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Synthesis and structural characterization of new mixed-ring indenyl derivatives of molybdenum containing phosphorus ligands

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Abstract

Reaction of $NaBH_4$ with $[IndCpMo(dppe)](BF_4)_2$ (**1**) in acetone yields $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ (**2**) quantitatively. The hydride addition takes place at the external face of the Cp ring. Dissolution of **2** in dichloromethane gives $[IndMo(\eta^4\text{-}C_5H_5\text{-}exo\text{-}CH_2Cl)(dppe)]BF_4$, as confirmed by elemental analysis, IR and ^1H NMR spectroscopy. The similar dication $[IndCpMo\{P(OMe)_3\}_2](BF_4)_2$ (**4**) reacts with $NaBH_4$, in a solvent dependent manner. In acetonitrile, $[IndMo(\eta^4\text{-}C_5H_6)\{P(OMe)_3\}_2]BF_4$ (**5**) is obtained and in acetone a $P(OMe)_3$ ligand is lost resulting in the asymmetric phosphite-hydride, $[IndCpMoH\{P(OMe)_3\}]^+$ (**6**). The molecular structures of $[IndMo(\eta^4\text{-}C_5H_6)\{P(OMe)_3\}_2]PF_6$ and $[IndCpMoH\{P(OMe)_3\}]PF_6$ were characterized by single-crystal X-ray diffraction.

Keywords: Molybdenum; Cyclopentadienyl; Indenyl; Hydride; Molybdenocene; Mixed-ring indenyl complexes

1. Introduction

A large number of reactions undergone by molybdenocene complexes of the type $[Cp'_2MoL_2]^{n+}$ ($Cp' = $ cyclopentadienyl ring, $\eta^5\text{-}C_5R_5$) do not involve the fragment Cp'_2Mo, which is remarkably stable [1]. However, nucleophilic addition to cyclopentadienyl ligands bonded to 18-electron organotransition metal cations is generally accepted to be stereospecific with the nucleophile approaching the uncoordinated face of the cyclopentadienyl ligand to yield η^4-cyclopentadiene complexes [2]. Earlier work has established that in the case of nucleophilic attack of hydride ion (H^-) on $[Cp_2MoL_2]^{n+}$ (M = Mo, W; L_2 = dppe (diphenylphosphinoethane) and other ligands; $n = 0, 1, 2$), the reaction center is one of the Cp rings [3]. Similarly, in the reaction of Cp_2MoCl_2 with $LiAlD_4$, D^- adds to one of the rings to give a partially ring-deuterated product [4], and the reaction of $Cp_2MoCl(Et)$ with alkylphosphines gives $CpMo(\eta^4\text{-}C_5H_4Et)Cl(PR_3)$ involving metal-to-ring migration of the ethyl group [5]. More recently, several other nucleophiles (R^-) have been shown to react with the dications $[Cp_2MoL_2]^{2+}$ (L = CO, PMe_3, L_2 = dppe) producing the cyclopentadiene complexes $[CpMo(\eta^4\text{-}C_5H_5R)L_2]^+$ (L_2 = dppe, R = H, Me, CH_2CN, CH_2PPh_3, SMe; L = CO or PMe_3, R = H) [6]. Indeed, there are more examples of the introduction of substituents on Cp ligands in group 6 metallocenes, in particular tungstenocene derivatives with exocyclic boron [7] or silyl substituents [8] have been reported but their formation results from a ligand transfer from the metal to the Cp ring. Also, a route to tungstenocene complexes with chiral metal centers was developed by Cooper following earlier scattered reports on nucleophilic addition at the Cp rings of Cp_2MX_2 complexes

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[9]. Möise and co-workers reported the ability of metallophosphide anions to undergo a direct Cp substitution on Cp_2MCl_2 (M = Mo, W), and explored the influence of steric and electronic factors on the Cp ring nucleophilic substitution on other metallocenes $(\eta^5\text{-}C_5H_4\text{-}^tBu)_2MCl_2$ [10]. However, the lack of convenient syntheses for the molybdenocene system limited for many years the corresponding exploration of the ring-substituted molybdenocene chemistry. Recent reports of routes to both substituted and unsubstituted bis-cyclopentadienyl complexes have changed this situation and helped the development of this area [11,12].

Investigations in our laboratory have focused on new methods to prepare bent metallocene complexes of molybdenum and tungsten containing substituted cyclopentadienyl ligands and η^5-cyclic analogues [13]. The synthetic approach is based on transformations of the diene complexes to provide a high yield route to metallocenes as well as differentially substituted chiral and pro-chiral metallocene analogues, namely the indenyl congeners $[IndCpML_2]^{2+}$. In this paper, we describe a new and high-yield route to some novel mixed ring molybdenum cations containing phosphorus ligands of the general formula $[IndMo(\eta^4\text{-}C_5H_6)L_2]^+$ [L = $P(OMe)_3$, L_2 = dppe], including X-ray crystallographic studies, and also present examples of their reactivity.

2. Results and discussion

2.1. Preparation of $[IndMo\{\eta^4\text{-}C_5H_5(R)\}(dppe)]BF_4$ (R = H, CH_2Cl) complexes

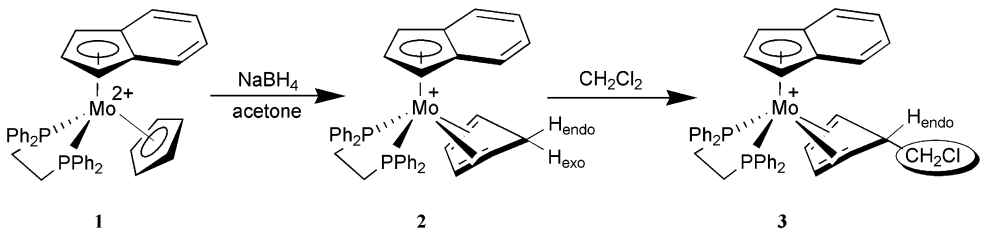
It was shown previously that H^- adds to the Cp ring of the dication in $[IndCpMo(dppe)](BF_4)_2$ (**1**) to afford the diene complex $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ (**2**) [14]. In fact, the preparation of pure **2** only occurs if acetone and diethyl ether are used. While attempting to crystallize **2** by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution at room temperature, brown crystals were obtained (Scheme 1). These crystals were identified as $[IndMo\{\eta^4\text{-}C_5H_5(CH_2Cl)\}(dppe)]BF_4$ (**3**) by elemental analysis, FTIR and ^1H NMR spectroscopy. The complex **3** can also be prepared by stirring in a CH_2Cl_2 solution for 48 h. Both **2** and **3** are quite stable at room temperature and can be handled in air for short periods of time.

The ^1H NMR spectrum of **3** shows the resonances of the η^5-indenyl, a multiplet pointing to the presence of the dppe phenyl group and the indenyl C_6 ring protons (H_{5-8}) at δ 7.42–6.82, a multiplet at δ 6.50 ppm ($H_{1/3}$) and a broad singlet at 5.32 ppm (H_2) (see Scheme 2 for numbering). The resonances for the η^4-cyclopentadiene ligand are typical of the *endo* conformation and reveal no evidence of rotamers involving different orientations of the η^4-cyclopentadiene ligand (invariance with temperature). In most diene complexes of general formula $[Cp'Mo(\eta^4\text{-diene})LL']^+$ the *endo* conformation of the diene is favored in spite of the fluxional behaviour that many of them present in solution [15]. The chemical shifts of the η^4-diene $C_5H_5(CH_2Cl)$ protons are very similar to those observed for the *endo* conformer of $[CpMo\{\eta^4\text{-}C_5H_5(R)\}(dppe)]PF_6$ (R = Me, PPh_3) [6] and, therefore, the $H_{b\text{-}c}$ was assigned as the lower field resonance at δ 4.98 ppm, followed by the $H_{a\text{-}d}$ and H_{endo} resonances at δ 4.23 and 2.85 ppm, respectively. The peak at δ 3.49 ppm was attributed to the chloromethyl group ($-CH_2Cl$) bonded to the saturated carbon. Also, the presence of $-CH_2Cl$ at the external face of the diene is implied by the absence of the C–H_{exo} vibration in the IR spectrum. Single crystal diffraction data obtained from low quality crystals and not completely refined is already of sufficient quality to confirm this stereochemistry [15b,15c].

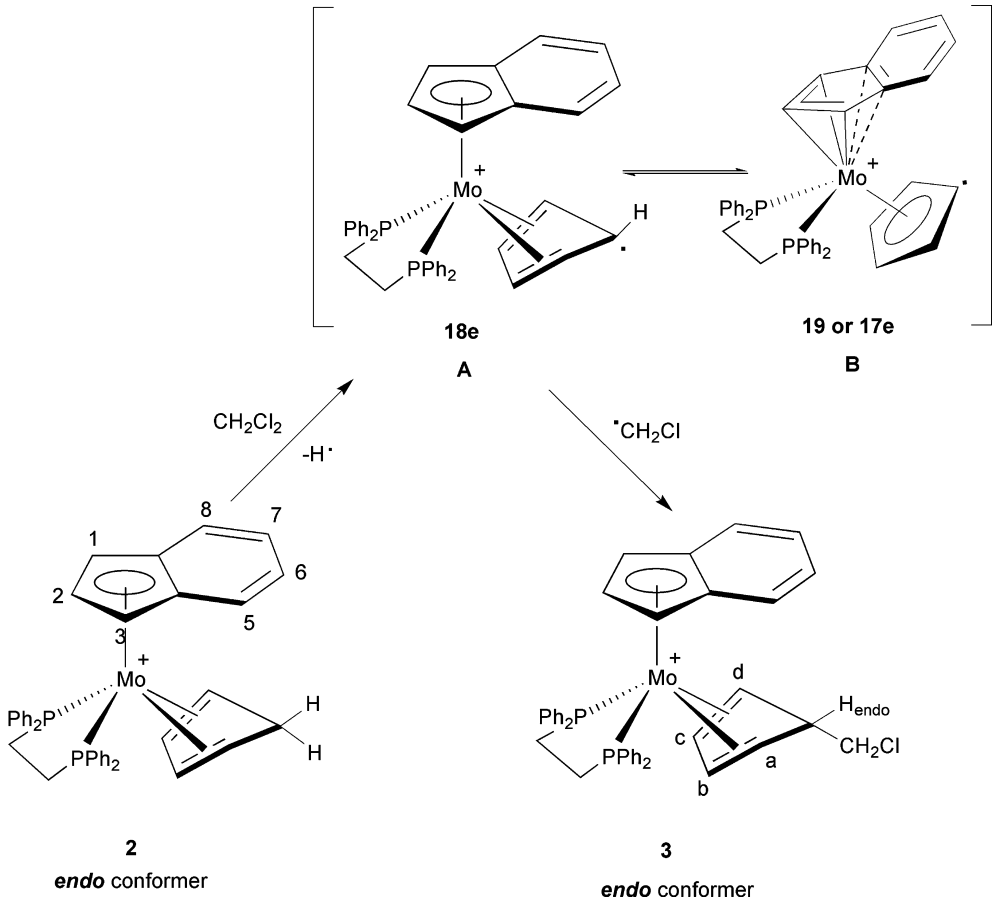
Similar trends are observed for the unsubstituted complex $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ (**2**) in $(CD_3)_2CO$, also assigned as the *endo* conformer (bridgehead CH_2 *cis* to the indenyl ring as in Scheme 1) [14]. However, concerning the chemical shifts of the methylene protons of the C_5H_6 ring, H_{endo} was assigned as the higher field resonance at δ 2.80 ppm and H_{exo} as the lower field resonance at δ 3.29 ppm. As expected, C–H_{exo} in **2** exhibits a distinct IR stretching vibration at 2768 cm^{-1}. For both compounds **2** and **3** a typical broad band between 1100 and 1000 cm^{-1}, attributed to a ν(B–F) absorption, is observed in the IR spectrum and is indicative of the presence of a tetrafluoroborate anion, suggesting a cationic molybdenum complex as counter-ion.

2.2. Mechanism of formation of $[IndMo(\eta^4\text{-}C_5H_5\text{-}exo\text{-}CH_2Cl)(dppe)]BF_4$

The observation that the CH_2Cl fragment of CH_2Cl_2 adds *exo* to the cyclopentadiene ligand of $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ is consistent with a radical mechanism on the basis of voltammetric studies and literature findings as summarized in Scheme 2 [16].



Scheme 1.



Scheme 2.

Oxidation of **2**, possibly caused by adventitious O_2 and/or light, leads to the loss of H· and formation of **A** which can be structurally reorganized to the radical cation **B**. The structure and spin distribution of this species should be rather similar to those calculated and measured experimentally for the isoelectronic radical cations $[IndCpMoL_2]^{+\cdot}$ (L = $P(OMe)_3$, $P(OH)_3$, CO) [17]. In these studies, it was shown that the flexibility of the coordination of the indenyl was the reason for the stabilization of this rare example of a molybdenocene complex in the Mo(III) oxidation state which is not observed for the isoelectronic $[Cp_2MoL_2]^{n+}$ analogues. Most of the spin density, as calculated for the model $[IndCpMo\{P(OH)_3\}_2]^{+\cdot}$, resides on the Mo atom and the C atoms of the Cp ring. Therefore, this initial H· abstraction produces the same result as the 1e reduction of the dication $[IndCpMo(dppe)]^{2+}$. The results of the cyclovoltammograms presented in Table 1 entirely support this interpretation. As expected, the CVs of **1** and its fully reduced Mo(II) derivative are the same confirming full chemical reversibility.

Under these circumstances it becomes clear that the *exo* addition of the chloromethyl radical (·CH_2Cl) to the radical cation complex $[IndCpMo(dppe)]^{+\cdot}$ should take place at the Cp ring where the spin density is higher [17]. This kind of reaction is not unprecedented [18]. For example, during the reaction of $Cp_2W(CO)$ with CCl_4 carried out in the dark, the addition of the ·CCl_3 radical to the cyclopentadienyl ligand and the chloride anion to the tungsten atom was observed and $CpW\{\eta^4\text{-}C_5H_5(CCl_3)\}(CO)Cl$ was formed [19]. In the present work, the cyclic voltammogram (CV) of $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ (**2**) in CH_2Cl_2 was compared with those obtained for the complexes $[IndCpMo(dppe)][BF_4]_2$ (**1**) and $(\eta^3\text{-}Ind)CpMo(dppe)$. Also, for comparison, the CV of $(\eta^3\text{-}Ind)CpMo(dppe)$ in CH_2Cl_2 was repeated in this work (Table 1).

The CVs of the complexes $[IndCpMo(dppe)][BF_4]_2$ (**1**) and $(\eta^3\text{-}Ind)CpMo(dppe)$ showed the expected similarities in two distinct quasi-reversible 1-electron reduction steps for the former and two reversible oxidation waves for the latter (Fig. 1). For $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ (**2**), part of the CV is similar to that of $(\eta^3\text{-}Ind)CpMo(dppe)$, showing that the loss of H· takes place on the time scale of the technique and the radical $[IndCpMo(dppe)]^{+\cdot}$ **B** is being formed. The separation between the waves is 150 mV for $[IndCpMo(dppe)](BF_4)_2$ (**1**) and also 150 mV for $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ (**2**). As proposed before [20] these small potential differences suggest marked stabilization of the final reduction product $(\eta^3\text{-}Ind)CpMo(dppe)$, by an $\eta^5 \rightarrow \eta^3$ hapticity shift concomitant with the second reduction, and also supports η^5-indenyl ligation in the first reduction product, $[(\eta^5\text{-}Ind)CpMo(dppe)]^+$ (Scheme 2).

Table 1
Cyclic voltammetry data for mixed ring dppe derivatives

Compound	$E_{p,a}$	$E_{p,c}$	$E_{p,1/2}$	I_a/I_c	Ref.
[IndCpMo(dppe)]$(BF_4)_2$ (**1**)	−0.30; −0.46	−0.37; −0.52	−0.34; −0.49	1.0; 0.9	[14]
[IndMo(η^4-C_5H_6)(dppe)]BF_4 (**2**)	−0.28; −0.44	−0.36; −0.51	−0.32; −0.48	1.0; 0.9	This work
(η^3-Ind)CpMo(dppe)	−0.29; −0.46	−0.36; −0.52	−0.33; −0.49	1.0; 0.9	[14]
	−0.24; −0.45	−0.31; −0.52	−0.28; −0.49	1.0; 0.9	This work

The voltammograms for **2** and (η^3-Ind)CpMo(dppe) were measured in CH_2Cl_2, in ca. 1.0 mM solutions, scan rate is 0.2 V s^{-1} and $E_{p,1/2}$ values are the average of the anodic and cathodic peak potentials. $E_{p,a}$, anodic sweep (peak potentials, V). $E_{p,c}$, cathodic sweep (peak potentials, V). $E_{p,a}$, $E_{p,c}$ and $E_{p,1/2}$ are referenced to SCE.

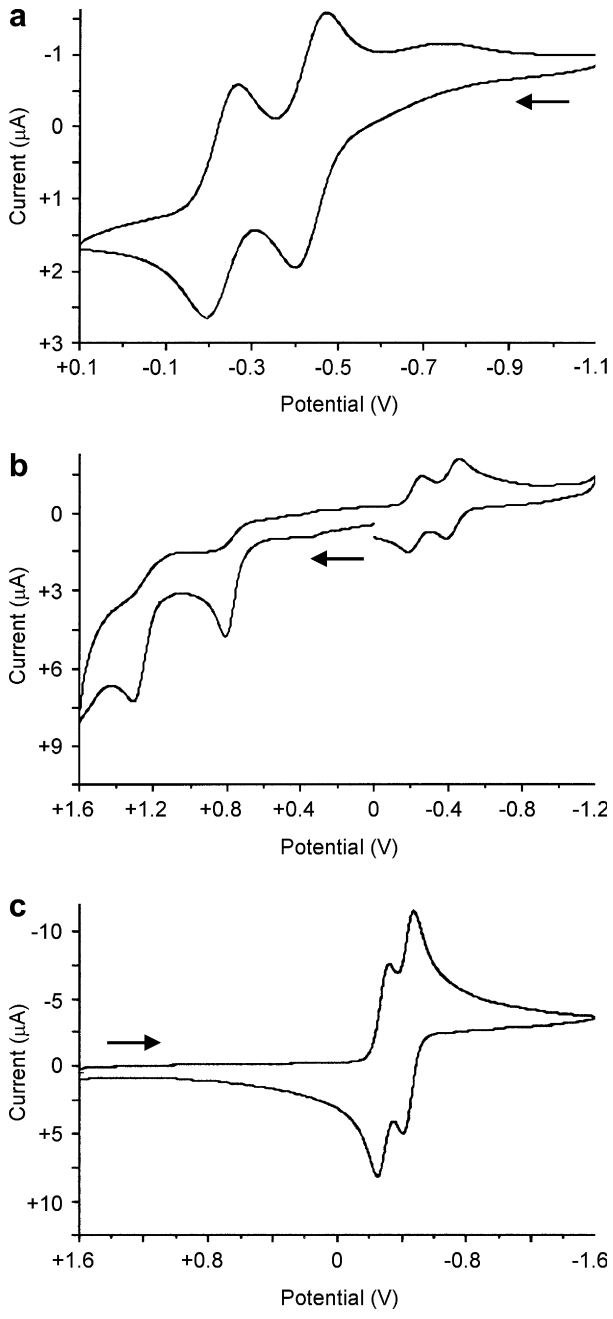


Fig. 1. Cyclic voltammograms of (a) (η^3-Ind)CpMo(dppe) in CH_2Cl_2; (b) [IndMo(η^4-C_5H_6)(dppe)]BF_4 (**2**) in CH_2Cl_2, and (c) [IndCpMo(dppe)]-$(BF_4)_2$ (**1**) in NCMe, with 0.1 M NBu_4PF_6, scan rate 0.2 V s^{-1}.

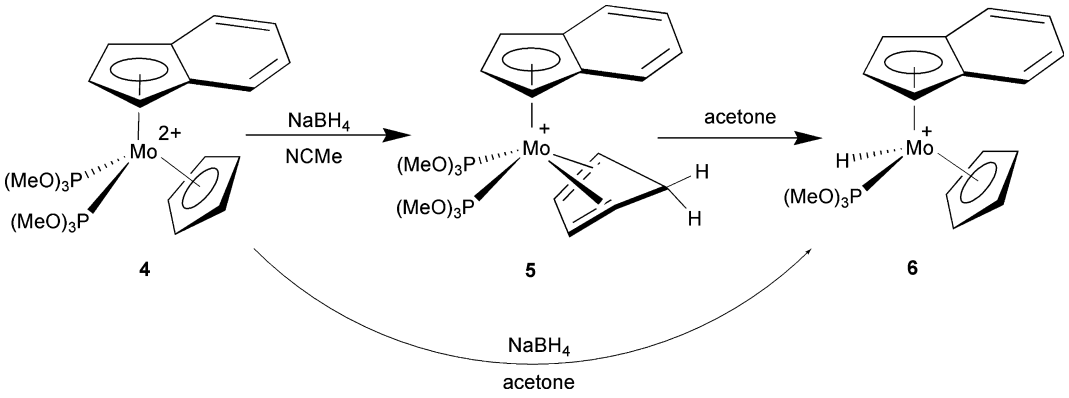
2.3. Preparation of $[IndMo(\eta^4\text{-}C_5H_6)\{P(OMe)_3\}_2]^+$ and $[IndCpMoH\{P(OMe)_3\}]^+$ complexes

Hydride additions also take place with the dication [IndCpMo{$P(OMe)_3$}$_2$]$(BF_4)_2$ (**4**). Complex **4** reacts with 1 equivalent of $NaBH_4$, in acetonitrile, to give the yellow complex [IndMo(η^4-C_5H_6){$P(OMe)_3$}$_2$]BF_4 (**5**), as depicted in Scheme 3. The choice of solvent determines the course of the reaction and hence when the reaction is carried out in acetone, complex **5** is not stable and looses a $P(OMe)_3$ ligand with H migration to molybdenum giving the asymmetric phosphite-hydride, [IndCpMoH-{$P(OMe)_3$}]$^+$ (**6**). Compounds **5**–**6** are moderately air and moisture sensitive. However, they are indefinitely stable under inert atmosphere at room temperature and both are completely insoluble in *n*-hexane and diethyl ether.

The diene complex [IndMo(η^4-C_5H_6){$P(OMe)_3$}$_2$]BF_4 (**5**) is not fluxional in CD_3CN, as concluded from the invariance of its ^{1}H NMR spectrum with temperature (from −30 °C to room temperature). However, in $(CD_3)_2CO$ complex **5** has a fluxional structure and broadening of the AB spin system of the methylene protons of the C_5H_6 ligand is observed at −70 °C, comparable with [IndM(η^4-C_5H_6)-$(CO)_2$]BF_4 (M = Mo, W) [13]. Both diene complexes {[IndM(η^4-C_5H_6)L_2]BF_4, L = CO, $P(OMe)_3$ (**5**)} are sensitive toward CO or $P(OMe)_3$ loss and H migration and, accordingly, give the corresponding metal-hydride complexes.

Complex **5** was assigned as the *endo* conformer (bridgehead CH_2 cis to the indenyl ring as in Scheme 3) by comparison of its ^{1}H NMR spectrum with the known congener [CpMo(η^4-C_5H_6)(dppe)]BF_4 [6]. In fact, the chemical shifts of the methylene protons of the C_5H_6 ring are very similar to those observed for [CpMo(η^4-C_5H_6)-(dppe)]BF_4 and, therefore, we assigned the H_{endo} as the higher field resonance at δ 2.87 ppm and the H_{exo} as the lower field resonance at δ 4.56 ppm. As expected, H_{exo} in **5** exhibits a distinct IR stretching vibration at 2764 cm^{-1}. A crystal structure determination of [IndMo(η^4-C_5H_6)-{$P(OMe)_3$}$_2$]PF_6 (**5**) also confirmed the overall molecular architecture (see below).

For the asymmetric hydride [IndCpMoH{$P(OMe)_3$}]-PF_6 (**6**) the ^{1}H NMR spectrum in CD_2Cl_2 shows the typical pattern for the resonances of the planar η^5-indenyl: two sets of signals for the C_6 ring protons (H_{5-8}), two singlets



Scheme 3.

for $H_{1/3}$ and a broad singlet for H_2 (see Scheme 2 for the numbering). The hydride resonance is observed as a doublet at δ −7.42 ppm with 46 Hz couplings to the phosphorus nuclei. An additional resonance due to the phosphite ligand P(O*Me*)$_3$ is observed at δ 3.62 ppm. The IR spectrum of **6** shows one weak ν(Mo–H) absorption at 1897 cm^{-1}. Recrystallization from CH_2Cl_2/Et_2O afforded single crystals suitable for structure determination by X-ray diffraction (see below).

2.4. Crystal structures of [IndMo(η^4-C_5H_6){P(OMe)$_3$}$_2$]-PF_6 and [IndCpMoH{P(OMe)$_3$}]PF_6

Both complexes are tetrahedral, and in [IndMo(η^4-C_5H_6){P(OMe)$_3$}$_2$]PF_6 (**5**) the molybdenum atom is bonded to the 5-membered ring of the indenyl group, the double bonds of the CpH and to two P(OMe)$_3$ groups (Fig. 2). Mo–C bond distances to Ind are in the range 2.24(2)–2.49(3) Å, with a mean value of 2.36(1) Å, and those to CpH are in the range 2.28(3)–2.41(2) Å with a mean value of 2.35(1) Å. In [IndCpMoH{P(OMe)$_3$}]PF_6 (**6**), the molybdenum is bonded to the Indenyl and Cp groups, to one P(OMe)$_3$ group, and to a hydrogen atom (Fig. 3). Mo–C bond distances to Ind are in the range 2.262(2)–2.419(2) Å, with a mean value of 2.328(1) Å, and those to Cp are in the range 2.282(2)–2.341(2) Å with a mean value of 2.303(1) Å. The geometry at the molybdenum atom is presented in Table 2. In both cases the tetrahedra are distorted with the angle involving the two organic ligands being the largest and that between the remaining ligands being smallest. The Mo–H distance of 1.57(3) Å is short but within the range found in the Cambridge Crystallographic Data Base [21], and not significantly shorter than the value of 1.59(3) Å found in the related compound (η^4-$C_5H_2Ph_4$)CpMoH[P(OMe)$_3$] [22]. Mo–Ind and Mo–Cp distances are similar to the values found in related compounds: Mo-η^5-Ind = 2.03(3) Å, Mo-η^4-CpH 2.06(3) Å in **5**; Mo-η^5-Ind = 1.986(2) Å, Mo-η^5-Cp = 1.966(2) Å in **6**; Mo-η^5-Ind = 2.019, 2.044 Å in [(Ind)$_2$Mo{P(OMe)$_3$}$_2$]-(PF_6)$_2$ [23]; Mo-η^5-Ind = 2.014 Å, Mo-η^5-Cp = 1.999 Å in [(η^5-Ind)CpMo{P-(OMe)$_3$}$_2$](BF_4)$_2$ [17]; Mo-η^3-Ind = 2.069 Å, Mo-η^5-Cp = 1.998 Å in [(η^3-Ind)CpMo-{P(OMe)$_3$}$_2$] [17].

3. Conclusions

In summary, we present the preparation of diene mixed ring complexes of the type [IndMo{η^4-C_5H_5(R)}L_2]$^+$ (L_2 = dppe or L = P(OMe)$_3$; R = H, CH_2Cl), which in the case of L = P(OMe)$_3$ can be used for the preparation

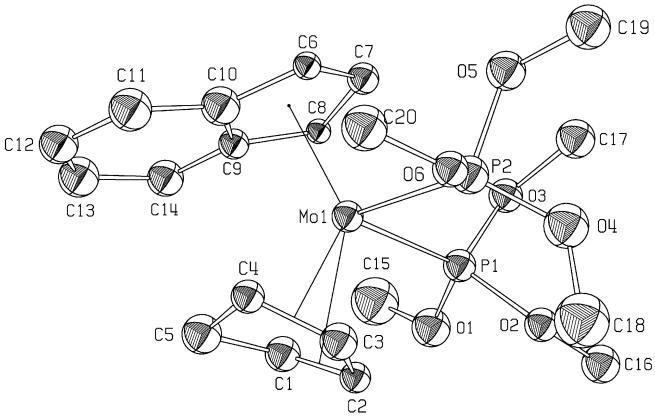


Fig. 2. Molecular structure of [IndMo(η^4-C_5H_6){P(OMe)$_3$}$_2$]PF_6 (**5**).

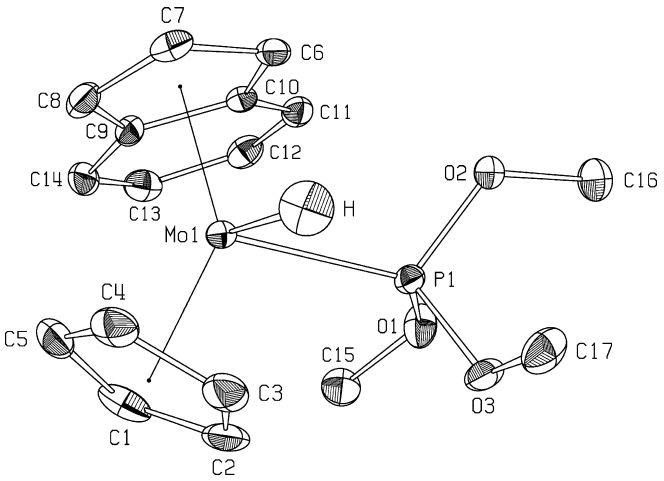


Fig. 3. Molecular structure of [IndCpMoH{P(OMe)$_3$}]PF_6 (**6**).

Table 2
Selected bond distances (Å) and angles (°) for **5** and **6**

	5	6
Mo1–CpH/Cp[a]	2.06(3)	1.966(2)
Mo1–Ind[a]	2.03(3)	1.986(2)
Mo1–P1	2.405(8)	2.427(1)
Mo1–P2	2.401(8)	–
Mo1–H20	–	1.57(3)
H20–Mo1–P1	–	74.5(9)
H20–Mo1–Ind	–	106.7(10)
H20–Mo1–Cp	–	97.7(10)
Ind–Mo1–CpH/Cp	137.3(8)	141.02(9)
Ind–Mo1–P1	111.0(6)	107.28(6)
Ind–Mo1–P2	110.1(6)	–
P1–Mo1–CpH/Cp	99.8(6)	108.27(6)
P2–Mo1–CpH	99.6(6)	–
P1–Mo1–P2	87.8(3)	–

[a] Cp and Ind are the centres of the cyclopentadienyl and the 5-ring of the indenyl group, CpH is the centre of the C_4H_4 of CpH.

of the asymmetric hydride complex, [IndCpMoH{$P(OMe)_3$}]PF_6 (**6**). Compound **6** is a mixed-ring indenyl hydride and, to the best of our knowledge, [IndCpMoH(CO)]$^+$ represents the only previously reported closely related example [13b], apart from the tungsten analogue [IndCpWH(CO)]$^+$ [24]. Furthermore, asymmetric hydrides such as **6** might – in view of the extensive chemistry of related bis-cyclopentadienyl hydrides [25] – be interesting starting materials for other asymmetric metallocene analogues containing halogenated and other ligands, which may provide a fine modulation of the electronic and stereochemical properties of these modified metallocenes. This work is also part of our general goal to extend the chemistry of mixed ring molybdenum systems and to raise their level of significance in comparison with those of Cp_2Mo complexes.

4. Experimental

4.1. Materials and methods

All preparations and manipulations were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by standard procedures, distilled under nitrogen and kept over 4 Å molecular sieves (3 Å for NCMe). Starting materials were obtained from commercial sources and used as received.

Microanalyses were performed at the ITQB (by C. Almeida). IR spectra were measured on a Mattson 7000 FT-IR spectrometer using KBr pellets. ^{1}H NMR spectra were measured on a Bruker AMX-300 spectrometer. Chemical shifts are quoted in parts per million from TMS.

The electrochemical measurements were performed with a BAS CV – 50 W – 1000 voltammetric analyser controlled by BAS/Windows data acquisition software. The solutions were purged with nitrogen and kept under an inert atmosphere throughout the measurements. Tetrabutylammonium hexafluorophosphate (0.1 M) in CH_2Cl_2 was used as the supporting electrolyte. A glass cell (BAS MF-1082 in a C-2 cell enclosed in a Faraday cage) was used with a carbon electrode as the working electrode, a 7.5 cm platinum wire (BAS MW-1032) with a gold-plated connector as the counter electrode, and a SSC (BAS MF-2063) as the reference electrode (exhibiting a potential ca. −44 mV relative to a saturated calomel electrode). The ferrocenium–ferrocene couple was used as an internal standard: under the experimental conditions used and for the scan rate of 0.2 V s^{-1}, $E_{1/2} = 0.46$ V and $i_{pa}/i_{pc} = 1.00$. The electrochemical behaviour of the complexes did not seem to be affected by the presence of ferrocene and vice versa.

[IndCpMo(dppe)]$(BF_4)_2$ (**1**) [14] and [IndCpMo{$P(OMe)_3$}$_2$]$(BF_4)_2$ (**4**) [17] were obtained as described previously.

4.2. Preparation of [IndMo(η^4-C_5H_6)(dppe)]BF_4 (2)

A solution of [IndCpMo(dppe)]$(BF_4)_2$ (0.30 g, 0.35 mmol) in acetone was treated with $NaBH_4$ (15 mg, 0.40 mmol) and the mixture was stirred for 3 h at room temperature. The resulting solution was filtered and taken to dryness to give compound **2** (0.26 g, 96%). Anal. Calc. for $C_{40}H_{37}BF_4P_2Mo$ (762.41): C, 63.01; H, 4.89. Found: C, 63.10; H, 4.86%. Selected IR (KBr, cm^{-1}): 3053 (m), 2971 (m), 2768 (m), 1697 (m), 1435 (m), 1084 (vs), 748 (s), 698 (vs), 523 (vs). ^{1}H NMR [$(CD_3)_2CO$, 300 MHz, 25 °C, δ ppm]: δ 7.79–6.90 (c, 24H, Ph + H_{5-8}); 6.37 (m, 2H, $H_{1/3}$); 5.61 (s (br), 1H, H_2); 5.03 (s (br), 2H, H_{b-c} of C_5H_6); 3.37 (s (br), 2H, H_{a-d}); 3.29 (d (br), 1H, H_{exo}); 2.80 (d (br), 1H, H_{endo}); 2.55 (c, 4H, CH_2 of dppe).

4.3. Preparation of [IndMo(η^4-C_5H_5-exo-CH_2Cl)(dppe)]BF_4 (3)

A solution of [IndMo(η^4-C_5H_6)(dppe)]BF_4 (**2**) (0.34 g, 0.50 mmol) in dichloromethane (20 ml) was stirred for 2 days. The volume was reduced by half and diethyl ether added to precipitate a brown solid which was filtered, washed with ether (2 × 10 ml) and dried in vacuum. Recrystallization from CH_2Cl_2/Et_2O (3:15) gave a brown microcrystalline product (0.39 g, 97%). Anal. Calc. for $C_{41}H_{38}BClF_4P_2Mo$ (810.88): C, 60.73; H, 4.72; Cl, 4.37; Mo, 11.83. Found: C, 60.86; H, 4.91; Cl, 4.22; Mo, 11.56%. Selected IR (KBr, cm^{-1}): 3053 (m), 2984 (m), 1483 (m), 1435 (s), 1084 (vs), 748 (s), 698 (vs), 521 (vs). ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C, δ ppm): δ 7.42–6.82 (c, 24H, Ph + H_{5-8}); 6.50 (m, 2H, $H_{1/3}$); 5.32 (s (br), 1H, H_2); 4.98 (s (br), 2H, H_{b-c} of C_5H_5R); 4.23 (s (br), 2H, H_{a-d} of C_5H_5R); 3.49 (s, 2H, CH_2Cl), 2.85 (s (br), 1H, H_{endo}); 2.52 (c, 4H, CH_2 of dppe).

4.4. Preparation of [IndMo(η^4-C_5H_6){$P(OMe)_3$}$_2$]BF_4 (5)

Addition of $NaBH_4$ (14.5 mg, 0.38 mmol) to a solution of [IndCpMo{$P(OMe)_3$}$_2$]$(BF_4)_2$ (**4**) (0.24 g, 0.34 mmol) in acetonitrile caused an immediate change of colour from

bright orange to dark orange. The solution was filtered and taken to dryness. Further recrystallization from NCMe/Et_2O gave light brown crystals (0.19 g, 92%). Anal. Calc. for $C_{20}H_{31}BF_4O_6P_2Mo$ (612.15): C, 39.24; H, 5.10. Found: C, 39.06; H, 4.93%. Selected IR (KBr, cm^{-1}): 3055 (m), 2840 (m), 2764 (w), 1483 (m), 1435 (s), 1055 (vs), 754 (s), 698 (s). ^1H NMR (CD_3CN, 300 MHz, −30 °C, δ ppm): 7.53–7.48 (m, 2H, H_{5-8}); 7.41 (d, 2H, $H_{1,2}$ of C_5H_6); 7.36–7.33 (m, 2H, H_{5-8}); 5.62 (m, 2H, $H_{1/3}$); 5.55 (t, 1H, H_2); 4.91 (d, 2H, $H_{3,4}$ of C_5H_6); 4.56 (m, 1H, H_{exo}); 3.68 (t, 18H, $P(OMe)_3$); 2.87 (m, 1H, H_{endo}).

Metathetical change of $[IndMo(\eta^4\text{-}C_5H_6)\{P(OMe)_3\}_2]^+$ was done by adding a saturated solution of LiCl to the dication precursor $[IndCpMo\{P(OMe)_3\}_2](BF_4)_2$ (**4**) in Me_2CO, which caused the immediate precipitation of the yellow complex $[IndCpMo\{P(OMe)_3\}_2]Cl_2$. This was washed with the same solvent and a saturated aqueous solution of KPF_6 was added to afford an orange precipitate, $[IndCpMo\{P(OMe)_3\}_2](PF_6)_2$ (**4a**), which was recrystallized from Me_2CO/Et_2O.

4.5. Preparation of [IndCpMoH{P(OMe)$_3$}]PF$_6$ (6)

Addition of $NaBH_4$ (14.5 mg, 0.38 mmol) to a solution of $[IndCpMo\{P(OMe)_3\}_2](PF_6)_2$ (0.28 g, 0.30 mmol) in Me_2CO caused an immediate change of colour from orange to brown and finally yellow after 2 h of reaction. The solution was filtered and taken to dryness. The residue was extracted with CH_2Cl_2 and washed several times with diethyl ether and hexane. Purification by recrystallization from dichloromethane/diethyl ether was possible, affording yellow crystals (0.15 g, 91%). Anal. Calc. for $C_{17}H_{22}O_3P_2F_6Mo$ (546.23): C, 37.88; H, 4.06. Found: C, 38.02, H; 3.92%. Selected IR (KBr, cm^{-1}): 3130 (m), 2949 (m), 2846 (w), 1897 (w), 1450 (m), 1262 (w), 1181 (m), 1029 (vs), 839 (vs), 795 (m), 760 (m), 557 (s). ^1H NMR (CD_2Cl_2, 300.13 MHz, r.t., δ ppm): 7.82–7.68 (m, 2H, H_{5-8}), 7.46–7.34 (m, 2H, H_{5-8}), 5.56 (t, 1H, $H_{1/3}$), 5.49 (t, 1H, $H_{1/3}$), 5.49 (m, 1H, H_2), 4.89 (d, 5H, Cp), 3.62 (d, 9H, $P(OMe)_3$), −7.42 (d, 1H, Mo–H).

4.6. X-ray crystallography

The structures were determined at 100 K using graphite monochromatized radiation. Data were collected on an Apex2 diffractometer [26]. Crystal data and experimental parameters are presented in Table 3. The data were corrected for Lorentz-polarization effects and for absorption [27]. The structures were solved by direct methods using SIR97 [28] and refined by least-squares (on F) using programs from the KRYSTAL package [29]. Hydrogen atoms were kept fixed in calculated positions with C–H = 0.95 Å and with isotropic displacement factors 20% larger than U_{eq} for the atoms to which they were bonded for the organic ligands. The hydrogen atom bonded to Mo was located from a difference synthesis and refined isotropically. Complex **5** diffracted very poorly and yielded so few significant reflections that only isotropic refinement

Table 3
Crystal data and structure refinement for compounds **5** and **6**

	5	**6**
Molecular formula	$[IndMo(\eta^4\text{-}C_5H_6)\{P(OMe)_3\}_2]PF_6$	$[IndCpMoH\{P(OMe)_3\}]PF_6$
Empirical formula	$C_{20}H_{31}F_6MoO_6P_3$	$C_{17}H_{22}F_6MoO_3P_2$
Formula weight (g mol^{-1})	670.30	546.26
Temperature (K)	100	100
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/n$
a (Å)	11.216(7)	11.8537(2)
b (Å)	18.01(1)	11.4218(2)
c (Å)	24.86(2)	15.6992(3)
β (°)	90.0	110.195(1)
V (Å^3)	5023(6)	1994.85(6)
Z	8	4
D_{calc} (Mg mm^{-1})	1.773	1.819
Absorption coefficient (mm^{-1})	0.794	0.888
F (000)	2720.0	1096.0
Radiation λ (Mo Kα) (Å)	0.71073	0.71073
θ Range	2.26–25.23	1.87–30.83
Reflections collected	162577	47170
Reflections independent	5093	6545
R_{int}	0.43	0.058
Reflections observed [$I > 3\sigma I$]	1431	4853
Final R indices[a] [$I > 3\sigma I$]	$R_1 = 0.098$, $wR_1 = 0.115$	$R_1 = 0.025$, $wR_1 = 0.032$
Refinable parameters	145	266
Goodness-of-fit	1.112	0.952
Residual electron density (e Å^{-3})	−3.9(2) to 2.9(2)2.5(2), −1.6(2)	−0.63(8) to 0.73(8)

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_1 = (\sum||F_o| - |F_c||)^2/\sum w|F_o^2|^{1/2}$, $w = 1/\{((\sum F_o^2) + B + (1 + A)F_o^2)^{1/2} - |F_o|\}^2$ with $A = 0.10$, $B = 10$. for **5** and 0.03 and 0.05 for **6**.

was feasible. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [30].

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Appendix A. Supplementary data

CCDC 610134, 610135 contains the supplementary crystallographic data for **5** and **6**. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.015.

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