

localized on the para than on the ortho carbon atoms of the ring. Hence, the LUMO is a metal-carbyne π antibond, largely localized on the ring and isolated in energy from the HOMO and from the next lowest unoccupied molecular orbital. If this is also true about the real osmium compound, the reported addition of nucleophile H^- to the para position of the ring may well be frontier rather than charge controlled.⁶³

Acknowledgment. We are grateful to Dr. Ulrich Schubert of the Technische Universität, München, West

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Germany, for preprints of articles and for a useful suggestion. This research was supported by the National Science Foundation (Grant CHE 7517744). N.M.K. has been a Fulbright Fellow since 1978 and is a Procter and Gamble Fellow for 1981-1982.

Registry No. *trans*-BrCr(CO)₄CMe, 51005-78-8; *trans*-BrCr(CO)₄CPh, 50701-13-8; *trans*-BrCr(CO)₄CNET₂, 57091-06-2; *trans*-ClCr(CO)₄CMe, 62938-49-2; *trans*-ICr(CO)₄CMe, 50701-14-9; *trans*-PMe₃Cr(CO)₄CMe⁺, 54460-85-4; *trans*-ClCr(CO)₄CPh, 68851-67-2; *trans*-ICr(CO)₄CPh, 50938-50-6; *mer*-BrCr(CO)₃(PMe₃)CMe, 52175-60-7; *cis*-BrCr(CO)₂(CNMe)₂CPh, 79992-51-1; *trans*-BrCr(CO)₂(CNMe)₂CPh, 800-37-5; *cis*-BrCr(CO)₂[P(OH)₃]₂CPh, 80028-17-7; *trans*-BrCr(CO)₂[P(OH)₃]₂CPh, 80080-80-4; *trans*(PH₃)-(PH₃)₂(CO)₂FeCPh⁺, 79992-52-2.

Synthesis and Molecular Structure of C₅H₅(P-*i*-Pr₃)Pd(η^1, η^3 -C₃H₄)Pd(P-*i*-Pr₃)Br: A Compound Formed through Insertion of Allene into a Metal-Metal Bond¹

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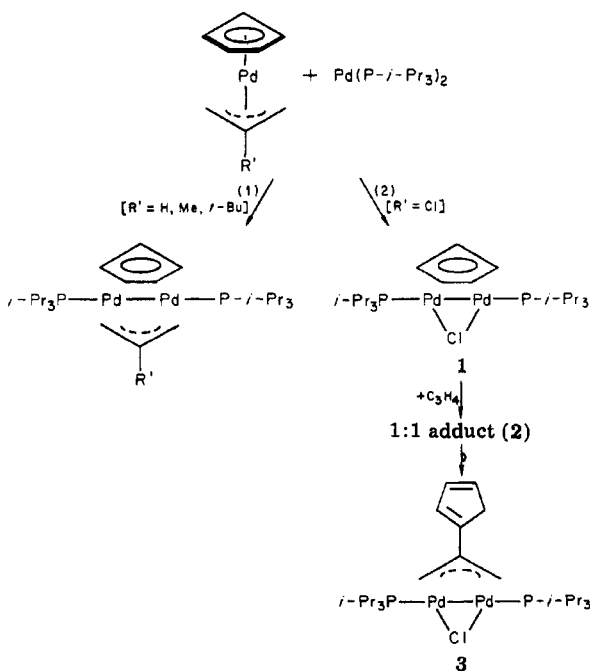
Received October 8, 1981

The reaction of $(\mu\text{-C}_5\text{H}_5)(\mu\text{-Br})\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2$ (4) with allene leads to a 1:1 adduct C₅H₅(P-*i*-Pr₃)Pd(η^1, η^3 -C₃H₄)Pd(P-*i*-Pr₃)Br (5) which has been characterized by elemental analysis, mass spectroscopy, NMR spectroscopy, and single-crystal X-ray investigations. The compound crystallizes in the space group C2/c with $a = 25.179$ (9) Å, $b = 17.173$ (8) Å, $c = 16.065$ (9) Å, $\beta = 91.86$ (4)°, and $V = 6943$ (6) Å³. Full-matrix least-squares refinement gave final discrepancy factors $R_1 = 0.064$ and $R_2 = 0.078$. The molecule contains a bridging allyl group which is (in 2-position) σ bonded to Pd(P-*i*-Pr₃)(η^5 -C₅H₅) and π bonded to Pd(P-*i*-Pr₃)Br. The Pd-Pd distance is 3.58 Å (almost 1 Å longer than in 4) indicating that the formation of 5 from 4 involves a real insertion of allene into the Pd-Pd bond. The structure of the previously described 1:1 adduct prepared from $(\mu\text{-C}_5\text{H}_5)(\mu\text{-Cl})\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2$ and allene is shown to be almost identical with that of 5.

There is much current interest in the chemistry of binuclear transition-metal compounds which may serve to activate small molecules such as CO, C₂H₂, C₂H₄, etc.² Recently, we have investigated the synthesis and reactivity of a new class of palladium and platinum complexes of the general composition $(\mu\text{-X})(\mu\text{-Y})\text{M}_2\text{L}_2$ in which the bridging ligands X and Y are C₅H₅, 2-R'C₃H₄, RCOO, SR, Cl etc. and L is a two-electron donor such as PR₃, P(OR)₃, or AsR₃.³ The most general route for the preparation of these complexes involves the reaction of (X)M(Y) (sometimes only stable as a dimer) with the coordinatively unsaturated compounds ML₂ (e.g., M(P-*i*-Pr₃)₂, M(P-*c*-Hx₃)₂, etc.) or suitable precursors (L')ML₂ where L', for example, is a substituted olefin.⁴

During our investigations of the synthesis of the complexes $(\mu\text{-X})(\mu\text{-Y})\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2$ with X = C₅H₅ and Y = 2-R'C₃H₄ from C₅H₅Pd(2-R'C₃H₄) and Pd(P-*i*-Pr₃)₂, we observed⁵ that for R' = H, Me, or *t*-Bu the expected product (C₅H₅)(2-R'C₃H₄)Pd₂(P-*i*-Pr₃)₂ is formed (eq 1) whereas for R' = Cl the corresponding compound 1 containing chloride rather than 2-chloroallyl as the bridging

ligand is obtained (eq 2). An alternative route to the complex 1 has been described by Felkin and Turner, who used C₅H₅Pd(P-*i*-Pr₃)Cl and Mg as starting material.⁶



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Table I. 1H NMR Data of 2 (X = Cl) and 5 (X = Br), in C_6D_6 ^a

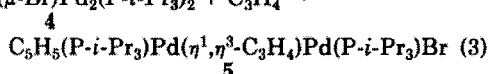
protons	2			5		
	δ	$J(PH)$	$J(H^1H^4)$	δ	$J(PH)$	$J(H^1H^4)$
C_5H_5	5.98 (d)	1.5		5.93 (d)	1.4	
H^1	5.27 (dd)	5.5	2.5	5.30 (dd)	5.6	2.6
H^2	4.17 (d)	8.0		4.15 (d)	9.0	
H^3	2.73 (b s)			2.80 (b s)		
H^4	3.55 (d)		2.5	3.70 (d)		2.6
PCH ^b	2.30 (m)			2.30 (m)		
$CHCH_3$ ^b	1.77 (m)			1.77 (m)		
	1.30 (m)			1.30 (m)		
	1.02 (m)			1.02 (m)		

^a δ in parts per million from Me₄Si (internal standard); J in hertz. ^b Due to the coordination to two different Pd atoms, the phosphine ligands are different and thus two signals for the PCH and two for the $CHCH_3$ protons are observed.

The observation that a freshly prepared solution containing the allene and compound 1 in benzene further reacts to give a new binuclear complex 2, which on warming isomerizes to form the substituted μ -allyl complex 3⁶ prompted us to study the reactivity of 1 and its analogues toward allene in more detail. In this paper we report the preparation of the bromide derivative of 2 and the X-ray structure of this compound which proves that its formation from $(C_5H_5)(Br)Pd_2(P-i-Pr_3)_2$ ⁶ involves a real insertion of allene into the Pd-Pd bond.

Results

The reaction of $(C_5H_5)(Br)Pd_2(P-i-Pr_3)_2$ (4) with allene



in toluene at room temperature leads to an orange-red solution which, on addition of pentane, afforded orange-red crystals. Elemental analysis and the mass spectrum indicated that the composition of the product 5 formally corresponds to a 1:1 adduct of 4 and allene; i.e., two palladium atoms are still present. The 1H NMR spectrum is characteristic of a complex containing an unsymmetrical π -bonded allylic ligand as found in $2-R'C_3H_4Pd(PR_3)_2X$ with X = halogen, alkyl, etc.⁷ The four allylic protons give rise to four different signals which not only have different chemical shifts but also have different P-H coupling constants. It has been proved by selective decoupling experiments that the P-H coupling of the cyclopentadienyl protons and of the allylic protons are due to two non-equivalent phosphorus atoms. From the 1H NMR data (Table I) there is no doubt that the structures of 5 and of the previously described compound 2⁵ are almost identical.

Crystal Data and Structure Determination of 5. Crystals of 5 which have been obtained from toluene/pentane are monoclinic with $a = 25.179$ (9) Å, $b = 17.173$ (8) Å, $c = 16.065$ (9) Å, $\beta = 91.86$ (4)°, and $V = 6943$ (6) Å³. The cell constants resulted from least-squares calculation using 15 strong reflections of the crystal in the range $24^\circ < 2\theta < 26^\circ$. The crystal was ground into a sphere of about 0.2-mm diameter. The space group is $C2/c$ ($Z = 8$) and the density $\rho(\text{pyk}) = 1.42$ g/cm³ and $\rho(\text{calcd}) = 1.37$ g/cm³.

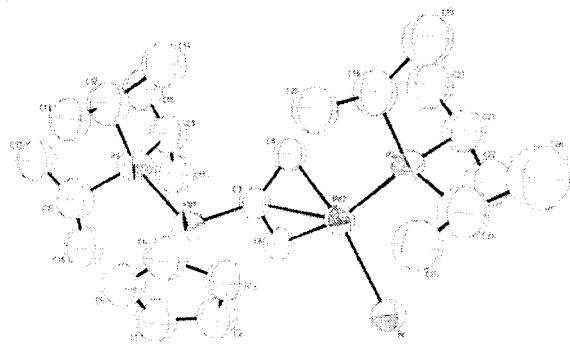


Figure 1. The molecular structure of $C_5H_5(P-i-Pr_3)Pd(\eta^1, \eta^3-C_3H_4)Pd(P-i-Pr_3)Br$ (5).

Intensity data were collected on a Syntex-P2₁ four circle automatic diffractometer using MoK α radiation (graphite monochromator, $\lambda = 0.71069$ Å, ω scan, $\Delta\omega = 1^\circ$) with 1720 symmetrically independent reflections measured in the range of $2^\circ < 2\theta < 35^\circ$. Corrections for absorption and extinction were not applied ($\mu_{Mo} = 2.34$ mm⁻¹). The heavy-atom part of the structure could be solved by direct methods (program SHELX⁸). Positions of the remaining atoms (except hydrogen) were located from Fourier and difference Fourier maps. Refinement of the atomic parameters by full-matrix least squares gave the final discrepancy factors $R_1 = 0.064$ and $R_2 = 0.078$ for 1720 reflections. All reflections were given unit weight. These calculations were carried out by means of the XTL program package⁹ on a NOVA 1200 minicomputer with structure factors for uncharged atoms as given in ref 10, corrected for anomalous dispersion. As the data set was limited (due to radiation damage) only Pd, Br, and P atoms were treated anisotropically, thus limiting the number of free variables to 150.

In the final difference Fourier map the maxima were smaller than 1.1 e/Å³. The highest peaks were in the regions of the methyl groups of the phosphine ligands which, in accordance with the thermal parameters of the carbon atoms C9-C26 and the variation of the C-C distances, point to a small disorder of these groups.

(8) SHELX Program, G. M. Sheldrick, 1976, unpublished.

(9) Syntex-XTL-Systems (1976), Syntex Analytical Instruments, Cupertino, CA.

(10) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 99-101.

(6) H. Felkin and G. K. Turner, *J. Organomet. Chem.*, 129, 429 (1977).

(7) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. 1, Academic Press, New York, 1971, p 207.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Pd1	0.2790 (1)	0.5539 (1)	0.3251 (1)	4.8 (1)	4.4 (1)	4.2 (1)	-0.2 (1)	-0.3 (1)	0.7 (1)
Pd2	0.1922 (1)	0.3919 (1)	0.3532 (1)	4.8 (1)	3.8 (1)	4.0 (1)	-0.0 (1)	-0.2 (1)	-0.1 (1)
Br	0.1437 (1)	0.3504 (2)	0.2220 (2)	7.9 (2)	6.0 (2)	4.8 (2)	0.4 (1)	-1.2 (1)	-1.4 (1)
P1	0.3522 (2)	0.5771 (4)	0.4054 (4)	4.6 (3)	5.0 (4)	5.2 (4)	-0.4 (3)	-0.0 (3)	1.2 (4)
P2	0.1220 (2)	0.3921 (4)	0.4408 (4)	4.6 (3)	4.5 (4)	4.3 (4)	-0.5 (3)	-0.5 (3)	-0.1 (3)

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
C1	0.2695 (11)	0.5987 (17)	0.1847 (17)	7.4 (7)	C14	0.2989 (12)	0.6033 (19)	0.5546 (19)	9.6 (9)
C2	0.2268 (11)	0.5522 (16)	0.2028 (17)	7.0 (7)	C15	0.4001 (11)	0.6313 (17)	0.3427 (19)	8.2 (8)
C3	0.1966 (9)	0.5824 (14)	0.2661 (16)	5.8 (6)	C16	0.4153 (10)	0.5908 (16)	0.2609 (18)	7.7 (7)
C4	0.2183 (10)	0.6660 (16)	0.2893 (17)	6.9 (7)	C17	0.4528 (12)	0.6585 (19)	0.3936 (20)	9.8 (9)
C5	0.2668 (10)	0.6662 (15)	0.2404 (17)	6.5 (7)	C18	0.1329 (10)	0.4586 (15)	0.5300 (16)	6.4 (7)
C6	0.2730 (8)	0.3817 (13)	0.3034 (14)	4.6 (6)	C19	0.0870 (11)	0.4579 (16)	0.5961 (18)	8.1 (8)
C7	0.2714 (8)	0.4412 (13)	0.3632 (15)	4.3 (5)	C20	0.1406 (10)	0.5464 (16)	0.4992 (17)	7.1 (7)
C8	0.2534 (8)	0.4189 (12)	0.4458 (14)	4.6 (5)	C21	0.1172 (10)	0.2947 (16)	0.4949 (17)	7.4 (7)
C9	0.3804 (11)	0.4904 (17)	0.4608 (18)	7.9 (8)	C22	0.1144 (12)	0.2283 (19)	0.4247 (20)	10.0 (9)
C10	0.4218 (11)	0.5071 (17)	0.5369 (19)	8.8 (8)	C23	0.1634 (11)	0.2828 (16)	0.5595 (18)	7.8 (7)
C11	0.4085 (12)	0.4419 (19)	0.3913 (20)	9.7 (9)	C24	0.0561 (12)	0.4031 (18)	0.3849 (19)	8.9 (8)
C12	0.3402 (11)	0.6466 (17)	0.4937 (19)	8.5 (8)	C25	0.0542 (11)	0.4880 (17)	0.3438 (18)	8.3 (8)
C13	0.3207 (10)	0.7268 (16)	0.4645 (17)	7.2 (7)	C26	0.0099 (17)	0.3700 (26)	0.4183 (27)	15.2 (14)

Table III. Bond Lengths (Å) in 5^a

Pd1-Pd2	3.575 (3)	C9-C10	1.61 (4)
Pd1-P1	2.250 (7)	C9-C11	1.58 (4)
Pd2-P2	2.294 (7)	C12-C13	1.53 (4)
Pd2-Br	2.505 (3)	C12-C14	1.63 (4)
Pd1-C1	2.39 (3)	C15-C16	1.55 (4)
Pd1-C2	2.33 (3)	C15-C17	1.61 (4)
Pd1-C3	2.31 (2)	C6-C7	1.41 (3)
Pd1-C4	2.38 (3)	C7-C8	1.47 (3)
Pd1-C5	2.38 (3)	P2-C18	1.85 (3)
Pd1-C7	2.04 (2)	P2-C21	1.89 (3)
Pd2-C6	2.22 (2)	P2-C24	1.87 (3)
Pd2-C7	2.17 (2)	C18-C19	1.60 (4)
Pd2-C8	2.16 (2)	C18-C20	1.60 (4)
P1-C9	1.86 (3)	C21-C22	1.60 (4)
P1-C12	1.89 (3)	C21-C23	1.55 (4)
P1-C15	1.85 (3)	C24-C25	1.60 (4)
		C24-C26	1.42 (5)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

The final atomic coordinates are listed in Table II, and selected intramolecular bond lengths and bond angles in Tables III, and IV, respectively.

The molecular structure is shown in Figure 1. The most characteristic feature is that the two different palladium-containing units, C₅H₅(P-*i*-Pr)₃Pd and Pd(P-*i*-Pr)₃Br, are bridged by a bent C₃H₄ group. The Pd-Pd distance of 3.58 Å in 5 is much longer than in 4 (2.61 Å), indicating that due to the insertion of the allene into the metal-to-metal bond the two palladium atoms in the resulting complex are no longer bonded to each other.

Whereas only the central carbon atom C(7) of the C₃H₄ group is σ bonded to Pd(1), all three allylic carbon atoms C(6)-C(8) are π bonded to Pd(2). The coordination in this part of the molecule is very similar to that in (π-allyl)-palladium complexes of the general composition 2-R'C₃H₄Pd(PR₃)₂X which means, for example, that the distance Pd(2)-C(8) which is trans to Br is significantly shorter than the distance Pd(2)-C(6). A comparison shows that the bond lengths and bond angles of the allyl-palladium moiety in 5 and in the complex 2-MeC₃H₄Pd(PPh₃)Cl¹¹ are very similar.

The bond length of the σ bond between the palladium atom Pd(1) and the carbon atom C(7) corresponds to the

Table IV. Bond Angles (Deg) in 5^a

P1-Pd1-C7	94.5 (6)	P1-Pd1-Pd2	123.9 (2)
P2-Pd2-Br	98.8 (2)	P2-Pd2-Pd1	124.2 (2)
P2-Pd2-C7	132.8 (6)	Br-Pd2-Pd1	113.5 (1)
Br-Pd2-C7	126.6 (6)		
C6-C7-C8	116.4 (19)		
Pd1-C7-C6	118.6 (16)		
Pd1-C7-C8	123.7 (16)		
Pd1-P1-C9	115.1 (9)	Pd2-P2-C18	112.3 (8)
Pd1-P1-C12	113.3 (10)	Pd2-P2-C21	110.1 (9)
Pd1-P1-C15	108.3 (10)	Pd2-P2-C24	113.3 (10)
C9-P1-C12	102.4 (13)	C18-P2-C21	101.5 (12)
C9-P1-C15	114.7 (13)	C18-P2-C24	114.7 (13)
C12-P1-C15	102.4 (13)	C21-P2-C24	103.9 (13)
P1-C9-C10	116.7 (19)	P2-C18-C19	114.8 (18)
P1-C9-C11	104.8 (19)	P2-C18-C20	111.0 (17)
P1-C12-C13	113.4 (20)	P2-C21-C22	107.9 (19)
P1-C12-C14	106.4 (15)	P2-C21-C23	111.6 (18)
P1-C15-C16	114.9 (20)	P2-C24-C25	107.7 (20)
P1-C15-C17	114.4 (20)	P2-C24-C26	120.3 (26)
C10-C9-C11	109.7 (23)	C19-C18-C20	108.1 (20)
C13-C12-C14	112.9 (23)	C22-C21-C23	113.1 (23)
C16-C15-C17	109.9 (23)	C25-C24-C26	120.5 (29)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

value which had been anticipated.¹² Together with the η⁵-cyclopentadienyl and the phosphine ligands, this part of the molecule is similar to that of other complexes C₅H₅Pd(PR'₃)₂R where R is alkyl, aryl, etc. It should be noted that the metal-substituted 2-PdC₃H₄ unit is not planar and that both palladium atoms are located on the same side of the allyl group.

Discussion

There are only a few examples describing the addition of allenes to M-M-bonded binuclear transition-metal complexes reported in the literature. Cotton and co-workers¹³ studied the reactions of (C₅H₅)₂M₂(CO)₄ compounds (M = Mo and W) which contain M-M triple bonds with various allenes C₃H₂R₂ (R = H and Me) and isolated the 1:1 adducts (C₅H₅)₂M₂(CO)₄(C₃H₂R₂). According to the X-ray structure of (C₅H₅)₂Mo₂(CO)₄(C₃H₄), the allene

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is V shaped (C-C-C = 146°) and bridges the Mo-Mo bond; it may be considered to form one olefin-metal bond to each molybdenum atom.

The structure of the binuclear palladium complex 5 is very different from that of Cotton's Mo₂ compound. It is not only that the C-C-C angle is much smaller but also, more important, that the bonding mode of the C₃H₄ moiety is not of the same type. As far as we know, there is precedent for the σ -alkyl-plus- π -allyl function of the C₃H₄ group only in two other complexes, namely, Fe₂(CO)₆L-(C₃H₄) (L = CO and PPh₃)¹⁴ and (C₅H₅)₂Ru₂(CO)₃(C₃H₄).¹⁵ The iron complexes differ from the Pd₂ compound 5 insofar as in both Fe₂(CO)₇(C₃H₄) and Fe₂(CO)₆PPh₃(C₃H₄) a M-M bond is still present. However, it is worth noting that the structural data for the bridging allyl ligand in 5 (C-C = 1.41 and 1.47 Å, C-C-C = 116.4°) and in Fe₂(CO)₆PPh₃(C₃H₄) (C-C = 1.41 and 1.45 ± 0.02 Å, C-C-C = 116 ± 1.3°)¹⁴ are very similar.

Experimental Section

NMR spectra were recorded on a Varian T 60 and mass spectra on a Varian MAT CH 7. All experiments were carried out under

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(15) A. F. Dyke, S. A. R. Knox, and P. J. Naish, *J. Organomet. Chem.*, 199, C47 (1980).

purified nitrogen. The synthesis of C₅H₅(P-*i*-Pr₃)Pd(η^1, η^3 -C₃H₄)Pd(P-*i*-Pr₃)Cl (2) has been described previously.⁵

Preparation of C₅H₅(P-*i*-Pr₃)Pd(η^1, η^3 -C₃H₄)Pd(P-*i*-Pr₃)Br (5). (μ -C₅H₅)(μ -Br)Pd₂(P-*i*-Pr₃)₂ (4) (0.55 g, 0.81 mmol)⁶ was dissolved in toluene (10 mL), and allene was bubbled through the solution for 30 min. An orange-red solution and a flocky precipitate resulted which was removed by filtration. The solution was concentrated in vacuo, and pentane was added. After the solution was left standing at 0 °C, orange-red crystals of 5 were formed which were washed with pentane and dried in vacuo: yield 0.3 g (53%); mp 86 °C; mass spectrum (70 eV), *m/e* 717 (32%, M⁺), 451 (56, M⁺ - PdP-*i*-Pr₃), 426 (98, Pd(P-*i*-Pr₃)₂⁺), 371 (95, C₅H₅Pd(C₃H₄)P-*i*-Pr₃⁺), 266 (100, PdP-*i*-Pr₃⁺).

Anal. Calcd for (C₅H₅)(C₃H₄)Pd₂(P-*i*-Pr₃)₂Br: C, 43.47; H, 7.20; Pd, 29.62. Found: C, 43.15; H, 7.08; Pd, 29.90.

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Registry No. 4, 57622-82-9; 5, 80048-98-2; allene, 463-49-0.

Supplementary Material Available: Table V, structure factors as observed and calculated for C₅H₅(P-*i*-Pr₃)Pd(η^1, η^3 -C₃H₄)Pd(P-*i*-Pr₃)Br (9 pages). Ordering information is given on any current masthead page.

The Reactivity of Fe₃(μ_3 -Te)₂(CO)₉ toward Lewis Bases. 1

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The compound Fe₃(μ_3 -Te)₂(CO)₉, 1, reacts with a range of Lewis bases, L, to form adducts Fe₃(μ_3 -Te)₂(CO)₉L where L = PPh₃, *t*-BuNC, CO, and amines. Spectroscopic evidence indicates that, contrary to previous suggestions, the base is bound to an iron center and not to the tellurium atoms. X-ray crystallography of the PPh₃ adduct proves this point: the structure consists of an isosceles triangle of iron atoms tethered by capping μ_3 -Te atoms. The basal Fe₂(CO)₆ unit contains a Fe-Fe bond while the apical Fe(CO)₃PPh₃ is octahedral, two coordination sites being occupied by the bridging tellurium atoms. We suggest that in 1 the μ_3 -Te moieties are constrained to acute (strained) ~60° Fe-Te-Fe angles which are fixed by Fe-Fe bonding. Upon adduct formation, one Fe-Fe vector elongates by 1.4 Å and one pair of the acute Fe-Te-Fe angles opens up to 98°. As such, 1 represents an unusual example of a strained metal cluster compound and the difference in its chemical behavior relative to the analogous but less strained Fe₃(μ_3 -E)₂(CO)₉ (E = S, Se) can thus be understood. Treatment of 1 with potentially chelating bis(tertiary phosphines) demonstrates that 1 is effectively coordinatively unsaturated with respect to only one base addition: in this way monodentate derivatives of Ph₂P(CH₂)_nPPh₂ (*n* = 1-3) were prepared. For Ph₂PCH₂CH₂PPh₂(dppe), the chelate-bridged bis cluster compound [Fe₃(μ_3 -Te)₂(CO)₉]₂(dppe) was isolated and characterized.

Introduction

Tellurium-containing transition metal clusters have been little studied¹⁻⁶ as they are few in number and they have

been assumed to be chemically analogous to the more numerous sulfur and selenium derivatives. Certain characteristics of tellurium suggest, however, that the chemistry of its transition metal clusters may prove distinctive. First, tellurium has a relatively large covalent radius (1.36 Å); therefore one might expect geometrical differences between tellurium-bridged clusters and those containing sulfur and

(1) Fe₃(μ_3 -Te)₂(CO)₉; Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* 1958, 296, 91.

(2) Fe₃(μ_3 -E)₂(CO)₉ (E = S, Se): Rosetti, R.; Cetini, G.; Gambino, O.; Stanghellini, P. L. *Atti Acad. Sci. Torino, U. Sci. Fis., Mat. Nat.* 1969-1970, 104, 127.

(3) Co₂Fe(μ_3 -Te)(CO)₉; Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* 1971, 93, 6032.

(4) Co₂(μ_3 -Te)₂(CO)₈(μ -CO)₂; Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* 1975, 97, 6904.

(5) Os₃(μ_3 -Te)₂(CO)₉; Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* 1979, 719.

(6) Fe₃Pt(μ_3 -Te)₂(CO)₉(PPh₃)₂; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* 1980, 99, C7. A full paper describing the structural aspects of this work has been submitted for publication.

(7) Fe₂(μ -Te)₂(CO)₆ and Fe₃(μ_3 -Te)₂(CO)₁₀; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* 1981, 20, 3583.

(8) The second paper in this series will describe the stereochemistry of substituted derivatives of Fe₃(μ_3 -Te)₂(CO)₉.