

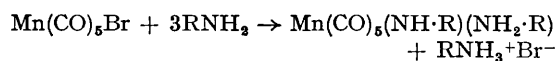
Alkylamido-carbonyl Complexes of Manganese(I)

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IN contrast to primary aromatic amines, ArNH_2 , which are known to react with $\text{Mn}(\text{CO})_5\text{Br}$ to yield products of the type, $\text{Mn}(\text{CO})_3(\text{NH}_2\cdot\text{Ar})_2\text{Br}$,^{1,2} primary aliphatic amines have been found to react

according to the following equation:



¹ W. Hieber and W. Schropp, Jr., *Z. Naturforsch.*, 1959, **14b**, 460.

² R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495.

No carbon monoxide is evolved in the reaction, and the infrared spectrum shows no evidence for the formation of formamides or 1,3-dialkylureas.

In a typical preparation methylamine is bubbled into a pentane solution of $\text{Mn}(\text{CO})_5\text{Br}$. The $\text{CH}_3\text{NH}_3^+\text{Br}^-$ is immediately filtered off and the pentane solution evaporated to dryness leaving a pale yellow solid. After washing with small amounts of pentane, and drying, the product analyzes for $\text{Mn}(\text{CO})_5(\text{NHCH}_3)(\text{NH}_2\text{CH}_3)$. Its infrared spectrum in pentane shows three sharp C—O stretching absorptions at 2077 (w), 1986 (vs), and 1939 cm^{-1} (s) but no strong absorptions in the 1500—1750 cm^{-1} region where an $\text{Mn}(\text{C}=\text{O})\text{NH}\cdot\text{Me}$ carbonyl group might be expected to absorb. This suggests that all seven groups are directly bonded to the metal. The proton n.m.r. spectrum of $\text{Mn}(\text{CO})_5(\text{NH}\cdot\text{Me})(\text{NH}_2\cdot\text{Me})$ in deuteriochloroform exhibits four different kinds of hydrogens whose chemical shifts are given in p.p.m. downfield with respect to tetramethylsilane: NH of

MeNH at 5.78 (broad), NH_2 of MeNH_2 at 3.11 (broad), CH_3 of MeNH at 2.92 (doublet), and CH_3 of MeNH_2 at 2.50 (triplet). The sharpness and position of the CH_3 resonances indicate that the compound is diamagnetic.

The spectral data suggest that the manganese is seven-co-ordinated in these compounds, and its formal electronic configuration must therefore exceed the next inert-gas configuration by two electrons. The scarcity of seven-co-ordinated metal carbonyl complexes whose E.A.N. exceeds that of the next inert gas makes these compounds of particular interest. A clarification of the structural problem awaits an X-ray-crystallographic investigation.

All primary amines, including n- and t-butylamine, ethylenediamine, isopropylamine, and cyclohexylamine, give analogous products, but secondary and tertiary amines do not.

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