Formation and Reactivity of Halogen Derivatives of (η^5-Cyclopentadienyl)thallium

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Reactions of chloro-, bromo-, or iodocyclopentadiene, generated in ethyl ether solution from cyclopentadienylthallium and *N*-halosuccinimides or iodine, with thallous ethoxide has afforded the respective (halocyclopentadienyl)thallium compounds in 72–96% yield. (Chlorocyclopentadienyl)thallium can also be formed in good yield from chlorocyclopentadiene, thallium(I) chloride, and potassium hydroxide in aqueous solution. These new reagents have served as convenient intermediates in the formation of the following compounds: $(\eta^5\text{-}C_5H_4X)_2Fe$ (X = Cl, Br); $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Cl)TiCl_2$; $(\eta^5\text{-}C_5H_4Cl)_2TiCl_2$; $(\eta^5\text{-}C_5H_4X)Mn(CO)_3$ (X = Cl, Br); $(\eta^5\text{-}C_5H_4X)Co(CO)_2$ (X = Cl, Br, I); $(\eta^5\text{-}C_5H_4Cl)Rh(CO)_2$; $(\eta^5\text{-}C_5H_4Cl)_2Ni$; and $(\eta^5\text{-}C_5H_4Cl)\text{-}Cu[P(C_2H_5)_3]$. A reaction between $(\eta^5\text{-}C_5H_4Br)Co(CO)_2$ and *n*-butyllithium in ethyl ether solution at −78 °C has generated $(\eta^5\text{-}C_5H_4Li)Co(CO)_2$, which reacts with carbon dioxide and with acetone to produce $(\eta^5\text{-}C_5H_4CO_2H)Co(CO)_2$ and $[\eta^5\text{-}C_5H_4C(CH_3)_2OH]Co(CO)_2$, respectively.

Introduction

η^5-Cyclopentadienyl derivatives of the transition metals represent the largest and most important class of organotransition-metal compounds at the present time, yet until very recently (η^5-cyclopentadienyl)metal compounds that contain reactive functional substituents were limited to the metalloaromatic compounds ferrocene [$(\eta^5\text{-}C_5H_5)_2Fe$], cymantrene [$(\eta^5\text{-}C_5H_5)Mn(CO)_3$], [$(\eta^5\text{-}C_5H_5)\text{-}Cr(CO)_2NO$], $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Ph_4)$, and a few analogues.[1–7] We have described a convenient and general route to (η^5-cyclopentadienyl)metal compounds which contain acyl substituents.[8] Routes to (η^5-cyclopentadienyl)metal compounds that contain halogen substituents were also desirable, since halogen derivatives of ferrocene have played a significant role in the development of ferrocene chemistry, including routes to ferrocenyllithium and ferrocenyl Grignard reagents, biferrocene and polyferrocenes, ferrocenyl ethers, esters, amines, sulfides, nitriles, etc.[1,2,4,9,10] Even the haloferrocenes must be prepared by indirect means, since ferrocene is oxidized under the conditions required for normal electrophilic aromatic halogenation.[1,2,4811,12] Besides the haloferrocenes, η^5-cyclopentadienyl derivatives of the transition metals that contain halogen substituents are presently limited to the halocymantrenes and rhenium analogues,[13–18] haloruthenocenes,[19,20] (η^5-iodocyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt,[6] and a few compounds of rhodium, rhenium, and iron derived from insertion of diazocyclopentadiene and phenylated derivatives into appropriate metal–halogen bonds.[18,21,22]

In this paper, we report a convenient, high-yield synthetic route to the halocyclopentadienylthallium compounds $(C_5H_4X)Tl$ (X = Cl, Br, I) and describe some reactions of these new reagents which demonstrate their general utility in the formation of many other (η^5-cyclopentadienyl)metal derivatives containing halogen substituents.

Results and Discussion

Formation and Properties of (Halocyclopentadienyl)thallium Compounds (5–7). Cyclopentadienylthallium (1) has long played a key role in the formation of η^5-cyclopentadienyl derivatives of the transition metals, since the initial reports of its synthetic applicability in the 1960s by Nesmeyanov et al.[23] and by Hunt and Doyle.[24] In addition to reactions with many transition-metal halides, 1 has found utility in the formation of cyclopentadienyl derivatives of mercury,[23] germanium,[25] tin,[26] actinide metals,[27–31] phosphorus,[32–34] and

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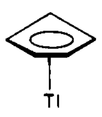
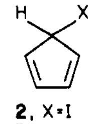
in organic synthesis.[35-42] Reagent 1 is an exceptionally useful intermediate, since it is readily available in nearly quantitative yield from reactions between thallous ion, potassium hydroxide, and cyclopentadiene under aqueous conditions,[24,43] reacts with metal halides, and is air stable for reasonable periods of time.

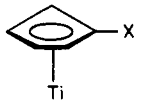
Breslow and co-workers have reported that 1 could be converted into iodocyclopentadiene (**2**) by reaction with iodine and into either chloro- (**3**) or bromocyclopentadiene (**4**) by by reactions with either *N*-chlorosuccinimide or *N*-bromosuccinimide, respectively.[36,37,44] Although the halocyclopentadienes **2**–**4** have not yet been isolated, they exhibit resonable stability in solution.[36-38] It therefore seemed reasonable that **2**–**4**, like cyclopentadiene itself, might react further with thallous ion to form halocyclopentadienylthallium compounds and that they might also undergo reactions similar to those of **1**.



1



2, X=I
3, X=Cl
4, X=Br



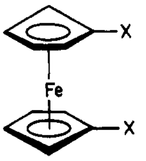
5, X=Cl
6, X=Br
7, X=I

Initial studies indicated that chlorocyclopentadiene (**3**), generated from **1** and *N*-chlorosuccinimide in ethyl ether solution, reacted readily with an aqueous mixture of thallium(I) chloride and potassium hydroxide to afford (chlorocyclopentadienyl)thallium (**5**) as a cream-colored powder in 74% yield. However, attempts to extend this approach to the synthesis of (bromocyclopentadienyl)thallium (**6**) and (iodocyclopentadienyl)thallium (**7**) were unsatisfactory, because **6** and **7** are appreciably more air sensitive than are **1** or **5**. When blending was carried out in the normal manner, **6** and **7** could be isolated only in very low yields as impure brown sludges.

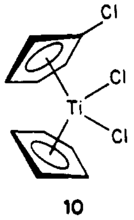
Subsequent studies showed that **5** could also be prepared conveniently in high purity and in 72% yield by a reaction of **3** in ethyl ether solution with thallous ethoxide conducted in a nitrogen atmosphere. This method was successfully extended to the bromo and iodo analogues. Thus, (bromocyclopentadienyl)thallium (**6**) was produced in 96% yield as a cream solid in high purity, whereas an analogous reaction of **2** with thallous ethoxide afforded (iodocyclopentadienyl)thallium (**7**) in 89% yield as a light yellow solid which was invariably contaminated with very small amounts of **1**. Compounds **5**–**7**, like **1**, are difficultly soluble in most common organic solvents, although they are slightly soluble in THF and in dimethyl sulfoxide. The ^{1}H NMR spectra of **5**–**7** in Me_2SO-d_6 exhibit two sets of apparent triplets representing the $H_{3,4}$ and $H_{2,5}$ protons of the substituted cyclopentadienyl rings. The order of deshielding for both sets of resonances is **7** > **6** > **5**. The IR spectra of **5**–**7** exhibit the usual bands expected for an η^5-cyclopentadienyl ring. The mass spectra of **5**–**7** exhibit molecular ion peaks, and the isotopic pattern was that expected for thallium and halogen in each case.

Chloro derivative **5** is slightly air sensitive and can be handled in air for short periods of time, while **6** and **7** are very air sensitive. Likewise, **5** can be vacuum sublimed as can **1**, whereas both **6** and **7** undergo extensive decomposition under sublimation conditions.

Reactions of (Halocyclopentadienyl)thallium Compounds (5–7) with Transition-Metal Halides. Our initial investigations concerning the potential synthetic utility of **5**–**7** involved formation of the 1,1′-dihaloferrocenes, since these compounds have previously been well characterized by us.[12] Reactions of 2 equiv of either **5** or **6** with ferrous chloride in benzene at reflux afforded 1,1′-dichloroferrocene (**8**) and 1,1′-dibromoferrocene (**9**)) in yields of 90% and 50%, respectively. Both products were identical with authentic samples of **8** and **9**.



8, X=Cl
9, X=Br



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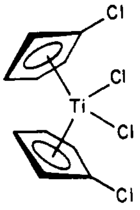

11

In view of the wide-spread utility of titanocene dichloride in organometallic chemistry and catalysis,[45] routes to halogenated derivatives were investigated. A reaction between **5** and (η^5-C_5H_5)$TiCl_3$ in refluxing THF generated 1-chlorotitanocene dichloride (**10**) in 82% yield. The ^{1}H NMR sppectrum of **10** (THF) contained two sharp *singlets* at δ 6.69 and 6.55. Integration indicated that the lower field resonance was due to the unsubstituted cyclopentadienyl ring protons, while the higher field peak represented the four protons of the substituted cyclopentadienyl ring. This assignment was further supported by the ^{1}H NMR spectrum of 1,1′-dichlorotitanocene dichloride (**11**) (vide infra), which exhibited a single sharp peak that was shifted upfield from the resonance for titanocene dichloride itself.[46]

1,1′-Dichlorotitanocene dichloride (**11**) could be prepared in 56% yield by a reaction between 2 equiv of **5** and titanium tetrachloride in refluxing benzene. The ^{1}H NMR spectrum of **11** in THF exhibited a sharp singlet for the cyclopentadienyl ring protons. The base peak in the mass spectrum of **11** corresponded to loss of one ring from the molecular ion, i.e., $(M - C_5H_4Cl)^+$. The remaining major peaks were atttributable to the molecular ion (M^+), $(M - Cl)^+$, $(M - C_5H_4Cl_2)^+$, $(TiCl_3)^+$, and $(C_5H_4Cl)^+$.

Reactions of **5** or **6** with $Br(CO)_5Mn$ in refluxing benzene or THF produced chlorocymantrene (**12**) and bromocymantrene (**13**) in yields of 77% and 30%, respectively.

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(44) We have also observed that **2** can be formed from reactions between **1** and either *N*-iodosuccinimide or iodine monochloride in ethyl ether solution, and can subsequently be converted into **7**. However, the reaction between **1** and I_2 followed by treatment with TlOEt is more satisfactory.

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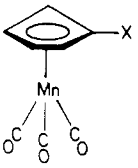
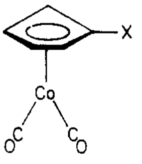
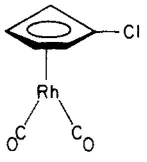
(46) The reason why the $H_{2,5}$ and $H_{3,4}$ protons of the substituted rings of **10** and **11** are coincidentally equivalent and appear as a singlet is not clear at the present time, although it is not necessarily a solvent effect. Thus, while **10** is only very slightly soluble in $CDCl_3$, the ^{1}H NMR spectrum of **10** in this solvent likewise revealed two singlets, integrating in a ratio of 5:4. Additional studies concerning the spectra of these compounds are in progress.

The products were isolated as yellow solids, and their ^{1}H NMR and IR spectra were identical with those previously reported.[15,18] These reactions are a convenient alternative route to halogenated cymantrenes.[47]


12, X=Cl
13, X=Br

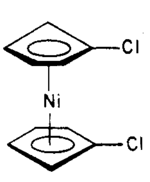

14, X=Cl
15, X=Br
16, X=I


17

Our previoius studies have shown that I_2 reacts with an equimolar amount of $Co_2(CO)_8$ in THF solution at room temperature with vigorous evolution of carbon monoxide and immediate formation of a deep green solution attributed to an iodocarbonylcobalt intermediate.[48] Reactions of the latter with (acylcyclopentadienyl)sodium reagents provided (η^5-acylcyclopentadienyl)dicarbonylcobalt complexes.[8,48] In a similar manner, all three (halocyclopentadienyl)thallium reagents **5–7** react with $Co_2(CO)_8$ + I_2 in THF solution to afford the respective (η^5-halocyclopentadienyl)dicarbonylcobalt complexes (**14–16**). Both **14** and **15** were obtained as deep red liquids in moderate yields and could be purified by column chromatography followed by vacuum distillation. The iodo complex **16**, however, was obtained in only 12% yield and was contaminated with (η^5-C_5H_5)Co(CO)$_2$ as evidenced by ^{1}H NMR analysis. Halogen derivatives **14–16** are best stored below −20 °C under an inert atmosphere. The ^{1}H NMR spectra of **14–16** in C_6D_6 each exhibited a pair of apparent triplets due to the $H_{3,4}$ and $H_{2,5}$ protons. The IR spectra contained two strong bands in the terminal metal carbonyl region which are characteristic of complexes of this type. The mass spectrum of **15** contained a molecular ion as well as a base peak at $(M - 2CO)^+$.

In a manner analogous to the formation of (η^5-C_5H_5)-Rh(CO)$_2$,[49] a reaction between 2 equiv of **6** and $[Rh(CO)_2Cl]_2$ in THF at 25 °C gave (η^5-chlorocyclopentadienyl)dicarbonylrhodium (**17**) as a gold-yellow liquid in 68% yield. The ^{1}H NMR spectrum of **17** exhibited an upfield multiplet for the $H_{3,4}$ protons and a lower field triplet for the $H_{2,5}$ protons. The splitting pattern is analogous to that observed for other substituted (η^5-cyclopentadienyl)dicarbonylrhodium complexes which contain electron-withdrawing substituents, in which the $H_{3,4}$ proton resonance is indicative of further coupling of these protons with the nucleus.[50,51] The IR spectrum of **17** contained two terminal carbonyl bands, whereas the mass spectrum exhibited a molecular ion as well as major peaks for the losses of one and two carbonyl substituents, respectively.

The utility of the (halocyclopentadienyl)thallium reagents **5–7** in the formation of substituted metallocenes is demonstrated by the reaction of **6** with $NiBr_2 \cdot 2DME$ to afford 1,1′-dichloronickelocene (**18**) in 49% yield. Compound **18** is relatively stable thermally and does not decompose below 100 °C under nitrogen. It is only slightly air-sensitive and is soluble in most organic solvents.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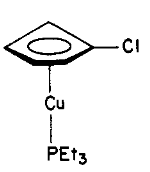
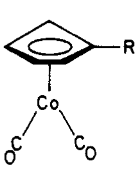

19


20, R=Li
21, R=COOH
22, R=C(CH$_3$)$_2$OH

Cyclopentadienylthallium (**1**) has previously been shown to be a valuable intermediate in the formation of (η^5-cyclopentadienyl)copper complexes.[52,53] A reaction between **5** and $[(PEt_3)CuCl]_4$ produced the first halogen-substituted derivative (η^5-chlorocyclopentadienyl)(triethylphosphine)copper (**19**) as a very air-sensitive solid in 81% yield. The ^{1}H NMR spectrum of **19** contained two apparent triplets due to the $H_{2,5}$ and $H_{3,4}$ protons as well as a multiplet for the coordinated phosphine substituent.

Reactions of (η^5-Bromocyclopentadienyl)dicarbonylcobalt (15). A wide variety of new halogen-substituted (η^5-cyclopentadienyl)transition-metal compounds are readily available through reactions of **5–7**. Further transformations of these derivatives should open up many possibilities in organic and organometallic syntheses. One example is provided by conversions of halogenated derivatives to organolithium intermediates which have been heretofor unavailable by other means.

As has been reported by Hedberg and Rosenberg,[54] the most satisfactory route to lithioferrocene is via the addition of *n*-butyllithium to bromo- or iodoferrocene at −78 °C. In an analogous fashion, (η^5-lithiocyclopentadienyl)dicarbonylcobalt (**20**) was prepared by the dropwise addition of *n*-butyllithium to a solution of **15** in ethyl ether at −78 °C. The reaction evidently goes rapidly to completion, since **15** could not be recovered from any reactions in which **20** was generated. Organolithium intermediate **20** is very unstable in solution, since even at −78 °C it darkens rapidly with concurrent formation of an insoluble black residue. The yields of subsequent products are appreciably lowered if the electrophile is not added within 5 min after completion of the halogen–lithium exchange reaction.

Reactions of **20** proceeded normally when conducted at low temperatures. Thus, carbonation of **20** followed by hydrolysis produced (η^5-carboxycyclopentadienyl)dicarbonylcobalt (**21**) in 56% yield, while a reaction with acetone afforded (η^5-1-methyl-1-(hydroxyethyl)cyclopentadienyl)dicarbonylcobalt (**22**) in 42% yield. Both compounds were shown to be identical with authentic samples prepared by reactions of (η^5-$C_5H_4CO_2CH_3$)Co(CO)$_2$ and [η^5-$C_5H_4C(O)CH_3$]Co(CO)$_2$, respectively.[8,48] From each reaction, small amounts of the hydrogenolysis product (η^5-C_5H_5)Co(CO)$_2$ could also be isolated.

Additional investigations of the formation of halogen-substituted cyclopentadienylmetal compounds of both transition and main-group metals are underway, as are studies on their reactivity and synthetic utility.

Experimental Section

All operations were carried out under a nitrogen atmosphere using Schlenk tube techniques except where specified. The nitrogen was deoxygenated with BTS catalyst and dried with H_2SO_4 and P_2O_5. Infrared spectra were recorded on either a Beckman IR-10 or a Perkin-Elmer 237B spectrophotometer. Solid samples were prepared as KBr pellets and liquid samples were prepared as liquid films on NaCl plates. ^{1}H NMR spectra were recorded on a Varian A-60 NMR spectrometer. Mass spectra were recorded

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on a Perkin-Elmer-Hitachi RMU 6L mass spectrometer. Melting points were obtained in sealed capillaries under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA 01003. Chromatography columns were packed dry under nitrogen, using 5% deactivated and deoxygenated Alfa-Ventron neutral alumina. Benzene, pentane, toluene, and methylene chloride were dried over CaH_2 and the distilled under argon. Ethyl ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were predried over sodium and distilled under argon from sodium–benzophenone. Benzene-d_6 and Me_2SO-d_6 were deoxygenated by three freeze–thaw cycles prior to use. Thallous ethoxide and dicobalt octacarbonyl were obtained from the Aldrich Chemical Co. and Strem Chemicals, Inc., respectively. (η^5-C_5H_5)$TiCl_3$,[55] C_5H_5Tl (1),[24] and $Mn(CO)_5Br$[56] were prepared by published procedures.

(Chlorocyclopentadienyl)thallium (5). Method A. Cyclopentadienylthallium (6.80 g, 25.2 mmol), *N*-chlorosuccinimide (3.36 g, 25.2 mmol), and 250 mL of ethyl ether were combined in a nitrogen-purged, 500-mL Schlenk flask equipped with a nitrogen sidearm inlet and a magnetic stirrer. The flask was immersed in an ice bath, and the reactants were stirred for 1 h. The resulting solution of chlorocyclopentadiene (**3**) was filtered through a glass wool plug on a glass frit. To the filtrate was added 3.14 g of thallous ethoxide (0.89 mL, 12.6 mmol). Formation of a flocculent, cream solid occurred rapidly. The solid was collected by filtration on a glass frit, washed with 2 × 20 mL of ether, and subsequently dried to give 2.75 g (72%) of **5**. An analytical sample, mp 140–142 °C (N_2), could be prepared by sublimation of the product at 95 °C (10^{-2} torr): NMR (Me_2SO-d_6) δ 5.76 (t, 2 H, $H_{2,5}$), 5.52 (t, 2 H, $H_{3,4}$); IR (KBr) 1720–1470 (br, w), 1430 (m), 1400 (m), 1350 (m), 1210 (w), 1160 (m), 1020 (m), 880 (m), 800 (s) cm^{-1}. MS, *m/e* 304 (M^+). Anal. Calcd for C_5H_4ClTl: C, 19.76; H, 1.33. Found: C, 19.73; H, 1.44.

Method B. A solution of chlorocyclopentadiene (**3**) in ethyl ether was prepared from cyclopentadienylthallium, *N*-chlorosuccinimide, and ethyl ether under conditions identical with those described in method A. The solution was filtered as above, and the filtrate was added to a 900-mL blender which contained 10.0 g of potassium hydroxide, 1.5 g (6.3 mmol) of thallous chloride, and 200 mL of water. The mixture was blended at high speed for 2 min, producing a flocculent precipitate. The solid was filtered through a glass frit, washed with 2 × 15 mL of water followed by 2 × 20 mL of absolute ethanol, and dried in vacuo to give 1.32 g (69%) of **5** as a cream powder.

(Bromocyclopentadienyl)thallium (6). Into a nitrogen-purged, 250-mL round-bottom flask equipped with a nitrogen inlet and a magnetic stirrer were placed 6.80 g (25.2 mmol) of cyclopentadienylthallium, 4.48 g (25.2 mmol) of *N*-bromosuccinimide, and 250 mL of ethyl ether. The flask was immersed in an ice bath, and the reactants were stirred at 0 °C for 1 h. The resulting solution of bromocyclopentadiene (**4**) was filtered through a glass wool plug on a glass frit. Dropwise addition of 3.52 g (1.00 mL, 14.1 mmol) of thallous ethoxide to the stirred filtrate at 0 °C resulted in rapid formation of a flocculent precipitate. The solid was collected by filtration on a glass frit and washed with 2 × 20 mL of ether. Subsequent drying of the product in vacuo produced 4.73 g (96%) of **6** as a cream solid. An analytical sample, decomp pt 130 °C (N_2), could be prepared by sublimation of the product at 85 °C (10^{-2} torr): NMR (Me_2SO-d_6) δ 5.83 (t, 2 H, $H_{2,5}$), 5.61 (t, 2 H, $H_{3,4}$); IR (KBr) 1665–1525 (br s), 1425 (w), 1360–1330 (br m), 1300 (m), 1240 (m), 1010 (w), 905 (w), 790 (m), 725 (s) cm^{-1}; MS, *m/e* 348 (M^+). Anal. Calcd for C_5H_4BrTl: C, 17.25; H, 1.16. Found: C, 17.51; H, 1.28.

(Iodocyclopentadienyl)thallium (7). A nitrogen-purged, 500-mL round-bottom flask fitted with nitrogen inlet, magnetic stirrer, and pressure-equalizing dropping funnel was immersed in an ice bath and charged with 50 mL of ethyl ether and 4.00 g (14.8 mmol) of cyclopentadienylthallium. Into the dropping funnel was placed a solution of 3.60 g (14.2 mmol) of iodine dissolved in 200 mL of ethyl ether. The iodine solution was then added dropwise to the stirred suspension of C_5H_5Tl over a 20-min period, and stirring was continued for an additional 40 min. The solution of iodocyclopentadiene (**2**) was subsequently filtered under nitrogen through a glass wool plug on a glass frit. Dropwise addition of 1.00 mL (3.52 g, 14.1 mmol) of thallous ethoxide to the stirred filtrate resulted in the immediate formation of a large amount of flocculent precipitate. The suspension was filtered, washed with 2 × 25 mL of ether, and dried in vacuo to give 4.95 g (89%) of **7** as a light yellow powder. The product was invariably contaminated with small amounts of C_5H_5Tl. Purification was best effected by vacuum sublimation at room temperature (to remove C_5H_5Tl), followed by sublimation of (iodocyclopentadienyl)thallium at 62 °C (10^{-2} torr). The product decomposes on heating over ca. 98 °C under nitrogen. NMR (Me_2SO-d_6) δ 5.90 (t, 2 H, $H_{2,5}$), 5.70 (t, 2 H, $H_{3,4}$); IR (KBr) 3100 (w), 2300 (m), 2080 (m), 1435 (w), 1345 (w), 1010 (br, m), 860 (m), 810 (s), 735 (vs) cm^{-1}; MS, *m/e* 396 (M^+). Anal. Calcd for C_5H_4ITl: C, 15.19; H, 1.02. Found: C, 15.58; H, 1.08.

(η^5-Chlorocyclopentadienyl)(η^5-cyclopentadienyl)dichlorotitanium (Chlorotitanocene Dichloride) (10). Into a nitrogen-purged 250-mL round-bottom flask equipped with a magnetic stirrer, reflux condenser, and mercury overpressure valve were added 2.19 g (10.0 mmol) of (η^5-cyclopentadienyl)trichlorotitanium, 3.04 g (10.0 mmol) of (chlorocyclopentadienyl)thallium, and 150 mL of THF. The reaction mixture was heated to reflux with stirring for 18 h, filtered through a glass frit, and concentrated to 10 mL under reduced pressure. Removal of the supernatant liquid by a pipet and drying of the residue in vacuo gave 2.32 g (82%) of **10** as red platelets. Vacuum sublimation at 100 °C (10^{-2} torr) for 18 h removed traces of (η^5-C_5H_5)$TiCl_3$ from the product. Further sublimation at 125 °C (10^{-2} torr) for 48 h gave an analytical sample of **10** as a light orange powder, mp 218–222 °C dec. The product underwent extensive thermal degradation during sublimation: NMR (THF, external Me_4Si) δ 6.69 (s, 5 H, C_5H_5), 6.55 (s, 4 H, C_5H_4Cl); IR (KBr) 3580–3300 (br, m), 3130 (s), 2800 (w), 2655 (w), 2560 (w), 2525 (w), 2450 (w), 1845 (w), 1670 (w), 1450 (vs), 1415 (m), 1375 (m), 1330 (w), 1195 (m), 1040 (m), 1025 (m), 1010 (m), 890 (m), 870 (m), 840 (s), 820 (vs) cm^{-1}. Anal. Calcd for $C_{10}H_9Cl_3Ti$: C, 42.37; H, 3.20; Cl, 37.52. Found: C, 42.15; H, 3.33; Cl, 37.51.

Bis(η^5-chlorocyclopentadienyl)dichlorotitanium (1,1′-Dichlorotitanocene Dichloride) (11). (Chlorocyclopentadienyl)thallium (3.04 g, 10.0 mmol) and benzene (100 mL) were placed into a nitrogen-purged, 500-mL round-bottom flask equipped with a nitrogen inlet, magnetic stirrer, and mercury overpressure valve. Titanium tetrachloride (0.50 mL, 0.86 g, 4.5 mmol) was added dropwise via a pipette to the stirred suspension, and the reaction mixture was heated to reflux for 4 h. At the end of this period, the solution was cooled to room temperature and the solvent was removed under reduced pressure. Extraction of the residue with toluene for 18 h in a Soxhlet extractor followed by removal of the solvent in vacuo gave 0.18 g (57%) of **11** as a brick-red solid. Sublimation of the product at 135 °C (10^{-2} torr) resulted in extensive loss of material due to thermal decomposition, although an analytical sample of **11** was obtained as deep red needles: mp 254–256 °C dec; NMR (THF, external Me_4Si) δ 6.61 (s, 8 H, C_5H_4Cl); IR (KBr) 3110 (vs), 1442 (s), 1365 (m), 1190 (m), 1040 (m), 885 (s), 830 (vs), 595 (br, m) cm^{-1}. MS: *m/e* 316 (M^+). Anal. Calcd for $C_{10}H_8Cl_4Ti$: C, 37.78; H, 2.54; Cl, 44.61. Found: C, 37.70; H, 2.57; Cl, 44.65.

(η^5-Chlorocyclopentadienyl)tricarbonylmanganese (Chlorocymantrene) (12). Into a nitrogen-purged, 250-mL round-bottom flask equipped with a nitrogen inlet, reflux condenser, and mercury overpressure valve was added 0.55 g (2.0 mmol) of bromopentacarbonylmanganese and 125 mL of THF. To the resulting yellow solution was added 0.60 g (2.0 mmol) of (chlorocyclopentadienyl)thallium, and the reaction mixture was heated to reflux with stirring for 4 h. At the end of this period, the mixture was filtered through a glass frit and the solvent was removed under reduced pressure. Sublimation of the resulting oily residue at 30 °C (10^{-2} torr) produced 0.36 g (77%) of yellow crystalline **12**: mp 24–25 °C (lit.[18] mp 24–25 °C); NMR (CCl_4, internal Me_4Si) δ 4.60 (t, 2 H, $H_{2,5}$), 4.88 (t, 2 H, $H_{3,4}$); IR (film, NaCl plates) 3125 (m), 2020 (vs), 1940 (vs), 1430 (s), 1393 (m), 1365 (s), 1175 (s), 1050 (sh), 1020 (s), 880 (s), 825 (s), 658 (s), 623 (s), 600 (s) cm^{-1}.

(η^5-Bromocyclopentadienyl)tricarbonylmanganese (Bromocymantrene) (13). In a manner similar to the preparation

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of **12**, a solution of 0.27 g (0.8 mmol) of (bromocyclopentadienyl)thallium, 0.21 g (0.8 mmol) of bromopentacarbonylmanganese, and 100 mL of THF were heated to reflux with stirring for 4 h. After being cooled to room temperature, the reaction mixture was filtered through a glass frit, the solvent was removed in vacuo, and the resulting oily residue was sublimed at 40 °C (10^{-2} torr) to afford 0.065 g (30%) of **13** as yellow crystals: mp 43–45 °C (lit.[18] mp 43–45 °C); NMR (CCl_4, internal Me_4Si) δ 4.95 (t, 2 H, $H_{2,5}$), 4.64 (t, 2 H, $H_{3,4}$).

1,1′-Dichloroferrocene (8). Into a 200-mL, nitrogen-purged Schlenk tube equipped with a stirring bar, reflux condenser, and mercury overpressure valve was added 250 mg (2.0 mmol) of iron(II) chloride,[57] 1.20 g (4.0 mmol) of (chlorocyclopentadienyl)thallium, and 50 mL of benzene. The reaction mixture was stirred at reflux for 24 h and then cooled and filtered through a glass frit, and the solvent was removed in vacuo, giving 450 mg (90%) of yellow **8**. Recrystallization of the product from hexane gave orange needles: mp 75–77 °C (lit.[58] mp 75–77 °C); NMR ($CDCl_3$, internal Me_4Si): δ 4.45 (t, 4 H, $H_{2,5}$), 4.16 (t, 4 H, $H_{3,4}$).

1,1′-Dibromoferrocene (9). This compound was prepared in a manner identical with the synthesis of **8** from 114 mg (0.90 mmol) of iron(II) chloride,[57] 570 mg (1.6 mmol) of bromocyclopentadienylthallium, and 100 mL of benzene. Removal of the solvent after reflux and filtration resulted in 160 mg (58%) of **9**. The product could be recrystallized from methanol as yellow-orange needles: mp 50–51 °C (lit.[59] mp 50–51 °C); NMR ($CDCl_3$, internal Me_4Si) δ 4.39 (t, 4 H, $H_{2,5}$), 4.13 (t, 4 H, $H_{3,4}$).

(η^5-Chlorocyclopentadienyl)dicarbonylcobalt (14). Into a nitrogen-purged, 600-mL Schlenk tube equipped with a magnetic stirrer and mercury overpressure valve was added 450 mg (1.3 mmol) of dicobalt octacarbonyl and 300 mL of THF. To this mixture was slowly added 330 mg (1.3 mmol) of iodine crystals, and the solution was stirred at 25 °C for 3 h. To the resulting green solution was added 800 mg (2.6 mmol) of (chlorocyclopentadienyl)thallium, and stirring was maintained for an additional 20 h. The reaction mixture was filtered through a glass frit, and the solvent was removed in vacuo. The residue was mixed with alumina in ethyl ether, the solvent was removed, and the coated product was placed on a 2 × 35 cm dry-packed column of alumina. Elution of the column with pentane brought down a single orange band. Removal of the solvent produced 300 mg (54%) of **14** as a deep red oil. An analytical sample was obtained by molecular distillation at 25 °C (10^{-3} torr): NMR (C_6D_6, external Me_4Si) δ 4.83 (t, 2 H, $H_{2,5}$), 4.17 (t, 2 H, $H_{3,4}$); IR (film, NaCl) 3125 (w), 2020 (vs), 1970 (vs), 1588 (w), 1430 (sh, m), 1408 (m), 1350 (m), 1260 (w), 1168 (m), 1030 (m), 980 (s), 805 (s) cm^{-1}. Anal. Calcd for $C_7H_4ClCoO_2$: C, 39.20; H, 1.88; Cl, 16.53. Found: C, 39.10; H, 1.92; Cl, 16.77.

(η^5-Bromocyclopentadienyl)dicarbonylcobalt (15). This compound was prepared in a manner analogous to the synthesis of **14** from 340 mg (1.0 mmol) of dicobalt octacarbonyl, 200 mL of THF, 254 mg (1.0 mmol) of iodine, and 700 mg (2.0 mmol) of (bromocyclopentadienyl)thallium. Chromatography afforded 293 mg of a deep red oil. NMR analysis indicated the product to be **15** (57%) contaminated by a very small amount of (η^5-cyclopentadienyl)dicarbonylcobalt. An analytical sample was prepared by two recrystallizations of the red oil from pentane at −78 °C, followed by molecular distillation at 25 °C (10^{-3} torr) immediately prior to analysis: NMR (C_6D_6, external Me_4Si) δ 4.86 (t, 2 H, $H_{2,5}$), 4.24 (t, 2 H, $H_{3,4}$); IR (film, NaCl) 3100 (w), 2955 (w), 2015 (vs), 1968 (vs), 1395 (m), 1345 (m), 1257 (m), 1150 (m), 1030 (m), 865 (m), 808 (s) cm^{-1}; MS, *m/e* 258 (M^+). Anal. Calcd for $C_7H_4BrCoO_2$: C, 32.46; H, 1.56. Found: C, 32.30; H, 1.66.

(η^5-Iodocyclopentadienyl)dicarbonylcobalt (16). This compound was prepared in a manner analogous to the synthesis of **14** from 1.08 g (3.2 mmol) of dicobalt octacarbonyl, 200 mL of THF, 802 mg (3.2 mmol) of iodine, and 2.50 g (6.3 mmol) of (iodocyclopentadienyl)thallium. NMR analysis of the red oil after chromatography and removal of the solvent at −40 °C (10^{-3} torr) indicated it was mixture of **16** (240 mg, 12%) and 70 mg (6%) of (η^5-cyclopentadienyl)dicarbonylcobalt: NMR (C_6D_6, external Me_4Si): δ 4.84 (t, 2 H, $H_{2,5}$), 4.28 (t, 2 H, $H_{3,4}$); IR (film, NaCl) 3100 (w), 2015 (vs), 1960 (vs), 1387 (m), 1340 (m), 1015 (m), 850 (m), 805 (s) cm^{-1}.

(η^5-Chlorocyclopentadienyl)dicarbonylrhodium (17). Into a nitrogen-purged 250-mL Schlenk tube was added 0.39 g (1.0 mmol) of dichlorotetracarbonyldirhodium,[60] 0.61 g (2.0 mmol) of (chlorocyclopentadienyl)thallium, and 75 mL of THF. The reaction mixture was stirred for 21 h at 25 °C. At the end of this period, the mixture was filtered through a glass frit and the filtrate treated with 5 g of alumina. The THF was removed in vacuo and the coated product placed on a 2 × 30 cm dry-packed alumina column. Elution of the column with pentane removed a single golden band. Evaporation of the solvent in vacuo gave 350 mg (68%) of **17** as a yellow oil. An analytical sample was obtained by molecular distillation at 25 °C (10^{-2} torr): NMR (C_6D_6, external Me_4Si) δ 5.42 (t, 2 H, $H_{2,5}$), 4.82 (t, 2 H, $H_{3,4}$); IR (film, NaCl) 3120 (w), 2045 (vs), 1975 (vs), 1443 (w), 1410 (m), 1344 (m), 1160 (m), 1050 (w), 1025 (m), 1000 (w), 875 (s), 785 (vs) cm^{-1}; MS, *m/e* 258 (M^+). Anal. Calcd for $C_7H_4ClO_2Rh$: C, 32.53; H, 1.56; Cl, 13.72. Found: C, 32.77; H, 1.79; Cl, 13.76.

Bis(η^5-chlorocyclopentadienyl)nickel (1,1′-Dichloronickelocene). The $NiBr_2 \cdot 2DME$ complex was prepared according to the procedure of King[61] from 0.22 g (3.8 mmol) of nickel powder, 0.20 mL (0.62 g, 3.9 mmol) of bromine, and 100 mL of dimethoxyethane (DME). The solvent was removed in vacuo and was replaced by 100 mL of THF. To the solution of $NiBr_2 \cdot 2DME$ in THF was added 2.44 g (8.0 mmol) of (chlorocyclopentadienyl)thallium. The solution was stirred for 12 h at 25 °C and filtered through a glass frit. Removal of the solvent in vacuo left a green oil. The latter solidified on cooling to 0 °C and was quickly transferred to a sublimer. Sublimation at 30 °C (10^{-2} torr) produced 472 mg (49%) of **18** as green needles: mp 36–37.5 °C; IR (Nujol) 3110 (vw), 1430 (m), 1337 (m), 1173 (m), 1018 (m), 887 (m), 825 (w), 772 (s) cm^{-1}; MS, *m/e* 256 (M^+). Anal. Calcd for $C_{10}H_8Cl_2Ni$: C, 46.59; H, 3.13; Cl, 27.51. Found: C, 46.55; H, 3.06; Cl, 27.63.

(η^5-Chlorocyclopentadienyl)(triethylphosphine)copper (19). A nitrogen-purged, 200-mL Schlenk tube was charged with 0.31 g (0.4 mmol) of chloro(triethylphosphine)copper tetramer,[62] 0.43 g (1.4 mmol) of chlorocyclopentadienylthallium, and 125 mL of pentane. The suspension was stirred for 18 h at 25 °C and filtered through a glass frit. The filtrate was concentrated to 50 mL under reduced pressure and then cooled to −78 °C, resulting in a cream solid. The supernatant liquid was removed via a pipette, and the solid was further purified by recrystallization from pentane at −78 °C. The product was dried at −78 °C (10^{-2} torr) for 3 h to afford 0.32 g (81%) of **19** as cream needles: mp 70–72 °C dec; NMR (C_6D_6, external Me_4Si) δ 6.31 (t, 2 H, $H_{2,5}$), 5.94 (t, 2 H, $H_{3,4}$), 1.13–0.40 (m, 15 H, C_2H_5); IR (KBr) 2970 (m), 2935 (m), 2905 (m), 2875 (m), 1520 (m), 1455 (m), 1375 (w), 1255 (m), 1115 (m), 1050 (m), 870 (sh), 850 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{19}ClCuP$: C, 46.98; H, 6.81. Found: C, 47.06; H, 6.78.

(η^5-Lithiocyclopentadienyl)dicarbonylcobalt (20). Into a nitrogen-purged, 250-mL Schlenk tube equipped with a magnetic stirrer and a mercury overpressure valve was added 0.96 g (3.7 mmol) of (η^5-bromocyclopentadienyl)dicarbonylcobalt and 40 mL of ethyl ether. The solution was cooled to −78 °C and treated dropwise with 2.00 mL (3.7 mmol) of *n*-butyllithium in hexane over a 5-min period to generate an air- and thermally-sensitive solution of **20**.

(η^5-Carboxycyclopentadienyl)dicarbonylcobalt (21). A solution of (η^5-lithiocyclopentadienyl)dicarbonylcobalt was prepared from 0.82 g (3.2 mmol) of (η^5-bromocyclopentadienyl)dicarbonylcobalt, 1.70 mL (3.2 mmol) of *n*-butyllithium in hexane, and 30 mL of ethyl ether as described above. The resulting solution was poured into a nitrogen-purged, 250-mL round-bottom flask which contained 30 mL of ethyl ether and 10 g of freshly crushed dry ice. The reaction mixture was allowed to warm to room temperature with stirring and was subsequently transferred into a nitrogen-purged 500-mL separatory funnel. The ether

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solution was extracted three times with 100-mL portions of deoxygenated water. The combined aqueous solution was extracted twice with 50-mL portions of ethyl ether and then acidified with 10% hydrochloric acid. The acidified solution was then extracted three times with 30-mL portions of ethyl ether, and the extracts were dried over magnesium sulfate. Filtration and removal of the solvent left 0.40 g (56%) of **21** as an orange solid. Recrystallization of the product from ethyl ether/pentane at –25 °C gave orange crystals, mp 135–137 °C (lit.[48] mp 135–138 °C). A mixture melting point of this product with an authentic sample was undepressed: NMR (acetone-d_6, internal Me_4Si) δ 5.64 (t, 2 H, $H_{2,5}$), 5.52 (t, 2 H, $H_{3,4}$), 8.94 (s, 1 H, OH); IR (KBr) 3100–2400 (m, br), 2035 (s), 1970 (s), 1670 (s, br) 1490 (s, br) 1490 (s), 1415 (m), 1370 (m), 1290 (s), 1155 (m), 1050 (w), 1030 (w), 1010 (w), 910 (m), 815 (m), 740 (m), 615 (m) cm^{-1}.

The initial ether solution after carbonation was dried over magnesium sulfate, filtered, and deposited on 5 g of alumina. Chromatography of the coated product on a 2 × 35 cm column of dry-packed alumina using pentane as the eluant removed an orange band, which afforded 20 mg (4%) of (η^5-cyclopentadienyl)dicarbonylcobalt as a red oil. Continued pentane elution removed a second orange band, which produced 30 mg of an unidentified red oil.

(η^5-1-Methyl-1-(hydroxyethyl)cyclopentadienyl)dicarbonylcobalt (22). A solution of (η^5-lithiocyclopentadienyl)dicarbonylcobalt was prepared from 0.52 g (2.0 mmol) of (η^5-bromocyclopentadienyl)dicarbonylcobalt, 1.07 mL (2.0 mmol) of *n*-butyllithium in hexane, and 30 mL of ethyl ether as previously described. Upon completion of the *n*-butyllithium addition, 1.00 mL (13.8 mmol) of deoxygenated, reagent grade acetone was immediately added to the solution. The solution was stirred for 30 min at –78 °C, treated with 3 mL of methanol, allowed to warm to 25 °C, and hydrolyzed with 50 mL of deoxygenated water. The reaction mixture was added to a 250-mL separatory funnel, the aqueous layer was removed, and the organic layer was washed with water until the aqueous extracts remained neutral. The organic layer was dried over magnesium sulfate, filtered, treated with 5 g of alumina, and concentrated to dryness in vacuo. The coated product was added to a 2 × 25 cm column of dry-packed alumina. Elution of the column with pentane produced an orange band, which after removal of the solvent gave 20 mg (6%) of (η^5-cyclopentadienyl)dicarbonylcobalt. Continued elution with pentane and 2:1 pentane/ether removed two additional orange bands, which produced 5 and 20 mg of unidentified red oils, respectively. Elution with 1:1 pentane/ether removed a fourth (major) band. Removal of the solvent afforded 200 mg (42%) of **22** as a dark red oil. NMR (C_6D_6, internal Me_4Si) δ 5.23 (t, 2 H, $H_{2,5}$), 5.06 (t, 2 H, $H_{3,4}$), 3.78 (s, 1 H, OH), 1.49 (s, 6 H, CH_3); IR (film, NaCl) 3750–3175 (br, vs), 3125 (m), 2995 (vs), 2945 (s), 2890 (s), 2010 (vs), 1965 (vs), 1500 (m), 1475 (m), 1460 (m), 1445 (m), 1390 (vs), 1330 (m), 1160 (s), 1125 (s), 1045 (m), 950 (s), 915 (m), 830 (s), 805 (m) cm^{-1}.

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Registry No. **1**, 34822-90-7; **2**, 36664-93-4; **3**, 41851-50-7; **4**, 41851-49-4; **5**, 94890-79-6; **6**, 94890-67-2; **7**, 94890-68-3; **8**, 1293-67-0; **9**, 1293-65-8; **10**, 94890-69-4; **11**, 94890-70-7; **12**, 12079-90-2; **13**, 12079-86-6; **14**, 94890-71-8; **15**, 94890-72-9; **16**, 94890-73-0; **17**, 94890-74-1; **18**, 94890-75-2; **19**, 94890-76-3; **20**, 94890-77-4; **21**, 94890-78-5; **22**, 79086-57-0; (η^5-c_5H_5)$TiCl_3$, 1270-98-0; $TiCl_4$, 7550-45-0; $BrMn(CO)_5$, 14516-54-2; $FeCl_2$, 7758-94-3; $Co_2(CO)_8$, 15226-74-1; (η^5-C_5H_5)$Co(CO)_2$, 12078-25-0; $[ClRh(CO)_2]_2$, 14523-22-9; $NiBr_2$·2DME, 18346-62-8; $[ClCu(PEt_3)]_4$, 55606-52-5.

Destabilization of μ-η^2-Carbon Monoxide and μ-η^2-Isocyanide Bridges in Dimanganese Compounds on Protonation of the Metal–Metal Bond

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Protonation of $Mn_2(\mu$-η^2-$CO)(CO)_4(dppm)_2$ in dichloromethane with $HBF_4 \cdot Et_2O$ at –80 °C gives $[Mn_2H(\mu$-η^2-$CO)(CO)_4(dppm)_2][BF_4]$ which was characterized by IR and NMR methods. It readily decomposes above –60 °C to $[Mn_2H(CO)_6(dppm)_2][BF_4]$ which can be isolated. Protonation of the neutral pentacarbonyl leads to a considerable destabilization of the formally four-electron-donating μ-η^2-carbonyl form as evidenced by the very large increase in ν(CO) associated with the bridging CO ligand from 1648 to 1787 cm^{-1}, by a greater than 9.4 kcal mol^{-1} lowering of the energy barrier to CO oscillation between the metal atoms, and by the facile thermal conversion to $[Mn_2H(CO)_6(dppm)_2]^+$ which contains only terminal CO ligands. The tolyl isocyanide compound $Mn_2(\mu$-η^2-CNC_6H_4Me-$4)(CO)_4(dppm)_2$ behaves almost identically, chemically, and spectroscopically, on protonation with $HBF_4 \cdot Et_2O$.

Introduction

The μ-η^2-carbonyl ligand in $Mn_2(CO)_5(dppm)_2$ (**1**; dppm = $Ph_2PCH_2PPh_2$) is formally a four-electron donor.[1-4] Intuitively one might expect that enhanced reactivity toward nucleophiles would be a feature of its chemistry. However, compound **1** was found to be generally not susceptible to nucleophilic attack,[5] and calculations indicating that the predominant component of the η^2-interaction is back-donation from the metal to the CO π^*

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