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Preliminary communication

Chemistry of transition-metal nitrogen complexes
III*. Reduction of tris-tertiary phosphine cobalt nitrogen complexes

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$Co(N_2)L_3$ complexes ($L = Ph_3P^1$, $n\text{-}Bu_3P$) react with sodium amalgam or n-butyllithium as indicated by the shift of the strong ν(N,N) band of the reaction mixture. Apparently several new complexes are formed depending on the reaction conditions. The observations are summarized in Table 1.

The reaction between n-BuLi and $Co(N_2)L_3$ leads to at least two classes of new nitrogen complexes, characterized by ν(N,N) bands around 2016–2006 cm^{-1} and 1904–1864 cm^{-1}. The formation of the compounds with the higher ν(N,N) values (2016–2006 cm^{-1}) required less n-BuLi than that of the complexes with lower ν(N,N) values. In the case of the trialkyl phosphine complexes the former compounds could be observed only in hexane as solvent and even then their formation was accompanied by a decomposition to cobalt metal. The compounds with lower frequencies (1904–1864 cm^{-1}) were formed when an excess of n-BuLi was used along with tetrahydrofuran as solvent.

The nature of the reactions taking place in the $Co(N_2)L_3$ + n-BuLi systems can be inferred from the following observations:

(a) When n-heptane was used as solvent with the triethylphosphine complex, n-hexane (identified by GLC) was formed.

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*For Part II, see ref.4.

TABLE 1

Starting nitrogen complex	Reducing agent	Solvent	ν(N,N) (cm^{-1})
$Co(N_2)(Ph_3P)_3$	–	THF	2093
	Na/Hg (excess) or n-BuLi (1 mole)	THF	~ 2040 (sh) 2016
	n-BuLi (excess)	THF	1904
$Co(N_2)(n\text{-}Bu_3P)_3$ [a]	–	hexane	2056
	n-BuLi	hexane	2018
	–	THF	2049
	N-BuLi (excess)	THF	1864
$Co(N_2)(Et_3P)_3$ [a]	–	hexane	2059
	n-BuLi	hexane	2014
	–	THF	2050
	n-BuLi (excess)	THF	1866

[a] These complexes were prepared *in situ* from $CoBr_2$ (in THF) or $Co(acac)_2$ (in hexane) and the appropriate phosphine under nitrogen by reduction with n-BuLi (2 moles).

(b) When the triphenylphosphine complex was used the band at 2016 cm^{-1} is replaced by that at 1904 cm^{-1} when an additional quantity of n-BuLi is added. This indicates that the compound with ν(N,N) of 2016 cm^{-1} is an intermediate in the formation of that with ν(N,N) of the 1904 cm^{-1}.

The same shifts of ν(N,N) were also achieved by treating $Co(N_2)(PPh_3)$ with $KPPh_2 \cdot$dioxane in THF, bands appearing at 2014 and 1904 cm^{-1}, respectively, when one or two moles of the phosphide were used.

(c) When iodobenzene was added to the mixture obtained from the triphenylphosphine complex, the infrared spectra showed that the original complex was regenerated.

The reactions occurring can probably be represented as follows:

$$\mathrm{Co(N_2)(Et_3P)_3 + n\text{-}BuLi \rightarrow Li(Et_2P)Co(N_2)(Et_3P)_2 + n\text{-}C_6H_{14}} \qquad (a)$$

$$\mathrm{Co(N_2)(Ph_3P)_3} \left\{ \begin{array}{l} \xrightarrow[-\ \mathrm{n\text{-}BuPh}]{+\ \mathrm{n\text{-}BuLi}} \mathrm{Li(Ph_2P)Co(N_2)(Ph_3P)_2} \xrightarrow[-\ \mathrm{n\text{-}BuPh}]{+\ \mathrm{n\text{-}BuLi}} \mathrm{Li_2(Ph_2P)_2Co(N_2)(Ph_3P)} \\ \xrightarrow[-\ \mathrm{Ph_3P}]{+\ \mathrm{Ph_2PK}} \mathrm{K(Ph_2P)Co(N_2)(Ph_3P)_2} \xrightarrow[-\ \mathrm{Ph_3P}]{+\ \mathrm{Ph_2PK}} \mathrm{K_2(Ph_2P)_2Co(N_2)(Ph_3P)} \end{array} \right. \qquad (b)$$

$$\left. \begin{array}{l} \mathrm{Li(Ph_2P)Co(N_2)(Ph_3P)_2} \\ \mathrm{Li_2(Ph_2P)_2Co(N_2)(Ph_3P)} \end{array} \right\rangle \xrightarrow[-\ \mathrm{LiI}]{+\ \mathrm{PhI}} \mathrm{Co(N_2)(Ph_3P)_3} \qquad (c)$$

Thus the complexes with ν(N,N) of 2016–2006 and 1904–1864 cm^{-1} are thought to have the formula (M) $[(K_2P)Co(N_2)(R_3P)_2]$ and $M_2[(R_2P)_2Co(N_2)(R_3P)]$, respectively (M = Li, Na, K).

N,N stretching frequencies of 1866–64 are the lowest values observed for transition metal nitrogen complexes, and indicate a very large contribution from Co→N back bonding. This can be explained by the accumulation of negative charge in the complexes.

Reduction of nitrogen to metal nitrides through metal–nitrogen complexes[2] is probably involved in nitrogen fixation by the Volpin–Shur systems[3]. Our observations suggest that the ligands in a nitrogen complex may play a significant part in this reduction by accepting electrons from the reductant and (partly) transferring them through the transition metal to the N_2 entity.

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