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Disproportionation of Diiron Nonacarbonyl in THF Solution: Formation and Structure of $Fe(THF)_4[HFe_3(CO)_{11}]_2$

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Introduction

The three known iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ were discovered by Mond[2] and Dewar[3] at the beginning of this century. Though Dewar noted the disproportionation reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ induced by pyridine and alumina, the true complexity of these reactions was only recently indicated. Electron spin resonance studies have revealed several odd-electron iron species intermediate in these reactions, suggesting that single-electron-transfer processes play an important part in the overall mechanisms.[4,5] Reactions are frequently both solvent and atmosphere dependent. In the case of solutions of $Fe_2(CO)_9$ in THF, the presence of a CO atmosphere leads to stabilization of the species in solution (presumably $(THF)Fe(CO)_4$),[6] whereas, under vacuum or another inert atmosphere, such as N_2 or Ar, these solutions undergo disproportionation to give red solutions which have been characterized as containing $HFe_3(CO)_{11}^-$ anions.[4] Recently the radical anion $Fe_3(CO)_{11}^{\bullet-}$ was found to decompose in THF to give the iron carbonylate anion $HFe_3(CO)_{11}^-$.[7] The characterization of these reaction mixtures has, in general, been incomplete. In most cases, the $HFe_3(CO)_{11}^-$ anion was extracted from the mixture using a suitable counterion before being identified; in other cases the presence of the anion was inferred from UV or IR spectra of the complex mixture. Such procedures leave the exact nature of the counterion undetermined and the source of the hydrogen atom ambiguous. Prompted by our results with other organic molecules,[8] we have reinvestigated the reaction of diiron nonacarbonyl with THF. We report here the structure of a minor product of this reaction: $Fe(THF)_4[HFe_3(CO)_{11}]_2$ (**1**), the first reported transition metal complex of the $HFe_3(CO)_{11}^-$ anion. We also note that the major product of this reaction does not contain the $HFe_3(CO)_{11}^-$ anion or the related radical anion $Fe_3(CO)_{11}^{\bullet-}$ though unfortunately the reactive and noncrystalline nature of this material prevented further characterization.

Table 1. Crystallographic Data for $[Fe(THF)_4[HFe_3(CO)_{11}]_{12}$ (**1**)

formula	$Fe_7C_{38}O_{26}H_{34}$	fw	1297.6
a, Å	9.336(2)	space group	$P\bar{1}$ (No. 2)
b, Å	11.078(3)	*T*, °C	−100
c, Å	12.499(3)	λ, Å	0.710 73
α, deg	79.76(2)	ρ_{calcd}, g cm^{-3}	3.67
β, deg	70.90(2)	μ, cm^{-1}	4.386
γ, deg	74.78(2)	R^a	0.0568
V, Å^3	1172.7(5)	R_w^b	0.100
Z	2		

[a] $R = \Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2$ for reflections with $F_o \geq 4\sigma(F_o)$. [b] $R_w = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^4)\}^{1/2}$, where the weight, *w*, is defined as follows: $w = 1/\{\sigma^2(|F_o|^2) + (0.02P)^2\}$; $P = [{}^1/_3(\text{maximum of 0 or } |F_o|^2) + {}^2/_3|F_o|^2]$.

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for Selected Atoms of $Fe(THF)_4[HFe_3(CO)_{11}]_2$ (**1**)

atom	*x*	*y*	*z*	U^a
Fe1	0.38013(7)	0.16910(6)	0.32115(5)	0.0250(2)
Fe2	0.13346(7)	0.13698(5)	0.26976(5)	0.0210(2)
Fe3	0.09975(7)	0.32483(5)	0.37681(5)	0.0203(2)
Fe4	0.0	0.5	0.0	0.0186(3)
C11	0.1034(5)	0.3139(4)	0.2229(3)	0.0201(14)
O11	0.0882(3)	0.3841(3)	0.1390(2)	0.0239(11)
O12	0.2233(3)	0.4509(3)	−0.1182(2)	0.0239(11)
O17	0.0570(3)	0.6554(3)	0.0357(2)	0.0257(11)
H23	0.072(5)	0.193(4)	0.394(4)	0.043(14)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct space unit cell vectors.

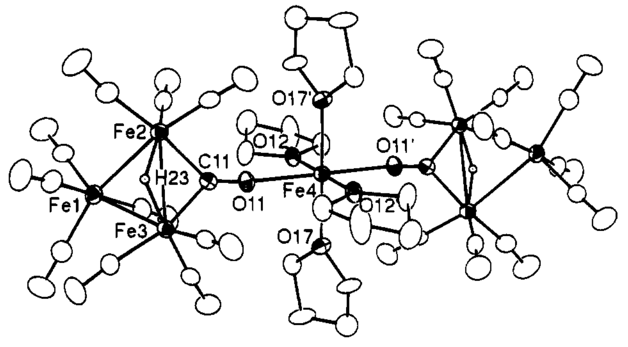

Figure 1. Thermal ellipsoid plot for $Fe(THF)_4[HFe_3(CO)_{11}]_2$, **1**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Results

Shaking a suspension of diiron nonacarbonyl in a mixture of benzene and THF sealed under vacuum results in slow reaction with the solvent mixture. Over a period of several days, the diiron nonacarbonyl (which is only sparingly soluble in the solvent mixture) is consumed and a dark green solution forms along with a flocculent red solid. The green color is due to formation of small quantities of triiron dodecacarbonyl ($Fe_3(CO)_{12}$). Heating the solution results in destruction of the $Fe_3(CO)_{12}$, leaving only the red solid and a reddish orange solution. The infrared spectrum of the red solid reveals only terminal CO stretches. $Fe(CO)_5$ is also formed in the reaction and was detected by infrared spectroscopy of the volatile components of the reaction mixture. Upon standing for several weeks, some of these reaction mixtures deposited small red tabular crystals of $Fe(THF)_4[HFe_3(CO)_{11}]_2$ (**1**) on the walls of the flask. Growth of these crystals was difficult to reproduce, and the ideal conditions for formation of **1** have yet to be determined. X-ray analysis of a single crystal indicated the structure shown in Figure 1. Selected bond distances and angles are given in Table 3. Infrared spectra of **1** show a bridging carbonyl stretch at 1590 cm^{-1} both in a KBr matrix and in chloroform solution. In tetrahydrofuran, however, the bridging carbonyl stretch is shifted to 1745 cm^{-1}. Control experiments with $Fe_2(CO)_9$ in benzene

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(1) (a) University of Colorado. (b) University of Texas at Austin.

(2) Mond, L.; Quincke, F. *J. Chem. Soc.* **1891**, *59*, 604. Mond, L.; Langer, C. *J. Chem. Soc.* **1891**, *59*, 1090.

(3) Dewar, J.; Jones, H. O. *Proc. R. Soc. London* **1905**, *76*, 538. Dewar, J.; Jones, H. O. *Proc. R. Soc. London* **1907**, *79*, 66.

(4) Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1980**, *19*, 465.

(5) Luo, F. H.; Yang, S. R.; Li, C. S.; Duan, J. P.; Cheng, C. H. *J. Chem. Soc., Dalton Trans.* **1991**, 2435. Yang, S. L.; Li, C. S.; Cheng, C. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1873.

(6) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

(7) Ragaini, F.; Ramage, D. L.; Song, J. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 12183.

(8) Brook, D. J. R. Ph.D. Thesis, University of Colorado, 1993.

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Table 3. Selected Bond Lengths and Angles for $Fe(THF)_4[HFe_3(CO)_{11}]_2$ (**1**)

Bond Lengths (Å)			
Fe1−Fe2	2.706(1)	Fe1−Fe3	2.679(1)
Fe2−Fe3	2.567(1)	Fe2−H23	1.65(5)
Fe2−C11	1.917(4)	Fe3−H23	1.52(5)
Fe3−C11	1.938(4)	C11−O11	1.214(5)
Fe4−O11	2.220(3)	Fe4−O12	2.121(2)
Fe4−O17	2.087(3)		
Bond Angles (deg)			
Fe2−Fe1−Fe3	56.94(3)	Fe1−Fe2−Fe3	61.00(3)
Fe2−H23−Fe3	108(2)	Fe2−C11−Fe3	83.5(2)
Fe2−C11−O11	137.9(4)	Fe3−C11−O11	138.6(3)
C11−O11−Fe4	165.0(3)	Fe1−Fe3−Fe2	62.06(3)
O11−Fe4−O12	90.2(1)	O11−Fe4−O17	89.4(1)
O12−Fe4−O17	90.9(1)		

alone confirm Dewar's early observation that, in hydrocarbon solvents, diiron nonacarbonyl decomposes to form $Fe(CO)_5$ and $Fe_3(CO)_{12}$.[3]

Discussion

Previous reports indicate that the solvolytic disproportionation of iron carbonyls is extremely sensitive to reaction conditions. Cotton reported that, under a CO atmosphere, THF solutions of $Fe_2(CO)_9$ were stable, behaving as solutions of $Fe(CO)_5$ and $(THF)Fe(CO)_4$, but rapidly exchanging CO. Under a flowing argon atmosphere, however, the solution turned dark red, presumably due to disproportionation.[6] Using slightly different conditions, Dawson and co-workers obtained complex mixtures of products from the $Fe_2(CO)_9$/THF system including $Fe_3(CO)_{12}$ from reaction under N_2 but the $HFe_3(CO)_{11}^-$ anion when the reaction occurred under vacuum.[4] Taking these previous results into consideration, we decided that use of a closed, evacuated reaction vessel would allow for effective removal of contaminant gases and overall more reproducible reaction conditions. We note that the closed system may cause marked differences in the course of the reaction. Notably, carbon monoxide, which is normally released to the atmosphere in the course of iron carbonyl disproportionations, will be confined to the reaction vessel where it may react with $Fe_2(CO)_9$ to produce $Fe(CO)_5$ or react with intermediate carbonylate anions to produce a variety of products. Under certain conditions carbon monoxide has even been known to prevent or reverse the disproportionation of iron carbonyl complexes.[9] Diluting the THF reagent with benzene results in greatly decreased solubility of the disproportionation products and facilitates their isolation and characterization. Control experiments indicate that benzene alone does not induce disproportionation.

Under these conditions, and using carefully dried solvents, the disproportionation reaction goes to completion, giving two major products, $Fe(CO)_5$ and an insoluble, extremely air-sensitive, purple-red precipitate. An infrared spectrum of the precipitate indicated the presence of only terminal CO groups, eliminating the possibility that it contains either the $HFe_3(CO)_{11}^-$ or $Fe_3(CO)_{11}^{2-}$ anion. The material was ESR silent, eliminating the possibility that the material contained the $Fe_3(CO)_{11}^{\bullet -}$ radical anion. Analysis indicates an extremely high iron content (greater than 50% Fe by weight) for this solid, but unfortunately the insolubility and extreme reactivity of the material prevented further characterization. Occasionally, when allowed to stand for several weeks, the reaction mixture also gave red crystals of the previously unknown complex $Fe(THF)_4[HFe_3(CO)_{11}]_2$ (**1**). The slow rate of deposition of these crystals suggests that this salt is formed as a further reaction of the red solid, though the possibility of its being formed in a parallel reaction has not been eliminated. The difficulty experienced in reproducing the crystallization suggests the influence of an as yet unidentified catalyst or reagent. Introduction of traces of water as proton source did not detectably influence the reaction. Introduction of halide ions (as tetrabutylammonium bromide) induced rapid disproportionation, giving a red precipitate containing $HFe_3(CO)_{11}^-$ ions but did not yield the compound **1**. It is quite possible that very small traces of halide in the reaction mixture are required to produce **1**.

The product $Fe(THF)_4[HFe_3(CO)_{11}]_2$ provides the first example of the $HFe_3(CO)_{11}^-$ anion acting as a ligand toward a transition metal. It has long been known that $HFe_3(CO)_{11}^-$ forms hydrogen bonds through the bridging carbonyl[10] and is protonated[11] and methylated[12] at the bridging carbonyl; however, no other metal complexes of this anion were previously characterized. The anion is unusual among iron carbonylate anions in its behavior. The anions $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, and $Fe_3(CO)_{11}^{2-}$ all form metal−metal bonds with other metals;[13] even with alkali metals, interaction primarily occurs between metal centers.[14]

Examination of the structure indicates that the actual metal−OC interaction is weak. The Fe^{2+}−OC bond (2.220(3) Å) is significantly longer than either of the two independent Fe^{2+}−THF bonds (2.121(2) and 2.087(3) Å, respectively). Of the two metal−THF ligand distances, one is comparable to and the other shorter than those observed in the $Fe(THF)_6^{2+}$ cation.[15] This suggests that the THF ligands are more tightly bonded to compensate for the weak Fe^{2+}−$HFe_3(CO)_{11}$ bonding. The $HFe_3(CO)_{11}^-$ anion itself is only slightly distorted by coordination to Fe^{2+}. The bond distances and angles observed are all comparable to those in the bis(triphenylphosphine)nitrogen(1+) (PPN) salt of $HFe_3(CO)_{11}^-$ with the exception of the angle between the planes of the Fe−Fe−Fe triangle and the Fe−CO−Fe bridge.[16] In **1** this angle is 108°, slightly larger than that found in the uncoordinated ligand (102°). This contrasts with the *O*-methyl derivative of $HFe_3(CO)_{11}^-$ where the angle closes to 91°.[12] This opening of the carbonylate anion may well be a simple steric influence; there is a weak van der Waals contact between one of the axial CO ligands and a THF hydrogen atom.

The infrared spectra of **1** reveal further information about the metal−ligand interactions. Both solid **1** and solutions of **1** in chloroform show bridging CO stretches at 1590 cm^{-1}. This is consistent with the crystal structure and indicates that the

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(9) Fachinietti, G.; Fochi, G.; Funaioli, T.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1987**, 89.

(10) Chen, C. K.; Cheng, C. H.; Hseu, T. H. *Organometallics* **1987**, *6*, 868.

(11) Hodal, H. A.; Shriver, D. F.; Ammlung, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5239.

(12) Shriver, D. F.; Lehman, D.; Strope, D. *J. Am. Chem. Soc.* **1975**, *97*, 1594.

(13) Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2090. Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2098. Deck, W.; Powell, A. K.; Vahrenkamp, H. *J. Organomet. Chem.* **1992**, *428*, 353. Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 3242.

(14) Teller, R. G.; Finke, R. G.; Collman, J. P.; Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1977**, 99, 1104. Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 2434.

(15) Spak, W.; Pohl, S. *Z. Anorg. Allg. Chem.* **1987**, *552*, 186.

(16) The structure of the PPN salt of $HFe_3(CO)_{11}^-$ has been reported twice in the literature: Iiskola, E.; Pakkanen, T. A.; Pakkanen, T. T.; Venalainen, T. *Acta Chem. Scand., Ser. A* **1983**, *37*, 125. Deck, W.; Powell, A. K.; Vahrenkamp, H. *J. Organomet. Chem.* **1991**, *411*, 451. Both the reported unit cells are essentially identical; however, the latter structure shows a terminal carbonyl shifted by 0.5 Å into a semibridging position. Though it is unclear whether this effect is a crystallographic artifact or a genuine structural feature, we have based our analysis on the earlier structure determination since it appears to be more representative of the $HFe_3(CO)_{11}^-$ anion in general.

molecular structure is maintained in chloroform solution. In THF solution the bridging carbonyl is shifted back to the more typical position of 1749 cm^{-1}, indicating the displacement of the carbonylate anion and formation of the $Fe(THF)_6^{2+}$ cation. Similar shifts have been observed for the bridging carbonyl of $HFe_3(CO)_{11}^-$ anions when hydrogen bonded to dialkylammonium ions.[10]

Conclusions

The structure determination of $Fe(THF)_4[HFe_3(CO)_{11}]_2$ provides the first example of the $HFe_3(CO)_{11}^-$ anion acting as a transition metal ligand. Unfortunately the mechanism of formation of this product is unclear; the reaction of $Fe_2(CO)_9$ with THF apparently does not produce $HFe_3(CO)_{11}^-$ as a major product under the reaction conditions investigated. The reaction further illustrates the complex nature of iron carbonyl disproportionations and their subtle dependence on reaction conditions; clearly, more work is needed before they can be completely understood.

Experimental Section

All manipulations were performed under an inert atmosphere (either Ar, N_2, or vacuum) using a Vacuum Atmospheres drybox and standard Schlenk techniques. Tetrahydrofuran (THF) and benzene were distilled from sodium benzophenone ketyl. Diiron nonacarbonyl was purchased from the Strem Chemical Co. and used as received. Samples were analyzed for iron by digestion in ULTREX grade nitric acid followed by colorimetry using potassium thiocyanate.

Reaction of $Fe_2(CO)_9$ with THF in Benzene. Diiron nonacarbonyl (526 mg, 1.45 mmol) was placed in a thick-walled glass tube fitted with a Teflon needle valve closure. Benzene (20 mL) was added followed by tetrahydrofuran (2 mL) and the mixture freeze−pump (0.1 mmHg)−thaw degassed for three cycles. After the final evacuation, the needle valve was closed and the tube allowed to warm to room temperature. The mixture was shaken continuously using a mechanical shaker until no visible traces of the diiron nonacabonyl remained (2 days). At this point, the tube contained a dark green solution and a red precipitate. Heating the mixture in an oil bath at 60 °C for 24 h completed the reaction, giving a dark reddish brown suspension. Filtration under an N_2 atmosphere gave 123 mg of a dark purple-red solid. This showed IR bands (KBr) at 2002, 1950 cm^{-1}. The solid material gave no ESR signal. Analysis indicated the material contained 56% Fe by weight. The nonvolatile, insoluble, and extremely air-sensitive nature of the material prevented further characterization. The filtrate contained only $Fe(CO)_5$, as indicated by infrared spectroscopy. Repetition of the reaction with benzene previously saturated with water produced identical results.

$Fe(THF)_4[HFe_3(CO)_{11}]_2$ (1). Diiron nonacarbonyl (370 mg) was combined with 11 mL of benzene (previously saturated with distilled water) and 1 mL of THF. The mixture was freeze (−196 °C)−pump (0.1 mmHg)−thaw degassed for three cycles and sealed in a thick-walled glass tube with a Teflon needle valve. The tube was shaken until all the diiron nonacarbonyl had dissolved (3 days) and a red precipitate had formed. This suspension was allowed to stand over a period of 1 month, during which time dark red plates of **1** grew on the walls of the reaction vessel. These showed IR bands at (KBr) 2073, 2000, 1975, 1958, 1938, 1589 cm^{-1}; ($CHCl_3$) 1590 cm^{-1}; and (THF) 1750 cm^{-1}; and a UV ($CHCl_3$) shoulder at 500 nm. A plate-shaped crystal of approximate dimensions 0.10 × 0.30 × 0.47 mm was selected for X-ray diffraction measurements. The data were collected at 173 K on a Nicolet P3 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo Kα radiation ($\lambda = 0.710\,73$ Å). Relevant crystallographic data are listed in Table 1. Four reflections (−1,1,2; 0,−1,2; 0,−2,1; −1,1,−2) were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.976 to 1.01. The data were corrected for Lp effects. An absorption correction was applied based on differences in observed and calculated structure factors using the routine SHELXA.[17] Data reduction and decay correction were performed using the SHELXTL-Plus software package.[18] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares[19] with anisotropic thermal parameters for all non-H atoms except for one carbon atom on a THF group that was observed to be disordered. The hydrogen atoms were calculated in idealized positions (C−H 0.96 Å) with isotropic temperature factors set to 0.08 Å^2. The bridging hydrogen atom, H23, was located from a ΔF map and refined with an isotropic temperature factor. The structure was refined on F_o^2 using SHELXL93.[20] The function, $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.184P)^2 + 0.412P]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. Neutral-atom scattering factors and values used to calculate the linear absorption coefficient were taken from ref 20. Other computer programs used in this work are listed elsewhere.[21] All figures were generated using SHELXTL-Plus.[19] Positional parameters for selected atoms are listed in Table 2. Select bond lengths and angles are listed in Table 3. Full tables of positional and thermal parameters, bond lengths, and bond angles and additional structural diagrams are located in the Supporting Information.

Decomposition of $Fe_2(CO)_9$ in Benzene. Diiron nonacarbonyl (670 mg, 1.84 mmol) was combined with 10 mL of benzene, and the mixture was freeze−pump−thaw degassed and sealed in a glass reaction tube under vacuum. The mixture was allowed to stand for 72 h and then heated at 60 °C for 24 h to complete the reaction. After this period, the reaction tube contained a deep green solution and black blocky crystals of $Fe_3(CO)_{12}$, identified by IR spectroscopy. The solution was evaporated under vacuum, and the volatile components were collected in a liquid nitrogen trap. IR spectroscopy indicated only the presence of benzene and $Fe(CO)_5$.

Reaction of $Fe_2(CO)_9$ with Tetrabutylammonium Bromide in THF/Benzene. Diiron nonacarbonyl (513 mg, 1.4 mmol), tetra-*n*-butylammonium bromide (131 mg, 0.4 mmol), THF (2 mL), and benzene (23 mL) were combined in a glass reaction tube. The mixture was freeze (−196 °C)−pump (0.1 mmHg)−thaw degassed and sealed under vacuum. The tube was agitated with a mechanical shaker for 12 h, after which the mixture consisted of a bright red solid and red solution. IR spectroscopy of the solid indicated that it contained uncoordinated $HFe_3(CO)_{11}^-$ anions (bridging CO stretch at 1745 cm^{-1}). No IR absorption corresponding to a coordinated bridging carbonyl was observed.

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Supporting Information Available: Full tables listing details of data collection and refinement, atomic coordinates, bond lengths, and bond angles and figures showing the complete atomic labeling scheme and a packing diagram for **1** (8 pages). Ordering information is given on any current masthead page.

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(17) Sheldrick, G. M. *SHELXA. A computer program to estimate systematic errors in the data by differences in the observed and calculated structure factor amplitudes*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1993.

(18) Sheldrick, G. M. *SHELXTL-PLUS*, Version 4.1; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(19) Sheldrick, G. M. *J. Appl. Crystallogr.*, in press.

(20) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Press: Boston, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(21) Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607−1613.