Synthesis of *trans*-[Mo(N_2)$_2$(dippe)$_2$] [dippe = 1,2-bis(diisopropylphosphino)ethane] and Related Derivatives, Protonation of Co-ordinated Dinitrogen and Crystal Structures of *trans*-[MoF(NNH_2)(dippe)$_2$][BF_4] and *trans*-[$MoCl_2$(dippe)$_2$][BF_4]†

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Reduction of [$MoCl_3$(thf)$_3$] (thf = tetrahydrofuran) with sodium dispersion or sodium amalgam in the presence of dinitrogen and 1,2-bis(diisopropylphosphino)ethane (dippe) gave low, but reproducible, yields of the bis(dinitrogen) complex *trans*-[Mo(N_2)$_2$(dippe)$_2$] **1**. This reacted very slowly with H_2 to yield the known tetrahydride [MoH_4(dippe)$_2$] **2**, which is more conveniently prepared by reaction of [$MoCl_4$(MeCN)$_2$] with dippe and Na[BH_4]. Complex **1** reacted with 2 equivalents of HBF_4 in Et_2O to give the hydrazido(2−) complex *trans*-[MoF(NNH_2)(dippe)$_2$][BF_4], the crystal structure of which has been determined. When the reduction of [$MoCl_3$(thf)$_3$] in the presence of dippe was performed under argon instead of dinitrogen the yellow, 16-electron, paramagnetic complex [$MoCl_2$(dippe)$_2$] **4** was obtained. In accordance with its co-ordinatively unsaturated character, **4** reacted with CO in thf yielding seven-co-ordinate, diamagnetic [MoCl(CO)$_2$(dippe)$_2$]Cl **5**. It also underwent one-electron oxidation by reaction with Ag[BF_4] in CH_2Cl_2, furnishing 15-electron [$MoCl_2$(dippe)$_2$][BF_4] **6**, the crystal structure of which was also determined.

Several aspects of dinitrogen transition-metal chemistry have been studied, particularly those relevant to the biochemical action of nitrogenases, prompting investigations into the chemistry, structure and function of molybdenum complexes containing dinitrogen fragments, either in the form of formally neutral N_2 or in reduced and protonated states.[1] In most cases, mono-, bi- or poly-dentate phosphines act as co-ligand in these complexes. The protonation of dinitrogen bound to molybdenum or tungsten, to give ammonia and/or hydrazine, has been studied,[2] and several intermediate complexes have been isolated and characterised.[3] However, the mechanism is not completely elucidated. As a part of our studies on the effects of bulky ligands on the activation of small molecules by transition-metal complexes, we carried out the synthesis and characterisation of molybdenum bis(dinitrogen) and related complexes, containing the sterically demanding, strong electron-releasing diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe) as co-ligand.

Results and Discussion

Synthesis of trans-[Mo(N_2)$_2$(dippe)$_2$].—When [$MoCl_3$(thf)$_3$] is reduced with sodium dispersion or sodium amalgam in tetrahydrofuran (thf), in the presence of dinitrogen and dippe, the red-orange, crystalline, bis(dinitrogen) adduct [Mo(N_2)$_2$(dippe)$_2$] **1** is isolated in low, but reproducible yields (*ca.* 20%), as inferred from analytical and spectral data. No other material can be isolated from the reaction mixture. Attempts to increase the yields of this preparation by changing the reaction conditions (reducing agent, dinitrogen pressure, reaction time) have been unsuccessful. It has not been possible to prepare **1** by displacement of monodentate phosphine ligands by dippe in a bis(dinitrogen) complex such as *cis*-[Mo(N_2)$_2$(PMe_3)$_4$].[4] The low yields in the synthesis of **1** have been the main obstacle in the development of the present work.

The IR spectrum of complex **1** displays one strong $\nu(N{\equiv}N)$ absorption band centred at 1900 cm^{-1}. This value falls in the range of frequencies observed for $\nu(N{\equiv}N)$ in other molybdenum bis(dinitrogen) phosphine complexes.[5] The presence of a single $\nu(N{\equiv}N)$ band suggests a *trans* arrangement of dinitrogen ligands. This was confirmed by the ^{31}P-{^1H} NMR spectrum, which consists of one sharp singlet at δ 65.5. No evidence for the formation of the *cis* isomer has been observed.

Stirring a thf solution of complex **1** under 1 atm (*ca.* 10^5 Pa) of hydrogen for 3 d yielded only small amounts of the tetrahydride complex [MoH_4(dippe)$_2$] **2** mixed with unreacted starting dinitrogen complex, as inferred from IR and NMR spectral data. Complex **2** has been previously prepared by metal-vapour synthesis techniques, and its crystal structure determined, although the hydride atoms were not located.[6] We have developed a more convenient synthesis of **2**, by reaction of [$MoCl_4$(MeCN)$_2$] with Na[BH_4] in the presence of dippe. Yields of 50–60% are achieved in this way. The spectral properties of **2** have been thoroughly studied and discussed elsewhere,[6] and no further comments will be made.

Protonation Reactions of trans-[Mo(N_2)$_2$(dippe)$_2$].—Molybdenum and tungsten bis(dinitrogen) complexes react with acids to form different species depending upon the nature of the acid, solvent, and co-ligands in the starting dinitrogen complex. In some instances ammonia and/or hydrazine are the ultimate nitrogen-containing products, although generally this is not the case with dinitrogen complexes containing diphosphines.[1]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Positional parameters for *trans*-[MoF(NNH$_2$)(dippe)$_2$][BF$_4$] **3**

Atom	*x*	*y*	*z*
Mo(1)	0.615 42(3)	0.696 48(2)	0.119 57(1)
Mo(2)	0.674 96(4)	0.053 13(2)	0.375 92(1)
P(1)	0.540 7(1)	0.797 62(5)	0.147 92(4)
P(2)	0.679 8(1)	−0.059 87(6)	0.384 24(4)
P(3)	0.413 9(1)	0.638 37(6)	0.088 74(4)
P(4)	0.491 5(1)	0.007 63(6)	0.325 39(4)
P(5)	0.820 2(1)	0.757 85(5)	0.143 21(4)
P(6)	0.641 6(1)	0.163 77(6)	0.378 21(4)
P(7)	0.696 7(1)	0.602 13(5)	0.081 48(4)
P(8)	0.827 9(1)	0.100 14(6)	0.437 77(4)
F(1)	0.464 7(4)	0.464 7(2)	0.163 5(1)
F(2)	0.101 8(6)	0.239 4(2)	0.352 8(1)
F(3)	0.556 5(5)	0.425 7(2)	0.216 0(2)
F(4)	0.032 9(5)	0.172 4(2)	0.299 4(2)
F(5)	0.388 0(6)	0.469 4(3)	0.227 5(2)
F(6)	0.128 3(6)	0.254 7(2)	0.285 8(2)
F(7)	0.556 7(5)	0.525 7(2)	0.218 5(2)
F(8)	0.222 7(6)	0.187 3(4)	0.313 4(2)
F(11)	0.618 6(2)	0.725 3(1)	0.061 02(8)
F(22)	0.556 5(2)	0.059 4(1)	0.424 62(8)
N(11)	0.612 6(3)	0.669 9(2)	0.169 6(1)
N(12)	0.621 8(5)	0.649 9(2)	0.207 8(1)
N(21)	0.781 5(4)	0.053 9(2)	0.335 0(1)
N(22)	0.866 3(5)	0.059 1(2)	0.304 9(2)
C(10)	0.551 6(4)	0.850 8(2)	0.107 1(2)
C(11)	0.390 9(4)	0.805 2(2)	0.174 5(2)
C(15)	0.658 3(5)	0.830 5(2)	0.189 2(2)
C(20)	0.812 1(5)	−0.098 9(2)	0.361 2(2)
C(22)	0.666 1(5)	−0.089 5(2)	0.437 2(2)
C(24)	0.545 5(5)	−0.102 6(2)	0.354 1(2)
C(30)	0.342 2(5)	0.673 6(2)	0.043 8(2)
C(33)	0.283 9(5)	0.617 2(2)	0.122 8(2)
C(37)	0.453 1(5)	0.564 9(2)	0.062 2(2)
C(40)	0.474 6(5)	0.024 0(2)	0.269 1(2)
C(42)	0.501 5(5)	−0.074 2(2)	0.315 4(2)
C(44)	0.330 3(5)	0.013 8(3)	0.344 2(2)
C(50)	0.905 8(5)	0.724 0(2)	0.185 9(2)
C(51)	0.785 1(4)	0.832 4(2)	0.170 1(2)
C(55)	0.937 8(4)	0.779 1(2)	0.103 8(2)
C(60)	0.751 3(5)	0.202 5(2)	0.343 9(2)
C(66)	0.486 1(5)	0.190 1(2)	0.372 2(2)
C(68)	0.693 2(5)	0.198 2(2)	0.432 6(2)
C(70)	0.840 9(4)	0.605 1(2)	0.050 9(2)
C(73)	0.577 0(5)	0.571 2(2)	0.040 6(2)
C(77)	0.701 4(5)	0.541 4(2)	0.116 8(2)
C(80)	0.997 4(5)	0.092 5(2)	0.438 3(2)
C(86)	0.824 0(5)	0.182 4(2)	0.442 6(2)
C(88)	0.774 5(5)	0.081 3(2)	0.491 5(2)
C(101)	0.439 7(5)	0.842 0(2)	0.076 5(2)
C(102)	0.580 9(6)	0.917 7(2)	0.122 9(2)
C(111)	0.379 6(6)	0.765 5(3)	0.209 9(2)
C(112)	0.361 7(5)	0.868 8(3)	0.190 7(2)
C(201)	0.932 8(6)	−0.074 2(3)	0.384 0(2)
C(202)	0.817 9(7)	−0.101 2(3)	0.313 0(2)
C(221)	0.656 7(7)	−0.157 6(3)	0.435 3(2)
C(222)	0.560 7(6)	−0.064 3(3)	0.462 9(2)
C(301)	0.235 3(5)	0.709 7(3)	0.059 0(2)
C(302)	0.306 7(6)	0.632 5(3)	0.002 3(2)
C(331)	0.184 5(6)	0.572 0(3)	0.099 5(3)
C(332)	0.328 9(6)	0.594 3(3)	0.162 7(3)
C(401)	0.425 1(6)	0.085 1(3)	0.265 9(2)
C(402)	0.592 4(6)	0.017 9(3)	0.244 4(2)
C(441)	0.309 2(5)	−0.010 1(3)	0.386 9(2)
C(442)	0.227 5(6)	−0.014 6(4)	0.311 5(2)
C(501)	1.010 0(5)	0.688 6(2)	0.167 6(2)
C(502)	0.947 1(7)	0.765 0(3)	0.226 0(2)
C(551)	0.877 8(5)	0.806 9(3)	0.067 5(2)
C(552)	1.047 9(5)	0.821 1(3)	0.124 0(2)
C(601)	0.789 0(7)	0.269 7(3)	0.356 3(3)
C(602)	0.713 1(7)	0.188 6(3)	0.296 6(2)
C(661)	0.403 9(6)	0.172 5(3)	0.408 0(2)
C(662)	0.479 4(6)	0.257 0(3)	0.369 4(3)
C(701)	0.882 7(6)	0.545 3(3)	0.029 8(2)
C(702)	0.831 5(6)	0.648 1(3)	0.017 4(2)
C(771)	0.813 4(6)	0.551 5(2)	0.147 3(2)
C(772)	0.686 6(6)	0.476 2(2)	0.095 3(2)
C(801)	1.073 2(6)	0.133 3(3)	0.473 6(2)
C(802)	1.049 2(5)	0.101 9(3)	0.394 5(2)
C(881)	0.841 4(6)	0.030 1(3)	0.505 6(2)
C(882)	0.776 9(6)	0.132 6(3)	0.527 9(2)
B(1)	0.498 1(9)	0.471 7(3)	0.206 1(3)
B(2)	0.121 7(8)	0.215 2(3)	0.313 5(2)

Table 2 Selected bond distances (Å) and angles (°) for complex **3**

Mo(1)–P(1)	2.540(1)	Mo(2)–P(2)	2.589(1)
Mo(1)–P(3)	2.555(1)	Mo(2)–P(4)	2.575(1)
Mo(1)–P(5)	2.557(1)	Mo(2)–P(6)	2.534(1)
Mo(1)–P(7)	2.535(1)	Mo(2)–P(8)	2.584(1)
Mo(1)–F(11)	2.017(2)	Mo(2)–F(22)	2.013(3)
Mo(1)–N(11)	1.743(4)	Mo(2)–N(21)	1.742(4)
N(11)–N(12)	1.332(5)	N(21)–N(22)	1.340(6)
F(4) ··· H(N4)	2.10	F(7) ··· H(N2)	2.04
P(1)–Mo(1)–P(3)	101.57(4)	P(2)–Mo(2)–P(4)	79.43(4)
P(1)–Mo(1)–P(5)	78.55(4)	P(2)–Mo(2)–P(6)	169.71(5)
P(1)–Mo(1)–P(7)	171.79(4)	P(2)–Mo(2)–P(8)	100.27(4)
P(1)–Mo(1)–F(11)	87.06(8)	P(2)–Mo(2)–F(22)	88.05(8)
P(1)–Mo(1)–N(11)	94.2(1)	P(2)–Mo(2)–N(21)	96.0(1)
P(3)–Mo(1)–P(5)	174.45(5)	P(4)–Mo(2)–P(6)	99.54(4)
P(3)–Mo(1)–P(7)	79.02(4)	P(4)–Mo(2)–P(8)	169.09(4)
P(3)–Mo(1)–F(11)	82.58(8)	P(4)–Mo(2)–F(22)	88.35(8)
P(3)–Mo(1)–N(11)	96.7(1)	P(4)–Mo(2)–N(21)	94.6(1)
P(5)–Mo(1)–P(7)	100.06(4)	P(6)–Mo(2)–P(8)	78.78(4)
P(5)–Mo(1)–F(11)	91.90(8)	P(6)–Mo(2)–F(22)	81.68(8)
P(5)–Mo(1)–N(11)	88.8(1)	P(6)–Mo(2)–N(21)	94.2(1)
P(7)–Mo(1)–F(11)	84.89(8)	P(8)–Mo(2)–F(22)	80.74(8)
P(7)–Mo(1)–N(11)	93.9(1)	P(8)–Mo(2)–N(21)	96.3(1)
F(11)–Mo(1)–N(11)	178.7(1)	F(22)–Mo(2)–N(21)	175.3(1)
Mo(1)–N(11)–N(12)	174.7(4)	Mo(2)–N(21)–N(22)	175.3(3)

Other cases involve complete dinitrogen loss. The protonation of co-ordinated dinitrogen is clearly a complex process in which several metal-containing species are involved. We have investigated the protonation of **1** in diethyl ether, using HBF$_4$·Et$_2$O as acid. Addition of HBF$_4$·Et$_2$O (*ca.* 2 equivalents) to an ether solution of **1** immediately produces a precipitate, which, upon recrystallisation from acetone–Et$_2$O, yielded red-pink crystals. The IR spectrum of these crystals shows bands at 3190, 3280 and 3350 cm^{-1}, attributable to ν(NH) of a protonated dinitrogen ligand. A strong, broad band, centred at 1050 cm^{-1} is also present, and it is assigned to the [BF$_4$]$^-$ anion. Microanalysis, together with spectral data, indicates a formulation of this compound as the diamagnetic hydrazido(2−) complex [MoF(NNH$_2$)(dippe)$_2$][BF$_4$] **3**. The ^{31}P-{^{1}H} NMR spectrum consists of one doublet centred at δ 57.3 ($^2J_{PF}$ = 32.4 Hz), which suggests a *trans* arrangement of equivalent phosphorus atoms coupled to one fluorine nucleus, as expected. This pattern has also been observed for other fluorohydrazido(2−) complexes [MF(NNH$_2$)(L–L)$_2$]$^+$ (M = Mo or W, L–L = tertiary diphosphine).[7,8] The protons of the NH$_2$ ligand do not appear in the ^{1}H NMR spectrum. It is well known that this kind of proton exchanges very easily in protic media. For other hydrazido(2−) complexes the relevant signals in the ^{1}H NMR spectra (when observed) disappear upon addition of water.[8,9] In our case the exchange may be promoted by traces of water present in the solvent, (CD$_3$)$_2$CO.

Complex **3** has been structurally characterised by X-ray analysis. The crystal structure consists of two independent complex cations and anions. Atomic positions are shown in Table 1, and selected bond lengths and angles in Table 2.

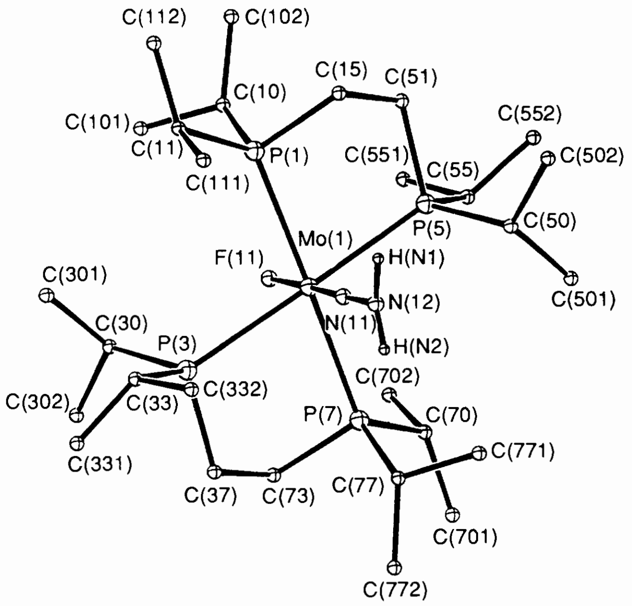

Fig. 1 Structure of one of the very similar cations *trans*-$[MoF(NNH_2)(dippe)_2]^+$ of complex **3**, indicating the atom numbering scheme. Hydrogen atoms, except those of the hydrazido(2−) ligand, have been omitted for clarity

The structure of the cation *trans*-$[MoF(NNH_2)(dippe)_2]^+$ is shown in Fig. 1. The co-ordination around the Mo atom is octahedral, with the four phosphorus atoms in the equatorial plane, and fluoride and hydrazide(2−) ligands in mutually *trans* positions. The N–N–Mo linkages are essentially linear for both independent complex cations. The Mo–N(1) and Mo–N(2) distances are 1.743(4) and 1.742(4) Å respectively, very short, as in the related complexes $[MoF(NNH_2)(dppe)_2]^+$ [7] and $[MoCl(NNH_2)(tdpme)(PPh_3)]^+$ [tdpme = 1,1,1-tris(diphenylphosphinomethyl)ethane].[10] The N–N separations of 1.332(5) and 1.340(6), which are also similar to those found for $[MoF(NNH_2)(dppe)_2]^+$ and $[MoCl(NNH_2)(tdpme)(PPh_3)]^+$, indicate some double-bond character throughout the Mo–N–N moieties. The bond distances Mo–F, 2.017(2) and 2.013(3), are very similar to the value of 1.992(8) reported in $[MoF(NNH_2)(dppe)_2]^+$. The Mo–P distances are also very similar to those found for similar molybdenum complexes.[7,10]

Hydrogen bonds between one fluorine atom in the $[BF_4]^-$ anion and the hydrogen atoms of the hydrazide(2−) ligand have been found, but these interactions are weaker than the hydrogen bond described in ref. 7, the distances F ··· H(N) being 2.10 and 2.04 Å instead of the reported value of 1.79 Å for the complex $[MoF(NNH_2)(dppe)_2][BF_4]$. It is interesting that three ν(NH) bands are observed in the IR spectrum of complex **3**, which however only contains two N–H bonds, and therefore only two bands are expected. This could be attributable to a solid-state effect, due to the presence of two symmetry-independent complex cations in the crystal, combined with the fact that hydrogen bonding between the $[BF_4]^-$ anion and the hydrogen atoms of the hydrazide(2−) ligand is also present.

Synthesis of $[MoCl_2(dippe)_2]$ *and Related Complexes.*—The reduction of $[MoCl_3(thf)_3]$ in the presence of phosphines under argon instead of dinitrogen is a known synthetic route to 16-electron complexes of the type *trans*-$[MoCl_2(PR_3)_4]$ or *trans*-$[MoCl_2(L–L)_2]$,[11,12] which are useful starting materials for the preparation of other low-valent molybdenum complexes. The reduction of $[MoCl_3(thf)_3]$ with sodium dispersion in thf under argon in the presence of dippe yielded a yellow, crystalline material, which is isolated in *ca.* 60% yield. This compound has been identified as $[MoCl_2(dippe)_2]$ **4** by its microanalysis. It is paramagnetic, displaying broad resonances in the ^1H NMR spectrum, and having an effective magnetic moment of 2.8 μ_B at 293 K in benzene solution. This value is similar in magnitude to that found for other similar complexes such as *trans*-$[MoCl_2(dmpe)_2]$ (2.65 μ_B) (dmpe = $Me_2PCH_2CH_2PMe_2$)[13] and *trans*-$[MoCl_2(PMe_3)_4]$ (2.75 μ_B).[11] All compounds with the donor set $MoCl_2P_4$ structurally characterised so far display a *trans* stereochemistry, and this is also the most likely structure for **4**.

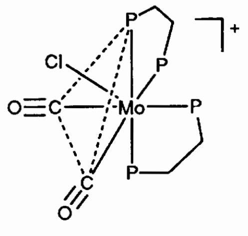

Fig. 2 Proposed structure for the seven-co-ordinate cation $[MoCl(CO)_2(dippe)_2]^+$ of complex **5**

In accord with its co-ordinatively unsaturated character, complex **4** reacts with CO in thf to yield yellow solutions, from which bright yellow crystals of seven-co-ordinate, 18-electron, diamagnetic $[MoCl(CO)_2(dippe)_2]Cl$ **5** were isolated. The IR spectrum displays two strong ν(C≡O) bands, at 1905 and 1823 cm^{-1}, which point to a *cis* or cisoid disposition of the carbonyl ligands. The $^{31}P-\{^1H\}$ NMR spectrum consists of a series of multiplets corresponding to an ABCD spin system. This also suggests a *cis* or cisoid arrangement of the phosphine ligands, despite the bulk of the substituent at the phosphorus atoms. Most seven-co-ordinate derivatives of the type $MX(CO)_2(L–L)_2$ (M = Mo^{II} or Ta^I, X = halide; L–L = tertiary diphosphine) have capped trigonal-prismatic structures, with the capping ligand added at a P_4 face.[13–15] This type of structure implies the equivalence of the phosphorus atoms, and therefore one singlet is observed in the $^{31}P-\{^1H\}$ NMR spectra of these complexes. This is not the case for **5**. There are several possible structures consistent with the non-equivalence of the phosphorus atoms, and the presence of two ν(C≡O) bands in the IR spectrum. One possible idealised structure is shown in Fig. 2, this being a capped octahedron, in which one chloride is added as capping ligand to one face of the octahedral moiety *cis*-$Mo(CO)_2(dippe)_2$, although it is more probable that an intermediate geometry between capped octahedral and capped trigonal prismatic is taken up, the actual structure being, in part, determined by the steric effects of the bulky isopropyl substituents.

It is interesting that compound **5** is stereochemically rigid at room temperature, despite the fact that stereochemical non-rigidy is a characteristic feature of seven-co-ordination.[16] However, it has been reported that an increase in the size of the substituents at phosphorus in the series of compounds $[TaI(CO)_2(Me_2PCH_2CH_2PR_2)_2]$ (R = Me, Et or Pr^i) also increases the stereochemical rigidity, as inferred from the higher energy of the barrier to methyl group exchange in those complexes with bulkier substituents at the phosphine ligands.[14] Unfortunately, crystals of **5** suitable for X-ray structure analysis could not be obtained.

Complex **4** is readily oxidised with $Ag[BF_4]$ in dichloromethane yielding the mononuclear molybdenum(III) cationic complex *trans*-$[MoCl_2(dippe)_2][BF_4]$ **6**, which has been unequivocally characterised by X-ray crystal structure analysis. The molybdenum atoms of the cation *trans*-$[MoCl_2(dippe)_2]^+$ are at special positions in the crystal, lying on centres of symmetry. Fig. 3 shows the molecular structure of one of the virtually identical cations *trans*-$[MoCl_2(dippe)_2]^+$. Final co-ordinates for all non-hydrogen atoms are listed in Table 3, selected bond lengths and angles in Table 4. The co-ordination around molybdenum is octahedral, with the chloride ligands in mutually *trans* positions. The bond lengths found for Mo–Cl, 2.397(2) and 2.392(2) Å, match that reported for *trans*-

Table 3 Positional parameters for *trans*-[$MoCl_2$(dippe)$_2$][BF_4] **6**

Atom	*x*	*y*	*z*
Mo(1)	0	0	0
Mo(2)	0.5	0	0.5
Cl(1)	−0.115 7(1)	0.136 3(2)	0.009 61(9)
Cl(2)	0.635 3(1)	0.110 8(2)	0.524 1(1)
P(1)	0.107 1(1)	0.136 2(2)	0.080 71(9)
P(2)	0.015 4(1)	0.094 5(2)	−0.104 05(8)
P(3)	0.556 0(1)	−0.121 5(3)	0.602 1(1)
P(4)	0.413 2(1)	0.172 2(2)	0.538 88(9)
F(1)	0.736(1)	0.031 6(8)	0.202 0(4)
F(2)	0.656(1)	−0.011 1(9)	0.267 2(5)
F(3)	0.784(1)	0.015(2)	0.297 0(6)
F(4)	0.716(1)	0.158(1)	0.263 9(6)
C(12)	0.088 1(5)	0.092 1(7)	0.156 1(3)
C(21)	0.002 1(6)	−0.033 5(6)	−0.154 9(4)
C(34)	0.623 9(6)	−0.243 1(7)	0.582 1(4)
C(43)	0.331 4(5)	0.213 5(7)	0.469 8(4)
C(100)	0.230 2(5)	0.130 2(8)	0.091 4(4)
C(101)	0.269 5(6)	0.006 9(9)	0.102 2(5)
C(102)	0.279 6(6)	0.209(1)	0.143 2(5)
C(110)	0.082 2(8)	0.295 4(7)	0.076 0(5)
C(111)	0.121 4(6)	0.364 2(8)	0.032 5(5)
C(112)	0.019 6(8)	0.345 8(8)	0.104 5(7)
C(200)	−0.076 1(5)	0.195 8(6)	−0.137 5(3)
C(201)	−0.059 7(6)	0.320 9(7)	−0.112 3(4)
C(202)	−0.103 7(6)	0.199 4(8)	−0.207 4(4)
C(220)	0.119 7(6)	0.167 7(7)	−0.112 2(4)
C(221)	0.200 8(6)	0.095(1)	−0.083 7(4)
C(222)	0.125 1(7)	0.203(1)	−0.176 9(5)
C(300)	0.631 7(8)	−0.047(2)	0.665 6(7)
C(301)	0.586 8(9)	0.020(1)	0.708 0(5)
C(302)	0.720 6(7)	−0.058(1)	0.676 5(5)
C(330)	0.476 8(8)	−0.203(2)	0.636 2(6)
C(331)	0.400(1)	−0.222(2)	0.618 9(9)
C(332)	0.523(1)	−0.286(2)	0.690 4(7)
C(400)	0.347 2(5)	0.143 0(6)	0.598 0(3)
C(401)	0.319 9(5)	0.248 9(8)	0.631 2(4)
C(402)	0.265 0(6)	0.070 3(8)	0.571 0(4)
C(440)	0.480 2(6)	0.308 3(7)	0.557 9(4)
C(441)	0.542 2(6)	0.299 2(9)	0.620 9(5)
C(442)	0.430 0(7)	0.424 3(8)	0.552 1(5)
B	0.732(3)	0.056(2)	0.252(1)

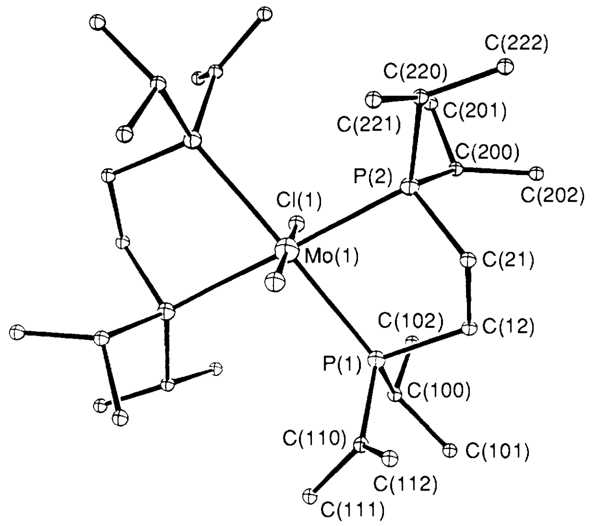

Fig. 3 Structure of one of the virtually identical cations *trans*-[$MoCl_2$(dippe)$_2$]$^+$ of complex **6**, showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity

[$MoCl_2$(dmpe)$_2$][$SnCl_3$] [2.401(2) Å].[13] The Mo–P separations are in the range 2.611–2.665 Å, considerably larger than those reported for [$MoCl_2$(dmpe)$_2$][$SnCl_3$] (2.523–2.534 Å); this is possibly due to the steric effects caused by the bulky substituents at the dippe ligands.

Compound **6** is paramagnetic, with an effective magnetic moment of 4.0 μ_B at 293 K in chloroform solution, which is, within experimental error, close to the spin-only value of 3.87 μ_B for a complex with three unpaired electrons; *trans*-[$MoCl_2$(dmpe)$_2$][PF_6][13] has an effective magnetic moment of 3.65 μ_B. This compound was prepared by oxidation of *trans*-[$MoCl_2$(dmpe)$_2$] with $AgPF_6$, a method analogous to that used by us for the preparation of **6**. Other authors have used the same method for the preparation of *trans*-[$MoCl_2$(dppe)$_2$][PF_6].[17] Molybdenum(III) complexes of the type [MoX_2(L–L)$_2$]X (X = Cl or Br) have also been obtained as products of the reaction of the corresponding bis(dinitrogen) adducts [$Mo(N_2)_2$(L–L)$_2$] with a large excess of HCl or HBr. For instance, the reaction of [$Mo(N_2)_2$(depe)$_2$] (depe = $Et_2PCH_2CH_2PEt_2$) with 10 molar equivalents of HX (X = Cl or Br) causes complete loss of dinitrogen from the complex. In the case of HBr, 2 mol of N_2 were recovered, and the yellow, crystalline product isolated in this case was characterised as [$MoBr_2$(depe)$_2$]Br.[3]

Table 4 Selected bond distances (Å) and angles (°) for complex **6**

Mo(1)–Cl(1)	2.397(2)	Mo(2)–Cl(2)	2.392(2)
Mo(1)–P(1)	2.665(2)	Mo(2)–P(3)	2.652(3)
Mo(1)–P(2)	2.619(2)	Mo(2)–P(4)	2.611(2)
Cl(1)–Mo(1)–P(1)	93.93(6)	Cl(2)–Mo(2)–P(3)	88.17(8)
Cl(1)–Mo(1)–P(2)	91.42(6)	Cl(2)–Mo(2)–P(4)	89.18(7)
P(1)–Mo(1)–P(2)	77.95(6)	P(3)–Mo(2)–P(4)	78.76(7)

Experimental

All synthetic operations were performed under a dinitrogen atmosphere, following standard Schlenk techniques. Tetrahydrofuran, diethyl ether, and light petroleum (b.p. 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane[18] was obtained according to the literature. Tetrafluoroboric acid and 50% sodium dispersion in mineral oil were supplied by Aldrich. Infrared spectra were recorded on a Perkin-Elmer 882 spectrophotometer, in Nujol mulls, NMR spectra on a Varian Unity 400 MHz spectrometer, with chemical shifts given in ppm relative to $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P-{^1H}). Microanalyses were by Mr. Colin Macdonald, at the AFRC-IPSR Nitrogen Fixation Laboratory, University of Sussex, or by Butterworth Laboratories Ltd., Middlesex, UK. Magnetic moments were determined in solution by the Evans method.[19]

trans-*Bis*[1,2-*bis*(*diisopropylphosphino*)*ethane*]*bis*(*dinitrogen*)*molybdenum*(0) **1**.—To a slurry of fresh [$MoCl_3(thf)_3$] (0.42 g, 1 mmol) in thf (20 cm^3) were added dippe (0.6 cm^3, 2 mmol) and the mixture stirred at room temperature for some minutes. In the meantime, sodium dispersion (0.28 g of a 50% dispersion in mineral oil) was placed in a Schlenk flask. The sodium dispersion was washed with light petroleum in order to remove mineral oil, and thf (10 cm^3) added. The solution containing [$MoCl_3(thf)_3$] and dippe in thf was added *via* cannula to the stirred sodium dispersion. The mixture was stirred under dinitrogen overnight at room temperature. The resulting dark brown suspension was then centrifuged or filtered through Celite, and the solvent removed *in vacuo*, leaving a dark oil. Treatment of this oil with methanol yielded orange-red microcrystals, which were filtered off and recrystallised from diethyl ether. Yield: 0.13 g, 19%. Complex **1** can also be prepared in similar yields using 1% Na–Hg instead of sodium dispersion (Found: C, 49.3; H, 9.75; N, 7.6. $C_{28}H_{64}MoN_4P_4$ requires C, 49.7; H, 9.45; N, 8.3%). IR: ν(N≡N) 1910 cm^{-1}. ^{31}P-{^{1}H} NMR (C_6D_6): δ 65.5 (s).

Bis[1,2-*bis*(*diisopropylphosphino*)*ethane*]*tetrahydridomolybdenum*(IV) **2**.—The complex [$MoCl_4(MeCN)_2$] (0.64 g, 2 mmol) was suspended in thf (20 cm^3) and dippe (0.6 cm^3, 2 mmol) was added. The mixture was stirred for 1 h at room temperature then the solvent was removed *in vacuo*. The resulting orange solid was slurried in ethanol (30 cm^3), and dippe (0.6 cm^3, 2 mmol) added. This mixture was treated with solid Na[BH_4] (0.5 g, excess). It was stirred for 1 h at room temperature. A white precipitate was obtained, which was filtered off and dissolved in thf. The solution was filtered through Celite and concentrated. Addition of ethanol and cooling to −20 °C yielded colourless crystals. Yield: 0.63 g, 50% (Found: C, 53.7; H, 11.0. $C_{28}H_{68}MoP_4$ requires C, 53.8; H, 10.9%). IR: ν(MoH) 1775 and 1790 (sh) cm^{-1}. NMR (C_6D_6): ^{1}H, δ −6.18 (br m, MoH_4); ^{31}P-{^{1}H}, δ 104.6 (s).

trans-*Bis*[1,2-*bis*(*diisopropylphosphino*)*ethane*]*fluoro*[*hydrazido*(2−)]*molybdenum*(IV) *Tetrafluoroborate* **3**.—A solution of complex **1** (0.1 g, 0.15 mmol) in Et_2O (15 cm^3) was treated with HBF_4·Et_2O (2.5 equivalents). A salmon-pink precipitate was immediately formed. It was filtered off, washed with diethyl ether, and dried *in vacuo*. The product was dissolved in the minimum amount of acetone. The filtered solution was layered with diethyl ether and cooled to −20 °C. Well formed crystals were obtained, which were collected, washed with diethyl ether, and dried *in vacuo*. Yield: 0.06 g, 53% (Found: C, 44.1; H, 8.70; N, 3.5. $C_{28}H_{66}BF_5MoN_2P_4$ requires C, 44.4; H, 8.75; N, 3.7%). IR: ν(NH) 3190, 3280 and 3350 cm^{-1}. ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$], δ 57.3 (d, $^2J_{PF}$ = 32.4 Hz).

Bis[1,2-*bis*(*diisopropylphosphino*)*ethane*]*dichloromolybdenum*(II) **4**.—A mixture of fresh [$MoCl_3(thf)_3$] (0.42 g, 1 mmol) and dippe (0.6 cm^3, 2 mmol) in thf (20 cm^3) was transferred under argon to a flask containing sodium dispersion (0.28 g of a 50% dispersion in mineral oil), which had been previously washed with light petroleum, as indicated in the procedure for the synthesis of compound **1**. The reaction mixture was stirred under argon for 2 h. Then the brown suspension was filtered through Celite or centrifuged. Yellow crystals began to form when the solution was concentrated. Methanol was added, completing the precipitation of the yellow, crystalline material. It was filtered off, washed with light petroleum and dried *in vacuo*. This air-sensitive product was recrystallised from thf or thf–MeOH. Yield: 0.41 g, 60% (Found: C, 48.5; H, 9.40, Cl, 10.6; P, 18.0. $C_{28}H_{64}Cl_2MoP_4$ requires C, 48.6; H, 9.25, Cl, 10.3; P, 17.9%); μ_{eff} = 2.8 μ_B.

Bis[1,2-*bis*(*diisopropylphosphino*)*ethane*]*dicarbonylchloromolybdenum*(II) *Chloride* **5**.—Carbon monoxide was bubbled through a thf solution of complex **4** (0.3 g, 0.43 mmol). The yellow solution was stirred under CO at room temperature for 3 h then concentrated and cooled to −20 °C, yielding bright yellow crystals which become opaque upon isolation. They were filtered off, washed with light petroleum and dried *in vacuo*. This product can be recrystallised from acetone or acetone–Et_2O. Yield: 0.21 g, 65% (Found: C, 47.9; H, 8.60. $C_{30}H_{64}Cl_2MoO_2P_4$ requires C, 48.2; H, 8.55%). IR: ν(C≡O) 1905 and 1823 cm^{-1}. ^{31}P-{^{1}H} NMR ($CDCl_3$): ABCD spin system, δ 55.17 (P_A), 36.19 (P_B), 89.01 (P_C), 87.96 (P_D), $J(P_AP_B)$ = 163.3, $J(P_AP_C)$ = 42.8, $J(P_AP_D)$ = 30.1, $J(P_BP_C)$ = 21.7, $J(P_BP_D)$ = 52.0 and $J(P_CP_D)$ = 41.3 Hz.

Table 5 Summary of data for the crystal structure analysis of compounds **3** and **6**

Formula	$C_{28}H_{66}BF_5MoN_2P_4$	$C_{28}H_{64}BCl_2F_4MoP_4$
M	756.5	778.4
Crystal system	Triclinic	Monoclinic
Space group	$C\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a/Å	10.828(1)	15.372(3)
b/Å	22.470(2)	11.315(1)
c/Å	31.295(2)	22.395(2)
α/°	97.014(6)	
β/°	91.238(7)	102.13(1)
γ/°	94.730(6)	
U/Å^3	7527.8(2)	3808(2)
Z	8	4
D_c/g cm^{-3}	1.335	1.358
λ/Å	0.710 69 (Mo-Kα)	1.5418 (Cu-Kα)
μ/cm^{-1}	5.51 (Mo-Kα)	61.36 (Cu-Kα)
F(000)	3200	1636
Unique reflections	9746	5984
Observed reflections	6984 ($I > 3\sigma_I$)	3644 ($I > 2\sigma_I$)
No. of parameters	739	364
R	0.034	0.051
R' ($w = \sigma_F^{-2}$)	0.042	0.061
Goodness of fit	1.33	2.19

trans-*Bis*[1,2-*bis*(*diisopropylphosphino*)*ethane*]*dichloromolybdenum*(III) *Tetrafluoroborate* **6**.—To a solution of complex **4** (0.25 g, 0.36 mmol) in CH_2Cl_2 (15 cm^3) was added solid Ag[BF_4] (0.07 g, 0.36 mmol). A dark precipitate and an orange solution were obtained. The mixture was centrifuged or filtered through Celite. The solvent was removed *in vacuo* yielding an orange powder. This was recrystallised from dichloromethane–diethyl ether as orange prisms, which were filtered off, washed with diethyl ether, and dried *in vacuo*. Yield: 0.16 g, 58% (Found: C, 43.0; H, 8.10; Cl, 9.5; P, 15.8. $C_{28}H_{64}BCl_2F_4MoP_4$ requires C, 43.2; H, 8.20; Cl, 9.1; P, 15.9%). μ_{eff} = 4.0 μ_B.

Crystal Structure Analyses.—Relevant crystal and crystal-structure-analysis data for compounds **3** and **6** are given in Table 5.

trans-[$MoF(NNH_2)(dippe)_2$][BF_4] **3**. Crystals of complex **3** are orange-red prisms. One, *ca.* 0.14 × 0.18 × 0.31 mm, was mounted on a glass fibre, and, after preliminary photographic examination, was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell dimensions (by refinement from goniometer settings of 25 reflections, θ *ca.* 10.5°, each centred in four orientations) and for measurement of diffraction intensities (to θ_{max} = 22.5°). During processing, intensities were corrected for Lorentz-polarisation effects, absorption (by semiempirical, ψ-scan methods) and by Bayesian statistical methods to remove negative net intensities. No deterioration correction was necessary.

9746 Unique reflections were used for structure analysis and refinement, by means of the SHELX 86[20] and SHELX 93 programs.[21] The molybdenum atoms were located by the Patterson method. The model was expanded until all non-hydrogen atoms were located. Approximately one-half of the hydrogen atoms, including those on the hydrazido(2−) fragment, were located on a regular Fourier difference map. The remaining hydrogen atoms were placed at idealised positions. Only non-hydrogen atoms were allowed to refine anisotropically. Full-matrix least-square methods gave the final values R = 0.034 and R' = 0.042 ($w = \sigma_F^{-2}$) for 6984 reflections with $I > 3\sigma_I$.

trans-[$MoCl_2(dippe)_2$][BF_4] **6**. A prismatic-shaped crystal, *ca.* 0.45 × 0.35 × 0.10 mm, was mounted on a glass fibre, and transferred to an AFC6S-Rigaku automatic diffractometer (with graphite-monochromated Cu-Kα radiation), where accurate cell parameters were obtained from the settings of 25 high-angle reflections. Intensity data were measured for a set of 5984 unique reflections. During processing, corrections were applied for Lorentz and polarisation effects, for deterioration (−3.7%), and absorption (from semiempirical ψ-scan methods).

The structure was solved by conventional Patterson methods, and refined by full-matrix least squares. Anisotropic thermal parameters were allowed for all non-hydrogen atoms in the complex. Hydrogen atoms were included at idealised positions and were not refined. At convergence, $R = 0.051$ and $R' = 0.061$ for 3644 reflections having $I > 2\sigma_I$ and weighted $w = \sigma_F^{-2}$. The peaks obtained in a final difference map were less than 0.7 e $Å^{-3}$ in intensity.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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