Synthesis and characterization of new rhodium and iridium complexes containing the heterodifunctional ligand (diphenylphosphino)cyclopentadienyl

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We are currently investigating the effects of stoichiometry and conditions on the reaction of 1 with $Cu_2(C_6H_6)(SO_3CF_3)_2$. A multinuclear complex of 1 has been isolated with excess $Cu_2(C_6H_6)(SO_3CF_3)_2$. The synthesis of Cu(I) complexes of the cyclyne 1 with other anions that may promote stacking and related silver chemistry are being explored.

Acknowledgment. We thank Professors M. E. Kenney, R. G. Salomon, and F. L. Urbach for helpful discussions. J.D.F. thanks the BFGoodrich Co. for financial support through the BFGoodrich Fellowship at CWRU. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and an Olin Corporation Charitable Trust Grant of the Research Corp. for partial support of this work.

Supplementary Material Available: Tables of data collection and structure solution details, bonds lengths and angles, and atomic positional and thermal parameters (10 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(24) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* 1985, *107*, 1979–1985.

Synthesis and Characterization of New Rhodium and Iridium Complexes Containing the Heterodifunctional Ligand (Diphenylphosphino)cyclopentadienyl

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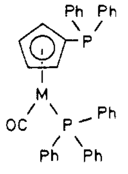
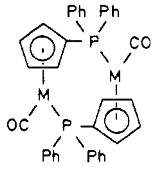
Summary: The new complexes $(\eta^5\text{-}C_5H_4)PPh_2M(CO)(PPh_3)$ (**1a**, M = Rh; **1b**, M = Ir), $[(\eta^5\text{-}C_5H_4)PPh_2]_2M_2(CO)_2$ (**2a**, M = Rh; **2b**, M = Ir), and $IrCl(CO)Ph_2P(\eta^5\text{-}C_5H_4)Ir(CO)(PPh_3)_2$ (**3b**) have been prepared and characterized. In the mononuclear complexes **1a** and **1b**, the heterodifunctional ligand possesses a free phosphine group that may attach to a second metal center as illustrated by the conversion of **1a** into the dinuclear complex **2a**. Complexes **2a** and **2b** have dinuclear symmetrical structures where the metallic centers are linked by two bridging (diphenylphosphino)cyclopentadienyl ligands in a "head-to-tail" configuration.

The heterodifunctional ligands containing a cyclopentadienide ring, directly linked to a phosphine group as in the (diphenylphosphino)cyclopentadienide anion (dppc)[2] or by a molecular chain as in (dimethyl((diphenylphosphino)methyl)silyl)cyclopentadienide[3] and ((diphenylphosphino)ethyl)cyclopentadienide[4] anions, have received significant attention in recent years because of their potential ability to join two metallic centers.[3,5-8]

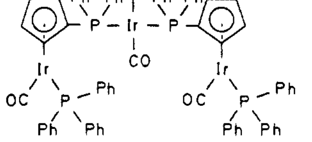
Following our investigations on the synthesis and properties of new polymetallic complexes,[5,9] we report here our preliminary results on the interaction of the ligand $Ph_2P(C_5H_4)Li$ with $[RhCl(CO)(PPh_3)]_2$ and *trans*-$IrCl(CO)(PPh_3)_2$ to form new monometallic (**1a** and **1b**), dimetallic (**2a** and **2b**), and trimetallic (**3b**) species.



1a, M = Rh
1b, M = Ir



2a, M = Rh
2b, M = Ir



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Addition of lithium (diphenylphosphino)cyclopentadienide to half an equimolar amount of the chloro-bridged dirhodium complex $Rh_2Cl_2(CO)_2(PPh_3)_2$ in toluene at 0 °C leads readily to the formation of a yellow precipitate of the dimetallic species **2a** and an orange solution containing the monometallic species **1a** together with free triphenylphosphine (eq 1).

$$\tfrac{1}{2}[RhCl(CO)(PPh_3)]_2 \xrightarrow[\substack{0\ ^\circ C,\ toluene\\ -LiCl}]{Li(C_5H_4)PPh_2} \underset{70\%}{\mathbf{1a}} + \underset{30\%}{\mathbf{2a}} + 2PPh_3 \tag{1}$$

Complexes **1a** and **2a** were fully characterized by mass spectra and IR spectra in the $\nu(CO)$ region as well as ^{31}P and ^{1}H NMR spectra.[10] The $^{31}P\{^1H\}$ spectrum of **1a** in CD_2Cl_2 exhibits two signals of equal intensities: a doublet centered at +52.28 ppm with a doublet spacing of 198 Hz corresponding to a triphenylphosphine ligand bonded to an 18-electron rhodium(I) center and a singlet at −21.20 ppm indicative of a noncoordinated tertiary phosphine group. The $^{31}P\{^1H\}$ NMR spectrum of **2a**, exhibiting a typical pattern of an AA′XX′ spin system (δ 41.08 ($J_{P\text{-}Rh}$ = 200 Hz)), points out a symmetrical structure in which the phosphorus atom of each of both difunctional ligands

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(2) Mathey, F.; Lampin, J. P. *Tetrahedron* 1975, *31*, 2685–2690.

(3) (a) Shore, N. E. *J. Am. Chem. Soc.* 1979, *101*, 7410–7412. (b) Shore, N. E.; Benner, L. S.; La Belle, B. *Inorg. Chem.* 1981, *20*, 3200–3208.

(4) Charrier, C; Mathey, F. *J. Organomet. Chem.* 1979, *170*, C41–C43.

(5) Moïse, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* 1984, *231*, C43–C48.

(6) (a) Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A.; L. *Organometallics* 1982, *1*, 1591–1596. (b) Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* 1983, *105*, 7574–7580. (c) Casey, C. P.; Nieff, F. *Organometallics* 1985, *4*, 1218–1220.

(7) Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, *105*, 3882–3886.

(8) Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* 1986, *5*, 888–894.

(9) (a) El Amane, M.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* 1985, *4*, 773–780. (b) Delavaux, B.; Chaudret, B.; Taylor, N. J.; Arabi, S.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* 1985, 805–807. (c) Maisonnat, A.; Poilblanc, R. *C. R. Acad. Sci., Ser. 2* 1984, 69–71.

(10) For **1a**: electron-impact MS (70 eV), *m/e* 610 (M^+) plus fragment ions from which one corresponds to the loss of one CO group; IR (ν(CO), in hexane) 1956 cm^{-1}. For **2a**: electron-impact MS, *m/e* 760 plus fragment ions corresponding to successive loss of two CO groups; IR (ν(CO), CH_2Cl_2) 1946 cm^{-1}. Anal. Calcd for $C_{36}H_{28}O_2P_2Rh_2$: C, 56.85; H, 3.71. Found: C, 57.68; H, 4.07.

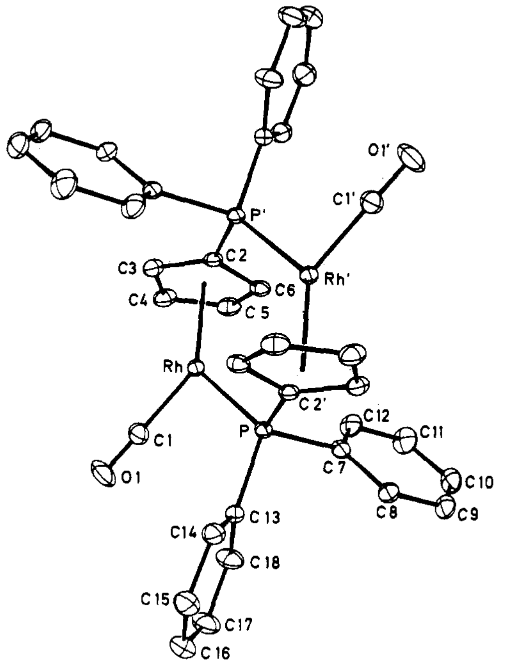

Figure 1. Molecular geometry and atom-labeling scheme for **2a**. Selected bond distances (Å) and angles (deg) include the following: Rh–C(1) = 1.831 (4), Rh–C(2) = 2.321 (4), Rh–C(3) = 2.307 (5), Rh–C(4) = 2.263 (5), Rh–C(5) = 2.294 (4), Rh–C(6) = 2.248 (3), C(1)–O(1) = 1. 144 (5), Rh–P = 2.237 (1), Rh···Rh′ = 4.3029 (6), P–C(2)′ = 1.804 (4), P–C(7) = 1.841 (5), P–C(13) = 1.841 (4); C(1)–Rh-P = 91.5 (2), Rh–P–C(2)′ = 113.7 (2), Rh–P–C(7) = 116.4 (1), Rh–P–C(13) = 117.3 (1), Rh–C(1)–O(1) = 177.0 (4).

is bonded to an 18-electron rhodium center according to an "head-to-tail" arrangement. X-ray diffraction preliminary data[11] (Figure 1) confirm this assumption.

Noteworthy, the ν(CO) absorptions of **1a** and **2a** compare well with that of (η^5-C_5H_5)Rh(CO)(PPh_3), i.e. 1957 cm^{-1} in hexane.[12]

The quantitative conversion of **1a** into the dirhodium species **2a** with the concomitant formation of free triphenylphosphine was obtained upon heating at 60 °C for 10 h a toluene solution of **1a**. **2a** was collected as a yellow precipitate (eq 2).

$$2 \times \mathbf{1a} \xrightarrow[\text{60 °C, 10 h}]{\text{toluene}} \mathbf{2a} + 2PPh_3 \qquad (2)$$

The reverse reaction of pure **2a** with triphenylphosphine was not observed, even upon heating the toluene reaction mixture for several hours.

Reaction 1 (eq 1) was monitored at -70 °C by ^{31}P NMR. After 15 min of reaction time, the NMR spectrum recorded at the same temperature indicated a total consumption of both the starting rhodium material and the dppc ligand and the formation of five major intermediates,[13] together with free triphenylphosphine. The values of the $J_{P\text{-}Rh}$ coupling constants are unambiguous indications[14] of the coordination of the phosphorus end of dppc on rhodium(I) atoms in square-planar configurations. The series of NMR signals is therefore attributed to mono- and binuclear rhodium(I) species normally expected for a reaction of a phosphine ligand with chloro-bridged RhL_2Cl_2 complexes.[15]

Owing to the low thermal stability of these intermediate species, the study of the mechanism of their conversion into **1a** and /or **2a** is not yet completed. Still, it may be assumed that the further steps leading to **2a** consist for each intermediate in nucleophilic substitution by the Cp^- free end of the coordinated dppc, including in every cases elimination of Cl^- ligands.

Addition of lithium (diphenylphosphino)cyclopentadienide to *trans*-IrCl(CO)(PPh_3)$_2$ (Ir/LiCpP molar ratio ca. 1:1) in toluene at 70 °C leads within 5 min to the formation of a yellow precipitate of the dimetallic species **2b** and an orange solution containing free triphenylphosphine, the monometallic species **1b**, and the trimetallic species **3b** (eq 3).[16]

$$\textit{trans}\text{-IrCl(CO)(PPh}_3)_2 \xrightarrow[\text{toluene, 70 °C; 5 min, -LiCl}]{\text{Li(C}_5\text{H}_4\text{)PPh}_2} \underset{70\%}{\mathbf{1b}} + \underset{25\%}{\mathbf{2b}} + \underset{5\%}{\mathbf{3b}} + PPh_3 \qquad (3)$$

1b, **2b**, and **3b** have been fully characterized by chemical analyses, mass spectra, IR in the ν(CO) region, and ^{31}P and ^{1}H NMR spectra.[17] $^{31}P\{^1H\}$ NMR and IR spectra of **1b** and **2b** indicate molecular structures similar to those of their rhodium analogues.

The $^{31}P\{^1H\}$ NMR spectrum of **3b** exhibits two singlets (δ +10.86, +16.18) of equal intensities. The former is attributed to equivalent phosphorus nuclei of two triphenylphosphine groups while the latter is attributed to equivalent phosphorus nuclei of two dppc ligands. This result, together with the IR (ν(CO)) spectrum, is consistent with the proposed structure for **3b** that may be viewed as the result of the attachment of two species of type **1b** by the phosphine end of dppc on a 16-electron Ir(I) center, according to a mutual trans arrangement.

The observed distribution of **1b**, **2b**, and **3b** (eq 3) in the reactional mixture is independent of the reaction time. We checked that addition of a slight excess of dppc to the reaction mixture leads to the complete disappearance of **3b** while **1b** and **2b** were the only observed products. Moreover, addition of the difunctional ligand to an equimolar amount of pure **3b** yielded quantitatively **1b** and **2b** according to eq 4.

$$\mathbf{3b} + Li(C_5H_4)PPh_2 \xrightarrow{-LiCl} 2 \times \mathbf{1b} + {}^1/_2\mathbf{2b} + 2PPh_3 \qquad (4)$$

Contrasting with our observations when rhodium was involved, the conversion of **1b** into **2b** was not observed

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[11] Crystal data: $C_{36}H_{28}O_2P_2Rh_2$; a = 9.475 (1), b = 9.527 (1), c = 9.145 (1) Å, α = 99.80 (1)°, β = 109.86 (1)°, γ = 90.36 (1)°, V = 763.2 (3) Å^3, triclinic, space group C_i^1—$P\bar{1}$, Z = 1. A total of 3511 intensity data were recorded in ω–2θ scan mode on a CAD4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). Full-matrix least-squares refinement with 2938 reflections having $F_o^2 > 3\sigma(Fo^2)$ led to a final R of 0.032.

[12] Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *12*, 2658–2663.

[13] Four intermediates are characterized by single doublets centered at 35.6 ($J_{P\text{-}Rh}$ = 120 Hz), 32.3 ($J_{P\text{-}Rh}$ = 120 Hz), 31.2 ($J_{P\text{-}Rh}$ = 127 Hz), and 26.3 ppm ($J_{P\text{-}Rh}$ = 120 Hz), respectively, and one intermediate is characterized by two doublets of doublets of equal intensity, centered at 23.56 ($J_{P\text{-}Rh}$ = 120 Hz, $J_{P\text{-}P}$ = 55 Hz) and 23.14 ppm ($J_{P\text{-}Rh}$ = 119 Hz, $J_{P\text{-}P}$ = 55 Hz), respectively.

[14] The $^1J_{P\text{-}Rh}$ coupling constants lie in quite different ranges, i.e. 190–200 and 120–130 Hz, respectively, as the phosphine end of the dppc ligand is bonded to 18e rhodium(I) centers (e.g. in CpRh(CO)L) or to square-planar 16e rhodium(I) centers.

[15] Gallay, J.; de Montauzon, D.; Poilblanc, R. *J. Organomet. Chem.* **1972**, *38*, 179–197.

[16] Under similar experimental conditions, the reaction of sodium cyclopentadienide on *trans*-IrCl(CO)(PPh_3)$_2$ leads to (η^5-C_5H_5)Ir(CO)(PPh_3). Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2653–2657.

[17] For **1b**: electron-impact MS (70 eV), *m/e* two principal peaks at 730 and 732 (M^+) plus fragment ions corresponding to the loss of one CO and one PPh_3 group; IR (ν(CO)) 1948 cm^{-1} in hexane and 1928 cm^{-1} in dichloromethane; $^{31}P\{^1H\}$ NMR (101.1 Hz, CD_2Cl_2), two singlets at +16.08 and −20.56 ppm. Anal. Calcd for $C_{36}H_{29}OP_2Ir$: C, 59.09; H, 3.99. Found: C, 58.01; H, 4.02. For **2b**: electron-impact MS, *m/e* three principal peaks at 936, 938, and 940 (M^+) plus fragment ions corresponding to the loss of two CO groups; IR (ν(CO)), CH_2Cl_2) 1934 cm^{-1}; $^{31}P\{^1H\}$ NMR (101.1 MHz, CD_2Cl_2) one singlet at +4.54 ppm. Anal. Calcd for $C_{36}H_{28}O_2P_2Ir_2$: C, 46.05; H, 3.01. Found: C, 45.88; H, 2.62. For **3b**; IR (ν(CO), CH_2Cl_2) 1952 (m) and 1929 (s) cm^{-1}. Anal. Calcd for $C_{73}H_{58}O_3P_4Ir_3$: C, 51.00; H, 3.40. Found: C, 51.76; H, 3.71.

under the same experimental conditions.

The complexes $(\eta^5\text{-}C_5H_5)Ir(CO)_2$, $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, and $(\eta^5\text{-}C_5Me_5)M(PMe_3)(R)(H)$ (M = Rh, Ir) are well-known for generating reactive species capable of intermolecular oxidative addition to single C–H bonds in saturated hydrocarbons.[18–20] We are presently investigating our new compounds with a similar purpose.

Registry No. **1a**, 106520-04-1; **1b**, 106500-77-0; **2a**, 106500-79-2; **2b**, 106500-78-1; **3b**, 106520-03-0; $[RhCl(CO)(PPh_3)]_2$, 34676-63-6; *trans*-$IrCO(CO)(PPh_3)_2$, 15318-31-7; $Li(C_5H_4)PPh_2$, 83272-80-4.

Supplementary Material Available: Tables of fractional atomic coordinates, hydrogen atomic positional and thermal parameters, final anisotropic thermal parameters, bond lengths and angles, interatomic distances, and least-squares planes (6 pages); a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[18] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352–354. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121–1122. Perlana, R. A.; Bergman, R. G. *Organometallics.* **1984**, *3*, 508–510.

[19] (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190–7191. (b) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, *624*–626.

[20] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663.

Uncommon Structural Features of $[Cp_2Zr\text{–}OC(Ph)\text{–}Mo(CO)_5]_2O$, a Zr–O–Zr-Bridged Tetranuclear Bis(carbene)metal Complex Exhibiting a Planar σ-Framework

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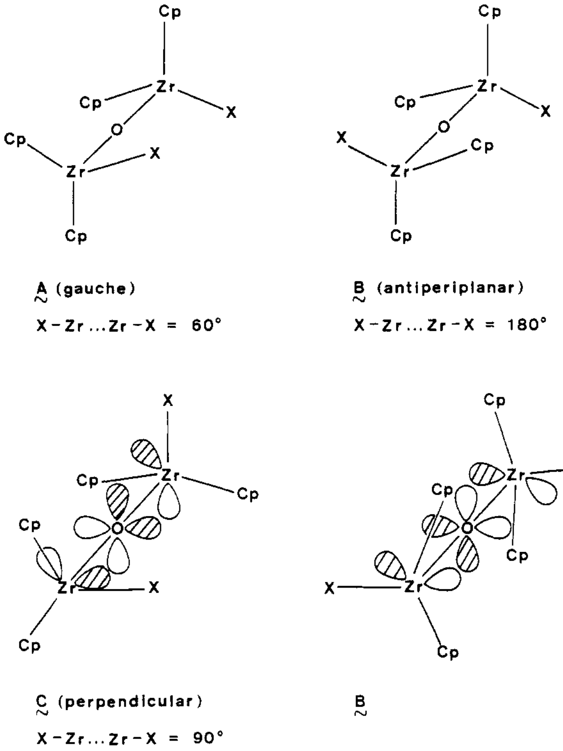
Summary: Thermally in situ generated $(\eta^2\text{-}1,2\text{-di}$dehydrobenzene)zirconocene reacts with $M(CO)_6$ (M = W, Mo) to give the benzannelated five-membered metallacyclic zirconoxycarbene complexes **4a,b**. Controlled hydrolysis of **4a** (M = W) with $CuSO_4\cdot 5H_2O$ yields the tetranuclear Zr–O–Zr-bridged bis(carbene) complex $[(CO)_5W\text{–}C(Ph)O\text{–}Cp_2Zr\text{–}O\text{–}ZrCp_2\text{–}OC(Ph)\text{–}W(CO)_5]$ (**5a**). The molecular structure of the molybdenum analogue **5b** was determined by X-ray diffraction. **5b** crystallizes in the monoclinic space group *C2/c* with cell parameters *a* = 28.666 (5) Å, *b* = 11.257 (2) Å *c* = 16.884 (2) Å, and β = 125.84 (1)°. **5b** is characterized by a completely planar σ-framework (Zr–O–Zr* = 180°). The most remarkable structural feature of **5b** is the trans arrangement of the voluminous $(CO)_5Mo$–carbene units at the Zr–O–Zr bridge. This favored antiperiplanar conformation is unique among the family of early-transition-metal $Cp_2M(X)\text{–}O\text{–}M(X)Cp_2$ compounds.

Connection of two pseudotetrahedral bent metallocene units Cp_2MX through a bridging oxygen atom leads to binuclear μ-oxo-metallocene complexes $(Cp_2MX)\text{–}O\text{–}(Cp_2MX)$ usually exhibiting a near to linear M–O–M linkage.[1–7] The stereochemical situation of such an arrangement could principally be similar to that of ordinary

Chart I. Schematic Representation of Possible Local Conformational $(Cp_2ZrX)_2O$ Minima[a]



[a] Orbitals drawn for B and C only serve to denote the planes of preferred electronic interaction.

Table I. A Comparison of Selected Structural Data of $(Cp_2MX)_2O$ Compounds Including 5b

M	X	X–M···M–X[a]	M–O–M	M–O[b]	ref
Zr	O–C(Ph)Mo-$(CO)_5$	180	180	1.958 (1)	this work
Zr	S–Ph	61.7	165.8	1.968 (3) 1.964 (3)	1
Zr	Cl	74.3	168.9	1.94 (1) 1.95 (1)	2
Zr	CH_3	90	174.1	1.948 (1)	3
Ti	$-CF_3C{=}CH\text{-}CF_3$	54.1 53.7	170	1.857 (6)	4
Ti^{+}[c]	$[H_2O]$	74.1	175.8	1.829 (2)	5
Ti	$-PhC{=}CHPh$	68	168.8	1.85 (1) 1.86 (1)	6
Nb^{+}[d]	Cl	72.5	169.3	1.88 (1)	7

[a] Dihedral angle θ. [b] Bond distance in Å and bond angles in deg. [c] ClO_4^- salt. [d] BF_4^- salt.

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[1] Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179.

[2] Clarke, J. F.; Drew, M. B. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2267.

[3] Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

[4] Rausch, M. D.; Sikora, D. J.; Hrncir, D. C.; Hunter, W. E.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 3817.

[5] Thewalt, U.; Kebbel, B. *J. Organomet. Chem.* **1978**, *150*, 59.

[6] Shur, V. B.; Bernadyuk, S. Z.; Burlakov, V. V.; Andrianov, V. G.; Yanovsky, A. I.; Struchkov, Y. T.; Vol'pin, M. E. *J. Organomet. Chem.* **1983**, *243*, 157.

[7] Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 2290.

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