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Bis-indenyl molybdenum(IV) halide complexes: synthesis and X-ray studies

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A stepwise route to bis-indenyl halide derivatives of molybdenum is reported. Treatment of $[Ind_2Mo(CO)_2][BF_4]_2$ with one equivalent of Bu_4NBr in CH_2Cl_2 yielded $[Ind_2Mo(CO)Br][BF_4]$ (**1**). When **1** was refluxed in NCMe and irradiated with a 60 W tungsten bulb $[Ind_2Mo(NCMe)Br][BF_4]$ (**2**) was isolated. The reaction of $[Ind_2Mo(CO)Br][BF_4]$ with LiBr afforded Ind_2MoBr_2 (**3**). The Ind_2MoCl_2 (**4**) analogue has been prepared directly by reaction of $[Ind_2Mo(CO)_2][BF_4]_2$ with LiCl.

The reaction of Ind_2MoBr_2 with $AlMe_3$ in toluene produces the bromo-methyl species $Ind_2MoBrMe$ (**5**). Treatment of Ind_2MoBr_2 with $TlPF_6$ in the presence of $P(OMe)_3$ afforded $[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ (**6**) which was readily reduced by two equivalents of cobaltocene to yield the neutral species $Ind_2Mo\{P(OMe)_3\}_2$ (**7**). Reaction of $[Ind_2Mo(CO)_2][BF_4]_2$ with $P(OMe)_3$ in dichloromethane yielded $[Ind_2Mo(CO)Cl][BF_4]$ (**8**). The molecular structures of $[Ind_2Mo(CO)X][BF_4]$ [X = Cl (**8**) or Br (**1**)], Ind_2MoBr_2 (**3**) and $[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ (**6**) have been determined by single crystal X-ray diffraction. The synthesis and characterisation of $[(\eta^3\text{-Ind})Mo(CO)_2]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**9**) is also reported.

Introduction

In contrast to the well developed chemistry of bis-cyclopentadienyl complexes of Group 6 metals, the number of their bis-indenyl counterparts is very small, reflecting difficulties found in their synthesis. The early examples reported are $(C_9H_7)_2Cr$,[1] $(\eta^5\text{-Ind})W(\eta^3\text{-Ind})(CO)_2$[2] and $(\eta^5\text{-Ind})Mo(\eta^3\text{-Ind})(dppe)$.[3] Recent investigations in our laboratory have focused on the chemistry of mixed ring (Cp)(indenyl)molybdenum(IV) complexes[4] but a simple route into the bis-indenyl complexes, namely $(\eta^5\text{-Ind})Mo(\eta^3\text{-Ind})(CO)_2$ has only recently been achieved.[5] This simple, high yield synthesis allows us to explore the chemistry of the bis-indenylmolybdenocenes. In the present paper we describe the synthesis of bis-indenyl halides of molybdenum $[Ind_2Mo(CO)X][BF_4]$ (X = Cl and Br), $[Ind_2Mo(NCMe)Br][BF_4]$, Ind_2MoBr_2, and the first alkyl derivative of this family, $Ind_2MoBrMe$. The synthesis of $[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ and $[Ind_2Mo\{P(OMe)_3\}_2]$ is also discussed.

We have also synthesized the novel *ansa*-(dimethylsilyl)-bis(cyclopentadienyl) molybdenum $[(\eta^3\text{-Ind})Mo(CO)_2]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**9**) by the reaction of $IndMoCl_3(CO)_2$ with the dilithium salt of the dimethylsilyl-bridged bis-cyclopentadienyl ligand $[Me_2Si(\eta^5\text{-}C_5H_4)_2]^{2-}$. Mononuclear *ansa*-metallocenes of tungsten and molybdenum have been reported in the literature but to our knowledge this is the first example of a dinuclear symmetric compound of molybdenum.[6]

Results and discussion

Reaction of $[Ind_2Mo(CO)_2][BF_4]_2$ with one equivalent of tetrabutylammonium bromide in dichloromethane at room temperature gives the purple monocation $[Ind_2Mo(CO)Br][BF_4]$ (**1**) characterized by a ν(CO) stretching vibration at 2036 cm^{-1}. Irradiation of a refluxing solution of **1** in NCMe with a 60 W tungsten bulb leads to the formation of $[Ind_2Mo(NCMe)Br][BF_4]$ (**2**) as a pink-red powder (Scheme 1). The crystal structure of **1** has been determined by X-ray diffraction studies (see below).

The ^1H NMR spectra of complexes **1** and **2** present the typical resonances expected for an η^5-Ind asymmetric complex: four resonances in the aromatic region at δ 7.74, 7.65, 7.45 and 7.27 (H^{5-8}), two multiplets at δ 7.17 and 6.36 ($H^{1/3}$) and a multiplet at δ 6.22 (H^2) for compound **1** and four multiplets at δ 7.57, 7.45, 7.32 and 7.27 (H^{5-8}), two multiplets at δ 7.12 and 6.25 ($H^{1/3}$) and a multiplet at δ 5.98 (H^2) for compound **2**. The IR and the ^1H NMR data on the coordinated NCMe ligand in **2** are similar to those already reported for the corresponding Ind_2-Mo congeners.[5] The coordinated NCMe molecule displays in the ^1H NMR spectrum a singlet at δ 2.12 and ν(NC) stretching vibrations at 2318 and 2291 cm^{-1}.

Treatment of **1** with one equivalent of LiBr in a refluxing acetone solution gives Ind_2MoBr_2 (**3**) as a green crystalline solid. Irradiation of a mixture of $[Ind_2Mo(CO)_2][BF_4]_2$ with excess of LiCl in a refluxing dichloromethane suspension directly forms Ind_2MoCl_2 (**4**) in high yield as a green microcrystalline complex (Scheme 1). Unexpectedly, the similar reaction of $[Ind_2Mo(CO)_2][BF_4]_2$ with LiBr does not afford the halide Ind_2MoBr_2, instead unidentified decomposition products are formed. The bis-indenyl halides **3** and **4** are soluble in chlorinated solvents (chloroform and dichloromethane) as well as in aromatic hydrocarbons (benzene, toluene) in contrast to the practically insoluble $IndCpMoX_2$[4b] and Cp_2MoX_2.[7]

The ^1H NMR spectrum of **3** presents one multiplet in the aromatic region at δ 7.31–7.18 (H^{5-8}), a doublet at δ 5.72 ($H^{1/3}$) and a triplet at δ 5.46 (H^2). A similar ^1H NMR spectrum was obtained for Ind_2MoCl_2 (**4**), one multiplet at δ 7.34–7.05 (H^{5-8}), a doublet at δ 5.81 ($H^{1/3}$) and a triplet at δ 5.53 (H^2). The crystal structure of **3** has been determined by X-ray diffraction studies (see below).

In total contrast to its bis-cyclopentadienyl congener, the bis-indenyl molybdenum bromide Ind_2MoBr_2 (**3**) is unexpectedly unreactive towards nucleophiles failing to react with NaSPh,

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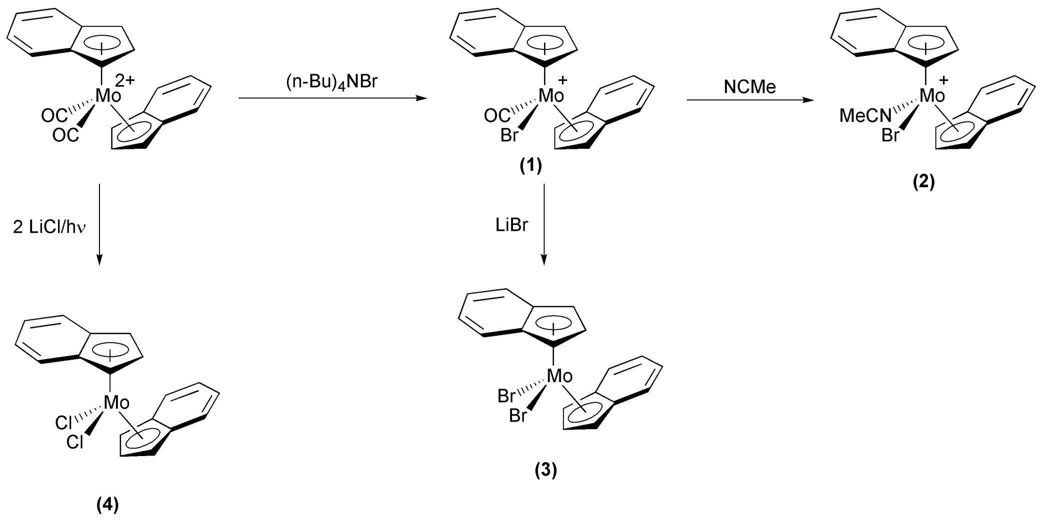
MeMgCl and $LiB[CH(CH_3)C_2H_5]_3H$. This lack of reactivity of the bis-indenylMo(IV) core towards nucleophiles may be the result of the steric protection offered to the metal by the indenyl ligands preventing approach of the nucleophile in substitution reactions. In fact, **3** reacts with $AlMe_3$ in a refluxing dichloromethane solution to yield $Ind_2MoBrMe$ (**5**) as a blue solid. Furthermore, substitution of the bromide is readily achieved in the presence of $TlPF_6$. Reaction of **3** with two equivalents of thallium hexafluorophosphate in the presence of excess of trimethylphosphite gives $[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ (**6**) as a red crystalline solid. Derivative **6** is readily reduced by two equivalents of cobaltocene in toluene to give the ring-slipped neutral species $Ind_2Mo\{P(OMe)_3\}_2$ (**7**) as a yellow solid (Scheme 2). This behaviour parallels that observed for the mixed ring complexes $[Cp(Ind)MoL_2]^{2+}$ as reported elsewhere.[8] When Ind_2MoBr_2 (**3**) was treated with one equivalent of thallium hexafluorophosphate in the presence of styrene no reaction was observed.

The ^1H NMR spectrum of complex **6** presents the expected resonances for a η^5-Ind complex: a multiplet at δ 7.72 (H^{5-8}), a doublet at δ 6.36 ($H^{1/3}$) and a triplet at δ 5.98 (H^2). The protons of the methyl group of $P(OMe)_3$ display a singlet at δ 4.09. The ^1H NMR spectrum of **7** shows the H^2 and $H^{1/3}$ resonances at δ 5.46 and 5.72, respectively, shifted upfield from their positions in the η^5-coordination mode, as has also been reported for the bis(indenyl) complex $IndMo(\eta^3\text{-}Ind)(CO)_2$.[5] The crystal structure of **6** has been determined by X-ray diffraction studies (see below).

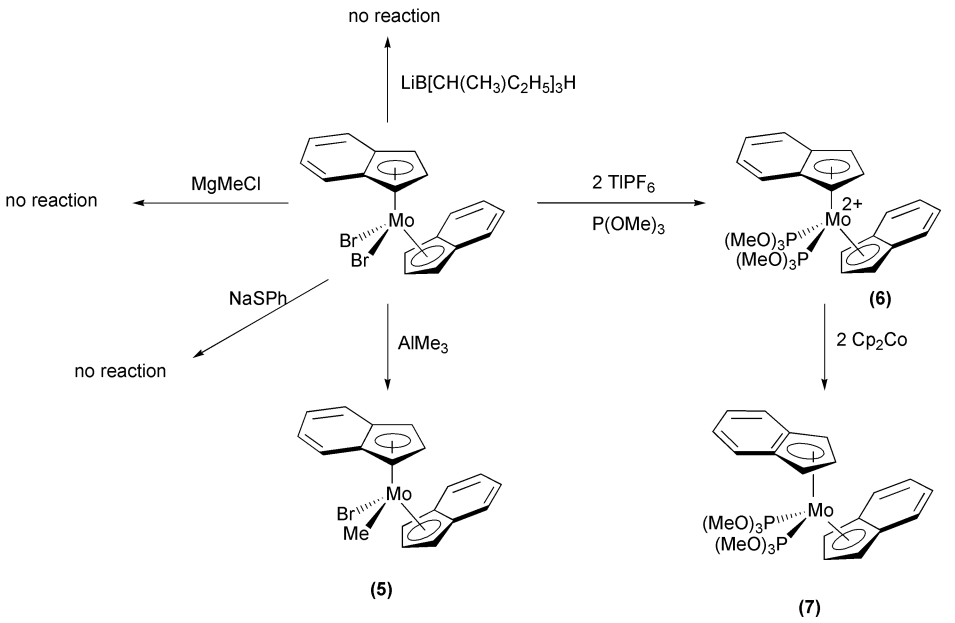
The ^1H NMR spectrum of **5** in C_6D_6 shows three multiplets in the aromatic region at δ 6.91, 6.78 and 6.53 (H^{5-8}), two multiplets at δ 4.56 and 4.29 ($H^{1/3}$), a multiplet at δ 3.56 (H^2) and a singlet at δ 0.3 for the protons of the methyl group.

The reaction of $[Ind_2Mo(CO)_2][BF_4]_2$ with excess of $P(OMe)_3$ in dichloromethane yields $[Ind_2Mo(CO)Cl][BF_4]$ (**8**) which has been characterized by IR, ^1H NMR and X-ray diffraction studies (see below). This result was rather unexpected because no chloride ions were present in the reactants. Therefore, the chloride must come from the solvent. No radical reaction is likely to take place in this mixture and, therefore, we put forward the following explanation for this reaction. Since CO is easily dissociated in these dications, an intermediate species $[Ind_2Mo(CO)(ClCH_2Cl)][BF_4]_2$ can be formed. Nucleophilic attack of the trimethylphosphite at the coordinated CH_2Cl_2 ligand can then lead to **8** together with $[ClCH_2P(OMe)_3]BF_4$. Such nucleophilic attacks at coordinated haloalkanes have been documented.[9]

We have also synthesised the novel *ansa*-metallocene $[(\eta^3\text{-}Ind)Mo(CO)_2]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ (**9**) by the reaction of

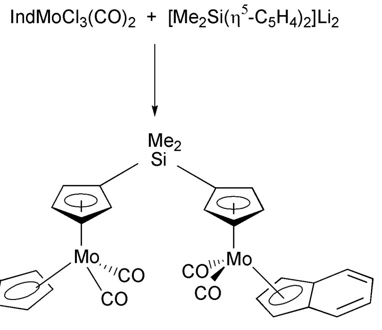


Scheme 1



Scheme 2

$IndMoCl_3(CO)_2$ with the lithium salt $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Li_2$ (Reaction 1). Compound **9** was isolated as a red solid. This synthetic strategy has already been reported by us for the synthesis of $Ind_2Mo(CO)_2$[5] and $IndMo(\eta^3\text{-Flu})(CO)_2$ (Flu = fluorenyl, $C_{13}H_9$).[10]



(1)

(9)

The ^1H NMR spectrum of **9** in CD_2Cl_2 shows the resonances for the bridging $DMSCp_2$ protons at δ 4.80 and 4.69 as two set of pseudotriplets due to an AA′BB′ system, and a singlet at δ 0.40 for the methyl protons of the $DMSCp_2$. The resonance at δ 0.40 for the methyl protons of the $DMSCp_2$ supports the assignment of the $DMSCp_2$ unit as a bridging ligand. It has been reported that a spectral feature that differentiates the mono- and di-nuclear complexes is related to the chemical shifts observed for the methyl protons of the bridging silyl groups in the $DMSCp_2$ ligand.[11] In mononuclear complexes (chelating ligand) these protons generate signals at higher fields (δ −0.01 to 0.00) than in dinuclear complexes (bridging ligand) (δ 0.16 to 1.44). This effect may be attributed to the greater rigidity in the mononuclear complexes and therefore to a more efficient shielding of these protons by the conjugated π system in the neighboring rings. The lower rigidity in the dinuclear complexes favors the rotation around the $Si\text{–}C_{ipso}$ (Cp) bond, thus reducing the shielding effect of the π system. The ^1H NMR spectrum of **9** confirms the η^3-indenyl coordination: a triplet for H^2 at δ 7.26, two multiplets for $H^{5\text{–}8}$ at δ 6.59 and 6.46 and a doublet for $H^{1/3}$ at δ 5.04.[4b]

Crystallographic studies

The solid state structures of the complexes $[Ind_2Mo(CO)Br][BF_4]$ (**1**), Ind_2MoBr_2 (**3**), $[Ind_2Mo\{P(OMe)_3\}_2][BF_4]_2$ (**6**) and $[Ind_2Mo(CO)Cl][BF_4]$ (**8**) were determined by single crystal X-ray diffraction. Molecular dimensions associated with the molybdenum coordination sphere for these four complexes are listed in Table 1. ORTEP diagrams showing the overall structures and atomic notation scheme adopted are presented in Figs. 1, 2, 3 and 4 for **1**, **3**, **6** and **8** respectively. All four complexes exhibit a pseudo tetrahedral environment comprising the centroids of two C_5 rings of both indenyl ligands and the donor atoms of two monodentate ligands (Br and CO in $\mathbf{1}^+$, two Br in **3**, two $P(OMe)_3$ in $\mathbf{6}^{2+}$ and Cl and CO in **8**).

The asymmetric unit of **3** comprises four discrete molecules of $[Ind_2Mo_2Br_2]$ held together only by van der Waals forces. These molecules display comparable dimensions. So in this discussion average values for the structural parameters are used unless otherwise stated. The four independent molecules correspond to four different conformational isomers present in the crystal structure, this structural feature is discussed later.

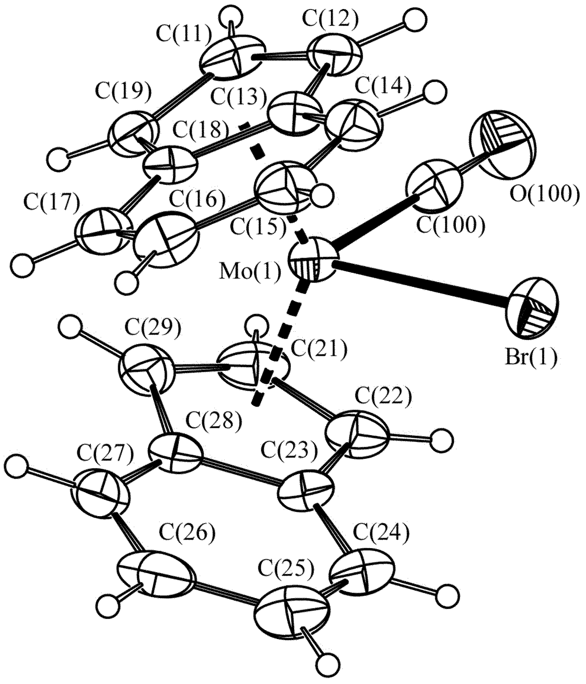


Fig. 1 An ORTEP view of the $[Ind_2Mo(CO)Br]^+$ cation in **1** with thermal ellipsoids drawn at the 30% probability level.

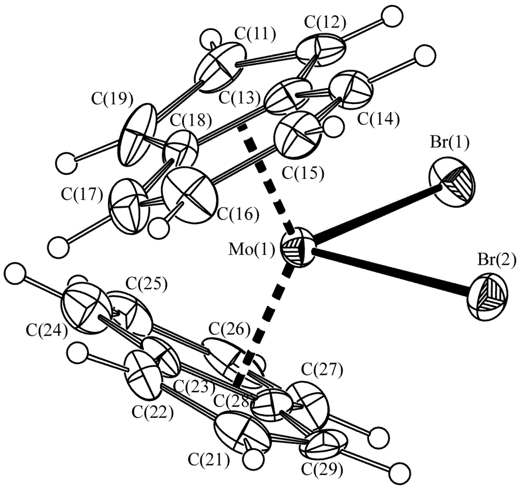


Fig. 2 An ORTEP view of Ind_2MoBr_2 complex **3** (molecule 1). Thermal ellipsoids are drawn at the 30% probability level.

Complexes **1** and **8** have quasi “isomorphous” structures. These two complexes display similar molecular dimensions (bond distances, bond angles and torsion angles) apart from the Mo–halogen distances. In fact the root mean square deviations (RMS) in the atomic positions of the non-hydrogen atoms of the $Ind_2Mo(CO)$ fragment between the two structures is only 0.188 Å. Furthermore the Mo–Br distance of 2.633(1) Å in **1** is 0.155 Å longer than the Mo–Cl of 2.478(3) Å distance in **8** leading to a slight increase of 10 Å^3 in the unit cell volume of **1**. The value of the Mo–Br distance in **1** is similar to the average value found for **3** of 2.632(1) Å. The distances found for Mo–L and Mo–L′ bonds naturally reflect the electronic properties of the molybdenum and the ligands L and L′, being the values quoted in Table 1 for Mo–P, Mo–C, Mo–Br and Mo–CO bonds within the expected values.[12] In spite of the natural differences between the Mo–Cl, Mo–CO and Mo–Br distances **1**, **3** and **8** have similar L–Mo–L′ angles of 80.8(3), 82.8(1), 81.9(4)° respectively. **6** with an average Mo–P distance of 2.446(1) Å displays a slightly wider angle of 87.0(1)°, reflecting the presence of two bulkier ligands $P(OMe)_3$ in the molybdenum coordination sphere.

The range distances found for the bonds between the molybdenum and the carbon atoms of the two indenyl ligands, listed in Table 1, indicates unequivocally that in all four complexes these two ligands are linked to the metal centre through their C_5 rings in an η^5-fashion. Furthermore, when η^5 hapticity is present the carbon atoms of the C_5 ring of the indenyl ligand are approximately planar and a small Ω folding angle would be

Table 1 Selected molecular dimensions associated with the molybdenum coordination sphere in complexes **1**, **3**, **6** and **8**

Complex	**1**	**3**	**6**	**8**
$[\mathrm{MoInd_2LL'}]^{n+}$	L = Br; L′ = C(100)	L = Br(1); L′ = Br(2)	L = P(1); L′ = P(2)	L = Cl; L′ = C(100)
Distances/Å				
Mo–L	2.633(1)	2.635(1) 2.618(1) 2.646(1) 2.642(2)	2.442(1)	2.478(3)
Mo–L′	1.992(10)	2.614(1) 2.629(1) 2.644(1) 2.630(1)	2.469(2)	1.997(15)
Mo–η-C_5H_5[a]	2.261(8)–2.445(8)	2.242(11)–2.472(10) 2.275(10)–2.534(11) 2.271(11)–2.469(10) 2.204(11)–2.429(10)	2.263(5)–2.449(5)	2.265(13)–2.491(12)
Mo–η-C_5H_5′[a]	2.254(8)–2.483(7)	2.268(11)–2.466(10) 2.268(11)–2.466(10) 2.254(12)–2.546(11) 2.262(11)–2.492(10)	2.272(5)–2.531(5)	2.262(11)–2.453(11)
Mo–Cp[b]	2.014	2.017 2.036 2.027 2.043	2.019	2.031
Mo–Cp′[b]	2.016	2.029 2.081 2.043 2.044	2.044	2.006
Angles/°				
L–Mo–L	80.8(3)	83.32(5) 83.00(5) 82.36(5) 82.41(5)	87.0(1)	81.9(4)
Cp–Mo–Cp[a]	135.3	133.5 133.9 134.6 133.7	136.5	135.5
Dihedral angles/°[c]				
Ω	7.2, 6.1	6.3, 6.7 5.0, 6.7 5.8, 3.6 4.5, 2.1	3.5, 6.1	5.5, 5.4
λ	3.7	173.6 173.2 11.7 15.4	92.2	6.1
β	95.9, 91.6	90.1 88.7 86.9, 92.8 84.3, 97.6 100.0, 82.3	177.2, 93.3	91.6,98.2

[a] Mo–η-C_5H_5 and Mo–η-C_5H_5 denotes the range of bond lengths between the molybdenum centre and carbon atoms of the five-membered ring of the indenyl ligands ligands. [b] Cp and Cp′represent the centroids of the η-C_5H_5 rings. [c] The dihedral angles are defined in the text.

expected. This structural parameter was proposed by Crabtree, Faller and Habib[13] precisely to characterise the $\eta^3 \longrightarrow \eta^5$ ring slippage of the indenyl π systems and has been extensively used.[5]

For the four structures described in this work the Ω folding angle is given by the dihedral angle between the planes [C(19), C(18), C(13), C(12)] and [C(19), C(11), C(12)]. The Ω parameter take values of 7.2 and 6.1° in **1**, 5.4 and 4.8° in **3**, 3.5 and 6.1° in **6** and 5.5 and 5.4° in **8**, which are perfectly consistent with an η^5 coordination mode for both indenyl ligands leading to a formal 18 electron species. In this context, in the related complex $[\mathrm{IndMo}(\eta^3\text{-Ind})(\mathrm{CO})_2]$[5] the η^5-indenyl ring exhibits a small folding of 3° comparable to that found for the quoted complexes while the η^3-indenyl ligand shows a pronounced bending with a Ω angle of 20.8°, typical of η^3-coordination.

Fig. 5 shows a top view of two of the four molecules present in the asymmetric unit of complex **3**. It is clear from this figure that these two structures correspond to two different geometric arrangements of the two indenyl ligands, called here a and b. In the crystal there are four molecules of $[\mathrm{Ind_2Mo_2Br_2}]$ two with conformation a and two with conformation b. These two conformations can be characterised using the indenyl rotation angle, λ, defined as the angle between the projections of the two vectors determined by the centroids of the five- and six-membered rings on the plane L–M–L′.[1] Thus, for a fully eclipsed arrangement of the two η-ligands, a λ angle of 0° is expected, while a fully staggered arrangement will correspond to a λ angle of 180°. The λ value for two molecules is 173.6 and 173.2° respectively indicating that in both a partially staggered arrangement is adopted while in the remaining two the λ angle takes the values of 11.7 and 15.4° respectively, consistent with almost eclipsed arrangements. In complex **6** the λ angle has a value of 92.2°, showing an intermediate situation between the staggered and eclipsed arrangements.

Another noteworthy structural feature is apparent from Fig. 6, which shows a top view of **6**: the two indenyl ligands adopt a different orientation relatively to the P–Mo–P bond angle. This structural feature is characterised by the β angle, defined as the average angle between the vectors joining the centroids of the five- and six-membered rings of each indenyl ligand on the L–Mo–L′ plane and the vector formed by the centroid of L and L′ donor atoms with the molybdenum centre

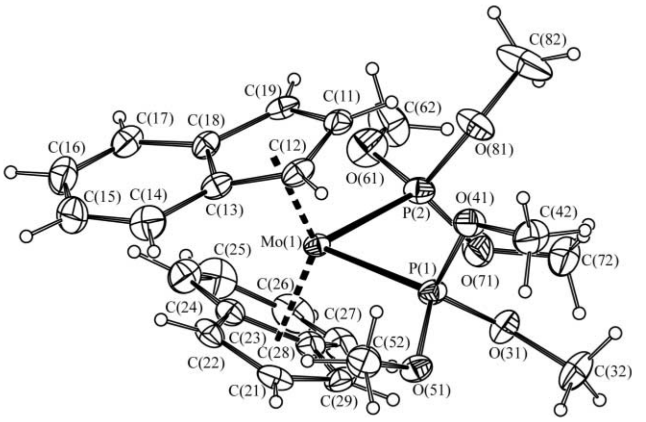


Fig. 3 An ORTEP view of the $[Ind_2MoP(OMe)_3]^{2+}$ cation in **6** with thermal ellipsoids drawn at the 20% probability level. For clarity only the atoms quoted in the text are labelled but the atomic notation adopted for indenyl rings is the same as that given in Figs. 1 and 2.

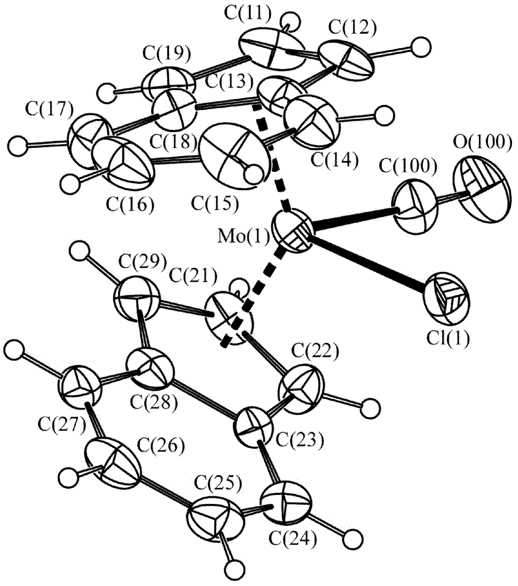
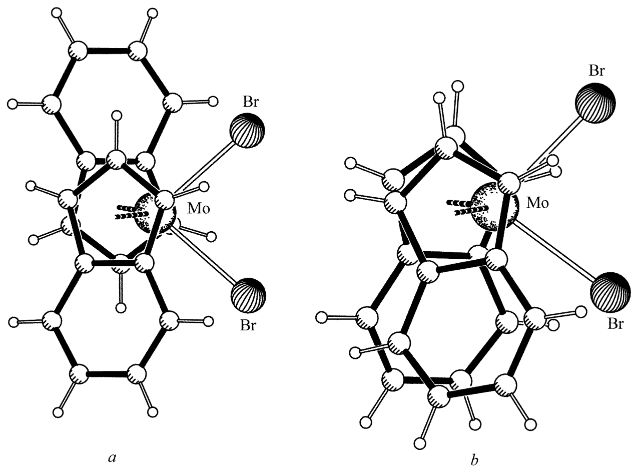


Fig. 4 An ORTEP view of the $[Ind_2Mo(CO)Cl]^+$ cation in **8** with thermal ellipsoids drawn at the 30% probability level.



a *b*

Fig. 5 Molecular projections of the two independent molecules (1 left and 3 right) of $[Ind_2MoBr_2]$ **3** on the plane Br–Mo–Br illustrating the two different geometric arrangements adopted by the four molecules of the asymmetric unit of **3**.

(see Scheme 3). The β angle has values of 177.2 and 93.3° for complex **6** while in the three remaining complexes, the two indenyl ligands have comparable β angles of *ca.* 90° (see Table 1). Obviously, the difference |λ − β| automatically gives the orientation of the second indenyl ligand. However, if this expression is used slightly different values are obtained for the second indenyl compared to those quoted in Table 1. This small discrepancy is due to the fact in the X-ray structure the line defined by the centroid and the metal centre intersects the indenyl ring near 90°.

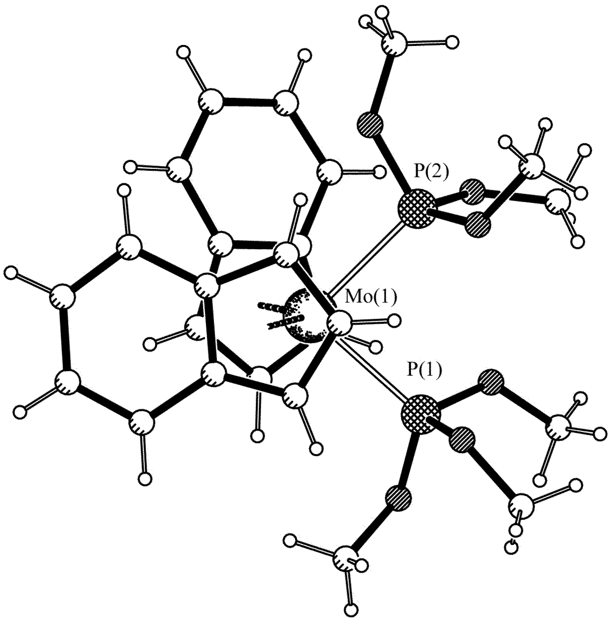
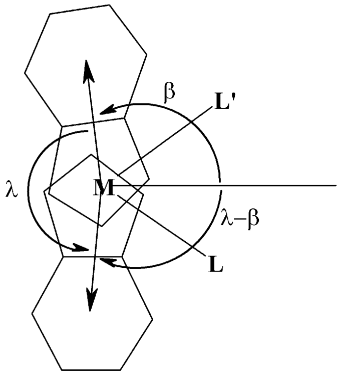


Fig. 6 Molecular projection of $[Ind_2Mo\{P(OMe)_3\}_2]^{2+}$ showing the conformation between eclipsed and staggered indenyl arrangements adopted by this cation.



Scheme 3

This crystallographic study shows clearly that the conformation adopted by $[(\eta^5\text{-Ind})_2MLL']^{n+}$ systems is characterised by the λ and β rotation angles with the preferred values determined in each case by intramolecular interactions between the ligands assembled in the molybdenum coordination sphere. Furthermore, the two different conformational isomers found in the crystal of **1** are consistent with the well-known fluxionality of π-indenyl ligands, also indicating that the arrangement adopted by these ligands is determined by crystal packing effects. However, it is important to note that electronic effects can also govern the structural preferences of these systems. Thus, for example, in the complex $[IndMo(\eta^3\text{-Ind})(CO)_2]$ the two indenyl ligands adopt an eclipsed arrangement with λ and β parameters of 179.4 and 2.6° respectively.[5]

Conclusions

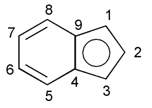
The synthesis of a number of simple derivatives of the Ind_2-Mo(IV) systems was accomplished and the products fully characterized. Although their chemistry shows a clear parallel to that of the well studied Cp_2M(IV) counterparts, interesting differences have already been found. The most important difference is the unexpected inertness of Ind_2MoBr_2 towards nucleophilic substitution. In fact, Cp_2MoBr_2 and $IndCpMoBr_2$ are readily substituted by a range of nucleophiles, namely thiolates to give $Cp_2Mo(SR)_2$ and $IndCpMo(SR)_2$. Under the same conditions Ind_2MoBr_2 is totally unreactive. On the other hand, substitution can be achieved using halide abstractors and, therefore, forcing dissociative conditions. This fact indicates that indenyl ring slippage is not important in this particular substitution mechanism and that the steric bulk of the indenyl ligand is actually blocking the access of nucleophiles to the metal. However, as shown by the ready conversion of $[(\eta^5\text{-Ind})_2\text{Mo}\{P(OMe)_3\}_2]^{2+}$ to $[(\eta^5\text{-Ind})(\eta^3\text{-Ind})\text{Mo}\{P(OMe)_3\}_2]$, redox induced ring-slippage is actually facile in this system. The other interesting difference between $[Cp_2MoL_2]^{2+}$ and $[Ind_2MoL_2]^{2+}$ systems seems to be the much higher electrophilicity of the latter capable of promoting activation the L ligands, *e.g.* CH_2Cl_2, towards nucleophilic attack. Further work regarding both the mechanistic and catalytic implications of both observations is under way in our laboratories.

Experimental

All manipulations were performed in an inert atmosphere using standard Schlenk techniques or in an inert atmosphere glovebox. Solvents were purified by distillation from an appropriate drying/deoxygenated agent. NMR spectra were recorded on a Bruker AMX 300 spectrometer. Infrared spectra were recorded on a Unicam Mattson model 7000 FTIR spectrophotometer using KBr pellets. Elemental analyses were performed in our laboratories (ITQB). $[Ind_2Mo(CO)_2][BF_4]_2$ and $IndMoCl_3(CO)_2$ were prepared following the previously published procedure.[5]

Preparation of complexes

$[Ind_2Mo(CO)Br][BF_4]$ 1. To a suspension of $[Ind_2Mo(CO)_2][BF_4]_2$ (1 g, 1.80 mmol) in dichloromethane (50 cm^3) was added one equivalent of n-Bu_4NBr (0.58 g, 1.80 mmol) and the mixture was stirred for 16 h at room temperature. The formation of a purple suspension was observed. The solid was filtered off, washed with Et_2O, and dried under vacuum. Crystals of $[Ind_2Mo(CO)Br][BF_4]$ **1** (0.72 g, 80%) suitable for X-ray analysis were obtained from an acetone–Et_2O mixture. (Found: C, 44.95; H, 2.65. $C_{19}H_{14}MoOBrBF_4$ requires C, 45.19; H, 2.79%); ν_{max}/cm^{-1} (CO) 2036vs (KBr); δ_H (Me_2CO-d$_6$; standard $SiMe_4$) 7.74 (1 H, m, H$^{5-8}$), 7.65 (1 H, m, H$^{5-8}$), 7.45 (1 H, m, H$^{5-8}$), 7.27 (1 H, m, H$^{5-8}$), 7.17 (1 H, m, H$^{1/3}$), 6.36 (1 H, m, H$^{1/3}$) and 6.22 (1 H, m, H^2) (see Scheme 4 for numbering).



Scheme 4

$[Ind_2Mo(NCMe)Br][BF_4]$ 2. A solution of $[Ind_2Mo(CO)Br][BF_4]$ (0.5 g, 0.96 mmol) in acetonitrile (50 cm^3) was refluxed and irradiated with a 60 W tungsten lamp for 10 h. A pink-red solution was formed, the solution was filtered through Celite, and the filtrate was taken to dryness to yield $[Ind_2Mo(NCMe)Br][BF_4]$ **2** (0.48 g, 94%) as a pink solid. (Found: C, 44.87; H, 2.96; N, 2.54. $C_{20}H_{17}MoNBrBF_4$ requires C, 44.98; H, 3.21; N, 2.62%); ν_{max}/cm^{-1} (NCMe) 2318 and 2291vs (KBr); δ_H (Me_2CO-d$_6$; standard $SiMe_4$) 7.57 (2 H, m, H$^{5-8}$), 7.45 (2 H, m, H$^{5-8}$), 7.32 (2 H, m, H$^{5-8}$), 7.27 (2 H, m, H$^{5-8}$), 7.12 (2 H, m, H$^{5-8}$), 6.25 (2 H, m, H$^{1/3}$), 5.98 (2 H, m, H^2) and 2.12 (3 H, s, NCMe) (see Scheme 4 for numbering).

Ind_2MoBr_2 3. Solid LiBr (0.11 g, 1.30 mmol) was added to a solution of $[Ind_2Mo(CO)Br][BF_4]$ (0.68 g, 1.30 mmol) in acetone (50 cm^3). The mixture was refluxed and irradiated with a 60 W tungsten lamp for 3 h. A green solution was formed, the volatiles were removed under vacuum and a green solid was extracted with dichloromethane. Recrystallization from CH_2Cl_2–Et_2O gave green crystals of Ind_2MoBr_2 **3** (0.44 g, 71%) suitable for X-ray analysis. (Found: C, 44.36; H, 2.81. $C_{18}H_{14}MoBr_2$ requires C, 44.48; H, 2.90%); δ_H (CD_2Cl_2; standard $SiMe_4$) 7.31–7.18 (4 H, m, H$^{5-8}$), 5.72 (2 H, d, H$^{1/3}$) and 5.46 (1 H, t, H^2) (see Scheme 4 for numbering).

Ind_2MoCl_2 4. To a suspension of $[Ind_2Mo(CO)_2][BF_4]_2$ (0.40 g, 0.72 mmol) in dichloromethane (50 cm^3) was added LiCl (0.06 g, 1.44 mmol) and the mixture was refluxed and irradiated with a 60 W tungsten lamp for 10 h. A green solution was obtained. The dichloromethane solution was filtered through Celite and the filtrate was concentrated to dryness to give a crystalline green solid of Ind_2MoCl_2 **4** (0.19 g, 68%). (Found: C, 54.32; H, 3.28. $C_{18}H_{14}MoCl_2$ requires C, 54.44; H, 3.55%); δ_H (CD_2Cl_2; standard $SiMe_4$) 7.34–7.05 (4 H, m, H$^{5-8}$), 5.81 (2 H, d, H$^{1/3}$) and 5.53 (1 H, t, H^2) (see Scheme 4 for numbering).

$Ind_2MoBrMe$ 5. To a solution of Ind_2MoBr_2 (0.37 g, 0.76 mmol) in dichloromethane (50 cm^3) was added $AlMe_3$ (0.76 cm^3, 1.52 mmol) and the mixture was refluxed for 16 h. The mixture reaction was taken to dryness and the residue was extracted with toluene. The toluene solution was concentrated to dryness to yield the title compound **5** (0.17 g, 71%) as a blue solid. (Found: C, 54.08; H, 3.95. $C_{19}H_{17}MoBr$ requires C, 54.18; H, 4.07%); δ_H (C_6D_6; standard $SiMe_4$) 6.91, 6.78, 6.53 (8 H, m, H$^{5-8}$), 4.56 (2 H, m, H$^{1/3}$), 4.29 (2 H, m, H$^{1/3}$), 3.56 (2 H, m, H^2) and 0.30 (3 H, s, Mo–CH_3) (see Scheme 4 for numbering).

$[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ 6. A solution of Ind_2MoBr_2 (0.36 g, 0.74 mmol) in acetone (50 cm^3) was treated with excess $P(OMe)_3$ (0.5 cm^3, 4.24 mmol) and $TlPF_6$ (0.51 g, 1.48 mmol), and the mixture was stirred for 1 h at room temperature. The mixture was taken to dryness and the residue was extracted with dichloromethane to yield a red crystalline solid of $[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ **6** (0.58 g, 92%). Crystals suitable for X-ray analysis were obtained from a CH_2Cl_2–Et_2O mixture. (Found: C, 33.18; H, 3.81. $C_{24}H_{32}MoO_6P_4F_{12}$ requires C, 33.35; H, 3.73%); δ_H (Me_2CO-d$_6$; standard $SiMe_4$) δ 7.72 (4 H, m, H$^{5-8}$), 6.36 (2 H, d, H$^{1/3}$), 5.98 (1 H, t, H^2) and 4.09 (9 H, s, Me) (see Scheme 4 for numbering).

$Ind_2Mo\{P(OMe)_3\}_2$ 7. A solution of Cp_2Co (0.13 g, 0.69 mmol) in toluene was added to a stirred solution of $[Ind_2Mo\{P(OMe)_3\}_2][PF_6]_2$ (0.30 g, 0.69 mmol) in toluene at room temperature and the mixture was stirred for 2 h. The solvent was removed under vacuum and the residue extracted with hexane to yield a yellow solid of the title compound **7** (0.39 g, 83%). (Found: C, 50.32; H, 5.71. $C_{24}H_{32}MoO_6P_2$ requires C, 50.19; H, 5.62%); δ_H (C_6D_6-d$_6$; standard $SiMe_4$) 6.88 (2 H, m, H$^{5-8}$), 6.51 (2 H, m, H$^{5-8}$), 5.46 (2 H, d, H^2), 5.72 (1 H, t, H$^{1/3}$) and 3.30 (9 H, s, Me) (see Scheme 4 for numbering).

Reaction of $[Ind_2Mo(CO)_2][BF_4]_2$ with $P(OMe)_3$. To a suspension of $[Ind_2Mo(CO)_2][BF_4]_2$ (0.2 g, 0.36 mmol) in dichloromethane (30 cm^3) was added $P(OMe)_3$ (0.1 cm^3, 0.84 mmol) and the mixture was stirred for 3 h at room temperature. The purple solid which formed was filtered off, washed with Et_2O and characterized as $[Ind_2Mo(CO)Cl][BF_4]$ (**8**) (0.13 g, 76%). Single crystals suitable for X-ray analysis were obtained from acetone–Et_2O solution. (Found: C, 47.97; H, 2.98. $C_{19}H_{14}MoOClBF_4$ requires C, 47.89; H, 2.96%); ν_{max}/cm^{-1} (CO) 2033vs (KBr); δ_H (Me_2CO-d$_6$; standard $SiMe_4$) 7.28 (4 H, m, H$^{5-8}$), 7.19 (4 H, m, H$^{5-8}$), 6.80 (2 H, m, H$^{1/3}$), 6.25 (2 H, m, H$^{1/3}$) and 6.02 (2 H, m, H^2) (see Scheme 4 for numbering).

$[(\eta^3\text{-Ind})Mo(CO)_2]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2]$ 9. A mixture of $[Me_2Si(\eta^5\text{-}C_5H_4)_2]Li_2$ (0.31 g, 1.6 mmol) and $IndMoCl_3(CO)_2$

Table 2 Crystal data and structure refinement details for complexes **1**, **3**, **6** and **8**

	1	**3**	**6**	**8**
Formula	$[Ind_2Mo(CO)Br][BF_4]$	Ind_2MoBr_2	$[Ind_2Mo\{POMe_3\}_2][PF_6]_2$	$[Ind_2Mo(CO)Cl][BF_4]$
Empirical formula	$C_{19}H_{14}BBrF_4MoO$	$C_{18}H_{14}Br_2Mo$	$C_{24}H_{32}F_{12}MoO_6P_4$	$C_{19}H_{14}BClF_4MoO$
M_w	520.95	486.05	864.32	476.50
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/c$	$P\bar{1}$
T/K	293(2)	293(2)	293(2)	293(2)
a/Å	8.928(11)	15.134(17)	12.447(17)	8.897(14)
b/Å	9.285(14)	14.522(19)	18.044(23)	9.332(14)
c/Å	12.402(17)	29.774(33)	14.977(19)	12.334(17)
α/°	96.67(1)	(90)	(90)	97.25(1)
β/°	97.05(1)	104.27(1)	99.99(1)	97.51(1)
γ/°	112.66(1)	(90)	(90)	113.11(1)
V/Å^3	926(1)	6342(2)	3313(7)	916(2)
Z	2	16	4	2
D_c/Mg m^{-3}	1.867	2.036	1.733	1.728
μ/mm^{-1}	2.908	5.857	0.694	0.906
Reflections collected	3186	20536	11295	3257
Independent reflections [R(int)]	3186 [0.0000]	11030 [0.0589]	6352 [0.0241]	3257 [0.0000]
Data/restraints/parameters	3186/0/245	11030/0/758	6352/0/431	3257/18/242
R_1, wR_2 [$I > 2\sigma(I)$]	0.0655, 0.1893	0.0678, 0.1437	0.0613, 0.1714	0.1053, 0.2240
R_1, wR_2 (all data)	0.0910, 0.2216	0.1382, 0.1746	0.0853, 0.1910	0.1684, 0.2527

(0.60 g, 1.6 mmol) was weighed into a Schlenk tube in a glovebox and tetrahydrofuran (50 cm^3) was added to the mixture. The reaction was stirred for 10 h at room temperature and all the volatiles were removed under vacuum. The residue was extracted with hexane, the red hexane solution was concentrated to dryness and the title compound, **9**, (0.46 g, 80%) was isolated as a red solid. (Found: C, 56.32; H, 3.90. $C_{34}H_{28}Mo_2O_4Si$ requires C, 56.67; H, 3.92%); ν_{max}/cm^{-1} (CO) 1959 and 1880 (KBr,); δ_H (CD_2Cl_2; standard $SiMe_4$) δ 7.26 (2 H, t, H^2), 6.59 (4 H, m, H$^{5-8}$), 6.46 (4 H, m, H$^{5-8}$), 5.04 (4 H, d, H$^{1/3}$), 4.80 (4 H, m, Cp), 4.69 (4 H, m, Cp) and 0.40 (6H, s, $SiMe_2$) (see Scheme 4 for numbering).

Crystallography

Data collection and processing. Crystal data together with pertinent refinement details are given in Table 2. The X-ray single crystal data for all four complexes were collected with a MAR research Image Plate system equipped with graphite-monochromated Mo-Kα radiation at the University of Reading. The crystals were positioned 70 mm from the image plate. 95 frames were measured at 2° intervals with a counting time adequate for the diffraction pattern exhibited by the crystal under investigation. Data analysis was carried out with the XDS program.[14] An empirical absorption correction using a version of DIFABS,[15] modified for image plate geometry, was applied to the intensities of **1** and **3** respectively. The intensities of **6** and **8** were not corrected for absorption effects.

CCDC reference numbers 167778–167781.

See http://www.rsc.org/suppdata/dt/b1/b106540h/ for crystallographic data in CIF or other electronic format.

Structure analysis and refinement. All structures were solved by direct methods with SHELXS.[16] The fluorine atoms of the BF_4 anion in **8** were disordered over two positions. Thus, the counter-ion was introduced in the process refinement in two tetrahedral sites with refined population parameters of x and $1 - 0.41$, being equal to 0.59(2).

All non-hydrogen atoms were refined with anisotropic thermal displacements, apart from the disordered fluorine atoms in **8**, which were refined independently with individual isotropic temperature factors. All hydrogen atoms were allowed for as riding atoms and were assigned isotropic thermal parameters equivalents to 1.2 times of those of the atoms to which they were bonded. The structures were then refined by full matrix least-squares methods on F^2 with SHELXL using the weighting scheme with standard form until convergence was achieved.[17] The ORTEP molecular diagrams presented were drawn with PLATON graphical software.[18]

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References

1 D. O'Hare, V. J. Murphy and N. Kaltsoyannis, *J. Chem. Soc., Dalton Trans.*, 1993, 383.
2 A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, V. G. Andriano, Yu. T. Struchkov, S. J. Andrae, Yu. A. Ustynyuk and S. G. Malyugina, *J. Organomet. Chem.*, 1978, **159**, 189.
3 R. Poli, S. P. Mattamana and L. R. Falvello, *Gazz. Chim. Ital.*, 1992, **122**, 315.
4 (*a*) C. C. Romão, *Appl. Organomet. Chem.*, 2000, **14**, 539548; (*b*) J. R. Ascenso, C. G. de Azevedo, I. S. Gonçalves, E. Herdtweck, D. S. Moreno, M. Pessanha and C. C. Romão, *Organometallics*, 1995, **14**, 3901.
5 M. G. B. Drew, V. Félix, I. S. Gonçalves, C. C. Romão and B. Royo, *Organometallics*, 1998, **17**, 5782.
6 (*a*) S. L. J. Conway, T. Dijkstra, L. H. Doerrer, J. C. Green, M. L. H. Green and A. H. H. Stephens, *J. Chem. Soc., Dalton Trans.*, 1998, 2689; (*b*) L. Labella, A. Chernega and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1995, 395; (*c*) A. Chernega, J. Cook, M. L. H. Green, L. Labella, S. J. Simpson, J. Souter and A. H. H. Stephens, *J. Chem. Soc., Dalton Trans.*, 1997, 3225.
7 R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1967, 1155.
8 C. A. Gamelas, E. Herdtweck, J. P. Lopes and C. C. Romão, *Organometallics*, 1999, **18**, 506.
9 A. Igau and J. A. Gladysz, *Organometallics*, 1991, **10**, 2327 and references cited therein.
10 M. J. Calhorda, I. S. Gonçalves, E. Herdtweck, C. C. Romão, B. Royo and L. F. Veiros, *Organometallics*, 1999, **18**, 3956.
11 T. Cuenca, J. C. Flores, R. Gómez, P. Gómez-Sal, M. Parra-Hake and P. Royo, *Inorg. Chem.*, 1993, **32**, 3608.
12 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchel, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comp. Sci.*, 1991, **31**, 187.
13 J. W. Faller, R. H. Crabtree and A. Habib, *Organometallics*, 1985, **4**, 929.
14 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
15 DIFABS: N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
16 SHELXS-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467–473.
17 G. M. Sheldrick, SHELX-97, University of Göttingen, 1997.
18 A. L. Spek, PLATON, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.