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Indenyl compounds with constrained hapticity: effect of strong intramolecular coordination.

Ondřej Mrózek,[a] Jaromír Vinklárek,[a] Zdeňka Růžičková,[a] and Jan Honzíček*[b]

Abstract: A series of cyclopentadienyl and indenyl molybdenum(II) compounds with intramolecularly coordinated pyridine arm, including scorpionate-like species bearing two irreversibly coordinated arms on indenyl core, was synthesized and characterized. All presented structural types were confirmed by X-ray diffraction analysis. Due to π-basicty of pyridine, the intramolecular interaction is considerably stronger than in case of analogous species bearing tertiary amines in the side chain. Although the starting compounds for syntheses are isostructural, the reaction outcomes differ considerably. The cyclopentadienyl precursor gives a pentacoordinated η5-ChN-compound while the indenyl analogue produces a hexacoordinated species with unprecedented η5-ChN-coordination mode of the indenyl ligand representing an unusual example of so-called indenyl effect. The unusually high stability of η5-ChN-coordination compounds toward η5 to η6 haptotropic rearrangement was clarified by theoretical calculations. As the strong intramolecular interaction prevents rotation of indenyl, it cannot reach a conformation suitable for η6 rearrangement. As a result, the low hapticity is effectively locked.

Introduction

Cyclopentadienyl compounds of the transition metals attract considerable attention since ferrocene, (η5-Cp)2Fe (Cp = C5H5), was discovered in early 1950’s.[1] In the last decade, an increasing number of new ring-substituted cyclopentadienyl compounds has appeared in the literature.[2] The variations in cyclopentadienyl ligand periphery often result in dramatic changes in physical, chemical and biological properties of the corresponding compounds.[3] These changes can be, in particular cases, attributed to electronic and steric effects caused by the partial or full replacement of the hydrogen atoms by other groups.[4] A formal replacement of the cyclopentadienyl ligand with indenyl, a congener with annulated benzene ring (Ind = C9H7), usually accelerates the rates of substitution reactions due to a lower energetic barrier of the haptotropic shift of the ligand. This so-called “indenyl effect” has been initially attributed to enhanced stability of η5-intermediates in the association reaction pathway as a consequence of the aromatic gain of the adjacent six-membered ring.[5] Although this approach is sometimes still accepted, it neglects different thermodynamic stability of η5-Cp and η5-Ind species that may play a crucial role in rearrangement as revealed by Veiros et al.[6] They have demonstrated that the acceleration of associative substitution reactions is a direct consequence of the different bonding of the ligands to the metal in η5 and η6 coordination modes. Hence, (η5-Cp)-M bond is considerably stronger than the (η5-Ind)-M while (η5-Cp)-M is weaker than (η5-Ind)-M bond. This is reflected in higher stability of η5-Cp complexes and η5-Ind intermediates or transition states proving both a thermodynamic and a kinetic origin of the “indenyl effect” in associative reactions. Some other mechanisms of the indenyl effect have been proposed for dissociative processes those are naturally not consistent with η5-η5 rearrangement. The electron deficient intermediate could be stabilized by interaction with six-membered ring.[7] Although nature of the intermediate was not fully clarified, the indenyl ligand could achieve η6-coordination mode that was documented later on low valent zirconium species.[8] When dissociative substitution reaction involves the “spin forbidden” mechanism, the acceleration could be attributed to lower barrier of spin crossover as recently evidenced on iron(II) compounds.[9]

The molybdenum(II) compounds were found to be very suitable for the investigation of η5-η5 rearrangements due to pronounced stability of η5-indenyl species. Hence, they are often accessible from η6-species by simple association of 2e donor into the coordination sphere of molybdenum(II) [10-13] or 2e reduction of molybdenum(IV) compounds.[14] The aim of the present work is to demonstrate the effect of annulated benzene ring on reactivity of cyclopentadienyl molybdenum compounds bearing strong N-donor in the side chain. The unprecedented structural motif consisting of η2-indenyl species with strong intramolecular coordination does NOT undergo usual η2-η5 rearrangement due to kinetic stabilization as evidenced by combined experimental/theoretical study. To best of our knowledge, this is the first example of “locking” the species in η3-coordination mode by intramolecular coordination.

Results and Discussion

Synthesis of allyl molybdenum precursors
The starting (2-pyridyl)methyl-substituted congeners of [(η5-C5H5)(η5-Cp)M(CO)3] (Cp = Cp, Ind) were prepared using a general procedure developed by Faller et al.[15] Functionalized cyclopentadiene C2H5NCH2C5H5 (3) and indene 3-
(C$_5$H$_4$NCH$_2$)$_2$C$_9$H$_7$ (4), necessary for the assembly, were synthesized using reaction of freshly distilled 2-(chloromethyl)pyridine with sodium cyclopentadienide (1-Na) and sodium indenide (2-Na), respectively (Scheme 1).

The indene 4 was further used for synthesis of isotopically substituted derivative 1-D-3-(C$_5$H$_4$NCH$_2$)$_2$C$_9$H$_7$ (4-D) and 1,3-disubstituted indene 1,3-(C$_5$H$_4$NCH$_2$)$_2$C$_9$H$_7$ (5), see Scheme 2. $^1$H and $^{13}$C($^1$H) NMR spectroscopic measurements reveal that the compound 3 forms a mixture tautomers. At room temperature, 1- and 2-isomer appear in molar ratio 1.2 : 1. In case of compound 4, only one tautomer was detected after the distillation purification step. The analytically pure sample of 1,3-disubstituted indene 5 was obtained after chromatographic purification step. The obtained sample was not contaminated with 1,1-isomer (expected side product) as evidenced by NMR measurements but its appearance in the product crude is not fully disproved. In case of 4-D, the efficiency of labeling was verified by $^1$H NMR spectroscopy. The spectrum reveals that one hydrogen atom on $sp^3$ carbon of indene framework is fully substituted with deuterium.

Lithium cyclopentadienide 3-Li, prepared by deprotonation of cyclopentadienes 3 with n-ButLi, react with chloride complex [(η$^5$-C$_5$H$_5$)Mo(CO)$_2$(NMe)$_2$Cl] (6) to give cyclopentadienyl complex [(η$^5$-C$_5$H$_5$)(η$^5$-C$_5$H$_5$NCH$_2$C$_9$H$_7$)Mo(CO)$_2$] (7), see Scheme 3. Indenyl complexes [(η$^5$-C$_5$H$_5$)(η$^5$-1-(C$_5$H$_4$NCH$_2$)$_2$C$_9$H$_7$)Mo(CO)$_2$] (8), [(η$^5$-C$_5$H$_5$)(η$^5$-1,3-(C$_5$H$_4$NCH$_2$)$_2$C$_9$H$_7$)Mo(CO)$_2$] (9) and isotopically labeled species [(η$^5$-C$_5$H$_5$)(η$^5$-1-(C$_5$H$_4$NCH$_2$)-3-[D]C$_5$H$_5$)Mo(CO)$_2$] (8-[D]) were prepared accordingly starting from indenes 4, 5, and 4-D, respectively.

The alternative route is available for lithium indenide 4-Li. It is given by hydrolithiation reaction of benzofulvene 4' using Super-Hydride. The starting 4' was prepared in medium yield by condensation of indene (2) with 2-pyridinecarboxaldehyde. The $^1$H and $^{13}$C($^1$H) NMR measurements revealed appearance of the less steric hindered E-isomer only. This assignment was confirmed by X-ray diffraction analysis; see Figure 1. The molecule 4' is almost planar structure. The dihedral angle between plane of the benzofulvene moiety and the pyridine ring is 3.72(5)$^\circ$.

Infrared spectrum of the cyclopentadienyl molybdenum compound 7 shows two CO stretching bands at 1927 and 1838 cm$^{-1}$. Higher wavenumbers observed for indenyl derivatives 8 and 9 (~1933 and ~1854 cm$^{-1}$) reflect lower electron density on central metals that is caused by weaker donor properties of the indenyl ligand. Raman spectrum, measured for 9, verifies the assignment of the band at lower frequency to symmetric vibration mode ($\nu_s$) as evident from considerably higher
intensity. $^1$H NMR spectra of the compounds 7–9 reveals presence of two conformers arising from two distinct orientations of the allyl ligand. This behavior is in line with counterparts bearing unsubstituted cyclopentadienyl and indenyl ligands.\[15\]

Deuterium substituted indene 4-D was used for synthesis of molybdenum compound selectively labeled in the position 3 of the indenyl ligand 8-[D]. High efficiency of the labeling (65%) is due to lower acidity of deuterium at the $sp^3$ carbon atom of 4-D when compared corresponding proton.

**Figure 2.** ORTEP drawing of molecule $[\eta^3$-$C_3H_5)(\eta^5$-$C_5H_4NCH_2C_5H_4)Mo(CO)_2]$ present in crystal structure of 7. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level. Only one of two crystallographically independent molecules is shown for clarity.

**Figure 3.** ORTEP drawing of molecule $[\eta^3$-$C_3H_5)(\eta^5$-$1,3-(C_5H_4NCH_2)C_9H_5)Mo(CO)_2]$ present in crystal structure of 9. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

**Table 1.** Geometric parameters of the tetracoordinated molybdenum complexes.$^{[a]}$

<table>
<thead>
<tr>
<th></th>
<th>7$^{[b]}$</th>
<th>7$^{[c]}$</th>
<th>9</th>
</tr>
</thead>
<tbody>
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<td>Mo–Cg(C$_5$)</td>
<td>2.014(3)</td>
<td>2.022(3)</td>
<td>2.027(2)</td>
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<tr>
<td>Mo–Cg(C$_3$)</td>
<td>2.043(6)</td>
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<td>2.048(3)</td>
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<td>Mo–C(CO)</td>
<td>1.966(6)</td>
<td>1.948(6)</td>
<td>1.938(3)</td>
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<tr>
<td>Cg(Cg)–Mo–Cg(C$_5$)</td>
<td>78.2(2)</td>
<td>79.4(2)</td>
<td>80.0(2)</td>
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<tr>
<td>C(CO)–Mo–C(CO)</td>
<td>127.0(4)</td>
<td>127.2(2)</td>
<td>126.9(1)</td>
</tr>
</tbody>
</table>

[a] Distances are given in Å; angles are given in °. [b] Two crystallographically independent molecules in the unit cell.

Structures of molybdenum compounds 7 and 9 were determined by X-ray diffraction analysis. The molecules have a distorted tetrahedral structure with two carbonyl ligand, $\eta^3$-allyl and $\eta^5$-coordinated $\pi$-ligand around molybdenum in the formal oxidation state II. Pyridine arms are not coordinated that obeys the 18-electron rule.$^{[16]}$

**Cyclopentadienyl molybdenum compounds with intramolecular coordination**

Reaction of cyclopentadienyl molybdenum compound 7 with HBF$_4$·Et$_2$O in presence of acetonitrile gives dicationic complex 10 with protonated pyridine arm. In acetonitrile solution, this compound undergoes slow deprotonation that is accompanied by exchange of MeCN ligand with pyridine of the side chain, see Scheme 5. The appeared compound with intramolecularly bonded pyridine arm (11) is inert toward strong acids in presence of coordinating solvents (e.g. HBF$_4$·Et$_2$O/MeCN) that demonstrates high stability of ($\eta^5$:CN-C$_3H_4NCH_2C_5H_4$)Mo$^{\text{II}}$ moiety. Putative intermediate of the deprotonation reaction, $[\eta^5$:C$_3H_4NCH_2C_5H_4)Mo(CO)_2(NCMe)$_2][BF_4]$ was not observed probably due to fast coordination of the pyridine arm that is driven by strong chelating effect.

**Scheme 5.** Reactivity of cyclopentadienyl compound 7. Reagents: a) HBF$_4$·Et$_2$O (2 eq./MeCN), b) acetone.

Infrared and Raman spectra of the compounds 10 and 11 show two CO stretching bands at higher wavelengths than observed.
for allyl precursor 7 that is in line with lower electron density on central metal. Intramolecular coordination of pyridine was easily recognized by $^1$H NMR spectroscopy since the compound 10 is $C_3$ symmetric while the species with coordinated pyridine arm 11 belongs to the point group $C_1$. This decrease of the molecular symmetry is distinct mainly on the pattern of signals assigned to methylene bridge and cyclopentadienyl ring. Hence, magnetically equivalent protons of CH$_2$ group in 10 give one singlet at 4.10 ppm while a quartet AB ($\Delta$$\delta_{AB}$ = 0.09 ppm, $^{2}J$ = 19.8 Hz) at 4.39 ppm was observed for compound 11. Furthermore, the $C_3$-symmetric species 10 gives two pseudo-triplets (AA'BB' spin system) at 5.66 and 5.96 for four protons of cyclopentadienyl ring while lower symmetric compound 11 show four multiplets (ABCD spin system) at 5.19–6.65 ppm.

The crystal structures of the compounds 10 and 11 were determined by X-ray diffraction analysis (Figs 4 an 5). Both compounds have a distorted square-pyramidal structure with $\eta^5$-bonded cyclopentadienyl ligand in the apical position and two carbonyls in adjacent vertices of the basal plane. In 10, two acetonitrile ligands occupy the remaining vertices of the basal plane. In case of 11, these two positions are occupied with acetonitrile ligand and intramolecularly bonded pyridine. Bond distance Mo–N [2.229(4)–2.238(4) Å] is considerably shorter than reported for species bearing intramolecularly coordinated tertiary amine [(η$^5$-NMe$_2$NCH$_2$CH$_2$C$_6$H$_4$)Mo(CO)$_2$I] [2.380(3) Å] [17] but comparable with more nucleophilic primary amine [(η$^5$-N$_2$NCH$_2$CH$_2$C$_6$H$_4$)Mo(CO)$_2$(PPh$_3$)]PF$_6$ [2.254(8) Å]. [18]

Acetonitrile ligand of the compound 11 could be easily exchanged by 2e-ligands such as pyridine of chloride, see Scheme 6. $^1$H NMR spectra of the products 12 and 13 show a pattern consistent with $C_1$ molecular symmetry. Methylene
groups of the intramolecular bridge give quartets AB (12: $\delta$ = 4.55 ppm, $\Delta\delta_{AB}$ = 0.30 ppm, $^2J = 19.8$ Hz; 13: $\delta$ = 4.26 ppm, $\Delta\delta_{AB}$ = 0.06 ppm, $^2J = 19.8$ Hz) that is typical for rigid low-symmetric compounds. Protons of cyclopentadienyl ring appear as four multiplets of the ABCD spin system.

Infrared and Raman spectra of the neutral chloride complex 13 show the CO stretching bands at considerably lower wavenumbers than cationic analogues bearing acetonitrile (11) or pyridine ligand (12). It is due to higher electron density on metal that enhances back donation into $\pi$-orbitals of carbonyl ligands.

Structures of 12 and 13, elucidated by analytical and spectroscopic measurements, were further verified by X-ray diffraction analysis (Figs. 6 and 7). In case of 12, the bond distance between molybdenum atom and nitrogen of the pyridine ligand [Mo–N2 = 2.230(3) Å] is very similar to intramolecularly coordinated pyridine arm [Mo–N2 = 2.256(3) Å]. Evidently, the chelate effect on the bond distance Mo–N1 is here compensated with weaker trans effect of the carbonyl ligands [N1–Mo–C13 = 150.1(2)$^\circ$, N2–Mo–C12 = 104.9(2)$^\circ$].

The compounds 12 and 13 are inert toward excess of pyridine and [Me4N]Cl, respectively. It suggests considerably stronger intramolecular interaction than recently reported for analogues with tertiary amines connected to cyclopentadienyl ring via ethylene bridge. Due to $\pi$-basicity of pyridine, the ($\eta^5$-N,N-C5H4NCH2C5H4)MoII moiety of 11 is not disrupted by strong N,N-chelators (e.g., bpy, phen). We note that tertiary amine-functionalized analogues give under similar conditions solely species without intramolecular interaction [($\eta^5$-R2NCH2CH2C5H4)Mo(CO)2(phen)][BF4].

### Table 2. Geometric parameters of the pentacoordinated molybdenum complexes

<table>
<thead>
<tr>
<th></th>
<th>10$^{[b]}$</th>
<th>11$^{[b]}$</th>
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<th>12$^{[a]}$</th>
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<td>Mo–Cg(C5)</td>
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<td>1.981(1)</td>
<td>1.985(3)</td>
<td>1.9767(3)</td>
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<td>Mo–C(CO)</td>
<td>1.981(4)</td>
<td>1.999(4)</td>
<td>2.017(4)</td>
<td>2.009(4)</td>
<td>2.028(4)</td>
<td>1.942(2)</td>
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<td>Mo–N1</td>
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<td>1.942(4)</td>
<td>1.954(4)</td>
<td>1.947(4)</td>
<td>1.924(4)</td>
<td>1.993(9)</td>
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<tr>
<td>Mo–X$^{[d]}$</td>
<td>2.165(3)</td>
<td>2.156(3)</td>
<td>2.150(3)</td>
<td>2.155(3)</td>
<td>2.230(3)</td>
<td>2.4910(4)</td>
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<tr>
<td>C(CO)–Mo–C(CO)</td>
<td>74.6(2)</td>
<td>76.3(2)</td>
<td>77.7(2)</td>
<td>75.8(2)</td>
<td>78.8(2)</td>
<td>77.3(1)</td>
</tr>
<tr>
<td>X–Mo–N$^{[d]}$</td>
<td>78.4(2)</td>
<td>77.9(2)</td>
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<td>78.85(4)</td>
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<tr>
<td>$\alpha^{[d]}$</td>
<td>0.3(3)</td>
<td>3.0(3)</td>
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<td>1.1(3)</td>
<td>8.3(2)</td>
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<tr>
<td>$\beta^{[d]}$</td>
<td>10.2(5)</td>
<td>1.3(5)</td>
<td>8.6(5)</td>
<td>1.2(4)</td>
<td>0.8(2)</td>
<td></td>
</tr>
</tbody>
</table>

[a] Distances are given in Å; angles are given in $^\circ$. [b] Three crystallographically independent molecules in the unit cell. [c] $X = N2$, [N3, 11; 12: X = N2; 13: X = C1]. [d] $\alpha$ represents orientation of the pyridine toward axis defined by Mo–Cg(C5). It is defined as absolute value of dihedral angle Cg(C5)–Mo1–N1–C7. [e] $\beta$ represents twisting of the coordinated arm. It is defined as absolute value of dihedral angle C1–C6–C7–N1.

### Indenyl molybdenum compounds with intramolecular coordination

Reaction of indenyl molybdenum compound 8 with HBF4⋅Et2O in presence of acetonitrile ligands, similarly as in case of cyclopentadienyl analogue 7, to exchange of $\eta^5$-allyl ligand with acetonitrile ligands. Surprisingly, the standard work up does not give expected pentacoordinated species with $\eta^1$-bonded indenyl but solely hexacoordinated $\eta^3$-indenyl complex with intramolecularly coordinated pyridine arm 14, see Scheme 7.
indenyl ligand, the signal of H\textsuperscript{2} appears at considerably lower field than H\textsuperscript{1} while \(\eta^5\)-species have the signal of H\textsuperscript{2} at higher field. This relation is, of course, applicable on our species bearing a substituent in position 1 but only after unambiguous assignment of two doublets (\(\Delta J = 3.9\) Hz) to H\textsuperscript{2} and H\textsuperscript{3}. It led us to use deuterium labeled derivative \textbf{8-[D]} for synthesis of \textbf{14-[D]} (Scheme 7). The labeling results in considerable decrease of the doublet at 5.14 ppm (H\textsuperscript{3}) in intensity and in broadening of signal at 6.83 ppm (H\textsuperscript{2}) due to spin-spin interactions H\textsuperscript{2}–[D]\textsuperscript{3}. This experiment unambiguously revealed \(\eta^1\)-coordination mode of the indenyl ligand that was confirmed in solid state by X-ray diffraction analysis (Fig. 8).

**Figure 8.** ORTEP drawing of cation \(\left[\eta^3:\kappa N-1-(C_7H_7CH_2)C_9H_6\right]Mo(CO)2(NCMe)_2\) present in crystal structure of \textbf{14-CH\textsubscript2Cl\textsubscript2}. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

**Scheme 7.** Reactivity of indenyl compounds 8 and 8-[D]. Reagents: a) HBF\textsubscript{4}·Et\textsubscript{2}O (1 eq.), MeCN (2 eq.), CH\textsubscript{2}Cl\textsubscript{2}, b) phen, MeCN, c) [Me\textsubscript{4}N][Cl].

Exchange of acetonitrile ligands does not disrupt coordination of the pyridine arm as demonstrated on reactions with 1,10-phenanthroline and [Me\textsubscript{2}N][Cl], see Scheme 7. In both cases, only products of simple ligand exchange were isolated. The retention of indenyl ligand hapticity in the species \textbf{15} and \textbf{16} was confirmed by deuterium labeling study. Similarly as observed for compound \textbf{14}, the signal the indenyl proton H\textsuperscript{2} appears in \textsuperscript{1}H NMR spectra at considerably lower filed than signal of H\textsuperscript{3}. Although the appearance of dichloride \textbf{16} seems to be obvious, it is rather unusual. From mechanistic point of view, one may expect formation of pentacoordinated species with coordination sphere resembling the recently described chloride complex \(\left[\eta^1\cdot\eta^5-4,7-\text{Me}_2\text{C}_9\text{H}_5\right]\text{Mo(CO)}_2(\text{py})(\text{Cl})\).\textsuperscript{[12]} The unusual stability of the compound \textbf{16} is probably not only a result of constrained geometry but also due to high energetic barrier of the \(\eta^3\cdot\eta^2\)-indenyl ring slippage as will be discussed in detail later on compound \textbf{14}.

Crystal structures of \textbf{14}, \textbf{15} and \textbf{16}·1/2Me\textsubscript{2}CO were determined by X-ray diffraction analysis (Figures 8–10). The molecules have a distorted octahedral structure with one face occupied by centroid of the indenyl ligand and two carbonyl ligands. The opposite octahedral face is occupied by nitrogen atom of pyridine arm and two donor atoms of remaining ligands. Due to short intramolecular bridge, the pyridine arm and indenyl are in cis-configuration. High values of envelop fold angle \(\Omega = 25.0(5)\)–26.3(6)°\textsuperscript{[12]} and \(\Delta(M–C) = 0.830(5)\)–0.871(4) Å, observed for indenyl ligand, verifies the \(\eta^1\)-coordination mode. The indenyl ligand takes configuration with C\textsubscript{6}-ring above carbonyls that is common for the hexacoordinated molybdenum compounds without intramolecular coordination.\textsuperscript{[12, 13, 20]} The \(\eta^2\cdot\kappa N\)-coordination mode of the s functionalized indenyl ligand is unprecedented. Hence, the more conventional \(\eta^5\cdot\kappa N\) was reported for number of lanthanide \textsuperscript{[21]} and group IV metal...
The species of intermediate hapticity between $\eta^1$ and $\eta^2$ was described on nickel complex $\eta^1\eta^2\kappa^\eta^\delta^{-1}N\left(C_5H_4NCH_2\right)C_9H_6\text{Ni(PPh}_3\text{)}[\text{BPh}_4]$. This species has shown considerably lower values of $\Omega$ $[1.48(14)^\circ]$ and $\Delta(M–C)$ $[0.242(3)\text{ Å}]$ than observed for $\eta^1\eta^3$–molybdenum complexes reported here; see Table 3. In contrast to cyclopentadienyl compounds 11–13, the indenyl complexes do not have the plane of pyridine ring parallel to the axis Cg–Mo and the arm is twisted as evident from considerably higher values of the parameter $\alpha [34.2(3)–38.0(3)^\circ]$ and $\beta [19.6(6)–31.2(5)^\circ]$, respectively (cf. with data in Table 2). Furthermore, the intramolecular bond Mo–N1 is considerably longer than observed for cyclopentadienyl species 11–13. The prolongation, observed for indenyl compounds, is due to more efficient trans effect of the carbonyl ligands. This phenomenon also clarifies the systematically longer bonds Mo–$X_{\text{eq}}$ when compared to Mo–$X_{\text{ax}}$, see Table 3.

| Table 3. Geometric parameters of the hexacoordinated molybdenum complexes. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                             | 14 CH$_2$Cl$_2$             | 15                          | 16 $^{1/2}$Me$_2$CO$^{[\text{IN}]b}$ | 16 $^{1/2}$Me$_2$CO$^{[\text{IN}]b}$ | 18                          |
| Mo–Cg(C$_3$)                | 2.069(4)                    | 2.063(4)                    | 2.078(4)                    | 2.043(5)                    | 2.051(1)                    |
| Mo–C(CO)                    | 2.002(4)                    | 1.978(4)                    | 1.960(5)                    | 1.947(6)                    | 1.979(2)                    |
| Mo–N1                       | 2.270(3)                    | 2.274(3)                    | 2.282(4)                    | 2.268(4)                    | 2.284(2)                    |
| Mo–$X_{\text{eq}}$          | 2.222(4)                    | 2.259(3)                    | 2.568(2)                    | 2.544(2)                    | 2.302(2)                    |
| Mo–$X_{\text{ax}}$          | 2.162(4)                    | 2.200(4)                    | 2.517(2)                    | 2.506(2)                    | 2.167(2)                    |
| $X_{\text{eq}}$–Mo–Cg(C$_3$)$^{[\text{IE}]b}$ | 172.9(2)                   | 171.6(2)                   | 175.2(2)                   | 176.6(2)                   | 171.7(1)                   |
| C(CO)–Mo–C(CO)              | 82.6(2)                     | 82.0(2)                     | 81.6(2)                     | 82.3(2)                     | 80.6(1)                     |
| N1–Mo–$X_{\text{eq}}$       | 83.7(2)                     | 88.0(2)                     | 87.0(1)                     | 86.1(1)                     | 95.2(1)                     |
| $\Omega$ $^{[\text{IE}]b}$  | 25.5(5)                     | 26.3(4)                     | 25.0(5)                     | 26.3(6)                     | 26.9(3)                     |
| $\Delta(M–C)$ $^{[\text{IT}]b}$ | 0.842(4)                 | 0.87(1)                     | 0.830(5)                    | 0.849(6)                    | 0.842(3)                    |
| $\alpha$ $^{[\text{ID}]b}$  | 34.2(3)                     | 35.0(3)                     | 35.3(3)                     | 38.0(3)                     | 40.2(2)$^{[\text{II}]b}$   |
| $\beta$ $^{[\text{II}]b}$   | 31.2(5)                     | 26.3(5)                     | 26.6(5)                     | 19.6(6)                     | 23.8(3)$^{[\text{II}]b}$   |

[a] Distances are given in Å; angles are given in $.\quad$ [b] Two crystallographically independent molecules in the unit cell. [c] 14 CH$_2$Cl$_2$, 15, 17: $X_{\text{eq}}$ = N2; 16 $^{1/2}$Me$_2$CO: $X_{\text{eq}}$ = Cl1. [d] 14 CH$_2$Cl$_2$, 15, 17: $X_{\text{ax}}$ = N3; 16 $^{1/2}$Me$_2$CO: $X_{\text{ax}}$ = Cl2. [e] $\Omega$ is the envelope fold angle defined as the angle between planes defined by C1, C2 and C3 and that of C1, C3, C4 and C5.$^{[\text{IE}]b}$ [f] $\Delta(M–C)$ represents the differences in the metal–carbon bonds. It is defined as the difference between the averages of the metal–carbon distances Mo–C4 and Mo–C5 and those of Mo–C1, Mo–C2 and Mo–C3.$^{[\text{IT}]b}$ [g] $\alpha$ is defined as absolute value of dihedral angle Cg(C3)–Mo1–N1–C11. [h] $\beta$ is defined as absolute value of dihedral angle C1–C10–C11–N1. [i] The values for the second coordinated arm are $\alpha = 35.3(2)^\circ$; $\beta = 25.3(3)^\circ$. Indenyl complex bearing two pyridine arms 9 reacts with HBF$_4 \cdot$Et$_2$O to give dicationic species 17, see Scheme 8. In this compound, one pyridine arm is protonated while the second one is intramolecularly coordinated to the central metal. The indenyl ring is $\eta^2$-bonded as evident from low-fielded signal of H$^2$ ($\delta = 7.18$ ppm). The methylene group of the uncoordinated arm gives quartets AB with very low value of the $\Delta\delta_{\text{AB}}$ (0.04 ppm). Considerably higher separation appears in the coordinated arm

Figure 10. ORTEP drawing of anion $\left(\eta^2\kappa^\eta^\delta^{-1}N\left(C_5H_4NCH_2\right)C_9H_6\text{Ni(PPh}_3\text{)}[\text{BPh}_4]\right)^{-}$ present in crystal structure of 16 $^{1/2}$Me$_2$CO.

The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level. Only one of two crystallographically independent molecules is shown for clarity.
The pyridinium ring in side arm of 17 could be deprotonated by excess of pyridine. This process is accompanied with exchange of the MeCN ligand (in cis-position to indenyl) with pyridine of the side chain to gives novel scorpionate-like compound 18 with two irreversibly coordinated arms on indenyl core. Due to steric hindrance, the MeCN ligand (in trans-position to indenyl) is not exchanged by pyridine. Nevertheless, it could be exchanged by less demanding chloride ligand to give compound 19, see Scheme 9.

The compounds with two intramolecularly bonded pyridine arms (18 and 19) are \(C_2\) symmetric as evident from pattern of the \(^1H\) NMR spectra. In both cases, methylene groups give one quartet AB with \(\Delta\delta \approx 19.5\) Hz (18: \(\Delta\delta_{AB} = 0.27\) ppm, 19: \(\Delta\delta_{AB} = 0.39\) ppm). The indenyl proton \(H_2\) appears at low field (18: 6.38 ppm, 19: 6.26 ppm) that is consistent with \(\eta^2\)-coordination mode. In case of the compound 18, the proposed molecular structure was confirmed in solid state by X-ray diffraction analysis, see Figure 11. The molecule has a distorted octahedral structure of approximate \(C_2\) symmetry. The tridentate indenyl ligand is coordinated symmetrically as revealed from similar bond lengths Mo–N, see Table 3. The \(\eta^2\)-coordination mode of indenyl is evidenced by high values of ring slip parameters \(\Omega\) [26.9(3)°] and \(\Delta(M–C)\) [0.842(3) Å].

Theoretical studies

Unusually high stability of the \(\eta^2\)-indenyl molybdenum compounds led us to theoretical investigation of haptotropic rearrangement for the compound 14. From mechanistic point of view, the rearrangement should be associated with abstraction of one acetonitrile ligand to obey 18e rule.\(^{[16]}\) Before exploration of the putative pathways for the species 14, the energy profile of indenyl molybdenum species without intramolecular interaction, \([\eta^2\text{-}3\text{-Ind} \text{Mo(CO)}_2(\text{NCMe})_2][\text{BF}_4]\), was investigated. It will be used for comparative purposes since preceding experimental study provides a clear identification of equilibrium reaction between A and D'.\(^{[26]}\) We note that this system was previously a subject of theoretical studies \(^{[10, 26]}\) but full energy profile of the rearrangement is still missing. The minima and the transition states were optimized at density functional level of theory (B3LYP) and the corresponding structures are shown in the energy profiles together with selected geometric parameters.

The energy is always referred to the starting compound. The mechanism of the haptotropic rearrangement for \([\eta^2\text{-}3\text{-Ind} \text{Mo(CO)}_2(\text{NCMe})_2][\text{BF}_4]\) is shown in Figure 12. In accordance with previous theoretical studies,\(^{[10, 26]}\) the hexacoordinated species with \(C_6\)-ring of indenyl ligand above carbonyls (A) shows lowest electronic energy. Nevertheless, the product of rearrangement \([\eta^2\text{-}3\text{-Ind} \text{Mo(CO)}_2(\text{NCMe})_2][\text{BF}_4]\), appearing via dissociative mechanism, is favored at room temperature on entropic grounds as revealed from negative value of Gibbs free energy obtained for conformer D’ (\(\Delta G = –8.3\) kcal·mol\(^{-1}\)). The spontaneous release of acetonitrile well correlates with our recent experiments those give single crystals of D’ from acetonitrile solution.\(^{[27]}\)

Since opposite orientation of the indenyl ligand toward Mo(CO)\(_2\) moiety is observed for the species A and D’, the haptotropic rearrangement have to include the 180° rotation of the indenyl ligand. The rotation barrier of \(\eta^2\)-bonded indenyl ligand is 9.3 kcal·mol\(^{-1}\). The conformer with the indenyl rotated \(\sim 90^\circ\) (B) has an energy 5.9 kcal·mol\(^{-1}\) and the conformer \(C\) with 180° rotation (\(C_6\)-ring trans to carbonyls) 7.8 kcal·mol\(^{-1}\). The rotation of the \(\eta^2\)-bonded indenyl ligand in pentacoordinated species D’ is also kinetically allowed as evidenced by low energy barrier of 8.5 kcal·mol\(^{-1}\). The transition states of ring slippage step were calculated for three pairs of conformers with the same orientation of indenyl ligand (TS\(_{AF}\), TS\(_{BE}\), and TS\(_{CO}\)). The lowest barrier (16.9 kcal·mol\(^{-1}\)) appears between conformers C and D having \(C_6\)-ring of indenyl ligand trans to carbonyl ligands. In appropriate transition state (TS\(_{CO}\)), the indenyl ring slips from \(\eta^2\) to \(\eta^3\), as evidenced by folding angle (\(\Omega\)) of 15.6°, while
The dissociation of the Mo–Nax bond is underway with a distance of 2.93 Å and a Wiberg index (WI) of 0.23, indicating a weak interaction. The pathways of the ring slippage starting from conformers A and B are kinetically disfavored owing to considerably higher activation energies (TS_{AB}: 33.1 kcal·mol⁻¹, TS_{BC}: 24.5 kcal·mol⁻¹). Consequently, the preferred pathway comprises 180° rotation of η³-bonded indenyl ligand (A → B → C) followed with η³ to η⁵ indenyl ring slippage accompanied with acetonitrile abstraction (C → D') that is a rate determining step.

![Figure 12](image1.png)

Figure 12. Energy profile (B3LYP) for haptotropic rearrangement of the indenyl ligand in molybdenum complex [(η³-Ind)Mo(CO)₂(NCMe)₃][BF₄]. The energy is given in kcal·mol⁻¹ and referred to reagent A. The structures of transition states related to indenyl rotation (TS_{AB}, TS_{BC}, TS_{DE} and TS_{EF}) are omitted for clarity.

In case of compound 14, the observed isomer with C₆-ring of indenyl ligand above carbonyls (14-A), is thermodynamically favored as confirmed by theoretical calculations. Hence, the virtual isomer with C₆-ring above Mo(CO)(NCMe) moiety (14-B) is 5.0 kcal·mol⁻¹ less stable (ΔG = 5.2 kcal·mol⁻¹). We note that further suggested isomer with C₆-ring trans to carbonyls is not an energetic minimum due to strain of the coordinated pyridine arm. As the rotation of the indenyl ligand is restricted by strong intramolecular interaction, the observed species 14-A could only rearrange to 14-C' while the thermodynamically favored product 14D' is only available from virtual isomer 14-B, see Figure 13. The transition 14-A → 14C' is not kinetically allowed due to high activation energy (41.7 kcal·mol⁻¹). In accordance to aforementioned system without intramolecular coordination, the η³ to η⁵ slippage is more convenient in the other orientations of the indenyl ligand. Hence, the transition 14-B → 14D' shows considerably lower activation energy (17.5 kcal·mol⁻¹) and significant free energy gain (ΔG = −9.9 kcal·mol⁻¹). As the isomer for the kinetically allowed pathway (14-B) is not available in the reaction mixture, the η³ to η⁵ cannot proceed under mild conditions.

![Figure 13](image2.png)

Figure 13. Energy profile (B3LYP) of haptotropic rearrangement of the indenyl ligand in complex 14. The energy is given in kcal·mol⁻¹ and referred to reagent 14-A.
Conclusions

In conclusion, we have demonstrated an unusual example of indenyl effect on cyclpentadienyl and indenyl molybdenum compounds with pyridine in the side chain (7 and 8). Although the species are isosttructural, their reactivity differs considerably. The cyclpentadienyl compound 7 produces rather convenient pentacoordinated $\eta^5$-xN-species 11 while hexacoordinated species with unprecedented $\eta^5$-xN-coordination mode 14 was synthesized from the indenyl analogue 8 under similar reaction conditions. Further experiments, performed on both products, have confirmed the irreversible character of intramolecular coordination. The unusually high stability of indenyl complex 14 toward $\eta^3$ to $\eta^2$ haptotropic rearrangement was clarified by theoretical calculations. Since strong intramolecular interaction prevents rotation of indenyl ligand, it cannot achieve conformation suitable for haptotropic rearrangement. Thus, the intramolecular coordination performs as a lock preserving low hapticity of the indenyl ligand.

Experimental Section

Methods and materials. All operations were performed under nitrogen atmosphere using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods.[28] Starting materials were available commercially or prepared according to literature procedures: NaCp (1),[24] NaH (2),[25] $\{\eta^5$-C₅H₅)Mo(CO)₂(NCMe)₂Cl][ (6).,[15]

Measurements. Infrared and Raman spectra were recorded on a Nicolet iS50 FTIR spectrometer equipped a Raman module (Nd:YAG laser emitting at 1064 cm⁻¹). The infrared spectra were recorded in the 4000–400 cm⁻¹ region (resolution 1 cm⁻¹) using Diamond Smart Orbit ATR. Raman spectra were recorded in the 4000–100 cm⁻¹ region (resolution 2 cm⁻¹) in glass capillaries. The $^1$H and $^{13}$C{¹H} NMR spectra were recorded on a Bruker Avance 400 and Bruker Avance 500 spectrometers at 300 K in CDCl₃, CD₃CN, acetone-d₆.

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In the synthesis of 3-(C₅H₄NCH₂)₂C₉H₆, the crude product was vacuum distilled using Kugelrohr apparatus (300°C, 6 Pa). Yield: 4.00 g (19 mmol, 42%). Orange liquid. Analytical and spectroscopic data are in line with those published elsewhere.[35]
Synthesis of \([\{(\text{C}_2\text{H}_2\text{N})\text{C}_4\text{H}_2\text{NCH}_2\text{C}_9\text{H}_6\text{N}\}\text{Mo(CO)}_2])\) (7). A solution of 3 (1.57 g, 10 mmol) in THF (40 mL) was cooled to 0°C, treated with a solution of \(\text{BuLi in hexane (6.55 µL , 1.6 mol/L, 10 mmol)}\) dropwise. The reaction mixture was stirred at room temperature overnight. The volatiles were removed under vacuum and the crude product was extracted with hexane (3 × 70 mL) at 60°C. The solvent was vacuum evaporated. The product was recrystallized from the mixture hexane/EtO at −80°C and vacuum dried. Yield: 1.88 g (5.4 mmol, 54%). Yellow viscous liquid. Anal. Calc. for C_{20}H_{17}MoNO_2: C, 60.16; H, 4.29; N, 3.01. Found: C, 55.28; H, 4.48; N, 3.86.

\[\text{Mp: 64.7 °C. Anal. Calcd. for C}_{20}\text{H}_{17}\text{MoNO}_2: C, 60.16; H, 4.29; N, 3.01.}\]

\[\text{IR (ATR; cm}^{-1}\text{): 1933 vs [ν(C=O)]. Raman (cm}^{-1}\text{): 1853 vs [ν(C=O)].}\]

When the reaction was carried out with 4D, 5D-[\(\text{BF}_2\)] was obtained, for which the signals at 5.83 and 5.89 ppm in the \(^1\text{H}\) NMR spectrum decreased in intensity (35% of initial intensity) and those at 5.73 and 5.79 ppm were seen as a broadened singlet.

Synthesis of \([\{(\text{C}_2\text{H}_2\text{N})\text{C}_4\text{H}_2\text{NCH}_2\text{C}_9\text{H}_6\text{N}\}\text{Mo(CO)}_2])\) (9). The reaction was carried out as described for compound 7 but with indene derivative 5 (2.97 g; 10 mmol). Yield: 1.14 g (3.2 mmol, 32%). Yellow crystals. Mp. 133 °C. Anal. Calc. for C_{19}H_{16}MoNO_2: C, 63.88; H, 4.52; N, 5.59. H NMR (CDCl_3, 400 MHz, 3.5 : 1 mixture of \(\text{C}_5\text{H}_{12}\text{NCH}_2\text{C}_9\text{H}_6\text{N}\)) 8.47 (ddd, 3 \(\text{H}, \text{H}, 1\text{H}) = 7.3 \text{ Hz, 1H,}

\[\text{[\{(\text{C}_2\text{H}_2\text{N})\text{C}_4\text{H}_2\text{NCH}_2\text{C}_9\text{H}_6\text{N}\}\text{Mo(CO)}_2])\} (11). A solution of 7 (0.7 g, 2 mmol) in MeCN (5 mL) was cooled to 0°C and treated with HBF_4·EtOH (550 µL, 4 mol dropwise). The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated. Crude product was washed with EtO_2 (2 × 5 mL), recrystallized from the mixture MeCN/EtO and vacuum dried. Yield 0.49 g (0.86 mmol, 43%).

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Synthesis of [(η⁵-1H)C₅H₄NCH₂C₅H₄]Mo(CO)₂(pyz)][BF₄] (12). A solution of 11 (0.87 g, 2 mmol) in CH₂Cl₂ (5 mL) was treated with pyridine (1 mL, 12 mmol) and stirred at room temperature overnight. The volatiles were vacuum evaporated. The crude product was washed with Et₂O (2 × 10 mL), recrystallized from the mixture CH₂Cl₂/Et₂O and vacuum dried. Yield: 0.85 g (1.8 mol%, 90%). Raman (cm⁻¹): [ν(BF)], 2285(6) [ν(CO)], 1982(6) vs [ν(BF)]. Raman (cm⁻¹): 1982(6) [ν(CO)], 1988(10) [ν(CO)].

Synthesis of [(η⁵-1H)C₅H₄NCH₂C₅H₄]Mo(CO)₂(pyz)][BF₄] (15). A solution of 14 (1.05, 2 mmol) in MeCN (5 mL) was treated with 1,10-phenanthroline (0.36 g, 2 mmol). The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated. The crude product was washed with CH₂Cl₂ (3 × 5 mL), recrystallized from MeCN/Et₂O and vacuum dried. Yield: 1.11 g (1.78 mmol, 89%). Purple crystals. Mp: 155°C (dec). Anal. Calcd. for C₉₆H₇₃N₉O₃Mo: C, 70.00; H, 5.33; N, 9.13; O, 15.54. Found: C, 70.01; H, 5.34; N, 9.11; O, 15.54.

Synthesis of [(η⁵-1H)C₅H₄NCH₂C₅H₄]Mo(CO)₂(pyz)][BF₄] (13). A solution of 11 (0.87 g, 2 mmol) in acetonitrile (5 mL) was treated with Me[N(CF₃)₂] (0.22 g, 2 mmol) and stirred at room temperature overnight. The volatiles were vacuum evaporated and the remaining solid was extracted with CH₂Cl₂ (5 × 7 mL). The white precipitate of [Me[N(CF₃)₂]]Mo(CO)₂(pyz) was filtered off and the volatiles of the filtrate were vacuum evaporated. The crude product was recrystallized from acetonitrile/Et₂O and vacuum dried. Yield: 0.63 g (1.83 mmol, 92%). Purple crystals. Mp: 150°C (dec). Anal. Calcd. for C₇₀H₆₁N₉O₃Mo: C, 74.44; H, 6.25; N, 9.07. Found: C, 74.43; H, 6.26; N, 9.08.

Synthesis of [(η⁵-1H)C₅H₄NCH₂C₅H₄]Mo(CO)₂(pyz)][BF₄] (14). A solution of 8 (0.8 g, 2 mmol) in the mixture of CH₂Cl₂ (5 mL) and MeCN (208 μL, 4 mmol) was cooled to 0°C and treated with HBF₄·Et₂O (275 μL, 2 mmol) dropwise. The reaction mixture was stirred at room temperature overnight and volatiles were vacuum evaporated. The remaining solid was dissolved in acetonitrile (7 mL), stirred at room temperature overnight and vacuum evaporated. This step was repeated with MeCN. The obtained crude product was washed with CH₂Cl₂ (5 mL) and recrystallized from MeCN/Et₂O and vacuum dried. Yield: 0.59 (1.12 mmol, 56%). Mp: 138°C (dec). Red crystals. Anal. Calcd. for C₇₀H₆₁N₉O₃Mo: C, 74.65; H, 6.34; N, 9.07. Found: C, 74.81; H, 6.36; N, 9.08.
Synthesis of [Me₂N]([η⁵-x:n-1-(C₅H₄NCH₂)C₉H₅]Mo(CO)₂Cl₂] (16). A solution of 14 (1.05, 2 mmol) in acetone (5 mL) was treated with [Me₆N]Cl (440 mg, 4 mmol). The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated. The remaining solid was extracted with CH₂Cl₂ (7 mL) and white precipitate of [Me₄N][BF₄] was filtrated off. The volatiles of the filtrate were vacuum evaporated and remaining solid was washed with Et₂O (5 mL) and white precipitate of the pyridinium salt (C₉H₅N–H₂O) was vacuum evaporated. The light brown solution was decanted. Remaining orange precipitate was washed with methanol (3 × 5 mL) and vacuum dried. Yield: 0.38 g (0.78 mmol, 78 %). Crystals. Mp: 139 °C (dec). Anal. Calcd. for C₁₅H₁₁BF₄MoN: C, 56.98; H, 3.54; N, 5.78. Found: C, 57.18; H, 3.45; N, 5.65. H NMR (DMSO-d₆, 500.20 MHz): δ = 3.82, 4.21 (2 × d, J_H = 19.4 Hz, 4H, H2, C₉H₅), 6.26 (s, 1H, H2, C₉H₅), 6.68 (m, 4H, H₂−₇, C₉H₅), 7.28 (d, J_H = 7.4 Hz, 2H, H4, C₉H₅), 7.97 (d, J_H = 7.8 Hz, 2H, H3, C₉H₅). 1H NMR (MeCN-d₃, 500 MHz): δ = 3.82 ppm, 2 (J_H = 4.6 Hz, 4H, H2, C₉H₅), 6.23−6.37 (m, 4H, H₂−₇, C₉H₅), 7.29−7.31 (d, J_H = 12.2 Hz, 2H, H4, C₉H₅), 7.54−7.56 (d, J_H = 8.5 Hz, 2H, H3, C₉H₅). IR (ATR; cm⁻¹) 1935 vs [ν(CO)], 1842 vs [ν(CO)].

X-ray crystallography: The X-ray data for the crystals of the compounds 4', 7', 9, 10, 11, 12, 13, 14, 16, 15, 16, 17 were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Data reductions were performed with DENOVO-SMN.[34] The absorption was corrected by integration methods.[35] Structures were solved by direct methods (SIR92)[36] and refined by full-matrix least squares based on F²(SHELXL97).[37] Hydrogen atoms were mostly localized on a difference Fourier map. However, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were calculated into idealized positions (riding model) and assigned temperature factors U_H = 1.2(Ueq(pivot atom)) or 1.5Ueq for the methyl moiety with C−H = 0.98, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in aromatic rings or the allyl moiety, respectively. Thermal ellipsoids of fluorine atoms of tetrafluoroborate anion in 11 were improved with standard ISOR instruction implemented in SHELXL software.[38] In 10, the same problem was solved by splitting of four fluorine atoms to two positions with nearly equal occupancy by using SAME, RIGU and EADP instructions in SHELXL-2013.[39] There are residual electron maxima and small cavities within the unit cell probably originated from the disordered solvent (acetonitrile) in the structure of 15. PLATON/SQUEEZE[40] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 306 Å³ was found. 78 electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be three molecules of acetonitrile per unit cell which results in 66 electrons per unit cell. The same procedure was used for structure of 14 resulting in a potential solvent volume of 100 Å³ and 46 electrons. The calculated stoichiometry of solvent was calculated to be one molecule of dichloromethane per unit cell which results in 42 electrons per unit cell. Moreover, the fluorine atoms in disordered tetrafluoroborate anion were split into two positions with occupancy 7.3. CCDC 1486921−1486931 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational details: All calculations were performed with the GAUSSTAIN 09 software package[41] using the B3LYP gradient-corrected exchange-correlation functional[42] in combination with the LanL2TZ basis set[43] augmented with a f-polarization function[44] for Mo and the standard 6-31G(d,p) basis set[45] for the remaining elements. The geometry optimizations were carried out without crystal symmetry constraints. Transition state optimizations were performed with synchronous transit-guided quasi-Newton method (STQN).[46] Frequency calculations were performed to confirm the nature of minima and stationary points. One imaginary frequency was observed for each transition state and none for minima. Each transition state was further confirmed by following the intrinsic reaction coordinate (IRC) on both sides.[47] The solvent effects were considered in all energy calculations using polarizable continuum model (PCM).[48] The free energy changes at 298.15 K were then calculated from equation: ΔG = ΔH − TΔS.

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Keywords: hapticity • cyclopentadienyl • indenyl • molybdenum • intramolecular coordination


The unusual example of a low hapticity lock is reported on indenyl compounds with intramolecularly coordinated pyridine arms. The combined experimental and theoretical study reveals a high stability of $\eta^3:κN$- and $\eta^3:κN,N$-coordination compounds toward $\eta^3$ to $\eta^5$ haptotropic rearrangement.

O. Mrózek, J. Vinklárek, Z. Růžičková, J. Honzíček

Indenyl compounds with constrained hapticity: effect of strong intramolecular coordination.