to $(Et_3P)_2\overline{Pt(2\text{-}C_6H_4CMe_2CH_2)}$ (**3**) *tert*-butylbenzene. Although it is undetectable (by NMR) during cyclization of **1** in the range +60 to −20 °C, there is a suspicion that **2** may lie on the mechanistic pathway between **1** and **3** either by a second aromatic C–H scission via B or by reversion to A (Scheme I)[7] by aliphatic C–H activation. The rate of conversion of **2** to **3** ($k_{35^\circ C} = 1.5 \times 10^{-5}$ s^{-1}) is, however, considerably slower than that of **1** to **3** ($k_{35^\circ C} = 1.8 \times 10^{-4}$ s^{-1}). This effectively excludes **2** as a thermal intermediate between **1** and **3**, in toluene solution at least. Corresponding isomerization of the dineopentylplatinum analogue was also shown to be unimportant during its metallacyclization.[1n]

It remained of interest to discover if metallacyclization of **2** occurs by aromatic or aliphatic H migration. To this end we examined the reactions of deuterated analogues *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6HD_3CMe_3)$ (**2a**)[8] and *cis*-$(Et_3P)_2Pt(CH_2CMe_2C_6D_5)(2\text{-}C_6H_4CMe_3)$ (**2b**). In thermolyses of **2a** in benzene[9] at 65 °C, an average of 28% of transferred hydrogen originates from the *tert*-butyl group.[10] Thence we estimate[11] that the difference in activation energy, $\Delta\Delta G^{\ddagger}_{338K}$ is 7.0 ± 1.0 kJ mol^{-1} in favor of aromatic site activation via B (Scheme I), in spite of the crystallographic indications that the aromatic C–H bonds are conformationally the less accessible (vide infra). On the other hand, rearrangement of **2b** at 54 °C yields both **3**-d_0 and **3**-d_4 in 73:27 ratio. The kinetic isotope effect on metallacyclization of **1** has now been established: k_H/k_D = 3.4. Adopting a similar value as reasonable for **2b** compared with **2**, with statistical allowance for differing aromatic and aliphatic site availabilities, leads to an estimate of $\Delta\Delta G^{\ddagger}_{327K} = 4.5 \pm 1.0$ kJ mol^{-1}, again in favor of aromatic C–H activation. Qualitatively similar conclusions have emerged from recent studies on intermolecular attack on C–H bonds,[1a,e,g] but the relatively small energy difference indicated here is not necessarily a truly quantitative measure of discrimination between aromatic and aliphatic sites; the two pathways followed in this case do not have strictly comparable intermediates, and the intimate nature of the mechanisms and their rate limiting steps are not yet known. Experiments aimed at more precise understanding are in progress. Similar controls clearly operate for the related isopropylphenyl derivative *cis*-$(Et_3P)_2Pt(CH_2CMe_2Ph)(2\text{-}C_6H_4CHMe_2)$ (**4**) which also cyclizes predominantly to **3** and isopropylbenzene.

The slower cyclization, via aromatic activation, of **2** (and **4**) compared with **1** may have a primarily steric origin. The molecular structure shows that the phenyl ring of the neophyl ligand is oriented away from the metal. Any approach by this group toward the metal will be hindered (relative to **1**) by the bulky *tert*-butyl substituent obstructing one axial entry to the coordination sphere. Some such conformational restriction is maintained in solution; the two methyl elements of the neophyl ligand give rise to different chemical shifts at 1.61 and 1.18 ppm in the ^{1}H NMR spectrum of **2** at ambient temperature. Restricted rotation about either or both of the Pt–C bonds accounts for this; the consequent absence of a molecular plane of symmetry places the methyl groups in diastereotopic environments. These signals show no significant change at temperatures up to the onset of metallacyclization. We are thus unable to distinguish which ligand is conformationally locked, nor can we estimate the rotational barrier(s). It is conceivable, of course, that surmounting this restriction is part of the energetic requirement for metallacyclization. The related species *cis*-$(Et_3P)_2Pt(2\text{-}C_6H_4CHMe_2)Me$ displays similar nonequivalence of the methyl substituents of the isopropyl group, clearly due to restricted platinum–aryl rotation. These signals do coalesce below cyclization temperatures, and we are evaluating the energetics of this system.[12]

In methanol/tetrahydrofuran (1:1) solution at 0 °C, we find by ^{31}P NMR that **2** is indeed formed as an accompaniment to **3** to a relative extent of 1–2%. The reasons for such an apparent increase in steric congestion[13] are not entirely clear, but a polar, coordinating solvent may favor the isomeric configurations of A from which the reductive C–H elimination which yields **2** becomes more likely (Scheme I).

Acknowledgment. We thank Sue Johnson and Dick Sheppard for NMR measurements. We are also grateful to the SERC for studentship awards (to D.C.G. and D. J.W.) and additionally British Petroleum for a CASE award (to L.G.J.). Thanks are also due to Johnson-Matthey for their generous loan of platinum and to the SERC and the Royal Society for equipment grants in support of our studies.

Registry No. 1, 88863-88-1; 2, 102869-70-5; 3, 88863-91-6.

Supplementary Material Available: Listings of structure factors, atom coordinates and temperature factors, bond angles, and bond lengths (22 pages). Ordering information is given on any masthead page.

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[7] Both isomers A and B have only one coordinated Et_3P. Cyclizations of **1** and **2** are both inhibited by the presence of Et_3P in solution, consistent with phosphine dissociation as a prerequisite step (cf. ref 1n,o). While the behavior of **1** is straightforward, rearrangement of **4** to **3** in presence of Et_3P is more complex and occurs partly via competitive pathways and new *trans*-diorganoplatinum species which are still being evaluated: Griffiths, D. C.; Young, G. B., unpublished observations.

[8] Preparation of 2-bromo-*tert*-butylbenzene-*3,5,6*-d_3 (see ref 5) leads to appreciable H/D scrambling on C_3 and C_5 (which become C_6 and C_4, respectively, in **2**) at the reduction step. This does not affect the integrity of labeling experiments since the extent of site deuteration can be precisely measured by ^{1}H NMR.

[9] Reactions were carried out in benzene-d_6 since the peaks due to residual methyl protons in toluene-d_8 overlap with C_2 hydrogens in **3** (see ref 10).

[10] Relative extents of aromatic and aliphatic C–H migration are determined from the amount of H substitution on C_7 in **3** (see Scheme I for numbering), measured from the 250-MHz ^{1}H NMR spectrum by comparing the integral for that signal with that for the hydrogens on C_2 as internal standard.

[11] From $\Delta\Delta G^{\ddagger} = RT \ln (k_1/k_2)$, where k_1 and k_2 are the rate constants for aliphatic and aromatic C–H activation respectively. Since formation of **3** is irreversible the ratio k_1/k_2 is that of the products, after statistical adjustment.

[12] Rzepa, H. R.; Wilkes, D. J.; Young, G. B., unpublished observations.

[13] We have not yet been able to obtain crystallographic data on **1** (or **3**), for a critical comparison.

A General Route to $C_6H_6(CO)_2Mn\text{–}R$ Complexes via $C_6H_6(CO)_2Mn^-Na^+$. Alkyl Group Migrations from Manganese to the Coordinated Arene Ring

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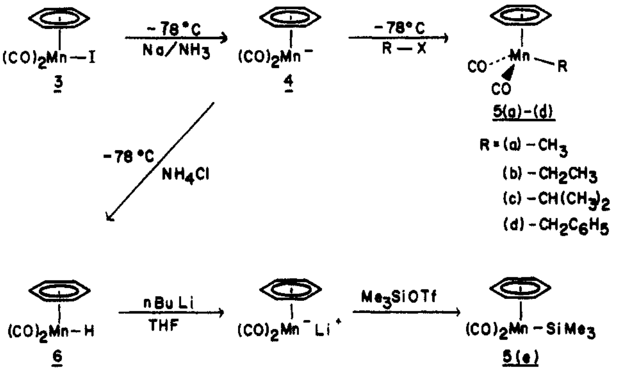
Summary: A convenient and general entry into $C_6H_6(CO)_2Mn\text{–}R$ complexes has been achieved via preparation of $C_6H_6(CO)_2MnI$ and reduction in $Na/NH_3(l)$ to yield $C_6H_6(CO)_2Mn^-$ followed by alkylation with R–X (R = $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, $-CH_2C_6H_5$, $-Si(CH_3)_3$, –H). A study of the migration of alkyl groups from manganese to the arene ring to give 6-endo-substituted cyclohexadienyl complexes is reported.

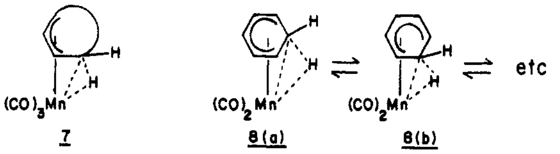
0276-7333/86/2305-1745$01.50/0

We recently described the synthesis of $C_6H_6(CO)_2Mn-CH_3$ (**1**) via dimethyl cuprate addition to $C_6H_6Mn(CO)_3^+$ (**2**) and the unique methyl migration from manganese to the arene ring in **1**.[1] On the basis of this migration reaction and the similarity between $C_6H_6(CO)_2Mn-R$ and the well-studied $Cp(CO)_2Fe-R$ systems, the potential for synthetic utility of (arene)$(CO)_2Mn-R$ derivatives is evident. A general and convenient entry into these complexes was sought. We report here: (1) preparation of a series of complexes $C_6H_6(CO)_2Mn-R$ (R = -Me, -Et, -*i*-Pr, $-CH_2C_6H_5$, $-SiMe_3$, -H) via in situ generation of $C_6H_6(CO)_2Mn^-$ and reaction with R-X and (2) a study of the migration of various alkyl groups from the manganese center to the arene ring.

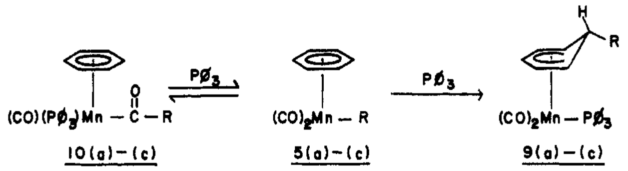
On the basis of the addition of hard nucleophiles at coordinated CO in **2**[2] and the stability of $C_6Me_6(CO)_2Mn-X$ (X = Cl, Br, I) complexes,[3] a convenient synthesis of $C_6H_6(CO)_2Mn-I$ (**3**)[4] was achieved by decarbonylation of **2** with Me_3NO in the presence of $Et_4N^+I^-$ (CH_2Cl_2, 25 °C, 60% yield).[5] Addition of **3** to $Na/NH_3(l)$ results in reduction and generation of $C_6H_6(CO)_2Mn^-$ (**4**). The in situ alkylation of **4** (-78 °C) with CH_3I, CH_3CH_2I, $(CH_3)_2CH-Br$, or $C_6H_5CH_2Cl$ gives the corresponding alkyl derivatives **5** in moderate yields: **5a**, R = $-CH_3$ (56%); **5b**, R = $-CH_2CH_3$ (58%); **5c**, R = $-CH(CH_3)_2$ (33%); **5d**, R = $-CH_2C_6H_5$ (54%).[6]



Protonation of **4** using ammonium chloride yields the hydride **6** (60%).[7] As with $C_6Me_6(CO)_2MnH$,[8] deprotonation of **6** (BuLi, THF) gives cleanly the anion **4**[9] and serves as the best source of the anion in THF free of ammonia. Alkylation of **4** generated in this fashion gives higher yields of $C_6H_6(CO)_2MnR$ derivatives (e.g., R = $-CH(CH_3)_2$, 75%) and allows use of electrophiles incompatible with NH_3. For example, reaction with $(CH_3)_3SiOTf$ gives $C_6H_6(CO)_2Mn-SiMe_3$(**5e**) in 60% yields.[10] Although (diene)$Mn(CO)_3H$ derivatives (**7**) invariably adopt an agostic structure containing a three-center, two electron M···H···C bond,[11] $C_6H_6(CO)_2MnH$ adopts a classical terminal structure. All ring hydrogens and ring carbons appear equivalent by NMR spectroscopy. If the structure were agostic and equivalence achieved by a rapid degenerate fluxional process (**8a** ⇌ **8b** ⇌ etc.), then a substantial $J_{C_{ring}-H_{Mn}}$ would be expected (ca. 12-14 Hz) from averaging one relatively large J_{CH} of ca. 80-85 Hz[11] with five small J_{CH} of ca. 0 Hz. The $J_{C_{ring}-H_{Mn}}$ value observed is less than 1 Hz ruling out the agostic structure.[12]



Treatment of solutions of **5a-c** (0.025 M) with $(C_6H_6)_3P$ (0.025 M) at 76 °C results in formation of 6-*endo*-$C_6H_6R(CO)_2Mn(PPh_3)$ complexes (**9a-c**).[13] Prior to formation of compounds **9**, ^1H NMR studies show that the alkyl complexes equilibrate with the acyl species **10a-10c**.[14] The ratios of alkyl to acyl at 76 °C under these conditions are ca. 25:1 for R = $-CH_3$, 2:1 for R = $-CH_2CH_3$, and 1:5 for R = $-CH(CH_3)_2$. Approximate times for 50% conversion of **5** to **9** in benzene at 76 °C are 3850 (R = $-CH_3$), 169 (R = -Et), and 8 min (R = $-CH(CH_3)_2$).[14] ^1H NMR studies in C_6D_6 reveal that arene ring exchange occurs (C_6H_6 is replaced by C_6D_6) and rates are comparable to the alkyl migrations.[15]



Treatment of **5d** (R = $-CH_2Ph$) under similar conditions (76 °C, 10 h) results in disappearance of starting material, but formation of **9d** in only very low yields.[16] The $C_6H_6Mn-SiMe_3$ complex is stable in benzene in the presence of PPh_3 for 80 h at 76 °C.

The hydride **6** is remarkably unreactive. At 76 °C in the presence of 3 equiv PPh_3, little reaction occurs after 4 h; further heating (40 h) results in formation of $C_6H_7(CO)_2MnPPh_3$ (**11**) (ca. 50%) together with small amounts of other products which include $Mn_2(CO)_{10}$ annd $C_6H_7(CO)_3Mn$. No formyl species are detected in these reactions. Indicative of a different mechanism for hydrogen migration relative to alkyl migration are results using $C_6H_6(CO)_2MnD$. Thermolysis leads to only *partial* D transfer to the

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[1] Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 1730.

[2] (a) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754. (b) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 62.

[3] Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445.

[4] Spectral properties of **3**: ^1H NMR (CD_2Cl_2) δ 5.67 (s); IR (ν_{CO}, CH_2Cl_2) 1998 (s), 1952 (s) cm^{-1}f ^{13}C NMR (C_6D_6) 93.5. Anal. Calcd for $C_8H_6MnO_2I$: C, 30.41; H, 1.91. Found: C 30.15; H, 1.94.

[5] **3** has also been prepared by D. P. Eyman by a similar method: Eyman, D. P., private communication.

[6] Compounds **5** were prepared from the reaction of **3** with RX in $NH_3(l)$ at -78 °C followed by addition of THF, removal of NH_3 and THF in vacuo, and extraction with hexane. See supplementary material for spectral and analytical data for **5a-d**.

[7] **6**: ^1H NMR (C_6D_6) δ 4.55 (s, C_1H_6), -9.43 (s, H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 89.6 (C_6H_6); IR (ν_{CO}, hexane) 1985 (s), 1938 (s) cm^{-1}. Exact mass calcd for $C_8H_7O_2Mn$: 189.9826. Found: 189.9831.

[8] Eyman, D. E. *Abstracts of Papers*, 188th National Meeting of the American Chemical Society, Philadelphia, PA; American Chemical Society: Washington, DC, 1984; No. 262.

[9] **4** (lithium salt): IR (ν_{CO}, THF) 1840, 1700 cm^{-1}.

[10] See supplementary material for spectral and analytical data for **5e**.

[11] (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *Organometallics* **1982**, *104*, 2117. (c) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 648. (d) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649. (e) Brookhart, M.; Timmers, F. *Organometallics* **1985**, *4*, 1365.

[12] **6**: ^{13}C line width = 0.65 Hz with selective decoupling of the arene ring ^1H signal.

[13] See supplementary material for spectral and analytical data for **9a-c**.

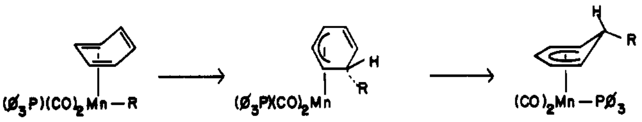
[14] Rates of R migration to the arene ring parallel rate of R migration to CO, M(CO)R → M-COR: (a) Crawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405. (b) Green, M.; Westlake, D. J. *J. Chem. Soc. A* 1971, 367. (c) Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 1978. (d) Craig, P. J.; Green, M. *J. Chem. Soc. A* **1969**, 157.

[15] Approximate time for 50% incorporation of C_6D_6 into equilibrating acyl/alkyl complexes: 1925 (R = CH_3), 120 (R = Et), and 6 min (R = *i*-Pr).

[16] Major products contained no arene ring signal but could not be positively identified.

ring with 11 containing only 0.25 D all in the 6-exo position. No 6-endo D incorporation is noted.

The detailed mechanism of the alkyl reaction is not yet clear, but several points should be noted. First, alkyl migrations from the acyl complex **10** to give directly the product can be ruled out. In the presence of a 12-fold excess of PPh_3, the **5c** $\rightleftharpoons$ **10c** equilibrium strongly favors acyl (>99:1) and the rate of isopropyl migration is greatly retarded rather than accelerated. Secondly, the surprising lack of endo migration of the hydride suggests that the mechanism is not simply irreversible migration of –R from manganese to the arene ring followed by PPh_3 trapping of the 16-electron cyclohexadienyl intermediate as was originally suggested by us.[1] Were this the case, hydrogen migration is expected to be much more rapid than alkyl migration, contrary to our observations. An attractive mechanistic alternative is the intermediacy of an (η^4-arene)$(CO)_2(PPh_3)$Mn–R complex **12**. On the basis of simple diene analogues,[11] alkyl migration is expected to be rapid in this system and the arene exchange reactions suggest accessibility of η^4-arene intermediates competitive with migration.[15] In this regard and in support of differing pathways for H vs. R migration, it is interesting to note that $C_6H_6(CO)_2$Mn–H *does not* exhibit appreciable arene ring exchange at 76 °C after 30 h (C_6D_6, presence or absence of PPh_3). This suggests that η^4-arene intermediates in the hydride system are not accessible at temperatures employed and may account for the lack of facile hydrogen migration. Further synthetic and mechanistic investigations are in progress.



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Acknowledgment is made to the National Institutes of Health (Grant 1R01 GM23938) for support of this research.

Registry No. 2, 41656-02-4; 3, 100858-02-4; **5a**, 65643-62-1; **5b**, 103191-65-7; **5c**, 103191-66-8; **5d**, 103191-67-9; **5e**, 103191-69-1; **6**, 103191-68-0; **9a**, 83681-38-3; **9b**, 103191-70-4; **9c**, 103191-71-5; **10a**, 83681-39-4; **10b**, 103191-72-6; **10c**, 103191-73-7; **11**, 95344-58-4.

Supplementary Material Available: Spectroscopic and analytical data for **5a–e**, **9a–c**, and **10a–c**, (2 pages). Ordering information is given on any current masthead page.

Formation and Structure of a Ferraphosphacyclopentenone

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Summary: Reaction of $Na(C_5H_5)Fe(CO)_2$ with $(C_6H_5)P(Cl)\{N[Si(CH_3)_3]_2\}$ in THF results in the formation of a metallophosphane complex $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}]$. This complex combines readily with $CF_3C{\equiv}CCF_3$, and a compound of composition $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}](CF_3C{\equiv}CCF_3)$ is isolated. The structure of the compound has been determined by single-crystal X-ray diffraction techniques and found to contain a ferraphosphacyclopentenone unit: $(C_5H_5)(CO)\overline{Fe\text{-}C(O)C(CF_3){=}C(CF_3)P}(C_6H_5)\{N[Si(CH_3)_3]_2\}$.

It has been demonstrated that the combination of the highly nucleophilic group 8 metal carbonylates $Na(C_5H_5)Fe(CO)_2$ and $Na[C_5(CH_3)_5]Fe(CO)_2$ with monohalophosphines P(X)(Y)(Cl) results in the formation of metallophosphanes $(C_5H_5)Fe(CO)_2[P(X)(Y)]$, which contain a terminal, pyramidal phosphorus atom.[1–6] The phosphorus atom in these complexes should serve as a site for nucleophilic reactivity and several reports which confirm this assumption have recently appeared.[2,4,6] We report here the synthesis of a metallophosphane $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}]$ (**1**) and the formation of a novel ferraphosphacyclopentenone complex, $(C_5H_5)(CO)\overline{FeC(O)C(CF_3){=}C(CF_3)P}(C_6H_5)\{N[Si(CH_3)_3]_2\}$ (**2**) through nucleophilic attack of the pyramidal phosphorus center on the activated acetylene $CF_3C{\equiv}CCF_3$.

Combination of $Na(C_5H_5)Fe(CO)_2$ with $(C_6H_5)P(Cl)\{N[Si(CH_3)_3]_2\}$[7] in equimolar amounts in tetrahydrofuran at 25 °C (12 h) resulted in a blood red solution containing $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}]$ (**1**). The solution was filtered to remove NaCl, the THF[8] solution evaporated to dryness, extracted with benzene, and filtered to remove remaining traces of NaCl, and the filtrate evaporated to dryness. **1** was recovered in 90% yield as a dark red microcrystalline solid which was characterized by analytical and spectroscopic techniques.[9] Elemental analysis and mass spectrometric data confirm the composition of **1**. An infrared spectrum shows the expected two-band pattern, 2007 and 1960 cm^{-1}, in the terminal carbonyl stretching

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(1) Cooke, M.; Green, M.; Kirkpatrick, D. *J. Chem. Soc. A* **1968**, 1507.

(2) Angerer, W.; Sheldrick, W. S.; Malisch, W. *Chem. Ber.* **1985**, *118*, 1261. Malisch, W.; Angerer, W.; Cowley, A. H.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1811.

(3) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230. Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254.

(4) Related complexes $(C_5H_5)Fe(CO)_2[P(CF_3)_2]$ and $(C_5H_5)Fe(CO)_2(PPh_2)$ prepared from $[(C_5H_5)Fe(CO)_2]_2$ and $(CF_3)_4P_2$ or Ph_4P_2 have been reported: (a) Dobbie, R. C.; Mason, P. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1124. (b) Dobbie, R. C.; Mason, R. R. *Ibid.* **1974**, 2439. (c) Barrow, M. J.; Sim, G. A. *Ibid.* **1975**, 291. (d) Dobbie, R. C.; Mason, P. R. *Ibid.* **1976**, 189. (e) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1972**, *36*, 63.

(5) Several other metallophosphane complexes which appear to contain pyramidal phosphorus environments have also been reported: Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc.* **1984**, 865. Bohle, D. S.; Rickard, C. E. F.; Roper, W. R. *Ibid.* **1985**, 1594. Bohle, D. S.; Roper, W. R. *J. Organomet. Chem.* **1984**, *273*, C4. Ebsworth, E. A. V.; Gould, R. O.; McManus, N. T.; Rankin, D. W. H.; Walkinshaw, M. D.; Whitelock, J. D. *J. Organomet. Chem.* **1983**, *249*, 227. Ebsworth, E. A. V.; Gould, R. O.; McManus, N. T.; Pilkington, N. J.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1984**, 2561.

(6) Related chemistry with pyramidal phosphorus atom environments in $CpMo(CO)_3(PX_2)$ complexes has been reported: Malisch, W.; Kuhn, M. *J. Organomet. Chem.* **1974**, *73*, C1. Maisch, R.; Ott, E.; Buchner, W.; Malisch, W. *J. Organomet. Chem.* **1985**, *286*, C31. Malisch, W.; Maisch, R.; Colquhoun, I. J.; McFarlane, W. *Ibid.* **1981**, *220*, C1. Maisch, R.; Barth, M.; Malisch, W. *Ibid.* **1984**, *260*, C35. Gudat, D.; Niecke, E.; Malisch, W.; Hofmockel, U.; Quashie, S.; Cowley, A. H.; Arif, A. M.; Krebs, B.; Dartmann, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1687.

(7) $Na(C_5H_5)Fe(CO)_2$ was prepared from Na/Hg amalgam reduction of $[(C_5H_5)Fe(CO)_2]_2$ in THF, and it was used without isolation. The phosphane was prepared from $PhPCl_2$ and $NaN(SiMe_3)_2$ in Et_2O by a procedure similar to that described for related phosphanes: Zeiss, W.; Feldt, C.; Weis, J.; Dunkel, G. *Chem. Ber.* **1978**, *111*, 1180.

(8) Abbreviations used in the text include THF = tetrahydrofuran, Cp = cyclopentadienide, Me = methyl, and Ph = phenyl.

(9) **1** was isolated under inert-atmosphere conditions. Characterization: mp 150–153 °C; mass spectrum (70 eV), *m/e* 445 (M^+), 417 ($M - CO^+$), 389 ($M - 2CO^+$), 268 ($PhP[N(SiMe_3)_2]^+$); IR (carbonyl region, cyclohexane) 2007 (vs), 1960 (vs); ^{1}H NMR (25 °C, CH_2Cl_2/CD_2Cl_2) δ 7.3 (m, phenyl), 4.8 (Cp), 0.09 ($SiMe_3$); $^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2) δ 131–125.5 (m, phenyl), 88.06 (Cp, d, $^2J_{CP} = 4.6$ Hz), 1.9 ($SiMe_3$); $^{31}P\{^1H\}$ NMR (THF, H_3PO_4 standard) δ 110. Anal. Calcd for $FePSi_2O_2NC_{19}H_{28}$: N, 3.1; C, 51.2; H, 6.3. Found: N, 3.2; C, 51.5; H, 6.2.

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