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

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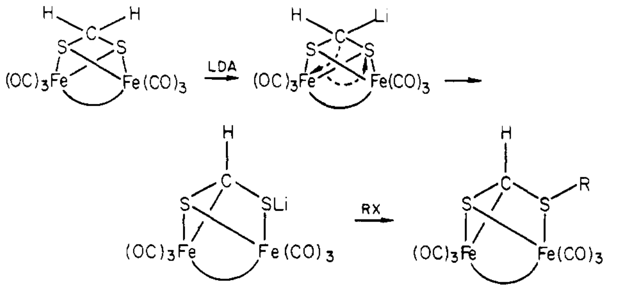
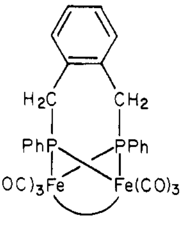
Summary: The reaction of α,α'-dibromo-*o*-xylene with $(\mu\text{-PhPH})_2Fe_2(CO)_6$ and excess Et_3N produces $[(\mu\text{-}o\text{-}C_6H_4(CH_2)_2)(PhP)_2]Fe_2(CO)_6$, **1**, in 46% yield. The deprotonation of **1** by *n*-butyllithium in THF yields a carbanion that undergoes an intramolecular nucleophilic 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^2_{2h}, 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^5_{2h}, 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.

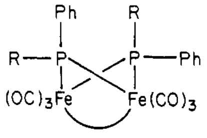


(1)

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]

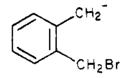


1

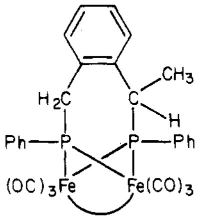


2

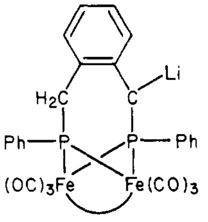
R =



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

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(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}.

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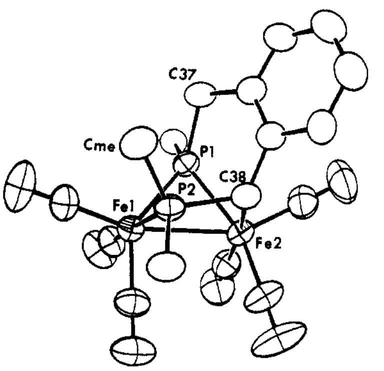


Figure 1. The molecular structure of 5 (50% probability thermal ellipsoids). Phenyl rings indicated by a single atom for clarity.

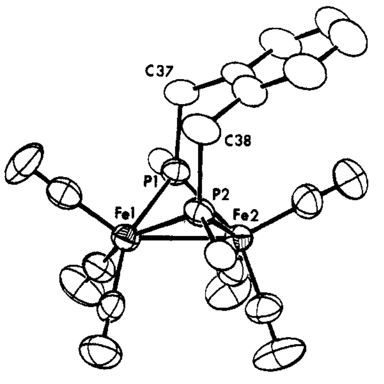


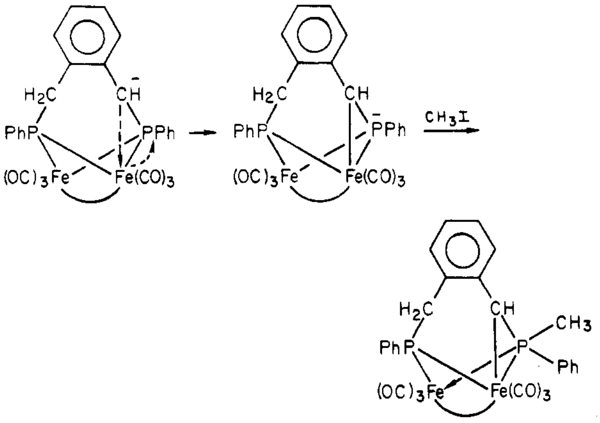
Figure 2. The molecular structure of 1 (50% probability thermal ellipsoids). Phenyl rings indicated by a single atom for clarity.

When a green solution containing 4 as prepared above was warmed to −20 °C and kept at that temperature for 1 h, a cherry red solution resulted. Cooling back to −78 °C caused no color change. Addition of an excess of iodomethane at −78 °C followed by reaction for 1 h at room temperature gave an orange-red solution from which were isolated (by the workup procedure described above) yellow crystals of a new product, mp 208–210 °C, in 53% yield that analysis showed to be isomeric with 3.[7] That this new product has a different structure was indicated, in particular, by its ^{31}P NMR spectrum. Hexacarbonyldiiron complexes with two bridging alkylphenylphosphido ligands usually show δ_P in the range 120–180 ppm and J(P–P) in the range 120–180 Hz (cf. 2, δ_P 141.2 and 145.7 (AX quartet with J(P–P) = 129.0 Hz). The ^{31}P NMR spectrum of the new product showed a low-field phosphido resonance at 182.5 ppm and a high-field tertiary phosphino resonance at 30.8 ppm (AX quartet with J(P–P) = 19.5 Hz).

If lithium reagent 4 had undergone intramolecular nucleophilic attack at an iron atom, followed by Fe–P heterolysis, a phosphide anion would result. Two modes of reaction are possible, as shown in eq 2 and 3, to give either 5 or 6, respectively. Compound 5 does not contain a

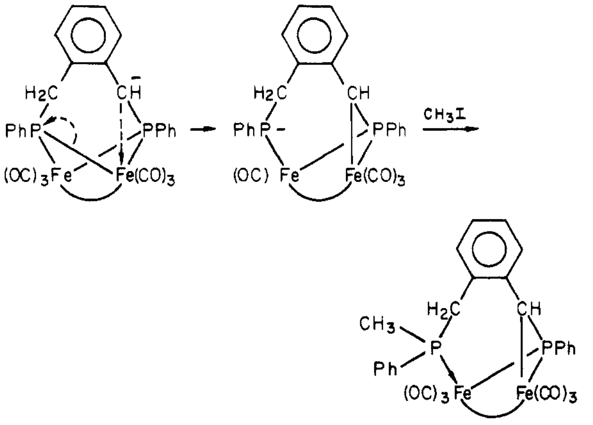
Table I. Selected Bond Lengths (Å) and Angles (deg)

	1	5
Fe1-Fe2	2.628 (2)	2.684 (1)
P2-C38	1.876 (9)	1.820 (4)
P1-C37	1.880 (8)	1.866 (3)
Fe2-C38		2.139 (3)
Fe1-P1	2.214 (2)	2.222 (1)
Fe1-P2	2.225 (2)	2.235 (1)
Fe2-P1	2.230 (2)	2.190 (1)
Fe2-P2	2.221 (2)	
Fe2-Fe1-P1	54.04 (6)	51.98 (3)
Fe2-Fe1-P2	53.68 (6)	73.01 (3)



(2)

5



(3)

6

strained three-membered ring and thus may be considered the more likely product. The rearranged product, whether it is 5 or 6, has the possibility of existing in the form of two diastereomers since the tertiary phosphine phosphorus atom and the adjacent carbon atom are chiral centers. However, only one isomer was observed by ^1H and ^{31}P NMR spectroscopy. This probably is due to the stability of the intermediate three-coordinate phosphorus anion toward pyramidal inversion.

Since the NMR and the IR spectra of the rearranged product could not distinguish between structures 5 and 6, a single-crystal X-ray diffraction study of this product, as well as of the starting material 1 was undertaken. X-ray crystallography has confirmed[11] 5 to be the rearranged

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(7) Anal. Calcd for $C_{27}H_{20}O_8Fe_2P_2$: C, 52.81; H, 3.28. Found: C, 52.80; H, 3.39. 90-MHz ^1H NMR ($CDCl_3$): δ 1.02 (d, J(P–H) = 8.3 Hz, 3 H, CH_3), 3.21 (dd, $J(P_1$–H) = 10.5 Hz, $J(P_2$–H) = 17.8 Hz, 1 H, methine CH), 3.85 (d, J(P–H) = 12.2 Hz, 2 H, CH_2), 7.01–7.77 (complex m, arene H). ^{31}P NMR ($CHCl_3$): δ_P 30.8, 182.5 (AX quartet, J(P–P) = 19.5 Hz). IR ($CHCl_3$): ν(C≡O) 2047 (s), 2005 (vs), 1981 (vs), 1958 (s), 1942 (sh) cm^{-1}.

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(10) Crystal data: $C_{26}H_{18}O_6P_2Fe_2 \cdot CH_2Cl_2$, M_r 685.0, monoclinic space group $P2_1/c$ (no. 14), a = 11.996 (1) Å, b = 13.592 (2) Å, c = 16.891 (2) Å, β = 109.80 (1)°, ρ_{cald} = 1.76 g/mL, Z = 4, μ(Mo Kα) = 15.2 cm^{-1}. Intensity data (5288 reflections, 3.0° ≤ 2θ ≤ 50.0°, $h,h,\pm l$, ω scan) were recorded on a Nicolet P3F four-circle diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. The 2553 reflections with $I > 3.0\sigma(I)$ were corrected for Lorentz, decay, polarization, and absorption effects. Final R = 0.069 and final R_w = 0.095.

(11) Crystal data: $C_{27}H_{20}O_6P_2Fe$, M_r 613.1, monoclinic, space group $P2_1/n$ (no. 14), a = 11.670 (2) Å, b = 14.581 (2) Å, c = 16.674 (2) Å, β = 109.47 (1)°, ρ_{cald} = 1.52 g/mL, Z = 4, (Mo Kα) = 12.7 cm^{-1}. Intensity data (7734 reflections, 3.0 ≤ 2θ ≤ 55.0°, $h,k,\pm l$, ω scan) were recorded on a Nicolet P3F four-circle diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. The 4158 reflections with $I > 3.0\sigma(I)$ were corrected for Lorentz decay, polarization, and absorption effects. Final R = 0.047 and final R_w = 0.068.

product shown in Figure 1. The molecular structure of its precursor 1[10] is shown in Figure 2. The initial Fe and S atom positions were determined by using MULTAN-11/82 and the Enraf-Nonius Structure Determination Package. All remaining non-hydrogen atom positions were located by subsequent difference Fourier techniques. Selected bond distances and angles are compared in Table I. The Fe1–Fe2 bond distance in 1 (2.628 (2) Å) is nearly identical with the Fe1–Fe2 distance in $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$[12] (2.623 (2) Å).[12] The Fe–P bond lengths observed for 1 are approximately 0.01 Å shorter than the Fe–P values found for the $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$[12] dimer (range 2.228 (3)–2.240 (3) Å). In general, the geometry of 1 closely resembles that of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ dimer.

The molecular structure of **5** shows significant structural changes from 1 although the Fe1–Fe2 bond distance increases by only 0.056 Å upon the substitution of P2 by C in the Fe2 coordination sphere. The Fe–Fe distances in $[\mu\text{-}CH_3C(O)CH_2CHS_2]Fe_2(CO)_6$[1] and $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$[16] are both 2.485 (1) Å. Replacement of a S atom in the Fe_2S_2 core with a C atom (e.g.,[1] $[\mu\text{-}CH_3C(O)CH_2SCHS]Fe_2(CO)_6$) results in an increase of 0.142 Å in the Fe–Fe distance (2.627 Å).

The P1-C38 bond distance of 1.820 (4) Å is not appreciably shorter than a typical P–C single bond (e.g., P2–CMe = 1.845 (4) Å), indicating only nominal multiple-bond character. The Fe2–C38 bond length of 2.139 (3) Å is longer than the Fe–C distances observed[17] in $Fe_2(CO)_5(PPh_2Me)(\mu\text{-}PPh_2)(\mu\text{-}C(O)Me)$ (1.962 (7) Å) and the $Fe_2(CO)_6$ complexes of dithioformic acid esters, HC(S)SR. The Fe–C distances found in $[\mu\text{-}CH_3C(O)CH_2SCHS]Fe_2(CO)_6$ is 1.998 (4) Å while the same distance[14] in $[\mu\text{-}CH_3SC(C_4SH_3)S]Fe_2(CO)_6$ is 2.007 (3) Å. The Fe–C distance in[15] the structurally similar $[\mu\text{-}SCH_2(C_6H_4)CHS(C_2H_5]Fe_2(CO)_6$[16] is 2.072 (a) Å, longer than the distance found in the "unrestrained" dithioformic acid ester iron dimer but shorter than that observed in the phosphido analogue.

The intramolecular attack at a metal atom by carbanions generated in a *neutral* tertiary phosphine ligand has been reported previously,[8,9] but, to the best of our knowledge, this is the first case of such a reaction sequence involving a phosphido ligand.

Acknowledgment. We are grateful to the National Science Foundation (Grants NSF-CHE-83-40747 at MIT and NSF-CHE-83-05046 at Texas A&M) for support of this work, to Union Carbide Corp. for the award of a fellowship to T.G.W., and to the Robert A. Welch Foundation for a fellowship to A.M.M.

Registry No. $1\cdot CH_2Cl_2$, 90343-31-0; **2**, 90343-32-1; **3**, 90343-33-2; **4**, 90343-34-3; **5**, 90343-35-4; $(\mu\text{-}PhPH)_2Fe_2(CO)_6$, 39049-79-1; Fe, 7439-89-6; α,α'-dibromo-*o*-xylene, 91-13-4.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, temperature factor expressions, bond distances, and bond angles for 1 and 5 and a listing of observed and calculated structure factor amplitudes for 1 and 5 (50 pages). Ordering information is given on any current masthead page.

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1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene: A Photochemical Source of Dimethylsilylene[1]

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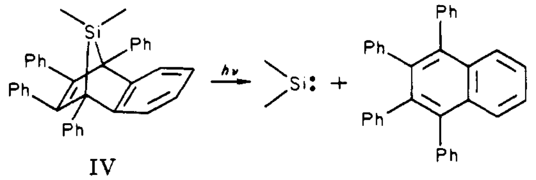
Received February 22, 1984

Summary: 1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene (IV) was synthesized in 83% yield by an improved procedure. Photolysis of IV at room temperature proved to be an excellent source of dimethylsilylene that could be efficiently scavenged by methanol, 1,2-diphenylacetylene, or benzil to yield the corresponding adducts. Laser flash photolysis experiments showed that the photoexcited state of IV decomposed to give dimethylsilylene and triplet 1,4,5,6-tetraphenylnaphthalene within 20–30 ns of the start of the laser pulse.

Photolysis of dodecamethylcyclohexasilane[2] (I) has generally been used to generate dimethylsilylene at room temperature.[3,4] However, the procedure has a number of disadvantages.

First, photolysis does not lead to a simple distribution of products.[3] Decamethylcyclopentasilane (II) and dimethylsilylene are formed initially but simply begin the cascade summarized in Scheme I, in which other polysilanes are rapidly formed.[3] Of these polysilanes, III is rapidly oxidized adding further complexity to product analyses and workup.[3] Second, since the detailed photochemistry of the smaller cyclic polysilanes is unknown, it becomes difficult to ascertain whether compounds containing two or more dimethylsilylene moieties arise from repeated insertions of that moiety or whether they derive directly from the photolysis of the cyclic polysilanes themselves.[3,10]

We have found that photolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene[14] (IV) is an excellent source of dimethylsilylene that obviates many of these problems (eq 1).



(1)

IV

V

The compound was synthesized by a improved method that was similar to that used by Neumann[15,16] for the preparation of the germanium analogue. Thus, 1,1-di-

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(1) Issued as NRCC publication no. 23279.

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