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NOVEL DINITROGEN-COBALT COMPLEXES $[Co(N_2)(PR_3)_3Mg(THF)_2]$ WHICH LIBERATE HYDRAZINE ON HYDROLYSIS

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New dinitrogen-cobalt complexes with the formula of $[CoN_2(PR_3)_3$-$Mg(THF)_2]$ (PR_3 = PPh_3 and PPh_2Et) have been obtained by the reaction of $CoH(N_2)(PPh_3)_3$ with diethylmagnesium and by the reaction of $Co(acac)_3$, PPh_2Et and $MgEt_2$ under nitrogen; the N_2 contained in the complexes was found to be converted into hydrazine and a small amount of ammonia on hydrolysis.

Although $CoH(N_2)(PPh_3)_3$ **1**1) represents one of the first examples of N_2-containing complexes prepared by direct binding of gaseous nitrogen with transition metal complexes,1,2) the reduction of the ligated dinitrogen to ammonia or hydrazine has eluded various attempts3) despite that some early transition metal complexes are known to liberate their coordinated dinitrogen as ammonia and/or hydrazine, on hydrolysis.4) With the view that putting more electrons into **1** might lead the ligated dinitrogen to a more activated form capable to react with protons we have examined the reactions of **1** with various reducing agents. Although the reactions of **1** with Na, Li, and BuLi failed resulting only in release of N_2, the reaction of diethylmagnesium with **1** led to a cobalt complex containing magnesium and a ligated dinitrogen, which could be converted partially into hydrazine on hydrolysis. A cobalt complex with a similar composition containing N_2 and magnesium was recently prepared by R. Hammer et al. from a system containing $CoCl_2$, trimethylphosphine and magnesium in tetrahydrofuran,5) but the reduction of the ligated dinitrogen was not described. This communication provides the first example of cobalt dinitrogen complex which release the ligated N_2 as hydrazine on protonation. Furthermore, these complexes are, to our knowledge, the second examples among Group VIII transition metal complexes in which the ligated dinitrogen is reduced.6)

Complex **1** was mixed with about 3 equiv of diethylmagnesium in tetrahydrofuran (THF) at -40°C under nitrogen and stirred for a day at 0°C. A reddish brown precipitate deposited from the dark red solution with evolution of 2 mol equiv of a mixture of ethane (90 %) and ethylene (10 %). The precipitate was filtered and washed with THF and ether below 0°C to give a complex with a composition of $Co(N_2)$-$(PPh_3)_3Mg(THF)_2$ **2** in a yield of 80 %. A similar complex containing diphenylethylphosphine ligands was also prepared by the reaction of $Co(acac)_3$, PPh_2Et and $MgEt_2$ in THF under nitrogen (yield, 11 %).

$$CoH(N_2)(PPh_3)_3 + MgEt_2 \xrightarrow[THF]{0^\circ C} \underset{\textbf{2}}{Co(N_2)(PPh_3)_3Mg(THF)_2}$$

$$Co(acac)_3 + 3PPh_2Et + MgEt_2 + N_2 \xrightarrow[THF]{0\,^{\circ}C} \underset{\mathbf{3}}{Co(N_2)(PPh_2Et)_3Mg(THF)_2}$$

Preparation of similar complexes with other tertiary phosphine ligands was attempted using PPh_2Me, $PPhEt_2$, $PPhMe_2$, and $P(C_6H_{11})_3$ without success. The reaction of $Co(acac)_3$, $MgEt_2$ and 1,2-bis(diphenylphosphino)ethane(dpe) gave the known complex $CoH(dpe)_2$. Lack of a suitable solvent has prevented the recrystallization of **2**, whereas the more soluble complex **3** was purified by reprecipitation from a benzene-hexane mixture. Complexes **2** and **3** decomposed in vacuo at 76-78°C and 80-82°C, respectively, with release of nitrogen gas. The iodolysis of these complexes also released nitrogen. Complexes **2** and **3** are so air sensitive that the microanalysis was not feasible. The results of macroanalysis of **2** and **3** are summarized in Table 1.

Table 1 Analytical Data of Complexes $Co(N_2)L_3Mg(THF)_2$ (**2**, L = PPh_3; **3**, L = PPh_2Et)

L		Co[a]	Mg[b]	L[c]	N_2[d]	THF[e]
PPh_3	found	5.72	2.57	76.1	2.61	14.0
	calcd.	5.66	2.33	75.6	2.69	13.9
PPh_2Et	found	6.53	2.83	70.5	2.84	f
	calcd.	6.56	2.70	71.6	3.12	16.1

Methods of analysis.
a Co, colorimetric determination
b Mg, EDTA chelate titration.
c Phosphine; GLC analysis after reaction with HCl.
d N_2, measured by means of a Toepler pump after decomposition with I_2 in ether.
e THF, **2** GLC analysis after reaction with HCl.
f THF, **3** analyzed by NMR spectrum.

Infrared spectra of **2** and **3** taken in Nujol mulls indicate a strong and broad band at 1840 cm^{-1} and 1835 cm^{-1}, respectively. When the spectrum of **2** is taken in KBr disc another peak at 2090 cm^{-1}, which is identical with the $\nu(N_2)$ band of **1**, is usually observed in addition to the strong 1840 cm^{-1} band, the relative intensities of both bands being variable depending on the conditions to prepare the KBr discs. We assign the band at 1840 cm^{-1} to the $\nu(N_2)$ band of complex **2** and the band at 2090 cm^{-1} to that of the starting complex **1** which was reverted from **2** on interaction with moisture contained in the KBr powder. In fact, treatment of **2** with water afforded the starting material **1**. On the other hand, the related complex $[Co(N_2)(PMe_3)_3]_2Mg(THF)_4$[5)] has been reported to show two IR bands at 2064 and 1830 cm^{-1} in a Nujol mull, the latter being assigned to the stretching of cobalt hydride formed by partial internal oxidative addition of the trimethylphosphine ligand to cobalt. In the present complexes, however, assignment of the band at 1840 cm^{-1} to $\nu(Co\text{-}H)$ is not reasonable since a perdeuterated complex $Co(N_2)[P(C_6D_5)_3]_3Mg\cdot(THF)_2$[7)] still shows the band at 1840 cm^{-1}. The observation of $\nu(N_2)$ band at a similar region (1845 cm^{-1}) in $NaCo(N_2)$-(tertiary phosphine)$_3$ complex in a Nujol mull has been made by Aresta et al.[8)]

Complexes **2** and **3** react with protic media to form hydrazine and a small amount of ammonia (Table 2). The best yield of hydrazine (0.29 mol per cobalt) was obtained when **2** was treated with concentrated sulfuric acid. In treatment of **2** with hydrogen

Table 2 Reactions of Complexes **2** and **3** with Protic Media[a]

Complex	Proton Donor	Solvent	gas evolved H_2	gas evolved N_2	N-compounds N_2H_4	N-compounds NH_3	total H_2	total N_2
2	conc.H_2SO_4	—	0.52	0.56	0.29	0.03	1.11	0.87
2	HCl	Et_2O	0.85	0.68	0.21	0.02	1.28	0.90
2	HCl	DME[b]	1.48	0.77	0.14	trace	1.76	0.91
2	HCl	THF	1.06	0.82	—	0.01	1.07	0.82
2	H_2O	THF	0.86	1.05	—	trace	0.86	1.05
3	HCl	Et_2O	0.96	0.79	0.11	0.01	1.20	0.91

[a] Liberated amounts of N_2 and H_2 were measured by a Toepler pump and gas liquid chromatography and are given in mol/complex.

[b] DME = dimethoxyethane

chloride the yield of hydrazine is influenced by solvent employed. Formation of hydrazine was found to be severely hindered when THF was used. Complex **3** was found to give less hydrazine than **2** when treated with HCl in ether. In each case, as summarized in Table 2, the combined amounts of dinitrogen and its protonated derivatives corresponded to about 1 mol per cobalt atom. Failure to obtain crystals of **2** and **3** in a form suitable for X-ray analysis prevented establishment of molecular structures. Diamagnetism of the complexes suggests a dimeric structure or an ortho-metallated structure. Complex **3** was found to be non-conductors in THF.

The possibility of ortho-metallation in complex **2** may be excluded on the basis of the following experimental evidence. Treatment of **2** with I_2, CH_3COCl, and DCl, respectively, followed by extraction with ether gave only PPh_3 which contained no I, CH_3CO, or D expected to be introduced at the ortho position for the ortho-metallated structure. With respect to the bonding mode of magnesium contained in transition metal complexes two cases are known. One involves a magnesium atom bridging two dinitrogen molecules bonded respectively to cobalt atoms.[5)] In the other case, magnesium is directly bonded to a transition metal.[9)] It remains to be established which is the case for the present complexes.

Further reaction of butyl lithium replaced magnesium from complex **2** and gave a crystalline complex containing Co, PPh_3, N_2 and Li showing an IR band at 1900 cm^{-1} ascribable to $\nu(N_2)$. Characterization of the complex is in progress.

References and Notes

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