Preparation of *mer*-$[\mathrm{Mo(N_2)_3(PPr^n{}_2Ph)_3}]$[*] from *trans*-$[\mathrm{Mo(N_2)_2(PPr^n{}_2Ph)_4}]$; its *X*-Ray Crystal Structure, Spectroscopic Properties, and Protonation to give Ammonia

Stewart N. Anderson, David L. Hughes, and Raymond L. Richards
A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ

The compound *trans*-$[\mathrm{Mo(N_2)_2(PPr^n{}_2Ph)_4}]$ (**1**), prepared by magnesium reduction of $[\mathrm{MoCl_3(thf)_3}]$ (thf = tetrahydrofuran) or $\mathrm{MoCl_5}$ in thf together with $\mathrm{PPr^n{}_2Ph}$ under $\mathrm{N_2}$, reacts with $\mathrm{N_2}$ in benzene or thf to give *mer*-$[\mathrm{Mo(N_2)_3(PPr^n{}_2Ph)_3}]$ (**2**) in high yield. The *mer* configuration is confirmed by an *X*-ray crystal structure determination which shows the compound to have *d*(Mo–N) = 2.050(9), 1.984(9), and 2.015(8), *d*(N–N) = 1.092(10), 1.124(9), and 1.103(9) Å. The longest N–N and shortest Mo–N distances are for the unique $\mathrm{N_2}$ ligand. Spectroscopic (i.r.; ^{31}P, ^{15}N, and ^{95}Mo n.m.r.) properties of the complexes are reported. Protonation of compounds (**1**) and (**2**) in methanol with $\mathrm{H_2SO_4}$ gave ammonia [0.3 and 1.3 mol $\mathrm{NH_3}$ per Mo atom for (**1**) and (**2**) respectively]. The occurrence of analogues of compound (**2**) with $\mathrm{PEt_2Ph}$ and $\mathrm{PBu_3}$ is discussed.

As part of our investigations of the reactions of dinitrogen at transition-metal sites,[1] we have recently examined the effect of increasing steric bulk of phosphine co-ligands on the type of dinitrogen complex which can be synthesised for molybdenum and tungsten.[2,3] We expected to obtain different types of dinitrogen co-ordination for bulky phosphine co-ligands as opposed to those observed for smaller phosphines and indeed we have obtained for tungsten the new types of compound $[\{\mathrm{W(N_2)_2(PR_2Ph)_3}\}_2(\mu\text{-}\mathrm{N_2})]$ and $[\mathrm{W(\eta^6\text{-}C_6H_5PR_2)(N_2)(PR_2Ph)_2}]$ (R = Et or Pr^n) which have been described elsewhere.[2]

It was clear from the preparation of the above dinuclear complexes of tungsten that the restricted access afforded to large phosphines at the metal opened up more sites for dinitrogen ligation and in the case of molybdenum the first tris(dinitrogen) complex *mer*-$[\mathrm{Mo(N_2)_3(PPr^n{}_2Ph)_3}]$ was obtained,[3] which is described in detail herein.

Results and Discussion

Preparation, Structure, and Spectroscopic Properties.—When $[\mathrm{MoCl_3(thf)_3}]$[4] (thf = tetrahydrofuran) is reduced with magnesium under dinitrogen in the presence of $\mathrm{PPr^n{}_2Ph}$, bright red *trans*-$[\mathrm{Mo(N_2)_2(PPr^n{}_2Ph)_4}]$ (**1**) can be isolated in good yield. It has the expected[1] single $\mathrm{N_2}$ i.r. band at 1 930 cm^{-1} (Table 1) and we sought to confirm its *trans* structure by determination of its ^{31}P-$\{^1$H$\}$ n.m.r. spectrum in benzene solution under dinitrogen. The observed spectrum did not, however, consist solely of the broad singlet normally observed for *trans*-tetraphosphine complexes,[5] but in addition, the resonance of the free phosphine at -167.3 p.p.m. was observed, together with a complex multiplet in the range -118 to -122 p.p.m. [relative to $\mathrm{P(OMe)_3}$].

Over a period of about 45 min, the intensity of the free phosphine resonance grew and the multiplet resolved into a doublet–triplet pattern, typical of a meridional arrangement of phosphine ligands, the intensity of this resonance pattern being close to three times that of the free phosphine resonance. Correspondingly, the colour of the solution changed from red to yellow-orange. Addition of methanol to this final solution gave yellow crystals which showed three N–N stretching bands in the i.r. spectrum and analysed as $[\mathrm{Mo(N_2)_3(PPr^n{}_2Ph)_3}]$ (Table 1). The reaction thus is as given in equation (1).

$$trans\text{-}[\mathrm{Mo(N_2)_2(PPr^n{}_2Ph)_4}] + \mathrm{N_2} \longrightarrow mer\text{-}[\mathrm{Mo(N_2)_3(PPr^n{}_2Ph)_3}]\ (\mathbf{2}) + \mathrm{PPr^n{}_2Ph} \quad (1)$$

Compound (**2**) was subsequently prepared from (**1**) in thf solution (Experimental section). The *mer* configuration of compound (**2**), assigned from the ^{31}P-$\{^1$H$\}$ n.m.r. spectrum, was confirmed by an *X*-ray structure determination as shown in Figure 1.

The complex molecule has octahedral co-ordination about the Mo atom and the three dinitrogen ligands are in the meridional arrangement (as are the three phosphine ligands). There are significant deviations from octahedral geometry at the Mo atom; the bulky phosphine groups push the dinitrogen ligands together so that not only are the N–Mo–N angles rather less than 90 and 180°, but also the *trans*-Mo–N(1) and –N(3) distances appear rather longer than Mo–N(2), the overlap of orbitals of Mo with N(1) and N(3) being reduced by the deviation from orthogonality. Correspondingly, the N(1)–N(11) and N(3)–N(31) distances appear to be shorter than N(2)–N(21). Competition for available molybdenum orbitals between the *trans*-dinitrogen ligands is also expected to cause them to have slightly longer (Mo–N) and shorter (N–N) bond distances compared with those of the unique dinitrogen.

As noted above, the ^{31}P-$\{^1$H$\}$ n.m.r. spectrum of compound (**2**) showed the expected doublet–triplet pattern (Table 1). The ^{15}N n.m.r. spectrum of the approximately 50% ^{15}N-enriched compound showed the following resonances (Figure 2 and Table 1): two doublets [-25 (intensity 1) and -40.3 (intensity 2) p.p.m., relative to $\mathrm{CD_3NO_2}$] assigned to N(21) and [N(11) plus N(31)] respectively, a double doublet at -44.4 p.p.m., assigned to N(2) [which is expected to have the largest coupling to *trans*-phosphorus[5]], and a resonance assigned to the N(1) and N(3) equivalent nuclei. The assignment of the metal-bound (N$_\alpha$) resonance to high field of the N$_\beta$ resonance follows from the generally observed pattern of these resonances in dinitrogen complexes[5] and the N–N coupling of 5—6 Hz is typical of terminal dinitrogen.

---

[*] *mer*-Tris(dinitrogen-*N*)tris(di-n-propylphenylphosphine)molybdenum.

Supplementary data available (No. SUP 56551, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Physical properties of dinitrogen complexes of molybdenum

Compound	Analyses[a]/%			I.r.[b]/cm⁻¹	N.m.r.[c]
	C	H	N		
trans-$[Mo(N_2)_2(PPr^n_2Ph)_4]$	62.2 (62.1)	8.2 (8.3)	6.1 (6.0)	1 930s	−118.1 (br s) (^{31}P)
mer-$[Mo(N_2)_3(PPr^n_2Ph)_3]$	56.7 (56.7)	7.7 (7.5)	11.0 (11.0)	2 080w, 1 985s, 1 965s	−118.3 (t), −120.3 (d); ^1J(PP) 15 (^{31}P) −25 [d ^1J(NN) 6, N(21)], −40.3 [d, ^1J(NN), 5, N(11) + N(31)], −44.4 [dd, ^2J(NP) 8, N(2)], −46.1 [br s, N(1) + N(3)] (^{15}N) −392 [q, J(MoP) 177.6, $W_{\frac{1}{2}}$ 10 Hz] (^{95}Mo)

[a] Calculated values in parentheses. [b] Nujol mulls. [c] δ Values in p.p.m., J values in Hz; ^{31}P relative to $P(OMe)_3$, ^{15}N to CD_3NO_2, ^{95}Mo to $[MoO_4]^{2-}$, saturated solution at pH 11 in water; all in thf solution. br = Broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quintet.

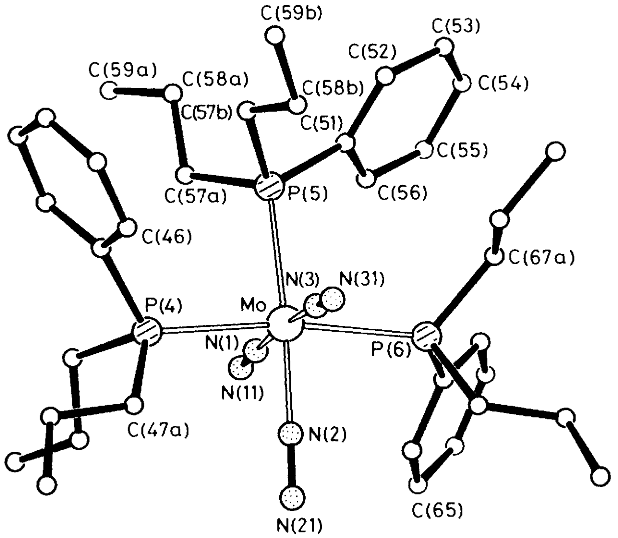

Figure 1. A view of the complex *mer*-$[Mo(N_2)_3(PPr^n_2Ph)_3]$. The labelling of the phosphine ligands of P(4) and P(6) corresponds to that for the P(5) ligands

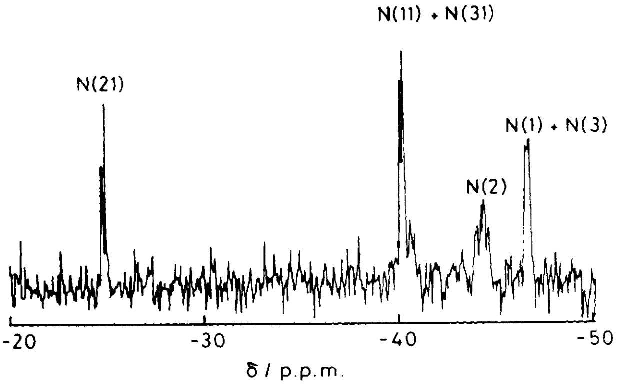

Figure 2. The ^{15}N n.m.r. spectrum of *mer*-$[Mo(^{15}N_2)_3(PPr^n_2Ph)_3]$

The ^{95}Mo spectrum of compound (**2**) shows a well resolved quartet [J(MoP) 177.6 Hz, $W_{\frac{1}{2}}$ 10 Hz], thus the phosphorus nuclei appear equivalent as far as the ^{95}Mo resonance is concerned, although they are inequivalent according to ^{31}P n.m.r. spectroscopy. Thus J(MoP) is essentially equal for the three phosphorus nuclei, giving a deceptively simple spectrum, as we have also observed in other mixed-phosphine dinitrogen complexes, such as *trans*-$[Mo(N_2)_2(PMe_2Ph)_2(Ph_2PCH_2CH_2PPh_2)]$, where the ^{95}Mo resonance is a simple quintet.[6] The ^{95}Mo chemical shift of (**2**), at −392 p.p.m. (relative to $[MoO_4]^{2-}$, Table 1) is the lowest resonance for any dinitrogen complex, which reflects the relatively low position occupied by dinitrogen in the ^{95}Mo spectrochemical series of ligands.[7]

Addition of PPr^n_2Ph to a solution of compound (**2**) in thf under argon showed no formation of (**1**) in the ^{31}P n.m.r. spectrum.

Occurrence of Analogues.—Previous investigation of dinitrogen complexes, with PEt_2Ph as co-ligand gave only *trans*-$[Mo(N_2)_2(PEt_2Ph)_4]$ (**3**).[8] When we repeated this work, however, we obtained in addition to (**3**) a red solid which had a high nitrogen content [typically 9.9% compared to 6.9% (calc.) for (**3**)] and strong i.r. absorbances at 1 920, 1 940, 1 958, and 1 970 cm⁻¹. These i.r. bands varied in relative intensity for different preparations, suggesting a mixture of complexes, and a ^{31}P-{^1H} n.m.r. spectrum of one of these samples showed two sets of triplets and two sets of doublets, indicating a mixture containing at least two complexes with the *mer*-$(PEt_2Ph)_3$ arrangement. These data indicate the presence of an analogue of (**2**) and possibly also one of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$,[2] but we were unable to isolate a pure compound. We also note that the compound reported[9] as *trans*-$[Mo(N_2)_2(PBu_3)_4]$ has an i.r. spectrum of the same pattern as (**2**) (bands at 2 080, 1 985, and 1 965 cm⁻¹). Impure solids which we obtained from attempts to prepare this compound also had a nitrogen content too high for *trans*-$[Mo(N_2)_2(PBu_3)_4]$ alone and the product probably contains *mer*-$[Mo(N_2)_3(PBu_3)_3]$.

Protonation Reactions.—When treated with H_2SO_4 in methanol, compounds (**1**) and (**2**) give ammonia (0.32 and 1.3 mol NH_3 per Mo atom respectively). The yield of ammonia from (**1**) is low relative to other bis(dinitrogen) complexes of molybdenum which generally give about 0.7 mol NH_3 per Mo atom (P = PMe_2Ph or $PMePh_2$),[10] whereas that from (**2**) is considerably higher than that from (**1**) and its analogues. During the course of reactions of this type, loss of phosphine occurs with the formation of intermediate hydrazido(2−)-complexes.[11] Since compound (**2**) contains the easily displaceable dinitrogen ligand rather than phosphine, the reaction pathway to ammonia might be facilitated for (**2**) and examination of the detail of this reaction will be reported in due course. Very little hydrazine was observed from reactions of (**1**) and (**2**).

Experimental

Air-sensitive materials were handled by standard Schlenk or vacuum techniques. N.m.r. spectra were measured with JEOL FX90Q or Bruker WM360 instruments, i.r. spectra with a

Table 2. Final atomic co-ordinates (fractional, × 10^4) of the non-hydrogen atoms of *mer*-$[Mo(N_2)_3(PPr^n{}_2Ph)_3]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	−119.1(5)	2 260.5(5)	7 369.3(4)	C(53)	−4 150(7)	3 060(6)	6 199(6)
N(1)	71(5)	3 446(5)	7 693(4)	C(54)	−4 150(8)	3 653(7)	6 756(6)
N(11)	185(6)	4 067(6)	7 899(5)	C(55)	−3 316(7)	3 962(6)	7 152(6)
N(2)	882(5)	1 970(5)	8 277(5)	C(56)	−2 479(7)	3 668(6)	6 971(5)
N(21)	1 453(7)	1 824(6)	8 796(6)	C(57a)	−928(6)	3 725(5)	5 825(5)
N(3)	−238(5)	1 074(5)	7 124(4)	C(58a)	−1 619(9)	4 126(8)	5 155(8)
N(31)	−268(6)	418(5)	7 016(5)	C(59a)	−1 289(10)	4 889(11)	4 901(10)
P(4)	1 155(2)	2 339(1)	6 598(1)	C(57b)	−1 627(6)	2 189(5)	5 297(5)
C(41)	898(6)	2 081(5)	5 541(5)	C(58b)	−1 897(7)	1 311(6)	5 350(5)
C(42)	847(6)	2 636(6)	4 948(5)	C(59b)	−2 199(8)	941(6)	4 540(6)
C(43)	576(7)	2 398(7)	4 152(6)	P(6)	−1 209(2)	2 067(1)	8 310(1)
C(44)	376(7)	1 611(7)	3 980(7)	C(61)	−1 206(6)	2 924(5)	8 986(5)
C(45)	451(7)	1 058(7)	4 541(6)	C(62)	−1 981(7)	3 391(6)	9 005(5)
C(46)	694(6)	1 272(6)	5 333(5)	C(63)	−1 922(8)	4 073(7)	9 482(6)
C(47a)	2 110(6)	1 631(6)	6 973(5)	C(64)	−1 075(8)	4 272(7)	9 945(6)
C(48a)	2 965(8)	1 606(7)	6 568(6)	C(65)	−301(8)	3 807(7)	9 924(6)
C(49a)	3 733(9)	1 090(10)	6 998(9)	C(66)	−371(7)	3 148(6)	9 449(5)
C(47b)	1 801(6)	3 283(5)	6 584(5)	C(67a)	−2 456(6)	1 827(5)	7 986(5)
C(48b)	2 396(7)	3 528(6)	7 379(6)	C(68a)	−2 622(7)	1 060(6)	7 523(6)
C(49b)	2 958(9)	4 271(8)	7 342(6)	C(69a)	−3 657(8)	854(7)	7 244(7)
P(5)	−1 314(2)	2 765(1)	6 223(1)	C(67b)	−850(6)	1 227(5)	9 021(5)
C(51)	−2 460(6)	3 092(5)	6 399(5)	C(68b)	−1 460(7)	1 078(6)	9 642(6)
C(52)	−3 305(7)	2 779(6)	6 011(6)	C(69b)	−1 112(8)	391(7)	10 192(6)

Table 3. Molecular dimensions, distances (Å) and angles ( ), with e.s.d.s in parentheses

(*a*) In the co-ordination sphere of Mo

Mo–N(1)	2.050(9)	N(1)–Mo–N(2)	88.7(3)	N(3)–Mo–P(4)	88.9(2)	N(1)–Mo–P(6)	90.9(2)
Mo–N(2)	1.984(9)	N(1)–Mo–N(3)	175.7(3)	N(1)–Mo–P(5)	86.1(2)	N(2)–Mo–P(6)	85.1(2)
Mo–N(3)	2.015(8)	N(2)–Mo–N(3)	87.1(3)	N(2)–Mo–P(5)	174.3(2)	N(3)–Mo–P(6)	88.3(2)
Mo–P(4)	2.483(2)	N(1)–Mo–P(4)	91.2(2)	N(3)–Mo–P(5)	98.2(2)	P(4)–Mo–P(6)	170.7(1)
Mo–P(5)	2.512(2)	N(2)–Mo–P(4)	85.8(2)	P(4)–Mo–P(5)	91.9(1)	P(5)–Mo–P(6)	97.3(1)
Mo–P(6)	2.497(2)						

(*b*) In the ligands

N(1)–N(11)	1.092(10)	C(47a)–C(48a)	1.537(13)	C(53)–C(54)	1.375(13)	C(61)–C(62)	1.373(12)
N(2)–N(21)	1.124(9)	C(48a)–C(49a)	1.487(15)	C(54)–C(55)	1.372(13)	C(61)–C(66)	1.370(12)
N(3)–N(31)	1.103(9)	C(47b)–C(48b)	1.530(12)	C(55)–C(56)	1.399(13)	C(62)–C(63)	1.393(13)
P(4)–C(41)	1.842(9)	C(48b)–C(49b)	1.487(13)	C(57a)–C(58a)	1.532(13)	C(63)–C(64)	1.374(13)
P(4)–C(47a)	1.839(9)	P(5)–C(51)	1.832(9)	C(58a)–C(59a)	1.450(17)	C(64)–C(65)	1.371(14)
P(4)–C(47b)	1.830(9)	P(5)–C(57a)	1.863(9)	C(57b)–C(58b)	1.517(12)	C(65)–C(66)	1.358(13)
C(41)–C(42)	1.368(12)	P(5)–C(57b)	1.845(8)	C(58b)–C(59b)	1.512(12)	C(67a)–C(68a)	1.498(12)
C(41)–C(46)	1.406(12)	C(51)–C(52)	1.383(12)	P(6)–C(61)	1.839(9)	C(68a)–C(69a)	1.526(13)
C(42)–C(43)	1.411(13)	C(51)–C(56)	1.379(12)	P(6)–C(67a)	1.834(9)	C(67b)–C(68b)	1.538(12)
C(43)–C(44)	1.358(14)	C(52)–C(53)	1.409(13)	P(6)–C(67b)	1.864(9)	C(68b)–C(69b)	1.508(13)
C(44)–C(45)	1.324(13)						
C(45)–C(46)	1.392(12)						

Mo–N(1)–N(11)	176.8(9)	C(44)–C(45)–C(46)	120.9(11)	C(52)–C(51)–C(56)	118.0(9)	C(61)–P(6)–C(67b)	101.2(4)
Mo–N(2)–N(21)	178.3(8)	C(41)–C(46)–C(45)	119.6(9)	C(51)–C(52)–C(53)	119.7(9)	C(67a)–P(6)–C(67b)	100.1(4)
Mo–N(3)–N(31)	176.8(7)	P(4)–C(47a)–C(48a)	118.6(7)	C(52)–C(53)–C(54)	121.0(10)	P(6)–C(61)–C(62)	123.3(7)
Mo–P(4)–C(41)	119.3(3)	C(47a)–C(48a)–C(49a)	112.6(10)	C(53)–C(54)–C(55)	119.9(11)	P(6)–C(61)–C(66)	118.4(7)
Mo–P(4)–C(47a)	111.6(3)	P(4)–C(47b)–C(48b)	114.7(6)	C(54)–C(55)–C(56)	118.8(10)	C(62)–C(61)–C(66)	118.1(9)
C(41)–P(4)–C(47a)	101.3(4)	C(47b)–C(48b)–C(49b)	113.7(8)	C(51)–C(56)–C(55)	122.6(9)	C(61)–C(62)–C(63)	121.0(10)
Mo–P(4)–C(47b)	119.3(3)	Mo–P(5)–C(51)	118.8(3)	P(5)–C(57a)–C(58a)	116.8(7)	C(62)–C(63)–C(64)	119.1(11)
C(41)–P(4)–C(47b)	101.1(4)	Mo–P(5)–C(57a)	111.4(3)	C(57a)–C(58a)–C(59a)	113.7(11)	C(63)–C(64)–C(65)	119.8(11)
C(47a)–P(4)–C(47b)	101.3(4)	C(51)–P(5)–C(57a)	98.9(4)	P(5)–C(57b)–C(58b)	118.0(6)	C(64)–C(65)–C(66)	120.2(11)
P(4)–C(41)–C(42)	123.8(7)	Mo–P(5)–C(57b)	121.9(3)	C(57b)–C(58b)–C(59b)	111.5(8)	C(61)–C(66)–C(65)	121.8(10)
P(4)–C(41)–C(46)	117.8(7)	C(51)–P(5)–C(57b)	102.5(4)	Mo–P(6)–C(61)	112.9(3)	P(6)–C(67a)–C(68a)	113.3(6)
C(42)–C(41)–C(46)	118.3(9)	C(57a)–P(5)–C(57b)	99.4(4)	Mo–P(6)–C(67a)	122.8(3)	C(67a)–C(68a)–C(69a)	114.0(8)
C(41)–C(42)–C(43)	120.4(10)	P(5)–C(51)–C(52)	124.0(7)	C(61)–P(6)–C(67a)	104.1(4)	P(6)–C(67b)–C(68b)	117.0(6)
C(42)–C(43)–C(44)	119.3(11)	P(5)–C(51)–C(56)	117.9(7)	Mo–P(6)–C(67b)	113.1(3)	C(67b)–C(68b)–C(69b)	113.1(9)
C(43)–C(44)–C(45)	121.5(12)						

Unicam SP2000 instrument, and mass spectra with an MS10 spectrometer. Analyses were by Mr. C. Macdonald of these Laboratories.

Preparation of trans-[Mo(N_2)$_2$(PPr$^n_2$Ph)$_4$] (**1**).—(*a*) The compound [MoCl$_3$(thf)$_3$] (1.25 g), PPr$^n_2$Ph (1.8 g), and magnesium turnings (2 g) were stirred together in thf under dinitrogen for 3 h. The red solution was then filtered and the solvent removed under vacuum. The residue was dissolved in benzene (30 cm^3) and methanol (100 cm^3) was added. The solution was reduced in volume to 50 cm^3 and cooled to −20 °C which produced a red crystalline *solid* which was filtered off, washed with methanol, and dried under vacuum (1.5 g, 55%).

(*b*) Molybdenum(v) chloride (3.55 g) was added slowly under an atmosphere of N_2 to a solution of PPr$^n_2$Ph (9.5 g) in thf (120 cm^3). The solution was stirred for 10 min then cooled to 10 °C in an ice–salt bath. Magnesium turnings (*ca.* 4 g) were added and the solution stirred at 10 °C for 3 h. The red solution formed was worked up as in (*a*), yield 2.2 g (25%).

Preparation of mer-[Mo(N_2)$_3$(PPr$^n_2$Ph)$_3$] (**2**).—Compound (**1**) (1 g) was stirred in thf (20 cm^3) under dinitrogen for 60 min during which time the colour of the solution changed from deep red to yellow-orange. Methanol (50 cm^3) was added and after cooling to −20 °C, yellow *crystals* were formed which were filtered off, washed with methanol, and dried under vacuum (0.75 g, 90%).

Protonation of Complexes (**1**) *and* (**2**).—The technique used in both cases was the same, as exemplified by the reaction of complex (**1**) with sulphuric acid in methanol. Methanol (20 cm^3) was distilled at −196 °C under vacuum onto (**1**) (55.8 mg) in a flask with an attached tipper containing sulphuric acid (1.0 cm^3). The solution was warmed to *ca.* 20 °C and the sulphuric acid carefully tipped into the methanol. After stirring for 16 h the solution was frozen at −196 °C and the non-condensible gas determined with a Toepler pump (1.25 mol N_2 per Mo atom). Solvent was removed under vacuum and the residue distilled from base (NaOH, 15 cm^3, 20% aqueous solution) under argon into 0.5 N sulphuric acid. The ammonia and hydrazine content of the solution were then determined colorimetrically[10] (0.32 mol NH_3 per Mo, 0.02 mol N_2H_4 per Mo). The corresponding yields for complex (**2**) were 1.32 mol NH_3 and 0.01 mol N_2H_4 together with 1.95 mol N_2 and 0.35 mol H_2 per Mo atom.

Crystal Structure Determination.—Crystal data. $C_{36}H_{57}MoN_6P_3$, $M = 762.75$, monoclinic, space group $P2_1/n$ (equivalent to $P2_1/c$, no. 14), $a = 14.531(4)$, $b = 16.594(5)$, $c = 17.270(5)$ Å, $\beta = 101.06(2)°$, $U = 4\,086.9$ Å^3, $Z = 4$, $D_c = 1.239$ g cm^{-3}, $F(000) = 1\,608$, μ(Mo-K_α) = 4.6 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å; crystal size *ca.* 0.07 × 0.30 × 0.43 mm.

Crystals are translucent, dull yellow, thin diamond-shaped plates. After preliminary photographic examination, accurate cell dimensions and diffraction intensities were measured on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation. There was considerable crystal deterioration (*ca.* 30%) over the period of measurement, and corrections for this, for Lorentz-polarisation effects, and by Bayesian methods[12] (to ensure no negative intensities) were made. For $\theta < 20°$, 3 802 unique reflections were measured; of these, 2 366 had $I > 2\sigma(I)$. No absorption corrections were applied.

The structure was derived readily from Patterson and electron-density maps, and the positions of all hydrogen atoms were calculated with idealised geometries (the end methyl groups in staggered conformations). Refinement by full-matrix least-squares methods[13] was smooth and rapid except for some of the methyl groups where large thermal parameters suggested some site disorder. The principal sites in every case are in the extended *trans* arrangement of the n-propyl groups. Attempted refinement of atoms in sites of minor occupancy was not satisfactory.

Refinement has thus converged with $R = 0.091$ and $R' = 0.083$ for all 3 802 reflections with weights $w = (\sigma_F^2 + 0.001\,49F^2)^{-1}$.

Scattering curves were from ref. 14. The Mo, P, N, and methyl C atoms were refined anisotropically, the remaining C atoms isotropically. The final co-ordinates of the non-hydrogen atoms are in Table 2, and molecular dimensions in Table 3.

In addition to the SHELX computer program[13] (used for the structure determination and refinement), other major programs used in this analysis included GEOM[15] (for molecular geometry calculations) and ORTEP[16] (for the diagram).

The principal intermolecular contacts, at normal van der Waals distances, were noted not to involve the phenyl groups, but to be between the methyl end groups, some across centres of symmetry, others between unrelated methyl groups.

References

1 R. L. Richards, in 'Nitrogen Fixation,' eds. A. Müller and W. E. Newton, Plenum, London, 1983; J. Chatt and R. L. Richards, *J. Organomet. Chem.*, 1982, **239**, 65.

2 S. N. Anderson, D. L. Hughes, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1982, 1291; *J. Chem. Soc., Dalton Trans.*, 1986, 245.

3 S. N. Anderson, D. L. Hughes, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1984, 958.

4 J. R. Dilworth and R. L. Richards, *Inorg. Synth.*, 1980, **20**, 119.

5 S. Donovan-Mtunzi, J. Mason, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1984, 469.

6 M. Hughes, J. Mason, and R. L. Richards, unpublished work; M. Hughes, D. Phil. Thesis, Open University, 1985.

7 S. Donovan-Mtunzi, M. Hughes, G. J. Leigh, J. Mason, H. Modh-Ali, and R. L. Richards, *J. Organomet. Chem.*, 1983, **246**, C1.

8 M. Aresta and A. Sacco, *Gazz. Chim. Ital.*, 1972, **102**, 755.

9 T. A. George and C. D. Seibold, *Inorg. Chem.*, 1973, **12**, 2544.

10 J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1977, 1852.

11 S. N. Anderson, J. Chatt, M. E. Fakley, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1981, 1973.

12 BAYES, Program to apply Bayesian statistics to diffraction intensity measurements, J. D. Owen, Rothamsted Experimental Station, Harpenden, Herts., 1983.

13 SHELX, Program for crystal structure determination, G. M. Sheldrick, University of Cambridge, 1976.

14 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

15 GEOM, Suite of crystallographic programs for the calculation of molecular geometry, J. D. Owen, Rothamsted Experimental Station, Harpenden, Herts., 1981.

16 ORTEP, Report ORNL-3794 (revision of 1971), C. K. Johnson, Oak Ridge National Laboratory, Tennessee.

Received 16th September 1985; *Paper* 5/1598