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Transition metal derivatives of arenediazonium ions

XVI *. The synthesis, structural characterisation and chemical behaviour of (η -cyclopentadienyl)bis(arenediazo)-(triphenylphosphine)molybdenum(0) cations: versatile reagents for the synthesis of complexes containing the $[\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{R}^1)(\text{N}_2\text{C}_6\text{H}_4\text{R}^2)]^{2+}$ fragment

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Abstract

Procedures are described for the preparation of a series of cationic bis(arenediazo) complexes of general formula $[(\eta\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{R}^1)(\text{N}_2\text{C}_6\text{H}_4\text{R}^2)(\text{PPh}_3)]^+$ (VII). Although salts of VII are indefinitely stable in the solid state, they are highly labile in solution and either the phosphine ligand alone or both phosphine and cyclopentadienyl ligands can be displaced by a variety of donor species to yield new kinds of neutral, anionic or cationic bis(arenediazo) complexes. The complex $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)(\text{PPh}_3)]\text{PF}_6$, [VIIIf] PF_6 and its neutral precursor $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)(\text{PPh}_3)$ (VIII) have been characterised by X-ray crystallographic methods. Crystals of [VIIIf] PF_6 are triclinic, space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 13.031(4)$, $b = 14.413(4)$, $c = 11.140(5)$ Å and $\alpha = 93.17(3)$, $\beta = 104.73(3)$, and $\gamma = 115.77(3)^\circ$. Crystals of VIII are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 11.549(2)$, $b = 8.881(4)$, $c = 26.197(11)$ Å and $\beta = 91.27(2)^\circ$. Both structures were determined by the heavy-atom method and refined to final R values of 0.0421 (for 4090 observed reflections, [VIIIf] PF_6) and 0.0323 (for 3081

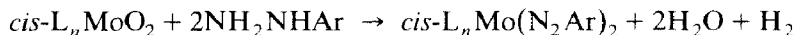
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observed reflections, VIII). The arenediazo ligands in both complexes are bonded to Mo in the "singly-bent" coordination mode with Mo–N 1.838(4), 1.840(4) Å and N–N 1.211(6), 1.196 Å in [VII]PF₆ and Mo–N 1.820(3) and N–N 1.244(4) Å in VIII.

Introduction

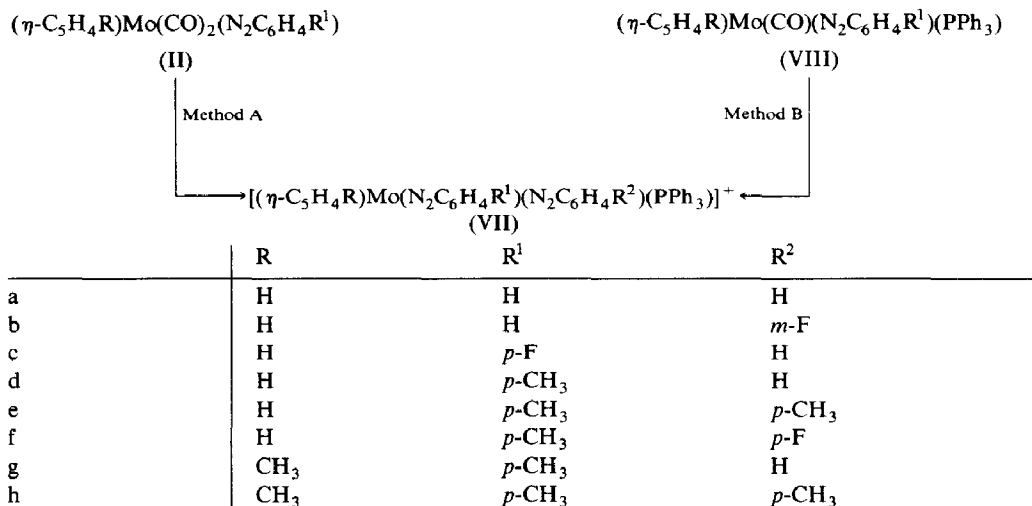
Because of the close structural and electronic relationship that exists between the nitrosonium and diazonium cations, the three molecular fragments *cis*-[M(NO)₂]²⁺, *cis*-[M(NO)(N₂Ar)]²⁺ and *cis*-[M(N₂Ar)₂]²⁺ (M = Cr, Mo, W) form an isoelectronic and quasi-isostructural homologous series. The first member of the series has been characterised in a wide range of coordination environments [1] and we have described complexes containing the second member of the series in a recent communication [2]. The chemically interesting [3] *cis*-bis(arenediazo)molybdenum fragment *cis*-[Mo(N₂Ar)₂]²⁺ may be generated by a formal condensation and redox reaction between monoarylhydrazines and *cis*-dioxomolybdenum complexes.



Originally described by Chatt et al. [4], this reaction has been elegantly exploited by Zubietta and co-workers for the synthesis of mono- and di-nuclear *cis*-bis(arenediazo) complexes with a variety of co-ligands [3,5,6] as well as tetra-, hexa- and octa-nuclear polyoxomolybdates containing one or more *cis*-bis(arenediazo)molybdenum(0) units [3,7]. We present here details of an alternative and complementary synthetic procedure for the preparation of complexes containing the *cis*-bis[Mo(N₂Ar)₂]²⁺ fragment. Some of the results described here have been published in preliminary form [8].

Results and discussion

Our interest in bis(arenediazo) complexes of molybdenum stems from our discovery that a complex of this type, namely (η-C₅H₄CH₃)MoCl(N₂C₆H₄F-*p*)₂ (I) is formed in low yield along with the main product (η-C₅H₄CH₃)Mo(CO)₂(N₂C₆H₄F-*p*) (II) when Na[(η-C₅H₄CH₃)Mo(CO)₃] is treated with one equivalent of [*p*-FC₆H₄N₂]BF₄ in tetrahydrofuran (THF) at –78°C followed by a work-up employing CH₂Cl₂ as solvent [9]. Suspecting that reaction of II with arenediazonium cation was a key step in the formation of I, we investigated the reaction of complexes of the general type (η-C₅H₄R)Mo(CO)₂(N₂C₆H₄R¹) (III) with equimolar quantities of [R²C₆H₄N₂]BF₄ under similar conditions in the expectation of isolating the cationic bis(arenediazo) complexes [(η-C₅H₄R)Mo(N₂C₆H₄R¹)(N₂C₆H₄R²)(L)]⁺ (IV, L = CO or THF) and developing a general synthesis of molybdenum bis(arenediazo) complexes. Although IV is almost certainly formed at low temperatures in these reactions (see below), work-up at room temperature produced only intractable CO-free materials. These results parallel our earlier inability to isolate the cationic nitrosyl-arenediazo complexes [(η-C₅H₅)Mo(N₂C₆H₄R)(CO)]⁺ (V) [2] so that of the isoelectronic and isostructural series composed of IV, V and [(η-C₅H₅)Mo(NO)₂(CO)] (VI), only the latter is isolable at room temperature [10]. This is an unexpected result since the stronger π-acceptor char-



Scheme 1. Method A: $[\text{R}^2\text{C}_6\text{H}_4\text{N}_2]^+$ at -75°C , PPh_3 at -35°C . Method B: $[\text{R}^2\text{C}_6\text{H}_4\text{N}_2]^+$ at -75°C .

acter of $[\text{NO}]^+$ vis-a-vis $[\text{ArN}_2]^+$ would lead one to predict lability of the CO ligand in the sequence $\text{VI} > \text{V} > \text{IV}$ rather than – as appears to be the case – the reverse.

That a complex of type IV is indeed formed at low temperatures is indicated by the fact that addition of triphenylphosphine to the reaction mixture at -35°C followed by work-up at room temperature allows isolation of an analogous species $[(\eta\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{R}^1)(\text{N}_2\text{C}_6\text{H}_4\text{R}^2)(\text{PPh}_3)]^+$ (VII) in which the CO (or solvent molecule) in IV has been replaced by triphenylphosphine (Method A, Scheme 1). These complexes could also be prepared by treating the phosphine-substituted arenediazo complexes $(\eta\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{R}^1)(\text{PPh}_3)$ (VIII) with the appropriate arenediazonium salt in THF at -75°C (Method B, Scheme 1). While the “one-pot” nature of method A has the advantage of convenience we have experienced some difficulty in purifying the products prepared by this route; possibly due to contaminants produced by competing reaction between $[\text{R}^2\text{C}_6\text{H}_4\text{N}_2]^+$ and PPh_3 . Consequently, Method II is the preferred route to complexes of type VII. In the hope of extending this synthesis of cationic bis(arenediazo) complexes to molybdenum substrates other than those containing the coordinated cyclopentadienide anion, we investigated the reactions of the hydrotris(1-pyrazolyl)borate complexes $\text{HBpz}_3\text{Mo}(\text{CO})_2(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)$ (IX) and $\text{HBpz}_3\text{Mo}(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)(\text{PPh}_3)$ (X) (pz = 1-pyrazolyl) with $[p\text{-CH}_3\text{C}_6\text{H}_4\text{N}_2]^+$. Rather surprisingly, since it possesses a potentially more electron-rich molybdenum atom than does the analogous cyclopentadienide complex II, no reaction took place with IX. While X did react, the properties of the unstable green monocarbonyl cation which resulted indicate that it is to be formulated as the 17-electron oxidation product $[\text{HBpz}_3\text{Mo}(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)(\text{PPh}_3)]^+$ (XI) analogous to the known isoelectronic cationic nitrosyl complex $[\text{HB}(3,5\text{-Me}_2\text{pz})_3\text{Mo}(\text{NO})(\text{CH}_3\text{CN})_2]^+$ (XII, 3,5-Me₂pz $\equiv$ 3,5-dimethyl-1-pyrazolyl) [11]. The origin of the contrasting behaviour of analogous η -cyclopentadienyl and poly-1-pyrazolylborato complexes is not entirely clear but seems likely to include steric inhibition of attack at the metal centre in the latter and/or destabilisation of intermediate 7-coordinate diazonium-substrate adducts.

The BF_4^- and PF_6^- salts of the new cationic bis(arenediazo) complexes VII are intensely purple microcrystalline solids which appear to be indefinitely stable in the normal laboratory atmosphere and moderately stable in solution in non-halogenated solvents so long as air is excluded. Microanalytical and IR data are in Table 1 and ^1H NMR data are in the experimental section. In accord with the evident stability of the cations, the complexes of type VII are formulated as "three-legged piano-stool" species in which both arenediazo ligands adopt the singly-bent coordination mode. This is established by our X-ray crystallographic study of VIIf (see below). Isotopic labelling of VIIa with ^{15}N at the molybdenum-coordinated nitrogen (i.e. N_α) in one or both arenediazo ligands (Table 1) identified three IR bands in the $1500\text{--}1660\text{ cm}^{-1}$ region which are associated with the *cis*-bis(arenediazo) N–N stretching vibration and revealed the vibrational coupling with skeletal vibrations of the arene ring which is common for arenediazo ligands in the singly-bent coordination mode [12,13]. The ^1H NMR spectra show no unusual features and are similar to those of the bis(nitrosyl) analogues $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})_2(\text{L})]^+$ (XIII, $\text{L} = \text{PPh}_3$ etc.) (but unlike the nitrosyl-arenediazo cations $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{N}_2\text{Ar})(\text{PPh}_3)]^+$ (XIV) in showing long-range coupling between the cyclopentadienide protons and the phosphine phosphorus nucleus ($^3J(\text{H-P}) = 1.2\text{ Hz}$) [2,10]. The ^{19}F NMR spectra of VIIb and VIIc have been discussed elsewhere [12]. Although the nitrosyl-arenediazo cation (XIV) reacts readily with various nucleophiles, we have had only limited success in characterising the products [2]. The bis(arenediazo) cations VII are similarly reactive but here clean displacement of phosphine or phosphine and cyclopentadienide ligands is observed, leading to the wide range of new bis(arenediazo) complexes summarised in Scheme 2. Careful treatment of VIId with a slight excess of $[\text{PPN}]\text{X}$ ($\text{PPN}^+ = \mu\text{-nitrido-bis(triphenylphosphonium)}$ cation, $\text{X} = \text{Cl, Br, CN}$) or $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]\text{I}$ selectively displaced the phosphine ligands to produce the bright red neutral halo- and cyano-complexes of the type $(\eta\text{-C}_5\text{H}_5)\text{MoX}(\text{N}_2\text{C}_6\text{H}_4\text{-CH}_3\text{-}p)$ (XV) which are closely related to the structurally characterised [9] chloro-complex I and are assumed to have similar "three-legged piano-stool" structures. The IR spectra of the complexes of type XV (Table 1) show two strong bands in the $1500\text{--}1620\text{ cm}^{-1}$ which are assigned to $\nu(\text{NN})$ although this conclusion can only be tentative in the absence of ^{15}N labelling studies. The cationic complexes VII also reacted rapidly with NO_3^- , N_3^- and NCO^- as evidence by an instantaneous purple to red colour change when solutions of VII were treated with the appropriate $[\text{PPN}]^+$ salt. Displacement of the phosphine ligand was confirmed by the absence of coupling to phosphorus in the cyclopentadienyl resonances of the crude products but work-up yielded no characterisable materials.

We extended the chemistry described above to a study of the reactions of the cations of type VII with the diethyldithiocarbamate anion $((\text{C}_2\text{H}_5)_2\text{NCS}_2^-, \text{dtc}^-)$ in the hope that the bidentate nature of the nucleophile would produce a complex (i.e. XX, Fig. 1) in which one of the arenediazo ligands would be forced into the (unknown for Mo) doubly-bent coordination mode. While complexes of type XX may well be formed as transient species, treatment of VII with one equivalent of $\text{Na}[\text{dtc}]$ resulted in displacement of phosphine and cyclopentadienide ligands and led only to formation of the purple bis(dithiocarbamate) complexes XVI in low yield (Scheme 2). Yields of XVI were improved by employing a 2/1 ratio of dithiocarbamate to complex VII. Complexes of type XVI had previously been isolated from the reaction of $(\text{dtc})_2\text{MoO}_2$ with two equivalents of arylhydrazine [4],

Table 1

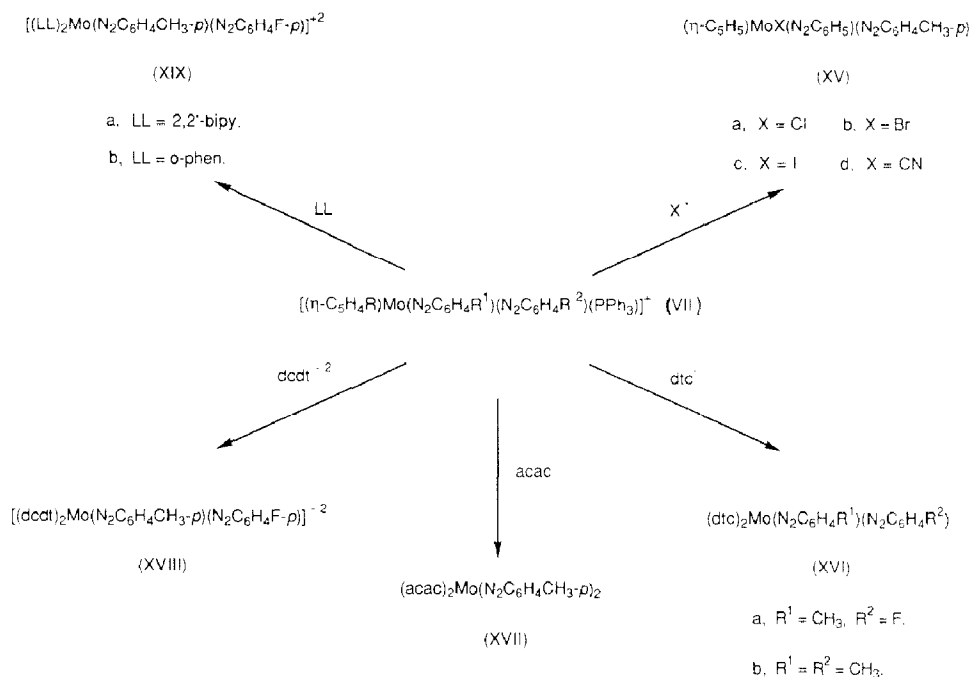
Infrared ^a and microanalytical data

Complex	$\nu(\text{NN})$ (cm ⁻¹)	Analysis (Found (calc.) (%))		
		C	H	N
VIIa ^{b,c}	1655m 1621s 1547s	58.61 (58.36)	4.07 (4.20)	7.53 (7.77)
VIIb ^b	1651m 1622s 1546s	57.29 (56.93)	4.33 (3.96)	7.35 (7.59)
VIIc ^b	1650m 1618s 1553s	56.77 (56.93)	4.31 (3.96)	7.69 (7.59)
VIIId ^b	1653m 1622s 1555s	59.32 (58.88)	4.85 (4.39)	7.49 (7.63)
VIIe ^b	1651m 1623s 1563s	59.37 (59.38)	4.97 (4.56)	7.37 (7.49)
VIIIf ^b	1647s 1651s 1561s	57.29 (57.46)	4.00 (4.15)	7.69 (7.45)
VIIIf ^d		53.87 (53.35)	4.31 (3.85)	7.37 (6.91)
VIIg ^b	1653m 1624s 1555s	59.02 (59.38)	4.39 (4.56)	7.57 (7.49)
VIIh ^b	1652m 1624s 1567s	60.14 (59.86)	5.09 (4.76)	7.03 (7.35)
XI ^b	1505m 1480m ^{e,f}	51.79 (52.21)	4.44 (4.00)	13.72 (13.92)
XVa ^g	1610s 1520s ^e	51.49 (51.38)	4.37 (4.07)	13.41 (13.32)
XVb ^h	1604s 1622s ^e	46.77 (46.47)	3.92 (3.68)	11.85 (12.04)
XVc	1610s 1524s ^e	42.53 (42.21)	3.59 (3.34)	10.63 (10.94)
XVd	1614s 1535s ^e	55.50 (55.48)	4.31 (4.16)	16.91 (17.02)
XVIa ⁱ	<i>j</i>	43.15 (43.52)	4.47 (4.92)	13.68 (13.14)
XVIb ^k	<i>j</i>	45.30 (45.70)	5.56 (5.43)	13.07 (13.32)
XVII	<i>j</i>	54.17 (54.14)	5.68 (5.30)	10.91 (10.52)
XVIII ^b	<i>j</i>	66.25 (65.87)	4.57 (4.22)	8.03 (8.26)
XIXa ^b	<i>j</i>	48.17 (48.09)	3.62 (3.30)	13.15 (13.60)
XIXb ^b	<i>j</i>	51.23 (50.95)	3.48 (3.12)	13.07 (12.85)

^a In CH₂Cl₂ solution, s = strong, m = medium, sh = shoulder. ^b BF₄⁻ salt. ^c ¹⁵N labelling at one N_α atom shifts these bands to 1645m, 1612s and 1536s. With both N_α atoms labelled the bands are at 1627m, sh, 1610s and 1531s. ^d PF₆⁻ salt. ^e Tentative assignment. ^f $\nu(\text{CO})$ 1990s cm⁻¹. ^g Cl, 8.46 (8.42)%. ^h Br, 17.28 (17.17)%. ⁱ S, 20.64 (20.20)%. ^j Not assigned-see text. ^k S, 20.59 (20.33)%. ^l s, 7.31 (7.56)%.

a reaction which – unlike that described above – necessitates that both arendiazo ligands be identical.

That the replacement of the 2-electron donor triphenylphosphine together with the 6-electron donor cyclopentadienide anion in VII by a pair of 4-electron donating



Scheme 2.

bidentate ligands is a general process is illustrated by the reactions with the 2,4-pentanedionato anion ($acac^-$), the 1,1-dicyano-2,2-dithiolate dianion ($ddct^{2-}$) and with 2,2'-bipyridyl or *o*-phenanthroline (bipy and *o*-phen respectively) which are summarized in Scheme 2. By this means, new neutral (XVII), dianionic (XVIII) and dicationic (XIX) bis(arenediazo)molybdenum complexes have been isolated in moderate yield. Complexes XVII–XIX are dark, reddish-brown air-stable solids. The ionic species XVIII and XIX were isolated as their salts with $[PPN]^+$ and $[BF_4]^-$ respectively. Rapid colour changes indicate that VII reacts also with a variety of other polydentate ligands, among them $[p-CH_3C_6H_4N=NNC_6H_4CH_3-p]^-$, $[H_2Bpz_2]^-$ and $[HBpz_3]^-$. Only in the case of the latter reagent could a characterisable product be isolated and its structure has been described by us elsewhere [14]. In view of its general lability we were surprised to find that VII did not react with

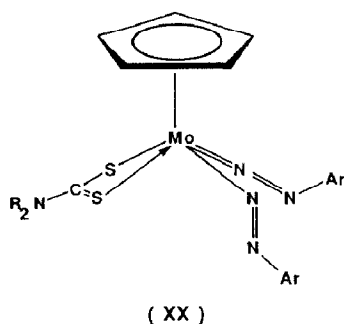


Fig. 1.

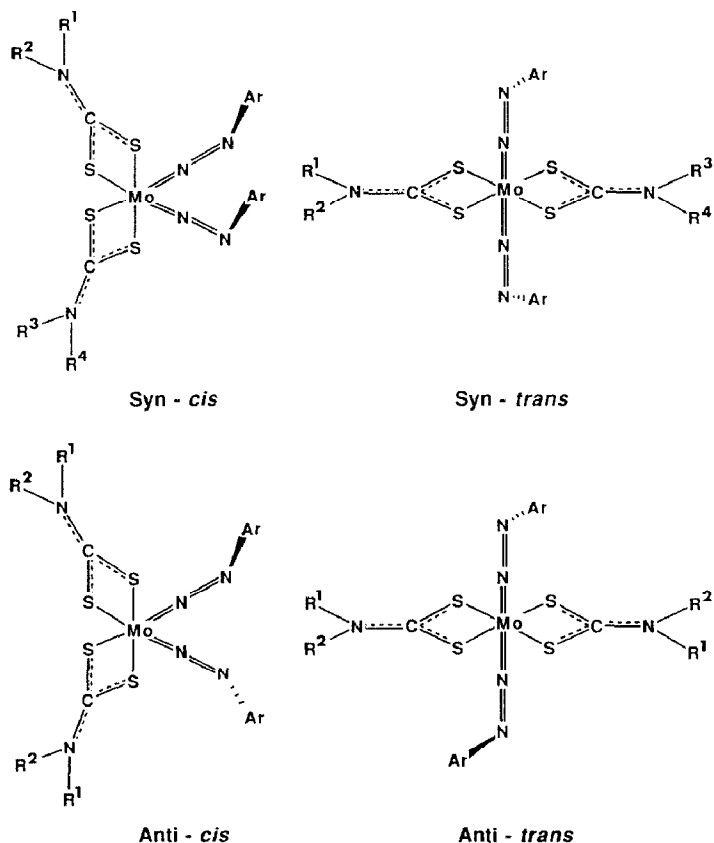


Fig. 3.

The angular $N_{\alpha}-N_{\beta}-C$ fragment of the latter will lie in, or close to, a plane containing N_{α} , the metal atom and three meridional co-ligands of the octahedral coordination sphere [19]. In bis(arenediazo) complexes, the bending of the two ligands may be in the same (*syn*) or opposite (*anti*) directions and one or other of these conformations has been observed in all the structurally characterised examples [3,5-7,9,20]. In addition there is a single example, the complex $[(\text{acac})\text{Mo}(\text{OCH}_3)(\text{N}_2\text{C}_6\text{H}_5)_2]_2$, in which both *syn* and *anti* isomers have been separately isolated and crystallographically characterised [21]. An additional feature of interest of the latter compound is the ^1H NMR spectrum which indicates that in solution the isomers undergo rapid *syn-anti* interconversion at room temperature. As illustrated in Fig. 3, four isomers must be considered for the bis(diethyldithiocarbamato)bis(arenediazo) complexes XVI and in *none* of them are all the dithiocarbamate alkyl groups equivalent. The *anti-cis* and *anti-trans* isomers have two different alkyl environments whereas all four alkyl groups are inequivalent in the *syn-cis* and *syn-trans* structures. That two (rather than four) sets of ethyl resonances are observed in the ^1H NMR spectrum of XVIb (Experimental section) rules out rigid *syn* structures but does not allow us to distinguish between *anti-cis* and *anti-trans* isomers. Neither can we rule out stereochemical non-rigidity involving rapid *syn-anti* interconversion. The ^1H NMR spectrum of the bis(nitrosyl) complex $[(\text{CH}_3)_2\text{NCS}_2]_2\text{Mo}(\text{NO})_2$ shows a reversible temperature dependence and at ca. 150°C the methyl

Although crystallographically useful crystals of the complexes XVI–XIX could not be obtained, we were more successful with the key cationic precursor $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)(\text{PPh}_3)]\text{PF}_6$, [VIIIf] PF_6 , and with the neutral monoarenediazo complex from which VIIIf is derived, $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{-CH}_3\text{-}p)(\text{PPh}_3)$ (VIII). Stereoscopic views of the molecular structures of [VIIIf] PF_6 and VIII, together with the crystallographic numbering schemes, are shown in Figs. 4 and 5 respectively. Crystal and refinement data are in Table 2 while final fractional coordinates and details of the molecular geometry for [VIIIf] PF_6 are in Tables 3 and 4 and Tables 5 and 6 for VIII.

Crystals of the [VIIf]PF₆ complex contain discrete cations and anions separated by normal Van der Waals distances. The coordination about Mo is formally octahedral with the cyclopentadienide ligand occupying three facial sites and the remaining positions taken up by the two arenediazo ligands and the triphenylphos-

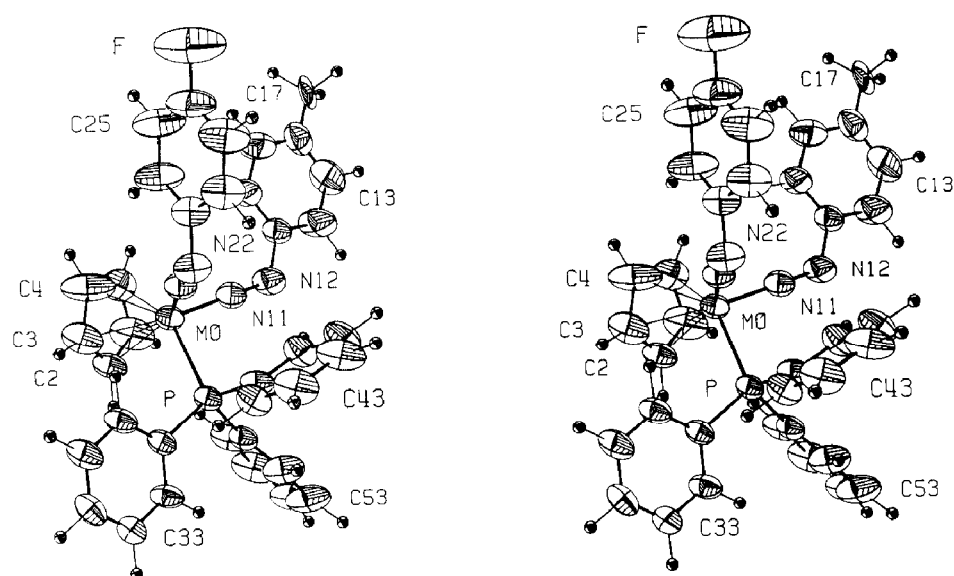


Fig. 4. A stereoview of [VIIIf] with our numbering scheme. Ellipsoids are at the 50% level.

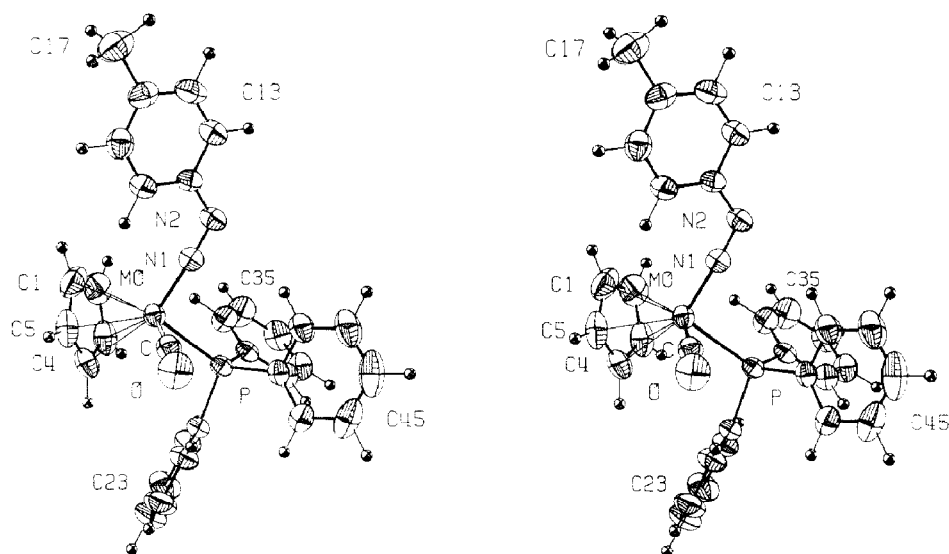


Fig. 5. A stereoview of [VIII] with our numbering scheme. Ellipsoids are at the 50% level.

phine ligand. The two arenediazo ligands are bound to molybdenum in the “singly-bent” coordination mode (Mo–N(11)–N(12) 175.9(4), N(11)–N(12)–C(11) 123.0(4); Mo–N(21)–N(22) 173.2(4), N(21)–N(22)–C(21) 122.9(4)°) and adopt a *syn* config-

Table 2

Crystal and refinement data for [VIII]PF₆ and VIII

	[VIII]PF ₆	VIII
Formula	C ₃₆ H ₃₁ F ₇ MoN ₄ P ₂	C ₃₁ H ₂₇ MoN ₂ OP
F.W.	810.6	570.5
Crystal class	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal dimensions (mm)	0.16 × 0.21 × 0.56	0.08 × 0.18 × 0.20
<i>a</i> (Å)	13.031(4)	11.549(2)
<i>b</i> (Å)	14.413(4)	8.881(4)
<i>c</i> (Å)	11.140(5)	26.197(11)
α (°)	93.17(3)	
β (°)	104.73(3)	91.27(2)
γ (°)	115.77(3)	
<i>V</i> (Å ³)	1789(3)	2686(3)
<i>D_c</i> (g cm ⁻³)	1.51	1.41
<i>Z</i>	2	4
<i>F</i> (000)	820	1168
μ (cm ⁻¹)	5.1	5.6
Total number of independent reflections	4976	3960
Number of reflections with <i>I</i> > 3σ(<i>I</i>)	4090	3081
2θ _{max} (°)	46	47
Final <i>R</i>	0.0421	0.0323
Final <i>R_w</i>	0.0441	0.0351

Table 3

Final fractional coordinates for [VII_f]·PF₆

Atom	x	y	z
Mo	0.38695(4)	0.23407(3)	0.18131(4)
N(11)	0.4746(3)	0.2354(3)	0.0747(4)
N(12)	0.5279(4)	0.2392(3)	0.0006(4)
N(21)	0.5022(3)	0.2379(3)	0.3198(4)
N(22)	0.5744(4)	0.2297(3)	0.4057(4)
C(11)	0.6307(4)	0.3327(4)	−0.0019(5)
C(12)	0.6718(5)	0.3296(4)	−0.1026(6)
C(13)	0.7707(6)	0.4151(5)	−0.1111(6)
C(14)	0.8293(5)	0.5030(4)	−0.0189(6)
C(15)	0.7867(5)	0.5048(4)	0.0827(6)
C(16)	0.6857(5)	0.4192(4)	0.0899(5)
C(17)	0.9328(5)	0.5938(4)	−0.0222(7)
C(21)	0.6875(4)	0.3153(4)	0.4732(5)
C(22)	0.7764(5)	0.2915(4)	0.5359(5)
C(23)	0.8883(5)	0.3699(5)	0.6019(6)
C(24)	0.9081(5)	0.4706(5)	0.6059(6)
C(25)	0.8220(6)	0.4970(5)	0.5461(6)
C(26)	0.7100(5)	0.4183(4)	0.4777(6)
F(1)	1.0219(4)	0.5538(4)	0.6755(5)
P(1)	0.29008(10)	0.03946(9)	0.15631(11)
C(31)	0.1847(4)	−0.0151(3)	0.2453(4)
C(32)	0.0834(4)	−0.1113(4)	0.2005(5)
C(33)	0.0109(4)	−0.1532(4)	0.2756(5)
C(34)	0.0400(4)	−0.0993(4)	0.3953(5)
C(35)	0.1402(4)	−0.0033(4)	0.4404(5)
C(36)	0.2128(4)	0.0389(4)	0.3656(4)
C(41)	0.4038(4)	−0.0009(3)	0.2177(4)
C(42)	0.4049(4)	−0.0541(4)	0.3172(5)
C(43)	0.4929(5)	−0.0840(4)	0.3589(5)
C(44)	0.5811(5)	−0.0603(4)	0.3027(5)
C(45)	0.5825(5)	−0.0068(4)	0.2053(5)
C(46)	0.4942(4)	0.0237(4)	0.1625(5)
C(51)	0.2107(4)	−0.0381(4)	−0.0035(4)
C(52)	0.2029(5)	−0.1359(4)	−0.0303(5)
C(53)	0.1407(6)	−0.1961(4)	−0.1510(5)
C(54)	0.0855(5)	−0.1579(5)	−0.2433(5)
C(55)	0.0941(5)	−0.0610(5)	−0.2174(5)
C(56)	0.1572(4)	−0.0005(4)	−0.0977(5)
C(1)	0.2588(5)	0.2880(5)	0.0510(5)
C(2)	0.1966(4)	0.2264(4)	0.1263(5)
C(3)	0.2537(5)	0.2774(4)	0.2504(6)
C(4)	0.3527(6)	0.3698(5)	0.2562(6)
C(5)	0.3570(5)	0.3772(4)	0.1333(7)
P(2)	0.67579(14)	0.68281(12)	0.34039(16)
F(21)	0.7344(4)	0.7808(3)	0.2786(4)
F(22)	0.5725(4)	0.6281(4)	0.2208(5)
F(23)	0.6215(4)	0.5884(3)	0.4059(5)
F(24)	0.7535(5)	0.6400(4)	0.3001(5)
F(25)	0.7839(4)	0.7398(4)	0.4640(4)
F(26)	0.6101(5)	0.7330(4)	0.3919(6)

Table 4

Molecular dimensions for [VII_f]·PF₆*(a) Bond lengths*

Mo–N(11)	1.840(4)	C(31)–C(32)	1.383(6)
Mo–N(21)	1.838(4)	C(31)–C(36)	1.387(7)
Mo–P(1)	2.489(2)	C(32)–C(33)	1.385(7)
Mo–C(1)	2.350(7)	C(33)–C(34)	1.378(8)
Mo–C(2)	2.350(7)	C(34)–C(35)	1.375(7)
Mo–C(3)	2.359(7)	C(35)–C(36)	1.384(7)
Mo–C(4)	2.343(7)	C(41)–C(42)	1.383(6)
Mo–C(5)	2.326(7)	C(41)–C(46)	1.386(6)
N(11)–N(12)	1.196(6)	C(42)–C(43)	1.378(7)
N(12)–C(11)	1.438(6)	C(43)–C(44)	1.371(8)
N(21)–N(22)	1.211(6)	C(44)–C(45)	1.364(8)
N(22)–C(21)	1.419(6)	C(45)–C(46)	1.389(7)
C(11)–C(12)	1.367(7)	C(51)–C(52)	1.378(7)
C(11)–C(16)	1.350(7)	C(51)–C(56)	1.378(7)
C(12)–C(13)	1.372(8)	C(52)–C(53)	1.382(8)
C(13)–C(14)	1.364(9)	C(53)–C(54)	1.372(9)
C(14)–C(15)	1.386(9)	C(54)–C(55)	1.360(9)
C(14)–C(17)	1.424(7)	C(55)–C(56)	1.380(7)
C(15)–C(16)	1.383(7)	C(1)–C(2)	1.397(8)
C(21)–C(22)	1.381(7)	C(1)–C(5)	1.405(9)
C(21)–C(26)	1.377(7)	C(2)–C(3)	1.376(8)
C(22)–C(23)	1.369(8)	C(3)–C(4)	1.377(9)
C(23)–C(24)	1.354(9)	C(4)–C(5)	1.392(10)
C(24)–C(25)	1.368(9)	P(2)–F(21)	1.578(6)
C(24)–F(1)	1.416(7)	P(2)–F(22)	1.502(6)
C(25)–C(26)	1.377(8)	P(2)–F(23)	1.556(6)
P(1)–C(31)	1.823(4)	P(2)–F(24)	1.533(6)
P(1)–C(41)	1.811(5)	P(2)–F(25)	1.561(6)
P(1)–C(51)	1.824(5)	P(2)–F(26)	1.526(6)

(b) Bond angles

N(11)–Mo–N(21)	92.5(2)	N(11)–N(12)–C(11)	123.0(4)
N(11)–Mo–P(1)	93.1(1)	N(12)–C(11)–C(12)	116.3(5)
N(21)–Mo–P(1)	87.2(1)	N(12)–C(11)–C(16)	122.6(4)
N(11)–Mo–C(1)	97.6(3)	C(12)–C(11)–C(16)	121.0(5)
N(21)–Mo–C(1)	158.7(3)	C(11)–C(12)–C(13)	119.9(5)
P(1)–Mo–C(1)	110.8(2)	C(12)–C(13)–C(14)	120.5(5)
N(11)–Mo–C(2)	127.1(3)	C(13)–C(14)–C(15)	118.9(5)
N(21)–Mo–C(2)	140.4(3)	C(13)–C(14)–C(17)	123.0(6)
P(1)–Mo–C(2)	89.4(2)	C(15)–C(14)–C(17)	118.2(6)
C(1)–Mo–C(2)	34.6(3)	C(14)–C(15)–C(16)	120.6(5)
N(11)–Mo–C(3)	153.6(3)	C(15)–C(16)–C(11)	119.1(5)
N(21)–Mo–C(3)	109.1(3)	N(21)–N(22)–C(21)	122.9(4)
P(1)–Mo–C(3)	107.8(2)	N(22)–C(21)–C(22)	117.1(5)
C(1)–Mo–C(3)	57.1(3)	N(22)–C(21)–C(26)	122.6(5)
C(2)–Mo–C(3)	34.0(3)	C(22)–C(21)–C(26)	120.3(5)
N(11)–Mo–C(4)	128.4(3)	C(21)–C(22)–C(23)	120.5(5)
N(21)–Mo–C(4)	101.5(3)	C(22)–C(23)–C(24)	118.2(5)
P(1)–Mo–C(4)	135.5(2)	C(23)–C(24)–C(25)	123.0(5)
C(1)–Mo–C(4)	57.8(3)	C(23)–C(24)–F(1)	119.9(6)
C(2)–Mo–C(4)	57.0(3)	C(25)–C(24)–F(1)	117.1(6)
C(3)–Mo–C(4)	34.1(3)	C(24)–C(25)–C(26)	118.9(5)
N(11)–Mo–C(5)	98.3(3)	C(25)–C(26)–C(21)	119.2(5)

Table 4 (continued)

(b) Bond angles

N(21)–Mo–C(5)	125.0(3)	P(1)–C(31)–C(32)	122.2(4)
P(1)–Mo–C(5)	145.0(2)	P(1)–C(31)–C(36)	118.2(3)
C(1)–Mo–C(5)	35.0(3)	C(32)–C(31)–C(36)	119.5(4)
C(2)–Mo–C(5)	57.4(3)	C(31)–C(32)–C(33)	120.1(5)
C(3)–Mo–C(5)	57.0(3)	C(32)–C(33)–C(34)	120.0(4)
C(4)–Mo–C(5)	34.7(3)	C(33)–C(34)–C(35)	120.3(4)
Mo–N(11)–N(12)	175.9(4)	C(34)–C(35)–C(36)	119.8(5)
Mo–N(21)–N(22)	173.2(4)	C(35)–C(36)–C(31)	120.3(4)
Mo–P(1)–C(31)	115.0(2)	P(1)–C(41)–C(42)	123.1(4)
Mo–P(1)–C(41)	109.2(2)	P(1)–C(41)–C(46)	118.1(3)
Mo–P(1)–C(51)	117.9(2)	C(42)–C(41)–C(46)	118.8(4)
C(31)–P(1)–C(41)	104.2(2)	C(41)–C(42)–C(43)	120.6(4)
C(31)–P(1)–C(51)	105.1(2)	C(42)–C(43)–C(44)	120.1(5)
C(41)–P(1)–C(51)	104.2(2)		
C(43)–C(44)–C(45)	120.3(5)		
C(44)–C(45)–C(46)	120.1(5)		
C(45)–C(46)–C(41)	120.2(4)		
P(1)–C(51)–C(52)	119.7(4)		
P(1)–C(51)–C(56)	120.8(4)		
C(52)–C(51)–C(56)	119.5(4)		
C(51)–C(52)–C(53)	120.0(5)		
C(52)–C(53)–C(54)	119.6(5)		
C(53)–C(54)–C(55)	120.5(5)		
C(54)–C(55)–C(56)	120.0(5)		
C(55)–C(56)–C(51)	120.4(5)		
C(2)–C(1)–C(5)	106.6(5)		
C(1)–C(2)–C(3)	108.5(5)		
C(2)–C(3)–C(4)	109.0(5)		
C(3)–C(4)–C(5)	107.7(5)		
C(4)–C(5)–C(1)	108.3(5)		
F(21)–P(2)–F(22)	91.0(3)		
F(21)–P(2)–F(23)	178.0(3)		
F(21)–P(2)–F(24)	88.3(3)		
F(21)–P(2)–F(25)	88.8(3)		
F(21)–P(2)–F(26)	90.5(3)		
F(22)–P(2)–F(23)	91.1(3)		
F(22)–P(2)–F(24)	94.2(3)		
F(22)–P(2)–F(25)	179.5(3)		
F(22)–P(2)–F(26)	91.7(3)		
F(23)–P(2)–F(24)	91.7(3)		
F(23)–P(2)–F(25)	89.2(3)		
F(23)–P(2)–F(26)	89.2(3)		
F(24)–P(2)–F(25)	85.4(3)		
F(24)–P(2)–F(26)	174.0(3)		
F(25)–P(2)–F(26)	88.7(3)		

uration, with both arenediazo phenyl groups directed away from the phosphine ligand. In this respect the structure is similar to that of the homologous nitrosyl-arenediazo cation $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)(\text{PPh}_3)]\text{PF}_6$ (XIV) (in which the single arenediazo ligand is also directed away from the phosphine ligand) [2] but differs from the structure of the related neutral bis(arenediazo) complex (η -

Table 5

Final fractional coordinates (Mo, P $\times 10^5$, others $\times 10^4$) for $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PPh}_3)(\text{N}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p)$ with estimated standard deviations in parentheses

Atom	x	y	z
Mo	7238(3)	18328(4)	15771(1)
P	24931(9)	9265(12)	12086(4)
O	2333(3)	3792(4)	2263(1)
N(1)	363(3)	3278(4)	1108(1)
N(2)	21(3)	4202(4)	781(1)
C	1737(4)	3103(5)	1993(1)
C(1)	−1100(4)	1219(6)	1887(2)
C(2)	−875(4)	168(6)	1501(2)
C(3)	83(4)	−674(5)	1679(2)
C(4)	436(4)	−141(5)	2153(2)
C(5)	−299(5)	1036(6)	2282(2)
C(11)	−847(4)	5263(5)	919(1)
C(12)	−1290(4)	6196(5)	532(2)
C(13)	−2162(4)	7208(5)	640(2)
C(14)	−2600(4)	7334(5)	1123(2)
C(15)	−2135(4)	6425(5)	1502(2)
C(16)	−1265(4)	5390(5)	1407(2)
C(17)	−3537(4)	8418(6)	1238(2)
C(21)	3187(4)	−417(5)	1647(1)
C(22)	3164(4)	−1965(5)	1544(2)
C(23)	3553(5)	−2965(5)	1910(2)
C(24)	3959(5)	−2469(7)	2374(2)
C(25)	3997(5)	−945(6)	2478(2)
C(26)	3602(4)	72(5)	2116(2)
C(31)	2437(4)	−120(4)	605(1)
C(32)	3444(4)	−506(5)	359(1)
C(33)	3396(4)	−1396(5)	68(2)
C(34)	2345(5)	−1905(6)	−258(2)
C(35)	1349(4)	−1522(6)	−22(2)
C(36)	1391(4)	−618(6)	408(2)
C(41)	3571(3)	2368(5)	1071(1)
C(42)	3192(4)	3568(5)	766(2)
C(43)	3945(5)	4694(6)	634(2)
C(44)	5075(5)	4652(6)	802(2)
C(45)	5462(4)	3495(6)	1107(2)
C(46)	4709(4)	2324(5)	1238(2)

$\text{C}_5\text{H}_5\text{MoCl}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)_2$ (I) in which the arenediazo ligands take up an *anti* configuration [9]. While the factors which determine the adoption of *syn* or *anti* bis(arenediazo) configurations are not clear [21] it seems probable that avoidance of unfavourable intramolecular interactions with the phosphine ligand (rather than electronic or crystal-packing effects) are responsible for the configurations adopted by VIIf and XIV. The Mo–N and N–N distances in VIIf fall well within the range which has been established for bis(arenediazo) complexes of molybdenum [3,5–7,15]. We note that the Mo–N distances in VIIf (1.838(4), 1.840(4) Å) are significantly shorter than the corresponding bond length in the analogous nitrosyl-arenediazo cation XIV (1.876(3) Å). This effect may be attributed to the greater π -acceptor capacity of $[\text{NO}]^+$ vis-a-vis $[\text{ArN}_2]^+$ which reduces the *d*-orbital electron density

Table 6

Molecular dimensions for [VIII]

(a) Bond lengths (Å)

Mo–P	2.417(1)	C(13)–C(14)	1.378(6)
Mo–N(1)	1.820(3)	C(14)–C(15)	1.378(6)
Mo–C	1.942(4)	C(14)–C(17)	1.485(6)
Mo–C(1)	2.338(4)	C(15)–C(16)	1.388(6)
Mo–C(2)	2.370(4)	C(21)–C(22)	1.401(6)
Mo–C(3)	2.363(4)	C(21)–C(26)	1.378(5)
Mo–C(4)	2.341(4)	C(22)–C(23)	1.374(6)
Mo–C(5)	2.323(4)	C(23)–C(24)	1.368(7)
P–C(21)	1.830(4)	C(24)–C(25)	1.381(8)
P–C(31)	1.834(4)	C(25)–C(26)	1.380(6)
P–C(41)	1.828(4)	C(31)–C(32)	1.384(5)
O–C	1.153(5)	C(31)–C(36)	1.376(5)
N(1)–N(2)	1.244(4)	C(32)–C(33)	1.371(5)
N(2)–C(11)	1.429(5)	C(33)–C(34)	1.379(6)
C(1)–C(2)	1.405(7)	C(34)–C(35)	1.361(7)
C(1)–C(5)	1.381(7)	C(35)–C(36)	1.384(6)
C(2)–C(3)	1.407(7)	C(41)–C(42)	1.397(6)
C(3)–C(4)	1.380(6)	C(41)–C(46)	1.376(5)
C(4)–C(5)	1.393(7)	C(42)–C(43)	1.375(7)
C(11)–C(12)	1.398(5)	C(43)–C(44)	1.369(8)
C(11)–C(16)	1.381(5)	C(44)–C(45)	1.370(8)
C(12)–C(13)	1.384(6)	C(45)–C(46)	1.402(6)

(b) Bond angles (°)

P–Mo–N(1)	98.5(1)	C(3)–Mo–C(5)	57.1(2)
P–Mo–C	85.0(1)	C(4)–Mo–C(5)	34.8(2)
P–Mo–C(1)	146.8(1)	Mo–P–C(21)	109.2(1)
P–Mo–C(2)	115.0(1)	Mo–P–C(31)	120.0(1)
P–Mo–C(3)	90.1(1)	Mo–P–C(41)	115.5(1)
P–Mo–C(4)	98.1(1)	C(21)–P–C(31)	102.6(2)
P–Mo–C(5)	131.7(1)	C(21)–P–C(41)	106.9(2)
N(1)–Mo–C	95.5(2)	C(31)–P–C(41)	101.3(2)
N(1)–Mo–C(1)	101.8(2)	Mo–N(1)–N(2)	174.1(3)
N(1)–Mo–C(2)	102.5(2)	N(1)–N(2)–C(11)	118.2(5)
N(1)–Mo–C(3)	132.4(2)	Mo–C–O	175.8(3)
N(1)–Mo–C(4)	158.4(2)	Mo–C(1)–C(2)	73.9(3)
N(1)–Mo–C(5)	129.7(2)	Mo–C(1)–C(5)	72.2(3)
C–Mo–C(1)	118.5(2)	C(2)–C(1)–C(5)	109.3(4)
C–Mo–C(2)	150.3(2)	Mo–C(2)–C(1)	71.4(3)
C–Mo–C(3)	132.1(2)	Mo–C(2)–C(3)	72.4(3)
C–Mo–C(4)	99.6(2)	C(1)–C(2)–C(3)	105.7(4)
C–Mo–C(5)	92.4(2)	Mo–C(3)–C(2)	73.0(3)
C(1)–Mo–C(2)	34.7(2)	Mo–C(3)–C(4)	72.1(3)
C(1)–Mo–C(3)	56.9(2)	C(2)–C(3)–C(4)	109.3(4)
C(1)–Mo–C(4)	57.3(2)	Mo–C(4)–C(3)	73.8(3)
C(1)–Mo–C(5)	34.5(2)	Mo–C(4)–C(5)	71.9(3)
C(2)–Mo–C(3)	34.6(2)	C(3)–C(4)–C(5)	107.8(4)
C(2)–Mo–C(4)	57.7(2)	Mo–C(5)–C(1)	73.4(3)
C(2)–Mo–C(5)	57.9(2)	Mo–C(5)–C(4)	73.3(3)
C(3)–Mo–C(4)	34.1(2)	C(1)–C(5)–C(4)	108.0(4)
N(2)–C(11)–C(12)	117.0(3)	P–C(41)–C(42)	116.2(3)
N(2)–C(11)–C(16)	123.5(3)	P–C(41)–C(46)	124.6
C(12)–C(11)–C(16)	119.5(4)	C(42)–C(41)–C(46)	119.3(4)
C(11)–C(12)–C(13)	119.6(4)	C(41)–C(42)–C(43)	120.5(4)

(continued)

Table 6 (continued)

(b) Bond angles (°)			
C(12)–C(13)–C(14)	121.6(4)	C(42)–C(43)–C(44)	120.2(5)
C(13)–C(14)–C(15)	117.9(4)	C(43)–C(44)–C(45)	120.3(4)
C(13)–C(14)–C(17)	121.5(4)	C(44)–C(45)–C(46)	120.2(4)
C(15)–C(14)–C(17)	120.5(4)	C(41)–C(46)–C(45)	119.6(4)
C(14)–C(15)–C(16)	122.1(4)		
C(11)–C(16)–C(15)	119.3(4)		
P–C(21)–C(22)	120.8(3)		
P–C(21)–C(26)	119.5(3)		
C(22)–C(21)–C(26)	119.1(3)		
C(21)–C(22)–C(23)	119.7(3)		
C(22)–C(23)–C(24)	120.8(4)		
C(23)–C(24)–C(25)	120.0(4)		
C(24)–C(25)–C(26)	119.9(4)		
C(21)–C(26)–C(25)	120.6(4)		
P–C(31)–C(32)	120.8(3)		
P–C(31)–C(36)	120.0(3)		
C(32)–C(31)–C(36)	119.0(3)		
C(31)–C(32)–C(33)	120.2(4)		
C(32)–C(33)–C(34)	120.3(4)		
C(33)–C(34)–C(35)	120.0(4)		
C(34)–C(35)–C(36)	120.0(4)		
C(31)–C(36)–C(35)	120.5(4)		

available for back bonding to the *p*-fluorobenzenediazo ligand in XIV compared with that in VIIIf and hence reduces the effective Mo–N_α bond-order in the former. The arenediazo N_α–N_β distances in the two complexes are not significantly different. Strong *trans* bond-lengthening effects have been observed in several bis(arene-diazo) complexes [3,5–7,22] but while the bonds from Mo to that portion of the cyclopentadienide ligand which is effectively *trans* to the two arenediazo ligands (i.e. Mo–C(1), 2.350(5), Mo–C(2) 2.350(5), Mo–C(3) 2.359(5) Å) are indeed somewhat longer than the bonds to the two remaining carbon atoms (Mo–C(4) 2.343(5), Mo–C(5) 2.326(5) Å) the effect is only significant for Mo–C(5) vis-a-vis Mo–C(3). The Mo–P (phosphine) distance and the dimensions with the triphenylphosphine ligand are in agreement with the expected values [23–26].

Crystals of VIII contain discrete well-separated molecules and – as with VIIIf – the geometry around the molybdenum atom is distorted octahedral with the cyclopentadienide ligand occupying three facial sites and the carbonyl, arenediazo and triphenylphosphine ligands filling the other three sites. The *p*-toluenediazo ligand is bonded to molybdenum in the “singly-bent” form (Mo–N(1)–N(2) 174.1(3), N(1)–N(2)–C(11) 118.2(3)°) and the bending of the ligand is, as in VIIIf, such as to minimize interaction with the triphenylphosphine ligands. Since formation of VIIIf from VIII involves replacement of CO by the more powerfully π -withdrawing *p*-fluorobenzenediazonium cation the degree of back-bonding to the *p*-toluenediazo ligand in VIII would be expected to be greater than that in VIIIf and, although the effect is small, this is reflected in the Mo–N_α bond lengths: 1.820(3) Å in VIII and 1.840(4) Å in VIIIf. While the Mo–C and C–O bond lengths are unexceptional [24–27] the Mo–P(phosphine) bond length of 2.417(1) Å is significantly shorter than

that in VIIf (2.489(2) Å) and is also shorter than the range of Mo–P bond distances in “piano-stool” molecules tabulated by Reisner et al. (2.436(3)–2.5175(8) Å) [29].

Conclusions

The results described here convincingly demonstrate that the cations $[(\eta\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{R}^1)(\text{N}_2\text{C}_6\text{H}_4\text{R}^2)(\text{PPh}_3)]^+$ (VII) have considerable potential as reagents for the facile introduction of the $[\text{Mo}(\text{N}_2\text{Ar})_2]^{2+}$ fragment into a variety of different coordination environments. Salts of cation VII are readily prepared in high yield, are air- and moisture-stable and we have encountered no deterioration in multigram samples which were exposed to the normal laboratory atmosphere for several years. While our route to bis(organodiazido) complexes based on VII lacks the facility for preparing alkyl- or aroyl-diazo complexes which is a feature of the oxomolybdenum-hydrazine route, it has the countervailing advantage of the ability to generate $[\text{Mo}(\text{N}_2\text{Ar})_2]^{2+}$ fragments where the two aryl groups are not identical and to combine this fragment with a wider range of co-ligands. We have no reason to suppose that we have exhausted the versatility of VII and our studies of its chemistry are continuing.

Experimental

Published procedures were employed for the synthesis of isotopically normal and ^{15}N -enriched arenediazonium tetrafluoroborates and hexafluorophosphates starting from the appropriate arylamine and NaNO_2 or $\text{Na}^{15}\text{NO}_2$ [30] as well as for the preparations of complexes III and VIII [31], IX [32], X [33] and for $(\text{CN})_2\text{C}=\text{C}(\text{SNa})_2 \cdot 3\text{H}_2\text{O}$ [34]. All other reagents and solvents were commercial samples and were used as received. Preparations were carried out under an atmosphere of dry, oxygen-free nitrogen but work-up procedures were not protected from the air. IR spectra were recorded on a Perkin Elmer 257 spectrophotometer and ^1H NMR spectra were obtained with a Perkin Elmer Hitachi R20-A spectrometer operating at 60 MHz and 34°C. Microanalyses were determined by the staff of the microanalytical laboratory of University College, Cork and are collected in Table 1.

Preparation of bis(arendiazo) cations of the general type $[(\eta\text{-C}_5\text{H}_5\text{R})\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{R}^1)(\text{N}_2\text{C}_6\text{H}_4\text{R}^2)(\text{PPh}_3)]^+$ (VII)

Method A. Benzenediazonium tetrafluoroborate (1.92 g, 10 mmol) was added portionwise to a stirred solution of $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{N}_2\text{C}_6\text{H}_5)$ (3.22 g, 10 mmol) in acetone at -78°C . After 15 min the solution was warmed slowly to -35°C and solid triphenylphosphine (2.62 g, 10 mmol) was added in small portions. After a further 15 min at -35°C the cooling bath was removed and the solution was allowed to warm spontaneously to room temperature. The solvent was removed in vacuo and the purple residue was recrystallised several times from CH_2Cl_2 /ether and from acetone/ether to yield pure $[(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{N}_2\text{C}_6\text{H}_5)_2(\text{PPh}_3)]\text{BF}_4$, [VIIa] BF_4 , as purple air-stable microcrystals in ca. 40% yield.

Method B. The procedure was basically the same as Method A except that $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{N}_2\text{C}_6\text{H}_5)(\text{PPh}_3)$ (5.56 g, 10 mmol) was employed as starting

material and the phosphine addition step was omitted. The yield of [VIIa]BF₄ by this method was ca. 70%.

Other complexes prepared by these procedures are listed in Table 1.

Reaction of HBpz₃Mo(CO)(N₂C₆H₄CH₃-p)(PPh₃), (X), with p-toluenediazonium tetrafluoroborate

The diazonium salt (0.29 g, 1.41 mmol) was added slowly to a stirred solution of complex X (1.01 g, 1.41 mmol) in acetone at -78°C. The solution was slowly warmed to room temperature during which the colour changed to greenish-black. Removal of the solvent in vacuo and recrystallisation of the residue from CH₂Cl₂/ether gave [HBpz₃Mo(CO)(N₂C₆H₅)(PPh₃)]BF₄ (XI), as an unstable olive-green powder (0.32 g, 28%).

Reaction of [(η-C₅H₅R)Mo(N₂C₆H₅)(N₂C₆H₄CH₃-p)(PPh₃)]⁺ (VIIId) with halide and cyanide anions

Solid [PPN]Cl (0.42 g, 0.73 mmol) was added to a stirred solution of [VIIId]BF₄ (0.5 g, 0.68 mmol) in 10 ml CH₂Cl₂ producing an immediate colour change from purple to blood red. After 30 min, diethyl ether (35 ml) was added and the solution was cooled to -78°C and filtered at that temperature. Concentration of the filtrate to dryness and recrystallisation of the residue from a mixture of CH₂Cl₂ and 40–60° petroleum yielded red crystalline XVa, (0.19 g, 66%).

Complexes XVb–XVd were similarly prepared using [PPN]Br, [(C₆H₅)₃PCH₃]⁺ and [PPN]CN respectively.

Preparation of (Et₂NCS₂)₂Mo(N₂C₆H₄R¹)(N₂C₆H₄R²) (XVI)

A stirred solution of [VIIIf]BF₄ (3.76 g, 4.99 mmol) in acetone (60 ml) was treated portionwise with solid (C₂H₅)₂NCS₂Na · 3H₂O (2.25 g, 10 mmol) and the reaction mixture was stirred for 8 h at room temperature. The solvent was removed in vacuo and the crude purple residue was dissolved in CH₂Cl₂. Diethyl ether (35 ml) was added to the solution and concentration of the filtered solution to dryness gave a purple solid which was further purified by chromatography on alumina (activity III). Elution was 1/1 pentane/diethyl ether yielded purple crystalline XVIa (1.42 g, 45%).

Complex XVIIb was prepared in a similar fashion.

Preparation of (acac)₂Mo(N₂C₆H₄CH₃-p)₂ (XVII)

Solid thallium(I) acetylacetonate, Tl(acac) (3.03 g, 20 mmol) was added to a stirred solution of [VIIe]BF₄ (3.81 g, 5.0 mmol) in acetone (50 ml). After ca. 2 min the purple colour of the starting material had been replaced by deep red and after a further 30 min the solvent was removed in vacuo. The red residue was taken up in CH₂Cl₂ (20 ml), diethyl ether (150 ml) was added and the mixture was filtered through Celite and concentrated to dryness. The red oily residue was purified by dry-column chromatography eluting with a 1/2 mixture of n-pentane and diethyl ether. The red band was removed from the column with CH₂Cl₂. Removal of the solvent in vacuo and recrystallization of the residue from diethyl ether/hexanes yielded red microcrystalline (acac)₂Mo(N₂C₆H₄CH₃-p)₂ (XVII) (1.49 g, 56%).

Preparation of [PPN]₂[(dcdt)₂Mo(N₂C₆H₄CH₃-p)(N₂C₆H₄F-p)] (XVIII)

Solid (CN)₂C=C(SNa)₂ · 3H₂O (1.20 g, 5 mmol) and [PPN]Cl (2.87 g, 5 mmol) were added to a stirred solution of [VIIIf]BF₄ (1.88 g, 2.5 mmol) in acetone. After ca. 2 h the solvent was removed in vacuo. The brownish-red residue was dissolved in CH₂Cl₂ and the solution was washed several times with water. The organic layer was separated, dried with anhydrous MgSO₄ and concentrated to dryness on the rotary evaporator. The crude brown solid was extracted several times with water at ca. 70 °C and the dried residue was recrystallised four times from CH₂Cl₂/methanol to give pure XVIII (1.48 g, 35%).

Preparation of the complexes [(LL)₂Mo(N₂C₆H₄CH₃-p)(N₂C₆H₄F-p)][BF₄]₂ (XIX) (LL = 2,2'-bipy, o-phen)

Solid 2,2'-bipyridyl (0.31 g, 2.0 mmol) and NaBF₄ (0.11 g, 1.0 mmol) were added to a solution of [VIIIf]BF₄ (0.75 g, 1.0 mmol) in 20 ml acetone. After ca. 20 min the solution was diluted with water and the mixture extracted with CH₂Cl₂. The CH₂Cl₂ extracts were washed thoroughly with water, dried (MgSO₄) and concentrated to small volume. The crude product was precipitated with diethyl ether and recrystallised several times from acetone/diethyl ether and CH₂Cl₂/diethyl ether to give pure XIXa (0.37 g, 45%).

Complex XIXb was prepared similarly.

¹H NMR spectra

[VIIa]BF₄ (CDCl₃, Me₄Si) δ 7.97–7.09 (multiplet, 25 H, N₂Ar and PPh₃), 6.20 (d, ³J(P–H) = 1.2 Hz, 5H, C₅H₅) ppm. Except where stated otherwise, the measurement conditions and the assignments for the following spectra are as for [VIIa]BF₄ above.

[VIIb]BF₄ δ 7.95–7.10 (m, 24H), 6.14 (d, ³J(P–H) = 1.0 Hz, 5H) ppm. [VIIc]BF₄ δ 7.96–7.09 (m, 24H), 6.15 (d, ³J(P–H) = 1.0 Hz, 5H) ppm. [VIId]BF₄ δ 7.96–7.10 (m, 24H), 6.05 (d, ³J(P–H) = 1.2 Hz), 2.35 (s, 3H, N₂C₆H₄CH₃-p) ppm. [VIIe]BF₄ (acetone-*d*₆) δ 7.79–7.50 (m, 15H, PPh₃), 7.26 (s, 8H, N₂Ar), 6.29 (d, ³J(P–H) = 1.8 Hz, 5H), 2.37 (s, 6H, N₂C₆H₄CH₃-p) ppm. [VIIf]BF₄ δ 7.84–7.10 (m, 24H), 6.06 (d, ³J(P–H) = 1.2 Hz, 5H), 2.37 (s, 3H, N₂C₆H₄CH₃-p) ppm. [VIIg]BF₄ δ 7.95–7.05 (m, 24H), 6.10–5.70 (m, 4H, C₅H₄CH₃), 2.40 (s, 3H, N₂C₆H₄CH₃-p), 2.04 (s, 3H, C₅H₄CH₃) ppm. [VIIh]BF₄ δ 7.84–7.04 (m, 23H), 6.06–5.70 (m, 4H, C₅H₄CH₃), 2.38 (s, 6H, N₂C₆H₄CH₃-p), 1.99 (s, 3H, C₅H₄CH₃) ppm.

XVa (CD₂Cl₂, Me₄Si) δ 7.54–7.05 (m, 9H, N₂Ar), 6.10 (s, 5H, C₅H₅), 2.33 (s, 3H, N₂C₆H₄CH₃-p) ppm. For the following compounds, the measurement conditions and assignments are as for XVa unless stated otherwise. XVb δ 7.55–7.07 (m, 9H), 6.09 (s, 5H), 2.33 (s, 3H) ppm. XVc (CDCl₃) δ 7.85–7.02 (m, 9H), 6.11 (s, 5H), 2.33 (s, 3H) ppm. Xvd (CDCl₃) δ 7.60–7.03 (m, 9H), 6.12 (s, 5H), 2.34 (s, 3H) ppm.

XVIa (CDCl₃, Me₄Si) δ 7.50–6.80 (m, 8H, N₂Ar), 3.8 (broad q, *J* ≈ 8 Hz, 8H, S₂CN(CH₂CH₃)₂), 2.3 (s, 3H, N₂C₆H₄CH₃-p), 1.30, 1.24 (overlapping t, *J* = ca. 8 Hz, 12H, S₂CN(CH₂CH₃)₂) ppm. XVIb (CD₂Cl₂, Me₄Si) δ 7.19 (q, 8H, N₂Ar), 3.82, 3.79 (overlapping q, *J* = ca. 8 Hz, 8H, S₂CN(CH₂CH₃)), 1.35, 1.27 (overlapping t, *J* = ca. 8 Hz, 12H, S₂CN(CH₂CH₃)₂) ppm.

XVII (CD₂Cl₂, Me₄Si) δ 7.23 (q, 8H, N₂Ar), 5.58 (s, 2H, H(3) of acac ligands), 2.32 (s, 6H, N₂C₆H₄CH₃-p), 2.26, 1.98 (s, 6H each, CH₃ groups of acac ligands) ppm.

XIXa (CD_2Cl_2 , Me_4Si) δ 9.69–6.60 (overlapping m, 24H, 2,2'-bipy and N_2Ar), 2.25 (s, 3H, $\text{N}_2\text{C}_6\text{H}_4\text{CH}_3$ -*p*) ppm. XIXb (CD_2Cl_2 , Me_4Si) δ 9.40–6.44 (overlapping m, 24H, *o*-phen and N_2Ar), 2.23 (s, 3H, $\text{N}_2\text{C}_6\text{H}_4\text{CH}_3$ -*p*) ppm.

Collection and reduction of X-ray data

Purple-black crystals of $[\text{VIIIf}]\text{PF}_6$ were grown by using a very slow current of nitrogen to evaporate a saturated solution of the complex in CH_2Cl_2 /ethanol containing a small quantity of PPh_3 . Red crystals of complex VIII were grown by slow evaporation of a concentrated solution in a mixture of CH_2Cl_2 and 40–60 °C petroleum. Crystal data and details of the refinement for $[\text{VIIIf}]\text{PF}_6$ and VIII are collected in Table 2. Accurate cell parameters were determined by least-squares calculations based on the angular settings for 25 automatically centred reflections using an Enraf–Nonius CAD4 diffractometer. Data were corrected for Lorentz and polarisation effects but not for absorption. The coordinates of the molybdenum atoms were obtained from analysis of the three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement [35] was by full-matrix, least-squares calculations, initially with isotropic, then with anisotropic vibration parameters.

Difference maps were computed at intermediate stages in the refinement and revealed maxima in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealised positions and included in the final rounds of calculations but not refined. Scattering factors used in the structure-factor calculations were taken from the literature [36] and allowance was made for anomalous dispersion [36]. Final difference maps were devoid of significant features. The structure factor listings, calculated hydrogen coordinates and thermal parameters are available from one of the authors (G.F.) on request.

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