Stabilization of \( \eta^3 \)-indenyl compounds by sterically demanding \( N,N \)-chelating ligands in the molybdenum coordination sphere†

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A series of \( \eta^3 \)-indenyl molybdenum compounds [(\( \eta^3 \)-4,7-Me₂C₉H₅)Mo(CO)₂(\( \eta^3 \)-N,L)]Cl (\( \eta^3 \)-N,L = bipy, phen, pyma) isostuctural with well-known \( \eta^3 \)-allyl compounds, was synthesized from the recently established halide synthons [(\( \eta^3 \)-4,7-Me₂C₉H₅)Mo(CO)₂(\( \mu \)-Cl)]₃. The low stability of the hexacoordinated \( \eta^3 \)-indenyl molybdenum species in solution has been overcome by a modification of the chelating ligand. Hence, the dissociation of the compounds bearing ligands with methyl groups beside nitrogen donor atoms (e.g. 6,6′-Me₂-bipy, 2,9-Me₂-phen, 2,9,9-Me₂-4,7-Ph₂-phen) is strongly disfavored due to the steric requirements of the substituents. The considerable discrimination of the pentacoordinated species enables the use of [(\( \eta^3 \)-4,7-Me₂C₉H₅)Mo(CO)₂(2,9-Me₂-phen)]BF₄ for the assembly of derivatives bearing other halides and pseudohalides in the coordination sphere of molybdenum. The current study further describes some other new indenyl complexes accessible from [(\( \eta^3 \)-4,7-Me₂C₉H₅)Mo(CO)₂(\( \mu \)-Cl)]₂. All structural types presented in this experimental study were supported by X-ray crystallographic data.

Introduction

Organometallic molybdenum compounds are currently under comprehensive scrutiny due to their interesting properties. Allyl compounds [(\( \eta^3 \)-C₅H₅)Mo(CO)₂(\( \eta^3 \)-N,L)]Cl (\( \eta^3 \)-N,L = \( N,N \)-chelating ligand) show a rich coordination chemistry and have found several applications in organic synthesis and catalysis.1-11 Promising cytotoxic properties have been observed for cationic cyclopentadienyl and indenyl compounds [(\( \eta^3 \)-Cp′)Mo(CO)₂(\( \eta^3 \)-N,L)][BF₄] (Cp′ = Cp = C₅H₅, Ind = C₅H₅₂, where \( \eta^3 \)-N,L is \( N,N \)-, \( P,P \)- or \( S,S \)-chelating ligands, and its congeners with substituted \( \pi \)-ligands.12-14 Neutral cyclopentadienyl compounds [(\( \eta^3 \)-Cp′)Mo(CO)₂X] (Cp′ = substituted Cp, X = anionic ligand) are well-established precursors of catalysts for oxidation reactions (e.g. olefin epoxidation or sulfoxidation).15-21 Recently, we have described a synthesis of [(\( \eta^3 \)-Ind]Mo(CO)₂(\( \mu \)-Cl)]₂ (1; Scheme 1) that was found to be a versatile synthon for various \( \eta^3 \)-indenyl compounds.22 Furthermore, this compound seems to be a suitable pre-catalyst for isomerization of α-pinene oxide to campholenic aldehyde23 and a precursor of hydrolytically active species for promoted hydrolysis of phosphoesters.24

Although the cyclopentadienyl and indenyl molybdenum compounds have often a similar molecular structure, a different reactivity is expected since a replacement of the cyclopentadienyl ligand with the indenyl accelerates reaction rates due to a lower energetic barrier of the haptoptropic shift of the \( \pi \)-ligand.25-29 The kinetic “indenyl effect” has been comprehensively scrutinized on various molybdenum compounds by Romão and Calhorda.30-32 For instance, they have recently demonstrated that the indenyl compound [(\( \eta^3 \)-Ind]Mo(CO)₂–[\( \kappa^2 \)-ttcn)]BF₄ (ttcn = 1,4,7-trithiaclononane) undergoes an acid-activated C-S cleavage to give [(\( \eta^3 \)-Ind]Mo(CO)₂–[\( \kappa^2 \)-{SCH₂CH₂S}]}BF₄, while the cyclopentadienyl analogue is stable under similar conditions.33 An activation of coordinated ligand was also observed for complexes with \( \eta^4 \)-bonded spiro-[2.4]hepta-4,6-diene. The cyclopentadienyl compound [(\( \eta^3 \)-Cp′)Mo(CO)₂(\( \mu \)-Cl)]₂–[\( \kappa^2 \)-ttcn]}BF₄ undergoes a facile C-S cleavage to give [(\( \eta^3 \)-Ind]Mo(CO)₂–[\( \kappa^2 \)-{SCH₂CH₂S}]}BF₄, while the cyclopentadienyl analogue is stable under similar conditions.34

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Scheme 1 Molecular formula of 1.
Results and discussion

Reactions of \( \left[ \left( \eta^5\text{-4,7-Me}_2\text{C}_9\text{H}_6 \right) \text{Mo(CO)}_2(\mu-\text{Cl}) \right]_2 \) (2) with py, bpy, phen and pyma

Reaction of \( \left[ \left( \eta^5\text{-4,7-Me}_2\text{C}_9\text{H}_6 \right) \text{Mo(CO)}_2(\mu-\text{Cl}) \right]_2 \) (2) with pyridine (py) gives a monomeric compound with \( \eta^5 \)-bonded indenyl ligand \( \left[ \eta^5\text{-4,7-Me}_2\text{C}_9\text{H}_6 \right] \text{Mo(CO)}_2(\text{py})\text{Cl} \) (3), see Scheme 2. The expected \( \eta^1 \)-indenyl species, which could appear upon coordination of further py molecule to molybdenum, was not detected even when a large excess of the reagent was used. Although the compound 3 is a structural analogue of the previously described cyclopentadienyl compound \( \left[ \eta^5\text{-Cp} \right] \text{Mo(CO)}_2(\text{py})\text{Cl} \), the original route is not suitable for 3 due to a low stability of the indenyl precursor \( \left[ \eta^5\text{-Ind} \right] \text{Mo(CO)}_2\text{Cl} \) at elevated temperature.

\(^{1}\text{H} \text{NMR} \) spectrum shows the signal of \( \text{H}^2 \) at a high field that is typical for the species with \( \eta^5 \)-coordinated indenyl ligand. The spectrum pattern with magnetically inequivalent protons \( \text{H}^1 \) and \( \text{H}^1 \) imply the \( \text{C}_1 \) point symmetry for the molecule of 3 that is fully in agreement with the solid state structure revealed by single crystal X-ray analysis (Fig. 1 and Table 1). The molecule of 3 has a square pyramidal structure with the \( \eta^5 \)-bonded indenyl ligand in the apical position. The basal plane is occupied with two \( \text{cis} \)-coordinated carbonyl ligands, one chloride and the nitrogen donor atom of pyridine. The \( \eta^5 \)-coordination mode of the indenyl ligand is confirmed by a low value of the envelope fold angle \( \left[ \varphi = 7.4(2)^\circ \right] \) and also by \( \Delta(M-C) \left[ 0.212(2) \AA \right] \).

From a mechanistic point of view, the \( \eta^5 \)–\( \eta^1 \) rearrangement of the indenyl ligand is stimulated by a coordination of two \( 2\)e donors to molybdenum that could be further enforced by a chelating effect. Nevertheless, this process is further complicated by a coordination or abstraction of chloride as will be documented on the reactions with 2,2’-bipyridine (bpy), 1,10-phenanthroline (phen) and trans-N-(2-pyridylmethylene)-aniline (pyma).

Reaction of 2 with two equivalents of bpy, phen and pyma gives, after standard work up, the desired \( \eta^1 \)-indenyl compounds \( \left[ \left( \eta^5\text{-4,7-Me}_2\text{C}_9\text{H}_6 \right) \text{Mo(CO)}_2(\text{N,NL})\text{Cl} \right] \) (4a: \( N,NL = \text{bpy} \), 5a: \( N,NL = \text{phen} \), 6a: \( N,NL = \text{pyma} \)), see Scheme 3. Infrared spectra of the solid-state samples show two CO stretching bands at low frequencies (Table 2) indicating the proposed neutral
structure. Hence, cationic complexes [(η²-Ind)Mo(CO)₂L₂]⁺ have much lower electron density on molybdenum atom than neutral compounds with slipped indenyl ring [(η²-Ind)Mo(CO)₂L₂Cl] as could be documented on the CO stretching band frequencies of the pairs bearing monodentate ligands (cf. data for compounds bearing DMF or MeCN in Table 2).

The solid state structure of the compound 6a was determined by X-ray diffraction analysis, see Fig. 2. The molecule has a distorted octahedral structure. When the bond Cg(C₃)–Mo is defined as the principal axis, indenyl and chloride occupy the axial positions while the cis-coordinated carbonyl ligands and the nitrogen donor atoms of pyma are in the equatorial plane. High values of Ω [23.1(6)°] and Δ(M–C) [0.849(6) Å], observed for indenyl ligand, are in line with desired η⁴-coordination mode.22,42,43 According to the initial aim, the compound 6a is isostructural with allyl complex [(η³-C₃H₅)Mo(CO)₂(pyma)Cl] (6-allyl) that was also confirmed by X-ray diffraction analysis (cf. Fig. 2 and 3). The allyl counterpart 6-allyl was prepared by a ligand exchange reaction starting from [(η³-C₃H₅)Mo(CO)₂(NCMe)₂]Cl and pyma. The geometric parameters of 6a and 6-allyl, describing the coordination sphere of molybdenum, are very similar (see Table 3). Only the distance Mo–Cg(C₃) in 6a is longer due to an electron-withdrawing character of the annulated benzene ring that weakens the donor properties of indenyl.

Although the indenyl compounds 4a–6a are isostructural with the well-known allyl complexes [(η³-C₃H₅)Mo(CO)₂(N,N)L]⁺ they behavior in solution is very different. The allyl compounds are stable in solution of common organic solvents while a dissolution of the η³-indenyl compounds 4a–6a, even in non-coordinating solvents, leads to a chloride abstraction to give cationic pentacoordinated species [(η³-C₄H₇)Mo(CO)₂(N,N,L)⁺]⁺ (4b: N,N,L = bipy, 5b: N,N,L = phen, 6b: N,N,L = pyma) as evidenced by the ¹H NMR spectroscopy, see Scheme 3. The complexes bearing bipy (4a) and phen (5a) undergo a complete ionization in solution while the compound 6a only a

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### Table 1 Geometric parameters of the neutral and cationic pentacoordinated molybdenum species

|                  | 3a          | 4b-BF₄      | 5b-9·CH₂Cl₂ | 8-BF₄      | 10b-BF₄·0.5(Mc₂-phen-HBF₄) |
|------------------|-------------|-------------|-------------|-------------|----------------------------|
| Mo–Cg(C₃)       | 2.0236(9)   | 1.9979(12)  | 2.004(3)    | 1.990(2)    | 2.0154(18)                 |
| Mo–C(CO)        | 1.929(2)    | 1.960(3)    | 1.950(9)    | 1.968(3)    | 1.945(6)                   |
| Mo–N–Mo–C(CO)   | 1.956(2)    | 1.970(3)    | 1.980(9)    | 1.969(4)    | 1.957(6)                   |
| Mo–N–C(C)       | 2.280(2)    | 2.190(2)    | 2.196(5)    | 2.180(4)    | 2.244(4)                   |
| (C(CO)–Mo–C(C)  | 72.71(10)   | 74.72(12)   | 74.6(4)     | 74.3(2)     | 69.5(2)                    |
| N–Mo–N          | —           | 73.3(2)     | 78.93(14)   | 74.45(13)   |                           |
| Phl–Phl²        | 7.4(2)      | 5.3(1)      | 5.7(6)      | 6.7(5)      | 6.3(4)                     |
| Δ(M–C)³         | 0.212(2)    | 0.149(3)    | 0.157(8)    | 0.160(5)    | 0.178(4)                   |
| Δ0.212(2)       | 0.149(3)    | 0.157(8)    | 0.160(5)    | 0.178(4)    |                           |

* Distances are given in Å; angles and dihedral angles are given in °. Pl¹ is defined by Mo and two nitrogen donor atoms; Pl² is defined by two nitrogen donor atoms and two adjacent carbon atoms of the chelate ring. 'Ω' is the envelope fold angle defined for the indenyl ligand as the angle between planes defined by C3, C4 and C5 and that of C1, C2, C3 and C5.41 Δ(M–C) represents the differences in the metal–carbon bonds. It is defined for the indenyl compounds as the difference between the averages of the metal–carbon distances M–C1 and M–C2 and those of M–C3, M–C4, and M–C5.41 Mo–Cl = 2.4998(6) Å; N–Mo–Cl = 82.24(4)°.

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### Table 2 Summary of the infrared data for the molybdenum complexes

|                 | ν₁(CO) | ν₂(CO) | Ref. |
|-----------------|--------|--------|------|
| 4a              | 1940   | 1862   |      |
| 4b-BF₄          | 1970   | 1894   |      |
| [(η²-Ind)Mo(CO)₂(bpy)][BF₄] | 1974 | 1878 | 13   |
| 5a              | 1919   | 1844   |      |
| 5b-BF₄          | 1967   | 1889   |      |
| [(η²-Ind)Mo(CO)₂(phen)][BF₄] | 1968 | 1874 | 13   |
| 6a              | 1934   | 1855   |      |
| [(η²-Ind)Mo(CO)₂(NCMe)₂]Cl | 1954 | 1851 | 23   |
| [(η²-Ind)Mo(CO)₂(NCMe)₂][BF₄] | 1970 | 1880 | 23   |
| [(η²-Ind)Mo(CO)₂(DMF)₂]Cl | 1934 | 1839 | 24   |
| [(η²-Ind)Mo(CO)₂(DMF)₂][BF₄] | 1962 | 1865 | 24   |

* The stretching frequencies are given in cm⁻¹.
The cis-coordinated carbonyl ligands and two nitrogen donor atoms of remaining ligands form the basal plane. The structural parameters, describing the coordination sphere of molybdenum, are in line with data of structurally related cyclopentadienyl and indenyl compounds described previously.\textsuperscript{13,14,24-46}

The reaction of 2 with lower than stoichiometric amount of \textit{bpy} or \textit{phen} gives a material insoluble in common organic solvents that strongly contrasts with properties of the starting compounds as well as the products 4a and 5a. Elemental analysis of the products together with their insolubility suggests an appearance of the ionic pair consisting of a large complex cation and a large complex anion \([\{\eta^5\text{-}4,7\text{-}\text{Me}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2\text{(N,NL)}\}^+\text{[}\{\eta^5\text{-}4,7\text{-}\text{Me}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2\text{Cl}_2\text{]}^–\text{[}\text{BF}_4\text{]}^–\text{[}\text{N,NL}\text{]}\text{]}\). The crystal structure of 5b-9 is stabilized by intramolecular \(\pi\text{-}\pi\) stacking involving phenanthroline ligand of 5b and indenyl ligand of 9. The distance between the centroid of central phenanthroline ring and centroid of the \(\text{C}_6\text{-}\text{ring}\) of the indenyl ligand was found to be 3.493(5) Å.

Since the anionic complex (9) is unprecedented an alternative method of the synthesis was developed. It is given by the reaction of 2 with a common source of chlorides. Namely, the soluble ammonium salt, \([\text{Me}_4\text{N}]\{\{\eta^5\text{-}4,7\text{-}\text{Me}_2\text{C}_9\text{H}_5\}\text{Mo(CO)}_2\text{Cl}_2\}^–\text{[}\text{Me}_4\text{N}\text{]}\text{]}\) (MeN-9), was prepared by the reaction of 2 with [Me₄N]Cl (Scheme 6). The infrared spectra of MeN-9 show the CO stretching bands at low wavenumbers \([v_\text{CO}]: 1936, 1922 \text{ cm}^{-1}\); \(v_\text{CO}\): 1820 \text{ cm}^{-1}\) that is consistent with the high electron density on molybdenum. The appearance of two bands of the \(v_\text{CO}\) is due to a vibration coupling of the carbonyl ligands in the crystal lattice. \(^1\)H NMR spectrum of MeN-9 shows a typical pattern of the \(\eta^5\text{-}\text{indenyl}\) ligand with a highfielded signal of H\(^2\) (\(\delta = 4.87\) ppm).

Reaction of 2 with sterically demanding N,N-chelating ligands

Dissociation of the complexes bearing \textit{bpy}, \textit{phen} and \textit{pyma} led us to a more sterically demanding \(N,N\)-chelating ligand,
2,9-dimethyl-1,10-phenanthroline (2,9-Me2-phen), in an attempt to stabilize the $\eta^1$-indenyl species in solution. The product of the reaction between $[\eta^3-4,7$-$\text{Me}_2C_9H_5]\text{Mo(CO)}_2(\mu$-$\text{Cl})_2$ and 2,9-Me2-phen shows similar frequencies of the CO stretching bands ($n_a$(CO): 1927 cm$^{-1}$; $n_s$(CO): 1848 cm$^{-1}$) as observed for the hexacoordinated species 4a–6a that implies a similar molecular structure in the solid state, $[\eta^3-4,7$-$\text{Me}_2C_9H_5]\text{Mo(CO)}_2(2,9$-$\text{Me}_2$-$\text{phen})\text{Cl}$ (10a), see Scheme 7. The enhanced stability of 10a in solution was confirmed by $^1$H NMR spectroscopy. Hence, the spectrum shows only one set of signals. The signal of the indenyl proton H2 appears at high field ($\delta = 5.84$ ppm) that is typical for $\eta^3$-coordination mode. The observed spectrum pattern is consistent with $C_6$ molecular symmetry that confirms a configuration with the nitrogen donor atoms of the chelating ligand in trans-positions to the cis-coordinated carbonyl ligands. The X-ray structure analyses of 10a-$\text{CH}_2\text{Cl}_2$ and 10a-$\text{CHCl}_3$ confirm appearance of this isomer in the solid state, see Fig. 7. The $\eta^3$-coordination mode of the indenyl ligand is evidenced by slipping parameters $\Omega$ ($\sim$23$^\circ$) and $\Delta$(M–C) ($\sim$0.84 Å), see Table 3.

Although the coordination sphere of molybdenum seems to be very similar to the pyma complex 6a (cf. bond distances and bond angles in Table 3), the methyl groups in the near neighborhood of carbonyl ligands prevent an appearance of a planar chelate cycle. Hence, the methyl groups of 2,9-Me2-phen are forced below the equatorial plane, defined by molybdenum and carbonyl ligands, that causes an envelope folding of the chelate cycle of $\sim$14$^\circ$. This distortion is caused by steric repulsion of the
methyl groups with the carbonyl ligands as evidenced by short nonbonding distances C(CH$_3$)$_2$-C(CO) of 3.064(4)–3.138(4) Å those are considerably shorter than sum of van der Waals radii of two carbon atoms (3.4 Å). The folding of the chelate cycle seems to be independent on nature of η$_2$-ligands. Hence, the η$_2$-allyl analogue 10-allyl is distorted in the same way as 10a; cf. Fig. 7 and 8 and Pl$_1$–Pl$_3$ in Table 3.

The high stability of 10a toward the loss of chloride suggests that the cationic complex bearing 2,9-Me$_2$-phen, 10b-BF$_4$, should be a suitable precursor for the assembly of hexacoordinated complexes bearing various anionic 2e ligands (Scheme 8). The starting 10b-BF$_4$, was synthesized using the standard protocol outlined above for 4b-BF$_4$. The X-ray diffraction analysis of the 10b-BF$_4$·0.5(Me$_2$-phen·HBF$_4$) reveals the expected square-pyramidal structure (Fig. 9) with the η$_5$-coordinated indenyl ligand as documented by slippage parameters [Ω = 6.3(4); Δ(M–C) = 0.178(4) Å]. The folding of the chelate cycle [Pl$_1$–Pl$_2$ = 22.4(2)$^\circ$] is, in this case, much heavier than observed for 2,2’-bipyridine analogue 4b-BF$_4$ [7.8(2)$^\circ$] and even that in hexacoordinated species 10a [10.0(2)–14.4(2)$^\circ$]. This distortion is

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**Table 3** Geometric parameters of the neutral hexacoordinated molybdenum species$^a$

|       | 6a     | 6-allyl | 10a·CH$_2$Cl$_2$ | 10a·CH$_2$Cl$_2$ | 10a·CHCl$_3$ | 10a·Me$_2$Cl | 10-allyl |
|-------|--------|---------|-----------------|-----------------|--------------|-------------|---------|
| Mo–Cg(C$_5$) | 2.1027(18) | 2.040(2) | 2.106(3) | 2.109(2) | 2.120(16) | 2.040(5) | 2.126(3) |
| Mo–X | 2.4736(14) | 2.4957(5) | 2.4649(7) | 2.4761(7) | 2.4690(7) | 2.4858(4) | 2.6189(4) |
| Mo–C(CO) | 1.977(7) | 1.957(3) | 1.952(2) | 1.953(2) | 1.945(3) | 1.9466(14) | 1.958(3) |
| Mo–N | 1.964(5) | 1.959(3) | 1.958(2) | 1.957(2) | 1.966(2) | 1.9498(15) | 1.960(3) |
| Mo–Cl | 2.231(6) | 2.248(2) | 2.277(2) | 2.279(2) | 2.280(2) | 2.2984(11) | 2.261(2) |
| Mo–Cl | 2.262(4) | 2.279(2) | 2.283(2) | 2.281(2) | 2.287(2) | 2.2958(11) | 2.283(2) |
| Cg(C$_3$)–Mo–X | 173.35(8) | 175.83(9) | 174.81(7) | 175.27(6) | 176.05(6) | 177.20(6) | 175.49(8) |
| C(CO)–Mo–C(CO) | 79.1(3) | 78.02(11) | 76.15(10) | 77.30(10) | 75.27(12) | 76.75(6) | 75.07(12) |
| N–Mo–N | 73.25(18) | 72.39(7) | 74.26(6) | 73.85(7) | 73.59(7) | 73.06(4) | 74.37(9) |
| Pl$_1$–Pl$_2$ | 2.0(3) | 0.4(1) | 10.0(2) | 14.4(2) | 13.2(2) | 14.11(8) | 9.8(2) |
| Ω | 23.1(6) | — | 23.2(3) | 23.4(2) | 22.5(3) | — | 21.3(5) |
| Δ(M–C)$^b$ | 0.849(6) | — | 0.840(3) | 0.847(3) | 0.838(3) | — | 0.805(3) |

$^a$ Distances are given in Å; angles and dihedral angles are given in °. $^b$ Two crystallographically independent molecules in the unit cell. $^c$ For definition see footnote of Table 1.

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**Table 4** Geometric parameters of the anionic molybdenum species [η$_5$-4,7-Me$_2$C$_9$H$_5$]Mo(CO)$_2$Cl$_2$$^-$ present in the crystal structure of 5b·9-CH$_2$Cl$_2$$^a$

|       | 6a     | 6-allyl | 10a·CH$_2$Cl$_2$ | 10a·CH$_2$Cl$_2$ | 10a·CHCl$_3$ | 10a·Me$_2$Cl | 10-allyl |
|-------|--------|---------|-----------------|-----------------|--------------|-------------|---------|
| Mo–Cg(C$_5$) | 2.036(4) | C(CO)–Mo–C(CO) | 74.0(4) | 74.0(4) | — | — | — |
| Mo–C(CO) | 1.942(9) | C(CO)–Mo–Cl | 81.56(8) | 81.56(8) | — | — | — |
| Mo–Cl | 2.495(2) | Ci–Mo–Cl | 9.9(10) | 9.9(10) | — | — | — |
| Mo–Cl | 2.514(2) | Ci–Mo–Cl | 0.239(10) | 0.239(10) | — | — | — |

$^a$ Distances are given in Å; angles and dihedral angles are given in °. $^b$ For definition see footnote of Table 1.

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**Scheme 6** Synthesis of [Me$_4$N][η$_5$-4,7-Me$_2$C$_9$H$_5$]Mo(CO)$_2$Cl$_2$ (Me$_4$N-9).
accompanied with prolongation of the bonds Mo–N (cf. 10b-BF$_4$·0.5(Me$_2$-phen·HBF$_4$) with 4b-BF$_4$ and 5b-9·CH$_2$Cl$_2$ in Table 1). These observations imply that a repulsion of the phenanthroline methyl groups from the carbonyl ligands is weaker for hexacoordinated species and seems to be a driving force for its stabilization in solution. The crystal structure of 10b-BF$_4$·0.5(Me$_2$-phen·HBF$_4$) reveals π–π stacking interactions involving two molecules of cationic complex 10b and a protonated ligand. The distance between centroid of the central phenanthroline rings are 3.598(3) Å.

The instability of the pentacoordinated cationic species in presence of free monoanionic ligands was evidenced on reactions of 10b-BF$_4$ with a series of halides and pseudohalides. An appearance of the hexacoordinated species [([η$^5$-4,7-Me$_2$C$_9$H$_5$]-Mo(CO)$_2$(2,9-Me$_2$-phen)X] (10a: X = Cl, 10c: X = Br, 10d: X = I, 10e: X = NCO, 10f: X = NCS) is documented by the infrared and NMR spectroscopy. The compounds 10c–10f are stable in solution. The $^1$H NMR spectra of the isolated products confirm that the dissociation reaction is highly disfavored similarly as in case of the parent chloride complex 10a. The infrared spectra reveal that cyanate ligand in 10e and thiocyanate ligand in 10f are bonded to molybdenum via the nitrogen donor atom. It is documented by low stretching frequencies of the C–N bonds (10e: 2195 cm$^{-1}$, 10f: 2063 cm$^{-1}$). This observation is in line with literature data reported for allyl analogues [([η$^5$-C$_3$H$_5$]-Mo(CO)$_2$(Ph$_3$PCH$_2$CH$_2$PPP)(NCO)]$^{49}$ [([η$^5$-C$_3$H$_5$]Mo(CO)$_2$(phen)·(NCS))]$^{50,51}$ [([η$^5$-C$_3$H$_5$]Ph)Mo(CO)$_2$(phen)(NCS)]$^{52}$ [([η$^5$-C$_3$H$_5$]Mo(CO)$_2$(NCMe)$_2$(NCS)]$^{53}$ Structure of the bromide complex 10c was determined by X-ray analysis, see Fig. 10. The coordination sphere of the central metal is very similar as in case of the chloride analogue 10a. The bond distance Mo–Br was found to be shorter [2.6189(4) Å] than in case of similar allyl complexes [([η$^5$-C$_3$H$_5$]-Mo(CO)$_2$(N,N-L)Br)] ($^1$N$_2$L = bppy: 2.650(3) Å, $^1$N$_2$L = phen: 2.645(2) Å) that is a result of different donor properties of the ligand in trans- position to bromide.$^{54}$

The instability of the pentacoordinated cationic species in presence of free monoanionic ligands was evidenced on reactions of 10b-BF$_4$ with a series of halides and pseudohalides. An appearance of the hexacoordinated species [([η$^5$-4,7-Me$_2$C$_9$H$_5$]-Mo(CO)$_2$(2,9-Me$_2$-phen)X] (10a: X = Cl, 10c: X = Br, 10d: X = I, 10e: X = NCO, 10f: X = NCS) is documented by the infrared and NMR spectroscopy. The compounds 10c–10f are stable in solution. The $^1$H NMR spectra of the isolated products confirm that the dissociation reaction is highly disfavored similarly as in case of the parent chloride complex 10a. The infrared spectra reveal that cyanate ligand in 10e and thiocyanate ligand in 10f are bonded to molybdenum via the nitrogen donor atom. It is documented by low stretching frequencies of the C–N bonds (10e: 2195 cm$^{-1}$, 10f: 2063 cm$^{-1}$). This observation is in line with literature data reported for allyl analogues [([η$^5$-C$_3$H$_5$]-Mo(CO)$_2$(Ph$_3$PCH$_2$CH$_2$PPP)(NCO)]$^{49}$ [([η$^5$-C$_3$H$_5$]Mo(CO)$_2$(phen)·(NCS))]$^{50,51}$ [([η$^5$-C$_3$H$_5$]Ph)Mo(CO)$_2$(phen)(NCS)]$^{52}$ [([η$^5$-C$_3$H$_5$]Mo(CO)$_2$(NCMe)$_2$(NCS)]$^{53}$ Structure of the bromide complex 10c was determined by X-ray analysis, see Fig. 10. The coordination sphere of the central metal is very similar as in case of the chloride analogue 10a. The bond distance Mo–Br was found to be shorter [2.6189(4) Å] than in case of similar allyl complexes [([η$^5$-C$_3$H$_5$]-Mo(CO)$_2$(N,N-L)Br)] ($^1$N$_2$L = bppy: 2.650(3) Å, $^1$N$_2$L = phen: 2.645(2) Å) that is a result of different donor properties of the ligand in trans-position to bromide.$^{54}$
A variation of the electronic properties of the bidentate ligands has only minor effect on stability of the \( \eta^1 \)-indenyl complexes as documented on experiments with series of modified \( N,N \)-chelating ligands, namely 3,4,7,8-Me\(_4\)-phen, 2,9-Me\(_2\)-4,7-Ph\(_2\)-phen, 4,4'-Me\(_2\)-bpy and 6,6'-Me\(_2\)-bpy. Although the donor ability of the 1,10-phenanthroline ligands decreases in the line 3,4,7,8-Me\(_4\)-phen > 2,9-Me\(_2\)-4,7-Ph\(_2\)-phen > 2,9-Me\(_2\)-phen > phen,\(^{25,26}\) the stability of the molybdenum complexes does not follow this relation. Derivatives bearing methyl groups beside the nitrogen donor atom (i.e. 2,9-Me\(_2\)-phen and 2,9-Me\(_2\)-4,7-Ph\(_2\)-phen) form much more stable complexes (10a and 12a) than the rest of the series (i.e. phen and 3,4,7,8-Me\(_4\)-phen), see Schemes 3, 9 and 10. Hence, complexes 10a and 12a are stable in solution, while compounds 5a and 11a undergo dissociation giving cationic complexes 5b-Cl and 11b-Cl, respectively. These observations reveal that the stability of the products is mainly influenced by steric effects of the chelating ligands, overshadowing the electronic ones. Similar conclusion was achieved based on experiments with dimethyl substituted 2,2'-bipyridines. Although donor ability of 4,4'-Me\(_2\)-bpy is comparable to 6,6'-Me\(_2\)-bpy, only the later ligand gives a stable hexacoordinated species (14a) that does not undergo dissociation in solution and cloud be easily synthesized by reaction of 14b-BF\(_4\) with common source of chlorides (e.g. [Me\(_4\)N]Cl), see Scheme 10. In contrary, 4,4'-Me\(_2\)-bpy produces complex with ionic structure (13b-Cl) both in solution and in solid state, see Scheme 9.

**Conclusions**

Although sterically demanding ligands are commonly used for the stabilization of low-coordinate metal compounds\(^{27,28}\) or complexes in a low oxidation state,\(^{29,30}\) an application of this approach for the stabilization of low hapticity of the indenyl ligand is rather unusual.\(^{25}\) In current study, we clearly demonstrated that modification of the steric properties of a \( N,N \)-chelating ligand is a suitable approach for the hapticity adjustment in the indenyl molybdenum compounds. Hence, powerful steric effect of methyl groups in positions beside nitrogen donor atoms activates \([\eta^5,\eta^7-\text{Me}_2\text{C}_9\text{H}_5\text{Mo(CO)}_2\text{]n}])\) toward association of 2e anionic ligand (e.g. halide) that is otherwise highly disfavored. Such nucleophile-induced indenyl ring slippage enables the assembly of \( \eta^1 \)-indenyl species isostructural with highly attended allyl complexes. This observation strongly contrasts with less demanding ligands (e.g. bpy, 4,4'-Me\(_2\)-bpy, phen, 3,4,7,8-Me\(_4\)-phen) those form pentacoordinated cationic species \([\eta^5,\eta^7-\text{Me}_2\text{C}_9\text{H}_5\text{Mo(CO)}_2\text{]n}(\text{N}_\text{L})])\) in solution and desired \( \eta^1 \)-compounds were stable only in particular cases in the solid state.

**Experimental section**

**Methods and materials**

All operations were performed under nitrogen using conventional Schlenk-line techniques. The solvents were purified and dried by standard methods.\(^{31}\) Starting materials were available commercially or prepared according to literature procedures: \([\eta^5,\eta^7-\text{Me}_2\text{C}_9\text{H}_5\text{Mo(CO)}_2\text{]N}])\) (2),\(^{22}\) \([\eta^5,\eta^7-\text{Me}_2\text{C}_9\text{H}_5\text{Mo(CO)}_2\text{]N}(\text{N}_\text{L})])\) (7),\(^{22}\) \([\eta^5,\eta^7-\text{Me}_2\text{C}_9\text{H}_5\text{Mo(CO)}_2\text{]N}(\text{N}_\text{L})])\)\(^{a2}\) The infrared spectra were recorded in the 4000–400 cm\(^{-1}\) region (resolution 2 cm\(^{-1}\)) on a Nicolet Magna 6700 FTIR spectrometer using a Diamond Smart Orbit ATR.\(^{1}\)H and \(^{13}\)C\(^{1}\)H) NMR spectra were measured on a Bruker Avance 400 and a Bruker Avance 500 spectrometers at room temperature. The chemical shifts are given in ppm relative to TMS.

**Synthesis of 6,6'-dimethyl-2,2'-bipyridine (6,6'-Me\(_2\)-bpy)**

A solution of bpy (1.00 g, 6.4 mmol) in THF (100 mL) was cooled at \(-50 \, ^{\circ}\text{C}\) treated with MeLi (17 mL, 1.6 mol L\(^{-1}\), 27.2 mmol) and stirred at this temperature for 1 h. The solution was warmed to room temperature, stirred for another 1 h and then refluxed overnight. After cooling at room temperature, the reaction mixture was transferred into a mixture ice-water. The organic layer was separated and the aqueous layer was extracted three times with CH\(_2\)Cl\(_2\). The combined organic layers were drier with MgSO\(_4\) and filtered. The volatiles were vacuum evaporated on a rotavapor. Resulting brown oil was oxidized by a saturated solution of KMnO\(_4\) in acetone until formation of MnO\(_2\) ceased. The MnO\(_2\) was removed by vacuum filtration through short pad of celite on a glass frit. Acetone was vacuum evaporated on a rotavapor and the crude product was purified by column chromatography on silica (hexane/ethyl acetate =

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**Scheme 9** Reaction of 2 with two equivalents of 3,4,7,8-Me\(_4\)-phen and 4,4'-Me\(_2\)-bpy.

**Scheme 10** Syntheses of complexes bearing 2,9-Me\(_2\)-4,7-Ph\(_2\)-phen and 6,6'-Me\(_2\)-bpy.
Synthesis of \(\left(\eta^2-4,7\text{-Me}_{2}C_9H_5\right)\text{Mo} \left(\text{CO}\right) \left(pyr\right)\text{Cl} \) (3)

\[
\left(\eta^2-4,7\text{-Me}_{2}C_9H_5\right)\text{Mo} \left(\text{CO}\right) \left(pyr\right)\text{Cl} \quad \text{(3)}
\]

\[
\text{C}_{27}H_{19}Cl\text{MoN}_{2}O_{2}
\]

\[
\begin{align*}
\text{C} & \quad 58.78; \\
\text{H} & \quad 3.75; \\
\text{N} & \quad 5.59.
\end{align*}
\]

\[\text{Found: C, 58.33; H, 3.96; N, 5.43.}

\[\text{1H NMR (CDCl}_3; 400 MHz; \delta (ppm)): 9.41 (dd, } J^\text{1H,1H} = 5.4 \text{ Hz, } J^\text{1H,1H} = 1.2 \text{ Hz, 2H, phen}), 8.62 (dd, } J^\text{1H,1H} = 8.1 \text{ Hz, } J^\text{1H,1H} = 1.2 \text{ Hz, 2H, phen}), 8.07 (s, 2H, phen), 7.94 (dd, } J^\text{1H,1H} = 8.2 \text{ Hz, } J^\text{1H,1H} = 5.2 \text{ Hz, 2H, phen}), 6.45 (d, } J^\text{1H,1H} = 2.8 \text{ Hz, 2H, C}_{9}\text{H}_{5} \left(5-Me_{2}\right), 0.39 (2H, s, C_{9}H_{5}, H^1_{a}), 0.39 (2H, s, C_{9}H_{5}, H^1_{a}), 1.86 (s, 6H, C_{9}H_{5}).
\]

Synthesis of \(\left(\eta^2-4,7\text{-Me}_{2}C_9H_5\right)\text{Mo} \left(\text{CO}\right) \left(pyr\right)\text{Cl} \) (5a)

Steps of the synthesis followed the procedure for the compounds \(4b\)-BF_{4}. Reagents: \(\left[\eta^2-4,7\text{-Me}_{2}C_9H_5\right]\text{Mo} \left(\text{CO}\right) \left(pyc\right)\text{BF}_{4}\) (5b-BF_{4}). Reagents: \(\left[\eta^2-4,7\text{-Me}_{2}C_9H_5\right]\text{Mo} \left(\text{CO}\right) \left(pyc\right)\text{BF}_{4}\) (5b-BF_{4}).

\[\text{Found: C, 57.17; H, 3.19; N, 4.42.}

\[\text{1H NMR (CDCl}_3; 400 MHz; \delta (ppm)): 9.41 (dd, } J^\text{1H,1H} = 5.4 \text{ Hz, } J^\text{1H,1H} = 1.2 \text{ Hz, 2H, phen}), 8.62 (dd, } J^\text{1H,1H} = 8.1 \text{ Hz, } J^\text{1H,1H} = 1.2 \text{ Hz, 2H, phen}), 8.07 (s, 2H, phen), 7.94 (dd, } J^\text{1H,1H} = 8.2 \text{ Hz, } J^\text{1H,1H} = 5.2 \text{ Hz, 2H, phen}), 6.45 (d, } J^\text{1H,1H} = 2.8 \text{ Hz, 2H, C}_{9}\text{H}_{5} \left(5-Me_{2}\right), 0.39 (2H, s, C_{9}H_{5}, H^1_{a}), 0.39 (2H, s, C_{9}H_{5}, H^1_{a}), 1.86 (s, 6H, C_{9}H_{5}).
\]

Synthesis of \(\left(\eta^2-4,7\text{-Me}_{2}C_9H_5\right)\text{Mo} \left(\text{CO}\right) \left(pyc\right)\text{Cl} \) (6a)

Steps of the synthesis followed the procedure for the compounds \(4a\). Reagents: \(\left[\eta^2-4,7\text{-Me}_{2}C_9H_5\right]\text{Mo} \left(\text{CO}\right) \left(pyc\right)\text{Cl} \) (5b-BF_{4}). Reagents: \(\left[\eta^2-4,7\text{-Me}_{2}C_9H_5\right]\text{Mo} \left(\text{CO}\right) \left(pyc\right)\text{BF}_{4}\) (5b-BF_{4}).

\[\text{Found: C, 57.17; H, 3.19; N, 4.42.}

\[\text{1H NMR (CDCl}_3; 400 MHz; \delta (ppm)): 9.41 (dd, } J^\text{1H,1H} = 5.4 \text{ Hz, } J^\text{1H,1H} = 1.2 \text{ Hz, 2H, phen}), 8.62 (dd, } J^\text{1H,1H} = 8.1 \text{ Hz, } J^\text{1H,1H} = 1.2 \text{ Hz, 2H, phen}), 8.07 (s, 2H, phen), 7.94 (dd, } J^\text{1H,1H} = 8.2 \text{ Hz, } J^\text{1H,1H} = 5.2 \text{ Hz, 2H, phen}), 6.45 (d, } J^\text{1H,1H} = 2.8 \text{ Hz, 2H, C}_{9}\text{H}_{5} \left(5-Me_{2}\right), 0.39 (2H, s, C_{9}H_{5}, H^1_{a}), 0.39 (2H, s, C_{9}H_{5}, H^1_{a}), 1.86 (s, 6H, C_{9}H_{5}).
\]
1.73 (s, 3H of a, CH₂), 1.57 (s, 3H of b, CH₃). FTIR (ATR, cm⁻¹): 1934 vs [ν(CO)], 1855 vs [ν(CO)]. Single crystals of 6a suitable for X-ray diffraction analysis were prepared by overlayering of the CHCl₃ solution with hexane.

**Synthesis of [(η⁵-C₅H₅)Mo(CO)₂(pyma)Cl] (6-allyl)**

[(η⁵-C₅H₅)Mo(CO)₂(NCMe)Cl] (200 mg, 0.64 mmol) was dissolved in CH₂Cl₂ (50 mL) and treated with pyma (117 mg, 0.64 mmol). The solution was stirred at room temperature overnight. The volatiles were vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture CH₂Cl₂/ether and vacuum dried. Yield: 250 mg (95%, 0.61 mmol).

Dark pale powder. Mp: 160–170 °C (dec.). Anal. calcld for C₁₇H₁₇BF₄MoN₂O₂: C, 44.00; H, 3.69; N, 6.04. Found: C, 43.88; H, 3.70; N, 6.12. 1H NMR (CD₃CN; 400 MHz; δ (ppm)): 8.84 (d, J(1H,1H) = 5.1 Hz, 1H, pyma), 8.53 (s, 1H, pyma), 8.10 (td, J(1H,1H) = 7.8 Hz, J(1H,1H) = 1.4 Hz 1H, pyma), 7.98 (d, J(1H,1H) = 7.6 Hz, 1H, pyma), 7.65–7.40 (m, 6H, pyma), 3.32 (t, J(1H,1H) = 9.2 Hz, 1H, pyma), 3.16 (dd, J(1H,1H) = 6.2 Hz, J(1H,1H) = 3.3 Hz, 1H, syn-C₅H₅), 2.48 (dd, J(1H,1H) = 6.2 Hz, J(1H,1H) = 3.3 Hz, 1H, syn-C₅H₅), 1.31 (d, J(1H,1H) = 9.2 Hz, 1H, anti-C₅H₅). FTIR (ATR, cm⁻¹): 1929 vs [ν(CO)], 1845 vs [ν(CO)].

Single crystals of 6-allyl suitable for X-ray diffraction analysis were prepared by overlayering of the CH₂Cl₂ solution with hexane.

**Synthesis of [(η⁵-C₅H₅)Mo(CO)₂(pyma)Cl] (8-BF₄)**

[(η⁵-C₅H₅)Mo(CO)₂(NCMe)Cl] (23 mg, 0.15 mmol) was dissolved in acetone (50 mL) and treated with [Me₄N][BF₄] (1.49 mmol). The volatiles were vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture CH₂Cl₂/ether and vacuum dried. Yield: 220 mg (83%, 0.50 mmol). Red powder. Mp: 150–160 °C (dec.). Anal. calcld for C₃₁H₂₃BF₄MoN₂O₂: C, 60.18; H, 4.82; N, 3.36. 1H NMR (CDCl₃; 400 MHz; δ (ppm)): 8.30 (d, J(1H,1H) = 8.2 Hz, 2H, C₁₂H₄N₂), 8.29 (s, 6H, pyma), 6.31 (d, J(1H,1H) = 2.6 Hz, 2H, C₉H₅), 2.56 (s, 6H, CH₃CN), 1.97 (s, 6H, CH₃). FTIR (ATR, cm⁻¹): 1970 vs [ν(CO)], 1897 vs [ν(CO)], 1040 vs [ν(BF₄)]. Single crystals of 8-BF₄ suitable for X-ray diffraction analysis were prepared by overlayering of the MeCN solution with EtO₂.

**Synthesis of [(η⁵-C₅H₅)Mo(CO)₂(bpy)]([(η⁵-C₅H₅)Mo(CO)₂][μ-Cl])₂ (db-9)**

[(η⁵-C₅H₅)Mo(CO)₂(bpy)][[(η⁵-C₅H₅)Mo(CO)₂][μ-Cl]]₂ (2; 100 mg, 0.15 mmol) was dissolved in CH₂Cl₂ (50 mL) and treated with bpy (23 mg, 0.15 mmol). The solution was stirred at room temperature overnight. The precipitate was decanted. The product was washed with ether, CH₂Cl₂ and vacuum dried. Yield: 85 mg (69%, 0.10 mmol). Red powder. Mp: 140–150 °C (dec.). Anal. calcld for C₃₂H₂₄Cl₂Mo₂N₂O₄: C, 52.90; H, 3.70; N, 3.43. Found: C, 52.82; H, 3.79; N, 3.51. FTIR (ATR, cm⁻¹): 1950 vs [ν(CO)], 1930 vs [ν(CO)], 1875 vs [ν(CO)], 1837 vs [ν(CO)].

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**Synthesis of [(η⁵-4,7-Me₂C₈H₅)Mo(CO)₂(phen)]([(η⁵-4,7-Me₂C₈H₅)Mo(CO)₂][μ-Cl])₂ (5b-9)**

Steps of the synthesis followed the procedure for the compounds 4b-9. Reagents: [(η⁵-4,7-Me₂C₈H₅)Mo(CO)₂][μ-Cl]₂ (2; 100 mg, 0.15 mmol) and phen (27 mg, 0.15 mmol). Yield: 95 mg (75%, 0.11 mmol). Red powder. Mp: 140–150 °C (dec.). Anal. calcld for C₃₂H₂₄Cl₂Mo₃N₂O₄: C, 54.24; H, 3.59; N, 3.33. Found: C, 54.38; H, 3.62; N, 3.10. FTIR (ATR, cm⁻¹): 1954 vs [ν(CO)], 1876 vs [ν(CO)], 1824 vs [ν(CO)].

Single crystals of 5b-9 CH₂Cl₂ suitable for X-ray diffraction analysis were prepared by overlayering of the CH₂Cl₂ solutions of the starting materials.

**Synthesis of [Me₄N][[(η⁵-4,7-Me₂C₈H₅)Mo(CO)₂][μ-Cl]]₂ (Me₄N-9)**

[(η⁵-4,7-Me₂C₈H₅)Mo(CO)₂][μ-Cl]₂ (2; 100 mg, 0.15 mmol) was dissolved in acetone (50 mL) and treated with [Me₄N][Cl] (82 mg, 0.75 mmol). The solution was stirred at room temperature overnight. The volatiles were vacuum evaporated. The residue was dissolved in CH₂Cl₂ and filtered over short pad of Celite. The volatiles were vacuum evaporated. The crude product was washed with ether and recrystallized from the mixture CH₂Cl₂/ether and vacuum dried. Yield: 220 mg (83%, 0.50 mmol). Red powder. Mp: 140–150 °C (dec.). Anal. calcld for C₁₇H₁₃ClMoN₂O₂: C, 49.72; H, 3.68; N, 6.82. Found: C, 49.61; H, 3.70; N, 6.94. 1H NMR (CD₃CN; 400 MHz; δ (ppm)): 8.84 (d, J(1H,1H) = 5.1 Hz, 1H, pyma), 8.32 (s, 1H, pyma), 8.10 (td, J(1H,1H) = 7.8 Hz, J(1H,1H) = 1.4 Hz, 1H, pyma), 7.98 (d, J(1H,1H) = 7.6 Hz, 1H, pyma), 7.65–7.40 (m, 6H, pyma), 3.33 (t, J(1H,1H) = 9.2 Hz, 1H, pyma), 6.22 (s, 2H, syn-C₅H₅), 6.07 (d, J(1H,1H) = 3.3 Hz, 1H, syn-C₅H₅), 1.31 (d, J(1H,1H) = 9.2 Hz, 1H, anti-C₅H₅). FTIR (ATR, cm⁻¹): 1929 vs [ν(CO)], 1845 vs [ν(CO)].

Single crystals of 6-allyl suitable for X-ray diffraction analysis were prepared by overlayering of the CH₂Cl₂ solution with hexane.
1927 vs [\(\nu_v(\text{CO})\)], 1848 vs [\(\nu_v(\text{CO})\)]. Single crystals of 10a·CHCl₃ suitable for X-ray diffraction analysis were prepared by overlaying of the CHCl₃ solution with hexane. Single crystals of 10a·CHCl₃ suitable for X-ray diffraction analysis were prepared by overlaying of the CHCl₃ solution with ether.

**Synthesis of \(\left[\(\text{\(1\)}\right.\left.\text{\(H\)}\right.\right] \text{C}_2\text{H}_3\text{Mo(\text{CO})}_2(\text{2,9-Me}_2\text{-phen})\text{Cl}\) (10-allyl)**

Steps of the synthesis followed the procedure for the compounds 6-allyl. Reagents: \(\left[\(\text{\(1\)}\right.\left.\text{\(H\)}\right.\right] \text{C}_2\text{H}_3\text{Mo(\text{CO})}_2(\text{NCMe})\text{Cl}\) (200 mg, 0.64 mmol) and 2,9-Me₂-phen (135 mg, 0.64 mmol). Yield: 260 mg (93%, 0.66 mmol). Dark orange powder. Mp: 150–160 °C (dec.). Anal. calc'd for C₂₇H₂₄BrMoN₂O₂: C, 52.39; H, 3.92; N, 6.41. Found: C, 52.38; H, 3.86; N, 6.49. ¹H NMR (acetone-d₆, 400 MHz; δ (ppm)): 8.60 (d, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 8.3 Hz, 2H, C₉H₅N₂), 8.07 (s, 2H, C₁₂H₂₈N₂), 3.27 (s, 6H, CH₃), 2.69 (d, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 6.2 Hz, 2H, syn-C₉H₅C), 1.13 (d, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 9.0 Hz, 2H, anti-C₉H₅C). FTIR (ATR, cm⁻¹): 1929 vs [\(\nu_s(\text{CO})\)], 1836 vs [\(\nu_v(\text{CO})\)]. Single crystals of 10a·CHCl₃ suitable for X-ray diffraction analysis were prepared by overlaying of the CHCl₃ solution with ether.

**Synthesis of \(\left[\(\text{\(2\)}\right.\left.\text{\(H\)}\right.\right] \text{C}_2\text{H}_3\text{Mo(\text{CO})}_2(\text{2,9-Me}_2\text{-phen})\text{Cl}\) (10b-BF₄)**

Steps of the synthesis followed the procedure for the compounds 10b-BF₄. Reagents: \(\left[\(\text{\(2\)}\right.\left.\text{\(H\)}\right.\right] \text{C}_2\text{H}_3\text{Mo(\text{CO})}_2(\text{NCMe})\text{Cl}\] (224 mg, 1.08 mmol) and 2,9-Me₂-phen (135 mg, 0.64 mmol). Yield: 505 mg (96%, 1.03 mmol). Red powder. Mp: 160–170 °C (dec.). Anal. calc'd for C₂₇H₂₄BrMoN₂O₂: C, 47.39; H, 3.86; N, 5.78. ¹H NMR (CDCl₃; 400 MHz; δ (ppm)): 8.50 (d, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 8.3 Hz, 2H, C₁₂H₂₈N₂), 7.96 (s, 2H, C₁₂H₂₈N₂), 7.86 (d, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 8.3 Hz, 2H, C₁₂H₂₈N₂), 6.27 (d, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 2.9 Hz, 2H, C₁₂H₂₈N₂), 6.04 (s, 2H, C₁₂H₂₈N₂), 5.45 (t, \(\text{\(J\)}(\text{\(H\)},\text{\(H\)})\) = 2.9 Hz, 1H, CH₉H₅C), 3.60 (s, 6H, (CH₃)₂C₁₂H₂₈N₂), 1.74 (s, 6H, (CH₃)₂C₁₂H₂₈N₂). ¹³C NMR (CDCl₃; 101 MHz; δ (ppm)): 252.5 (2C, CO), 166.5, 164.2, 132.9, 131.5, 121.0 (5 × [\(\text{\(1\)}\right.\left.\text{\(C\)}\right.]), 140.2, 130.0, 127.3, 127.3 (4 × C₁₂H₂₈N₂) and C₁₂H₂₈N₂), 90.6 (1C, C₁₂ of C₁₂H₂₈N₂), 79.9 (2C, C₁₂ of C₁₂H₂₈N₂), 32.8 (2C, C₁₂H₂₈N₂(CH₃)), 18.6 (2C, C₁₂H₂₈N₂(CH₃)). FTIR (ATR, cm⁻¹): 1946 vs [\(\nu_v(\text{CN})\)], 1867 vs [\(\nu_v(\text{CO})\)]. Single crystals of 10b-BF₄·0.5(2Me₂-phen·HBF₄) suitable for X-ray diffraction analysis were prepared by overlaying of the crude product in CH₂Cl₂ with hexane.
(CH$_3$)$_2$SnH$_2$). FTIR (ATR, cm$^{-1}$): 2063 vs [v(CN)], 1925 vs [v$_3$(CO)], 1849 vs [v$_4$(CO)].

**Synthesis of ([η$^5$-4,7-Me$_2$C$_9$H$_8$]Mo(CO)$_2$(3,4,7,8-Me$_4$-phen)Cl) (11a)**

Steps of the synthesis followed the procedure for the compounds 4a. Reagents: [[([η$^5$-4,7-Me$_2$C$_9$H$_8$]Mo(CO)$_2$)[µ-Cl]]$_2$ (2; 50 mg, 76 µmol) and 3,4,7,8-Me$_4$-phen (35 mg, 0.15 mmol). Yield: 50 mg (93%, 88 µmol). Red powder. Mp: 140–150 °C (dec.). Anal. calc. for C$_37$H$_{25}$ClMoN$_2$O$_2$: C, 62.47; H, 4.05; N, 5.44. Found: C, 62.76; H, 4.07; N, 5.50. 

**1H NMR (CD$_2$Cl$_2$; 400 MHz; δ (ppm))**: 8.19 (d, j$^1$(H,H) = 8.2 Hz, 2H, C$_9$H$_5$N$_2$), 5.93 (d, j$^2$(H,H) = 2.8 Hz, 2H, C$_9$H$_5$N$_2$), 1.86 (s, 6H, (CH$_3$)$_2$C$_9$H$_8$)$_2$), 1.72 (s, 6H, (CH$_3$)$_2$C$_9$H$_8$)$_2$), 1.65 (s, 6H, (CH$_3$)$_2$C$_9$H$_8$)$_2$), 1.60 (s, 6H, (CH$_3$)$_2$C$_9$H$_8$)$_2$). FTIR (ATR, cm$^{-1}$): 1944 vs [v$_4$(CO)], 1893 vs [v$_4$(CO)], 1877 s [v$_4$(CO)].

**Synthesis of ([η$^5$-4,7-Me$_2$C$_9$H$_8$]Mo(CO)$_2$(4,4'-Me$_2$-bpy)][Cl] (13b-Cl)**

Steps of the synthesis followed the procedure for the compounds 4a. Reagents: [[([η$^5$-4,7-Me$_2$C$_9$H$_8$]Mo(CO)$_2$)[µ-Cl]]$_2$ (2; 50 mg, 76 µmol) and 4,4'-Me$_2$-bpy (28 mg, 0.15 mmol). Yield: 75 mg (96%, 0.15 mmol). Red powder. Mp: 130–140 °C (dec.). Anal. calc. for C$_35$H$_{23}$ClMoN$_2$O$_2$: C, 62.09; H, 4.06; N, 5.45. Found: C, 62.33; H, 4.11; N, 5.53. 

**1H NMR (CD$_2$Cl$_2$; 400 MHz; δ (ppm))**: 8.12 (d, j$^1$(H,H) = 8.4 Hz, 2H, C$_9$H$_5$N$_2$), 7.85 (d, j$^2$(H,H) = 8.4 Hz, 2H, C$_9$H$_5$N$_2$). FTIR (ATR, cm$^{-1}$): 1942 vs [v$_4$(CO)], 1893 vs [v$_4$(CO)].

**Synthesis of ([η$^5$-4,7-Me$_2$C$_9$H$_8$]Mo(CO)$_2$(6,6'-Me$_2$-bpy)][BF$_4$] (14a)**

Steps of the synthesis followed the procedure for the compounds 10a. Reagents: [[([η$^5$-4,7-Me$_2$C$_9$H$_8$]Mo(CO)$_2$(6,6'-Me$_2$-bpy)][BF$_4$] (12b-BF$_4$); 30 mg, 53 µmol) and [Me$_2$N][Cl] (58 mg, 0.53 mmol). Yield: 27 mg (99%, 52 µmol). Purple powder. Mp: 170–180 °C (dec.). Anal. calc. for C$_38$H$_25$ClMoN$_2$O$_2$: C, 62.09; H, 4.11; N, 5.45. 

**1H NMR (CD$_2$Cl$_2$; 400 MHz; δ (ppm))**: 8.12 (d, j$^1$(H,H) = 7.8 Hz, 2H, C$_9$H$_5$N$_2$), 7.97 (d, j$^2$(H,H) = 7.8 Hz, 2H, C$_9$H$_5$N$_2$). FTIR (ATR, cm$^{-1}$): 1930 vs [v$_4$(CO)], 1852 vs [v$_4$(CO)].

**X-ray crystallography**

The X-ray data for the crystals of the compounds 3, 4b-BF$_4$, 5b-9-CH$_3$Cl$_2$, 6a-6-allyl, 8-BF$_4$, 10a-CH$_2$Cl$_2$, 10a-CHCl$_3$, 10a-allyl,
10b-BF$_4$ - 0.5(phen-HBF$_4$) and 10c and were obtained at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Data reductions were performed with DENZO-SMN. The absorption was corrected by integration methods and only in cases of 5b-9-CH$_2$Cl$_2$ and 6a it was performed analytically using SADABS software. Structures were solved by direct methods (SIR92) and refined by full-matrix least squares based on $F^2$ (SHELXL). Thermal ellipsoids of C13 and C14 atoms in 5b-9-CH$_2$Cl$_2$, of F1, F3 and F4 atoms in 8-BF$_4$ and of F1 atom in 10b-BF$_4$ - 0.5(phen-HBF$_4$) were treated with standard ISOR instruction implemented in SHELXL97 software. 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 $U_{eq}$(H) = 1.2[$U_{eq}$(pivot atom)] or 1.5$U_{eq}$ 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.

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