

# New Synthetic Pathway to Mono- and Bis-indenyl Complexes of Molybdenum(IV)

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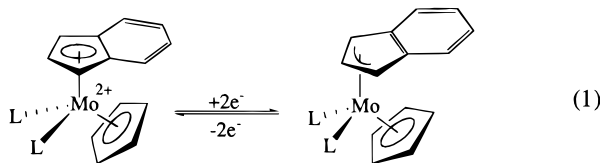
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The complex  $\text{IndMoCl}_3(\text{CO})_2$  ( $\text{Ind} = \eta^5\text{-C}_9\text{H}_7$ ) has been synthesized by the reaction of  $\text{IndMo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2$  with HCl gas in dichloromethane at 25 °C. Thermal decarbonylation of  $\text{IndMoCl}_3(\text{CO})_2$  in chloroform gives paramagnetic  $\text{IndMoCl}_3$  ( $\mu_{\text{eff}} = 1.48 \mu_{\text{B}}$ ). A consistent stepwise route to bis-indenyl derivatives of molybdenum is available upon treatment of  $\text{IndMoCl}_3(\text{CO})_2$  with KInd in THF at low temperature. The complex  $\text{IndMo}(\eta^3\text{-Ind})(\text{CO})_2$  is obtained in high yield and opens a convenient entry into bis-indenyl molybdenum chemistry. The reaction of  $\text{IndMo}(\eta^3\text{-Ind})(\text{CO})_2$  with  $\text{Ph}_3\text{CBF}_4$ , in  $\text{CH}_2\text{Cl}_2$ , yields  $[\text{Ind}_2\text{Mo}(\text{CO})_2][\text{BF}_4]_2$ . Solvolysis of  $[\text{Ind}_2\text{Mo}(\text{CO})_2][\text{BF}_4]_2$  in acetonitrile affords  $[\text{Ind}_2\text{Mo}(\text{CO})(\text{NCMe})][\text{BF}_4]_2$  and  $[\text{Ind}_2\text{Mo}(\text{NCMe})_2][\text{BF}_4]_2$ . The reaction of  $[\text{Ind}_2\text{Mo}(\text{NCMe})_2][\text{BF}_4]_2$  with  $[\text{Bu}_4\text{N}][\text{S}_2\text{CNET}_2]$  forms the dithiocarbamate complex  $[\text{Ind}_2\text{Mo}(\text{S}_2\text{CNET}_2)][\text{BF}_4]$ . The molecular structures of  $\text{IndMo}(\eta^3\text{-Ind})(\text{CO})_2$  and  $[\text{Ind}_2\text{Mo}(\text{S}_2\text{CNET}_2)][\text{BF}_4]$  have been determined by single-crystal X-ray diffraction.

## Introduction

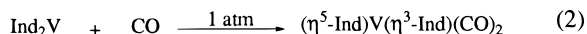
The organometallic chemistry of molybdenum(IV) is largely dominated by the chemistry of the bent metallocenes  $\text{Cp}_2\text{MX}_2$ , which is very well established mainly by the continued contribution from the group of M. L. H. Green after the discovery of these compounds in 1961.<sup>1</sup>

To modify the reactivity of this type of complex, we have recently started a systematic study of the synthetic pathways to mono- and bis-substituted Mo and W metallocene analogues, of general formulas  $\text{CpCp}'\text{MX}_2$  and  $\text{Cp}'_2\text{MX}_2$ , respectively. The mixed ring indenyl derivatives  $\text{IndCpML}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) revealed a number of interesting reversible 2e redox processes, eq 1, which are still under investigation.<sup>2</sup>



The obvious extension of these studies to the bis-indenyl complexes, which are expected to be more

reactive as a result of their increased electronic and structural flexibility, has been hampered by the difficulties found in their synthesis. With the outstanding exception of the catalytically important group 4 ansa bridged or unbridged bis-indenylmetallocenes  $\text{Ind}_2\text{ZrX}_2$ ,<sup>3</sup> bis-indenyl complexes have been little studied. The more relevant contributions comprise the structural systematics of indenyl distortion along the family of sandwich derivatives  $\text{Ind}_2\text{M}$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ )<sup>4</sup> and the ready addition of CO to  $\text{Ind}_2\text{V}$  in eq 2.<sup>5</sup>



In the case of group 6 metals the only known bis-indenyl derivatives are  $(\text{C}_9\text{Me}_7)_2\text{Cr}$ ,<sup>6</sup>  $(\eta^5\text{-Ind})\text{W}(\eta^3\text{-Ind})(\text{CO})_2$ ,<sup>7</sup>  $(\eta^5\text{-Ind})\text{Mo}(\eta^3\text{-Ind})(\text{CO})_2$ ,<sup>2a</sup> and  $(\eta^5\text{-Ind})\text{Mo}(\eta^3\text{-Ind})(\text{dppe})$ .<sup>8</sup> However,  $(\eta^5\text{-Ind})\text{Mo}(\eta^3\text{-Ind})(\text{CO})_2$  is difficult to prepare, and its W congener was obtained in a reported 1.5% yield.<sup>7</sup>

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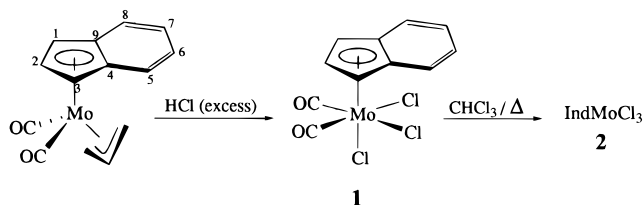
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## Scheme 1



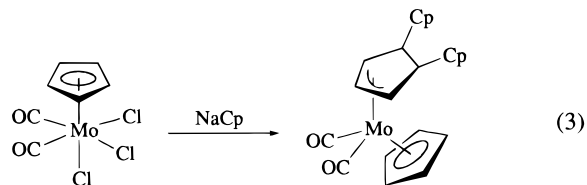
Despite many efforts, the chemistry of the half-sandwich complexes Cp'MoX<sub>3</sub> or their derivatives Cp'MoX<sub>3</sub>L<sub>2</sub> (Cp' = Cp, RCp), which are potential intermediates for the synthesis of the Cp'<sub>2</sub>MoX<sub>2</sub> derivatives, has remained difficult to control from the synthetic point of view, and no example of an indenyl derivative has been reported so far.<sup>9</sup>

In the present paper we describe a simple synthesis of IndMoCl<sub>3</sub>(CO)<sub>2</sub>, which is found to be a convenient entry to the synthesis of the target bis-indenyl molybdenocene analogues Ind<sub>2</sub>MoX<sub>2</sub>, some of which are structurally characterized.

## Results and Discussion

**1. Synthesis.** The indenyl complex IndMoCl<sub>3</sub>(CO)<sub>2</sub> (**1**) is appropriately synthesized by the reaction of IndMo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> with excess HCl gas in dichloromethane at room temperature. The method is particularly suitable since the corresponding allyl precursor, IndMo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>, is conveniently available from Mo(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)-Cl(CO)<sub>2</sub>(NCMe)<sub>2</sub> and KInd in almost quantitative yield.<sup>10</sup> The IR spectrum of **1** shows two strong ν(C≡O) absorptions at 1961 and 1880 cm<sup>-1</sup>. Due to instability in solution, we were not able to obtain any NMR data on **1**. As a matter of fact, IndMoCl<sub>3</sub>(CO)<sub>2</sub> appears to be stable toward CO loss at room temperature in the solid state but decarbonylates completely in refluxing chloroform to afford an insoluble solid that analyzes correctly for IndMoCl<sub>3</sub> (**2**) (Scheme 1). The trichloride **2** is a paramagnetic complex with μ<sub>eff</sub> = 1.48 μ<sub>B</sub>. This value is similar to the one reported for the analogue CpMoCl<sub>3</sub> (μ<sub>eff</sub> = 1.25 μ<sub>B</sub>).<sup>11b</sup> The low solubility prevents recrystallization to form single crystals suitable for X-ray analysis. However, consistent analytical data on **2** and the similar decarbonylation reported for CpMoCl<sub>3</sub>(CO)<sub>2</sub><sup>11b</sup> support this formulation. Of course, its low electron count strongly suggests that IndMoCl<sub>3</sub> (**2**) should be best formulated as an oligomeric species [IndMoCl<sub>3</sub>]<sub>n</sub> like the related (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)MoCl<sub>3</sub>, which is a dimer, but no molecular weight measurements were feasible.<sup>12</sup>

Reactions of IndMoCl<sub>3</sub> with NaCp or IndK did not afford any tractable product under a variety of experimental conditions and were, therefore, discarded as a synthetic method for the preparation of IndCpMoCl<sub>2</sub> or Ind<sub>2</sub>MoCl<sub>2</sub>. On the other hand, the reaction of IndMoCl<sub>3</sub>(CO)<sub>2</sub> (**1**) with KInd in THF at low temperature affords IndMo(η<sup>3</sup>-Ind)(CO)<sub>2</sub> (**3**) as a red crystalline solid in high yield (Scheme 2). This compound had been previously obtained and spectroscopically characterized by a less obvious route and in a smaller yield.<sup>2a</sup> Although very useful for our purposes, this reaction is quite surprising considering that the parallel reactions of CpMCl<sub>3</sub>(CO)<sub>2</sub> (M = Mo, W) with NaCp led to an entirely different family of compounds which are derived from Cp<sup>-</sup> addition to one coordinated Cp ring, as depicted in eq 3.<sup>14</sup>



The solid-state structure of **3** (see Crystallography) reveals two differently bound rings in compliance with the 18e rule and the known structure of IndW(η<sup>3</sup>-Ind)(CO)<sub>2</sub>.<sup>7</sup>

Reaction of **3** with 2 equiv of triphenylcarbenium tetrafluoroborate in dichloromethane at room temperature gives the yellow dication [Ind<sub>2</sub>Mo(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**4**) characterized by ν(C≡O) stretching vibrations at 2119 and 2085 cm<sup>-1</sup>. As expected from these high wavenumbers, the CO ligands are rather labile. This prevented NMR studies because the compound reacts with the solvents in which it is soluble. The same difficulty was found with the related dications [Cp<sub>2</sub>Mo(CO)<sub>2</sub>]<sup>2+</sup> and [IndCpMo(CO)<sub>2</sub>]<sup>2+</sup>.<sup>2a</sup>

Accordingly, dissolution of **4** in acetonitrile leads to rapid substitution, forming [Ind<sub>2</sub>Mo(CO)(NCMe)][BF<sub>4</sub>]<sub>2</sub> (**5**). The only ν(C≡O) stretching vibration at 2054 cm<sup>-1</sup> suggests high lability for CO substitution. In fact, irradiation of a refluxing solution of **5** in NCMe with a 60 W tungsten bulb leads to the formation of [Ind<sub>2</sub>Mo(NCMe)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**6**) as a pink-red powder in high yield.

The <sup>1</sup>H NMR spectra of **5** and **6** are compatible with the η<sup>5</sup>-coordination mode of the indenyl ligands. For [Ind<sub>2</sub>Mo(NCMe)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**6**) the spectrum presents one multiplet in the aromatic region at δ 7.46 (H<sup>5-8</sup>), a doublet at δ 6.37 (H<sup>1/3</sup>), and a triplet at δ 6.03 ppm for H<sup>2</sup>. This pattern is slightly different in the case of the less symmetric complex **5**, which shows two resonances in the aromatic region at δ 7.76, 7.55 (H<sup>5-8</sup>), two doublets at δ 7.40, 6.71 (H<sup>1/3</sup>), and a triplet at δ 6.12 (H<sup>2</sup>) ppm. However, no sign of ring-slippage is observed in NCMe solution because that would change the <sup>1</sup>H NMR resonances considerably, particularly that of H<sup>2</sup> as we know from previous data on the ring-slippage of [IndMo(CO)<sub>2</sub>(NCMe)<sub>2</sub>]<sup>+</sup> complexes.<sup>13</sup> The IR and NMR data on the coordinated NCMe ligand in both **5** and **6** are essentially similar to the one already reported for the corresponding Cp<sub>2</sub>Mo and IndCpMo congeners. The coordinated NCMe molecule displays in the <sup>1</sup>H NMR spectrum a singlet at δ 2.12 ppm.

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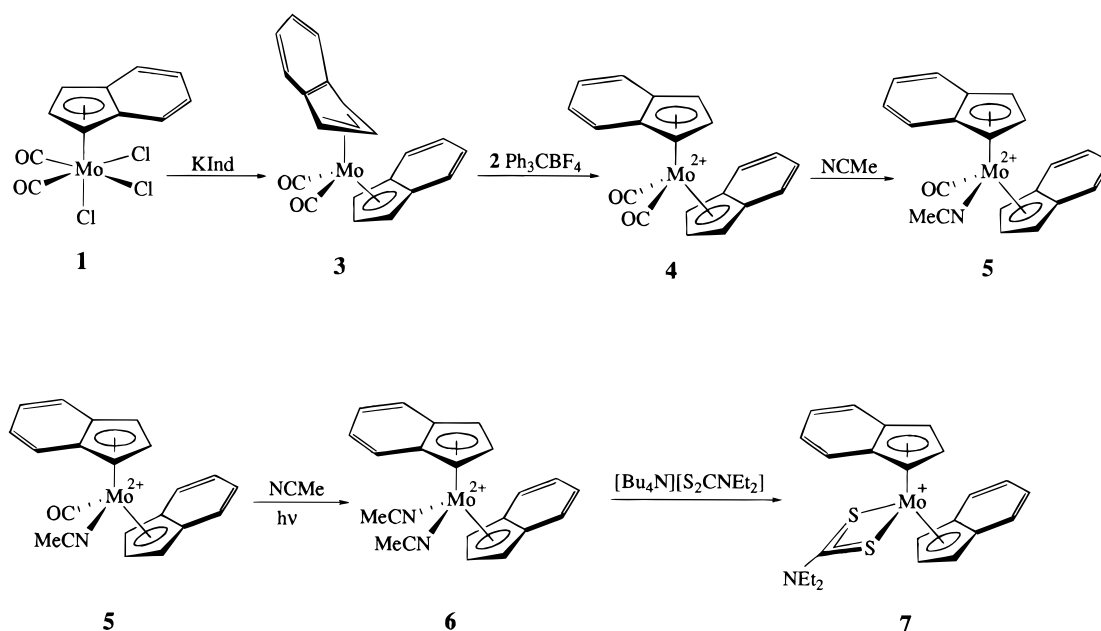
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Scheme 2



In previous studies we noted that related bis-nitrile dications  $[\text{IndCpMo}(\text{NCMe})_2]^{2+}$  undergo ready nitrile substitution without competing nucleophilic addition to the indenyl ring and are, therefore, the ideal starting material for the synthesis of other  $[\text{IndCpMoX}_2]$  derivatives.<sup>2a,c</sup> This same observation applies to the bis-indenyl complex **6**. In fact, the reaction of  $[\text{Ind}_2\text{Mo}(\text{NCMe})_2][\text{BF}_4]_2$  with the tetrabutylammonium salt of diethyldithiocarbamate,  $[\text{Bu}_4\text{N}][\text{S}_2\text{CNET}_2]$ , in dichloromethane, yields  $[\text{Ind}_2\text{Mo}(\text{S}_2\text{CNET}_2)][\text{BF}_4]$  (**7**) in high yield. The  $^1\text{H}$  NMR spectrum of **7** presents one multiplet in the aromatic region at  $\delta$  7.13 ( $\text{H}^{5-8}$ ), a doublet at  $\delta$  6.34 ( $\text{H}^{1/3}$ ), a triplet at  $\delta$  5.31 ( $\text{H}^2$ ), and two resonances for the two equivalent ethyl groups, a quartet at  $\delta$  3.49 and a triplet at  $\delta$  1.09 ppm. The crystal structure of **7** has been determined by X-ray diffraction.

**2. Crystallography.** The crystal structures of the metal complexes  $\text{IndMo}(\eta^3\text{-Ind})(\text{CO})_2$  (**3**) and  $[\text{Ind}_2\text{Mo}(\text{S}_2\text{CNET}_2)][\text{BF}_4]$  (**7**) were determined using single-crystal X-ray diffraction analysis.

The unit cell of complex **3** contains four discrete molecules. The unit cell of the complex **7** is built up from an asymmetric unit composed of two cations  $[\text{Ind}_2\text{Mo}(\text{S}_2\text{CNET}_2)]^+$ , **7**<sup>+</sup>, and two anions  $\text{BF}_4^-$ . In the crystal structure, one of the anions is disordered with fluorine atoms occupying two alternative positions. The bond lengths and angles found for both independent cations are identical within the standard limits. Therefore, in the present discussion, the average values will be used for these structural parameters; otherwise is stated.

Table 1 gives selected bond distances and angles for the two complexes.

The molecular diagram with the corresponding crystallographic labeling scheme is shown in Figure 1 for cation **7**<sup>+</sup>.

The range of distances observed for the 10 Mo–C bonds, 2.251(11)–2.464(9) Å, shows that the two indenyl ligands are coordinated to the molybdenum atom in a  $\eta^5$  fashion. The Mo coordination sphere, comprising the centroids of both  $\text{C}_5$  rings and two sulfur atoms of the bidentate ligand  $\text{S}_2\text{CNET}_2$ , can be described as a pseudo-

**Table 1. Selected Bond Distances and Angles for the Bis-indenyl Complexes **3** and **7**<sup>+</sup><sup>a</sup>**

	<b>7</b> <sup>+</sup> [L = S(11); L' = S(12); Cn = Cp]	<b>3</b> [L = C(11); L' = C(13); Cn = Cm]
Bond Lengths (Å)		
Mo–L	2.457(3), 2.477(3)	1.953(15)
Mo–L'	2.471(3), 2.483(2)	1.947(14)
Mo–Cn	2.019, 2.020	2.148
Mo–Cp*	2.018, 2.025	2.034
Angles (deg)		
L–Mo–L'	70.1(1), 69.5(1)	80.3(5)
Cn–Mo–Cp*	135.4, 136.0	137.4
Cn–Mo–L	107.2, 107.6	91.6
Cn–Mo–L'	109.9, 108.2	90.6
Cp*–Mo–L	106.4, 107.3	119.6
Cp*–Mo–L'	108.7, 108.6	120.9

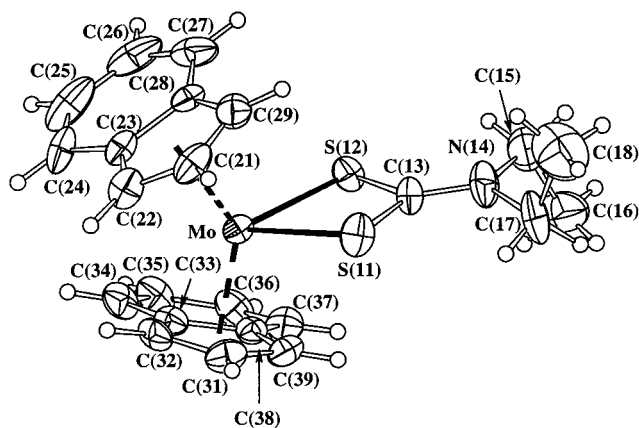
<sup>a</sup> Cp denotes the centroid of the five-member ring C(21)–C(29) for complex **7**<sup>+</sup>. Cm represents the midpoint of the two carbon atoms adjacent to the six-member ring (atoms C(22) and C(29), see Figure 2) for complex **3**. Cp\* denotes the centroid of the five-member ring C(31)–C(39) for these complexes. The italic values reported for complex **3** refer to the second molecule present in the asymmetric unit.

tetrahedron. The average metal-to- $\text{C}_5$  ring centroid distances is 2.020 Å, and the corresponding centroid–Mo–centroid angle has a value of 135.7°. The average Mo–S bond distances are 2.472(3) Å, and the S–Mo–S angle is 69.8(1)°. This geometry agrees well with those found for  $d^2$  (biscyclopentadienyl)MoL<sub>2</sub> derivatives, such as  $\text{Cp}_2\text{Mo}(\text{S}^n\text{Bu})_2\text{FeCl}_2$ <sup>15</sup> and  $[\text{Cp}_2\text{Mo}(\text{S}^t\text{Bu})_2\text{NiCp}][\text{BF}_4]$ .<sup>16</sup>

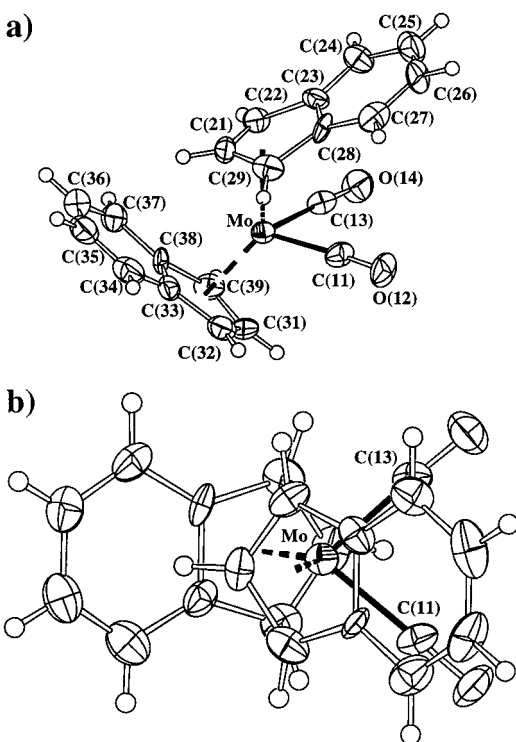
Figure 2a shows the molecular structure of complex **3** with the atomic labeling scheme used. The indenyl ligand, comprising the carbon atoms C(31) to C(39), is  $\eta^5$  coordinated to the molybdenum center with five Mo–C distances in the range 2.44(1)–2.32(1) Å. The other indenyl ligand is linked to the metal center by only three carbon atoms: C(21) [2.21(1) Å], C(22) [2.44(1) Å], and C(29) [2.42(1) Å]. The remaining two carbon atoms of the  $\text{C}_5$  ring, C(23) and C(28), are away from the

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**Figure 1.** Molecular structure of complex  $[\text{Ind}_2\text{Mo}(\text{S}_2\text{-CNEt}_2)]^+$ : a side view with the labeling adopted. The ellipsoids are drawn at the 30% probability level.



**Figure 2.** Molecular structure of complex  $\text{IndMo}(\eta^3\text{-Ind})(\text{CO})_2$ : (a) a side view with the labeling adopted; (b) a top view showing the configuration adopted by the indenyl ligands. The ellipsoids are drawn at the 40% probability level.

molybdenum by 3.17(1) and 3.14(1) Å, respectively, leading to a  $\eta^3$  coordination for this ligand. Two carbonyl ligands complete the coordination sphere of this complex. As observed for dithiocarbamate complex **7**, the coordination environment of the metal center is also a pseudo-tetrahedron. The molybdenum is 2.148 Å from the centroid of the  $\text{C}_5$  ring [C(31)–C(39)] and 2.034 Å from the midpoint determined by the atoms C(22) and C(29), leading to a centroid–Mo–midpoint angle of 137.4°. The average Mo–CO bond distance is 1.950(14) Å, and the corresponding OC–Mo–CO angle is 80.3(5)°. Similar geometric arrangements, with similar structural parameters within experimental errors, were found for the related species  $(\eta^5\text{-Ind})\text{W}(\eta^3\text{-Ind})(\text{CO})_2^7$  and  $\text{CpMo}(\eta^3\text{-Ind})(\text{CO})_2$ .<sup>2a</sup>

Table 2 lists relevant structural parameters for the characterization of complexes **3** and **7**<sup>+</sup> together with data for other related bis-indenyl derivatives.

The  $\eta^5$  or  $\eta^3$  coordination mode of the indenyl ligands can be easily characterized through the folding angle ( $\Omega$ ), proposed by Crabtree, Faller, and Habib.<sup>19</sup> When  $\eta^5$  hapticity is present, the indenyl ligand is almost planar and a very small value for the  $\Omega$  angle will be expected. Thus, small  $\Omega$  angles are reported for both indenyl ligands in cation **7**<sup>+</sup> [4.0° and 3.0°]. In complex **3**, one indenyl ligand shows an  $\Omega$  angle of 3.0°, consistent with a  $\eta^5$  coordination, while the other exhibits a  $\Omega$  angle of 20.8° that indicates a pronounced bending of the indenyl ligand, characteristic of a  $\eta^3$  coordination, along the vector C(22)–C(29). Slightly wider  $\Omega$  angles of 25.6° were determined for the  $\eta^3$ -indenyl ligand in the complexes  $\text{IndW}(\eta^3\text{-Ind})(\text{CO})_2$  (**8**) and  $\text{IndMo}(\eta^3\text{-Ind})(\text{dppe})$  (**10**). In contrast, in complex  $\text{IndV}(\eta^3\text{-Ind})(\text{CO})_2$  (**9**), the  $\eta^3$ -indenyl ligand displays a small bending with an  $\Omega$  angle of 12.0°. Furthermore, the related complexes  $\text{CpMo}(\eta^3\text{-Ind})(\text{CO})_2$ <sup>2a</sup> and  $\text{CpMo}(\eta^3\text{-Ind})\{\text{P}(\text{OMe})_3\}_2$ <sup>20</sup> show for the  $\eta^3$ -indenyl ligand bending angles of 21.3° and 21.7°, respectively, which are similar to that observed for complex **3**.

The configuration adopted by the two indenyl ligands in the  $[\text{Ind}_2\text{MLL}]^{n+}$  systems can be fully characterized using  $\lambda$  and  $\beta$  angles quoted in the Table 2 and depicted in Schemes 3 and 4, respectively.

The rotation angle ( $\lambda$ ) gives the relative orientation of the two indenyl ligands and is defined for the  $[(\eta^5\text{-Ind})_2\text{MLL}]^{n+}$  systems 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'. When one  $\eta^3$ -indenyl ligand is considered in this definition, the centroid of the corresponding five-member ring is replaced by the midpoint of the two carbon atoms adjacent to the six-member ring, e.g., atoms C(22) and C(29) in complex **3**, Figure 2. The  $\lambda$  angle takes the values of 0° and 180°, respectively, for a fully eclipsed and staggered arrangement of the two indenyl ligands (Scheme 3). For complex **7**<sup>+</sup> the two different values found for  $\lambda$ , 11.3° and 0.4°, correspond to the two cations present in the asymmetric unit. These values show that in the solid state the indenyl ligands in these two molecules exhibit slightly different, almost eclipsed arrangements. An extreme situation was observed for complex  $\text{Ind}_2\text{Ti}(\text{CO})_2$  (**11**). The two molecules in the asymmetric unit have  $\lambda$  angles of 174.6° and 16.6°, indicating that in one molecule the indenyl ligands adopt a nearly full staggered configuration, while in the other, these ligands show an almost eclipsed arrangement. These two complexes reflect the fluxionality of the indenyl ligands and suggest that in certain cases the packing effects have influence on the configuration adopted by these ligands. In complex **3**, the indenyl ligands display a nearly fully staggered arrangement, with a  $\lambda$  angle of 179.3°, which is nearly identical with those reported for the isoelectronic tung-

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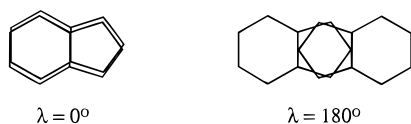
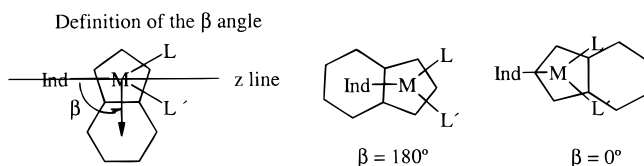
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**Table 2. Comparison of Crystal Structures of Some Bis-indenyl Complexes**

complex	$\Omega$	$\lambda$	$\beta$	ref
$[\text{Ind}_2\text{Mo}(\text{S}_2\text{CNEt}_2)]^+$ ( <b>7</b> <sup>+</sup> )	$\eta^5$ -Ind, 4.0 $\eta^5$ -Ind, 3.0	0.4, 11.3	105.7, 99.4 92.2, 99.5	this work
$\text{IndMo}(\eta^3\text{-Ind})(\text{CO})_2$ ( <b>3</b> )	$\eta^3$ -Ind, 20.8 $\eta^5$ -Ind, 3.0	179.4	2.6 177.4	this work
$\text{IndW}(\eta^3\text{-Ind})(\text{CO})_2$ ( <b>8</b> )	$\eta^3$ -Ind, 25.6 $\eta^5$ -Ind, 1.2	178.4	0.6 179.3	<b>8</b>
$\text{IndV}(\eta^3\text{-Ind})(\text{CO})_2$ ( <b>9</b> )	$\eta^3$ -Ind, 12.0 $\eta^5$ -Ind, 4.4	179.4	5.9 173.8	<b>5</b>
$\text{IndMo}(\eta^3\text{-Ind})(\text{dppe})$ ( <b>10</b> )	$\eta^3$ -Ind, 25.6 $\eta^5$ -Ind, 3.7	88.4	179.1 88.0	<b>9</b>
$\text{Ind}_2\text{Ti}(\text{CO})_2$ ( <b>11</b> ) <sup>a</sup>	$\eta^5$ -Ind, 3.6, 4.1 $\eta^5$ -Ind, 3.8, 2.9	174.6, 16.6	88.5, 97.2 107.3, 85.4	<b>17</b>
$\text{Ind}_2\text{Zr}(\text{CO})_2$ ( <b>12</b> )	$\eta^5$ -Ind, 3.9 $\eta^5$ -Ind, 3.2	3.3	99.8 96.4	<b>18</b>

<sup>a</sup> This complex contains two molecules in the asymmetric unit.

**Scheme 3****Scheme 4**

sten complex **8** and the 17e vanadium complex **9**, which have  $\lambda$  angles of 178.4° and 179.4°, respectively. In contrast, **10**, which bears one dppe ligand, has a  $\lambda$  angle of 88.4°, corresponding to a partially staggered arrangement for the two  $\pi$  ligands.

The  $\beta$  angle is defined for the  $[(\eta^5\text{-Ind})_2\text{MLL}']^{n+}$  systems as the angle that the projection of the vector, determined by the centroids of the five- and the six-membered rings on the LML' plane, makes with  $z$  line. This line is given by the intersection of the LML' plane with the plane defined by the metal center and by the centroids of the five-membered rings of the two indenyl ligands. Hence, this structural parameter reflects the orientation of an indenyl ligand with respect to that line (Scheme 4). For an  $\eta^3$ -indenyl ligand the centroid of the five-membered ring is replaced by the midpoint considered in the definition of the  $\lambda$  angle (see above).

The  $\beta$  angles reported for complex **7**<sup>+</sup> as well as for the other two isoelectronic complexes  $\text{Ind}_2\text{Ti}(\text{CO})_2$  (**11**) and  $\text{Ind}_2\text{Zr}(\text{CO})_2$  (**12**) indicate that the two indenyl rings are almost perpendicular to the  $z$  line. It is interesting to note that the complex **11**, containing two molecules in the asymmetric unit, displays identical  $\beta$  angles and very different  $\lambda$  angles (see above). In other words, the relative orientation of the two indenyl rings to the  $z$  line is independent of the conformation of these ligands, determined exclusively by the  $\lambda$  angle.

Figure 2b shows the projection of a molecular structure of complex **3** on the OC–Mo–CO plane. The  $\eta^3$ -indenyl ring is cis to the carbonyl ligands, with the six-membered ring on the same side of these ligands, leading to a  $\beta$  angle of 2.6°. The  $\eta^5$ -indenyl ring is trans relative to the carbonyl ligands, with a  $\beta$  angle of 177.4°. This type of conformation is also present in the W and

V complexes, **8** and **9**, respectively. When complexes of type  $[(\eta^5\text{-Ind})\text{M}(\eta^3\text{-Ind})\text{LL}']^{n+}$  have bulky ligands in the coordination sphere, such as dppe in **10**, the two rings exhibit different orientations. A trans orientation relative to the two Mo–P bonds is preferred by the  $\eta^3$ -indenyl ligand, leading to a  $\beta$  angle of 179.1°. The  $\eta^5$ -indenyl has a perpendicular orientation relative to the  $z$  line ring, with a  $\beta$  angle of 88.0°. This conformation may be the result of the minimization of the steric interactions between the indenyl and dppe ligands.

In conclusion, this set of structural results suggests that the conformation adopted by indenyl ligands is determined, case to case, by a delicate balance between packing, steric, and electronic effects. In an attempt to shed some light on the role of the steric and electronic effects on the structural preferences of the bis-indenyl complexes, molecular mechanics and orbital calculations at the dft level are in progress.

**Conclusions**

The results presented above open an alternative, high-yield synthesis of mono- and bis-indenyl complexes of Mo(IV) which were either unknown, e.g.,  $\text{IndMoCl}_3$  derivatives, or needed more complex and indirect synthetic routes, like the  $[\text{Ind}_2\text{Mo}^{\text{IV}}\text{L}_2]^{n+}$  derivatives. The somewhat subtle differences between the chemistry of the more reactive indenyl complexes and their parent Cp analogues leave the hope that the above complexes may lead to a varied and rich chemistry of an oxidation state of molybdenum which has been mainly limited to the stoichiometric chemistry of  $\text{Cp}_2\text{MoX}_2$  complexes.

**Experimental Section**

All operations were carried out under an atmosphere of dinitrogen with standard Schlenk-line and glovebox techniques. Solvents were purified by conventional methods and distilled under nitrogen prior to use. NMR spectra were measured on a Bruker CXP 300 spectrometer, and IR spectra were measured on a Unicam Mattson model 7000 FTIR spectrometer.

Room-temperature magnetic susceptibility measurements were carried out by a modified Gouy method with a Johnson Matthey balance. The magnetic susceptibility data were corrected for the diamagnetism of the ligands before conversion to magnetic moments.

$\text{IndMo}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2$ <sup>2,10</sup> and  $\text{Ph}_3\text{CBF}_4$ <sup>21</sup> were prepared as published.

Table 3. Crystal Data and Refinement Details for Metal Complexes 3 and 7

	3	7
empirical formula	C <sub>20</sub> H <sub>14</sub> MoO <sub>2</sub>	C <sub>23</sub> H <sub>24</sub> BF <sub>4</sub> MoNS <sub>2</sub>
<i>M</i>	382.25	561.30
cryst system	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	11.077(13)	8.810(11)
<i>b</i> /Å	6.734(8)	40.114(42)
<i>c</i> /Å	21.161(24)	13.106(16)
$\beta$ /deg	100.59(1)	91.98(1)
<i>V</i> /Å <sup>3</sup>	1552(3)	4629(9)
<i>Z</i>	4	8
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.636	1.611
$\mu$ (mm <sup>-1</sup> )	0.852	0.791
<i>F</i> (000)	768	2272
$\theta$ range/deg	3.18–26.05	2.77–25.99
index ranges <i>hkl</i>	0 ≤ <i>h</i> < 13, −7 ≤ <i>k</i> ≤ 7, −25 ≤ <i>l</i> ≤ 25	0 ≤ <i>h</i> ≤ 10, −48 ≤ <i>k</i> ≤ 49, −14 ≤ <i>l</i> ≤ 15
no. of reflns collected	3677	12 402
no. of unique reflns	2043 ( <i>R</i> <sub>int</sub> = 0.0239)	6701 ( <i>R</i> <sub>int</sub> = 0.0580)
no. of refined params	209	579
goodness-of-fit on <i>F</i> <sup>2</sup>	1.219	1.139
<i>R</i> and <i>R<sub>w</sub></i> [ <i>I</i> > $\sigma$ 2( <i>I</i> )]	0.0651, 0.1812	0.0839, 0.1731
(all data)	0.0773, 0.1859	0.1151, 0.1864
<i>a</i> and <i>b</i> in weighting scheme	0.0461; 24.06	0.0491; 35.00
largest diff peak and hole/e Å <sup>-3</sup>	1.732 and −0.877	0.797 and −0.704

**Preparation of IndMoCl<sub>3</sub>(CO)<sub>2</sub> (1).** Gaseous HCl was bubbled through a solution of IndMo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub> (1.82 g, 5.91 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) for 3 min, and the reaction mixture was stirred for a further 3 h to ensure completion of the reaction. The pink-red precipitate was filtered off, washed with Et<sub>2</sub>O, and dried under vacuum. Yield: 1.65 g (75%). Selected IR (KBr, cm<sup>-1</sup>): 1961, 1880, vs,  $\nu$ (C≡O). Anal. Calcd for C<sub>11</sub>H<sub>7</sub>MoCl<sub>3</sub>O<sub>2</sub>: C, 35.43; H, 1.87. Found: C, 35.22; H, 1.83.

**Preparation of IndMoCl<sub>3</sub> (2).** Solid IndMoCl<sub>3</sub>(CO)<sub>2</sub> (1.13 g, 3.67 mmol) was suspended in 50 mL of CHCl<sub>3</sub>, and the mixture was refluxed for 2 days. Gas evolution and the formation of a dark brown suspension were observed. The solid was filtered off, washed with Et<sub>2</sub>O, and dried under vacuum. Yield: 1.11 g (95%). Anal. Calcd for C<sub>9</sub>H<sub>7</sub>MoCl<sub>3</sub>: C, 34.05; H, 2.22. Found: C, 33.89; H, 2.18.

**Preparation of IndMo( $\eta^3$ -Ind)(CO)<sub>2</sub> (3).** A mixture of KInd (0.41 g, 2.70 mmol) and IndMoCl<sub>3</sub>(CO)<sub>2</sub> (1 g, 2.67 mmol) was weighed in a Schlenk tube in the glovebox and placed in a cold bath at −60 °C. Precooled THF was added, and the temperature was slowly raised to room temperature. After 16 h, the mixture was taken to dryness and the residue was extracted with dichloromethane. The solution obtained was concentrated to dryness to yield the title compound **3** as a red solid. Crystals suitable for X-ray analysis were obtained from a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture. Yield: 0.9 g (90%). Anal. Calcd for C<sub>20</sub>H<sub>14</sub>MoO<sub>2</sub>: C, 62.31; H, 3.50. Found: C, 62.50; H, 3.67. Selected IR (KBr, cm<sup>-1</sup>): 1944, 1851, vs,  $\nu$ (C≡O). <sup>1</sup>H NMR (NCMe-*d*<sub>3</sub>, 300 MHz, room temperature,  $\delta$  ppm): 6.69–6.66 (m, 8 H, H<sub>5–8</sub>), 5.11 (d, 4 H, H<sub>1/3</sub>), 4.80 (t, 2 H, H<sub>2</sub>) (see Scheme 1 for numbering).

**Preparation of [Ind<sub>2</sub>Mo(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (4).** Solid Ph<sub>3</sub>CBF<sub>4</sub> (1.4 g, 4.29 mmol) was added to a solution of IndMo( $\eta^3$ -Ind)(CO)<sub>2</sub> (0.82 g, 2.14 mmol) in dichloromethane at room temperature. The reaction mixture was stirred for 8 h, and a green precipitate was separated from the solution. The solid was filtered off, washed with Et<sub>2</sub>O, and dried under vacuum. Yield: 1.05 g (89%). Anal. Calcd for C<sub>20</sub>H<sub>14</sub>MoO<sub>2</sub>B<sub>2</sub>F<sub>8</sub>: C, 43.17; H, 2.52. Found: C, 42.90; H, 2.40. Selected IR (KBr, cm<sup>-1</sup>): 2119, 2085, vs,  $\nu$ (C≡O).

**Preparation of [Ind<sub>2</sub>Mo(CO)(NCMe)][BF<sub>4</sub>]<sub>2</sub> (5).** A solution of [Ind<sub>2</sub>Mo(CO)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (0.40 g, 0.72 mmol) in acetonitrile (30 mL) was stirred for 2 h at room temperature. The initial green color of the solution became orange. After concentration to ca. 15 mL and addition of Et<sub>2</sub>O, a crystalline orange precipitate was obtained. The solid was filtered off, washed with hexane, and dried under vacuum. Yield: 0.37 g (90%).

Anal. Calcd for C<sub>21</sub>H<sub>17</sub>MoONB<sub>2</sub>F<sub>8</sub>: C, 44.32; H, 3.0; N, 2.46. Found: C, 44.08; H, 3.0; N, 2.30. Selected IR (KBr, cm<sup>-1</sup>): 2054, vs,  $\nu$ (C≡O); 2328, 2297, w,  $\nu$ (N≡C). <sup>1</sup>H NMR (NCMe-*d*<sub>3</sub>, 300 MHz, room temperature,  $\delta$  ppm): 7.76 (m, 4 H, H<sub>5–8</sub>), 7.55 (m, 4 H, H<sub>5–8</sub>), 7.40 (d, 2 H, H<sub>1/3</sub>), 6.71 (d, 2 H, H<sub>1/3</sub>), 6.12 (t, 2 H, H<sub>2</sub>), 2.12 (s, 3 H) (see Scheme 1 for numbering).

**Preparation of [Ind<sub>2</sub>Mo(NCMe)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (6).** A solution of [Ind<sub>2</sub>Mo(CO)(NCMe)][BF<sub>4</sub>]<sub>2</sub> (0.95 g, 2.67 mmol) in acetonitrile (60 mL) was refluxed and irradiated with a 60 W tungsten lamp for 4 h. A pink-red solution was formed, the solution was filtered through Celite, and the filtrate was taken to dryness to yield a pink-red solid, which was washed with Et<sub>2</sub>O. Yield: 0.87 g (87%). Anal. Calcd for C<sub>22</sub>H<sub>20</sub>MoN<sub>2</sub>B<sub>2</sub>F<sub>8</sub>: C, 45.39; H, 3.46; N, 4.12. Found: C, 45.11; H, 3.37; N, 4.11. Selected IR (KBr, cm<sup>-1</sup>): 2320, 2291, w,  $\nu$ (N≡C). <sup>1</sup>H NMR (NCMe-*d*<sub>3</sub>, 300 MHz, room temperature,  $\delta$  ppm): 7.46 (m, 8 H, H<sub>5–8</sub>), 6.37 (d, 4 H, H<sub>1/3</sub>), 6.03 (t, 2 H, H<sub>2</sub>), 2.14 (s, 6 H) (see Scheme 1 for numbering).

**Preparation of [Ind<sub>2</sub>Mo(S<sub>2</sub>CNEt<sub>2</sub>)][BF<sub>4</sub>]<sub>2</sub> (7).** A solution of tetrabutylammonium diethyldithiocarbamate (0.10 g, 0.25 mmol) in dichloromethane was added to a stirred solution of [Ind<sub>2</sub>Mo(NCMe)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (0.14 g, 0.25 mmol) in dichloromethane at room temperature. The reaction mixture was stirred for 10 h at room temperature. The solution was filtered through Celite, and the filtrate was taken to dryness and washed with Et<sub>2</sub>O to yield the title compound **7** as a red solid. Recrystallization from NCMe/Et<sub>2</sub>O gave red crystals suitable for X-ray analysis. Yield: 0.13 g (93%). Anal. Calcd for C<sub>23</sub>H<sub>24</sub>MoS<sub>2</sub>NBF<sub>4</sub>: C, 49.21; H, 4.27; N, 2.49; S, 11.41. Found: C, 48.92; H, 4.21; N, 2.38; S, 11. Selected IR (KBr, cm<sup>-1</sup>): 1944, 1851, vs,  $\nu$ (C≡O). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, room temperature,  $\delta$  ppm): 7.13 (m, 8 H, H<sub>5–8</sub>), 6.34 (d, 4 H, H<sub>1/3</sub>), 5.31 (t, 2 H, H<sub>2</sub>), 3.49 (q, 4 H, Et), 1.09 (t, 6 H, Et) (see Scheme 1 for numbering).

**X-ray Crystallography. Data Collection and Processing.** Table 3 lists the pertinent crystallographic data together with refinement details for complexes **3** and **7**. The X-ray single-crystal data for the two complexes were collected with a MAR Research Image Plate system using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å). The crystals were positioned at 70 mm from the image plate; 95 frames were measured at 2° intervals with counting times of 10.5 and 5 min, respectively. Data analysis was carried out with the XDS program.<sup>22</sup> Intensities were not corrected for absorption effects.

**Structure Analysis and Refinement.** The positions of

molybdenum atoms were obtained by direct method, while the positions of remaining non-hydrogen atoms were found from successive difference Fourier synthesis. From earliest difference Fourier maps calculated for complex **7** it was clear that one of the BF<sub>4</sub> anions was disordered, with fluorine atoms occupying two sites. So, a disordered model with fluorine atoms positioned on two alternative positions with refined occupation factors was considered for this anion. A refined value of 0.57 was obtained for major disorder component.

Hydrogen atoms of the three structures were included in the refinement at idealized geometric positions, giving isotropic thermal parameters equal to 1.2 times those of the atoms to which they were bonded. All non-hydrogen atoms were refined using anisotropic thermal parameters, except the disordered fluorine atoms in **7**, which were refined with isotropic thermal parameters.

The structures were refined by least-squares method on  $F^2$  until convergence was achieved. The final refinements were made using a weighting scheme with the form  $w = 1/[\sigma^2(F_o^2) + (a)^2 + bP]$ , where  $P = [\max(F_o^2) + 2F_o^2]/3$ . The values of the parameters  $a$  and  $b$  are given in Table 3.

The structures were solved and refined using the programs SHELXS and SHELXL within the SHELX97 package.<sup>23</sup> The molecular diagrams were drawn with the XPMA and ZORTEP programs.<sup>24</sup>

**Acknowledgment.** This work was supported by PRAXIS XXI under project 2/2.1/QUI/316/94. B.R. thanks PRAXIS XXI for a grant. V. F. thanks the British Council and FCT for a travel grant.

**Supporting Information Available:** Atomic coordinates, thermal parameters, and bond lengths and angles for **3** and **7** (26 pages). Ordering information is given on any current masthead page.

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