placing chlorine atoms bound to gallium with bulky pentamethylcyclopentadienyl ligands. For this series of dimeric chlorine bridged molecules, regular changes in bond distances and bond angles as well as in distances between similar but nonbonded atoms in the four-membered rings occur (Table VI). As the molecule changes from $[GaCl_3]_2$ to $[Ga(C_5Me_5)Cl_2]_2$ to $[Ga(C_5Me_5)_2Cl]_2$, the Ga–Cl bridge bonding distances increase significantly. The Cl–Ga–Cl ring angles decrease whereas the Ga–Cl–Ga ring angles increase in the series. These changes in ring angles are also reflected with an increase in the nonbonding Ga···Ga distance and with a decrease in the nonbonding Cl···Cl distance within the four-membered rings of the series. As the Ga_2Cl_2 ring dimensions and angles change, the terminal Ga–Cl distances and the angles between the terminal groups change. The observed changes in the dimensions of the molecules in this series also affect the calculated densities of the compounds. The observation that $[Ga(C_5Me_5)_2Cl]_2$ has the longest Ga–Cl (bridge) distances is also reflected in the ease of dissociation of the dimer. Only monomers are observed in benzene solution according to cryoscopic molecular weight data. The Ga–C distances in the two (pentamethylcyclopentadienyl)gallium compounds are comparable (Table VI) and similar to the average Ga–C distances in $Ga(C_5H_5)_3$[1] (2.05 [3] Å), $Ga(C_6H_5)_3$[16] (1.947 [1] Å), $MeGa(O_2CMe)_2$[17] (1.946 Å), $Me_2GaN_2C_5H_7$[18] (1.995 and 1.969 Å), and $KGa(CH_2SiMe_3)_3H$[19] (2.04 (1) and 2.02 (1) Å). Thus, in both new (pentamethylcyclopentadienyl)gallium compounds, the cyclopentadienyl ligand has no unusual structural features or bonding characteristics. The pentamethylcyclopentadienyl ring is acting as a simple monodentate ligand.

Acknowledgment. This work was supported by the National Science Foundation through Grants CHE-81-3316 (O.T.B.) and CHE-81-11137 (J.L.A.).

Registry No. $[Ga(C_5Me_5)_2Cl]_2$, 97210-83-8; $[Ga(C_5Me_5)Cl_2]_2$, 97210-84-9; $GaCl_3$, 13450-90-3; LiC_5Me_5, 51905-34-1.

Supplementary Material Available: Tables VII-S, VIII-S, and X-S, showing a complete listing of interatomic distances and angles, anisotropic thermal parameters for gallium and chlorine atoms and isotropic thermal parameters for carbon atoms, and calculated structure factor amplitudes for $[Ga(C_5Me_5)_2Cl]_2$, respectively, and Tables IX-S and XI-S, showing anisotropic thermal parameters for all non-hydrogen atoms and the calculated structure factor amplitudes for $[Ga(C_5Me_5)Cl_2]_2$, respectively (22 pages). Ordering information is given on any current masthead page.

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Communications

Pentamethylcyclopentadienyl Acetylacetonate Complexes of Iron(II), Cobalt(II), and Nickel(II). Convenient Synthetic Entries to Mono-η^5-C_5Me_5 Derivatives

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Received March 26, 1985

Summary: The reactions between $M(acac)_2$ (M = Fe, Co, and Ni; acac = acetylacetonate) and 1 mol of LiC_5Me_5 cleanly yield $(\eta^5\text{-}C_5Me_5)M(acac)$ (**2**, M = Fe; **6**, M = Co; **7**, M = Ni). **2** reacts with CO to give $(\eta^5\text{-}C_5Me_5)Fe(CO)(acac)$ (**3**) with methylmagnesium iodide under CO to give $(\eta\text{-}C_5Me_5)Fe(CO)_2CH_3$ (**4**) and with benzene–$AlCl_3$ followed by NH_4PF_6 to give $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**5**). **2**, **6**, and **7** react with NaC_5H_5 to give $(\eta^5\text{-}C_5Me_5)M(\eta^5\text{-}C_5H_5)$ (**10**, M = Fe; **11**, M = Co; **12**, M = Ni) in high yield. The reactions of **2** with lithium salts of 3,4-dimethyl(*p*-bromophenyl)cyclopentadiene and 2,3,4,5-tetramethyl(*p*-bromophenyl)cyclopentadiene afford $(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5H_2Me_2\text{-}p\text{-}C_6H_4Br)$ (**15**) and $(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}C_5Me_4\text{-}p\text{-}C_6H_4Br)$ (**16**).

The first-row transition-metal organometallic chemistry generally starts with the binary metal carbonyls. Noncarbonyl organometallic complexes starting with other easily accessible binary compounds would provide entries to a broader spectrum of complexes.

Along this line, we report a general method of synthesis of the precursors $(\eta^5\text{-}C_5Me_5)M(acac)$, essential materials for the synthesis of a variety of mono-η^5-C_5Me_5 derivatives.

We find that a convenient procedure to the known $Fe(acac)_2$[1] consists of adding stoichiometric[2] amounts of acetylacetone and piperidine to an ether slurry of the easily available complex $FeCl_2{\cdot}2THF$[3] (THF = tetrahydrofuran) followed by filtration of the piperidine hydrochloride formed, removal of the ether under vacuum, and washing with pentane (eq 1). Crude **1** obtained in this way (50–60% yield) can be used in further reactions.

$$FeCl_2{\cdot}2THF \xrightarrow[\text{2. piperidine}]{\text{1. acetylacetone}} \underset{1}{Fe(acac)_2} + C_5H_{11}NHCl \qquad (1)$$

Whereas the reaction of $FeCl_2{\cdot}2THF$ with 1 equiv of C_5Me_5Li in THF yields only $(\eta^5\text{-}C_5Me_5)_2Fe$,[4] under all conditions examined, $Fe(acac)_2$ reacts cleanly to afford $(\eta^5\text{-}C_5Me_5)Fe(acac)$ (**2**) (eq 2).

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(1) Buckingham, D. A.; Gorges, R. C.; Henry, J. T. *Aust. J. Chem.* **1967**, *20*, 281.

(2) If excess of piperidine is added, complex $Fe(acac)_2(piperidine)_2$ is isolated.

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$$\mathrm{Fe(acac)_2 + C_5Me_5Li \xrightarrow[-80\ ^\circ C\ to\ 25\ ^\circ C]{THF} \underset{\mathbf{2}}{(\eta^5\text{-}C_5Me_5)Fe(acac)} + Li(acac)} \quad (2)$$

Solutions of **2** in THF are very air sensitive but thermally stable at room temperature. Although **2** has not been isolated, it has been characterized in solution through the following reactions.

Red-orange pentane solutions of **2** rapidly absorb carbon monoxide to afford brown $(\eta^5\text{-}C_5Me_5)Fe(CO)(acac)$ **3**[5] (eq 3) in 25% yield. Sublimation of the residue obtained upon removal of solvent "in vacuo" gives **3** as nearly black, air-sensitive, analytically pure crystals with ν_{CO} at 1930 cm^{-1} (Nujol).

$$\mathrm{(\eta^5\text{-}C_5Me_5)Fe(acac) + CO \xrightarrow{pentane} \underset{\mathbf{3}}{(\eta^5\text{-}C_5Me_5)Fe(CO)(acac)}} \quad (3)$$

Similarly solutions of **2** in THF react with CH_3MgI at −78 °C under carbon monoxide (1 atm) followed by warming to 25 °C to give $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_3$ (**4**)[5,6] as yellow crystals in 60% yield (eq 4).

$$\mathrm{(\eta^5\text{-}C_5Me_5)Fe(acac) + CH_3MgI \xrightarrow[-78\ ^\circ C\ to\ 25\ ^\circ C]{THF,\ CO\ (1\ atm)} \underset{\mathbf{4}}{(\eta^5\text{-}C_5Me_5)Fe(CO)_2CH_3} + MgI(acac)} \quad (4)$$

If THF is removed in vacuo from the solution of **2**, prepared as above (eq 2), extraction with pentane to remove insoluble Li(acac) and removal of pentane "in vacuo" followed by addition of benzene and $AlCl_3$ (3 mol/mol of iron) immediately give $[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_6)]^+PF_6^-$ (**5**)[7] in 60% yield after hydrolysis and the usual workup with $NaPF_6$ (eq 5).

$$\mathrm{(\eta^5\text{-}C_5Me_5)Fe(acac) \xrightarrow[2.\ NaPF_6/H_2O]{1.\ AlCl_3\text{-}benzene} \underset{\mathbf{5}}{[(\eta^5\text{-}C_5Me_5)Fe(\eta^6\text{-}C_6H_6)]^+PF_6^-}} \quad (5)$$

Investigations are underway to determine the exact structure of the intermediate **2**.

Brown $(\eta^5\text{-}C_5Me_5)Co(acac)$, **6**,[5] and dark red $(\eta^5\text{-}C_5Me_5)Ni(acac)$, **7**,[5] are prepared as **2** in 60–70% yield after crystallization from pentane (or sublimation at 100 °C (10^{-3} torr)) and give satisfactory elemental analysis. A crucial point is that C_5Me_5H must be very pure to perform the synthesis of **2**, **6**, and **7**.

$$\mathrm{M(acac)_2 + C_5Me_5Li \xrightarrow[-78\ ^\circ C\ +\ 25\ ^\circ C]{THF} (\eta^5\text{-}C_5Me_5)M(acac) + Li(acac)} \quad (6)$$

$$\mathbf{6},\ \mathrm{M = Co}$$
$$\mathbf{7},\ \mathrm{M = Ni}$$

6 reacts with a stoichiometric amount of CO and CH_3MgI to give the green crystalline dimer **8**[5] (ν_{CO} 1850 cm^{-1} (Nujol)), as shown in eq 7. Compound **8** is analogous to the $[(\eta^5\text{-}C_5H_5)Co(CO)(CH_3)]_2$ previously reported.[8]

$$\mathrm{2[6] + 2CH_3MgI + 2CO \rightarrow \underset{\mathbf{8}}{[(\eta^5\text{-}C_5Me_5)Co(CO)(CH_3)]_2} + 2MgI(acac)} \quad (7)$$

7 reacts with CO and CH_3MgI as shown in eq 8.

$$\mathrm{7 + CH_3MgI \xrightarrow{CO\ (1\ atm)} \underset{\mathbf{9}}{(\eta^5\text{-}C_5Me_5)Ni(CO)(CH_3)} + MgI(acac)} \quad (8)$$

Compound **9**[5] is isolated as a volatile and thermally unstable violet liquid (ν_{CO} 2000 cm^{-1} (neat)). Details of these reactions will be reported in the full paper.

2, **6**, and **7** react with C_5H_5Na in THF to give the mixed metallocenes $(\eta^5\text{-}C_5Me_5)M(\eta^5\text{-}C_5H_5)$ (M = Fe,[5] Co,[9] Ni[10]) in excellent yields after removal of Na(acac) by extraction of the residue with pentane and crystallization (eq 9). Spectroscopic and analytical data are in accord with literature values.

$$\mathrm{(\eta^5\text{-}C_5Me_5)M(acac) + C_5H_5Na \xrightarrow[-78\ ^\circ C\ to\ 25\ ^\circ C]{THF} (\eta^5\text{-}C_5Me_5)M(\eta^5\text{-}C_5H_5) + Na(acac)} \quad (9)$$

$$\mathbf{10},\ \mathrm{M = Fe\ (86\%)}$$
$$\mathbf{11},\ \mathrm{M = Co\ (63\%)}$$
$$\mathbf{12},\ \mathrm{M = Ni\ (60\%)}$$

Other examples of syntheses of mixed ferrocenes containing functionalized substituents were performed in the same fashion. Thus, the lithium salts of 1-(*p*-bromophenyl)-3,4-dimethylcyclopentadiene (**13**)[11] and 1-(*p*-bromophenyl)-2,3,4,5-tetramethylcyclopentadiene (**14**)[12] react with **2** (eq 10) to give the new complexes **15**[5] and **16**[5] obtained in 57–58% yields after recrystallization in ethanol and pentane, respectively.

$$\mathrm{2 + Li(C_5Me_2R_2\text{-}\mathit{p}\text{-}C_6H_4Br) \xrightarrow[-Li(acac)]{THF} (\eta^5\text{-}C_5Me_5)M(\eta^5\text{-}C_5Me_2R_2\text{-}\mathit{p}\text{-}C_6H_4Br)} \quad (10)$$

$$\mathbf{15},\ \mathrm{R = H\ (58\%)}$$
$$\mathbf{16},\ \mathrm{R = Me\ (57\%)}$$

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(5) **3**: ν_{max} (Nujol) 1930, 1580, 1513 cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 1.38 (15 H, s), 1.64 (6 H, s), 4.9 (1 H, s); mass spectra, $M^+ = 318$, calcd for $C_{16}H_{22}O_3Fe$ $M^+ = 318$. Anal. Calcd for $C_{16}H_{22}O_3Fe$: C, 60.4; H, 6.97. Found: C, 60.8; H, 6.73. **4**: ν_{max} (Nujol) 1930, 1985 cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 1.40 (15 H, s), 0.05 (3 H, s); mass spectra, $M^+ = 262$, calcd for $C_{13}H_{18}O_2Fe$ $M^+ = 262$. Anal. Calcd for $C_{13}H_{18}O_2Fe$: C, 59.56; H, 6.92. Found: C, 59.37; H, 7.01. **6**: ν_{max} (Nujol) 1600, 1515 cm^{-1}; mass spectra, $M^+ = 293$, calcd for $C_{15}H_{22}O_2Co$ $M^+ = 293$. Anal. Calcd for $C_{15}H_{22}O_2Co$: C, 61.43; H, 7.56. Found: C, 61.43; H, 7.51. **7**: ν_{max} (Nujol) 1570, 1515 cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 64.2 (15 H, br s), −2.1 (6 H, s), −10 (1 H, s); mass spectra, $M^+ = 293$, calcd for $C_{15}H_{22}O_2Ni$ $M^+ = 293$. Anal. Calcd for $C_{15}H_{22}O_2Ni$: C, 61.55; H, 7.55. Found: C, 61.25; H, 7.60. **8**: ^{1}H NMR (C_6D_6, 90 MHz) δ −1.50 (6 H, s), 1.32 (30 H, s); ν_{max} (Nujol) 1850 cm^{-1}. **9**: ^{1}H NMR (C_6D_6, 90 MHz) δ 0.04 (3 H, s), 1.60 (15 H, s); ν_{max} (neat) 2000 cm^{-1}. **10**: ^{1}H NMR (C_6D_6, 90 MHz) δ 1.87 (15 H, s), 3.52 (5 H, s); mass spectra, $M^+ = 256$, calcd for $C_{15}H_{20}Fe$ $M^+ = 256$. Anal. Calcd for $C_{15}H_{20}Fe$: C, 70.33; H, 7.87. Found: C, 70.51; H, 7.79. **13**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.893 (3 H, s), 1.970 (3 H, s), 3.230 (2 H, s), 6.663 (1 H, s), 7.274, 7.303, 7.373, 7.401 (AA′BB′, 4 H); mass spectra, $M^+ = 249$, calcd for $C_{13}H_{13}Br$ $M^+ = 249$. Anal. Calcd for $C_{13}H_{13}Br$: C, 62.07; H, 5.26. Found: C, 62.39; H, 5.49. **14**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.939 (3 H, d, $J = 1.5$ Hz), 1.860 (3 H, s), 1.924 (3 H, s), 2.007 (3 H, s), 3.159 (1 H, q, $J = 1.5$ Hz) 7.083, 7.111, 7.447, 7.474 (AA′BB′, 4 H); mass spectra, $M^+ = 277$, calcd for $C_{15}H_{17}Br$ $M^+ = 277$. Anal. Calcd for $C_{15}H_{17}Br$: C, 64.99; H, 6.18. Found: C, 65.20; H, 6.22. **15**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.582 (15 H, s), 1.824 (6 H, s), 3.886 (2 H, s), 7.112, 7.141, 7.347, 7.375 (AA′BB′, 4 H); mass spectra, $M^+ = 439$, calcd for $C_{23}H_{27}BrFe$ $M^+ = 439$. Anal. Calcd for $C_{23}H_{27}BrFe$: C, 62.89; H, 6.19. Found: C, 62.49; H, 6.13. **16**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.639 (15 H, s), 1.757 (6 H, s), 1.773 (6 H, s), 7.289, 7.317, 7.425, 7.453 (AA′BB′, 4 H); mass spectra, $M^+ = 467$, calcd for $C_{25}H_{31}BrFe$ $M^+ = 467$. Anal. Calcd for $C_{25}H_{31}BrFe$: C, 64.26; H, 6.79. Found: C, 64.26; H, 6.79.

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(11) **11**: to a solution of *p*-C_6H_4BrLi prepared from *p*-$C_6H_4Br_2$ (131 mmol in 130 mL of ether) and *n*-BuLi in hexanes (131 mmol) was added slowly 3,4-dimethylcyclopent-2-en-1-one[13] (132 mmol in 20 mL of ether). The mixture was stirred for 1 h and then hydrolyzed with saturated NH_4Cl solution. The ethereal solution was dried, concentrated to ca. 100 mL, and *p*-toluenesulfonic acid monohydrate (16 mmol) was added and the mixture stirred for 5 min. The solid formed was filtered, washed with $NaHCO_3$ solution and then with water, and finally dried. The crude product was recrystallized from chloroform giving 21.6 g of **11** as white crystals (66%).

(12) **12**: this was prepared in the same manner as **11** using 2,3,4,5-tetramethylcyclopent-2-en-1-one[14] (131 mmol). The product was recrystallized from chloroform giving 16.6 g of **12** as yellow crystals (45.7%).

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We intend to extend the strategy presented here with other ligands and metals.

Acknowledgment. We are greatly indebted to Professors Didier Astruc, John E. Bercaw, and Clifford A. Bunton for helpful discussions and miscellaneous analysis. We also with to thank Barbara J. Burger for her help in the preparation of this manuscript.

Registry No. **1**, 14024-17-0; **2**, 97210-26-9; **3**, 97210-27-0; **4**, 52409-66-2; **5**, 76747-93-8; **6**, 97210-28-1; **7**, 97210-29-2; **8**, 97210-30-5; **9**, 97210-31-6; **10**, 83928-47-6; **11**, 97210-32-7; **12**, 75730-73-3; **13**, 97190-28-8; **14**, 97190-29-9; **15**, 97210-33-8; **16**, 97210-34-9; C_5Me_5Li, 51905-34-1; MeI, 74-88-4; $Co(acac)_2$, 14024-48-7; $Ni(acac)_2$, 3264-82-2; C_5H_5Na, 4984-82-1; p-$C_6H_4Br_2$, 106-37-6; 3,4-dimethylcyclopent-2-en-1-one, 30434-64-1; 2,3,4,5-tetramethylcyclopent-2-en-1-one, 54458-61-6.

Thallium(I)-Promoted Substitution Reactions of Chloromethyl Complexes of Iron and Molybdenum with Uncharged Nucleophiles

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Summary: $TlBF_4$ has been used as an electrophilic promotor for substitution of chloride in $[Fe(\eta^5\text{-}C_5H_5\text{-}(CO)_2CH_2Cl]$ and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3CH_2Cl]$ by a wide range of uncharged nucleophiles. The resulting fluoroborate onium salts are obtained in high yield.

Nucleophilic substitution of halide in halomethyl complexes L_nMCH_2X would appear to be an attractive approach to the preparation of a variety of other alkyl complexes. Indeed, a number of successful substitution reactions of such compounds have been reported.[1] However, some attempts to substitute the halide in certain halomethyl complexes by neutral nucleophiles have met with only limited success. In particular, Moss and co-workers report very erratic results in reactions of various phosphines with $[FeCp(CO)_2CH_2Cl]$ (A) and that some compounds, including $[MoCp(CO)_3CH_2Cl]$ (B) (Cp = η^5-C_5H_5), fail to give any halide substitution product at all.[1g] Attempts in our laboratory to substitute A with either $HNEt_2$ or NEt_3 were unsuccessful.[2] We now wish to report that $TlBF_4$ can be used to promote halide substitution by a variety of neutral nucleophiles in both A and B to give the onium salts in excellent yield.

A list of the compounds prepared by the thallium promoted method with yields and spectroscopic data are given in Table I. All of the compounds were prepared by stirring a suspension of 1.2–2 equiv of $TlBF_4$ in a methylene chloride solution of A[1f] or B[3] (3–5 mmol in 25 mL) and 1–5 equiv of nucleophile at room temperature.[4,5] Reactions of A were complete in 5–20 h whereas B reacted much more slowly, and 2–4 days were required to achieve conversions of 50–60%. It is important to note that there is no evidence for loss of B to other reactions and that greater conversions can likely be achieved with longer reaction times. Attempts to perform reactions of B at higher temperature resulted in the formation of other products.[6] Workup involved filtration to remove thallium salts, concentration, and addition of hexane to crystallize the products.[7] Characterization of the new compounds in Table I on the basis of IR and NMR spectral data and elemental analyses[8] was straight forward.

Of the compounds listed in the table only **1** and some of its analogues have been previously prepared by direct reaction of A with the phosphines.[1g] The other known complexes **5**[9a] and **6**[9b] were prepared by an alternative route, as was the methyl analogue of **2**.[10] We believe that the thallium(I)-promoted reaction is superior to these methods.

In principle, it should be possible to perform anion substitution reactions with thallium salts whose solubility is comparable or greater than that of thallium chloride. We have observed that A reacts rapidly with TlOEt and more slowly with the less soluble TlOAc. Infrared spectra of the reaction mixtures indicate that $[FeCp(CO)_2CH_2OEt]$[1f] and $[FeCp(CO)_2CH_2OC(O)CH_3]$[1f] are the only detectable carbonyl containing species present.

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[2] Attempts were made by using both $HNEt_2$ or NEt_3 in THF with and without added $AgBF_4$. Sepelak, D. J.; Barefield, E. K., unpublished results.

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[4] Reactions of A with Me_2S and PMe_2Ph were attempted without addition of $TlBF_4$. After 16 h the dimethyl sulfide reaction mixture was completely homogeneous and A was the only detectable (infrared and ^1H NMR spectra) iron carbonyl product. After 16 h the PMe_2Ph reaction contained a white precipitate that was identified as $[PhPMe_3]Cl$ based on its ^1H NMR spectrum (Knoll, L. *J. Organomet. Chem.* **1979**, *182*, 77). Most of the A had reacted to give a monocarbonyl species which was probably $[FeCp(CO)(PMe_2Ph)_2]^+$ [ν_{CO} 1966 cm^{-1} (lit.,[1g] ν_{CO} 1967 cm^{-1})]. A small amount of starting material remained. There was no evidence for the presence of **1**.

[5] Complexes A and B do not react with $TlBF_4$ in CH_2Cl_2 in the absence of nucleophile. Complex A does however react with $TlBF_4$ in Me_2SO, CH_3CN, and THF. The products of these reactions have not been characterized.

[6] No attempts were made to separate the product mixtures, but the infrared and ^1H NMR spectra suggested that CO substitution products were formed when reaction mixtures containing NEt_3 and PMe_2Ph were heated.

[7] $\{FeCp(CO)_2[CH_2P(OMe)_3]\}BF_4$ has a melting point below room temperature. It separated as a viscous oil upon addition of hexane to the CH_2Cl_2 solution.

[8] All products in Table I gave satisfactory elemental analyses.

[9] (a) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869. (b) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473.

[10] Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6542.

0276-7333/85/2304-1682$01.50/0