Organometallics **1983,** *2,* 733-740

Amphoteric Ligands. 3. Reactions of Alkylmetal Carbonyls with (Aluminoamino)phosphine Ligands. Structure of $(\eta\text{-}C_5H_5)(CO)Fe(C(CH_3)OAl(C_2H_5)_2N(C(CH_3)_3)P(C_6H_5)_2)$

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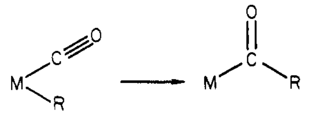
Amphoteric ligands $Ph_2PNRAlR'_2$ react with alkylmetal carbonyl complexes to induce facile migrations. The reaction of $Ph_2PN\text{-}t\text{-}BuAlEt_2$ with $CpFe(CO)_2Me$ (Cp = $\eta^5\text{-}C_5H_5$) gives as major product the chelated acyl complex $Cp(CO)Fe(C(Me)OAlEt_2N\text{-}t\text{-}BuPPh_2)$, along with smaller amounts of $Cp(CO)Fe(O\text{-}(CH{=}CH_2)AlEt_2N\text{-}t\text{-}BuPPh_2)$. An intermediate leading to these products was characterized crystallographically as $Cp(CO)Fe(C(Me)OAlEt_2N\text{-}t\text{-}BuPPh_2)$. Crystal data: triclinic; space group $P\bar{1}$; a = 10.474 (2) Å, b = 15.677 (3) Å, c = 9.707 (1) Å; α = 97.98 (1)°, β = 115.01 (1)°, γ = 71.81 (1)°; Z = 2; final R = 0.049 for 4303 reflections used. The molecule consists of a five-membered heterocycle, $C(Me)OAl(Et)_2N(t\text{-}Bu)P(Ph)_2$, bonded in η^2(C, O) fashion to a Cp(CO)Fe fragment, with Fe–C = 1.983 (3) Å, Fe–O = 1.969 (2) Å, and C–O = 1.401 (3) Å.

Introduction

The so-called insertion or migration reaction (1) has received continuing attention in organotransition-metal chemistry since it was first reported.[1,2] In recent years interest has been considerably reinforced because of relevance to synthesis gas conversion, a potentially important route for coal utilization. There appears to be general agreement that step 1 is responsible for at least some of the C–H and/or C–C bond formations during the *homogeneously* catalyzed transformation of CO plus H_2 to organic compounds.[3] Whether such steps are important in heterogeneous catalysis is still a matter for debate.[4,5]


(1)

Of particular concern is the hydride migration (eq 1, R = H) to give a formyl complex, M–CHO. It is clear from comparing the known chemistry of hydridometal carbonyls to that of alkylmetal carbonyls that this is a less favorable process than alkyl migration; it is not certain whether this is due to kinetic or thermodynamic (or both) barriers.[6] Assuming this step is indeed a key part of a homogeneous system for CO reduction and taking note of the fact that all homogeneous systems found so far to catalyze synthesis gas conversion require unacceptably high pressure and/or temperature, the need for methods to assist such migration reactions appears obvious.

Shriver has shown that addition of certain Lewis acids can substantially accelerate *alkyl* migration reactions as in (2).[7] Only the strongest Lewis acids are successful, however;[8] this may restrict the applicability of this approach to catalytic systems, as such strong Lewis acids will generally not survive the presence of CO reduction products (alcohols, water). Furthermore, the more difficult hydride migration has not been shown to be effected by addition of Lewis acids.[7,9] We postulated that a complex incorporating an amphoteric ligand—a ligand containing both a Lewis base center to attach to a metal *and* a Lewis acid to bind oxygen—could provide additional facilitation for migration reactions as a result of the intramolecular nature of the interaction. This might make it possible to overcome the limitations cited above.

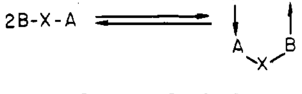
(2)

1 2

In this paper we report on the reactivity of a class of amphoteric ligand—(aluminoamino)phosphines—with $CpFe(CO)_2Me$ (1) and other alkylmetal carbonyls. In a subsequent paper, we shall discuss the behavior of these ligands toward hydridometal carbonyls.[10] Preliminary accounts of portions of this work have appeared previously.[11]

Results and Discussion

Synthesis of Amphoteric Ligands. In principle there are two approaches to construction of the desired systems: addition of a preformed amphoteric ligand to a complex, or attachment of a Lewis acid to a ligand that is already part of a complex. The first has (at least) two potential difficulties. First, the amphoteric ligand B–X–A (where B is a Lewis base center, X a connecting atom or group of atoms, and A a Lewis acid center) will have a natural tendency to self-aggregate (eq 3) and thus inhibit reaction.



(3)

Secondly, if the complex to which the amphoteric ligand is added has alternate sites for reaction (for example, an electrophilic center on a ligand), a product with other than

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[1] Wojcicki, A. *Adv. Organomet. Chem.* **1973,** *11,* 87–145.

[2] Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980,** *33,* 195–225.

[3] Fahey, D. R. *J. Am. Chem. Soc.* **1981,** *103,* 136–141.

[4] Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980,** *102,* 6181–6182.

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[6] Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1980,** *100,* 7224–7236.

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[8] Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982,** *21,* 1272–1273.

[9] Otto, E. E. H.; Britzinger, H. H. *J. Organomet. Chem.* **1979,** *170,* 209–216.

[10] Labinger, J. A. et al., manuscript in preparation.

[11] Labinger, J. A.; Miller, J. S. *J. Am. Chem. Soc.* **1982,** *104,* 6856–6858. Grimmett, D. L.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Ibid.* **1982,** *104,* 6858–6859.

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the target structure may result. Nonetheless, while the second approach above appears conceptually more attractive, we have found it synthetically much more difficult, as reagents for attaching the Lewis acid tend to cause destructive side reactions of the complex. Hence the present discussion will deal with the first route only.

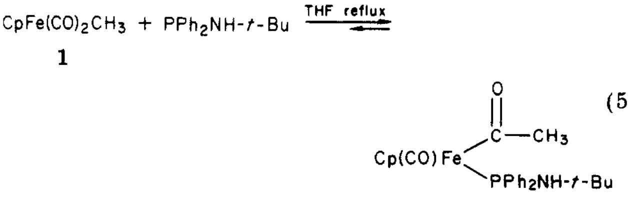
A number of potentially amphoteric ligands are known in the literature, but in general they exist in solution as strongly bonded oligomers. For example, Ph_2PAlEt_2 is reported as a dimer;[12] we find it to be unreactive toward 1 and related compounds. Dimerization can of course be disrupted by adding a Lewis base such as THF or R_3N, but this would only make the Lewis base center available for bonding to metal.[13] The Lewis acid center would still be blocked. The amino-linked compound Ph_2PN-*t*-$BuAlEt_2$ (**3a**), prepared by heating Et_3Al with PPh_2NH-*t*-Bu, has been reported to be monomeric in benzene (according to cryoscopy)[14] and hence should be a more suitable choice. We have prepared **3a** and related compounds **3b–f** by an alternate, more general route (eq 4).

$$R_2PCl + R'NH_2 \rightarrow R_2PNHR' \xrightarrow{BuLi} \xrightarrow{R''_2AlCl} \underset{\mathbf{3a-f}}{R_2P\text{-}NR'\text{-}AlR''_2} \quad (4)$$

a, R = Ph, R′ = *t*-Bu, R″ = Et; **b**,R = Ph, R′ = *t*-Bu, R″ = Me; **c**, R = Ph, R′ = *t*-Bu, R″ = Ph; **d**, R = Ph, R = *i*-Pr, R″ = Et; **e**, R = Ph, R = *i*-Pr, R″ = Me; **f**, R = Ph, R′ = Ph, R″ = Me

The two previously known members of this class, **3a** and **3d**, were reported as respectively monomeric and trimeric in benzene;[14] this would be consistent with the relative amount of steric crowding in the two compounds. It was noted, though, that partial hydrolysis may have led to erroneously low molecular weights.[14] Our NMR studies indicate that **3a** is not monomeric in benzene solution.[15] In particular, the methine carbon signal (CMe_3) in the ^{13}C NMR spectrum appears as a triplet, which indicates coupling to *two* ^{31}P nuclei; the same feature is present in the ^{13}C spectrum of other ligands examined, suggesting that all of these species are aggregated. Reactivity generally correlates with increasing steric bulk (vide infra), as one would expect if dissociation to monomers is required for interaction with complexes.

Reactions of Amphoteric Ligands with $CpFe(CO)_2(CH_3)$ (1). Compound 1 is convenient for demonstrating facilitated migration, as it does not undergo migration under ordinary conditions. Thus the aminophosphine PPh_2NH-*t*-Bu does not react with 1 in benzene at room temperature; slow (and reversible) formation of acetyl 4 occurs in refluxing THF (eq 5). In contrast, a benzene solution of 1 and **3a** darkens over a period of minutes. The reaction may be followed in a number of ways; most informative is the ^2H NMR spectrum of the reaction of 1-d_3 with **3a** (Figure 1). Rapid disappearance of the starting material signal (δ 0.3) is accompanied by growth of a new signal at δ 1.5. During the next several hours the latter is gradually replaced by a strong signal at δ 2.7 plus three weaker, equal intensity signals at δ 4.0, 4.5, and 6.0. A small amount of 1 is regenerated as well.



1

(5)

4

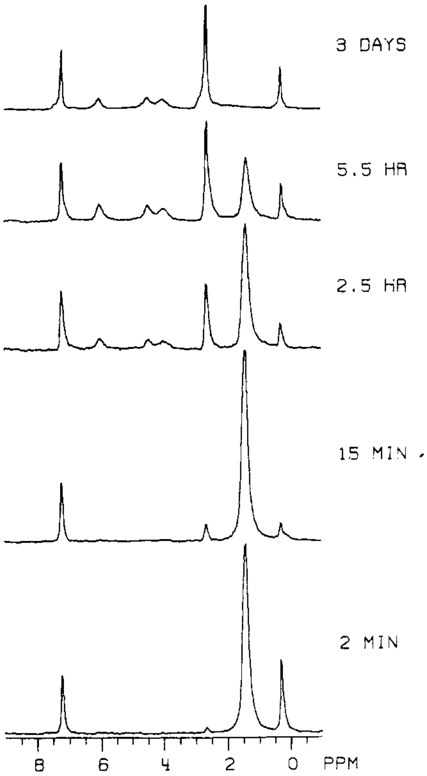
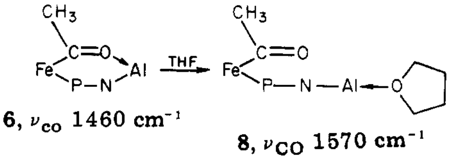


Figure 1. ^2H NMR spectrum as a function of time for the reaction of $CpFe(CO)_2CD_3$ with Ph_2PN-*t*-$BuAlEt_2$ in benzene; C_6D_6 added as reference.

The intermediate 5 corresponding to the peak at δ 1.5 can be easily isolated after short reaction times and has been shown crystallographically to be derived from addition of the phosphorus center to carbon rather than to metal (see below). On dissolution in benzene, 5 gradually converts to 6 and 7, the products exhibiting the ^2H signals observed after longer reaction times. Complex 6 is by far the major component (>75%) and can be fully characterized spectroscopically, although it has not proven possible to isolate it in pure form. All attempts at crystallization lead to impure oils, while chromatography causes immediate decomposition. Nonetheless, the spectral parameters (see Experimental Section for complete enumeration) are fully consistent with 6 being the expected chelated acyl. In particular the following are observed:

(i) The IR spectra of Lewis acid stabilized acyls such as 2 show ν_{CO} in the range 1360–1480 cm^{-1}.[7] Although for 6 this region is partially obscured by ligand vibrations, a shoulder can be observed at 1460 cm^{-1}; addition of a small amount of THF causes this shoulder to disappear and a new peak to appear at 1570 cm^{-1}, suggesting eq 6.



(6)

6, ν_{CO} 1460 cm^{-1}

8, ν_{CO} 1570 cm^{-1}

(ii) The ^{13}C NMR spectrum of 6 shows a doublet at extremely low field, 330.8 ppm (J_{PC} = 27.5 Hz), assigned to acyl carbon. A model for 6 was generated by adding

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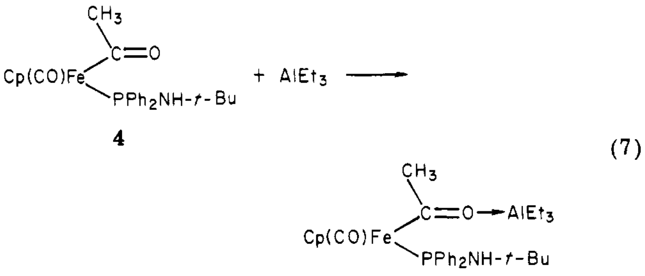
[12] Issleib, K.; Deylig, H. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 198–199; Johnson, A. W.; Dahl, G. H. *Can. J. Chem.* **1965**, *43*, 1338–1344.

[13] For an example of such a situation, see: Beachley, O. T.; Bueno, C.; Churchill, M. R.; Tessier-Youngs, C. *Inorg. Chem.*, in press.

[14] Clemens, D. F.; Sisler, H. H.; Brey, W. S. *Inorg. Chem.* **1966**, *5*, 527–533.

[15] Churchill, M. R.; Labinger, J. A. et al., unpublished results.

$AlEt_3$ to 4, since simple acyls such as 4 are known to form adducts with Lewis acids.[16] The acetyl carbon resonance



4

(7)

9

in 4 (277.8 ppm (J_{PC} = 26.7 Hz)) shifts to 323.8 ppm (J_{PC} = 29.0 Hz) in 9, in excellent agreement with the shift for 6. The downfield shift presumably reflects greater contribution from alkylidene-like resonance forms (eq 8); a similar trend (though not so pronounced) was found in ion-pairing studies of $[Fe(COCH_3)(CO)_4]^-$ with cations of varying Lewis acidity.[17]

(8)

The NMR spectra of 4 and 9 show several other features of some interest. Most notably, the NH proton in the ^1H NMR exhibits considerably differing shifts and coupling constants: δ 5.0 (J_{PH} = 9.5 Hz) in 4; δ 3.1, (J_{PH} = 16 Hz) in 9. This is probably due to a hydrogen-bonding interaction between that proton and the acetyl oxygen in 4, as shown crystallographically for a closely related compound;[18] this interaction would not be present in 9 as the oxygen is tied up by Al. Also, the ^{13}C NMR spectra show that the phenyl groups in both compounds are nonequivalent, a consequence of the chiral Fe center.

(iii) While the ^{31}P shifts for 4, 8, and 9 are all within a few parts per million of one another, the shift for 6 is about 15 ppm to higher field. This appears to be a manifestation of the so-called ring contribution: shifts for coordinated phosphorus that is part of a chelate ring are systematically different from those of acyclic analogues. It has been claimed that this phenomenon is sufficiently general to be used as a test for the presence of chelation and for ring size. Typical values for Δ_R are −20 to −60 ppm for four-membered rings; +20 to +40 ppm for five-membered rings; −5 to −15 ppm for six-membered rings.[19] The value for 6 is thus consistent with the six-membered ring in the postulated structure.

Complete spectral characterization of 7 is not possible, as it is a minor component. The broad signals at δ 6.0 and 4.5 in the ^2H NMR spectrum correspond to double doublets in the ^1H spectrum, with *J*'s = 14, 6 and 14, 2 Hz, respectively (the signal at δ 4.0 is hidden by a Cp signal). By comparison to an analogous product in a reaction of $CpMo(CO)_3(CH_3)$ (see below), these signals are assigned to a vinyloxy group, $CH_2{=}CHO$. Formation of these products will be discussed below. Still another side reaction must be involved in the regeneration of small amounts of starting material 1 as this is *not* accompanied by any free 3a: the ^{31}P NMR spectrum of a solution of 5 that has been allowed to stand for some time shows a number of weak signals in the vicinity of the free ligand shift (but none of the latter itself).

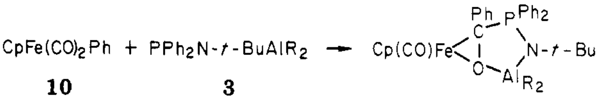
Table I. NMR Parameters (in δ, Coupling Constants in Hz) for Vinyloxy Groups

complex	H_a	H_b	H_c	J_{ab}	J_{ac}	J_{bc}
$CH_2{=}CHOAc$	7.2	4.4	4.7	6.4	13.8	1.4
7	6.0	4.0	4.5	6	14	2
12	6.4	4.1	4.4	6.2	14.3	1.6
15	6.6		4.6		12	
$[Cp(CO)_2$-$Fe(\eta^2$-$CH_2{=}CHOMe)]^+$ [a]	7.8	2.7	3.1	4.5	12.0	3.0

[a] Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381-391.

The last-mentioned side reaction appears to become more dominant in reactions of several of the other amphoteric ligands with 1. For example, in the reaction of 1 with equimolar 3b, NMR signals similar to those observed for 5, 6, and 7 can be detected over the course of the reaction. However, at completion 1 is the major Fe-containing species detected. Furthermore, even in the presence of excess 3b, the ligand was completely consumed. The nature of the destructive side reactions remains unclear. Reactivity as indicated by color changes does seem to correlate with steric bulk of the ligand: benzene solutions of 1 and ligand darken over periods of several hours for 3d, 15–30 min for 3b, several minutes for 3a, and virtually instantaneously for 3c. This general trend would be expected if dissociation of the ligand into monomers governs the rate of reaction.

Reactions of Other Metal Complexes. The ability of 3a to facilitate methyl migration led us to try other metal alkyls, including some for which migration is generally difficult or unknown. Disappointingly, neither $CpFe(CO)_2(SiMe_3)$ nor $CpFe(CO)_2(\eta^1\text{-}Cp)$ reacted at all with 3a. $CpFe(CO)_2(CF_3)$ gave an immediate color change, but the NMR showed at least three different major products; this system was not pursued. $CpFe(CO)_2Ph$[20] (10) reacts with 3a to give 11a, the analogue of 5. However, 11 shows absolutely no tendency to react any further, even on heating or in the presence of excess 3a or simple phosphine ligands. As with 1, the reaction of 3b with 10 proceeds much more slowly, but the decomposition pathways do not operate here, so 11b was readily isolated.



10 **3** **11**

(9)

Several complexes of other metals were also examined. $MeMn(CO)_5$ reacts rapidly with 3a, but only broad, featureless NMR peaks could be observed; products were not characterized. $Cp_2NbMe(CO)$ is inert to 3a; it has been suggested that alkyl migration is particularly unfavorable for this complex.[9] $CpMo(CO)_3Me$ reacts rapidly with 3a, but the system is exceedingly complex: at least five major Cp signals are seen in the NMR, and the products could not readily be sorted out. However, the reaction of this complex with 3d is cleaner (albeit much slower). A product sufficiently pure to assign NMR resonances was obtained; the three double doublet signals (Table I) identify the product 12 as containing a vinyloxy group, analogous to iron product 7. The structures of 7 and 12 are formulated as shown, with a metal–oxygen bond, to satisfy the 18-electron rule. An alternate formulation with a coordinated

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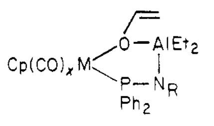
(16) Stimson, R. E.; Shriver, D. F. *Inorg. Chem.* **1980**, *19*, 1141–1145.

(17) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766–4772.

(18) Korp, J. D.; Bernal, I. *J. Organomet. Chem.* **1981**, *220*, 355–364.

(19) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

(20) The rate of phenyl migration from Mn to CO appears to be slower than that of methyl migration, although this is by no means unequivocally a general result; see: Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299–311, as well as references cited above.[1,2]



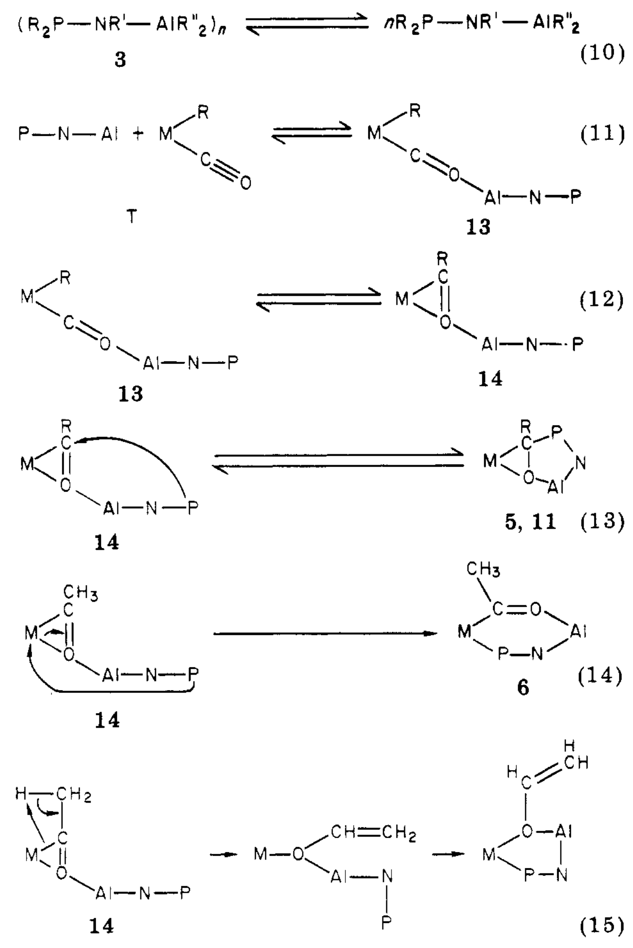
7, M = Fe, R = *t*-Bu, x = 1
12, M = Mo, R = *i*-Pr, x = 2

C=C double bond would not be consistent with either the NMR shifts (Table I) or the observation of a C=C stretching band at 1617 cm^{-1} in the IR spectrum.

Mechanistic Aspects. The proposed mechanism for the above transformations is summarized in eq 10–15 (Scheme I). As noted previously, reactivity seems to be largely governed by the dissociation equilibrium (10), as rates depend more upon the nature of the ligand than on the metal complex (except, of course, for those complexes which do not react at all). The existence of an intermediate such as **13** seems required by the rates of these reactions; simple trapping by Lewis acid of small equilibrium amounts of simple insertion product could not account for the reactivity observed.[8] Instead, the Lewis acid is proposed to activate the complex for insertion, presumably by interacting with the CO oxygen as shown. We were not able to detect **13** or any other intermediate by IR spectroscopy.

Actual migration takes place at step 12; an alternate route in which P–C bond formation precedes migration cannot be ruled out but seems less likely in view of the ready migrations observed in the presence of simple Lewis acids;[7] also, in this mechanism P–C bond formation (eq 13) can be viewed as nucleophilic addition to a more or less carbene-like carbon center, generally found to be facile in stable oxygen-substituted carbene complexes (eq 16).[21]

Scheme I



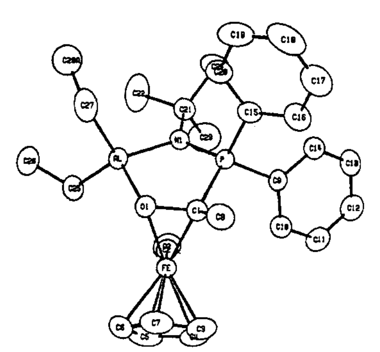
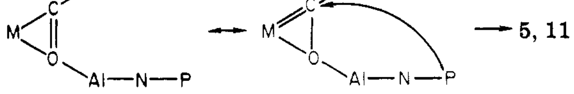


Figure 2. Perspective view of complex **5a** (hydrogen atoms have been omitted for clarity).

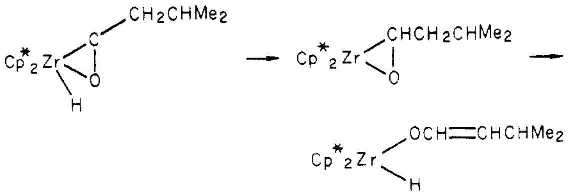


14 (16)

The O–M interaction in intermediate **14** is postulated on the grounds of the 18-electron rule as well as the fact that stereochemical considerations suggest the intermediacy of an η^2-acyl in migration reactions of **1** without Lewis acid promoters.[22]

The key intermediate **14** can undergo P–C bond formation, P–M bond formation, or a hydride shift to give the three main products observed. The first is the kinetically favored route, probably because of geometric reasons—a five-membered ring is thus formed. Rearrangement of **5** to **6** is most likely driven by more favorable metal–ligand bonding: the combination η^1-acyl plus η^1-phosphine should provide a more stable bonding situation than the η^2-ketone-like ligand in **5**, making **6** a thermodynamically preferred structure. The stability of **11**, in contrast to **5**, is intriguing; if the ligand may be viewed as a coordinated ketone-like molecule (see below), then the additional stabilization of **11** may be ascribed to conjugation—that is, **5** and **11** bear the same relationship as acetone and acetophenone.

The 1,2 hydride shift that leads to compounds **7** and **12** can also be understood in terms of the substantial carbenoid character of **14**; such rearrangements are found for both free oxycarbenes and alkylidene complexes.[23] There is also precedent for formation of a vinyloxy ligand from an acyl in the case of a zirconium complex (eq 17), where



(17)

15

the strong O–Zr interaction presumably provides the driving force. However, labeling studies show that **15** is not the result of a simple 1,2 shift: the acyl (carbenoid) carbon inserts into a Zr–H rather than a C–H bond.[24]

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[21] Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32.

[22] Flood, T. C. *Top. Stereochem.* **1981**, *12*, 89–90. Brunner, H.; Vogt, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 405–406; *Chem. Ber.* **1981**, *114*, 2186–2207.

[23] For example, see: Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895–896.

[24] Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–2724.

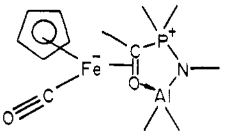
Table II. Atomic Coordinates for 5a

atom	*x*	*y*	*z*
Fe	0.73482 (4)	0.77990 (3)	0.64193 (5)
P	0.54410 (7)	0.75530 (5)	0.27079 (8)
Al	0.39218 (9)	0.77673 (6)	0.4736 (1)
O(1)	0.5267 (2)	0.8403 (1)	0.5216 (2)
O(2)	0.7602 (3)	0.5911 (2)	0.6307 (3)
N(1)	0.4498 (2)	0.7087 (2)	0.3167 (3)
C(1)	0.6086 (3)	0.8279 (2)	0.4340 (3)
C(2)	0.7360 (3)	0.6684 (2)	0.6216 (4)
C(3)	0.9029 (4)	0.8410 (3)	0.7020 (5)
C(4)	0.9575 (4)	0.7576 (4)	0.7588 (5)
C(5)	0.8948 (5)	0.7526 (3)	0.8596 (5)
C(6)	0.7988 (4)	0.8372 (4)	0.8592 (4)
C(7)	0.8070 (5)	0.8914 (3)	0.7606 (5)
C(8)	0.6187 (4)	0.9137 (2)	0.3909 (4)
C(9)	0.6957 (3)	0.6828 (2)	0.2262 (3)
C(10)	0.8340 (3)	0.6540 (3)	0.3376 (4)
C(11)	0.9452 (4)	0.5949 (3)	0.3025 (5)
C(12)	0.9201 (4)	0.5656 (3)	0.1565 (4)
C(13)	0.7844 (4)	0.5953 (3)	0.0451 (4)
C(14)	0.6718 (3)	0.6531 (2)	0.0777 (4)
C(15)	0.4322 (3)	0.8274 (2)	0.1059 (3)
C(16)	0.4939 (4)	0.8574 (2)	0.0281 (4)
C(17)	0.4082 (5)	0.9184 (3)	−0.0893 (4)
C(18)	0.2634 (6)	0.9499 (3)	−0.1277 (5)
C(19)	0.1975 (5)	0.9232 (3)	−0.0511 (5)
C(20)	0.2839 (4)	0.8604 (2)	0.0660 (4)
C(21)	0.4014 (3)	0.6275 (2)	0.2395 (3)
C(22)	0.2941 (4)	0.6174 (3)	0.2960 (5)
C(23)	0.5328 (5)	0.5427 (3)	0.2797 (6)
C(24)	0.3299 (4)	0.6353 (3)	0.0685 (4)
C(25)	0.4281 (4)	0.7114 (3)	0.6508 (4)
C(26)	0.2962 (4)	0.7067 (3)	0.6741 (4)
C(27)	0.1881 (4)	0.8723 (3)	0.3926 (4)
C(28A)[a]	0.0585 (8)	0.8420 (5)	0.3256 (9)
C(28B)[a]	0.1494 (10)	0.8912 (7)	0.4081 (11)
H(1)	0.891 (5)	0.869 (3)	0.601 (6)
H(2)	1.007 (5)	0.713 (3)	0.743 (6)
H(3)	0.916 (4)	0.703 (3)	0.903 (4)
H(4)	0.751 (5)	0.859 (3)	0.898 (5)
H(5)	0.754 (4)	0.965 (3)	0.729 (5)
H(6)	0.696 (3)	0.903 (2)	0.356 (4)
H(7)	0.638 (3)	0.946 (2)	0.468 (3)
H(8)	0.546 (4)	0.940 (2)	0.317 (4)
H(9)	0.854 (3)	0.683 (2)	0.425 (4)
H(10)	1.029 (4)	0.583 (3)	0.369 (4)
H(11)	0.990 (4)	0.511 (3)	0.145 (4)
H(12)	0.765 (3)	0.574 (2)	−0.049 (3)
H(13)	0.581 (3)	0.668 (2)	0.006 (3)
H(14)	0.604 (4)	0.836 (3)	0.079 (4)
H(15)	0.452 (4)	0.944 (2)	−0.145 (4)

[a] Atom C(28) exhibited disorder; C(28A) and C(28B) were refined at 60% and 40% occupancy, respectively.

Such a path is not available to **14**, having no metal-bound hydrogen.

Structure of Complex 5a. The molecular structure of **5a** is shown in Figure 2. Atomic parameters, selected bond distances, and bond angles are enumerated in Tables II–IV. The molecule consists of a five-membered heterocycle, $\overline{\mathrm{C(Me)OAl(Et)_2N(}t\mathrm{\text{-}Bu)P(Ph)_2}}$, bonded in η^2(C, O) fashion to the Cp(CO)Fe fragment. Perhaps the most attractive valence-bond description of the bonding is that of a ketone (actually an acylphosphonium ion), which has an additional O–Al interaction, acting as a two-electron π donor to the 16-electron fragment $[CpFe(CO)]^-$:



While this zwitterionic formation should not be taken completely literally, spectral parameters are generally in accord with substantial charge separation. The low frequency for the terminal CO stretch (1887 cm^{-1}) suggests substantial electron density on Fe, while the ^{31}P NMR parameters for **5a** (shift and P–C coupling constants) are very similar to those found for the phosphonium salt $[MePPh_2N\text{-}t\text{-}BuAlEt_2]^+I^-$ (see Experimental Section for parameters).

Table III. Selected Bond Distances (Å)

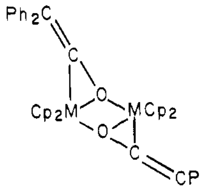
Fe–O(1)	1.969 (2)	N(1)–C(21)	1.503 (3)
Fe–C(1)	1.983 (3)	N(1)–Al	1.936 (2)
O(1)–C(1)	1.401 (3)	Al–C(25)	1.963 (3)
C(1)–C(8)	1.510 (4)	Al–C(27)	2.083 (5)
C(1)–P	1.827 (2)	Al–O(1)	1.842 (2)
P–C(9)	1.822 (2)	Fe–C(2)	1.729 (3)
P–C(15)	1.818 (2)	C(2)–O(2)	1.166 (3)
P–N(1)	1.619 (2)	Fe–Cp[a]	2.084

[a] Average Fe–C distance for cyclopentadienyl ring carbons.

Table IV. Selected Bond Angles (deg)

O(1)–C(1)–P	110.1 (2)	N(1)–Al–O(1)	92.22 (8)
O(1)–C(1)–C(8)	114.5 (2)	C(25)–Al–C(27)	113.4 (2)
P–C(1)–C(8)	113.1 (2)	Al–O(1)–C(1)	119.4 (1)
C(1)–P–N(1)	103.2 (1)	O(1)–Fe–C(1)	41.53 (8)
C(9)–P–C(15)	104.1 (1)	Fe–C(1)–C(8)	119.3 (2)
P–N(1)–Al	111.3 (1)	Fe–C(1)–P	122.1 (1)
P–N(1)–C(21)	125.0 (2)	Fe–O(1)–Al	118.08 (9)
Al–N(1)–C(21)	123.5 (2)	Fe–C(2)–O(2)	167.8 (3)

Relatively few complexes of η^2(C, O)-bonded ketones or aldehydes have been characterized structurally; some parameters are collected and compared to those of **5a** in Table V. Perhaps the closest analogues are the diphenylketene complexes **16** and **17**, which have the feature of the η^1-O bond to a second metal atom found in **5a**. (A



16, M = Ti
17, M = Zr

closer analogue is $[Cp_2Zr(Ph_2CO)]_2$,[25] which is proposed to have the same basic structure as **17** with ketone instead of ketene ligands; the structure has not been determined.)

The η^2 ligand–metal bonding can be viewed in the same terms as metal–olefin bonding.[26] The C–O bond distance of 1.401 Å is substantially lengthened from free ketone C=O distances; as a model one might take the recently determined acylphosphine $Ph_2PCOCHCl_2$, for which C–O is 1.196 Å.[27] Comparing values cited in Table V, the C–O distance is **5a** is the longest, with the exception of the remarkable 1.59 Å for the Os(CH$_2$O) complex **18**. Perhaps a more apt comparison is to the Fe(CH$_2$O) complex **19**; the longer C–O and shorter Fe–C and Fe–O in **5a** indicate stronger back-donation, consistent with the high negative charge at Fe. The Fe–C distance in **5a** is somewhat longer than Fe–O; the same situation is present in all the other complexes in Table V (although the difference is much larger in two of the examples). By way of contrast, in η^2-*acyl* complexes M–C is notably *shorter* than M–O. This is especially notable for later transition metals: for two complexes Ru(η^2-COR)I(CO)(PPh$_3$)$_2$, Ru–C values are 1.88

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Table V. Structural Parameters (Distances in Å, Angles in deg) for η^2-Ketone and -Aldehyde Complexes

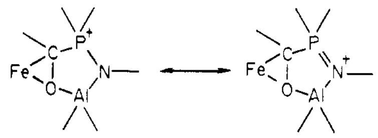
complex	C-O	M-C	M-O	O-M'[a]	β[b]	R-C-R[c]	ref
5a	1.401	1.983	1.969	1.842	50.7	113.1	this work
$[Cp_2Ti(Ph_2C{=}C{=}O)]_2$ (**16**)	1.311	2.099	2.037	2.250	38.8[d]		29
$[Cp_2Zr(Ph_2C{=}C{=}O)]_2$ (**17**)	1.371	2.204	2.164	2.165	33.6[d]		30
$Os(CO)_2(PPh_3)_2(H_2C{=}O)$ (**18**)	1.59	2.191	2.038		*e*	*e*	31
$Fe(CO)_2(P(OMe)_3)_2(H_2C{=}O)$ (**19**)	1.32	2.03	2.00		*e*	*e*	32
$Ni(P(C_6H_{11})_3)_2(PhHC{=}O)$	1.325	1.983	1.867		*e*	*e*	33
$Ni(PEt_3)_2(Ph_2C{=}O)$	1.335	1.974	1.849		63.4	119.3	34
$Ni(PPh_3)_2((CF_3)_2C{=}O)$	1.32	1.89	1.87		48	112	35
$CpMo(CO)(\eta^2\text{-}Ar_2CNHMe)(PhHC{=}O)$	1.333	2.258	2.071		*e*	*e*	36

[a] η^1-O interaction with second metal atom, if present. [b] Bending-back angle; see text. [c] Angle between substituents on carbonyl carbon. [d] These values for ketenes (here C-C-O angle minus 90°) should not be strictly comparable with the rest. [e] Not determined or not reported.

(3) and 1.92 (1) Å and Ru-O distances 2.47 (2) and 2.36 (1) Å.[28]

The geometry at C(1) also shows distortion towards sp^3 hybridization: the angle C(8)-C(1)-P has been reduced from the ideal sp^2 angle of 120° (the corresponding value for $Ph_2PCOCHCl_2$ is 115.6° (average for two independent molecules), however)[27] to 113.1 (2)°. The "bending-back" angle (β, the angle between the C-O vector and the normal to the plane defined by C(8), C(1), and P) is 50.7°. This is a rather large value (90° would correspond to no bending back); olefin complexes generally exhibit β of less than 60° only when strongly electron-withdrawing substituents are present. The value of β for **5a** is smaller than the "tetrahedral" value[26] of 55.7°, a situation which also is found only for the most electronegative ligands. Bending back at oxygen, which has only one substituent, is defined by δ, the torsional angle Fe-C(1)-O(1)-Al, which in **5a** is 111.6°, again near the top of the range normally observed.[26]

The five-membered heterocyclic ring is not quite planar; the least-squares plane makes an angle of 111.2° with that defined by Fe, C(1), and O(1). Geometries about both Al and P are roughly tetrahedral, although the endocyclic bond angles are significantly more acute that the rest; in contrast, the geometry about N is very nearly planar, suggesting substantial P=N character:



This is also consistent with the relatively short P-N distance. One of the ethyl groups on Al exhibits disorder; the structure was refined assuming a twofold rotational disorder about the Al-C(27) bond (i.e., two positions for the methyl group C(28)). The O(1)-Al bond appears to be considerably stronger than the O-M' bonds in **16** and **17**; it is a full 0.4 Å shorter than the O-Ti bond in **16**.

The iron atom exhibits the expected pseudotetrahedral geometry (that is, viewing the Cp as a single ligand and the η^2 grouping as two ligands). In comparison to CpFe(CO)(PPh$_2$NHCHMePh)(COMe) (**20**),[18] the Fe-C(2) bond is somewhat shorter (1.729 vs. 1.749 Å) and the C(2)-O(2) bond longer (1.116 vs. 1.128 Å), consistent with greater back-bonding in **5a**. The Fe-C(2)-O(2) angle (167.8 (3)°) is distorted from linearity more than is usual for terminal metal carbonyls; the remainder of the structure reveals no obvious cause. Also, the Cp ligand in **5a** is rather less regular than in **20**, and the average Fe-C(Cp) distance is shorter (2.084 (26) Å for **5a**; 2.131 (9) Å for **20**). The Cp plane is nearly parallel to the C(1)-O(1) axis.

Experimental Section

General Procedures. All operations were carried out under argon by using standard Schlenk techniques or a Vacuum Atmospheres Corp. glovebox. All reagents were obtained commercially and used without further purification unless otherwise specified. Solvents were distilled from sodium benzophenone ketyl under argon before use. NMR spectra were recorded on Varian EM-360 and Nicolet NT-200 instruments; all NMR data are for benzene-d_6 solution except where noted.

Ligand Syntheses. (*tert*-Butylamino)diphenylphosphine was prepared according to a published procedure,[37] (isopropylamino)diphenylphosphine was prepared analogously, and (phenylamino)diphenylphosphine by a slightly different route.[38] For preparation of $Ph_2PN\text{-}t\text{-}BuAlEt_2$ (**3a**), a solution of $Ph_2PNH\text{-}t\text{-}Bu$ (30 g, 0.116 mol) in 100 mL of toluene was treated dropwise with 48.6 mL of an *n*-butyllithium solution (2.4 M in hexane, 0.116 mol). After addition was complete, 99 g of a 25% solution of Et_2AlI in hexane (0.116 mol) was added slowly. The resulting suspension was stirred for 2 h; the precipitated LiI was filtered off; solvent was removed under vacuum; and the product was recrystallized by dissolving in hot toluene, adding hexane, and cooling. A 40-g (61%) sample of white crystalline solid was obtained. This compound was also successfully prepared by a literature route (heating the aminophosphine directly with Et_3Al),[14] but the latter was not found to work for AlR_3 where R = Me or Ph. NMR data for **3a** agree approximately with published values (the ^{31}P value shows the largest difference); the latter were not determined by the most accurate methods.[14] Although this and other ligands appear highly pure by NMR spectroscopy we were not able to obtain satisfactory analyses, probably because of decomposition during transit or handling: ^1H NMR δ 8.3 (m), 7.25 (m, Ph), 1.35 (s, *t*-Bu), 1.2 (t, J = 8 Hz, $AlCH_2CH_3$), 0.25 (q, J = 8 Hz, $AlCH_2CH_3$); ^{13}C NMR 136.0, 133.8, 130.1, 128.2 (Ph), 58.6 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 10.4 ($AlCH_2CH_3$), 5.9 ($AlCH_2CH_3$); ^{31}P NMR 25.0 ppm. Variable-temperature NMR and crystallographic studies on **3a** will be reported separately.[15]

The following amphoteric ligands were prepared similarly: $Ph_2PN\text{-}t\text{-}BuAlMe_2$ (**3b**): from Me_2AlCl; recrystallized from hot benzene as it is considerably less soluble than **3a**; ^1H NMR δ 8.1 (m), 7.2 (m, Ph), 1.2 (s, *t*-Bu), -0.5 (t, J_{PH} = 2 Hz, $AlCH_3$); ^{13}C NMR δ 135.6, 133.8, 130.0, 128.2 (Ph), 58.6 ($C(CH_3)_3$), 33.7 ($C(CH_3)_3$), -4.2 ($AlCH_3$); ^{31}P NMR 26.6 ppm.

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Ph_2PN-*t*-$BuAlPh_2$ (**3c**): this ligand was not obtained pure (by NMR), probably because the commercially obtained Ph_2AlCl was far from pure; the NMR spectrum of the product prepared as above showed major signals at (^1H) δ 1.0 (*t*-Bu; also complex Ph signals) and (^{31}P) 25.0 ppm.

Ph_2PN-*i*-$PrAlEt_2$ (**3d**): this compound is also in the literature;[14] ^1H NMR δ 7.9 (m), 7.2 (m, Ph), 3.4 (m, $CH(CH_3)_2$), 1.1 (m, $CH(CH_3)_2$ plus $AlCH_2CH_3$), 0.4 (m, $AlCH_2CH_3$); ^{13}C NMR δ 135–127 (m, Ph), 50.3 ($CH(CH_3)_2$), 25.8 ($CH(CH_3)_2$), 10.5 ($AlCH_2CH_3$), 4.5 ($AlCH_2CH_3$); ^{31}P NMR 33.2 ppm.

Ph_2PN-*i*-$PrAlMe_2$ (**3e**): ^1H NMR δ 7.7–6.9 (m, Ph), 2.9 (m, $CH(CH_3)_2$), 0.7 (d, $CH(CH_3)_2$), –1.3 ($AlCH_3$); ^{31}P NMR 34.5 ppm.

$Ph_2NPhAlMe_2$ (**3f**): ^1H NMR δ –0.1 ($AlCH_3$ (plus phenyl signals)); ^{31}P NMR 29.6 ppm.

Reactions of Amphoteric Ligands with Metal Complexes. $CpFe(CO)_2CH_3$ (1),[39] $CpMo(CO)_3CH_3$,[39] $CpFe(CO)_2(\eta^1\text{-}Cp)$,[40] $CpFe(CO)_2SiMe_3$,[41] and $Cp_2Nb(CO)CH_3$[9] were all prepared by literature routes (or minor modifications thereof). $CpFe(CO)_2CD_3$ was prepared similarly by using CD_3I. $CpFe(CO)_2Ph$ was prepared by the literature route[42] except that the crude intermediate $CpFe(CO)_2(COPh)$ was photolyzed directly without isolation; a yield of 75% was obtained, in contrast to the overall 12% reported.[42]

Reactions were generally carried out by mixing equimolar amounts of ligand and complex in C_6D_6 solution in the drybox, transferring the solution (with filtration if necessary) to an NMR tube, and following the reaction by NMR spectroscopy. Frequently mixtures of products resulted (shown by more than one new Cp signal); attempts at crystallization from aliphatic solvents usually gave some enrichment in one or more component but rarely led to pure crystalline product, while all attempts at chromatographic separation led to complete decomposition. Hence some of the identifications are based entirely on spectroscopic evidence.

$Cp(CO)Fe(C(CH_3)OAlEt_2N$-*t*-$BuPPh_2)$ (5a). A mixture of 1 (215 mg, 1.1 mmol) and **3a** (380 mg, 1.1 mmol) was dissolved in 3 mL of toluene. Within 30 s a dark color developed and intensified over the next few minutes. A 3-mL sample of heptane was added, and the solution was filtered through glass wool and cooled to –40 °C. After 5 h large black crystals were separated by decantation; a second crop was obtained on cooling the supernatant overnight; total yield 0.5 g, 83%. **5a** is quite stable as a solid in inert atmosphere but readily rearranges in solution: ^1H NMR δ 8.8 (m), 7.2 (m, Ph), 4.3 (s, Cp), 1.84 (t), 1.65 (t, *J* = 8 Hz, $Al(CH_3CH_3)_2$), 1.50 (d, *J* = 16 Hz, $CH_3COAlNP$), 1.3 (s, *t*-Bu), 0.8 (m, $Al(CH_2CH_3)_2$); ^{13}C NMR (toluene-d_8, –20 °C) δ 217.9 (d, *J* = 3.4 Hz, FeCO), 136–132 (m, Ph), 80.6 (s, Cp), 58.4 (d, *J* = 68.6 Hz, FeCOAlNP), 54.5 (d, *J* = 7.1 Hz, $C(CH_3)_3$), 34.0 (d, *J* = 6.3 Hz, $C(CH_3)_3$), 28.9 (d, *J* = 21.2 Hz, $CH_3COAlNP$), 11.1 (s), 11.0 (s, $Al(CH_2CH_3)_2$), 6.5 (s), 5.7 (s, $Al(CH_2CH_3)_2$); ^{31}P NMR 33.0 ppm; IR (Nujol) ν_{CO} 1887 cm^{-1}.

$Cp(CO)Fe(C(CH_3)OAlEt_2N$-*t*-$BuPPh_2)$ (**6**) forms as major product when a benzene solution of 1 and **3a**, or of isolated **5a**, is allowed to stand for about 1 day at room temperature. The NMR shows that other species are present (see Results and Discussion) up to about 20% of the total, but the key ^1H NMR parameters for **6** can be readily distinguished: δ 7.7 (m), 7.2 (m, Ph), 3.8 (d, *J* = 0.8 Hz, Cp), 2.7 (s, CH_3CO), 1.73 (t), 1.65 (t, *J* = 8 Hz, $Al(CH_2CH_3)_2$), 1.2 (s, *t*-Bu), 0.7 (m, $Al(CH_2CH_3)_2$). The ^{13}C NMR spectrum was somewhat more complex, but the following signals could be identified: δ 330.8 (d, *J* = 27.5 Hz, FeCOAlNP), 218.5 (d, *J* = 29.3 Hz, FeCO), 87.0 (s, Cp), 54.0 ($C(CH_3)_3$), 52.3 (CH_3CO), 34.0, ($C(CH_3)_3$). ^{31}P NMR: 84.1 ppm. IR (CH_2Cl_2): ν_{CO} 1940, 1460 sh cm^{-1}. On addition of THF, the IR peak at 1460 cm^{-1} disappears and is replaced by a peak at 1570 cm^{-1}; the major ^{31}P peak shifts from 84.1 to 100.3 ppm; both of these are consistent with conversion of **6** to **8** (see Results and Discussion).

$Cp(CO)Fe(C(C_6H_5)OAlEt_2N$-*t*-$BuPPh_2)$ (11a). A solution of 0.8 mmol each of **10** and **3a** in 1 mL of C_6D_6 was prepared in the drybox. By the time the NMR could be run (15 min) starting material signals were completely gone and replaced by those of the product; the NMR showed no further changes on allowing the solution to stand for 4 days or on heating to 50 °C for several hours. Evaporation of solvent and addition of hexane gave **11a** as a brown solid (0.31 g, 65%): ^1H NMR δ 9.3 (m), 7.3 (m), 6.85 (m, Ph), 4.1 (s, Cp), 1.66 (t), 1.53 (t, $Al(CH_2CH_3)_3$), 1.13 (s, *t*-Bu), 0.35 (m, $Al(CH_2CH_3)_2$); ^{31}P NMR 30.1 ppm; IR (Nujol) ν_{CO} 1886 cm^{-1}. Anal. Calcd for $C_{33}H_{39}AlFeNO_2P$: C, 66.56; H, 6.60; P, 5.20. Found: C, 65.36; H, 6.48; P, 5.50.

$Cp(CO)Fe(C(C_6H_5)OAlMe_2N$-*t*-$BuPPh_2)$ (11b). A solution of 0.4 mmol each of **10** and **3b** in 1 mL of C_6D_6 was allowed to stand for 2 h; NMR spectroscopy showed complete conversion to product. Solvent was evaporated, the residue dissolved in a minimum of toluene, excess hexane added, and the solution cooled to –40 °C, yielding 120 mg (54%) of brown crystals: ^1H NMR δ 9.4 (m), 7.3 (m), 6.9 (m, Ph), 4.1 (s, Cp), 1.2 (s, *t*-Bu); 0.25 (s), –0.1 (s, $AlCH_3)_2$); ^{31}P NMR 30.1 ppm.

$Cp(CO)_2Mo(O(CH{=}CH_2)AlEt_2N$-*i*-$PrPPh_2)$ (12). A solution of 2 mmol each of $CpMo(CO)_3CH_3$ and **3d** in 6 mL of toluene was allowed to stand for 10 days; it gradually became dark red. Addition of an equal volume of hexane and cooling to –40 °C overnight gave an oily red solid, which exhibited only broad, very weak NMR signals. The supernatant was evaporated to dryness and extracted with hexane; evaporation of the extract gave a red oil that contained **12** in about 75% purity (by ^1H NMR) and at least three minor components. Attempted crystallization from hexane at –78 °C gave a solid that turned to an oil on warming to room temperature and which was only marginally more pure: ^1H NMR δ 7.8 (m), 7.2 (m, Ph), 6.4 (dd, *J* = 14.3, 6.2 Hz, $OCH{=}CH_2$), 4.4 (dd, *J* = 14.4, 1.6 Hz), 4.1 (dd, *J* = 6.3, 1.6 Hz, $OCH{=}CH_2$), 4.7 (s, Cp (plus weaker impurity Cp signals at δ 5.0, 4.75, and 4.65)). The intensities of the preceding signals agreed with expected values to within experimental error. The aliphatic region ($AlCH_2CH_3$ plus $CH(CH_3)_2$) was too complex to assign: ^{31}P NMR 85.6 ppm (plus several weaker impurity peaks); IR (heptane) ν_{CO} 1966 (vs), 1939 (s), 1894 (vs) cm^{-1}, $\nu_{C=C}$ 1617 (m) cm^{-1}.

$[CH_3PPh_2N$-*t*-$BuAlEt_2]^+I^-$. A solution of 0.35 g of **3a** (1 mmol) in 2.5 mL of benzene was treated with 0.215 g of MeI (1.5 mmol), allowed to stand for 1 h, and then evaporated to dryness. The residual solid was dissolved in 2 mL of warm toluene, and the solution was filtered, treated with heptane to the cloud point, and cooled overnight at –40 °C to give 0.38 g (64%) white crystalline solid: ^1H NMR δ 7.7 (m), 7.2 (m, Ph), 2.3 (d, *J* = 13 Hz, CH_3P), 1.45 (t, $AlCH_2CH_3$), 1.2 (s, *t*-Bu), 0.5 (q, $AlCH_2CH_3$); ^{13}C NMR, δ 132.6 (s, Ph_{para}), 132.0 (d, *J* = 10 Hz, Ph_{meta}), 130.8 (d, *J* = 91.3 Hz, Ph_{ipso}), 129.0 (d, *J* = 12 Hz, Ph_{ortho}), 58.2 (d, *J* = 4.6 Hz, $C(CH_3)_3$), 34.0 (d, *J* = 7.1 Hz, $C(CH_3)_3$), 21.2 (d, *J* = 74.3 Hz, CH_3P), 11.4 (s, $AlCH_2CH_3$), 11.0 (s, br, $AlCH_2CH_3$); ^{31}P NMR 32.5 ppm.

$CpFe(CO)(PPh_2NH$-*t*-$Bu)(COCH_3)$ (4). The procedure used by Brunner et al. for preparation of a number of complexes of type $CpFe(CO)(PPh_2NHR)(COCH_3)$[43] was followed; **4** was obtained after chromatography in 79% yield as a yellow-orange oil: ^1H NMR δ 7.8 (m), 7.25 (m, Ph), 5.0 (d, *J* =9.5 Hz, NH), 4.1 (d, *J* = 1.2 Hz, Cp), 2.85 (d, *J* = 0.6 Hz, CH_3CO), 1.0 (s, *t*-Bu); ^{13}C NMR δ 277.8 (d, *J* = 26.7 Hz, CH_3CO), 220.4 (d, *J* = 32.1 Hz, FeCO), 140.9 (d, *J* = 51.5 Hz), 138.1 (d, *J* = 46.1 Hz, Ph_{ipso}), 132.9 (d, *J* = 11.1 Hz), 131.4 (d, *J* = 10.5 Hz, Ph_{ortho}), 130.0 (d, *J* = 1.5 Hz), 129.0 (d, *J* = 1.7 Hz, Ph_{para} (the Ph_{meta} signals are presumably obscured by solvent); 85.0 (s, Cp), 54.7 (d, *J* = 15.0 Hz, $C(CH_3)_3$), 51.2 (d, *J* = 6.4 Hz, CH_3CO), 32.0 (d, *J* = 3.8 Hz, $C(CH_3)_3$); ^{31}P NMR 99.8 ppm; IR (Nujol) 1925 cm^{-1} (terminal CO), 1592 cm^{-1} (acyl CO).

$CpFe(CO)(PPh_2NH$-*t*-$Bu)(CO(AlEt_3)CH_3)$ (9). One equivalent of $AlEt_3$ (toluene solution) was added to a C_6D_6 solution of **4**; the solution darkened from yellow-orange to brown but

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remained clear: ^{1}H NMR δ 7.7 (m (remainder of Ph signal obscured by toluene peak), Ph), 4.0 (d, J = 1 Hz, Cp), 3.12 (d, J = 16 Hz, NH), 2.44 (s, CH_3CO), 1.66 (t, $AlCH_2CH_3$), 0.95 (s, *t*-Bu), 0.45 (q, $AlCH_2CH_3$); ^{13}C NMR 323.8 (d, J = 29.0 Hz, $CH_3COAlEt_3$), 217.3 (d, J = 31.1 Hz, FeCO), 138.0 (d, J = 51.0 Hz), 136.5 (d, J = 52.9 Hz, Ph_{ipso}), 132.9 (d, J = 11.5 Hz), 131.0 (d, J = 10.8 Hz, Ph_{ortho}), 130.8 (d, J = 1.7 Hz), 130.2 (d, J = 1.3 Hz, Ph_{para}), 86.6 (s, Cp), 55.5 (d, J = 8.2 Hz, $C(CH_3)_3$), 50.8 (d, J = 3.0 Hz, $CH_3COAlEt_3$), 32.0 (d, J = 3.7 Hz, $C(CH_3)_3$); ^{31}P NMR 96.5 ppm.

X-ray Crystallographic Data. Large, well-shaped brownish black crystals of **5a**, obtained as described above, were sent to Molecular Structures Corp., College Station, TX, for analysis. A nearly spherical crystal of approximate diameter 0.40 mm was mounted in a glass capillary in a random orientation. Preliminary examination revealed the crystal to be triclinic, with cell parameters a = 10.474 (2) Å, b = 15.677 (3) Å, c = 9.707 (1) Å, α = 97.98 (1)°, β = 115.01 (1)°, γ = 71.81 (1)°, V = 1373.1 Å^3, Z = 2, and space group $P\bar{1}$.

Data were collected on an Enraf-Nonius CAD4 computer-controlled diffractometer, using graphite-monochromated Mo K$\bar{\alpha}$ radiation, at a temperature of 23 ± 1 °C. The ω–θ scan technique was used, with scan rates from 2 to 20°/min, to a maximum 2θ of 56.0°. A total of 6816 reflections were collected, of which 6602 were unique. As a check on stability, three representative reflections were monitored over time; these showed a loss of intensity over the course of data collection of 151 ± 7 counts/h; a linear decay correction was applied. Lorentz and polarization corrections were applied to the data; no absorption correction was made.

Structure Solution and Refinement. The structure was solved by direct methods. Using 350 reflections (minimum E of 1.45) and 4000 relationships, a total of 16 phase sets were produced. A total of 24 atoms were located from an E map prepared from the phase set with probability statistics: absolute figure of merit = 1.31, residual = 0.24, and psi zero = 1.200. The remaining atoms were located in succeeding difference Fourier syntheses. A disorder was noted in the region of atoms C27 and C28A. A twofold rotational disorder (about the Al–C27 bond) was assumed, with a 3:2 occupancy ratio for C28A and C28B, respectively. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The temperature factors for the *tert*-butyl and ethyl group hydrogens were fixed and not refined. The disordered hydrogen atoms were not located. The largest peaks in the final difference map were less than half as high as those that yielded C(28B) and were in the region of the ethyl group. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$.

The standard deviation on intensities, $\sigma(F_o^2)$, is defined as follows: $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz–polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.050.

Scattering factors were taken from Cromer and Waber.[44] Anomalous dispersion effects were included in F_c;[45] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[44] Only the 4303 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 420 variable parameters and converged (largest parameter shift was 0.48 times its esd) with unweighted and weighted agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.068$. The standard deviation of an observation of unit weight was 1.93. The highest peak in the final difference Fourier had a height of 0.93 e/Å with an estimated error based on ΔF of 0.08. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

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Supplementary Material Available: Listings of thermal parameters (Table VI), complete bond lengths (Table VII) and angles (Table VIII), least-squares planes (Table IX), observed and calculated structure factor amplitudes (Table X), torsional angles (Table XI), and intermolecular contacts (Table XII) for compound **5a** (42 pages). Ordering information is given on any current masthead page.

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Preparation of Cyclometalladisiloxanes of the Type M(SiMeROSiMeR) (R = Phenyl and Benzyl) and the Catalyzed Redistribution of $(HRMeSi)_2O$[1]

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New cyclometalladisiloxanes, $L_nM(SiMeROSiMeR)$ (R = C_6H_5, $C_6H_5CH_2$), have been prepared from the interation of disiloxanes $(HRMeSi)_2O$ with low-valent complexes. L_4Pt (L = Ph_3P) selectively reacts with the *RR* and *SS* enantiomers to give only the metallacycles with Ph groups on opposite sides of the ring. The formation of the benzyl analogue is not stereoselective; both cis and trans isomers form. The reactions of $L_2(CO)ClIr$ with $(HRMeSi)_2O$ yield two isomers when R = $C_6H_5CH_2$ and all three possible isomers when R = C_6H_5. These metallacycles are catalyst precursors in a reaction that causes extensive redistribution of groups on silicon via Me/H, Ph/H, Ph/Me, and SiO/R exchanges.

Introduction

Certain classes of organosilanes will undergo redistribution reactions of the type shown in eq 1 when treated

$$R_4Si + R'_4Si \rightarrow 2R_{4-n}R'_nSi \ (n = 1\text{–}4) \quad (1)$$

with catalytic quantities of transition-metal complexes. In order for the redistribution reaction to occur at low temperatures, there must be at least one Si–H bond or an activated Si–Si bond if the catalyst is a typical low-valent complex, e.g., $L_2(CO)ClIr$, $L_2Pt(C_2H_4)$, or L_2PdCl_2 (L = Ph_3P unless otherwise stated).[1c]

Curtis and Greene observed that cyclometalladisiloxanes of type 1 were active as catalysts for the disproportionation

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[1] This paper is part 6 in the series "Small Ring Metallacycles" and part 5 of "Metal-Catalyzed Redistributions of Organosilanes". For earlier papers, see: (a) Curtis, M. D.; Greene, J.; Butler, W. M. *J. Organomet. Chem.* **1979**, *164*, 371. (b) Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362. (c) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

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