

The Strong Base Trinitrosylcobalt

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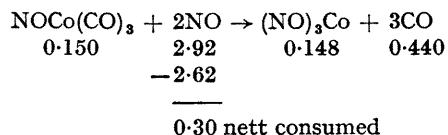
Summary The new compound $(\text{NO})_3\text{Co}$ exerts strong-base action through lone-pair electrons on cobalt, as demonstrated especially by its formation of a stable adduct with the weak Lewis acid trimethylboron.

THE novel trico-ordinate complex $(\text{NO})_3\text{Co}$ has been made from $\text{Co}_2(\text{CO})_8$ 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 $(\text{NO})_3\text{Co}$ in solution. We have studied most fully the adduct $(\text{NO})_3\text{CoBMe}_3$, because the weakness of BMe_3 as a Lewis acid makes a good test of base strength.

For the synthesis of $(\text{NO})_3\text{Co}$ it is expedient to heat $\text{Co}_2(\text{CO})_8$ with NO in a sealed tube, first producing $\text{NOCo}(\text{CO})_3$, and then to expose this to more NO in a separate

experiment. The mmole stoichiometry of such an experiment is as follows.



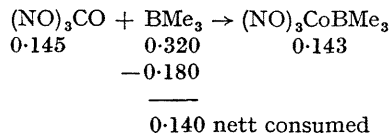
This reaction was observable after a few minutes under direct sunlight (through Pyrex) at 25°. In the dark at 60°, it could be completed in 4 days, by occasional removal of the liberated CO. There seemed to be at least one CO-bridged intermediate—possibly $(\text{NO})_2\text{Co}(\text{CO})_2\text{Co}(\text{NO})_2$.

The formula $(\text{NO})_3\text{Co}$ 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 $(\text{NO})_3\text{Co}$,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 $(\text{NO})_3\text{CoBMe}_3$ was formed exothermally in benzene solution, with mmole stoichiometry as follows:



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 $(\text{NO})_3\text{Co}$ and $\text{B}(\text{CH}_3)_3$, but not the parent ion of the adduct nor any higher numbers. Other *m/e* numbers, possibly

assignable to $\text{CoB}(\text{CH}_3)_3$, $(\text{NO})_3\text{CoBC}_3\text{H}_3$, $(\text{NO})_2\text{CoBC}_2\text{H}_4$, $\text{NOCoBC}_3\text{H}_3$, and $\text{NOCoBC}_3\text{H}_5$, lend some further support to the formation $(\text{NO})_3\text{CoB}(\text{CH}_3)_3$. 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 $(\text{NO})_3\text{CoBMe}_3$ indicates that $(\text{NO})_3\text{Co}$ 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 $(\text{C}_5\text{H}_5)_2\text{-WH}_2$ ⁴ and $(\text{C}_5\text{H}_5)_2\text{ReH}$,⁵ have been described, but proved too weak to hold BMe_3 . It appears that $(\text{NO})_3\text{Co}$ 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.