J. Am. Chem. Soc. **1995**, *117*, 11745−11748

Can Spin State Change Slow Organometallic Reactions?

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Received August 15, 1995⊗

Abstract: Diamagnetic $Tp^{i\text{-}Pr,Me}Co(CO)_2$ ($Tp^{i\text{-}Pr,Me}$ = hydrotris(3-iso-propyl-5-methylpyrazolyl)borato) has been prepared and structurally characterized by X-ray diffraction. In solution it spontaneously loses carbon monoxide to yield paramagnetic $Tp^{i\text{-}Pr,Me}Co(CO)$, a complex with a triplet spin ground state. In the presence of CO, the two complexes are in equilibrium (i.e. $Tp^{i\text{-}Pr,Me}Co(CO) + CO \leftrightarrow Tp^{i\text{-}Pr,Me}Co(CO)_2$), and measurements of the temperature dependence of the equilibrium constant by variable temperature ^1H NMR spectroscopy have been used to determine the thermochemical parameters $\Delta H = -12.9(2)$ kcal and $\Delta S = -32(1)$ eu. The CO exchange reaction is fast on the NMR time scale at ambient temperature, but it can be frozen out below 224 K, the temperature of coalescence. At 224 K the rate constants for the dissociation and binding of CO were $k_{-1} = 6(1) \times 10^3\ s^{-1}$ and $k_1 = 3(1) \times 10^9\ M^{-1}\ s^{-1}$, respectively. This reaction represents an interconversion between a triplet and a singlet molecule by a typical organometallic two-electron process, and it is exceedingly fast. Based on this observation it is argued that the notion of "spin-blocking" of organometallic reactions is inappropriate.

Introduction

A recent paper by Schrock et al. has once again raised the question whether organometallic reactions can be "spin-blocked", i.e. slowed significantly by the need for a high-spin (triplet) starting material to cross over to a low-spin (singlet) surface on the pathway to a diamagnetic product.[1] The hypothesis that different ground-state spin multiplicities might raise the activation barriers of organometallic transformations was originally put forward by Collman.[2] However, since an experimental test explicitly designed to test this speculation failed to support it,[3] the notion seemed abandoned.[4] In connection with our general exploration of the reactivity of paramagnetic organometallics, any systematic effects of spin state changes on reaction rates would be of interest. Herein we report our observations regarding an extremely facile interconversion between an organometallic triplet and a singlet.

Tris(pyrazolyl)borate (Tp) ligands (recently rechristened "scorpionates")[5] are often considered the coordination chemist's equivalent of the quintessential "organometallic" ligand, namely the cyclopentadienyl (Cp) moiety. However, while there exist many pairs of complexes differing only by substitution of one for the other, the greater steric demand of the nitrogen tripod is readily apparent, and subject to straightforward augmentation besides. By the simple expedient of introducing large alkyl substituents in the 3-position of the pyrazole ring, so-called "tetrahedral enforcers" are created, owing their name to the tendency to leave room for only one additional ligand to bind to the metal atom.[6] For example, we have used the $Tp^{t\text{-}Bu,Me}$ ligand to prepare 4-coordinate complexes of the type $Tp^{t\text{-}Bu,Me}Co{-}L$ ($Tp^{t\text{-}Bu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borato, L = CO, N_2, C_2H_4, etc.).[7] These paramagnetic 16-electron complexes stand in stark contrast to the familiar closed-shell compounds $CpCo(L)_2$ and $Cp^*Co(L)_2$. A system straddling this divide, namely the carbonyls $Tp^{i\text{-}Pr,Me}Co(CO)_n$ ($Tp^{i\text{-}Pr,Me}$ = hydridotris(3-iso-propyl-5-methylpyrazolyl)borato, n = 1,[8] 2), coexists in a readily observable equilibrium.

Results and Discussion

Depending on the CO pressure, the $Tp^{i\text{-}Pr,Me}Co$ moiety binds one or two carbonyl ligands. Thus, exposure of a concentrated pentane solution of $[Tp^{i\text{-}Pr,Me}Co)_2(\mu\text{-}N_2)]$ to an overpressure (P > 2 atm) of CO and cooling to 0 °C yielded brown crystals of $Tp^{i\text{-}Pr,Me}Co(CO)_2$. While susceptible to ligand loss in solution (see below), solid $Tp^{i\text{-}Pr,Me}Co(CO)_2$ proved stable enough for a crystal structure determination; its molecular structure is shown in Figure 1 and selected interatomic distances and angles are listed in Table 1. The five-coordinate cobalt adopts a nearly perfect square-pyramidal coordination geometry, with one of the pyrazole rings supplying the apical nitrogen ligand. The angles between the latter and the four basal ligands average 97° (range: 90.5−105.5°), and the cobalt does not deviate significantly from the C_2N_2 plane defined by these ligands (0.25 Å). The metal−ligand distance to the apical nitrogen (Co−N(21) = 2.087(11) Å) is the longest of the three Co−N distances, yet on average (Co-N_{avg} = 2.02 Å) these distances are entirely typical for a tris(pyrazolyl)borato coordinated to Co(I). Tris(pyrazolyl)borate complexes have a remarkable tendency to adopt coordination geometries derived from octahedral coordination by removal of one or several ligands. Thus the disposition of the two carbonyl ligands with respect to the symmetry axis of the TpCo fragment of $Tp^{i\text{-}Pr,Me}Co(CO)_2$ (see **A** in Scheme 1) is distinctly different from that found in, e.g., $CpCo(CO)_2$,[9] which more closely approximates a trigonal bipyramidal complex (see **B**). Nevertheless, the two complexes

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⊗ Abstract published in *Advance ACS Abstracts*, November 15, 1995.

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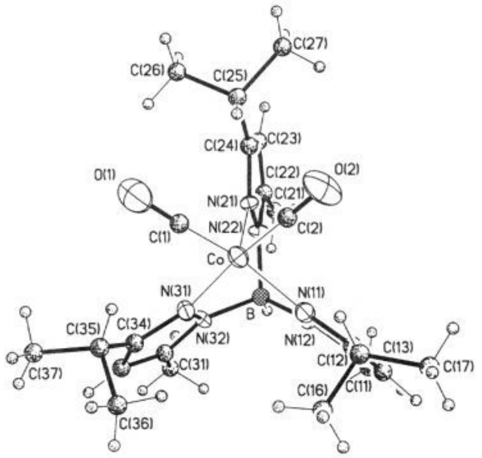
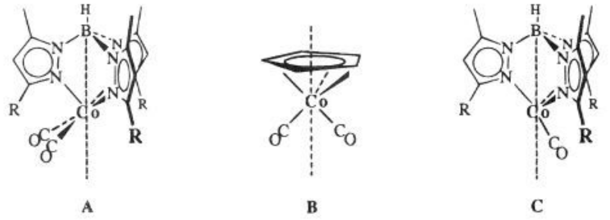


Figure 1. The molecular structure of $Tp^{i\text{-}Pr,Me}Co(CO)_2$. Selected interatomic distances and angles are listed in Table 1.

Table 1. Selected Interatomic Distances and Angles for $Tp^{i\text{-}Pr,Me}Co(CO)_2$

	Distances (Å)		
Co−N(11)	2.002(12)	Co−N(21)	2.087(11)
Co−N(31)	1.985(8)	Co−C(1)	1.696(19)
Co−C(2)	1.729(15)	C(1)−O(1)	1.179(23)
C(2)−O(2)	1.162(18)		
	Angles (deg)		
N(11)−Co−N(21)	91.9(5)	N(11)−Co−N(31)	85.5(4)
N(21)−Co−N(31)	90.5(4)	N(11)−Co−C(1)	162.5(7)
N(11)−Co−C(2)	92.1(7)	N(21)−Co−C(1)	105.5(7)
N(21)−Co−C(2)	99.4(7)	N(31)−Co−C(1)	94.3(6)
N(31)−Co−C(2)	169.8(7)	C(1)−Co−C(2)	85.0(8)
Co−C(1)−O(1)	173.4(16)	Co−C(2)−O(2)	177.5(14)

Scheme 1



are closely related; most importantly, both are closed-shell species, the 18-electron configurations of which result in bulk diamagnetism.

Dissolution of brown $Tp^{i\text{-}Pr,Me}Co(CO)_2$ in organic solvent resulted in the immediate release of 1 equiv of carbon monoxide and quantitative formation of green $Tp^{i\text{-}Pr,Me}Co(CO)$. Indeed, under typical laboratory conditions (ambient temperature, absence of CO) the monocarbonyl is the stable compound in this system, much as it was for other sterically hindered tris(pyrazolyl)borato cobalt complexes (e.g. $Tp^{t\text{-}Bu,Me}Co(CO)$, $Tp^{Np}Co(CO)$).[10] The spectroscopic data for $Tp^{i\text{-}Pr,Me}Co(CO)$ were also very similar; specifically, the IR spectrum (KBr) showed a single ν_{C-O} stretch at 1940 cm^{-1}, and the ^1H NMR spectrum revealed a set of isotropically shifted resonances consistent with a paramagnetic complex. Accordingly, the effective magnetic moment of $Tp^{i\text{-}Pr,Me}Co(CO)$ in the solid state measured $\mu_{eff} = 3.1(1)\ \mu_B$. This value is consistent with the presence of two unpaired electrons; the ground state of this 16-electron d^8 complex is a triplet. While we have not determined the crystal structure of $Tp^{i\text{-}Pr,Me}Co(CO)$, there is no reason to believe that it deviates significantly from that of $Tp^{Np}Co(CO)$, which has been structurally characterized.[10] For reasons well understood, these monocarbonyls adopt structures best described as "cis-divacant octahedra" (see **C** in Scheme 1), i.e. the single CO ligand is bent away from the 3-fold axis of the Tp ligand and is situated approximately trans to one of the pyrazolyl nitrogens.

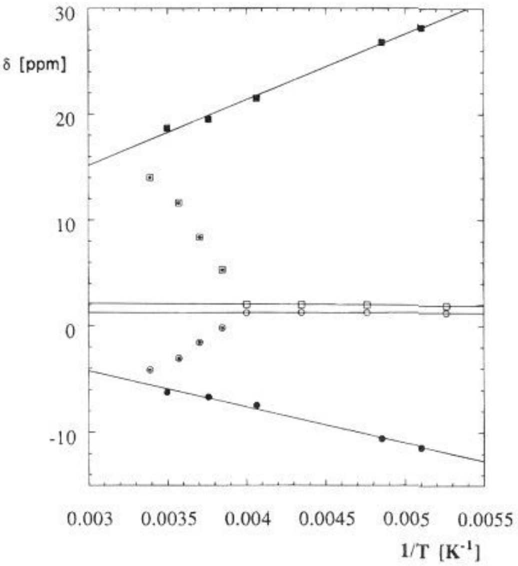


Figure 2. Temperature dependence of the chemical shifts of $Tp^{i\text{-}Pr,Me}Co(CO)_2$ (pz-CH*Me*$_2$, ○; pz-*Me*, □) and $Tp^{i\text{-}Pr,Me}Co(CO)$ (pz-CH*Me*$_2$, ●; pz-*Me*, ■), and equilibrium mixtures of both (pz-CH*Me*$_2$, ⊙, pz-*Me*, ⊡). Note the linear $1/T$ dependence of the shifts of the paramagnet and the intermediate shifts (i.e. concentration weighted averages) of the mixtures.

$$Tp^{i-Pr,Me}Co(CO) + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Tp^{i-Pr,Me}Co(CO)_2 \qquad (1)$$

$$K_{eq} = \frac{[Tp^{i-Pr,Me}Co(CO)_2]}{[Tp^{i-Pr,Me}Co(CO)][CO]}$$

Exposure of $Tp^{i\text{-}Pr,Me}Co(CO)$ solutions to CO gas at various pressures and temperatures allowed the spectroscopic observation of equilibrium mixtures of mono- and dicarbonyl (see eq 1). For example, solution IR spectra (toluene) showed the appearance of two new bands at 2016 and 1939 cm^{-1}, as ν_{CO} of the monocarbonyl (1946 cm^{-1}) diminished in intensity. Most informative, however, was NMR spectroscopy; we have used the pressure and temperature dependence of ^1H NMR spectra to determine the thermochemical parameters of the equilibrium in toluene-d_8. Equilibrium mixtures showed NMR resonances with chemical shifts intermediate between those of pure $Tp^{i\text{-}Pr,Me}Co(CO)$ and $Tp^{i\text{-}Pr,Me}Co(CO)_2$. Figure 2 depicts some representative data; note, that the resonances of paramagnetic $Tp^{i\text{-}Pr,Me}Co(CO)$ exhibited a linear dependence of δ on $1/T$ as expected from the Curie law, while the resonances of diamagnetic $Tp^{i\text{-}Pr,Me}Co(CO)_2$ (observable only at high p_{CO} and low T) were essentially temperature independent. The actual shifts of mixtures were concentration weighted averages of these extremes; in combination with solubility data for CO in toluene these spectra permitted determination of the equilibrium constants K_{eq} (eq 1). A van't Hoff analysis of the temperature dependence of the latter (see Figure 3) yielded the thermochemical parameters governing the equilibrium as $\Delta H = -12.9(2)$ kcal/mol and $\Delta S = -32(1)$ eu. While the negative entropy of reaction is not surprising for a ligand association reaction,

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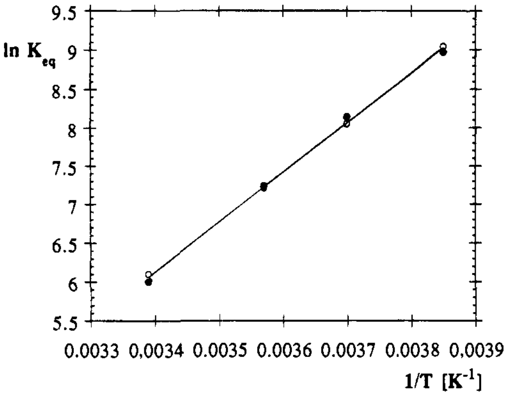

Figure 3. Temperature dependence of the equilibrium constant for the CO exchange reaction (eq 1) at two initial CO pressures (P_{CO} = 0.64 atm, ●; P_{CO} = 0.7 atm, ○—note that upon cooling P_{CO} changed and was recalculated for each temperature; see Experimental Section); $\Delta H = -12.9(2)$ kcal, $\Delta S = -32(1)$ eu.

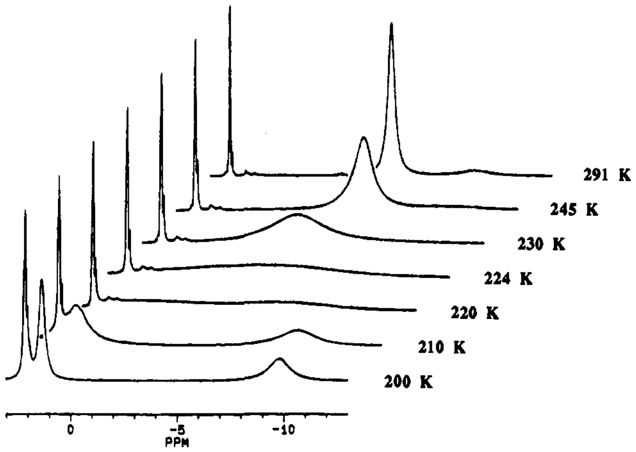

Figure 4. Variable-temperature ^{1}H NMR spectra of a mixture of $Tp^{i\text{-}Pr,Me}Co(CO)$ and $Tp^{i\text{-}Pr,Me}Co(CO)_2$ under CO. Only the region of the isopropyl groups is shown.

the enthalpy of reaction is remarkably small. Typical bond dissociation energies for homoleptic metal carbonyls of the first row transition metals range between 25 and 41 kcal/mol,[4] and at ca. 13 kcal/mol the second CO ligand of $Tp^{i\text{-}Pr,Me}Co(CO)_2$ must rank as one of the most weakly bound carbonyls in any 18-electron complex.[11] We suggest that steric encumbrance of the cobalt by the "tetrahedral enforcer" ligand is solely responsible for the bond weakening. Consistent with this notion, even more hindered complexes (e.g. $Tp^{t\text{-}Bu,Me}Co(CO)$) showed no signs of CO binding under comparable conditions.

Finally, we wish to address the dynamics of the reaction. As noted above, only one set of averaged resonances was observed in ^{1}H NMR spectra of $Tp^{i\text{-}Pr,Me}Co(CO)_2/Tp^{i\text{-}Pr,Me}Co(CO)$ mixtures in the temperature interval used for the equilibrium measurements (T = 260−295 K). The CO dissociation/association equilibrating the two complexes is fast on the NMR time scale at these temperatures. However, NMR spectra at even lower temperatures revealed a coalescence phenomenon and ultimately that led to the observation of individual resonances of both species. A set of representative spectra is shown in Figure 4; the temperature of coalescence was judged to be T_c = 224 K. For the purposes of our argument only an approximate estimate of the rates of interconversion is required; thus we have opted against a complete bandshape analysis of the spectra and extraction of the associated activation parameters. However, as the concentrations of $Tp^{i\text{-}Pr,Me}Co(CO)_2$ and $Tp^{i\text{-}Pr,Me}Co(CO)$ were close to equal at the coalescence temperature, and since the difference in their resonance frequencies ($\delta\nu$) and the rate constant for their interconversion (k) substantially exceed the band widths in the absence of exchange, the rate constant at the coalescence temperature could be determined from the relationship $k_c = 2.22\cdot\delta\nu$.[12] At 224 K, the first order rate constant for the ligand dissociation of $Tp^{i\text{-}Pr,Me}Co(CO)_2$ is $k_{-1} = 6(1) \times 10^3$ s^{-1}; extrapolation of the equilibrium constants to the same temperature ($K_{eq}(224\text{ K}) = 4.4 \times 10^5$ M^{-1}) then yielded the second-order rate constant for CO binding as $k_1 = 3(1) \times 10^9$ M^{-1} s^{-1}, simply by detailed balancing. The latter rate approaches diffusion control, leaving little room for any kinetic barrier. Insertion of k_{-1} into the Eyring equation yielded $\Delta G^{\ddagger}$ = 9.1 kcal; however, we note that much of this barrier is due to the thermodynamics of the equilibrium, which favors $Tp^{i\text{-}Pr,Me}Co(CO)_2$ by ΔG = 5.7 kcal at 224 K.

Conclusions

The reaction in eq 1 converts an organometallic triplet molecule into a singlet by way of an archetypal organometallic transformation, namely ligand dissociation/binding. The reaction is so fast as to rule out any appreciable activation barrier, no matter what the origin (including "spin-blocking"). Other fast organometallic spin crossover reactions are known; for example, chromocene (a ground state triplet) reacts rapidly, and reversibly, with CO at −78 °C to form the diamagnetic adduct $Cp_2Cr(CO)$.[13] To gauge the possible impact of "spin-forbiddeness" on reactions of transition metal compounds, it is informative to consider spin crossover complexes.[14] Rates of intersystem crossing processes for such compounds in solution are generally very fast ($k > 1 \times 10^5$ s^{-1}).[15,16] It seems thus implausible, that changes in spin state should slow organometallic transformations as a general rule.

Experimental Section

Commercial reagents were used as supplied. All manipulations of air-sensitive compounds were carried out under an inert atmosphere in a Vacuum Atmospheres inert-atmosphere drybox or using standard Schlenk and high-vacuum techniques. $[Tp^{i\text{-}Pr,Me}Co](N_2)$ and $Tp^{i\text{-}Pr,Me}Co(CO)$ were synthesized as previously described.[8] Solvents were purified by distillation from sodium benzophenone ketyl. Toluene-d_8 and benzene-d_6 were dried with Na and stored over Na/K. ^{1}H NMR spectra were collected on a WM 250 Bruker spectrometer, using a Bruker VT 1000 variable temperature unit as required. Infrared spectra under CO pressure were obtained using an *in situ* internal reflectance FTIR reaction monitoring system (Applied Systems React IR). UV/vis/NIR spectra were obtained on a Bruins Instruments Omega 20 spectrophotometer. Solid-state IR spectra (KBr) were obtained with a Mattson Instruments Alpha Centauri FTIR. Magnetic moments (at room temperature) were measured using a Johnson-Matthey Magnetic Susceptibilities balance.

[Hydrotris(3-isopropyl-5-methylpyrazolyl)borato](dicarbonyl)cobalt(I), $Tp^{i\text{-}Pr,Me}Co(CO)_2$. A concentrated pentane solution of $[Tp^{i\text{-}Pr,Me}Co]_2(N_2)$ was placed under 3 atm of CO in a glass ampule . The solution was cooled to 0 °C overnight, yielding brown crystals of $Tp^{i\text{-}Pr,Me}Co(CO)_2$. The mother liquor was then decanted from the crystals, and the ampule was evacuated and brought into the drybox. The crystals were coated with oil, to retard the loss of CO, and mounted

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Table 2. Crystallographic Data for $Tp^{i\text{-}Pr,Me}Co(CO)_2$

(a) Crystal Parameters	
formula	$C_{23}H_{34}BCoN_6O_2$
formula wt	496.3
cryst system	monoclinic
space group	$P2_1/n$
a, Å	9.320(2)
b, Å	31,731(8)
c, Å	9,402(3)
β, deg	108.23(3)
V, Å^3	2640,8(12)
Z	4
crystal dimens, mm	0.38 × 0.42 × 0.48
crystal color	red-brown
D(calc), g cm^{-3}	1.248
μ(Mo Kα), cm^{-1}	6,79
(b) Data Collection	
diffractometer	Siemens R3m/V
monochromator	highly oriented graphite crystal
radiation	Mo Kα ($\lambda = 0.71073$ Å)
T, K	296
2*θ* scan range, deg	4.0 to 40.0
data collected (*h,k,l*)	$-8 \leq h \leq 8, 0 \leq k \leq 30, -4 \leq l \leq 9$
no. of reflcns collected	2626
no. of indep. reflections	2436
no. of obsd ref ($F_o > n\sigma(F_o)$)	1325 ($F > 4.0\sigma(F)$)
stad. reflcns	3 measured every 197 reflections
var. in stand, %	<1
(c) Refinement	
R(*F*), %	6,63
R(*wF*), %	8.29
Δ/σ(max)	0,089
$\Delta(\rho)$, e Å^{-3}	0.51
N_o/N_v	7.4
GOF	1.67

in glass capillaries for X-ray diffraction. For the ^{1}H NMR, IR, and UV/vis/NIR spectroscopic characterization $Tp^{i\text{-}Pr,Me}Co(CO)_2$ was generated in situ using various pressures of CO. ^{1}H NMR (toluene-d_8) 1.20 (18H), 1,90 (9H), 3.69 m (3H), and 5.37 (3H) ppm; internal reflectance FTIR (toluene, 1 atm of CO at 263 K) ν_{CO} 2016 and 1939 cm^{-1}; UV/vis/NIR (toluene, 3 atm CO) 433 nm ($\epsilon = 1123$ M^{-1} cm^{-1}).

Crystal Structure Determination of $Tp^{i\text{-}Pr,Me}Co(CO)_2$. Crystallographic data are collected in Table 2. All samples were found to diffract weakly and diffusely. No data were available beyond 2*θ*(Mo Kα) = 40°. Diffraction symmetry and systematic absences in the data uniquely allowed the assigned space group. Azimuthal scans indicated that corrections for absorption were not required, and none were applied. The Co atom was located by Patterson methods, and the structure completed by the usual procedures. To conserve data only atoms with $Z > 6$ were refined anisotropically. Hydrogen atoms were included as idealized contributions. All software is contained in the SHELXTL library (ver 4.2, G. Sheldrick, Siemens XRD, Madison, WI).

Variable-Temperature ^{1}H NMR. In a drybox NMR tubes fitted with 14/20 ground glass joints were charged with carefully weighed amounts (ranging from 10 to 15 mg) of $Tp^{i\text{-}Pr,Me}Co(CO)$. Toluene-$d_8$ was then vacuum transferred into the tube, and finally the solution was exposed to CO gas ($P < 1.0$ atm). After equilibration, the CO pressure in the NMR tube was measured with a U-tube manometer. The NMR tube was then flame sealed and variable-temperature NMR data were recorded at 250 MHz. As the exchange reaction was fast on the NMR time scale, the observed resonances were concentration weighted averages of the known chemical shifts of $Tp^{i\text{-}Pr,Me}Co(CO)$ and $Tp^{i\text{-}Pr,Me}Co(CO)_2$. Concentrations were corrected for the thermal contraction of the solvent using the temperature dependence of the density of toluene: $d_T = [0.8845 - 0.009159(T - 298)]$ g·cm^{-3}.[17] The applicable concentrations of CO were calculated by correcting for the amount of CO bound to the metal due to temperature-dependent shifts in the equilibrium ($n_{CO} = n_{CO,initial} - \Delta n_{Tp^{i\text{-}Pr,Me}Co(CO)_2}$) and using an extrapolation of tabulated values of the solubility of CO in toluene.[18] This calculation was performed for each of the individual temperatures, as the temperature change causes a decrease in solubility but an increase in the conversion to diamagnetic product.

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy (ER14273 to K.H.T.).

Supporting Information Available: Tables giving the positional and thermal parameters of $Tp^{i\text{-}Pr,Me}Co(CO)_2$ (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions,

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