Journal of Organometallic Chemistry, 282 (1985) 75–84
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TRANSITION METAL DERIVATIVES OF ARENEDIAZONIUM IONS

XIII *. INDIRECT SYNTHESIS OF A BIS(ARENEDIAZO) DERIVATIVE OF THE HYDROTRIS(1-PYRAZOLYL)BORATOTRICARBONYLMOLYBDENUM ANION: THE CRYSTAL AND MOLECULAR STRUCTURE OF HYDROTRIS(1-PYRAZOLYL)BORATOBIS(*p*-TOLUENEDIAZO)-FLUOROMOLYBDENUM(0) $MoF(N_2C_6H_4Me\text{-}p)_2[HB(C_3H_3N_2)_3]$

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(Received August 24th, 1984)

Summary

Although the anion $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ reacts readily with excess $[ArN_2]^+$ to give a cationic bis-arenediazo derivative $[Mo(N_2Ar)_2(L)(\eta\text{-}C_5H_5)]^+$ (L = CO or solvent) the analagous hydrotris(1-pyrazolyl)borato complexes are not accessible via the reaction of either $[Mo(CO)_3\{HB(C_3H_3N_2)_3\}]^-$ or $Mo(N_2Ar)(CO)_2[HB(C_3H_3N_2)_3]$ with $[ArN_2]^+$. This reactivity difference can be ascribed to the reluctance of molybdenum poly(1-pyrazolyl)borato complexes to form 7-coordinate intermediates. However the bis(arenediazo) complex $MoF(N_2C_6H_4Me\text{-}p)_2[HB(C_3H_3N_2)_3]$ (I) is accessible via an indirect route involving reaction of the kinetically labile complex $[Mo(N_2C_6H_4Me\text{-}p)_2(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ (XI) with $Tl[HB(C_3H_3N_2)_3]$. Crystals of I are monoclinic, space group $P2_1/n$ with four molecules in a unit-cell of dimensions *a* 10.354(4), *b* 8.289((1), *c* 30.402(7) Å and β 99.78(3)°. The structure was solved by the heavy-atom method and refined by full-matrix least squares calculations. All hydrogen atoms were located from difference syntheses. Final $R = 0.030$ for 3812 reflections with $I > 3\sigma(I)$. Complex I has octahedral geometry and approximate mirror symmetry with the two arenediazo ligands bound to Mo in the "singly-bent" (formal $[ArN_2]^+$) coordination mode (Mo–N–N 176.1(2), 175.2(2); N–N–C both 118.2°; Mo–N both 1.832(3), N–N 1.217(4), 1.226(3) Å) and the Mo–F bond length is 1.965(2) Å. The orientation of

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* For part XII see ref. 1.

0022-328X/85/$03.30

the bending of the two arenediazo ligands is ascribed to steric crowding within the molybdenum coordination sphere. The Mo–N (pyrazolyl) bond lengths show a pronounced *trans*-effect (Mo–N *trans* to F = 2.173(2), Mo–N *trans* to $[N_2C_6H_4Me\text{-}p]$ 2.211, 2.210(3) Å].

Introduction

The chemistry of the Group VIb transition metals affords numerous examples of organometallic bis(nitrosyl) complexes. Moreover recent studies have shown that readily accessible compounds of this type such as $[Cr(NO)_2(\eta\text{-}C_5H_5)]_2$ $CrCl(NO)_2(\eta\text{-}C_5H_5)$ and $[W(NO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ exhibit interesting chemical properties and can be converted into new bis(nitrosyl) complexes of unusual molecular architecture and/or electronic structure [2–4]. In sharp contrast, few examples of the closely-related Group VIb bis(arenediazo) complexes have been synthesised, fewer-still have been structurally characterised and very little is known about their chemical behaviour [5–11]. We are currently engaged in a program aimed at the preparation and the chemical and structural characterisation of compounds of this type. Herein we describe the synthesis and the crystal and molecular structure of a new member of the class: hydrotris(1-pyrazolyl)boratobis(*p*-toluenediazo)fluoromolybdenum(0), $MoF(N_2C_6H_4Me\text{-}p)_2\{HB(C_3H_3N_2)_3\}$ (I).

Results and discussion

Recent work in these laboratories [5,9] has established that the carbonyl anion $[Mo(CO)_3(\eta\text{-}C_5H_4R)]^-$ (II) (R = H, Me) reacts with an excess of $[ArN_2]^+$ at $-70°C$ to yield highly-reactive cationic bis-arenediazo complexes $[Mo(N_2Ar)_2(L)(\eta\text{-}C_5H_4R)]^+$ (III, L = CO or solvent). This reaction undoubtedly proceeds via initial formation of the neutral arenediazo complex $Mo(CO)_2(N_2Ar)(\eta\text{-}C_5H_4R)$ (IV) and we have shown that pre-formed IV reacts with one equivalent of $[ArN_2]^+$ to yield III. Since the chemistry of η-cyclopentadienyl and hydrotris(1-pyrazolyl)borato complexes of molybdenum often show close parallels we sought to extend this synthesis of bis-arenediazo complexes by investigating the reaction of $[Mo(CO)_3\{HB(C_3H_3N_2)_3\}]^-$ (V) with excess $[ArN_2]^+$. However this reaction, yielded only the neutral arenediazo complex $Mo(CO)_2(N_2Ar)[HB(C_3H_3N_2)_3]$ (VI) whether carried out at $-70°C$ or at room temperature. Pre-formed complex VI was also completely inert to further reaction with $[ArN_2]^+$ under similar conditions.

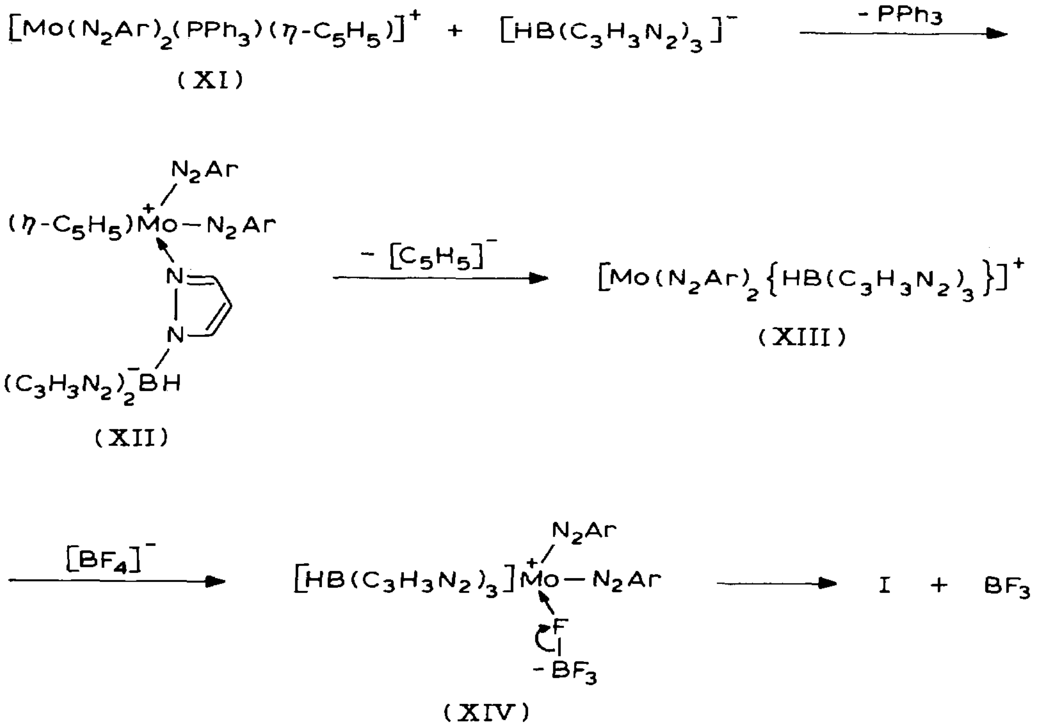
It has been suggested that the initial interaction between a metal carbonyl and a transition metal substrate involves a complex in which the metal behaves as a Lewis base and the diazonium cation as a Lewis acid [12]. Viewed in this light the inertness of VI, vis-a-vis IV, to further reaction with $[ArN_2]^+$ is rather surprising since the former complex should contain a more basic metal atom than the latter [13]. We believed that the critical factor operating here is steric rather than electronic in nature. Recent work in these laboratories and elsewhere [14,15] strongly suggests that poly(1-pyrazolyl)borato molybdenum complexes, unlike their η-cyclopentadienyl analogues, do not readily tolerate 7-coordinate structures with bulky monodentate ligands. The formation of a bis(arenediazo) complex from VI would necessarily involve formation of a cationic 7-coordinate intermediate $[Mo(N_2Ar)_2$-

$(CO)_2\{HB(C_3H_3N_2)_3\}]^+$ (VII). The poly(1-pyrazolyl)borato complex (VII) contains two bulky arenediazo ligands bound to molybdenum. Furthermore one of these is forced to adopt the doubly-bent coordination mode (thus further exacerbating steric crowding) if the complex is to avoid an unfavourable 20-electron configuration. Consequently interaction between VI and $[ArN_2]^+$ is likely to be seriously inhibited.

An alternative route to bis(arenediazo) complexes containing poly(1-pyrazolyl)borate ligands was suggested by Trofimenko's observation that the allyl complex $Mo(\eta^3\text{-}C_3H_5)(CO)_2[HB(3,5\text{-}Me_2C_3HN_2)_3]$ (VIII) ($3,5\text{-}Me_2C_3HN_2 \equiv$ 3,5-dimethyl-1-pyrazolyl) is indirectly accessible from the reaction of $[HB(3,5\text{-}Me_2C_3HN_2)_3]^-$ with $MoCl(MeCN)_2(CO)_2(\eta^3\text{-}C_3H_5)$ (IX) despite the fact that steric crowding prevents reaction of $[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^-$ (X) with allyl halides [16]. Direct reaction of X with allyl halides would involve a crowded 7-coordinate intermediate or transition state. However complex IX (whether via prior halide or MeCN ligand dissociation or η^3–η^1 transformation of the allyl group, or both) could react with the hydrotris(1-pyrazolyl)borato anion in a stepwise fashion via a series of 6-coordinate intermediates. By analogy it seemed possible that the hydrotris(1-pyrazolyl)borato anion might react with the bis(arenediazo) complex $[Mo(N_2C_6H_4Me\text{-}p)_2(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ (XI) (in which both cyclopentadienyl and phosphine ligands are kinetically very labile [5]) to afford a hydrotris(1-pyrazolyl)boratobis(arenediazo)molybdenum complex without the necessity for the intervention of a 7-coordinate intermediate. Complex XI did indeed react very rapidly with $Tl[HB(C_3H_3N_2)_3]$ in ether/dichloromethane solvent. The infrared spectrum of the scarlet crystalline product (I) showed the presence of the $[HB(C_3H_3N_2)_3]^-$ ligand (ν(BH) at 2495 cm^{-1}) while the absence of an absorption band due to $[BF_4]^-$ and the solubility of I in non-polar solvents suggested that it was a non-ionic species. The ^1H NMR spectrum of I was consistent with its formulation as a stereochemically rigid octahedral complex of the type $MoX(N_2C_6H_4Me\text{-}p)_2\{HB(C_3H_3N_2)_3\}$ in which the cyclopentadienide and phosphine ligands of XI had been replaced by $[HB(C_3H_3N_2)_3]^-$ and a unidentate anionic ligand X^-. Both microanalytical data and a molecular-weight determination on I indicated that X^- was likely to be a fluoride anion.

Based on the known chemistry of XI [5] we suggest that its reaction with $[HB(C_3H_3N_2)_3]^-$ follows the sequence outlined in Scheme 1. Dissociation of the phosphine ligand followed by reaction with $[HB(C_3H_3N_2)_3]^-$ would yield XII in which the hydrotris(1-pyrazolyl)borate is bound to molybdenum in a monodentate fashion. Chelation of the remaining two pyrazolyl groups to molybdenum (accompanied by successive $\eta^5 \to \eta^3 \to \eta^1$ transformations of the cyclopentadienyl ligand) and ultimately loss of cyclopentadienide anion would generate a transient coordinatively unsaturated cation XIII. We suggest that XIII is stabilised by forming a weakly-bound complex XIV with $[BF_4]^-$ anion from which the metal atom than abstracts fluoride to form the final product I. While there is precedent in molybdenum chemistry for the final two steps in this sequence [17,18–21] the proposed pathway contrasts with the behaviour of the closely-related bis(arenediazo) species $[Mo(N_2C_6H_4\text{-}p)_2(L)(\eta\text{-}C_5H_4Me)]^+$ (XV) (L = CO or THF). Despite its considerable lability this cation does not react with the $[BF_4]^-$ counter-ion. It instead abstracts chloride from CH_2Cl_2 solvent (which is also present during formation of I) and generates the neutral chloro complex $MoCl(N_2Ar)_2\{\eta\text{-}C_5H_4Me)$ (XVI) [9]. We therefore felt that it was desirable to subject I to an X-ray crystallographic investiga-

SCHEME 1. Ar = C_6H_4Me-*p*.



tion in order to establish unambiguously that the sixth ligand is indeed fluoride and in the process to extend the relatively limited range of structural information on bis(arenediazo) complexes.

A stereoscopic view of the molecular structure of I is shown in Fig. 1 together with the crystallographic numbering scheme. Final fractional coordinates for I are listed in Table 1 and details of the molecular geometry are summarised in Table 2. Crystals of I contain discrete molecules separated by normal Van der Waals distances. In agreement with our deductions from the spectroscopic evidence the overall geometry of I is octahedral. The $[HB(C_3H_3N_2)_3]^-$ ligand occupies three

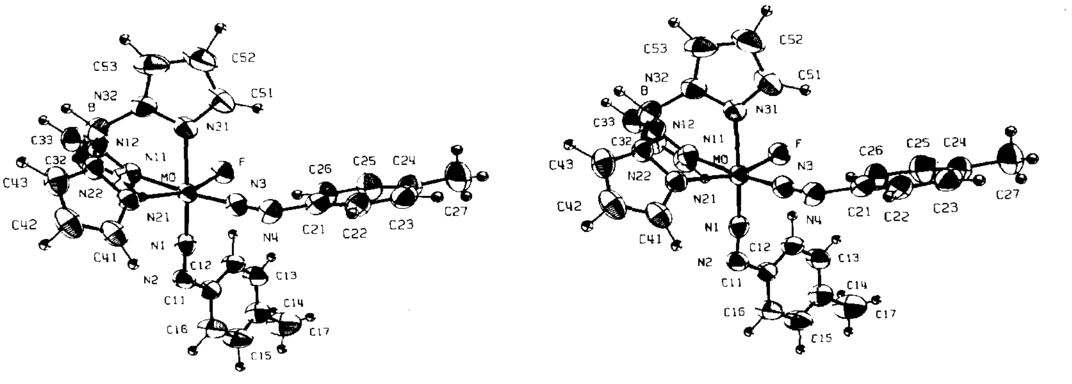


Fig. 1. Stereoview of I with the crystallographic numbering scheme.

adjacent coordination sites. The three remaining coordination positions contain two *p*-toluenediazo ligands and covalently bonded fluoride respectively. The molecule as a whole has approximate mirror symmetry (through Mo, B, F and the pyrazolyl ring atoms N(21), N(22), C(41)–C(43)). The Mo–F distance in I (1.965(2) Å) may be compared with the Mo–F bond length of 1.992(8) Å in the cationic hydrazido(−2) complex $[MoF(NNH_2)(dppe)_2]^+$ (dppe ≡ 1,2-bis(diphenylphosphino)ethane) which is the only other six-coordinate monofluoro molybdenum complex to have been structurally characterised [17].

The bond angles within the $[Mo(N_2C_6H_4Me\text{-}p)_2]$ structural unit of I (Mo–N–N 176.1(2), 175.2(2); N–N–C both 118.2°) establish that both *p*-toluenediazo ligands adopt the "singly-bent" (i.e. formal $[ArN_2]^+$) coordination mode. The angular

TABLE 1

FINAL FRACTIONAL COORDINATES ($Mo \times 10^5$, others $\times 10^4$) $MoF(N_2C_6H_4Me\text{-}p)_2[HB(C_3H_3N_2)_3]$ (I) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*
Mo	22373(2)	11291(3)	37612(1)
F	826(2)	2338(2)	3389(1)
N(1)	1740(2)	1519(3)	4302(1)
N(2)	1445(2)	1690(4)	4670(1)
N(3)	1432(2)	−845(3)	3726(1)
N(4)	969(2)	−2210(3)	3690(1)
N(11)	3342(2)	3410(3)	3754(1)
N(12)	4517(2)	3466(3)	3606(1)
N(21)	4194(2)	315(3)	4049(1)
N(22)	5257(2)	714(3)	3865(1)
N(31)	2978(3)	640(3)	3134(1)
N(32)	4177(3)	1154(3)	3073(1)
C(11)	219(3)	2406(4)	4699(1)
C(12)	−600(3)	3058(4)	4334(1)
C(13)	−1770(3)	3722(4)	4390(1)
C(14)	−2181(4)	3730(4)	4799(1)
C(15)	−1392(4)	3044(5)	5152(1)
C(16)	−172(4)	2418(5)	5114(1)
C(17)	−3521(5)	4391(7)	4840(2)
C(21)	−312(3)	−2414(4)	3441(1)
C(22)	−748(3)	−3985(4)	3346(1)
C(23)	−1944(3)	−4259(4)	3096(1)
C(24)	−2778(3)	−2982(5)	2933(1)
C(25)	−2334(4)	−1424(4)	3040(1)
C(26)	−1127(3)	−1124(4)	3288(1)
C(27)	−4085(4)	−3287(6)	2650(2)
C(31)	3045(3)	4923(4)	3832(1)
C(32)	3996(4)	5954(4)	3737(1)
C(33)	4904(4)	4995(4)	3604(1)
C(41)	4626(3)	−538(4)	4419(1)
C(42)	5971(4)	−704(5)	4467(1)
C(43)	6334(3)	102(4)	4118(1)
C(51)	2402(4)	−40(5)	2753(1)
C(52)	3244(5)	68(6)	2440(1)
C(53)	4336(4)	797(6)	2657(1)
B	5118(3)	1885(5)	3464(1)

TABLE 2

PRINCIPAL INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN I WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Interatomic distances

Mo–F	1.965(2)	C(24)–C(25)	1.391(5)
Mo–N(1)	1.832(3)	C(24)–C(27)	1.497(5)
Mo–N(3)	1.832(3)	C(25)–C(26)	1.369(5)
Mo–N(11)	2.211(3)	N(11)–N(12)	1.368(3)
Mo–N(21)	2.173(2)	N(11)–C(31)	1.322(4)
Mo–N(31)	2.210(3)	N(12)–C(33)	1.330(4)
N(1)–N(2)	1.217(4)	N(12)–B	1.544(4)
N(2)–C(11)	1.418(4)	N(22)–B	1.546(5)
C(11)–C(12)	1.386(4)	C(41)–C(42)	1.382(5)
C(11)–C(16)	1.390(4)	C(42)–C(43)	1.360(5)
C(12)–C(13)	1.367(4)	N(31)–N(32)	1.356(4)
C(13)–C(14)	1.382(5)	N(31)–C(51)	1.334(4)
C(14)–C(15)	1.357(5)	N(32)–C(53)	1.335(5)
C(14)–C(17)	1.517(5)	N(32)–B	1.528(5)
C(15)–C(16)	1.388(4)	C(51)–C(52)	1.398(6)
N(3)–N(4)	1.226(3)	C(52)–C(53)	1.351(6)
N(4)–C(21)	1.421(4)	C(31)–C(32)	1.371(5)
C(21)–C(22)	1.389(4)	C(32)–C(33)	1.344(5)
C(21)–C(26)	1.392(4)	N(21)–N(22)	1.357(3)
C(22)–C(23)	1.359(5)	N(21)–C(41)	1.340(4)
C(23)–C(24)	1.403(5)	N(22)–C(43)	1.343(4)

(b) Bond angles

F–Mo–N(1)	97.6(1)	C(22)–C(23)–C(24)	121.2(3)
F–Mo–N(3)	97.8(1)	C(23)–C(24)–C(25)	117.3(3)
F–Mo–N(11)	83.9(1)	C(23)–C(24)–C(27)	121.2(3)
F–Mo–N(21)	160.3(1)	C(25)–C(24)–C(27)	121.5(3)
F–Mo–N(31)	86.0(1)	C(24)–C(25)–C(26)	122.2(3)
N(1)–Mo–N(3)	90.8(1)	C(25)–C(26)–C(21)	119.3(3)
N(1)–Mo–N(11)	94.7(1)	Mo–N(11)–N(12)	121.5(2)
N(1)–Mo–N(21)	94.5(1)	Mo–N(11)–C(31)	132.3(2)
N(1)–Mo–N(31)	176.0(1)	N(12)–N(11)–C(31)	105.8(3)
N(3)–Mo–N(11)	173.9(1)	N(11)–N(12)–C(33)	108.6(3)
N(3)–Mo–N(21)	97.5(1)	N(11)–N(12)–B	119.1(2)
N(3)–Mo–N(31)	90.4(1)	C(33)–N(12)–B	132.2(3)
N(11)–Mo–N(21)	79.7(1)	N(12)–C(33)–C(32)	109.6(3)
N(11)–Mo–N(31)	83.9(1)	C(31)–C(32)–C(33)	105.0(3)
N(21)–Mo–N(31)	81.6(1)	N(11)–C(31)–C(32)	110.9(3)
Mo–N(1)–N(2)	176.1(2)	Mo–N(21)–N(22)	121.7(2)
N(1)–N(2)–C(11)	118.2(3)	Mo–N(21)–C(41)	131.1(2)
N(2)–C(11)–C(12)	123.1(3)	N(22)–N(21)–C(41)	107.2(2)
N(2)–C(11)–C(16)	117.5(3)	N(21)–N(22)–C(43)	108.9(3)
C(12)–C(11)–C(16)	119.4(3)	N(21)–N(22)–B	120.3(2)
C(11)–C(12)–C(13)	119.5(3)	C(43)–N(22)–B	130.3(3)
C(12)–C(13)–C(14)	121.9(3)	N(22)–C(43)–C(42)	108.7(3)
C(13)–C(14)–C(15)	118.2(3)	C(41)–C(42)–C(43)	105.9(3)
C(13)–C(14)–C(17)	120.1(4)	C(42)–C(41)–N(21)	109.2(3)
C(15)–C(14)–C(17)	121.6(3)	Mo–N(31)–N(32)	121.4(2)
C(14)–C(15)–C(16)	121.8(3)	Mo–N(31)–C(51)	131.1(2)
C(15)–C(16)–C(11)	119.1(3)	C(51)–N(31)–N(32)	107.4(3)
Mo–N(3)–N(4)	175.2(2)	N(31)–N(32)–C(53)	108.8(3)
N(3)–N(4)–C(21)	118.2(2)	N(31)–N(32)–B	119.7(3)

TABLE 2 (continued)

(b) Bond angles

N(4)-C(21)-C(22)	117.5(3)	C(53)-N(32)-B	131.3(3)
N(4)-C(21)-C(26)	123.0(3)	N(32)-C(53)-C(52)	109.5(4)
C(22)-C(21)-C(26)	119.5(3)	C(51)-C(52)-C(53)	105.3(3)
C(21)-C(22)-C(23)	120.6(3)	C(52)-C(51)-N(31)	109.0(4)

Mo-N-N-C moieties lie close to two mutually perpendicular planes defined by the atoms of the octahedral molybdenum coordination sphere as would be anticipated for interaction of the arenediazo ligand π^* orbitals with a pair of molybdenum t_{2g} orbitals. The planes of the arenediazo ligand aryl groups also lie close to the Mo-N-N-C plane with interplanar angles of 7.3 and 9.0° respectively. The Mo-N bonds (both 1.832(3) Å), N-N bonds (1.217(4), 1.226(3) Å) and N-C bonds (1.418, 1.421(4) Å) of the coordinated arenediazo ligands in (I) are similar in length to the comparable bonds in the closely-related bis(*p*-fluorophenyldiazo) complex $MoCl(N_2C_6H_4F\text{-}p)_2(C_5H_4Me)$ (XVI) [9]. However some significant differences may also be discerned between the geometries of the $[Mo(N_2Ar)_2]$ structural units in these two complexes. In complex I both of the arenediazo aryl groups are *cis*-oriented with respect to the fluoride ligand (the relevant torsion angles are F-Mo...N(4)-C(21), 4.7° and F-Mo...N(2)-C(11), 3.3°). However in complex XVI one aryl group is *cis*-oriented and one *trans* with respect to the chloride ligand. In a recent theoretical study of the bonding in transition metal arenediazo complexes DuBois and Hoffmann have speculated that electronic factors may dictate the direction of bending of a "singly-bent" arenediazo ligand with respect to the other ligands in an octahedral coordination sphere [22]. In the present case, however, the determining factor is likely to be steric in nature. A *trans* orientation with respect to the fluoride ligand of one or both of the arenediazo ligands in (I) would produce impossibly short non-bonded contacts with the bulky pyrazolyl groups. The orientations actually adopted by the arenediazo ligand phenyl groups in I lead to *ortho* C-H...F distances [C(12)-H...F (H...F 2.58 Å) and C(26)-H...F (H...F 2.62 Å)] which are normal Van der Waals contacts. Whether the mutually *trans* orientation of the arenediazo aryl groups in the *cis*-$[Mo(N_2Ar)_2]$ moiety which is observed in XVI and also in $Mo(N_2C_6H_4OCH_3\text{-}p)_2L$ (where L is the dianion of *N*,*N*-dimethyl-*N*,*N*-bis(ethylenethio)ethylenediamine) [11] is the electronically preferred orientation for this structural unit in the absence of severe steric constraints will not be clear until further structures have been examined. The angle at molybdenum between the two arenediazo ligands is somewhat smaller in I than the corresponding angle in XVI (90.8(1) versus 93.2(1)°) and this difference may also be the result of the greater steric demand of the poly(1-pyrazolyl)borato ligand in I. The near-identity of the two Mo-N-N bond-angles in I also contrasts with the situation in XVI where one of the *p*-fluorobenzenediazo ligands is significantly distorted from the idealised "singly-bent" geometry (Mo-N-N 167.4(2)°) [9] due to crystal-packing effects.

The $[\{HB(C_3H_3N_2)_3\}Mo]$ moiety in I has normal geometry [23] with N-Mo-N angles of 79.7, 81.6 and 83.9(1)°. The Mo-N bonds show a pronounced *trans*-effect, the bond *trans* to the fluorine ligand (2.173(2) Å) being considerably shorter than the two bonds *trans* to the *p*-toluenediazo ligands (2.211, 2.210(3) Å).

Experimental

The compounds $Tl[HB(C_3H_3N_2)_3]$ and $[Mo(N_2C_6H_4Me\text{-}p)_2(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ (XI) were prepared by literature methods [24,5]. IR spectra were recorded on a Perkin–Elmer 257 spectrometer and were calibrated with respect to a standard polystyrene film. A Perkin–Elmer/Hitachi R20A spectrometer operating at 60 MHz and ambient temperature was employed for ^1H NMR measurements. Microanalysis and molecular weight determinations were carried out by the staff of the Microanalytical Laboratory at University College, Cork.

Reaction of $Tl[HB(C_3H_3N_2)_3]$ *with complex XI.* A solution of $Tl[HB(C_3H_3N_2)_3]$ (2.09 g, 5.0 mol) in diethyl ether containing 10% CH_2Cl_2 was added dropwise under nitrogen to a stirred solution of XI (3.74 g, 5.0 mmol) in CH_2Cl_2. Addition was accompanied by a colour change from deep purple to wine red. After 8 h at room temperature the solution was filtered through Celite and concentrated to ca. 10 ml under reduced pressure. Diethyl ether was added to the concentrated solution which was again filtered and then reduced in volume to ca. 10 ml. Slow addition of 100 ml of n-pentane produced a scarlet microcrystalline precipitate of complex I which was collected by filtration and recrystallised from CH_2Cl_2/hexane. Yield 2.40 g, 85%. (Found: C, 49.10; H, 4.24; B, 2.21; Mo, 16.48; N, 24.36. $C_{23}H_{24}BFMoN_{10}$ calcd.: C, 48.78; H, 4.27; B, 1.91; Mo, 16.94; N, 24.73%). Molecular weight (vapour-phase osmometry in CH_2Cl_2): Found 567.0, $C_{23}H_{24}BFMoN_{10}$ calcd.: 566.3. IR (CH_2Cl_2) 2495(w)(ν(BH)), 1539, 1485(s)(ν(NN), tentative assignment) cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si) (ppm) δ 7.90–7.09 (complex multiplet, 14 H, aromatic protons of p-Me $C_6H_4N_2$ ligands and H(3), H(5) protons of $HB(C_3H_3N_2)_3$ ligand); 6.29 (triplet, J ca. 2.0 Hz, 1H, H(4) of $HB(C_3H_3N_2)_3$ ligand *trans* to F); 6.14 (triplet, J 2.0 Hz, 2H, H(4) of $HB(C_3H_3N_2)_3$ ligand *trans* to p-$MeC_6H_4N_2$ ligands); 2.35 (singlet, 6H, CH_3 protons of p-$MeC_6H_4N_2$ ligands) ppm. Dark red crystals of I which were suitable for an X-ray diffraction study were obtained by slow evaporation of a solution in dichloromethane-ethanol.

Crystal data for I. $MoF(N_2C_6H_4Me\text{-}p)_2[HB(C_3H_3N_2)_3]$, $C_{23}H_{24}BFMoN_{10}$, $M_r = 566.3$, Monoclinic, a 10.354(4), b 8.289(1), c 30.402(7) Å, β 99.78(3)°, U 2571.4 Å^3, $Z = 4$, $D_c = 1.46$, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 48 cm^{-1}. Space group $P2_1/n$ (C_{2h}^5, No. 14) from systematic absences $h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$.

Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections (with θ in the range 10–20°) measured on an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected with a small ($0.26 \times 0.37 \times 0.41$ mm) crystal to a maximum θ of 25 and 4504 unique data were obtained. After corrections for Lorentz and polarization effects and for absorption, the data wtih $I > 3\sigma(I)$ (3812) were labelled observed and used in structure solution and refinement. All calculations were carried out on the Amdahl V5 computer with our programs for data reduction; the SHELX [25] program system was used in subsequent calculations.

Structure solution and refinement

The coordinates of the molybdenum atom were obtained from an analysis of a three-dimensional Patterson function and the remaining non-hydrogen atoms were located in a heavy-atom-phased Fourier summation. Refinement was by full-matrix least-squares calculations initially with isotropic and then with anisotropic vibration parameters. A difference map, computed at an intermediate stage in the refinement, revealed maxima (0.77–0.37 e Å^{-3}) in positions expected for all the hydrogen atoms; these were then allowed for in geometrically idealised positions (C–H, 0.95 Å) and included in the final rounds of calculations. An overall isotropic thermal parameter was refined for the hydrogens of each methyl group and for the remaining hydrogen atoms. In the final refinement cycles a weighting scheme of the form $\sqrt{w} = 1/[\sigma^2 F + pF^2]^{1/2}$ was employed where the final p-parameter was 0.00300. Scattering factors used in the structure factor calculations were taken from the literature [26,27] and allowance was made for anomalous dispersion [28]. Refinement converged with $R = 0.0290$ and $R_w = [\Sigma w\Delta^2/\Sigma wF_0^2]^{1/2} = 0.0505$ for the reflections with $I > 3\sigma(I)$. A final difference map was devoid of any significant features. The structure factor listing, calculated hydrogen coordinates, a stereoview of the unit cell and tables of thermal parameters are available on request from the authors at the University of Guelph.

Acknowledgements

We are grateful to the Department of Education of the Irish Republic for a Maintenance Grant (to M.E.D.) and to the NSERC (Canada) for support (G.F.).

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