The Strong Base Trinitrosylcobalt

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Summary The new compound $(NO)_3Co$ exerts strong-base action through lone-pair electrons on cobalt, as demonstrated especially by its formation of a stable adduct with the weak Lewis acid trimethylboron.

The novel trico-ordinate complex $(NO)_3Co$ has been made from $Co_2(CO)_8$ and NO by quantitative high-vacuum methods. Its i.r. spectrum (in cyclohexane) shows N–O stretching at 1860 and 1795 cm^{-1}, and no band in the NO-bridging region (*ca.* 1400 cm^{-1}). The two observable N–O stretching modes indicate a pyramidal C_{3v} structure rather than a planar D_{3h} arrangement. This means that the Co–NO σ-bonds are based upon a tetrahedral hybridization of cobalt, with potentially base-active sp^3 lone-pair electrons on cobalt.

Such base action is demonstrated by the formation of adducts from BF_3, B_2H_6, or BMe_3, with $(NO)_3Co$ in solution. We have studied most fully the adduct $(NO)_3CoBMe_3$, because the weakness of BMe_3 as a Lewis acid makes a good test of base strength.

For the synthesis of $(NO)_3Co$ it is expedient to heat $Co_2(CO)_8$ with NO in a sealed tube, first producing $NOCo(CO)_3$, and then to expose this to more NO in a separate experiment. The mmole stoicheiometry of such an experiment is as follows.

$$\begin{array}{cccc} NOCo(CO)_3 + & 2NO \rightarrow & (NO)_3Co + & 3CO \\ 0{\cdot}150 & 2{\cdot}92 & 0{\cdot}148 & 0{\cdot}440 \\ & -2{\cdot}62 & & \\ \hline & 0{\cdot}30 \text{ nett consumed} & & \end{array}$$

This reaction was observable after a few minutes under direct sunlight (through Pyrex) at 25°. In the dark at 60°, it could be completed in 4 days, by occasional removal of the liberated CO. There seemed to be at least one CO-bridged intermediate—possibly $(NO)_2Co(CO)_2Co(NO)_2$.

The formula $(NO)_3Co$ was confirmed by the high-vacuum thermal decomposition of a 0·206 mmole sample to give 0·202 mg.-atom of lustrous metallic cobalt and 0·612 mmole of NO, authenticated by its known vapour pressures. The results of tensiometric molecular-weight determinations (in dry, degassed benzene or carbon tetrachloride) were 132 or 136; calc., 149.

Unlike the product previously claimed as $(NO)_3Co$,[1] our compound appears black (or deep red in solution), does not sublime under high vacuum below 100° (above which temperature NO is lost), and is rapidly destroyed by air or moisture. Accordingly, it appears that we have made the first authentic samples of this substance.

The adduct $(NO)_3CoBMe_3$ was formed exothermally in benzene solution, with mmole stoicheiometry as follows:

$$\begin{array}{lll} (NO)_3CO & + \; BMe_3 & \rightarrow (NO)_3CoBMe_3 \\ 0{\cdot}145 & \quad 0{\cdot}320 & \qquad 0{\cdot}143 \\ & -0{\cdot}180 & \\ \hline & 0{\cdot}140 \text{ nett consumed} & \end{array}$$

It seemed to be reasonably stable in the open air, or *in vacuo* up to 45°, above which temperature it was possible to remove some BMe_3 (proved by its i.r. spectrum); at higher temperatures there was simultaneous loss of NO. The mass spectrum showed m/e numbers corresponding to $(NO)_3Co$ and $B(CH_3)_3$, but not the parent ion of the adduct nor any higher numbers. Other m/e numbers, possibly assignable to $CoB(CH_3)_3$, $(NO)_3CoBC_3H_3$, $(NO)_2CoBC_2H_4$, $NOCoBC_3H_8$, and $NOCoBC_3H_5$, lend some further support to the formation $(NO)_3CoB(CH_3)_3$. The i.r. spectrum (mull in hexachlorobutadiene) showed C–H stretching at 2925 and 2895 cm^{-1} and N–O stretching only at 1845 and 1766 cm^{-1}, meaning that the BMe_3 could not have been attached to an NO group.

The stability of the adduct $(NO)_3CoBMe_3$ indicates that $(NO)_3Co$ is a stronger base than either ammonia or trimethylamine, which hold BMe_3 far more weakly.[2,3] Other neutral-molecule transition-element bases, such as $(C_5H_5)_2WH_2$[4] and $(C_5H_5)_2ReH$,[5] have been described, but proved too weak to hold BMe_3. It appears that $(NO)_3Co$ is the strongest non-ionic transition-element base yet found, and deserves a full study of its reactions analogous to those of ammonia or tertiary amines.

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[1] L. Schlecht, G. Hamprecht, and F. Spoun, Fr. P., 740,095 (1932); Ger. P., 613,400 (1935); U.S. P., 1,992,637 (1935).
[2] A. Stock and F. Zeidler, *Ber.*, 1921, **54B**, 531.
[3] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 1079.
[4] D. F. Shriver, *J. Amer. Chem. Soc.*, 1963, **85**, 3509; M. P. Johnson and D. F. Shriver, *ibid.*, 1966, **88**, 301.
[5] H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 125.