Compared Reductive Chemistry of Molybdenocene and Indenyl-Substituted Complexes

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Reduction of [IndCpMo(L)Br]Br (L = **1a**, CO; **2**, NCMe) with Cp_2Co in the presence of two equivalents of the ligand L′ gives the ring-slipped neutral complexes [(η^3-Ind)CpMoL′$_2$] (L′ = **5**, CO; **6**, 1/2 dppe; **7**, PMe_3; **8**, $P(OMe)_3$; **9**, CN*t*Bu) in good yield. Products **7**, **8**, and **9**, but not [IndCpMoL′], are also formed in the presence of only 1 equivalent of L′ in modest yields. In the case of the reduction of [IndCpMo(L)Br]Br [L = **2**, NCMe; **3a**, CN*t*Bu; **4**, $P(OMe)_3$] mixtures of the complexes, [(η^3-Ind)CpMoL$_2$] (**8**, **9**) and [(η^5-Ind)CpMoL] [L = **11**, $P(OMe)_3$; **12**, CN*t*Bu] were obtained. The only product of formal type [(η^5-Ind)CpMoL] that could be prepared by these methods was the alkyne complex [(η^5-Ind)CpMo(η^2-PhC≡CPh)] (**10**). These results contrast with the well-known reductions of similar bis-cyclopentadienyl cations [Cp_2Mo(L)Br]$^+$, which produce [Cp_2MoL] complexes under the same conditions. The reduction of the dications [Cp_2MoL_2][BF_4]$_2$ [L = CO; $P(OMe)_3$] with Cp_2Co is now reported to afford the neutral complexes [CpMo(η^3-C_5H_5)(CO)$_2$] (**13**) and [Cp_2Mo($P(OMe)_3$)] (**14**), respectively, showing that the stability of the ring-slipped complexes is dependent on the other ligands. From DFT and EHMO calculations used to probe the bonding and the energetics of these ring slippage processes it is concluded that weak π acceptor ligands favour η^5-Ind → η^3-Ind slippage and disfavour η^5-Cp → η^3-Cp slippage at the $CpMoL_2$ fragment. Redox-induced ring slippages involve very similar energies for both indenyl and cyclopentadienyl complexes and should be able to produce more examples of the otherwise rare η^3-Cp coordination mode.

Introduction

We have recently reported the synthesis of a variety of indenyl analogues of molybdenocene and tungstenocene in the +4 oxidation state, [$IndCpMX_2$].[1] The chemistry of these complexes follows closely the chemistry of the corresponding metallocene derivatives, [Cp_2MX_2]. The most interesting reaction type observed so far is the facile, reversible, chemical and electrochemical reduction of several dications [$IndCpML_2$]$^{2+}$ to the ring-slipped neutral, 18e complexes [(η^3-Ind)CpML$_2$] (L = CO, dppe, PMe_3, bipy, CN*t*Bu).[2] Although the strictly parallel reductions of the corresponding metallocene dications [Cp_2ML_2]$^{2+}$ have never been reported, the general rule holding for the reductions of Cp_2M^{IV} complexes is the formation of Cp_2ML species, e.g. L = CO,[3] CNR,[4] (η^2-NCMe),[5] (η^2-C_2Ph_2),[3][6] (η^2-C_2H_4),[7] PR_3,[8] (η^2-CO_2).[9] Such species have played a central role in revealing the chemistry of the very reactive and electron-rich [Cp_2M^{II}] fragment (M = Mo, W). The only exception is the reduction of [Cp_2WCl(CO)]$^+$ under a CO atmosphere, to give [(η^3-Cp)CpW$(CO)_2$].[3b]

With the aim of continuing the comparative study of the chemistry of the [Cp_2Mo] and [IndCpMo] fragments, we set out to synthesize the Mo^{II} mixed-ring complexes [IndCpMoL] that might give access to the as yet unstudied [$IndCpMo^{II}$] fragment. As described in the present paper, in spite of the numerous different synthetic variations used, IndCpMo(η^2-C_2Ph_2) was the only such complex that we could isolate. Instead, the unexpectedly effective synthesis of ring-slipped complexes of type [(η^3-Ind)CpMoL$_2$] took place even at Mo/L = 1:1 ratios, suggesting that the electron-rich complexes [IndCpMoL] undergo facile ligand addition in contrast to their Cp_2MoL analogues. The comparison of the behaviour of the [IndCpMo] and [Cp_2Mo] fragments towards ring slippage was then studied by reduction of the corresponding cationic Mo^{IV} complexes under similar conditions. DFT and EHMO calculations were used to study these ring slippages and provide the energetic relationships between [(η^5-Cp′)CpMoL$_2$]$^{2+}$, [(η^3-Cp′)CpMoL$_2$], and [(η^5-Cp′)CpMoL] (Cp′ = Cp, Ind) complexes.

Results

Chemical Studies

In order to prepare the target [IndCpMoL] complexes we considered the methods that are well established for the synthesis of [Cp_2MoL] complexes. From all these methods, reductive dehalogenation from [IndCpMo(L)Br]$^+$ [L = **1**, CO; **2**, NCMe; **3**, CN*t*Bu; **4**, $P(OMe_3)_3$] was selected as the most practical method since we improved a convenient syn-

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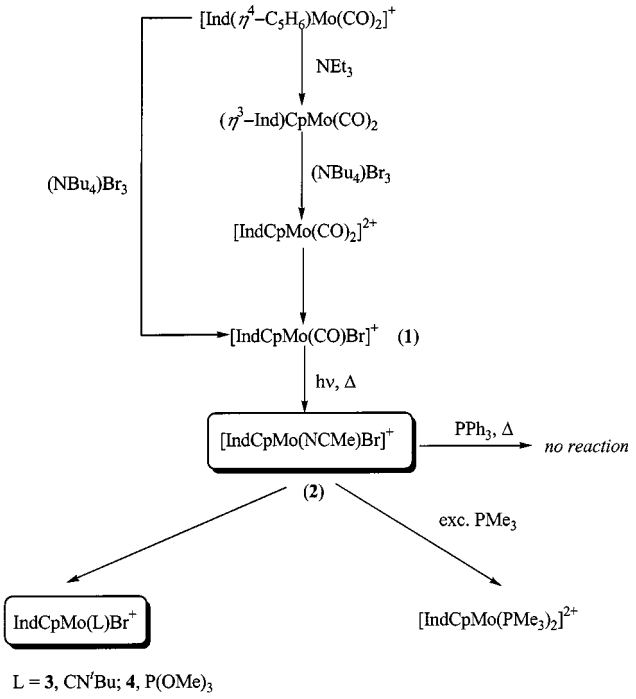
thesis of the appropriate starting halides **1** and **2**, whose congeners $[IndCpMo(L)X]^+$ (X = Cl, I) are known.[1] In fact, oxidation of $[(\eta^3\text{-Ind})CpMo(CO)_2]$ (**5**) with $(NBu_4)Br_3$ leads to the immediate precipitation of the white oxidation product $[IndCpMo(CO)_2]Br_2$, identified by comparison of its IR and ^{1}H-NMR spectra with those of an authentic sample;[1] further stirring of the suspension leads to substitution of one carbonyl ligand, affording [IndCpMo(CO)Br]Br (**1a**), as depicted in Scheme 1. The oxidation of $[IndMo(\eta^4\text{-}C_5H_6)(CO)_2]BF_4$ with $(NBu_4)Br_3$ is even better because it avoids the preparation of **5** and leads to $[IndCpMo(CO)Br]BF_4$ (**1b**) in 70% yield.



Scheme 1. Reaction sequence for the synthesis of the cationic $IndCpMo^{(IV)}$ derivatives

Refluxing **1a** in NCMe solution under visible light irradiation gave rise to complex **2** in 90% yield. Simple substitution of NCMe in **2** with CN*t*Bu and $P(OMe)_3$ afforded **3** and **4**. The characterization of these complexes was straightforward from their ^{1}H-NMR data and elemental analysis. The ^{1}H-NMR pattern of the indenyl ligand in **1**, **3**, and **4** is typical for η^5-coordination in asymmetric complexes, as resonances are doubled and occasionally superimposed, because the (normally equivalent) pairs of indenyl protons are now diastereotopic and, therefore, exhibit different chemical shifts. Complex **2**, on the other hand, shows only one resonance for protons $H^{1/3}$, probably due to a fast isomerization process in solution. This behaviour was also observed in the previously reported complex $[IndCpMo(NCMe)Cl]BF_4$.[1] Surprisingly, no reaction occurred between **2** and PPh_3, probably due to steric hindrance; the congener complex $[IndCpMo(PPh_3)Cl]BF_4$ has been prepared by the facile reaction of the dichloride $[IndCpMoCl_2]$ with PPh_3 in the presence of $TlBF_4$.[1] Reaction of **2** with PMe_3 under mild conditions readily gave the reported dication $[IndCpMo(PMe_3)_2]^{2+}$.[2]

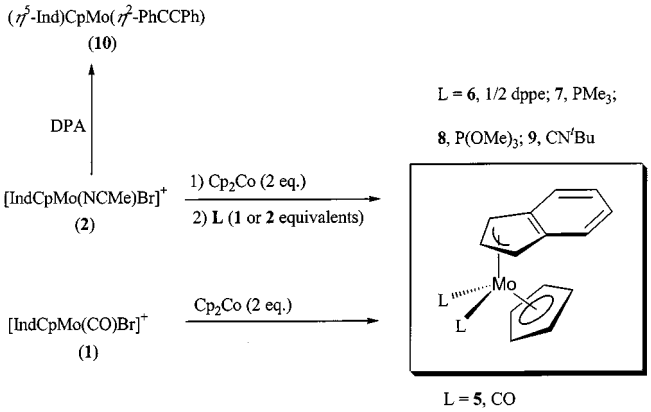
Reduction of [IndCpMo(CO)Br]Br with Cp_2Co gave a dark solution. The hexane-soluble extract is $[(\eta^3\text{-Ind})CpMo(CO)_2]$ (**5**), identified by comparison of its IR and ^{1}H-NMR spectra with those of an authentic sample.[1] The IR spectrum displays two characteristic stretching vibrations of the *cis* carbonyl ligands, at $\tilde{\nu}$ 1959 and 1888 cm^{-1}. We could not observe the formation of the intermediate complex IndCpMo(CO) and the yield of the reaction is relatively low (40%).

The metallocene fragments $[Cp_2M^{II}]$ (M = Mo, W) produce one of the most striking examples of side-on coordinated nitriles in complexes $[Cp_2M(\eta^2\text{-NCMe})]$.[5] These complexes are readily available by reduction of $[Cp_2MX_2]$ and provide one of the most useful starting materials for the preparation of other $[Cp_2ML]$ complexes, since the η^2-NCMe ligand is quite labile.[4][8]

We therefore attempted the reduction of $[IndCpMo(NCMe)Br]^+$ (**2**) with Cp_2Co in acetonitrile solvent. A brown-red solution was formed but, in spite of many attempts, we were unable to isolate any complex from the reaction mixture. Decomposition products were similarly obtained in the reduction of $[IndCpMoCl_2]$ with Na/Hg in NCMe, the method used for the synthesis of the $[Cp_2Mo(\eta^2\text{-NCMe})]$ analogues.

However, the chemical evidence described below points to the formation of some labile acetonitrile derivative of the fragment [IndCpMo], which can only be formulated as $[(\eta\text{-Ind})CpMo(NCMe)_x]$, that decomposes upon loss of NCMe solvent.

Treatment of the brown-red solutions of this compound with *one equivalent* of several ligands (L) affords the ring-slipped neutral complexes $[(\eta^3\text{-Ind})CpMoL_2]$ [**7**, L = PMe_3; **8**, L = $P(OMe)_3$; **9**, L = CN*t*Bu] instead of the intended congeners [IndCpMoL] (as depicted in Scheme 2). Compounds **7**–**9** are formed in < 50% yields (ca. 30%), as expected. In the case of PPh_3 no tractable product was obtained.



Scheme 2. Reductive reactions of the $IndCpMo^{(IV)}$ cations

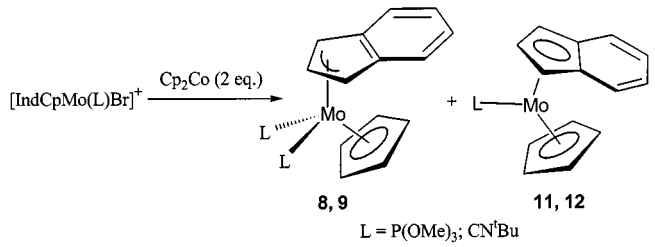
On the other hand, reaction with 1 equivalent of diphenylacetylene (DPA) produces $[(\eta^5\text{-Ind})CpMo(\eta^2\text{-PhC}\equiv\text{CPh})]$ (**10**) in 80% yield. The analytical and ^{1}H-NMR

data agree with a structure with η^5-indenyl and only one DPA molecule, which is the same type of structure present in the analogous $[Cp_2Mo(\eta^2\text{-PhC}{\equiv}CPh)]$.[10] In fact, **10** presents the ^{1}H-NMR chemical shift pattern expected for η^5-coordination of the indenyl ligand in a neutral complex, with two multiplets for benzenoid protons H^{5-8} (δ = 6.93−6.90 and δ = 6.75−6.72), a triplet for H^2 (δ = 5.53), a doublet for $H^{1/3}$ (δ = 3.85), and a singlet for the Cp ring (δ = 4.21). Another reaction leading to **10** is discussed below.

Of course, the yields of complexes **7** to **9** increase to much higher values (ca. 50−90%) when *two equivalents* of the ligand L are used. Reaction with dppe affords [(η^3-Ind)CpMo(dppe)] (**6**). In the case of P(^{i}Pr)$_3$ (2 equiv.) no tractable product was obtained.

Complexes **6**−**9** have been previously prepared by reduction of the respective dications $[IndCpMoL_2]^{2+}$ with Cp_2Co;[2][11] reported preparations of **6** and **8** also include deprotonation of the cyclopentadiene cations $[IndMo(\eta^4\text{-}C_5H_6)(dppe)]BF_4$ and $[IndMo(\eta^4\text{-}C_5H_6)(P(OMe)_3)_2]BF_4$ with NEt_3.[2][11]

Reduction of [IndCpMo(L)Br]Br complexes [L = **3a**, CN*t*Bu; **4**, P(OMe)$_3$] produced mixtures of the respective [(η^5-Ind)CpMoL] [L = **11**, P(OMe)$_3$; **12**, CN*t*Bu] and [(η^3-Ind)CpMoL$_2$] (**8** and **9**), as depicted in Scheme 3. All attempts to separate the two products were unsuccessful due to their similar solubility properties. However, their presence in the mixtures is easily recognized by ^{1}H-NMR spectroscopy; *trihapto* and *pentahapto* complexes present distinctly different patterns of chemical shifts.[2]



Scheme 3. Reduction of the cations $[IndCpMo(L)Br]^+$

Complex [(η^5-Ind)CpMo(CN*t*Bu)] (**12**) presents the expected ^{1}H-NMR pattern for η^5-coordination mode of the indenyl ligand in a neutral complex. Signals in the ^{1}H-NMR spectrum of the mixture in C_6D_6 related to complex [(η^3-Ind)CpMo(CN*t*Bu)$_2$] are in agreement with those of an authentic sample (see Experimental Section).[2] A similar assignment was made for the resonances in the mixture of **11** and **8** (see Experimental Section).

In order to be able to compare the properties of the Cp_2M and IndCpM complexes, the reduction of some dications $[Cp_2MoL_2]^{2+}$ was carried out under the same conditions reported for the reduction of several mixed-ring dications $[IndCpMoL_2]^{2+}$.[2] Somewhat unexpectedly, the previously reported neutral complex [(η^3-Cp)CpMo(CO)$_2$][1] (**13**) was now obtained, in high yield (80%), upon reduction of $[Cp_2Mo(CO)_2]^{2+}$ with Cp_2Co. The reaction of $[Cp_2Mo(P(OMe)_3)_2]^{2+}$ under similar conditions affords [Cp_2Mo(P(OMe)$_3$)] (**14**), instead of [(η^3-Cp)CpMo(P(OMe)$_3$)$_2$]. This behaviour differs from that of the indenyl congener $[IndCpMo(P(OMe)_3)_2]^{2+}$, which is readily reduced to the neutral complex [(η^3-Ind)CpMo(P(OMe)$_3$)$_2$] (**8**).[11] The dication $[Cp_2Mo(CNtBu)_2]^{2+}$ (**15**) proved to be resistant to reduction by both Cp_2Co and Na/Hg.

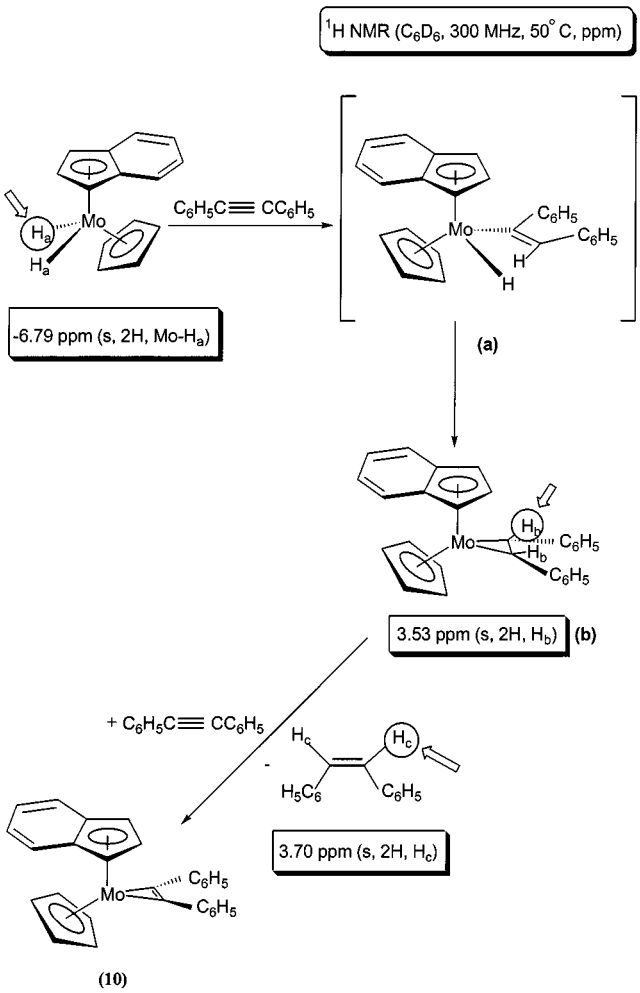
The complex [(η^5-Ind)CpMo(η^2-PhC≡CPh)] (**10**), the only one in which the stoichiometry [IndCpMoL] is preferred over the ring-slipped complexes of stoichiometry [(η^3-Ind)CpMoL$_2$], is the final product of DPA insertion across the Mo−H bonds in $[IndCpMoH_2]$. Nakamura and Otsuka,[12] as well as Herberich and Okuda,[13] studied the analogous reaction between DPA and $[Cp_2MoH_2]$. Assuming the same mechanism, Scheme 4 summarizes our observations and relevant chemical shifts for this experiment. Reaction of the dihydride and DPA in a 1:2 ratio was monitored by ^{1}H-NMR spectroscopy in C_6D_6. After 1 h at room temperature no reaction had occurred. At 50°C, the resonances corresponding to the protons of stilbene, both coordinated (H_b at δ = 3.53 in intermediate **b**; Scheme 4) and free (H_c at δ = 3.70), immediately appeared. The vinyl-hydride intermediate **a** could not be observed because of the very fast second insertion step. Signals at δ = 5.26 and δ = 4.21 can be ascribed to the Cp rings of **b** and **10**, respectively. After 3 h at 50°C neither $[IndCpMoH_2]$ nor the stilbene complex **b** were present (the former was monitored by its characteristic hydride signal at δ = − 6.79 and the latter by its resonance at δ = 3.53), revealing the presence of **10** and some free DPA.

Theoretical Studies

The previously described experiments indicate that the [IndCpMo] fragment produces only with difficulty the monoligand [IndCpMoL] derivatives, leading preferentially to the slipped [(η^3-Ind)CpMoL$_2$] species. On the other hand, for the [Cp_2MoL] complexes a different pattern is observed. [Cp_2MoL] complexes seem favoured over [(η^3-Cp)CpMoL$_2$], the only example of the latter being [(η^3-Cp)CpMo(CO)$_2$], which is easily accessible by reduction of its dicationic precursor.

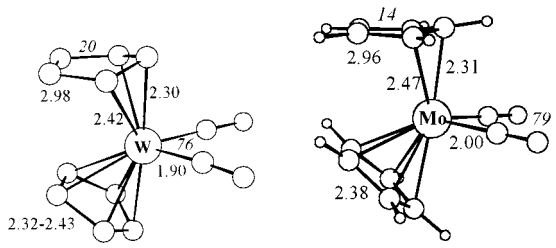
We therefore performed DFT calculations[14] in order to find out the relative stabilities of these types of compounds, both for the biscyclopentadienyl and the indenylcyclopentadienyl systems. We started the calculations for models with L = CO but, in order to understand the different reactivities of the systems as a function of the ligand, the same study was repeated for L = P(OMe)$_3$.

The geometry of the following six compounds was optimized: [(η^5-Ring)CpMo(CO)$_2$]$^{2+}$ (**I**), [(η^3-Ring)CpMo(CO)$_2$] (**II**) and [(η^5-Ring)CpMo(CO)] (**III**) (Ring = **a**, Ind; **b**, Cp). The indenyl derivatives **Ia** and **IIa** are studied in detail using DFT calculations in another work,[11] and the reliability of the theoretical approach has been checked by comparing the optimized geometries with the available structures of the indenyl derivatives.[1] The remaining indenyl complex



Scheme 4. Insertion of DPA across the Mo−H bonds

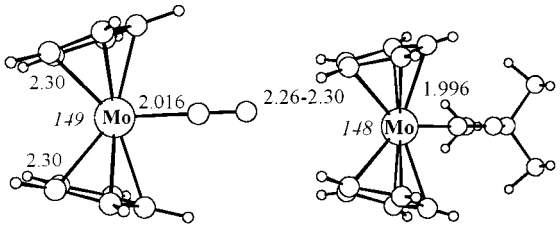
type (**IIIa**) has not been isolated and the optimized geometry cannot be compared with that of a known species. Concerning the biscyclopentadienyl complexes, there is a structure of the tungsten analogue of **IIb** [(η^3-Cp)CpW(CO)$_2$][15] and of the *tert*-Butylnitrile derivative of **IIIb** [$Cp_2Mo(CNtBu)$],[4] which can be used for comparison. The molybdenum and tungsten compounds are usually very similar as far as their geometric characteristics are concerned and therefore they can be compared. The main features of the geometry of [(η^3-Cp)CpW(CO)$_2$] and those of our optimized [(η^3-Cp)CpMo(CO)$_2$] are shown in Scheme 5 (left and right, respectively).



Scheme 5. Relevant distances and angles in [(η^3Cp)CpW(CO)$_2$] (left, exp.) and [(η^3Cp)CpMo(CO)$_2$] (right, calcd.)

The agreement is very good, both for distances and angles, except for the folding of the Cp ring, which is 6° less in the model than in the tunsgten compound. It should be remembered that, in the optimization procedure, the C−C and C−H distances of one Cp ring were kept fixed, with only the position of the ring being allowed to change. The second ring was totally optimized, in order to allow it to become η^3 if necessary (it always started as η^5).

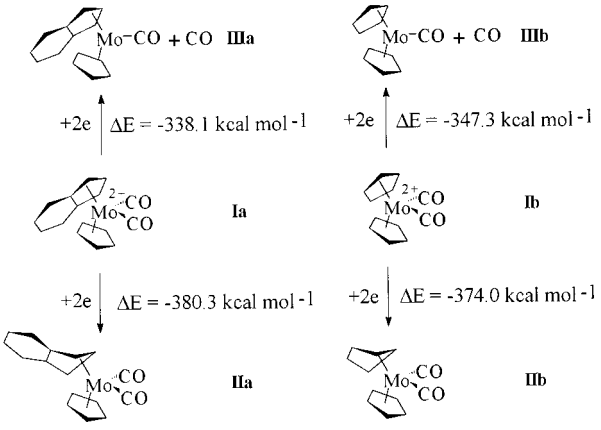
There is no carbonyl complex of type **III** structurally characterized, and the most similar to [$Cp_2Mo(CO)$] is [$Cp_2Mo(CNtBu)$],[4] the isonitrile ligand being also a π-acceptor. There are not so many parameters to compare in this situation, but the agreement between Mo−C distances and the Cp−Mo−Cp angle is acceptable, considering that it is not exactly the same species (Scheme 6).



Scheme 6. Relevant distances and angles in [$Cp_2Mo(CO)$] (left, calcd.) and [$Cp_2Mo(CNtBu)$] (right, exp.)

Finally, compound **I** $[Cp_2Mo(CO)_2]^{2+}$ has not been structurally characterized, but belongs to the large family of the [Cp_2MoL_2] complexes.[16] Both the Mo−C distances (ca. 2.35 Å), the C−Mo−C angle (139°) and the Cp−Mo−Cp angle (88°) fit in the general pattern.

The relative energies of the six compounds are given in Scheme 7, taking into account that to make the numbers directly comparable we added one molecule of free CO on going from **I** to **III**.



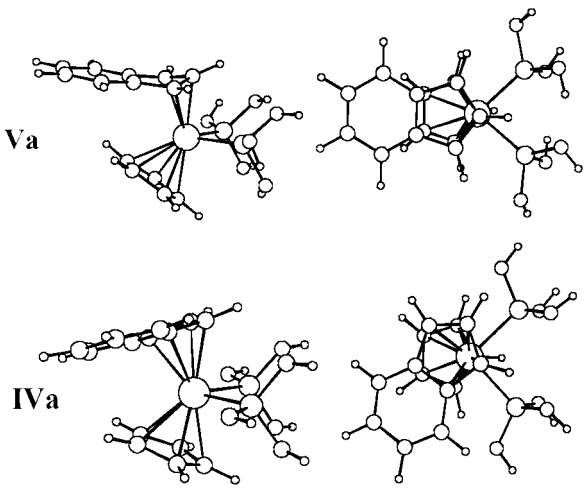
Scheme 7. Relative DFT energies of CO complexes

The energies of the final products are much lower for the η^3 species than for the monoligand derivative, both for Cp and Ind derivatives. Even taking into account the fact that

entropy should favour **IIIa** and **IIIb**, that difference is significant. Indeed, the experimental results show the formation of this species when the ligands are carbonyls, i.e. strong π-acceptors. When carbonyls are replaced by other ligands, such as phosphites, only the monoligand complex is formed for Ring = Cp and a mixture of both species is detected for the Ind system.

We therefore also performed DFT calculations for the corresponding phosphite complexes [L=P(OH)$_3$], [(η^5-Ring)CpMo(L)$_2$]$^{2+}$ (**IV**), [(η^3-Ring)CpMo(L)$_2$] (**V**), and [(η^5-Ring)CpMo(L)] (**VI**) (Ring = **a**, Ind; **b**, Cp), using P(OH)$_3$ instead of P(OMe)$_3$. The geometries of the six complexes were fully optimized.

The calculations on **IVa** and **Va** are also been discussed in another work, along with the description of the X-ray structures of the parent phosphite compounds.[11] It might be important to stress that the conformation of the indenyl ring in the η^3-coordination is different from that in the η^5-coordination. This is easily seen in Scheme 8, where the side and top views of [(η^5-Ind)CpMo(L)$_2$]$^{2+}$ (**IVa**) and [(η^3-Ind)CpMo(L)$_2$] (**Va**) are shown.

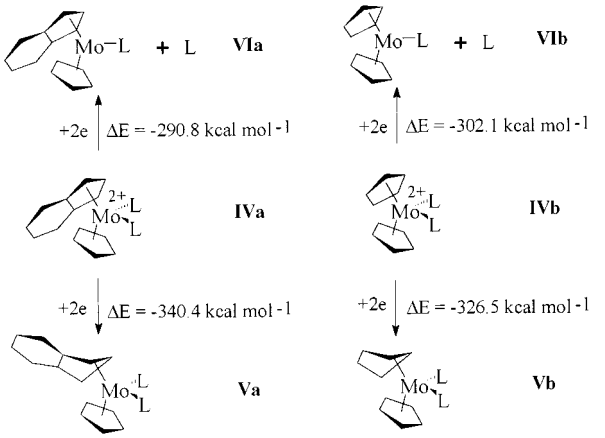


Scheme 8. Side (left) and top (right) views of the structures of complexes **Va** and **IVa**

For the η^3-Ind derivative, the ring is slipped away from the two L (phosphite) ligands and lies trans to them. The folding is plainly seen. The change of coordination to η^5 results in a planar ligand, so that the Ind ring approaches the Cp ring. Steric repulsion forces a rotation of the ring. This change in conformation of the ligand accompanying a change of hapticity has already been observed and analysed in another family of compounds.[17] The distances and angles in the geometries of the calculated complexes are within the range of expected values.

The relative energies of the six species are given in Scheme 9, the energy of **V** being adjusted with the energy of free P(OH)$_3$, as performed previously for the CO series of compounds.

The most striking feature is the similarity of Schemes 7 and 9, at first sight, and the very small difference of energy in the parallel redox processes that form [(η^3-Ind)CpMoL$_2$] and [(η^3-Cp)CpMoL$_2$] from their corresponding cations. A further comparison of these values is found in the Discussion. However, the understanding of the relative stability of the several species involved, namely, the reason why η^3-Ring derivatives are more stable for indenyl than Cp and why carbonyls stabilize η^3-Cp rings, can be traced qualitatively by extended Hückel calculations performed on the same models. The first important aspect when comparing Cp and Ind is that η^5-Cp binds more strongly than η^5-Ind. The calculated bonding energy (DFT calculation) between Cp$^-$ or Ind$^-$ and the CpMo(CO)$^+$ fragment is −237.5 and −221.4 kcal mol^{-1}, respectively. The reason is clearly seen on the molecular orbital diagram of Figure 1, where one compares the binding of each of the two rings to the CpMo(CO)$^+$ fragment.



Scheme 9. Relative DFT energies of P(OH)$_3$ complexes

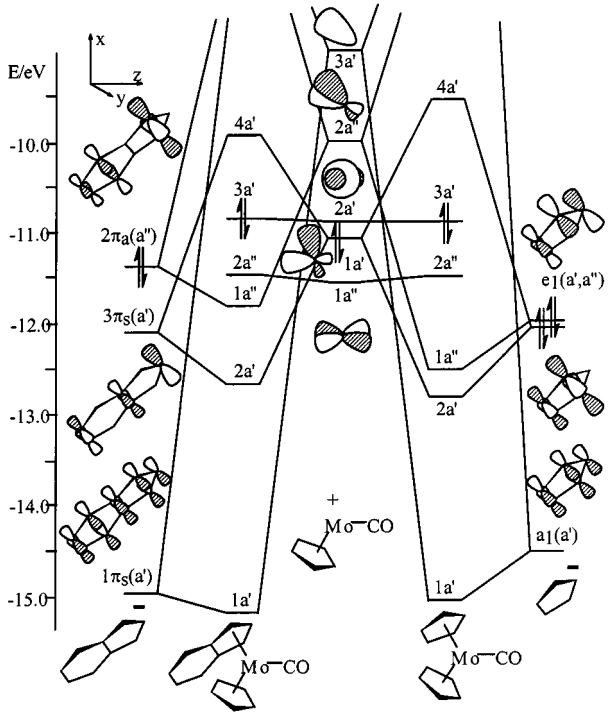
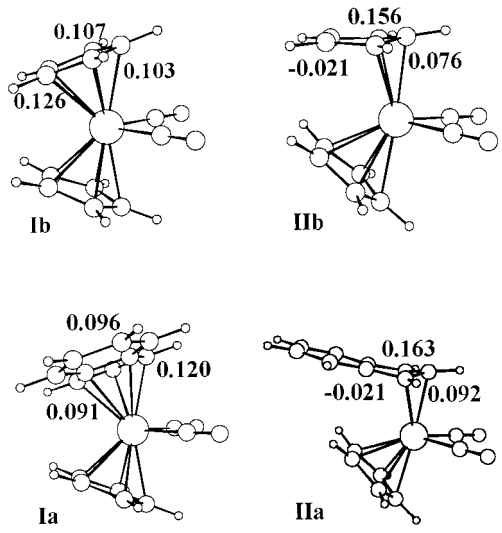


Figure 1. Molecular orbital diagram for the interaction between one η^5-Ind ring (left)/η^5-Cp (right) and the CpMo(CO)$^+$ fragment

Both rings formally donate three pairs of electrons into empty levels of the metal fragment. These electrons come from the lowest energy, totally symmetric a_1, and from the e_1 set in the Cp. The a_1 level is similar for the indenyl (lower energy, owing to the largest number of the carbon atoms and to bonding interactions), but those corresponding to the e_1 set are different, as not all the carbon atoms from the C_5 ring contribute to the orbital, and their contributions are smaller, as sketched on the left side of the drawing and discussed elsewhere.[18] As a result, the overlap between Ind−CpMo(CO) is smaller (0.45) than between Cp−CpMo(CO) (0.58) and the resulting bonding molecular orbitals have higher energies (1a″ is 18.5 kcal mol^{-1} higher and 2a′ is 2.3 kcal mol^{-1} higher for Ind, see diagram in Figure 1).

The same diagram can help us to understand why a η^3-coordination mode is more favorable for the indenyl ring. Upon bending, only three carbon atoms remain coordinated to the metal. For the Cp ring this is an effective loss of overlap, as the five carbon atoms were all strongly bound to the metal, while for the indenyl unit the two hinge atoms, which do not participate in all indenyl π orbitals, are much less affected by this distortion. This can be seen by the Mo−C overlap populations in Scheme 10, where we compare compounds **I** and **II**.



Scheme 10. Mo−C overlap populations (EHMO) in complexes **Ia,b** and **IIa,b**

The overlap populations between fragments lead us to the same conclusion, but in a different way. In fact, the Ring-[CpMo(CO)$_2$] overlap populations are 0.54 for Ring = η^5-Cp, 0.40 for Ring = η^5-Ind, 0.26 for Ring = η^3-Cp, and 0.30 for Ring = η^3-Ind. Another contribution to this behaviour is that the energy required to distort Cp is larger than that needed to distort Ind, as in the latter the orbitals of the resulting benzene ring are much stabilized relative to those of the ethylene formed from Cp. Brintzinger and co-workers attempted to understand these problems,[15c] but the lack of structural information at the time makes the results of their calculations difficult to compare.

When the carbonyl groups are replaced by other ligands, which are not (or are weaker) π-acceptors, the small stabilization provided to the bonding of the η^3-Cp ring by back-donation to the carbonyls is lost, and this explains the much higher energy of the comparable phosphite derivative. Other derivatives become more competitive.

Discussion

[Cp$_2$MoL] complexes are well known for being very electron-rich d^4 species. Their chemistry is, therefore, essentially characterized by oxidative addition reactions to the carbene-like metal fragment, as well as protonation and methylation with Mo−H and Mo−CH$_3$ formation, both of which reflect the nucleophilicity and basicity of the metal centre. Ligand substitution, L for L′, has also been reported for several complexes. Replacement of Cp by indenyl was expected to give 18e complexes with overall analogous reactivity since they would present the same type of high energy metal-based lone pairs. However, the results reported above point to the appearance of a new type of reactivity around [IndCpMoL] complexes. In fact, these complexes failed to be prepared by reductive methods analogous to those employed for [Cp$_2$MoL] and, even under stoichiometries favouring the formation of [IndCpMoL], ring-slipped [(η^3-Ind)CpMoL$_2$] complexes were always observed. The only exceptions were found for the diphenyl acetylene complex, [IndCpMo(η^2-C$_2$Ph$_2$)], *tert*-Butyl isocyanide and phosphite complexes [IndCpMo(CN*t*Bu)] and [IndCpMo(P(OMe)$_3$)], which are formed simultaneously with [(η^3-Ind)CpMo(CN*t*Bu)$_2$] and [(η^3-Ind)CpMo{P(OMe)$_3$], respectively.

These results mean that the metal centre in [IndCpMoL] complexes readily accepts 2e donors according to the Equation (a).

$$[\text{IndCpMoL}] + \text{L} \rightleftharpoons [(\eta^3\text{-Ind})\text{CpMoL}_2] \quad \text{(a)}$$

In this equation the equilibrium seems to be shifted to the right hand side. For all that has been reported in the literature, the similar Equation (b) represents an equilibrium that is, in most cases, shifted to the left hand side.

$$[\text{Cp}_2\text{MoL}] + \text{L} \rightleftharpoons [(\eta^3\text{-Cp})\text{CpMoL}_2] \quad \text{(b)}$$

The only known exception is described in this work for L = CO. In general, these results are normal insofar as they fit in with the well established higher tendency of the indenyl ligand to undergo $\eta^5 \rightarrow \eta^3$ ring slippage when compared with the Cp ligand. However, the term tendency is qualitative and the very fact that there are unpredictable exceptions prompted us to attempt some quantification of the energetics involved in these ring slippages. The results of the

DFT calculations, which are summarized in schemes 7 and 9, can be written according to Equations (c)−(f).

$$[IndCpMo(CO)] + CO \rightleftharpoons [(\eta^3\text{-Ind})CpMo(CO)_2]\ \Delta E_1 = -42.2\ \text{kcal mol}^{-1} \quad (c)$$

$$[Cp_2Mo(CO)] + CO \rightleftharpoons [(\eta^3\text{-Cp})CpMo(CO)_2]\ \Delta E_2 = -26.7\ \text{kcal mol}^{-1} \quad (d)$$

$$[IndCpMo\{P(OH)_3\}] + P(OH)_3 \rightleftharpoons [(\eta^3\text{-Ind})CpMo\{P(OH)_3\}_2]\ \Delta E_3 = -49.6\ \text{kcal mol}^{-1} \quad (e)$$

$$[Cp_2Mo\{P(OH)_3\}] + P(OH)_3 \rightleftharpoons [(\eta^3\text{-Cp})CpMo\{P(OH)_3\}_2]\ \Delta E_4 = -24.4\ \text{kcal mol}^{-1} \quad (f)$$

From these energy differences, the following conclusions may be drawn:

(i) Both the indenyl and cyclopentadienyl ring slippages in Equations (a) and (b) are exothermic, but they are entropically disfavoured association processes (ΔE is negative in all equations).

(ii) The ring slippage of the indenyl complexes is more exothermic than that of the cyclopentadienyl congeners regardless of the nature of the ligand L ($|\Delta E_1| > |\Delta E_2|$; $|\Delta E_3| > |\Delta E_4|$).

(iii) Weaker π-acceptor ligands L favour the ring slippage of indenyl and disfavour the ring slippage of cyclopentadienyl, therefore widening the energy gap between the two similar transformations ($\Delta E_3 - \Delta E_4 = -25.1$ kcal mol^{-1}; $\Delta E_1 - \Delta E_2 = -15.4$ kcal mol^{-1}).

The last conclusion means that CO-containing fragments will level out the differences between indenyl and cyclopentadienyl slippage by facilitating the latter due to orbital stabilization of the η^3-Cp ligand, as shown in the EHMO studies. For the same reasons, indenyl slippages will be favoured in systems carrying weak π-acceptors and/or π-donors where the corresponding Cp slippages become strongly disfavoured. One might then set the value of ca. 15 kcal/mol as the lowest energy difference between a Cp and an indenyl ring slippage on the same fragment when it contains strong π-acceptor ligands. All other ligands will be less favourable for Cp ring slippage. This type of ligand dependence of the ring slippage has been experimentally observed and authenticated by DFT calculations for the reaction according to Equation (g) which takes place for L = NCMe but is thermodynamically forbidden for L = CNMe.[17]

$$[IndMo(CO)_2(L)_2]^+ + NCMe \rightleftharpoons [(\eta^3\text{-Ind})Mo(CO)_2(L)_2(NCMe)]^+ \quad (g)$$

Whereas the result of the second conclusion was largely expected due to the more facile ring slippages of indenyl relative to cylopentadienyl, the result of the first conclusion is not so obvious given the fact that the trihapto coordination of Cp has proven to be very difficult to achieve experimentally. We believe that one of the main difficulties is the need to overcome the entropy factor. The use of redox-induced ring slippage seems to be the most favourable method to achieve difficult ring slippages because it does not involve changes in the number of ligands in the coordination sphere. As a matter of fact, as depicted in Scheme 7, the reductions of the dications **Ia** and **Ib** to give the ring slipped products **IIa** and **IIb**, respectively, differ very little in energy (6.2 kcal mol^{-1}) and allow a simple synthesis of the thermally sensitive $[(\eta^3\text{-Cp})CpMo(CO)_2]$ complex. The mild conditions of the synthesis of $[(\eta^3\text{-Cp})CpW(CO)_2]$ by reduction of $[Cp_2W(CO)Cl]$ under a CO atmosphere (1 atm)[3b] are similar to our conditions and strongly contrast with the 100 atm of CO pressure necessary to prepare it from $[Cp_2W(CO)]$, according to Equation (b).[15b] Related observations were made for CO addition to $[Cp_2Cr(CO)]$.[15d] A classical example is the formation of the $[Ru(\eta^4\text{-}C_6R_6)(\eta^6\text{-}C_6R_6)]$ by reduction of its dicationic precursor $[Ru(\eta^6\text{-}C_6R_6)_2]$,[19a] but there are many other examples of these redox-induced slippages.[2][19] The formation of the ring slipped product **Vb** might appear likely from our calculations, as ΔE_4 is not too different from ΔE_2. The fact that such product has never been detected may be related to kinetic factors.

The examples reported in this work show the remarkable capacity of the $CpMo(CO)_2$ fragment to stabilize rather elusive trihapto-coordinated hydrocarbon ligands like η^3-Cp or the exocyclic-coordination of the fluorenyl ligand in $[(\eta^3\text{-}C_{13}H_9)(Ind)Mo(CO)_2]$.[20] The only examples of a different behaviour were the complexes $[IndCpMo(\eta^2\text{-}C_2Ph_2)]$ and the *tert*-Butyl isocyanide complex [IndCpMo(CN*t*Bu)]. We believe that the formation of the latter is favoured not only by the fact that CN*t*Bu is a good π-acceptor but also because $[(\eta^3\text{-Ind})CpMo(CNtBu)_2]$ is a rather bulky species. On the other hand, the coordination of the acetylene molecule may involve significant oxidative addition as in the analogous $[Cp_2Mo(\eta^2\text{-}C_2Ph_2)]$.[10] In this case the complex may be better considered as a Mo^{IV} species where no ring slippage is expected to occur.

Experimental Section

General: All experiments were carried out under dry nitrogen using Schlenk techniques. Solvents were dried by standard procedures (tetrahydrofuran, diethyl ether, toluene, and pentane over Na/benzophenone ketyl; dichloromethane, and acetonitrile with CaH_2), distilled under argon and kept over 4-Å molecular sieves (3 Å for NCMe). − Microanalyses were performed in our laboratories (ITQB). − ^{1}H NMR spectra were obtained with a Bruker AMX 300 spectrometer. − Infrared spectra were recorded with a Perkin−Elmer 457 and with a Unican Mattson Mod 7000 FTIR spectrophotometer using KBr pellets. − PMe_3,[21] $[(\eta^3\text{Ind})\text{-}CpMo(CO)_2]$, $[Ind(\eta^4C_5H_6)Mo(CO)_2]BF_4$, [IndCpMo(NCMe)-Cl]$BF_4$, $[IndCpMoH_2]$, $[Cp_2Mo(CO)_2][BF_4]_2$,[1] $[Cp_2Mo(P(OMe)_3)_2][BF_4]_2$[22] were prepared as described previously.

Preparation of [IndCpMo(CO)Br]Y (1). − Method (a): Treatment of a solution of $[(\eta^3\text{-Ind})CpMo(CO)_2]$ (0.45 g, 1.35 mmol) in CH_2Cl_2 with $(NBu_4)Br_3$ (0.65 g, 1.35 mmol) led to the immediate formation of a white precipitate of $[IndCpMo(CO)_2][Br]_2$. The mixture was stirred for 15 h and the purple precipitate of [IndCpMo(-CO)Br]Br (**1a**) was filtered off and washed with CH_2Cl_2. Yield: 60%. − **Method (b):** A solution of $[Ind(\eta^4\text{-}C_5H_6)Mo(CO)_2]BF_4$ (0.21 g, 0.50 mmol) in CH_2Cl_2 was treated with $(NBu_4)Br_3$ (0.24 g, 0.50 mmol) and stirred overnight. The violet precipitate of [IndCpMo(CO)Br]BF_4 (**1b**) was separated by filtration in 70% yield

and washed with CH_2Cl_2. – $C_{15}H_{12}Br_2MoO$ (464.01): calcd. C 38.82, H 2.61; found C 38.75, H 2.12. – Selected IR (KBr): $\tilde{\nu}$ = 3077, 2045 (*sv*, CO), 1539, 1413, 946, 856, 760 cm^{-1}. – ^1H NMR ([D_6]acetone, 300 MHz, room temp.): δ = 7.95 (m, 1 H, H^{5-8}), 7.74 (m, 2 H, H^{5-8}), 7.57 (m, 1 H, H^{5-8}), 7.12 (m, 1 H, H^{1-3}), 6.65 (t, 1 H, H^{1-3}), 6.45 (m, 1 H, H^{1-3}), 6.34 (s, 5 H, Cp).

Preparation of [IndCpMo(NCMe)Br]Br (2): A solution of [IndCpMo(CO)Br]Br (0.07 g, 0.15 mmol) in NCMe was refluxed and irradiated with a 60 Watt tungsten bulb for 5 h. The solution was evaporated to dryness and the residue efficiently extracted with CH_2Cl_2. The purple powder was obtained in 90% yield upon evaporation of the solvent. The product was purified by recrystallization from CH_2Cl_2/Et_2O. – $C_{16}H_{15}Br_2MoN$ (477.05): calcd. C 40.28, H 3.17, N 2.94; found C 40.48, H 3.49, N 3.32. – Selected IR (KBr): $\tilde{\nu}$ = 3100, 2317, 2278, 1427, 802, 758 cm^{-1}. – ^1H NMR (CD_3CN, 300 MHz, room temp.): δ = 7.35 [s (br), 4 H, H^{5-8}], 5.98 (t, 1 H, H^2), 5.83 (d, 2 H, $H^{1/3}$), 5.33 (s, 5 H, Cp), 2.12 (s, 3 H, CH_3).

Preparation of [IndCpMo(CNCMe$_3$)X]Y (3). – Method (a): A solution of [IndCpMo(NCMe)Br]Br (0.11 g, 0.23 mmol) in CH_2Cl_2 was treated with excess CN*t*Bu (0.25 mL) and refluxed overnight. The solution was evaporated to dryness to afford the grey complex [IndCpMo(CNCMe$_3$)Br]Br (**3a**) in 80% yield. This was recrystallized from CH_2Cl_2/Et_2O. – $C_{28}H_{39}Br_2MoN$ (645.38): calcd. C 52.11, H 6.09, N 2.17; found C 52.44, H 6.17, N 2.60. – Selected IR (KBr): $\tilde{\nu}$ = 3102, 2982, 2191, 1449, 1373, 1194, 1084, 845, 764 cm^{-1}. – ^1H NMR (CD_3CN, 300 MHz, room temp.): δ = 7.69–7.67 (m, 1 H, H^{5-8}), 7.56–7.54 (m, 2 H, H^{5-8}), 7.47–7.43 (m, 1 H, H^{5-8}), 6.02 (t, 1 H, H^{1-3}), 5.92 (t, 1 H, H^{1-3}), 5.75 [s (br), 1 H, H^{1-3}], 5.58 (s, 5 H, Cp), 1.60 (s, 9 H, CH_3). – **Method (b):** Treatment of a solution of [IndCpMo(NCMe)Cl]BF_4 (0.18 g, 0.40 mmol) in CH_2Cl_2 with excess CN*t*Bu (0.14 mL) at room temperature led to an immediate color change from green to dark violet. After stirring for 4 h the reaction mixture was concentrated to ca. 5 mL and Et_2O was added and caused the precipitation of the grey-violet complex [IndCpMo(CNCMe$_3$)Cl]BF_4 (**3b**), which was recrystallized from CH_2Cl_2/Et_2O in 85% yield. – $C_{19}H_{21}BClF_4MoN$ (481.58): calcd. C 47.39, H 4.40, N 2.91; found C 47.48, H 4.25, N 3.41. – Selected IR (KBr): $\tilde{\nu}$ = 3095, 2982, 2193, 1449, 1373, 1194, 1084, 845, 764 cm^{-1}. – ^1H NMR ([D_6]acetone, 300 MHz, room temp.): δ = 7.89 (d, 1 H, H^{5-8}), 7.70–7.54 (m, 2 H, H^{5-8}), 7.40 (d, 1 H, H^{5-8}), 6.22 [s (br), 1 H, H^{1-3}], 5.97 (s, 1 H, H^{1-3}), 5.83 [s (br), 1 H, H^{1-3}], 5.79 (s, 5 H, Cp), 1.68 (s, 9 H, CH_3).

Preparation of [IndCpMo(P(OMe)$_3$)Br]Br (4): A solution of [IndCpMo(NCMe)Br]Br (0.21 g, 0.43 mmol) in CH_2Cl_2 was treated with excess $P(OMe)_3$ (2.5 mL) and refluxed for 4 h. The solution was evaporated to dryness to afford the complex in 80% yield. The complex was recrystallized from CH_2Cl_2/Et_2O. – $C_{17}H_{21}Br_2MoO_3P$ (560.08): calcd. C 36.46, H 3.78; found C 36.65, H 3.49. – Selected IR (KBr): $\tilde{\nu}$ = 3082, 2942, 1425, 1541, 1134, 1042, 716 cm^{-1}. – ^1H NMR (CD_2Cl_2, 300 MHz, room temp.): δ = 7.45 (d, 1 H, H^{5-8}), 7.36–7.27 (m, 2 H, H^{5-8}), 7.21 (d, 1 H, H^{5-8}), 6.08 (m, 1 H, H^{1-3}), 5.72 (d, 1 H, H^{1-3}), 5.01 (t, 5 H, Cp), 4.50 [s (br), 1 H, H^{1-3}], 3.67 {d, 9 H, $P(OMe)_3$, [J_{PH} = 9.0 Hz]}.

Attempted Preparation of [IndCpMo(PMe$_3$)Br]Br: A solution of [IndCpMo(NCMe)Br]Br (0.20 g, 0.42 mmol) in CH_2Cl_2 was treated with excess PMe_3 (0.15 mL) and stirred for 3 h at room temperature. The pink precipitate of [IndCpMo(PMe$_3$)$_2$]Br_2 was filtered off and washed with CH_2Cl_2. Yield: 50%. – $C_{20}H_{30}Br_2MoP_2$ (588.16): calcd. C 39.91, H 5.02; found C 39.74, H 5.52. – Selected IR (KBr): $\tilde{\nu}$ = 3366, 3092, 2912, 1423, 1300, 965, 845, 779 cm^{-1}. – ^1H NMR (CD_3CN, 300 MHz, room temp.): δ = 7.72–7.68 (m, 4 H, H^{5-8}), 6.09 (m, 2 H, $H^{1/3}$), 5.48 (t, 1 H, H^2), 5.17 (t, 5 H, Cp, [$^3J_{PH}$ = 2.1 Hz]), 1.66–1.62 (t, 18 H, CH_3).

Preparation of Complexes [(η^3-Ind)CpMoL$_2$] (5–9): A suspension of [IndCpMo(L)Br]Br (L = **5**, CO; **6** to **9**, NCMe) in toluene (or NCMe) was treated with a solution of Cp_2Co (2 equiv.) in the same solvent at 0°C. Addition of the ligand (1 or 2 mol) caused an immediate change and after 2 h stirring at room temperature the solution was separated from [Cp_2Co]Br by filtration. The solvent was removed under vacuum and the residue extracted with Et_2O (3 × 30 mL). The product, which separated upon concentration and cooling of the extract, was identified by comparison of its IR and ^1H-NMR spectra with those of an authentic sample.[1,2,11]

Preparation of [(η^3-Ind)CpMo(CO)$_2$] (5): [IndCpMo(CO)Br]Br: 0.30 g, 0.65 mmol; Cp_2Co: 0.24 g, 1.29 mmol. Light protection. Purple microcrystalline complex (η^3-Ind)$CpMo(CO)_2$. Yield: 40%.

Preparation of [(η^3-Ind)CpMo(dppe)] (6): [IndCpMo(NCMe)Br]Br: 0.20 g, 0.42 mmol; Cp_2Co: 0.16 g, 0.84 mmol; dppe: 0.17 g, 0.42 mmol. Orange complex. Yield: 80%.

Preparation of [(η^3-Ind)CpMo(PMe$_3$)$_2$] (7). – (a) [IndCpMo(NCMe)Br]Br: 0.21 g, 0.44 mmol; Cp_2Co: 0.16 g, 0.87 mmol; PMe_3: 0.087 mL, 0.87 mmol. Orange complex. Yield, 90%. – **(b)** [IndCpMo(NCMe)Br]Br: 0.21 g, 0.44 mmol; Cp_2Co: 0.16 g, 0.87 mmol; PMe_3: 0.044 mL, 0.44 mmol. Orange complex. Yield: 45%.

Preparation of [(η^3-Ind)CpMo(P(OMe)$_3$)$_2$] (8). – (a) [IndCpMo(NCMe)Br]Br: 0.359 g, 0.752 mmol; Cp_2Co: 0.285 g, 1.504 mmol; $P(OMe)_3$: 2.5 mL, excess. Orange complex. Yield, 80%. – **(b)** [IndCpMo(NCMe)Br]Br: 0.179 g, 0.374 mmol; Cp_2Co: 0.142 g, 0.748 mmol; $P(OMe)_3$: 44 μL, 0.374 mmol. Orange complex. Yield: 40%.

Preparation of [(η^3-Ind)CpMo(CNCMe$_3$)$_2$] (9). – (a) [IndCpMo(NCMe)Br]Br: 0.27 g, 0.35 mmol; Cp_2Co: 0.13 g, 0.70 mmol; CN*t*Bu: 0.10 mL, excess. Reaction solvent: NCMe. Orange complex. Yield, 50%. – **(b)** [IndCpMo(NCMe)Br]Br: 0.27 g, 0.35 mmol; Cp_2Co: 0.13 g, 0.70 mmol; CN*t*Bu: 0.039 mL, 0.35 mmol. Reaction solvent: NCMe. Orange complex. Yield, 30%.

Preparation of [(η^5-Ind)CpMo(η^2-PhCCPh)] (10): A suspension of [IndCpMo(NCMe)Br]Br (0.20 g, 0.42 mmol) in toluene was treated with a solution of Cp_2Co (0.16 g, 0.84 mmol) in the same solvent at 0°C. Addition of DPA (0.075 mL, 0.42 mmol) caused an immediate change and after 2 h stirring at room temperature the solution was separated from [Cp_2Co]Br by filtration. The solvent was removed under vacuum and the residue extracted with Et_2O (3 × 30 mL). The garnet-like complex separated upon concentration and cooling of the extract to give 80% yield. – $C_{28}H_{22}Mo$ (454.43): calcd. C 74.01, H 4.88; found C 74.40, H 4.90. – Selected IR (KBr): $\tilde{\nu}$ = 3505, 3067, 1580, 1486, 1414, 1261, 824, 756 cm^{-1}. – ^1H NMR (C_6D_6, 300 MHz, room temp.): δ = 7.69 (d, Ph), 7.52–7.49 (m, Ph), 7.32 (t, Ph), 6.99–6.97 (m, Ph), 6.93–6.90 (m, 2 H, H^{5-8}), 6.75–6.72 (m, 2 H, H^{5-8}), 5.53 (t, 1 H, H^2), 4.21 (s, 5 H, Cp), 3.85 (d, 2 H, $H^{1/3}$).

Attempted Ppreparation of [(η^5-Ind)CpMoL] (11, 12) by Reduction of [IndCpMo(L)Br]Br: Treatment of a solution of [IndCpMo(L)Br]Br [L = $P(OMe)_3$, $CNCMe_3$] in NCMe with a solution of Cp_2Co (2 equiv.) in the same solvent, at 0°C, caused an immediate change. After 2 h stirring at room temperature the solvent was removed under vacuum and the residue extracted with toluene (3 × 30 mL). Upon evaporation of the solvent and washing of the residue with cold pentane, a mixture of two complexes, [(η^3-Ind)$CpMoL_2$] and [(η^5-Ind)CpMoL], was obtained. The previously

reported complexes [(η^3-Ind)CpMoL$_2$] were identified by comparison of the IR and ^{1}H-NMR spectra of the mixture with those of an authentic sample.[2][11]

Attempted Isolation of [(η^5-Ind)CpMo(P(OMe)$_3$)] (11): [IndCpMo{P(OMe)$_3$}Br]Br: 0.07 g, 0.125 mmol; Cp_2Co: 0.045 g, 0.25 mmol. Orange powder (mixture of two complexes). − Selected IR (KBr) $\tilde{\nu}$ = 3104, 2944, 1417, 1109, 1044, 1012, 808, 717 cm^{-1}. − ^{1}H NMR (C_6D_6, 300 MHz, room temp.); [(η^5-Ind)CpMo{P(OMe)$_3$}]: δ = 7.33−7.26 (m, 2 H, H$^{5-8}$), 7.06−7.00 (m, 2 H, H$^{5-8}$), 5.85 [t (br), 1 H, H^2], 5.71 (m, 2 H, H$^{1/3}$), 4.23 (d, 5 H, Cp, [J_{PH} = 1.8 Hz]), 3.76 {d, 9 H, P(OMe)$_3$, [J_{PH} = 10.8 Hz]}. − [(η^3-Ind)CpMo{P(OMe)$_3$}$_2$]: δ = 6.57−6.50 (m, 4 H, H$^{5-8}$), 4.58 (t, 5 H, Cp, [J_{PH} = 1.8 Hz]), 3.90−3.87 (m, 3 H, H$^{1-3}$), 3.24 {t, 18 H, P(OMe)$_3$, [J_{PH} = 10.8 Hz]}.

Attempted Isolation of [(η^5-Ind)CpMo(CNCMe$_3$)] (12): [IndCpMo(CNCMe$_3$)Br]Br: 0.09 g, 0.14 mmol; Cp_2Co: 0.052 g, 0.28 mmol; orange powder (mixture of two complexes). − Selected IR (KBr); [(η^5-Ind)CpMo(CNCMe$_3$)]: $\tilde{\nu}$ = 2934, 1934, 1728, 1456, 1198, 1036, 800, 737 cm^{-1}. − ^{1}H NMR (C_6D_6, 300 MHz, room temp.); [(η^5-Ind)CpMo(CNCMe$_3$)]: δ = 7.64−7.61 (m, 2 H, H$^{5-8}$), 6.93−6.90 (m, 2 H, H$^{5-8}$), 5.84 [s (br), 1 H, H^2], 5.65 [s (br), 2 H, H$^{1/3}$], 5.11 (s, 5 H, Cp), 1.22 (s, 9 H, CH_3). − [(η^3-Ind)CpMo(CNCMe$_3$)$_2$]: δ = 6.81 (t, 1 H, H^2), 6.64−6.61 (m, 2 H, H$^{5-8}$), 6.51−6.48 (m, 2 H, H$^{5-8}$), 4.80 (s, 5 H, Cp), 4.41 (d, 1 H, H$^{1/3}$), 1.04 (s, 18 H, CH_3).

Preparation of [(η^3-C_5H_5)CpMo(CO)$_2$] (13): A suspension of [Cp_2Mo(CO)$_2$][BF_4]$_2$ (0.27 g, 0.60 mmol) in toluene was treated with a solution of Cp_2Co (0.23 g, 1.21 mmol) in the same solvent at 0°C. After 3 h stirring at room temperature the solution was separated from [Cp_2Co]Br by filtration. The solvent was removed under vacuum and the residue extracted with hexane (3 × 30 mL). The green powder that separated upon concentration and cooling of the extract was identified by comparison of its IR and ^{1}H-NMR spectra with those of an authentic sample.[1] Yield, 80%.

Preparation of [Cp_2Mo(P(OMe)$_3$)] (14): A suspension of [Cp_2Mo{P(OMe)$_3$}$_2$][BF_4]$_2$ (0.34 g, 0.53 mmol) in NCMe was treated with a solution of Cp_2Co (0.23 g, 1.21 mmol) in the same solvent at 0°C. After 3 h stirring at room temperature the solvent was removed under vacuum and the residue extracted with Et_2O (3 × 30 mL). The brown powder was separated upon evaporation of the solvent. Yield: 30%. − $C_{13}H_{19}MoO_3P$ (350.21): calcd. C 44.59, H 5.47; found C 44.40, H 5.50. − Selected IR (KBr): $\tilde{\nu}$ = 3104, 2926, 1416, 1036, 866 cm^{-1}. − ^{1}H NMR (C_6D_6, 300 MHz, room temp.): δ = 4.14 (d, 10 H, Cp, [J_{PH} = 4.8 Hz]), 3.29 {t, 9 H, P(OMe)$_3$, [J_{PH} = 5.7 Hz]}.

Preparation of [Cp_2Mo(CNCMe$_3$)$_2$][BF_4]$_2$ (15): A solution of [Cp_2Mo(NCMe)$_2$][BF_4]$_2$ (0.34 g, 0.71 mmol) in CH_2Cl_2/NMF (2:1) was treated with excess CN*t*Bu (0.50 mL) and refluxed overnight. The solution was concentrated under vacuum (until the only remaining solvent was NMF) and Et_2O/EtOH (30:1) was added to precipitate the yellow complex. The compound was washed with CH_2Cl_2. Yield: 90%. − $C_{20}H_{28}B_2F_8MoN_2$ (566.01): calcd. C 42.44, H 4.99, N 4.95; found C 42.35, H 5.22, N 4.42. − Selected IR (KBr): $\tilde{\nu}$ = 3119, 3047, 2992, 2226, 2114, 1417, 1377, 1204, 1065, 872 cm^{-1}. − ^{1}H NMR (CD_3CN, 300 MHz, room temp.): δ = 5.92 (s, 10 H, Cp), 1.55 (s, 18 H, CH_3).

Molecular Orbital Calculations. − Extended Hückel Calculations: EH calculations were performed using the ICON8 program[23a,b] with modified H_{ij} values.[23c] The basis set for the metal atoms consisted of *n*s, *n*p and (*n* − 1)d orbitals. The s and p orbitals were described by single Slater-type wave functions, and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions. The parameters used for Mo were [H_{ii} (eV), ζ]: 5s −8.77, 1.960; 5p −5.60, 1.900; 4d −11.06, 4.542, 1.901 (ζ_2), 0.5899 (C_1), 0.5899 (C_2). Standard parameters were used for other atoms. − The calculations were performed on model complexes with idealised geometries taken from the real structures quoted along the text. Thus, [(η^m-Ind)CpMo(CO)$_2$]$^{n+}$ (*m* = 3, *n* = 0 or *m* = 5, *n* = 2) and [(η^3-Cp)CpMo(CO)$_2$] complexes have a distorted tetrahedral geometry with C_s symmetry and Cp/Ind−Mo−Cp and CO−Mo−CO angles of 140° and 80°, respectively. The bis(η^5-Cp) model, [Cp_2Mo(CO)$_2$]$^{2+}$, has C_{2v} symmetry and the same L−Mo−L angles as mentioned above. The trihapto coordination mode of the indenyl and Cp ligands was accomplished by a 30° folding of those ligands. The mono-carbonyl models, [(Ind/Cp)CpMo(CO)], have a Cp/Ind−Mo−Cp angle of 140°, their symmetries being C_s for the Ind complex and C_{2v} for the Cp species. The bond lengths (Å) were as follows: M−(C_5 ring centroid) 2.00, M−C(CO) 2.00, C−O 1.15, C−C 1.40, C−H 1.08. − **DFT Calculations:** Density functional calculations[14] were carried out on model compounds based on the structures of the complexes described in the text, under C_s symmetry or no symmetry, using the Amsterdam Density Functional (ADF) program[24] developed by Baerends and co-workers.[25] The slipping, folding and position of the cyclopentadienyl and indenyl rings, the Mo−C(CO) distance and position of the carbonyl groups were optimized for the six carbonyl complexes. A full optimization was performed for the six phosphite complexes, using P(OH)$_3$ as a model for P(OMe)$_3$. Vosko, Wilk, and Nusair′s local exchange correlation potential was used,[26] with Becke′s nonlocal exchange[27] and Perdew′s correlation corrections.[28] The geometry optimization procedure was based on the method developed by Versluis and Ziegler,[29] using the nonlocal correction terms in the calculation of the gradients. The core orbitals were frozen for Mo ([1−4]s, [1−4]p, 3d) and C, N, O (1s), P (1s, 2s, 2p). Triple-ζ Slater-type orbitals (STO) were used for H 1s; C, N, O 2s and 2p; P 3s and 3p; Mo 5s, 5p, and 4d. One polarization function was added for H, C, N, O, and P.

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