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Paramagnetic Organometallic Complexes. Synthesis of 17-Electron Cyclopentadienylcobalt Complexes

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The thermally stable 17-electron complexes $[(\eta^5\text{-}C_5H_5)CoL_2][BF_4]$ (**2**; L = tertiary phosphines and phosphites) have been synthesized by one-electron oxidation of the corresponding 18-electron complexes, **1**. Metathesis of L_2CoX_2 (X = halogen) with thallium cyclopentadienide gives $(\eta^5\text{-}C_5H_5)CoXL$ (**3**), which may be further treated with thallium tetrafluoroborate to give **2**. Complexes **2** may be further oxidized to the diamagnetic 16-electron complexes $[(\eta^5\text{-}C_5H_5)CoL_2][BF_4]_2$ (**5**). Treating **5** (L = PEt_3) with 1 equiv of PEt_3 gives the unusual phosphonium complex $[(\eta^5\text{-}C_5H_4PEt_3)CoH(PEt_3)_2][BF_4]$ (**7**).

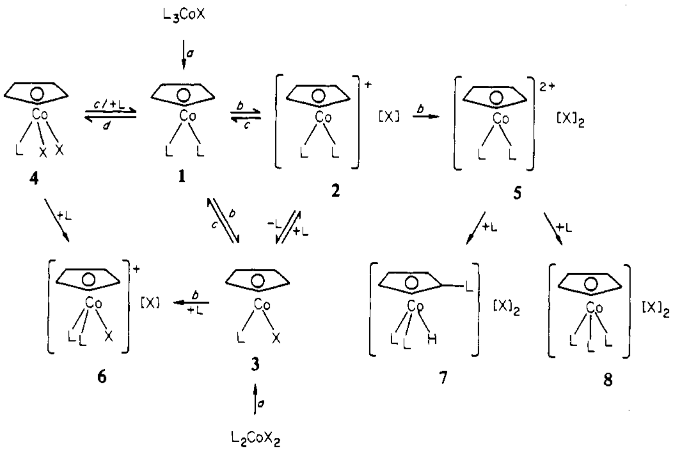
Paramagnetic organometallic species have been detected or implicated in a number of catalytic processes.[1] Despite increasing interest, relatively little is known about the behavior of these odd-electron species, and their role in a reaction sequence often is unclear.

Recently, surprisingly thermally stable 17-electron complexes of cyclopentadienylmanganese(II), -iron(III), and -molybdenum(III) with group 5 donor ligands were synthesized by one-electron oxidation of the corresponding diamagnetic 18-electron complexes.[2] Paramagnetic cyclopentadienylcobalt[3] and -nickel(I)[4] complexes have also been generated through one-electron reduction, and in the cobalt case this usually leads to dinuclear species. Herein we report that one-electron oxidation of cyclopentadienylcobalt(I) complexes may also lead to the isolation of thermally stable mononuclear 17-electron complexes.

Results

Preparation of Diamagnetic Cyclopentadienylcobalt(I) Complexes. A summary of the synthetic results is shown in Scheme I. Many procedures start with L_2CoX_2 complexes (L = PR_3; R = alkyl or aryl; X = Cl, Br, I) which are obtained in high yield by treatment of CoX_2 (hydrated or anhydrous) with the appropriate ligand in ethanol.[5] They are highly colored (blues, greens, and browns), air-stable, paramagnetic complexes which are somewhat soluble in donor solvents such as tetrahydrofuran (THF). The complex $(Ph_3P)_3CoCl$ was obtained by reduction of $(Ph_3P)_2CoCl_2$ in the presence of excess ligand. Three methods of reduction have been reported by Aresta, Rossi, and Sacco,[6] i.e., $NaBH_4$, Zn, or electrochemical reduction. We found zinc reduction unsatisfactory because of the need to destroy excess zinc with acid, which in turn destroys some of the product. On the other hand, modification of the reported electrochemical reduction method led to a simple high-yield procedure allowing isolation of 15–20-g quantities of this bright green, reasonably air-stable solid. However, we have not been able to extend this synthesis to other phosphines or phosphites. Isolation of some phosphite derivatives using zinc reduction has been previously reported.[7,8]

Scheme I



^{a} TlCp. ^{b} AgX. ^{c} Zn. ^{d} X_2 or 2AgX.

The complexes $CpCoL_2$ (**2**) (Cp = $\eta^5\text{-}C_5H_5$) were prepared by modification of various literature procedures. The preparation of $CpCo(PPh_3)_2$ (**1a**) using Grignard reduction of $CpCoI_2(PPh_3)$ has been described.[9] We found that zinc reduction of the latter in the presence of PPh_3 gave **1a**. Simpler yet, the reaction of $(Ph_3P)_3CoCl$ with thallium cyclopentadienide (TlCp) gives a very high yield of **1a**. More generally, treating L_2CoCl_2 with TlCp and zinc also gives $CpCoL_2$ [**1a**, L = PPh_3; **1b**, L = PEt_3; **1c**, L = $PEtPh_2$; **1d**, L_2 = 1,2-bis(diphenylphosphino)ethane (DPPE)]. Similar preparations for Co and Rh complexes have been reported by Werner et al.[10,11] These methods are useful when L = tertiary phosphine but are less successful with phosphites. Harder, Müller and Werner[12] have reported the synthesis of $CpCo(P(OMe)_3)_2$ (**1e**) by reaction of Cp_2Co with excess $P(OMe)_3$ at elevated temperatures. We have found that addition of 1 equiv of 2-butyne leads to a much higher yield under less severe conditions. This may result from the formation of a labile intermediate upon reaction of Cp_2Co with butyne[13] (eq 1). We have also found that the reaction of $CpCoI_2(CO)$[14] with

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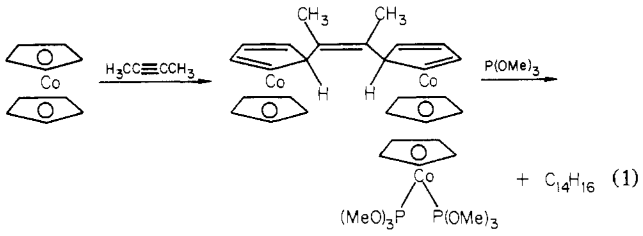


(1)

1e

2 equiv of $P(OPh)_3$ and excess zinc gives $CpCo[P(OPh)_3]_2$ (**1f**) in high yield.

Preparation and Characterization of Paramagnetic Cobalt(II) Products. Treating the diamagnetic complex $CpCo(PPh_3)_2$ (**1a**) with 1 equiv of $AgBF_4$ in THF led to deposition of silver metal and the isolation of the one-electron oxidation product $[CpCo(PPh_3)_2][BF_4]$ (**2a**) in high yield. This product was also obtained in good yield by the sequential treatment of $(Ph_3P)_2COCl_2$ with thallium cyclopentadienide (TlCp) and thallium tetrafluoroborate ($TlBF_4$), presumably through the intermediate $CpCoCl(PPh_3)$ (**3a**) (vide infra). The light brown, crystalline complex **2a** is air sensitive but thermally very stable, melting with decomposition at 250 °C under nitrogen atmosphere. The infrared spectrum (KBr) is very similar to that of the parent compound (**1a**) except for the addition of a strong, broad absorption centered at ca. 1060 cm^{-1}, assigned to the BF_4 counterion. The complex is paramagnetic, containing one unpaired electron ($\mu_{eff} = 1.6\ \mu_B$) as determined by the Evans NMR method,[15] and is formally a 17-electron complex. It is unclear why the effective magnetic moment (μ_{eff}) is below the spin-only value of 1.73 μ_B; possibly diamagnetism of the ligands is sufficient to cause the lowering.

The oxidation of **1a** by other silver salts results in different products. The use of AgCl results in the isolation of $CpCoCl(PPh_3)$ (**3a**) in good yield. It is also obtained in good yield from the reaction of $(Ph_3P)_2CoCl_2$ with TlCp.[16] The deep red, crystalline complex (**3**, L = PPh_3, X = Cl) is air sensitive and thermally stable (mp 120 °C dec) though less so than **2**. It also is paramagnetic with one unpaired electron ($\mu_{eff} = 1.8\ \mu_B$). The infrared spectrum (KBr) is fairly similar to that of the parent compound (**1**, L = PPh_3), the primary differences being the increase in intensity of the bands at 1400 and 810 cm^{-1}, both assigned to the cyclopentadienyl ring, and the appearance of a medium-intensity absorption at 305 cm^{-1} (ν_{Co-Cl}). The derivatives with X = Br or I were obtained similarly. With AgCN we obtained a diamagnetic cobalt(III) complex, which will be described below.

Similar reactions and products were obtained for the systems in which L = PEt_3. The reaction of $(Et_3P)_2CoX_2$ (X = Cl) with TlCp led to the isolation of $CpCoCl(PEt_3)$ (**3**) in low yield. For X = Br a compound which analyzed as a mixture of **2** and **3** was obtained, and for X = I only **2** (X = I) was isolated in high yield. In each of the three cases, treatment of the reaction mixture with 1 equiv of $TlBF_4$ led to the isolation of **2** (X = BF_4) in high yield. These results and those with L = PPh_3 described above suggest that there is an equilibrium (eq 2) which is strongly influenced by the relative

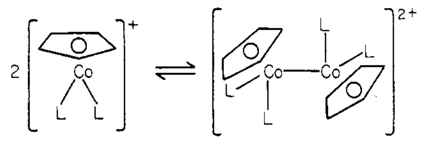
$$\underset{\mathbf{3}}{[\mathrm{CpCoXL}]} + \mathrm{L} \rightleftharpoons \underset{\mathbf{2}}{[\mathrm{CpCoL_2}]\mathrm{X}} \qquad (2)$$

steric requirements of X and L. Complexes **2** and **3** (L = PEt_3) are red-brown, air-sensitive, and thermally stable. They are paramagnetic, containing one unpaired electron. The infrared spectra of these complexes are notable for their well-defined absorptions at ca. 3100 cm^{-1} assigned to ν_{CH} of the cyclopentadienyl group. An exception to this is found for **2** (L = PEt_3, X = I) where the $\nu_{CH}(Cp)$ is broadened and lowered in energy (ca. 3060 cm^{-1}). If this compound is treated with $TlBF_4$, the isolated product again has the band at 3100 cm^{-1}. We believe this is due to Cp hydrogen bonding with the iodide counterion.[17a]

For the system with L = $PEtPh_2$, treating $(Ph_2EtP)_2CoX_2$ with TlCp and $TlBF_4$ results in the isolation of the paramagnetic complex **2** (L = $PEtPh_2$, X = BF_4) in good yield. In the absence of $TlBF_4$, we encountered difficulty in isolating pure products presumably because of the equilibrium of eq 2. Crystals could be obtained at −30 °C, which were stable in the presence of the mother liquor even at room temperature. However, upon separation from the liquor, they melted to a brown oil. No attempt was made to characterize these oils.

When the chelating ligand 1,2-bis(diphenylphosphino)ethane (DPPE) was used, a related problem was encountered. Treatment of $(DPPE)CoX_2$ (X = Br or I) with TlCp resulted in the precipitation of TlX and subsequent isolation of maroon paramagnetic complexes. It is not clear whether the halogen is coordinated with DPPE being monodentate or if X is not coordinated and DPPE is bidentate. However, upon treatment of either reaction mixture with $TlBF_4$, a color change to *green* occurs. Thus far we have been unable to isolate this green product.

Turning to systems containing phosphites, for [L = $P(O\text{-}i\text{-}Pr)_3$] ($i$-Pr = $i\text{-}C_3H_7$), we have isolated the paramagnetic complex **2** (L = $P(O\text{-}i\text{-}Pr)_3$, X = BF_4) in good yield by sequential treatment of anhydrous CoI_2 with 2 equiv of $P(O\text{-}i\text{-}Pr)_3$ and 1 equiv each of TlCp and $TlBF_4$. The solution-phase effective magnetic moment (1.5 μ_B) is lower than described above for the case where L = PPh_3, suggesting the possibility of a monomer–dimer equilibrium (eq 3). However, variable-temperature measurements over the range −80 to +30 °C revealed no change in the effective magnetic moment. The reason for the low value remains unclear.[17b]



(3)

The green crystalline complex $[CpCo(P(OPh)_3)_2][BF_4]$ (**2**) was obtained in good yield by silver oxidation of $CpCo(P(OPh)_3)_2$ (**1**). Surprisingly, the yield and purity of the product declined the longer the reaction mixture was allowed to stir. The impurity is apparently highly paramagnetic because the magnetic moment is greater in the impure product.

Attempts to prepare similar compounds by oxidation of **1** (L = $P(OR)_3$, R = Me, Et, i-Pr) were unsuccessful. Treating **1** [L = $P(OMe)_3$] with silver ion does not result in the immediate precipitation of silver metal, and an unstable complex which apparently contains silver ion can be isolated. It is probably related to the recently reported rhodium–silver complexes reported by Connelly, Lucy, and Galas.[18]

Attempts to prepare **2** [L = $P(OR)_3$ (R = Me, Et), X = BF_4] by treatment of CoX_2 with $P(OR)_3$, TlCp, and $TlBF_4$ resulted in the precipitation of TlX, yielding yellow solutions from which uncharacterized oils are obtained.

Cobalt(III) Complexes. All the paramagnetic cobalt(II) complexes described above are readily oxidized further with silver salts to cobalt(III) complexes. In addition, in several

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(17) (a) X-ray crystal structure analysis of $[CpCo(PEt_3)_2]I$ by J. F. Whitney reveals that the iodide couterions are in a position to interact with the cyclopentadienyl hydrogens. (b) Solution-phase molecular weight determinations were attempted but were unsuccessful due to insolubility in suitable solvents.

(18) Connelly, N. G.; Lucy, A. R.; Galas, A. M. R. *J. Chem. Soc., Chem. Commun.* **1981**, 43–44.

instances attempted one-electron oxidation led to two-electron oxidation of half the starting material.

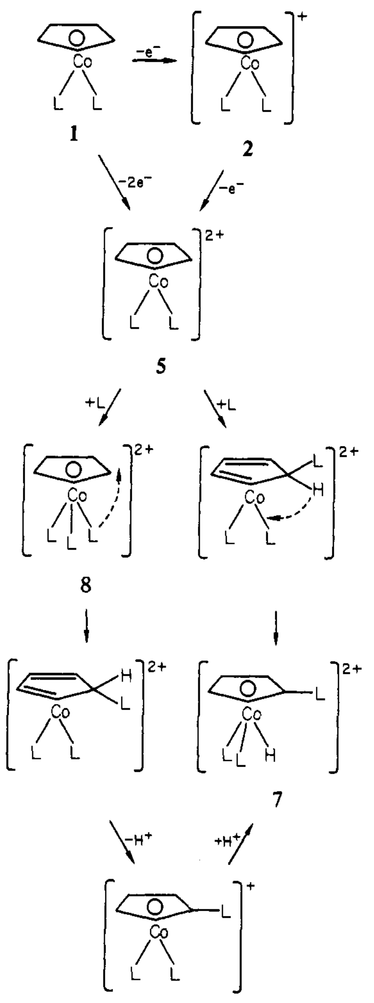
When $CpCo(PPh_3)_2$ (**1**) was oxidized with AgCN, the only characterized product was $CpCo(CN)_2(PPh_3)$ (**4**). This diamagnetic Co(III) product was obtained in high yield when 2 equiv of AgCN was used. It is an air-stable and thermally stable yellow, crystalline compound. The infrared spectrum (KBr) displays a medium-intensity absorption at 2130 cm^{-1} (ν_{CN}). The ^1H NMR spectrum gives a phenyl multiplet at τ 2.5 and a sharp singlet at τ 4.9 (relative integration 15:5). A number of similar complexes (**4**), where X = I and L = CO, PR_3, $P(OR)_3$, or nitrogen donor ligands, have previously been reported.[14] They were derived from the oxidation of $CpCo(CO)_2$ with I_2 to give $CpCoI_2(CO)$ with subsequent substitution of the carbonyl group.

Treating $[CpCo(PPh_3)_2][BF_4]$ (**2**) with 1 equiv of $AgBF_4$ affords the diamagnetic "16-electron" complex $[CpCo(PPh_3)_2][BF_4]_2$ (**5**). The same product is isolated upon oxidation of $CpCo(CO)(PPh_3)$ with $AgBF_4$. The pale yellow, air-stable solid exhibits an infrared spectrum (KBr), which reveals the presence of Cp, PPh_3, and BF_4. The ^1H NMR spectrum shows two PPh_3 groups per Cp group, the latter giving a sharp singlet at τ 4.25. No evidence for a metal hydride resonance could be found in a relatively concentrated CD_2Cl_2 solution.

In the L = PEt_3 system different Co(III) complexes are isolated. When $(Et_3P)_2CoCl_2$ is treated sequentially with TlCp and $AgBF_4$, oxidation takes place instead of metathesis, and the diamagnetic crystalline complex $[CpCoCl(PEt_3)_2][BF_4]$ (**6**) is isolated in good yield, presumably through the intermediacy of **3**. Besides absorptions typical for coordinated cyclopentadienyl, PEt_3, and BF_4 counterion, the infrared spectrum (KBr) shows a weak absorbance at 310 cm^{-1} (ν_{Co-Cl}). The ^1H NMR spectrum shows a Cp singlet at τ 4.65 and PEt_3 multiplets at τ 8.0 and 8.9.

On the other hand, when $[CpCo(PEt_3)_2][BF_4]$ (**2**) is treated with 1 equiv of $AgBF_4$ in THF, deposition of silver metal occurs, and a dark solution similar to that of **6** is obtained from which only an uncharacterized oil could be separated. However, if this dark solution is treated dropwise with 1 equiv of PEt_3, a dramatic color change to yellow occurs, and a diamagnetic solid is isolated in good yield. The infrared spectrum shows bands for Cp, PEt_3, and BF_4 and is otherwise unremarkable. However, the ^1H NMR spectrum reveals a complex pattern (see Experimental Section) revealing the presence of a substituted cyclopentadienyl ring (multiplets of intensity 2 at τ 3.7 and 4.4) and a metal hydride (triplet of intensity 1 at τ 25.4). These data and the elemental analysis are consistent with the formulation $[(Et_3PC_5H_4)CoH(PEt_3)_2][BF_4]_2$ (**7**), which is an isomer of the expected product **8**. Werner and Hofmann[19] recently reported the reaction of $CpCo(PMe_3)_2$ (**1**) with alkyl halides (RX) to give the similar complexes $[(RC_5H_4)CoH(PMe_3)_2][X]$. They proposed and gave evidence for the intermediacy of $[CpCoRL_2]X$, followed by intramolecular migration of R to the cyclopentadienyl ring, followed by loss of a ring proton and reattack on the cobalt center. A similar reaction path using the neutral phosphine ligand (L) instead of an alkyl group is represented by the counterclockwise path of Scheme II. It is interesting to note that whereas there is precedence for the migration of alkyl or aryl groups to cyclopentadienyl rings,[20] we are unaware of any reports of phosphine migration. An alternative is the more direct clockwise pathway of Scheme II, incorporating intermolecular attack of (L) on the cyclopentadienyl ring in a position exo to the metal with transfer of a ring proton to the metal. The attack of phosphines on organic ligands of cationic complexes has been reported for other systems,[21] and we favor it here on the basis of steric considerations. It should be noted that while we have found no evidence for **8** (L = PEt_3), the less sterically crowded complex **8** (L = PMe_3) has been isolated by Werner and Hofmann.[10] Also, we have been unable to convert $[CpCoCl(PEt_3)_2][BF_4]$ (**6**) to either **7** or **8** by reaction of PEt_3 and $TlBF_4$ either sequentially or concurrently; it appears that instead the cyclopentadienyl group is displaced.

Scheme II



In the systems where L = $P(OR)_3$ (R = Me, Et, *i*-Pr) the reaction of either **1** or **2** with $AgBF_4$ in the presence of free ligand afforded the diamagnetic complexes $[CpCo(P(OR)_3)_3][BF_4]_2$ (**8**) in good yields. The same complexes can be obtained by sequential treatment of $CpCoI_2(CO)$ with 3 equiv of $P(OR)_3$ and 2 equiv of $TlBF_4$. No evidence for complexes **3**, **6**, or **7** was detected with these ligands. However, treatment of $CpCoI_2(CO)$ with 1 equiv of $P(OR)_3$ does give the corresponding complex **4**.

Oxidation of $CpCo(CO)_2$. Oxidation of $CpCo(CO)_2$ with 1 equiv of $AgBF_4$ causes evolution of gas and deposition of silver metal, leading to the isolation of an apparently air-stable, off-white solid. The infrared spectrum suggests the presence of Cp, BF_4, and THF. We find no IR carbonyl bands. The product is highly paramagnetic with $\chi = 1.62 \times 10^{-5}$. Treatment of this product with phosphines or phosphites has

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(19) Werner, H.; Hofmann, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 794; **1978**, *17*, 464.

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given no recognized products, and so the structure of the complex remains unclear.

Conclusions

It appears that stable paramagnetic organocobalt(II) complexes can be isolated, provided the ligands are sufficiently bulky to prevent dimerization of the Co(II) complex (eq 2) or disproportionation to Co(I) and Co(III) complexes. Accordingly, treatment of any of the isolated complexes **2** with $P(OMe)_3$ results in immediate disproportionation to diamagnetic products. The disproportionation reaction will be discussed in a later paper. All of the paramagnetic Co(II) complexes can be further oxidized to Co(III) containing two or three ligands, depending on the steric requirements of the ligand. However, sterics alone do not control the geometry of the Co(III) complex as revealed by the formation of **7** when L = PEt_3. Also it is surprising that treating **5** (L = PPh_3) with PEt_3 does not convert it to **7** but merely substitutes one of the PPh_3 groups. If the ligands are small enough, i.e., PMe_3 or $P(OR)_3$, *it* appears that **8** will be formed.

Experimental Section

All reactions and manipulations were carried out under nitrogen unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under nitrogen. All other solvents were purged with nitrogen and stored over 4A molecular sieves.

Proton NMR spectra and Evans method magnetic susceptibility measurements[15] were obtained at 60 MHz unless otherwise noted. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 283B spectrophotometer. Melting points were taken under nitrogen.

$(Ph_3P)_3CoCl$. An electrolytic H-cell (1 L) separated by a Nafion perfluorosulfonic acid membrane was connected to a Princeton Applied Research Model 173 Potentiostat/Galvanostat. LiCl (25 g) was dissolved in absolute EtOH (1 L), and half of the solution was placed in one half of the cell with a Pt-gauze anode. The remaining solution, in which PPh_3 (17 g) was dissolved with warming, was placed in the other half of the cell over a mercury-pool cathode. $CoCl_2{\cdot}6H_2O$ (5.0 g) was dissolved in a minimum amount of EtOH and added to the PPh_3 solution (Hg cathode), and controlled-potential (1.25 V vs. Ag/AgCl reference) electrolysis was carried out until the theoretical amount of current had been passed (ca. 2024 faradays, ~24 h). A bright green solid slowly separated from the blue solution. The mercury was drained away and the green suspension filtered to give a green solid, which was washed with two 50-mL portions of Et_2O and then pentane and dried under vacuum (17.4 g, 94%).

$(\eta\text{-}C_5H_5)Co(PPh_3)_2$. A green suspension of $(Ph_3P)_3CoCl$ (4.90 g, 5.6 mmol) in THF (250 mL) was treated with TlC_5H_5 (1.51 g, 5.6 mmol), giving a deep red solution with a white precipitate over a 15-min period. Stirring was continued for 3 h and the mixture filtered. Heptane (100 mL) was added to the red filtrate and the solution volume reduced to about 80 mL by aspiration. Red microcrystals separated and were filtered off and washed with pentane (3.06 g, 85%): mp 159–160 °C; ^1H NMR (C_6D_6) τ 2.2 (m, 12), 3.0 (m, 18), 5.5 (t, 5, J = 1.5 Hz).

$(\eta\text{-}C_5H_5)Co(PEt_3)_2$. $(Et_3P)_2CoI_2$ (6.00 g, 10.9 mmol) in THF (250 mL) was treated with TlC_5H_5 (2.94 g, 10.9 mmol) and excess Zn powder for 4 h at room temperature. The mixture was filtered and stripped down to a brown oil, which was extracted with warm pentane. The extract was allowed to evaporate slowly, leaving a brown solid (2.2 g, 55%): ^1H NMR (C_6D_6) τ 5.35 (s, 5), 8.85 (m, 30).

$(\eta\text{-}C_5H_5)Co(P(OMe)_3)_2$. $(\eta\text{-}C_5H_5)_2Co$ (3.00 g, 15.9 mmol) was treated with 2-butyne (0.41 g, 7.7 mmol) and $P(OCH_3)_3$ (9.45 g, 76 mmol) in heptane (30 cm^3) and heated under reflux for 3 h. The solvent was evaporated under vacuum, and the residue was distilled under vacuum at ~150 °C to give a red oil. Crystallization from pentane at −35 °C gave an orange, crystalline solid (4.36 g; 74% yield): ^1H NMR (acetone-d_6) τ 5.35 (s, 5), 6.5 (t, 18, J = 6 Hz).

$(\eta\text{-}C_5H_5)Co(P(OPh)_3)_2$. $(\eta\text{-}C_5H_5)CoI_2(CO)$ (2.00 g, 4.6 mmol) in THF (100 mL) was treated with $P(OPh)_3$ (2.42 mL, 9.2 mmol), which caused evolution of gas, and then with excess zinc powder (0.5 g) for 3 h. The mixture was filtered and stripped to an orange solid, which was extracted with warm pentane. The orange pentane solution was reduced in volume by aspiration, giving an orange microcrystalline solid (1.55 g). The filtrate was allowed to evaporate slowly at −10 °C, giving well-formed orange crystals (0.75 g; mp 130 °C; total yield 67%): ^1H NMR (acetone-d_6) τ 2.7 (m, 30), 6.0 (s, 5).

$[(\eta\text{-}C_5H_5)Co(PPh_3)_2][BF_4]$. (a) $(\eta\text{-}C_5H_5)Co(PPh_3)_2$ (2.00 g, 3.1 mmol) dissolved in THF (50 mL) was treated with $AgBF_4$ (0.60 g, 3.1 mmol) and stirred at room temperature for 1 h. Filtration gave a black solid which was extracted with CH_2Cl_2. The combined filtrate and extract were treated dropwise with hexane. Filtration gave a golden microcrystalline solid (1.95 g, 86%), mp 250 °C dec.

(b) $(Ph_3P)_3CoCl$ (2.0 g, 2.3 mmol) suspended in THF (50 mL) was treated with TlC_5H_5 (0.61 g, 2.3 mmol) for 0.5 h and filtered, $AgBF_4$ (0.44 g, 2.3 mmol) was added, and stirring was continued for a further 0.5 h. Filtration gave a black solid (0.28 g). The brown filtrate was treated with hexane. Filtration and washing with pentane gave a golden solid (1.40 g, 83%): mp 250 °C; magnetic susceptibility (CH_2Cl_2) $\chi = 1.38 \times 10^{-6}$, $\mu_{eff} = 1.6\ \mu_B$. Anal. Calcd: C, 66.94; H, 4.76. Found: C, 66.89; H, 4.87.

(c) $(Ph_3P)_2CoCl_2$ (10.00 g, 15.3 mmol) dissolved in THF (500 mL) was treated with TlC_5H_5 (4.11 g, 15.3 mmol) and $TlBF_4$ (4.45 g, 15.3 mmol) and stirred overnight. Filtration gave a tan solid, which was extracted with CH_2Cl_2, and the extract was treated with hexane to give a golden microcrystalline solid (6.8 g, 60%), mp 250 °C. The filtrate from above was reduced in volume and treated with hexane to give a golden solid (3.7 g, 33%), which has a melting point of 230 °C, suggesting it is impure (combined yield of about 90%).

$(\eta\text{-}C_5H_5)CoCl(PPh_3)$. (a) $(Ph_3P)_2CoCl_2$ (6.80 g, 10.4 mmol) was suspended in THF (250 mL), and the mixture was treated with TlC_5H_5 (2.80 g, 10.4 mmol) and stirred overnight. The maroon suspension was filtered (2.9 g of green solid recovered), and the solvent level was reduced and treated with hexane, which caused a maroon solid to separate. Recrystallization of the maroon solid from methylene chloride/hexane gave a maroon, microcrystalline solid (3.06 g, 70%): mp 150 °C dec; magnetic susceptibility (CH_2Cl_2) $\chi = 3.2 \times 10^{-6}$, $\mu_{eff} = 1.8\ \mu_B$. Anal. Calcd: C, 65.50; H, 4.75; Cl, 8.40. Found: C, 65.11, 65.30; H, 4.73, 4.79; Cl, 9.01.

(b) $(\eta\text{-}C_5H_5)Co(PPh_3)_2$ (2.00 g, 3.1 mmol) dissolved in THF (50 mL) was treated with AgCl (0.44 g, 3.1 mmol). After 1 h of stirring, the solid silver (0.36 g; theory 0.33 g) was separated by filtration and the level of solvent was reduced to about 10 mL. Heptane (25 mL) was added, and the solution allowed to stand for 0.5 h, resulting in the formation of deep maroon crystals (0.85 g, 65%), which were identified by IR, melting point, and magnetic susceptibility.

$(\eta\text{-}C_5H_5)CoBr(PPh_3)$. $(Ph_3P)_2CoBr_2$ (4.00 g, 5.4 mmol) was dissolved in THF (200 mL), and the solution was treated with TlC_5H_5 (1.45 g, 5.4 mmol) and stirred at room temperature for 4 h. A green-tinted, white solid was separated by filtration, leaving a deep red solution. Heptane (50 mL) was added, and the volume was reduced (to about 70 mL). Filtration gave a brown, microcrystalline solid (1.77 g, 71%; mp 125 °C dec), which was dried under high vacuum at 50 °C for 3 h: magnetic susceptibility (CH_2Cl_2) $\chi = 2.63 \times 10^{-6}$, $\mu_{eff} = 1.7\ \mu_B$. Anal. Calcd: C, 59.2; H, 5.1. Found: C, 58.4; H, 4.1.

$(\eta\text{-}C_5H_5)CoI(PPh_3)$. $(Ph_3P)_2CoI_2$ (4.00 g, 4.8 mmol) dissolved in THF (100 mL) was treated as above with TlC_5H_5 (1.29 g, 4.8 mmol). The product was isolated as above as red-black crystals (1.44 g, 59%) and dried under vacuum at 50 °C (mp 135 °C dec). Anal. Calcd: C, 53.8; H, 3.9. Found: C, 54.3; H, 3.9.

$[(\eta\text{-}C_5H_5)Co(PEt_3)_2]I$. $(Et_3P)_2CoI_2$ (3.0 g, 5.5 mmol) was suspended in THF (100 mL) and treated with TlC_5H_5 for 4 h. Separation of the yellow solid by filtration gave a deep red filtrate, which was treated with heptane (50 mL) and reduced in volume. Filtration gave red-brown crystals (1.66 g, 82%): mp 149 °C; magnetic susceptibility (CH_2Cl_2) $\chi = 2.48 \times 10^{-6}$, $\mu_{eff} = 1.7\ \mu_B$. Anal. Calcd: C, 41.90; H, 7.19. Found: C, 41.85; H, 7.24.

$[(\eta\text{-}C_5H_5)Co(PEt_3)_2][BF_4]$. (a) $[(\eta\text{-}C_5H_5)Co(PEt_3)_2]I$ (1.65 g, 3.4 mmol) dissolved in THF (100 mL) was treated with $TlBF_4$ (1.00 g, 3.4 mmol) for 1.5 h. A brown solid was separated by filtration and extracted with CH_2Cl_2, leaving a yellow solid (TlI). Slow treatment of the extract with hexane resulted in a light brown precipitate (1.08 g, 72%): mp 175 °C, discoloring at 289 °C dec; magnetic susceptibility (CH_2Cl_2) $\chi = 2.55 \times 10^{-6}$, $\mu_{eff} = 1.7\ \mu_B$. Anal. Calcd: C, 45.63; H, 7.83. Found: C, 45.61; H, 7.80.

(b) $(Et_3P)_2CoCl_2$ (10.00 g, 27.3 mmol) dissolved in THF (500 mL) was treated with TlC_5H_5 (7.35 g, 27.3 mmol) for 0.5 h, $TlBF_4$ (7.95 g, 27.3 mmol) was added, and stirring was continued for a further 3 h. Hexane (100 mL) was added, and filtration gave a light brown solid, which was extracted with CH_2Cl until no further coloration of the solvent occurred. Treatment of the extract with hexane (300 mL, dropwise with stirring) caused a solid to separate. Filtration gave a brown microcrystalline solid (9.53 g, 78%).

(c) $(\eta\text{-}C_5H_5)Co(PEt_3)_2$ (1.00 g, 2.8 mmol) dissolved in THF (80 mL) was treated with $AgBF_4$ (0.54 g, 2.8 mmol) for 1 h. Filtration gave a black solid, which was extracted with CH_2Cl_2, giving a brown solution and leaving a black solid (Ag). The brown extract was treated with hexane to give a brown-black crystalline product (0.79 g). The above filtrate gave additional product (0.12 g) when treated with hexane; total yield 0.91 g, 74%.

$(\eta\text{-}C_5H_5)CoCl(PEt_3)$. $(Et_3P)_2CoCl_2$ (3.0 g, 8.2 mmol) dissolved in THF (100 mL) was treated with TlC_5H_5 (2.21 g, 8.2 mmol) as above for 3 h. Separation of a white solid by filtration gives a burgundy-colored filtrate. The filtrate was reduced in volume, treated with heptane, and refiltered, giving a small amount of green solid. The volume was reduced further and filtered, giving maroon-black crystals (0.15 g), mp 65 °C. Anal. Calcd: C, 47.57; H, 7.20. Found: C, 47.40; H, 7.34.

$(\eta\text{-}C_5H_5)CoBr(PEt_3)_2$. $(Et_3P)_2CoBr$ (4.0 g, 8.8 mmol) dissolved in THF (100 mL) was treated as above with TlC_5H_5 (2.36 g, 8.8 mmol). Filtration and isolation as above gave maroon crystals (0.21 g), which may be a mixture of $[CpCoL_2]Br$ and CpCoBrL. Anal. Calcd for $CpCoL_2Br$: C, 46.36; H, 7.9. Calcd for CpCoBrL: C, 41.0; H, 6.2 (for $CpCoBr(PEt_3)$). Found: C, 44.92; H, 7.33.

$[(\eta\text{-}C_5H_5)Co(PEtPh_2)_2][BF_4]$. $(Ph_2EtP)_2CoCl_2$ (3.00 g, 5.4 mmol) dissolved in THF (200 mL) was treated with TlC_5H_5 (1.45 g, 5.4 mmol) and $TlBF_4$ (1.56 g, 5.4 mmol) as above. Isolation as above gave a brown microcrystalline solid (2.23 g, 65%): mp 176–177 °C; magnetic susceptibility (CH_2Cl_2) $\chi = 1.70 \times 10^{-6}$, $\mu_{eff} = 1.65\ \mu_B$. Anal. Calcd: C, 61.97; H, 5.48. Found; C, 61.81; H, 5.49.

$(Ph_2EtP)_2CoX_2$ with TlC_5H_5 (X = Cl, Br, I). $(Ph_2EtP)CoX_2$ was treated with an equimolar amount of TlC_5H_5 in THF at room temperature for 3 h. Filtration yielded a stoichiometric amount of TlX. Addition of heptane and reduction in volume followed by standing at −30 °C overnight led to the isolation of brown crystals, which melted in the absence of the mother liquor.

$(\eta\text{-}C_5H_5)CoBr(Ph_2PCH_2CH_2PPh_2)$. $(DPPE)CoBr_2$ (4.00 g, 6.5 mmol) suspended in THF (100 mL) was treated with TlC_5H_5 (1.74 g, 6.5 mmol) overnight. The mixture was filtered, treated with heptane (25 mL), and reduced in volume. Filtration gave a maroon solid (1.09 g, 28%): mp 145–147 °C; magnetic susceptibility (CH_2Cl_2) $\chi = 1.18 \times 10^{-6}$, $\mu_{eff} = 1.3\ \mu_B$. Anal. Calcd; C, 61.79; H, 4.82. Found: C, 61.05; H, 4.70.

$(\eta\text{-}C_5H_5)CoI(PH_2PCH_2CH_2PPh_2)$. $(DPPE)CoI_2$ (4.00 g, 5.6 mmol) suspended in THF (100 mL) was treated with TlC_5H_5 (1.51 g, 5.6 mmol) for 3 h. The mixture was filtered, treated with heptane, and stripped of solvent. The resulting violet solid was washed with THF and hexane to give a violet solid (3.7 g, >95%), mp 183–185 °C. Anal. Calcd: C, 57.32; H, 4.47. Found: C, 57.28; H, 4.92.

$[(\eta\text{-}C_5H_5)Co(P(O\text{-}i\text{-}Pr)_3)_2][BF_4]$. Anhydrous CoI_2 (1.00 g, 3.2 mmol) and $P(O\text{-}i\text{-}Pr)_3$ (1.33 g, 1.53 mL, 6.4 mmol) dissolved in THF (200 mL) were treated with TlC_5H_5 (0.86 g, 3.2 mmol) and stirred for 0.5 h. Addition of $TlBF_4$ (0.93 g, 3.2 mmol) with continued stirring for 3 h resulted in a brown solution with a yellow precipitate. Filtration gave a brown solution, which was evaporated to a brown oil and extracted with CH_2Cl_2. The extract was treated with Et_2O and allowed to evaporate slowly under nitrogen. Filtration gave a yellow-green crystalline solid, which was washed with pentane (1.00 g, 50%): mp 95 °C; magnetic susceptibility (CH_2Cl_2) $\chi = 1.45 \times 10^{-5}$, $\mu_{eff} = 1.5\ \mu_B$. Anal. Calcd; C, 44.0; H, 7.50. Found: C, 43.8; H, 7.76.

$[(\eta\text{-}C_5H_5)Co(P(OPh)_3)_2][BF_4]$. $(\eta\text{-}C_5H_5)Co(P(OPh)_3)_2$ (1.00 g, 1.3 mmol) dissolved in THF (25 mL) was treated with a solution of $AgBF_4$ (0.30 g, 1.5 mmol) in THF (20 mL). After addition, the mixture was immediately filtered. The gray solid was extracted with CH_2Cl_2 and treated with hexane, giving a green solid (0.20 g), mp 163 °C. The filtrate was treated with hexane to give green crystals (0.35 g), mp 155 °C. An analytical sample was recrystallized from CH_2Cl_2/hexane; magnetic susceptibility (CH_2Cl_2) 1.6 μ_B. Anal. Calcd: C, 59.2; H, 4.2. Found: C, 57.4; H, 4.4.

$[(\eta\text{-}C_5H_5)Co(PPh_3)_2][BF_4]_2$. (a) $(\eta\text{-}C_5H_5)Co(CO)(PPh_3)$ (2.0 g, 4.8 mmol) dissolved in THF (100 mL) was treated with $AgBF_4$ (0.94 g, 4.8 mmol) for 1 h. Filtration gave a gray solid, which was extracted with CH_2Cl_2, giving a yellow solution and leaving silver metal (0.4 g). Treatment of the extract with hexane gave a light yellow solid (1.29 g, 65% based on $AgBF_4$): mp 260 °C; ^1H NMR (CD_2Cl_2) τ 2.8 (m, 30), 4.25 (s, 5). Anal. Calcd: C, 59.85; H, 4.26; P, 7.54. Found: C, 59.87; H, 4.49; P, 7.16.

(b) $[(\eta\text{-}C_5H_5)Co(PPh_3)_2][BF_4]$ (1.00 g, 1.4 mmol) suspended in THF (50 mL) was treated dropwise with a solution of $AgBF_4$ (0.28 g, 1.4 mmol) in THF (10 mL). After 5 min the mixture was filtered. The gray solid was extracted with CH_2Cl_2, and the yellow extract was treated with hexane to give a yellow solid (0.12 g). The filtrate above was treated with hexane to give a pale yellow solid (0.70 g; mp 260 °C).

$(\eta\text{-}C_5H_5)Co(CN)_2PPh_3$. (a) $(\eta\text{-}C_5H_5)Co(PPh_3)_2$ (2.00 g, 3.1 mmol) dissolved in THF (150 mL) was treated with AgCN (0.83 g, 6.2 mmol) for 2 h with stirring. The mixture was evaporated to dryness and extracted with CH_2Cl_2, giving a yellow solution, which was treated with hexane, resulting in a yellow crystalline solid (1.23 g, 91%; mp 250 °C dec). A sample was dried in vacuo at 50 °C for 24 h to remove CH_2Cl_2 of crystallization. Anal. Calcd: C, 68.49; H, 4.57; N, 6.39. Found: C, 68.43; H, 4.86; N, 6.34.

$[(\eta\text{-}C_5H_5)CoCl(PEt_3)_2][BF_4]$. $(Et_3P)_2CoCl_2$ (2.00 g, 5.5 mmol) dissolved in THF (150 mL) was treated with TlC_5H_5 (1.47 g, 5.5 mmol), resulting in a color change from blue to deep red and precipitation of a white solid. After 1 h the mixture was filtered (1.30 g of white solid; theory for TlCl 1.31 g) and the red filtrate treated with $AgBF_4$. A rapid color change to red-brown occurred with precipitation of a light-colored solid, which darkened over a period of about 1 h. The mixture was filtered and the dark precipitate extracted repeatedly with warm THF until little color was washed away (ca. 1 L). The extracts were combined, and the volume was reduced to about 100 mL. Filtration gave a black, microcrystalline solid, which was washed with pentane (1.85 g, 70%): ^1H NMR (CD_2Cl_2) τ 4.65 (s, 5), 8.0 (m, 14), 8.9 (m, 21). Anal. Calcd: C, 42.28; H, 7.25. Found: C, 42.42; H, 7.29.

$[(\eta\text{-}C_5H_4PEt_3)CoH(PEt_3)_2][BF_4]_2$. $[(\eta\text{-}C_5H_5)Co(PEt_3)_2][BF_4]$ (0.21 g, 0.5 mmol) suspended in THF (80 mL) was treated with $AgBF_4$ (0.09 g, 0.5 mmol), resulting in a deep brown solution with precipitated silver metal. The brown solution was separated by filtration and treated with PEt_3 (0.1 mL), causing an immediate color change to yellow and precipitation of a yellow solid, which was filtered off and washed with pentane (0.27 g, 88%): mp 153–154 °C; ^1H NMR (acetone-d_6, 220 MHz) τ 3.7 (m, 2), 4.4 (m, 2), 7.2 (dq, 6, J = 13.5, 7.5 Hz), 8.0 (dq, 12, J = 7.5, 7.5 Hz), 8.6 (dt, 9, J = 20, 7.5 Hz), 8.75 (dt, 18, J = 15, 7.5 Hz), 25.4 (t, 1, J = 77 Hz). Anal. Calcd: C, 42.33; H, 7.67. Found: C, 42.49; H, 7.77.

$[(\eta\text{-}C_5H_5)Co(P(OCH_3)_3)_3][BF_4]_2$. $(\eta\text{-}C_5H_5)Co(CO)I_2$ (0.50 g, 1.2 mmol) dissolved in THF (100 mL) was treated with $P(OCH_3)_3$ (0.5 mL), causing a color change to red-brown with precipitation of a solid. Addition of $TlBF_4$ (1.0 g, 3.4 mmol) with vigorous stirring for 0.5 h caused the mixture to turn bright yellow. The mixture was filtered, the solid extracted with CH_2Cl_2 again, and the extract treated with hexane, resulting in a yellow solid (0.30 g): mp 245–246 °C dec; ^1H NMR τ 4.1 (s, 5), 5.9 (virtual quartet, 27).

$[(\eta\text{-}C_5H_5)Co(P(OEt)_3)_3][BF_4]_2$. $((EtO)_3P)_3CoCl$ (2.42 g, 4.1 mmol) dissolved in THF (100 mL) was treated with TlC_5H_5 (1.10 g, 4.1 mmol) for 1 h. The mixture was filtered and filtrate treated with $AgBF_4$ (0.80 g, 4.1 mmol) for 1.5 h with stirring. Filtration gave a black solid, which was extracted with CH_2Cl_2, giving a green solution. Addition of Et_2O caused precipitation of a yellow solid (1.30 g; 40% based on L_3CoCl, 80% based on $AgBF_4$): mp 220–221 °C dec; ^1H NMR τ 3.9 (s, 5), 5.4 (m, 18), 8.5 (t, 27). Anal. Calcd: C, 36.7; H, 6.3. Found: C, 35.0; H, 6.3.

$[(\eta\text{-}C_5H_5)Co(P(O\text{-}i\text{-}Pr)_3)_3][BF_4]_2$. $(\eta\text{-}C_5H_5)Co(P(O\text{-}i\text{-}Pr)_3)_2$ (10.0 g, 18.5 mmol) dissolved in THF (100 mL) with excess $P(O\text{-}i\text{-}Pr)_3$ (10 mL) was treated with $AgBF_4$ (7.1 g, 36.5 mmol) for 1 h with stirring. Filtration gave a yellow-gray solid, which was extracted with CH_2Cl_2. THF was added to the yellow extract and the volume reduced, giving a yellow, microcrystalline solid (10.3 g, 60%): mp 130 °C dec; ^1H NMR τ 4.2 (s, 5), 4.85 (m, 9), 8.4 (d, 54). Anal. Calcd: C, 41.6; H, 7.4. Found: C, 41.5; H, 7.2.

$(\eta\text{-}C_5H_5)Co(CO)_2$ with $AgBF_4$. $(\eta\text{-}C_5H_5)Co(CO)_2$ (1.80 g, 10.0 mmol) dissolved in THF (100 mL) was treated with $AgBF_4$ (1.95 g, 10.0 mmol) for 1 h. Filtration gave a gray solid, which was extracted with CH_2Cl_2. The extract was treated with hexane, giving a yellow solid (1.44 g): mp 164 °C dec; magnetic susceptibility (CH_2Cl_2) $\chi = 1.65 \times 10^{-5}$.

Registry No. **1a**, 32993-07-0; **1b**, 79639-49-9; **1c**, 80719-04-6; **1e**, 32677-72-8; **1f**, 32611-34-0; **1**, L = CO and PPh_3, 12203-85-9; **1**, L

= P(O-*i*-Pr)$_3$, 80719-05-7; **1**, L = CO, 12078-25-0; **2a**, 80719-07-9; **2**, L = PEt$_3$, X = I, 80719-08-0; **2**, L = PEt$_3$, X = BF$_4$, 80719-10-4; **2**, L = PEt$_3$, X = Br, 80719-11-5; **2**, L = PPh$_2$Et, X = BF$_4$, 80719-13-7; **2**, L = DPPE, X = Br, 80719-14-8; **2**, L = DPPE, X = I, 80719-15-9; **2**, L = P(O-*i*-Pr)$_3$, X = BF$_4$, 80719-17-1; **2**, L = P(OPh)$_3$, X = BF$_4$, 80719-19-3; **3a**, 72859-67-7; **3**, L = PPh$_3$, X = Br, 80719-20-6; **3**, L = PPh$_3$, X = I, 80719-21-7; **3**, L = PEt$_3$, X = Cl, 80719-22-8; **4**, L = CO, X = I, 12012-77-0; **4**, L = PPh$_3$, X = CN, 38531-03-2; **5**, L = PPh$_3$, X = BF$_4$, 80719-24-0; **6**, L = PEt$_3$, X = Cl, BF$_4$, 80719-26-2; **7**, L = PEt$_3$, X = BF$_4$, 80719-28-4; **8**, L = P(OMe)$_3$, X = BF$_4$, 80737-24-2; **8**, L = P(OEt)$_3$, X = BF$_4$, 80737-26-4; **8**, L = P(O-*i*-Pr)$_3$, X = BF$_4$, 80719-30-8; (Ph$_3$P)$_3$CoCl, 26305-75-9; (Et$_3$P)$_2$CoI$_2$, 31933-55-8; (η-C$_5$H$_5$)$_2$Co, 1277-43-6; (Ph$_3$P)$_2$CoCl$_2$, 14126-40-0; (Ph$_3$P)$_2$CoBr$_2$, 14126-32-0; (Ph$_3$P)$_2$CoI$_2$, 14056-93-0; (Et$_3$P)$_2$CoCl$_2$, 14784-62-4; (Et$_3$P)$_2$CoBr, 14784-57-7; (Ph$_2$EtP)$_2$CoBr$_2$, 14916-44-0; (Ph$_2$EtP)$_2$CoI$_2$, 31880-18-9; (Ph$_2$EtP)$_2$CoCl$_2$, 14916-45-1; (DPPE)CoBr$_2$, 34775-49-0; (DPPE)CoI$_2$, 34775-39-8; ((EtO)$_3$P)$_3$CoCl, 15488-43-4.

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A New Route to Thiocarbonyl–Iron Complexes: Preparation of Fe^{II}[porphyrin][C(Cl)SR] Carbene Complexes and Their Conversion to Fe^{II}[porphyrin][CS] Complexes

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The reaction of trichloromethyl–thioalkyl compounds including the widely used fungicides Captan and Folpet with iron(II) porphyrins in the presence of a reducing agent in excess leads to the formation of new carbene complexes, Fe[porphyrin][C(Cl)SR], whose stabilities are strongly dependent on the nature of the R substituent. Upon treatment by a catalytic amount of FeCl$_2$ or CuCl$_2$, some of them are decomposed into thiocarbonyliron(II)–porphyrin complexes, Fe[porphyrin][CS], in nearly quantitative yields. Various Fe[porphyrin][CS][L] complexes have thus been obtained by this method and characterized by UV–visible, IR, and ^{1}H and ^{13}C NMR spectroscopy. They are very stable to dioxygen and nucleophiles but react with primary amines R′NH$_2$ in excess to give the Fe[porphyrin][CNR′][R′NH$_2$] complexes. Reduction of C$_6$H$_5$SCHCl$_2$ by iron(II) tetraphenylporphyrin, Fe[TPP], leads to the Fe[TPP][CHSC$_6$H$_5$] complex, which is the first example of an iron(II) porphyrin complex bearing a secondary CHR carbene.

Introduction

Polyhalogenated compounds are widely used as industrial solvents, insecticides, fungicides, or volatile anaesthetics. It has been indicated[1] that they lead to cytochrome P450–iron(II)–carbene complexes upon reductive metabolization (eq 1).

$$\underset{\mathbf{1}}{\mathrm{RCCl_3}} + \mathrm{Fe[P]} \xrightarrow[-2\mathrm{Cl}^-]{2e^-} \underset{\mathbf{2}}{\mathrm{Fe[P][C(Cl)R]}} \qquad (1)$$

P = porphyrin or cytochrome P450

This has been recently confirmed by the preparation of carbene–iron(II) porphyrin complexes (**2**) upon reduction of polyhalogenated compounds by iron(II) porphyrins in the presence of an excess of reducing agent (eq 1).[2,3] The carbenic structure of complexes **2** has been established by their elemental analysis and various spectroscopic studies as well as by an X-ray diffraction analysis[3b] in the case of the dichlorocarbene complex Fe[TPP][CCl$_2$][H$_2$O].[3a,4]

Various organic compounds containing the SCCl$_3$ moiety display fungicidal activity. Among them, Folpet **3a**[4] and especially Captan **3b**[4] are broad spectra, nonpersistent fungicides, which are widely used for various fungus diseases of seeds, plants, and fruits.[5] Their activities have been related to the presence of the SCCl$_3$ group, which is metabolized in part into thiophosgene and carbonyl sulfide.[6]

We have studied the reduction of RSCCl$_3$ compounds by iron(II) porphyrins in order to mimic their reductive metabolism by cytochrome P450–iron(II) and also to have an access to the unknown carbene complexes of the type Fe^{II}[P][C(Cl)SR] that one could expect from eq 1.

We report, in this paper,[7] the preparation and properties of such carbene complexes, Fe[TPP][C(Cl)SR], and a new simple method of preparation of iron thiocarbonyl complexes based on the unexpected property of the aforementioned carbene complexes to eliminate RCl upon treatment by FeCl$_2$ or CuCl$_2$. The properties of some thiocarbonyl–iron(II) porphyrin complexes, Fe[P][CS][L], obtained by this reaction are also discussed.

Results and Discussion

(I) Reaction of Iron(II) Porphyrins with RSCCl$_3$ and RSCHCl$_2$ in the Presence of an Excess of Reducing Agent. The reduction of the RSCCl$_3$ compounds **3a**–**3d** and of dichloromethyl benzyl thioether, **3e**, by iron(II) tetraphenylporphyrin has been done under argon in a biphasic medium (CH$_2$Cl$_2$ or C$_6$H$_6$–H$_2$O) with sodium dithionite as a reducing agent (method A). Compounds **3d** and **3e** can also be reduced in dichloromethane–methanol solutions with iron powder as a

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