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Equilibration between a Phosphine−Cobalt Complex and an Analogous Complex Containing an N-Heterocyclic Carbene: The Thermodynamics of a Phosphine−Carbene Exchange Reaction

Ryan W. Simms, Mark J. Drewitt, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada, K7L 3N6

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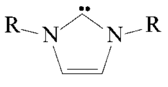
The reaction of $CpCo(PPh_3)Me_2$ with the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) does not result in complete substitution of the PPh_3, as expected, but rather in an equilibrium mixture of $CpCo(PPh_3)Me_2$, IPr, $CpCo(IPr)Me_2$, and PPh_3. Determination of the equilibrium constants for this unusual reaction over the temperature range 30−50 °C shows that $\Delta H° = -24.4 \pm 1.7$ kJ mol^{-1}, $\Delta S° = -65.8 \pm 5.5$ J mol^{-1} K^{-1}, and thus that it is entropy factors arising from steric crowding in $CpCo(IPr)Me_2$ that prevent complete substitution. Evidence for steric crowding is found in a comparison with the crystal structures of $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO). The smaller, more basic PMe_3 does displace IPr completely from $CpCo(IPr)Me_2$.

Phosphine complexes are used extensively in catalytic processes, generally stabilizing reaction intermediates through their electronic and steric properties.[1] N-Heterocyclic carbenes (**A**, R = alkyl, aryl), available with a wide variety of functionalities and often regarded as phosphine mimics, offer a new range of electronic and steric influence to catalytic systems.[2] The main advantage of N-heterocyclic carbenes over even the most basic phosphines is their greater electron-donating ability, resulting in complexes with improved stabilities.[2a,c,3] Indeed, N-heterocyclic carbenes readily displace coordinated phosphines in a variety of environments, and it is generally accepted that it is the strength of the metal carbene bond that is the reason for the general stability of carbene complexes.[2]



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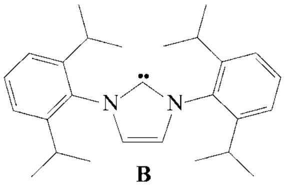

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We recently initiated a study of N-heterocyclic carbene complexes of cobalt by attempting to substitute the phosphine of the compound $CpCo(PPh_3)Me_2$ by the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**B**; henceforth IPr). Hoping to prepare the compound $CpCo(IPr)Me_2$, ligand exchange between the free carbene IPr and $CpCo(PPh_3)Me_2$ (**1**) was attempted. To our surprise, however, the reaction of $CpCo(PPh_3)Me_2$ with IPr did not proceed to completion, but reached equilibrium as in eq 1.

$$CpCo(PPh_3)Me_2 + IPr \rightleftharpoons CpCo(IPr)Me_2 + PPh_3 \quad (1)$$

As displacement of N-heterocyclic carbenes by phosphines had not previously been reported, this unexpected behavior provided a welcome opportunity to obtain equilibrium constant data and, thence, thermodynamic data for the interchange of phosphine and carbene ligands. The only previous thermochemical study of carbene complexes produced just enthalpic data and showed that, in compounds of the type Cp*RuLCl (L = carbene of type A, PCy_3, P^iPr_3), the ruthenium−carbene bonds are generally stronger than the ruthenium−phosphine bonds except when R is the very bulky adamantyl group.[2f,3a,b] We now describe the results of a quantitative equilibrium constant study, complemented by a comparison of the electronic and steric effects of the ligands PPh_3, IPr, and PMe_3 (which completely displaces IPr from $CpCo(IPr)Me_2$) based on spectroscopic (IR, NMR) and crystallographic data. While this work was in progress, a somewhat similar phosphine−carbene exchange was reported by Titcomb et al. for palladium(0) complexes,[4] although the relationship between the Co(III) and Pd(0) systems is not as yet clear.

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* Corresponding author. E-mail: bairdmc@chem.queensu.ca. Fax: (613) 533-6669.

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Experimental Section

All manipulations were carried out under argon using standard Schlenk techniques or in a nitrogen-filled glovebox. Solvents, including deuterated solvents for NMR studies, were dried and distilled under nitrogen or argon immediately prior to use. All chemicals (Aldrich, Strem Chemicals) were used as received. $CpCo(PPh_3)Me_2$,[5] $CpCo(PPh_3)(CO)$,[6] $CpCo(PMe_3)(CO)$,[7] and IPr[8] were prepared as described in the literature. NMR spectra were measured on a Bruker Avance-400 spectrometer; IR spectra, on a Bruker IFS 25 spectrometer. Microanalyses were performed by Canadian Microanalytical Services Ltd, Vancouver, British Columbia.

Synthesis of $CpCo(IPr)Me_2$. A solution of 1.12 g of $CpCo(PPh_3)Me_2$ (2.68 mmol) and 1.08 g of IPr (2.77 mmol) in toluene (20 mL) was stirred for 4 h at 40 °C. Removal of the solvent in vacuo produced an oily solid, which was chromatographed on basic alumina (25 cm × 15 mm, 1:9 by volume toluene/hexanes) under argon. The first orange band was collected, and the solvent was removed in vacuo. The resulting red solid was recrystallized (−30 °C, 1:4 by vol toluene/hexanes) to give dark red needles. Yield: 0.13 g (8.9%). ^1H NMR (toluene-d_8): δ 0.21 (s, 6H, Co-Me), 1.01 (d, J_{HH} 6.8 Hz, 12H, CH*Me$_2$*), 1.43 (d, J_{HH} 6.8 Hz, 12H, CH*Me$_2$*), 3.06 (dq, J_{HH} 6.8 Hz, 4H, *CH*Me$_2$), 4.23 (s, 5H, Cp), 6.50 (s, 2H, NCH), 7.13 (d, J_{HH} 7.6, 4H, *m*-$C_6H_3(CHMe_2)_2$), 7.26 (t, J_{HH} 7.6, 2H, *p*-$C_6H_3(CHMe_2)_2$). $^{13}C\{^1H\}$NMR (toluene-d_8, −30 °C): δ −16.3 (Co-Me), 22.5, 26.5, 29.0 (CH*Me$_2$*), 87.4 (Cp), 123.6 (N*CC*), 126.0, 129.8, 139.1, 146.2 (*C$_6$*H$_3$(CHMe$_2$)$_2$), the carbene carbon resonance was not observed. Anal. Calcd for $C_{34}H_{47}CoN_2$: C, 75.25; H, 8.73; N, 5.16. Found: C, 75.43; H, 8.83; N, 5.16.

Synthesis of CpCo(IPr)(CO). A solution of 1.7 g of $CpCo(CO)_2$ (9.5 mmol) and 3.40 g of IPr (8.7 mmol) in toluene (50 mL) was stirred 16 h at 50 °C. The solvent was removed in vacuo until ∼5 mL remained, and then 50 mL of hexanes was added. The solution was cooled to −30 °C, producing dark red crystals, which were collected and dried in vacuo. Yield: 3.38 g (72%). ^1H NMR (toluene-d_8): δ 1.04 (d, J_{HH} 7 Hz, 12H, $CHMe_2$), 1.41 (d, J_{HH} 7 Hz, 12H, $CHMe_2$), 3.05 (dq, J_{HH} 7 Hz, 4H, $CHMe_2$), 4.28 (s, 5H, Cp), 6.58 (s, 2H, NCH), 7.15 (m, 6H, *m*- and *p*-$C_6H_3(CHMe_2)_2$). ^1H NMR (CD_2Cl_2): δ 1.10 (d, J_{HH} 6.6 Hz, 12H, $CHMe_2$), 1.38 (d, J_{HH} 6.6 Hz, 12H, $CHMe_2$), 2.90 (dq, J_{HH} 6.6 Hz, 4H, $CHMe_2$), 4.13 (s, 5H, Cp), 7.05 (s, 2H, NCH), 7.45 (m, 6H, *m*- and *p*-C_6H_3(i-Pr)$_2$). $^{13}C\{1H\}$NMR (toluene-d_8, −30 °C): δ 22.6, 26.1, 29.1 (s, $CHMe_2$), 81.3 (s, Cp), 124.2 (s, NCC), 126.1, 129.9, 138.2, 146.2 (s, $C_6H_3(CHMe_2)_2$), the carbene and carbonyl carbon resonances were not observed. IR ν_{CO} (hexanes): 1921 cm^{-1}. Anal. Calcd for $C_{33}H_{41}CoN_2O$: C, 73.32; H, 7.64; N, 5.18. Found: C, 73.02; H, 7.84; N, 5.09.

Monitoring the Carbene−Phosphine Exchange. In a representative experiment, 0.5 mL of toluene-d_8 was added to 8.3 mg of $CpCo(PPh_3)Me_2$ (0.02 mmol) and 7.8 mg of IPr (0.02 mmol) in a 5 mm NMR tube. The ligand substitution reaction was monitored by changes in the ^1H NMR spectra (single pulse) of the reaction mixture with time. The relative amounts of $CpCo(PPh_3)Me_2$, IPr, and $CpCo(IPr)Me_2$ were determined from the integrated area of the singlets at δ 4.20 (Cp in $CpCo(IPr)Me_2$), 4.45 (Cp in $CpCo(PPh_3)Me_2$), and 6.70 (NCH in free IPr). At equilibrium, the ^{31}P NMR spectrum confirmed the ratio of $CpCo(PPh_3)Me_2$ to PPh_3. The approach to equilibrium was monitored at five different temperatures (30, 35, 40, 45, and 50 °C), as well as by the reverse reaction of $CpCo(IPr)Me_2$ with PPh_3 at 30 °C.

X-ray Crystallography. Crystals of $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO) were mounted and sealed on glass fibers with epoxy glue. Data for each of the compounds were collected on a CCD-detector-equipped SMART system with graphite-monochromated Mo Kα radiation (λ 0.71073 Å) operated at 50 kV and 35 mA at 23 °C over the 2θ range of 4−56. The data were processed on a Pentium PC using the Siemens SHELXTL (version 5.0) software package, an empirical absorption correction being applied for the crystals. The data were corrected for Lorentz−polarization effects. Neutral atoms scattering factors were taken from Cromer and Waber.[9a] The structures were solved by direct methods; full-matrix least-squares refinements on *F* were performed with Crystals and the hydrogen atoms were placed geometrically and allowed to ride on their respective carbon during refinement.[9b] The figures of the structure were generated with ORTEP-III.[9c]

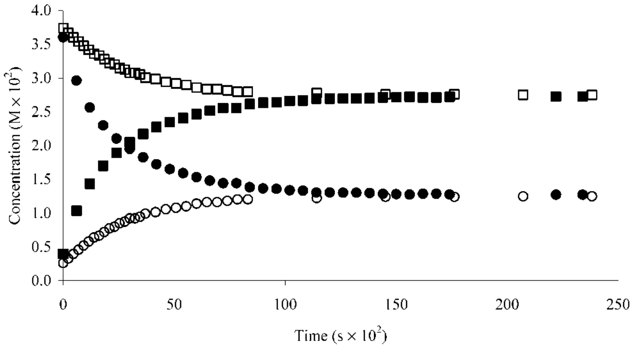

Figure 1. Approach to the equilibrium at 30 °C $CpCo(PPh_3)Me_2 + IPr \rightleftharpoons CpCo(IPr)Me_2 + PPh_3$: (a) forward direction (●) $CpCo(PPh_3)Me_2$, (■) $CpCo(IPr)Me_2$; (b) reverse direction (○) $CpCo(PPh_3)Me_2$, (□) $CpCo(IPr)Me_2$.

Results and Discussion

Equilibrium Studies. The new compound $CpCo(IPr)Me_2$ was prepared by the slow equilibration of a mixture of $CpCo(PPh_3)Me_2$ and IPr in toluene at 30 °C followed by chromatographic separation of the products at room temperature. Yields were invariably low because of partial decomposition on the column, but the compound was obtained pure and was characterized by elemental analyses, by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and crystallographically (see below). By monitoring the ^1H NMR spectrum of a reaction involving equimolar amounts of $CpCo(PPh_3)Me_2$ and IPr in toluene at 30 °C, the system was observed to approach equilibrium over about 4 h (Figure 1). To verify that equilibrium had indeed been achieved, the reverse reaction, involving equimolar amounts of $CpCo(IPr)Me_2$ and PPh_3, at 30 °C, was also monitored (Figure 1). As is seen, equilibration had certainly been achieved over this time span.

The equilibrium constants were measured at five temperatures, 30, 35, 40, 45, and 50 °C, with results as summarized in Table 1. A plot of ln(K_{eq}) vs 1/T is shown in Figure 2, and from this the thermodynamic values were calculated to be $\Delta H° = -24.4 \pm 1.7$ kJ mol^{-1}, $\Delta S° = -65.8 \pm 5.5$ J mol^{-1} K^{-1}. As is expected, the value of $\Delta H°$ does indeed suggest that the Co−IPr bond is stronger than the Co−PPh_3 bond, with the difference

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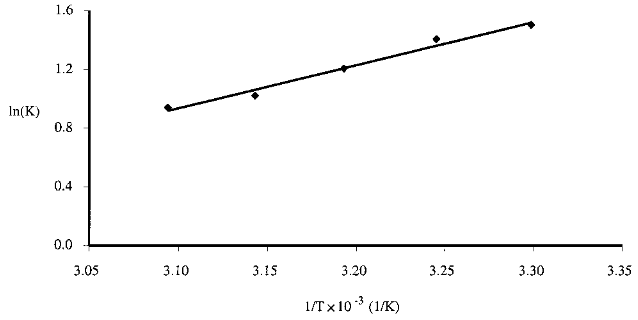


Figure 2. Plot of $\ln(K_{eq})$ vs $1/T$.

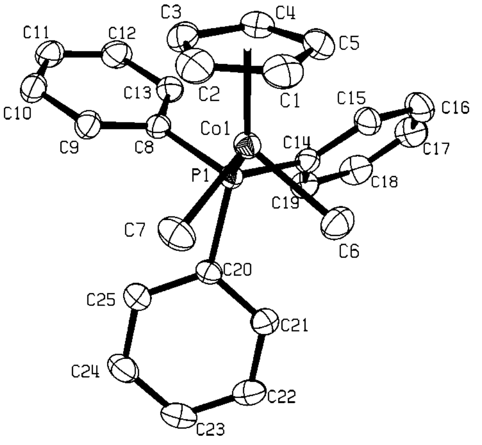


Figure 3. Molecular structure of $CpCo(PPh_3)Me_2$ with ellipsoids drawn at 30% probability. Hydrogen atoms are removed for clarity.

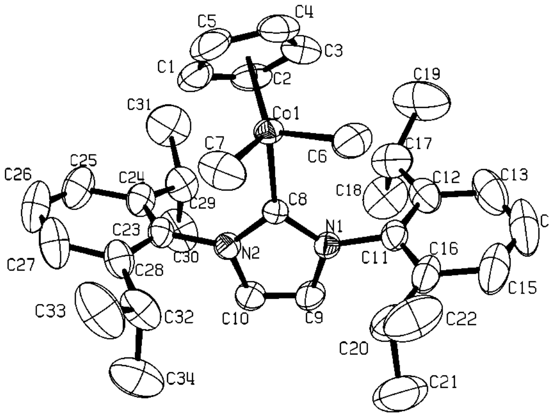


Figure 4. Molecular structure of $CpCo(IPr)Me_2$ with ellipsoids drawn at 30% probability. Hydrogen atoms are removed for clarity.

Table 1. Equilibrium Constants

temperature (K)	K_{eq}
303	4.49
308	4.08
313	3.34
318	2.78
323	2.56

in metal−carbene and metal−phosphine bond strengths being somewhat larger than has been reported for complexes of the type Cp*RuLCl (L = phosphine, carbene).[3] While it is the exothermicity of the ligand exchange reaction that is the driving force for the forward direction of eq 1, the very negative $\Delta S°$ for the forward reaction clearly counters at least in part the enthalpy change, leading to the establishment of equilibrium rather than the more commonly observed total displacement of phosphine.

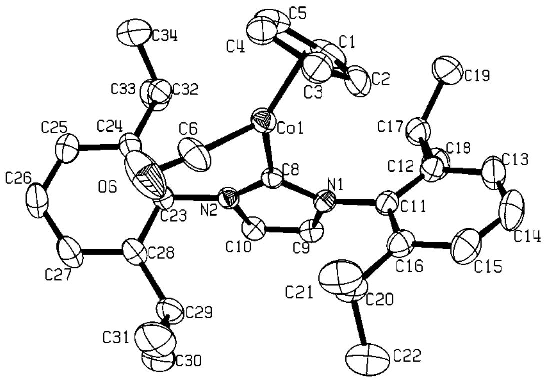


Figure 5. Molecular structure of CpCo(IPr)(CO) with ellipsoids drawn at 30% probability. Hydrogen atoms are removed for clarity

Table 2. ^{1}H NMR in Toluene-d_8

	δ(Cp)	δ(Me)
$CpCo(IPr)Me_2$	4.20	0.18
$CpCo(PMe_3)Me_2$	4.37	0.08
$CpCo(PPh_3)Me_2$	4.45	0.46
CpCo(IPr)(CO)	4.28	

In an effort to better understand the origins of the enthalpic and entropic influences, we undertook a spectroscopic (IR, NMR) study of the compounds $CpCo(PPh_3)Me_2$,[5] $CpCo(PMe_3)(CO)$,[7] $CpCo(IPr)Me_2$, $CpCo(PMe_3)Me_2$,[10] and CpCo(IPr)(CO) in order to assess the relative donor abilities of the ligands PPh_3, IPr, and PMe_3 in the cobalt system. In addition, we also undertook a structural comparison of the compounds $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO) in an attempt to gain further insight into the steric factors involved. The new compound CpCo(IPr)(CO) was prepared by reaction of IPr with $CpCo(CO)_2$ and was characterized by elemental analyses, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy, and single-crystal X-ray diffraction (see below).

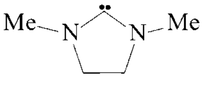
Electronic Factors. The ^{1}H NMR chemical shifts of the cyclopentadienyl and cobalt-methyl resonances of the cobalt(III) compounds can be expected to reflect the electron-donating abilities of the ligands and are summarized in Table 2. As can be seen, the upfield shifts of the cyclopentadienyl ring and methyl group resonances of $CpCo(PMe_3)Me_2$ and $CpCo(IPr)Me_2$ relative to those of $CpCo(PPh_3)Me_2$ are consistent with the presumed greater electron-donating abilities of PMe_3 and IPr relative to that of PPh_3, although no distinction can be made between PMe_3 and IPr. Interestingly, the cyclopentadienyl chemical shift of the cobalt(I) compound CpCo(IPr)(CO) lies between those of the cobalt(III) compounds $CpCo(PMe_3)Me_2$ and $CpCo(IPr)Me_2$, consistent with the strong back-bonding properties of the carbonyl ligand to the lower oxidation state cobalt(I).

Carbonyl stretching frequencies also provide useful comparisons of the relative electron-donating abilities of the different ligands, and the new complex CpCo(IPr)(CO) (ν_{CO} 1921 cm^{-1}, pentane) was found to have a carbonyl stretching frequency similar to that of $CpCo(PMe_3)(CO)$ (ν_{CO} 1923 cm^{-1}, pentane),[7] somewhat higher than that of the analogous cobalt(I) complex of **C** (ν_{CO}

Table 3. Crystal Data for $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO)

	$CpCo(PPh_3)Me_2$	$CpCo(IPr)Me_2$	CpCo(IPr)(CO)
chemical formula	$C_{25}H_{26}CoP$	$C_{34}H_{41}CoN_2$	$C_{33}H_{41}CoN_2O$
fw (g mol^{-1})	416.39	542.69	540.63
temp (K)	296(2)	293(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	8.2212(15)	19.029(6)	10.355(2)
b (Å)	16.001(3)	10.159(3)	18.183(4)
c (Å)	15.946(3)	16.538(5)	16.238(3)
β (deg)	102.116(4)	92.384(5)	104.644(4)
volume ($Å^3$)	2050.9(7)	3194.2(17)	2958.1(4)
Z	4	4	4
ρ(calc) (Mg/m^3)	1.348	1.128	1.21
μ (mm^{-1})	0.921	0.560	0.607
F(000)	874	1170	1154
θ range (deg)	1.82 to 28.29	2.14 to 28.40	1.71 to 27.39
index ranges	$-10 \le h \le 10$	$-25 \le h \le 24$	$-12 \le h \le 13$
	$-21 \le k \le 21$	$-13 \le k \le 13$	$-23 \le k \le 24$
	$-20 \le l \le 21$	$-21 \le l \le 21$	$-20 \le l \le 21$
no. of reflns collected	15 010	23 530	21 755
ind reflns (R_{int})	4844 (0.01)	7690 (0.01)	6966 (0.01)
GOF	1.0124	0.9953	1.0522
final R indicies [$I > 2\sigma(I)$]	$R = 0.0265$	$R = 0.0329$	$R = 0.0359$
	$R_w = 0.0303$	$R_w = 0.0365$	$R_w = 0.0364$
largest diff peak and hole (e $Å^{-3}$)	0.41 and −0.23	0.48 and −0.17	0.31 and −0.17

1915 cm^{-1}, pentane)[11] but considerably lower than that of $CpCo(PPh_3)(CO)$ (ν_{CO} 1937 cm^{-1}, pentane).[6]



C

These are among the lowest carbonyl stretching frequencies observed for complexes of the type CpCoL(CO)[11] and suggest that IPr is indeed a strong σ-donor ligand. These data are consistent with the ^1H NMR data discussed above, and thus, as might be expected, electron σ-donating abilities appear to vary in the order $PPh_3 < PMe_3 \approx IPr$.

Since IPr in $CpCo(IPr)Me_2$ behaves in this series of compounds as a strong σ-bond donor similar to PMe_3, it was of interest to ascertain how PMe_3 would behave in an equilibrium such as that of eq 1. It was found that addition of a 2-fold excess of PMe_3 to an equilibrium mixture of $CpCo(PPh_3)Me_2$, IPr, $CpCo(IPr)Me_2$, and PPh_3 at 30 °C resulted (^1H NMR) in the formation of $CpCo(PMe_3)Me_2$ as the only cobalt-containing species, consistent with previous observations that the sterically less demanding PMe_3 in $CpCo(PMe_3)Me_2$ exhibits little tendency to dissociate.[10] To our knowledge, this is the first instance reported where a phosphine ligand has completely displaced a coordinated carbene ligand.

Steric Factors. Steric effects are the most likely candidate to provide a rationale of the entropy change involved in the chemistry of eq 1. Steric effects have been shown to have a major affect on the thermal stabilities of a variety of types of metal−carbene complexes[3] and to have a major influence on the extent of phosphine dissociation in a number of metal−phosphine complexes.[12] The strongly negative value of $\Delta S°$ found for eq 1 presumably reflects significant loss of internal motion in the products relative to the reactants, and crystal structures of $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO) were obtained (Figures 3, 4, 5, respectively) in an effort to identify the nature of the presumed steric strain in $CpCo(IPr)Me_2$. The crystallographic data are summarized in Table 3, and selected bond distances, bond angles, and torsion angles are presented in Table 4.

The complexes $CpCo(PPh_3)Me_2$ and $CpCo(IPr)Me_2$ assume conventional pseudo-tetrahedral piano stool structures, while CpCo(IPr)(CO) essentially retains the trigonal structure of its precursor, $CpCo(CO)_2$. The bonding of PPh_3 with the cobalt atom in $CpCo(PPh_3)Me_2$ is normal, the Co−P bond length (2.1500(4) Å) being similar to that in the Co(III) complex **D** (2.146(1) Å)[13] but shorter than those in $Co(CH_2Ph)(dimethyl\ glyoximate)_2(PPh_3)$ (2.399(3) Å)[14] and the cobalt(I) complex **E** (2.227(4) Å).[15]

The average Co−C(Cp) distances in $CpCo(PPh_3)Me_2$ (2.106(4) Å), $CpCo(IPr)Me_2$ (2.119(7) Å), and CpCo(IPr)(CO) (2.094(8) Å) are comparable to those of Cp−Co compounds as diverse as Cp_2Co (2.096 Å),[16] compound **D** (2.091 Å),[13] a cobalt(II) complex containing **C**, CpCo(SPh)(**C**) (2.10 Å),[11] and $[CpCo(PEt_3)_2]BF_4$ (2.083 Å).[17] The compound $CpCo(IPr)Me_2$ has a longer Co−C(carbene) bond length (1.914(2) Å) than does CpCo(IPr)(CO) (1.888(3) Å), but both are similar to those of the cobalt carbene compounds **E** (1.974(15) Å),[17] **F** (1.929(8) Å),[18] and CpCo(SPh)(**C**) (1.902(3) Å).[11] The finding of shorter Cp−Co and Co−C(carbene) bonds in the Co(I) complex CpCo(IPr)(CO) than in the Co(III) complex $CpCo(IPr)Me_2$ is surprising and probably indicates a greater degree of steric crowding in the latter.

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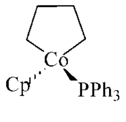
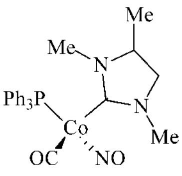
Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for the Compounds $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO)

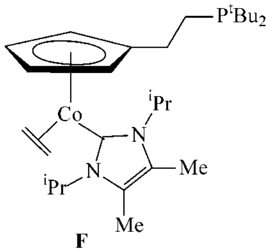
	$CpCo(PPh_3)Me_2$	$CpCo(IPr)Me_2$	CpCo(IPr)(CO)
Co−C(1)	2.0910(18)	2.137(3)	2.074(4)
Co−C(2)	2.0987(19)	2.126(3)	2.119(4)
Co−C(3)	2.1221(18)	2.125(3)	2.108(3)
Co−C(4)	2.1150(18)	2.094(3)	2.066(3)
Co−C(5)	2.1036(18)	2.111(3)	2.100(4)
$Co-Cp_{av}$	2.106(4)	2.119(7)	2.094(8)
Co−L	2.1500(4)	1.914(2)	1.888(3)
Co−C(6)	2.0094(19)	1.981(3)	1.699(4)
Co−C(7)	1.9992(18)	1.952(3)	
L−Co−C(6)	91.08(6)	96.72(12)	96.83(14)
L−Co−C(7)	94.07(6)	93.51(13)	
C(6)−Co−C(7)	85.88(9)	84.84(19)	
C(8)−N(1)−C(11)		130.25(19)	126.7(2)
C(8)−N(2)−C(23)		128.4(2)	126.3(2)
C(8)−N(1)−C(11)−C(16)		100.8(4)	67.9(4)
C(8)−N(2)−C(23)−C(28)		93.0(4)	96.6(4)



D

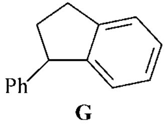


E



F

The C(carbene)−N−C(aryl) bond angles in $CpCo(IPr)Me_2$ (128.4(2)°, 130.25(19)°) are large compared to those of free N-heterocyclic carbenes, which range from 121.9° to 123.5°,[19] consistent with significant steric compression on coordination in $CpCo(IPr)Me_2$. Indeed, the C(carbene)−N−C(aryl) bond angles in $CpCo(IPr)Me_2$ are larger than in the five-coordinate, biscarbene ruthenium complexes $RuCl_2({=}CHPh)(IPr)(PCy_3)$ (127.37(19)°, 127.4(2)°) and $RuCl_2(IPr)(PCy_3)$(3-phenylindenylid-1-ene) (128.2(4)°, 129.2(4)°; 3-phenylindenylid-1-ene = **G**).[20] On the other hand, the C(carbene)−N−C(aryl) bond angles of the complexed IPr in more symmetric, less crowded CpCo(IPr)(CO) are smaller and essentially identical (126.7(2)°, 126.3(2)°), although larger than those of the compound Cp*Ru(IPr)Cl (124.1(2)°, 124.3(2)°).[8]



G

Further comparisons show that the Me−Co−Me bond angle is smaller in $CpCo(IPr)Me_2$ (84.84(19)°) than in $CpCo(PPh_3)Me_2$ (85.88(9)°), again consistent with greater steric compression in the IPr compound. Similarly, the average of the Me−Co−P bond angles of $CpCo(PPh_3)Me_2$ (92.575°) is smaller than the average of the Me−Co-carbene bond angles (94.935°) of $CpCo(IPr)Me_2$. The C(carbene)−Co−CO bond angle in CpCo(IPr)(CO) (96.83(14)°) is greater than the C(carbene)−Co−Cl in Cp*Ru(IPr)Cl (90.6°)[8] but less than the P−Co−P bond angle in the possibly more sterically demanding environment of $[CpCo(PEt_3)_2]BF_4$ (101.21(3)°).[17]

Thus there is considerable evidence that $CpCo(IPr)Me_2$ is a relatively crowded molecule, exhibiting considerable steric strain, and we therefore examined its solid state structure in greater detail in an effort to identify further evidence for steric congestion. Interestingly, even though the isopropyl groups of $CpCo(IPr)Me_2$ are oriented with the methyl groups pointing away from the $CpCoMe_2$ moiety in order to minimize steric repulsions, the torsional angles between the plane of the imidazol-2-ylidene five-membered ring and those of the two 2,6-diisopropylphenyl rings are 81° and 88°. In contrast, the same torsional angles in CpCo(IPr)(CO) and in the free carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene[19] are 72°, 78° and 71°, 80°, respectively. It would appear that the $CpCoMe_2$ unit forces the 2,6-diisopropylphenyl rings into orientations that minimize interactions of the isopropyl groups with the other ligands. In contrast, the CpCo(CO) unit of CpCo(IPr)(CO) appears to be able to intermesh with the carbene ligand so not to significantly distort the carbene from the free structure.

The sterically congested environment in $CpCo(IPr)Me_2$ is also evident from some nonbonding distances between the atoms of different ligands. Among the notable features of the structure are the close contacts between each cobalt methyl group and one of the isopropyl methine carbon atoms of the IPr ligand; the distances C(7)−C(32) and C(6)−C(20) are 3.388 and 3.704 Å, respectively. The van der Waals radius of a methyl group has been estimated to lie in the range 1.72−2.23 Å,[21] depending on the orientation, and that of an isopropyl group is presumably somewhat greater. Thus the sums of the van der Waals radii of the interacting methyl and isopropyl methine groups in $CpCo(IPr)Me_2$ are presumably in the range 3.44 to >4.5 Å, and the interatomic distances noted above do indeed indicate significant nonbonded repulsive interactions. While this steric crowding in $CpCo(IPr)Me_2$ can be demonstrated only in the solid state, it is presumably a factor in solution and would undoubtedly contribute to loss of internal motions within the coordinated IPr ligand. The crowding around the cobalt would prevent

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the phenyl rings on the IPr ligand from rotating freely, greatly reducing the degrees of freedom of the coordinated IPr relative to free IPr; this would contribute to the large negative $\Delta S°$ observed and favors the reverse direction of the equilibrium.

Finally, we note that the CpCo(CO) moiety in CpCo(IPr)(CO) is orientated such that the plane of the imidazol-2-ylidene ring is at an angle of about 44° relative to that of the Cp(centroid)−Co−CO plane. Thus the carbene ligand lies midway between the probable sterically favored structure, in which the Cp(centroid)−Co−CO plane is perpendicular to the imidazol-2-ylidene ring of the carbene, and the possible electronically favored structure in which the essentially vacant p orbital on the carbene carbon is in a position to overlap optimally with the HOMO of the bent (C_s) CpCo(CO) moiety.[22] However, we note that π back-donation from metals to coordinated carbenes is generally believed to be negligible.[2c]

Summary

The reaction of $CpCo(PPh_3)Me_2$ with IPr does not result in complete substitution of the PPh_3, as expected, but rather in an equilibrium mixture of $CpCo(PPh_3)Me_2$, IPr, $CpCo(IPr)Me_2$, and PPh_3. Determination of the equilibrium constants for this unusual reaction over the temperature range 30−50 °C shows that $\Delta H° = -24.4 \pm 1.7$ kJ mol^{-1}, $\Delta S° = -65.8 \pm 5.5$ J mol^{-1} K^{-1}, and thus that it is entropy factors arising from steric crowding in $CpCo(IPr)Me_2$ that prevent complete substitution. Evidence for steric crowding is found in a comparison with the crystal structures of $CpCo(PPh_3)Me_2$, $CpCo(IPr)Me_2$, and CpCo(IPr)(CO). The smaller, more basic PMe_3 does displace IPr completely from $CpCo(IPr)Me_2$.

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Supporting Information Available: Crystal structure details. This material is available free of charge via the Internet at http://pubs.acs.org.

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