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Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 5. Evidence for a Highly Selective Backside Attack by Strong Nucleophiles on a μ-Phosphido Center

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At −78 °C *n*-butyllithium, methyllithium, and lithium triethylborohydride react cleanly with [μ-1,2-phenylenebis(phenylphosphido)-*P*,*P*′]hexacarbonyldiiron (**1**) to give initially a single diastereomeric anion, *cis*-[μ-[2-(*exo*-R-*endo*-phenylphosphino)phenyl]phenylphosphido-*P*](μ-carbonyl)pentacarbonyldiiron anion (**9a**, R = *n*-Bu; **9b**, R = Me; **9c**, R = H), which is the result of a backside attack on a phosphido moiety. The initial anion **9** establishes an equilibrium with an isomer (**10**, as **9** except exo and endo positions exchanged) upon warming. Stereochemical assignments are based on the methyl iodide trapping of **9a** obtained from *n*-BuLi to give *cis*-[μ-[2-(*exo*-*n*-butyl-*endo*-phenylphosphino)phenyl]phenylphosphido-*P*](μ-acetyl)pentacarbonyldiiron (**11a**) and of **10b** from MeLi to give *cis*-[μ-[2-(*exo*-phenyl-*endo*-methylphosphino)phenyl]phenylphosphido-*P*](μ-acetyl)pentacarbonyldiiron (**13b**). The structures of **11a** and **13b** were determined by single-crystal X-ray diffraction. A rationale is presented for the nature of the equilibration of **9** and **10** as well as for the site attack by the nucleophile on **1**. X-ray data were collected at −110 °C on a Syntex $P2_1$ autodiffractometer and refined by the full-matrix least-squares method. For **11a**: a = 11.071 (2) Å, b = 13.756 (2) Å, c = 10.498 (1) Å, α = 97.64 (1)°, β = 117.15 (1)°, γ = 82.76 (1)°, triclinic, $P1$, Z = 2; R_1 = 0.038 and R_2 = 0.034 for 5014 reflections with $F_o \geq 4\sigma_{F_o}$. The molecule contains two pseudooctahedral iron moieties bonded to each other and bound by a μ-phosphido and a μ-acetyl group in a cis relationship. For **13b**: a = 10.531 (2) Å, b = 17.610 (5) Å, c = 28.896 (19) Å, orthorhombic, *Pbca*, Z = 8; R_1 = 0.061 and R_2 = 0.052 for 3704 reflections with $F_o \geq 4\sigma_{F_o}$. The core structure is very similar to **11a**.

Introduction

In recent years interest in various bridged di- and polynuclear transition-metal complexes has been quite intense,[2] particularly due to the increased stability of such complexes toward metal–metal bond scission. Bridging phosphido moieties have been especially heavily investigated in this regard,[3] due to their similarity to the ubiquitous tertiary phosphine ligand. Many recent papers, however, have dealt with cases in which the μ-phosphido ligand does not survive certain reaction conditions[4] Our entry into this area was based on the expectation that the interposition of a link such as a 1,2-phenylene group between two μ-phosphido groups would lend additional stability to a bimetallic complex relative to the unlinked congener (e.g., **1** more stable than **2**). Indeed, we found that **1** had a half-life ca. 30-fold greater than **2** in mesitylene at 165 °C.[5]

The 1,2-phenylene link between bridging groups has allowed the isolation of some highly unusual transition-metal complexes.[6] We have also found substantially altered chemistry exhibited by complexes containing the μ-1,2-phenylenebis(phosphido) unit, relative to the unlinked bis(μ-phosphido) grouping. For example, two-electron reduction cleaves the iron–iron bond in **2** but a phosphido–iron bond in **1**.[8] Obviously, the ensuing chemistry of the corresponding dianions with electrophiles is quite different. The differences in chemistry between **1** and **2** extend to the reactivity toward strong anionic nucleophiles, and herein we report the results of the reactions of carbanions and hydride nucleophiles with **1**.

By way of background, Collman and his co-workers have observed that the reaction of **2** with methyl- or phenyllithium (eq 1) gave the corresponding anionic acyl complexes **3**,[7] which were characterized by single-crystal X-ray diffraction by Dahl and his co-workers.[9] Wojcicki and his group[4g] have reported that lithium triethylborohydride gives **4** upon reaction with **2** and that with excess tri-

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(1) For the preceding paper in this series, see: Kyba, E. P.; Hassett, K. L.; Sheikh, B.; McKennis, J. S.; King, R. B.; Davis, R. E. *Organometallics* **1985**, *4*, 994.

(2) See, inter alia: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Roberts, D. A.; Geoffroy, G. L. *Compr. Organomet. Chem.* **1982**, *6*, 763. (c) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379.

(3) Comments regarding metal–metal bond stabilization by μ-PR_2 and related ligands may be found in inter alia: (a) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394. (b) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (c) Braunstein, P.; Mott, D.; Fars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79. (d) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1379. (e) Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860. (f) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53. (g) Ritchey, J. M.; Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T *J. Am. Chem. Soc.* **1985**, *107*, 501. (h) Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 189.

(4) (a) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782. (b) Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazong, A. M. *Ibid.* **1984**, *3*, 1121. (c) Wojcicki, A.; Shyu, S.-G. *Ibid.* **1984**, *3*, 809. (d) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Ibid.* **1984**, *3*, 814. (e) Yu, Y.-F.; Chou, C.-N.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Balducci, G. *J. Am. Chem. Soc.* **1984**, *106*, 3704. (f) Geoffroy, G. L.; Rosenberg, S.; Shulman, P. M.; Whittle, R. R. *Ibid.* **1984**, *106*, 1519. (g) Yu, Y.-F.; Gallucci, J.; Wojciccki, A. *Ibid.* **1983**, *105*, 4826. (h) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53. (i) Breen, M. J.; Geoffroy, G. L. *Ibid.* **1982**, *1*, 1437.

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(6) (a) Kyba, E. P.; Mather, J. D.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371. (b) Kyba, E. P.; Hassett, K. L.; Sheikh, B.; McKennis, J. S.; King, R. B.; Davis, R. E. *Organometallics* **1985**, *4*, 994. (c) Kyba, E. P.; Davis, R. E.; Hassett, K. L.; McKennis, J. S.; Sheikh, B. *Phosphorus Sulfur* **1983**, *18*, 275.

(7) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

(8) McKennis, J. S.; Kyba, E. P. *Organometallics* **1983**, *2*, 1249.

(9) Ginsburg, R. E.; Berg, J. M.; Rothrock, R. K.; Collman, J. P.; Hodgson, K. O.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 7218.

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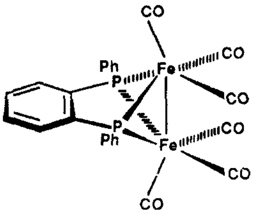

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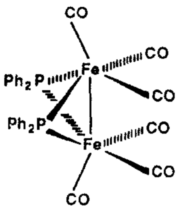

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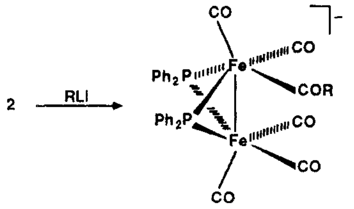
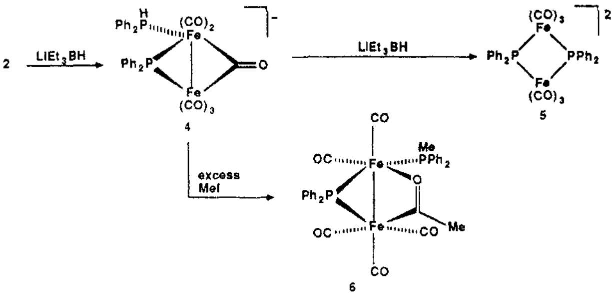


(1)

3a, R = Me
3b, R = Ph

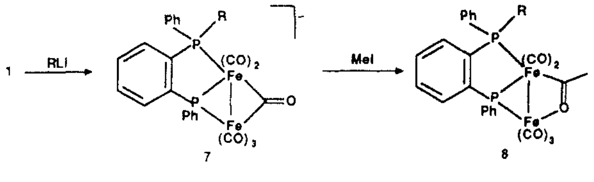
ethylborohydride, this proceeds ultimately to the dianion 5 (eq 2), previously described by Collman[7] and structurally



(2)

characterized by Dahl.[10] More recently, Shyu and Wojcicki found that 4 is produced via initial hydride attack at carbonyl to give 3 (R = H) followed by deinsertion to give a metal hydride and then reductive elimination of the P-H moiety.[11] Species 4 reacted with excess MeI to give the neutral μ-acyl species 5, whose structure was determined by single-crystal X-ray crystallography.[4g]

In contrast to these results in which organolithium and borohydride nucleophiles attack the metal-bound carbonyl group in 2, we find that alkyllithium species and triethylborohydride react with 1 to give anion 7 (eq 3). This



(3)

upon alkylation with methyl iodide gives 8, ignoring, for the moment, stereochemical details in both 7 and 8. A priori, the generation of 7 might involve the following: a backside nucleophilic attack on the phosphido phosphorus site with inversion of this atom; an attack on the carbonyl group, followed by deinsertion and reductive elimination of the P-R moiety,[4g,11] which would be the equivalent of a frontside attack on the phosphido group; an electron-transfer radical combination which would probably result in random stereochemistry at the phosphorus atom attacked. Our results, summarized in Scheme I, show that the production of 7 is a highly selective S_N2-like backside attack.

Table I. ^{31}P{H} NMR Absorptions of Complexes 1, 2, and 9–14[a]

complex	^{31}P{H} (multiplicity) [J_{PP}, Hz]
1	138.1 (s)
2	142.5 (s)
9a	140.2 (d), 69.2 (d) [37]
10a	141.3 (d), 68.6 (d) [37]
9b	141.8 (d), 57.7 (d) [43]
10b	140.1 (d), 59.5 (d) [43]
9c	142.9 (d), 40.5 (d) [37, ^{31}P, J_{PH} = 330]
10c	136.5 (d), 46.6 (d) [37, ^{31}P, J_{PH} = 330]
11a	198.0 (d), 71.5 (d) [24]
12a	203.6 (d), 87.5 (d) [36]
13a	199.1 (d), 73.5 (d) [26]
14a	203.0 (d), 84.3 (d) [35]
11b	196.0 (d), 58.7 (d) [25]
12b	201.8 (d), 72.6 (d) [36]
13b	195.2 (d), 63.1 (d) [27]
14b	199.9 (d), 77.5 (d) [38]

[a] Spectra were determined in $CDCl_3$ solution for 1, 2, and 10–14 and in THF solution for 9 and 10.

Results

In order to probe the stereochemistry of the production of 7, the reaction was carried out at −80 °C in a ^{31}P NMR spectrometer. A THF solution of 1 in an NMR tube was frozen at −196 °C, and 1.2 equiv of a hexane solution of n-BuLi was added while the tube was immersed in a liquid-nitrogen bath. The mixture was then placed in a dry ice–acetone bath until it liquified to give a deep red solution. The NMR tube was then transferred to the ^{31}P NMR spectrometer, and a clean spectrum was observed, consisting of only two doublets (see Table I for all the ^{31}P NMR data in this work) which indicated a single anionic species assigned (vide infra) as **9a**. The downfield doublet was due to the μ-phosphido moiety and the upfield doublet, to the coordinated tertiary phosphine.[12] The sample was then warmed to room temperature and monitored by ^{31}P NMR spectroscopy for 24 h, during which time a second anion, **10a**, was formed: ratio **9a**:**10a** = 3:2. The solution was then heated at 70 °C for 3 h at which point the ratio **9a**:**10a** = 1:1. No further change in the ratio occurred on additional heating. A bridging CO absorption was observed in the IR spectrum at 1650 cm^{-1}. This solution was then treated with a large excess of methyl iodide to give a mixture of four isomers, a observed by ^{31}P{H} NMR spectroscopy: **11a**:**12a**:**13a**:**14a** = 43:10:43:4; (**11a** + **12a**):(**13a** + **14a**) = 1.1:1. This mixture was quantitated by HPLC to give a yield of **11a**–**14a** of 79%. In contrast, when **9a** was treated at −78 °C with excess MeI and then warmed to room temperature for 3 h, the ratio of products was **11a**:**12a**:**13a**:**14a** = 88:7:4:1; (**11a** + **12a**):(**13a** + **14a**) = 19:1. Since (**11a** + **12a**) are derived from **9a** (vide infra), this latter experiment indicates that only 5% leakage to **10a** occurred during electrophilic trapping of **9a**, i.e., MeI is a reasonable kinetic trap for **9a**. The major component **11a** was isolated as red crystals by a combination of extraction, chromatography, and recrystallization techniques in 24% from the thermodynamic trapping experiment. The results of a single-crystal X-ray structure determi-

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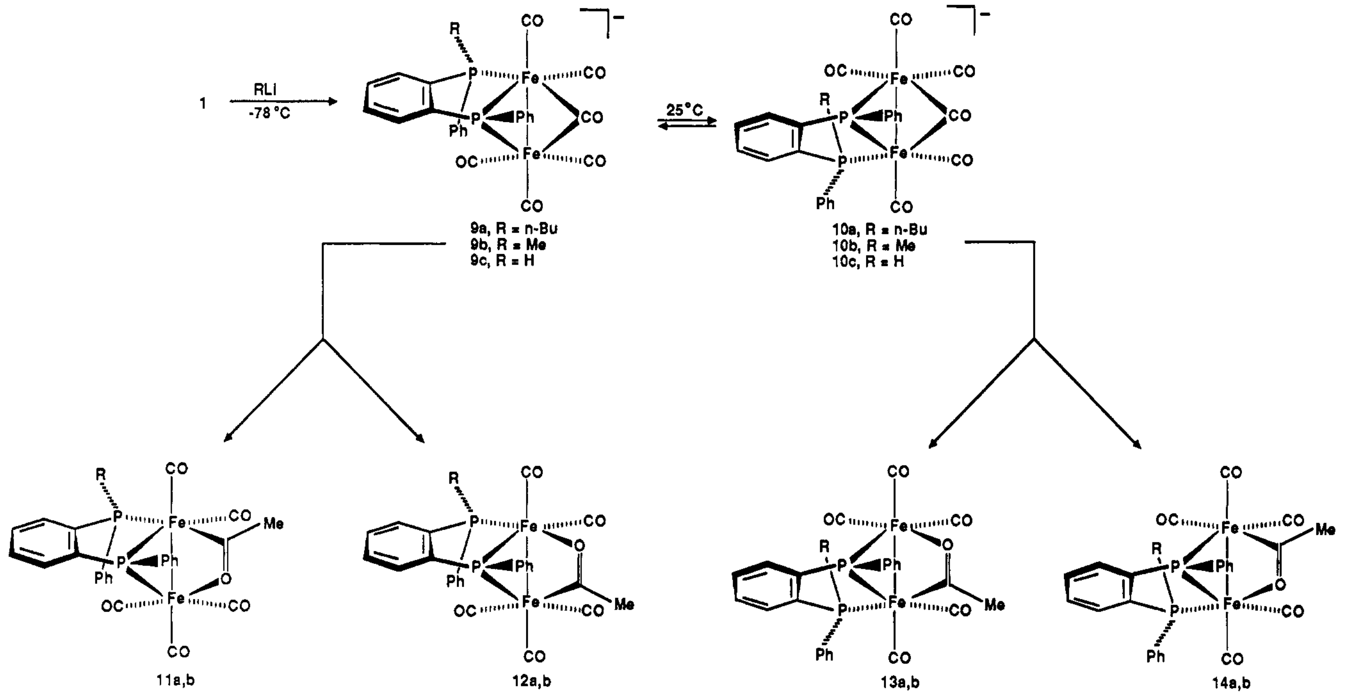
[10] Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

[11] Shyu, S.-G.; Wojcicki, A., submitted for publication.

[12] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

[13] Scheme I has been constructed on the basis of the stereochemical outcomes of processes which occur starting from the enantiomer shown as 9. It is understood that all the chiral complexes 9–14 exist as racemates.

Scheme I



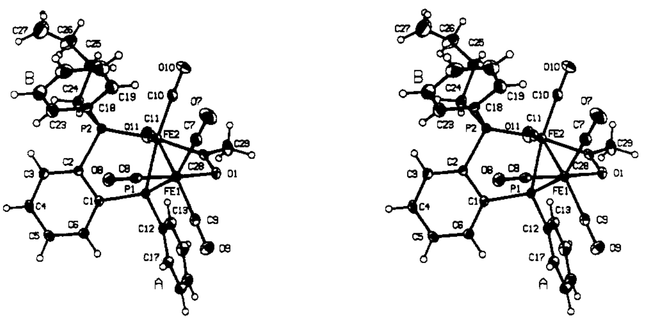


Figure 1. ORTEP stereoview plot of **11a**, showing the non-hydrogens as 35% equiprobability ellipsoids.

nation of this species is shown as an ORTEP plot in Figure 1, which confirms the stereochemistry depicted in **11a**. It was not possible to resolve cleanly the other components **12a–14a**.

Substrate **1** was reacted with MeLi at −80 °C exactly as described above for *n*-BuLi. Again a very clean ^{31}P{H} NMR spectrum was observed, consisting only of a pair of doublets (Table I), which is assigned to **9b** (Scheme I). Upon warming to room temperature a new anionic species, assigned as **10b** was formed. After 10 h the ratio of **9b**:**10b** = 1:4 was invariant as a function of time. A μ-CO stretching frequency was observed at 1650 cm^{-1} in the IR spectrum. Treatment of this mixture with excess MeI for 6 h gave a mixture of isomers as observed by ^{31}P{H} NMR spectroscopy, in the following ratio: **11b**:**12b**:**13b**:**14b** = 16:4:61:19; (**11b** + **12b**):(**13b** + **14b**) = 1:4. This mixture was isolated in 83% yield following chromatography on alumina. The major isomer **13b** was isolated as red crystals by careful crystallization from hexane. Its structure was determined by X-ray crystallography, and the result is presented as an ORTEP plot in Figure 2. An attempt at a kinetic quench of anion **9b** with a large excess of MeI at 25 °C gave the following ratio of products: **11b**:**12b**:**13b**:**14b** = 52:8:30:10; (**11b** + **12b**):(**13b** + **14b**) = 3:2. Thus there was 40% leakage of **9b** to **10b** during the trapping process.

Finally, the reaction of **1** with LiHBEt$_3$ gave results analogous to those above. Great care had to be taken to monitor the reaction by ^{31}P{H} NMR spectroscopy at short intervals, since the attack by the hydride was slow and the rearrangement process was much more facile than with the alkyllithium reagents. Anion **9c** was formed exclusively in the initial stages of the reaction and at equilibrium the ratio of **9c**:**10c** = 1:3.

Discussion

Stereochemistry of Nucleophilic Attack. The stereochemical question being probed is the direction of attack by the nucleophile on the μ-phosphido site. Backside attack on the prochiral phosphido centers in **1** will generate

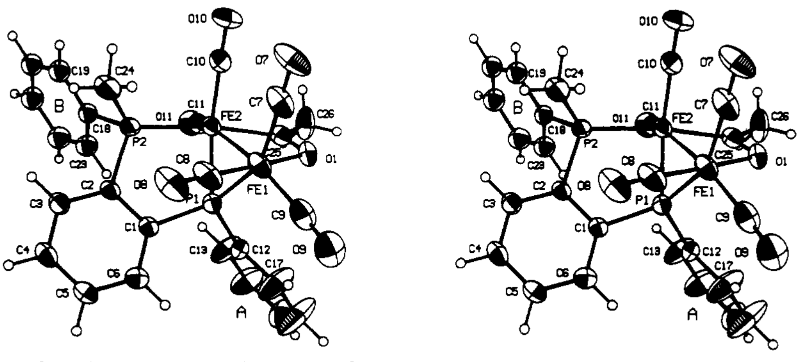


Figure 2. ORTEP stereoview plot of **13a** showing the non-hydrogens as 35% equiprobability ellipsoids. The disordered phenyl ring B is shown in the position of major occupancy.

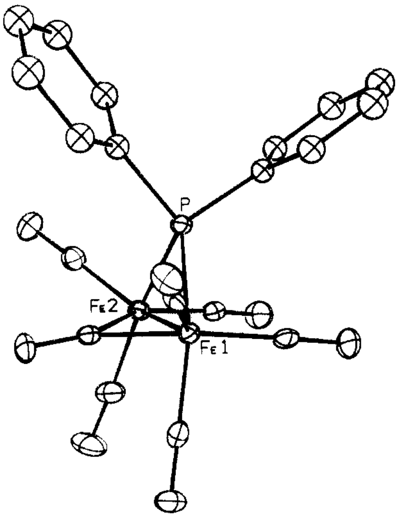


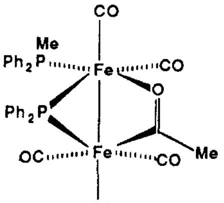
Figure 3. ORTEP plot of the $(\mu\text{-}Ph_2P)(\mu\text{-}CO)Fe_2(CO)_6^-$ complex.[14]

a racemic mixture of **9**, one enantiomer of which is shown.[13] Complex **9** is drawn with the μ-phosphido and μ-CO cis, although we have no direct physical evidence for this. Attempts were made to isolate a crystalline form of **9**, to no avail. There is precedent for our structural assignment in the work of Osterloh, who determined the structure of $[(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_6Fe_2]^-$ (**15**) by X-ray cyrstallography and found the bridging groups to be cis as shown in Figure 3.[14] In addition, theoretical work has rationalized the Fe_2X_2 core (X = three-electron donor) in the $(\mu\text{-}X)_2Fe_2(CO)_6$ species as an "open book" geometry with a "bent" iron–iron bond.[15] One may view the $(\mu\text{-}CO)^-$ ligand also as a three-electron donor, so that the basic orbital structure of the $Fe_2X_2(CO)_6$ species is maintained in the anionic $[(\mu\text{-}CO)(\mu\text{-}X)Fe_2(CO)_6]^-$ species, hence cis bridging groups.

Examination of a molecular model of **1** reveals that if *backside* attack by R^- occurs, the original Ph group on the μ-P would reside in the "endo" pocket of the complex and the R in the "exo" position, as shown in **9**. Transformation of **9** into the new diastereomer **10** involves the exchange of positions by R and Ph. This could occur by a decoordination–inversion of phosphine mechanism, but we consider this unlikely, since the inversion barrier at a tertiary phosphine is above 30 kcal/mol.[16] More likely is a 1,2 shift of phosphine from one iron center to another, as shown in Scheme I. The net result is the exchange of exo–endo positions by R and Ph. Such a process would probably involve concomitant movement of the carbonyl groups, accounting for the observed significant barrier to isomerization.

The assignment of structures **9** and **10** rests on the structures of **11a** and **13b**, the products of trapping by MeI of the kinetic anion **9a** and thermodynamic anion **10b**. (Attempts to trap the **9c**$\rightleftharpoons$**10c** species led only to **11b**–**14b**, as has also been observed by Wojcicki with his system.[4g]) The assumption is that methylation of the anion leaves the coordinated tertiary phosphine untouched. Examination of the ORTEP plot of **11a** in Figure 1 shows that the *n*-Bu group is in the exo position, hence our placement of this group in the analogous position in **9a**. If our model is correct, then the thermodynamic anion should generate the MeI trapped product with the nucleophile endo. We were unable to obtain this product pure starting with *n*-BuLi, but we were successful with MeLi. It is clear from the ORTEP plot of **13b** in Figure 2 that indeed the original nucleophile is now in the endo position, consistent with our proposed **9** to **10** isomerization.

A complicating feature of the MeI trapping of **9** and/or **10** is that each anion gives a major and a minor product. In neither case (*n*-Bu nor Me system) have we been successful in isolating the minor isomers **12** and **14**. We postulate that the only difference between **12** and **11** or **14** and **13** is the orientation of the bridging acyl group. Our assignment of these structures rests primarily on their $^{31}P\{H\}$ NMR spectra in comparison to their more abundant congeners. In all cases, the tertiary phosphine resonance in the minor isomer (**12**, **14**) is quite deshielded (11–16 ppm) relative to the corresponding major isomers (**11**, **13**). This is consistent with the tertiary phosphine being coordinated to the iron atom which is ligated by the oxygen atom of the acyl group. The μ-phosphido group is also deshielded, but less so (4–6 ppm) in the minor isomers. Since we have been unable to observe a spectrum of the major isomer in the absence of the minor one, the suspicion is that the minor isomer is in rapid equilibrium with the major one, although we have seen no evidence of fluxionality in the $^{31}P\{H\}$ NMR spectrum down to −80 °C. Wojcicki and his co-workers have determined the structure of **16**, which has the μ-acyl group with the same orientation as in the postulated structures of the minor isomers **12** and **14**. Although it is conceivable that the minor isomers differ from the major ones by having the two bridging groups trans rather than cis about the pseudooctahedral iron atoms, we favor the alternative discussed above for two reasons. First, there are now five (two in this work, plus those of Wojcicki[4g] and Carty[3h]) such structures, all with −P and −COR cis, and second, theoretical work favors the cis orientation (vide supra).[15]



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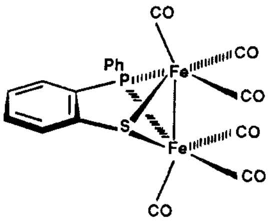

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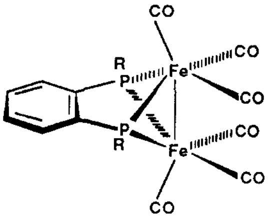
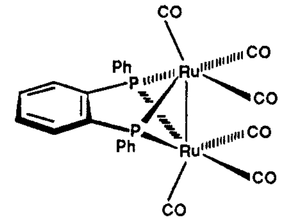


18a, R = mesityl
18b, R = Me
18c, R = t-Bu



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Structures 11a and 13b Compared to 16. The $(\mu\text{-}P)(\mu\text{-}COMe)Fe_2$ cores of the two structures determined in this work (**11a**, **13b**) are virtually superimposable. They are also very similar to **16**, except for the orientation of the μ-acyl group, which has the oxygen bound to the iron atom which bears the tertiary phosphine in **16** but to the other iron atom in **11a** and **13b**. All three structures have the μ-ligands cis, i.e., with folded $(\mu\text{-}P)(\mu\text{-}COMe)Fe_2$ cores. The tertiary phosphine ligand in **11a** and **13b** is perforce, cis to the μ-P moiety and trans to the carbon atom of the μ-acyl group. In contrast, **6** has the tertiary phosphino

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(14) Osterloh, W. T. Ph.D. Dissertation, The University of Texas at Austin, 1982. Complex **15** was obtained by photolysis of $[[(CO)_4Fe]_2PPh_2]^-$, which was prepared from $(Et_4N)_2Fe_2(CO)_8$ and Ph_2PCl in dichloromethane.

(15) (a) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F. *Inorg. Chem.* **1975**, *14*, 3103. (b) Burdett, J. K. *J. Chem. Soc., Dalt. Trans.* **1977**, 423.

(16) Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 3090.

Table II. Selected Nonbonded Internuclear Distances (Å) in Complexes 11a and 13b

11a		13b	
C18···C10	3.699	C24···C19	3.358
C18···C7	4.289	C24···C3	3.330
C18···C8	3.278	C24···C10	3.395
C18···C3	3.593	C24···C7	4.405
C18···C25	3.379	C24···C8	3.548
C19···C10	3.379	C18···C11	3.187
C19···C7	3.609	C18···C3	3.380
C19···C8	3.386		
C19···C24	3.797	C23···C11	3.241
C19···C25	3.869	C23···C2	3.281
C23···C8	5.236		
C23···C3	2.908		
C23···C24	4.177		
C24···C11	3.373		
C25···C11	3.721		
C27···C24	3.162		

group trans to the μ-P moiety but cis to the μ-acyl oxygen atom. In fact, Wojcicki et al. have shown that in solution **6** is in equilibrium with **16**, which is analogous to our two structures, **11a** and **13b**, except for the orientation of the μ-acyl group. We have been unable to observe any fluxional behavior in either **11a** or **13b**, aside from the fact that in solution samples of highly purified **11a** or **13b** always have present the minor isomers (**12a** and **14b**, respectively), even though no evidence for these isomers was found in the crystal structure determinations.

Examination of the ORTEP plots of **11a** and **13b** reveals that the endo position of the substituent on the tertiary phosphine (that occupied by Ph in **11a** and Me in **13b**) is a relatively constained cavity with walls defined by C10, C7, C8, C3, and C25 (**11a**) or C19 (**13b**). Nonbonded distances of the substituent in the endo position and the constraining atoms are given in Table II. With **13b**, all but one of the nonbonded distances are in the 3.33–3.55 Å range, indicative of a tight fit. Were a propyl group to replace a hydrogen atom on the methyl group in **13b**, i.e., to give **13a**, it would be constratined to occupy the region in space between the benzo group and phenyl ring B. The nonbonded distances of the phenyl ring in the endo cavity in **11a** are also given in Table II. Most of these are also in the 3.3–3.6 Å range, although there is one quite close contact, C23···C3 (2.908 Å). It is clear from the examination of a model of **11a** that Ph group B is quite constrained in terms of rotation about the C18–P2 bond.

In order to consider the intramolecular nonbonded interactions in **9** and **10** and how they may affect the equilibrium between them, it is necessary to assume that the corresponding interactions in the μ-acyl species **11a** and **13b** are similar. Comparison of the structures **15** and **16** indicates that replacement of a (μ-CO)⁻ by a μ-COMe results in only minor changes in the remaining structure. Thus it is reasonable to assume that the walls of the endo cavity in **9** and **10** are approximately as in **11a** and **13b**. Given that, it is easy to rationalize that **9b** is more stable than **10b**, since the smaller methyl group is in the more constrained endo cavity. It might at first glance by surprising that **9a** and **10a** are equal in energy since the *n*-Bu group is considered to be a smaller group than Ph on the basis of chair cyclohexane *A* values.[17] In fact, placing the Ph group in the exo position imposes an additional barrier in the endo cavity and further constrains the number of degrees of conformational freedom available to an *n*-Bu group in this position. If the phenyl ring in the exo position were able to rotate by 90° to remove C19 (see Figure 2) as a barrier, then more than likely **10a** would be more stable than **9a**. This is not possible because of the close proximity of C11 (Figure 2) to this phenyl ring. With the hydride nucleophile, it is somewhat bothersome that the equilibrium **9c** ⇌ **10c** only favors the latter by a factor of 3, especially in light of the methyl case favoring the endo position by a factor of 4. Since the coordination of a secondary phosphine acidifies the P–H substantially,[18] we suspect that this moiety is involved in hydrogen bonding with the THF solvent, making it behave as if it were larger than it would be in the absence of this phenomenon.

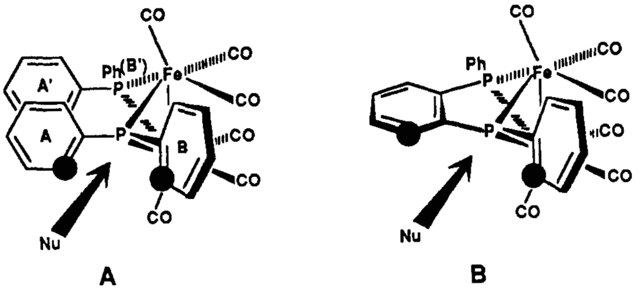

Figure 4. A. Nucleophilic approach to the phosphido center in complex **2**. B. Nucleophilic approach to the phosphido center in complex **1**.

In summary, the evidence described above strongly favors an S_N2-like backside attack by MeLi, *n*-BuLi, and Et_3BHLi on the μ-phosphido group with the $Fe_2(CO)_6^-$ moiety as the leaving group, as outlined in Scheme I.

Regioselectivity of Electrophilic Sites in 1 and 2. A fundamental question to be answered is why R⁻ attacks the metal carbonyl in **2** but the μ-phosphido group in **1**. Consideration of the structures **1** and **2** allows one to put forth a reasonable postulate. A drawing of **2** that emphasizes pertinent steric interactions is shown in Figure 4A and is based on the structural determination by Dahl and his group.[19] Phenyl rings B and B′ must be in the positions shown to minimize interactions with the carbonyl groups. This places the ortho carbon atoms which are highlighted with solid circles a comfortable >4 Å apart. If nucleophilic attack is backside, then the approach by the nucleophile must be almost exactly between the highlighted carbon atoms, as indicated. There are four identical approaches, only one of which is shown. There is simply insufficient room for the nucleophile to achieve close enough approach to achieve a transition state, and thus only the carbonyl groups are attacked.

Although we have been unable to obtain crystals of X-ray quality of **1**, we do have structure determinations on **17**,[20] **18a**,[20] and **19**,[21] all of which indicate that the structure drawn in Figure 4B is a reasonable representation. The key feature is that the phenyl groups A and A′ have been removed and replaced with the 1,2-phenylene moiety, which has its major steric bulk perpendicular to that of the A and A′ phenyl groups. The effect of this is to open a clear pathway for the nucleophile into the μ-P atom. Apparently, in the absence of steric effects, the nucleophiles described above prefer to attack the phosphido rather than the carbonyl center.

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Work that we will report elsewhere indicates that the regioselectivity of attack on species such as **1** and **2** and their congeners is subject to delicately balanced factors. Thus, we have found that PhLi attacks only carbonyl in **1**, similar to **2**.[7] The bulkiness of the substituent on P in **1** affects the regioselectivity: **18b** reacts analogously to **1** with alkyllithium species, but **18a** and **18c** give attack only at carbonyl. Also, **19** is attacked by alkyllithiums and lithium triethylborohydride only at carbonyl.

Conclusions. Nucleophilic attack by lithium alkyls and lithium triethylborohydride on the μ-phosphido group in **1** proceeds with a highly stereoselective backside attack with the hexacarbonyldiiron anionic moiety as the leaving group. The initially formed anion **9** is stable at −78 °C but upon warming rearranges to an isomer, probably via a 1,2 tertiary phosphine shift from one iron to the other. At equilibrium, the second-formed isomer **10** is the more stable with MeLi and $LiHBEt_3$ as nucleophiles but equal in energy to the initial (kinetic) isomer with *n*-BuLi. The structures of the anions **9** and **10** formed were deduced from the X-ray crystal structures of the MeI trapping products **11a** and **13b** of the kinetic isomer **9a** (n-Bu^- as nucleophile) and the thermodynamic isomer **10b** (Me^- as nucleophile), respectively.

Experimental Section

General Information. Proton magnetic resonance spectra were obtained on a Varian EM-390 or a Varian FT-80 spectrometer. Carbon-13 NMR spectra were determined on a Varian FT-80 spectrometer at 20.1 MHz. Proton-decoupled ^{31}P NMR spectra were determined on a Varian FT-80 or Bruker WH90 spectrometer at 32.2 and 36.4 MHz, respectively. All spectra were determined in $CDCl_3$ solution unless otherwise stated. Chemical shifts are given in parts per million relative to Me_4Si for ^{13}C and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative. *All ^{31}P NMR spectra are reported only in Table I.* Analytical HPLC determinations were carried out on a Waters ALC 204 instrument, equipped with a UV detector (280 nm) and a Waters μ-Porasil 10 μm, 3.9 mm i.d. × 30 cm column. HPLC quantitative analyses were performedd by using a digital integrator (Hewlett-Packard 3390A reporting integrator). Response factors were determined at 280 nm utilizing pure samples.

All reactions were performed under dry nitrogen or argon atmosphere. All concentrations of solutions were carried out on a rotary evaporator under water aspirator pressures unless otherwise noted. Solutions were dried with anydrous magnesium sulfate. The alumina used was neutral, activity 1, 80–200 mesh, and was used as supplied from Fisher Scientific Co. Tetrahydrofuran and diethyl ether were purified by distillation from benzophenone ketyl. The ligand 1,2-bis(phenylphosphino)benzene was prepared as described previously.[22]

[μ-1,2-Phenylenebis(phenylphosphido)-*P*,*P*′]hexacarbonyldiiron (1). Nonacarbonyldiiron (12.0 g, 33.0 mmol) was added to a magnetically stirred solution of *o*-bis(phenylphosphino)benzene (10.8 g, 36.7 mmol) in benzene (125 mL). The mixture was brought to reflux over a period of ca. 10 min. After 15 min, more $Fe_2(CO)_9$ (9.0 g) was added. Over the next 4.5 h, an additional 25 g of $Fe_2(CO)_9$ in five approximately equal portions was added. After three more hours at reflux, the reaction mixture was allowed to cool to room temperature over a period of 3.5 h. The reaction mixture was then filtered through Celite and concentrated. The viscous residue was taken up in a small quantity of benzene and chromatographed over alumina. Elution with benzene–hexane (2:3, v/v) gave a yellow band, which afforded **3** as a yellow microcrystalline solid (12.1 g, 58%). An analytically pure sample was obtained by recrystallization from benzene–hexane: mp 196–197 °C dec [lit.[23] mp 200–201 °C dec]. IR and ^{31}P NMR data for **3** agree with that previously reported.[23]

Reaction of 1 with *n*-Butyllithium at −78 °C, Followed by Thermal Equilibration. An 8-mm NMR tube with **1** (103.8 mg, 0.180 mmol) was degassed and THF (1.0 mL) added. It was then inserted into a 10-mm NMR tube which contained acetone-d_6 (deuterium lock) and frozen in a liquid nitrogen bath. A hexane solution of 3.03 M *n*-butyllithium (0.070 mL, 0.21 mmol) was added and the mixture warmed in a dry ice–acetone bath to give a deep red solution. This was then placed in the ^{31}P NMR probe at −80 °C, and a single species, **9a**, was observed (see Table I). The temperature of the probe was raised in 20° increments to −20 °C with no change. At room temperature a new species, **10a** (Table I), was observed. The ratio of **9a**:**10a** after 1.5 h at room temperature was 4:1 and after 24 h was 3:2. The sample was heated at 70 °C for 3 h to rpoduce a 1:1 ratio. Further heating did not cause the ratio to change. At this point the IR spectrum exhibited absorptions at ν_{CO} = 2000 (m), 1980 (m), 1940 (s), 1900 (s), and 1650 (m) cm^{-1}.

Reaction of 1 with *n*-Butyllithium at −78 °C, Followed by Methyl Iodide Quench. A solution of 1.45 M *n*-butyllithium in hexanes (0.10 mL, 0.145 mmol) was added to a solution of **1** (50.85 mg, 0.0889 mmol) in THF (0.50 mL) in an NMR tube at −78 °C to give a red solution. To this solution was added iodomethane (0.30 mL), and the NMR tube was placed in a −64 °C bath for 30 min. This was then warmed to room temperature for 3.5 h. Analysis by ^{31}P NMR spectroscopy gave the product distribution **11a**:**12a**:**13a**:**14a** = 88:7:4:1.

Reaction of 1 with n-Butyllithium at −78 °C, Followed by Thermal Equilibration and Methyl Iodide Quench. Isolation of 11a. A solution of 4.0 M *n*-butyllithium in hexanes (0.053 mL, 0.212 mmol) was added to a solution of **1** (100.0 mg, 0.175 mmol) in THF (3.0 mL) at −78 °C to give a red solution. This was boiled at reflux for 16 h. The ^{31}P NMR spectrum showed the corresponding signals for **9a** and **10a** in a 1:1 ratio. Excess iodomethane (2.0 mL) was added and the solution stirred at room temperature for 2 h. This was concentrated and passed through a silica filtration column using benzene as eluent. The filtrate was diluted to 100 mL with benzene for quantitation by HPLC using a silica column and 0.5% ethyl acetate in hexanes as eluent. This gave a yield of 79% for all isomers. The ^{31}P NMR spectrum had signals corresponding to **11a**:**12a**:**13a**:**14a** in a ratio of 43:10:43:4. The benzene solution was concentrated and dissolved in hot hexanes and then cooled to −20 °C to give **11a** as an orange solid (27 mg, 24%), mp 147–149 °C dec. Crystallization from mixture of ethyl acetate–hexanes produced red X-ray quality crystals: ^1H NMR (C_6D_6) δ 8.05 (m, 2 H), 7.72 (m, 2 H), 7.3 (m, 1 H), 7.1 (complex m, 7 H), 6.83 (m, 2 H), 2.40 (m, 1 H), 2.03 (s, 3 H), 2.00 (m, 1 H), 1.70 (m, 2 H), 1.34 (m, 2 H), 0.83 (t, *J* = 7 Hz, 3 H); ^{13}C NMR δ 303.0 (dd, *J* = 25, 19 Hz), 217.6 (dd, *J* = 7, 6 Hz) 216.8 (dd, *J* = 26, 15), 212.5 (br s), 150.4 (dd, *J* = 40, 36 Hz), 138.6 (dd, *J* = 41, 30), 135.1–127.5 (m), 47.2 (d, *J* = 10 Hz), 34.2 (d, *J* = 26 Hz), 26.5 (s), 24.2 (d, *J* = 15 Hz), 13.6 (s); IR (CH_2Cl_2) ν_{CO} 2040 (m), 1980 (s), 1960 (m), 1920 (m), 1481 (w), 1435 (w) cm^{-1}.

Anal. Calcd for $C_{29}H_{26}Fe_2O_6P_2$: C, 54.07; H, 4.07. Found: C, 53.82; H, 4.18.

Reaction of 1 with Methyllithium at −78 °C, Followed by Thermal Equilibration. The reaction was carried out exactly as for the *n*-butyllithium experiment (above) to give only **9b** at −78 °C (by ^{31}P NMR spectroscopy). Upon warming, a new species **10b** was formed, and after 10 h, the ratio of **9b**:**10b** = 1:4 was invariant as a function of time: IR ν_{CO} 1990 (s), 1940 (s), 1900 (s), 1655 (m) cm^{-1}.

Reaction of 1 with Methyllithium at −78 °C, Followed by Thermal Equilibration and Methyl Iodide Quench. Isolation of 13b. A solution of **1** (300 mg, 0.51 mmol) in THF (15 mL) was treated dropwise with a 1.55 M ethereal solution of methyllithium (0.70 mL, 1.09 mmol). After 10 h at room temperature, a ^{31}P NMR spectrum was determined on the dark red solution, which showed a ratio of **9b**:**10b** = 1:4. Methyl iodide (1.82 g, 12.8 mmol) was added, and the reaction mixture was stirred for 7.5 h and then concentrated. A ^{31}P NMR spectrum of this mixture revealed the presence only of **11b**:**12b**:**13b**:**14b** in the proportion 16:4:61:19. The mixture was chromatographed on alumina by using benzene as an eluent, to give a red oil (259 mg, 83%) which slowly solidified

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Table III. Crystallographic Summary for **11a** and **13b**

	11a	**13b**
	A. Crystal Data (–110 °C)[a]	
a, Å	11.071 (2)	10.531 (2)
b, Å	13.756 (2)	17.610 (5)
c, Å	10.498 (1)	28.896 (19)
α, deg	97.64 (1)	90.0
β, deg	117.15 (1)	90.0
γ, deg	82.76 (1)	90.0
V, Å^3	1406.15	5358.84
d_{calcd}, g cm^{-3} (–110 °C)	1.521	1.498
empirical formula	$Fe_2P_2C_{29}H_{26}O_6$	$Fe_2P_2C_{26}H_{20}O_6$
fw	644.16	602.06
cryst system	triclinic	orthorhombic
space group	*P*1 bar	*Pbca*
Z	2	8
F(000), electrons	708	2448
	B. Data Collection (–110 °C)[b]	
radiatn, λ, Å	Mo Kα 0.710 69	
mode	ω scan	
scan range	symmetrically over 1.0° about $K\alpha_{1,2}$ maximum	
background	offset 1.0 and –1.0 in ω from $K\alpha_{1,2}$ maximum	
scan rate, deg min^{-1}	3.0–6.0	
2θ range, deg	4.0–55.0	
exposure time, h	80	47
stability anal.		
computed s	–0.0004 (1)	–0.0009 (4)
computed t	–0.000003 (2)	–0.00002 (8)
correction range (on I)	0.989–1.000	0.989–1.001
total reflctns measd	6460	6160
data cryst vol, mm^3	0.0091	0.0545
data cryst faces	{–1,0,1}, {100}, {001}, {011}	{102}, {021}
abs coeff μ(Mo Kα), cm^{-1}	12.15	12.69
transmissn factor range	0.784–0.886	0.650–0.716
	C. Structure Refinement[c]	
ignorance factor, p	0.02	0.02
reflctns used, $F_o \geqslant 4\sigma(F_o)$	5014	3704
no. of variables	434	300
R_1, R_2	0.038, 0.034	0.061, 0.052
R_1 for all data	0.058	0.107
goodness of fit, s	1.53	1.96
max shift/esd (non-H)	0.884	1.240
max shift/esd (H)	0.778	1.994
max peak in diff map, e Å^{-3}	1.06	0.54

[a] Unit-cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with 20.09° < 2θ < 23.94° for **11a** and 30 reflections with 23.49° < 2θ < 26.03° for **13b**. [b] Syntex P2$_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect B*: *Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B*: *Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1511. [c] Relevant expressions are as follows, where in this table F_o and F_c represent respectively the observed and calculated structure factor amplitudes. Function minimized was $\Sigma w(F_o - F_c)^2$, where $w = (\sigma_F)^{-2}$. $R_1 = \Sigma|(F_o - F_c)|/\Sigma F_o$. $R_2 = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$.

upon standing at –20 °C. This was carefully recrystallized from hexanes to give **13b** as dark red crystals of X-ray quality: mp 120–122.5 °C; ^{1}H NMR δ 8.1–7.3 (complex m, 14 H), 2.1 (s, 0.6 H), 2.0 (s, 2.4 H), 1.9 (d, $^2J_{P-H}$ = 7.8 Hz, 2.4 H), 1.75 (d, $^2J_{P-H}$ = 9.0 Hz, 0.6 H); ^{13}C NMR δ 212.7 (s), 147–128 (m), 48.0 (s), 47.7 (s), 15.5 (d, $^1J_{P-C}$ = 24 Hz); IR (C_2Cl_4) ν_{CO} 2045 (s), 2032 (m), 1988 (vs), 1972 (s), 1958 (s), 1482 (w), 1435 (vw) cm^{-1}.

Reaction of 1 with Methyllithium at –78 °C, Followed by a Methyl Iodide Quench. A solution of 0.90 M methyllithium in ether (0.20 mL, 0.18 mmol) was added to a solution of **1** (55.50 mg, 0.097 mmol) in THF (0.50 mL) at –78 °C. To this solution was added methyl iodide (0.30 mL), and the temperature was maintained at –78 °C for 1 h before warming to room temperature. Analysis by ^{31}P NMR spectroscopy gave the product distribution **11b**:**12b**:**13b**:**14b** = 52:8:30:10.

Reaction of 1 with Lithium Triethylborohydride at –60 °C. An 8-mm NMR tube with **1** (85.2 mg, 0.149 mmol) was degassed and THF (1.0 mL) added. This NMR tube was inserted into a 10-mm NMR tube which contained acetone-d_6 and then frozen in a liquid-nitrogen bath. A THF solution of 1.1 M lithium triethylborohydride was added and the solution warmed in a dry ice–acetone bath. This was then placed in the ^{31}P NMR probe at –60 °C. After an hour, approximately 10% had reacted to give **9c** exclusively. An additional equivalent of hydride (0.16 mL, 1.1 M, 0.160 mmol) was added. The reaction was approximately 30% complete after a total time of 3 h and a second species, **10c**, was observed (ratio **9c**:**10c** = 3:1). The temperature of the NMR probe was raised to –52 °C, and after 5.5 hours from the start of the reaction the ratio of **9c**:**10c** was 3:1 at 37% reaction completion. The temperature was raised to –38 °C, and after 7-h total time the ratio of **9c**:**10c** was 1:3 at 56% reaction completion. The solution was allowed to stand at room temperature overnight to give a **9c**:**10c** ratio of 1:3 with no **1**.

Crystallographic Analysis. For each substance, a single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Syntex P2$_1$ autodiffractometer, where it was maintained in a cold (–110 °C) stream of dry nitrogen for the duration of the diffraction experiments. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystals for intensity

Table IV. Fractional Coordinates and Isotropic or Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms for 11a

atom	*x*	*y*	*z*	*U*
Fe1	0.54504 (4)	0.88055 (3)	−0.24484 (4)	0.0181 (2)
Fe2	0.53173 (4)	0.68761 (3)	−0.25462 (4)	0.0188 (2)
P1	0.64577 (7)	0.78406 (5)	−0.06571 (7)	0.0171 (3)
P2	0.38522 (7)	0.68932 (5)	−0.16020 (8)	0.0194 (3)
O7	0.3368 (3)	0.9192 (2)	−0.5371 (2)	0.0527 (12)
O9	0.7083 (2)	1.0535 (2)	−0.1434 (2)	0.0387 (11)
O8	0.3596 (2)	0.96513 (15)	−0.1261 (2)	0.0295 (9)
O11	0.6632 (3)	0.4954 (2)	−0.1636 (3)	0.0429 (12)
O10	0.3460 (2)	0.6313 (2)	−0.5544 (2)	0.0459 (11)
O1	0.6742 (2)	0.80706 (14)	−0.3159 (2)	0.0237 (8)
C1	0.5907 (3)	0.7824 (2)	0.0731 (3)	0.0181 (10)
C2	0.4718 (3)	0.7349 (2)	0.0308 (3)	0.0188 (10)
C3	0.4313 (3)	0.7193 (2)	0.1335 (3)	0.0251 (12)
C4	0.5052 (3)	0.7541 (2)	0.2755 (3)	0.0282 (13)
C5	0.6196 (3)	0.8046 (2)	0.3166 (3)	0.0260 (12)
C6	0.6627 (3)	0.8178 (2)	0.2161 (3)	0.0229 (11)
C7	0.4192 (3)	0.9011 (2)	−0.4264 (3)	0.0285 (13)
C9	0.6439 (3)	0.9879 (2)	−0.1843 (3)	0.0245 (12)
C8	0.4317 (3)	0.9309 (2)	−0.1742 (3)	0.0212 (11)
C11	0.6086 (3)	0.5707 (2)	−0.2017 (3)	0.0264 (12)
C10	0.4151 (3)	0.6554 (2)	−0.4367 (3)	0.0281 (13)
C12	0.8312 (3)	0.7802 (2)	0.0309 (3)	0.0206 (11)
C13	0.9102 (3)	0.6929 (2)	0.0371 (3)	0.0302 (13)
C14	1.0513 (3)	0.6909 (3)	0.1134 (4)	0.0368 (15)
C15	1.1127 (3)	0.7755 (3)	0.1821 (4)	0.0362 (14)
C16	1.0361 (3)	0.8637 (3)	0.1761 (4)	0.0336 (14)
C17	0.8952 (3)	0.8660 (2)	0.1000 (3)	0.0263 (12)
C18	0.2212 (3)	0.7631 (2)	−0.2369 (3)	0.0232 (11)
C19	0.1670 (3)	0.7907 (3)	−0.3757 (3)	0.0344 (14)
C20	0.0419 (4)	0.8445 (3)	−0.4357 (4)	0.046 (2)
C21	−0.0298 (3)	0.8702 (3)	−0.3573 (4)	0.045 (2)
C22	0.0216 (3)	0.8436 (3)	−0.2205 (4)	0.043 (2)
C23	0.1470 (3)	0.7906 (3)	−0.1602 (4)	0.0345 (14)
C24	0.3274 (3)	0.5717 (2)	−0.1534 (3)	0.0281 (13)
C25	0.2541 (4)	0.5163 (2)	−0.3012 (4)	0.043 (2)
C26	0.1722 (4)	0.4356 (2)	−0.2998 (5)	0.048 (2)
C27	0.0441 (4)	0.4771 (4)	−0.2945 (6)	0.067 (2)
C28	0.6588 (3)	0.7181 (2)	−0.3186 (3)	0.0224 (11)
C29	0.7421 (4)	0.6466 (3)	−0.3734 (4)	0.037 (2)

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

Table V. Fractional Coordinates and Isotropic or Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms for 13b

atom	*x*	*y*	*z*	*U*
Fe1	0.13414 (7)	0.21259 (5)	0.10069 (3)	0.0508 (3)
Fe2	−0.02872 (7)	0.10603 (4)	0.12691 (2)	0.0417 (2)
P1	−0.03638 (13)	0.22524 (8)	0.14569 (4)	0.0386 (4)
P2	−0.19755 (15)	0.13138 (9)	0.08208 (5)	0.0524 (5)
O1	0.2054 (3)	0.1537 (2)	0.15433 (12)	0.0520 (14)
O7	0.2763 (5)	0.1187 (3)	0.0331 (2)	0.093 (2)
O8	−0.0001 (4)	0.2921 (3)	0.02765 (13)	0.084 (2)
O9	0.2966 (4)	0.3471 (3)	0.1135 (2)	0.089 (2)
O10	0.0737 (4)	−0.0096 (2)	0.06441 (14)	0.074 (2)
O11	−0.1719 (4)	0.0224 (2)	0.19646 (14)	0.071 (2)
C1	−0.1749 (3)	0.2726 (2)	0.12162 (10)	0.037 (2)
C2	−0.2482 (3)	0.2288 (2)	0.09154 (10)	0.042 (2)
C3	−0.3526 (3)	0.2611 (2)	0.06922 (10)	0.052 (2)
C4	−0.3836 (3)	0.3370 (2)	0.07696 (10)	0.055 (2)
C5	−0.3102 (3)	0.3808 (2)	0.10703 (10)	0.051 (2)
C6	−0.2058 (3)	0.3486 (2)	0.12936 (10)	0.046 (2)
C7	0.2225 (6)	0.1537 (4)	0.0600 (2)	0.065 (2)
C8	0.0534 (6)	0.2595 (4)	0.0565 (2)	0.064 (2)
C9	0.2353 (6)	0.2929 (4)	0.1094 (2)	0.067 (2)
C10	0.0318 (5)	0.0355 (3)	0.0891 (2)	0.052 (2)
C11	−0.1161 (5)	0.0555 (3)	0.1681 (2)	0.051 (2)
C12	−0.0200 (4)	0.2611 (2)	0.20398 (12)	0.042 (2)
C13	−0.0968 (4)	0.2307 (2)	0.23869 (12)	0.082 (3)
C14	−0.0833 (4)	0.2554 (2)	0.28429 (12)	0.092 (3)
C15	0.0070 (4)	0.3106 (2)	0.29518 (12)	0.087 (3)
C16	0.0838 (4)	0.3410 (2)	0.26047 (12)	0.153 (5)
C17	0.0703 (4)	0.3162 (2)	0.21487 (12)	0.114 (4)
C18	−0.3511 (8)	0.0758 (4)	0.0997 (3)	0.041 (3)
C19	−0.4045 (8)	0.0217 (4)	0.0703 (3)	0.053 (3)
C20	−0.5158 (8)	−0.0158 (4)	0.0831 (3)	0.055 (4)
C21	−0.5737 (8)	0.0008 (4)	0.1254 (3)	0.064 (4)
C22	−0.5203 (8)	0.0549 (4)	0.1548 (3)	0.070 (4)
C23	−0.4090 (8)	0.0924 (4)	0.1420 (3)	0.059 (3)
C18A	−0.3311 (11)	0.0838 (5)	0.0846 (4)	0.040 (3)
C19A	−0.3631 (11)	0.0278 (5)	0.0526 (4)	0.060 (4)
C20A	−0.4717 (11)	−0.0163 (5)	0.0592 (4)	0.070 (5)
C21A	−0.5481 (11)	−0.0044 (5)	0.0980 (4)	0.063 (6)
C22A	−0.5161 (11)	0.0516 (5)	0.1301 (4)	0.078 (5)
C23A	−0.4076 (11)	0.0957 (5)	0.1234 (4)	0.062 (4)
C24	−0.1780 (13)	0.1265 (8)	0.0192 (3)	0.101 (4)
C25	0.1244 (5)	0.1048 (3)	0.1634 (2)	0.049 (2)
C26	0.1541 (7)	0.0507 (5)	0.2025 (3)	0.077 (3)

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

data collection. A summary of the pertinent crystal data and details of the X-ray diffraction data collection and processing is presented in Table III, and crystallographic coordinates for **11a** and **13b** appear in Tables IV and V, respectively. The measured intensities were reduced and assigned standard deviations as described elsewhere,[24] including corrections for absorption based on measured crystal shape.

The structures were solved[25] by the heavy-atom method, using heavy-atom positions determined from sharpened Patterson maps. Both structures were refined by the full-matrix least-squares method, using the program SHELX-76. Neutral atom scattering factors[26] for H, C, O, P, and Fe were used, including real and imaginary corrections for anomalous dispersion.

The structure solution of **11a** proceeded without incident to final convergence, with the two phenyl rings treated as rigid groups and the hydrogen atoms in these rings as well as in the *n*-butyl group calculated in ideal positions. Because of the large total number of parameters, the refinement was carried out by blocking the structure into two parts. One block had the two Fe and two P atoms, the carbonyl groups, and the C(Me)O bridge; the other block had the benzo bridge, the two phenyl rings, the *n*-butyl, and the two P atoms.

The non-hydrogen atoms of **13b** were refined isotropically, until convergence was reached at R_1 = 0.130 and R_2 = 0.130. These unusually high *R* indexes and the erratic behavior of the U values and the shift/parameter ratios of phenyl ring B (attached to P2) indicated some difficulty with this portion of the structure. A series of difference density maps eventually revealed the presence of disorder in this phenyl ring. In the subsequent successful refinement of this structure, the phenyl rings and the benzo bridge were treated as rigid groups, constrained with C–C = 1.395 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°. The occupancy ratio for the disordered phenyl group was determined by refinement to be 0.56 (2):0.44 (2).[27]

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(24) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallog. Cryst. Chem.* **1976**, *B32*, 381.

(25) Principal computer programs: least-squares lattice parameters, LSLAT by K. N. Trueblood; absorption correction, SYABS, a local verion of ORABS by W. R. Busing and H. A. Levy as modified by J. M. Williams; full-matrix least-squartes and Fourier calculations, SHELX-76 by G. M. Sheldrick; thermal ellipsoid plots, ORTEP-II by C. K. Johnson. Various data processing programs of local origin, including: statistical analysis of check reflections, SYSTD by T.-H. Hseu; data reduction, INCON and FTABLE by R. E. Davis; preparation of computer-typed tables of atomic parameters, bond lengths, and bond angles, FUER by S. B. Larson.

(26) Scattering factors for H, C, O, and P were used as programmed in SHELX-76. Values for Fe were obtained from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974, Vol. IV.

(27) See note at the end of the paper regarding availability of supplementary materials.

F573, and R.E.D., Grant No. F233).

Registry No. 1, 57139-08-9; **2**, 19599-68-9; **9a**, 100700-54-7; **9b**, 100700-57-0; **9c**, 100700-60-5; **10a**, 100837-22-7; **10b**, 100837-25-0; **10c**, 100837-27-2; **11a**, 100700-55-8; **11b**, 100700-58-1; **12a**, 100700-56-9; **12b**, 100700-59-2; **13a**, 100837-23-8; **13b**, 100895-70-3; **14a**, 100837-24-9; **14b**, 100837-26-1; nonacarbonyldiiron, 15321-51-4; *o*-bis(phenylphosphino)benzene, 38023-29-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional crystallographic coordinates, thermal parameters, and full listings of bond lengths and angles (77 pages). Ordering information is given on any current masthead page.

Ligand Exchange Reaction of Ferrocene with 2,4,6-Triphenylphosphabenzene. Synthesis and Structural Study of Isomeric (η^5-Phosphacyclohexadienyl)(η^5-cyclopentadienyl)iron(II) Complexes Containing a η^5-Phosphadienyl Unit

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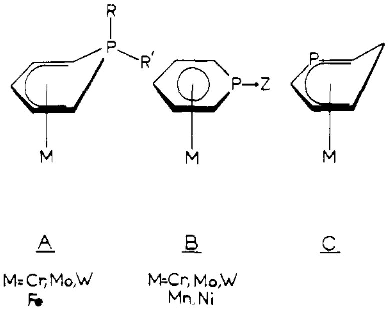
The reaction of 2,4,6-triphenylphosphabenzene with ferrocene and aluminum chloride gives a transient (η^6-2,4,6-triphenylphosphabenzene)(η^5-cyclopentadienyl)iron cation which reacts with water to give (η^5-2,4,6-triphenyl-1-hydrophosphabenzene 1-oxide)(η^5-cyclopentadienyl)iron, a secondary phosphine oxide complex. Reduction of this complex with trichlorosilane affords, depending on the conditions used, four isomeric (η^6-2,4,6-triphenylhydrophosphabenzene)(η^5-cyclopentadienyl)iron compounds, three of which possess the unprecedented η^5-phosphadienyl ligand. The X-ray crystal structure of one of these complexes is presented. The interconversion of the isomeric η^5-2,4,6-triphenylhydrophosphabenzene complexes has been studied by using 2,4,6-triphenylphosphabenzene-*1,3*-d_2 as ligand. The aforementioned (η^6-phosphabenzene)(η^5-cyclopentadienyl)iron cationic complex could be obtained by hydride abstraction from (η^5-2,4,6-triphenyl-2-hydrophosphabenzene)(η^5-cyclopentadienyl)iron.

Introduction

Several organometallic complexes in which a π-ligand has the phosphabenzene structure are now known. The π-complexes that have been prepared so far can be classified according to two types, A and B (Chart I). In structure A[2] a metal is coordinated by a η^5-dienyl ligand. In this type of compound, the phosphorus atom is not coordinated to the metal and has no specific role in the metal–ligand interaction. Indeed, compounds have been isolated in which the phosphorus atom had the structural properties of a phosphine,[2f] a phosphine oxide or sulfide,[2g] or a phosphonium salt.[2a–e]

In structure B,[3] a metal is complexed by the η^6 aromatic phosphabenzene ligand. In this case, the phosphorus atom is bonded to the metal. It still possesses a lone pair and can act as a two-electron ligand.

Chart I



Another interesting complex would be type C (Chart I). This type of complex would be similar to structure A in the sense that, in structure C, a η^5-dienyl ligand would also be present, but bonding of the phosphorus atom to the metal would be similar to that in structure B. No compound of type C (η^5-phosphadienyl) has been previously reported in the literature.

So far, complexes of type B have been synthetized with the chromium triad,[3a–d,g] manganese,[3f] and nickel.[3e] In order to expand this series, we wanted to prepare a (cyclopentadienyl)(phosphabenzene)iron(II) cation by the well-known ligand exchange reaction with ferrocene.[4] We now wish to report on this and on the synthesis and structure of some of the previously unknown complexes of type C as well.

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