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Molybdenum–carbon functionalities supported by a quadridentate Schiff-base ligand: the reactivity of *trans*-dichloro[*N*,*N*′-bis(salicylidene)-*o*-phenylenediaminato]molybdenum(IV) ‡

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The parent compounds *trans*-[Mo(salophen)Cl_2] **1** [salophen = *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine dianion] and *trans*-[Mo(tbsalophen)Cl_2] **2** [tbsalophen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-*o*-phenylenediamine dianion] were obtained from the corresponding Schiff bases and [$MoCl_4(MeCN)_2$]. The alkylation of **1** proceeded very differently depending on the alkylating agent. The reaction with $(PhCH_2)_2Mg$ led to the formation of *trans*-[Mo(salophen)$(PhCH_2)_2$] **3**, containing two alkyl groups at the metal, while with Mg(mes)Br (mes = 2,4,6-$Me_3C_6H_2$) arylation occurred both at the imino carbons and at the metal, *via* a rather complex mechanism. Reduction of **1** led to an intermediate Mo(salophen), which was intercepted by PhCCPh. The plausible intermediate metallocyclopropene rearranged with the migration of one of the carbons to an imino group and dimerization of the monomeric unit. The salophen ligand displayed a bridging bonding mode in the dimer, containing a Mo=Mo fragment and two bridging vinyl functionalities. The proposed structures are supported by three X-ray analyses.

Over the last two decades the M(η-C_5H_5)$_2$ moiety has become representative of an organometallic fragment which can be used in the stabilization of M–C bonds and in a wide variety of metal-assisted reactions. In the meantime very few attempts have been made to move away from this convenient fragment and to improve upon it. One strategy is the use of alkoxo groups as ancillary ligands,[1] a second consists of the replacement of at least one C_5H_5 ring with an amido group,[2] while a third makes use of macrocyclic ligands, which until recently have been confined to co-ordination chemistry in its strictest sense. The only popular use of these macrocycles has been in the formation of organometallic derivatives of the pairs Fe, Ru, and Co, Rh in porphyrin chemistry,[3] with other cases being spread over a range of metals. In the case of early transition metals five major approaches can be mentioned, in chronological order: the use of (*i*) tetradentate Schiff bases, *i.e.* salen;[4] (*ii*) dibenzotetramethyltetraaza[14]annulenes;[5] (*iii*) the porphyrin skeleton;[6] (*iv*) *meso*-octaalkylporphyrinogen;[7] (*v*) calix[4]arenes.[8]

Whilst using tetradentate Schiff bases as ancillary ligands in the organometallic chemistry of titanium(IV) and zirconium(IV) it was discovered that, though very reactive metal–carbon bonds could be formed, the alkyl or aryl groups migrated to the highly electrophilic imino carbons of the ligand.[4a,d] The use of lower oxidation states, namely Ti^{III}, rendered the imino groups less electrophilic and enabled the isolation and study of M–C bond functionalities.[4c]

The present study describes how a molybdenum(IV) bonded to the tetradentate salophen ligand [*N*,*N*′-bis(salicylidene)-*o*-phenylenediamine dianion] behaves in the alkylation reaction and the formation of Mo–C functionalities. This is quite a rare co-ordination environment for molybdenum engaged in organometallic derivatization, and it can be usefully extended to other macrocyclic ligands.

Experimental

General

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Proton NMR and IR spectra were recorded on AC-200, DPX-400 Bruker, and Perkin-Elmer FT 1600 instruments, respectively. Magnetic susceptibility measurements were made on a MPMS5 SQUID susceptometer (Quantum Design Inc.) operating at a magnetic field strength of 3 kG.

Syntheses

Compound 1. Tri-*n*-butylamine (19 cm^3, 79.2 mmol) was added to an orange solution of H_2salophen (11.39 g, 36.0 cm^3) in thf (350 cm^3). The complex [$MoCl_4(MeCN)_2$] (11.5 g, 36 mmol) was then added and the resulting black suspension refluxed for 1 d. The black microcrystalline solid was filtered off and dried *in vacuo* (16.6 g, 83%) (Found: C, 52.15; H, 4.03; N, 5.15. $C_{24}H_{22}Cl_2MoN_2O_3$ requires C, 52.10; H, 4.01; N, 5.06%). IR (Nujol): $\tilde{\nu}_{max}$/cm^{-1} 1600s and 1567s. $\mu_{eff} = 2.75\ \mu_B$ at 300 K.

Compound 2. Tri-*n*-butylamine (19 cm^3, 80 mmol) was added to a light yellow solution of H_2tbsalophen [*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-*o*-phenylenediamine] (19.6 g, 36 mmol) in thf (300 cm^3). The complex [$MoCl_4(MeCN)_2$] (11.6 g, 36 mmol) was then added, and the resulting black suspension refluxed for 1 d. The black microcrystalline solid was filtered off and dried *in vacuo* (17.0 g, 66%). Crystals suitable for X-ray analysis were grown from thf solution (Found: C, 61.32; H, 6.63; N, 3.88. $C_{36}H_{46}Cl_2MoN_2O_2$ requires C, 61.28; H, 6.57; N, 3.97%). IR (Nujol): $\tilde{\nu}_{max}$/cm^{-1} 1600m and 1572m. $\mu_{eff} = 2.65\ \mu_B$ at 300 K.

Compound 3. Dibenzylmagnesium (28.5 cm^3, 0.3 M in thf, 8.5 mmol) was added to a frozen brown suspension of compound **1** (4.7 g, 8.5 mmol) in benzene (200 cm^3)–1,4-dioxane (5 cm^3). The solution slowly changed from dark brown to dark red. It was stirred overnight. The resulting dark red suspension was taken to dryness and benzene (200 cm^3) added. The suspension was

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‡ *Non-SI units employed*: G = 10^{-4} T, $\mu_B = 9.27 \times 10^{-24}$ J T^{-1}.

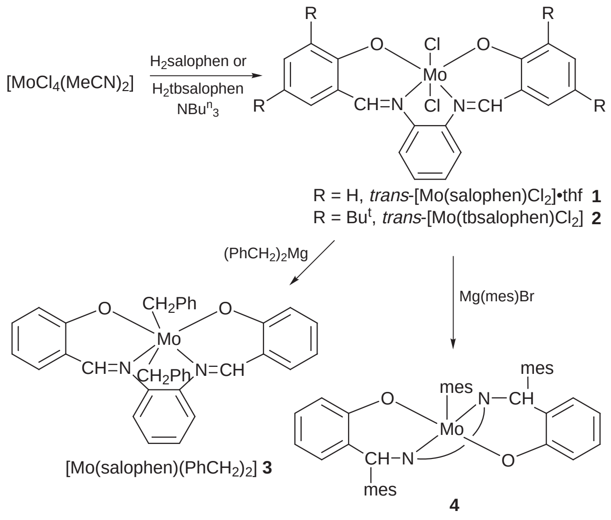
then filtered, taken to dryness and *n*-hexane (60 cm^3) added. The reddish brown solid was then collected and dried *in vacuo* (3.6 g, 71%) (Found: C, 68.5; H, 4.80; N, 4.45. $C_{34}H_{28}MoN_2O_2$ requires C, 68.92; H, 4.76; N, 4.73%). IR (Nujol): $\tilde{\nu}_{max}$/cm^{-1} 1599m and 1576m. $\mu_{eff} = 2.53$ μ_B at 300 K. The hydrolysis of **3** by aqueous HCl gave $PhCH_3$ (GC-MS) in the expected 1:2 Mo:$PhCH_3$ ratio.

Compound 4. Mesitylmagnesium bromide (22.8 cm^3, 0.83 M in thf, 19 mmol), was added dropwise to a frozen brown suspension of compound **1** (5.3 g, 9.5 mmol) in benzene (200 cm^3)–1,4-dioxane (4 cm^3). The mixture slowly changed from dark brown to dark green and was stirred overnight. The resulting dark green suspension was taken to dryness and benzene (200 cm^3) added. The green mixture was then filtered, taken to dryness and *n*-hexane (50 cm^3) added. The greenish brown precipitate was collected and dried *in vacuo* (4.1 g, 67%). Crystals suitable for X-ray analysis were grown in an *n*-hexane solution (Found: C, 73.16; H, 6.23; N, 3.90. $C_{47}H_{47}MoN_2O_2$ requires C, 73.52; H, 6.17; N, 3.65%). IR (Nujol): $\tilde{\nu}_{max}$/cm^{-1} 1569m. $\mu_{eff} = 1.83$ μ_B at 300 K.

Compound 5. Compound **1** (7.2 g, 13.0 mmol), Na (0.6 g, 26.0 mmol) and PhCCPh (2.9 g, 16.0 mmol) were added to thf (200 cm^3) and the mixture was stirred for 5 d. It slowly changed from violet to dark green. The resulting solution was then filtered (to remove NaCl), concentrated (50 cm^3) and diethyl ether (50 cm^3) added. The dark green precipitate was collected and dried *in vacuo* (6.8 g, 80%). Crystals suitable for X-ray analysis were grown in a thf–*n*-hexane solution (Found: C, 68.79; H, 5.24; N, 3.48. $C_{76}H_{64}Mo_2N_4O_6$ requires C, 68.85; H, 5.50; N, 3.82%). IR (Nujol): $\tilde{\nu}_{max}$/cm^{-1} 1589s and 1533m. $\mu_{eff} = 0.9$ μ_B at 300 K.

X-Ray crystallography

Suitable crystals were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[9] Crystal data and details associated with data collection are given in Table 1. Data were obtained using a single-crystal diffractometer (Rigaku AFC6S) at 133 K. For intensities and background the individual reflection profiles were analysed.[10] The structure amplitudes were obtained after the usual Lorentz-polarization corrections, and the absolute scale was established by the Wilson method.[11] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. Data for all complexes were then corrected for absorption using a semiempirical method.[12] The function minimized during the least-squares refinements was $\Sigma w(\Delta F^2)^2$. Anomalous scattering corrections were included in all structure factor calculations.[13*b*] Scattering factors for neutral atoms were taken from ref. 13(*a*) for non-hydrogen atoms and from ref. 14 for H. Structure solutions were based on the observed reflections [$I > 2\sigma(I)$] while the refinements were based on the unique reflections having $I > 0$. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map.[15] Refinements were done by full-matrix least squares first isotropically and then anisotropically for all non-H atoms except for the disordered atoms in **2** and **5**. The hydrogen atoms were located in a Fourier-difference map and introduced in the refinements as fixed atom contributions ($U_{iso} = 0.05$ Å^2). The H atoms associated with the disordered carbon atoms were ignored. In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ [with $P = (F_o^2 + 2F_c^2)/3$ was applied with a resulting in the value of 0.0634, 0.1052, 0.0513 for **2**, **4** and **5** respectively]. All calculations were performed using SHELXL 93.[16] The final difference map for **5** showed no unusual features, with no significant peaks above the general background. For **2** two residual peaks of 0.98 and 0.90 e Å^{-3} were found in proximity to the metal atom in the direction of the Mo(1)–N(2) and Mo(1)–O(1) bonds (general background 0.40 e Å^{-3}). For **4** two residual peaks of 1.32 and 1.28 e Å^{-3} were found in proximity to the metal atom along the Mo(1)–C(41) and Mo(1)–N(1) bonds (general background 0.43 e Å^{-3}).



Scheme 1

The refinement of complex **4** was straightforward. In **2** the C(26), C(27), C(28) methyl carbon atoms of a *tert*-butyl group showed high thermal parameters indicating the presence of disorder. The atoms were then split over two positions (A and B) isotropically refined with site occupation factors of 0.5. In complex **5** the thf solvent molecule of crystallization was found to be heavily affected by disorder which was solved by splitting the atoms over three positions, A, B and C, isotropically refined with site occupation factors of 0.5, 0.25 and 0.25, respectively. During refinement the C–O and C–C bond distances within the disordered thf molecules were constrained to 1.42(1) and 1.54(1) Å respectively. The isotropic model applied to the disordered atoms in **2** and **5** was the most satisfactory obtained after unsuccessful attempts to allow the 'partial' atoms to vary anisotropically.

CCDC reference number 186/1001.

See http://www.rsc.org/suppdata/dt/1998/2395/ for crystallographic files in .cif format.

Results and Discussion

The synthesis of the parent compounds **1** and **2** was carried out by treating [$MoCl_4(MeCN)_2$] with H_2salophen in the presence of a base, *i.e.* $Bu^n{}_3N$ (Scheme 1). Both compounds were obtained as microcrystalline black solids. They have the expected d^2 high-spin configuration with a magnetic moment of 2.75–2.65 μ_B at 300 K. The structures of **1** and **2** were clarified by X-ray analysis carried out on the more soluble derivative **2**.

A SCHAKAL[17] view of complex **2** is given in Fig. 1, with selected bond distances and angles in Table 2. Complex **2** crystallizes with a thf molecule. The co-ordination around molybdenum is pseudo-octahedral, two chlorine atoms being bonded to a Mo(tbsalophen) moiety in a *trans* arrangement [Cl(1)–Mo–Cl(2) 179.2(1)°] (Fig. 1). The Mo–Cl bond distances are not significantly different from each other and are in good agreement with those found for instance in [Mo(acacen)Cl_2] [H_2-acacen = 4,4′-ethylenedinitrilobis(pentan-2-one)],[18] while the Mo–O and Mo–N bond distances are significantly shorter and longer respectively than those in [Mo(acacen)Cl_2]. However, they fall in the range of values found for molybdenum Schiff base complexes [1.920(2)–2.112(2) and 2.070(6)–2.304(3) Å for Mo–O and Mo–N respectively].[18–20] The Mo atom lies on the N_2O_2 core which shows considerable tetrahedral distortion (Table 3). The normal to the mean co-ordination plane forms a dihedral angle of 1.7(1)° with the Cl–Mo–Cl line. The two six-membered chelation rings are slightly folded with respect to the N···O lines (Table 3). The metal lies nearly on the *o*-phenylene moiety, the maximum displacement from the mean plane

Table 1 Experimental data for the X-ray diffraction studies on crystalline complexes **2**, **4** and **5**

	2	**4**	**5**
Formula	$C_{36}H_{46}Cl_2MoN_2O_2{\cdot}C_4H_8O$	$C_{47}H_{47}MoN_2O_2$	$C_{68}H_{48}Mo_2N_4O_4{\cdot}2C_4H_8O$
M	777.7	767.8	1321.2
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$Pbcn$ (no. 60)
a/Å	13.648(3)	9.188(2)	24.185(4)
b/Å	15.105(5)	30.228(4)	14.435(2)
c/Å	11.149(3)	13.615(2)	17.044(2)
α/°	108.48(3)		
β/°	105.37(2)	103.99(2)	90
γ/°	63.91(2)		
U/Å^3	1936.3(10)	3669.2(11)	5950.2(15)
Z	2	4	4
D_c/g cm^{-3}	1.334	1.390	1.475
μ/cm^{-1}	44.08	32.83	39.85
Transmission coefficients	0.669–1.000	0.643–1.000	0.822–1.000
Unique data used in refinement ($I > 0$)	6516	5959	4919
Unique observed data [$I > 2\sigma(I)$]	4910	4104	3303
No. parameters refined	430	469	412
R	0.051	0.068	0.042
$wR2$	0.143	0.196	0.121

$\lambda = 1.541\ 78$ Å; $R = \Sigma|\Delta F|/\Sigma|F_o|$ calculated on the unique observed data [$I > 2\sigma(I)$]; $wR2 = (\Sigma w|\Delta F^2|^2/\Sigma w|F_o^2|^2)^{\frac{1}{2}}$ calculated on the unique data with $I > 0$.

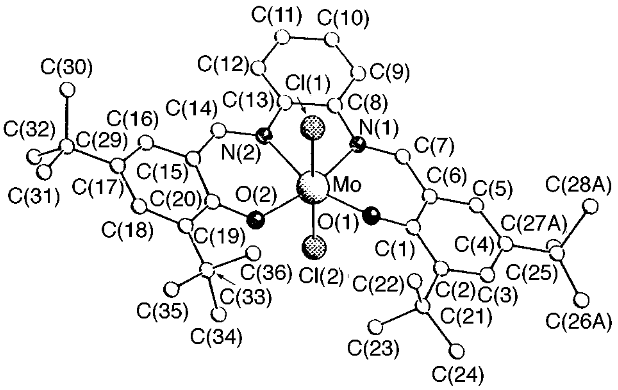


Fig. 1 A SCHAKAL drawing of complex **2**. Disorder affecting the C(25)–C(28) *tert*-butyl group has been omitted for clarity

through all the atoms including Mo being 0.042(5) for N(2). The tetrasubstituted Schiff base assumes a stacked conformation, the two peripheral aromatic rings being parallel [dihedral angle between them 1.0(2)°, stacking distance 0.97(2) Å] and tilted up and down with respect to the N_2O_2 core by 21.2(4)° (mean).

The alkylation of compound **1** with $Mg(CH_2Ph)_2$ leads to the expected *trans*-dibenzyl derivative **3**. The proposed structure is supported by the presence in the IR spectrum of the C=N band at 1599 cm^{-1}, and hydrolysis gave the expected amount of $PhCH_3$ confirming the presence of both benzyl groups at the metal without any migration to the imino carbons.

The reaction of compound **1** with Mg(mes)Br (mes = mesityl) led to **4** the formation of which requires the arylation of both the imino carbons and the metal, along with the oxidation of Mo^{IV} to Mo^{V}. The oxidation remains quite obscure since we cannot invoke a disproportionation reaction Mo^{V} to Mo^{III} because **4** is formed in a yield of *ca.* 70%. The arylation at the imino groups is the consequence of a preliminary oxidation of the metal to Mo^{V} which enhances the electrophilicity of the imino groups. The structure of **4** is shown in Fig. 2, with selected bond distances and angles in Table 2.

Complex **4** contains two mesityl groups bonded to the two C(7) and C(14) imino carbon atoms of a salophen ligand [C(7)–C(21) 1.550(9), C(14)–C(31) 1.543(10) Å]. A third mesityl group is σ bonded to molybdenum(V) which achieves five-co-ordination involving the N_2O_2 set of donor atoms at the base (Fig. 2). Molybdenum is 0.088(1) Å out of the plane through

Table 2 Selected bond distances (Å) and angles (°) for complexes **2** and **4**

	2	**4**
Mo–X*	2.400(1)	2.120(6)
Mo–Cl(2)	2.397(1)	
Mo–O(1)	1.928(5)	1.944(6)
Mo–O(2)	1.930(3)	1.938(6)
Mo–N(1)	2.129(4)	1.958(5)
Mo–N(2)	2.131(5)	1.994(7)
O(1)–C(1)	1.341(5)	1.361(10)
O(2)–C(20)	1.346(6)	1.365(10)
N(1)–C(7)	1.309(7)	1.510(10)
N(1)–C(8)	1.432(9)	1.400(10)
N(2)–C(13)	1.431(7)	1.391(9)
N(2)–C(14)	1.306(6)	1.494(10)
C(6)–C(7)	1.424(10)	1.522(10)
C(7)–C(21)		1.550(9)
C(14)–C(15)	1.427(8)	1.495(9)
C(14)–C(31)		1.543(10)
N(1)–Mo–N(2)	76.4(2)	79.6(3)
O(2)–Mo–N(2)	85.9(2)	84.7(2)
O(2)–Mo–N(1)	160.0(2)	127.9(2)
O(1)–Mo–N(2)	160.4(2)	166.2(2)
O(1)–Mo–N(1)	86.1(2)	92.7(2)
O(1)–Mo–O(2)	112.7(2)	91.1(2)
Cl(1)–Mo–Cl(2)	179.2(1)	
N(1)–Mo–C(41)		109.2(3)
O(2)–Mo–C(41)		122.2(2)
N(1)–C(7)–C(6)	127.2(5)	115.4(5)
C(6)–C(7)–C(21)		111.4(5)
N(1)–C(7)–C(21)		112.9(6)
N(2)–C(14)–C(15)	126.9(5)	106.2(5)
N(2)–C(14)–C(30)		110.2(6)
C(15)–C(14)–C(31)		119.4(6)

* X = Cl(1) for complex **2** and C(41) for complex **4**.

the σ-bonded aromatic ring at a Mo–C(41) distance of 2.120(6) Å falling in the range of values observed for Mo–$C_{\sigma\text{-aryl}}$ bonds [mean 2.151(10) Å].[21] The C(41)–C(46) ring is nearly perpendicular to the N_2O_2 core, the dihedral angle between them being 83.0(1)°. Molybdenum is out of the N_2O_2 core toward the apical aromatic carbon by 0.536(1) Å. The N_2O_2 core shows remarkable tetrahedral distortions (Table 3). The co-ordination polyhedron should be described as a distorted trigonal bipyramid involving the N(1), O(1), C(41) atoms in the equatorial plane and the O(1) and N(2) atoms at the apices. Molybdenum is out of the equatorial plane by 0.099(1) Å toward O(1). The double

Table 3 Comparison of relevant structural parameters (distances in Å, angles in °) within the Mo(salophen) units for complexes **2**, **4** and **5**

		2	**4**	**5**
Distances of atoms from the N_2O_2 cores	O(1)	−0.159(5)	−0.264(6)	0.019(4)
	O(2)	0.159(5)	0.281(6)	−0.031(4)
	N(1)	0.118(5)	0.320(6)	−0.002(3)
	N(2)	−0.095(4)	−0.338(6)	0.009(3)
	Mo	0.010(2)	0.536(1)	0.987(1)
Distances of atoms from the O(1)C(3)N(1) mean planes	O(1)	−0.041(4)	−0.076(6)	−0.007(3)
	N(1)	0.049(5)	0.103(6)	0.029(4)
	C(1)	0.085(5)	0.066(7)	0.006(5)
	C(6)	−0.019(6)	0.080(7)	0.035(5)
	C(7)	−0.077(6)	−0.166(7)	−0.060(5)
	Mo	0.524(1)	0.361(1)	0.722(1)
Distances of atoms from the $O_2C_3N_2$ cores	O(2)	0.032(4)	0.179(5)	0.104(3)
	N(2)	−0.044(5)	−0.229(6)	−0.142(3)
	C(14)	0.077(6)	0.424(7)	0.455(4)
	C(15)	0.004(6)	−0.126(7)	−0.193(4)
	C(20)	−0.080(6)	−0.247(7)	−0.313(6)
	Mo	−0.516(2)	0.132(1)	1.118(1)
Folding* along the N(1)···O(1) line		20.9(2)	15.4(2)	26.7(2)
Folding along the N(2)···O(2) line		20.4(2)	10.7(2)	45.3(2)
Angle between Mo–N(1)–O(1) and Mo–N(2)–O(2) planes		11.0(2)	53.0(2)	54.6(1)
Angle between the mean O(1)C(3)N(1) and O(2)C(3)N(2) planes		11.2(2)	45.6(2)	79.8(1)
Torsion angle N(1)–C(8)–C(13)–N(2)		4.6(8)	−5.1(9)	−4.0(6)

* The folding is defined as the dihedral angle between the Mo,N,O and OC_3N planes of a six-membered chelation ring.

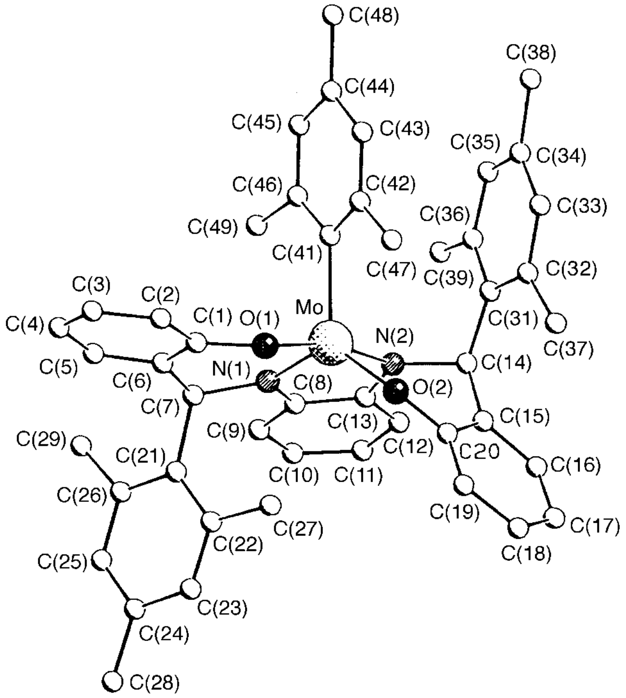
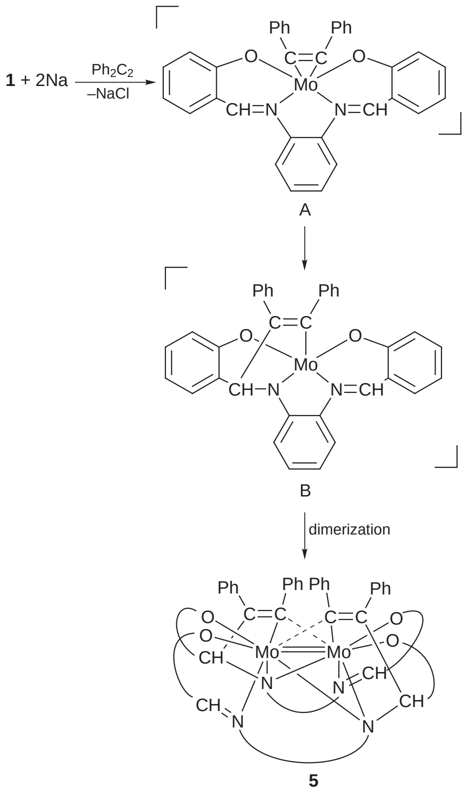


Fig. 2 A SCHAKAL drawing of complex **4**

arylation of salophen leads to a tetraanionic ligand, which would account for the marked shortening of the Mo–N distances compared with those of complex **2** (see Table 2). The Mo–O distances are not significantly different from those in complex **2**. The conformation of the Mo(salophen) moiety is strongly affected by arylation which moves the two mesityl ligands to the opposite sides of the co-ordination plane. As a result the two C(41)–C(46) and C(31)–C(36) rings become nearly parallel to each other to avoid steric interactions [dihedral angle 23.1(2)°]. As a consequence the peripheral C(15)–C(20) aromatic ring is pushed down to produce a half-umbrella conformation and a strong puckering of the N(2)···O(2) six-membered ring (Table 3). The deformation of the Schiff base is clearly indicated by the dihedral angle of 48.1(2)° between the C(15)–C(20) ring and the N_2O_2 core. The N(1)···O(1) six-membered chelation ring undergoes a minor distortion upon arylation, mainly as a result of the sp^3 character of the C(7) carbon atom (Table 3), the dihedral angle between the C(1)–C(6) ring and N_2O_2 core being 18.7(2)°. The metal lies approximately on the *o*-phenylene moiety, the maximum displacement from the mean plane through all the atoms including Mo being 0.086(6) Å for N(2). The orientation of the C(21)–C(26) ring which is nearly perpendicular to the N_2O_2 core [dihedral angle 86.5(2)°] means that the C(27) *o*-methyl group approaches the six-co-ordination site of molybdenum [Mo···H(271) 2.56 Å, C(41)–Mo···H(271) 152.3°]. Rotation of the mesityl groups C(31)–C(36) and C(41)–C(46) around the C–C and Ti–C bonds respectively is inhibited by mutual steric interactions, and rotation of the third mesityl group around the C(7)–C(21) bond is forbidden by steric interaction with the phenylene bridge.

With the purpose of accessing other kinds of M–C bonds, we attempted the reduction of compound **1** in the presence of diphenylacetylene. This reaction led to the formation of the dimeric complex **5**, *via* a complex pathway. The reduction of **1** in the absence of any reactive substrate would probably produce a metal–metal bonded dimer, as in the case of [Mo(acacen)Cl_2], leading to [(acacen)Mo≡Mo(acacen)].[20] In the presence of diphenylacetylene the intermediate Mo^{II} is intercepted by PhCCPh (see species **A** in Scheme 2) and finally one of the M–C bonds of the metallacyclopropene migrates to one of the imino carbons. This event leads to loss of the square-planar rigid arrangement of the salophen ligand and allows dimerization of the monomeric unit, as shown for **5** in Scheme 2.

The structure of complex **5** is shown in Fig. 3, with selected bond distances and angles in Table 4. Complex **5** is a dimeric unit which contains two tetraanionic ligands L (Fig. 3) derived from the alkylation of the C(14) imino carbon atom [C(14)–C(21) 1.502(6) Å] by PhCCPh. The complex has a crystallographically imposed C_2 symmetry (Fig. 4). In a dimer each ligand exhibits a tris-chelating behaviour toward the Mo atom through the O(1), N(1) and N(2) atoms while it binds the Mo′



Scheme 2

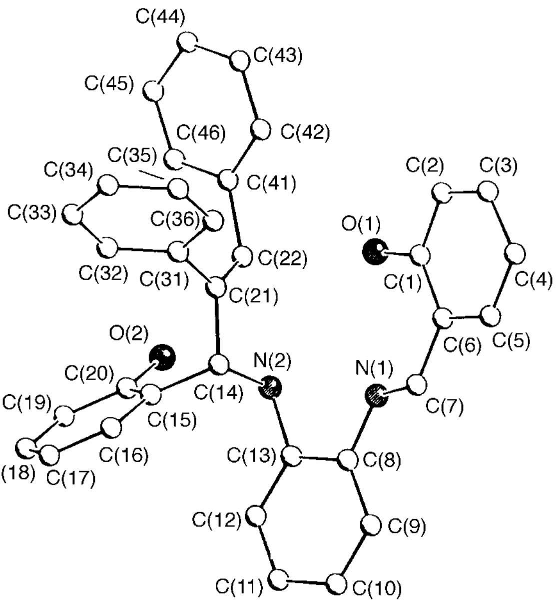


Fig. 3 A SCHAKAL drawing of the ligand in complex **5** with the numbering scheme adopted

Table 4 Selected bond distances (Å) and angles (°) for complex **5**

Mo(1)–Mo(1′)	2.544(1)	N(1)–C(7)	1.295(6)
Mo(1)–O(1)	2.007(3)	N(1)–C(8)	1.407(7)
Mo(1)–N(1)	2.220(4)	N(2)–C(13)	1.441(5)
Mo(1)–N(2)	2.114(4)	N(2)–C(14)	1.494(6)
Mo(1)–N(2′)	2.176(3)	C(6)–C(7)	1.434(8)
Mo(1)–C(22)	2.528(5)	C(14)–C(15)	1.503(7)
Mo(1)–C(22′)	2.226(5)	C(14)–C(21)	1.502(6)
Mo(1′)–O(2)	2.002(2)	C(21)–C(22)	1.354(7)
O(1)–C(1)	1.320(6)	C(21)–C(31)	1.483(7)
O(2)–C(20)	1.336(6)	C(22)–C(41)	1.503(6)
N(2′)–Mo(1)–C(22′)	72.0(2)	N(1)–C(7)–C(6)	124.0(5)
N(2)–Mo(1)–N(2′)	73.0(1)	N(2)–C(14)–C(21)	106.6(4)
N(2)–Mo(1)–C(22)	67.1(1)	N(2)–C(14)–C(15)	110.2(4)
N(1)–Mo(1)–C(22′)	165.6(2)	C(15)–C(14)–C(21)	109.9(4)
N(1)–Mo(1)–N(2′)	104.9(1)	C(14)–C(21)–C(31)	116.1(4)
N(1)–Mo(1)–N(2)	72.8(2)	C(14)–C(21)–C(22)	117.2(4)
O(1)–Mo(1)–C(22′)	97.9(1)	C(22)–C(21)–C(31)	126.5(4)
O(1)–Mo(1)–N(2′)	165.3(1)	Mo(1′)–C(22)–C(21)	113.1(3)
O(1)–Mo(1)–N(1)	82.2(1)	C(21)–C(22)–C(41)	114.8(4)
O(2′)–Mo(1)–C(22)	156.9(1)	Mo(1′)–C(22)–C(41)	125.8(4)

Primes denote the transformation $-x$, y, $1.5 - z$.

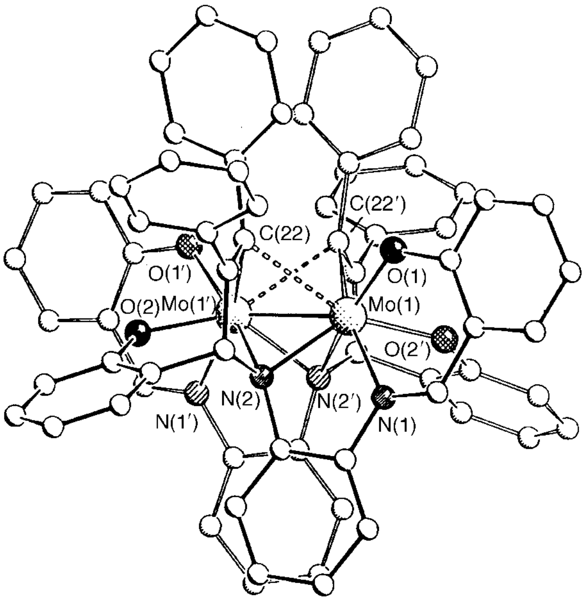


Fig. 4 A SCHAKAL drawing of complex **5**. Primes denote a transformation of $-x$, y, $1.5 - z$

atom (′ $-x$, y, $1.5 - z$) through the O(1), N(2) and C(22) atoms (Table 4). This results in the formation of a five-membered metallacycle [N(2), C(14), C(21), C(22), Mo(1′)]. The Mo(1)–C(22′) [2.226(5) Å] and C(21)–C(22) [1.354(7) Å] bond distances are in the range found for Mo–C(R)=CR$_2$ functionalities [Mo–C$_{av}$ 2.193(8), C=C$_{av}$ 1.346(4) Å].[21] The group of N(2), C(14), C(21), C(22) atoms gives rise to another metallacycle with Mo(1) if the C(22)– Mo(1) contact distance of 2.528(5) Å is taken into account. The hypothesis that this contact distance can be explained by a weak π interaction rather than mere geometrical effects is supported by the pyramidality of the C(22) carbon atom, which is out of the plane passing through the three bonded atoms [C(21), C(41), Mo(1′)] by 0.239(5) Å, but not by the C(21)–C(22) distance [1.354(7) Å] which is not significantly longer than a localized double bond. The Mo(1)···C(21) [3.023(5) Å] and Mo(1′)–C(21) [3.025(5) Å] distances rule out any possible η^2-C=C interaction with the metal. Considering the Mo(1)–C(22) interaction the metal atoms exhibit seven-coordination which could be described as a monocapped distorted octahedron (Fig. 5) with the N(1), O(1), N(2′), C(22′) atoms defining the equatorial plane and the O(2′) and C(22) atoms at the apices. The N(2) atom is capping the N(1), N(2′), C(22) face. In a dimer the two octahedra share the C(22)–N(2′) edge. The two Mo–N(2) distances are significantly different [Mo–N(2) 2.114(4), Mo–N(2′) 2.176(3) Å]. In spite of the bridging role of N(2) these values are significantly shorter than the Mo–N(1) distance [2.220(4) Å] as a consequence of the alkylation of the C(14) imino carbon. The Mo–O bond distances are significantly longer than those observed in complexes **2** and **4**. The Mo–Mo′ distance [2.544(1) Å][22] suggests a double metal–metal bond. The alkylation by PhCCPh strongly affects the conformation of the original Schiff base, the N$_2$O$_2$ inner core being removed by the twist of the O(2)–C(20)–C(15) phenoxide moiety which forms a dihedral angle of 57.4(2)° with the *o*-phenylene ring. Nevertheless, the four N and O donor atoms still define a plane (Table 3). The dihedral angle between the *o*-phenylene ring and the O(1)–C(1)–C(6) phenoxide moiety is

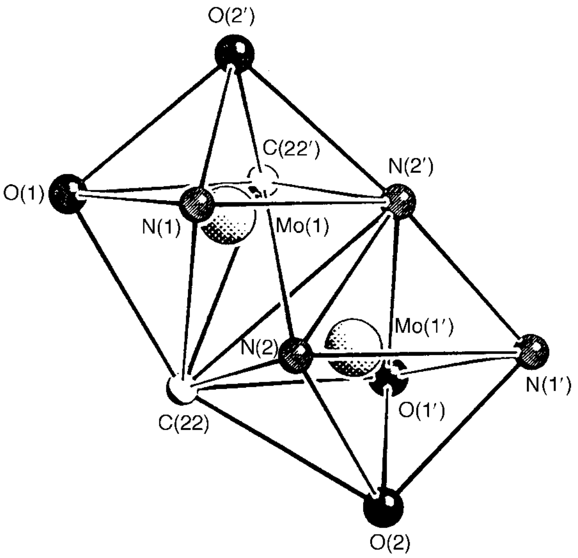


Fig. 5 A SCHAKAL drawing of the co-ordination polyhedra in complex **5**. Primes denote a transformation of −*x*, *y*, 1.5 − *z*

13.3(2)°. The mean planes through the two OC$_3$N moieties are nearly perpendicular forming a dihedral angle of 79.8(1)°.

Conclusion

This report deals with unprecedented Mo–C bond functionalities supported by a tetradentate Schiff-base ligand. The organometallic functionalization of the parent compound [Mo(salophen)Cl$_2$] **1** led to the formation of a bis(benzyl)-molybdenum(IV) derivative, containing two alkyl groups *trans* to each other in *trans*-[Mo(salophen)(PhCH$_2$)$_2$]. However, the arylation of **1** occurred both at the metal and at the imino groups of the salophen ligand with the formation of an unusual molybdenum(V) aryl derivative. The metal and the electrophilic carbon of the imino groups were also involved when the Mo(salophen) intermediate, produced from the reduction of **1**, was intercepted by PhCCPh, leading to a dimeric Mo=Mo′ compound containing two bridging vinyl functionalities.

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