Molybdenum(VI) and Molybdenum(V) Nitrido-complexes and a μ-Nitrido-molybdenumrhenium Complex

By JOSEPH CHATT and JONATHAN R. DILWORTH*
(*A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton* BN1 9QJ)

Summary Trimethylsilyl azide is a convenient reagent for the preparation of molybdenum(VI) and molybdenum(V) nitrido-complexes, most of which are air-stable crystalline solids; the 7-co-ordinate complexes, $[MoN(S_2CNR_2)_3]$ (R = alkyl), are obtained from $[MoCl_4(thf)_2]$, the silyl azide, and $Me_3SiS_2CNR_2$, or from $[MoCl(S_2CNR_2)_3]$ and azides.

LIMITED series of nitrido-complexes of rhenium(V),[1] osmium(VI),[2] and ruthenium(VI)[3] are known but very few nitrido-complexes of other metals. We are interested in molybdenum nitrido-complexes as models for intermediates in the degradation of dinitrogen in nitrogenase and here report methods for their preparation.

Apart from the complex formulated as $K_3[MoNO_3]$,[4] there are a few ill characterised molybdenum nitrido-complexes. These were obtained by the reaction of (explosive) chlorine azide[5] or of tetraethylammonium azide[6] with molybdenum pentachloride. We have found neither route satisfactory; indeed the tetra-alkylammonium azide route gave only molybdenum oxo-complexes.[7] We now report an easy general method and list some typical products in the Table. All are air-stable crystalline solids except (III) which hydrolyses in air.

The addition of trimethylsilyl azide (tmsa) to a suspension of $[MoCl_4(MeCN)_2]$ or $[MoCl_4(thf)_2]$ (thf = tetrahydrofuran) in suitable dry solvents (see Table) produces clear orange-red solutions with evolution of dinitrogen. From these solutions molybdenum(VI) nitrido-complexes, *e.g.*, (I), (II), and (III) are obtained by the addition of the appropriate ligands. Sodium azide can be used in place of tmsa, but only in methyl cyanide as solvent.

Addition of triphenylphosphine to the solution from $[MoCl_4(thf)_2]$ and tmsa in dichloromethane (solution A) causes reduction to yield the paramagnetic nitrido-complex (IV) μ_{eff} = 1·52 B.M.), which is also obtained from $[MoCl_3(thf)_3]$, tmsa and triphenylphosphine. The e.s.r. spectrum of (IV) at 20° confirms its formulation, showing a 1:2:1 triplet due to splitting by two phosphorus nuclei (hyperfine constant 24·5 G) and weak satellites due to molybdenum isotopes with spin $I = 5/2$ (hyperfine constant 49 G).

The 7-co-ordinate complex $[MoN(S_2CNEt_2)_3]$ (VII) is

Molybdenum(VI) and molybdenum(V) nitrido-complexes

	Complex	Colour	M.p. (t/°C)[a]	ν (Mo≡N)[b] cm^{-1}	Reaction solvent
(I)	$[MoCl_3N(bipy)]$	Brown	> 300	1009	MeCN
(II)	$[MoCl_3N(OPPh_3)_2]$	Yellow	255—257[d]	1038	Benzene
(III)	$[Et_4N]\ [MoCl_5N]$[c]	Ochre	296—298[d]	1032	CH_2Cl_2
(IV)	$[MoCl_2N(PPh_3)_2]$	Yellow	237—240[d]	1049	CH_2Cl_2
(V)	$[MoCl_2N(bipy)]$	Pink	> 300	948	thf
(VI)	$[MoN(S_2CNMe_2)_3]$	Yellow	240—242[d]	1019	CH_2Cl_2
(VII)	$[MoN(S_2CNEt_2)_3]$	Yellow	225—227[d]	1015	MeCN

[a] Measured in sealed evacuated tubes. [b] Measured as Nujol mulls. [c] See ref. 5. [d] Decomp.

prepared by the addition of 3 mol. of trimethylsilyl *NN*-diethyldithiocarbamate[8] to solution (A), but more conveniently by the reaction of $[MoCl(S_2CNR_2)_3]$[9] (R_2 = Me_2, Et_2, or $[CH_2]_5$) with tmsa or sodium azide in methyl cyanide.

The reaction of $[ReNCl_2(PMe_2Ph)_3]$ with $[MoCl_4(MeCN)_2]$ in dichloromethane yields the bridged nitride $[(PMe_2Ph)_3Cl_2ReNMoCl_4(MeCN)]$, a purple-red air-stable paramagnetic solid (μ_{eff} = 2·33 B.M.). It is more stable than the Re–N–Pt bridged species previously reported[10] but the addition of methanol regenerates from it the parent rhenium nitrido-complex.

Preliminary experiments show that tmsa can be used analogously to prepare tungsten nitrido-complexes but $[VCl_3(MeCN)_3]$ yields an azido-complex.

We thank Drs. R. C. Bray and D. A. Lowe for recording the e.s.r. spectra.

(*Received*, 19*th March* 1974; *Com.* 315.)

[1] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.
[2] W. P. Griffith and D. Pawson, *J.C.S. Chem. Comm.*, 1973, 418.
[3] W. P. Griffith and D. Pawson, *J.C.S. Dalton*, 1973, 1315.
[4] A. Rosenheim and F. Jacobsohn, *Z. Anorg. Chem.*, 1906, **50**, 297.
[5] W. Kolitsch and K. Dehnicke, *Z. Naturforsch.*, 1970, **25b**, 1080.
[6] R. D. Bereman, *Inorg. Chem.*, 1972, **11**, 1149.
[7] J. Chatt, G. J. Leigh, and F. B. Normanton, unpublished observations.
[8] H. Breederveld, *Rec. trav. Chim.*, 1962, **81**, 276.
[9] M. W. Bishop, J. Chatt, and J. R. Dilworth, to be published.
[10] J. Chatt and B. T. Heaton, *Chem. Comm.*, 1968, 274.