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

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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 -basicity 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 $\eta^5\text{:}\kappa\text{N}$ -compound while the indenyl analogue produces a hexacoordinated species with unprecedented $\eta^3\text{:}\kappa\text{N}$ -coordination mode of the indenyl ligand representing an unusual example of so-called indenyl effect. The unusually high stability of $\eta^3\text{:}\kappa\text{N}$ -coordination compounds toward η^3 to η^5 haptotropic rearrangement was clarified by theoretical calculations. As the strong intramolecular interaction prevents rotation of indenyl, it cannot reach a conformation suitable for η^3 to η^5 rearrangement. As a result, the low hapticity is effectively locked.

Introduction

Cyclopentadienyl compounds of the transition metals attract considerable attention since ferrocene, $(\eta^5\text{-Cp})_2\text{Fe}$ ($\text{Cp} = \text{C}_5\text{H}_5$), 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 ($\text{Ind} = \text{C}_9\text{H}_7$), usually accelerates the rates of substitution reactions due to a lower energetic barrier of the haptotropic shift of the π -ligand. This so-

called "indenyl effect" has been initially attributed to enhanced stability of η^3 -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 $\eta^5\text{-Cp}$ and $\eta^5\text{-Ind}$ 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 η^5 and η^3 coordination modes. Hence, $(\eta^5\text{-Cp})\text{-M}$ bond is considerably stronger than the $(\eta^5\text{-Ind})\text{-M}$ while $(\eta^3\text{-Cp})\text{-M}$ is weaker than $(\eta^3\text{-Ind})\text{-M}$ bond. This is reflected in higher stability of $\eta^5\text{-Cp}$ complexes and $\eta^3\text{-Ind}$ 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 $\eta^5\text{-}\eta^3$ 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 η^9 -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 $\eta^5\text{-}\eta^3$ rearrangements due to pronounced stability of η^3 -indenyl species. Hence, they are often accessible from η^5 -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 η^3 -indenyl species with strong intramolecular coordination does NOT undergo usual $\eta^3\text{-}\eta^5$ 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 η^3 -coordination mode by intramolecular coordination.

Results and Discussion

Synthesis of allyl molybdenum precursors

The starting (2-pyridyl)methyl-substituted congeners of $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-Cp}')\text{Mo}(\text{CO})_2]$ ($\text{Cp}' = \text{Cp}, \text{Ind}$) were prepared using a general procedure developed by Faller *et al.*^[15] Functionalized cyclopentadiene $\text{C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_5$ (**3**) and indene 3-

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($\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_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).

Scheme 1. Synthesis of functionalized cyclopentadiene **3** and indene **4**. Reagents: a) $\text{C}_5\text{H}_4\text{NCH}_2\text{Cl}/\text{THF}$.

The indene **4** was further used for synthesis of isotopically substituted derivative 1-D-3-($\text{C}_5\text{H}_4\text{NCH}_2$) C_9H_6 (**4-D**) and 1,3-disubstituted indene 1,3-($\text{C}_5\text{H}_4\text{NCH}_2$) $_2\text{C}_9\text{H}_6$ (**5**), see Scheme 2. ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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 ^1H NMR spectroscopy. The spectrum reveals that one hydrogen atom on sp^3 carbon of indene framework is fully substituted with deuterium.

Scheme 2. Synthesis of functionalized indenenes **4-D** and **5**. Reagents: a) $\text{D}_2\text{O}/\text{THF}$; b) $\text{C}_5\text{H}_4\text{NCH}_2\text{Cl}/\text{THF}$.

Scheme 3. Synthesis of molybdenum compounds **7–9** and **8-[D]**.

Lithium cyclopentadienide **3-Li**, prepared by deprotonation of cyclopentadienes **3** with *n*-BuLi, react with chloride complex $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{NCMe})_2\text{Cl}]$ (**6**) to give cyclopentadienyl complex $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2]$ (**7**), see Scheme 3. Indenyl complexes $[(\eta^3\text{-C}_3\text{H}_5)\{\eta^5\text{-1-(C}_5\text{H}_4\text{NCH}_2\text{C}_9\text{H}_6)\}\text{Mo}(\text{CO})_2]$ (**8**), $[(\eta^3\text{-C}_3\text{H}_5)\{\eta^5\text{-1,3-(C}_5\text{H}_4\text{NCH}_2)_2\text{C}_9\text{H}_5\}\text{Mo}(\text{CO})_2]$ (**9**) and isotopically labeled species $[(\eta^3\text{-C}_3\text{H}_5)\{\eta^5\text{-1-(C}_5\text{H}_4\text{NCH}_2\text{-3-[D]C}_9\text{H}_5)\}\text{Mo}(\text{CO})_2]$ (**8-[D]**) were prepared accordingly starting from indenenes **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 ^1H and $^{13}\text{C}\{^1\text{H}\}$ 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 $3.72(5)^\circ$.

Scheme 4. Synthesis of **4-Li** via fulvene intermediate. Reagents: a) $\text{C}_5\text{H}_4\text{NCHO}$, MeONa/MeOH ; b) $\text{Li}[\text{Et}_3\text{BH}]/\text{Et}_2\text{O}$.

Figure 1. ORTEP drawing of benzofulvene **4'**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 50% probability level.

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 (ν_s) as evident from considerably higher

intensity. ^1H 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 $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2]$ 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.

Table 1. Geometric parameters of the tetracoordinated molybdenum complexes.^[a]

	7 ^[b]	7 ^[b]	9
Mo–Cg(C ₅)	2.014(3)	2.022(3)	2.027(2)
Mo–Cg(C ₃)	2.043(6)	2.053(3)	2.048(3)
Mo–C(CO)	1.966(6) 1.941(4)	1.948(6) 1.936(4)	1.938(3) 1.936(3)
C(CO)–Mo–C(CO)	78.7(2)	79.4(2)	80.0(2)
Cg(C ₅)–Mo–Cg(C ₃)	127.0(4)	127.2(2)	126.9(1)

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

tetrahedral structure with two carbonyl ligand, η^3 -allyl and η^5 -coordinated π -ligand around molybdenum in the formal oxidation state II. Pyridine arms are not coordinated that obeys the 18-electron rule.^[16]

Figure 3. ORTEP drawing of molecule $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-1,3-(C}_5\text{H}_4\text{NCH}_2)_2\text{C}_9\text{H}_5)\text{Mo}(\text{CO})_2]$ 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.

Cyclopentadienyl molybdenum compounds with intramolecular coordination

Reaction of cyclopentadienyl molybdenum compound **7** with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ 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. $\text{HBF}_4 \cdot \text{Et}_2\text{O}/\text{MeCN}$) that demonstrates high stability of $(\eta^5\text{-}k\text{N-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}^{\text{II}}$ moiety. Putative intermediate of the deprotonation reaction, $[(\eta^5\text{-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{NCMe})_2][\text{BF}_4]$, 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) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (2 eq.)/MeCN, b) acetone.

Structures of molybdenum compounds **7** and **9** were determined by X-ray diffraction analysis. The molecules have a distorted

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 ^1H NMR spectroscopy since the compound **10** is C_s 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 ($\Delta\delta_{\text{AB}} = 0.09$ ppm, $^2J = 19.8$ Hz) at 4.39 ppm was observed for compound **11**. Furthermore, the C_s -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.

Figure 4. ORTEP drawing of dication $[(\eta^5\text{-C}_5\text{H}_4\text{NHCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{NCMe})_2]^{2+}$ present in crystal structure of **10**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

The crystal structures of the compounds **10** and **11** were determined by X-ray diffraction analysis (Figs 4 and 5). Both compounds have a distorted square-pyramidal structure with η^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 $[(\eta^5\text{-}k\text{N-Me}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2\text{I}]$ [2.380(3) Å]^[17] but comparable with more nucleophilic primary amine $[(\eta^5\text{-}k\text{N-H}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{PPh}_3)][\text{PF}_6]$ [2.254(8) Å].^[18]

Figure 5. ORTEP drawing of cation $[(\eta^5\text{-}\kappa\text{N-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{NCMe})]^{+}$ present in crystal structure of **11**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level. Only one of three crystallographically independent molecules is shown for clarity.

Scheme 6. Reactivity of cyclopentadienyl compound **11**. Reagents: a) Py/ CH_2Cl_2 , b) $[\text{Me}_4\text{N}]\text{Cl}/\text{acetone}$.

Figure 6. ORTEP drawing of cation $[(\eta^5\text{-}\kappa\text{N-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{py})]^{+}$ present in crystal structure of **12**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

Acetonitrile ligand of the compound **11** could be easily exchanged by 2e-ligands such as pyridine or chloride, see Scheme 6. ^1H 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.

Figure 7. ORTEP drawing of molecule $[(\eta^5\text{-}\kappa\text{N-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2\text{Cl}]$ present in crystal structure of **13**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

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 π^* -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 [$\text{Mo-N2} = 2.230(3)$ Å] is very similar to intramolecularly coordinated pyridine arm [$\text{Mo-N2} = 2.256(3)$ Å]. Evidently, the chelate effect on the bond distance Mo–N1 is here compensated with weaker *trans* effect of the carbonyl ligands [$\text{N1-Mo-C13} = 150.1(2)^\circ$, $\text{N2-Mo-C12} = 104.9(2)^\circ$].

The compounds **12** and **13** are inert toward excess of pyridine and $[\text{Me}_4\text{N}]\text{Cl}$, respectively. It suggests considerably stronger intramolecular interaction than recently reported for analogues with tertiary amines connected to cyclopentadienyl ring via ethylene bridge.^[19] Due to π -basicity of pyridine, the $(\eta^5\text{-}\kappa\text{N-C}_5\text{H}_4\text{NCH}_2\text{C}_5\text{H}_4)\text{Mo}^{\text{II}}$ moiety of **11** is not disrupted even 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 $[(\eta^5\text{-R}_2\text{NCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_2(\text{phen})][\text{BF}_4]$.^[19]

Table 2. Geometric parameters of the pentacoordinated molybdenum complexes.^[a]

	10	11 ^[b]	11 ^[b]	11 ^[b]	12	13
Mo–Cg(C ₅)	1.980(1)	1.964(1)	1.968(2)	1.961(1)	1.985(3)	1.9767(3)
Mo–C(CO)	1.981(4) 1.966(3)	1.999(4) 1.942(4)	2.017(4) 1.954(4)	2.009(4) 1.947(4)	2.028(4) 1.928(4)	1.942(2) 1.993(2)
Mo–N1	–	2.229(4)	2.238(4)	2.234(4)	2.256(3)	2.237(2)
Mo–X ^[c]	2.165(3) 2.167(3)	2.156(3)	2.150(3)	2.155(3)	2.230(3)	2.4910(4)
C(CO)–Mo–C(CO)	74.6(2)	76.3(2)	77.7 (2)	75.8(2)	78.8(2)	77.3(1)
X–Mo–N ^[c]	78.4(2)	77.9(2)	78.0(2)	79.0(2)	78.8(1)	78.85(4)
α ^[d]	–	0.3(3)	3.0(3)	0.2(3)	1.1 (3)	8.3(2)
β ^[e]	–	10.2(5)	1.3(5)	8.6(5)	1.2 (4)	0.8(2)

[a] Distances are given in Å; angles are given in °. [b] Three crystallographically independent molecules in the unit cell. [c] **10**: X = N2, N3 **11**, **12**: X = N2; **13**: X = Cl1. [d] α 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] β 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 $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in presence of acetonitrile leads, similarly as in case of cyclopentadienyl analogue **7**, to exchange of η^3 -allyl ligand with acetonitrile ligands. Surprisingly, the standard work up does not give expected pentacoordinated species with η^5 -bonded indenyl but solely hexacoordinated η^3 -indenyl complex with intramolecularly coordinated pyridine arm **14**, see Scheme 7.

The infrared spectrum shows two bands in range typical for terminal carbonyl ligands. The hapticity of indenyl ligand was elucidated from ^1H NMR measurements. Since the compound **14** gives one set of sharp signals at room, consistent with C_1 molecular symmetry, fluxional behavior is not expected in solution. According to previous studies on indenyl compounds without substituents in five-membered ring,^[10, 12, 13] the chemical shifts of $\text{H}^{1/3}$ and H^2 are diagnostic for hapticity elucidation. Hence, in case of the organometallic compounds bearing η^3 -

indenyl ligand, the signal of H^2 appears at considerably lower field than $H^{1/3}$ while η^5 -species have the signal of H^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 ($^2J = 3.9$ Hz) to H^2 and H^3 . It led as to use deuterium labeled derivative **8**-[D] for synthesis of **14**-[D] (Scheme 7). The labeling results in considerable decrease of the doublet at 5.14 ppm (H^3) in intensity and in broadening of signal at 6.83 ppm (H^2) due to spin-spin interactions H^2 -[D]³. This experiment unambiguously revealed η^3 -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 $[(\eta^3:\kappa N-1-(C_5H_4NCH_2)C_9H_6)Mo(CO)_2(NCMe)_2]^+$ present in crystal structure of **14**-CH₂Cl₂. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

Figure 9. ORTEP drawing of cation $[(\eta^3:\kappa N-1-(C_5H_4NCH_2)C_9H_6)Mo(CO)_2(phen)]^+$ present in crystal structure of **15**. 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) HBF₄·Et₂O (1 eq.), MeCN (2 eq.)/CH₂Cl₂, b) phen/MeCN, c) [Me₄N]Cl/acetone.

Exchange of acetonitrile ligands does not disrupt coordination of the pyridine arm as demonstrated on reactions with 1,10-phenanthroline and [Me₄N]Cl, see Scheme 7. In both cases,

only products of simple ligand exchange were isolated. The retention of indenyl ligand hapticity in the species **15** and **16** was confirmed by deuterium labeling study. Similarly as observed for compound **14**, the signal the indenyl proton H^2 appears in ¹H NMR spectra at considerably lower field than signal of H^3 .

Although the appearance of dichloride **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 $[(\eta^5-4,7-Me_2C_9H_5)Mo(CO)_2(py)Cl]$.^[12] The unusual stability of the compound **16** is probably not only a result of constrained geometry but also due to high energetic barrier of the $\eta^3:\eta^5$ -indenyl ring slippage as will be discussed in detail later on compound **14**.

Crystal structures of **14**, **15** and **16**·¹/₂Me₂CO 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 [$\Omega = 25.0(5)$ – $26.3(6)^\circ$] and $\Delta(M-C)$ [0.830(5)–0.871(4) Å], observed for indenyl ligand, verifies the η^3 -coordination mode. The indenyl ligand takes configuration with C₆-ring above carbonyls that is common for the hexacoordinated molybdenum compounds without intramolecular coordination.^[12, 13, 20] The $\eta^3:\kappa N$ -coordination mode of the *s* functionalized indenyl ligand is unprecedented. Hence, the more conventional $\eta^5:\kappa N$ was reported for number of lanthanide^[21] and group IV metal

compounds.^[22] The species of intermediate hapticity between η^5 and $\eta^{2:1}$ was described on nickel complex $[(\eta^{5 \rightarrow 2:1}: \kappa N-1-(C_5H_4NCH_2)C_9H_6)Ni(PPh_3)][BPh_4]$. This species has shown considerably lower values of Ω [11.48(14)°] and $\Delta(M-C)$ [0.242(3) Å] than observed for $\eta^3: \kappa N$ -molybdenum complexes reported here; see Table 3.^[23] 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 parameters α [34.2(3)–38.0(3)°] and β [19.6(6)–31.2(5)°], 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_{eq} when compared to Mo–X_{ax}, see Table 3.

Figure 10. ORTEP drawing of anion $[(\eta^3: \kappa N-1-(C_5H_4NCH_2)C_9H_6)Mo(CO)_2Cl_2]^-$ present in crystal structure of **16** · $\frac{1}{2}Me_2CO$. 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.

Table 3. Geometric parameters of the hexacoordinated molybdenum complexes.^[a]

	14 ·CH ₂ Cl ₂	15	16 · $\frac{1}{2}Me_2CO$ ^[b]	16 · $\frac{1}{2}Me_2CO$ ^[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) 1.966(4)	1.978(4) 1.957(4)	1.960(5) 1.934(5)	1.947(6) 1.932(6)	1.979(2) 1.963(2)
Mo–N1	2.270(3)	2.274(3)	2.282(4)	2.268(4)	2.284(2)
Mo–X _{eq} ^[c]	2.222(4)	2.259(3)	2.568(2)	2.544(2)	2.302(2)
Mo–X _{ax} ^[d]	2.162(4)	2.200(4)	2.517(2)	2.506(2)	2.167(2)
X _{ax} –Mo–Cg(C ₃) ^[d]	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 _{eq} ^[c]	83.7(2)	88.0(2)	87.0(1)	86.1(1)	95.2(1)
Ω ^[e]	25.5(5)	26.3(4)	25.0(5)	26.3(6)	26.9(3)
$\Delta(M-C)$ ^[f]	0.842(4)	0.871(4)	0.830(5)	0.849(6)	0.842(3)
α ^[g]	34.2(3)	35.0(3)	35.3(3)	38.0(3)	40.2(2) ^[i]
β ^[h]	31.2(5)	26.3(5)	26.6(5)	19.6(6)	23.8(3) ^[i]

[a] Distances are given in Å; angles are given in °. [b] Two crystallographically independent molecules in the unit cell. [c] **14**·CH₂Cl₂, **15**, **17**: X_{eq} = N2; **16**· $\frac{1}{2}Me_2CO$: X_{eq} = Cl1. [d] **14**·CH₂Cl₂, **15**, **17**: X_{ax} = N3; **16**· $\frac{1}{2}Me_2CO$: X_{ax} = Cl2. [e] Ω 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.^[24] [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.^[24] [g] α is defined as absolute value of dihedral angle Cg(C3)–Mo1–N1–C11; [h] β is defined as absolute value of dihedral angle C1–C10–C11–N1. [i] The values for the second coordinated arm are α = 35.3(2)°; β = 25.5(3)°.

Indenyl complex bearing two pyridine arms **9** reacts with HBF₄·Et₂O 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 η^3 -bonded as evident from low-fielded signal of H² (δ = 7.18 ppm). The methylene group of the uncoordinated arm gives quartets AB with very low value of the $\Delta\delta_{AB}$ (0.04 ppm). Considerably higher separation appears in the coordinated arm

($\Delta\delta_{AB} = 0.28$ ppm) that is in line with observations on structurally related complexes **14**–**16**. 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.

Scheme 8. Reactivity of indenyl compound **9**. Reagents: a) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (3 eq.)/MeCN.

Scheme 9. Reactivity of indenyl compound **17**. Reagents: a) py b) $[\text{Me}_4\text{N}]\text{Cl}$ /acetone.

Figure 11. ORTEP drawing of cation $[(\eta^3\text{-}kN,N\text{-}1,3\text{-}(\text{C}_5\text{H}_4\text{NCH}_2)_2\text{C}_9\text{H}_5)\text{Mo}(\text{CO})_2(\text{NCMe})]^{+}$ present in crystal structure of **18**. The labeling scheme for all non-hydrogen atoms is shown. Thermal ellipsoids are drawn at the 30% probability level.

The compounds with two intramolecularly bonded pyridine arms (**18** and **19**) are C_s symmetric as evident from pattern of the ^1H NMR spectra. In both cases, methylene groups give one quartet AB with $^2J \sim 19.5$ 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 η^3 -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_s symmetry. The tridentate indenyl ligand is coordinated symmetrically as revealed from similar bond lengths Mo–N, see Table 3. The η^3 -coordination mode of indenyl is evidenced by high values of ring slip parameters Ω [26.9(3) $^\circ$] and $\Delta(\text{M}–\text{C})$ [0.842(3) Å].

Theoretical studies

Unusually high stability of the η^3 -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, $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\text{NCMe})_3][\text{BF}_4]$, was investigated. It will be used for comparative purposes since preceding experimental study provides a clear identification of equilibrium reaction between **A** and **D'**.^[25] 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 $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\text{NCMe})_3][\text{BF}_4]$ 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 $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\text{NCMe})_2][\text{BF}_4]$, 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 $\text{Mo}(\text{CO})_2$ moiety is observed for the species **A** and **D'**, the haptotropic rearrangement have to include the 180 $^\circ$ rotation of the indenyl ligand. The rotation barrier of η^3 -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 $^\circ$ rotation (C_6 -ring *trans* to carbonyls) 7.8 kcal·mol $^{-1}$. The rotation of the η^5 -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_{CD}**). 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_{CD}**), the indenyl ring slips from η^3 to η^5 , as evidenced by folding angle (Ω) of 15.6 $^\circ$, while

dissociation of the Mo–N_{ax} bond is underway with a distance of 2.93 Å and a Wiberg index (WI) [28] 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**_{AF}: 33.1 kcal·mol^{−1};

TS_{BE}: 24.5 kcal·mol^{−1}). Consequently, the preferred pathway comprises 180° rotation of η^3 -bonded indenyl ligand (**A** → **B** → **C**) followed with η^3 to η^5 indenyl ring slippage accompanied with acetonitrile abstraction (**C** → **D'**) that is a rate determining step.

Figure 12. Energy profile (B3LYP) for haptotropic rearrangement of the indenyl ligand in molybdenum complex $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\text{NCMe})_3][\text{BF}_4]$. 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**_{D'E'} and **TS**_{E'F'}) 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 ($\Delta G = 5.2$ 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 η^3 to η^5 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 ($\Delta G = -9.9$ kcal·mol^{−1}). As the isomer for the kinetically allowed pathway (**14-B**) is not available in the reaction mixture, the η^3 to η^5 cannot proceed under mild conditions.

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 cyclopentadienyl and indenyl molybdenum compounds with pyridine in the side chain (**7** and **8**). Although the species are isostructural, their reactivity differs considerably. The cyclopentadienyl compound **7** produces rather convenient pentacoordinated η^5 : κ N-species **11** while hexacoordinated species with unprecedented η^3 : κ N-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 η^3 to η^5 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.^[29] Starting materials were available commercially or prepared according to literature procedures: NaCp (**1**),^[30] NaInd (**2**),^[31] [$(\eta^3$ -C₃H₅)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 ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 and Bruker Avance 500 spectrometers at 300 K in CDCl₃, CD₃CN, acetone-d₆ and DMSO-d₆. The chemical shifts are given in ppm relative to TMS. Mass spectrometry was performed on a quadrupole mass spectrometer (LCMS 2010, Shimadzu, Japan). The sample was injected into the mass spectrometer with infusion mode at a constant flow rate of 10 μ L/min. Electrospray ionization-mass spectrometry (ESI-MS) was used for the identification of analyzed samples.

Synthesis of C₅H₄NCH₂Cl. A solution of KOH (15 g, 0.27 mol) in distilled water (150 mL) was cooled to 0°C and treated with C₅H₄NCH₂Cl·HCl (21.3 g, 0.13 mol). The reaction mixture was extracted with CH₂Cl₂ (4 $\times$ 50 mL) and combined organic layers were dried with magnesium sulfate. The volatiles were evaporated on rotavapor and the crude product was vacuum distilled at 74°C (10 Torr). Yield: 14.9 g (0.12 mol, 90%). Colorless liquid. Analytical and spectroscopic data are in line with those published elsewhere.^[32]

Synthesis of C₅H₄NCH₂C₅H₅ (3**).** A solution of NaCp (**1**; 4.40 g, 50 mmol) in THF (150 mL) was cooled to 0°C, treated with C₅H₄NCH₂Cl (5.87 g, 46 mmol) dropwise and stirred at room temperature overnight. The reaction mixture was poured into distilled water (75 mL) and crude product was extracted with CH₂Cl₂ (4 $\times$ 50 mL). Combined organic layers were dried with magnesium sulfate. The volatiles were evaporated on rotavapor and the crude product was vacuum distilled using Kugelrohr apparatus (150°C, 10 Torr). Yield: 4.55 g (29 mmol, 63%). Pale yellow liquid. Analytical and spectroscopic data are in line with those published elsewhere.^[33]

Synthesis of 3-(C₅H₄NCH₂)C₉H₇ (4**).** The reaction was carried out as described for compound **3** but with NaInd (**2**; 6.91 g, 50 mmol). 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.^[33]

Synthesis of 1-D-3-(C₅H₄NCH₂)C₉H₆ (4-D**).** A solution of 3-(C₅H₄NCH₂)C₉H₇ (**4**; 5.18 g, 25 mmol) in THF (30 mL) was cooled to 0°C, treated with a solution of ⁿBuLi in hexane (15.6 mL, 1.6 mol/L, 25 mmol) dropwise and stirred for 30 min. at this temperature. The reaction mixture was treated with D₂O (3 mL, 165 mmol) dropwise, allowed to warm up to room temperature, slowly poured into distilled water (50 mL) and extracted with CH₂Cl₂ (4 $\times$ 50 mL). Combined organic layers were dried with magnesium sulfate. The volatiles were evaporated on rotavapor and the product was vacuum distilled using Kugelrohr apparatus (240°C, 6 Pa). Yield: 4.4 g (21 mmol, 72%). Orange liquid. ¹H NMR (CDCl₃, 400.13 MHz): δ = 3.44 (m, 1H, H¹, C₉H₆), 4.20 (s, 2H, CH₂), 6.33 (m, 1H, H², C₉H₆), 7.20 (ddd, ³J(¹H,¹H) = 7.5 Hz, ³J(¹H,¹H) = 5.1 Hz, ⁴J(¹H,¹H) = 0.7 Hz, 1H, H^{4/5}, C₅H₄N), 7.24–7.35 (m, 3H, H⁴⁻⁷, C₉H₆), 7.39 (d, ³J(¹H,¹H) = 7.6 Hz, H^{4/7}, C₉H₆), 7.53 (d, ³J(¹H,¹H) = 7.6 Hz, H^{3/6}, C₅H₄N), 7.63 (td, ³J(¹H,¹H) = 7.6 Hz, ⁴J(¹H,¹H) = 1.7 Hz, H^{4/5}, C₅H₄N), 8.65 (d, ³J(¹H,¹H) = 4.6 Hz, H^{3/6}, C₅H₄N).

Synthesis of 1-(C₅H₄NCH)C₉H₆ (4'**).** A solution of sodium methanolate (10.8 g, 200 mmol) in methanol (250 mL) was treated with indene (10 mL, 86 mmol) and 2-pyridinecarboxaldehyde (5.68 g, 53 mmol). The reaction mixture was heated under reflux for 1h and then stirred at room temperature overnight. The solution was diluted with water (300 mL) and extracted with pentane (5 $\times$ 200 mL). The combined organic layers were dried with magnesium sulfate and volatiles were vacuum evaporated on rotavapor. The crude product was purified by column chromatography on silica (hexane : Et₂O – 1 : 1). Yield: 5.22 g (25 mmol, 48%). Yellow crystals. Mp: 114 °C. Anal. Calcd. for C₁₅H₁₁N: C, 87.77; H, 5.40; N, 6.83. Found: C, 87.59; H, 5.36; N, 6.91. ¹H NMR (CDCl₃; 500.20 MHz): δ = 7.06 (dd, ³J(¹H,¹H) = 5.6 Hz, ⁴J(¹H,¹H) = 1.5 Hz, 1H, H³, C₉H₆), 7.21–7.34 (m, 1H of C₅H₄N, H⁵ and 3H of C₉H₆, H⁴⁻⁷), 7.41 (s, 1H, C₉H₆CHC₅H₄N), 7.56 (d, ³J(¹H,¹H) = 7.9 Hz, 1H, H², C₅H₄N), 7.65 (d, ³J(¹H,¹H) = 5.6 Hz, 1H, H², C₉H₆), 7.71 (d, ³J(¹H,¹H) = 7.3 Hz, 1H, H^{4/7}, C₉H₆), 7.75 (ddd, ³J(¹H,¹H) = 7.9 Hz, ³J(¹H,¹H) = 7.6 Hz, ⁴J(¹H,¹H) = 1.9 Hz, 1H, H⁴, C₅H₄N), 8.75 (ddd, ³J(¹H,¹H) = 4.8 Hz, ⁴J(¹H,¹H) = 1.7 Hz, ⁵J(¹H,¹H) = 0.8 Hz, 1H, H⁶, C₅H₄N). ¹³C{¹H} NMR (CDCl₃; 125.77 MHz): δ = 119.7 (1C, C^{4/7}, C₉H₆), 121.3 (1C, C^{5/6}, C₉H₆), 122.6 (1C, C^{4/7}, C₉H₆), 125.6 (1C, C⁵, C₅H₄N), 125.9 (1C, C₉H₆CHC₅H₄N), 126.2 (1C, C³, C₅H₄N), 127.6 (1C, C², C₉H₆), 128.4 (1C, C^{5/6}, C₉H₆), 136.1 (1C, C³, C₉H₆), 136.9 (1C, C⁴, C₅H₄N), 150.0 (1C, C⁶, C₅H₄N), 137.8, 142.7, 143.2 (3 $\times$ 1C_q, C₉H₆), 155.7 (1C_q, C², C₅H₄N). Single crystals suitable for X-ray diffraction analysis were prepared by a slow evaporation of Et₂O solution.

Synthesis of 1,3-(C₅H₄NCH₂)₂C₉H₆ (5**).** A solution of 3-(C₅H₄NCH₂)C₉H₇ (**4**; 5.18 g, 25 mmol) was cooled to 0°C, treated with a solution of ⁿBuLi in hexane (15.6 mL, 1.6 mol/L, 25 mmol) dropwise and stirred for 30 min. at this temperature. The reaction mixture was treated with C₅H₄NCH₂Cl (3.10 g, 25 mmol) dropwise, stirred at room temperature overnight and then poured into distilled water (75 mL). Crude product was extracted with CH₂Cl₂. Combined organic layers were dried with magnesium sulfate. The volatiles were evaporated on the rotavapor and crude product was purified by column chromatography on silica (ethyl acetate). Yield: 1.56 g (5.2 mmol, 21%). Pale yellow liquid. Anal. Calcd. for C₁₅H₁₁N: C, 86.50; H, 6.77; N, 6.73. Found: C, 86.67; H, 6.69; N, 6.85. ¹H NMR (CDCl₃, 400.13 MHz): δ = 2.91 (dd, ²J(¹H,¹H) = 13.5 Hz, ³J(¹H,¹H) = 8.8 Hz, 1H, 1-(C₅H₄NCH₂)C₉H₆), 3.25 (dd, ²J(¹H,¹H) = 13.5 Hz, ³J(¹H,¹H) = 6.7 Hz, 1H, 1-(C₅H₄NCH₂)C₉H₆), 4.02 (dd, ³J(¹H,¹H) = 8.8 Hz, ³J(¹H,¹H) = 6.7 Hz, 1H, C₉H₆), 4.06 (s, 2H, 3-(C₅H₄NCH₂)C₉H₆), 6.20 (s, 1H, H², C₉H₆), 7.04–7.24 (m, 8H, H^{3,4} of (C₅H₄NCH₂)₂C₉H₆, H⁴⁻⁷ of C₉H₆), 7.51, 7.57 (2 $\times$ td, ³J(¹H,¹H) = 7.6 Hz, ⁴J(¹H,¹H) = 1.5 Hz, 2H, H⁵, C₅H₄N), 8.53, 8.59 (2 $\times$ d, ³J(¹H,¹H) = 4.7 Hz, 2H, H⁶, C₅H₄N). ¹³C{¹H} NMR (CDCl₃, 100.61 MHz): δ = 37.4, 40.4 (2 $\times$ 1C, CH₂), 49.2 (1C, C¹, C₉H₆), 119.9, 121.4, 121.6, 122.9, 123.2,

123.7, 124.9, 126.7, 135.6, 136.4, 136.6, 149.3, 149.4 (13 × 1C, C^{2,4-7} of C₉H₆, C³⁻⁶ of (C₅H₄NCH₂)₂C₉H₆, 140.9, 144.5, 147.9 (3 × 1C_q, C^{3,3A,7A}, C₉H₆), 159.5, 160.3 (2 × 1C_q, C², (C₅H₄NCH₂)₂C₉H₆).

Synthesis of [(η³-C₃H₅)(η⁵-C₅H₄NCH₂C₅H₄)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 ⁿBuLi in hexane (6.55 μL, 1.6 mol/L, 10 mmol) dropwise and stirred for 30 min. at room temperature. The reaction mixture was cooled to -80°C and treated with a solution of [(η³-C₃H₅)Mo(CO)₂(NCMe)₂Cl] (3.1 g, 10 mmol) in THF (30 mL) dropwise. The mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated and 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/Et₂O at -80°C and vacuum dried. Yield: 1.88 g (5.4 mmol, 54%). Yellow viscous liquid. Anal. Calcd. for C₁₆H₁₅MoNO₂: C, 55.03; H, 4.33; N, 4.01. Found: C, 55.28; H, 4.48; N, 3.86. ¹H NMR (CDCl₃, 400.13 MHz, 3.5 : 1 mixture of **7a** (exo-C₃H₅) and **7b** (endo-C₃H₅)): δ = 0.88 (d, ³J(H¹,H¹) = 10.8 Hz, 2H of **a**, H^{anti}, C₃H₅), 1.62 (d, ³J(H¹,H¹) = 10.3 Hz, 2H of **b**, H^{anti}, C₃H₅), 2.66 (d, ³J(H¹,H¹) = 7.0 Hz, 2H of **a**, H^{syn}, C₃H₅), 2.73 (s-br, 2H of **b**, H^{syn}, C₃H₅), 3.59 (m, 1H of **b**, H^{meso}, C₃H₅), 3.66 (s, 2H of **a** and 2H of **b**, CH₂), 3.88 (m, 1H of **a**, H^{meso}, C₃H₅), 5.12 (dd, ³J(H¹,H¹) = 2.1 Hz, ⁴J(H¹,H¹) = 2.1 Hz, 2H of **a** and 2H of **b**, C₅H₄), 5.21 (dd, ³J(H¹,H¹) = 2.1 Hz, ⁴J(H¹,H¹) = 2.1 Hz, 2H of **a** and 2H of **b**, C₅H₄), 7.09 (ddd, ³J(H¹,H¹) = 7.5 Hz, ³J(H¹,H¹) = 4.9 Hz, ⁴J(H¹,H¹) = 0.8 Hz, 1H of **a** and 1H of **b**, H⁵, C₅H₄N), 7.12 (d, ³J(H¹,H¹) = 7.9 Hz, 1H of **a** and 1H of **b**, H³, C₅H₄N), 7.56 (ddd, ³J(H¹,H¹) = 7.9 Hz, ³J(H¹,H¹) = 7.5 Hz, ³J(H¹,H¹) = 1.8 Hz, 1H of **a** and 1H of **b**, H⁴, C₅H₄N), 8.47 (ddd, ³J(H¹,H¹) = 4.9 Hz, ⁴J(H¹,H¹) = 1.8 Hz, ⁵J(H¹,H¹) = 0.9 Hz, 1H of **a** and 1H of **b**, H⁶, C₅H₄N). ¹³C{¹H} NMR (CDCl₃, 125.77 MHz): δ = 37.4 (1C of **a** and 1C of **b**, CH₂), 38.0 (2C of **a**, C^{1,3}, C₃H₅), 40.9 (2C of **a**, C^{1,3}, C₃H₅), 68.7 (1C of **a**, C², C₃H₅), 89.8 (2C of **a** and 2C of **b**, C₄H₅), 92.4 (2C of **a** and 2C of **b**, C₄H₅), 111.0 (1C_q of **a** and 1C_q of **b**, C₄H₅), 121.6 (1C of **a** and 1C of **b**, C⁵, C₅H₄N), 122.7 (1C of **a** and 1C of **b**, C⁵, C₅H₄N), 136.7 (1C of **a** and 1C of **b**, C⁴, C₅H₄N), 149.2 (1C of **a** and 1C of **b**, C⁶, C₅H₄N), 159.3 (1C_q of **a** and 1C_q of **b**, C², C₅H₄N), 237.6 (2C of **a** and 2C of **b**, CO). IR (ATR; cm⁻¹): 1927 vs [ν_a(CO)], 1838 vs [ν_s(CO)]. Single crystals of **7** suitable for X-ray diffraction analysis were prepared by slow evaporation of hexane solution under inert atmosphere.

Synthesis of [(η³-C₃H₅)(η⁵-1-(C₅H₄NCH₂)C₉H₆)Mo(CO)₂] (8). Method A: The reaction was carried out as described for compound **7** but with indene derivative **4** (2.07 g; 10 mmol). Yield: 2.63 g (6.6 mmol, 66%). Method B: A solution of **4'** (2.05 g, 10 mmol) in Et₂O (80 mL) was treated with a solution of Super-Hydride in THF (10 mL, 1.0 mol/L, 10 mmol). The reaction mixture was stirred overnight. The white precipitate was decanted, washed with Et₂O (3 × 10 mL) and vacuum dried. The white solid was dissolved in THF (40 mL), cooled to -80°C and treated with a solution of [(η³-C₃H₅)Mo(CO)₂(NCMe)₂Cl] (3.1 g, 10 mmol) in THF (30 mL) dropwise. The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated and crude product was extracted with hexane (3 × 70 mL) at 60°C. The solvent was vacuum evaporated. The product was recrystallized from mixture hexane/Et₂O at -80°C and vacuum dried. Yield: 2.48 g (6.2 mmol, 62%). Yellow crystals. Mp: 64.7 °C. Anal. Calcd. for C₂₀H₁₇MoNO₂: C, 60.16; H, 4.29; N, 3.01. Found: C, 60.02; H, 4.39; N, 2.85. ¹H NMR (CDCl₃, 400.13 MHz, 3.8 : 1 mixture of **8a** (exo-C₃H₅) and **8b** (endo-C₃H₅)): δ = -0.88 (d, ³J(H¹,H¹) = 10.9 Hz, 1H of **b**, H^{anti}, C₃H₅), -0.72 (d, ³J(H¹,H¹) = 10.7 Hz, 1H of **b**, H^{anti}, C₃H₅), 0.22 (m, 1H of **a**, H^{meso}, C₃H₅), 0.86 (d, ³J(H¹,H¹) = 11.1 Hz, 1H of **a**, H^{anti}, C₃H₅), 0.96 (d, ³J(H¹,H¹) = 11.2 Hz, 1H of **a**, H^{anti}, C₃H₅), 2.21 (d, ³J(H¹,H¹) = 7.3 Hz, 1H of **a**, H^{syn}, C₃H₅), 2.28 (d, ³J(H¹,H¹) = 7.4 Hz, 1H of **a**, H^{syn}, C₃H₅), 3.44–3.28 (m, 3H of **b**, H^{syn}, H^{meso}, C₃H₅), 4.35 (ABq, Δδ_{AB} = 0.06, ²J(H¹,H¹) = 15.5 Hz, 2H of **a**, CH₂), 4.39 (ABq, Δδ_{AB} = 0.24, ²J(H¹,H¹) = 15.5 Hz, 2H of **b**, CH₂), 5.73 (d, ³J(H¹,H¹) = 2.7 Hz, 1H of **b**, H², C₉H₆), 5.79 (d, ³J(H¹,H¹) = 2.7 Hz, 1H of **a**, H², C₉H₆), 5.83 (d, ³J(H¹,H¹) = 2.7 Hz, 1H of **b**, H³, C₉H₆), 5.89 (d, ³J(H¹,H¹) = 2.7 Hz, 1H of **a**, H³, C₉H₆), 6.88–7.28 (m, 6H of **a** and 6H of **b**, H⁴⁻⁷ of C₉H₆ and H^{3,5} of C₅H₄N), 7.57 (dd-br, ³J(H¹,H¹) = 7.8 Hz, ³J(H¹,H¹) = 7.6 Hz, 1H of **a** and 1H of **b**, H⁴, C₅H₄N), 8.50 (d-br, ³J(H¹,H¹) = 4.6 Hz, 1H of **a** and 1H of **b**, H⁶, C₅H₄N). IR (ATR; cm⁻¹): 1933 vs [ν_a(CO)], 1854 vs [ν_s(CO)].

When the reaction was carried out with **4-D**, **8-[D]** was obtained, for which the signals at 5.83 and 5.89 ppm in the ¹H 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 [(η³-C₃H₅)(η⁵-1,3-(C₅H₄NCH₂)₂C₉H₅)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. Calcd. for C₂₆H₂₂MoN₂O₂: C, 63.68; H, 4.52; N, 5.71. Found: C, 63.73; H, 4.59; N, 5.59. ¹H NMR (CDCl₃, 400.13 MHz, 3.5 : 1 mixture of **9a** (exo-C₃H₅) and **9b** (endo-C₃H₅)): δ = -0.77 (d, ³J(H¹,H¹) = 10.6 Hz, 2H of **b**, H^{anti}, C₃H₅), 0.51 (tt, ³J(H¹,H¹) = 11.1 Hz, ³J(H¹,H¹) = 7.3 Hz, 1H of **a**, H^{meso}, C₃H₅), 0.88 (d, ³J(H¹,H¹) = 11.1 Hz, 2H of **a**, H^{anti}, C₃H₅), 2.16 (d, ³J(H¹,H¹) = 7.3 Hz, 2H of **a**, H^{syn}, C₃H₅), 3.23–3.43 (m, 3H of **b**, H^{syn}, H^{meso}, C₃H₅), 4.31 (ABq, Δδ_{AB} = 0.07, ²J(H¹,H¹) = 15.5 Hz, 2H of **a**, CH₂), 4.35 (ABq, Δδ_{AB} = 0.19, ²J(H¹,H¹) = 15.5 Hz, 2H of **b**, CH₂), 5.93 (s, 1H of **b**, H², C₉H₅), 5.97 (s, 1H of **a**, H², C₉H₅), 6.93 (dd, ³J(H¹,H¹) = 6.5 Hz, ⁴J(H¹,H¹) = 3.1 Hz, 2H of **b**, H⁴⁻⁷, C₉H₅), 7.00 (dd, ³J(H¹,H¹) = 6.5 Hz, ⁴J(H¹,H¹) = 3.1 Hz, 2H of **a**, H⁴⁻⁷, C₉H₅), 7.09–7.22 (m, 6H of **a** and 6H of **b**, H⁴⁻⁷ of C₉H₅ and H^{3,5} of C₅H₄N), 7.56 (m, 2H of **a** and 2H of **b**, H⁴, C₅H₄N), 8.50 (m, 2H of **a** and 2H of **b**, H⁶, C₅H₄N). IR (ATR; cm⁻¹): 1934 vs [ν_a(CO)], 1853 vs [ν_s(CO)]. Raman (cm⁻¹): 1919(3) [ν_a(CO)], 1838(10) [ν_s(CO)]. Single crystals of **9** suitable for X-ray diffraction analysis were prepared by sublimation in vacuum-sealed (1 Pa) ampule at 110°C.

[(η⁵-C₅H₄NHCH₂C₅H₄)Mo(CO)₂(NCMe)₂][BF₄]₂ (10). A solution of **7** (0.7 g, 2 mmol) in MeCN (5 mL) was cooled to 0°C and treated with HBF₄·Et₂O (550 μL, 4 mmol) dropwise. The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated. Crude product was washed with Et₂O (2 × 5 mL), recrystallized from the mixture MeCN/Et₂O and vacuum dried. Yield 0.49 g (0.86 mmol, 43%). Red crystals. Mp: 137 °C (dec). Anal. Calcd. for C₁₇H₁₇B₂F₈MoN₃O₂: C, 36.15; H, 3.03; N, 7.44. Found: C, 36.25; H, 3.16; N, 7.29. ¹H NMR (CD₃CN, 400.13 MHz): δ = 2.49 (s, 6H, NCCCH₃), 4.06 (s, 2H, CH₂), 5.66 (dd, ³J(H¹,H¹) = 2.2 Hz, ⁴J(H¹,H¹) = 2.1 Hz, 2H, C₅H₄), 6.96 (dd, ³J(H¹,H¹) = 2.2 Hz, ⁴J(H¹,H¹) = 2.1 Hz, 2H, C₅H₄), 7.94–7.99 (m, 2H, H^{3,5}, C₅H₄NH), 8.56 (ddd, ³J(H¹,H¹) = 8.0 Hz, ³J(H¹,H¹) = 8.0 Hz, ⁴J(H¹,H¹) = 1.0 Hz, 1H, H⁴, C₅H₄NH), 8.65 (t-br, ³J(H¹,H¹) = 4.8 Hz, 1H, H⁶, C₅H₄NH), 13.2 (s-br, 1H, C₅H₄NH). IR (ATR; cm⁻¹): 2324 vs [ν_a(CN)], 2296 vs [ν_s(CN)], 1981 vs [ν_a(CO)], 1905 vs [ν_s(CO)], 1026 vs-br [ν(BF)]. Raman (cm⁻¹): 2323(5) [ν_a(CN)], 2289(10) [ν_s(CN)], 1984(4) [ν_a(CO)], 1917(8) [ν_s(CO)]. Single crystals of **10** suitable for X-ray diffraction analysis were prepared by diffusion of hexane into saturated solution of **10** in CH₂Cl₂.

[(η⁵-κN-C₅H₄NCH₂C₅H₄)Mo(CO)₂(NCMe)][BF₄] (11). A solution of **7** (0.7 g, 2 mmol) in the mixture of CH₂Cl₂ (5 mL) and MeCN (105 μL, 2mmol) was cooled to 0°C and treated with HBF₄·Et₂O (225 μL, 2 mmol) dropwise. The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated. The remaining solid was dissolved in acetone (10 mL) and stirred overnight. The volatiles were vacuum evaporated, crude product was recrystallized from the mixture acetone/Et₂O and vacuum dried. Yield 0.64 g (1.48 mmol, 74%). Purple crystals. Mp: 140 °C (dec). Anal. Calcd. for C₁₅H₁₃BF₄MoN₂O₂: C, 41.31; H, 3.00; N, 6.42. Found: C, 41.16; H, 3.09; N, 6.50. Positive-ion MS (MeCN): *m/z* = 351 (100%) [M]⁺, 310 [M – MeCN]⁺. ¹H NMR (acetone-d₆, 400.13 MHz): δ = 2.66 (s, 3H, NCCCH₃), 4.39 (ABq, Δδ_{AB} = 0.09 ppm, ²J(H¹,H¹) = 18.2 Hz, 2H, CH₂), 5.19 (ddd, ³J(H¹,H¹) = 2.6 Hz, ³J(H¹,H¹) = 2.6 Hz, ⁴J(H¹,H¹) = 1.6 Hz, 1H, C₅H₄), 5.80 (ddd, ³J(H¹,H¹) = 2.7 Hz, ³J(H¹,H¹) = 2.7 Hz, ⁴J(H¹,H¹) = 1.6 Hz, 1H, C₅H₄), 6.23 (ddd, ³J(H¹,H¹) = 2.7 Hz, ⁴J(H¹,H¹) = 1.6 Hz, ⁴J(H¹,H¹) = 1.6 Hz, 1H, C₅H₄), 6.65 (ddd, ³J(H¹,H¹) = 2.8 Hz, ⁴J(H¹,H¹) = 1.6 Hz, ⁴J(H¹,H¹) = 1.6 Hz, 1H, C₅H₄), 7.38 (dd, ³J(H¹,H¹) = 7.5 Hz, ³J(H¹,H¹) = 5.8 Hz, 1H, H⁵, C₅H₄N), 7.48 (ddd, ³J(H¹,H¹) = 8.1 Hz, ⁴J(H¹,H¹) = 1.5 Hz, ⁵J(H¹,H¹) = 0.8 Hz, 1H, H³, C₅H₄N), 7.95 (ddd, ³J(H¹,H¹) = 7.9 Hz, ³J(H¹,H¹) = 7.9 Hz, ⁴J(H¹,H¹) = 1.6 Hz, 1H, H⁴, C₅H₄N), 8.43 (ddd, ³J(H¹,H¹) = 5.9 Hz, ⁴J(H¹,H¹) = 1.5 Hz, ⁵J(H¹,H¹) = 0.7 Hz, 1H, H⁶, C₅H₄N). ¹³C{¹H} NMR (acetone-d₆, 125.77 MHz): δ = 36.3 (1C, CH₂),

86.7, 87.8, 88.1, 104.0 (4 × 1C, C₅H₄), 124.7 (1C, C⁵, C₅H₄N), 125.8 (1C, C³, C₅H₄N), 133.1 (1C_q, C₅H₄), 140.2 (1C, C⁴, C₅H₄N), 155.6 (1C, C⁶, C₅H₄N), 175.8 (1C_q, C², C₅H₄N), 248.8, 251.8 (2 × 1C, CO). IR (ATR; cm⁻¹): 2285 vs [v(CN)], 1982 vs [v_a(CO)], 1866 vs [v_s(CO)], 1030 vs-br [v(BF)]. Raman (cm⁻¹): 2285(6) [v(CN)], 1982(7) [v_a(CO)], 1898(10) [v_s(CO)]. Single crystals of **11** suitable for X-ray diffraction analysis were prepared by diffusion of hexane into saturated solution of **11** in CH₂Cl₂.

Synthesis of [(η⁵-κN-C₅H₄NCH₂C₅H₄)Mo(CO)₂(py)](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. Crude product was washed with Et₂O (2 × 10 mL), recrystallized from the mixture CH₂Cl₂/Et₂O and vacuum dried. Yield: 0.85 g (1.8 mmol, 90%). Mp: 130 °C (dec). Red crystals. Anal. Calcd. for C₁₈H₁₅BF₄MoN₃O₂: C, 45.60; H, 3.19; N, 5.91. Found: C, 45.73; H, 3.22; N, 5.83. Positive-ion MS (MeCN): *m/z* = 389 (100%) [M]⁺, 351 [M - py + MeCN]⁺, 310 [M - py]⁺. ¹H NMR (acetone-d₆, 400.13 MHz): δ = 4.40, 4.70 (2 × d, ²J(¹H,¹H) = 18.2 Hz, 2H, CH₂), 5.35 (ddd, ³J(¹H,¹H) = 2.8 Hz, ³J(¹H,¹H) = 2.8 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, C₅H₄), 5.89 (ddd, ³J(¹H,¹H) = 2.7 Hz, ³J(¹H,¹H) = 2.7 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, C₅H₄), 6.16 (ddd, ³J(¹H,¹H) = 2.9 Hz, ⁴J(¹H,¹H) = 1.6 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, C₅H₄), 6.77 (ddd, ³J(¹H,¹H) = 2.9 Hz, ⁴J(¹H,¹H) = 1.6 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, C₅H₄), 7.17 (dd, ³J(¹H,¹H) = 7.5 Hz, ³J(¹H,¹H) = 6.0 Hz, 1H, H⁵, C₅H₄N), 7.53, (ddd, ³J(¹H,¹H) = 8.1 Hz, ⁴J(¹H,¹H) = 1.5 Hz, ⁵J(¹H,¹H) = 0.7 Hz, 1H, H³, C₅H₄N), 7.61 (dt, ³J(¹H,¹H) = 7.7 Hz, ³J(¹H,¹H) = 6.4 Hz, 2H, H^{3,5}, C₅H₅N), 7.87 (dd, ³J(¹H,¹H) = 7.8 Hz, ³J(¹H,¹H) = 7.8 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, H⁴, C₅H₄N), 8.07, (tt, ³J(¹H,¹H) = 7.7 Hz, ⁴J(¹H,¹H) = 1.5 Hz, 1H, H⁴, C₅H₅N), 8.19 (d, ³J(¹H,¹H) = 5.9 Hz, ⁴J(¹H,¹H) = 1.5 Hz, ⁵J(¹H,¹H) = 0.7 Hz, 1H, H⁶, C₅H₄N), 9.11 (dd, ³J(¹H,¹H) = 6.4 Hz, ⁴J(¹H,¹H) = 1.5 Hz, 2H, H^{2,6}, C₅H₅N). ¹³C{¹H} NMR (acetone-d₆, 125.77 MHz): δ = 36.6 (1C, CH₂), 86.5, 87.1, 88.1, 106.8 (4 × 1C, C₅H₄), 124.7 (1C, C⁵, C₅H₄N), 126.1 (1C, C³, C₅H₄N), 127.7 (2C, C^{3,5}, C₅H₅N), 133.3 (1C_q, C₅H₄), 140.3 (1C, C⁴, C₅H₄N), 140.5 (1C, C⁴, C₅H₅N), 154.5 (1C, C⁶, C₅H₄N), 158.3 (2C, C^{2,6}, C₅H₅N), 175.4 (1C_q, C², C₅H₄N), 249.5, 250.1 (2 × 1C, CO). IR (ATR; cm⁻¹): 1997 vs [v_a(CO)], 1840 vs [v_s(CO)], 1030 vs-br [v(BF)]. Raman (cm⁻¹): 2009(4) [v_a(CO)], 2003(4) [v_a(CO)], 1851(10) [v_s(CO)]. Single crystals of **12** suitable for X-ray diffraction analysis were prepared by diffusion of hexane into saturated solution of **12** in CH₂Cl₂.

Synthesis of [(η⁵-κN-C₅H₄NCH₂C₅H₄)Mo(CO)₂Cl](13**).** A solution of **11** (0.87 g, 2 mmol) in acetone (5 mL) was treated with [Me₄N]Cl (0.22 g, 2 mmol) and stirred at room temperature overnight. The volatiles were vacuum evaporated and remaining solid was extracted with CH₂Cl₂ (7 mL). The white precipitate of [Me₄N][BF₄] was filtrated off and the volatiles of the filtrate were vacuum evaporated. The crude product was recrystallized from acetone/Et₂O and vacuum dried. Yield: 0.63 g (1.83 mmol, 92%). Purple crystals. Mp: 150 °C (dec). Anal. Calcd. for C₁₃H₁₀ClMoNO₂: C, 45.44; H, 2.93; N, 4.07. Found: C, 45.62; H, 2.85; N, 3.94. ¹H NMR (acetone-d₆, 400.13 MHz): δ = 4.46 (ABq, Δδ_{AB} = 0.05 ppm, ²J(¹H,¹H) = 18.0 Hz, 2H, CH₂), 5.98 (ddd, ³J(¹H,¹H) = 2.5 Hz, ³J(¹H,¹H) = 2.5 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, C₅H₄), 5.62 (ddd, ³J(¹H,¹H) = 2.7 Hz, ³J(¹H,¹H) = 2.7 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, C₅H₄), 6.01 (ddd, ³J(¹H,¹H) = 2.9 Hz, ⁴J(¹H,¹H) = 1.7 Hz, ⁴J(¹H,¹H) = 1.7 Hz, 1H, C₅H₄), 6.03 (ddd, ³J(¹H,¹H) = 2.8 Hz, ⁴J(¹H,¹H) = 1.7 Hz, ⁴J(¹H,¹H) = 1.7 Hz, 1H, C₅H₄), 7.22 (dd, ³J(¹H,¹H) = 7.6 Hz, ³J(¹H,¹H) = 5.7 Hz, 1H, H⁵, C₅H₄N), 7.31 (d, ³J(¹H,¹H) = 7.9 Hz, 1H, H³, C₅H₄N), 7.79 (td, ³J(¹H,¹H) = 7.8 Hz, ⁴J(¹H,¹H) = 1.7 Hz, 1H, H⁴, C₅H₄N), 8.34 (d, ³J(¹H,¹H) = 5.7 Hz, 1H, H⁶, C₅H₄N). ¹³C{¹H} NMR (CD₃CN, 125.77 MHz): δ = 36.2 (1C, CH₂), 86.2, 87.02, 87.04, 108.3 (4 × 1C, C₅H₄), 123.7 (1C, C⁵, C₅H₄N), 124.6 (1C, C³, C₅H₄N), 131.1 (1C_q, C₅H₄), 139.2 (1C, C⁴, C₅H₄N), 156.7 (1C, C⁶, C₅H₄N), 173.6 (1C_q, C², C₅H₄N), 252.8, 264.3 (2 × 1C, CO). IR (ATR; cm⁻¹): 1945 vs [v_a(CO)], 1827 vs [v_s(CO)]. Raman (cm⁻¹): 1950(8) [v_a(CO)], 1846(10) [v_s(CO)]. Single crystals of **13** suitable for X-ray diffraction analysis were prepared by diffusion of hexane into saturated solution of **13** in CH₂Cl₂.

Synthesis of [(η³-κN-1-(C₅H₄NCH₂)C₉H₆)Mo(CO)₂(NCMe)₂](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 acetone (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 C₂₁H₁₈BF₄MoN₃O₂: C, 47.85; H, 3.44; N, 7.97. Found: C, 47.61; H, 3.42; N, 7.87. Positive-ion MS (MeCN): *m/z* = 414 [M - CO]⁺, 401 (100%) [M - MeCN]⁺, 373 [M - MeCN - CO]⁺, 360 [M - 2MeCN]⁺. ¹H NMR (CD₃CN, 400.13 MHz): δ = 4.03, 4.27 (2 × d, ²J(¹H,¹H) = 19.8 Hz, 2H, CH₂), 5.14 (d, ³J(¹H,¹H) = 3.9 Hz, 1H, H³, C₉H₆), 6.45–6.61 (m, 4H, H^{4–7}, C₉H₆), 6.83 (d, ³J(¹H,¹H) = 3.9 Hz, 1H, H², C₉H₆), 7.33 (dd, ³J(¹H,¹H) = 7.6 Hz, ³J(¹H,¹H) = 5.6 Hz, 1H, H⁵, C₅H₄N), 7.62 (d, ³J(¹H,¹H) = 7.8 Hz, 1H, H³, C₅H₄N), 7.84 (d, ³J(¹H,¹H) = 5.6 Hz, 1H, H⁶, C₅H₄N), 7.93, (ddd, ³J(¹H,¹H) = 7.7 Hz, ³J(¹H,¹H) = 7.7 Hz, ⁴J(¹H,¹H) = 1.6 Hz, 1H, H⁴, C₅H₄N). ¹³C{¹H} NMR (CD₃CN, 125.77 MHz): δ = 35.8 (1C, CH₂), 73.1 (1C, C³, C₉H₆), 86.0 (1C_q, C¹, C₉H₆), 98.8 (1C, C², C₉H₆), 116.1, 117.2, 124.8, 124.9 (4 × 1C, C^{4–7}, C₉H₆), 123.8 (1C, C⁵, C₅H₄N), 124.5 (1C, C³, C₅H₄N), 139.5 (1C, C⁴, C₅H₄N), 146.0, 147.6 (2 × 1C_q, C^{3a,7a}, C₉H₆), 150.2 (1C, C⁶, C₅H₄N), 161.8 (1C_q, C², C₅H₄N), 221.1, 221.4 (2 × 1C, CO). IR (ATR; cm⁻¹): 2317 vs [v_a(CN)], 2284 vs [v_s(CN)], 1967 vs [v_a(CO)], 1904 vs [v_s(CO)], 1029 vs-br [v(BF)]. Raman (cm⁻¹): 2316(3) [v_a(CN)], 2284(10) [v_s(CN)], 1988(2) [v_a(CO)], 1900(4) [v_s(CO)]. Single crystals of **14**·CH₂Cl₂ suitable for X-ray diffraction analysis were prepared by diffusion of Et₂O into saturated solution of **14** in CH₂Cl₂. When the reaction was carried out with **8**·[D], **14**·[D] was obtained, for which the signal at 5.14 ppm in the ¹H NMR spectrum decreased in intensity (35 % of initial intensity) and that at 6.83 ppm was seen as a broadened singlet.

Synthesis of [(η³-κN-1-(C₅H₄NCH₂)C₉H₆)Mo(CO)₂(phen)](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. Crude product was washed with CH₂Cl₂ (3 × 5 mL), recrystallized from MeCN/Et₂O and vacuum dried. Yield: 1.11 g (1.78 mmol, 89%). Brown crystals. Mp: 155 °C (dec). Anal. Calcd. for C₂₉H₂₀BF₄MoN₃O₂: C, 55.71; H, 3.22; N, 6.72. Found: C, 55.55; H, 3.09; N, 6.64. Positive-ion MS (MeCN): *m/z* = 540 (100%) [M]⁺, 512 [M - CO]⁺, 484 [M - 2CO]⁺. ¹H NMR (acetone-d₆, 400.13 MHz): δ = 4.37, 4.66 (2 × d, ²J(¹H,¹H) = 19.8 Hz, 2H, CH₂), 5.51 (d, ³J(¹H,¹H) = 3.9 Hz, 1H, H³, C₉H₆), 5.99 (ddd, ³J(¹H,¹H) = 5.2 Hz, ⁴J(¹H,¹H) = 1.1 Hz, ⁴J(¹H,¹H) = 1.1 Hz, 1H, H⁶, C₅H₄N), 6.51–6.70 (m, 2H of C₉H₆ (H^{4–7}) and 2H of C₅H₄N (H^{4,5})), 6.71 (dd, ³J(¹H,¹H) = 7.2 Hz, ⁴J(¹H,¹H) = 0.7 Hz, 1H, H³, C₅H₄N), 7.40 (d, ³J(¹H,¹H) = 3.9 Hz, 1H, H², C₉H₆), 7.81 (m, 2H, H^{4–7}, C₉H₆), 8.14 (dd, ³J(¹H,¹H) = 8.2 Hz, ³J(¹H,¹H) = 5.2 Hz, 1H, H^{3/8}, C₁₂H₈N₂), 8.39 (dd, ³J(¹H,¹H) = 8.3 Hz, ³J(¹H,¹H) = 5.2 Hz, 1H, H^{3/8}, C₁₂H₈N₂), 8.43 (ABq, Δδ_{AB} = 0.04 ppm, ³J(¹H,¹H) = 8.7 Hz, 2H, H^{5,6}, C₁₂H₈N₂), 8.93 (dd, ³J(¹H,¹H) = 8.2 Hz, ⁴J(¹H,¹H) = 1.3 Hz, 1H, H^{4/7}, C₁₂H₈N₂), 9.11 (dd, ³J(¹H,¹H) = 8.3 Hz, ⁴J(¹H,¹H) = 1.4 Hz, 1H, H^{4/7}, C₁₂H₈N₂), 9.51 (dd, ³J(¹H,¹H) = 5.2 Hz, ⁴J(¹H,¹H) = 1.3 Hz, 1H, H^{2/9}, C₁₂H₈N₂), 10.1 (dd, ³J(¹H,¹H) = 5.2 Hz, ⁴J(¹H,¹H) = 1.3 Hz, 1H, H^{2/9}, C₁₂H₈N₂). ¹³C{¹H} NMR (CD₃CN, 125.77 MHz): δ = 36.8 (1C, CH₂), 73.0 (1C, C³, C₉H₆), 86.5 (1C_q, C¹, C₉H₆), 98.6 (1C, C², C₉H₆), 116.6 (1C, C³, C₄H₅N), 118.4, 124.8, 125.7, 125.9, 126.0 (5 × 1C, C₄H₅N (C^{4,5}), C₉H₆ (C^{4–7}), 126.5 (1C, C^{3/8}, C₁₂H₈N₂), 127.5 (1C, C^{3/8}, C₁₂H₈N₂), 128.9 (1C, C^{5/6}, C₁₂H₈N₂), 129.4 (1C, C^{5/6}, C₁₂H₈N₂), 132.0, 132.2, 142.0, 144.7 (4 × 1C_q, C₁₂H₈N₂), 140.2 (1C, C^{4/7}, C₁₂H₈N₂), 140.4 (1C, C^{4–7}, C₉H₆), 141.4 (1C, C^{4/7}, C₁₂H₈N₂), 147.4, 148.6 (2 × 1C_q, C^{3a,7a}, C₉H₆), 147.9 (1C, C⁶, C₄H₅N), 153.8 (1C, C^{2/9}, C₁₂H₈N₂), 158.5 (1C, C^{2/9}, C₁₂H₈N₂), 163.5 (1C_q, C², C₄H₅N), 224.7, 222.4 (2 × 1C, CO). IR (ATR; cm⁻¹): 1921 vs [v_a(CO)], 1861 vs [v_s(CO)], 1030 vs-br [v(BF)]. Raman (cm⁻¹): 1941(10) [v_a(CO)], 1846(5) [v_s(CO)]. Single crystals of **15** suitable for X-ray diffraction analysis were prepared by diffusion of Et₂O into saturated solution of **15** in MeCN. When the reaction was carried out with **14**·[D], **15**·[D] was obtained, for which the signal at 5.51 ppm in the ¹H NMR

spectrum decreased in intensity (35 % of initial intensity) and that at 7.40 ppm was seen as a broadened singlet.

Synthesis of $[\text{Me}_4\text{N}][\{\eta^3\text{-}\kappa\text{N-1-(C}_5\text{H}_4\text{NCH}_2\text{)}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2\text{Cl}_2\text{]} (16)$. A solution of **14** (1.05, 2 mmol) in acetone (5 mL) was treated with $[\text{Me}_4\text{N}]\text{Cl}$ (440 mg, 4 mmol). The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated. The remaining solid was extracted with CH_2Cl_2 (7 mL) and white precipitate of $[\text{Me}_4\text{N}][\text{BF}_4]$ was filtrated off. The volatiles of the filtrate were vacuum evaporated. Crude product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ and vacuum dried. Yield: 0.78 g (1.56 mmol, 78%). Mp: 147°C (dec). Light orange crystals. Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{Cl}_2\text{MoN}_2\text{O}_2$: C, 50.12; H, 4.81; N, 5.57. Found: C, 50.04; H, 4.88; N, 5.43. Negative-ion MS (MeCN): $m/z = 429$ (100%) $[\text{M}]^-$. ^1H NMR (acetone- d_6 , 500.20 MHz): $\delta = 3.43$ (s, 12H, $(\text{CH}_3)_4\text{N}$), 3.74, 4.04 (2 $\times$ d, $^2J(\text{H}^1, \text{H}^1) = 19.1$ Hz, 2H, CH_2), 4.58 (d, $^3J(\text{H}^1, \text{H}^1) = 3.9$ Hz, 1H, H^3 , C_9H_5), 6.24–6.37 (m, 4H, H^{4-7} , C_9H_5), 6.88 (d, $^3J(\text{H}^1, \text{H}^1) = 3.9$ Hz, 1H, H^2 , C_9H_5), 7.14 (dd, $^3J(\text{H}^1, \text{H}^1) = 7.6$ Hz, $^3J(\text{H}^1, \text{H}^1) = 5.6$ Hz, 1H, H^5 , $\text{C}_5\text{H}_4\text{N}$), 7.47 (d, $^3J(\text{H}^1, \text{H}^1) = 7.8$ Hz, 1H, H^3 , $\text{C}_5\text{H}_4\text{N}$), 7.77 (ddd, $^3J(\text{H}^1, \text{H}^1) = 7.8$ Hz, $^3J(\text{H}^1, \text{H}^1) = 7.6$ Hz, $^4J(\text{H}^1, \text{H}^1) = 1.7$ Hz, 1H, H^4 , $\text{C}_5\text{H}_4\text{N}$), 8.58 (dd, $^3J(\text{H}^1, \text{H}^1) = 5.6$ Hz, $^4J(\text{H}^1, \text{H}^1) = 1.5$ Hz, 1H, H^6 , $\text{C}_5\text{H}_4\text{N}$). IR (ATR; cm^{-1}): 1928 vs $[\nu_a(\text{CO})]$, 1842 vs $[\nu_s(\text{CO})]$. Single crystals of $16 \cdot 1/2\text{Me}_2\text{CO}$ suitable for X-ray diffraction analysis were prepared by diffusion of Et_2O into saturated solution of **16** in acetone. When the reaction was carried out with **14-[D]**, **16-[D]** was obtained, for which the signal at 4.58 ppm in the ^1H NMR spectrum decreased in intensity (35 % of initial intensity) and that at 6.88 ppm was seen as a broadened singlet.

Synthesis of $[\{\eta^3\text{-}\kappa\text{N-1-(C}_5\text{H}_4\text{NCH}_2\text{)}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2(\text{NCMe})_2][\text{BF}_4]_2 (17)$. A solution of **9** (0.98 g, 2 mmol) in MeCN (5 mL) was cooled at 0°C and treated with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.82 mL, 6 mmol) dropwise. The reaction mixture was stirred at room temperature overnight. The volatiles were vacuum evaporated and remaining solid was washed with Et_2O (5 mL) and CH_2Cl_2 (5 mL). Crude product was recrystallized from MeCN/ Et_2O and vacuum dried. Yield: 1.08 g (1.54 mmol, 77%). Red crystals. Mp: 133 °C (dec). Anal. Calcd. for $\text{C}_{27}\text{H}_{23}\text{B}_2\text{F}_8\text{MoN}_4\text{O}_2$: C, 46.00; H, 3.29; N, 4.75. Found: C, 45.88; H, 3.32; N, 4.84. ^1H NMR (CD_3CN , 400.13 MHz): $\delta = 4.05$, 4.33 (2 $\times$ d, $^2J(\text{H}^1, \text{H}^1) = 19.9$ Hz, 2H, $\text{C}_5\text{H}_4\text{NCH}_2$), 4.18 (ABq, $\Delta\delta_{\text{AB}} = 0.04$ ppm, $^2J(\text{H}^1, \text{H}^1) = 16.9$ Hz, 2H, $\text{C}_5\text{H}_4\text{NCH}_2$), 6.33 (d, $^3J(\text{H}^1, \text{H}^1) = 7.2$ Hz, 1H, $\text{H}^{4/7}$, C_9H_5), 6.45 (dd, $^3J(\text{H}^1, \text{H}^1) = 7.5$ Hz, $^3J(\text{H}^1, \text{H}^1) = 7.3$ Hz, 1H, $\text{H}^{5/6}$, C_9H_5), 6.58 (dd, $^3J(\text{H}^1, \text{H}^1) = 7.5$ Hz, $^3J(\text{H}^1, \text{H}^1) = 7.2$ Hz, 1H, $\text{H}^{5/6}$, C_9H_5), 6.64 (d, $^3J(\text{H}^1, \text{H}^1) = 7.1$ Hz, 1H, $\text{H}^{4/7}$, C_9H_5), 7.18 (s, 1H, H^2 , C_9H_5), 7.29–7.55 (m, 4H of $\text{C}_5\text{H}_4\text{N}$ and 4H of $\text{C}_5\text{H}_4\text{NH}$), 13.1 (m, 1H, $\text{C}_5\text{H}_4\text{NH}$). IR (ATR; cm^{-1}): 1958 vs $[\nu_a(\text{CO})]$, 1873 vs $[\nu_s(\text{CO})]$.

Synthesis of $[\{\eta^3\text{-}\kappa\text{N,N-1,3-(C}_5\text{H}_4\text{NCH}_2\text{)}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2(\text{NCMe})][\text{BF}_4] (18)$. Complex **17** (0.49, 1 mmol) was dissolved in pyridine (5 mL). The reaction mixture was stirred at room temperature overnight. The excess of the pyridine was vacuum evaporated and remaining solid was extracted with CH_2Cl_2 (7 mL). The white precipitate of the pyridinium salt was filtrated off and volatiles of the filtrate were vacuum evaporated. Crude product was recrystallized from MeCN/ Et_2O and vacuum dried. Yield: 0.27 g (0.46 mmol, 46%). Red crystals. Mp: 137 °C (dec). Anal. Calcd. for $\text{C}_{25}\text{H}_{20}\text{BF}_4\text{MoN}_3\text{O}_2$: C, 52.02; H, 3.49; N, 7.28. Found: C, 52.10; H, 3.41; N, 7.44. Positive-ion MS (MeCN): 492 (100%) $[\text{M}]^+$, 464 $[\text{M} - \text{CO}]^+$, 451 $[\text{M} - \text{MeCN}]^+$, 423 $[\text{M} - \text{CO} - \text{MeCN}]^+$, 395 $[\text{M} - 2\text{CO} - \text{MeCN}]^+$. ^1H NMR (CD_3CN , 500.20 MHz): $\delta = 4.04$, 4.31 (2 $\times$ d, $^3J(\text{H}^1, \text{H}^1) = 19.6$ Hz, 4H, CH_2), 6.38 (s, 1H, H^2 , C_9H_5), 6.58 (m, 4H, H^{4-7} , C_9H_5), 7.34 (dd, $^3J(\text{H}^1, \text{H}^1) = 7.6$ Hz, $^3J(\text{H}^1, \text{H}^1) = 5.8$ Hz, 2H, H^5 , $\text{C}_5\text{H}_4\text{N}$), 7.60 (d, $^3J(\text{H}^1, \text{H}^1) = 8.0$ Hz, 2H, H^3 , $\text{C}_5\text{H}_4\text{N}$), 7.90 (dd, $^3J(\text{H}^1, \text{H}^1) = 8.0$ Hz, $^3J(\text{H}^1, \text{H}^1) = 7.6$ Hz, 2H, H^4 , $\text{C}_5\text{H}_4\text{N}$), 8.05 (d, $^3J(\text{H}^1, \text{H}^1) = 5.8$ Hz, 2H, H^6 , $\text{C}_5\text{H}_4\text{N}$). IR (ATR; cm^{-1}): 1952 vs $[\nu_a(\text{CO})]$, 1874 vs $[\nu_s(\text{CO})]$. Single crystals of **18** suitable for X-ray diffraction analysis were prepared by diffusion of Et_2O into saturated solution of **14** in MeCN.

Synthesis of $[\{\eta^3\text{-}\kappa\text{N,N-1,3-(C}_5\text{H}_4\text{NCH}_2\text{)}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2\text{Cl}] (19)$. A solution of **17** (0.58 g, 1 mmol) in acetone (5 mL) was treated with

$[\text{Me}_4\text{N}]\text{Cl}$ (0.11 g, 1 mmol). The reaction mixture was stirred at room temperature overnight. The light brown solution was decanted. Remaining orange precipitate was washed with methanol (3 $\times$ 5 mL) and vacuum dried. Yield: 0.38 g (0.78 mmol, 78 %). Orange crystals. Mp: 139 °C (dec). Anal. Calcd. for $\text{C}_{23}\text{H}_{17}\text{ClMoN}_2\text{O}_2$: C, 56.98; H, 3.54; N, 5.78. Found: C, 57.18; H, 3.45; N, 5.65. ^1H NMR (DMSO- d_6 , 500.20 MHz): $\delta = 3.82$, 4.21 (2 $\times$ d, $^3J(\text{H}^1, \text{H}^1) = 19.4$ Hz, 4H, CH_2), 6.26 (s, 1H, H^2 , C_9H_5), 6.46 (m, 4H, H^{4-7} , C_9H_5), 7.37 (dd, $^3J(\text{H}^1, \text{H}^1) = 7.4$ Hz, $^3J(\text{H}^1, \text{H}^1) = 5.6$ Hz, 2H, H^5 , $\text{C}_5\text{H}_4\text{N}$), 7.62 (d, $^3J(\text{H}^1, \text{H}^1) = 7.7$ Hz, 2H, H^3 , $\text{C}_5\text{H}_4\text{N}$), 7.91 (ddd, $^3J(\text{H}^1, \text{H}^1) = 7.7$ Hz, $^3J(\text{H}^1, \text{H}^1) = 7.4$ Hz, $^4J(\text{H}^1, \text{H}^1) = 1.6$ Hz, 2H, H^4 , $\text{C}_5\text{H}_4\text{N}$), 8.38 (dd, $^3J(\text{H}^1, \text{H}^1) = 5.6$ Hz, $^4J(\text{H}^1, \text{H}^1) = 1.3$ Hz, 2H, H^6 , $\text{C}_5\text{H}_4\text{N}$). IR (ATR; cm^{-1}): 1935 vs $[\nu_a(\text{CO})]$, 1862 vs $[\nu_s(\text{CO})]$, 1850 vs $[\nu_s(\text{CO})]$.

X-ray crystallography: The X-ray data for the crystals of the compounds **4'**, **7**, **9**, **10**, **11**, **12**, **13**, **14**· CH_2Cl_2 , **15**, **16**· $1/2\text{Me}_2\text{CO}$ and **18** were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Data reductions were performed with DENZO-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 F^2 (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 recalculated into idealized positions (riding model) and assigned temperature factors $U_{\text{iso}}(\text{H}) = 1.2[U_{\text{eq}}(\text{pivot atom})]$ or $1.5U_{\text{eq}}$ for the methyl moiety with C–H = 0.96, 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 SHELXL97 software.^[37] 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.^[38] 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/SQUEZZE^[39] 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 GAUSSIAN 09 software package^[40] using the B3LYP gradient-corrected exchange–correlation functional^[41] in combination with the LanL2TZ basis set^[42] augmented with an f-polarization function^[43] for Mo and the standard 6-31G(d,p) basis set^[44] for the remaining elements. The geometry optimizations were carried out without symmetry constraints. Transition state optimizations were performed with synchronous transit-guided quasi-Newton method (STQN).^[45] 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.^[46] The solvent effects were considered in all energy calculations using polarizable continuum model (PCM).^[47] The free energy changes at 298.15 K were then calculated from equation: $\Delta G = \Delta H - T\Delta S$.

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FULL PAPER

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 $\eta^3:\kappa N$ - and $\eta^3:\kappa N,N$ -coordination compounds toward η^3 to η^5 haptotropic rearrangement.

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Page No. – Page No.

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