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Synthesis and reactivity of mixed-ring indenyl complexes of molybdenocene

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Abstract

The complex $[IndCpMo(NCMe)_2][BF_4]_2$ provides a suitable entry to the synthesis of $IndCpMoBr_2$ and $IndCpMoMe_2$. The latter, also available from $IndCpMoX_2$ (X = Cl, Br) and MeMgCl, reacts with HCl to give IndCpMoCl(Me) which, in turn reacts with NaSPh to yield IndCpMo(SPh)(Me). Cyclic voltammetry shows that these three alkyl complexes undergo a 1e reversible oxidation to 17 e Mo^V cations. IndCpMoCl(Me) is oxidized by $[Cp_2Fe]BF_4$ to afford $[IndCpMoCl(Me)]BF_4$ in 95% yield. Reaction of $[IndCpMo(NCMe)_2][BF_4]_2$ with $KBPz_4$ in CH_2Cl_2/NMF leads to $[IndCpMo(\kappa^2\text{-}BPz_4)]BF_4$. Taken together with previous reports these results show that the indenyl ring slows down substitutional chemistry at the $Cp'_2Mo(IV)$ fragment (Cp′ = Cp, Ind) by steric reasons, overshadowing any acceleration due to a possible indenyl effect.

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

1. Introduction

Molybdenocene derivatives in the oxidation state (IV) have the general formulae Cp_2MoXY, $[Cp_2MoXL]^+$ and $[Cp_2MoL_2]^{2+}$, in which X and Y represent σ-bonded one electron ligands (e.g., alkyls, hydrides, thiolates) and L represents two electron donor ligands (olefins, amines, phosphines, nitriles, CO, CNR, etc.) [1–3]. In terms of synthesis, this very well established chemistry derives from the dihydride Cp_2MoH_2 and the corresponding dihalides Cp_2MoX_2 that are readily prepared from it. Halide substitution then yields the variety of products mentioned above.

In contrast, our previously devised method of preparing the mixed-ring IndCpMo(IV) complexes led us directly to $[IndCp'Mo(CO)_2]^{2+}$ and $(\eta^3\text{-Ind})Cp'Mo(CO)_2$ complexes (Cp′ = Cp, Ind) [4a,4b]. The very interesting chemistry of these species was studied in terms of their redox-induced indenyl-slippage processes leaving behind the study of many other types of derivatives and reactions of the IndCpMo fragment. Indenyl complexes usually possess a higher reactivity than their Cp analogues, due either to their higher ground state energy or to facile haptotropic rearrangements (the indenyl effect) [5,6]. It is, therefore, expected that IndCpMo derivatives might exhibit enhanced reactivity compared with their parent metallocenes, namely in what concerns insertion chemistry or associatively driven reactions. In order to be able to draw conclusions on this issue, we set out to explore synthetic routes to the relevant starting complexes from the dication $[IndCpMo(CO)_2]^{2+}$.

Accordingly, we now report on the reactivity of $[IndCpMo(CO)_2]^{2+}$ and on improved routes to some fundamental mixed ring complexes like $IndCpMoX_2$, IndCpMoX(SR) and IndCpMoCl(Me) derivatives. The

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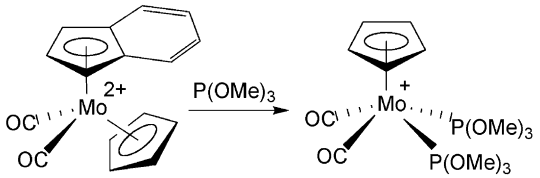
data gathered on these studies is compared to that of their $Cp_2Mo(IV)$ and $Ind_2Mo(IV)$ analogues in order to ascertain the influence of the indenyl ligand on the chemistry of molybdenocenes.

2. Results

2.1. Synthetic studies

Reaction of $[IndCpMo(CO)_2]^{2+}$ with excess $P(OMe)_3$, under reflux and irradiation, gives the analytically pure complex $[CpMo\{P(OMe)_3\}_2(CO)_2]BF_4$ (**1**), with a Cp signal at δ 5.80 ppm in the ^1H NMR spectrum and two characteristic CO stretching vibrations in the IR, at 1995 and 1915 cm^{-1}, Eq. (1).



(1)

The lability of the CO ligands in $[IndCpMo(CO)_2]^{2+}$ is expected on the basis of the values for their CO stretching vibrations (2129 and 2089 cm^{-1}, Ref. [4b]) indicating very low π-backdonation. It is, therefore, surprising that CO substitution from $[IndCpMo(CO)_2]^{2+}$ by Cl^- or Br^- is not a straightforward process and is sensitive to the solvents and salts used. This problem is also shared by the chemistry of $[Ind_2Mo(CO)_2]^{2+}$. In fact, Ind_2MoCl_2 could be made easily by this process (using LiCl in CH_2Cl_2) whereas Ind_2MoBr_2 was obtained from LiBr in acetone but not in CH_2Cl_2 [7]. Even the reported preparation of $IndCpMoCl_2$ (**2**) from $[IndCpMoCl(CO)]BF_4$ in the presence of LiCl in acetone can yield some surprises if the starting materials are not freshly distilled or if the irradiation period is longer than needed. An IR inspection in the CO stretching region determines the exact period of time required [4b]. Following this careful method, we were now able to prepare $IndCpMoI_2$ (**3**) by refluxing and irradiating $[IndCpMoI(CO)]BF_4$ [4a,4b] in the presence of $(NBu_4)I$. However, the dibromide $IndCpMoBr_2$ (**4**) resisted synthesis by this method being finally prepared in 80% yield by reaction of $[IndCpMo(NCMe)_2]^{2+}$ with 2 equivalents of $(NBu_4)Br$ in acetone, Eq. (2).

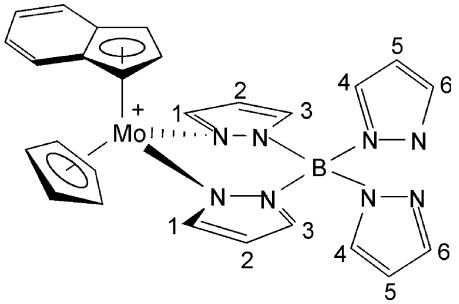
$$[IndCpMo(NCMe)_2][BF_4]_2 \xrightarrow{Bu_4NBr} IndCpMoBr_2\ (\mathbf{4}) \quad (2)$$

Alternatively, we also prepared **3** by reaction of $IndCpMo(SPh)_2$ (prepared from **2** [4b]) with excess MeI, a process already known in $Cp_2Mo(IV)$ chemistry [2].

The dihalide complexes **2**–**4** are stable to air oxidation during several weeks and are insoluble in chlorinated solvents as well as in ether or hexane. They are also insoluble in water but are hydrolysed slowly. In an attempt to prepare **4** by a totally different methodology, the reaction of $IndMoBr_3$ with Cp^- transfer agents was devised as a viable alternative (Scheme 1). The readily available $IndMo(\eta^3\text{-}C_3H_5)(CO)_2$ was protonated with $HBF_4 \cdot Et_2O$ and then treated with 1 equivalent of $(NBu_4)Br_3$ to give the green complex $IndMoBr_3(CO)_2$ (**5**) in good yield.

The IR spectrum shows two strong $\nu(C\equiv O)$ absorptions at 2101 and 2072 cm^{-1}. These values are comparable with those for the chloro tungsten analogue $IndWCl_3(CO)_2$ (2065 and 2002 cm^{-1}) [8a]. The ^1H NMR spectrum in $(CD_3)_2CO$ is compatible with the η^5-coordination mode of the indenyl ligand and the spectrum presents one multiplet in the aromatic region at δ 7.64–7.42 (H^{5-8}), a doublet at δ 6.25 ($H^{1/3}$) and a triplet at δ 5.82 ppm for H^2. Decarbonylation of **5** in solution takes place after a short period of time as is the case with $IndMCl_3(CO)_2$ (M = Mo, W), [8]. But, in contrast to the latter, the product obtained could not be positively identified as the desired $IndMoBr_3$ and was not further characterized. This shortcoming prevented the completion of Scheme 1.

Reaction of $[IndCpMo(NCMe)_2]^{2+}$ with $KBPz_4$ led to $[IndCpMo(\kappa^2\text{-}BPz_4)]BF_4$ (**6**) isolated in good yield. The indenyl ligand in **6** presents a typical η^5 chemical shift pattern, with a doublet for $H^{1/3}$ at δ 6.69 ppm and a triplet for H^2 at δ 6.40 ppm, unequivocally assigned and distinguished from the peaks of the BPz_4^- ligand by irradiation experiments. The triplets at δ 6.46 and 6.26 ppm are attributed to H_5 and H_2 of BPz_4^-, respectively, because of their multiplicity and integrated area. The triplet at δ 6.46 ppm (H_5) is transformed into a doublet by irradiation of the doublets at δ 7.18 or δ 7.01 ppm, which are assigned to H_4 and H_6. Irradiation of the triplet at δ 6.26 ppm (H_2) affects the doublets at δ 7.63 (H_3) and 6.53 (H_1) ppm (see also compound **7** in Scheme 2 for numbering).



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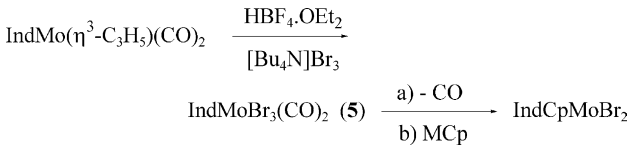
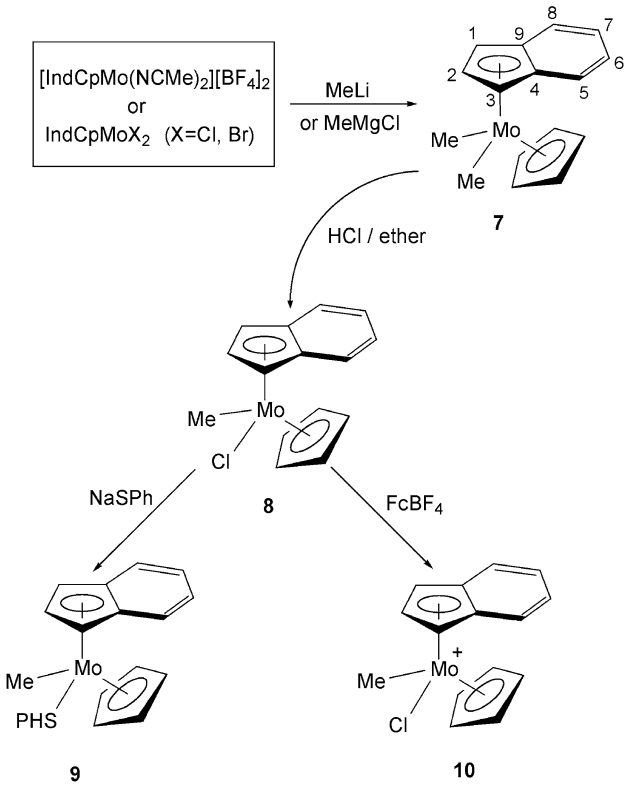


Scheme 1.



Scheme 2.

Reaction of **2** or **4** with MeMgCl or MeLi affords moderate yields of the dimethyl complex IndCpMoMe$_2$ (**7**). Somewhat surprisingly, **7** can also be obtained from $[IndCpMo(NCMe)_2]^{2+}$ upon reaction with MeMgCl in Et_2O/THF. **7** is a deep blue complex in contrast to the orange Cp_2MoMe_2 [9]. Its ^{1}H NMR spectrum presents the resonance for the Cp protons (δ 3.85 ppm) as well as for the Ind protons (δ 4.76 ppm for the H^2 triplet, 4.09 for the $H^{1/3}$ doublet). The CH_3 resonances appear as a singlet at δ 0.33 ppm in C_6D_6. These values are significantly shifted relative to those of Cp_2MoMe_2 (δ 4.20 ppm, Cp; 0.19 ppm, CH_3). The EI mass spectrum presents the molecular ion at *m*/*z* 306 as well as two peaks corresponding to stepwise loss of one and two CH_3 groups.

Reaction of **7** with HCl in Et_2O affords a quantitative yield of blue IndCpMoCl(Me) (**8**). Being chiral-at-metal **8** presents a complex set of resonances for the indenyl protons due to the fact that they are now diastereoptopic. The Cp and CH_3 resonances at δ 4.72 ppm and δ 0.53 are slightly deshielded relative to those in **7**, as expected.

Reaction of **8** with NaSPh gives IndCpMo(SPh)(Me) (**9**) in low yield. Again, this asymmetric compound presents a complex set of indenyl resonances in its ^{1}H NMR spectrum (three broad singlets at δ 5.55, 5.25 and 4.44 ppm). In comparison to the ^{1}H NMR spectrum of **7**, the Cp resonance of **8** is slightly shielded whereas the CH_3 resonance is more deshielded.

Reaction of **8** with $[Cp_2Fe]BF_4$, at room temperature in NCMe gives the green paramagnetic cation [IndCpMoCl(Me)]BF_4 (**10**) in 95% isolated yield. This reaction is entirely similar to that reported for $Cp_2MoCl(Me)$ and attests for the chemical stability of the IndCpMo(V) fragment and its 17 e complexes [10]. These reactions are summarized in Scheme 2.

2.2. Electrochemical studies

The electrochemical data of complexes IndCpMoMe$_2$ (**7**), IndCpMoX(Me) [X = Cl (**8**), SPh (**9**)] and the cationic [IndCpMo(κ^2-BPz_4)]BF_4 (**6**) were obtained in dichloromethane (containing 0.1 M tetrabutylammonium hexafluorophosphate) and are summarized in Table 1.

The cyclic voltammograms (CV) of complexes **7**, **8** and **9** all present one reversible redox couple assigned to the $Mo^{IV/V}$ oxidation (within the solvent limits, ca. −1.5 to +1.6 V). The peak separations, ΔE_p for each redox couple ranged from 60 to 80 mV in CH_2Cl_2, which at the present experimental conditions are plausibly suggestive of one-electron reversible processes. Replacement of one Cl (in **8**) by one CH_3 (in **7**) makes oxidation of IndCpMo(IV) to IndCpMo(V) easier by 350 mV: the half wave potentials ($E_{1/2}$) of **7** and **8** are −0.22 and +0.13 V, respectively. For the congeners Cp_2MoMe_2 and $Cp_2MoCl(Me)$ the similar values of −0.27 and +0.12 V ($\Delta E_{1/2}$ = 390 mV) were found in the same solvent [10]. The chloro-alkyl derivative **8** reacts instantaneously in the electrochemical cell when the solvent is NCMe (blue to violet solution), as observed for $Cp_2MoBr(Me)$ [10].

The relative shifts of the peak potentials reflect the variations in the overall donor/acceptor abilities of the ligands and ease of oxidation decreases in the order IndCpMoMe$_2$ > IndCpMoCl(Me) > IndCpMo(SPh)(Me).

Table 1
Electrochemical data in CH_2Cl_2 at room temperature[a]

Compound	E_{pa}[b]	E_{pc}[c]	$E_{1/2}$
IndCpMoMe$_2$ (**7**)	−0.19	−0.26	−0.22
IndCpMoCl(Me) (**8**)	+0.17	+0.09	+0.13
IndCpMo(SPh)(Me) (**9**)	+0.20	+0.14	+0.17
[IndCpMo(κ^2-Bpz_4)]BF_4 (**6**)	−0.69	−0.87	−0.78
	−1.01	−1.16	−1.09
[IndCpMo(H_2biim)][BF_4]$_2$[d]	−0.90	−0.99	−0.94
	−1.16	−1.26	−1.21

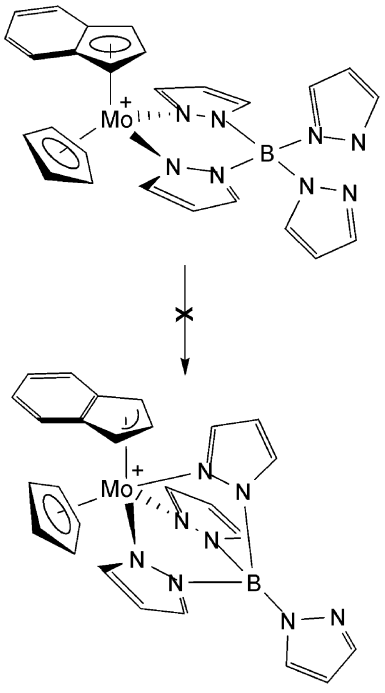
[a] All the voltammograms were measured in ca. 1.0 mM solutions. Potentials in V vs. SCE; scan rate is 200 mV s^{-1} and $E_{1/2}$ values are the average of the anodic and cathodic peak potentials.
[b] E_{pa} anodic sweep (peak potentials, Volts).
[c] E_{pc} cathodic sweep (peak potentials, Volts).
[d] [Ref. [6a]] the voltammogram was measured in NCMe.

In contrast to the previous complexes, the cationic complex **6** is electroactive on the cathodic part of the CV and electrochemically silent on the anodic part of the same. This means that there is no $Mo^{IV/V}$ oxidation. Instead, it undergoes two consecutive reductions that are assigned to $Mo^{IV/III}$ and $Mo^{III/II}$, a process that can be interpreted assuming indenyl η^5–η^3 slippage (η^5-Ind)CpMo(IV) → (η-Ind)CpMo(III) and (η-Ind)-CpMo(III) → (η^3-Ind)CpMo(II). Many similar processes have been observed and reported by us and studied in depth [6]. However, this is the first involving the reduction of a monocation to a monoanion [(η^3-IndCpMo(κ^3-BPz_4)]$^-$ as the final product. We have not attempted to isolate this product chemically but its identity can be safely assumed even on the basis of the similarities of the redox potentials to those previously reported, namely with N-heterocyclic bidentate ligands such as [IndCpMo(Bipy)][BF_4]$_2$ (E_{pa} = −0.59 V), [IndCpMo(^{t}Bu$_2$Bipy)][BF_4]$_2$ (E_{pa} = −0.60 V), and [IndCpMo(H_2biim)][BF_4]$_2$ (E_{pa} = −0.90 V) (H_2biim = bis-imidazole) [6a]. These observations leave the neutral Mo^{IV} biscyanide complex IndCpMo(CN)$_2$ as the only one in this system where both oxidative $Mo^{IV/V}$ and reductive $Mo^{IV/III/II}$ processes are observed [6a,6b]. As a matter of fact, charge effects seem to prevent cationic complexes [IndCpMoXL]$^+$ and [IndCpMoL$_2$]$^{2+}$ from undergoing oxidation to Mo(V). On the other hand, among the neutral Cp'_2MoX_2 complexes (Cp′ = Cp, Ind) the biscyanides are, so far, the only capable of undergoing reversible reductions, certainly due to the strong π-acidity of the CN-ligand. Indeed, there is not much electronic difference, in terms of orbitals, between the species in the two series of redox cascades [IndCpMo(CO)$_2$]$^{2+/+/0}$ and [IndCpMo(CN)$_2$]$^{0/-1/-2}$, and the electrochemical and ESR characterization of both processes reveals strong similarities [6b].

3. Discussion

Presently [IndCpMo(CO)$_2$]$^{2+}$ is the only entry for the synthesis of derivatives of the IndCpMo(IV) fragment. However, direct CO substitution to give IndCpMX_2, [IndCpMoXL]$^+$ or [IndCpMoL$_2$]$^{2+}$ complexes is not a straightforward process due to the high reactivity of the bis-carbonyl dications. In fact, until now the synthetic use of [IndCpMo(CO)$_2$][BF_4]$_2$ has been limited to the preparation of the nitrile precursors [IndCpMo(NCMe)(CO)][BF_4]$_2$ and [IndCpMo(NCMe)$_2$][BF_4]$_2$ and related isonitrile complexes, both the result of slow CO substitutions [4b,6a]. The first reactivity problem posed by [IndCpMo(CO)$_2$]$^{2+}$ is the unusually high electrophilicity of its rings. Accordingly, $P(OMe)_3$ adds to the indenyl ligand in [IndCpMo(CO)$_2$]$^{2+}$ to give [CpMo{$P(OMe)_3$}$_2$(CO)$_2$]BF_4 (**1**) (Eq. (1)). We had previously reported that a similar reaction with dppe yields [CpMo(CO)$_2$(dppe)]$^+$ [6a] in a simple parallel to the H^- and PMe_3 addition to one Cp ring in the case of the corresponding [Cp_2Mo(CO)$_2$]$^{2+}$ complexes (L = PMe_3, 1/2 dppe, CO) [11]. It is, nevertheless surprising that even the weak nucleophile $P(OMe)_3$ affords similar results. It is also interesting to note that the indenyl ligand is more prone to undergo addition of phospine nucleophiles than the Cp ring.

In spite of the expected lability of the CO ligands in [IndCpMo(CO)$_2$]$^{2+}$ we do not have any reasonable explanation to account for the erratic reactivity of this complex with weak nucleophiles like the halides. However, the possible formation of ring-slipped intermediates (or transition states) that might decompose in unexpected ways seemed attractive in view of the established observation that such species are induced by weak, specially π-donor, nucleophiles [12]. In order to test this hypothesis [IndCpMo(NCMe)$_2$]$^{2+}$ was reacted with $KBPz_4$, a multidentate anion that might stabilize a putative ring-slipped complex like [(η^3-Ind)CpMo(κ^3-BPz_4)]$^+$. The formation of **6** indicates that ligand induced ring-slippage in the [IndCpMoL$_2$]$^+$ complexes to afford [(η^3-Ind)CpMoL$_3$]$^+$ adducts (Eq. (3)) is not a thermodynamically favoured process leading to isolable species, in contrast to the ready redox induced ring-slippage undergone by **6** itself as seen in the CV studies, and by several dicationic complexes [IndCpMoL$_2$]$^{2+}$ to give (η^3-Ind)CpMoL$_2$ [6b].



(3)

The fact that indenyl slipped species are not isolated does not mean that indenyl slippage is absent in the nucleophilic substitution reactions of IndCpMo(IV) complexes. This can only be ascertained by kinetic studies

that compare reaction rates of substitution reactions in similar IndCpMo(IV), $Cp_2Mo(IV)$ and $Ind_2Mo(IV)$ species. However, some conclusions can be already drawn out of the existing data. The results in Scheme 2 on the straightforward halide substitution by CH_3^- and PhS^- nucleophiles on the $IndCpMoX_2$ complexes, parallel those established a long time ago for the congener Cp_2MoX_2 complexes. However, they strongly contrast to the total lack of reactivity of Ind_2MoX_2 towards nucleophiles. In fact Ind_2MoMe_2 cannot be made from the parent dichloride and CH_3MgCl but can be prepared from Ind_2MoCl_2 and the Lewis acidic, Cl^- abstractor, $AlMe_3$ [7]. Also, Ind_2MoX_2 does not react with PhS^- and $[HB(CHMeEt)_3]^-$. All of these reactions readily take place with Cp_2MoX_2 and $IndCpMoX_2$ complexes. This contrast suggests that steric congestion around the metal in the Ind_2MoX_2 complexes prevents the nucleophile from reaching the metal, thereby blocking the reaction. Space around the metal is more readily available in the Cp containing complexes, enabling the reaction.

Strange as it may seem for a family of complexes studied over the last four decades, there is, to the best of our knowledge, no mechanistic study on the nucleophilic substitution reactions of Cp_2MoX_2 complexes. Certainly it is known to all those working with such compounds that halide abstracting reagents and polar solvents strongly favour halide substitution, implying that a dissociative pathway is favoured over an associative one. This is not unexpected since the Cp_2MoX_2 complexes are 18 e species and the Cp ring is not very prone to undergo the ring-slippage rearrangements expected for an associative mechanism. However, the situation might be different for the indenyl containing analogues since the indenyl ring is prone to elicit the required haptotropic shifts. In a detailed study of an associative reaction taking place at the $Cp_2Mo(IV)$ fragment (the insertion of acetylenes into the Mo–H bond of Cp_2MoH_2) Nakamura and Otsuka, almost 30 years ago, were led to conclude that a rearrangement of the wedge like structure of the molybdenocene to an excited structure with parallel rings plays a central role in explaining some of the results [13]. They also noted clear differences brought about by the simple introduction of one CH_3 substituent to the Cp ring. Such a rearrangement will have obvious energetic changes upon replacement of Cp by Ind. It follows that for $Ind_2Mo(IV)$ complexes any possible acceleration caused by the indenyl effect is overshadowed by the steric bulk of the indenyl ligand which blocks the access of nucleophiles to the metal [7].

On the other hand the introduction of indenyl ligands in the molybdenocene structure does not disturb the electronic properties related to redox behaviour in any dramatic fashion. The changes recorded so far present a smooth picture with regard to the Mo(IV)/Mo(V) redox process. Naturally, the reductive behaviour is significantly changed upon indenyl introduction due to the possibility of accomodating extra electrons provided by the η^5–η^3 shift of the indenyl ligand. Again going from the IndCpMo(IV) to the $Ind_2Mo(IV)$ fragment derivatives does not introduce any substantial difference in the reductive or ring-slippage behaviour.

4. Conclusions

The synthesis of neutral mixed-ring molybdenocenes IndCpMoXY from $[IndCpMo(CO)_2]^{2+}$ is limited to the dihalides and even so unexpectedly unreliable. In contrast, the dicationic complex $[IndCpMo(NCMe)_2][BF_4]_2$ provides feasible routes to $IndCpMoX_2$ by nucleophilic substitution of the NCMe ligand, free of competition with nucleophilic attack to the indenyl ring or the CO ligand. The chemistry of the $IndCpMoX_2$ and Cp_2MoX_2 complexes (X = CH_3, Cl, SPh) is very similar but bears some significant differences relative to that of their Ind_2MoX_2 congeners. These comparisons suggest that: (i) the existence of accessible free space around the metal is a decisive factor in the reaction of Cp'_2MoX_2 metallocenes towards nucleophiles; (ii) contrary to the initial expectations, indenyl-slippage does not apparently play an overwhelming role in the activation of the substitutional chemistry of molybdenocenes. The lack of ring-slippage in the complex $[IndCpMo(\kappa^2\text{-}BPz_4)]^+$ with dangling ligands well suited to coordinate the metal and stabilize a ring-slipped complex, gives further support to this last conclusion.

5. Experimental

5.1. Materials and methods

All experiments were carried out under N_2 atmosphere by Schlenk techniques. Solvents were dried by standard procedures, distilled under nitrogen or argon and kept over 4 Å molecular sieves.

Microanalyses were performed at the ITQB (C. Almeida). Infrared spectra were recorded on a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets and/or in solution. ^1H NMR spectra were obtained with a Bruker CXP 300 spectrometer.

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. 0.1 M tetrabutylammonium hexafluorophosphate 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.

$KBPz_4$ [14], $[IndCpMo(CO)_2][BF_4]_2$ [4a], $[IndCpMo(NCMe)_2][BF_4]_2$ [4a], $IndCpMoCl_2$ [4a] and [IndCpMoI(CO)]BF_4 [4a,4b] were prepared as described previously.

5.2. Preparation of $[CpMo\{P(OMe)_3\}_2(CO)_2]BF_4$ (1)

A suspension of $[IndCpMo(CO)_2][BF_4]_2$ (0.30 g, 0.59 mmol) in CH_2Cl_2 was treated with excess $P(OMe)_3$ (4 ml), refluxed and irradiated with a 60 W tungsten bulb for 2 h. The resulting yellow solution was evaporated under vacuum until the only remaining liquid was $P(OMe)_3$. An oil separated upon addition of Et_2O and an orange powder was obtained by washing it with cold Et_2O/EtOH (10/1). Further recrystallization from EtOH/Et_2O afforded the pure complex **1**, in 80% yield. Anal. Found: C, 28.29; H, 3.94. Calc. for $C_{13}H_{23}BF_4O_8P_2Mo$: C, 28.29, H, 4.20%. Selected IR (KBr, cm^{-1}): *v* 3050 (m); 2957 (w); 1995 (vs, CO), 1915 (vs, CO); 1483 (m); 1084 (vs, B-F); 795 (s); 725 (m); 605 (m). ^1H NMR [$(CD_3)CO$, 300 MHz, r.t., δ ppm]: 5.80 (s (br), 5H, Cp); 3.88 (t, 18H, $P(OMe)_3$).

5.3. Preparation of $IndCpMoI_2$ (3)

Method a: A solution of [IndCpMoI(CO)]BF_4 (0.34 g, 0.66 mmol) in CH_2Cl_2 was refluxed and irradiated with a 60 W tungsten bulb for 36 h, in the presence of $(NBu_4)I$ (0.50 g, 1.36 mmol). The supernatant solution was filtered and the dark brown microcrystalline precipitate washed with Me_2CO and Et_2O. Yield, 70%.

Method b: A solution of $IndCpMo(SPh)_2$ (0.33 g, 0.66 mmol) in CH_2Cl_2 was allowed to react with excess CH_3I (0.08 ml, 1.36 mmol) for 4 h at room temperature. The supernatant solution was filtered and the dark brown precipitate washed with Me_2CO and Et_2O. Yield, 75%. Anal. Found: C, 31.23; H, 2.49. Calc. for $C_{14}H_{12}I_2Mo$: C, 31.73, H, 2.28%. Selected IR (KBr, cm^{-1}): *v* 3098 (m), 1422 (m), 1211 (w), 829 (s), 750 (s).

5.4. Preparation of $IndCpMoBr_2$ (4)

A suspension of $[IndCpMo(NCMe)_2][BF_4]_2$ (0.35 g, 0.66 mmol) in Me_2CO was allowed to react with $(NBu_4)Br$ (0.44 g, 1.36 mmol) for 12 h at room temperature. The supernatant solution was filtered and the violet precipitate washed with Me_2CO and Et_2O. Yield, 80%. Anal. Found: C, 38.78; H, 2.89. Calc. for $C_{14}H_{12}Br_2Mo$: C 38.57, H 2.77%. Selected IR (KBr, cm^{-1}): *v* 3111 (m), 1604 (w), 1537 (w), 1427 (m), 1337 (w), 1014 (w), 773 (s).

5.5. Preparation of $IndMoBr_3(CO)_2$ (5)

A solution of $IndMo(\eta^3\text{-}C_3H_5)(CO)_2$ (0.34 g, 1.09 mmol) in CH_2Cl_2 was treated with HBF_4. Et_2O (1 equivalent). After 10 min, $(NBu_4)Br_3$ (0.53 g, 1.09 mmol) was added and the reaction was continued for 1/2 h at room temperature. The supernatant solution was filtered and the green precipitate was washed with CH_2Cl_2 (3 × 30 ml) to yield the pure compound in 70% yield. Anal. Found: C, 25.99; H, 1.31. Calc. for $C_{11}H_7O_2Br_3Mo$: C, 26.07, H, 1.39%. Selected IR (KBr, cm^{-1}): *v* 3100 (w), 3050 (m), 2101 (vs, CO), 2072 (vs, CO), 1445 (w), 1069 (m), 756 (w). ^1H NMR [$(CD_3)CO$, 300 MHz, r.t., δ ppm]: 7.64 (m, 2H, H^{5-8}); 7.42 (m, 2H, H^{5-8}); 6.25 (d, 2H, $H^{1/3}$); 5.82 (t, 1H, H H^2).

5.6. Preparation of $[IndCpMo(\kappa^2\text{-}Bpz_4)]BF_4$ (6)

A solution of $[IndCpMo(NCMe)_2][BF_4]_2$ (0.31 g, 0.58 mmol) in CH_2Cl_2/NMF (20/1) was treated with $KBPz_4$ (0.18 g, 0.58 mmol) at room temperature. After stirring for 7 h the violet solution was filtered and the CH_2Cl_2 evaporated under vacuum. Upon addition of Et_2O/EtOH (30/1) and washing with Et_2O, a violet powder was obtained. This was recrystallized from EtOH/Et_2O in 85% yield. Anal. Found: C, 48.88; H, 3.33; N, 17.30. Calc. for $C_{26}H_{24}B_2F_4N_8Mo$: C, 48.64, H, 3.77, N, 17.45%. Selected IR (KBr, cm^{-1}): *v* 3109 (m), 1508 (m), 1437 (m), 1397 (s), 1294 (s), 1221 (m), 1084 (vs, B-F), 833 (s), 764 (s). ^1H NMR [$(CD_3)_2CO$, 300 MHz, r.t., δ ppm]: 7.79 (d, 2H, H_3 of BPz_4, [^3J = 1.5 Hz]); 7.63 (d, 1H, H_1 of BPz_4, [^3J = 1.5 Hz]); 7.55–7.51 (m, 2H, H^{5-8}); 7.18 (d, 2H, H_4 of BPz_4, [^3J = 3.0 Hz]); 7.15–7.12 (m, 2H, H^{5-8}); 7.01 (d, 2H, H_6 of BPz_4, [^3J = 2.1 Hz]); 6.69 (d, 2H, $H^{1/3}$); 6.53 (d, 1H, H_1 of BPz_4, [^3J = 2.1 Hz]); 6.46 (t, 2H, H_5 of BPz_4, [^3J = 2.4 Hz]); 6.40 (t, 1H, H^2); 6.26 (t, 2H, H_2 of BPz_4, [^3J = 3.0 Hz]); 5.69 (s, 5H, Cp).

5.7. Preparation of $IndCpMoMe_2$ (7)

Method a: A suspension of $[IndCpMo(NCMe)_2][BF_4]_2$ (0.3 g, 0.56 mmol) in Et_2O was allowed to react with excess of a 3 M solution of MeMgCl in THF (0.45 ml, 1.35 mmol) from −20 °C to room temperature, for 4 h. The reaction mixture was filtered after addition of H_2O (0.3 ml) and the solution taken to dryness under vacuum. The residue was extracted with hexane and the extracts were taken to dryness to afford a blue powder in 40% yield.

Method b: A suspension of $IndCpMoBr_2$ (0.06 g, 0.14 mmol) in Et_2O was allowed to react with excess of a 3 M solution of MeMgCl in THF (0.15 ml), from −20 °C to room temperature, for 1 h. The reaction mixture was filtered after addition of H_2O (0.5 ml) and the solution taken to dryness under vacuum. The residue was extracted with hexane and the extracts were taken to dryness to afford a blue powder in 50% yield.

Method c: A suspension of $IndCpMoCl_2$ (0.24 g, 0.70 mmol) in Et_2O was allowed to react with excess of a 1.6 M solution of MeLi in the same solvent (0.95 ml), from −20 °C to room temperature, for 2 h. The reaction mixture was filtered after addition of H_2O (0.2 ml) and the solution taken to dryness under vacuum. The residue was extracted with hexane and the extracts were taken to dryness to afford a blue powder in 40% yield.

Method d: A suspension of $IndCpMoCl_2$ (0.24 g, 0.70 mmol) in Et_2O was allowed to react with excess of a 3 M solution of MeMgCl in THF (0.56 ml, 1.68 mmol), from −20 °C to room temperature, for 1 h. The reaction mixture was filtered after addition of H_2O (0.1 ml) and the solution taken to dryness under vacuum. The residue was extracted with hexane (or pentane) and the extracts were taken to dryness to afford a blue powder in 40% yield. Anal. Found: C, 62.51; H, 5.68. Calc. for $C_{16}H_{18}Mo$: C, 62.75, H, 5.92%. MS (EI),(*m*/*z*): 306 (M^+); 290 ($M^+ - CH_3$); 276 ($M^+ - 2CH_3$). Selected IR (KBr, cm^{-1}): *v* 3098 (m), 2990 (w), 2895 (w), 1427 (w), 1020 (m), 941 (m), 910 (m), 843 (m), 758 (m), 710 (m). ^1H NMR (C_6D_6, 300 MHz, r.t., δ ppm): 6.89–6.81 (m, 4H, H^{5-8}); 4.76 (t, 1H, H^2); 4.09 (d, 2H, $H^{1/3}$); 3.85 (s, 5H, Cp); 0.33 (s, 6H, CH_3).

5.8. Preparation of IndCpMoCl(Me) (**8**)

A solution of $IndCpMoMe_2$ (0.20 g, 0.66 mmol) in Et_2O was allowed to react with a 1 M solution of HCl in the same solvent (0.66 ml, 0.66 mmol) at room temperature, for 1/2 h. The blue crystalline precipitate, formed in quantitative yield, was washed with Et_2O. Anal. Found: C, 55.15; H, 4.66. Calc. for $C_{15}H_{15}ClMo$: C, 55.15, H, 4.63%. Selected IR (KBr, cm^{-1}): *v* 3115 (m), 2967 (m), 2891 (s), 1449 (w), 1339 (m), 806 (m), 760 (s). ^1H NMR [$(CD_3)_2CO$, 300 MHz, r.t., δ ppm]: 7.44–7.41 (m, 2H, H^{5-8}); 7.26–7.22 (m, 2H, H^{5-8}); 5.47 (t, 1H, H^{1-3}); 5.08 (t, 1H, H^{1-3}); 4.80 (t, 1H, H^{1-3}); 4.72 (s, 5H, Cp); 0.53 (s, 3H, CH_3).

5.9. Preparation of IndCpMo(SPh)(Me) (**9**)

A solution of IndCpMoCl(Me) (0.09 g, 0.27 mmol) in CH_2Cl_2 was allowed to react with $NaSC_6H_5$ (0.04 g, 0.27 mmol) at room temperature, for 15 h. The reaction mixture was filtered and the solution taken to dryness under vacuum. The residue was extracted with Et_2O (3×20 ml) and the extracts were taken to dryness to afford a green powder in 30% yield. Anal. Found: C, 63.22; H, 5.24. Calc. for $C_{21}H_{20}MoS$: C, 63.00, H, 5.03%. Selected IR (KBr, cm^{-1}): *v* 3100 (w), 2965 (w), 1262 (m), 1096 (m), 1022 (m), 926 (m), 901 (m), 824 (s). ^1H NMR ($CDCl_3$, 300 MHz, r.t., δ ppm): 7.53–7.24 (m, 9H, Ph + H^{5-8}); 5.55 (s (br), 1H, H^{1-3}); 5.25 (s (br), 1H, H^{1-3}); 4.68 (s, 5H, Cp); 4.44 (s (br), 1H, H^{1-3}); 0.64 (s, 3H, CH_3).

5.10. Preparation of [IndCpMoCl(Me)]BF_4 (**10**)

A solution of IndCpMoCl(Me) (0.05 g, 0.15 mmol) in NCMe was treated with $[Cp_2Fe]BF_4$ (0.04 g, 0.15 mmol) at room temperature. There was an immediate change from blue to green and the reaction mixture was taken to dryness under vacuum after stirring for 1/2 h. The green powder was washed with Et_2O (3×20 ml). Yield, 95%. Anal. Found: C, 43.88; H, 3.78. Calc. for $C_{15}H_{15}BClF_4Mo$: C, 43.57, H, 3.66%. Selected IR (KBr, cm^{-1}): *v* 3100 (m), 2891 (w), 1537 (w), 1441 (m), 1036 (vs, B-F), 858 (s), 768 (s).

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