Molybdenum(IV) Complexes with Terminal Imido- and Nitrido-Ligands The Crystal and Molecular Structures of $[MoN(N_3)(Ph_2P(CH_2)_2PPh_2)_2]$ and $[MoBr(NH)(Ph_2P(CH_2)_2PPh_2)_2]Br\cdot MeOH$

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The structures of $[MoN(N_3)(Ph_2P(CH_2)_2PPh_2)_2]$ *(I) and* $[MoBr(NH)(Ph_2P(CH_2)_2PPh_2]Br\cdot MeOH$ *(II) have been determined. Crystal data (I): Space Group P1.* a = *11.540(2),* b = *13.102(2),* c = *9.612(2)* Å, α = *99.58(1),* β = *108.88(1),* γ = *110.46(1)°,* V = *1211.50* Å^3, *Z = 1; 2731 reflections to give R = 0.061. Crystal data (II): Space Group* $P2_1/n$; a = *18.111(2)* Å, b = *16.548(3)* Å, c = *18.064(2)* Å, α = *90.0°,* β = *105.30(1)°,* γ = *90.0°;* V = *5395.15* Å^3; *Z = 4; 1837 reflections to give R = 0.054. In I the geometry is pseudooctahedral and the Mo–nitride distance is unusually long at 1.79(2)* Å. *The* trans *azido-group' is nearly linear* ($\angle Mo-N_1-N_2$ = *167.1(11)°) suggesting strong* π*-interaction of the* N_3^- *ion with the metal. In II the overall geometry is again pseudo-octahedral with a metal–imido nitrogen distance of 1.73(2)* Å *lying in the normal range for imido complexes. The* trans *Mo–Br distance (2.612(4)* Å*) suggests that the imido-ligand exerts no* trans *influence.*

Introduction

Metal nitrido- (M≡N) and imido- (M = NH) complexes continue to attract attention as possible intermediates in the reduction of co-ordinated dinitrogen to ammonia. The structures of a number of molybdenum nitrido-complexes have been determined, but these have invariably been for oxidation states five and six [1]. We here report the structure of the Mo(IV) nitrido-complex $[MoN(N_3)(dppe)_2]$ (I) (dppe = $Ph_2PCH_2CH_2PPh_2$) with an azido-anion *trans* to the nitride ligand. Complexes containing terminal imido (NH) ligands are rare and only one other structure has been reported for the complex $[MoO(NH)Cl_2(OPPh_2Et)_2]$ [2]. Furthermore, recent work in these laboratories [3] has demonstrated the formation of an imido-complex from coordinated dinitrogen by the sequence shown in equation (1):

$$[Mo(N_2)_2(dppe)_2] + 2RX \rightarrow$$

$$[Mo(NNR_2)X(dppe)_2]Br \xrightarrow[H^+]{2e\ reduction}$$

$$R_2 = (CH_2)_5 [Mo(NH)Br(dppe)_2]Br + R_2NH \qquad (1)$$

In this paper we also report the X-ray structure of $[Mo(NH)Br(dppe)_2]Br$ (II) to confirm the presence of a terminally ligated NH ligand. The preparation of complexes (I) and (II) by reaction of $[Mo(N_2)_2(dppe)_2]$ with trimethylsilyl azide has been reported previously [3].

Experimental

Collection, Reduction and Refinement of the X-ray Diffraction Data

The pertinent details of the X-ray structural studies of $[MoN(N_3)(dppe)_2]$ and $[MoBr(NH)(dppe)_2]Br\cdot MeOH$ are summarised in Tables I and II, respectively, and further details are provided below.

$[MoN(N_3)(dppe)_2]$

Since the complex crystallises in the triclinic space group P1, the Mo atom was placed at the cell origin 0, 0, 0. Introduction of a heavy atom at the origin of the cell in the acentric space group P1 creates a false centre of symmetry at the origin, a problem enhanced

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TABLE I. Summary of Crystal Data and Experimental Details for the Structural Study of $[MoN(N_3)(Ph_2PCH_2CH_2PPh_2)_2]$.

(A) Crystal Parameters[a] at 23 °C

a = 11.540(2) Å
b = 13.102(2) Å
c = 9.612(2)
α = 99.58(1)°
β = 109.88(1)°
γ = 110.46(1)°

V = 1211.50 Å^3
Space Group: P1
Z = 1
D_{calc} = 1.30 g cm^{-3}
D_{obs} = 1.29(2) g cm^{-3}
(flotation)

(B) Measurement of Intensity Data

Crystal dimensions:	0.20 × 0.18 × 0.22 mm
Instrument:	Nonius CAD4 automated diffractometer
Radiation:	MoK_α (λ = 0.71073 Å), graphite monochromator
Scan mode:	ω
Scan rate:	Variable, within the limits of 2° to 20°/min
Scan range:	$0 < 2\theta < 45.0°$
Scan length:	1.2°
Background measurement:	10 s at either end of the 2θ scan range
Standards:	3 every 200 reflections
No. of reflections collected:	3614

(C) Reduction of Intensity Data and Summary of Structure and Refinement[b]

Data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion

No. of reflections used:	2731 with $I \geqslant 3\sigma(I)$
Absorption coefficient:	4.38 cm^{-1}
Absorption correction:	None (Tmax/Tmin = 1.04, based on ψ scans for 5 medium intensity reflections)
Structure solution:	Mo atom located from sharpened Patterson map. All non-hydrogen atoms located on subsequent difference Fourier maps.
Atomic scattering factors:	Mo, P, N and C from ref. c. H from ref. g.
Anomalous dispersion[d]:	Mo and P atomic scattering factors corrected for both real and imaginary components of anomalous scattering
Final discrepancy factors[e]:	R = 0.061
	Rw = 0.082
Goodness of Fit[f]:	2.03

[a] From a least squares fitting of the setting angles of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using versions of the Nicolet SHELXTL interactive crystallographic software package as described in G. M. Sheldrick, 'Nicolet SHELXTL Operations Manual'; Nicolet XRD Corp. Cupertino, CA 1979. D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A, 24,* 321 (1968). [u] 'International Tables for X-ray Crystallography', Vol. III, Kynoch Press, 1962. [e] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o\|$, $Rw = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2\}^{1/2}$; $w = 1/\sigma_F^2$. [f] $GOF = \{\Sigma w(|F_o - F_c|)^2/(NO - NV)\}^{1/2}$ where NO is the number of observations and NV is the number of variables. [g] R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).

by the near centrosymmetric displacement of the diphosphine ligands in the equatorial plane.

Symmetry problems such as these are usually resolved by insertion of one atom at a time into the model, that atom being the one with the greatest value of electron density on the Fourier map. Application of this method converged at a value of R_1 = 0.089 but did not resolve the position of the nitrido-nitrogen, N4.

The initial model contained only the molybdenum atom, four phosphorus atoms, and N_3 from the azide group. Atom N3 was included because it contributed most to the acentricity of the structure. Carbon atoms were inserted in groups of two to five until all 52 had been located. At this stage, a final $F_{(obs)}$ map revealed the positions of the nitrido nitrogen and N1 and N2 of the azide group. Although tedious, this was

TABLE II. Summary of Crystal Data and Experimental Details for the Structural Study of $[MoBr(NH)(Ph_2PCH_2CH_2PPh_2)_2]Br \cdot MeOH$.

(A) Crystal Parameters[a] at 23 °C

a = 18.111(2) Å
b = 16.548(3) Å
c = 18.064(2) Å
α = 90.0°
β = 105.30(1)°
γ = 90.0°

V = 5395.15 Å^3
Space Group: $P2_1/n$
Z = 4
D_{calc} = 1.35 g cm^{-3}
D_{obs} = 1.38(1) g cm^{-3}

(B) Measurement of Intensity Data

Crystal dimensions:	0.18 × 0.29 × 0.16 mm
Instrument:	Nicolet R3/m automated diffractometer
Radiation:	MoK_α (λ = 0.71073 Å), graphite monochromator
Scan mode:	Coupled θ(crystal) – 2θ(counter)
Scan rate:	Variable, within limits of 1.0 to 30.0°/min
Scan range:	$0 < 2\theta \leqslant 45°$
Scan length:	1.2° in θ
Background measurement:	10 s at each end of the 2θ scan
Standards:	3 reflections every 100 data
No. of data collected:	4493

(C) Reduction of Intensity Data and Summary of Structure Solution and Refinement[b]

Data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion.

No. of reflections used:	1837 with $F_{obs} \geqslant 6\sigma(F_{obs})$
Absorption coefficient:	14.52 cm^{-1}
Absorption correction:	None (Tmax/Tmin = 1.12, based on ψ scans for 5 axial reflections)
Structure Solution:	Mo and Br atoms located from sharpened Patterson map. All other non-hydrogen atoms located on subsequent difference Fourier maps.
Atomic scattering factors:	Mo, Br, P, O, N and C from reference c. H atomic scattering factors from reference g.
Anomalous dispersion[d]:	Mo, Br and P atomic scattering factors corrected for both real and imaginary components of anomalous scattering.
Final discrepancy factors[e]:	R = 0.054 Rw = 0.069
Goodness of Fit[f]:	1.21

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[a] From a least squares fitting of the setting angles of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32 K of 16-bit words using versions of the Nicolet software package described in G. M.Sheldrick, 'Nicolet SHELXTL Operations Manual', Nicolet XRD Corp.Cupertino, CA, 1979. [c] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A, 24*, 321 (1968). [d] 'International Tables for X-ray Crystallography', Vol. III, Kynoch Press, 1962. [e] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $Rw = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2\}^{1/2}$; $w = 1/\sigma_F^2$. [f] $GOF = \{\Sigma w(|F_1| - |F_c|)^2/(NO - NV)\}^{1/2}$ where NO is the number of observations and NV is the number of variables. [g] R. F. Stewart, E. R. Davidson and W. T. Simpson, *J Chem. Phys., 42*, 3175 (1965).

the only method to reveal the position of the nitrido nitrogen.

Refinement of the positional parameters and isotropic temperature factors for all non-hydrogen atoms converged to a value R_1 = 0.112. Introduction of hydrogen atoms at calculated positions and anisotropic temperature factors for all non-hydrogen atoms converted to value R_1 = 0.061 (Table I). Hydrogen atom positions and isotropic temperature factors were introduced as fixed contributors to the refinement. An analysis of variance indicated that the weighting scheme was adequate. The final difference Fourier map showed no excursions of electron density greater than 1 e Å^3, and these were found within 1 Å of the Mo.

TABLE III. Final Positional Parameters for [MoN(N_3)($Ph_2PCH_2CH_2PPh_2$)$_2$].

Atom	*x*	*y*	*z*
Mo	1.0000(0)	1.0000(0)	1.0000(0)
P1	1.0444(4)	0.8990(5)	1.1978(6)
P2	0.8097(4)	0.8344(4)	0.7625(6)
P3	1.1896(5)	1.1643(4)	1.2332(5)
P4	0.9594(4)	1.1033(5)	0.8055(6)
N1	1.124(1)	0.957(1)	0.892(1)
N2	1.183(1)	0.943(1)	0.810(1)
N3	1.239(2)	0.931(1)	0.732(2)
N4	0.889(2)	1.024(2)	1.081(3)
C1	1.183(2)	0.849(2)	1.226(3)
C2	1,193(2)	0.792(2)	1.097(2)
C3	1.286(3)	0.750(2)	1.109(4)
C4	1.371(3)	0.768(3)	1.262(3)
C5	1.364(3)	0.819(2)	1.400(3)
C6	1.268(2)	0.859(2)	1.373(2)
C7	0.904(2)	0.775(2)	1.190(3)
C8	0.775(2)	0.781(2)	1.162(3)
C9	0.664(3)	0.690(3)	1.152(3)
C10	0.667(3)	0.581(3)	1.155(3)
C11	0.787(3)	0.580(2)	1.177(3)
C12	0.904(2)	0.671(2)	1.204(3)
C13	0.851(2)	0.713(2)	0.724(2)
C14	0.919(2)	0.695(2)	0.633(3)
C15	0.963(3)	0.620(3)	0.588(2)
C16	0.947(3)	0.556(3)	0.681(2)
C17	0.876(4)	0.547(3)	0.783(4)
C18	0.826(2)	0.634(2)	0.784(2)
C19	0.631(2)	0.770(2)	0.739(3)
C20	0.546(2)	0.664(2)	0.638(3)
C21	0.411(2)	0.613(2)	0.616(3)
C22	0.364(2)	0.674(3)	0.679(4)
C23	0.446(2)	0.783(2)	0.785(3)
C24	0.584(2)	0.832(2)	0.815(2)
C25	1.151(2)	1.282(2)	1.282(3)
C26	1.173(3)	1.367(2)	1.182(3)
C27	1.133(2)	1.446(3)	1.215(4)
C28	1.064(2)	1.457(3)	1.299(4)
C29	1.036(2)	1.370(2)	1.377(3)
C30	1.071(3)	1.278(2)	1.376(3)
C31	1.362(2)	1.230(2)	1.254(2)
C32	1.466(3)	1.348(2)	1.354(3)
C33	1.595(3)	1.379(3)	1.368(2)
C34	1.636(2)	1.324(3)	1.300(2)
C35	1.553(3)	1.208(3)	1.196(2)
C36	1.396(2)	1.161(2)	1.169(3)
C37	1.010(2)	1.224(2)	0.805(2)
C38	1.212(2)	1.223(2)	0.834(3)
C39	1.332(2)	1.312(2)	0.851(4)
C40	1.325(2)	1.409(2)	0.837(3)
C41	1.204(3)	1.416(3)	0.803(5)
C42	1.086(3)	1.327(2)	0.805(3)
C43	0.826(2)	1.142(2)	0.769(2)
C44	0.742(3)	1.141(3)	0.635(3)
C45	0.630(3)	1.172(3)	0.619(3)
C46	0.614(3)	1.218(3)	0.732(3)
C47	0.697(3)	1.221(3)	0.877(3)
C48	0.811(3)	1.195(2)	0.909(3)
C49	1.095(2)	1.008(2)	1.384(3)
C50	1.215(4)	1.111(3)	1.415(3)
C51	0.906(3)	0.998(2)	0.616(2)
C52	0.781(3)	0.877(3)	0.585(2)

TABLE IV. Final Atomic Positional Parameters for [MoBr(NH)($Ph_2PCH_2CH_2PPh_2$)$_2$]Br·MeOH.

Atom	*x*	*y*	*z*
Mo	0.9734(1)	0.799(1)	0.2208(1)
Br1	1.0054(2)	0.9409(2)	0.1752(2)
Br2	0.5429(3)	0.8670(2)	0.2386(2)
P1	0.8551(5)	0.8625(4)	0.2485(5)
P2	0.8734(6)	0.7674(4)	0.1021(4)
P3	1.0895(6)	0.7608(4)	0.1815(4)
P4	1.0777(7)	0.8273(5)	0.3389(5)
N1	0.9524(15)	0.7059(13)	0.2529(11)
C1	0.846(1)	0.9712(9)	0.264(1)
C2	0.838(1)	1.024(1)	0.204(1)
C3	0.830(1)	1.1064(9)	0.214(1)
C4	0.830(1)	1.1368(9)	0.283(1)
C5	0.838(1)	1.084(1)	0.343(1)
C6	0.846(1)	1.002(1)	0.224(1)
C7	0.820(1)	0.819(1)	0.3218(8)
C8	0.868(1)	0.769(1)	0.3751(9)
C9	0.842(1)	0.739(1)	0.4339(9)
C10	0.768(1)	0.757(1)	0.439(1)
C11	0.720(1)	0.806(1)	0.386(1)
C12	0.746(1)	0.837(1)	0.3273(9)
C13	0.768(2)	0.845(1)	0.166(2)
C14	0.775(2)	0.766(1)	0.127(2)
C15	0.853(2)	0.837(1)	0.024(1)
C16	0.779(1)	0.855(1)	−0.0169(9)
C17	0.767(2)	0.904(1)	−0.0796(9)
C18	0.829(2)	0.936(1)	−0.101(1)
C19	0.903(1)	0.918(1)	−0.0602(9)
C20	0.916(2)	0.868(1)	0.002(1)
C21	0.884(1)	0.671(1)	0.062(1)
C22	0.888(1)	0.664(1)	−0.011(1)
C23	0.891(2)	0.588(1)	−0.041(1)
C24	0.890(1)	0.5186(9)	0.001(1)
C25	0.885(2)	0.526(1)	0.074(1)
C26	0.882(1)	0.602(1)	0.105(1)
C27	1.095(1)	0.782(1)	0.0862(8)
C28	1.118(1)	0.856(1)	0.064(1)
C29	1.109(1)	0.871(1)	−0.111(8)
C30	1.078(1)	0.813(1)	−0.641(8)
C31	1.054(1)	0.739(1)	−0.420(8)
C32	1.063(1)	0.723(1)	0.0332(8)
C33	1.125(1)	0.657(1)	0.1943(9)
C34	1.198(2)	0.638(1)	0.188(1)
C35	1.225(1)	0.559(1)	0.197(1)
C36	1.180(1)	0.499(1)	0.2164(9)

(continued on facing page)

TABLE IV. *(continued)*

Atom	*x*	*y*	*z*
C37	1.107(1)	0.517(1)	0.223(1)
C38	1.079(1)	0.596(1)	0.212(1)
C39	1.165(2)	0.813(1)	0.239(2)
C40	1.171(2)	0.799(2)	0.320(2)
C41	1.078(2)	0.764(1)	0.416(1)
C42	1.070(2)	0.680(1)	0.407(1)
C43	1.071(2)	0.629(1)	0.463(9)
C44	1.061(2)	0.661(1)	0.529(1)
C45	1.059(2)	0.744(1)	0.539(1)
C46	1.068(2)	0.796(1)	0.482(1)
C47	1.099(1)	0.927(1)	0.380(1)
C48	1.167(2)	0.944(1)	0.433(1)
C49	1.176(1)	1.020(1)	0.468(1)
C50	1.118(2)	1.077(1)	0.450(1)
C51	1.050(2)	1.059(2)	0.396(1)
C52	1.040(1)	0.984(1)	0.361(1)
O	0.574(2)	0.048(1)	0.203(1)
C53	0.633(3)	0.043(2)	0.175(2)

Final atomic positional parameters for non-hydrogen atoms are presented in Table III. Anisotropic temperature factors for all non-hydrogen atoms, calculated hydrogen atom positions, and a listing of observed and calculated structure factors are available as supplementary materials. Table V lists relevant bond lengths and angles.

[MoBr(NH)(dppe)$_2$]Br·MeOH

Shiny purple crystals of the complex were observed to become opaque with time under exposure to the X-ray beam. Although encasing the crystals in a film of epoxy alleviated this problem, the intensity of the standard reflections decreased to 75% of the original values after exposure for two days, necessitating the use of a second crystal to complete the data set. A crystal of dimensions 0.20 × 0.19 × 0.20 mm was chosen, and 20 reflections of varying intensities used to normalise the data sets.

In the final cycles of refinement, hydrogen atoms were introduced as fixed contributors. The poor quality of the final difference Fourier map precluded location of the imido-hydrogen. The final map showed excursion of electron density (1.5 Å^3) near the Mo and Br atoms. Inspection of the function $\Sigma w\Delta^2$ for reflections ordered according to $|F_o|$ and (sin θ/λ) showed satisfactory consistency, indicating an adequate weighting scheme.

Final atomic positional parameters are listed in Table IV. Relevant bond lengths and angles are presented in Table VI. Final atomic thermal parameters, calculated hydrogen atom positions, and structure factor listings are available in supplementary tables.

TABLE V. Selected Bond Lengths (Å) and Angles (°) for [$MoN(N_3)(Ph_2PCH_2CH_2PPh_2)_2$].

Mo–P1	2.506(9)	P1–Mo–P2	101.3(3)
Mo–P2	2.521(6)	P1–Mo–P3	79.3(3)
Mo–P3	2.492(6)	P1–Mo–P4	179.0(3)
Mo–P4	2.497(9)	P1–Mo–N1	95.5(6)
Mo–N1	2.20(2)	P1–Mo–N4	83.3(6)
Mo–N4	1.79(2)	P2–Mo–P3	179.3(3)
N1–N2	1.23(3)	P2–Mo–P4	79.7(3)
N2–N3	1.16(3)	P2–Mo–N1	81.2(7)
P–C, ave.	1.84(4)	P2–Mo–N4	94.9(6)
C–C, ring ave.	1.41(5)	P3–Mo–P4	99.9(3)
		P3–Mo–N1	98.3(6)
		P3–Mo–N4	85.6(5)
		P4–Mo–N1	84.3(5)
		P4–Mo–N4	96.9(6)
		N1–Mo–N4	175.5(8)
		Mo–N1–N2	167.1(11)
		N1–N2–N3	179.0(12)

TABLE VI. Selected Bond Lengths (Å) and Angles (°) for [$MoBr(NH)(Ph_2PCH_2CH_2PPh_2)_2$]Br·MeOH.

Mo–P1	2.559(9)	P1–Mo–P2	79.5(3)
Mo–P2	2.519(9)	P1–Mo–P3	169.6(3)
Mo–P3	2.485(8)	P1–Mo–P4	102.7(4)
Mo–P4	2.539(10)	P1–Mo–Br1	88.1(2)
Mo–Br1	2.612(4)	P1–Mo–N1	91.3(9)
Mo–N1	1.73(2)	P2–Mo–P4	99.0(3)
P–C, ave.	1.83(2)	P2–Mo–P4	177.8(4)
C–C, ring, ave.	1.40(4)	P2–Mo–Br1	94.0(2)
		P2–Mo–N1	86.9(8)
		P3–Mo–P4	79.0(4)
		P3–Mo–Br1	81.7(3)
		P3–Mo–N1	98.9(10)
		P4–Mo–Br1	86.6(3)
		P4–Mo–N1	92.5(8)
		Br1–Mo–N1	178.8(9)

Results and Discussion

Description of Structures

Perspective views of the molecular geometries of [$MoN(N_3)(dppe)_2$] and [$MoBr(NH)(dppe)_2$]$^+$ are presented in Figs. 1 and 2.

[MoN(N$_3$)(dppe)$_2$]

The structure of [$MoN(N_3)(dppe)_2$] consists of discrete monomers, as shown in Fig. 1. The Mo is coordinated to the four phosphorus atoms of the two chelating diphosphine ligands, the nitrido nitrogen N4, and N1 of the linear azide group generating a distorted octahedral arrangement. The local symmetry at the Mo is approximately C_{4v}, with the

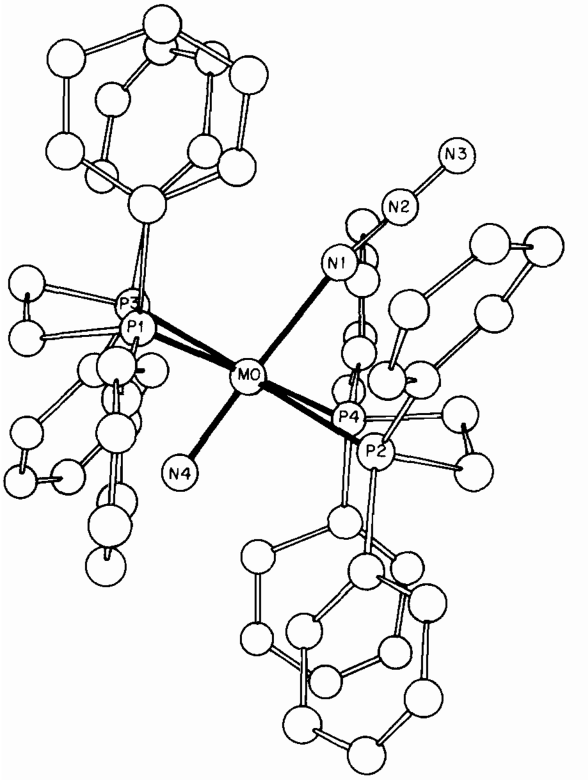

Fig. 1. Perspective view of the molecular geometry of [MoN(N$_3$)(dppe)$_2$].

P donors occupying the equatorial plane and the axial positions defined by the nitrido-N4 and the azido-N1. The molybdenum–phosphorus bond lengths are unexceptional at 2.498(9) Å (ave.). The methylene bridges of the two diphos ligands lie in an eclipsed configuration.

The Mo–N (nitrido) distance of 1.79(2) Å is considerably longer than that found in other octahedral nitrido-complexes which generally lie in the range 1.61–1.66 Å [1]. The only complex with a comparable metal–nitrido distance is [ReCl$_2$N(PEt$_2$Ph)$_3$] where the Re≡N bond length is 1.79 Å [5]. In this instance the exceptionally long metal–nitride bond was ascribed to steric compression induced by three bulky phosphine ligands. Although it is possible that steric effects may also force the nitride-ligand away from the metal in [MoN(N$_3$)(dppe)$_2$], there is little evidence of abnormally long metal nitrogen bond lengths in complexes such as [MoCl(N$_2$HC$_8$H$_{17}$)(dppe)$_2$] [6] or indeed in [MoBr(NH)(dppe)$_2$]Br discussed below. Furthermore the linearity of the N–Mo–N(3)–N(2)–N(1) system suggests strong electron delocalisation through an extended π-system.

This complex provides the first example to our knowledge of a completely linear terminally ligated azido-ligand [7]. This suggests that π-bonding of the azido-ligand to the molybdenum may occur at the expense of the nitride ligand bonding causing the abnormally long Mo–N(4) distance. The situation is complicated by the strong *trans* influence of both ligands, that of nitride being well documented as being large [1, 7]. The *trans*-influence has been postulated to be transmitted via π- or σ-bonding systems although recently evidence was presented that inductive σ-effects may well be dominant [8].

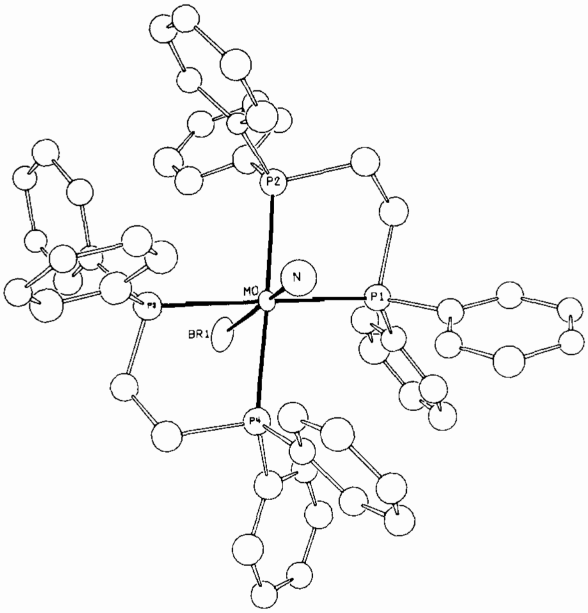

Fig. 2. Perspective representation of the molecular geometry of [MoBr(NH)(dppe)$_2$]$^+$.

[MoBr(NH)(dppe)$_2$]Br

The molybdenum atom is octahedrally co-ordinated enjoying approximately C_{4v} symmetry with the equatorial plane defined by the P atoms of the dppe ligands. The imido- and Br ligands occupy axial positions and the Mo–Br distance of 2.614(4) Å suggests that no significant *trans* influence is exerted by the NH ligand. The Mo–N distance of 1.73(2) Å lies well within the range of 1.70–1.73 Å found for other imido-complexes. Regrettably the data was not of sufficiently high quality to locate the imido-proton, but simple electron-counting arguments suggest the Mo–N–H system should be linear with the NH ligand formally functioning as a four-electron donor. The observed Mo imido-distance certainly supports this formalism.

Summary

Some metal–nitrogen bond lengths for derivatives with metal–nitrogen multiple bonds are collected in

TABLE VII. Metal–Nitrogen Bond Lengths and Relevant Structural Features.

Complex	Formal Metal Oxidation State	Mo–N, Å	Mo–N–X, degr. (X)	Mo–L (*trans*) (L)	Mo–L (*cis*) (L)	Ref.
1. Nitrido-complexes						
[MoN(S$_2$CNEt$_2$)$_3$]	VI	1.62	–	2.85(S)	2.53(S)	a
[{MoN(S$_2$CNEt$_2$)$_3$}$_2$Mo(S$_2$CNEt$_2$)$_3$] [PF$_6$]$_3$	VI	1.66	–	2.74(S)	2.49(S)	b
[MoN(N$_3$)(dppe)$_2$]	IV	1.79(2), nitrido-N	–	c	2.504(7) (P)	d
		2.20(2), azido-N	167.1(11), (N)			
2. Imido-complexes						
[Mo(NPh)$_2$(S$_2$CNEt$_2$)$_2$]	VI	1.754(4)	169.4(4), (C)	2.602(2), (S)	2.458(2), (S)	e
		1.789(4)	139.4(4), (C)	2.755(2), (S)		
[Mo(NPh)Cl$_2$(S$_2$CNEt$_2$)$_2$]CHCl$_3$	VI	1.734(4)	166.8(3), (C)	2.467(1), (Cl)	2.469(1), (Cl)	f
[Mo(NC$_6$H$_4$CH$_3$)(μ-S)(S$_2$P(OEt)$_2$)]$_4$	V	1.72(1)	170.8(11), (C)	2.704(4), (S)	2.366(4), (S)	g
[MoCl$_2$(NH)O(OPR$_3$)$_2$]	VI	1.70(1)	157(10), (H)	2.21(0)	2.22 (O)[h]	i
[WBr(NH)(dppe)$_2$]Br	IV	1.73(2)	Not observed	2.612(4), (Br)	2.523(9), (P)	l
3. Hydrazido- and Diazenido- Complexes						
[MoO(N$_2$Ph$_2$)L][j]	VI	1.778(3)	172.9(2), (N)	2.359(3), (N)	2.464(3), (N)[k]	m
[Mo(N$_2$C$_6$H$_4$OCH$_3$)$_2$L][j]	VI	1.82(1)	169.4(6), (N)	2.32(1), (N)	2.462(3), (N)	m
[MoO(N$_2$Me$_2$)(C$_9$H$_6$NO)$_2$]	VI	1.800	155.5, (N)	2.123, (O)	2.019(0)	m

[a] M. W.Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse and M. Motevalli, *J. Chem. Soc. Chem. Comm.*, 780 (1976). [b] M. B. Hursthouse and M. Motevalli, *J. Chem. Soc. Dalton Trans.*, 1362 (1979). [c] Imido- and azido-groups are mutually *trans*. [d] This work. [e] B. L. Haymore, E. A. Maata, R. A. D. Wentworth, *J. Am. Chem. Soc.*, *101*, 2063 (1979). [f] E. A. Maata, B. L. Haymore and R. A. D. Wentworth, *Inorg. Chem.*, *19*, 1055 (1980). [g] B. L. Haymore, E. A. Maata and R. A. D. Wentworth, *J. Am. Chem. Soc.*, *101*, 2063 (1979). [h] Oxygenation of OPR$_3$ group *trans* to *oxo*-group and thus experiencing strong *trans*-influence. [i] J. Chatt, R. Choukroun, J. R. Dilworth, J. Hyde, P. Vella and J. Zubieta, *Trans. Met. Chem.*, *4*, 59 (1979). [j] L = $^{-}$SCH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$N(CH$_3$)CH$_2$CH$_2$S^{-}. [k] Amine nitrogen atom is *trans* to oxo-group. [l] J. R. Dilworth, R. L. Henderson, J. Hutchinson and J. Zubieta, unpublished results. [m] P. L. Dahlstrom, J. R. Dilworth, P. Shulman and J. Zubieta, *Inorg. Chem.*, in press. [n] P. L. Dahlstrom, J. R. Dilworth and J. Zubieta, unpublished results.

Table VII together with indication of the *trans*-influence of the multiply bonded nitrogen ligand. Generally it appears that the range for Mo≡N is 1.62 to 1.66 Å whereas that for Mo≡NR (R = aryl, alkyl or H) is 1.70 to 1.75 Å. The metal-nitrogen bonds in hydrazido(2−)-complexes are generally somewhat longer, between 1.78 and 1.80 Å.

It is tempting to ascribe the long Mo–N of 1.79 Å in $[MoN(N_3)(dppe)_2]$ to the presence of a strongly π-bonded azide ligand *trans* to the nitride rather than steric effects. The π-bonding of the azide is revealed by the unusual near linear Mo–N–N–N– system and that the metal–azide bond is not particularly long despite its position *trans* to the nitride ligand with its high *trans* influence.

However in $[ReCl_2N(PEt_2Ph)_3]$ the Re≡N is long, and there is no strongly π-bonding ligand *trans* to nitride. Here the importance of steric compression is shown by the bending of the phosphine ligands away from the nitride nitrogen [5]. Clearly at this stage it is not possible to find any single factor responsible for these abnormally long metal–nitride bonds. The extension of the metal nitride bond does not appear to effect the reactivity of the nitride nitrogen as in both $[MoN(S_2CNEt_2)_3]$ and $[ReCl_2N(PMe_2Ph)_3]$ it has substantial nucleophilic character. The ^{15}N nmr chemical shifts for the nitride ligands are relatively close at 36.7 and 64.8 ppm (wrt to CH_3NO_2) respectively [9]. Although it is difficult to correlate such shifts, the similarity of the values suggests that extension of the metal nitride distance by about 0.2 Å (~12%) does not cause a gross electronic redistribution at the nitride nitrogen.

In the case of $[MoBr(NH)(dppe)_2]Br$ the bromide ion almost certainly exerts little *trans* influence and the Mo=NH bond length of 1.73 Å is very much in the range found for other imido-complexes. Also the molybdenum bromide distance itself indicates that the NH ligand shows no *trans* influence. This is in accord with previous observations that linear imido-ligands cause little lengthening of *trans* bonds. Thus although the imido hydrogen was not located in the structure determination there is little doubt that the complex contains the NH ligand functioning as a formally four electron donor.

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