DALTON
FULL PAPER

Bis(isodiazene) and related complexes of molybdenum(VI). Syntheses and structures of $[Mo(OTf)_2(NNPh_2)_2(py)_2]$, $[MoCl(OTf)(NNPh_2)\{NC_5H_3(CH_2C(O)Ph_2)_2\text{-}2,6\}]$, $[\{MoCl(NNPh_2)_2(\mu\text{-}Cl)(NH_2Bu^t)\}_2]$ and $[MoTp'Cl(NNPh_2)_2]$ $[OTf = O_3SCF_3, Tp' = \text{tris(3,5-dimethylpyrazolyl)hydroborate}]$

Jonathan R. Dilworth,*[a] **Vernon C. Gibson,***[b] **Nicola Davies,**[a] **Carl Redshaw,**[b]
Andrew P. White[b] **and David J. Williams**[b]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.*
E-mail: Jon.Dilworth@chemistry.oxford.ac.uk
[b] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY.*
E-mail: v.gibson@ic.ac.uk

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Possible routes to $[Mo(NNPh_2)_2R_2]$, where R = alkyl or aryl groups, have been investigated including the interaction of $[MoCl_2(NNPh_2)_2(dme)]$ **1** (dme = 1,2-dimethoxyethane) with the standard alkylating agents LiR, RMgX, R_2Mg or R_2Zn under various conditions of solvent and temperature. There was, however, no evidence to suggest alkylation had taken place. Treatment of **1** with two equivalents of silver trifluoromethanesulfonate, silver triflate (AgOTf), in the presence of pyridine gave the golden-yellow bis(triflate) complex $[Mo(OTf)_2(NNPh_2)_2(py)_2]$ **2** in good yield. In the presence of an excess of bipy (2,2′-bipyridine) the known dicationic species $[Mo(NNPh_2)_2(bipy)_2]^{2+}$ was isolated as its PF_6^- salt. Attempts to replace triflate by alkyl groups in **2** were unsuccessful. A similar reaction of **1** with silver triflate in the presence of the bulky tridentate alkoxide 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine (H_2L) led to loss of an $NNPh_2$ group (presumably as hydrazine) and formation of the green mono-isodiazene complex $[MoCl(OTf)(NNPh_2)(L)]$ **3**. The compound $[Mo(CH_2CMe_2Ph)_2(NBu^t)_2]$ underwent partial imido ligand exchange with an excess of 1,1-diphenylhydrazine hydrochloride to give the brown bis(isodiazene) chloro-bridged dimer $[\{MoCl(NNPh_2)_2(\mu\text{-}Cl)(NH_2Bu^t)\}_2]$ **4**. A chloride substitution reaction of **1** with potassium tris(3,5-dimethylpyrazolyl)hydroborate, (KTp′) afforded the bis(isodiazene) complex $[MoTp'Cl(NNPh_2)_2]$ **5**. The crystal and molecular structures of **2**–**5** have been determined. The complexes all contain linear isodiazene groups with Mo–N distances in the range 1.755(6) to 1.768(7) Å. In **2** the molybdenum(VI) centre has a pseudo octahedral geometry with axial pyridines and *cis*-triflate groups. In six-co-ordinate **3** the pyridinediolate ligand has a meridional donor atom arrangement with an equatorial isodiazene ligand. The binuclear compound **4** has slightly asymmetric chloro bridges coplanar with the terminal isodiazene ligands. Complex **5** is octahedral, having a facially co-ordinated Tp′ ligand and linear $NNPh_2$ ligands.

The present studies arose from attempts to synthesize isodiazene† analogues of the four-co-ordinate molybdenum(VI) organoimido complexes $[Mo(NC_6H_3Pr^i_2\text{-}2,6)(CHCMe_2Ph)(OR)_2]$ $[R = CMe_3, CMe_2(CF_3)$ or $CMe(CF_3)_2]$, which have found widespread use in ring-opening metathesis polymerization (ROMP).[2] This objective has been difficult to achieve, due primarily to surprising problems in alkylating the direct isodiazene analogues of imido-complexes which themselves can readily be alkylated in high yield. Nevertheless, a series of new molybdenum(VI) isodiazene compounds has been isolated and structurally characterized.

Results and discussion

A number of possible routes to $[Mo(NNPh_2)_2R_2]$ (where R = alkyl or aryl) have been studied, including the interaction of $[MoCl_2(NNPh_2)_2(dme)]$ **1**[1] with the standard alkylating agents LiR, RMgX, R_2Mg or R_2Zn (R = Me, CH_2CMe_3 or CH_2SiMe_3) using a wide range of solvents and reaction conditions. There was, however, no evidence from any of the reactions to suggest clean alkylation had taken place. For example interaction of **1** with an excess of $Zn(CH_2CMe_2Ph)_2$ in diethyl ether at room temperature for 12 h afforded **1**·MeCN, after work-up and recrystallization from MeCN (characterised by ^1H NMR and microanalysis) as the only tractable product.

In view of the failure to substitute the chloride ligands of compound **1** we turned to the trifluoromethanesulfonate (triflate, OTf) ligand which is known to be a better leaving group than chloride. Golden-yellow $[Mo(OTf)_2(NNPh_2)_2(py)_2]$ **2** was obtained as an air and moisture sensitive compound in good yield (50–60%) upon treatment of **1** with two equivalents of silver triflate in acetonitrile and subsequent addition of pyridine (see Experimental section). Crystals suitable for a structure determination were obtained by diffusion of diethyl ether into a dichloromethane solution of **2**. Solutions of the complex deteriorate in light and were therefore stored in the dark. The X-ray analysis shows **2** to have approximate molecular C_2 symmetry (Fig. 1), the molybdenum co-ordination geometry being distorted octahedral with *cis* O_3SCF_3 groups [O(5)–Mo–O(6) 73.6(3)°] *trans* to a pair of *cis* isodiazene ligands [N(1)–Mo–N(3) 104.1(3)°], the remaining sites being occupied by pyridine ligands [N(7)–Mo–N(8) 168.2(3)°] Table 1. The two equatorial Mo–N bond lengths [1.765(8) and 1.768(7) Å] and the associated N=N distances [*ca.* 1.31 Å] are very close to those found in other isodiazene complexes.[3] There are departures from linearity at both N(1) and N(3), the angles being 164.2(6) and

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† We have in an earlier publication[1] discussed the problems of nomenclature and bonding in NNR_2 ligands and advocated the use of the isodiazene designation as being the most generally applicable.

Table 1 Selected bond lengths (Å) and angles (°) for compound **2**

Mo–N(3)	1.765(8)	Mo–N(1)	1.768(7)
Mo–O(6)	2.203(7)	Mo–N(8)	2.212(8)
Mo–N(7)	2.216(8)	Mo–O(5)	2.266(6)
N(1)–N(2)	1.328(10)	N(3)–N(4)	1.299(11)
N(3)–Mo–N(1)	104.1(3)	N(3)–Mo–O(6)	164.1(4)
N(1)–Mo–O(6)	91.4(3)	N(3)–Mo–N(8)	90.1(3)
N(1)–Mo–N(8)	93.6(3)	O(6)–Mo–N(8)	85.3(3)
N(3)–Mo–N(7)	98.4(3)	N(1)–Mo–N(7)	92.2(3)
O(6)–Mo–N(7)	84.3(3)	N(8)–Mo–N(7)	168.2(3)
N(3)–Mo–O(5)	90.8(3)	N(1)–Mo–O(5)	165.0(3)
O(6)–Mo–O(5)	73.6(3)	N(8)–Mo–O(5)	86.0(3)
N(7)–Mo–O(5)	85.8(3)	N(2)–N(1)–Mo	164.2(6)
N(1)–N(2)–C(32)	119.9(6)	N(1)–N(2)–C(26)	118.6(6)
C(32)–N(2)–C(26)	121.6(6)	N(4)–N(3)–Mo	171.7(7)
N(3)–N(4)–C(46)	122.4(7)	N(3)–N(4)–C(52)	117.4(7)
C(46)–N(4)–C(52)	118.1(6)		

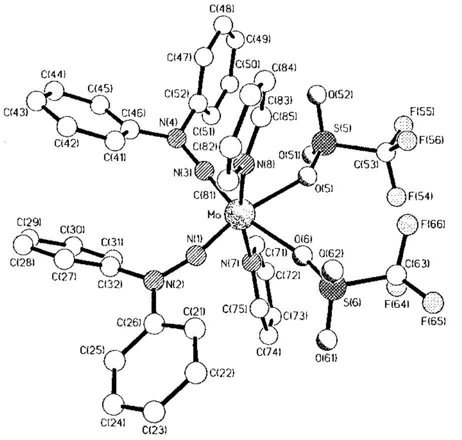

Fig. 1 View of the molecular structure of compound **2** (hydrogen atoms omitted for clarity as in all Figures).

171.7(7)° respectively; the former deviation is at the lower end of the range anticipated for a "linear" isodiazene ligand. For both ligands, the N–Ph bonds lie approximately coplanar with the (isodiazene)N_2O_2 co-ordination plane. The two axial Mo–N (pyridyl) distances [2.212(8) and 2.216(8) Å] are noticeably shorter than the normal value [*ca* 2.30 Å] observed for such systems. The Mo–O (triflate) bonds differ significantly and have distances [2.203(7) and 2.266(6) Å] that are slightly longer than typical values observed for co-ordination to molybdenum, possibly reflecting the *trans* influence of the isodiazene ligands.

A related organoimido complex *cis*$[W(OTf)_2(NBu^t)_2(NH_2Bu^t)_2]$, formed on protonation of $[W(NBu^t)_2(NH_2Bu^t)_2]$ with triflic acid, has been structurally characterised.[4] Reaction of **1** with bipy and silver triflate in acetonitrile afforded, after work-up, the known[5] dication $[Mo(NNPh_2)_2(bipy)_2]^{2+}$ as its PF_6^- salt.

All attempts to obtain stable isodiazene/alkyl derivatives by substitution of the triflate ligands of compound **2** *via* interaction with standard alkylating agents were unsuccessful. Interaction of **1** with silver triflate and the bulky tridentate alkoxide 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine (H_2L) afforded green $[MoCl(OTf)(NNPh_2)(L)]$ **3**, which has *v*(Mo–Cl) at 489 cm^{-1} and *v*(NN) at 1590 cm^{-1} in the IR spectrum. The structure has been confirmed by an X-ray analysis (Fig. 2). The co-ordination geometry is best described as distorted octahedral with a triflate and a chloride ligand occupying the *trans* sites; the isodiazene group is *trans* to the pyridine ring of the tridentate pyridinediolate ligand. The meridional arrangement of the pyridinediolate is similar to its co-ordination mode in the dioxo complexes $[Mo(O)_2L(Me_2SO)]$ and $[Os(O)_2L(NH_2Bu^t)]$,[6] the pyridine ring being twisted by *ca.* 32° out of the equatorial co-ordination plane. The pattern of bonding to, and within, the isodiazene ligand is essentially the same as observed in **2** (Table 2), and there is also a retention of near coplanarity between the two N–Ph bonds and the equatorial co-ordination plane. The co-ordination of the tridentate pyridinediolate ligand is characterized by a pair of short Mo–O bonds [1.861(5) and 1.878(5) Å] and a long Mo–N (pyridine) distance [2.319(6) Å]. The Mo–Cl distance is typical at 2.393(2) Å, as is the Mo–O bond to the triflate ligand [2.181(5) Å]. It is interesting that there is a short intramolecular contact of 2.86 Å between one of the triflate oxygen atoms, O(50), and the α-nitrogen atom, N(34), of the isodiazene ligand with the O···N vector being essentially orthogonal to the equatorial co-ordination plane. However, this is not due to the presence of hydrogen bonding as the N–N distance remains unaffected, and the diamagnetism of the complex is not consistent with the presence of a formally monoanionic hydrazide(1−) ligand. There is nothing noteworthy in the packing of the molecules.

Table 2 Selected bond lengths (Å) and angles (°) for compound **3**

Mo–N(34)	1.763(6)	Mo–O(1)	1.861(5)
Mo–O(9)	1.878(5)	Mo–O(48)	2.181(5)
Mo–N(3)	2.319(6)	Mo–Cl	2.393(2)
N(34)–N(35)	1.306(8)		
N(34)–Mo–O(1)	98.6(3)	N(34)–Mo–O(9)	96.9(3)
O(1)–Mo–O(9)	163.8(2)	N(34)–Mo–O(48)	94.3(2)
O(1)–Mo–O(48)	85.5(2)	O(9)–Mo–O(48)	88.8(2)
N(34)–Mo–N(3)	178.4(2)	O(1)–Mo–N(3)	81.8(2)
O(9)–Mo–N(3)	82.8(2)	O(48)–Mo–N(3)	87.3(2)
N(34)–Mo–Cl	89.8(2)	O(1)–Mo–Cl	93.3(2)
O(9)–Mo–Cl	91.4(2)	O(48)–Mo–Cl	175.9(1)
N(3)–Mo–Cl	88.7(2)	N(35)–N(34)–Mo	169.5(6)
N(34)–N(35)–C(41)	119.5(6)	N(34)–N(35)–C(47)	117.1(6)
C(41)–N(35)–C(47)	123.3(5)		

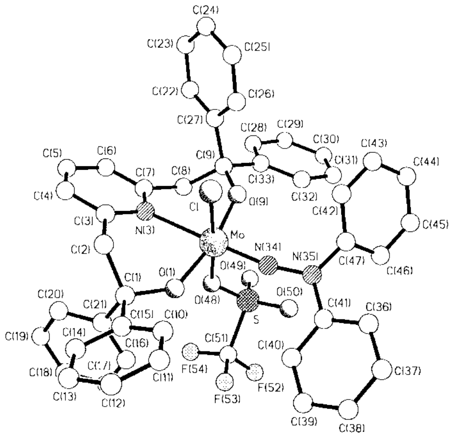

Fig. 2 View of the molecular structure of compound **3**.

Although we were unable to alkylate compounds **1** and **2** it seemed possible that an imido ligand exchange reaction of $[MoR_2(NBu^t)_2]$ with 1,1-diphenylhydrazine hydrochloride, similar to that observed for $[MoCl_2(NBu^t)_2(dme)]$ to give $[MoCl_2(NNPh_2)_2(dme)]$,[1] would provide an entry into alkylated isodiazene species. However, the reaction of $[Mo(CH_2CMe_2Ph)_2(NBu^t)_2]$ with $Ph_2NNH_2{\cdot}HCl$ (two equivalents) in refluxing dme afforded after work-up an orange-brown crystalline solid **4** in high yield (*ca.* 75%). The infrared spectrum showed N–H stretches at *v* 3289 and 3179 cm^{-1}, while the ^1H NMR spectrum contained resonances in the region for aromatic protons, *tert*-butyl protons and a signal at *ca.* δ 4.1 due to NH. The structure was determined by X-ray diffraction. An ORTEP[7] representation of the molecule is shown in Fig. 3 and selected bond lengths and angles are given in Table 3.

The binuclear compound **4** adopts a centrosymmetric edge-shared bi-octahedral geometry with slightly asymmetric chloro

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

Mo–N(3)	1.755(6)	Mo–N(1)	1.758(6)
Mo–N(5)	2.255(6)	Mo–Cl(2)	2.468(2)
Mo–Cl(1)	2.566(1)	Mo–Cl(1′)	2.642(2)
N(1)–N(2)	1.333(8)	N(3)–N(4)	1.321(8)
N(3)–Mo–N(1)	107.1(3)	N(3)–Mo–N(5)	92.2(2)
N(1)–Mo–N(5)	101.2(3)	N(3)–Mo–Cl(2)	92.8(2)
N(1)–Mo–Cl(2)	93.0(2)	N(5)–Mo–Cl(2)	162.9(2)
N(3)–Mo–Cl(1)	162.3(2)	N(1)–Mo–Cl(1)	90.6(2)
N(5)–Mo–Cl(1)	83.2(2)	Cl(2)–Mo–Cl(1)	87.10(6)
N(3)–Mo–Cl(1′)	87.3(2)	N(1)–Mo–Cl(1′)	165.6(2)
N(5)–Mo–Cl(1′)	76.1(2)	Cl(2)–Mo–Cl(1′)	87.85(6)
Cl(1)–Mo–Cl(1′)	75.00(5)	Mo–Cl(1)–Mo′	105.00(5)
N(2)–N(1)–Mo	168.9(5)	N(1)–N(2)–C(17)	118.4(5)
N(1)–N(2)–C(11)	120.2(5)	C(17)–N(2)–C(11)	119.6(5)
N(4)–N(3)–Mo	170.7(5)	N(3)–N(4)–C(23)	120.7(5)
N(3)–N(4)–C(29)	116.9(5)	C(23)–N(4)–C(29)	122.3(4)

Table 4 Selected bond lengths (Å) and angles (°) for compound **5**

Mo–Cl(1)	2.451(2)	Mo–N(1)	1.790(4)
Mo–N(3)	1.780(4)	Mo–N(5)	2.279(5)
Mo–N(7)	2.191(4)	Mo–N(9)	2.303(5)
N(1)–N(2)	1.310(6)	N(3)–N(4)	1.312(6)
Cl(1)–Mo–N(1)	96.0(1)	Cl(1)–Mo–N(3)	92.2(1)
Cl(1)–Mo–N(5)	88.3(1)	Cl(1)–Mo–N(7)	170.2(1)
Cl(1)–Mo–N(9)	88.3(1)	N(1)–Mo–N(3)	105.8(2)
N(1)–Mo–N(5)	89.5(2)	N(1)–Mo–N(7)	91.7(2)
N(1)–Mo–N(9)	164.0(2)	N(3)–Mo–N(5)	164.6(2)
N(3)–Mo–N(7)	91.4(2)	N(3)–Mo–N(9)	89.4(2)
N(5)–Mo–N(7)	85.9(2)	N(5)–Mo–N(9)	75.3(2)
N(7)–Mo–N(9)	82.6(2)	Mo–N(1)–N(2)	174.0(4)
N(1)–N(2)–C(1)	121.1(5)	N(1)–N(2)–C(7)	118.0(5)
C(1)–N(2)–C(7)	120.7(5)	Mo–N(3)–N(4)	178.2(4)
N(3)–N(4)–C(13)	120.0(5)	N(3)–N(4)–C(19)	118.1(4)
C(13)–N(4)–C(19)	121.5(5)		

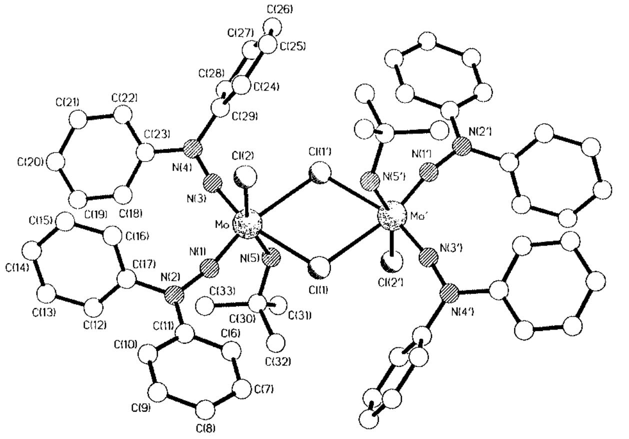

Fig. 3 View of the molecular structure of compound **4**.

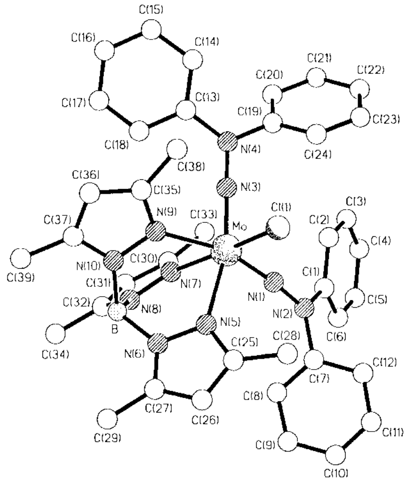

Fig. 4 View of the molecular structure of compound **5**.

bridges [Mo–Cl(1) 2.566(1) and Mo–Cl(1′) 2.642(2) Å] which are coplanar with the terminal isodiazene ligands. The main equatorial angular distortions [Cl(1)–Mo–Cl(1′) 75.0(1) and N(1)–Mo–N(3) 107.1(3)°] arise from the chloride bridging ligands and steric interactions between the bulky diphenylisodiazene ligands whose geometries are essentially the same as in both **2** and **3**, with a retention of near coplanarity of the N–Ph bonds with the (isodiazene) N_2Cl_2 co-ordination plane. The terminal axial Mo–Cl distances are long, at 2.468(2) Å, whereas the associated *trans* Mo–N bond is normal at 2.255(6) Å. The co-ordination geometry to the *tert*-butylamine ligand is noticeably distorted, with the Mo–N bonds being inclined by *ca.* 75° to the equatorial co-ordination plane, this distortion probably being due to a weak intramolecular N–H···Cl hydrogen bond to the proximal axial chlorine atom on the adjacent molybdenum centre [N···Cl 3.50, H···Cl 2.61 Å, N–H···Cl 172°]. The only feature of note in the packing of the molecules is a weak π–π stacking between symmetry related phenyl rings in adjacent molecules [mean interplanar separation 3.20 Å, centroid–centroid separation 3.97 Å]. Clearly the hydrazine hydrochloride effects hydrogen transfer to both imido and alkyl groups with loss of the latter as hydrocarbon.‡

The reaction of compound **1** with KTp′ (Tp′ = tris(3,5-dimethylpyrazolyl)hydroborate) in refluxing thf affords after work-up red-brown prisms of $[MoTp'Cl(NNPh_2)_2]$ **5**. The ^1H NMR spectrum exhibits peaks at δ 5.29 and 5.76 (ratio 2:1) attributable to the pyrazolyl ring protons, and four methyl peaks at δ 1.79, 1.94, 2.27 and 2.51 (ratio 3:6:6:3) consistent with inequivalent pyrazole rings in the ratio 2:1. The X-ray analysis of **5**, shown in Fig. 4, reveals the molybdenum centre to have a distorted octahedral geometry with a conventional *fac* co-ordination for the Tp′ ligand, the other sites being occupied by a pair of isodiazene ligands and a chloride ion. All the co-ordination distances are unexceptional (Table 4), and there is the anticipated enlargement of the angle between the *cis*-co-ordinated isodiazene moieties [N(1)–Mo–N(3) 105.8(2)°]. The geometries of these two ligands are essentially the same as those observed for **2**, **3** and **4**, with again a retention of near coplanarity of both sets of N–Ph bonds with their associated equatorial co-ordination plane. There are no notable intermolecular contacts. The structure of the related complex $[MoTp(NNPh_2)_2Cl]$ (Tp = hydrotris(pyrazolyl)borate) has been described,[8] and the bond lengths and angles are similar to those of **5**.

Conclusion

Attempts to alkylate isodiazene complexes such as $[MoCl_2(NNPh_2)_2(dme)]$ under analogous conditions to those used for $[MoCl_2(NBu^t)_2(dme)]$ were unsuccessful. The precise reasons for this are unclear, but the comparative inertness of the halides in the bis(isodiazene) complexes would be consistent with a lower formal oxidation state. DFT Calculations on isodiazene complexes have suggested an overall charge on the ligand closer to 1− than 2−, in accordance with the recently reported calculations of Carrillo and co-workers.[8] The bond lengths within the $M–N–NR_2$ systems were very similar to those observed previously with complexes of this type, and provide little direct information on formal metal oxidation state.

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‡ The reaction corresponds to the transfer of all the hydrogens on $2R_2NNH_2{\cdot}HCl$ with loss of 2 equivalents of alkane and 1 of Bu^tNH_2 per molybdenum.

Table 5 Crystal data, data collection and refinement parameters[a] for compounds **2**–**5**

	2	**3**	**4**	**5**
Formula	$C_{36}H_{30}F_6MoN_6O_6S_2$	$C_{46}H_{37}ClF_3MoN_3O_5S$	$C_{56}H_{62}Cl_4Mo_2N_{10}$	$C_{39}H_{42}BClMoN_{10}$
Formula weight	916.7	1059.6	1208.8	793.0
Space group, number	Ia, 9[b]	$P\bar{1}$, 2	$P2_1/n$, 14	$P2_1/n$, 14
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
T/K	293	223	293	291
a/Å	18.874(1)	12.900(2)	10.609(1)	15.56(1)
b/Å	10.753(1)	14.588(3)	18.777(2)	13.67(1)
c/Å	19.600(1)	14.795(3)	14.606(1)	18.86(1)
α/°	—	119.41(2)	—	—
β/°	97.97(1)	91.32(1)	106.57(1)	105.09(3)
γ/°	—	95.50(2)	—	—
V/Å^3	3939.7(3)	2406.4(8)	2788.8(4)	3871(9)
Z	4	2	2[c]	4
D_c/g cm^{-3}	1.546	1.462	1.440	1.360
F(000)	1856	1078	1240	1640
μ/mm^{-1}	4.43	0.60	5.81	0.44
No. unique reflections				
measured	3332	5708	4621	7065
observed	3009[d]	4210[d]	3289[d]	5027[e]
No. of variables	491	514	286	469
$R1$	0.046	0.063	0.059	0.049
$wR2$	0.113	0.149	0.133	0.081

[a] Detail in common: graphite monochromated radiation. [b] I-Centered cell used as C-centered cell has $\beta = 129.8°$. [c] The molecule has crystallographic C_i symmetry. $|I_o| > 2\sigma(|I_o|)$. [e] $|I_o| > 3\sigma(|I_o|)$

Experimental

General

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Imperial College. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (^{1}H), 75.0 (^{13}C) and 376.3 MHz (^{19}F); chemical shifts are referenced to the residual protio impurity of the deuteriated solvent. The IR spectra (Nujol mulls, KBr windows) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. The starting materials $[MoCl_2(NNPh_2)_2(dme)]$ **1**,[1] and $[Mo(CH_2Ph)_2(NBu^t)_2]$[9] were prepared as described in the literature. The ligand H_2L was prepared by the previously published procedure.[6b] All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparations

$[Mo(OTf)_2(NNPh_2)_2(py)_2]$ 2. Compound **1** (1.1 g, 1.77 mmol) and silver triflate (0.92 g, 3.58 mmol) in MeCN (40 cm^3) were stirred for 4 h. After filtration and removal of volatiles the residue was redissolved in CH_2Cl_2 (30 cm^3) and pyridine (0.29 cm^3, 3.58 mmol) added. At this stage the flask was wrapped in foil. Stirring was continued for 12 h and after filtering a diethyl ether layer was added and left to diffuse for 2–3 d affording **2** as large golden prisms. Yield 0.96 g, 59%. Found: C, 45.3; H, 3.1; N, 7.9. $C_{36}H_{30}F_6MoN_6O_6S_2\cdot CH_2Cl_2$ requires C, 44.4; H, 3.2; N, 8.4%. IR: 2359w, 1608m, 1588s, 1345s, 1323s, 1205s, 1152s, 1069s, 1023s, 920m, 833m, 804m, 751s, 692s, 632s, 558s, 497m, 446m and 425s cm^{-1}. ^{1}H NMR (CH_2Cl_2): δ 8.71 (d, 4 H, $^4J_{HH} = 5.2$ Hz, o-H of C_5H_5N) and 8.42–6.91 (multiplets, 26H, aryl H and m-, p-H of C_5H_5N). ^{19}F NMR ($CDCl_3$): δ −78.5.

$[Mo(NNPh_2)_2(bipy)_2]^{2+}$. Compound **1** (1.4 g, 2.25 mmol) and bipy (0.35 g, 2.24 mmol) were stirred in CH_2Cl_2 (30 cm^3) for 4 h. After removal of volatiles, silver triflate (1.16 g, 4.51 mmol) and MeCN (40 cm^3) were added. After stirring for 12 h, bipy (0.35 g, 2.24 mmol) was added and stirring continued for 3 h. The volatiles were removed *in vacuo* to afford an orange-red oily solid to which $[Bu^n{}_4N]PF_6$ (1.8 g, 4.65 mmol) in MeOH (30 cm^3) was added. After 5 min stirring, the suspension was filtered and the mother-liquor cooled (−20 °C) to afford red cubes. The remaining solid was redissolved in warm MeOH (*ca.* 40 cm^3) and left to stand at ambient temperature for 2–3 d affording a further crop of orange-red cubes. Overall yield 1.9 g, 80%. Found: C, 49.6; H, 3.4; N, 10.4. $C_{44}H_{36}F_{12}MoN_8P_2$ requires C, 49.7; H, 3.4; N, 10.5%. ^{1}H NMR (CD_3CN): δ 9.2 (dd, 2 H, α-H_{bipy}), 8.66 (d, 2 H, α′-H_{bipy}), 8.48 (m, 4 H, β-H_{bipy}), 8.07–7.96 (m, 4 H, β-H_{bipy}) and 7.23–7.06 (overlapping br m[20H, aryl H] + m[4 H, γ-H_{bipy}]).

$[MoCl(OTf)(NNPh_2)(L)]$ 3. **1** (1.0 g, 1.61 mmol) and silver triflate (0.82 g, 3.2 mmol) in MeCN (40 cm^3) were stirred for 4 h. After filtration and removal of volatiles, the residue was redissolved in CH_2Cl_2 (30 cm^3) and H_2L (0.76 g, 1.61 mmol) was added. Stirring was continued for 12 h and after filtering a diethyl ether layer was added and left to diffuse for 2–3 d affording **3** as green needles. Yield 0.96 g, 64%. Found: C, 58.6; H, 3.9; N, 4.4. $C_{46}H_{37}ClF_3MoN_3O_5S$ requires C, 59.2; H, 4.0; N, 4.5%. IR: 2363w, 1951w, 1716w, 1605w, 1590m, 1574w, 1332s, 1262s, 1234s, 1199s, 1125m, 1093m, 1063s, 1022s, 991s, 946s, 920s, 877m, 843m, 817m, 787m, 775m, 761m, 750s, 702s, 676m, 633m, 609m, 601w, 584w, 561w, 528w, 513w, 489w, 459w and 436w cm^{-1}. ^{1}H NMR (acetone-d$_6$): δ 4.15 (s, 4 H, CH_2) and 6.78–7.81 (overlapping multiplets, 33 H, aryl H). ^{19}F NMR (acetone-d$_6$): δ −78.0.

$\{MoCl(NNPh_2)_2(\mu\text{-}Cl)(NH_2Bu^t)\}_2]$ 4. The compound $[Mo(CH_2CMe_2Ph)_2(NBu^t)_2]$ (3.5 g, 6.95 mmol) and $Ph_2NNH_2\cdot HCl$ (3.1 g, 14.03 mmol) were combined in a dry-box. Then dme (80 cm^3) was added and the system refluxed for 12 h affording an orange-brown solution. After removal of volatiles, the residue was extracted into toluene–pentane (1:2) and cooled to give large brown prisms. Yield 3.1 g, 74%. Found: C, 55.8; H, 5.2; N, 12.5. $C_{28}H_{31}Cl_2MoN_5$ requires C, 55.6; H, 5.2; N, 11.6%. IR: 3289w, 3179w, 1586m, 1340m, 1301m, 1261s, 1207m, 1159m, 1094s, 1025s, 929w, 895w, 801s, 748m, 689m, 629m, 543w, 474w and 455w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 18 H, $(CH_3)_3C$), 4.13 (d, 4 H, NH_2) and 6.75–8.17 (overlapping multiplets, 40 H, aryl H).

[MoTp′Cl(NNPh$_2$)$_2$] 5. Tetrahydrofuran (20 cm^3) was added to compound **1** (1.0 g, 1.61 mmol) and KTp′ (0.54 g, 1.61 mmol) in a thick-walled 'rotaflo' ampoule. After refluxing for 12 h the volatiles were removed *in vacuo* and the residue was extracted with hot MeCN (25 cm^3) affording on-cooling red-brown crystals of **5**. Yield 0.41 g, 35% (isolated yield). Found: C, 58.8; H, 5.2; N, 17.7. $C_{39}H_{42}BClMoN_{10}$ requires C, 59.1; H, 5.2; N, 17.7%. IR: 2360m, 2342m, 1588w, 1542w, 1289m, 1261s, 1208w, 1155w, 1093s, 1022s, 800s, 757w, 723w and 693w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.79 (s, 3 H, pz CH$_3$), 1.94 (s, 6 H, pz CH$_3$), 2.27 (s, 6 H, pz CH$_3$), 2.51 (s, 3 H, pz CH$_3$), 5.29 (s, 2 H, pz CH), 5.76 (s, 1 H, pz CH), 6.79 and 6.94 (2 × br s, 20 H, aryl H). ^{13}C-{^{1}H} NMR (CDCl$_3$) : chemically inequivalent pyrazol rings A and B (ratio 2 : 1), δ 12.5(A)/13.0(B) (5-CH$_3$), 14.5(B)/15.1(A) (3-CH$_3$), 29.7 (CH$_2$), 106.5(A)/106.6(B) (C-4), 119.6, 121.7, 122.0, 125.3, 128.7, 128.9, 129.1, 129.2 (aryls), 142.5(A)/143.9(B) (C-3) and 151.4(A)/152.9(B) (C-5).

X-Ray crystallography

A summary of the crystal data, data collection and refinement parameters for compounds **2**–**5** is given in Table 5. Data were collected on Siemens P4 diffractometers using ω–scans. Structures were solved by the heavy atom method. All the major occupancy non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 for **2**–**4** [16] but on F for **5**.[11] The crystals of **4** were found to contain full and partial occupancy dichloromethane solvent molecules distributed over multiple sites; only the major occupancy atoms were refined anisotropically. In **3** both of the O_3SCF_3 groups exhibited rotational disorder about the S–C bonds, with the fluorine atoms occupying both the staggered (75%) and eclipsed (25%) conformations; only the major occupancy fluorine atoms were refined anisotropically. In **3**–**5** the pendant phenyl rings were refined as idealized rigid bodies. The C–H hydrogen atoms in all of the complexes were placed in calculated positions, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ [$U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C–Me/N})$] for **2**–**4**, and $1.3U_{\mathrm{eq}}(\mathrm{C})$ for **5**, and allowed to ride on their parent atoms. The N–H hydrogen atoms in **4** were located from a ΔF map and refined subject to a distance constraint (0.90 Å). The polarity of **3** was unambiguously determined by both an R-factor test ($R^+ = 0.046$, $R^- = 0.052$) and by use of the Flack parameter, which refined to a value of $-0.01(2)$.

CCDC reference number 186/1539.

See http://www.rsc.org/suppdata/dt/1999/2695/ for crystallographic files in .cif format.

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