$(OC)_3Fe^{-\cdot}$, $(OC)_3FeD^{-\cdot}$, and $(OC)_3FeH^{-\cdot}$ and possible H/D exchange in $(OC)_3FeH^-$ (*m/z* 141),[1] the ratio $[(OC)_3FeD^-/(OC)_3FeH^-)] = 2.2$.

The large amount of $(OC)_3FeD^-$ formed in this reaction requires that the major bond-forming process is that of Fe–D formation yielding **3**.[10] However, the significant amount of $(OC)_3FeH^-$ produced could arise from rearrangement of **1** → **2** or **3** → **5** followed by fragmentation. Since the rearrangement of **1** → **2** is the microscopic reverse of the **3** → **4** rearrangement, it is reasonable that partial H/D exchange (via diene isomerization **3** → **4** → **5**) is competitive with unimolecular fragmentation of **3**. While we cannot exclude minor formation of **1** in this reaction, the presence of **1** is not required to account for the observed products.

The minor product *m/z* 193 formed in the reaction of $(\eta^2\text{-1,3-}C_6H_8)Fe(CO)_3^{-\cdot}$ (*m/z* 220) with H atoms (eq 1c) increases by 1 amu to *m/z* 194 in the reaction of *m/z* 220 with D atoms. The overall process is substitution of a CO ligand by the H or D atom. Three structures were considered possible for the negative ion *m/z* 193, the 18-electron species $(\eta^4\text{-1,3-}C_6H_8)Fe(CO)_2(H)^-$, and the two 16-electron complexes $(\eta^4\text{-1,3-}C_6H_8)Fe(CO)(CHO)^-$ and $(\eta^3\text{-}C_6H_9)Fe(CO)_2^-$. However, the latter two 16-electron complexes would be expected to readily add H_2 in a secondary reaction yielding the corresponding dihydrides as we have observed with other coordinatively unsaturated complex negative ions, e.g., $(OC)_4Mn^-$,[11] $(OC)_3Fe^{-\cdot}$,[12] and $(\eta^4\text{-1,3-}C_4H_6)Fe(CO)^{-\cdot}$.[5] The fact that *m/z* 193 (or 194) does not react with H_2 (or D_2) under these conditions or with extended reaction times (changing $\bar{v}$ from 80 to 32 m/s) eliminates the two 16-electron structures for *m/z* 193 from further consideration. Since some H/D rearrangement may have occurred in *m/z* 194, this anion may be composed of a mixture of $(\eta^4\text{-1,3-}C_6H_8)Fe(CO)_2(D)^-$ and $(\eta^4\text{-1,3-}C_6H_7D)Fe(CO)_2(H)^-$.

The fact that H/D exchange was not observed in unreacted *m/z* 220 suggests that the fragmentation/rearrangement of **3** occurs on every bond-forming collision. The source of the $(OC)_3Fe^{-\cdot}$ fragmentation product in these reactions appears to be the η^3-allyl ion **4** which decomposes by loss of the cyclohexenyl radical. Therefore, formation of the three primary negative ion products in the reaction of $(\eta^2\text{-1,3-}C_6H_8)Fe(CO)_3^{-\cdot}$ with H atoms are readily explained via initial production of a single, vibrationally excited intermediate $[(\eta^2\text{-1,3-}C_6H_8)Fe(CO)_3(H)^-]^*$. In the reaction of *m/z* 220 with D atoms, **3** is the intermediate and H/D exchange between Fe and the diene ligand and decarbonylation (→ *m/z* 194) are only modestly competitive with loss of the cyclohexadiene ligand from the excited intermediate.

We conclude that the reaction of $(\eta^2\text{-1,3-}C_6H_8)Fe(CO)_3^{-\cdot}$ with H and D atoms occurs principally (or exclusively) by initial formation of the Fe–H(D) bond. This is in contrast to the gas-phase reactions of various anions with neutral transition-metal carbonyl complexes which demonstrated that nucleophilic addition to the carbonyl[13] and other ligands (e.g., $\eta^6\text{-}C_6H_6$)[2] were the low-energy pathways. We expect to contribute further to the development of bond-forming induced decomposition (BFID) reactions between anions and reactive atomic species as a tool to aid in structural assignments of gas-phase negative ions.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $(\eta^4\text{-1,3-c-}C_6H_8)Fe(CO)_3$, 12152-72-6; $(\eta^2\text{-1,3-c-}C_6H_8)Fe(CO)_3^{-\cdot}$, 101471-50-5; H, 12385-13-6; D, 16873-17-9.

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[11] McDonald, R. N.; Jones, M. T., unpublished results.

[12] McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095–6096.

[13] Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5369–5375 and references therein.

A Convenient Synthesis of Symmetrical and Unsymmetrical 1,2-Bis(phosphino)benzenes as Ligands for Transition Metals

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The reaction of 1,2-bis(phosphino)benzene with 6 equiv of phosgene gives 1,2-bis(dichlorophosphino)benzene (**4**) in 45–55% yields. Species **4** reacts with 2 equiv of *t*-BuMgCl or PhZnCl to give 1,2-bis(*tert*-butylchlorophosphino)- (**5a**) and 1,2-bis(phenylchlorophosphino)benzene (**5c**), respectively. The former can be isolated in 56% yield as the $MgCl_2$ adduct, but **5c** must be reduced to 1,2-bis(phenylphosphino)benzene in order to facilitate isolation. The bis(secondary phosphine) 1,2-bis[(2,4,6-trimethylphenyl)phosphino]benzene (**6g**) was prepared in good yield from the reaction of **4** and the organozinc reagent obtained from (2,4,6-trimethylphenyl)magnesium bromide and zinc chloride, followed by LAH reduction. Compounds **5a,c** react readily with 2 equiv of MeMgBr to give the corresponding symmetrical 1,2-bis(tertiary phosphino)benzenes in high yields. Reaction of **4** with 1 equiv of PhZnCl or *t*-BuZnCl gives 1-(phenylchlorophosphino)- (**8a**) or 1-(*tert*-butylphosphino)-2-(dichlorophosphino)benzene (**8b**), respectively. These could be reduced or carried on to unsymmetrical bis(tertiary phosphines) in good yields. The complexes 1-μ-PR^1-2-μ-PR^2$C_6H_4Fe_2(CO)_6$ ($R^1 = R^2 = t\text{-Bu}$; $R^1 = t\text{-Bu}$, $R^2 = Ph$; $R^1 = R^2 = 2,4,6\text{-}Me_3C_6H_2$) have been prepared in good yields and fully characterized.

Introduction

We have described a convenient synthesis of 1,2-bis(dimethoxyphosphoryl)benzene (**1**), which served as a precursor to 1,2-bis(phosphino)benzene (**2**).[1] We also reported that double deprotonation followed by alkylation gave **3a,b** and that **3a** could be transformed into **3c** by a

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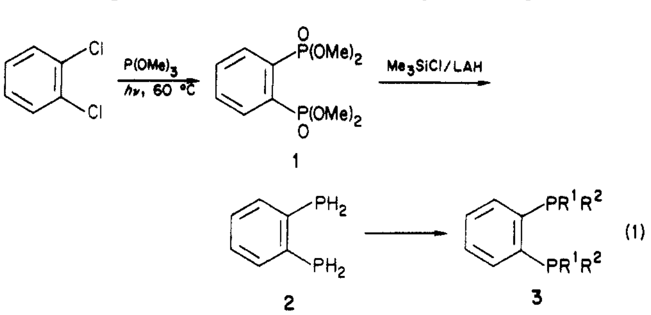
[1] Kyba, D. P.; Liu, S.-T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.

0276-7333/86/2305-1189$01.50/0

second deprotonation–methylation sequence (eq 1).[1] This route allows easy access to 1,2-bis(alkylphosphino)- and 1,2-bis(dialkylphosphino)benzenes, where the alkyl group can be methyl, primary alkyl,[2] and at least some secondary (e.g., *i*-Pr) alkyl groups. These types of compounds are highly entropically organized diphosphines which can serve as excellent ligands for transition metals; the 1,2-bis(secondary phosphino)benzenes are precursors to bis(μ-phosphido)dimetal systems,[3] and the 1,2-bis(tertiary phosphino)benzenes can give rise to unusual properties of coordinated transition metals.[4]

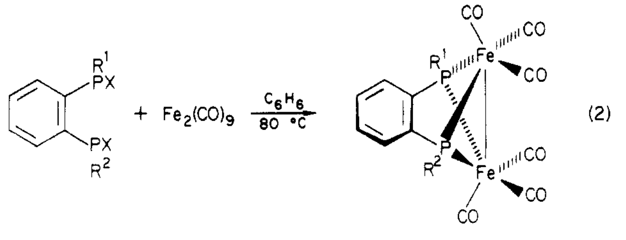


(1)

The above method for the formation of carbon–phosphorus bonds works best for methyl and primary alkyl species and may well fail for branched secondary alkyl systems, due to the intervention of an E2 rather than a displacement reaction, although we have not investigated this aspect. Certainly the formation of tertiary carbon- and aromatic carbon–phosphorus bonds using the **2** → **3** route would be doomed to failure. Thus we have developed an alternate approach which utilizes *electrophilic* rather than nucleophilic phosphorus sites and which has allowed considerable flexibility in the types of ligands which can be synthesized.

Results and Discussion

The reaction of bis(primary phosphine) **2** with phosgene[5] (6 equiv) in dichloromethane at −78 °C gave the tetrachloride **4** (Scheme I) in about 50% yield after distillation under vacuum. Table I summarizes ^{31}P NMR and other data for all of the compounds shown in Scheme I and eq 2. When a stoichiometric (4 equiv) amount of phosgene was used the yield dropped to 25%, but increasing the amount of phosgene beyond 6 equiv did not increase the yield above ca. 50%. Other reagents such as oxalyl chloride and thionyl chloride gave much poorer yields of **4**. Species **4** has been prepared before by a much longer and more expensive route, starting with *o*-bromoaniline.[6]



(2)

12, R^1 = R^2 = *t*-Bu
13, R^1 = *t*-Bu, R^2 = Ph
14, R^1 = R^2 = 2,4,6-Me$_3$C$_6$H$_2$
15, R^1 = R^2 = Ph

Table I. Percentage Yields and ^{31}P NMR Data for the Diphosphines Shown in Scheme I and the Complexes in Eq 2[a]

diphosphine	% yield	^{31}P NMR chem shifts δ (multiplicity, *J* (Hz), amount of diastereomer)
4	54	154.0 (s)
5a·MgCl$_2$	56	106.4 (s)
5b	81	136.3 (s, 65%), 127.6 (s, 35%)
5c	*b*	73.7 (s, 41%), 68.0 (s, 54%)
6a	77	−9.8 (s, 36%), −18.6 (s, 64%)
6b	58	−23.3 (s, 44%), −25.8 (s, 56%)[c]
6d	71	−43.0 (s, 46%), −44.0 (s, 54%)
6e	92	−35.5 (s, 20%), −36.1 (s, 80%)
6f	85	−13.8 (s)
6g	62	−83.2 (s, 56%), −83.7 (s, 44%)
10a	65	−15.2 (d, 95), −42.5 (d, 95); −17.6 (d, 58), −45.7 (d, 58), diastereomeric ratio 50:50
10b·2MgBrCl		−12.8 (d, 228), −35.4 (d, 228); −12.8 (d, 225), −36.0 (d, 225), diastereomeric ratio 57:43, respectively
10b	33	−24.3 (d, 159), −33.5 (d, 159); −24.0 (d, 160), −36.9 (d, 160), diastereomeric ratio 41:59, respectively
8a	*b*	155.8 (d, 406), 67.5 (d, 406)
8b	*b*	161.7 (d, 479), 97.1 (d, 479)
11a	23	−43.3 (d, 66) −124.4 (d, 66)
11b	55	−14.4 (d, 73), −124.3 (d, 73)
12	90	179.9
13	52	185.5 (d, 96.5), 143.0 (d, 96.5)[d]
14	54	108.5[d]

[a] Spectra determined on ca. 0.1 M solutions in CDCl$_3$, except for **4** where C$_6$D$_6$ was used. The diastereomeric ratios were determined by integration, and no attempt was made to account for differences in relaxation times; see: Shortt, A. B.; Durham, L. J.; Mosher, H. S. *J. Org. Chem.* **1983**, *48*, 3125. [b] Not isolated. [c] Before distillation the diastereomeric ratio was 79:21, respectively. [d] Acetone-d_6 solvent.

With the electrophilic diphosphine **4** in hand, we investigated phosphorus–carbon bond-forming reactions. It is well-known[7] that the reaction of Grignard reagents with multiple P–Cl bonds is difficult to control unless the Grignard reagent is bulky. Indeed we were able to react **4** cleanly with 2.0 equiv of *t*-BuMgCl to give **5a** as its monomagnesium chloride complex in 56% yield after distillation.[8] Further transformations on this complex gave high yields of the bis(secondary phosphine) **6a** and bis(tertiary phosphine) **6b**, both as diastereomeric mixtures. The reaction of **5a** and excess *t*-BuMgCl in THF at reflux gave a material which exhibited a sharp singlet in the ^{31}P NMR spectrum at δ 6.0 (spectrum determined prior to workup). All attempts to isolate a pure material from this solution led to the generation of multitudinous products as monitored by ^{31}P NMR. At the moment we do not know if **6c** is the material responsible for the signal at δ 6.0 and is very unstable or if it is a compound of as yet unknown composition.

One strategy which has been utilized to control the substitution at a tricoordinated phosphorus atom is to make the leaving groups quite different, e.g., Cl and NEt$_2$.[9]

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[2] Synthesis of **3** (R^1 = H, R^2 = Et and R^1 = R^2 = Et) as well as **3d** proceeds with about the same facility as that for **3c**: Liu, S.-T., unpublished results.

[3] McKennis, J. S.; Kyba, E. P. *Organometallics* **1983**, *2*, 1249.

[4] (a) Sethulakshmi, C. N.; Subramainan, S.; Bennett, M. A.; Manoharan, P. T. *Inorg. Chem.* **1979**, *18*, 2520. (b) Warren, L. F.; Bennett, M. A. *Ibid.* **1976**, *15*, 3126. (c) Warren, L. F.; Bennett, M. A. *J. Am. Chem. Soc.* **1974**, *20*, 1892. (d) Roberts, N. K.; Wild, S. B. *Ibid.* **1981**, *20*, 1900. (e) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.

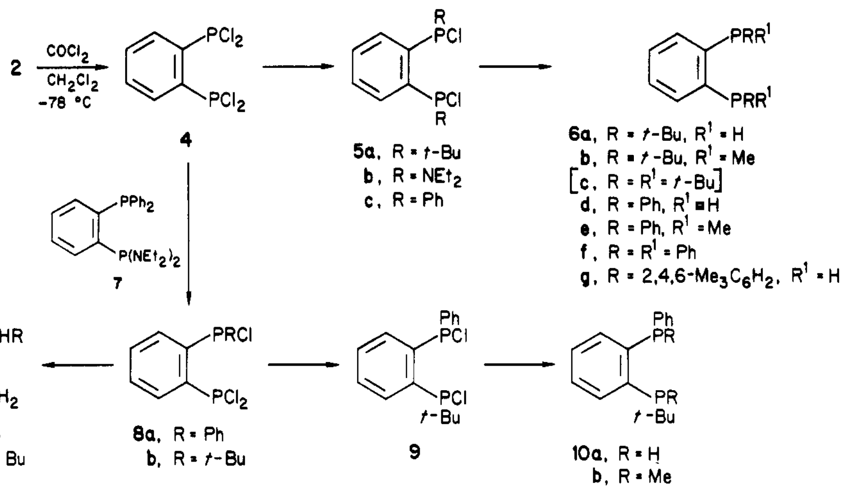
[5] Henderson, W. A., Jr.; Buchler, S. A.; Day, N. E.; Grayson, M. *J. Org. Chem.* **1961**, *26*, 4770.

[6] Drewelies, K.; Latscha, H. P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 638.

[7] Fild, M.; Schmutzler, R. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 4, pp 75–79.

[8] In the reactions involving *t*-BuMgCl and P–Cl bonds, we did not observe any reduction as was the case with Ph$_2$PCl + *t*-BuMgCl: Grim, S. O.; McFarland, W.; Davidoff, E. F. *J. Org. Chem.* **1967**, *32*, 781.

Scheme I

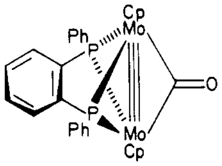


Thus we synthesized **5b** and reacted it with 2 equiv of PhMgBr at -78 °C, which gave a high yield of a 1:2 mixture of **5c** and **7**. Various modifications of the procedure did not change this ratio substantially, and thus we abandoned this approach. Instead, we established first that the reaction of **4** does indeed give mixtures upon reaction with PhMgBr. We then investigated less reactive reagents, in particular, phenylcadmium and phenylzinc species. Both reagents gave **5c** as the only species visible in the ^{31}P NMR spectrum upon reaction with **4** prior to workup. Subsequent manipulations and reactions showed clearly that the zinc species was reagent of choice. Thus the solution derived from the reaction of equimolar quantities of PhMgBr and anhydrous $ZnCl_2$ was treated with **4** (molar ratio Ph^-:4 = 2.0) at -78 °C. After the solution was warmed to room temperature, a ^{31}P NMR spectrum was taken which showed only two singlets at δ 73.7 and 68.0 (diastereomeric ratio ca. 2:3), consistent with the presence of **5c**. Attempts to isolate this species by distillation led to extensive decomposition. Thus this reaction mixture was treated directly with excess LAH to give the bis(secondary phosphine) **6d**[9] in 71% yield after distillation. This route of **1** → **2** → **4** → [**5c**] → **6d** is superior to those published[10,11] both in overall yield, and especially in the avoidance of odoriferous materials. Finally, treatment of the above-described crude reaction mixture of **5c** with a slight excess of MeMgCl gave **6e**[4d,e] in 92% yield (from **4**) as a mixture of diastereomers.

We have further extended the utility of **4** by effecting monosubstitution with 1.0 equiv of [PhMgBr + $ZnCl_2$] to give **8a**, cleanly, by ^{31}P NMR spectroscopy. After removal of the THF, attempts were made to remove selectively the inorganic salts by dissolution and precipitation from dichloromethane–hexane solutions, to no avail. Distillation (Kugelrohr, 165 °C, 60 μm) of the concentrated material gave only a 4% yield of **8a** and left a great deal of tarry material in the distillation pot. When the crude mixture of **8a** was treated with LAH, however, a three component mixture was obtained, which consisted of **11a**, **6d**, and **2** in a ratio of ca. 5:2:2 by ^{31}P NMR integration. Fractional vacuum distillation gave **11a** in 23% yield. It should be noted that there was no evidence for the chloride precursors to **6d** and **2** in the reaction mixture prior to LAH reduction. This might be indicative of randomization of the phenyl substituent on the phosphorus atoms during the LAH reduction.[12] We established in control experiments that **6d** and **2** do not revert to **11a** under thermal conditions or in THF solution in the presence of LAH. The *t*-Bu analogue **11b** was much better behaved; it was obtained in 55% yield via **8b**, which was reduced with LAH directly after the reaction of [*t*-BuMgCl + $ZnCl_2$] and **4**.

Finally, we have prepared two examples of disymmetric diphosphines. Reaction of **8a**, prepared in situ as described above, with 1.0 equiv of *t*-BuMgCl, gave **9**, which was reduced with LAH without workup to give **10a** in 65% overall yield from **4** (diastereomeric ratio 1:1). In addition, **10b** was isolated as a mixture of two chiral diastereomers in 33% overall yield from **4**, when **9** was treated in situ with a slight excess of MeMgBr.

We have utilized ligands **5a**, **10a**, and **6g** to synthesize the novel bis(μ-phosphido)diiron species **12–14**, respectively, as shown in eq 2. The structures of **12** and **14** have been determined by single-crystal X-ray crystallography;[13] both have been found to be unusually unreactive toward organolithium reagents.[14] We have described the use of **6d** as a precursor to complexes **15**[3] and **16**.[15]



16

In summary, we have described a general procedure for the synthesis of symmetric and disymmetric *o*-phenylenebis(primary, secondary, and tertiary phosphines), in which we use *o*-phenylenebis(dichlorophosphine) in selective carbon–phosphorus bond-forming reactions. Several bis(μ-phosphido) transition-metal complexes have been synthesized which illustrate some of the utility of the ligands prepared in this work.

Experimental Section

General Information. Proton magnetic resonance spectra were obtained in $CDCl_3$ solutions on a Varian EM-390 or a Nicolet NT 200 spectrometer. Carbon-13 and proton-decoupled phos-

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[9] Gerrard, W.; Hudson, H. R. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.: Wiley-Interscience: New York, 1972; Vol. 5, pp 99–100.

[10] (a) Mann, F. G.; Mercer, A. J. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1632. (b) Mann, F. G.; Mercer, A. J. H. *Ibid.* **1972**, 2548.

[11] Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139.

[12] We have observed such a phenomenon with **6d**. The details will be published elsewhere.

[13] Davis, R. E.; Hassett, K. L.; Kyba, E. P., unpublished results.

[14] Kyba, E. P.; Rines, S. P., manuscript in preparation.

[15] Kyba, E. P.; Mather, J. E.; Hassett, K. L.; McKennis, J. S.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 5371.

phorus-31 NMR spectra were determined in $CDCl_3$ solutions on Varian FT-80 spectrometers at 20.1 and 32.4 MHz, respectively. The ^{31}P NMR spectra are reported in Table I. 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.

Mass spectra (MS or HRMS) were determined on CEC-21-100 high-resolution instrument or a Du Pont 21-491 instrument at 70 eV.

Unless noted, all of the reactions, manipulations, and purification steps involving phosphines and organometallic species were performed under a dry nitrogen atmosphere. Air-sensitive liquids were transferred by Teflon flexneedles using nitrogen pressure or by syringe. All concentrations of solutions were carried out on a rotary evaporator under water aspirator pressures unless otherwise noted.

1,2-Bis(phosphino)benzene (**2**)[1] and *tert*-butylmagnesium chloride[16] were prepared as previously described. Tetrahydrofuran and diethyl ether were distilled under nitrogen from benzophenone ketyl, and dichloromethane was distilled under nitrogen from P_2O_5. The concentrations of the organolithium and organomagnesium reagents were determined by titration with aqueous acid using 9,10-phenanthroline as an indicator.

1,2-Bis(dichlorophosphino)benzene (4). Phosgene (183.1 g, 1.85 mol) was condensed into a solution of **2** (43.8 g, 30.8 mmol) in CH_2Cl_2 (1000 mL) at −78 °C. The apparatus included a dry ice condenser, gas inlet tube, and $NaOH/H_2O$ trap. The resulting solution was allowed to warm to room temperature, stirred for 10 h, and concentrated by using a rotary evaporator under high vacuum. The viscous, bright yellow-orange liquid was purified by vacuum distillation to give **4** (46.35 g, 54%) as a clear, colorless liquid: bp 132 °C (950 μm) [lit.[6] bp 97–99 °C (10^{-3} torr)]; ^1H NMR (C_6D_6) δ 8.0–7.8 (m, 2 H), 7.3–7.0 (m, 2 H).

[1,2-Bis(*tert*-butylchlorophosphino)benzene]magnesium Chloride Complex (5a·MgCl$_2$). A 2.32 M ether solution of *tert*-butylmagnesium chloride (19.9 mL, 46.4 mmol) was added to a solution of **4** (6.49 g, 23.2 mmol) in THF (160 mL) at −78 °C. The resulting solution was allowed to warm to room temperature over 8 h, then concentrated, and extracted with CH_2Cl_2. The combined organic extracts were concentrated and distilled under vacuum to give **5a**·$MgCl_2$[17] (5.38 g, 56%) as a colorless liquid which subsequently solidified: bp 134 °C (300 μm); ^1H NMR δ 8.0–7.8 (m, 2 H), 7.3–7.0 (m, 2 H), 1.04 (t, 18 H); ^{13}C NMR δ 142.2 (t, J = 6.3 Hz), 131.9 (t, J = 3.4 Hz), 130.1 (s), 36.8 (t, J = 16 Hz), 25.9 (t, J = 10 Hz); HRMS *m/e* 322.0584 (calcd 322.0574).

Anal. Calcd for $C_{14}H_{22}Cl_4MgP_2$: C, 51.71; H, 5.97. Found: C, 51.79; H, 5.80.

1,2-Bis[(diethylamino)chlorophosphino]benzene (5b). Diethylamine (55.5 g, 759 mmol) was added dropwise over 2 h to a solution of **4** (53.1 g, 190 mmol) in hexane (1.8 L) at −78 °C. The resulting solution was filtered, and the filtrate was concentrated and distilled under vacuum to give **5b** (54.0 g, 81%) as pale yellow liquid: bp 130–135 °C (200 μm); ^1H NMR δ 8.40–8.15 (m, 2 H), 7.43–7.20 (m, 2 H), 2.87 (dq, J_{HH} = 6 Hz, J_{PH} = 6 Hz, 4 H), 0.85 (dt, J_{HH} = 6 Hz, J_{PH} = 6 Hz, 6 H); ^{13}C NMR δ 149.3 (t, J = 5.0 Hz), 139.1 (s), 137.8 (s), 52.0 (t, J = 5.6 Hz), 21.4 (s); HRMS *m/e* 352.0785 (calcd 352.0792).

1,2-Bis(*tert*-butylphosphino)benzene (6a). A 2.11 M ether solution of *tert*-butylmagnesium chloride (12.4 mL, 26.2 mmol) was added to a solution of **4** (3.65 g, 13.0 mmol) in THF (100 mL) at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 5 h. It was recooled to −78 °C and treated with LAH (1.00 g, 26.3 mmol). The solution was allowed to warm to room temperature, stirred overnight, and then quenched with aqueous NaOH (6 M, 10 mL). The organic layer was separated, the salts were washed with diethyl ether (50 mL), and the organic extracts were combined, concentrated, and distilled under vacuum to give **6a** (2.55 g, 77%) as an air-sensitive, colorless liquid: bp 86–88 °C (150 μm); ^1H NMR δ 7.7–7.0 (m, 8 H), 3.85 (d, J = 225 Hz, 2 H), 1.03 (d, J = 15 Hz, 18 H), 4.38 (d, J = 213 Hz, 2 H), 1.00 (d, J = 15 Hz, 18 H); ^{13}C NMR δ 140.8 (s), 137.5 (t, J = 6.3 Hz), 128.0 (s), 30.8 (t, J = 5.1 Hz), 30.2 (t, J = 7.1 Hz); HRMS *m/e* 254.135 32 (calcd 254.135 77).

Anal. Calcd for $C_{14}H_{24}P_2$: C, 66.13; H, 9.51. Found: C, 66.27; H, 9.51.

1,2-Bis(*tert*-butylmethylphosphino)benzene (6b). A 1.78 M ether solution of *tert*-butylmagnesium chloride (36.0 mL, 64.1 mmol) was added to a solution of **4** (8.74 g, 31.2 mmol) in THF (180 mL) at −78 °C, and the resulting solution was allowed to warm to room temperature and stirred 5 h. The resulting solution was treated with a 2.8 M ether solution of methylmagnesium chloride (30 mL, 84.0 mmol) and stirred for 2 h. It was then quenched with saturated ammonium chloride (5 mL), the layers were separated, and the organic layer was concentrated. The residue was distilled under vacuum to give **6b** (5.96 g, 67.4%) as a colorless, air-sensitive liquid: bp 114–116 °C (180 μm); ^1H NMR δ 7.8–7.2 (m, 8 H), 1.25 (m, 6 H), 1.23 (m, 6 H), 1.15 (t, J = 6 Hz, 18 H), 0.97 (t, J = 6 Hz, 18 H); ^{13}C NMR δ 146.0 (t, J = 5.1 Hz), 144.3 (t, J = 6.1 Hz), 131.6 (s), 130.8 (s), 127.5 (s), 127.2 (s), 29.8 (t, J = 7.7 Hz), 29.2 (t, J = 6.0 Hz), 27.7 (t, J = 8.0 Hz), 26.7 (t, J = 8.1 Hz), 8.3 (t, J = 7.0 Hz), 5.1 (t, J = 5.9 Hz); HRMS *m/e* 282.1666 (calcd 282.1676).

Anal. Calcd for $C_{16}H_{28}P_2$: C, 68.18; H, 9.95. Found: C, 68.37; H, 10.00.

1,2-Bis(phenylphosphino)benzene (6d). Zinc Reaction. A 3.0 M ether solution of phenylmagnesium bromide (17.5 mL, 52.5 mmol) was added to anhydrous $ZnCl_2$ (7.15 g, 52.5 mmol) in THF (200 mL) and the resulting mixture stirred for 15 min. It was then cooled to −78 °C and treated with a solution of **4** (7.34 g, 26.2 mmol) in THF (30 mL) also at −78 °C. The mixture was allowed to warm to room temperature, stirred for 6 h, and then recooled to −78 °C. It was then treated with LAH (4.0 g, 110 mmol), allowed to warm to room temperature, and stirred overnight. The mixture was quenched with aqueous NaOH (4 M, 50 mL), the THF layer was separated, and the salts were washed with diethyl ether (100 mL). The combined organic extracts were concentrated and distilled under vacuum to give **6d** (5.50 g, 71%) as a colorless, air-sensitive, viscous oil, bp 170–174 °C (20 μm) [lit.[10a] bp 170–174 °C (50 μm)].

1,2-Bis(phenylphosphino)benzene (6d). Cadmium Reaction. A 3.0 M ether solution of phenylmagnesium bromide (4.86 mL, 14.6 mmol) was added to $CdCl_2$ (1.34 g, 7.29 mmol) in THF (130 mL) and the resulting mixture stirred for 45 min. It was then cooled to −78 °C and treated with a solution of **4** (2.04 g, 7.29 mmol) in THF (20 mL) also at −78 °C. The mixture was allowed to warm to room temperature, stirred for 4 h, and then recooled to −78 °C. It was then treated with LAH (500 mg, 13.2 mmol), allowed to warm to room temperature, and stirred overnight. The mixture was quenched with aqueous NaOH (4 M, 50 mL), the THF layer was separated, and the aqueous layer was washed with diethyl ether (75 mL). The combined organic extracts were concentrated and distilled under vacuum to give **6d** (960 mg, 45%) as a colorless, air-sensitive, viscous oil, bp 170–174 °C (43 μm) [Lit.[10a] bp 170–174 °C (50 μm)].

1,2-Bis(phenylmethylphosphino)benzene (6e). A 3.0 M ether solution of phenylmagnesium bromide (5.73 mL, 17.2 mmol) was added to anhydrous $ZnCl_2$ (2.34 g, 17.2 mmol) in THF (100 mL). The resulting mixture was stirred for 15 min, cooled to −78 °C, and treated with a solution of **4** (2.32 g, 8.29 mmol) in THF (30 mL) also at −78 °C. This was stirred at room temperature for 6 h, then treated with a 2.9 M ether solution of methylmagnesium bromide (6.55 mL, 19.0 mmol), and stirred three additional hours. The resulting solution was quenched with saturated ammonium chloride (20 mL), and the organic layer was separated and concentrated. The residue was passed through a short column of silica gel (10 g) utilizing ethyl acetate as an eluent. Upon concentration, **6e** (2.47 g, 92%) was obtained as pale yellow gum, which solidified upon standing; ^1H NMR (partial) δ 1.50 (t, J = 2 Hz), 1.37 (t, J = 2 Hz), meso and *dl* diastereomers, respectively (ratio 4:1) [lit.[4f] δ 1.60 (t, J = 4 Hz), 1.42 (t, J = 4 Hz)].

1,2-Bis(diphenylphosphino)benzene (6f). A 3.0 M ether solution of phenylmagnesium bromide (21.6 mL, 64.8 mmol) was added to **4** (4.02 g, 14.4 mmol) in THF (125 mL) at −78 °C, allowed to warm to room temperature, and stirred 8 h. The resulting solution was quenched with water (1 mL) and partitioned between water and dichloromethane. The organic extracts were washed

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(17) The presence of magnesium was confirmed by atomic absorption spectroscopy. We thank Thomas M. Rettberg and Professor James A. Holcombe for this determination.

with aqueous ammonium chloride (2 × 100 mL) and concentrated to give crude **6f** (6.61 g, 103%) as a yellow solid. It was passed through a short column of silica gel (20 g) with ethyl acetate as the eluent to give **6f** (5.47 g, 85%) as an off-white, air-stable solid: mp 182–183.5 °C (lit.[18] mp 186.5–187.5 °C); ^{1}H NMR δ 7.0–7.4 (m); MS *m/e* 446 (M$^+$).

1,2-Bis[(2,4,6-trimethylphenyl)phosphino]benzene (6g). A 1.47 M ether solution of mesitylmagnesium bromide (35.0 mL, 50.9 mmol) was added to anhydrous zinc chloride (6.93 g, 50.9 mmol) in THF (220 mL) and the resulting mixture stirred for 15 min. It was then cooled to −78 °C and treated with a solution of **4** (7.12 g, 25.4 mmol) in THF (25 mL) also at −78 °C. The mixture was allowed to warm to room temperature, stirred for 6 h, and then recooled to −78 °C. It was then treated with LAH (1.5 g, 39.5 mmol), allowed to warm to room temperature, and stirred overnight. The mixture was quenched with aqueous NaOH (4 M, 25 mL), the THF layer was separated, and the salts were washed with diethyl ether (100 mL). The organic extracts were combined and concentrated to give **6g** (9.62 g) as a crude yellow solid. The pure phosphine was obtained by precipitation from hexane to give **6g** (5.97 g, 62%) as a white powder and recrystallized from CH_2Cl_2 to give **6g**·$(0.1CH_2Cl_2)$: mp 158.5–161.5 °C; ^{1}H NMR δ 7.18–6.72 (m, 8 H), 2.41 (s, 12 H), 2.32 (s, 6 H); ^{13}C NMR δ 143.6 (t, *J* = 6.6 Hz), 139.1 (s), 138.3 (t, *J* = 3.6 Hz), 130.8 (t, *J* = 5.3 Hz), 129.1 (s), 127.9 (t, *J* = 20 Hz), 127.4 (s), 22.9 (t, *J* = 6.3 Hz), 21.1 (s); HRMS *m/e* 378.1672 (calcd 378.1666).

Anal. Calcd for $C_{24}H_{28}P_2\cdot(0.1CH_2Cl_2)$: C, 74.81; H, 7.35. Found: C, 74.44; H, 7.20.

1-(*tert*-Butylphosphino)-2-(phenylphosphino)benzene (10a). A 3.0 M ether solution of phenylmagnesium bromide (8.65 mL, 26.0 mmol) was added to anhydrous zinc chloride (3.54 g, 26.0 mmol) in THF (230 mL) and stirred for 15 min. The resulting solution was cooled to −78 °C and treated with **4** (7.27 g, 26.0 mmol) in THF (75 mL) also at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 3 h. It was subsequently recooled to −78 °C, treated with a 1.74 M ether solution of *tert*-butylmagnesium chloride (15.0 mL, 26.0 mmol), and then stirred at room temperature for 5 h. The solution was again cooled to −78 °C, LAH (1.00 g, 26.0 mmol) was added, and the resulting mixture was stirred overnight at room temperature. It was then quenched with aqueous NaOH (6 M, 30 mL), and the THF layer was separated. The salts were washed with diethyl ether (50 mL), and the combined organic extracts were concentrated, passed through a short column of degassed alumina, and distilled under vacuum to give **10a** (4.63 g, 65%) as colorless, air-sensitive liquid: bp 154–159 °C (600 μm); ^{1}H NMR δ 7.7–7.1 (m, 18 H), 5.63 (d, *J* = 223 Hz, 1 H), 5.20 (dd, *J* = 216, 12 Hz, 1 H), 4.40 (d, *J* = 216 Hz, 1 H), 4.05 (dd, *J* = 210, 12 Hz, 1 H), 1.13 (d, *J* = 12 Hz, 9 H), 1.10 (d, *J* = 12 Hz, 9 H); ^{13}C NMR (partial) δ 30.6 (m, P–$C(CH_3)_3$), 29.9 (m, P–$C(CH_3)_3$); HRMS *m/e* 274.10329 (calcd 274.10707).

1-(*tert*-Butylmethylphosphino)-2-(methylphenylphosphino)benzene (10b). A 3.02 M ether solution of phenylmagnesium bromide (2.65 mL, 8.00 mmol) was added to zinc chloride (1.09 g, 8.00 mmol) in THF (75 mL) for 15 min. The resulting solution was cooled to −78 °C and treated with **4** (2.23 g, 8.00 mmol) in THF (30 mL) also at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 3 h. It was subsequently recooled to −78 °C, treated with a 2.04 M ether solution of *tert*-butylmagnesium chloride (3.9 mL, 8.0 mmol), and then stirred at room temperature for 5 h. The resulting mixture was treated with a 2.55 M ether solution of methylmagnesium chloride (6.3 mL, 16.0 mmol) and stirred overnight. This was quenched with saturated NH_4Cl (100 mL), and the layers were separated. The organic extracts were then treated with a 0.1 M sodium hydroxide solution (100 mL), and the layers were separated. The aqueous layer was washed with dichloromethane (100 mL), and the organic layers were combined, filtered, dried, and concentrated to give a yellow oil (1.59 g, 64%). The oil was distilled under vacuum to yield **10b** (0.83 g, 33%) as an air-sensitive, colorless liquid: bp 100–103 °C (70 μm); ^{1}H NMR δ 7.80–7.15 (m, 18 H), 1.81 (d, *J* = 6 Hz, 6 H), 1.67 (d, *J* = 6 Hz, 2.4 H), 1.60 (d, *J* = 6 Hz, 3.6 H), 1.18 (d, *J* = 15 Hz, 7 H), 0.95 (d, *J* = 15 Hz, 11 H); ^{13}C NMR (partial) δ 30.4 (m), 27.7 (s), 27.5 (s), 12.8 (m), 6.0 (m); HRMS *m/e* 302.13464 (calcd 302.13532).

Anal. Calcd for $C_{18}H_{24}P_2$: C, 71.49; H, 8.02. Found: C, 70.77; H, 8.01.

When the above procedure was followed, except that the ammonium chloride quench was not followed by the sodium hydroxide treatment, then the complex **10b**·2MgBrCl was isolated as a white solid which was recrystallized from methanol (54%): mp 196–199 °C; ^{1}H NMR virtually identical with that of **10b**; ^{13}C NMR (partial) δ 31.1 (d, *J* = 3.0 Hz), 30.3 (d, *J* = 2.0 Hz), 26.1 (m), 13.0–4.0 (complex m).

Several attempts failed to obtain more acceptable combustion analytical data for **10b**, so that the bis(tertiary sulfide) derivative was prepared. Diphosphine **10b** (135 mg, 0.45 mmol) in THF (30 mL) was added to sulfur (125 mg, 0.48 mmol), and the mixture was stirred at 25 °C for 2.5 h. The resulting solution was concentrated and passed through a column of silica gel (3:1 CH_2Cl_2/hexanes, v/v) to give the bis(sulfide) (142 mg, 87%) as white crystals: mp 127–128 °C; ^{1}H NMR δ 7.9–7.4 (m, 18 H), 5.20 (s, 1 H, CH_2Cl_2), 2.54 (d, *J* = 12.5 Hz, 2.4 H), 2.48 (d, *J* = 12.55 Hz, 2.4 H), 2.26 (d, *J* = 12.5 Hz, 3.6 H), 1.88 (d, *J* = 13.0 Hz, 3.6 H), 1.14 (d, *J* = 17.0 Hz, 11 H), 1.05 (d, *J* = 17.0 Hz, 7 H); ^{31}P NMR (CH_2Cl_2) δ 66.6 (d, *J* = 4.4 Hz) and 39.7 (d, *J* = 4.4 Hz), 62.5 (d, *J* = 5.6 Hz), 41.0 (d, *J* = 5.6 Hz), diastereomeric ratio 41:59 (see Table I, footnote *a*).

Anal. Calcd for $C_{18}H_{24}P_2S_2\cdot0.4CH_2Cl_2$: C, 57.00; H, 6.54. Found: C, 57.28; H, 6.59.

(2-Phosphinophenyl)phenylphosphine (11a). A 3.0 M ether solution of phenylmagnesium bromide (8.90 mL, 26.7 mmol) was added to a solution of zinc chloride (3.64 g, 26.7 mmol) in THF (225 mL) and the mixture was stirred for 15 min before being cooled to −78 °C and treated with a solution of **4** (7.47 g, 26.7 mmol) in THF (20 mL) also at −78 °C. The resulting solution was allowed to warm to room temperature and stirred for 8 h; at this time an aliquot was analyzed by ^{31}P NMR which showed that there was a 10:1 ratio of **8a** [δ 155.8 (d, *J* = 406 Hz), 67.5 (d, *J* = 406 Hz] and **5c** [δ 68.1 (s)], respectively. Solid LAH (2.02 g, 53.2 mmol) was added to the mixture at −78 °C, and the resulting slurry was allowed to warm to room temperature and to stir for 10 h. The mixture was quenched with aqueous NaOH (4 M, 15 mL), the layers were separated, and the salts were washed with diethyl ether (100 mL). The combined organic extracts were concentrated to give a yellow oil. ^{31}P NMR analysis of the crude product showed a 5:2:2 ratio of **11a**, **6d**, and **2**, respectively. Fractional distillation under vacuum gave **11a** (1.28 g, 22%) as an air-sensitive, colorless liquid: bp 130–135 °C (300 μm); ^{1}H NMR 8.0–7.2 (br m, 9 H), 5.30 (dd, *J* = 201, 7 Hz, 2 H), 3.95 (dd, *J* = 219, 5 Hz, 1 H); ^{13}C NMR δ 134.7 (s), 133.9 (s), 128.9 (m), 127.2 (m); HRMS *m/e* 218.04068 (calcd 218.04142).

Anal. Calcd for $C_{12}H_{12}P_2$: C, 66.06; H, 5.54. Found: C, 66.30; H, 5.60.

(2-Phosphinophenyl)-*tert*-butylphosphine (11b). A 1.6 M ether solution of *tert*-butylmagnesium chloride (18.5 mL, 29.6 mmol) was added to a solution of zinc chloride (4.03 g, 29.6 mmol) in THF (250 mL) and the mixture stirred for 15 min before being cooled to −78 °C and being treated with a solution of **4** (8.28 g, 29.6 mmol) in THF (20 mL) also at −78 °C. The resulting solution was stirred at room temperature for 3 h, then cooled to −78 °C, and treated with LAH (1.68 g, 44.4 mmol). The resulting mixture was stirred at room temperature 8 h and then quenched with aqueous NaOH (4 M, 15 mL), and the layers were separated. The salts were washed with diethyl ether (100 mL), and the organic extracts were combined, concentrated, and distilled under vacuum to give **11b** (3.20 g, 55%) as an air-sensitive, colorless liquid: bp 67–69 °C (120 μm); ^{1}H NMR δ 7.8–7.2 (m, 4 H), 4.27 (br s, 1 H), 4.13 (d, *J* = 203 Hz, 2 H), 1.16 (dd, *J* = 12, 2 Hz, 9 H); ^{13}C NMR δ 137.5 (t, *J* = 5.4 Hz), 128.5 (d, *J* = 1.7 Hz), 127.6 (d, *J* = 3.1 Hz), 29.7–30.4 (m); HRMS *m/e* 198.07235 (calcd 198.07272).

[μ-1,2-Phenylenebis(*tert*-butylphosphido)-μ-*P*,*P*′]hexacarbonyldiiron (12). Nonacarbonyldiiron (11.6 g, 32.0 mmol) was added as a solid to a solution of **5a**·$MgCl_2$ (4.46 g, 10.7 mmol) in benzene (200 mL) under nitrogen and the mixture was stirred for 2 h before being heated at reflux for 10 h. The solution was cooled to room temperature and concentrated, and the product was isolated by column chromatography (alumina, benzene) to afford, after crystallization from hexane, **12** as orange crystals:

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[18] Hart, F. A. *J. Chem. Soc.* **1960**, 3324.

mp >120 °C dec (5.14 g, 90%); ^{1}H NMR (C_6D_6) δ 7.34–7.13 (br s, 2 H), 6.60–6.37 (m, 2 H), 1.40 (s, 6 H), 1.33 (br s, 6 H), 1.23 (s, 6 H); ^{13}C NMR δ 212.6 (t, J = 3.2 Hz, CO), 147.4 (t, J = 30.2 Hz), 129.0 (t, J = 8.4 Hz), 125.1 (t, J = 1.4 Hz), 37.0 (t, J = 8.5 Hz), 29.0 (s); IR (THF) ν_{CO} 2040 (s), 2003 (s), 1963 (b-s), 1924 (w) cm^{-1}; MS, *m/e* 532 (M$^+$).

Anal. Calcd for $C_{20}H_{22}Fe_2O_2P_2$: C, 45.15; H, 4.17. Found: C, 45.37; H, 4.33.

[μ-*P*-Phenyl-*P′*-*tert*-butyl-1,2-phenylenebis(phosphido)-μ-*P*,*P′*]hexacarbonyldiiron (13). Nonacarbonyldiiron (14.10 g, 38.8 mmol) was added as a solid to a solution of 1-(phenylphosphino)-2-(*tert*-butylphosphino)benzene (4.08 g, 14.9 mmol) in benzene (200 mL) under nitrogen, and the mixture was heated at reflux for 43 h. The dark blackish orange solution was concentrated and passed through alumina using hexane, to afford an orange powder, which was crystallized from hexane to give **13** (4.27 g, 52%) as orange crystals: mp >120 °C dec; ^{1}H NMR (C_6D_6) δ 7.83–7.47 (m, 2 H), 7.33–6.95 (5 H), 6.53–6.20 (m, 2 H), 1.33 (d, J_{P-H} = 17 Hz, 9 H); ^{13}C NMR (partial, C_6D_6) δ 205.05 (dd, J_{P1-C} = 4.2 Hz, J_{P2-C} = 2.9 Hz, *C*O), 30.48 (dd, J_{P1-C} = 7.1 Hz, J_{P2-C} = 9.0 Hz, *C*(CH_3)$_3$) 21.70 (d, J_{P-C} = 3.1 Hz, C(CH_3)$_3$); IR (THF) ν_{CO} 2048 (s), 2012 (s), 1979 (s), 1958 (s), 1929 (m) cm^{-1}; MS, *m/e* 552 (M$^+$).

Anal. Calcd for $C_{22}H_{18}Fe_2O_2P_2$: C, 47.87; H, 3.29. Found: C, 47.71; H, 3.40.

[μ-1,2-Phenylenebis[(2,4,6-trimethylphenyl)phosphido]-μ-*P*,*P′*]hexacarbonyldiiron (14). Nonacarbonyldiiron (6.10 g, 16.7 mmol) was added as a solid to a solution of 1,2-bis[(2,4,6-trimethylphenyl)phosphino]benzene (2.53 g, 6.69 mmol) in benzene (200 mL) under nitrogen and the mixture heated at reflux for 5 h. The dark blackish orange solution was concentrated and passed through alumina (hexane) to afford an orange powder which was crystallized from dichloromethane to give **14** (2.37 g, 54%) as an orange microcrystalline solid: mp >120 °C dec; ^{1}H NMR (C_6D_6) 7.20 (br s, 6 H), 6.76 (m, 2 H), 2.73 (s, 12 H), 1.98 (s, 6 H); ^{13}C NMR (partial, C_6D_6) δ 203.62 (s, CO), 21.82 (s, CH_3), 12.84 (s, CH_3); IR (THF) ν_{CO} 2068 (s), 2010 (s), 1982 (s), 1966 (s), 1952 (m) cm^{-1}; MS, *m/e* 656 (M$^+$).

Anal. Calcd for $C_{30}H_{26}Fe_2O_2P_2$: C, 54.91; H, 3.99. Found: C, 54.87; H, 4.19.

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Registry No. 2, 80510-04-9; 4, 82495-67-8; **5a**·$MgCl_2$, 101653-36-5; **5b**, 101653-20-7; **5c**, 101653-32-1; **6a**, 101653-21-8; **6b**, 101653-22-9; **6d**, 38023-29-9; *meso*-**6e**, 72091-02-2; *al*-**6e**, 72091-01-1; **6f**, 13991-08-7; **6g**, 101653-23-0; **8a**, 101653-31-0; **8b**, 101653-35-4; *meso*-**10a**, 101653-24-1; *al*-**10a**, 101653-25-2; *meso*-**10b**, 101653-26-3; *al*-**10b**, 101653-27-4; *meso*-**10b** (bis(sulfide)), 101653-29-6; *al*-**10b** (bis(sulfide)), 101653-30-9; **11a**, 101653-33-2; **11b**, 101653-34-3; **12**, 101653-37-6; **13**, 101653-38-7; 14, 101653-39-8; $Fe_2(CO)_9$, 15321-51-4; phosgene, 75-44-5; *tert*-butylmagnesium chloride, 677-22-5; methylmagnesium chloride, 676-58-4; phenylmagnesium bromide, 100-58-3; mesitylmagnesium bromide, 2633-66-1.

A ^{125}Te Mössbauer Study of Complexes Containing Metal–Tellurium Multiple Bonds

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The ^{125}Te Mössbauer isomer shifts, δ, and quadrupole splittings, Δ, have been measured at 4.2 K for the following compounds: (μ-Te)[V(CO)$_3$diphos]$_2$, where diphos = ethylenebis(diphenylphosphane) (δ = 0.17, Δ < 3.8 mm s^{-1}), (μ_3-Te)[Mn(CO)$_2$(η^5-C_5H_5)]$_3$ (δ = 0.18, Δ = 5.6 mm s^{-1}), (μ-Te)[Mn(CO)$_2$(η^5-C_5Me_5)]$_2$ (δ = 0.15, Δ = 6.5 mm s^{-1}), (μ-η^2-TeCH_2)[Mn(CO)$_2$(η^5-C_5Me_5)]$_2$ (δ = 0.20, Δ = 6.3 mm s^{-1}), and (μ-Te)-[Cr(CO)$_3$(η^5-C_5H_5)]$_2$ (δ = 0.38, Δ = 8.4 mm s^{-1}). The isomer shifts are essentially the same regardless of whether the tellurium is acting as a six-, four-, or two-electron donor. The very small quadrupole splittings of the first three listed compounds are evidence of multiple-bond character in the tellurium–metal bonds.

Introduction

Recently there has been considerable interest in transition metal complexes containing a ligand-free chalcogen as a bridging element.[1] Examples have been found[2-4] where, on the basis of X-ray structural determination of the metal–chalcogen bond length, the presence of a multiple bond, M=E or M≡E, has been invoked. It was of interest to explore the nature of the bonding in the tellurium analogues of these complexes using ^{125}Te Mössbauer spectroscopy.

The molecules that have been investigated are illustrated in Figure 1, where only the geometry about the tellurium is shown.

In (μ-Te)[V(CO)$_3$diphos]$_2$, where diphos = ethylenebis(diphenylphosphane), the V–Te–V linkage is presumably linear in analogy with the sulfur compound where the crystal structure has been determined.[2] In the latter the V–S bond length was found to be 217.2 pm in comparison with a V–S single bond length of 230 pm. This suggests the presence of V–E multiple-bond character, with the chalcogen acting as a six-electron donor.

$$\mathrm{diphos(CO)_3V{\equiv}E{\equiv}V(CO)_3diphos}$$

$$\mathrm{diphos(CO)_3V}\,\underline{\longleftarrow}\,\mathrm{E}\,\underline{\longrightarrow}\,\mathrm{V(CO)_3diphos}$$

In (μ_3-Te)[Mn(CO)$_2$(η^5-C_5H_5)]$_3$ the X-ray crystal structure shows the coordination about the tellurium to be trigonal planar,[3] the tellurium atom lying 3.4 (1) pm out of the Mn_3 plane. The Mn–Te bond lengths of 247 and 251 pm compare with an anticipated single bond length of 270 pm.[4] The bonding may be described in terms of three double bonds between tellurium and manganese, although some contribution from Te→Mn bonds cannot be ruled out. The tellurium is again serving as a six-electron donor.

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