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Reactions of Molybdenum Dinitrogen Complexes

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As extension of previous studies[1] we have investigated the reaction of *trans*-$Mo(N_2)_2dp_2$ (I) [dp = 1,2-bis(diphenylphosphino)ethane] with Lewis and Bronsted acids and with $[Ni(PCy_3)_2X]_2$ (X = Cl, Br; II, III).[2] We wish to report here the preparation and properties of some new ionic molybdenum dinitrogen complexes, the stoichiometry and chemical and spectroscopic properties of which have been determined, but we still need X-ray investigation for a full report on their structures (Table).

From the reaction of (I) with C_6H_5SCl (1 to 1 molar ratio) in toluene at –20 °C a salmon-pink compound $[Mo_2(N_2)_3(-SC_6H_5)_2dp_4]Cl_2 \cdot C_7H_8$ (IV), precipitated, which shows a strong i.r. band at 2040 cm^{-1} [$\nu(N_2)$, in Nujol mull] and a weak one at 1980 cm^{-1}. It loses N_2 in the solid state at room temperature and more easily in solution at temperatures above –20 °C. When the compound (IV) is heated at 50 °C it decomposes[6] according to reaction (1):

$$[Mo_2(N_2)_3(-SC_6H_5)_2dp_4]Cl_2 \rightarrow MoCl_2dp_2 + {} + Mo(N_2)_2dp_2 + (C_6H_5S)_2 + N_2 \qquad (1)$$

$Mo(N_2)_2dp_2$ can be recovered in variable yields owing to its decomposition under the experimental conditions.

At room temperature the reaction of (I) (one mol) with C_6H_5SCl (two mol) produces $MoCl_2dp_2$, $C_6H_5S-SC_6H_5$ and nitrogen.

Owsley[3] has reported that the $C_6H_5S^+$ cation is able to react with molecular nitrogen to give a not isolated species supposed to be $C_6H_5-S-N_2^+$ on the basis of its i.r. spectrum in solution. Thus, in our case C_6H_5SCl does not interact with the coordinated dinitrogen, as the i.r. band for $\nu(N_2)$ in the $Mo-N_2-SC_6H_5$ moiety should be at lower frequencies than in (I) [1982 cm^{-1}, in Nujol mull[1b]], but an oxidative addition to Mo(0) takes place to give a Mo(II) complex. Similar oxidative reactions are given by CH_2Cl_2 and CCl_4 which are converted into a 1,2-dichloroethane (V) (85% yield based on Mo) and C_2Cl_6 (70% yield) respectively. From the reaction of (I) with CCl_4 a pink very unstable complex is first formed [$\nu(N_2)$ at 2038 cm^{-1}] which converts into $MoCl_2dp_2$ and hexachloroethane.

From the reaction of (I) with (II) and (III) in benzene (1:1 molar ratio Mo to Ni), $MoCl(N_2)dp_2$ (VI) [$\nu(N_2)$ at 1970 cm^{-1}, in Nujol mull] and $MoBr(N_2)dp_2$ (VII) [$\nu(N_2)$ at 1965 cm^{-1}] are obtained. (VI) reacts with CH_2Cl_2 to give $MoCl_2dp_2$ and (V); (VII) gives (V) and $MoClBrdp_2$. From the reaction[6] of (I) with $HClO_4$ in toluene at –10 °C there separates a salmon-pink product analysing for $[Mo_2H_2(N_2)_3dp_4](ClO_4)_2 \cdot 2.5C_7H_8$ (VIII) which presents a strong i.r. band at 2036 cm^{-1} and a weak one at 1980 cm^{-1} [$\nu(N_2)$] and a weak band at 1822 cm^{-1} attributable to the ν(Mo–H) on the basis of exchange with deuterium.

(VIII) loses N_2 in the solid state at temperatures above –15 °C. When dissolved in acetone or ethanol at room temperature[6] it converts into a yellow compound analysing for $[MoH(N_2)dp_2](ClO_4)$, with evolution of 0.5 mol of N_2 per Mo atom.

(VIII) (one mol) treated with KOH (two mol) under argon in THF at –25 °C produces a mixture of (I) and $Mo(N_2)dp_2$ (IX) [$\nu(N_2)$ at 1950 cm^{-1}, in Nujol]. (IX) gives (I) under nitrogen in the solid state or in solution. When the reduction with KOH is carried out under nitrogen, (I) is the only product.

Excess of $HClO_4$ does not affect (VIII) suspended in toluene at temperatures below –25 °C,[6] even for prolonged reaction time, and produces complete

TABLE. Analytical Data of the Compounds (calculated values in parentheses).

Compound	Cl	Mo	N	P
$[Mo_2(N_2)_3(SC_6H_5)_2dp_4]Cl_2 \cdot C_7H_8$	3.38	8.53	3.56	11.0
	(3.15)	(8.53)	(3.73)	(11.03)
$[Mo_2H_2(N_2)_3dp_4](ClO_4)_2 \cdot 2.5C_7H_8$	3.15	8.35	3.55	10.9
	(3.08)	(8.35)	(3.65)	(10.8)
$[MoH(N_2)dp_2](ClO_4)$	3.58	10.0	2.80	12.19
	(3.48)	(9.41)	(2.74)	(12.15)
$[Mo_2H_2(CO)_2(N_2)dp_4](ClO_4)_2$	3.45	9.27	1.33	11.95
	(3.42)	(9.28)	(1.35)	(12.0)

loss of N_2[6] above –5 °C. Treatment of (VIII) with anhydrous HCl in toluene at –10 °C affords an orange–red complex analysing for $[MoCl(N_2H_2)dp_2]ClO_4$ [ν(N–H) at 3315 and 3205 cm^{-1}], analogous to the compound $[WCl(N_2H_2)dp_2]ClO_4$ described by Chatt.[4]

The reaction of solid (VIII) with CO at room temperature produces elimination of two mol of N_2 per mol of complex[6] and a carbonyl complex of formula $[Mo_2H_2(CO)_2N_2dp_4](ClO_4)_2$ (X) [ν(CO) at 1867, ν(Mo–H) at 1825 cm^{-1}, in Nujol]. No bands attributable to a bridging CO nor to $\nu(N_2)$, terminal or bridging, are evident in the i.r. spectrum. Treatment of solid (X), or its toluene solutions, with I_2 at 40 °C gives H_2 (0.5 mol), CO (1 mol), N_2 (0.5 mol) per Mo atom.[6] On the basis of analytical and spectroscopic data and chemical properties, complexes (IV), (VIII), (X) can be tentatively described as binuclear complexes of Mo(II) containing a dinitrogen bridging two seven-coordinate Mo atoms.

Attempts to confirm the presence of bridging N_2 by Raman spectra failed as compounds decomposed when irradiated.

Seven-coordinate Mo(II) or W(II) complexes containing coordinated dinitrogen are not very common. Miniscloux[5] and co-workers have reported the covalent complex $MoH_2(N_2)dp_2$, and Chatt[4] described a W(II) dinitrogen cationic complex of formula $[WH(N_2)_2dp_2]HCl_2 \cdot THF]$ which presents only one i.r. active band for N_2 stretching at 1995 cm^{-1} [1955 cm^{-1} in the parent *trans*-$W(N_2)_2dp_2$].

It seems justified to relate the shift to higher frequencies of the $\nu(N_2)$ band to the variation of both the oxidation state and coordination number of the metal, resulting in a less effective back π-bonding from the filled *d* orbitals of the metal to the antibonding π-orbital of N_2. This picture could as well explain the lability of coordinated dinitrogen in these complexes.

References

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6 This reaction has been carried out also in a suitable cell connected to a C. Erba Mod. C Fractovap gas chromatograph in order to determine the nature of the gas evolved and its amount. Stoichiometry of the reaction is given on these bases.