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Preparation, X-ray Molecular Structure Determination, and Chemical Properties of Dinitrogen-Coordinated Cobalt Complexes Containing Triphenylphosphine Ligands and Alkali Metal or Magnesium. Protonation of the Coordinated Dinitrogen to Ammonia and Hydrazine

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Treatment of $CoH(N_2)(PPh_3)_3$ (**1**) with diethylmagnesium gave a magnesium-containing complex **2** formulated as $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$ (THF = tetrahydrofuran). Subsequent reaction of **2** or direct reaction of **1** with LiBu afforded Li-containing complexes $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (**3**) and $[Co(N_2)(PPh_3)_3]Li(THF)_3$ (**4**) depending on the solvent employed. A Na-containing complex, $[Co(N_2)(PPh_3)_3]Na(THF)_3$ (**5**), was also obtained by the reaction of **1** with sodium metal. The molecular structures of **3** and **4** were fully established by X-ray structural analysis. These complexes are isomorphous and have a threefold symmetry with the N_2 ligand bridging Co and Li on its both ends with the N–N bond length of 1.167 (16) Å for **3** and 1.19 (4) Å for **4**. In contrast to **1** whose coordinated N_2 ligand is incapable of reacting with protic acids, the ligated N_2 in the electron-rich cobalt complexes **2–5** is attacked by concentrated H_2SO_4 to afford hydrazine and ammonia. These complexes provide the first examples of the conversion of dinitrogen coordinated to cobalt into hydrazine and ammonia on hydrolysis. The corresponding iron analogue having a ligating dinitrogen also was prepared by the reaction of $Fe(acac)_3$ with $MgEt_2$ in the presence of 2–6 equiv of PPh_3 under nitrogen. The complex was characterized as $[FeEt(N_2)(PPh_3)_2]_2Mg(THF)_4$ (**6**). Complex **6** also affords hydrazine and ammonia on acidolysis.

Introduction

In contrast to numerous reports concerning early transition-metal complexes containing dinitrogen, which can be transformed to hydrazine and/or ammonia on hydrolysis,[1] very few N_2-coordinated group 8 transition-metal complexes that show similar behavior are known. Only some poorly characterized N_2-containing iron complexes[2] have been reported to protonated to hydrazine on hydrolysis.

Hydrido(dinitrogen)tris(triphenylphosphine)cobalt(I) (**1**) represents one of the earliest dinitrogen complexes discovered,[3] and various attempts have been made without success to reduce the ligating dinitrogen. Treatment of **1** with protic acids, which readily convert the coordinated N_2 in molybdenum and tungsten analogues into ammonia and/or hydrazine, invariably causes liberation of the dinitrogen without protonation.

With the view that putting more electrons into **1** may cause the enhancement of the back-donation from cobalt to the ligating dinitrogen and make it reactive enough toward attack of protonic reagents, we have treated **1** with various reducing agents and prepared new cobalt complexes containing alkali metal or magnesium, triphenylphosphine, and N_2, which can be converted into hydrazine and ammonia on hydrolysis. Klein and co-workers recently reported trimethylphosphine-coordinated Co–N_2 complexes containing magnesium and potassium via different routes, but no detailed study was made on the reactivity of the ligating dinitrogen.[4,5] This paper deals with the preparation of the magnesium and alkali-metal-containing N_2-coordinated cobalt complexes, X-ray molecular structure determinations, and chemical properties of the cobalt–dinitrogen complexes. Preliminary results concerning a magnesium-containing cobalt–dinitrogen complex that liberates hydrazine were communicated previously.[6]

Results and Discussion

Table I summarizes the N_2-containing cobalt complexes prepared in the present study together with analytical and physical data. Since these complexes are extremely sensitive to oxygen and moisture and their microanalysis was not feasible, their compositions were determined on the basis of macroscopic chemical analysis and chemical reactions. Structures of two Co(I–) complexes containing lithium were fully established by X-ray crystallography.

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Table I. Analytical and Physical Data of the N_2-Containing Cobalt Complexes

complex	anal.[a] found (calcd) Co	M	N_2	THF or Et_2O	PPh_3	mp,[b] °C (dec)
$[Co(PPh_3)_3N_2]_2Mg(THF)_4$ (2)	5.5 (5.7)	Mg, 1.2 (1.2)	2.9 (2.7)	76 (76)	14 (14)	63-70
$[Co(PPh_3)_3N_2]Li(Et_2O)_3$ (3)	5.6 (5.3)	Li, 0.72 (0.63)	2.4 (2.5)	72 (71)	19 (20)	95-99
$[Co(PPh_3)_3N_2]Li(THF)_3$ (4)	5.2 (5.4)	Li, 0.67 (0.63)	2.6 (2.6)	71 (72)	20 (20)	98-102
$[Co(PPh_3)_3N_2]Na(THF)_3$ (5)	5.4 (5.3)	Na, 1.8 (2.1)	2.6 (2.5)	71 (71)	20 (19)	88-89

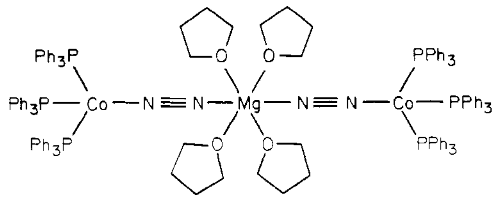
[a] Compositions of the complexes were determined by the macroscopic analysis, Co was determined by colorimetric determination, Mg, Li, and Na were determined by flame photomeric methods, N_2 was determined by measuring the volume of N_2 evolved on pyrolysis, and PPh_3 THF, and Et_2O were determined by GLC analysis after hydrolysis. [b] Under vacuum.

1. The Magnesium-Containing Complex $[Co(PPh_3)_3N_2]_2Mg(THF)_4$ (2). Treatment of $CoH(N_2)(PPh_3)_3$ (1) dissolved in tetrahydrofuran (THF) with diethylmagnesium in diethyl ether at low temperature (−20 to +5 °C) gave reddish brown needles of $[Co(PPh_3)_3N_2]_2Mg(THF)_4$ (2). Experimental conditions to

$$\underset{1}{2CoH(N_2)(PPh_3)_3} + MgEt_2 \xrightarrow{THF} \underset{2}{[Co(PPh_3)_3N_2]_2Mg(THF)_4} + 2C_2H_6 \quad (1)$$

prepare the pure complex are somewhat delicate. Tetrahydrofuran was most suitable as the reaction solvent, and the reaction temperature should not exceed 5 °C. Particularly critical for obtaining crystals was to leave the homogenous reaction mixture after the initial mixing without stirring.

During the course of our investigation on the PPh_3-containing dinitrogen complexes, preparation and characterization of a PMe_3-coordinated dinitrogen complex with a composition of $[Co(PMe_3)_3N_2]_2Mg(THF)_4$ analogous to that of 2 were reported.[4] Our attempts to obtain a suitable crystal of 2 for X-ray crystallography were not successful. From the chemical data and analogy with the PMe_3-coordinated complex we assume that our complex $[Co(PPh_3)_3N_2]_2Mg(THF)_4$ also possesses a structure containing magnesium connecting two ligating dinitrogen molecules, each coordinated to cobalt in an end-on manner as shown.



2

Complex 2 shows a strong IR band at 1840 cm^{-1} (Nujol) that is assigned to the $\nu(N_2)$ band of the coordinated dinitrogen. The complex is very sensitive to oxygen and water, and treatment of 2 with water instantly converts 2 into 1 that shows the $\nu(N_2)$ band at 2088 cm^{-1}. When

$$\underset{2}{[Co(PPh_3)_3N_2]_2Mg(THF)_4} + 2H_2O \rightarrow \underset{1}{2CoH(N_2)(PPh_3)_3} + Mg(OH)_2 + 4THF \quad (2)$$

the IR spectrum of 2 was measured as a KBr disk, from which a trace of water is difficult to remove, the spectrum always showed a band of moderate, variable intensity at 2088 cm^{-1} in addition to a band at 1840 cm^{-1}. This may be caused by partial conversion of 2 into 1 by reaction of 2 with a small amount of water contained in the KBr powder. Klein and co-workers[4] observed the IR bands of $[Co(PMe_3)_3N_2]_2Mg(THF)_4$, measured as a Nujol mull, at 2064 and 1830 cm^{-1} and assigned the former to the $\nu(N_2)$ band and the latter to the stretching vibration of a Co–H band formed by an internal metalation of the coordinated PMe_3 ligand. We suspect that the band of the PMe_3 complex at 2064 cm^{-1} may be due to the $\nu(N_2)$ band of $CoH(N_2)(PMe_3)_3$ or some form of the N_2-coordinated cobalt(I+) complex produced by interaction with a small amount of water and the band at 1830 cm^{-1} is to be assigned to the $\nu(N_2)$ band of $[Co(PMe_3)_3N_2]_2Mg(THF)_4$. The PMe_3-coordinated complex has the ligating N_2 with an N–N bond distance of 1.19 Å as determined by X-ray analysis. The IR band of 1830 cm^{-1} is considered to be in a resonable region to be assigned to the $\nu(N_2)$ band for a complex having an N–N distance of 1.19 Å.

The ^{31}P NMR spectrum of 2 measured in dioxane (containing 10% of benzene-d_6) showed two peaks at −8.62 ppm (higher field from the external reference of H_3PO_4 in D_2O) ascribable to the free PPh_3 and 46.74 ppm (very broad) due to the undissociated PPh_3. Since 2 containing THF is not suitable for molecular weight measurement by the freezing point depression method, a dioxane-containing crystalline complex of composition $[Co(PPh_3)_3N_2]_2Mg(dioxane)_4$ was prepared from 1 and diethylmagnesium in dioxane. The molecular weight of the complex observed in dioxane was found to be 550. The observed value is less than one-third of the calculated value for the $[Co(PPh_3)_3N_2]_2Mg$ entity but is close to the value of 591 calculated for the average of molecular weights of the $[Co(PPh_3)_2N_2]_2Mg$ entity and $2PPh_3$ formed by dissociation from 2 in solution in agreement with the observation of the free PPh_3 signal in the ^{31}P NMR spectrum of 2. Complex 2 was found to be nonconducting in dioxane, eliminating ionic dissociation.

When the reaction of 1 with $MgEt_2$ was carried out while the solution was stirred at 0 °C, a reddish brown, powdery material of composition $Co(PPh_3)_3N_2Mg(THF)_2$ was obtained in a yield of 80% as we preliminarily reported.[6] A sample of a similar composition, $Co(PEtPh_2)_3N_2Mg(THF)_2$, also was obtained by reaction of $Co(acac)_3$, $PEtPh_2$, and $MgEt_2$ in tetrahydrofuran under nitrogen in a yield of 11%. The ^1H NMR spectrum of this complex showed that the ratio of $PEtPh_2$ to THF was 3:2. Although the analytical data of these samples suggested the composition $Co(PR_3)_3N_2Mg(THF)_2$, it is possible that these samples include $[Co(PR_3)_3N_2]_2Mg(THF)_4$ and some magnesium-containing species, while the possibility of formation of complexes having a composition such as $Co(PR_3)_3N_2Mg(THF)_2Mg(THF)_2N_2Co(PR_3)_3$ cannot be ignored. Because we could not obtain these complexes containing Co and Mg in 1:1 ratio in crystalline form, further attempts at characterization of these complexes were abandoned.

2. Preparation of N_2-Coordinated Cobaltate Complexes Containing Alkali-Metal Cations. Treatment of 1 with an excess of *n*-butyllithium in a diethyl ether–hexane mixture at room temperature followed by crystallization at low temperatures (−20 to −30 °C) gave very air-sensitive black crystals of $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3)

Table II. Protonation of Cobalt Complexes Having N_2 and PPh_3 Ligands with Acids

complex	$\nu(N_2)$, cm^{-1}	acid[a]	evolved gas[b,c]		nitrogen hydrides[b]		N_2 blance[d]
			H_2	N_2	N_2H_4	NH_3	
$CoH(N_2)(PPh_3)_3$ (1)	2088	c	0.60	1.0			1.0
$[Co(PPh_3)_3N_2]_2Mg(THF)_4$ (2)	1840	s	0.57	0.72	0.26	0.06	1.0
$[Co(PPh_3)_3N_2]Li(Et_2O)_3$ (3)	1900	c	1.3	0.71	0.22	0.21	1.0
$[Co(PPh_3)_3N_2]Li(THF)_3$ (4)	1890	s	0.54	0.63	0.31	0.18	1.0
$[Co(PPh_3)_3N_2]Na(THF)_3$ (5)	1910	s	0.80	0.71	0.21	0.13	0.98
$[Co(PPh_3)_3N_2]Li(12\text{-crown-}4)_{1.5}$	1920	s	1.19	0.76	0.01	0.15	0.84
		c	1.45	0.81	0.01	0.17	0.91

[a] Complexes were hydrolyzed by concentrated H_2SO_4 (s) or by 10 molar excess of HCl in Et_2O (c) at room temperature. [b] mol/mol of Co or Fe. [c] Analysis of the gases was carried out by means of GLC (molecular sieve 5A column) after the gases were collected by using a Toepler pump. [d] Sum of N_2 liberated and nitrogen hydrides (converted into mol of N_2/Co).

in good yields. Similar treatment in a THF–hexane mixture of 1 with LiBu afforded a THF-coordinated analogue 4 in good yields. By a similar reaction of 1 with LiBu

$$\underset{1}{\mathrm{CoH(N_2)(PPh_3)_3}} + \mathrm{LiBu} \xrightarrow{\mathrm{Et_2O\text{–}hexane}} \underset{3}{\mathrm{[Co(N_2)(PPh_3)_3]Li(Et_2O)_3}} \quad (3)$$

$$\underset{1}{\mathrm{CoH(N_2)(PPh_3)_3}} + \mathrm{LiBu} \xrightarrow{\mathrm{THF\text{–}hexane}} \underset{4}{\mathrm{[Co(N_2)(PPh_3)_3]Li(THF)_3}} \quad (4)$$

carried out in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmed) an analogous complex, $[Co(N_2)(PPh_3)_3]Li(tmed)$, was obtained as black cubes.

The diethyl ether containing complex 3 can be transformed to the THF-containing complex 4 on recrystallization of 3 from THF and to a dioxane-containing reddish brown complex, $[Co(N_2)(PPh_3)_3]Li(dioxane)$, on crystallization of 3 from a dioxane–hexane mixture. Crown ether (12-crown-4) also replaces the coordinated ether ligands in 3 as evidenced by a shift of the $\nu(N_2)$ band to 1920 cm^{-1}, but isolation of the crown ether coordinated complex in a crystalline form was not successful. Employment of other crown ethers of a larger ring size such as 15-crown-5 and 18-crown-6 led to simple liberation of N_2, and no N_2-containing complex was obtained. In the preparation of the crown ether containing complex from 3 a triphenylphosphine ligand was not released into the solution and the ^1H NMR spectrum of the solution containing the crown ether complex showed 1.5 equiv of the crown ether per cobalt having three triphenylphosphine ligands. Further characterization of the complex was precluded by its instability. Complex 4 is avaliable also by a reaction of the magnesium-containing complex $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$ (2) with butyllithium.

The ^1H NMR spectrum of 4 showed the presence of the coordinated triphenylphosphine and THF protons. The $^{31}P\{^1H\}$ NMR spectrum of 4 in THF containing 10% of benzene-d_6 showed a singlet at −5.76 ppm (relative to the external H_3PO_4 reference in D_2O), which is shifted considerably upfield from the region where the ^{31}P chemical shift of the other PPh_3-containing complexes is observed (30–50 ppm). The upfield shift may arise from the high electron density of the Co(I−) complex. The ^7Li NMR signal of 4 was also observed as a singlet at −3.83 ppm relative to LiCl in D_2O, and no coupling to phosphorus was observed.

The corresponding sodium analogue $[Co(N_2)(PPh_3)_3]Na(THF)_3$ (5) was obtained as black crystals by treatment of the Mg–Co–N_2 complex 2 with sodium metal. The corresponding potassium analogue of 4 also was obtained by the reaction of 2 with potassium, but the complex could not be isolated in the pure state.

There are some precedents for the preparation of alkali-metal containing N_2-coordinated cobalt complexes having triphenylphosphine and diphenylethylphosphine as ligands.[7] In none of these reports, however, were any analytical data given, and evidence for formation of the N_2-containing complexes is based solely on observation of the $\nu(N_2)$ band in the region of 1835–2100 cm^{-1}. The PMe_3-coordinated Co(I−) complex containing potassium having the formula of $[Co(N_2)(PMe_3)_3K]_6$, prepared by Klein et al. during the progress of the present study, represents the only well-characterized example of N_2–Co^{I-} complex but its structure differs somewhat from that of our PPh_3-coordinated complex as revealed by X-ray crystallography.

All of the present complexes formally can be considered as alkali-metal salts of cobaltate and show sharp strong $\nu(N_2)$ bands as tabulated in Table II. The $\nu(N_2)$ band is considerably lowered (by 200 cm^{-1}) with respect to the starting Co(I+) complex 1, reflecting the back-donation from cobalt to the ligating dinitrogen. The influence of the coordinated ether type ligands on the $\nu(N_2)$ band is minor except for the crown ether coordinated complex that shows the highest $\nu(N_2)$ band at 1920 cm^{-1}. The effect of the crown ether to alter the protonolysis behavior of the N_2 complex also is seen as discussed later.

The partial ionic character of the lithium and sodium complexes in solution was confirmed by measuring the relative electric conductivities. They showed electric conductivities on the order of $^1/_5$ of that of $NaBPh_4$ in THF, whereas $[Co(PPh_3)_3N_2]_2Mg(THF)_4$ was nonconducting.

Treatment of 3 with an equimolar amount of carbon monoxide in THF solution causes a simple exchange of the dinitrogen ligand with CO to afford the anionic cobalt carbonyl complex $[Co(CO)(PPh_3)_3]Li(THF)_3$ with quantitative evolution of N_2 gas. This carbonyl complex shows a considerably low $\nu(CO)$ band at 1710 cm^{-1} (Nujol mull), reflecting the anionic nature of PPh_3–Co–CO moiety which results in the large back-donation from cobalt to the ligating CO.

$$\underset{3}{\mathrm{[Co(N_2)(PPh_3)_3]Li(Et_2O)_3}} + \mathrm{CO} \xrightarrow{\mathrm{THF}} \mathrm{[Co(CO)(PPh_3)_3]Li(THF)_3} + \mathrm{N_2} \quad (5)$$

3. Molecular Structures of $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3) and $[Co(N_2)(PPh_3)_3]Li(THF)_3$ 4.

A perspective view of the 3 molecule is given in Figure 1. Selected bond lengths and bond angles are listed in Table III. The molecule has a threefold symmetry, and the Co, N(1) and N(2), and Li atoms lie on a crystallographic threefold rotatory inversion axis. That is, the nitrogen

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Table III. Selected Bond Lengths (Å) and Bond Angles (deg) of 3 and 4[a]

Bond Lengths

$[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3)

Co-N(1)	1.707 (11)	N(1)-N(2)	1.167 (16)	O-C(19)	1.62 (3)
Co-P	2.160 (3)	Li-N(2)	1.96 (4)	O-C(20)	1.64 (4)
P-C(1)	1.864 (8)	Li-O	1.99 (4)	C(19)-C(21)	1.29 (5)
P-C(7)	1.852 (9)	C(7)-C(8)	1.417 (13)	C(20)-C(22)	1.34 (6)
P-C(13)	1.857 (9)	C(8)-C(9)	1.427 (15)	C(13)-C(14)	1.410 (13)
C(1)-C(2)	1.408 (12)	C(9)-C(10)	1.374 (19)	C(14)-C(15)	1.403 (16)
C(2)-C(3)	1.399 (14)	C(10)-C(11)	1.393 (21)	C(15)-C(16)	1.392 (18)
C(3)-C(4)	1.399 (15)	C(11)-C(12)	1.417 (20)	C(16)-C(17)	1.404 (17)
C(4)-C(5)	1.382 (16)	C(12)-C(7)	1.422 (16)	C(17)-C(18)	1.419 (16)
C(5)-C(6)	1.420 (15)			C(18)-C(13)	1.398 (14)
C(6)-C(1)	1.396 (12)				

$[Co(N_2)(PPh_3)_3]Li(THF)_3$ (4)

Co-N(1)	1.624 (26)	N(1)-N(2)	1.19 (4)	Li-O	1.99 (9)
Co-P	2.169 (7)	Li-N(2)	2.06 (9)	O-C(19)	1.54 (6)
P-C(1)	1.882 (19)	C(7)-C(8)	1.39 (4)	O-C(20)	1.68 (7)
P-C(7)	1.833 (22)	C(8)-C(9)	1.43 (4)	C(13)-C(14)	1.40 (4)
P-C(13)	1.826 (22)	C(9)-C(10)	1.39 (5)	C(14)-C(15)	1.43 (4)
C(1)-C(2)	1.39 (3)	C(10)-C(11)	1.31 (6)	C(15)-C(16)	1.38 (4)
C(2)-C(3)	1.42 (4)	C(11)-C(12)	1.48 (5)	C(16)-C(17)	1.39 (4)
C(3)-C(4)	1.38 (4)	C(12)-C(7)	1.47 (4)	C(17)-C(18)	1.42 (4)
C(4)-C(5)	1.35 (4)			C(18)-C(13)	1.44 (4)
C(5)-C(6)	1.46 (4)				
C(6)-C(1)	1.37 (4)				

Bond Angles

$[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3)

Co-P-C(1)	116.6 (3)	P-Co-N(1)	106.5 (4)	C(19)-O-C(20)	94.2 (16)
Co-P-C(7)	113.5 (3)	N(2)-Li-O	106.5 (15)	C(21)-C(19)-O	86.0 (21)
Co-P-C(13)	124.7 (3)	O-Li-O′	111.1 (18)	O-C(20)-C(22)	93.5 (25)
P-Co-P′	112.3 (2)	Li-O-C(19)	131.7 (16)	C(13)-C(14)-C(15)	120.1 (10)
C(1)-C(2)-C(3)	121.9 (9)	Li-O-C(20)	120.9 (16)	C(14)-C(15)-C(16)	120.3 (11)
C(2)-C(3)-C(4)	118.9 (10)	C(7)-C(8)-C(9)	119.4 (10)	C(15)-C(16)-C(17)	121.2 (12)
C(3)-C(4)-C(5)	120.1 (11)	C(8)-C(9)-C(10)	119.8 (12)	C(16)-C(17)-C(18)	117.8 (11)
C(4)-C(5)-C(6)	121.2 (11)	C(9)-C(10)-C(11)	121.2 (14)	C(17)-C(18)-C(13)	121.8 (10)
C(5)-C(6)-C(1)	119.2 (9)	C(10)-C(11)-C(12)	120.9 (14)	C(18)-C(13)-C(14)	118.9 (9)
C(6)-C(1)-C(2)	118.8 (8)	C(11)-C(12)-C(7)	118.3 (12)	P-C(13)-C(14)	124.9 (7)
P-C(1)-C(2)	118.2 (7)	C(12)-C(7)-C(8)	120.2 (9)	P-C(13)-C(18)	116.3 (7)
P-C(1)-C(6)	123.0 (7)	P-C(7)-C(8)	118.1 (7)		
		P-C(7)-C(12)	121.3 (8)		

$[Co(N_2)(PPh_3)_3]Li(THF)_3$ (4)

Co-P-C(1)	117.0 (7)	P-Co-N(1)	106.6 (10)	C(19)-O-C(20)	89 (3)
Co-P-C(7)	113.5 (8)	N(2)-Li-O	107 (4)	C(7)-C(8)-C(9)	121 (3)
Co-P-C(13)	125.1 (8)	O-Li-O′	112 (4)	C(8)-C(9)-C(10)	119 (3)
P-Co-P′	112.1 (3)	Li-O-C(19)	125 (4)	C(9)-C(10)-C(11)	121 (4)
C(1)-C(2)-C(3)	121 (3)	Li-O-C(20)	140 (4)	C(10)-C(11)-C(12)	124 (4)
C(2)-C(3)-C(4)	119 (3)	C(13)-C(14)-C(15)	121 (3)	C(11)-C(12)-C(7)	114 (3)
C(3)-C(4)-C(5)	120 (3)	C(14)-C(15)-C(16)	121 (3)	C(12)-C(7)-C(8)	120 (3)
C(4)-C(5)-C(6)	121 (3)	C(15)-C(16)-C(17)	122 (3)	P-C(7)-C(8)	120 (2)
C(5)-C(6)-C(1)	118 (3)	C(16)-C(17)-C(18)	118 (3)	P-C(7)-C(12)	119 (2)
C(6)-C(1)-C(2)	120 (2)	C(17)-C(18)-C(13)	122 (3)		
P-C(1)-C(2)	117 (2)	C(18)-C(13)-C(14)	117 (2)		
P-C(1)-C(6)	123 (2)	P-C(13)-C(14)	126 (2)		
		P-C(13)-C(18)	117 (2)		

[a] Estimated standard deviations are in parentheses.

molecule coordinates to the Co atom by the N(1) atom to form an end-on type coordination and weakly bonds to the Li by the N(2). The N(1)-N(2) bond length [1.167 (16) Å] seems to be longer than those in $CoH(N_2)(PPh_3)_3$ [1.123 (13) and 1.101 (12) Å],[8] whereas the Co–N(1) length [1.707 (11) Å] is much shorter than those in $CoH(N_2)(PPh_3)_3$ [1.829 (12) and 1.784 (13) Å]. The coordination geometry around the Co atom is tetrahedral [Co–P = 2.160 (3) Å, P–Co–P = 112.3 (2)°, and P–Co–N(1) = 106.5 (4)°]. Three Et_2O molecules coordinate to the Li by the O atoms. The bonding of PPh_3 with the Co atom is normal.

A crystal of 4 is isomorphous to that of 3. A molecule of 4 has a similar structure as that of 3. The molecular symmetry is 3, and the straight Co—N(1)≡N(2)—Li bonds lie on a 3 axis. The N(1)-N(2) and Co–N(1) bond lengths

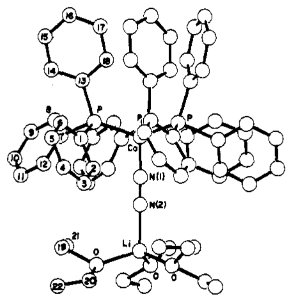

Figure 1. An ORTEP drawing of the $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3) molecule.

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[1.19 (4) and 1.624 (26) Å, respectively] show similar tendencies as those observed in **3**. Three THF molecules instead of Et_2O in **3** coordinate to the Li by their O atoms, although the location of β-carbon atoms of THF is somewhat uncertain.

4. Preparation of Iron–Dinitrogen Complexes and Attempted Synthesis of N_2 Complexes of Other Transition Metals. After the successful preparation of low-valent Co–N_2 complexes using diethylmagnesium, synthesis of dinitrogen complexes of other low-valent transition metals was attempted. Among the group 8 transition-metal complexes examined, only an iron–dinitrogen complex was obtained in crystalline form. As Fe–N_2 complexes reported so far, neutral[9] and cationic[10] Fe(II) and Fe(0) complexes containing tertiary phosphine ligands are known, but the coordinated dinitrogen was not able to be protonated, whereas characterization of N_2–Fe complexes that produce hydrazine on hydrolysis is not satisfactory.[2]

By reaction of $Fe(acac)_3$ with diethylmagnesium in the presence of dinitrogen and 2–6 equiv of PPh_3 in tetrahydrofuran below 0 °C black crystals containing dinitrogen were obtained. The complex is extremely air sensitive and insoluble in nonreacting solvents such as benzene, tetrahydrofuran, diethyl ether, dioxane, and hexane while methylene chloride, acetone, and methanol decompose it. Thus recrystallization of the complex was not feasible, and the complex was characterized after repeated washing with ether and hexane. As in the preparation of the corresponding Co–N_2–Mg complex, stirring of the reaction mixture after it became homogeneous had an adverse effect on getting the good crystals. On the basis of macroscopic analysis and chemical reactions of the iron complex the complex was characterized as $[FeEt(N_2)(PPh_3)_2]_2Mg(THF)_4$ (**6**). Complex **6** evolves 1 mol each of N_2 and C_2 hydrocarbon gas, which contained 96% ethylene, on thermolysis, whereas acidolysis with H_2SO_4 liberated the ethyl group as ethane and N_2 as hydrazine (0.11 mol/Fe) and ammonia (0.11 mol/Fe). The reaction with CH_3COCl released ethylene. The complex shows a strong broad $\nu(N_2)$ band at 1830 cm^{-1} in addition to the absorptions arising from the coordinated PPh_3 and THF ligands. Complex **6** is paramagnetic with a magnetic moment of $\mu_{eff} = 2.60$ μ_β. Thus, complex **6** may be formally regarded as a Fe(II) complex, presumably having a tetrahedral environment around Fe(II) with bridging N_2 and Mg entities similar to those in **2**. Attempts to obtain **6** as crystals suitable for X-ray crystallography failed. Attempts to prepare a Fe–N_2 complex by reaction of a known Fe–N_2 complex $FeH_2(N_2)(PPh_2Et)_3$ with Et_2Mg in THF were unsuccessful.

For obtaining N_2-coordinated complexes of other low-valent group 8 transition metals the reaction of $[Ni\{P(c\text{-}C_6H_{11})_3\}_2]_2N_2$[11] with Et_2Mg in THF was tried but only an ethylene-coordinated complex, $Ni(C_2H_4)\{P(c\text{-}C_6H_{11})_3\}_2$, was obtained. Treatment of $Ni(acac)_2$ in the presence of PPh_3 with $MgEt_2$ in THF afforded also an ethylene-containing complex, $Ni(C_2H_4)(PPh_3)_2$,[12] without producing an N_2-coordinated nickel complex. Reaction of $RhCl(PPh_3)_3$ with $MgEt_2$ gave $RhH(PPh_3)_3$, and no N_2 complex was available.

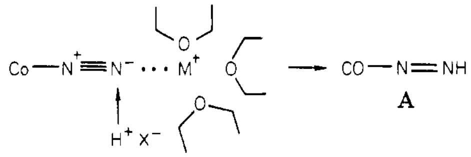
Table IV. Crystal Data of 3 and 4

	$[Co(N_2)(PPh_3)_3]$-$Li(Et_2O)_3$ (3) $C_{66}H_{75}LiN_2O_3P_3Co$	$[Co(N_2)(PPh_3)_3]$-$Li(THF)_3$ (4) $C_{66}H_{69}LiN_2O_3P_3Co$
fw	1103.1	1097.1
cryst system	trigonal	trigonal
space group	$R\bar{3}$	$R\bar{3}$
unit cell	(hexagonal lattice)	(hexagonal lattice)
a/Å	19.095 (2)	19.077 (2)
c/Å	28.455 (5)	28.569 (5)
V/Å^3	8984.9 (18)	9004 (2)
Z	6	6
D_{calcd}/g cm^{-3}	1.223	1.214
μ(Mo Kα)/cm^{-1}	4.27	4.26

Protonation of the Coordinated Dinitrogen. In contrast to complex 1, which does not liberate hydrazine or ammonia on protonolysis, the alkali-metal- or magnesium-containing cobalt complexes prepared in the present study all react with protonic acids to release hydrazine and ammonia as summarized in Table II, in which $\nu(N_2)$ bands are included also for comparison. The sum of ammonia and hydrazine produced on acidolysis accounted for about 20–30% of the coordinated dinitrogen, and the rest was liberated as N_2 without being protonated. In most cases the N_2 balance gave satisfactory values supporting the formulation of each complex.

It is noteworthy that the amount of N_2H_4 generated on acidolysis of the diethyl ether and THF-containing complexes **3** and **4**, respectively (0.22 and 0.31 mol/Co, respectively), dropped drastically when the ethers were replaced by the crown ether, to liberate ammonia as the principal protonolysis product. The effect of the nature of the acid employed was less marked.

In the protonolysis of the Co^{I-}–N_2–M^+ complex the proton may attack either the cobalt or the coordinate N_2. In the former case protonation of the ligating N_2 may not occur and it may be liberated as is. For the ligating dinitrogen bonded to coblat in the end-on manner to be reduced, the terminal nitrogen atom should be rendered nucleophilic enough by back-donation from the electron-rich Co(I–) entity and attacked by the proton.



A

The ensuing proton attack on the diazenido species A may give a hydrazido(2–) complex that is further protonated to afford hydrazine and/or ammonia depending on the site of further proton attack. Another possible pathway is the protonation of A to liberate diazene which disproportionates further to hydrazine and H_2. Although the route through the diazenido(1–) and hydrazido(2–) intermediates are established for acidolysis of molybdenum and tungsten dinitrogen complexes,[13] no information is presently available regarding the intermediacy of these diazenido or hydrazido species in the hydrolysis of the present complexes. It is intriguing, however, that modification of the environment around the end-on coordinated nitrogen by changing the nature of the coordinating ether ligands bound to the countercation, which is bonded to the terminal nitrogen, profoundly alters the protonolysis pathway.

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Table V. Experimental Conditions for X-ray Diffraction of 3 and 4

	$[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3)	$[Co(N_2)(PPh_3)_3]Li(THF)_3$ (4)
cryst size/mm	0.4 × 0.6 × 0.25	0.4 × 0.5 × 0.4
X-ray	Mo Kα	Mo Kα
monochromatization	Zr filter	graphite monochromator
wavelength/Å	0.710 69	0.710 69
peak intensity		
scan mode	θ-2θ	θ-2θ
scan speed/deg min^{-1}	4	4
scan width/deg	2.0 + 0.7 tan θ (1° below Kα_1 to 1° above Kα_2)	2.0 + 0.7 tan θ (1° below Kα_1 to 1° above Kα_2)
background		
scan mode	stationary crystal-stationary counter	stationary crystal-stationary counter
no. of measurements	2 (at both ends of a peak scan)	2 (at both ends of a peak scan)
measurement time/s	7.5	7.5
no. of std reflctns measd	4 (after every 60 reflections)	4 (after every 60 reflections)
no. of reflctns measd	4084	5260
collectn range	$+h,k,l$	$h,k,+l$
$2\theta_{max}$/deg	42.0	50.0
agreement between equiv reflctns, R_{sym}[a]	0.03	0.027
no. of independent reflctns measd	2160	3201
no. of reflctns obsd ($\lvert F\rvert > 3\sigma(F)$)	1288	2345

[a] $R_{sym} = \Sigma\,\lvert\lvert F\rvert - \langle\lvert F\rvert\rangle\rvert / \Sigma\langle\lvert F\rvert\rangle$; $\langle\lvert F\rvert\rangle$ is the average value of two or more equivalent reflections.

Change of the protonolysis product distribution was also noted in acidolysis of Co^{I-}–N_2–Li complexes containing dioxane and tetramethylethylenediamine (tmed) ligands. In the acidolysis of the dioxane-containing complex with HCl rather low yields of 0.05 mol/Co of hydrazine and 0.06 mol/Co of ammonia were formed while the tmed-containing complex liberated 0.07 mol/Co of hydrazine and 0.02 mol/Co of ammonia.

For investigating the protonolysis behavior of the ligating dinitrogen and probing the feasibility of designing a system by which the dinitrogen is reduced by dihydrogen, the reactions of the N_2–Co complexes with transition-metal hydrides that are available by interaction with H_2 were examined. The Mg- and Li-containing complexes 2 and 4 were treated with $CoH(CO)_4$ and $FeH_2(CO)_4$, which react themselves with H_2. Only 0.005–0.02 mol of NH_3 was formed per N_2 complex examined, and no hydrazine was detected. $Zr(\eta^5\text{-}C_5H_5)_2H_2$ showed a similar feeble reactivity while $LiAlH_4$ was totally nonreactive. The results are in contrast to the recently reported higher reactivities of molybdenum and tungsten dinitrogen complexes toward transition-metal and non-transition-metal hydrides.[13a,14]

The direct treatment of 4 with H_2 in ether formed the Co–H_2–Li complex as reddish brown crystals, which was converted into the known hydrido complex $H_3Co(PPh_3)_3$ by the reaction with water, with quantitative evolution of coordinated dinitrogen ligand, whereas the Co–H_2–Li complex could reproduce 4 with evolution of hydrogen gas on treatment with N_2 gas in THF, showing the reversible coordination of N_2 and H_2 to the Ph_3P–Co–Li moiety. Further characterization of this Co–H_2–Li complex was not feasible due to its instability.

Experimental Section

All manipulations were carried out under an atmosphere of dinitrogen or argon or in vacuo. Solvents, stored over $LiAlH_4$ after being dried and distilled in the usual manner, were directly introduced into the reaction flask by a trap to trap distillation method in order to avoid contamination with oxygen and moisture.

Infrared spectra were recorded on a Hitachi 295 spectrometer using KBr pellets or Nujol mull prepared under inert atmosphere. ^1H, ^{31}P, and ^7Li NMR spectra were measured on JEOL FX-100 spectrometer.

Due to the extreme sensitivity to air of the complexes reported here the microanalysis was not feasible and the macroscopic analysis was carried out to determine their compositions. Cobalt and iron contents were determined by colorimetric methods, magnesium and lithium by flame photometric methods, PPh_3, Et_2O, and THF by GLC analysis after hydrolysis of the complexes, and N_2 by measuring the amount of noncondensable gas with a Toepler pump after thermolyzing the complexes. Quantitative analysis of ammonia and hydrazine produced by acidolysis of the complexes was performed by colorimetric methods according to the literatures.[15,16]

$HCo(N_2)(PPh_3)_3$ was prepared as previously reported. BuLi was used as purchased. Diethylmagnesium was prepared as Et_2O solution of dioxane adduct $Et_2Mg(dioxane)_{1/2}$ from ethylmagnesium bromide and dioxane by the literature method.

Preparation of $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$ (2). To the orange homogeneous THF solution (25 mL) of $HCo(N_2)(PPh_3)_3$ (1.7 g, 2.0 mmol) was added an Et_2O solution of $Et_2Mg(dioxane)_{1/2}$ (3 mL, ca. 3 mmol) by means of a syringe at −30 °C. On stirring the system at the same temperature for a few minutes, it became a dark brown solution, and then the system was allowed to stand at 0 °C without stirring. After 10 h reddish brown fine crystals of $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$ (2) were formed. The products thus obtained were filtered, washed with a small amount of dry Et_2O at low temperature, and dried in vacuo (1.6 g, 81% yield).

Preparation of $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3) from 1. To the orange heterogeneous mixture of $HCo(N_2)(PPh_3)_3$ (2.6 g, 2.9 mmol) and Et_2O (20 mL) was added a hexane solution of BuLi (9 mL, 14 mmol) by means of a syringe at −30 °C. Stirring the system at room temperature for 15 h yielded a dark brown and almost homogeneous solution. After removal of the undissolved matter by filtration, the solution was concentrated to a half volume followed by addition of 10 mL of hexane. Standing the system for 1 day at −30 °C yielded slightly reddish black crystals of 3, which were filtered, washed with hexane at −50 °C, and dried in vacuo (2.0 g, 63%).

Preparation of 3 from 2. To the ether suspension (90 mL) of $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$ (2; 4.3 g, 2.1 mmol) was added a hexane solution of BuLi (ca. 10 mmol) by means of a syringe at −30 °C. On stirring the system at room temperature for 30 min, it became a dark brown homogeneous solution. Standing the

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Table VI. The Atomic Positional Parameters and Equivalent Temperature Factors with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq} (or *B*)/Å^2
		$[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3)		
Co	0	0	0.23018 (6)	3.1
N(1)	0	0	0.2902 (4)	4.3
N(2)	0	0	0.3312 (5)	6.4
P	0.07246 (12)	0.12474 (11)	0.20868 (7)	3.7
C(1)	0.1764 (5)	0.1822 (5)	0.2337 (3)	4.0
C(2)	0.1904 (6)	0.1593 (5)	0.2782 (3)	5.3
C(3)	0.2664 (6)	0.1998 (6)	0.2998 (4)	6.3
C(4)	0.3303 (6)	0.2642 (6)	0.2761 (4)	6.4
C(5)	0.3182 (6)	0.2863 (7)	0.2319 (4)	7.2
C(6)	0.2408 (5)	0.2463 (5)	0.2103 (4)	5.6
C(7)	0.0326 (5)	0.1900 (5)	0.2295 (3)	4.9
C(8)	−0.0351 (5)	0.1850 (6)	0.2060 (4)	5.9
C(9)	−0.0711 (7)	0.2298 (7)	0.2234 (4)	7.8
C(10)	−0.0416 (8)	0.2749 (7)	0.2637 (5)	9.2
C(11)	0.0240 (9)	0.2791 (8)	0.2877 (5)	9.8
C(12)	0.0633 (7)	0.2377 (6)	0.2708 (4)	7.1
C(13)	0.0956 (5)	0.1595 (5)	0.1467 (3)	4.1
C(14)	0.1050 (5)	0.2331 (6)	0.1297 (3)	5.4
C(15)	0.1183 (6)	0.2514 (7)	0.0816 (4)	7.0
C(16)	0.1236 (6)	0.1978 (7)	0.0507 (4)	7.3
C(17)	0.1180 (6)	0.1257 (7)	0.0667 (4)	7.3
C(18)	0.1033 (6)	0.1075 (6)	0.1153 (3)	6.1
Li	0	0	0.4002 (13)	8.4 (8)
O	0.0588 (6)	0.1144 (6)	0.4215 (4)	10.9 (3)
C(19)	0.0774 (14)	0.1978 (14)	0.3957 (8)	18.9 (8)
C(20)	0.1488 (16)	0.1535 (16)	0.4450 (9)	22.1 (10)
C(21)	−0.0002 (18)	0.1671 (17)	0.3943 (10)	24.3 (11)
C(22)	0.154 (3)	0.227 (3)	0.4528 (13)	31.7 (16)
		$[Co(N_2)(PPh_3)_3]Li(THF)_3$ (4)		
Co	0	0	0.26969 (14)	3.1
N(1)	0	0	0.2128 (9)	4.8
N(2)	0	0	0.1712 (11)	7.0
P	0.0730 (3)	0.1252 (3)	0.29144 (18)	4.0
C(1)	0.1781 (10)	0.1842 (10)	0.2663 (6)	4.1
C(2)	0.1908 (12)	0.1601 (12)	0.2228 (7)	5.4
C(3)	0.2677 (14)	0.2011 (13)	0.2007 (8)	6.6
C(4)	0.3312 (13)	0.2639 (15)	0.2240 (7)	6.6
C(5)	0.3198 (13)	0.2873 (14)	0.2667 (8)	7.6
C(6)	0.2411 (13)	0.2462 (13)	0.2897 (8)	6.8
C(7)	0.0332 (11)	0.1899 (12)	0.2716 (7)	4.8
C(8)	−0.0324 (13)	0.1876 (13)	0.2943 (8)	6.5
C(9)	−0.0683 (14)	0.2324 (14)	0.2770 (9)	7.8
C(10)	−0.039 (2)	0.2770 (19)	0.2360 (11)	11.1
C(11)	0.023 (2)	0.2811 (16)	0.2139 (10)	10.0
C(12)	0.0674 (16)	0.2398 (14)	0.2294 (8)	7.4
C(13)	0.0955 (11)	0.1597 (12)	0.3520 (6)	4.5
C(14)	0.1042 (12)	0.2320 (12)	0.3695 (7)	5.1
C(15)	0.1178 (13)	0.2503 (14)	0.4182 (8)	6.4
C(16)	0.1241 (14)	0.1978 (15)	0.4487 (7)	8.0
C(17)	0.1196 (13)	0.1264 (14)	0.4334 (8)	7.9
C(18)	0.1050 (12)	0.1077 (13)	0.3848 (8)	6.4
Li	0	0	0.099 (3)	8.4 (19)
O	0.0607 (13)	0.1153 (13)	0.0792 (7)	11.5 (6)
C(19)	0.060 (3)	0.186 (3)	0.1050 (14)	15.5 (13)
C(20)	0.149 (4)	0.182 (4)	0.0540 (18)	20.4 (18)

system at −30 °C without stirring yielded slightly reddish black crystals of $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (**3**), which were filtered, washed with hexane, and dried in vacuo at low temperature (3.4 g, 80%).

Preparation of $[Co(PPh_3)_3N_2]Li(THF)_3$ (4). By a similar procedure to the preparation of **3** from **1** except for using THF–Et_2O as solvent, the THF-containing complex $[Co(N_2)(PPh_3)_3]Li(THF)_3$ (**4**) was obtained from **1** and BuLi.

Complex **4** was also obtained by recrystallization of the ether-containing complex **3** in THF–Et_2O. To the THF solution (10 mL) of complex **3** (0.92 g) was added 20 mL of dry Et_2O by a trap to trap distillation. The resulting dark solution was cooled to −70 °C overnight to yield black crystals of $[Co(N_2)(PPh_3)_3]Li(THF)_3$ (**4**; 0.81 g, 90%).

Preparation of $[Co(N_2)(PPh_3)_3]Na(THF)_3$ (5). To a Schlenk tube containing $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$ (**2**) (1.44 g, 0.63 mmol) and sodium dispersion was added THF (20 mL) by a trap to trap distillation, and the system was stirred for 3 h at room temperature. After separation of unreactive sodium metals by filtration, the solvent was evaporated by pumping followed by addition of dry Et_2O (20 mL) to yield black crystals, which were recrystallized from THF–Et_2O to give black cubes of $[Co(N_2)(PPh_3)_3]Na(THF)_3$ (**5**; 0.98 g, 63%).

Preparation of $[EtFe(N_2)(PPh_3)_2]_2Mg(THF)_4$ (6). To a homogeneous THF solution (40 mL) of $Fe(acac)_3$ (0.7 g, 2.0 mmol) and PPh_3 (3.1 g, 12.0 mmol) was added an ethereal solution of $Et_2Mg(dioxane)_{1/2}$ (12 mL, 12 mmol) at −60 °C. The color of the system quickly changed from red to dark brown. After the temperature of the system was raised gradually to −20 °C, it was allowed to stand at 0 °C without stirring. After 3 days, black crystals of $[EtFe(N_2)(PPh_3)_2]_2Mg(THF)_4$ (**6**) were formed. The products were filtered, washed with Et_2O and hexane at −50 °C several times, and dried in vacuo: 1.0 g, 64% yield; mp 128–129 °C dec: IR (Nujol mull) $\nu(N_2)$ 1830 cm^{-1} (br, s). Anal. Calcd for $[EtFe(N_2)(PPh_3)_2]_2Mg(THF)_4$: Fe, 7.0, Mg, 1.5; N_2, 3.5; PPh_3, 66; THF, 18; Et, 3.7. Found: Fe, 6.9; Mg, 1.4; N_2, 3.5; PPh_3, 64; THF, 20; Et, 3.2.

Preparation of $[Co(CO)(PPh_3)_3]Li(THF)_3$. A 30-mL Schlenk tube containing a THF solution (7 mL) of $[Co(N_2)(PPh_3)_3]Li(Et_2O)_3$ (3; 0.46 g, 0.42 mmol) was sealed with a gas-tight rubber serum cap under an argon atmosphere. A 10.5-mL sample of carbon monoxide gas (0.43 mmol) was introduced by means of syringe, and the system was stirred at room temperature. After half a day, a complete consumption of carbon monoxide and a quantitative evolution of dinitrogen gas have been confirmed by means of GLC. Addition of dry Et_2O (7 mL) to the system yielded black crystals, which were recrystallized from THF–Et_2O to give black crystals of $[Co(CO)(PPh_3)_3]Li(THF)_3$: 0.31 g, 67% yield; mp 196–198 °C dec; IR (Nujol mull) $\nu(CO)$ 1710 cm^{-1} (br, s). Anal. Calcd: Co, 5.4. Found: Co, 5.4.

X-ray Crystal Structure Analysis of 3 and 4. Since the crystals of 3 and 4 are unstable in the moist air, they were sealed in thin-walled glass capillary tubes under an atmosphere of dinitrogen. Of the many crystals examined only a few but rather large crystals were found useful for the X-ray experiment. Crystal data of 3 and 4 are given in Table IV.

Preliminary X-ray work on 4 failed to determine the crystal system and space group. The smallest primitive unit cell was then determined by measuring the centered positions of 20 reflections that were searched out in the lower 2θ angular regions coupled with wide range variations of χ and ϕ angles. Using the parameters of this unit cell, reflection intensities of 310 reflections over all the octants within the diffraction sphere of 2θ up to 12° were measured by a quick θ–2θ scan technique (8° min^{-1} in 2θ scan rate and 1-s background count at both ends of a scan), from which the Laue group of the crystal was determined as $\bar{3}$ and the crystal system as trigonal (LAGCOD program). (Reflections indexed by using the smallest primitive cell are grouped by magnitudes of their $|F(hkl)|$ and d_{hkl}. Laue symmetry of reflection intensities of the crystal is determined by the statistics of the number of grouped reflections, and the primitive unit cell is then converted into the reduced unit cell.) The systematic absence of reflections ($-h + k + l = 3n + 1$ for hkl of hexagonal lattice) and the relationships $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})| = |F(khl)|$ and $|F(hk\bar{l})| \neq |F(khl)|$ revealed the corresponding space group as $R3$ or $R\bar{3}$. Crystals of 3 were found isostructural with those of 4.

Unit-cell dimensions(hexagonal lattice) of 3 and 4 were determined by least-squares fits of 2θ values of 25 high order reflections measured at 18 °C on a Rigaku automated, four-circle diffractometer. Integrated intensities were measured on the same diffractometer. Details for the experimental conditions are shown in Table V. Usual Lp corrections were made, but corrections for absorption ($(\mu R)_{max} < 0.3$ for both crystals) and extinction were ignored.

Both structures were solved by the heavy-atom method and refined by the block-diagonal least-squares procedure (HBLS V).[17] The quantity minimized was $\sum w(\Delta F)^2$. Hydrogen atoms were not located since the present study aims only to determine the chemical structures of 3 and 4. Anomalous dispersion of atoms was, therefore, not considered.

Approximate positions of the Co and P atoms of 4 were determined from the three-dimensional Patterson function. The highest peak located at (0, 0, 48/90) on corresponding to the Co–Co vector, determined the space group as $R\bar{3}$. The number of unobserved reflections of 4 was rather large, the β-carbon atoms of THF could not be located unambiguously, and the Li atom and the C and O atoms of THF were refined isotropically in the anisotropic refinement. The R ($R = \sum||F_o| - |F_c||/\sum|F_o|$) value was rather high as 0.120 for 1288 observed reflections (R_w (= $\{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ = 0.135). The atomic parameters are listed in Table VI. (Lists of observed and calculated structure factors and anisotropic temperature factors are deposited as supplementary material.)

All the non-hydrogen atoms of 3 were refined with anisotropic thermal parameters. The final R value was 0.091 for 2345 observed reflections (R_w = 0.091). The atomic parameters are also listed in Table VI.

Atomic scattering factors were taken from ref 18. Calculations were done on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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Registry No. 1, 16920-54-0; 2, 86528-87-2; 3, 86528-89-4; 4, 86528-90-7; 5, 86528-91-8; 6, 86528-92-9; $[Co(CO)(PPh_3)_3]Li(THF)_3$, 86528-94-1; $[Co(PPh_3)_3N_2]Li$(12-crown-4), 86561-50-4; $Fe(acac)_3$, 14024-18-1; $MgEt_2$, 557-18-6; LiBu, 109-72-8; sodium, 7440-23-5; ammonia, 7664-41-7; hydrazine, 302-01-2.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic temperature factors for 3 and 4 (15 pages). Ordering information is given on any current masthead page.

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[18] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 17–98.