The μ-Dinitrogen-bis{[1,2-bis(dimethylphosphino)ethane]hydrido-[η-(1,3,5-trimethylbenzene)]molybdenum} Cation

By **Malcolm L. H. Green** and **William E. Silverthorn**, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

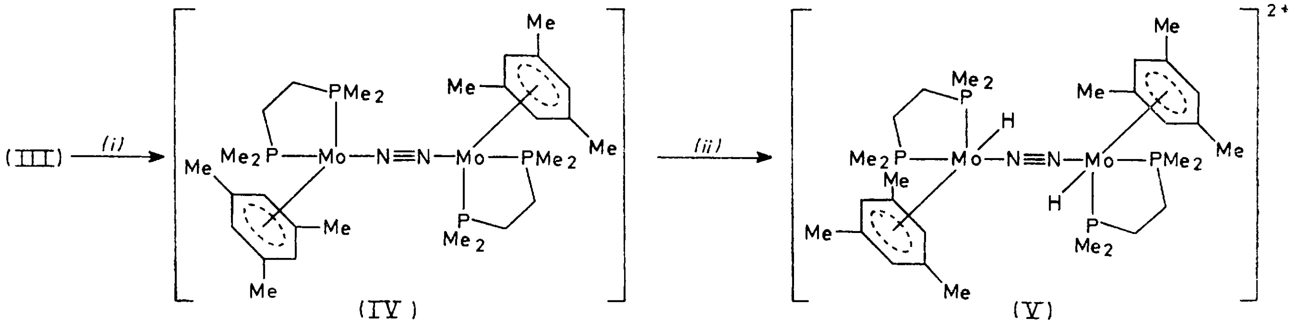
The complex $[(Me_3C_6H_3)(dmpe)Mo(\mu\text{-}N_2)Mo(dmpe)(Me_3C_6H_3)]$ [$Me_3C_6H_3$ = η-1,3,5-trimethylbenzene and dmpe = 1,2-bis(dimethylphosphino)ethane] has been protonated by tetrafluoroboric acid to give the cation $[(Me_3C_6H_3)(dmpe)HMo(\mu\text{-}N_2)MoH(dmpe)(Me_3C_6H_3)]^{2+}$. The complex $[(C_6H_6)Mo\{P(cy)_2Me\}_2(N_2)]$ (cy = cyclohexyl) is also described.

WE have shown that dinitrogen derivatives of the grouping [(η-arene)$Mo(PR_3)_2$] occur both with terminal or bridging dinitrogen as in $[(MeC_6H_5)Mo(PPh_3)_2(N_2)]$, (I), or $[(C_6H_6)(Ph_3P)_2Mo(\mu\text{-}N_2)Mo(PPh_3)_2(C_6H_6)]$, (II), respectively.[1] The complexes $[(C_6H_3R_3)Mo(PR'_3)_3]$ (R = H, R' = Et; R = R' = Me) protonated readily forming mono- and di-hydrido-cations $[(C_6H_3R_3)Mo(PR'_3)_3H_n]^{n+}$ (n = 1 or 2).[2] However, we were unable to prepare the analogous cations [(η-arene)$Mo(PR_3)_2(N_2)H]^+$. A possible reason for this is that the addition of a proton to the molybdenum in complexes (I) and (II) would cause an increase in positive charge on the metal atom. This in turn, would cause a decrease in back donation from the metal to the dinitrogen ligand, thus decreasing the metal–dinitrogen bond strength and increasing the ease of loss of dinitrogen. The present work describes attempts to overcome this problem by increasing the initial electron density on the metal atom by methyl substitution on the ligands.

Analytical and spectroscopic data

Complex	Colour	Analyses (%) [a] C	H	N	Selected i.r. data (cm^{-1}) $\bar{\nu}$(N≡N)	$\bar{\nu}$(Mo–H)
$[(C_6H_6)Mo\{P(cy)_2Me\}_2(N_2)]$	Orange	59·5 (61·2)	8·6 (9·0)	4·2 (4·5)	1 975vs [b]	
$[(Me_3C_6H_3)(dmpe)Mo(\mu\text{-}N_2)Mo(dmpe)(Me_3C_6H_3)]$	Purple	47·5 (47·6)	7·05 (7·4)	3·6 (3·7)	1 989ms [b] (1 973s [d]) [e]	
$[Me_3C_6H_3)(dmpe)HMo(\mu\text{-}N_2)MoH(dmpe)(Me_3C_6H_3)]\text{-}[BF_4]_2$ [f]	Red-brown	38·1 (38·5)	6·2 (6·2)	2·9 (3·0)	1 937vw [b]	1 815w [g]
$[(Me_3C_6H_3)(dmpe)HMo(\mu\text{-}N_2)MoH(dmpe)(Me_3C_6H_3)]\text{-}[PF_6]_2$	Red-brown	33·9 (34·0)	5·5 (5·5)	2·7 (2·65)	1 937vw [b]	1 793w [g]

[a] Calculated values are given in parentheses. [b] Nujol mull. [c] P, 16·3 (16·3); Mo, 25·6 (25·2) %. [d] In C_6D_6. [e] For the $^{15}N^{14}N$ derivative, 1 955ms; [b] for the $^{15}N^{15}N$ derivative, 1 923ms [b] and 1 920 cm^{-1} (KBr disc). [f] ^{1}H N.m.r. data: τ 4·69s (br), C_6H_3; 7—9c (broad), Me_3C_6 and dmpe; and 14·65,[g] d, [J(^{31}P–H) 81·6 Hz], Mo–H *cis* or *trans*. [g] Absent in the spectrum of the deuteriated analogue, Mo–^{2}H. [h] P, 17·6 (17·6); F, 21·8 (21·6); and Mo, 18·4 (18·1) %.



SCHEME (*i*) Na–Hg in thf, 1 atm N_2; (*ii*) HBF_4 in toluene–diethyl ether. The N–N distance in complex (IV) is 1·145 ± 0·007 Å

RESULTS AND DISCUSSION

Chemical Studies.—Treatment of the previously described[1] dimer $[(Me_3C_6H_3)(C_3H_5)Mo(\mu\text{-}Cl)_2Mo(C_3H_5)(Me_3C_6H_3)]$ with 1,2-bis(dimethylphosphino)ethane (dmpe), followed by addition of ammonium hexafluorophosphate to an aqueous extract of the reaction mixture, gave the salt $[(Me_3C_6H_3)Mo(C_3H_5)(dmpe)]PF_6$, (III) ($Me_3C_6H_3$ = η-1,3,5-trimethylbenzene and C_3H_5 = η-allyl). This is soluble in acetone, tetrahydrofuran (thf), and ethanol and solutions are kinetically stable to oxidation by dioxygen. Reduction using sodium amalgam of thf solutions of (III) under 1 atm dinitrogen gave deep purple crystals which the data in the Table and a crystal-structure determination show to be the complex $[(Me_3C_6H_3)(dmpe)Mo(\mu\text{-}N_2)Mo(dmpe)(Me_3C_6H_3)]$, (IV). This complex is readily oxidised in air and is soluble in toluene. A crystal-structure determination showed the molecule lies on a crystallographic centre of symmetry with the configuration given in the Scheme.[3] Nonetheless the i.r. spectrum of complex (IV) has a band near 1 980 cm^{-1}, in mulls and in benzene solutions, which must be assigned to a N≡N

---

[1] M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.

[2] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J.C.S. Dalton*, 1974, 1361.

[3] R. A. Forder, personal communication.

stretching frequency. This assignment was confirmed by the observation of three strong bands at 1 989s, 1 955vs, and 1 923s cm^{-1} in the mull spectrum of an isotopic mixture of complex (IV) containing $^{14}N\equiv{}^{14}N$, $^{14}N\equiv{}^{15}N$, and $^{15}N\equiv{}^{15}N$ systems (see the Table). Careful examination of a crystalline mass of a sample of complex (IV) suggested the presence of a small proportion of a different form. This may arise either from a different crystalline modification of complex (IV), or of an isomer of (IV) such as a non-centrosymmetric *cis*-isomer, or of a minor impurity such as $[(Me_3C_6H_3)Mo(dmpe)(N_2)]$. We do not have any evidence to distinguish between these possibilities. Attempts to measure the Raman spectrum of (IV) were unsuccessful.

Careful treatment of (IV) with tetrafluoroboric acid gives a salt which the data showed to be $[(Me_3C_6H_3)(dmpe)HMo(\mu\text{-}N_2)MoH(dmpe)(Me_3C_6H_3)][BF_4]_2$, (V). This salt gives moderately stable solutions in acetone and dimethyl sulphoxide. The formulation was suggested by the observation of a band in the i.r. spectrum at 1 815 cm^{-1} which may be assigned to a Mo–H stretching frequency. This band was absent in the i.r. spectrum of the dideuterio-analogue of (V). The ^1H n.m.r. spectrum of the salt showed a high-field doublet at τ 14·62 which may be assigned to a Mo–*H* coupling to only one ^{31}P nucleus. The proposed formulation for the salt was also supported by the observation that treatment of thf solutions of (V) with sodium amalgam reformed the parent complex (IV) in *ca.* 15% yield.

Several unsuccessful attempts were made with the salt (V) to achieve formation of further dinitrogen derivatives. For this purpose ^{15}N-enriched analogues of (V) were prepared using $^{15}N_2$. No $^{15}NH_3$ was detected following treatment of reaction products of (V) with dilute hydrochloric acid, or with dilute sulphuric acid in the presence of iron(II) sulphate. During these studies we became interested in trying to prepare a molybdenum dinitrogen derivative in which steric access to the molybdenum atom was restricted. The new ligand dicyclohexylmethylphosphine was prepared and used in turn to prepare the orange complex $[(Me_3C_6H_3)Mo\{P(cy)_2Me\}_2(N_2)]$. The evidence for the characterisation of this complex is given in the Table and the Experimental section.

EXPERIMENTAL

Preparations and reactions were carried out under an atmosphere of argon except where stated. Solvents were freshly distilled from calcium dihydride. I.r. spectra were measured on an Infracord 457 instrument and were calibrated using a polystyrene film. ^1H N.m.r. spectra were determined on a Japan Electron Optics laboratory instrument at 60 MHz; calibration was against external tetramethylsilane. The complex $[(Me_3C_6H_3)(C_3H_5)Mo(\mu\text{-}Cl)_2Mo(C_3H_5)(Me_3C_6H_3)]$ was prepared as described.[1]

(η-Allyl)[1,2-bis(dimethylphosphino)ethane][η-(1,3,5-trimethylbenzene)]molybdenum Hexafluorophosphate, (III).—The complex $[(Me_3C_6H_3)(C_3H_5)Mo(\mu\text{-}Cl)_2Mo(C_3H_5)(Me_3C_6H_3)]$ (1·5 g) in ethanol (50 cm^3) and 1,2-bis(dimethylphosphino)ethane (0·9 cm^3) were heated under reflux for 6 h. The solvent was then removed under reduced pressure, and the residue was extracted with water. The aqueous extract was treated with saturated ammonium hexafluorophosphate to give a yellow precipitate. This was recrystallised from dichloromethane–diethyl ether to give orange-red crystals. These were washed with diethyl ether and dried *in vacuo*, yield *ca.* 85%.

μ-Dinitrogen-bis{[1,2-bis(dimethylphosphino)ethane][η-(1,3,5-trimethylbenzene)]molybdenum}, (IV).—The salt (III) (3·0 g) in dry tetrahydrofuran (thf) (125 cm^3) under dinitrogen at 1 atm was treated with an excess of sodium amalgam (2%, 10 g) for 5 h. A further amount of the salt (2·0 g) was added and the mixture was stirred for another 4 h under an argon atmosphere. The resulting solution was decanted from the residual amalgam and solvent was removed under reduced pressure. The residue was washed with light petroleum (50 cm^3) and then extracted with warm benzene (150—200 cm^3; 50 °C). The extract was filtered and the filtrate was concentrated under reduced pressure (25 cm^3). The concentrate was cooled giving purple crystals (1·6 g) which were washed with light petroleum and dried under vacuum. The washings and mother liquors were combined and concentrated slowly (1 week) giving a further yield of purple crystals (0·4 g), total combined yield *ca.* 40%.

μ-Dinitrogen-bis{[1,2-bis(dimethylphosphino)ethane]-hydrido[η-(1,3,5-trimethylbenzene)]molybdenum} Bis(tetrafluoroborate), (V).—Complex (IV) (0·8 g) in dry toluene (400 cm^3) at −95 °C was treated with a solution of aqueous tetrafluoroboric acid (0·5 cm^3, 40%) in diethyl ether (50 cm^3) at −95 °C. The mixture was allowed to warm first to −10 °C and then, after 2 h, to room temperature for 2 h. The supernatant liquor was separated from the deep red-purple precipitate, which was then washed with dry diethyl ether (400 cm^3) and dried *in vacuo*, yield 0·83 g. The product was recrystallised from acetone at −10 °C (0·8 mg in 50 cm^3 concentrated to 5 cm^3), yield 0·8 g.

The hexafluorophosphate salt of the cation (V) was prepared as follows. The tetrafluoroborate salt (0·13 g) was slowly added to cold water (450 cm^3, 0 °C) with stirring giving a purple-red solution. The solution was filtered into a solution of ammonium hexafluorophosphate at 0 °C giving a red-brown solid. This was separated, washed with water (500 cm^3, 0 °C), and dried under vacuum at 40 °C, *ca.* 80%.

Di(cyclohexyl)methylphosphine.—Chlorodicyclohexylphosphine (5·0 g) in diethyl ether (25 cm^3) was added slowly (1 h) to methylmagnesium iodide in diethyl ether (22 cm^3 of 1·3M) at −15 °C.* The mixture was heated under reflux for 15 min then cooled to −15 °C and saturated aqueous ammonium chloride (50 cm^3) was added slowly. The ether layer was separated from the hydrolysed product and the remaining aqueous layer was extracted with diethyl ether (2 × 50 cm^3). The ether solutions were collected and concentrated giving an oil which was distilled at 112—114 °C (2 mmHg), yield 2·65 g. ^1H N.m.r. spectrum of the pure liquid: τ 7·71, t; 8·21, complex multiplet, (cy)$_2$ (22H); 8·69, rel. intensity 3, d [$J(^{31}P\text{–}Me)$ 4·5 Hz], Me.

(η-Benzene)bis(dicyclohexylmethylphosphine)dinitrogen-molybdenum.—The complex $[(C_6H_6)(C_3H_5)Mo(\mu\text{-}Cl)_2Mo(C_3H_5)(C_6H_6)]$ (1·0 g) in dry thf (75 cm^3) was heated with dicyclohexylmethylphosphine (1·3 cm^3) under reflux for 30 min until all the complex had dissolved. Excess of

---

* 1M = 1 mol dm^{-3}.

sodium amalgam (2%, 5·0 g) was then added and the mixture was stirred in the presence of excess of dinitrogen at atmospheric pressure for 40 h. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (100 cm^3). The resulting violet solution was separated and the residue was dissolved in dry thf (100 cm^3). After filtration the filtrate was treated with ethanol (100 cm^3) and solvent was removed from the mixture under reduced pressure until the total volume was 100 cm^3. Orange crystals which formed were collected, washed with ethanol, and dried *in vacuo*, yield 0·50 g (*ca.* 20%).

We thank the Petroleum Research Fund, administered by the American Chemical Society, for support.

[4/836 *Received, 25th April*, 1974]