

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  $[\text{GaCl}_3]_2$  to  $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$  to  $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$ , 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  $\text{Ga}_2\text{Cl}_2$  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  $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$  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  $\text{Ga}(\text{C}_5\text{H}_5)_3$ <sup>1</sup> (2.05 [3] Å),  $\text{Ga}(\text{C}_6\text{H}_5)_3$ <sup>16</sup> (1.947 [1] Å),  $\text{MeGa}(\text{O}_2\text{CMe})_2$ <sup>17</sup> (1.946 Å),  $\text{Me}_2\text{GaN}_2\text{C}_5\text{H}_7$ <sup>18</sup> (1.995 and 1.969 Å), and  $\text{KGa}(\text{CH}_2\text{SiMe}_3)_3\text{H}$ <sup>19</sup> (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.

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**Registry No.**  $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$ , 97210-83-8;  $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ , 97210-84-9;  $\text{GaCl}_3$ , 13450-90-3;  $\text{LiC}_5\text{Me}_5$ , 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  $[\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}]_2$ , respectively, and Tables IX-S and XI-S, showing anisotropic thermal parameters for all non-hydrogen atoms and the calculated structure factor amplitudes for  $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ , 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- $\eta^5\text{-C}_5\text{Me}_5$ Derivatives

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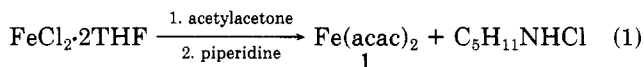
Received March 26, 1985

**Summary:** The reactions between  $\text{M}(\text{acac})_2$  ( $\text{M} = \text{Fe}, \text{Co}$ , and  $\text{Ni}$ ;  $\text{acac} = \text{acetylacetonate}$ ) and 1 mol of  $\text{LiC}_5\text{Me}_5$  cleanly yield  $(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{acac})$  (**2**,  $\text{M} = \text{Fe}$ ; **6**,  $\text{M} = \text{Co}$ ; **7**,  $\text{M} = \text{Ni}$ ). **2** reacts with  $\text{CO}$  to give  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})(\text{acac})$  (**3**) with methylmagnesium iodide under  $\text{CO}$  to give  $(\eta\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{CH}_3$  (**4**) and with benzene- $\text{AlCl}_3$  followed by  $\text{NH}_4\text{PF}_6$  to give  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\eta^6\text{-C}_6\text{H}_6)]^+\text{PF}_6^-$  (**5**). **2**, **6**, and **7** react with  $\text{NaC}_5\text{H}_5$  to give  $(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^5\text{-C}_5\text{H}_5)$  (**10**,  $\text{M} = \text{Fe}$ ; **11**,  $\text{M} = \text{Co}$ ; **12**,  $\text{M} = \text{Ni}$ ) 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  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_2\text{Me}_2\text{-}p\text{-C}_6\text{H}_4\text{Br})$  (**15**) and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\eta^5\text{-C}_5\text{Me}_4\text{-}p\text{-C}_6\text{H}_4\text{Br})$  (**16**).

The first-row transition-metal organometallic chemistry generally starts with the binary metal carbonyls. Non-carbonyl 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  $(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{acac})$ , essential materials for the synthesis of a variety of mono- $\eta^5\text{-C}_5\text{Me}_5$  derivatives.

We find that a convenient procedure to the known  $\text{Fe}(\text{acac})_2$ <sup>1</sup> consists of adding stoichiometric<sup>2</sup> amounts of acetylacetonate and piperidine to an ether slurry of the easily available complex  $\text{FeCl}_2 \cdot 2\text{THF}$ <sup>3</sup> ( $\text{THF} = \text{tetrahydrofuran}$ ) 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.



Whereas the reaction of  $\text{FeCl}_2 \cdot 2\text{THF}$  with 1 equiv of  $\text{C}_5\text{Me}_5\text{Li}$  in THF yields only  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}$ ,<sup>4</sup> under all conditions examined,  $\text{Fe}(\text{acac})_2$  reacts cleanly to afford  $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{acac})$  (**2**) (eq 2).

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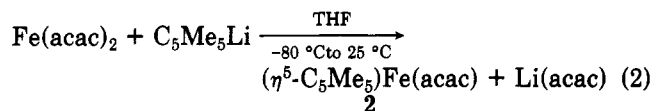
(1) Buckingham, D. A.; Gorges, R. C.; Henry, J. T. *Aust. J. Chem.* 1967, 20, 281.

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

(3) Herzog, S.; Gustav, K.; Kruger, E.; Oberender, H.; Schuster, R. Z. *Chem.* 1963, 428.

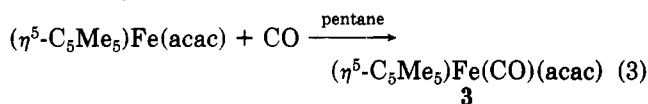
(4) King, R. B.; Bisnett, M. B. *J. Organomet. Chem.* 1967, 8, 287.

<sup>†</sup> Comision Chilena de Energia Nuclear.



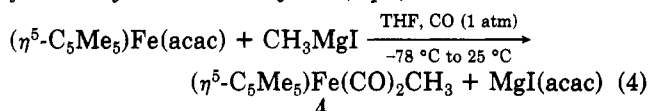
Solutions of **2** in THF are very air sensitive but thermally stable at room temperature. Although **2** has not been isolated, it has been characterized in solution through the following reactions.

Red-orange pentane solutions of **2** rapidly absorb carbon monoxide to afford brown  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}(\text{CO})(\text{acac})$  **3**<sup>5</sup> (eq 3) in 25% yield. Sublimation of the residue obtained upon

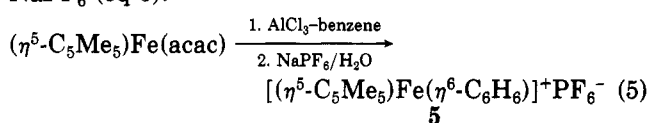


removal of solvent "in vacuo" gives **3** as nearly black, air-sensitive, analytically pure crystals with  $\nu_{\text{CO}}$  at 1930  $\text{cm}^{-1}$  (Nujol).

Similarly solutions of **2** in THF react with  $\text{CH}_3\text{MgI}$  at  $-78 ^\circ\text{C}$  under carbon monoxide (1 atm) followed by warming to  $25 ^\circ\text{C}$  to give  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}(\text{CO})_2\text{CH}_3$  (**4**)<sup>5,6</sup> as yellow crystals in 60% yield (eq 4).



If THF is removed in vacuo from the solution of **2**, prepared as above (eq 2), extraction with pentane to remove insoluble  $\text{Li}(\text{acac})$  and removal of pentane "in vacuo" followed by addition of benzene and  $\text{AlCl}_3$  (3 mol/mol of iron) immediately give  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}(\eta^6\text{-C}_6\text{H}_6)]^+\text{PF}_6^-$  (**5**)<sup>7</sup> in 60% yield after hydrolysis and the usual workup with  $\text{NaPF}_6$  (eq 5).



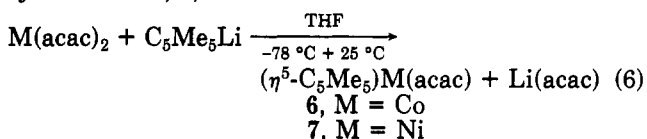
Investigations are underway to determine the exact structure of the intermediate **2**.

(5) **3**:  $\nu_{\text{max}}$  (Nujol) 1930, 1580, 1513  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 90 MHz)  $\delta$  1.38 (15 H, s), 1.64 (6 H, s), 4.9 (1 H, s); mass spectra,  $M^+ = 318$ , calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Fe}$   $M^+ = 318$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Fe}$ : C, 60.4; H, 6.97. Found: C, 60.8; H, 6.73. **4**:  $\nu_{\text{max}}$  (Nujol) 1930, 1985  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 90 MHz)  $\delta$  1.40 (15 H, s), 0.05 (3 H, s); mass spectra,  $M^+ = 262$ , calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Fe}$   $M^+ = 262$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Fe}$ : C, 59.56; H, 6.92. Found: C, 59.37; H, 7.01. **6**:  $\nu_{\text{max}}$  (Nujol) 1600, 1515  $\text{cm}^{-1}$ ; mass spectra,  $M^+ = 293$ , calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Co}$   $M^+ = 293$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Co}$ : C, 61.43; H, 7.56. Found: C, 61.43; H, 7.51. **7**:  $\nu_{\text{max}}$  (Nujol) 1570, 1515  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 90 MHz)  $\delta$  64.2 (15 H, br s), -2.1 (6 H, s), -10 (1 H, s); mass spectra,  $M^+ = 293$ , calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Ni}$   $M^+ = 293$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Ni}$ : C, 61.55; H, 7.55. Found: C, 61.25; H, 7.60. **8**:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 90 MHz)  $\delta$  -1.50 (6 H, s), 1.32 (30 H, s);  $\nu_{\text{max}}$  (Nujol) 1850  $\text{cm}^{-1}$ . **9**:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 90 MHz)  $\delta$  0.04 (3 H, s), 1.60 (15 H, s);  $\nu_{\text{max}}$  (neat) 2000  $\text{cm}^{-1}$ . **10**:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ , 90 MHz)  $\delta$  1.87 (15 H, s), 3.52 (5 H, s); mass spectra,  $M^+ = 256$ , calcd for  $\text{C}_{15}\text{H}_{20}\text{Fe}$   $M^+ = 256$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{20}\text{Fe}$ : C, 70.33; H, 7.87. Found: C, 70.51; H, 7.79. **13**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  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  $\text{C}_{13}\text{H}_{13}\text{Br}$   $M^+ = 249$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{13}\text{Br}$ : C, 62.07; H, 5.26. Found: C, 62.39; H, 5.49. **14**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  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  $\text{C}_{15}\text{H}_{17}\text{Br}$   $M^+ = 277$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{17}\text{Br}$ : C, 64.99; H, 6.18. Found: C, 65.20; H, 6.22. **15**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  1.532 (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  $\text{C}_{23}\text{H}_{27}\text{BrFe}$   $M^+ = 439$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{27}\text{BrFe}$ : C, 62.89; H, 6.19. Found: C, 62.49; H, 6.13. **16**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz)  $\delta$  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  $\text{C}_{25}\text{H}_{31}\text{BrFe}$   $M^+ = 467$ . Anal. Calcd for  $\text{C}_{25}\text{H}_{31}\text{BrFe}$ : C, 64.26; H, 6.79. Found: C, 64.26; H, 6.79.

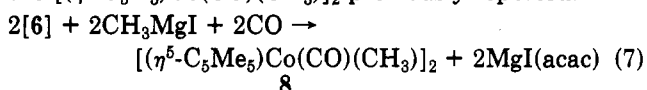
(6) Catheline, D.; Astruc, D. *Organometallics* 1984, 3, 1094.

(7) Hamon, J. R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* 1981, 103, 758.

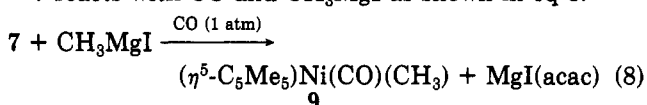
Brown  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Co}(\text{acac})$ , **6**,<sup>5</sup> and dark red  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ni}(\text{acac})$ , **7**,<sup>5</sup> are prepared as **2** in 60–70% yield after crystallization from pentane (or sublimation at  $100 ^\circ\text{C}$  ( $10^{-3}$  torr)) and give satisfactory elemental analysis. A crucial point is that  $\text{C}_5\text{Me}_5\text{H}$  must be very pure to perform the synthesis of **2**, **6**, and **7**.



**6** reacts with a stoichiometric amount of CO and  $\text{CH}_3\text{-MgI}$  to give the green crystalline dimer **8**<sup>5</sup> ( $\nu_{\text{CO}}$  1850  $\text{cm}^{-1}$  (Nujol)), as shown in eq 7. Compound **8** is analogous to the  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}(\text{CO})(\text{CH}_3)]_2$  previously reported.<sup>8</sup>

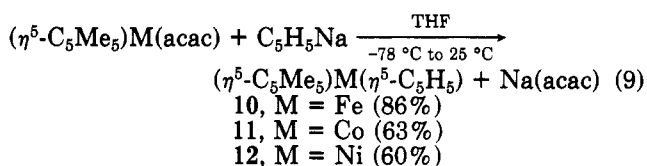


**7** reacts with CO and  $\text{CH}_3\text{MgI}$  as shown in eq 8.

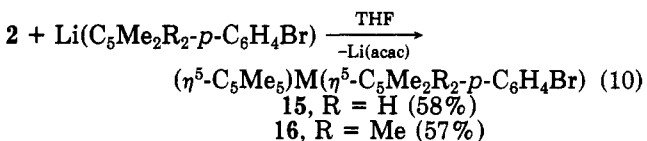


Compound **9**<sup>5</sup> is isolated as a volatile and thermally unstable violet liquid ( $\nu_{\text{CO}}$  2000  $\text{cm}^{-1}$  (neat)). Details of these reactions will be reported in the full paper.

**2**, **6**, and **7** react with  $\text{C}_5\text{H}_5\text{Na}$  in THF to give the mixed metallocenes  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{M}(\eta^5\text{-C}_5\text{H}_5)$  (M = Fe,<sup>5</sup> Co,<sup>9</sup> Ni<sup>10</sup>) in excellent yields after removal of  $\text{Na}(\text{acac})$  by extraction of the residue with pentane and crystallization (eq 9). Spectroscopic and analytical data are in accord with literature values.



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**)<sup>11</sup> and 1-(*p*-bromophenyl)-2,3,4,5-tetramethylcyclopentadiene (**14**)<sup>12</sup> react with **2** (eq 10) to give the new complexes **15**<sup>5</sup> and **16**<sup>5</sup> obtained in 57–58% yields after recrystallization in ethanol and pentane, respectively.



(8) Schore, N. E.; Iienda, C. S.; White, M. A.; Bryndza, H. E.; Maturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* 1984, 106, 7451.

(9) Kolle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 131.

(10) Werner, H.; Dernberger, Th. *J. Organomet. Chem.* 1980, 198, 97.

(11) **11**: to a solution of *p*- $\text{C}_6\text{H}_4\text{BrLi}$  prepared from *p*- $\text{C}_6\text{H}_4\text{Br}_2$  (131 mmol) in 130 mL of ether) and *n*-BuLi in hexanes (131 mmol) was added slowly 3,4-dimethylcyclopent-2-en-1-one<sup>13</sup> (132 mmol in 20 mL of ether). The mixture was stirred for 1 h and then hydrolyzed with saturated  $\text{NH}_4\text{Cl}$  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  $\text{NaHCO}_3$  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<sup>14</sup> (131 mmol). The product was recrystallized from chloroform giving 16.6 g of **12** as yellow crystals (45.7%).

(13) Conia, J. M.; Lerivenend, M. L. *Bull. Soc. Chim. Fr.* 1970, 2981.

(14) deVries, L. *J. Org. Chem.* 1960, 25, 1838.

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 wish 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 promoter for substitution of chloride in  $[Fe(\eta^5-C_5H_5)(CO)_2CH_2Cl]$  and  $[Mo(\eta^5-C_5H_5)(CO)_3CH_2Cl]$  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.<sup>1</sup> 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) ( $Cp = \eta^5-C_5H_5$ ), fail to give any halide substitution product at all.<sup>1a</sup> Attempts in our laboratory to substitute A with either  $HNEt_2$  or  $NEt_3$  were unsuccessful.<sup>2</sup> 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<sup>lf</sup> or B<sup>3</sup> (3–5 mmol in 25 mL) and 1–5 equiv of nucleophile at room temperature.<sup>4,5</sup> 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.<sup>6</sup> Workup involved filtration to remove thallium salts, concentration, and addition of hexane to crystallize the products.<sup>7</sup> Characterization of the new compounds in Table I on the basis of IR and NMR spectral data and elemental analyses<sup>8</sup> 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.<sup>1a</sup> The other known complexes 5<sup>9a</sup> and 6<sup>9b</sup> were prepared by an alternative route, as was the methyl analogue of 2.<sup>10</sup> 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  $[FeCp(CO)_2CH_2OEt]^{lf}$  and  $[FeCp(CO)_2CH_2OC(O)CH_3]^{lf}$  are the only detectable carbonyl containing species present.

(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.

(3) King, R. B.; Braitsch, D. M. *J. Organomet. Chem.* 1973, 54, 9.

(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 <sup>1</sup>H NMR spectra) iron carbonyl product. After 16 h the  $PMe_2Ph$  reaction contained a white precipitate that was identified as  $[PhPMe_2]Cl$  based on its <sup>1</sup>H NMR spectrum (Knoll, L. *J. Organomet. Chem.* 1979, 182, 77). Most of the A had reacted to give a monocarbonyl species which was probably  $[FeCp(CO)(PMe_2Ph)_2]^+$  [ $\nu_{CO}$  1966  $cm^{-1}$  (lit.,<sup>1a</sup>  $\nu_{CO}$  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 <sup>1</sup>H 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.

(1) Substitution in  $[FeCp(CO)_2CH_2X]$ : (a) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* 1983, 105, 5926. (b) Jensen, J. E.; Campbell, L. L.; Nakanishi, S.; Flood, T. C. *J. Organomet. Chem.* 1983, 244, 61. (c) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* 1976, 15, 1910. (d) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *J. Chem. Soc., Chem. Commun.* 1975, 336. (e) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* 1974, 72, C7. (f) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* 1967, 1508. Substitutions in  $[FeCp(CO)_2CH_2Cl]$  and  $[W(Cp)(CO)_3CH_2Cl]$  and attempted substitution in  $[MoCp(CO)_3CH_2Cl]$ ,  $[RuCp(CO)_2CH_2Cl]$ , and  $[M(CO)_5CH_2Cl]$  (M = Mn, Re): (g) Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* 1983, 1495. Substitutions in  $[PtL_2(CH_2X)(X)]$  (L = tertiary phosphine): (h) Engelter, C.; Moss, J. R.; Niven, M. L.; Nassimbeni, L. R.; Reid, G. *J. Organomet. Chem.* 1982, 232, C78. (i) Kermod, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Organomet. Chem.* 1982, 228, C71. (j) Kermod, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* 1981, 698. (k) Scherer, O. J.; Jungmann, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1981, 36B, 1663. Substitutions in  $[RhCp(L)_2CH_2I]^+$  (L = tertiary phosphine) and  $[RhCp(PMe_3)(CH_2I)(I)]$ : (l) Paul, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 316. (m) Werner, H.; Hofmann, L.; Paul, W. *J. Organomet. Chem.* 1982, 236, C65. (n) Werner, H.; Feser, R.; Paul, W.; Hofmann, L. *J. Organomet. Chem.* 1981, 219, C29. (o) Feser, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 940. Reduction of  $[Os(CH_2I)(CO)_2(PPh_3)_2]$  by  $BH_3^-$ : (p) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* 1980, 198, C7.  $\alpha$ -Halide exchange in a number of perfluoroalkyls: (q) Richmond, T. G.; Shriver, D. F. *Organometallics* 1984, 3, 305.