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Preliminary communication

Methyl- and hydrido(π-cyclopentadienyl)carbonyl nitrosylrhenium

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Reduction of the π-cyclopentadienyldicarbonylnitrosyl cation of manganese using borohydride affords the neutral dimer $[\pi\text{-}C_5H_5Mn(CO)NO]_2$ [1]. The mechanism of this reaction has not been elucidated, but it seemed to us that an unstable neutral hydride, $\pi\text{-}C_5H_5MnH(CO)NO$, might initially be formed. In the hope of isolating such a neutral hydride, we examined the borohydride reduction of the rhenium analog[2], $[\pi\text{-}C_5H_5Re(CO)_2NO]^+$. We report here the unexpected product of this reaction, as well as the novel rhenium hydride $\pi\text{-}C_5H_5ReH(CO)NO$ obtained by another route.

The reaction of $[\pi\text{-}C_5H_5Re(CO)_2NO]^+$ with $NaBH_4$ in tetrahydrofuran (THF) resulted in formation of the *methyl* derivative $\pi\text{-}C_5H_5ReCH_3(CO)NO$★. No dimer was formed, in contrast to the analogous manganese reaction★★. The red, crystalline compound (m.p. 75°) was stable in air for long periods, and sublimed readily at 50°/0.3 mm. The infrared spectrum (cyclohexane) showed bands at 1972 cm^{-1} (ν(CO)) and 1715 cm^{-1} (ν(NO)). The proton NMR spectrum in $CDCl_3$ showed two sharp singlets at τ 4.42 and 9.05 (intensities 5/3) assigned as C_5H_5 and CH_3 respectively.

In the mass spectrum, the molecular ion was the base peak, and fragments due to loss of CH_3, CO, or NO from the molecular ion were unambiguously identified. Peaks in the *m/e* range 280 ($C_5H_5ReCO^+$) to 187 (Re^+) were somewhat more complex. Doubly charged ions such as $C_5H_5ReCH_3(CO)NO^{2+}$, $C_5H_5Re(CH_3)CO^{2+}$, $C_5H_5ReNO^{2+}$, $C_5H_5ReCH_2{}^{2+}$, and $C_5H_5ReH^{2+}$ were observed in moderate to high abundance.

The relatively high yield (ca. 50%) of the methyl derivative suggests the reduction of a carbonyl group by borohydride ion. A similar phenomenon was observed by Treichel and Shubkin[3] in the borohydride reduction of $[\pi\text{-}C_5H_5M(CO)_3PPh_3]^+$ (where M = Mo, W). It is of interest that borohydride reduction of the rhenium cation in water–benzene affords the rather unstable $\pi\text{-}C_5H_5ReCH_2OH(CO)NO$ [4], which would presumably be an intermediate in the complete reduction of the carbonyl group to methyl.

★ Satisfactory elemental analyses for the new compounds have been obtained.

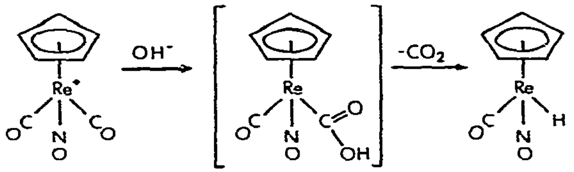
★★ Borohydride reduction of the manganese cation has been described[1] using water–benzene. We have repeated the reaction in THF, where it is extremely vigorous with much decomposition. The manganese dimer was detected by infrared spectroscopy, but no methyl derivative was observed.

Since [π-$C_5H_5Re(CO)NO]_2$ was not obtainable by borohydride reduction, we examined the reaction of [π-$C_5H_5Re(CO)_2NO]^+$ with triethylamine in water—acetone, conditions similar to those recently reported to form the manganese dimer from [π-$C_5H_5Mn(CO)_2NO]^+$ [5]. From the reaction with the rhenium cation, an orange liquid was obtained in rather good yield (~60%), and was characterized as π-$C_5H_5ReH(CO)NO$. The mass spectrum exhibited the strong molecular ion, and ions due to $C_5H_5ReH(NO)^+$, and $C_5H_5ReH(CO)^+$, together with the corresponding weak doubly-charged ions. As in the case of the methyl derivative, the *m/e* 187—280 region was more complex. The proton NMR spectrum showed a sharp singlet (intensity 5) at τ 5.02 and a broad signal (intensity 1) at τ 18.2 in C_6D_6 solution, in agreement with the proposed formulation. The infrared spectrum (cyclohexane) exhibited ν(CO) at 1979 cm^{-1} and ν(NO) at 1722 cm^{-1}.

Compared with most cyclopentadienyl transition metal hydrides π-$C_5H_5ReH(CO)NO$ is unusual both in terms of its relatively high thermal and oxidative stability and its reactions, factors which have thus far precluded synthesis of the dimer [π-$C_5H_5Re(CO)NO]_2$. For example, only unreacted starting material is recovered (with some decomposition) on heating the hydride at 90° for 20 h in a sealed tube.

We feel that formation of the hydride from [π-$C_5H_5Re(CO)_2NO]^+$ involves nucleophilic attack of hydroxide ion (or water) at the carbonyl carbon, resulting in a carboxylate intermediate which then undergoes decarboxylation to give the neutral hydride. The overall reaction is depicted in Scheme 1.

$$Et_3N + H_2O \rightleftharpoons Et_3NH^+ + OH^-$$



Facile loss of CO_2 from such an intermediate has ample precedent in related systems[6,7]. A similar mechanism is probably operative in the manganese reaction together with subsequent rapid dimerization of the presumably unstable manganese hydride.

Further reactions of π-$C_5H_5ReH(CO)NO$ will be described in detail in a future publication, and work is currently in progress on related nitrosyl hydrides of other transition metals.

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REFERENCES

1 R.B. King and M.B. Bisnette, *Inorg. Chem.*, 3 (1964) 791.
2 E.O. Fischer and H. Strametz, *Z. Naturforsch. B*, 23 (1968) 278.
3 P.M. Treichel and R.L. Shubkin, *Inorg. Chem.*, 6 (1967) 1328.
4 A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and L.L. Krasnoslobodskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1970) 860; *Bull. Acad. Sci. USSR*, (1970) 807.
5 T.A. James and J.A. McCleverty, *J. Chem. Soc., A*, (1970) 850.
6 A.J. Deeming and B.L. Shaw, *J. Chem. Soc. A*, (1969) 443.
7 H.C. Clark and W.J. Jacobs, *Inorg. Chem.*, 9 (1970) 1229.