s, *i*Pr-CH_3), 50.9 (d, $^3J_{CP}$ = 12.9 Hz, *i*Pr-*CH*), 117.3 (d, $^1J_{CC}$ = 2.2 Hz, *CHCH*), 126.1 (d, $^4J_{CP}$ = 1.1 Hz, aryl-CH_{para}), 128.7 (d, $^3J_{CP}$ = 4.0 Hz, aryl-CH_{meta}), 135.3 (d, $^2J_{CP}$ = 15.6 Hz, aryl-CH_{ortho}), 141.0 (d, $^1J_{CP}$ = 26.3 Hz, aryl-C_{ipso}), 164.3 (d, $^1J_{CP}$ = 86.4 Hz, NCN), 200.5 (d, $^2J_{CP}$ = 4.1 Hz, *CO*). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −80.9 (m, $^1J_{PW}$ = 112.3 Hz, *P*). $C_{20}H_{21}N_2O_5PW$ (584.21 g/mol): calcd.: 41.12, H 3.62, N 4.80; found: C 40.97, H 3.16, N 4.02. **HRMS LIFDI** (m/z): calculated for $C_{20}H_{21}N_2O_5PW$ [M$^+$]: 584.0692; found: 584.0685. **IR** (ATR[cm^{-1}]): 405 (m), 438 (m), 491 (m), 579 (s), 605 (m), 691 (m), 738 (s, ν_{CH}), 801 (m, δ_{CHoop}), 1023 (w), 1131 (vw), 1194 (vw), 1207 (m), 1260 (w), 1319 (vw), 1370 (w), 1396 (w), 1431 (m), 1464 (w), 1561 (w), 1578 (w), 1810 (vs, ν_{CO}), 1833 (vs, ν_{CO}), 1855 (s, ν_{CO}), 1880 (s), 1969 (s), 1996 (m), 2051 (w, ν_{CC}), 2968 (vw), 3140 (vw, ν_{CH}), 3168 (vw, ν_{CH}).

Synthesis of [Co(CO)$_2$(NO){(*i*Pr$_2$Im)PPh}] (16): A solution of (*i*Pr$_2$Im)PPh (**1**) (224 mg, 861 µmol) in 6 mL THF was added to a pre-cooled (−78 °C) solution of [Co(CO)$_3$(NO)] (149 mg, 861 µmol) in 6 mL THF. The mixture was allowed to warm up to room temperature and the solvent was removed under vacuum. The residue was suspended in *n*-pentane and filtered and the remaining solid was washed with *n*-pentane (2×5 mL) and dried *in vacuo* to afford 144 mg (357 µmol, 42%) of a red solid.**^{1}H NMR (500.1 MHz, C_6D_6, 25 °C)**: δ = 0.81 (d, 12H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-CH_3), 5.02 (d_{sept}, 2H, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 1.35 Hz, *i*Pr-*CH*), 6.07 (d_{br}, 2H, *CHCH*), 6.59–6.99 (m, 1H, *p*-CH_{Ar}), 7.04–7.07 (m, 2H, *o*-CH_{Ar}), 7.46–7.67 (m, 2H, *m*-CH_{Ar}) ppm. **^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K)**: δ = 22.3 (*i*Pr-CH_3), 50.9 (d, $^3J_{PC}$ = 12.4 Hz, *i*Pr-*CH*), 117.6 (d, $^4J_{PC}$ = 2.24 Hz, *CHCH*), 125.5 (d, $^4J_{PC}$ = 1.24 Hz, *p*-CH_{Ar}), 128.4 (*o*-CH_{Ar}), 133.9 (d, $^3J_{PC}$ = 15.4 Hz, *m*-CH_{Ar}), 144.1 (d, $^1J_{PC}$ = 31.9 Hz, q.-C_{Ar}), 163.7 (d, $^1J_{PC}$ = 91.2 Hz, NCN), the carbonyl carbon atom were not detected. **^{31}P NMR (202 MHz, C_6D_6)** δ = −45.5 (br, *P*). $C_{17}H_{21}CoN_3O_3P$ (405.3 g/mol): calcd.: 50.38, H 5.22, N 11.97; found: C 49.55, H 5.35, N 9.93. **HRMS LIFDI** (m/z): [M]+ for $C_{17}H_{21}CoN_3O_3P$ calcd.: 405.0647, found: 405.0639. **IR (ATR):** $\tilde{\nu}$ **[cm^{-1}]** = 499 (vs), 581 (vs), 670 (m), 699 (vs), 744(vs), 801 (w), 833 (w), 1023 (m), 1066 (m), 1135 (m), 1176 (m), 1209 (s), 1374 (m), 1435 (m), 1464 (m), 1560 (m), 1576 (m), 1694 (vs, $\nu_{N=O,\ str.}$), 1925 (vs, $\nu_{C\equiv O\ str.(B1)}$), 1992 (vs, $\nu_{C\equiv O,\ str.(A1)}$), 2873 (w, $\nu_{C\text{-}H,\ str.}$), 2934 (w, $\nu_{C\text{-}H,\ str.}$), 2981 (m, $\nu_{C\text{-}H,\ str.}$), 3059 (w, $\nu_{C\text{-}H,\ str.}$), 3144 (w, $\nu_{C\text{-}H,\ str.}$), 3171 (w, $\nu_{C\text{-}H,\ str.}$).

Synthesis of [(η^5-C_5Me_5)Co(C_2H_4){*i*Pr$_2$Im)PPh}] (17): (*i*Pr$_2$Im)PPh (**1**) (157 mg, 599 µmol) was added to a solution of [(η^5-C_5Me_5)Co(C_2H_4)$_2$] (150 mg, 599 µmol) in 15 mL toluene at room temperature and the mixture was stirred for additional 16 h. Immediately the formation of gaseous C_2H_4 and a color change to red was observed. The solvent was removed and the residue was suspended in 5 mL *n*-pentane, filtered off and washed with *n*-pentan (2×5 mL) and dried *in vacuo* to afford 98.3 mg (203.7 µmol, 34%) of a dark brown solid.**^{1}H NMR (500.1 MHz, C_6D_6, 298 K)**: δ = 0.71 (d_{br}, 2H, η^2-C_2H_4), 0.95 (d, 12H, $^3J_{HH}$ = 6.59 Hz, *i*Pr-CH_3), 1.37 (d, 2H, $^3J_{HH}$ = 8.08 Hz, η^2-C_2H_4), 1.93 (s, 15 H, η^5-$C_5(CH_3)_5$), 4.57 (sept, 2H, $^3J_{HH}$ = 5.80 Hz, *i*Pr-*CH*), 6.04 (d_{br}, 2H, *CHCH*), 7.05–7.09 (m, 1H, *p*-CH_{Ar}.), 7.19–7.23 (m, 2H, *m*-CH_{Ar}.), 8.30–8.33 (m, 2H, *o*-CH_{Ar}.) ppm. **^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C)**: δ = 9.88 (d, $^3J_{PC}$ = 5.07 Hz, η^5-$C_5(CH_3)_5$), 22.5 (*i*Pr-CH_3), 28.2 (η^2-C_2H_4), 49.1 (d, $^2J_{PC}$ = 12.7 Hz, *i*Pr-*CH*), 87.9 (d, $^2J_{PC}$ = 3.02 Hz, η^5-C_5Me_5), 116.3 (d, $^3J_{PC}$ = 2.73 Hz,*CHCH*), 125.5 (d, $^4J_{PC}$ = 0.9 Hz, *p*-CH_{Ar}.), 127.6 (d, $^3J_{PC}$ = 3.24 Hz, *m*-CH_{Ar}.), 136.4 (d, $^2J_{PC}$ = 14.6 Hz, *o*-CH_{Ar}.), 142.3 (d, $^1J_{PC}$ = 33.2 Hz, *q*-C_{Ar}.), 163.7 (d, $^1J_{PC}$ = 98.5 Hz, NCN). **^{31}P NMR (202 MHz, C_6D_6)** δ = 25.8 (br, *P*). $C_{27}H_{40}CoN_2P$ (482.53 g/mol): calcd.: 67.21, H 8.36, N 5.81; found: C 66.55, H 8.31, N 5.36. **HRMS LIFDI** (m/z): [M]+ for $C_{27}H_{40}CoN_2P$ calcd.: 482.2246, found: 482.2256.

Synthesis of [Ni(*i*Pr$_2$Im)$_2$(η^2-PhP=PPh)] (18): [Ni(COD)$_2$] (80 mg, 291 µmol) and (*i*Pr$_2$Im)PPh (**1**) (151 mg, 580 µmol) were dissolved in 9 mL of toluene at room temperature. The reaction mixture was stirred at room temperature for 2 d and additionally for 1 d at 80 °C. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration, the solid was washed with 7 mL of *n*-hexane and dried *in vacuo* to afford 76 mg (131 µmol; 45%) of a brown solid. **^{1}H NMR** (400.1 MHz, Toluol-d_8, 298 K): δ = 0.49 (s_{br}, 6H, *i*Pr-CH_3), 0.86 (s_{br}, 6H, *i*Pr-CH_3), 1.02 (s_{br}, 6H, *i*Pr-CH_3), 1.57 (s_{br}, 6H, *i*Pr-CH_3), 4.68 (s_{br}, 2H, *i*Pr-*CH*), 5.64 (s_{br}, 2H, *i*Pr-*CH*), 6.40 (s_{br}, 4H, *CHCH*), 6.85–6.93 (m, 4H, aryl-*CH*), 7.59–7.64 (m, 4H, aryl-*CH*). **^{1}H NMR** (500.1 MHz, Toluol-d_8, 248 K): δ = 0.47 (d, 6H, *i*Pr-CH_3), 0.89 (d, 6H, *i*Pr-CH_3), 0.95 (d, 6H, *i*Pr-CH_3), 1.57 (d, 6H, *i*Pr-CH_3), 4.77 (m, 2H, *i*Pr-*CH*), 5.66 (m, 2H, *i*Pr-*CH*), 6.28 (s, 2H, *CHCH*), 6.36 (s, 2H, *CHCH*), 6.92–6.96 (m, 4H, aryl-*CH*), 7.04–7.06 (m, 2H, aryl-*CH*), 7.67–7.69 (m, 4H, aryl-*CH*). **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6, 298 K): δ = 22.7 (s_{br}, *i*Pr-CH_3), 24.9 (s_{br}, *i*Pr-CH_3), 51.3 (s_{br}, *i*Pr-*CH*), 52.2 (s_{br}, *i*Pr-*CH*), 116.4 (s_{br}, *CHCH*), 124.0 (s, aryl-CH_{para}), 127.5 (t, aryl-CH_{meta}), 134.0 (t, N = $|^2J_{CP} + {}^3J_{CP}|$ = 26.0 Hz), 148.5 (t, N = $|^1J_{CP} + {}^2J_{CP}|$ = 37.0 Hz, aryl-C_{ipso}), 193.9 (t, $^2J_{CP}$ = 8.3 Hz). **^{31}P NMR** (162.0 MHz, C_6D_6, 298 K): δ = −40.9 (s, *P*). **^{31}P NMR** (162.0 MHz, Toluol-d_8, 298 K): δ = −42.9 (s, *P*). $C_{30}H_{42}N_4P_2Ni$ (579.33 g/mol): calcd.: 62.20, H 7.31, N 9.67; found: C 62.41, H 7.68, N 9.63. **HRMS LIFDI** (m/z): calculated for $C_{30}H_{42}N_4P_2Ni$ [M$^+$]: 578.2233; found: 578.2221. **IR** (ATR[cm^{-1}]): 477 (m), 536 (vw), 570 (vw), 674 (m), 689 (s), 734 (s), 791 (w, δ_{CHoop}), 878 (w, δ_{CHoop}), 1019 (m, δ_{CHip}), 1129 (w), 1211 (vs), 1286 (m), 1366 (m), 1402 (m), 1464 (m), 1574 (m), 1928 (w), 1981 (w), 2022 (w), 2079 (w), 2157 (m), 2179 (w), 2247 (w), 2308 (vw), 2964 (m, ν_{CH}), 2974 (m, ν_{CH}), 3042 (vw, ν_{CH}).

Crystallographic Details

Crystals were immersed in a film of perfluoropolyether oil on a nylon fiber and transferred to a Bruker D8 Apex-1 diffractometer with CCD area detector and graphite-monochromated Mo-K_α radiation or a Bruker D8 Apex-2 diffractometer with CCD area

Table 3. Crystal data collection and processing parameter for the molecular structure determination of the compounds **6**, **8**, **12** and **14**.

Chemical formula	(Me$_4$Im)PMes (**6**) $C_{16}H_{23}N_2P$	(*i*Pr$_2$Im)PH (**8**) $C_9H_{17}N_2P$	(*i*Pr$_2$Im)PS$_2$Ph (**12**) $C_{19}H_{29}N_2POS_2$	(*i*Pr$_2$Im)Te (**14**) $C_9H_{16}N_2Te$
Mass [g mol^{-1}]	274.33	184.21	396.53	279.84
Temperature [K]	100(2)	100(2)	100.00(10)	100(2)
Wavelength [Å]	0.71073	0.71073	1.54184	1.54184
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	C_c	$P2_12_12_1$	$P2_1/c$	P1
a [Å]	9.642(3)	8.491(2)	7.99220(10)	7.5231(4)
b [Å]	13.032(3)	11.146(3)	15.19500(10)	10.7141(5)
c [Å]	12.156(3)	11.794(3)	17.31640(10)	14.6650(8)
α [°]	90	90	90	83.973(4)
β [°]	97.963	90	94.0170(10)	75.485(4)
γ [°]	90	90	90	81.3058(4)
Volume [Å^3]	1512.7(7)	1116.2(5)	2097.76(3)	1128.39(10)
Z	4	4	4	4
Density [g cm^{-3}]	1.205	1.096	1.256	1.647
Abs. coeff. [mm^{-1}]	0.171	0.202	3.088	20.442
F (000)	592	400	848	544
Theta range θ [°]	2.644–26.738	2.514–26.825	2.9040–76.7090	3.120–77.508
Refl. collected	5893	10509	22314	23066
Indep. reflections	2319	2402	4281	4713
Refl. [$I > 2\sigma$(I)]	2212	2134	3973	4260
R_{int}	0.0296	0.0413	0.0370	0.0604
Data	2319	2402	4281	4713
Restraints	2	0	363	0
Parameter	179	118	306	225
*R*1/*wR*2 for [$I > 2\sigma$(I)]	0.0289/0.0693	0.0438/0.1039	0.0304/0.0796	0.0405/0.1102
*R*1/*wR*2 (all data)	0.0315/0.0706	0.0517/0.1071	0.0327/0.0812	0.0442/0.1133
diff. peak/hole [eÅ^{-3}]	0.235/−0.199	0.982/−0.218	0.367/−0.296	1.598/−1.055
GooF	1.046	1.064	1.044	1.113
CCDC	2041355	2041356	2041357	2041358

detector and graphite-monochromated Mo-K_α radiation equipped with an Oxford Cryosystems low-temperature device or a Rigaku XtaLAB Synergy-DW diffractometer with HyPix-6000HE detector and monochromated Cu-K_α equipped with an Oxford Cryo 800 cooling unit. Data were collected at 100 K. The images were processed with the Bruker or Crysalis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.[45] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were usually assigned to idealized positions and were included in structure factors calculations. Crystal data collection and processing parameter are given in Table 3. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 2041355 (**6**), CCDC 2041356 (**8**), CCDC 2041357 (**12**), CCDC 2041358 (**14**).

Computational Details

Calculations have been performed using the TURBOMOLE V7.2 program suite, a development of University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.[46] Geometry optimizations were performed using (RI-)DFT calculations[47] on a m4 grid employing the BP86[48] functional and a def2-TZVP basis set for titanium and for all other atoms the def2-TZVP basis sets.[49] Vibrational frequencies were calculated at the same level with the AOFORCE[50] module and all structures represented true minima without imaginary frequencies. Cartesian coordinates of the compounds are provided in the SI.

Acknowledgments

This work was supported by the Julius-Maximilians-University Würzburg. Open access funding enabled and organized by Projekt DEAL.

Keywords: *N*-Heterocyclic Carbenes · Phosphinidenes · Dehydrocoupling · Transition Metal Complexes

[1] a) U. Schmidt, *Angew. Chem.* **1975**, *87*, 535–540; *Angew. Chem. Int. Ed.* **1975**, *14*, 523–528; b) F. Mathey, *Dalton Trans.* **2007**, *19*, 1861–1868.
[2] a) F. Mathey, *Angew. Chem.* **1987**, *99*, 285–296; *Angew. Chem. Int. Ed.* **1987**, *26*, 275–286; b) H. Aktas, J. C. Slootweg, K. Lammertsma, *Angew. Chem.* **2010**, *122*, 2148–2159; *Angew. Chem. Int. Ed.* **2010**, *49*, 2102–2113; c) F. Mathey, N. Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *17*, 2938–2957; d) M. Vlaar, K. Lammertsma, *Eur. J. Org. Chem.* **2002**, *7*, 1127–1138; e) A. H. Cowley, *Acc. Chem. Res.* **1997**, *30*, 445–451.
[3] a) T. Krachko, J. C. Slootweg, *Eur. J. Inorg. Chem.* **2018**, *24*, 2734–2754; b) A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**,

119, 6994–7112; c) R. R. Rodrigues, C. L. Dorsey, C. A. Arceneaux, T. W. Hudnall, *Chem. Commun.* **2014**, *50*, 162–164; d) K. Schwedtmann, G. Zanoni, J. J. Weigand, *Chem. Asian J.* **2018**, *13*, 1388–1405; e) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678.

[4] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485; b) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667–668; c) D. Rottschäfer, B. Neumann, H.-G. Stammler, D. M. Andrada, R. S. Ghadwal, *J. Org. Chem.* **2020**, *85*, 14351–14359.

[5] a) P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *J. Chem. Soc. Chem. Commun.* **1987**, 1282–1283; b) R. Bohra, P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *Polyhedron* **1989**, *8*, 1884.

[6] a) Z. Hou, T. L. Breen, D. W. Stephan, *Organometallics* **1993**, *12*, 3158–3167; b) Z. Hou, D. W. Stephan, *J. Am. Chem. Soc.* **1992**, *114*, 10088–10089; c) J. Ho, Z. Hou, J. Drake, D. W. Stephan, *Organometallics* **1993**, *12*, 3145–3157; d) J. Ho, D. W. Stephan, *Organometallics* **1991**, *10*, 3001–3003.

[7] a) J. Ho, R. Rousseau, D. W. Stephan, *Organometallics* **1994**, *13*, 1918–1926; b) T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921.

[8] D. S. J. Arney, R. C. Schnabel, B. C. Scott, C. J. Burns, *J. Am. Chem. Soc.* **1996**, *118*, 6780–6781.

[9] a) A. T. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2002**, *21*, 3196–3202; b) A. T. Termaten, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2003**, *9*, 3577–3582.

[10] A. Schmidpeter, W. Gebler, F. Zwaschka, W. S. Sheldrick, *Angew. Chem.* **1980**, *92*, 767–768; *Angew. Chem. Int. Ed.* **1980**, *19*, 722–723.

[11] a) A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riedel, *Inorg. Chem.* **1997**, *36*, 2151–2158; b) A. J. Arduengo, H. V. R. Dias, J. C. Calabrese, *Chem. Lett.* **1997**, *26*, 143–144.

[12] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011–3015; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943.

[13] N. Hayakawa, K. Sadamori, S. Tsujimoto, M. Hatanaka, T. Wakabayashi, T. Matsuo, *Angew. Chem.* **2017**, *129*, 5859–5863; *Angew. Chem. Int. Ed.* **2017**, *56*, 5765–5769.

[14] A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem.* **2014**, *126*, 13786–13790; *Angew. Chem. Int. Ed.* **2014**, *53*, 13568–13572.

[15] M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2016**, *2016*, 649–658.

[16] a) D. Heift, Z. Benko, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 5920–5928; b) Z. Li, X. Chen, Y. Li, C.-Y. Su, H. Grützmacher, *Chem. Commun.* **2016**, *52*, 11343–11346.

[17] F. E. Hahn, D. Le Van, M. C. Moyes, T. von Fehren, R. Fröhlich, E. U. Würthwein, *Angew. Chem.* **2001**, *113*, 3241–3244; *Angew. Chem. Int. Ed.* **2001**, *40*, 3144–3148.

[18] A. K. Adhikari, T. Grell, P. Lönnecke, E. Hey-Hawkins, *Eur. J. Inorg. Chem.* **2016**, *2016*, 620–622.

[19] a) D. Schmidt, J. H. J. Berthel, S. Pietsch, U. Radius, *Angew. Chem.* **2012**, *124*, 9011–9015; *Angew. Chem. Int. Ed.* **2012**, *51*, 8881–8885; b) H. Schneider, D. Schmidt, U. Radius, *Chem. Commun.* **2015**, *51*, 10138–10141; c) S. Würtemberger-Pietsch, H. Schneider, T. B. Marder, U. Radius, *Chem. Eur. J.* **2016**, *22*, 13032–13036; d) H. Schneider, M. J. Krahfuß, U. Radius, *Z. Anorg. Allg. Chem.* **2016**, *642*, 1282–1286; e) H. Schneider, A. Hock, R. Bertermann, U. Radius, *Chem. Eur. J.* **2017**, *23*, 12387–12398; f) H. Schneider, A. Hock, A. D. Jaeger, D. Lentz, U. Radius, *Eur. J. Inorg. Chem.* **2018**, *2018*, 4031–4043; g) A. Hock, H. Schneider, M. J. Krahfuß, U. Radius, *Z. Anorg. Allg. Chem.* **2018**, *644*, 1243–1251; h) A. Hock, L. Werner, M. Riethmann, U. Radius, *Eur. J. Inorg. Chem.* **2020**, DOI: 10.1002/ejic.202000720; i) A. Hock, L. Werner, C. Luz, U. Radius, *Dalton Trans.* **2020**, *32*, 11108–11119.

[20] a) H. Schneider, D. Schmidt, U. Radius, *Chem. Eur. J.* **2015**, *21*, 2793–2797; b) S. Pietsch, U. Paul, I. A. Cade, M. J. Ingleson, U. Radius, T. B. Marder, *Chem. Eur. J.* **2015**, *21*, 9018–9021; c) S. Würtemberger-Pietsch, U. Radius, T. B. Marder, *Dalton* **2016**, *45*, 5880–5895; d) M. Eck, S. Würtemberger-Pietsch, A. Eichhorn, J. H. J. Berthel, R. Bertermann, U. S. D. Paul, H. Schneider, A. Friedrich, C. Kleeberg, U. Radius, T. B. Marder, *Dalton* **2017**, *46*, 3661–3680; e) A. F. Eichhorn, S. Fuchs, M. Flock, T. B. Marder, U. Radius, *Angew. Chem.* **2017**, *129*, 10343–10347; *Angew. Chem. Int. Ed.* **2017**, *56*, 10209–10213; f) U. S. D. Paul, U. Radius, *Eur. J. Inorg. Chem.* **2017**, 3362–3375; g) A. F. Eichhorn, L. Kuehn, T. B. Marder, U. Radius, *Chem. Commun.* **2017**, *53*, 11694–11696; h) L. Kuehn, M. Stang, S. Würtemberger-Pietsch, A. Friedrich, H. Schneider, U. Radius, T. B. Marder, *Faraday Discuss.* **2019**, *220*, 350–363; i) J. Lorkowski, M. Krahfuß, M. Kubicki, U. Radius, C. Pietraszuk, *Chem. Eur. J.* **2019**, *25*, 11365–11374.

[21] K. Pal, O. B. Hemming, B. M. Day, T. Pugh, D. J. Evans, R. A. Layfield, *Angew. Chem.* **2016**, *128*, 1722–1725; *Angew. Chem. Int. Ed.* **2016**, *55*, 1690–1693.

[22] K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 11795–11798.

[23] A. M. Tondreau, Z. Benkö, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545–1554.

[24] M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2016**, *2016*, 649–658.

[25] M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. A. Faradji, P. G. Pringle, *Dalton Trans.* **2016**, *45*, 5999–6003.

[26] a) O. Lemp, M. Balmer, K. Reiter, F. Weigend, C. von Hänisch, *Chem. Commun.* **2017**, *53*, 7620–7623; b) M. Balmer, Y. J. Franzke, F. Weigend, C. von Hänisch, *Chem. Eur. J.* **2020**, *26*, 192–197.

[27] D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2017**, *2017*, 3452–3458.

[28] K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* **2015**, 2416–2425.

[29] a) N. Kuhn, R. Fawzi, T. Kratz, M. Steinmann, G. Henkel, *Phosphorus Sulfur Silicon Relat. Elem.* **2006**, *108*, 107–119; b) N. Kuhn, G. Henkel, T. Kratz, *Chem. Ber.* **1993**, *126*, 2047–2049.

[30] a) G. P. Junor, J. Lorkowski, C. M. Weinstein, R. Jazzar, C. Pietraszuk, G. Bertrand, *Angew. Chem.* **2020**, *132*, 22212–22217; *Angew. Chem. Int. Ed.* **2020**, *59*, 22028–22033; b) A. Merschel, D. Rottschäfer, B. Neumann, H.-G. Stammler, R. S. Ghadwal, *Organometallics* **2020**, *39*, 1719–1729.

[31] T. G. Larocque, G. G. Lavoie, *New J. Chem.* **2014**, *38*, 499–502.

[32] A. Doddi, D. Bockfeld, A. Nasr, T. Bannenberg, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2015**, *21*, 16178–16189.

[33] D. Bockfeld, A. Doddi, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2016**, 3704–3713.

[34] R. Job, J. Rovang, *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 367–371.

[35] a) F. Hering, J. H. J. Berthel, K. Lubitz, U. S. D. Paul, H. Schneider, M. Härterich, U. Radius, *Organometallics* **2016**, *35*, 2806–2821; b) K. Lubitz, V. Sharma, S. Shukla, J. H. J. Berthel, H. Schneider, C. Hoßbach, U. Radius, *Organometallics* **2018**, *37*, 1181–1191.

[36] a) S. Dürr, B. Zarzycki, D. Ertler, I. Ivanović-Burmazović, U. Radius, *Organometallics* **2012**, *31*, 1730–1742; b) S. Dürr, D. Ertler, U. Radius, *Inorg. Chem.* **2012**, *51*, 3904–3909; c) B. Zarzycki, F. M. Bickelhaupt, U. Radius *Dalton* **2013**, *42*, 7468–7481; d) K. Lubitz, U. Radius, *Organometallics* **2019**, *38*, 2558–2572.

[37] a) H. Aktas, J. C. Slootweg, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2009**, *131*, 6666–6667; b) A. T. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2003**, *9*, 2200–2208.
[38] a) A. T. Arjan, H. Aktas, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2003**, *22*, 1827–1834; b) A. Doddi, D. Bockfeld, T. Bannenberg, M. Tamm, *Chem. Eur. J.* **2020**, *26*, 14878–14887; c) M. Peters, A. Doddi, T. Bannenberg, M. Freytag, P. G. Jones, M. Tamm, *Inorg. Chem.* **2017**, *56*, 10785–10793.
[39] see for example: a) J. Zhou, M. W. Kuntze-Fechner, R. Bertermann, U. S. D. Paul, J. H. J. Berthel, A. Friedrich, Z. Du, T. B. Marder, U. Radius, *J. Am. Chem. Soc.* **2016**, *138*, 5250–5253; b) Y.-M. Tian, X.-N. Guo, M. W. Kuntze-Fechner, I. Krummenacher, H. Braunschweig, U. Radius, A. Steffen, T. B. Marder, *J. Am. Chem. Soc.* **2018**, *140*, 17612–17623; c) U. S. D. Paul, C. Sieck, M. Hähnel, K. Hammond, T. B. Marder, U. Radius, *Chem. Eur. J.* **2016**, *22*, 11005–11014; d) U. S. D. Paul, U. Radius, *Chem. Eur. J.* **2017**, *23*, 3993–4009; e) U. S. D. Paul, U. Radius, *Organometallics* **2017**, *36*, 1398–1407; f) J. H. J. Berthel, L. Tendera, M. W. Kuntze-Fechner, L. Kuehn, U. Radius, *Eur. J. Inorg. Chem.* **2019**, 3061–3072; g) L. Kuehn, D. G. Jammal, K. Lubitz, T. B. Marder, U. Radius, *Chem. Eur. J.* **2019**, *25*, 9514–9521.
[40] G. Hierlmeier, A. Hinz, R. Wolf, J. M. Goicochea, *Angew. Chem. Int. Ed.* **2018**, *57*, 431–436; *Angew. Chem.* **2018**, *130*, 439–444.
[41] S. Gómez-Ruiz, E. Hey-Hawkins, *Dalton* **2007**, 5678–5683.
[42] a) T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *25*, 4196–4206; b) T. Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss, *Inorg. Synth.* **2011**, *35*, 78–83.
[43] A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
[44] G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
[45] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2014**, *70*, C1437.
[46] a) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. T. Weigend, *Mol. Sci.* **2014**, *4*, 91–100; b) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169.
[47] a) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354; b) M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104–111.
[48] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) J. Perdew, *Phys. Rev. B* **1986**, *34*.
[49] a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835; c) K. Eichkorn, O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652–660; d) F. Weigend, R. Ahlrichs, *Physical Chemistry Chemical Physsics* **2005**, *7*, 3297–3305; e) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.
[50] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103–107.

Manuscript received: October 30, 2020
Revised manuscript received: December 14, 2020
Accepted manuscript online: December 14, 2020

