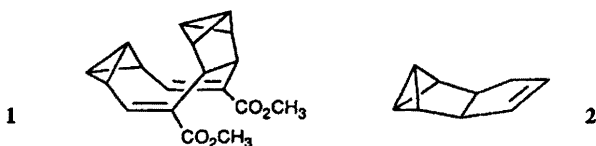


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Octahydro-1,2,3:4,5,6-dimethenopentalene-2-carbonitrile, the First Derivative of a Yet-Unknown $(CH)_{10}$ Hydrocarbon**

Manfred Christl,* Michael Türk, Eva-Maria Peters, Karl Peters, and Hans Georg von Schnering

The "nonconjugated" bisbicyclobutane **1** has interesting reactivity. Owing to the proximity of the two bicyclobutane units, they interact either directly or after an external reagent has attacked either of the two.^[1] In this context we have been interested in the synthesis of compounds in which two bicyclobutane



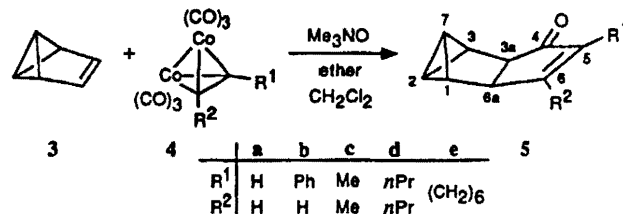
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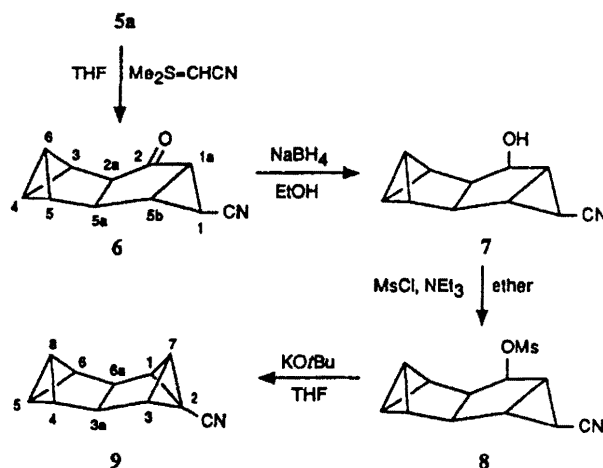
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units are next to one another but not linked directly. We report here on our first goal achieved in this area, the synthesis of the title compound **9**.

In analogy to the synthesis of octabisvalenecarbonitrile (pentacyclo[5.1.0.0^{2,4}.0^{3,5}.0^{6,8}]octane-3-carbonitrile) by Prinzbach et al.,^[2] the cyclopentenone derivative **5a** can be considered the key compound in the synthesis of **9**. We first contemplated a route starting with the allylic oxidation of hexahydro-1,2,3-methenopentalene **2**. In fact, compound **2** is known, but two preparations proceed in very low yields;^[3,4] a third, a six-step sequence starting with benzvalene (**3**), has an overall yield of roughly 10% and is also quite time-consuming.^[5]



The construction of cyclopentenones from olefins by the Pauson-Khand reaction^[6] seemed to be ideal for the one-step conversion of **3** into **5a**. Thus we treated **3** with the dicobalt complex **4a**, but thereby only isomerized **3** into benzene. The intended reaction proceeded readily, however, when trimethylamine oxide, a reagent known for accelerating such reactions,^[7] was added, and the desired product **5a** was isolated in 30–51% yield (see Experimental Procedure). Analogously, the derivatives **5b–e** were obtained in unoptimized yields of 33, 40, 43, and 35%, respectively.



By applying the reaction sequence recently used to transform tricyclo[4.1.0.0^{2,7}]hept-4-en-3-one into octabisvalenecarbonitrile,^[2] we converted **5a** into the target compound **9** in four steps. Treatment of **5a** with dimethylsulfonium cyanomethanide provided oxonitrile **6** and its diastereomer with the opposite configuration at C1 in a 1:1 ratio (54% yield). After separation by flash chromatography (basic Al_2O_3 , activity IV, diethyl ether), **6** was reduced with sodium borohydride to give hydroxynitrile **7** and its diastereomer (opposite configuration at C2) in a ratio of 4:1. Separation by flash chromatography (basic Al_2O_3 , activity IV, dichloromethane) provided the pure compounds in yields of 48 and 16%, respectively. Treatment of

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7 with methanesulfonyl chloride gave mesylate **8** (98%), which was converted into bisbicyclobutane **9** (83%) by reaction with potassium *tert*-butoxide in tetrahydrofuran. Compound **9** is the first derivative of the yet-unknown (CH)₁₀ hydrocarbon^[8] octahydro-1,2,3:4,5,6-dimethenopentalene (hexacyclo[4.4.0.0^{2,4}.0^{3,5}.0^{7,9}.0^{8,10}]decane).

The structures of **8** and **9** were confirmed by X-ray structure analyses.^[9] It is evident in Figure 1 that the cyclopropanecar-

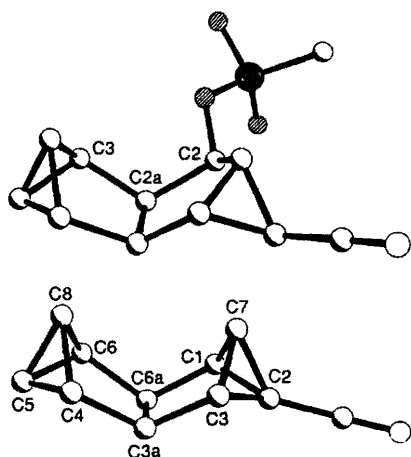
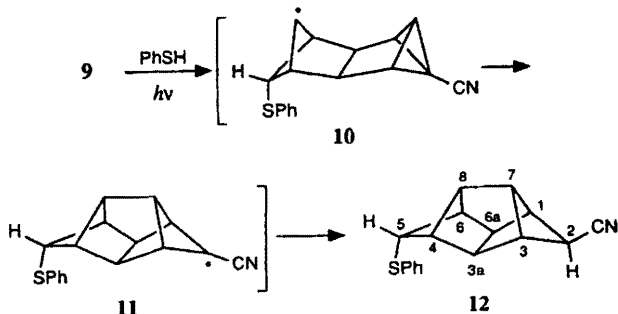


Fig. 1. X-ray crystal structures of **8** (top) and **9** (bottom) [9]. The central bonds in the bicyclobutane units have different lengths (143.6 (**8**), 145.6 (**9**, C5–C8), and 148.3 pm (**9**, C2–C7)), even though the flap angles of the bicyclobutane units are almost identical (111.1° (**8**), 110.5° (**9**, C4,5,6,8), and 111.7° (**9**, C1,2,3,7)). Thus the correlation between these bond lengths and flap angles [10] holds only for the unsubstituted bicyclobutane unit in **9**. The nitrile group in **9** causes the bonds of C2 within the three-membered rings [11] to be particularly long [C2–C1 (150.8 pm), C2–C3 (151.8 pm), and C2–C7]. The configuration of C2 is an inverted tetrahedron. The inversion parameter (angle between the bond vector C2–CN and the plane through C1, C2, C3) [12] is 174.6°. The *cis* annelation of the two five-membered rings in both **8** and **9** leads to relatively small distances between atoms that are not directly bonded [e.g. between C3 and the oxygen atom at C2 in **8** (280 pm) and between C7 and C8 in **9** (312 pm)], which results in large bond angles [C2–C2a–C3 (118.4°) in **8** and C1–C6a–C6 (116.4°) in **9**].

bonitrile unit and the mesylate group in **8** are *trans*. Thus the stereochemical prerequisite for the 1,3-elimination, in which the mesylate group is removed with inversion, is fulfilled. In **9** the distance between the bicyclobutane bridgehead atoms C7 and C8 is 312 pm.

This distance is small enough for a transannular reaction: irradiation of a solution of **9** and thiophenol in benzene furnished a 6:1 mixture of 1,3:4,6-ethane-1,2-diylidenepentalene (pentacyclo[5.3.0.0^{2,5}.0^{4,10}.0^{6,9}]decane) derivative **12** and its diastereomer (opposite configuration at C2) in 70% yield. This reaction is most likely a radical chain process analogous to the corresponding reaction of **1**.^[1] The cyclobutyl radicals **10** and **11** are assumed to occur as intermediates.



The IR, NMR, and mass spectra, as well as elemental analyses, obtained for all new compounds are in agreement with the assigned structures. Selected physical data are given in Table 1.

Table 1. Selected physical data for **5a**, **6**–**9**, and **12**: 200 or 400 MHz ¹H NMR spectra, 50, 63, or 100 MHz ¹³C NMR spectra, measured in CDCl₃; the assignments given in the NMR spectra are based on decoupling experiments, NOE effects, and ¹H, ¹³C COSY spectra.

5a : B.p. 50–55 °C/0.15 mbar; IR (neat): $\tilde{\nu}$ = 1703 cm ⁻¹ (C=O), 1582 (C=C); MS (70 eV), <i>m/z</i> (%): 132 (29) [M ⁺], 131 (100), 104 (42), 103 (60), 78 (42), 77 (22), 51 (21); ¹ H NMR: δ = 1.91 (dt, <i>J</i> (2,7) = 9.2, <i>J</i> (1,7) = <i>J</i> (3,7) = 1.7, <i>J</i> (3a,7) = <i>J</i> (6a,7) = 1.3 Hz; H7), 2.16 (dt, <i>J</i> (1,2) = <i>J</i> (2,3) = 1.7 Hz; H2), 2.23 (\approx dq, <i>J</i> (1,3) = 4.9 Hz; H1), 2.27 (\approx dq, <i>J</i> (3,6) = 0.3 Hz; H3), 2.50 (dt, <i>J</i> (3a,6a) = 5.4, <i>J</i> (3,3a) = 1.3 Hz; H3a), 3.13 (ddq, <i>J</i> (6,6a) = 2.5, <i>J</i> (1,6a) = <i>J</i> (5,6a) = 1.2 Hz; H6a), 5.94 (dd, <i>J</i> (5,6) = 5.8 Hz; H5), 7.42 (ddd; H6); ¹³ C NMR: δ = -0.5 (dt, <i>J</i> (C,H) = 219, 8, 6 Hz; C7), 10.5 (dd, 217, 6 Hz; C2), 35.1 (ddq, 170, 14, 4 Hz; C3), 37.5 (ddq, 168, 13, 4 Hz; C1), 49.7 (ddq, 140, 9, 5 Hz; C6a), 51.4 (quint, 140, 5 Hz; C3a), 134.2 (dt, 170, 4 Hz; C6), 164.3 (dq, 164, 3 Hz; C5), 210.7 (dm, 13 Hz; C4)
6 : M.p. 112–113 °C; IR (KBr): $\tilde{\nu}$ = 2243 cm ⁻¹ (C≡N), 1718 (C=O); ¹³ C NMR: δ = -0.3 (C6), 5.3 (C4), 8.9 (C1), 30.3 (C1a), 35.2 (C5b), 35.8, 37.5 (C3,5), 45.6 (C2a), 51.1 (C5a), 117.7 (CN), 210.5 (C2)
7 : M.p. 56–57 °C; IR (KBr): $\tilde{\nu}$ = 3220 cm ⁻¹ (broad, O-H), 2235, 2243 (C≡N); ¹³ C NMR: δ = 1.3 (C6), 4.2 (C4), 29.5, 33.3 (C1a,5b), 36.6, 37.2 (C3,5), 50.5 (C2a), 51.9 (C5a), 73.2 (C2), 120.1 (CN)
8 : M.p. 127–128 °C; IR (KBr): $\tilde{\nu}$ = 2238 cm ⁻¹ (C≡N); ¹³ C NMR: δ = 2.5 (C6), 4.9 (C4), 7.0 (C1), 30.2, 33.6 (C1a,5b), 34.4, 37.0 (C3,5), 38.1 (CH ₂), 51.4 (C2a), 52.3 (C5a), 80.9 (C2), 119.1 (CN)
9 : M.p. 78–79 °C; IR (KBr): $\tilde{\nu}$ = 2220 cm ⁻¹ (C≡N); MS (70 eV), <i>m/z</i> (%): 155 (14) [M ⁺], 154 (76), 153 (21), 140 (59), 128 (44), 127 (100), 126 (15), 115 (29), 78 (14), 77 (40), 76 (15), 63 (18), 52 (25), 51 (24), 50 (20), 39 (13); ¹ H NMR: δ = 1.78 (dt, <i>J</i> (5,8) = 9.2, <i>J</i> (4,5) = 1.8 Hz; H5), 1.83 (dt, <i>J</i> (4,8) = 1.7, <i>J</i> (3a,8) = 1.3 Hz; H8), 1.89 (m; H4,6), 2.34 (m; H3a,6a), 2.56 (dm; H1,3), 2.83 (tt, <i>J</i> (1,7) = 2.2, <i>J</i> (3a,7) = 1.5 Hz; H7); ¹³ C NMR: δ = 0.3 (dt, <i>J</i> (C,H) = 215, 8, 4 Hz; C8), 0.9 (s; C2), 7.0 (dd, 214, 4 Hz; C5), 15.7 (dt, 216, 8 Hz; C7), 34.6 (ddt, 165, 14, 4 Hz; C4,6), 43.5 (ddd, 169, 12, 5 Hz; C1,3), 48.5 (dq, 141, 6, 2 Hz; C3a,6a), 118.9 (d, 7 Hz; CN)
12 : M.p. 91–92 °C; IR (KBr): $\tilde{\nu}$ = 2237 cm ⁻¹ (C≡N); ¹ H NMR: δ = 2.35 (qt, <i>J</i> (4,8) = <i>J</i> (7,8) = 3.2, <i>J</i> (3a,8) = 1.6 Hz; H8), 2.67 (s; H2), 2.75 (br. s; H3a,6a), 3.00 (qt, <i>J</i> (1,7) = 3.5, <i>J</i> (3a,7) = 1.6 Hz; H7), 3.12 (br. d; H1,3), 3.15 (br. t; H4,6), 3.82 (t, <i>J</i> (4,5) = 2.8 Hz; H5), 7.15–7.32 (m; C ₆ H ₅); ¹³ C NMR: δ = 31.5 (C2), 43.9 (C3a,6a), 48.6 (C5), 50.0 (C8), 51.8 (C7), 55.4 (C1,3), 57.4 (C4,6), 121.4 (CN), 125.8 (<i>p</i> -C), 128.8, 129.1 (<i>m</i> -, <i>o</i> -C), 136.4 (<i>i</i> -C)

Experimental Procedure

5a: A moderate stream of acetylene (passed through a trap at -78 °C to remove acetone) was bubbled through a stirred, ice-cooled solution of octacarbonyldicobalt (82.0 g, 240 mmol) in dichloromethane (700 mL) under nitrogen until release of CO could no longer be detected (ca. 5 h). The solution was transferred to an addition funnel and added dropwise under nitrogen within 45 min to a stirred suspension of anhydrous trimethylamine *N*-oxide (135 g, 1.80 mol) in a solution of benzvalene (**3**) [13] (19.0 g, 243 mmol) in diethyl ether (300–450 mL) cooled to -75 °C. The mixture was stirred and allowed to warm to 20 °C over 2 h. Then a gentle stream of oxygen was passed through the mixture for 4 h. Diethyl ether was added repeatedly to replace the solvent that evaporated, such that the original volume was maintained. The brown precipitate was filtered off, the filtrate extracted with water (4 × 100 mL), the organic phase dried with K₂CO₃, and the solvent removed by distillation. Distillation of the yellow-brown residue at 50–55 °C/0.15 mbar gave 9.5 g (30–51%) **5a**, which was pale blue in the cooled (-30 °C) receiving flask but turned yellow-brown upon warming to 20 °C. Trace amounts of volatile cobalt-containing compounds were probably the source of these colors. Impurities are not evident in the NMR spectra. Compound **5a** purified by preparative gas chromatography (1.5 m column, 20% EGA on Volaspher[®] A2, 90 °C) was colorless. Spectroscopic data are given in Table 1.

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- [9] **8**: Monoclinic, $P2_1/c$; $a = 1379.1(5)$, $b = 826.0(4)$, $c = 1088.5(5)$ pm, $\beta = 108.87(3)$; 2992 measured reflections, of which 2641 with $F > 3\sigma(F)$ were considered independent; $R = 0.125$, $R_w = 0.120$. **9**: Monoclinic, $P2_1/n$; $a = 685.8(2)$, $b = 1796.7(4)$, $c = 662.1(1)$ pm, $\beta = 90.08(2)$; 2090 measured reflections, of which 1080 with $F > 3\sigma(F)$ were considered independent; $R = 0.055$, $R_w = 0.041$. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository numbers CSD-400696 (**8**) and CSD-400697 (**9**).
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The Use of Heterometallic Bridging Moieties To Generate Tractable Lanthanide Complexes of Small Ligands**

William J. Evans,* Reiner Anwander, Robert J. Doedens, and Joseph W. Ziller

Dedicated to Professor M. Frederick Hawthorne on the occasion of his 65th birthday

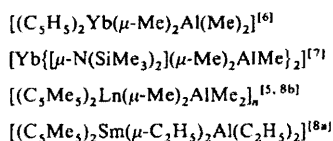
Lanthanide chemistry is dominated by large, anionic ligands which meet the steric and electronic demands of these large electropositive metals. On the other hand, the chemistry of simple lanthanide complexes of general formula LnZ_3 in which Z is a small anionic ligand such as methanide, methanolate, ethanolate, or dimethylamido, is poorly developed since these complexes are either unstable or insoluble.^[1, 2] The only homoleptic lanthanide complexes with small ligands which are tractable enough to be definitively characterized by X-ray crystallography are the hexamethyl "ate" complexes $[\text{LnMe}_6]^{3-}$ of the late lanthanides Ho, Er, and Lu.^[2]

We describe here a method for the synthesis of isolable, soluble lanthanide complexes of small ligands Z ($Z = \text{NMe}_2$, Me) which also provides a convenient route to heterometallic complexes which have component combinations of interest with respect to polymerization catalysis^[3] and the formation of materials from molecular precursors.^[4] We also report details of the first structurally characterized molecular complexes containing a lanthanide metal and gallium.^[5]

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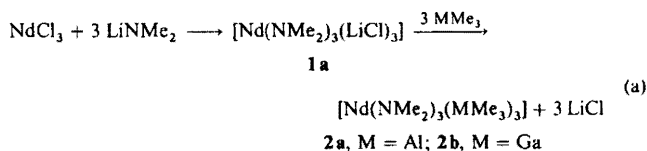
For many years it has been known that trialkylaluminum complexes will add to lanthanide complexes containing bulky stabilizing co-ligands to form bridged heterometallic species such as those given in Scheme 1.



Scheme 1. Examples of lanthanide heterometallic complexes.

Recently, we have shown that AlMe_3 will also bridge and stabilize metal ligand combinations such as $\text{Y}(\text{OCMe}_3)_3$ in $[\text{Y}\{\mu\text{-OCMe}_3(\mu\text{-Me})\text{AlMe}_2\}_3]^{[9]}$ and $[(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Y}(\text{OCMe}_3)_2]$ in $[(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Y}\{\mu\text{-OCMe}_3(\mu\text{-Me})\text{AlMe}_2\}_2]^{[10]}$. We now report that AlMe_3 will not only react with soluble reagents containing bulky ligands, but that it will also react with and solubilize the insoluble materials formed from reactions of lanthanide halides with small anionic ligands.

The reaction of anhydrous NdCl_3 with three equivalents of LiNMe_2 ($Z = \text{NMe}_2$) in THF at room temperature formed a blue material which was identified as **1a** [Eq. (a)]. Reaction of AlMe_3 or GaMe_3 with a suspension of **1a** in hexane yielded the hexane-soluble products **2a** (violet-blue) and **2b** (blue), respectively.



The intensely colored solutions of **2** are stable at room temperature. Evaporation of the solvent results in oily residues which solidify at -35°C . These solids slowly decompose at room temperature to form large colorless crystals of $[\{\text{Me}_2\text{NMMe}_2\}_2]$ ($\text{M} = \text{Al}, \text{Ga}$)^[11] which sublime to the top of the container. Compounds **2a** and **2b** can be isolated in 80% yield by crystallization of the initially isolated solids from hexane at -35°C ; the molecular structure of **2b** is shown in Figure 1.^[12]

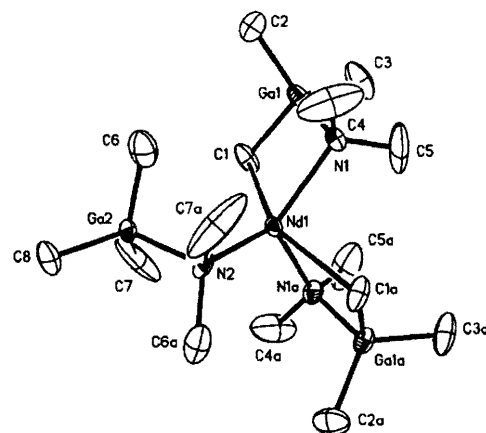


Fig. 1. Molecular structure of **2b**; the numbering is identical to that of isostructural **2a**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å] and angles [°] for **2b** are as follows (**2a** in brackets): Nd1–N1 2.395(5) [2.435(4)], Nd1–N2 2.362(10) [2.433(8)], Nd1–C1 2.749(7) [2.708(5)], Nd1–C6 3.28 [3.39], Nd1–C7 3.35 [3.21], Nd1–M1 3.276(1) [3.274(2)], Nd1–M2 3.242(1) [3.191(3)], Nd1–N1–M1 94.7(2) [96.0(1)], Nd1–C1–M1 84.3(2) [85.7(1)], N1–Nd1–C1 77.3(2) [74.7(1)], N1–M1–C1 103.0(3) [102.5(2)], Nd1–N2–M2 94.5(4) [92.6(3)].