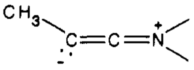
factors are indicative of a significant N–C $\pi$-bonding interaction which is believed to supercede and disrupt the metal–alkyne $\pi$-back-bonding, and this causes the ligand to shift from the normal triply bridging modes to this unusual edge-bridging mode.[7] The observed coordination can be understood in terms of the heteroallene resonance structure C for the ynamine ligand. A $\pi$-coordination of the carbon–carbon double bond to atom Os(1) should produce the bending observed at C(2), C(1)–C(2)–N = 128 (2)°. A $\sigma$-donation of the lone pair on carbon C(1) to Os(3) would produce the observed bridging coordination, and the ynamine would then serve as a four-electron donor as required by the EAN rule.



C

When refluxed in heptane solution for 15 min, compound 2 was decarbonylated and converted to the new compound $Os_3(CO)_9[\mu_3\text{-}H_2CCCN(CH_3)_2](\mu\text{-}H)$ (3) in 90% yield.[9] An ORTEP drawing of 3 is shown in Figure 2.[7,10] The molecule contains a triangular triosmium cluster with nine carbonyl ligands, a triply bridging $H_2CCCN(CH_3)_2$ ligand, and bridging hydride ligand.[11] The latter two ligands were formed by the activation of one of the C–H bonds on the *C*-methyl group of the ynamine ligand and the transfer of the hydrogen atom to the metal atoms. The $H_2CCCN(CH_3)_2$ ligand bridges the face of the cluster through three carbon atoms. As in 2, there is evidence for a strong C(2)–N $\pi$-bonding interaction: the nitrogen atom is planar; the C(2)–N distance is short, 1.33 (1) Å, and there is a hindered rotation about the C(2)–N bond that is slow on the $^1$H NMR time scale even at 100 °C.[12] Mechanistically, the loss of CO from 2 probably occurs at the CO-rich metal atom Os(2). The alkyne ligand might then assume a coordination similar to that in 1 that would bring the *C*-methyl group proximate to the metal atoms Os(1) and Os(3). Formally, this decarbonylated species would be electronically unsaturated, and this should facilitate an intramolecular attack at one of the C–H bonds of the methyl group to form the saturated product 3.[14] Further studies focused on the reactivity of activated ynamine ligand in 2 and 3 are in progress.

**Acknowledgment.** These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Johnson-Matthey Inc. for a loan of osmium tetraoxide.

**Registry No.** 2, 118496-12-1; 3, 94955-83-6; $Os_3(CO)_{10}(NCMe)_2$, 61817-93-4; $CH_3C{\equiv}CN(CH_3)_2$, 7223-38-3; Os, 7440-04-2.

**Supplementary Material Available:** Tables of crystallographic data, positional parameters, intramolecular distances, intramolecular angles, and anisotropic thermal parameters for compounds 2 and 3 (16 pages); listings of structure factor amplitudes for compounds 2 and 3 (36 pages). Ordering information is given on any current masthead page.

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(9) Yellow 3 was isolated by TLC on silica gel. IR ($\nu$(CO), cm$^{-1}$, in hexane): 2088 s, 2057 vs, 2035 vs, 2012 s, 2003 s, 1994 s, 1978 s, 1952 m. $^1$H NMR ($\delta$ in $CD_2Cl_2$): 3.52 (s, 3 H), 3.50 (s, 3 H), 2.10 (br, 2 H), −19.81 (s, br, 1 H). A satisfactory elemental analysis has been obtained.

(10) Crystals of 3, grown from hexane/$CH_2Cl_2$ solutions at 0 °C, belong to the monoclinic crystal system: space group $P2_1/n$, $a$ = 13.001 (2) Å, $b$ = 10.325 (1) Å, $c$ = 15.570 (2) Å, $\beta$ = 113.109 (9)°, Z = 4. The structure was solved by direct methods and was refined (3185 reflections) to the final values of the residuals, $R$ = 0.030 and $R_w$ = 0.034.

(11) The hydrogen atoms shown in Figure 2 were located and refined crystallographically.

(12) The ruthenium homologue of 3 is known but was prepared by a different method.[13]

(13) Aime, S.; Osella, D.; Arce, A. J.; Deeming, A. J.; Hursthouse, M. B.; Galas, A. M. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1981.

(14) The 2-butyne complex $Os_3(CO)_{10}(\mu_3\text{-}CH_3C_2CH_3)$ also undergoes activation of a CH bond on one of the methyl groups when it is decarbonylated.[15]

(15) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614.

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# Carbon Migration along the Fe–Fe Bond during the Transformation of $[(\mu\text{-}\eta^3\text{-}\overline{SCS(CH_2)_2S})Fe_2CO_5L]$ into $[(\mu\text{-}\eta^2\text{-}CH_2{=}CHS\ddot{C}\ddot{S})(\mu\text{-}CH_3S)Fe_2(CO)_5L]$

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*Laboratoire de Chimie Minérale, U.A. CNRS 254, and*
*Ecole Nationale Supérieure de Chimie*
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*Received June 20, 1988*

*Summary:* When they are treated with strong bases, cyclic trithiocarbonate complexes of type $[(\mu\text{-}\eta^3\text{-}\overline{SC(1)\text{-}S(CH_2)_2S})Fe_2(CO)_5L]$ (**3a** (L = CO) and **3b** [L = $P(OMe)_3$]) undergo ring opening. After S-alkylation the new complexes $[(\mu\text{-}\eta^3\text{-}SC(1)(SCH{=}CH_2)(\mu\text{-}SCH_3)Fe_2(CO)_5L]$ (**6a** (L = CO) and **6b** [L = $P(OMe)_3$]) are isolated and characterized. The X-ray structure of **6b** proves that this first sequence does not affect the metal coordination spheres. Under thermal activation **6a** and **6b** undergo a C(1)–(SCH$_3$) cleavage leading ultimately to the carbenic species $[(\mu\text{-}\eta^2\text{-}CH_2{=}CHS\ddot{C}(1)\ddot{S})Fe_2(CO)_5L(\mu\text{-}SCH_3)]$ (**5a** (L = CO) and **5b** [L = $P(OMe)_3$]). During this last step C(1) migrates along the Fe–Fe axis.

Ligand fragmentations and atom migrations in the coordination sphere of polynuclear transition-metal complexes are topics of current interest because unexpected transformations occur under electron-transfer catalysis,[1] under thermal activation,[2] by reaction with strong bases,[3,4] or during ligand exchange processes.[5] We have recently demonstrated that xanthates R–O–C(S)–S–R react with $Fe_2(CO)_9$ affording compounds **1a** which are the precursors of the carbenic complexes **2a**.[6] Under thermal activation

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(1) Lhadi, E. K.; Patin, H.; Darchen, A. *Organometallics* **1984**, *3*, 1128.

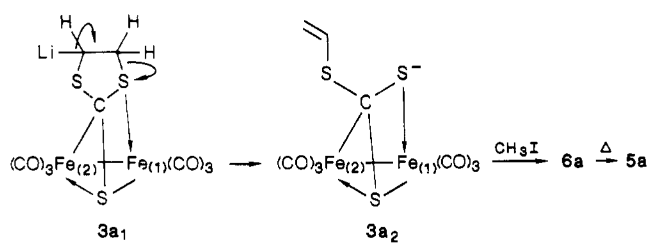
(2) Darchen, A.; Lhadi, E. K.; Grandjean, D.; Mousser, A.; Patin, H. *J. Organomet. Chem.* **1988**, *342*, C15.

(3) Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 1696.

(4) Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1121.

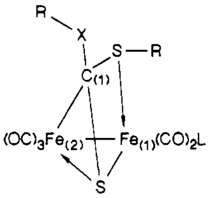
(5) Darchen, A.; Lhadi, E. K.; Patin, H. *J. Organomet. Chem.* **1987**, *327*, C47.

**Scheme I**

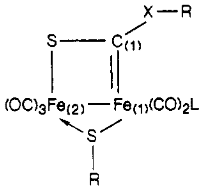


or electron-transfer catalysis the C(1)–Fe(2) and C(1)–SR bonds are broken; moreover, with use of labeling experiments, we have shown that C(1) migrates from Fe(2) to Fe(1) during the rearrangement **1b** → **2b**.[2,6]

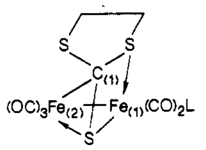
The trithiocarbonates R–S–C(S)–S–R also react with Fe$_2$(CO)$_9$ to give complexes **2c** but in that case **1c** could not be isolated.[7,8] The coordination compound **3a** obtained by complexation of ethylenetrithiocarbonate represents the cyclic analogue of **1c**. No fast chemical reaction occurs when **3a** was submitted to electron-transfer catalysis. On the other hand, under thermal activation the expected fragmentation of the heterocycle was not observed and complex **4** was formed by a bimolecular process, the nature of which has not yet been elucidated.[9] Finally, the behavior of **3** in the presence of strong nonnucleophilic bases has been studied and the results are described in this paper.



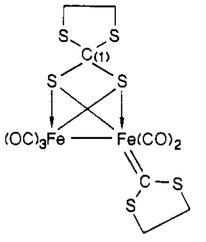
**1a**: L = CO, X = O
**b**: L = P(OMe)$_3$, X = O
**c**: L = CO, X = S



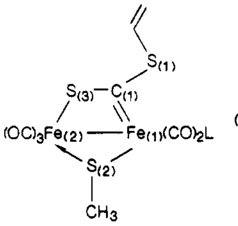
**2a**: L = CO, X = O
**b**: L = P(OMe)$_3$, X = O
**c**: L = CO, X = S



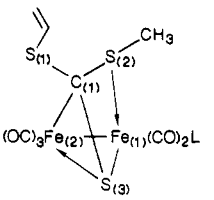
**3a**: L = CO
**b**: L = P(OMe)$_3$



**4**



**5a**: L = CO
**b**: L = P(OMe)$_3$



**6a**: L = CO
**b**: L = P(OMe)$_3$

Seyferth and co-workers have used successfully the following sequence on several binuclear hexacarbonyl compounds such as a methylene dithio-bridged complex and α,ω-dithioalkylene-bridged Fe$_2$(CO)$_6$ and dithioformate ester –Fe$_2$(CO)$_6$ coordination compounds: (i) hydrogen abstraction leading either to rearrangements by carbanionic attack on iron[3,4,10] or to ligand fragmentation[11] and (ii) reaction of the resulting anions with alkyl halides to afford new complexes. When we treated **3a** with lithium diisopropylamide (LDA) in THF, followed by addition of methyl iodide, the new carbenic complex **5a** was obtained.[12] The structure of **5a** was readily established by the usual analytical and spectroscopic techniques.[12] The $^1$H NMR spectrum is consistent with the presence of *S*-vinyl and *S*-methyl ligands. In $^{13}$C NMR spectrum the low-field resonance at 304 ppm proves the existence of a carbene linked to iron.[13] A small amount of **6a**, characterized by the high-field resonance of C(1) σ-bonded to iron (66 ppm),[14] is also obtained. Complex **6a** rearranges when heated at 55 °C to give **5a**. Consequently, ring opening

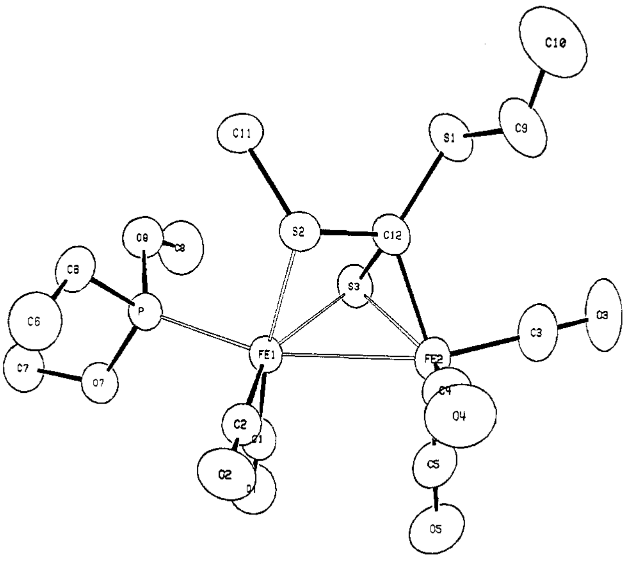


**Figure 1.** Molecular structure and labeling scheme for compound **6b**. Relevant bond distances (Å) and angles (deg): Fe(1)–Fe(2), 2.636 (1); Fe(1)–S(2), 2.307 (2); Fe(1)–S(3), 2.258 (1); Fe(1)–P, 2.182 (1); Fe(1)–C(1), 1.782 (5); Fe(1)–C(2), 1.787 (5); Fe(2)–S(3), 2.198 (1); Fe(2)–C(12), 2.008 (4); Fe(2)–C(3), 1.785 (5); Fe(2)–C(4), 1.774 (5); Fe(2)–C(5), 1.799 (5); C(12)–S(3), 1.772 (4); C(12)–S(2), 1.793 (4); C(12)–S(1), 1.778 (4); Fe(2)–Fe(1)–S(2), 75.34 (3); Fe(2)–Fe(1)–S(3), 52.69 (3); Fe(2)–Fe(1)–P, 159.13 (4); Fe(1)–Fe(2)–S(3), 54.79 (3); Fe(1)–Fe(2)–C(12), 69.7 (1); Fe(1)–S(3)–Fe(2), 72.52 (4); S(2)–Fe(1)–S(3), 78.06 (4); S(3)–Fe(2)–C(12), 49.6 (1); Fe(1)–S(2)–C(12), 81.4 (1); Fe(1)–S(3)–C(12), 83.3 (1); Fe(2)–S(3)–C(12), 59.6 (1); Fe(2)–C(12)–S(1), 128.5 (2); Fe(2)–C(12)–S(2), 105.7 (2); Fe(2)–C(12)–S(3), 70.8 (2); S(1)–C(12)–S(2), 117.8 (2), S(1)–C(12)–S(3), 116.6 (3); S(2)–C(12)–S(3), 107.5 (2).

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(6) Darchen, A.; Lhadi, E. K.; Patin, H. *New. J. Chem.* **1988**, *12*, 377.

(7) Patin, H.; Mignani, G.; Mahe, C.; Le Marouille, J. Y.; Southern, T. G.; Benoit, A.; Grandjean, D. *J. Organomet. Chem.* **1980**, *197*, 315.

(8) Dadamoussa, B. Thesis, Rennes, 1988.

(9) Lagadec, A.; Misterkiewicz, B.; Darchen, A.; Grandjean, D.; Mousser, A.; Patin, H. *Organometallics* **1988**, *7*, 242.

(10) Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. M. *Organometallics* **1984**, *3*, 1891.

(11) Seyferth, D.; Womack, G. B.; Gallagher, M. K.; Cowie, M.; Hames, B. M.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1987**, *6*, 283.

(12) A solution of **3a** (0.94 g, 2.25 mmol) in THF (50 mL) was prepared under argon and cooled to −70 °C. To this solution was added slowly a solution of lithium diisopropylamide (LDA) (0.37 g, 3.45 mmol) prepared under argon in THF (25 mL) and cooled to −70 °C. The red-brown mixture was allowed to stand for 30 min at the same temperature, and 1 mL (16.1 mmol) of CH$_3$I was added. The stirred mixture was slowly warmed to room temperature, and after 1 h it was filtrated. The residue obtained after distillation of THF under vacuum was dissolved in diethyl ether and chromatographed on silica plates (elution with hexane–Et$_2$O, 4/1). The strips of $R_f$ 0.76 and 0.89 were extracted and afforded after crystallization from pentane, respectively, 0.1 g (10%) of **6a** (yellow) and 0.81 g (83%) of **5a** (red). **6a**: mp 72–73 °C; mass spectrum, *m/z* calcd 429.802, found 429.803 (M$^{•+}$) for C$_{10}$H$_6$Fe$_2$O$_6$S$_3$; $^1$H NMR (CDCl$_3$) δ 2.42 (s, 3 H), 5.35 (d, *J* = 10 Hz, 1 H), 5.36 (d, *J* = 17 Hz, 1 H), 6.58 (dd, *J* = 10 Hz, *J* = 17 Hz, 1 H); $^{13}$C NMR (CDCl$_3$ at −55 °C) δ 32.7, 66.4 (CS), 115, 133, 203.3, 204.9, 206.8, 208.7, 212.0, 214.1; IR (KBr) 1960, 2000, 2050, 2090 cm$^{-1}$. **5a**: mp 80 °C; mass spectrum, *m/z* calcd 429.802, found 429.803 (M$^{•+}$); $^1$H NMR (CDCl$_3$) δ 2.57 (s, 3 H), 5.62 (d, *J* = 7 Hz, 1 H), 5.91 (d, *J* = 16 Hz, 1 H), 6.34 (dd, *J* = 7 Hz, *J* = 16 Hz, 1 H); $^{13}$C NMR (CDCl$_3$ at −55 °C) δ 24.6, 125, 137, 206.6, 206.8, 209.5, 210.6, 210.8, 211.0, 304.1 [C(1)]; IR (Nujol) 1980, 2010, 2030, 2050, 2090 cm$^{-1}$. Anal. Calcd for C$_{10}$H$_6$Fe$_2$O$_6$S$_3$:C, 27.93; H, 1.41; Fe, 25.97. Found: C, 27.99; H, 1.65; Fe, 25.52. A solution of **6a** (0.1 g) in dry acetone (20 mL) was refluxed overnight under N$_2$. After usual treatment and chromatography, 0.03 g of **5a** was obtained, identical with an authentic sample ($^1$H NMR and mixed melting point).

(13) Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J. Y.; Grandjean, D. *Inorg. Chem.* **1981**, *20*, 4351.

(14) Patin, H.; Misterkiewicz, B.; Le Marouille, J. Y.; Mousser, A. *J. Organomet. Chem.* **1986**, *314*, 173.

of the carbanion **3a**$_1$ affords the intermediate **3a**$_2$ which is alkylated at sulfur leading to **6a** and finally to **5a** (Scheme I).

The carbanion **3a**$_1$ may not be the kinetic product because the methylene protons $\alpha$ to the sulfur linked to Fe(1) probably are more acidic.[11] In addition, masked pathways can exist during all these transformations. Consequently, we have labeled specifically Fe(1) by replacement of a CO ligand with P(OMe)$_3$. Complex **3b** thus obtained[15] has been submitted to the same reaction sequence.[17] As expected, the coordination of P(OMe)$_3$ stabilizes complex **6b** by decreasing the electron demand on sulfur and consequently making the carbon–sulfur single bond less labile.[6] The structure of **6b** has been established by X-ray diffraction.[18] The ORTEP view (Figure 1) clearly shows that ring opening, followed by alkylation at the sulfur atom linked to iron, occurs without alteration of the metallic skeleton. Compound **6b** is analogous to **1b** previously described[2] with a sulfur atom, instead of oxygen linked to the tetragonal carbon atom C(1). When heated, **6b** undergoes the expected fragmentation giving rise to the carbenic complex **5b** which is in all respects identical with the monosubstituted phosphite derivative prepared independently from **5a**.[19] This transformation **5a** → **5b** is similar to **2a** → **2b** previously described in detail, the structure of **2b** being proved by an X-ray study.[20] In **6b** the P(OMe)$_3$ ligand is linked to Fe(1) while C(1) is bonded to Fe(2), but they are both coordinated to Fe(1) in complex **5b**. Consequently, owing to the phosphite ligand's reluctance to migrate, it is obvious that during the rearrangement the carbon atom C(1) discriminates between Fe(1) and Fe(2) to become bonded to the most electron-rich metal atom. This last step can only occur if in the transition state the carbon atom is bonded to both metal atoms.[2,5,6]

**Registry No.** **3a**, 90697-86-2; **3b**, 118459-31-7; **5a**, 118459-30-6; **5b**, 118459-33-9; **6a**, 118459-29-3; **6b**, 118459-32-8.

**Supplementary Material Available:** Tables of selected interatomic distances, selected bond angles, positional parameters, anisotropic thermal parameters and hydrogen parameters (6 pages); a listing of observed and calculated structure amplitudes (14 pages). Ordering information is given on any current masthead page.

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(15) To a solution of **3a** (2 g, 4.8 mmol) in dry acetone (15 mL) cooled to −80 °C was added P(OMe)$_3$ (0.56 mL, 4.8 mmol). After 3 h under argon at −80 °C, the solvent was partly removed under vacuum and the residue chromatographed on silica plates. The strip of $R_f$ 0.61 gave 0.2 g of **3a** and the strip of $R_f$ 0.26 afforded 1.5 g of **3b** (68%) after crystallization from hexane. **3b**: mp 90 °C; mass spectrum, $m/z$ calcd 511.820, found 511.821 ($M^{\bullet+}$). $^1$H NMR (CDCl$_3$) $\delta$ 2.12 (m, 1 H), 2.53 (m, 3 H), 3.22 [d, P(OMe)$_3$]; $^{31}$P NMR (toluene) $\delta$ 174.4; $^{13}$C NMR (toluene at −85 °C) $\delta$ 36.8, 50.4, 51.3 [P(OMe)$_3$], 76.5 (d, CS, $^3J$ = 4 Hz), 209.9 (d, $J$ = 6 Hz), 211.4 (d, $J$ = 24 Hz), 212.4 (d, $J$ = 3 Hz), 218.7 (2CO); IR (Nujol) 1932, 1972 (br), 2044 cm$^{-1}$. Anal. Calcd for $C_{11}H_{13}Fe_2O_8PS_3$: C, 25.80; H, 2.56; P, 6.05. Found: C, 26.01; H, 2.64; P, 5.90. The position of P(OMe)$_3$ was assigned by considering the low value of the $^3J_{P-C}$ coupling[16] and later by an X-ray diffraction study.[8]

(16) Lagadec, A.; Misterkiewicz, B.; Patin, H.; Mousser, A.; Le Marouille, J. Y. *J. Organomet. Chem.* **1986**, *315*, 201.

(17) A solution of **3b** (0.512 g, 1 mmol) in THF (50 mL) was treated at −70 °C, under argon, with a solution of LDA (0.150 g, 1.5 mmol) in 25 mL of THF. The reaction and treatment are conducted as for **3a**,[12] and we obtained 0.25 g (50%) of the orange compound **6b** ($R_f$ 0.45) and 0.08 g (15%) of the red compound **5b** ($R_f$ 0.54). **6b**: mp 103 °C; mass spectrum, $m/z$ calcd 525.836, found 525.839 ($M^{\bullet+}$); $^1$H NMR (CDCl$_3$) $\delta$ 2.27 (s, 3 H), 3.73 [d, P(OMe)$_3$], 5.26 (d, $J$ = 10 Hz, 1 H) 5.31 (d, $J$ = 17 Hz, 1 H), 6.52 (dd, $J$ = 10 Hz, $J$ = 17 Hz, 1 H); $^{13}$C NMR (CDCl$_3$ at 36 °C) $\delta$ 32.2, 52.5 [P(OMe)$_3$], 67.9 (CS), 115.2, 134.8, 212 (multiplet for 3 CO), 214.2 (multiplet for 2 CO); IR (Nujol) 1947, 1993, 2043 cm$^{-1}$. Anal. Calcd for $C_{12}H_{15}Fe_2O_8PS_3$: C, 27.37; H, 2.87; P, 5.88; S, 18.27. Found: C, 27.33; H, 2.90; P, 6.00; S, 18.03. Crystals suitable for the X-ray study were obtained from hexane. **5b**: mp 70 °C, mass spectrum, $m/z$ calcd 525.836, found 525.836 ($M^{\bullet+}$); $^1$H NMR (CDCl$_3$) $\delta$ 2.10 (s, 3 H), 3.73 [d, P(OMe)$_3$], 5.47 (d, $J$ = 14 Hz, 1 H), 5.80 (d, $J$ = 17 Hz, 1 H), 6.29 (dd, $J$ = 14 Hz, $J$ = 17 Hz, 1 H); $^{13}$C NMR (CDCl$_3$ at −55 °C) $\delta$ 23.4, 51.4 [P(OMe)$_3$], 122.7, 137.5, 206.1 ($J$ = 13 Hz), 211.3 ($J$ = 6 Hz), 213.5, 213.7 ($J$ = 19 Hz), 214.9 ($J$ = 4 Hz), 308.1 (carbene), at room temperature the carbene is at $\delta$ 309.5 (d, $J$ = 3.7 Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 176.7. Anal. Calcd for $C_{12}H_{15}Fe_2O_8PS_3$: C, 27.40; H, 2.87. Found: C, 27.86; H, 2.91.

(18) Crystal data for $C_{12}H_{15}Fe_2O_8PS_3$: space group $P\bar{1}$, $a$ = 7.887 (2) Å, $b$ = 11.756 (2) Å, $c$ = 12.502 (6) Å, $\alpha$ = 110.52 (3)°, $\beta$ = 100.30 (3)°, $\gamma$ = 103.04 (2)°, $V$ = 1014.5 Å$^3$, $\rho$(calcd) = 1.72 g cm$^{-3}$ for $M_r$ 526.11, $Z$ = 2, $\mu$ = 18.38 cm$^{-1}$, for Mo K$\alpha$. A red-orange parallelipipedic crystal of **6b** (approximate dimensions 0.05 × 0.22 × 0.46 mm) was studied on a CAD4 Enraf-Nonius diffractometer at room temperature with a Mo K$\alpha$ graphite-monochromatized radiation ($\lambda$ = 0.7107 Å). All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/60 computer using the SDP (structure determination package). A total of 3738 reflections were collected in the range $1° \leq \theta \leq 25°$. The structure was solved by the direct method using the MULTAN program and difference Fourier syntheses. The last refinement gave $R$ = 0.032 and $R_w$ = 0.043 for 2320 observations ($I > 3\sigma(I)$) and 236 refined parameters; GOF = 1.005. Hydrogen atoms are included as fixed contributors in idealized positions prior to the final least-squares refinement cycles. Their thermal parameters are obtained by multiplying by 1.3 the thermal parameters of the carbon atoms to which they are bonded, before the last refinement. The highest residual peak (0.5 e/Å$^3$) is located at 1.214 Å from the Fe(2) atom.

(19) A solution of **6b** (0.1 g) in acetone (15 mL) was refluxed under N$_2$ for 8 h. After chromatography the product is in all respects identical with complex **5b**. When **5a** (0.2 g) in acetone (10 mL) was treated with P(OMe)$_3$ (0.06 g) at room temperature under nitrogen for 3 h, we obtained after chromatography 0.17 g (85%) of **5b**, also identical with other samples (mixed melting point and spectroscopic data).

(20) Lhadi, E. K.; Patin, H.; Benoit, A.; Le Marouille, J. Y.; Darchen, A. *J. Organomet. Chem.* **1983**, *259*, 321.

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## The First Structural Evidence for the Insertion of an Unsubstituted Lead into a Carborane Cage

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*Summary:* The reaction of the monoanion of the *nido*-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_6$ (I) with anhydrous PbCl$_2$ in a 1:1 molar ratio in tetrahydrofuran (THF) at −23 °C produced a new plumbacarborane, *closo*-1-Pb-2,3-(SiMe$_3$)$_2$-2,3-$C_2B_4H_4$ (II), as an off-white, sublimable solid, in 25% yield. The X-ray crystal structure of II unambiguously showed that the apical lead atom, formally in a +2 oxidation state, is $\eta^5$-bonded to the planar face of the $C_2B_4$ carborane ligand and is located almost in the centroidal position above the $C_2B_3$ face. A pair of these plumbacarboranes form a molecular cluster with a crystallographic center of symmetry halfway between the two apical lead atoms in the crystal lattice; the clusters are layered almost symmetrically on top of each other along with benzene molecules of crystallization.

Of all the group 14 heterocarboranes the plumbacarboranes have been least studied.[1] The first icosahedral plumbacarborane was reported nearly 18 years ago by Rudolph et al.[2] Since this heterocarborane was insoluble

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(1) (a) Hosmane, N. S.; Maguire, J. A. *Molecular Structure* and *Energetics*; Greenberg, A., Liebman, J. F., Williams, R. E., Eds.; VCH: New York, 1988; Vol. 5, Chapter 14, pp 297–328 and references therein. (b) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1989**, *30*, 0000.

(2) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92*, 3351.

0276-7333/89/2308-0566$01.50/0