ORGANOMETALLICS

Subscriber access provided by CUNY CENTRAL OFFICE

Synthesis and characterization of new, air-stable closo-1-Os(CO)3-2,3-(Me3Si)2-2,3-C2B4H4

Narayan S. Hosmane, and Narayan N. Sirmokadam

Organometallics, **1984**, 3 (7), 1119-1121• DOI: 10.1021/om00085a028 • Publication Date (Web): 01 May 2002

Downloaded from http://pubs.acs.org on April 26, 2009

More About This Article

The permalink http://dx.doi.org/10.1021/om00085a028 provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

ACS Publications
High quality. High impact.

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

values for the heavier atoms have been submitted as supplementary material.

Of particular interest are the 206 reflections coded as having $I \leq 1.9\sigma(I)$; some statistics for these reflections are given in Table II. (The $70\bar{2}$ reflection is excluded, being a severe outlier with $F_o = 0.6$ and $F_c = 13.6$ for both refinements.) For the $P1$ description, the average value of $|F_c|$ is over twice that of F_o and the R index is a striking 1.24, clear evidence of the inappropriateness of the noncentrosymmetric description. On the other hand, the numbers are quite reasonable for the $P\bar{1}$ description. The message is clear and we repeat it:[2] if there is possible ambiguity between a centrosymmetric and a noncetrosymmetric description of a structure, the weak reflections are the ones most able to provide a choice. The common practice of deleting these reflections from the data set is a dangerous one and should be strongly discouraged.

The $P\bar{1}$ refinement has led to a considerably more reasonable molecular structure. For example, the Ge–C bond lengths are statistically equal at 1.970 (3) Å whereas they ranged from 1.896 to 2.050 Å for the $P1$ refinement, and the range of C–C distances is between 1.486 (9) and 1.544 (7) Å compared with 1.427–1.614 Å. Nevertheless, the two S–S distances, at 1.973 (3) and 2.051 (3) Å, remain severely disparate. It is probable that the disparity is related to the disorder of the central atom S(2). In particular, atom S(1,3) has a large anisotropic "temperature" factor, with its principal axis (U = 0.094 (1) A^2) oriented along the S(2)···S(2)′ direction; this atom may well occupy alternative sites that depend upon which S(2) site is occupied. Because of this situation, no reliable value can be assigned to either S–S distance; they could well be equal at about 2.01 Å. The Ge–S distance, for which we obtain the value 2.281 (2) Å, is less seriously in doubt because the bond is directed approximately perpendicular to the principal axis of S(1,3); possibly it should be lengthened slightly.

Acknowledgment. This investigation was supported by Public Health Service Research Grant GM 16966 from the National Institute of General Medical Sciences, National Institutes of Health.

Registry No. $[(C_6H_{11})_3Ge]_2S_3$, 85185-49-5.

Supplementary Material Available: Tables of coordinates and isotropic B's, assigned to the hydrogen atoms, and anisotropic U's (2 pages). Ordering information is given on any current masthead page.

---

(2) Marsh, R. E. *Acta Crystallogr., Sect. B* **1981**, *837*, 1985–1988.

Synthesis and Characterization of New, Air-Stable *closo*-1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$

Narayan S. Hosmane* and Narayan N. Sirmokadam

Department of Chemistry, Southern Methodist University
Dallas, Texas 75275

Received April 5, 1984

Summary: The *closo*-osmacarborane, 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$, has been synthesized by the reaction of Os$_3$(CO)$_{12}$ with either *closo*-Sn[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_4$ or *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$. The reaction of Os$_3$(CO)$_{12}$ with the *closo*-stannacarborane yielded the osmacarborane in gram quantities in almost quantitative yields, while *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$ produced the osmacarborane in much lower yields.

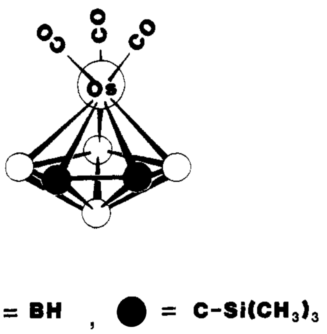


Figure 1. Proposed structure of 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$.

Although several hundred metallacarborane derivatives containing transition metals or main-group metals have been synthesized,[1,2] insertion of osmium metal into a carborane cage framework has never been reported. However, Shore et al. demonstrated the insertion of one BH unit into an osmium–carbonyl bond of $(\mu\text{-H})_2Os_3(CO)_{10}$ to produce $(\mu\text{-H})_3(CO)_9Os_3BCO$ in 85% yield.[3]

We have recently reported the synthesis of the carborane *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$[4] and the stannacarborane *closo*-Sn[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_4$.[5] We report herein the reaction of Os$_3$(CO)$_{12}$ with these new carboranes to produce the first osmacarborane having a pentagonal-bipyramidal geometry (Figure 1). This compound is isoelectronic and isostructural with known metallacarboranes[1,2] of the types C$_2$B$_4$H$_6$MLn, C$_2$B$_3$H$_5$(MLn)$_2$ [MLn = Fe(CO)$_3$, CoCp, Ni(PPh$_3$)$_2$, Pt(PEt$_3$)$_2$, GaR, BeNMe$_3$, AlR, Sn, Pb], C$_3$B$_3$H$_5$CH$_3$Mn(CO)$_3$, and C$_4$BH$_3$R$_2$[Mn(CO)$_3$]$_2$.

The reaction of Os$_3$(CO)$_{12}$ with *closo*-Sn[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_4$, in a molar ratio of 1:3, in the absence of a solvent at 150 °C produced 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$ as an air-stable, volatile (bp 148–149 °C at 10 torr of argon), colorless liquid; in addition, the side products, carbon monoxide and metallic tin (Sn^0), were produced in almost quantitative yields. The fact that this compound is obtained in gram quantities as a single volatile carborane product is in contrast with the results of the gas-phase reaction of Sn(CH$_3$)$_2$C$_2$B$_4$H$_4$ with (η^5-C$_5$H$_5$)Co(CO)$_2$ which produced a mixture of (η^5-C$_5$H$_5$)CoSn(CH$_3$)$_2$C$_2$B$_4$H$_4$, 1,2,3-(η^5-C$_5$H$_5$)Co(CH$_3$)$_2$C$_2$B$_4$H$_4$, and (η^5-C$_5$H$_5$)$_2$Co$_2$(CH$_3$)$_2$C$_2$B$_4$H$_4$ in low yields.[6] The reaction of Os$_3$(CO)$_{12}$ with *nido*-[(CH$_3$)$_3$Si]$_2$C$_2$B$_4$H$_6$ at 140 °C also produced the same *closo*-osmacarborane (Figure 1) in very low yield (<3%). The other detectable gaseous products were carbon monoxide and, presumably, hydrogen.

The electron-impact mass spectrum of 1-Os(CO)$_3$-2,3-[(CH$_3$)$_3$Si]$_2$-2,3-C$_2$B$_4$H$_4$ exhibited an intense parent grouping $[{}^{192}\mathrm{Os}({}^{12}\mathrm{C}{}^{16}\mathrm{O})_3({}^{12}\mathrm{CH}_3)_6{}^{28}\mathrm{Si}_2{}^{12}\mathrm{C}_2{}^{11}\mathrm{B}_4\mathrm{H}_4{}^+]$ with the major cutoff at m/e 494 and strong groups with local cutoffs at m/e 479, 466, 451, 423, 409, 395, 338, 323, 309 that correspond to the fragments Os(CO)$_3$(CH$_3$)$_5$Si$_2$C$_2$B$_4$H$_4^+$, Os(CO)$_2$(CH$_3$)$_6$Si$_2$C$_2$B$_4$H$_4^+$, Os(CO)$_2$(CH$_3$)$_5$Si$_2$C$_2$B$_4$H$_4^+$, Os(CO)(CH$_3$)$_5$Si$_2$C$_2$B$_4$H$_4^+$, Os(CO)(CH$_3$)$_4$Si$_2$C$_2$B$_4$H$_5^+$, Os-

---

(1) "Metal Interactions with Boron Clusters", Grimes, R. N., Ed. Plenum Press: New York, 1982 and references therein.

(2) Grimes, R. N. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982, Vol. 1, and references therein.

(3) Shore, S. G.; Jan, D. Y.; Hsu, L. Y.; Hsu, W. L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

(4) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N., submitted for publication.

(5) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics*, in press.

(6) Wong, K.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053.

0276-7333/84/2303-1119$01.50/0 © 1984 American Chemical Society

Table I. FT NMR Data of $Os(CO)_3[(CH_3)_3Si]_2C_2B_4H_4$ (^1H, 200.132, ^{11}B, 64.2, ^{13}C, 50.32, and ^{29}Si, 39.76 MHz)

nuclei	δ (*J*, Hz)^{a,b}		rel area	assignmt
^1H	5.38 (166)	broad	1	H_t (base)
	4.52 (160)	overlapping	2	H_t (base)
	3.75 (154)	quartets	1	H_t (apex)
	0.37	singlet	18	$(CH_3)_3Si$
^{11}B	15.80 (168)	doublet	1	B(5)-H (base)
	11.05 (158)	doublet	2	B(4,6)-H (base)
	2.70 (156)	doublet	1	B(7)-H (apex)
^{13}C	173.48	singlet		CO in $Os(CO)_3$
	89.93	singlet		cage carbons
	1.94 (119.8)	quartet		$(CH_3)_3Si$
^{29}Si	2.26 (4.3)	multiplets of 10 lines		$(CH_3)_3Si$

[a] $CDCl_3$ was used as solvent in all the spectra. [b] Chemical shifts (in ppm) are relative to (i) $(CH_3)_4Si$ for the nuclei ^1H, ^{13}C, and ^{29}Si and (ii) $BF_3O(C_2H_5)_2$ for ^{11}B, with a positive sign denoting a downfield shift.

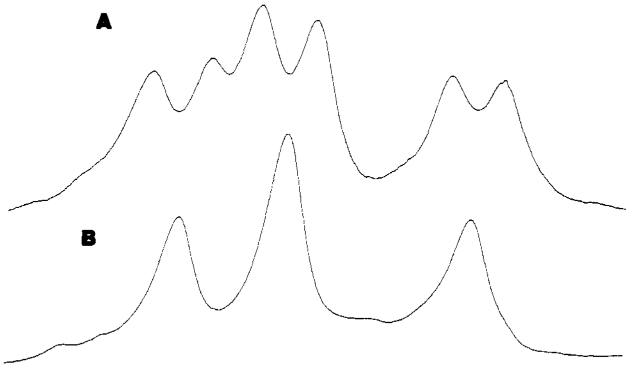


Figure 2. 64.2-MHz ^{11}B FT NMR spectra of $Os(CO)_3[(CH_3)_3Si]_2C_2B_4H_4$ (in $CDCl_3$): A, undecoupled; B, proton decoupled. Chemical shifts and coupling constants are reported in Table I.

$(CH_3)_5Si_2C_2B_4H_4^+$, $Os(CH_3)_3SiC_2B_4H_5^+$, $Os(CH_3)_2SiC_2B_4H_5^+$, and $Os(CH_3)SiC_2B_4H_6^+$, respectively. On the basis of natural isotopic distributions of osmium, boron, and silicon, the pattern of intensities is consistent with the compositions indicated. Intense peaks at *m/e* 73 and 45, corresponding to the $(CH_3)_3Si^+$ and $CH_3SiH_2^+$ fragments, respectively, were also observed.

The undecoupled and proton-decoupled ^{11}B pulse Fourier transform NMR spectra (Figure 2) and ^1H pulse Fourier transform NMR data (Table I) confirm the presence of four $B\text{-}H_{terminal}$ units with no bridging hydrogen atoms. The ^1H and ^{29}Si NMR data show only one type of trimethylsilyl group in the osmacarborane. Except for the large shift of the $B(7)\text{-}H_{apex}$ resonance, the ^{11}B NMR spectrum of the osmacarborane bears no similarity to that of the precursor $Sn[(CH_3)_3Si]_2C_2B_4H_4$, which has a single low-field doublet due to the overlapping of basal B(4)-H, B(5)-H, and B(6)-H resonances.[5] As can be seen in Figure 2, the nonequivalence of the basal boron atoms in the osmacarborane is similar to that found in $1\text{-}Fe(CO)_3\text{-}2,3\text{-}C_2B_4H_6$ and supports the presence of an $Os(CO)_3$ unit occupying one of the apical positions.[7] The ^{13}C pulse Fourier transform NMR spectrum (Figure 3) exhibits a singlet near 173 ppm, corresponding to three spectroscopically equivalent carbons of the $Os(CO)_3$ [δ(CO) in $Os_3(CO)_{12}$ is 176.4 ppm[8]], another singlet near 90 ppm (due to two equivalent cage carbons[9] heavily shielded due to the π bonding between cage carbons and osmium metal), and a quartet near 2 ppm, assigned to the six equivalent trimethylsilyl carbons.

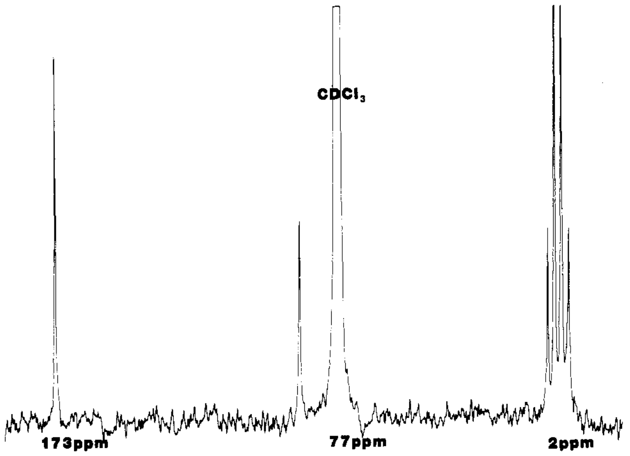


Figure 3. 50.32-MHz undecoupled ^{13}C FT NMR spectrum of $Os(CO)_3[(CH_3)_3Si]_2C_2B_4H_4$ (in $CDCl_3$). Chemical shifts and coupling constants are reported in Table I.

The IR,[10] NMR, and mass spectroscopic data of $Os(CO)_3[(CH_3)_3Si]_2C_2B_4H_4$ are all consistent with the proposed pentagonal-bipyramidal structure, which contains 16 skeletal valence electrtons (assigning two from $Os(CO)_3$, three from each $CSi(CH_3)_3$ and two from each BH unit).

The compound is highly miscible in THF, $CHCl_3$, CH_2Cl_2, CCl_4, $(C_2H_5)_2O$, $(CH_3)_2CO$, $(CH_3)_2C_2$, $(C_6H_5)C_2H$, etc. and stable in air and/or moisture. Because of these properties $Os(CO)_3[(CH_3)_3Si]_2C_2B_4H_4$ would be of great interest in the homogeneous catalytic studies.

The present synthesis of the *closo*-osmacarborane provides further evidence that the BH units of boranes or carboranes can effectively be replaced by units such as $M(CO)_3$ (M = Fe,[7] Ru,[11] or Os), which can act as a source of three atomic orbitals and two electrons for skeletal bonding. Complete replacement of all the BH groups of carboranes or boranes by such metal atom units would thus lead to metal clusters of predictable shapes.

This work, together with earlier studies,[4,5] suggests that the stannacarboranes of the type $1\text{-}Sn\text{-}2\text{-}[(CH_3)_3Si]\text{-}3\text{-}[R]\text{-}2,3\text{-}C_2B_4H_4$ [where R = $Si(CH_3)_3$, CH_3 or H] should be excellent precursors for the preparation of new mono-, di-, and/or polynuclear metal carbonyl cluster derivatives of the small carboranes. Studies on the reactions of stannacarboranes with various polynuclear metal carbonyl

---

[7] Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 6623.

[8] Forster, A.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W.; Robinson, B. H.; Jackson, W. G. *J. Chem. Soc., Chem. Commun.* **1974**, 1042.

[9] The ^{13}C chemical shifts (δ) observed for cage carbons in $[(CH_3)_3Si]_2C_2B_4H_6$ and $Sn[(CH_3)_3Si]_2C_2B_4H_4$ are 143.52 and 133.6 ppm, respectively.[4,5]

[10] IR ($CDCl_3$ vs. $CDCl_3$): 2950 (ms), 2890 (w), 2840 (sh), 2565 (vs), 2080 (vs), 2010 (vvs), 1405 (ms), 1252 (vs), 1158 (ms), 1110 (ms), 1095 (w), 1053 (ms), 840 (vs), 665 (w), 620 (ms), 585 (sh), 555 (vs), 485 (s), 468 (w), 445 (w), 420 (w), and 395 (vw) cm^{-1}.

[11] Siedle, A. R. *J. Organomet. Chem.* **1975**, *90*, 249.

[12] The reactions of $Os(CO)ClH(PPh_3)_3$ under mild conditions with the anions $[B_3H_8]^-$ and $[B_5H_8]^-$ yield *arachno*-$[(HOsB_3H_8)(CO)(PPh_3)_2]$ and *nido*-$[(OsB_5H_9)(CO)(PPh_3)_2]$, respectively: Bould, J.; Greenwood, N. N.; Kennedy, J. D. *J. Organomet. Chem.* **1983**, *249*, 11.

derivatives including $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, and $Co_4(CO)_{12}$ are presently underway in this laboratory.

Acknowledgment. This work was supported by a Cottrell grant from the Research Corp. and a Seed Grant from Southern Methodist University. N.N.S. thanks SMU for a Lazenby Postdoctoral Fellowship. We are indebted to Professor R. H. Neilson, Texas Christian University, for obtaining the mass spectra.

Registry No. 1-$Os(CO)_3$-2,3-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_4$, 90412-46-7; $Os_3(CO)_{12}$, 15696-40-9; *closo*-$Sn[(CH_3)_3Si]_2C_2B_4H_4$, 90388-43-5; *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$, 38117-58-7; Os, 7440-04-2; B, 7440-42-8.

Intramolecular Nucleophilic Attack at Iron in an Anionic Phosphido-Bridged $Fe_2(CO)_6$ Complex

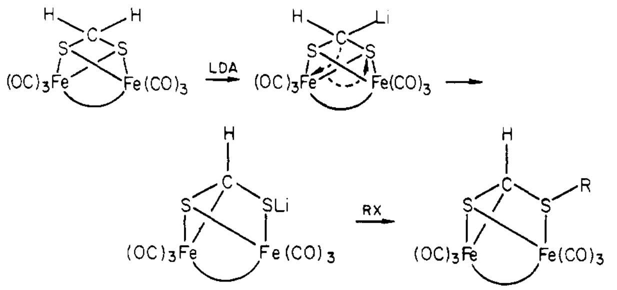
Dietmar Seyferth* and Timothy G. Wood
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

John P. Fackler, Jr., and Anthony M. Mazany
Department of Chemistry, Texas A&M University
College Station, Texas 77843

Received December 14, 1983

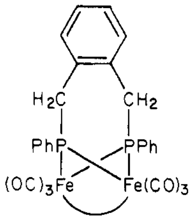
Summary: The reaction of α,α'-dibromo-*o*-xylene with $(\mu\text{-PhPH})_2Fe_2(CO)_6$ and excess Et_3N produces $[(\mu\text{-}o\text{-}C_6H_4(CH_2)_2)(PhP)_2]Fe_2(CO)_6$, **1**, in 46% yield. The deprotonation of **1** by *n*-butyllithium in THF yields a carbanion that undergoes an intramolecular nucleophilic attack at iron to form an Fe–C bond with concomitant Fe–P bond cleavage. Methylation of the phosphorus-centered anion permits the isolation of the cluster now incorporating a methine group bound to iron. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^2, No. 14) with a = 11.996 (1) Å, b = 13.592 (2) Å, c = 16.891 (2) Å, β = 109.80 (1)°, V = 2591.3 Å^3, and Z = 4. Full-matrix least-squares refinement provided a final R value of 0.069 based on 2553 unique reflections. Compound **5** crystallizes in the monoclinic space group $P2_1/n$ (C_{2h}^5, nonstandard setting No. 14) with a = 11.670 (2) Å, b = 14.581 (2) Å, c = 16.674 (2) Å, β = 109.47 (1)°, V = 2674.8 Å^3, and Z = 4. Full-matrix least-squares refinement yields a final value of 0.047 based on 4158 independent reflections. The Fe–CH bond distance (2.139 (3) Å) is longer than usually observed in similar diiron carbonyl clusters.

We have recently reported an example of intramolecular nucleophilic attack at iron in an anionic (alkylthio)$Fe_2(CO)_6$ complex (eq 1).[1] It was of interest to see how general such reactions were, and we describe here a similar process that occurs in an anionic phosphido-bridged $Fe_2(CO)_6$ complex.

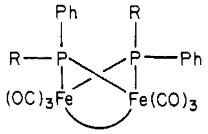


(1)

The starting material for this study was prepared by the reaction, under nitrogen, of α,α'-dibromo-*o*-xylene with $(\mu\text{-PhPH})_2Fe_2(CO)_6$[2,3] in the presence of an excess of triethylamine at −78 °C (0.5 h) and, subsequently, room temperature (12 h). The orange, crystalline solid product that was obtained was resolved by column chromatography into two components: **1**, a yellow solid, mp 242–244 °C dec, obtained in 46% yield,[4] and **2**, an orange solid, mp 144–146 °C, obtained in 25% yield.[5]

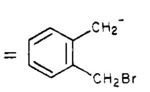


1

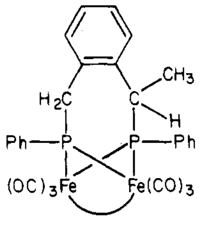


2

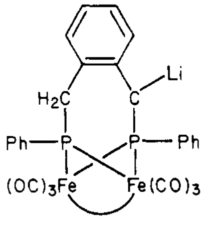
R =



Deprotonation of **1** was carried out by treating a THF solution of this compound at −78 °C under nitrogen with an equimolar quantity of *n*-butyllithium in hexane. A yellow-to-dark green color change was noted. Addition of a 3.3-fold excess of iodomethane at −78 °C caused an immediate color change to yellow. Removal of solvent, extraction of the residue with 30% CH_2Cl_2/petroleum ether, and filtration through a thin pad of silicic acid was followed by removal of solvent to give a 92% yield of **3**, mp 219–221 °C, as a mixture of diastereomers.[6] Thus, at −78 °C, the organolithium reagent **4** is stable.



3



4

---

[1] Seyferth, D.; Womack, G. B.; Song, L.-C.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 928.

[2] Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem.* **1972**, *11*, 1609, 1615.

[3] Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *J. Organomet. Chem.* **1981**, *222*, 273.

[4] The analytical sample was recrystallized from CH_2Cl_2/petroleum ether and was found to be a 1:1 CH_2Cl_2 solvate: ^1H NMR ($CDCl_3$) δ 3.11–3.68 (br m, CH_2, 4 H), 7.02–7.73 (complex m, arene H); ^{31}P NMR ($CHCl_3$) δ_P 136.2; IR ($CHCl_3$) $\nu(C{\equiv}O)$ 2047 (s), 2010 (vs), 1983 (s), 1967 (s) cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_6Fe_2P_2\cdot CH_2Cl_2$: C, 47.34; H, 2.94; Cl, 10.35. Found: C, 47.39; H, 3.24; Cl, 9.68.

[5] Anal. Calcd for $C_{34}H_{26}O_6Fe_2P_2Br_2$: C, 47.26; H, 3.03. Found: C, 47.63; H, 3.16. 250-MHz ^1H NMR ($CDCl_3$): δ 2.27 and 3.85 (both d, J(P–H) = 9.9 and 7.4 Hz, respectively, axial and equatorial P–CH_2, 4 H), 3.23 and 3.64 (both s, axial and equatorial $BrCH_2$, 4 H), 6.68–7.72 (complex m, arene H). ^{31}P NMR ($CHCl_3$): δ_P 141.2 and 145.7 (AX quartet, J(P–P) = 129.0 Hz). IR ($CHCl_3$): 2050 (s), 2006 (vs), 1981 (s), 1962 (s) cm^{-1}.

[6] Anal. Calcd for $C_{27}H_{20}O_6Fe_2P_2$: C, 52.81; H, 3.28. Found: C, 52.94; H, 3.38. 250-MHz ^1H NMR ($CDCl_2$): δ 1.00 and 1.63 (both dd J(H–H) = 7.3, 7.5 Hz, J(P–H) = 16.3, 16.3 Hz, respectively, 3 H, CH_3 of both diastereomers), 2.99–3.15 (overlapping dd's, both diastereotopic CH_2 of one diastereomer, 1 H), 3.86 and 4.15 (both dd, J(H–H) = 14.2, 14.2 Hz, J(P–H) = 14.0, 11.9 Hz, respectively, diastereotopic CH_2 of one diastereomer, 1 H), 3.46 and 3.65 (both m, J(H–H) = 7.5, 7.3 Hz, respectively, C*H*CH_3 of both diastereomers, 1 H), 6.83–7.77 (complex m, arene H). ^{31}P NMR ($CHCl_3$): δ_P 136.5, 152.0 (AX quartet, J(P–P) = 166.0 Hz, one diastereomer), 137.0, 154.3 (AX quartet, J(P–P) = 170.9 Hz, other diastereomer). IR ($CHCl_3$): $\nu(C{\equiv}O)$ 2049 (s), 2005 (vs), 1984 (s), 1965 (s) cm^{-1}.

0276-7333/84/2303-1121$01.50/0 © 1984 American Chemical Society