C-Sb-C bond angle are very close to those found in Sb$(CH_3)_3$ (216.3 (3) pm and 94.1 (5)°).[9] Perhaps the most interesting of the parameter values is the Sb-Sb bond length. At 281.8 (4) pm in the gas, this bond is certainly shorter[12] than in the crystal (286.2 (2)[2a] and 283.1 (1) pm[2b]). Presumably electron delocalization occurs in the crystal along the linear chains of Sb-Sb···Sb-Sb atoms, thereby lengthening the Sb-Sb bond relative to that in the monomeric gas and at the same time leading to a rather short intermolecular Sb···Sb contact. One supposes that relative to the crystal, a similar bond shortening occurs in the liquid where the rupture of the chains of Sb atoms by the melting process is consistent with the accompanying color change.[2a]

We had hoped to learn something about the rotomeric composition and then, by measurement of the temperature effect of the composition, to estimate the energy and entropy difference of the conformers. However, the difference between the scattering from the C···C terms in the anti and gauche forms of the molecule proved to be too small to measure. The reason is partly that this scattering is only a small part (less than 3%) of the total, but also that the two forms are otherwise distinguishable only by the fact that the anti form has two syn and two anti C···C distances, while the gauche form has three syn and one anti.

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Supplementary Material Available: Tables of the total scattered intensity, the final backgrounds, and the average molecular intensities (11 pages). Ordering information is given on any current masthead page.

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[12] In principle the types of distances in the crystal and gas should not be compared without taking into account the effects of thermal motion. Conversion of our electron diffraction r_g to r_α, a distance type more comparable to the uncorrected X-ray values, would increase the apparent difference by about 0.2 pm. It appears as if one of the reported X-ray values[2a] does not have the thermal motion corrections; these corrections may have been made in the other.

Extreme Electrophilicity of Coordinated Carbon Monoxide in $[CpCo(dppe)CO]^{2+}$

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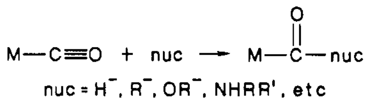
Unprecedented nucleophilic activation of coordinated carbon monoxide is achieved with $[CpCo(dppe)CO]^{2+}$. The synthesis of this and closely related dications is reported along with the crystal structure of $[CpCo(dppe)CO](PF_6)_2\cdot(CH_3)_2CO$. Crystal data: monoclinic, $P2_1/c$; $a = 13.308$ (3) Å, $b = 15.129$ (4) Å, $c = 20.266$ (8) Å; $\beta = 106.92$ (2)°; $V = 3903$ (2) Å^3; $Z = 4$; $R_F = 7.5\%$, $R_{wF} = 7.2\%$. The unusual reactivity of CO is demonstrated by direct attack on CO by relatively unreactive nucleophiles, such as aniline and higher alcohols. The arylcarbamoyl complex from aniline, $\{CpCo(dppe)[C(O)NHC_6H_5]\}^+$, whose molecular structure is reported as the $PF_6^-\cdot CH_3C(O)OC_2H_5$ salt, is the first synthesized by direct attack on CO. Crystal data: monoclinic, $C2/c$, $a = 22.553$ (5) Å, $b = 23.345$ (6) Å, $c = 19.303$ (6) Å; $\beta = 111.20$ (2)°; $V = 9475$ (4) Å^3; $Z = 8$; $R_F = 10.5\%$ $R_{wF} = 10.9\%$. An unusual type of angular disorder of the Cp ring is present in this complex. Soft nucleophiles displace CO from $[CpCo(dppe)CO]^{2+}$. The product of the reaction with C_6H_5SH produces a Co-S bond which was structurally characterized in the case of $[CpCo(dppp)(SC_6H_5)]PF_6\cdot C_6H_6\cdot(CH_3)_2CO$. Crystal data: monoclinic, $P2_1/c$; $a = 14.701$ (3) Å, $b = 16.276$ (6) Å, $c = 19.373$ (3) Å; $\beta = 105.24$ (1)°; $V = 4472$ (2) Å^3; $Z = 4$; $R_F = 5.2\%$, $R_{wF} = 5.4\%$.

Introduction

Activation of CO toward nucleophilic attack by attachment to a metal center (eq 1) is an important step in the Fischer-Tropsch process,[1] the water-gas shift reaction,[2] and selected organic syntheses involving homogeneous catalysis.[3] The electrophilicity of CO should be enhanced by association with metals having a high formal oxidation state and/or by incorporating CO into complexes with a net positive charge. Both of these features reduce the M→C≡O back-bonding and thereby mitigate against stability of the complex to the point that mononuclear, dicationic, metal-carbonyl complexes have been infrequently isolated.[4-6]



$$M{-}C{\equiv}O + nuc \longrightarrow M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}nuc \qquad (1)$$

$$nuc = H^-, R^-, OR^-, NHRR', etc$$

The pursuit of uncharacteristic reactions involving nucleophilic attack on coordinated ligands attached to Co(III)[7] led us to attempt the preparation of an unusually reactive Co(III)-CO bond. This paper describes several

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Table I. Selected Data for the Complexes Synthesized in This Work[a]

compd	$\delta(^1H)$	$\delta(^{31}P)$	ν_{CO}, cm^{-1}	elem. anal. found (calcd)	yield, %	mp, °C
$[CpCo(dppe)CO](PF_6)_2$[b]	6.61 (Cp) 3.81 (CH_2, d of d, J = 19.7, 3.5 Hz)	80.8	2100	C 46.14 (45.73) H 3.46 (3.48)	86	142 dec
$[CpCo(dppe)CO](BF_4)_2\cdot(CH_3)_2CO$	6.58 (Cp) 3.80 (CH_2, m)	80.5	2098	C 54.26 (54.00) H 4.91 (4.53)		
$[CpCo(dppp)CO](PF_6)_2$	6.61 (Cp) 2.8–3.7 (CH_2, m)	33.5	2081	C 46.68 (46.39) H 3.87 (3.66)	62	130 dec
$[Cp^*Co(dppe)CO](PF_6)_2$	1.78 (CH_3, t, J = 2.2 Hz)	74.0	2064	C 48.42 (48.80) H 4.16 (4.32)		170 dec
$[Cp^*Co(dppe)CO](BF_4)_2$	1.76 (CH_3, t, J = 2.2 Hz) 3.45 (CH_2, br)	73.5	2070	C 55.57 (55.95) H 4.89 (4.95)		195 dec
$[CpCo(dppe)C(O)OCH_3]PF_6$	5.40 (Cp) 2.81 (CH_3)	94.7	1640	C 53.3 (54.55) H 4.47 (4.44)	87	166–168 dec
$[Cp^*Co(dppe)C(O)OCH_3]BF_4$	1.32 (t, J = 1.9 Hz) 3.03 (CH_3)	72.9	1623			
$[Cp^*Co(dppe)C(O)OC_2H_5]BF_4$	1.32 (t, J = 1.0 Hz)	70.1	1635			
$[CpCo(dppe)C(O)OC_2H_5]PF_6$	5.37 (Cp) 3.20 (OCH_2, q, J = 7.1 Hz) 0.57 (CH_3, t, J = 7.1 Hz) 3.4 ($(CH_2)_2$, m)		1625	C 55.37 (55.15) H 4.55 (4.63)	81	184–186 dec
$[CpCo(dppe)C(O)OC_3H_7]PF_6$	5.39 (Cp) 3.41 (OCH_2) 3.12 (OCH_2CH_2) 1.07 ($OCCCH_3$)		1621	C 54.36 (55.71) H 4.62 (4.81)	72	177–178 dec
$[CpCo(dppe)C(O)OC_4H_9]PF_6$	5.40 (Cp) 3.22, 2.86, 1.20 (CH_2) 0.73 (CH_3)		1629	C 56.15 (56.26) H 4.69 (4.98)	60	156–157 dec
$[CpCo(dppe)C(O)CH_2CH(CH_3)_2]PF_6$	5.40 (Cp) 3.07 (CH_2, d, J = 6.6 Hz) 1.44 (CH, h, J = 6.7 Hz) 0.67 (CH_3, d, J = 6.7 Hz)		1621	C 56.59 (56.26) H 5.19 (4.98)	42	166–168 dec
$[CpCo(dppe)C(O)C_5H_{11}]PF_6$	5.39 (Cp)		1623	C 56.03 (56.79) H 4.98 (5.15)	51	168–169 dec
$[CpCo(dppe)C(O)C_6H_{13}]PF_6$	5.38 (Cp) 3.20 (OCH_2, t, J = 5.9 Hz) 3.1–3.4 ($(CH_2)_2$, m) 1.0–1.2 ($(CH_2)_4$, m) 0.85 (CH_3, t, J = 7.1 Hz)		1622	C 57.85 (57.30) H 5.49 (5.32)	50	166–167 dec
$\{CpCo(dppe)[C(O)NHC_6H_5]\}PF_6\cdot CH_3C(O)OC_2H_5$	5.64 (Cp) 3.1–3.3 ($(CH_2)_2$, m) 6.7–7.0 (NHC_6H_5, m)	95.2	1607 1590 (sh)	C 57.49 (57.61) H 4.94 (4.95)	85	
$[CpCo(dppp)(SC_6H_5)]PF_6\cdot C_6H_6\cdot(CH_3)_2CO$	5.15 (Cp) 2.58 ($(CH_2)_3$, m)	29.9			83	

[a] Abbreviations: d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, sh = shoulder, br = broad. [b] $\delta(^{13}C)$ 133 (m), 18.7 (Cp).

reactions of new, isolable, dicationic, metal–carbonyl complexes of this type[8] $[CpCo(P^\frown P)CO]^{2+}$ in which the electrophilicity of CO is unprecedented.

Results and Discussion

Synthesis and Structure of $[CpCo(dppe)CO]^{2+}$. $[CpCo(dppe)CO]^{2+}$ was prepared by reacting [CpCo(dppe)I]I with 2 equiv of $AgPF_6$ in acetone while CO was bubbled through the solution. This procedure is similar to that employed by Spencer and Werner[5] to prepare $\{CpCo[P(CH_3)_3]_2CO\}^{2+}$. The pale yellow product $[CpCo(dppe)CO](PF_6)_2$ is stable, but light-sensitive. Despite exhaustive attempts to purify this compound, the ^1H NMR spectrum showed a low percentage of an unidentified impurity and somewhat broadened lines. Later, while attempting another reaction, it was discovered serendipitously that the presence of a small amount of $C_6H_5C{\equiv}CH$ in the reaction led to crystallization of analytically pure $[CpCo(dppe)CO](PF_6)_2$ which displayed sharp NMR absorptions. The function of $C_6H_5C{\equiv}CH$ was not explored further but its advantageous effect was used thereafter to purify $[CpCo(dppe)CO](PF_6)_2$. The analogous complexes containing dppp in place of dppe, Cp* in place of Cp, and BF_4^- in place of PF_6^- were prepared in a like manner. Table I summarizes selected data and some of the properties of these complexes.

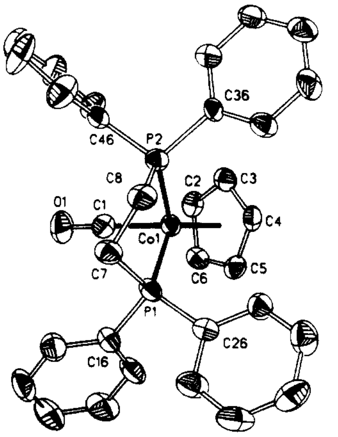

Figure 1. The cation of $[CpCo(dppe)CO](PF_6)_2\cdot(CH_3)_2CO$.

The crystal structure of $[CpCo(dppe)CO](PF_6)_2\cdot(CH_3)_2CO$ was determined. Table II gives the atomic coordinates while Table III gives selected bond distances and angles. A projection of the cation is shown in Figure 1.

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[8] Abbreviations used: Cp = η^5-C_5H_5; Cp* = $C_5(CH_3)_5$; $P^\frown P$ = ditertiary phosphine; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [CpCo(dppe)CO](PF$_6$)$_2$•(CH$_3$)$_2$CO

	x	y	z	U^a
Co(1)	−2487 (1)	9091 (1)	1327 (1)	42 (1)
P(1)	−1563 (2)	9363 (2)	2421 (1)	48 (1)
P(2)	−3684 (2)	8414 (2)	1735 (1)	47 (1)
P(3)	4813 (2)	7509 (2)	3838 (1)	59 (1)
P(4)	−381 (2)	6730 (2)	4417 (2)	60 (1)
F(1)	4627 (7)	8293 (5)	4278 (4)	147 (5)
F(2)	4928 (6)	6690 (5)	3391 (4)	141 (4)
F(3)	6006 (5)	7696 (6)	4047 (4)	153 (4)
F(4)	5000 (5)	6882 (4)	4482 (3)	113 (3)
F(5)	4619 (5)	8109 (5)	3179 (4)	132 (4)
F(6)	3600 (4)	7288 (5)	3631 (4)	105 (3)
F(7)	−544 (7)	5709 (4)	4415 (4)	137 (4)
F(8)	−1553 (7)	6783 (8)	4065 (7)	212 (7)
F(9)	−599 (10)	6802 (7)	5121 (5)	186 (7)
F(10)	−229 (9)	6676 (5)	3704 (4)	194 (6)
F(11)	−271 (6)	7754 (4)	4387 (4)	120 (4)
F(12)	756 (6)	6644 (7)	4750 (7)	220 (8)
O(1)	−1224 (6)	7501 (5)	1386 (4)	90 (4)
C(1)	−1721 (7)	8117 (6)	1361 (4)	55 (4)
C(2)	−2717 (7)	9197 (6)	258 (5)	57 (4)
C(3)	−3611 (8)	9472 (7)	421 (5)	54 (4)
C(4)	−3348 (7)	10193 (5)	889 (4)	51 (4)
C(5)	−2266 (7)	10371 (5)	994 (4)	51 (4)
C(6)	−1856 (7)	9748 (6)	625 (4)	50 (4)
C(7)	−2044 (6)	8545 (6)	2921 (4)	55 (4)
C(8)	−3240 (6)	8575 (6)	2676 (4)	59 (4)
C(11)	344 (5)	8494 (4)	2938 (3)	72 (5)
C(12)	1410	8370	3012	90 (6)
C(13)	1939	8949	2693	96 (6)
C(14)	1402	9652	2300	94 (6)
C(15)	336	9776	2225	75 (5)
C(16)	−193	9196	2544	49 (4)
C(21)	−794 (4)	10662 (5)	3390 (4)	73 (5)
C(22)	−851	11440	3747	83 (5)
C(23)	−1745	11970	3541	87 (6)
C(24)	−2583	11723	2977	79 (5)
C(25)	−2526	10945	2620	61 (4)
C(26)	−1631	10415	2826	48 (4)
C(31)	−5783 (5)	8279 (3)	943 (3)	62 (4)
C(32)	−6823	8565	708	70 (5)
C(33)	−7116	9363	944	70 (5)
C(34)	−6369	9873	1417	69 (5)
C(35)	−5329	9586	1652	58 (4)
C(36)	−5037	8789	1415	47 (4)
C(41)	−3697 (5)	6965 (5)	900 (4)	66 (5)
C(42)	−3862	6078	711	82 (5)
C(43)	−4088	5470	1166	98 (6)
C(44)	−4150	5750	1809	116 (8)
C(45)	−3985	6637	1997	87 (6)
C(46)	−3759	7244	1543	54 (4)
Ao	2816 (9)	4895 (8)	877 (6)	192 (7)
Ac(1)	2817 (20)	6065 (12)	94 (12)	210 (16)
Ac(2)	2354 (19)	5254 (16)	280 (11)	176 (13)
Ac(3)	1492 (16)	4762 (19)	−127 (15)	277 (18)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for the Structurally Characterized Complexes

[CpCo(dppe)CO](PF$_6$)$_2$·(CH$_3$)$_2$CO			
(a) Bond Distances (Å)			
Co(1)–CNT^a	1.711 (8)	C(1)–O(1)	1.14 (1)
Co(1)–P(1)	2.238 (2)	P(3)–F(av)	1.564 (8)
Co(1)–P(2)	2.243 (3)	P(4)–F(av)	1.545 (8)
Co(1)–C(1)	1.782 (9)		
(b) Bond Angles (deg)			
CNT–Co(1)–P(1)	128.3 (3)	P(1)–Co(1)–P(2)	87.9 (1)
CNT–CO(1)–P(2)	125.5 (3)	P(1)–Co(1)–C(1)	88.3 (3)
CNT–Co(1)–C(1)	121.9 (8)	P(2)–Co(1)–C(1)	93.9 (3)
Co(1)–C(1)–O(1)	179.3 (9)		
{CpCo(dppe)[C(O)NHC$_6$H$_5$]}PF$_6$·CH$_3$C(O)OC$_2$H$_5$			
(a) Bond Distances (Å)			
Co–CNT	1.75 (1)	C(8)–O(1)	1.18 (2)
Co–P(1)	2.218 (5)	C(8)–N(1)	1.34 (2)
Co–P(2)	2.182 (6)		
Co–C(8)	2.02 (2)		
(b) Bond Angles (deg)			
CNT–Co–P(1)	122.8 (4)	P(1)–Co–P(2)	87.4 (2)
CNT–Co–P(2)	130.2 (4)	P(1)–Co–C(8)	90.9 (5)
CNT–Co–C(8)	128.9 (5)	P(2)–Co–C(8)	83.0 (6)
Co–C(8)–O(1)	120 (1)		
Co–C(8)–N(1)	116 (1)		
[CpCo(dppp)(SC$_6$H$_5$)]PF$_6$·C$_6$H$_6$·(CH$_3$)$_2$CO			
(a) Bond Distances (Å)			
Co–CNT	1.718 (3)	Co–S	2.291 (2)
Co–P(1)	2.223 (2)	P–F(av)	1.552 (7)
Co–P(2)	2.225 (2)		
(b) Bond Angles (deg)			
CNT–Co–P(1)	124.8 (1)	P(1)–Co–S	86.1 (1)
CNT–Co–P(2)	125.0 (1)	P(2)–Co–S	88.3 (1)
CNT–Co–S	125.5 (1)	P(1)–Co–P(2)	95.9 (1)

^{a} CNT = centroid axis; distances and angles are to the major Cp ring orientation.

Despite the scarcity of dicationic metal–carbonyl complexes, there is little that is unusual about the structure of the [CpCo(dppe)CO]$^{2+}$ ion compared to other metal carbonyls. The CO bond distance of 1.14 (1) Å is typical of CO coordinated to cobalt. However, the Co(III)–CO bond has not been structurally characterized before. The diminished amount of π-back-bonding that would be expected of a Co(III)–CO bond in a dispositive complex leads to a relatively high value of ν_{CO} (2100 cm^{-1}). The Co–P bond distances of [CpCo(dppe)CO]$^{2+}$ (2.238–2.243 (3) Å) are comparable to those involving dppe in the analogous phosphite complex [CpCo(dppe)P(OCH$_3$)$_3$]$^{2+}$ (2.238–2.251 (3) Å).[9] It appears that the Co–P bond distance in these complexes is sensitive to the residual charge on the ion, being shorter for the residual charge of 1+ than 2+ (vide infra).

Reactions. ν_{CO} at 2100 cm^{-1} and δ(^{1}H$_{Cp}$) at 6.61 for [CpCo(dppe)CO](PF$_6$)$_2$ both suggest that the carbonyl ligand should be more electrophilic than in the analogous Co(III) complex[5] {CpCo[P(CH$_3$)$_3$]$_2$CO}$^{2+}$ (ν_{CO} = 2095 cm–^{1}; δ(^{1}H$_{Cp}$) 6.14 in the same solvent) where the phosphorus atoms are better electron donors. The reactions of [CpCo(dppe)CO]$^{2+}$ bear out this expectation.

For instance, many positive-charged metal–carbonyl complexes are sufficiently electrophilic that free alkoxide ion is not required to produce the carboalkoxy derivative[10,11] but instead react directly with primary alcohols as illustrated by eq 2. Only R = CH$_3$ and C$_2$H$_5$ reportedly

$$[\mathrm{CpCo(dppe)CO}]^{2+} + \mathrm{ROH} \rightarrow [\mathrm{CpCo(dppe)C(O)OR}]^{+} + \mathrm{H}^{+} \quad (2)$$

react[5] with {CpCo[P(CH$_3$)$_3$]$_2$CO}$^{2+}$, whereas [CpCo(dppe)CO]$^{2+}$ was found to react with R = CH$_3$ to n-C$_6$H$_{13}$ and (CH$_3$)$_2$CHCH$_2$ when the complex was warmed in the appropriate alcohol. Primary alcohols react, but secondary alcohols, tertiary alcohols, and phenol do not. The reaction with still higher alcohols is limited by the solubility of the complex in the alcohol. Table I summarizes some of the properties of these carboalkoxy compounds. Both δ(^{1}H$_{Cp}$),

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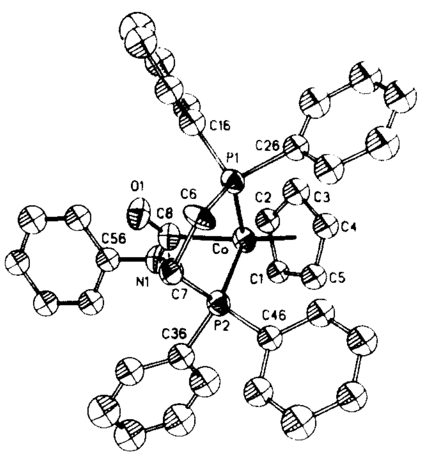

Figure 2. The cation of {CpCo(dppe)[C(O)NHC$_6$H$_5$]}PF$_6$·CH$_3$C(O)OC$_2$H$_5$. The depicted Cp ring represents the major populated (74%) position (see text).

which shifts upfield as a result of the reduction of the residual charge on the complex, and ν_{CO}, which shifts sharply to lower energy, are diagnostic of the reaction. $\nu_{C=O}$ shifts to lower frequency as R progresses from CH$_3$ to C$_2$H$_5$ but then levels off. The dicationic complexes with Cp* are less reactive toward the alcohols owing to the lower electrophilicity of the carbonyl carbon atom as suggested by ν_{CO}.

The reaction of coordinated CO with the higher alcohols suggests that [CpCo(dppe)CO]$^{2+}$ displays an unprecedented degree of electrophilicity. Success with eq 2 therefore stimulated an attempt to carry out the analogous reaction using a comparatively unreactive amine in place of ROH. Although direct attack of alkylamines on coordinated CO to produce the carboxamido complex is well-known,[11] the analogous reaction of an arylamine (eq 3) is unknown because aniline is a weaker base by a factor

$$[\mathrm{CpCo(dppe)CO}]^{2+} + 2\mathrm{C_6H_5NH_2} \rightarrow \{\mathrm{CpCo(dppe)[C(O)NHC_6H_5]}\}^{+} + \mathrm{C_6H_5NH_3}^{+} \quad (3)$$

of about 10^6 than an alkylamine. Reaction 3 occurs smoothly in 95% yield at room temperature after 1 h in aniline. The yellow, light-sensitive arylcarbamoyl complex is the first of its kind synthesized in this manner and demonstrates the remarkable degree of nucleophilic activation that can be achieved with coordinated carbon monoxide.

The cation of {CpCo(dppe)[C(O)NHC$_6$H$_5$]}PF$_6$·CH$_3$C(O)OC$_2$H$_5$ is shown in Figure 2. Table IV gives the atomic coordinates, and Table III gives selected bond distances and angles. Disorder of the solvent of crystallization and the Cp ring, in addition to the rapid data collection necessitated by severe crystal decay, contribute to larger than normal esds for the lighter atom positions. The C=O group is exo to the Cp ring, suggesting that nucleophilic attack occurs from the Cp side of the molecule. The short C(8)—N(1) bond distance, 1.34 (2) Å, indicates that there is significant double-bond character through the resulting carboxamido group. The Cp ring disorder is unusual in that it leads to two Cp locations which are distinguished by a 14° offset in the centroid–Co–centroid angle in the centroid axis–Co–C(8) plane. Heretofore, the Cp ring disorder in these types of molecules has been confined to rotation about the metal–centroid axis.[12] Two different angular positions of the Cp ring on the cobalt atom surface implies that a small potential barrier exists between them but, more importantly, that significant Cp ring slippage is possible on the surface of the Co(III) atom in response to crowding.

Table IV. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for {CpCo(dppe)[C(O)NHC$_6$H$_5$]}PF$_6$•CH$_3$C(O)OC$_2$H$_5$

atom	*x*	*y*	*z*	*U*
Co	2906 (1)	2992 (1)	7837 (1)	56 (1)^a
P(1)	2180 (2)	2316 (2)	7370 (3)	55 (2)^a
P(2)	2284 (2)	3343 (2)	8377 (3)	56 (2)^a
P(3)	0	778 (5)	7500	101 (5)^a
P(4)	5000	1702 (6)	7500	160 (9)^a
F(1)	500 (9)	327 (8)	7495 (12)	165 (10)^a
F(2)	479 (6)	1245 (7)	7453 (12)	168 (11)^a
F(3)	292 (7)	743 (11)	8371 (7)	191 (12)^a
F(4)	4307 (7)	1719 (15)	6968 (15)	278 (21)^a
F(5)	4747 (14)	1710 (14)	8140 (14)	276 (24)^a
F(6)	5000	2360 (8)	7500	462 (75)^a
F(7)	5000	1041 (11)	7500	256 (29)^a
O(1)	3021 (5)	2137 (5)	8903 (7)	78 (6)^a
N(1)	3837 (5)	2769 (6)	9290 (8)	66 (7)^a
C(1)	3593 (26)	3607 (23)	7851 (47)	58 (20)
C(2)	3756 (26)	3063 (23)	7643 (47)	65 (22)
C(3)	3269 (26)	2898 (23)	6968 (47)	73 (18)
C(4)	2805 (26)	3340 (23)	6758 (47)	69 (17)
C(5)	3005 (26)	3778 (23)	7304 (47)	65 (20)
C(1′)	3693 (22)	3532 (19)	8047 (37)	53 (11)
C(2′)	3864 (22)	2992 (19)	7837 (37)	82 (12)
C(3′)	3420 (22)	2856 (19)	7120 (37)	48 (14)
C(4′)	2975 (22)	3312 (19)	6886 (37)	47 (12)
C(5′)	3144 (22)	3730 (19)	7460 (37)	80 (14)
C(6)	1539 (6)	2403 (9)	7775 (10)	60 (8)^a
C(7)	1779 (8)	2741 (9)	8507 (10)	76 (8)^a
C(8)	3278 (7)	2559 (10)	8804 (10)	59 (9)^a
C(11)	1979 (7)	1140 (8)	7400 (11)	69 (5)
C(12)	2153 (9)	586 (10)	7471 (13)	92 (6)
C(13)	2770 (11)	425 (11)	7597 (15)	111 (8)
C(14)	3234 (9)	863 (10)	7633 (13)	92 (6)
C(15)	3072 (8)	1424 (9)	7632 (11)	76 (5)
C(16)	2430 (7)	1577 (8)	7490 (10)	66 (5)
C(21)	2057 (4)	2068 (6)	5910 (7)	90 (6)
C(22)	1784 (4)	2098 (6)	5137 (7)	94 (7)
C(23)	1217 (4)	2399 (6)	4800 (7)	91 (6)
C(24)	924 (4)	2669 (6)	5236 (7)	94 (6)
C(25)	1198 (4)	2639 (6)	6009 (7)	76 (5)
C(26)	1764 (4)	2339 (6)	6346 (7)	57 (4)
C(31)	3081 (6)	4132 (6)	9359 (7)	91 (6)
C(32)	3374 (6)	4398 (6)	10046 (7)	112 (8)
C(33)	3240 (6)	4216 (6)	10662 (7)	99 (7)
C(34)	2813 (6)	3768 (6)	10591 (7)	101 (7)
C(35)	2520 (6)	3502 (6)	9904 (7)	76 (5)
C(36)	2654 (6)	3684 (6)	9288 (7)	66 (5)
C(41)	1467 (5)	3881 (5)	7074 (6)	68 (5)
C(42)	972 (5)	4250 (5)	6684 (6)	71 (5)
C(43)	698 (5)	4603 (5)	7068 (6)	72 (5)
C(44)	919 (5)	4587 (5)	7843 (6)	99 (7)
C(45)	1414 (5)	4218 (5)	8233 (6)	76 (5)
C(46)	1688 (5)	3865 (5)	7848 (6)	54 (4)
C(51)	4200 (5)	1888 (5)	10075 (6)	72 (5)
C(52)	4522 (5)	1643 (5)	10769 (6)	90 (6)
C(53)	4775 (5)	1992 (5)	11394 (6)	76 (5)
C(54)	4707 (5)	2585 (5)	11325 (6)	76 (5)
C(55)	4385 (5)	2830 (5)	10630 (6)	71 (5)
C(56)	4132 (5)	2481 (5)	10005 (6)	68 (5)
O(61)	646 (7)	803 (8)	4604 (11)	125 (6)
O(62)	−205 (8)	1273 (9)	4384 (11)	134 (7)
C(61)	616 (17)	918 (17)	5667 (24)	169 (14)
C(62)	246 (33)	870 (27)	4923 (42)	302 (29)
C(63)	362 (25)	1049 (22)	3652 (29)	223 (20)
C(64)	703 (41)	882 (33)	3475 (45)	336 (45)
C(71)	3308 (22)	258 (20)	5084 (26)	230 (19)
C(72)	4258 (31)	72 (30)	5451 (37)	319 (28)
C(73)	3694 (25)	582 (24)	5102 (30)	243 (21)
C(74)	3569 (26)	−317 (25)	4570 (33)	281 (25)
C(75)	2994 (30)	759 (27)	5407 (37)	308 (29)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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(12) Miller, E. J.; Rheingold, A. L.; Brill, T. B. *J. Organomet. Chem.* **1984**, *273*, 377; **1985**, *282*, 399.

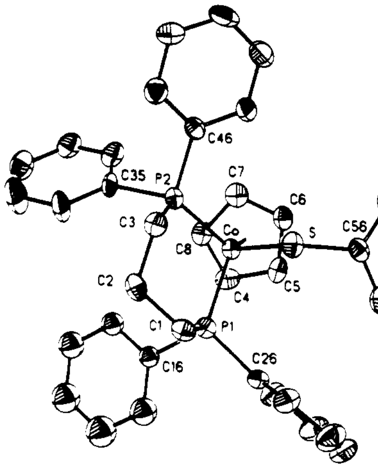

Figure 3. The cation of [CpCo(dppp)(SC$_6$H$_5$)]PF$_6$·C$_6$H$_6$·(CH$_3$)$_2$CO.

The reactions of {CpCo(dppe)[C(O)NHC$_6$H$_5$]} are comparable to those of other alkylcarbamoyl complexes.[11] For instance, CH$_3$OH displaces the amine to give [CpCo(dppe)C(O)OCH$_3$]$^+$ and C$_6$H$_5$NH$_2$.

Other successful reactions explored for [CpCo(dppe)CO]$^{2+}$ involving softer nucleophiles frequently resulted in displacement of the carbonyl ligand. For instance, sources of Br$^-$ react to produce [CpCo(dppe)Br]$^+$. Grignard reagents displace CO and alkylate the complex to [CpCo(dppe)R]$^+$. Likewise, thiophenol displaces CO to form [CpCo(dppe)(SC$_6$H$_5$)]$^+$, which was structurally characterized for [CpCo(dppp)(SC$_6$H$_5$)]PF$_6$·C$_6$H$_6$·(CH$_3$)$_2$CO. Table V gives the atomic coordinates, and Table III gives selected bond distances and angles for this complex. Figure 3 shows a projection of the cation. The Co–S bond distance (2.291 (2) Å) is somewhat longer than that in another six-coordinate CpCoSR complex, Cp$_2$Co$_2$(S$_2$C$_6$H$_4$)$_2$ (2.23–2.27 Å)[13] but is about equal to the sum of the Co and S covalent radii. The Co–P bond distances of 2.223 (2) and 2.225 (2) Å are shorter than those of the dications and fit the pattern noted above for monocations of these complexes.[9]

Consequently, [CpCo(dppe)CO]$^{2+}$ contains, perhaps, the most nucleophilic-activated CO of any metal–carbonyl complex yet isolated. It is able to engage in reactions that are apparently unprecedented in transition metal–carbonyl chemistry. Despite this, the compound also retains many of the traditional reaction characteristics of a metal carbonyl in that the products of nucleophilic attack resemble those of many less activated metal–carbonyl counterparts.

Experimental Section

All synthetic operations were performed under a nitrogen atmosphere. Acetone was dried by distillation from P$_2$O$_5$. Aniline was distilled from NaOH. All alcohols were sparged with N$_2$ for 15 min before use. Thiophenol was used as purchased; [CpCo(dppe)I]I and [CpCo(dppp)I]I were prepared as described elsewhere.[7a,b]

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker WA-250 spectrometer (δ_{Me_4Si} 0.0 ppm). ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WM-250 with δ relative to 85% external H$_3$PO$_4$. IR spectra were recorded in KBr pellets on a Perkin-Elmer 281B spectrometer. Elemental analyses were performed by Micro-Analysis, Wilmington, DE. Owing to their similarities in some cases, a complete set of data in Table I was not acquired for every compound.

[CpCo(dppe)CO](PF$_6$)$_2$·(CH$_3$)$_2$CO. In 300 mL of dry acetone with bubbling CO, AgPF$_6$ (3.918 g, 15.53 mmol), [CpCo(dppe)I]I (6.010 g, 7.76 mmol), and 0.5 mL of C$_6$H$_5$C≡CH were stirred for 2 h. The yellow-red solution was filtered through Celite and the acetone removed under vacuum. The crude product was washed with THF and dried under vacuum. The yellow, powdery product was recrystallized from acetone/ether at 0 °C in the dark. The acetone molecule of crystallization can be removed by evacuation. Analytical data and spectra were obtained on the solvent-free product. Substitution in the reaction of AgBF$_4$, {C$_5$(CH$_3$)$_5$]Co(dppe)I}I, and [CpCo(dppp)I]I all afford the respective dicationic metal–carbonyl salt (see Table I).

Table V. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å × 10^3) for [CpCo(dppp)(SC$_6$H$_5$)]PF$_6$•C$_6$H$_6$•(CH$_3$)$_2$CO

	x	y	z	U^a
Co	5005 (1)	8884 (1)	3178 (1)	30 (1)
P(1)	3953 (1)	9889 (1)	3074 (1)	33 (1)
P(2)	6243 (1)	9703 (1)	3268 (1)	32 (1)
P(3)	1311 (1)	7457 (1)	1154 (1)	62 (1)
S	5226 (1)	9016 (1)	4388 (1)	40 (1)
F(1)	778 (4)	6626 (3)	1224 (3)	101 (2)
F(2)	2206 (4)	7130 (4)	1705 (4)	159 (3)
F(3)	973 (5)	7827 (4)	1776 (3)	147 (4)
F(4)	1848 (4)	8279 (3)	1108 (3)	122 (3)
F(5)	1624 (5)	7066 (5)	537 (4)	182 (4)
F(6)	411 (4)	7780 (3)	618 (3)	142 (3)
C(1)	4390 (4)	10824 (3)	3577 (3)	36 (2)
C(2)	5262 (4)	11193 (3)	3416 (3)	39 (2)
C(3)	6159 (4)	10685 (4)	3700 (3)	38 (2)
C(4)	4111 (4)	8259 (4)	2319 (3)	41 (2)
C(5)	4174 (4)	7837 (3)	2967 (3)	41 (2)
C(6)	5118 (4)	7602 (4)	3245 (3)	42 (2)
C(7)	5645 (5)	7881 (4)	2796 (3)	44 (3)
C(8)	5014 (4)	8304 (4)	2215 (3)	41 (3)
C(11)	4003 (3)	10259 (3)	1673 (2)	47 (3)
C(12)	3647	10580	987	64 (3)
C(13)	2744	10919	791	83 (4)
C(14)	2197	10936	1280	89 (4)
C(15)	2553	10615	1965	63 (3)
C(16)	3456	10277	2162	37 (2)
C(21)	2302 (3)	9018 (3)	3008 (2)	48 (3)
C(22)	1558	8743	3270	63 (3)
C(23)	1438	9059	3910	72 (4)
C(24)	2063	9649	4288	68 (3)
C(25)	2807	9923	4026	50 (3)
C(26)	2927	9607	3386	37 (2)
C(31)	7119 (3)	9471 (3)	1434 (2)	55 (3)
C(32)	6985	10253	1130	64 (3)
C(33)	6629	10884	1471	81 (4)
C(34)	6407	10732	2116	59 (3)
C(35)	6540	9950	2421	36 (2)
C(36)	6896	9320	2080	47 (3)
C(41)	7487 (3)	8577 (2)	4160 (2)	43 (3)
C(42)	8377	8320	4554	55 (3)
C(43)	9166	8807	4578	59 (3)
C(44)	9064	9550	4206	57 (3)
C(45)	8174	9806	3812	46 (3)
C(46)	7385	9320	3789	34 (2)
C(51)	3856 (3)	8018 (3)	4697 (2)	47 (3)
C(52)	3549	7328	4999	64 (3)
C(53)	4196	6735	5341	70 (4)
C(54)	5152	6831	5380	69 (4)
C(55)	5459	7520	5078	57 (3)
C(56)	4812	8114	4736	38 (2)
C(61)	400 (6)	5388 (9)	2845 (4)	135 (7)
C(62)	185	4824	3321	144 (8)
C(63)	349	5025	4043	146 (9)
C(64)	729	5789	4290	155 (8)
C(65)	944	6353	3814	146 (8)
C(66)	780	6152	3091	137 (8)
O(1)	2639 (4)	2368 (3)	2975 (3)	96 (3)
C(71)	1462 (7)	1996 (8)	3497 (5)	152 (7)
C(72)	1810 (6)	2379 (5)	2949 (5)	73 (4)
C(73)	1121 (7)	2776 (7)	2353 (5)	125 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

[CpCo(dppe)C(O)OR]PF$_6$ (R = n-C$_x$H$_{2x+1}$; x = 1-6) and CH$_2$CH(CH$_3$)$_2$. [CpCo(dppe)CO](PF$_6$)$_2$, dissolved in the re-

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[13] Miller, E. J.; Brill, T. B.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 7580.

Table VI. Crystal Data Collection and Refinement Parameters for $[CpCo(dppe)CO](PF_6)_2 \bullet (CH_3)_2CO$ (1), $\{CpCo(dppe)[C(O)NHC_6H_5]\}PF_6 \bullet CH_3C(O)OC_2H_5$ (2), and $[CpCo(dppe)(SC_6H_5)]PF_6 \bullet C_6H_6 \bullet (CH_3)_2CO$ (3)

	1	2	3
formula	$C_{35}H_{35}CoF_{12}O_2P_4$	$C_{41}H_{43}CoF_6NO_3P_3$	$C_{47}H_{48}CoF_6OP_3S$
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$
a, Å	13.308 (3)	22.553 (5)[a]	14.701 (3)
b, Å	15.129 (4)	23.345 (6)	16.276 (6)
c, Å	20.266 (8)	19.303 (6)	19.373 (3)
β, deg	106.92 (2)	111.23 (2)	105.24 (1)
V, Å^3	3903 (2)	9475 (4)	4472 (2)
Z	4	8	4
cryst color	yellow-orange	orange	black
cryst dimens, mm	0.27 × 0.31 × 0.36	0.20 × 0.25 × 0.30	0.16 × 0.30 × 0.30
μ(Mo Kα), cm^{-1}	6.81	5.16	5.81
D(calcd), g cm^{-3}	1.53	1.21	1.38
diffractometer	Nicolet R3m/μ	Nicolet R3m/M	Nicolet R3m/μ
radiatn	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
monochromator	highly oriented graphite	highly oriented graphite	highly oriented graphite
scan technique	ω	$\theta/2\theta$	$\theta/2\theta$
2θ limit, deg	45	45	45
scan speed, deg min^{-1}	var 5–20	var 8–20	var 5–20
unique data	4817	4700	5888
R(int), %	2.79	1.61	1.62
unique date, $F_o \geq n\sigma(F_o)$	3056 (n = 3.5)	1995 (n = 5)	3545 (n = 5)
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/197 rflns
decay	6%	av 14%	4%
soln method	direct (Co + 4P)	direct (Co + 3P)	direct (Co + 3P)
R_F, R_{wF}	7.5, 7.2	10.5, 10.8	5.2, 5.4
GOF	1.58	1.73	1.29
data/parameter	7.0	7.6	8.3
Δ/σ	0.13	0.05	0.05
highest peak, e Å^{-3}	0.65	0.56	0.42
computer programs	SHELXTL(5.1) Nicolet Corp.	SHELXTL(5.1) Nicolet Corp.	SHELXTL(5.1) Nicolet Corp.

[a] Three specimens required. Dimensions of crystal and unit-cell parameters are the averages for the three data crystals of similar size.

spective alcohol, ROH, and warmed as appropriate, caused a color change to redish orange. For the higher alcohols the unreacted dication complex was filtered out. Evaporation of the solvent produced the desired product. The compounds can be further purified by chromatography on silica gel. When eluted with acetone/ether (50/50), a yellow-orange band came first. Evaporation of the solvent from this band gave pure yellow-orange compounds. Still higher alcohols probably will also react, but the dication salt becomes increasingly less soluble as the alkyl chain length increases. Raising the temperature beyond about 100 °C results in decomposition. See Table I for analytical data and some of the physical properties of these compounds.

$\{CpCo(dppe)[C(O)NHC_6H_5]\}PF_6{\cdot}CH_3C(O)OC_2H_5$. After stirring $[CpCo(dppe)CO](PF_6)_2$ (0.25 g, 0.30 mmol) in 4 mL of $C_6H_5NH_2$ under N_2 for 1 h at room temperature, the orange solution was poured into 150 mL of Et_2O and the resulting yellow precipitate of $\{CpCo(dppe)[C(O)NHC_6H_5]\}PF_6$ was filtered and dried under vacuum. The product was recrystallized from ethyl acetate at 0 °C.

$[CpCo(dppe)(SC_6H_5)]PF_6{\cdot}C_6H_6{\cdot}(CH_3)_2CO$. $[CpCo(dppe)CO]PF_6)_2$ (0.22 g, 0.26 mmol) was stirred with 2 mL of C_6H_5SH for 15 min. The red solution was then poured into 100 mL of diethyl ether. The resultant precipitate was filtered and washed several times with ether. The yellow-red crude product was further purified by chromatography on silica gel eluted with acetone/ether (50/50). A red band eluted first followed by the dark violet product. Crystals grew from acetone–benzene solution at 0 °C after 2–3 days.

Structural Determinations. Crystals were grown as described above in the synthesis of the compounds. Table VI provides crystal parameters and details of the data collection and refinement. All data were collected at 23 (1) °C and corrected for decay and *Lp* effects. No corrections for absorption or extinction were required. Due to excessive radiation decay in **2**, partial data from three specimens were collected and merged with interlayer scale factors. Efflorescence of the solvent, ethyl acetate, was not the cause for the decay; unexposed samples coated with epoxy cement, as were the data specimens, remained stable for several weeks. Where rigid-body constraint is indicated, the following parameters were used: strict planarity, six-membered rings (C–C = 1.395 Å), five-membered rings (C–C = 1.420 Å), and C–H = 0.96 Å.

1, $[CpCo(dppe)CO](PF_6)_2{\cdot}(CH_3)_2CO$. The space group was unambiguously determined from systematic absences. All non-hydrogen atoms were anisotropically refined and phenyl rings constrained to rigid bodies. A thermally noisy molecule of acetone, the recrystallization solvent, was located and refined. Hydrogen atom contributions were idealized and updated, but not refined.

2, $\{CpCo(dppe)[C(O)NHC_6H_5]\}PF_6{\cdot}CH_3C(O)OC_2H_5$. All ring carbon atom structures were constrained to rigid bodies. Two nonconcentric Cp ring orientations were located. A combined unit-constrained occupancy refined to 0.74/0.26 occupancy ratio. The lattice contains ethyl acetate in at least two sites in an approximately total occupancy of one per Co complex. The major site (occupancy 0.8) is ordered; the remaining site(s) were poorly resolved and not included. Except for the atoms of the two Cp ring orientations and the solvent molecule, all non-hydrogen atoms were refined anisotropically. The PF_6^- counterion is ordered and resides on two sites with crystallographic twofold rotational symmetry. Hydrogen atoms were treated as in **1**.

3, $[CpCo(dppe)(SC_6H_5)]PF_6{\cdot}C_6H_6{\cdot}(CH_3)_2CO$. The space group was unambigiously determined from systematic absences. Molecules of benzene and acetone were located in the lattice, one each per Co complex. The phenyl rings and benzene molecule were treated as rigid bodies. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as **1**.

Additional crystallographic data are available as supplementary material. In none of the structures were there any notheworthy interionic or ion–molecule contacts.

Acknowledgment. Dr. S. J. Landon conducted the original experiments leading to the preparation of $[CpCo(dppe)CO](BF_4)_2$.

Registry No. **1**, 104507-00-8; **2**, 104507-03-1; **3**, 104507-06-4; $[CpCO(dppe)CO](PF_3)_2$, 104506-99-2; $[CpCo(dppe)CO](BF_4)_2$, 104507-07-5; $[CpCo(dppp)Co](PF_6)_2$, 104531-53-5; $[Cp^*Co(dppe)CO](PF_6)_2$, 104507-09-7; $[Cp^*Co(dppe)CO](BF_4)_2$, 104507-10-0; $[CpCo(dppe)C(O)OCH_3]PF_6$, 104507-12-2; $[Cp^*Co(dppe)C(O)OCH_3]BF_4$, 104507-14-4; $[Cp^*Co(dppe)C(O)$-

$OC_2H_5]BF_4$, 104507-16-6; $[CpCo(dppe)C(O)OC_2H_5]PF_6$, 104507-18-8; $[CpCo(dppe)C(O)OC_3H_7]PF_6$, 104507-20-2; $[CpCo(dppe)C(O)OC_4H_9]PF_6$, 104507-22-4; $[CpCo(dppe)C(O)CH_iCH(CH_3)_2]PF_6$, 104507-24-6; $[CpCo(dppe)C(O)C_3H_{11}]PF_6$, 104507-26-8; $[CpCo(dppe)C(O)C_6H_{13}]PF_6$, 104507-28-0; CO, 630-08-0; [CpCo(dppe)I]I, 32842-39-0; [Cp*Co(dppe)I]I, 104507-29-1; [CpCo(dppp)I]I, 89463-02-5; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; C_oH_7OH, 71-23-8; C_4H_9OH, 71-36-3; $(CH_3)_2CHCH_2OH$, 78-83-1; $C_kH_{11}OH$, 71-41-0; $C_6H_{13}OH$, 111-27-3; $C_lH_5NH_2$, 62-53-3; C_6H_5SH, 108-98-5.

Supplementary Material Available: Tables of bond distances and angles and anisotropic thermal parameters for the three structures described in this paper (12 pages); listings of calculated and observed structure factors for the three structures described in this paper (51 pages). Ordering information is given on any current masthead page.

Functionalized Isocyanides as Ligands. 4.[1] Base-Promoted Cyclization Reactions of Free and Platinum(II)-Coordinated *o*-(Phosphoniomethyl)phenyl Isocyanide Tetrafluoroborates, *o*-($BF_4^-R_3P^+-CH_2)C_6H_4NC$. Synthesis and Spectroscopic Characterization of 1- and 2-Platinum(II)-Substituted Indole Derivatives and X-ray Structure of *trans*-$\{(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C}(PMe_3)]Cl\}BF_4\cdot C_2H_4Cl_2$

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The chloromethyl substituent of the isocyanide *o*-$(ClCH_2)C_6H_4NC$ easily reacts in CH_2Cl_2 with the tertiary phosphines PMe_3 and PMe_2Ph or in acetone in the presence of excess LiBr with the phosphines $PMePh_2$ and PPh_3 to give quantitatively the novel phosphonium-substituted isocyanides *o*-$(X^-R_3P^+-CH_2)C_6H_4NC$ (X = halide), which are more conveniently converted into their less hygroscopic tetrafluoroborate salts *o*-$(BF_4^-R^3P^+-CH_2)C_6H_4NC$ (L) ($PR_3 = PMe_3$ (L^1), PMe_2Ph (L^2), $PMePh_2$ (L^3), PPh_3 (L^4)). Attack of an appropriate base to the activated methylene group of the $R_3P^+-CH_2-$ substituent produces the highly reactive ylide function $R_3P^+-\dot{C}H^--$ which undergoes ring closure with the adjacent isocyano group via intramolecular attack of the ylide carbanion to the electrophilic isocyanide carbon (either free or metal-coordinated), affording an indole derivative. Thus, upon treatment in CH_2Cl_2 at room temperature with a 10-fold excess of the mild base NEt_3, the Pt(II)-coordinated ligands L in cationic complexes of the type *trans*- and *cis*-$[P_2Pt(L)X]BF_4$ (X = Cl, L = L^1–L^4, P = PPh_3 (**1–4**); X = CH_3, L = L^1, P = $PMePh_2$ (**5**), PMe_2Ph (**6**), PCy_3 (**7**); X = Cl, L = L^1, P_2 = *cis*-$Ph_2PCH{=}CHPPh_2$ (**8**)) undergo cyclization reactions to 2-Pt(II)-substituted indole derivatives of the type *trans*- and *cis*-$\{P_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C}(PR_3)]X\}BF_4$ (**9–15**), with reaction times depending on steric and electronic factors due to the ligand and metal substituents. The structures of the final compounds have been assigned on the basis of analytical, spectroscopic (IR and ^1H and ^{31}P NMR), and structural data. The solid-state structure of *trans*-$\{(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C}(PMe_3)]Cl\}BF_4\cdot C_2H_4Cl_2$ (**9**) has been determined by single-crystal X-ray diffractometry: space group $P2_1/m$, a = 10.434 (1) Å, b = 23.465 (2) Å, c = 11.725 (1) Å, β = 112.88 (2)°, Z = 2. The structural model was refined to R = 0.040 (R_w = 0.045) for 3961 independent reflections. The coordination geometry around the Pt(II) atom is square-planar with the carbenoid ligand perpendicular to the plane. The Pt–C(sp^2) and Pt–Cl bond lengths are 1.99 (1) and 2.369 (1) Å, respectively. Bond lengths within the indole system, which constitutes the carbenoid ligand, indicate extensive electronic delocalization. As a consequence, β-protonation at the indole ring occurs on treating **9** with HBF_4. Reaction of the stronger base $NaNH_2$ in THF at room temperature with the uncoordinated isocyanide L^4 affords the 3-(triphenylphosphonio)indolyl ligand: $\overline{N(o\text{-}C_6H_4)C(PPh_3)C}(H)$, which is found to coordinate to Pt(II) at the N(1) position of the indole ring as in the complexes *cis*-$\{(PPh_3)_2Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)C}(H)]Cl\}BF_4$ and *trans*-$(PPh_3)Cl_2Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)C}(H)]$.

Introduction

Suitably functionalized isocyanide ligands have proved synthetically useful reagents in organometallic chemistry to form a variety of heterocyclic systems. The two general routes reported so far to such cyclization reactions are closely related to the role of the function which can (i) spontaneously interact with the isocyanide[2] or (ii) activate the neighboring C–H bonds to form α-metalated iso-

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[1] For previous work on this area see ref 8, 9, and 14.

[2] Bartel, K.; Fehlhammer, W. P. *Angew. Chem., Int. Ed. Engl.* 1974, *13*, 599.