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Modified molybdenum and tungsten metallocenes and ring-slippage reactions: new compounds and revisited concepts[†]

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A systematic method for the synthesis of ring-modified metallocenes of Mo and W was developed producing a variety of substituted Cp-, indenyl- and fluorenyl-containing analogues Cp'_2ML_2. Preferred coordination of η^3-Flu in the exocyclic fashion was definitely established on experimental and theoretical grounds. The redox chemistry and electrochemistry of these complexes is coupled with ring-slippage between the extreme coordinations $[Cp(\eta^3\text{-}Cp')ML_2]$ and $[CpCp'ML_2]^{2+}$; ($Cp' = Cp$, Ind). DFT calculations reveal that $\eta^5 \rightarrow \eta^3$ Cp′ ring slippages are exothermic for both Cp and Ind rings. A subtle dependence of ring-slippage on the nature of the ancillary ligands has been explained with the help of DFT calculations. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: metallocenes; molybdenum; tungsten; ring-slippage; cyclopentadienyl complexes; indenyl complexes; fluorenyl complexes; DFT calculations

BACKGROUND AND INTRODUCTION

The dihydrides Cp_2MH_2 (Cp = cyclopentadienyl; M = Mo, W) were among the first reported examples of transition-metal hydrides and carbonyl-free organometallic compounds.[1] These metallocene complexes generated a wide variety of chemistry and proved very important in establishing a number of key reaction steps of organometallic chemistry, some of which are represented in Scheme 1. However, due to their kinetic and thermodynamic stability, which results from their electronic and coordinative saturation, they have found no use in catalytic reactions. In this respect they strongly contrast with their Group 4 congeners. On the other hand, this stability made them useful precursors for thermochemical studies and the first Mo–CH_3 mean bond dissociation energy obtained from $Cp_2Mo(CH_3)_2$ by Calado, Dias and Simões marked the beginning of a long stream of thermochemical data.[5,6]

The widely used replacement of the cyclopentadienyl ligand ($Cp = C_5H_5$) by the isoelectronic but much bulkier and electron-richer pentamethylcyclopentadienyl ($Cp^* = C_5Me_5$) made it very clear that the known reactivity of the Cp-containing complexes could be modified and eventually tuned by the use of 'modified Cp ligands' with different steric and electronic properties. In this respect the indenyl ligand ($Ind = C_9H_7$) provided a most interesting example when Basolo and co-workers revealed that it could accelerate some substitution reactions by a factor up to 10^8 relative to the analogous Cp-containing complexes.[7] This so called 'indenyl effect' suggested to us the possibility of enhancing the reactivity of the molybdenum and tungsten metallocenes in complexes of the type $IndCpMX_2$ and Ind_2MX_2 relative to their parent Cp_2MX_2 derivatives. The spectacular outburst of catalytic chemistry displayed by bis(indenyl)–titanium and –ziranium complexes which originated from the work of Kaminsky and Brintzinger,[8] reinforced our hope of modifying molybdenum and tungsten metallocene reactivity by means of systematic Cp ring replacement. The target molecules were then set as those complexes containing the following symmetric or differentially substituted metallocene-like fragments: Cp'_2M and $CpCp'M$ [$Cp' = Cp$, Cp^*, Ind, Flu(fluorenyl, $C_{13}H_9$)].

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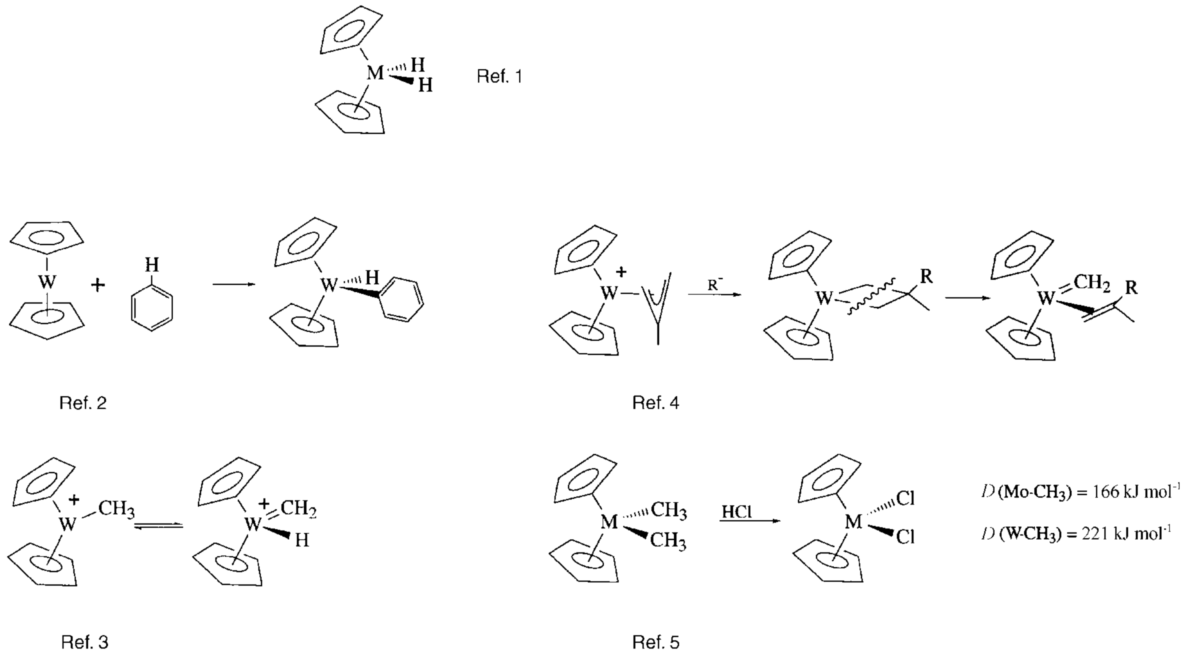


Scheme 1

SYNTHESIS OF Cp′-SUBSTITUTED METALLOCENE ANALOGUES

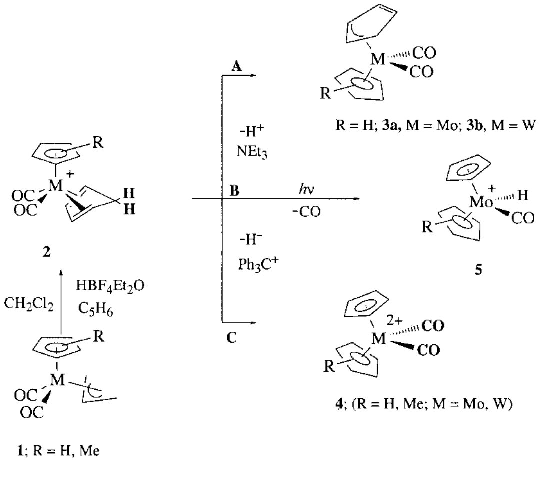
In contrast to the Group 4 metals, where stepwise halide replacement makes it possible to introduce Cp and Cp′ ligands as in Scheme 2, the tetrahalides of molybdenum and tungsten are known to produce the corresponding metallocenes by reaction with Cp′ anions only in the case of the symmetric complex Cp_2WCl_2[9] and related *ansa*-metallocene derivatives.[10]

We therefore developed a totally independent route to the target CpCp′Mo(W) complexes, based on the manipulation of the pentadienes coordinated to the $[Cp'M(CO)_2]^+$ fragment. The general approach is described in Scheme 3 for preparation of Cp_2Mo complexes (R = H) as well as mixed-ring Cp(MeCp)M derivatives.

The allyl complex **1**, which is readily available from $M(CO)_6$ in three high-yield steps, is protonated with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 and the resulting mixture treated with a cyclopentadiene to give **2**. The positive charge of the diene complex, coupled with the gain in resonance energy upon formation of the cyclopentadienyl C_5H_5 (C_5H_4R) ring, allows complex **2** to react with both a base like NEt_3 (H^+ abstraction) or an acid like Ph_3C^+ (H^- abstraction) forming the metallocene complexes **3** and **4**,

$$MCl_4 \xrightarrow{Cp'M'} Cp'MCl_3 \xrightarrow{Cp'M'(\text{or } Cp''M')} Cp'_2MCl_2$$
$$(\text{or } Cp'Cp''MCl_2)$$

Scheme 2

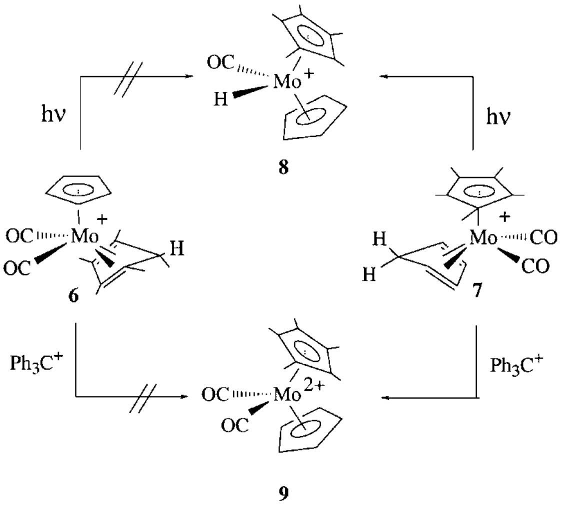


Scheme 3

respectively[11,12] Complex **3b** was already known for M = W[13] but it is easier to prepare by this method which gives virtually quantitative yields. The molybdenum analogue **3a** can also be obtained in high yield but it is temperature-sensitive and decomposes at room temperature with loss of CO to give the known $Cp_2Mo(CO)$. This simple synthesis shows that it is indeed possible to obtain the almost elusive η^3-Cp ligand under very mild conditions and, as judged from its IR ν(CO) stretching frequencies [ν(CO) $\approx$ 1955, 1865 cm^{-1}] is not extraordinarily electron-rich. In fact the starting allyl analogue **1** presents ν(CO) at *ca* 1946 and 1859 cm^{-1}.

Of course, the dicationic complexes **4** present very high ν(CO) stretching frequencies ($\approx$ 2135, 2095 cm^{-1}), suggesting a high degree of activation towards attack from nucleophiles (still unexplored) or substitution reactions. The latter have indeed been shown to yield a variety of products of the types $Cp(RCp)MX_2$, $[Cp(RCp)MXL]^+$ and $[Cp(RCp)ML_2\}^{2+}$ in parallel with the classical chemistry of the parent metallocenes.[14] The formation of the carbonyl hydride **5** is the third pathway for reaction of **2** as shown in Scheme 3. This pathway is dependent on CO dissociation from **2** followed by migration of H to the metal. Further manipulations of **5** produce a variety of Cp_2M and Cp(RCp)M derivatives by known, classical metallocene chemistry methods.[14]

The chemistry in Scheme 3 is an advantageous alternative to the synthesis of mixed-ring Cp(RCp) M(IV) complexes, a few examples of which had been obtained by Cooper from low-temperature reactions of $[Cp_2MXL]^+$ or $Cp(RCp)MX_2$ (X = halide) with RLi(MgX) reagents.[15] The attempts to extend this method to the very important Cp* ligand are depicted in Scheme 4. The mixed-ring dication $[CpCp^*Mo(CO)_2]^{2+}$ (**9**) is best prepared from **7**.[11b]



Scheme 4

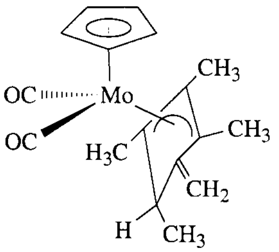
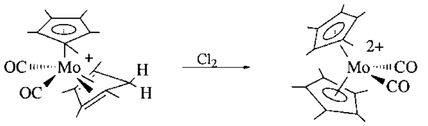


Figure 1 Structure **10**.

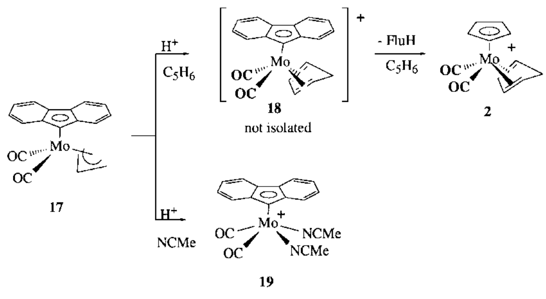
For steric reasons the methylenic H atom of the C_5Me_5H ligand of **6** does not react with Ph_3C^+. Probably for the same reason, deprotonation of **6** with NEt_3 does not produce the expected trihapto complex $Cp^*(\eta^3\text{-}Cp)Mo(CO)_2$ but, instead, the allylic complex $CpMo(\eta^3\text{-}C_4Me_4HCH_2)(CO)_2$ (**10**) which bears an exocyclic methylene group resulting from deprotonation at one CH_3 substituent (Fig. 1). The curious fact that the crystalline sample analysed by X-ray diffraction happened to be enantiomerically pure may be attributed to the preferential crystallization of this particular enantiomeric form.

The steric problems posed by the bulky Ph_3C^+ electrophile are easily overcome, however, by using Cl_2 gas as the electrophile for H^- abstraction. In this way it proved possible to synthesize the symmetrically disubstituted dication $[Cp^*_2Mo(CO)_2]^{2+}$ (**11**) as (Eqn [1]). This reaction is also applicable to the H^- abstractions mentioned in Scheme 3. This synthesis of the Cp^*_2Mo fragment is much simpler than the previously reported one, which dealt with rather more sensitive compounds in a nine-step procedure with very low overall yield.[16]

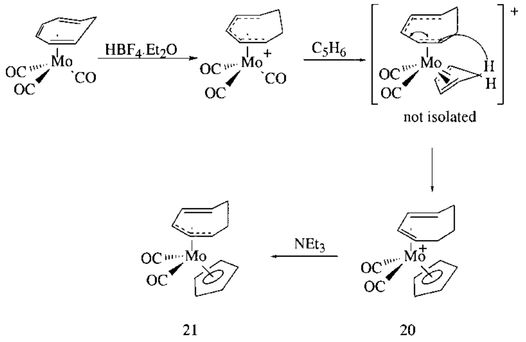


[1]

The substitution of one indenyl ring in the metallocene fragment also follows the routes



Scheme 5



Scheme 6

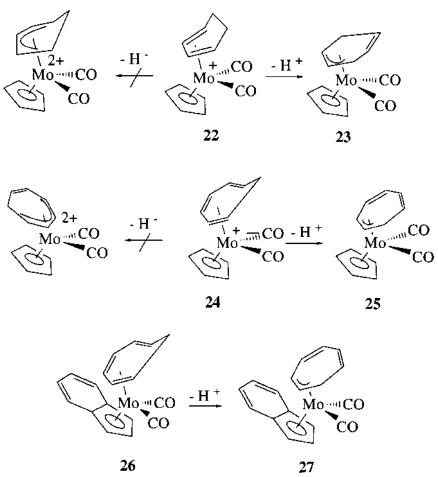
depicted in Scheme 3. Instead of **2**, the starting compound is now the cyclopentadiene cation $[\mathrm{IndM}(\eta^4\text{-}C_5H_6)(CO)_2]^+$ (**12**) (**12a**, M = Mo; **12b**, M = W). Light-induced CO loss followed by ring-to-metal H migration produces $[\mathrm{Cp(Ind)MH(CO)}]^+$ (**13**) and H^- abstraction (with either Ph_3C^+ or Cl_2) produces the dication $[\mathrm{Cp(Ind)M}(CO)_2]^{2+}$ (**14**). The high ν(CO) stretching frequencies (*ca* 2125, 2060 cm^{-1}) are, however, lower than those observed for the parent $[Cp_2M(CO)_2\}^{2+}$ (see above). The deprotonation of **12a** and **12b** gives the ring-slipped $\mathrm{Cp}(\eta^3\text{-Ind})\mathrm{M}(CO)_2$ (**15a** and **15b**, respectively). This is hardly surprising, considering the well-established ability of the indenyl ring to undergo ring-slippage, compared with the Cp ring.

Following the classical substitution reactions of molybdenum and tungsten metallocene derivatives in the +4 oxidation state,[14] complexes **13** and **14** were used as starting materials for the synthesis of a wide range of complexes of the general types $\mathrm{Cp(Ind)MX_2}$ (X = Cl, Br, I, SPh, Me) $[\mathrm{Cp(Ind)MXL}]^+$ (X = Cl, Br, I; L = CO, NCMe, PPh_3) and $[\mathrm{Cp(Ind)ML_2}\}^{2+}$ [L_2 = $(NCR)_2$, $(CNR)_2$, bipyridyl, $(PR_3)_2$, dppel; see below].

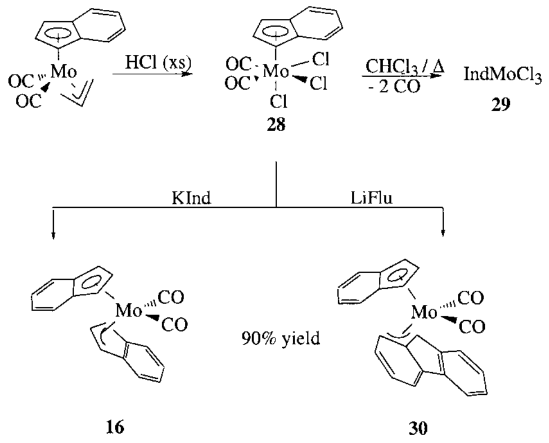
Still following the pathway A of Scheme 3, it was possible to isolate $\mathrm{Ind}(\eta^3\text{-Ind})\mathrm{Mo}(CO)_2$ (**16a**, M = Mo; **16b**, M = W) by simply protonating the starting $\mathrm{IndMo}(\eta^3\text{-}C_3H_5)(CO)_2$ complexes with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 and treating the reaction mixture with indene and NEt_3. No intermediate like **2** was isolated but the trihapto indenyl complexes **16** were obtained in moderate yields.[11b] Compound **16b** had been prepared before by Ustynyuk's group in a very low yield (1.5%). Although its chemistry was never developed it became one of the earliest structurally characterized examples of an η^3-indenyl ligand. An alternative and improved synthesis of these bis-indenyl compounds will, however, be described below.

Although rather general, the chemistry of Scheme 3 revealed several limitations when we attempted to substitute other pentadienyl analogues for Cp. The first limitation was met in the attempted synthesis of fluorenyl derivatives. As depicted in Scheme 5, protonation of **17** followed by treatment with C_5H_6 leads to isolation of the trivial complex **2** instead of the expected $(\mathrm{Flu})\mathrm{Mo}(\eta^4\text{-}C_5H_6)(CO)_2\}^+$ (**18**).

Protonation of **17** with HBF_4 followed by addition of 2 equiv of NCMe yields **19**, which has been isolated and characterized. This fact indicates that the fluorene ring is not directly protonated by HBF_4. The intramolecular abstraction of H (from coordinated C_5H_6) by the neighbouring fluorenyl ligand in **18**, followed by replacement of fluorene by excess C_5H_6, seems to be the best explanation for the formation of **2**. A similar H migration also explains the reaction of Scheme 6 which we



Scheme 7



Scheme 8

performed in order to attempt the synthesis of the mixed-ring molybdenocene of formula $[Cp(\eta^5\text{-}C_7H_9)Mo(CO)_2]^{2+}$ but which ended up in the synthesis of the allylic complex **21**.

Other attempts to prepare open pentadienyl derivatives of the dicationic type, by route **B** of Scheme 3, also failed because no reaction took place between the cations $[CpMo(\eta^4\text{-diene})(CO)_2)]^+$ (**22, 24, 26**) and Ph_3C^+ (Scheme 7). On the contrary, their deprotonation gave the $Cp'Mo(\eta^3\text{-allyl})(CO)_2$-type derivatives (**23, 25** and **27**) in very high yields. The chemistry of these compounds, namely their oxidation, is being studied.

A breakthrough in the synthesis of bis-indenyl metallocenes was achieved with the unexpected reaction of $IndMoCl_3(CO)_2$ (**28**) with KInd, which produces $Ind(\eta^3\text{-}Ind)Mo(CO)_2$ (**16**) in *ca*. 90% yield (Scheme 8). No Ind_2MoCl_2 is obtained. Since the 1:1 stoichiometry of the reagents used cannot explain both the substitution and reduction observed, we believe that Mo–Cl bonds are cleaved homolytically and the Cl radicals are being taken up by the solvent, but we did not ascertain their fate. However, this type of reactivity seems to be consistent because treatment of **28** with NaCp or LiFlu leads to $IndCpMo(CO)_2$ or the novel $Ind(\eta^3\text{-}Flu)Mo(CO)_2$ (**30**) (Scheme 8).

The latter complex is particularly interesting from the structural point of view because it represents the first clear-cut example of an exocyclic trihapto coordination of the fluorenyl ligand (Fig. 2) as revealed by X-ray diffraction analysis.[18] The actual preference for the exocyclic over the endocyclic coordination mode (Fig. 2) for η^3-fluorenyl was also confirmed by Density Functional Theory (DFT) calculations on **30** and also on the putative dianion $[Mn(\eta^3\text{-}Flu)(CO_3]^{2-}$.[18] The previous examples of similar structures were either too distorted towards the η^1-Flu coordination mode,[19] or present in rather sterically crowded *ansa*-metallocene analogues.[20] However, in the present case there is no doubt about the electronic preference for the exocyclic coordination mode. On the other hand, this also shows that the fragment $Cp'Mo(CO)_2$ has a remarkable tendency to stabilize the trihapto coordination of polyenyl ligands, giving rise to a vast family of $Cp'Mo(CO)_2(\eta^3\text{-}polyenyl)$ complexes of which some, bearing ligands such as η^3-Cp and η^3-Flu, are otherwise very rare.

Figure 2 Endocyclic (left) and exocyclic (right) coordination modes of η^3-flu.

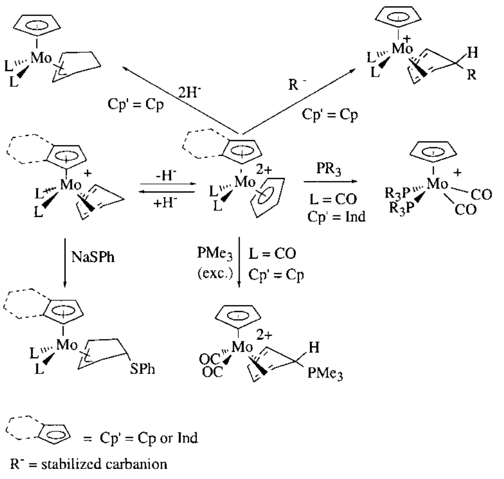
EXPLORATORY CHEMISTRY OF THE $CpCp'M(CO)_2$ COMPLEXES

The chemistry described in the previous section led to two main types of products, namely $Cp_2'M(CO)_2$ and $[Cp'_2M(CO)_2]^{2+}$ (where Cp′ = Cp, Ind Flu), which are related by the redox equation [2].

$$[Cp'_2M(CO)_2]^{2+} \underset{-2e}{\overset{+2e}{\leftrightharpoons}} [Cp'(\eta^3-Cp')M(CO)_2] \qquad [2]$$

M = Mo, W; Cp′ = Cp, Ind, Flu

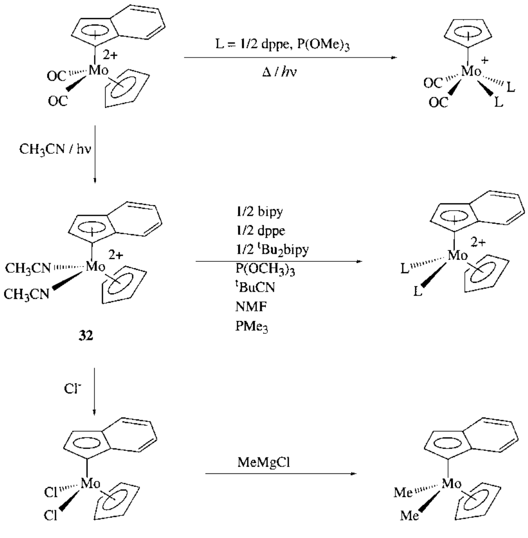
As was also pointed out above, the carbonyl ligand in the dicationic complexes is very labile and can be readily substituted by other ligands. This accounts for the easy solvolysis of $[Cp'_2M(CO)_2]^{2+}$ complexes in NCMe, which proceeds stepwise to give $[Cp'_2M(CO)(NCMe)]^{2+}$ (**31**) and $[Cp'_2M(NCMe)_2]^{2+}$ (**32**). However, the high positive charge of $[Cp'_2M(CO)_2]^{2+}$ complexes is strongly reflected in the reactivity of the Cp′ ring ligands, which undergo facile addition of nucleophiles.



Scheme 9

Scheme 9 shows several examples of these addition reactions.[21]

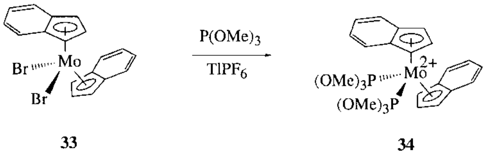
According to the Davies–Green–Mingos rules,[22] sequential addition of two nucleophiles should produce 1,2-disubstituted cyclopentenyl with both substituents on the same face of the ring. However, this double addition is not feasible except for the very small hydride nucleophile. In all other cases only one nucleophile either than hydride could be added as in the examples of Scheme 9.



Scheme 10

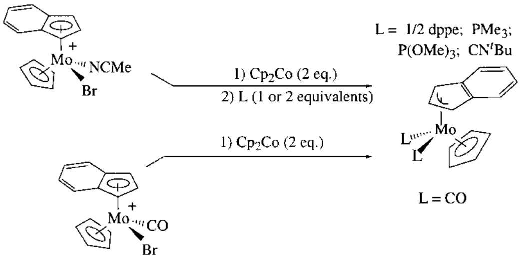
Interestingly, in the case of the mixed-ring dication$[\mathrm{CpIndMo(CO)_2}]^{2+}$ addition of phosphines or phosphites took place at the indenyl and not at the Cp ring (see Scheme 10 below). In practice, substitutions at the metal are rather straightforward when the bis-nitrile dications **32** are used. Addition of a drop of *N*-methylformamide catalyses the substitution reaction and leads to high yields of a variety of cationic complexes with the metal in the +4 oxidation state as depicted in Scheme 10 for the mixed-ring derivatives of the IndCpMo(IV) fragment.

The general similarity of this chemistry to that displayed by the parent metallocenes in the +4 oxidation state, e.g. Cp_2MX_2, is striking. Although on the basis of the 'indenyl effect' a general acceleration of some substitution reactions might be expected for the indenyl-containing complexes we are unable to confirm it in the absence of kinetic measurements. Quite on the contrary, the bis-indenyl complex Ind_2MoBr_2 (**33**) is unexpectedly unreactive towards nucleophiles, failing to react with PhS^- and MeMgCl for instance. In the case of the parent Cp_2MoBr_2 and even $IndCpMoBr_2$ such substitution reactions take place quite easily. This may be the result of the steric protection offered to the metal by the indenyl ligands preventing approach of the nucleophile in nucleophilic substitution reactions. Substitution of the bromides in **33** may, however, be achieved readily in the presence of $TlBF_4$, as exemplified in Eqn [3].



[3]

Since the molybdenocenes and tungstenocenes in the +2 oxidation state, with the general formula Cp_2ML ($L = PR_3$, NCR, CNR, CO, C_2H_4, C_2H_2,



Scheme 11

etc.), have an extensive and important chemistry, we decided to attempt the preparation of the analogue mixed-ring complexes IndCpMoL. Such species should be very electron-rich, and reactive in oxidative additions like those displayed by their Cp_2ML congeners.[23] The synthesis was attempted by means of the reductive pathways that have been tried successfully in the synthesis of the parent Cp_2M complexes. However, as summarized in Scheme 11, the general result obtained when $[Cp(Ind)MoBr(NCMe)]^+$ was reduced with Cp_2Co and the resulting solution was treated with the ligand L was the synthesis of the tetracoordinated $Cp(\eta^3\text{-}Ind)MoL_2$ derivatives. In the cases where the Mo:L ratio was 1:1 the yields were poor but they rose to almost quantitative when the ratio was adjusted to L:Mo $\geq$ 2:1. Even the reduction of $[CpIndMoBr(CO)]^+$ with Cp_2Co gave $IndCpMo(CO)_2$ (*ca* 40% yield) and not IndCpMoCO.

This means that the complexes IndCpMoL are electrophilic and are stabilized by addition of a second equivalent of L to give the ring-slipped compounds $Cp(\eta^3\text{-}Ind)MoL_2$. The only exception, so far, was found for L = CN(tBu), in which case a mixture of CpIndMo[CN(tBu)] and $Cp(\eta^3\text{-}Ind)Mo[CN(tBu)]_2$ was produced. The bulkiness of the CN(tBu) ligand may explain this result and the lower relative stability of the tetracoordinated bis-isonitrile complex. Under similar circumstances the reduction of the corresponding $[Cp_2Mo(NCMe)X]^+$ complexes produces the tricoordinated Cp_2MoL.[24]

The related two-electron (2e) redox processes of Eqn [2] also involve hapticity changes and are, therefore, redox-induced ring-slippage reactions. In the beginning both complexes in Eqn [2] were obtained by independent synthetic routes, namely the pathways A and B of Scheme 3. However, the cyclic voltammogram of $Cp(\eta^3\text{-}Ind)W(CO)_2$ in NCMe showed a single reversible oxidation wave corresponding to a 2e process. Since the voltammogram was found to be identical to that of the dication $[Cp(Ind)W(CO)_2]^{2+}$ it was proved that the transformations in Eqn [2] are electrochemically feasible, at least in this case. In the case of the corresponding molybdenum complex the wave is irreversible because the dication is readily solvolysed in NCMe solution. However, we later established that this reaction is chemically and electrochemically reversible for a large number of dications $[CpIndMoL_2]^{2+}$ [L = CO, P(OMe) dppe, (tBu)bipy, CN(tBu); bipy = bipyridyl] which produce the corresponding ring-slipped reduced complexes $Cp(\eta^3\text{-}Ind)ML_2$, many of which were prepared by independent chemical routes. In several cases the complexes display two separate 1e waves, suggesting that the intermediate monocations $[CpIndML_2]^+$ may be stable enough for isolation and characterization.[25] No analogous parent Group 6 metallocenes with the metal in the formal oxidation state +3 are known.

Most interestingly, reduction of $[Cp_2Mo(CO)_2]^{2+}$ with Cp_2Co gave the ring-slipped trihapto Cp complex $Cp(\eta^3\text{-}Cp)Mo(CO)_2$ in very high isolated yield. However, the similar reaction with $[Cp_2Mo\{P(OMe)_3\}_2]^{2+}$ gave $Cp_2MoP(OMe)_3$. On the other hand, it is known that $Cp_2W(CO)$[13] and Cp_2CrCO[26] react with CO to give $Cp(\eta^3\text{-}Cp)M(CO)_2$ only under very high CO pressure. The corresponding molybdenum complex could never be prepared by the same procedure, probably due to its thermal instability.[13a,c]

ENERGETICS OF THE RING-SLIPPAGE REACTIONS AT THE MOLYBDENOCENE FRAGMENT

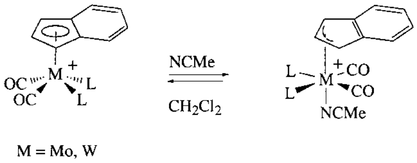
From the results above, it becomes clear that ring-slippage can be best induced by means of redox processes, even in the case of the less favourable and rarely observed η^5-Cp → η^3-Cp ring-slippage. In fact, DFT calculations perfomed by Calhorda and Veiros on the redox reaction of Eqns [4] and [5] show that the energy difference between the redox-induced ring-slippage of the Cp ligand and the indenyl ligands is very small.[27]

$$[Cp_2Mo(CO)_2]^{2+} \xrightarrow{+2e} [Cp(\eta^3\text{–}Cp)Mo(CO)_2] \quad \Delta E = -374.07\ \text{kcal mol}^{-1} \qquad [4]$$

$$[CpIndMo(CO)_2]^{2+} \xrightarrow{+2e} [Cp(\eta^3\text{–}Ind)Mo(CO)_2] \quad \Delta E = -380.3\ \text{kcal mol}^{-1} \qquad [5]$$

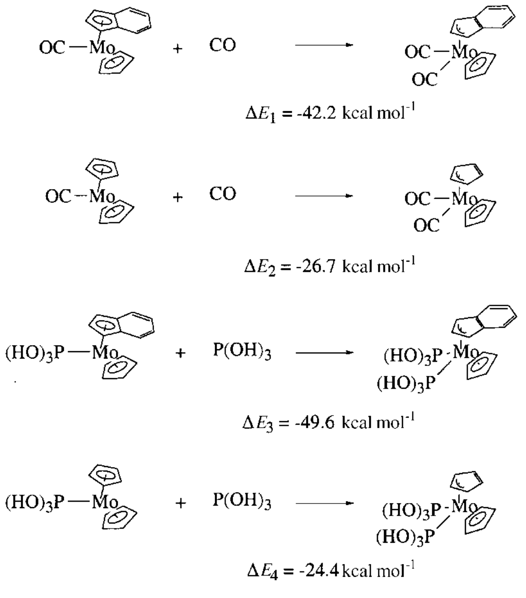
However, most of the arguments related to ring-slippage reactions involve the association or dissociation of one 2e donor from the coordination sphere of the ring-containing complex rather than redox reactions.

In this context, the kinetic evidence shows that indenyl undergoes these haptotropic changes more readily than Cp.[7] The fact that there are many more examples of complexes bearing the η^3-Ind ligand than the η^3-Cp ring provides circumstantial evidence in favour of the easier slippage of the indenyl ring. However, there are no values for the energy differences between these two types of ring-slippages which may allow a quantification of how ‘favourable’ the indenyl slippage is. Besides, the nature of the added or dissociated ligands and of the other ancillary ligands present is known to influence the ring-slippage process, as we were able to show in the recently reported study of the reaction in Eqn [6].[28] In this system, the indenyl slippage caused by addition of NCMe, which is the reaction solvent, is strongly dependent on the nature of the L ligands: it is not observed for L = PR_3, $P(OR)_3$, CNMe and $\frac{1}{2}$ bipy but it is rapid for L = NCMe, $OPPh_3$, DMF, $\frac{1}{2}$ acac. The most striking example of this subtle dependence was the fact that NCMe addition takes place for L = NCMe but not for L = CNMe. According to the DFT calculations performed for the model system with NCH and CNH, nitrile addition to the bis-isonitrile (**35**, L = CNH) complex is thermodynamically forbidden ($\Delta G^\circ > 0$) whereas nitrile addition to the bis-nitrile (**35**, L = NCH) complex is thermodynamically allowed for L ($\Delta G^\circ < 0$).[28]



[6]

This kind of ligand dependence is likely to be a general feature of haptotropic shifts and certainly plays a role in the case of the molybdenocene system, where ring-slippage of the Cp ring has been used to explain a number of reactions.[4,29]



Scheme 12

The isolated products of the reactions of Eqns. [7] and [8], both performed under the same conditions, clearly show that CO is favouring Cp slippage relative to $P(OMe)_3$.

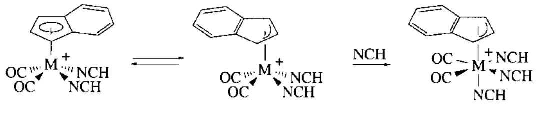
$$[Cp_2Mo(CO)_2]^{2+} \xrightarrow{+2e} [Cp(\eta^3-Cp)Mo(CO)_2] \quad [7]$$

$$[Cp_2Mo\{P(OMe)_3\}_2]^{2+} \xrightarrow{+2e} [Cp_2MoP(OMe)_3] + P(OMe)_3 \quad [8]$$

In order to shed some light on the energetics of the ligand-addition-induced ring-slippage reaction in the molybdenocene system, DFT calculations were performed on the reactions given in Scheme 12.[27] In order to simplify the calculations $P(OH)_3$ was used instead of $P(OMe)_3$.

From the calculated reaction enthalpies a few conclusions may be drawn. The first is the confirmation of the well-known fact that indenyl slippage is more favourable than cyclopentadienyl slippage. This is reflected in the more negative reaction enthalpies of the reactions ΔE_1 and ΔE_3 (Scheme 12) compared with ΔE_2 and ΔE_4 respectively. The second and much less obvious conclusion is that all the tested ring-slippage reactions, both for Ind and Cp, are exothermic. They probably do not occur more often because they are entropically disfavoured association reactions. A third conclusion concerns the influence of the ancillary ligands on the energetics of the ring-slippage. A comparison between the reaction enthalpies ΔE_2 and ΔE_4 shows that CO favours the slippage of the Cp ligand and shortens the gap between the energies of the Cp and Ind slippages. In contrast, the weaker π-acceptor $P(OH)_3$ widens this gap and clearly favours the slippage of the indenyl ring relative to the Cp.

Another interesting result of the theoretical calculations on the ring-slippage depicted in Eqn [6] is the strong suggestion that NCMe just traps the



37 **38** **39**

Scheme 13

electronically unsaturated η^3-indenyl species **38**, which is in a rapid pre-equilibrium with the 18-electron starting η^5-indenyl species **37**, as depicted in Scheme 13. Indeed, optimization of the energy and structure of a number of species formed upon lengthening of the Mo–NCH bond *trans* to the η^3-Ind ligand in the final complex **39** shows an increase in energy and involves a slight closing of the angles between the CO and L ligands on the equatorial plane, while retaining the η^3-Ind coordination even at the essentially non-bonding Mo–NCH distance of 3.67 Å.

This suggests that the transition state for the forward addition reaction presents a geometry and coordination sphere rather similar to those of **38**. In his original report on the indenyl effect, Basolo considered this type of mechanism as entirely consistent with his kinetic data and, therefore, a plausible alternative to what became the more widely accepted mechanistic interpretation of the indenyl effect which considers a bimolecular associative pathway. Kinetic investigations of reaction [6] are at present under way in order to ascertain the validity of this mechanistic model.

CONCLUSIONS AND PROSPECTS

The work described reveals a well-structured family of substituted metallocenes bearing cyclopentadienyl analogues. The chemistry and properties of these compounds need to be explored further but already provide the basis for an improved understanding of the synthesis, structure and energetics involved in the ring-slippage processes of cyclopentadienyl, indenyl and fluorenyl ligands. In this respect, DFT calculations have been extremely helpful for the prediction and interpretation of many results.

From the experimental and theoretical data gathered, we suggest that one should be able to prepare other complexes bearing the ring-slipped η^3-Cp ligand by using η^5-Cp $\rightarrow \eta^3$-Cp redox-induced slippages, at low temperature, starting from η^5-Cp complexes bearing CO ancillary ligands. The wide variety of available $[CpM(CO)_n]^{x+}$ complexes should provide ample ground for testing this prediction. Two such studies, by Cooper on the reduction of $(MeCp)Mn(CO)_3$[30] and Sweigart on the reduction of $CpFe(CO)_3$[31] which gave contradictory evidence for redox-induced ring-slippage (positive for Mn and negative for Fe), are already important contributions to the understanding of the subtle factors that seem decisive in these structural transformations.

A large amount of the chemistry and electrochemistry of the modified metallocene complexes of molybdenum and tungsten remains to be explored. Currently under way is the study of $Cp'_2M(III)$ derivatives of the $[Cp'_2ML_2]^+$ type, which are important species for the understanding of the structural changes undergone during the redox-induced haptotropic rearrangements and are totally unknown for their parent Cp_2ML_n metallocenes.

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