Exocyclic Coordination of the η^3-Fluorenyl Anion: Experimental and Theoretical Study

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Summary: The novel (η^5-Ind)Mo(η^3-Flu)(CO)$_2$ (Ind = indenyl, C_9H_7; Flu = fluorenyl, $C_{13}H_9$) can be readily prepared from (η^5-Ind)MoCl$_3$(CO)$_2$ and LiFlu in toluene (90% yield). X-ray crystallographic studies show an exocyclic η^3 coordination for the fluorenyl ligand, which is also predicted from dft calculations.

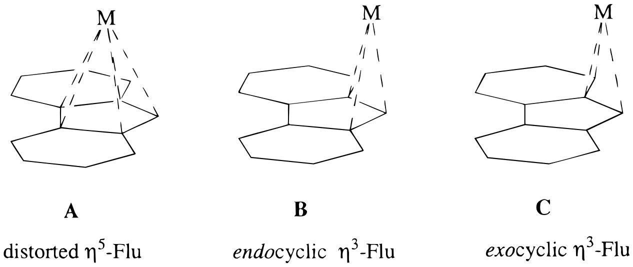
The ring-slippage of coordinated cyclic polyenic ligands is an established process whereby the central metal is able to adjust its electron count in response to some variation brought about by a redox process or a change of the number of ancillary ligands (loss or gain) in its coordination sphere.[1]

The simple cyclopentadienyl (Cp) ligand is rarely observed to coordinate in a η^3-Cp fashion to avoid losing its aromaticity. However, in the more extended π-systems such as indenyl (Ind) or fluorenyl (Flu) the ring-slippage processes become more facile mainly because some of these hapticity changes produce localized aromatic rings. Therefore, a significant number of η^3-Ind complexes have been characterized.[2]

The instability of many π-fluorenyl complexes in the presence of donor ligands and solvents has been attributed to the easy ring-slippage reactions of these complexes. However, the structure of different types of ring-slipped fluorenyl compounds is rather limited. The overwhelming majority of the examples characterized so far present either η^5or η^1 hapticities. In many cases the η^5-Flu coordination is sufficiently distorted to be taken as almost η^3-Flu since two carbons of the coordinated C5 ring are significantly further away from the metal than the other three, as depicted in **A** of Scheme 1.

A detailed observation of this kind of distortion in Flu$_2$ZrCl$_2$ suggests that it originates from stereochemical reasons.[3] In the limit this type of distortion leads to the η^3-Flu coordination mode **B**, where coordination takes place within the C5 ring of the Flu ligand like in the Cp and Ind cases. Structure **C**, represents another possibility of achieving the η^3-Flu coordination. One of the benzene rings regains aromaticity, and therefore, such a structure might be energetically favored.

Scheme 1



distorted η^5-Flu *endo*cyclic η^3-Flu *exo*cyclic η^3-Flu

Studies on the PEt$_3$-catalyzed isomerization of (η^6-Flu)Mn(CO)$_3$ to (η^5-Flu)Mn(CO)$_3$ reinforced the evidence favoring the exocyclic intermediate (or transition state), as already proposed by Basolo.[4] In 1989 the group of Jolly reported the compound Mo(η^3-Flu)(η^3-C$_3$H$_5$)$_3$, which, however, is so distorted as to be described as Mo(η^1-Flu)(η^3-C$_3$H$_5$)$_3$ in the CSD files.[5] Green and Bochmann[6,7] characterized the two ansa complexes [{Me$_2$C(η^5-C$_5$H$_4$)-(η^3-C$_{13}$H$_8$)}Zr(η^5-C$_5$H$_5$)Cl] and [Me$_2$C(C$_5$H$_4$)(η^3-C$_{13}$H$_8$)Zr(μ-H)Cl]$_2$Zr with *exo*cyclic η^3-Flu ligands. However, both complexes are sterically very crowded and distorted by the presence of the ansa-bridge and the bulky substituents. In both cases, the exocyclic coordination of the

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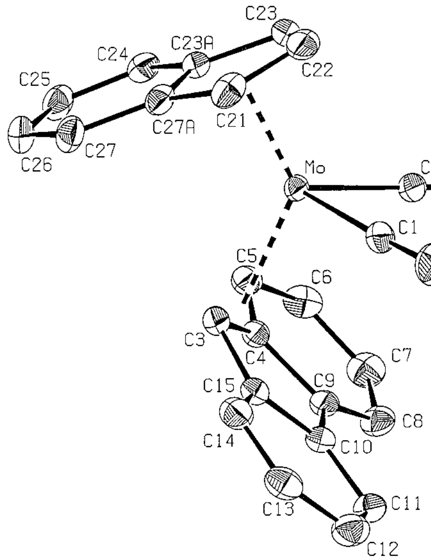

Figure 1. ORTEP drawing of the molecular structure of **1**. Thermal ellipsoids are at the 50% probability level. Selected bond lengths [pm] and angles [deg]: Mo−C1 194.6(2), Mo−C2 196.4(2), Mo−C3 233.4(2), Mo−C4 236.8(2), Mo−C5 249.7(2), Mo−C21 230.2(2), Mo−C22 230.3(2), Mo−C23 233.5(3), Mo−C23A 245.6(2), Mo−C27A 244.4(2); C1−Mo−C2 77.85(8), Mo−C1−O1 176.8(2), Mo−C2−O2 177.9(2), C3−C4−C5 129.0(2), C3−C15−C14 130.5(2), Flu−Mo−Ind 129.0.

fluorenyl may be easily interpreted as a way of relieving the stereochemical pressure around the metal.

The attempts to obtain a (η^3-ring)Mn(CO)$_3$(PEt$_3$) (ring = $C_{15}H_9^-$, cpp; $C_{13}H_9^-$, Flu) complex by PEt$_3$ addition to (η^5-ring)Mn(CO)$_3$ led only to (η^1-ring)Mn(CO)$_3$(PEt$_3$)$_2$ complexes.[3,8]

Our previous studies have shown that the 15e fragment CpM(CO)$_2$ is particularly suitable to stabilize trihapto C5 polyenyls such as the indenyl, e.g., CpMo(η^3-Ind)(CO)$_2$, and the more elusive η^3-Cp, e.g., (η^3-Cp)(η^5-Cp)M(CO)$_2$ (M = Mo, W).[2] This prompted us to attempt to use this versatile fragment to produce sterically unperturbed examples of η^3-Flu coordination.

Following a recently found reaction method,[2c] IndMoCl$_3$(CO)$_2$ was treated with LiFlu to give (η^5-Ind)Mo(η^3-Flu)(CO)$_2$ in 90% yield. The reaction was carried out in toluene, and the compound recrystallized from a toluene/hexane mixture.[2e] It decomposes in donor solvents such as NCMe or THF. The results of the X-ray crystal structure determination are depicted in Figure 1.[9]

The crystal structure consists of discrete monomeric units. Distances and angles around the central metal atom are in very good agreement with the data reported in the literature for another six structurally characterized allyl compounds of the general formula (η^5-Ind)Mo(η^3-allyl)(CO)$_2$.[10] The observed values for the ring-slippage parameters of the indenyl ligand are typical for η^5-coordination.[10a,11] The intramolecular interactions between H31 and C27 (275(3) pm) and between H51 and C24 (272(3) pm) are short but may be considered to lie in the range of the intramolecular H-bonding distances to aromatic rings.[12]

The ^{1}H NMR in C_6D_6 is entirely consistent with the solid-state structure revealing no fluxionality at room temperature. Upon warming to 50 °C the signals at δ 5.54 and 3.45 start to broaden due to exchange. Irradiation of the signal at δ 3.45 weakens the signal at δ 7.87 ppm. This is consistent with the exchange between protons H5 and H14, which is caused by the motion of the IndMo(CO)$_2$ fragment between the pseudoallylic positions defined by C5C4C3 and C3C15C14. Warming above 80 °C causes decomposition of the sample. This type of fluxionality was not observed in the more rigid ansa-bridged complexes [{Me$_2$C(η^5-C$_5$H$_4$)(η^3-C$_{13}$H$_8$)}Zr(η^5-C$_5$H$_5$)Cl] and [Me$_2$C(C$_5$H$_4$)(Flu)Zr(μ-H)Cl]$_2$.[6,7]

The unusual coordination mode **C** was therefore confirmed by these data. In contrast to the two other known exocyclic compounds,[6,7] neither ansa-bridging nor important steric crowding force the observed exocyclic bonding.

Dft calculations[13] (ADF program)[14] also showed the exocyclic coordination to be preferred. A geometry optimization was performed starting from (η^5-Ind)(η^5-Flu)Mo(CO)$_2$. In the final geometry, the exocyclic arrangement was found (**1**), the Mo−C distance pattern (Mo−C5 263.7, Mo−C4 237.5, Mo−C3 238.6 pm, for the fluorenyl ring; Mo−C21 232.3, Mo−C22 233.9, Mo−C23 243.0, Mo−C23A 257.9, Mo−C27A 248.2 pm for the indenyl ring) being similar to that found in the experimental structure (see Figure 1). A second geometry optimization, starting from the experimental structure coordinates, led to a similar Mo−C distance distribution (Mo−C5 252.6, Mo−C4 240.0, Mo−C3 237.0 pm, for the fluorenyl ring; Mo−C21 232.8, Mo−C22 231.7, Mo−C23 235.5, Mo−C23A 250.9, Mo−C27A 248.7 pm for the indenyl ring), but differed in the relative indenyl−fluorenyl orientation (**2**), which was the same as found in the X-ray-determined structure (**3**) (Scheme 2). Notice that the Mo−C distances in the C5 ring of the indenyl follow the typical distribution of three shorter + two

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[9] Crystal data and X-ray crystallography for $C_{24}H_{16}MoO_2$, **1**: $M = 432.33$, triclinic, P, $a = 945.25(4)$ pm, $b = 975.94(3)$ pm, $c = 987.60(4)$ pm, $\alpha = 92.739(2)°$, $\beta = 105.477(1)°$, $\gamma = 94.262(2)°$, $V = 873.43(6) \times 10^6$ pm^3; $Z = 2$; $\rho_{calcd} = 1.644$ g cm^{-3}, $F_{000} = 436$, $\mu = 0.77$ mm^{-1}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112653 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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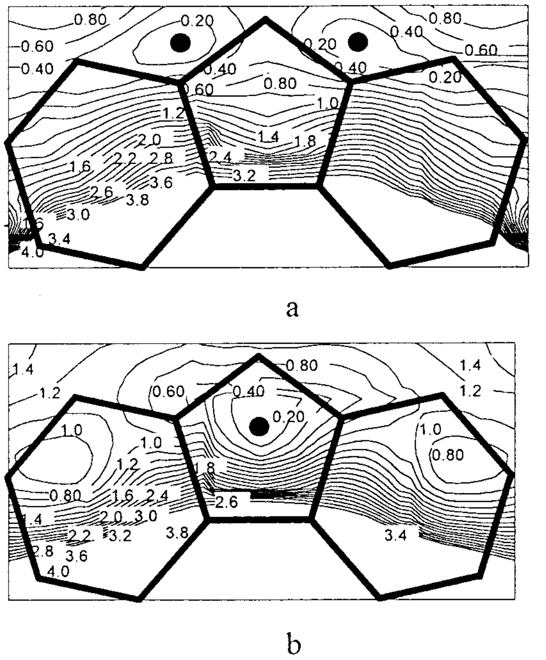


Figure 2. Potencial energy surfaces for the migration of a metal fragment across the fluorenyl ring (minima are given by black circles): (a) $[(\eta^5\text{-Ind})Mo(CO)_2]^+$, (b) $[(\eta^5\text{-Ind})Mo(CO)_2]^{3+}$. The grid used to build the surfaces has 0.5 Å between adjacent points in both directions.

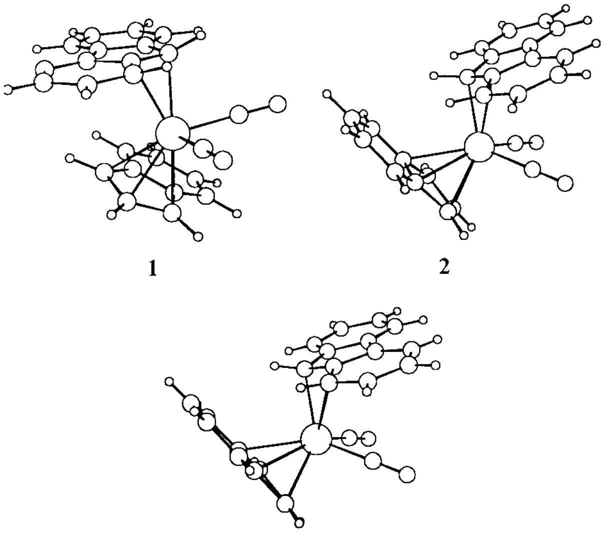
longer bonds.[15] On the other hand, all the Mo−C bonds relative to the fluorenyl ring, except those three mentioned above, are longer than 300 pm. The factors determining the coordination mode are electronic. There are no steric constraints, as also revealed in the X-ray structure (Figure 1).

The energies determined for **1**, **2**, and **3** were respectively −298.888, −299.078, and −289.37 eV, showing that local minima were found. They differ by the relative orientation of the two rings, but always exhibit the same exocyclic coordination mode.

We carried out a similar optimization of the geometry of the controversial $(\eta\text{-Flu})Mo(allyl)_3$[5] using DFT calculations and starting from the coordinates of the X-ray-determined structure. The final geometry exhibits a η^1-fluorenyl ring, showing that this coordination mode is not a consequence of the crystal-packing forces, but is favored even despite the unfavorable 16e count and results from the balance between Mo−fluorenyl interaction and allyl−allyl, allyl−fluorenyl repulsions. The Mo distance to the coordinated carbon atom is 238.8 pm, much shorter than the next Mo−C distance to a fluorenyl carbon (264.9 pm) and comparable to the Mo−C distance to the allyl carbons. The hydrogen attached to the coordinated carbon is located out of the plane of the fluorenyl, both in the X-ray and in the calculated geometry, a fact that is consistent with an sp^3 carbon.

A complementary study was performed using EH calculations.[16] A potential energy surface was calculated for the migration of the $(\eta^5\text{-Ind})Mo(CO)_2$ fragment accross the fluorenyl ring, as in the studies of Albright[1a] and of McGlinchey[8] for other rings, showing a minimum for the η^3-exocyclic coordination of the fluorenyl (Figure 2a). The concentration of lines on the side opposite the favored positions reflects the steric effect of the indenyl ligand coordinated to molybdenum. If two electrons are taken from the complex, the $(\eta^5\text{-Ind})Mo(CO)_2$ migrates to a η^5 coordination in the center of the ring (Figure 2b). To separate the steric from the electronic effect, similar calculations were performed for the migration of the sterically undemanding $Mn(CO)_3$ fragment. The preferred coordinations were η^5-FluMn(CO)$_3$ and exocyclic η^3-Flu for the reduced species $[FluMn(CO)_3]^{2-}$ following the patterns of the Mo complexes shown in Figure 2, parts b and a, respectively. The exocyclic coordination is due to electronic factors. Fluorenyl slips more easily than indenyl, because it binds less strongly to the metal when η.[5] This is shown in the overlap populations between each of the rings and the rest of the molecules: 0.26 for $(\eta^5\text{-Flu})^-$ and $(\eta^3\text{-Ind})Mo(CO)_2{}^+$, and 0.40 for $(\eta^5\text{-Ind})^-$ and $(\eta^3\text{-Flu})Mo(CO)_2{}^+$.

Scheme 2



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In summary we have characterized the otherwise elusive exocyclic η^3-Flu ligand in a situation where coordination is uniquely dependent on electronic factors.

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Supporting Information Available: Synthesis, characterization, theoretical details, and tables of crystal data and the structure determination, positional and displacement parameters, and bond distances and angles for $(\eta^5\text{-Ind})Mo(\eta^3\text{-Flu})(CO)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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