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### Preliminary communication

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

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$\text{Co}(\text{N}_2)\text{L}_3$  complexes ( $\text{L} = \text{Ph}_3\text{P}^1$ ,  $\text{n-Bu}_3\text{P}$ ) react with sodium amalgam or *n*-butyllithium as indicated by the shift of the strong  $\nu(\text{N},\text{N})$  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  $\text{Co}(\text{N}_2)\text{L}_3$  leads to at least two classes of new nitrogen complexes, characterized by  $\nu(\text{N},\text{N})$  bands around 2016–2006  $\text{cm}^{-1}$  and 1904–1864  $\text{cm}^{-1}$ . The formation of the compounds with the higher  $\nu(\text{N},\text{N})$  values (2016–2006  $\text{cm}^{-1}$ ) required less *n*-BuLi than that of the complexes with lower  $\nu(\text{N},\text{N})$  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  $\text{cm}^{-1}$ ) were formed when an excess of *n*-BuLi was used along with tetrahydrofuran as solvent.

The nature of the reactions taking place in the  $\text{Co}(\text{N}_2)\text{L}_3 + \text{n-BuLi}$  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

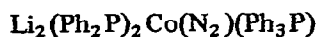
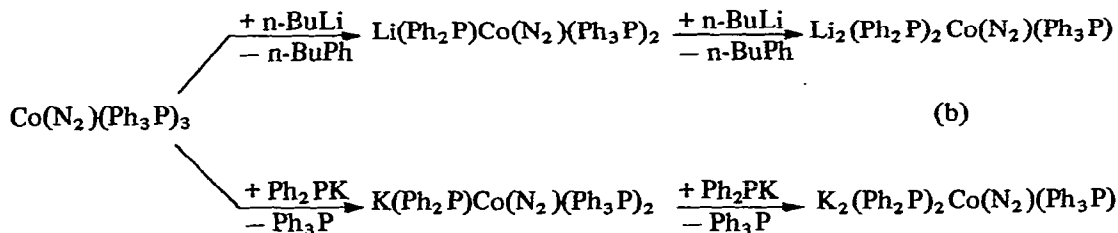
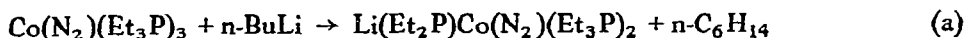
| Starting nitrogen complex                          | Reducing agent                     | Solvent | $\nu(\text{N,N})$<br>( $\text{cm}^{-1}$ ) |
|--|------------------------------------|---------|---|
| $\text{Co}(\text{N}_2)(\text{Ph}_3\text{P})_3$     | —                                  | THF     | 2093                                      |
|  | Na/Hg (excess)                     | THF     | 2040 (sh)                                 |
|  | or                                 |         |   |
|  | n-BuLi (1 mole)<br>n-BuLi (excess) | THF     | 2016<br>1904                              |
| $\text{Co}(\text{N}_2)(\text{n-Bu}_3\text{P})_3^a$ | —                                  | hexane  | 2056                                      |
|  | n-BuLi                             | hexane  | 2018                                      |
|  | —                                  | THF     | 2049                                      |
|  | N-BuLi (excess)                    | THF     | 1864                                      |
| $\text{Co}(\text{N}_2)(\text{Et}_3\text{P})_3^a$   | —                                  | hexane  | 2059                                      |
|  | n-BuLi                             | hexane  | 2014                                      |
|  | —                                  | THF     | 2050                                      |
|  | n-BuLi (excess)                    | THF     | 1866                                      |

<sup>a</sup>These complexes were prepared *in situ* from  $\text{CoBr}_2$  (in THF) or  $\text{Co}(\text{acac})_2$  (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  $2016 \text{ cm}^{-1}$  is replaced by that at  $1904 \text{ cm}^{-1}$  when an additional quantity of n-BuLi is added. This indicates that the compound with  $\nu(\text{N,N})$  of  $2016 \text{ cm}^{-1}$  is an intermediate in the formation of that with  $\nu(\text{N,N})$  of the  $1904 \text{ cm}^{-1}$ .

The same shifts of  $\nu(\text{N,N})$  were also achieved by treating  $\text{Co}(\text{N}_2)(\text{PPh}_3)$  with  $\text{KPPH}_2$ ·dioxane in THF, bands appearing at  $2014$  and  $1904 \text{ cm}^{-1}$ , respectively, when one or two moles of the phosphide were used.

(c) When indobenzene 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:



Thus the complexes with  $\nu(\text{N,N})$  of 2016–2006 and 1904–1864  $\text{cm}^{-1}$  are thought to have the formula  $(\text{M}) [(\text{K}_2\text{P})\text{Co}(\text{N}_2)(\text{R}_3\text{P})_2]$  and  $\text{M}_2 [(\text{R}_2\text{P})_2\text{Co}(\text{N}_2)(\text{R}_3\text{P})]$ , respectively ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ).

$\text{N,N}$  stretching frequencies of 1866–64 are the lowest values observed for transition metal nitrogen complexes, and indicate a very large contribution from  $\text{Co} \rightarrow \text{N}$  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<sup>2</sup> is probably involved in nitrogen fixation by the Volpin–Shur systems<sup>3</sup>. 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  $\text{N}_2$  entity.

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