Novel indenyl ligands bearing electron-withdrawing functional groups†

Iva Honzičková, a Jaromír Vinklárek, a Carlos C. Romão, b Zdeňka Růžičková a and Jan Honziček * c

A series of molybdenum complexes bearing new ligands is reported. The study covers a series of molybdenum compounds with the η5-coordinated indenyl ligand substituted with acyl-, ester- and amide-functions. This portfolio was extended by adding one representative with a η5-coordinated ester-substituted indenyl ligand. The functionalized indenes, necessary for the assembly, were prepared by convenient routes starting from inexpensive and readily available materials, enabling their production on a multigram scale. All structural types presented in this experimental study were supported by X-ray crystallographic data.

Introduction

The attachment of functional groups at cyclopentadienyl (Cp) rings of transition metal complexes can change considerably their electronic properties as well as the range of potential applications. 1,2 So far, many different substitution patterns have been developed for the Cp ligand but only a few of them cover electron-withdrawing substituents and are applicable for ligands with extended π-systems such as indenyl (Ind) or fluorenyl (Flu). These congeners of the Cp bearing annulated benzene rings show unique properties with consequent implications in the design of new catalytic systems. 3 Hence, the replacement of the Cp ligand with a larger π-system often has a strong effect on reactivity. 4 This so-called “indenyl effect” accelerates the reaction rates or switches the reaction pathway due to a lower energetic barrier of the haptotropic rearrangement of the π-ligand. 5 Recent studies have further revealed that a subtle modification of the indenyl ligand (e.g. replacement of one hydrogen with a methyl group) may play a crucial role in activation of coordinated ligands. 6,7

The modification of the indenyl ligand with electron-withdrawing substituents is rather rare. In 2000, Deck et al. extended a synthetic route giving perfluoroaryl-functionalized cyclopentadienides 5 on the indenes and described their rhénium complexes. 9 Some other strong electron-withdrawing substituents such as –F, 10 –CN, 11 –COOR, 12,13 –CONHR 14,15 and –COR 11,12,16 have been successfully attached on the Cp ring of various transition metal complexes using different strategies. However, the synthesis of the indenyl congeners has not been reported, although some of the suitable indene precursors are already known for several decades. 17

The aim of this study is to extend a family of indenyl ligands with ester-, amide- and acyl-functionalized derivatives. It will cover a series of modified indenes and unprecedented indenyl complexes. It is expected that a strong electron-withdrawing power of the attached functional groups will lead to more electron deficient metal centers that should be beneficial for their future application in catalysis. We decided to start our investigations with a familiar and well defined fragment, (η5-C5H5)Mo(CO)3, before moving into unexplored areas. The allyl molybdenum scaffold is accessible from the halide precursor [(η5-C5H4)Mo(CO)2(NCMe)X], which is an excellent starting material for the incorporation of a monoanionic π-ligand into the molybdenum coordination sphere. 15,16,18–20

Results and discussion

Ester-functionalized indenes

Three approaches for the synthesis of ester-functionalized indenes were examined. The obvious one using the reaction of sodium indenide with one equivalent of chloroformate was found to be ineffective since the 1,1-disubstituted derivative appears as a major product. In case of the methyl ester, 3-(MeOOC)C9H7 (2) and 1,1-(MeOOC)C9H6 (2a) were isolated in 2% and 15% yields, respectively (Scheme 1).

Alternatively, a series of ester-functionalized indenes (3–5) was prepared by an esterification of indene-3-carboxylic acid
Ester-functionalized indenyl molybdenum compounds

The ability of ester-functionalized indenyl ligands to form \( \eta^3 \)-coordination compounds was evidenced for the following molybdenum species. The series of ester-substituted indenes (3–5) was deprotonated with \( n \)-butyl lithium. The reaction of indenides (3-Li-5-Li) formed \( \textit{in situ} \) with the halide complex \([\eta^3-\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{NCMe})_2\text{Cl}]\) [6], accompanied by a loss of the stabilizing MeCN ligands, resulted in the formation of \( \eta^3 \)-indenyl compounds \([\eta^3-\text{C}_5\text{H}_5]\{\eta^3-1-(ROCO)\text{C}_5\text{H}_5\} \text{Mo}(\text{CO})_2\} \) (7–10), see Scheme 3.

The infrared and Raman spectra of compounds 7–10 show two CO stretching bands in a range typical for terminal carbonyl ligands, see Table 1. The CO stretching bands of the ester groups vary between 1702 and 1722 cm\(^{-1}\), thus revealing a very low delocalization of \( \pi \)-electrons of the C–O group and excluding an alternative \( \kappa \)-O-coordination mode of the functionalized indenyl ligand. The \( ^1 \text{H} \) NMR spectra of compounds 7–10 show the presence of two conformers arising from a different orientation of the \( \eta^3 \)-bonded allyl ligand. The signals of the allyl ligand were assigned to a conformer with the allyl ligand eclipsed with \( \text{OC-Mo-CO} \) (exo) and that with a staggered conformation (endo) according to data published for the unsubstituted analogue.\(^{19}\)

The solid state structure of compound 7 was determined by the single crystal X-ray analysis. The molecule has a distorted tetrahedral structure with allyl, indenyl and two carbonyl ligands around molybdenum in the formal oxidation state II, see Fig. 1. The geometric parameters describing the coordination sphere of molybdenum are listed in Table 2. The \( \eta^3 \)-coordinated allyl ligand is positionally disordered and splits into \( \text{exo} \)-conformer and \( \text{endo} \)-conformer. The molar ratio (exo/endo) was found to be 3:1 for compounds 7–10 correlating well with data published for monosubstituted derivatives of \([\eta^3-\text{C}_5\text{H}_5]\{\eta^3-\text{Ind}\} \text{Mo}(\text{CO})_2\} .\(^{7}\)

The dihedral angle between the \( C_5 \) ring of indenyl and a plane of the solid state structure of compound 7 was determined by the single crystal X-ray analysis. The molecule has a distorted tetrahedral structure with allyl, indenyl and two carbonyl ligands around molybdenum in the formal oxidation state II, see Fig. 1. The geometric parameters describing the coordination sphere of molybdenum are listed in Table 2. The \( \eta^3 \)-coordinated allyl ligand is positionally disordered and splits into \( \text{exo} \)-conformer and \( \text{endo} \)-conformer. The molar ratio (exo/endo) was found to be 3:1 for compounds 7–10 correlating well with data published for monosubstituted derivatives of \([\eta^3-\text{C}_5\text{H}_5]\{\eta^3-\text{Ind}\} \text{Mo}(\text{CO})_2\} .\(^{7}\)

The ester group is almost coplanar with the indenyl framework. The dihedral angle between the \( C_5 \) ring of indenyl and a plane defined by atoms C1, C10, O1 and O2 is 1.28(16)°.

Having obtained a series of molybdenum compounds with \( \eta^3 \)-bonded ester-substituted indenyl ligands, we sought to extend

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**Table 1** Summary of the infrared and Raman data for the ester-functionalized molybdenum complexes

|   | Infrared \( \nu(\text{C} \equiv \text{O}) \) cm\(^{-1}\) | Raman \( \nu(\text{C} \equiv \text{O}) \) cm\(^{-1}\) |
|---|---|---|
| 7 | 1934 | 1714 | 1944 |
|   | 1866 | 1861 |    |
| 8 | 1947 | 1712 |    |
|   | 1869 |    |    |
| 9 | 1932 | 1702 | 1942 |
|   | 1865 | 1856 | 1705 |
| 10 | 1944 | 1722 | 1946 |
|    | 1865 |    | 1714 |
| 12 | 1943 | 1694 |    |
|    | 1876 |    |    |
|    | 1828 |    |    |

\(^a\) The stretching frequencies are given in cm\(^{-1}\). \(^b\) The Raman spectrum was not obtained owing to luminescence.
the portfolio of such compounds by (i) adding a representative with a \( \eta^3 \)-coordinated ester-substituted indenyl ligand, (ii) introducing an acetyl substituent as a representative of a stronger electron-withdrawing substituent and (iii) developing a versatile route for amid-functionalized derivatives.

On the first count, we chose the mixed-indenyl species of type \( [\eta^3\text{-Ind}](\eta^3\text{-Ind})\text{Mo} \left( \text{CO}_2 \right) \). The methyl ester derivative \( [\eta^3\text{-1-(MeOCO)C}_9\text{H}_6](\eta^3\text{-Ind})\text{Mo} \left( \text{CO}_2 \right) \) (12) was prepared by a reaction of 2-Li with one equivalent of \( [\eta^3\text{-Ind}](\text{CO}_2)(\mu-\text{C})] \) (11) in a moderate isolated yield (43%), see Scheme 4. Coordination of the indenyl ligand was evidenced by infrared spectroscopy, which shows the stretching bands of the carbonyl ligands at frequencies \( \nu_1: 1943 \text{ cm}^{-1}; \nu_2: 1876, 1828 \text{ cm}^{-1} \) similar to those reported for the unsubstituted parent compound \( [\eta^3\text{-Ind}](\eta^3\text{-Ind})\text{Mo} \left( \text{CO}_2 \right)J \). The appearance of two bands of the \( \nu_1 \text{(CO)} \) is due to a vibration coupling of the carbonyl ligands in the crystal lattice. The CO stretching band of the ester group is almost parallel to the \( \eta^3 \)-coordinated \( \pi \)-system of the indenyl framework. The distance between the plane defined by three carbon atoms of 1-(MeOCO)C9H6 and a plane defined by atoms C1, C10 and O2 is 3.8(2) Å.

The crystal structure of 12 is stabilized by a sandwich \( \pi-\pi \) stacking involving the unsubstituted indenyl ligands of two neighboring molecules. The distance between the centroid of the five-membered ring \( \text{Cg(C12–C16)} \) and a plane defined by the parallel five-membered ring \( \text{[Pl(C12’–C16’)]} \) is 3.3075(10) Å. A T-shaped interaction between the face of the six-membered ring of the substituted indenyl ligand \( \text{C2–C6} \) and the six-membered ring vertex of the unsubstituted indenyl \( \text{C17’–H17’} \) connects the molecules into zig-zag chains along the \( \text{b-axis} \). The distance between the centroid \( \text{Cg(C2–C6)} \) and the carbon atom \( \text{C17’} \) is 3.532(2) Å.

The X-ray diffraction analysis reveals that the less donating ester-substituted indenyl ligand adopts the \( \eta^3 \)-coordination mode in the solid state, whereas the electron richer unsubstituted indenyl stays \( \eta^3 \)-coordinated, see Fig. 2. The hapticity of indenyl ligands is clearly elucidated from the slip parameters listed in Table 2. Hence, the substituted indenyl has considerably higher values of \( \Omega \) and \( \Delta(M-C) \) than the unsubstituted one. Compound 12 adopts a conformation, similar to the unsubstituted counterpart,23 with the \( \eta^3 \)-indenyl ligand in \( \text{exo-conformation and that of the C6-ring of the \( \eta^3 \)-indenyl facing away from the carbonyl ligands thereby avoiding repulsive interactions. The ester group is almost coplanar with the \( \eta^3 \)-coordinated \( \pi \)-system of the indenyl framework. The dihedral angle between a plane defined by three carbon atoms of \( \text{Ind} \) (C1, C4 and C5) and a plane defined by atoms C1, C10, O1 and O2 is 3.8(2) Å.

The \( \eta^3 \)-indenyl ring is stabilized by a sandwich \( \pi-\pi \) stacking involving the unsubstituted indenyl ligands of two neighboring molecules. The distance between the centroid of the five-membered ring \( \text{Cg(C12–C16)} \) and a plane defined by the parallel five-membered ring \( \text{[Pl(C12’–C16’)]} \) is 3.3075(10) Å. A T-shaped interaction between the face of the six-membered ring of the substituted indenyl ligand \( \text{C2–C6} \) and the six-membered ring vertex of the unsubstituted indenyl \( \text{C17’–H17’} \) connects the molecules into zig-zag chains along the \( \text{b-axis} \). The distance between the centroid \( \text{Cg(C2–C6)} \) and the carbon atom \( \text{C17’} \) is 3.532(2) Å.

Table 2 Geometric parameters of the molybdenum complexes \(^a\)

|          | 7        | 12       | 14       | 20       | 22 MeOH  |
|----------|----------|----------|----------|----------|----------|
| Mo-Cg(C1)| 2.0358(12)| 2.0203(10)| 2.0366(11)| 2.0229(10)| 2.0369(11)|
| Mo-Cg(C1)| 2.044(4)  | 2.1423(19)| 2.053(3) | 2.047(3) | 2.049(3) |
| Mo-C(CO)| 1.936(3)  | 1.943(2)  | 1.933(3) | 1.931(2) | 1.939(3) |
| Cg(C1)–Mo–Cg(C1)| 126.06(13) | 131.62(6) | 127.88(10) | 126.69(11) | 127.09(10) |
| C(CO)–Mo–C(CO)| 80.26(12) | 79.22(9)  | 79.15(13) | 82.79(9) | 78.04(11) |
| \( \Omega \) | 4.5(3)  | 4.4(2)  | 3.4(3) | 4.3(2) | 3.7(3) |
| \( \Delta(M-C) \) | 0.119(3) | 0.114(2)d | 0.106(3) | 0.104(2) | 0.105(3) |

\(^a\) Distances are given in Å; angles and dihedral angles are given in °. \(^b\) \( \Omega \) is the envelope fold angle defined for the indenyl ligand as the angle between planes defined by C1, C2 and C3 and that of C1, C3, C8 and C9. \(^c\) \( \Delta(M-C) \) 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–C8 and M–C9 and those of M–C1, M–C2, and M–C3.22 \( ^d \) Data for Ind. \(^e\) Data for 1-(MeOCO)C9H6.

exchange of the indenyl rings. This observation correlates well with the properties of the unsubstituted analogue \( [\eta^3\text{-Ind}](\eta^3\text{-Ind})\text{Mo} \left( \text{CO}_2 \right)J \), that gives only one set of signals for both indenyl ligands.24

**Scheme 4** Synthesis of a mixed indenyl molybdenum complex.
Acetyl-functionalized indenyl molybdenum compound

A similar strategy as described for indene was utilized for the synthesis of the acetyl-functionalized derivative 3-(MeCO)C9H7 (13). Hence, the reaction of sodium indenide with ethyl acetate produced indene in 38% isolated yield including a vacuum distillation step (Scheme 5). The protocol utilized inexpensive and readily available starting materials providing the product on a multigram scale. The vibrational spectra show a strong band of CO stretching in a range typical for the keto-group (IR: 1669 cm⁻¹; Raman: 1666 cm⁻¹). The 1H and 13C{1H} NMR spectra reveal the appearance of an isomer with the acetyl function in the 3-position of the indene framework. This observation is in line with the X-ray analysis of a single crystal obtained by recrystallization from hexane at low temperature. Hence, the acetyl group is attached to the sp² carbon atom of the indene framework, see Fig. 3. The bond length between the carbon atom C1 and the oxygen atom O1 is 1.222(2) Å that is within a range typical for the CO double bond.

Deprotonation of indene 13 with n-butyl lithium followed by addition of the allyl complex [(η⁵-C₅H₅)Mo(CO)₂(NCMe)₂Cl] (6) yields the desired η⁵-indenyl complex [(η⁵-C₅H₅)(η⁵-1-(MeCO)C₉H₆)-Mo(CO)₂] (14), see Scheme 6.

Infrared, Raman and ¹H NMR spectroscopy confirmed the successful assembly of the acetyl-functionalized indenyl molybdenum framework. Hence, the vibrational spectra of compound 14 show, in addition to stretching bands of the carbonyl ligands, a characteristic band of the C=O stretching at similar frequencies as observed for indene precursor 13, see Table 3. The ¹H NMR spectrum of compound 14 features a similar pattern as observed for the ester derivatives. The molar ratio of exo- and endo-conformers (3 : 1) is virtually the same as observed for the ester derivatives. This observation indicates that the abundance of given conformers is directed by the bulkiness of the modified indenyl ligand while electronic properties of the substituents play only a minor role.

X-ray crystallographic structure determination confirmed that the acetyl-substituted molybdenum compound 14 is isostructural with ester-derivative 7. The acetyl function is coplanar

|   | Infrared | Raman |
|---|----------|-------|
|   | ν(C=O) | ν(C=O) | ν(C=O) | ν(C=O) |
| 14 | 1936 | 1660 | 1932 | 1666 |
| 20 | 1858 | 1836 |       |       |
| 21 | 1932 | 1635 | 1931 | 1637 |
| 1859 | 1850 |       |       |       |
| 22 | 1940 | 1667 | 1948 | 1664 |
| 1852 | 1848 |       |       |       |

a The stretching frequencies are given in cm⁻¹.
Amide-functionalized indenyl molybdenum compounds

Finally, we have also investigated the scope of our synthetic protocol for compounds with amide-functions. The starting amide-substituted indenes were synthesized using two strategies. 

**tert-Butyl derivative** 15 was prepared by a reaction of lithium indenide (1-Li) with tert-butyl isocyanate, see Scheme 7. Rather inexpensive starting materials and an acceptable isolated yield (65%) predestinate this procedure for the use on a multigram scale. Unfortunately, the higher reactivity of aryl isocyanates precludes their use for the synthesis of aryl amides such as 16 and 19 (for structures, see Scheme 9). In fact, the reaction of phenyl isocyanate gives the acyl-substituted N,N-diphenyl urea 17 and the 1,3-disubstituted indene 18 as major outcomes in about 22% and 8% yields, respectively (based on indene). The desired 3-(PhNHCO)C9H7 (16) appears only as a minor product (in ~4% yield) that was separated from the reaction mixture by column chromatography (Scheme 8).

This led us to use 3-(ClCO)C9H7 prepared *in situ* for the synthesis of aryl amides 16 and 19, see Scheme 9. The carboxylic acid, 3-(HOCO)C9H7, was treated with thionyl chloride and the product reacted with anilines to give carboxamides 16 and 19 in satisfactory isolated yields.

Indenyl molybdenum compounds bearing the amide function group are accessible using the aforementioned protocol successfully used for the ester-derivatives. Deprotonation with *n*-butyl lithium followed by a metathesis reaction gave indenyl molybdenum compounds 20–22 in moderate isolated yields, see Scheme 10. The compounds were characterized by infrared, Raman and 1HN M R spectroscopy. The structures of compounds 20 and 22 were determined by X-ray diffraction analysis. The vibration spectra of compounds 20–22 show stretching bands of the carbonyl ligands at frequencies similar to those observed for ester-derivatives 7–10 (cf. data in Tables 1 and 3). Frequencies of N–H and C=O stretching bands of the amide functions are also consistent with the desired η^5^-coordination mode of the substituted indenyl ligands.

In case of compounds 20 and 22, a successful assembly of the [[η^3^-C3H3][η^5^-Ind]Mo(CO)2] moiety was further confirmed by the X-ray diffraction analysis, see Fig. 5 and 6. The carboxamide-functionalized indenyl ligands are η^5^-coordinated to the molybdenum as evidenced by ring slip parameters (Table 2). Surprisingly, only a very weak hydrogen bond (N1–H1···O1^1) was observed in the crystal lattice of with the indenyl framework. The dihedral angle between the C5 ring of indenyl and a plane defined by atoms C1, C10, O1 and O2 is 2.15(17)° (Fig. 4).
The derivatives of $[\eta^5-C_3H_5](\eta^5-Ind)Mo(CO)_2]$ bearing a strong electron-withdrawing functional group attached to the indenyl framework were prepared by a convenient route starting from functionalized lithium indenides. Since the availability of the ligand precursor is often a limiting factor of a synthetic protocol and consequent applications, attention was further given to low-cost pathways giving the ester-, acyl- and amide-functionalized indenes without the necessity of a tedious chromatographic purification step. On that count, one representative from each group was synthesized on the 6–14 g scale starting from common and inexpensive starting materials.

The herewith established substitution of the indenyl ligands with polar functional groups opens a novel pathway for chemical modifications of transition metal complexes and may accelerate their use in organic synthesis or catalysis.

**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. The starting materials were available commercially or prepared according to literature procedures: 3-(HOCO)C_9H_7, 21 [($\eta^5$-C_3H_5)Mo(CO)_2(\text{CNMe})_2\text{Cl}] (6), 18 [($\eta^5$-Ind)Mo(CO)_2(\mu-Cl)]_2 (11). 20

**Measurements**

Infrared and Raman spectra were measured on a Nicolet iS50 FTIR spectrometer equipped with a Raman module. The infrared spectra were recorded in the 4000–400 cm$^{-1}$ region (resolution 1 cm$^{-1}$) using a Diamond Smart Orbit ATR. Raman spectra were recorded in the 4000–100 cm$^{-1}$ region (resolution 2 cm$^{-1}$) in glass capillaries. The excitation source consisted of a Nd:YAG laser emitting at 1064 cm$^{-1}$. $^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance 400 and a Bruker Avance 500 spectrometers, respectively, at room temperature. The chemical shifts are given in ppm relative to TMS.

**Synthesis of 3-(MeOCO)C_9H_7 (2)**

Sodium indenide (1-Na), freshly prepared from indene (1; 11.7 mL, 0.10 mol) and sodium hydride (2.4 g, 0.10 mmol) in THF (150 mL), was treated with dimethyl carbonate (8.4 mL, 0.10 mol) and heated under reflux overnight. After cooling to room temperature, the reaction mixture was poured on an ice/water mixture and extracted with diethyl ether. The combined organic phases were washed with water, dried with magnesium sulfate and volatiles were vacuum evaporated on a rotavapor. The crude product was vacuum distilled (120 ºC, 660 Pa). Yield: 7.2 g (41 mmol, 41%). Pale yellow oil. Anal. Calc. for C_{11}H_{10}O_2: C: 75.84; H: 5.79. Found: C: 75.72; H: 5.85. $^1$H NMR (CDCl_3; 400 MHz; δ ppm): 7.94 (d, $^3$J(H,H) = 7.7 Hz, 1H, C_9H_7), 7.28 (d, $^3$J(H,H) = 7.5 Hz, 1H, C_9H_7), 7.24 (s, 1H, C_9H_7), 7.21 (t, $^3$J(H,H) = 7.5 Hz, 1H, C_9H_7), 7.10 (t, $^3$J(H,H) = 7.5 Hz, 1H, C_9H_7), 3.73 (s, 3H, COOCH_3), 3.26 (s, 2H, C_9H_7). $^{13}$C NMR (CDCl_3; 101 MHz; δ ppm): 164.3 (1C, C_9, COOME), 144.4 (1C, CH, C_9H_7), 143.3, ...
Reaction of 1-Na with CICOOMe

Sodium indene (1-Na), freshly prepared from indene (1, 11.7 mL, 0.10 mol) and sodium hydride (2.4 g, 0.10 mol) in THF (150 mL), was treated with methyl chloroformate (7.7 mL, 0.1 mol) and stirred at room temperature overnight. The reaction mixture was poured on an ice/water mixture and extracted with diethyl ether. The combined organic phases were dried with magnesium sulfate and washed with cold hexane (10 mL) and extracted several times. The steps of synthesis followed the procedure for compound 2. Reagents: 3-(HOCOC)C₆H₇ (0.80 g, 5.0 mmol), PhCH₂OH (5.4 g, 50 mmol). The crude product was purified by column chromatography on silica (diethyl ether/hexane = 1:9). Yield: 0.72 g (2.7 mmol, 54%). Colorless crystals. Mp = 110 °C. Anal. Calc. for C₁₇H₁₄O₂: C: 76.23; H: 5.30. Found: C: 76.75; H: 5.33.

Synthesis of 3-(PhCH₂OOC)C₆H₇ (4)

The steps of synthesis followed the procedure for compound 3. Reagents: 3-(HOCOC)C₆H₇ (0.80 g, 5.0 mmol), PhCH₂OH (5.4 g, 50 mmol). The crude product was purified by column chromatography on silica (diethyl ether/hexane = 1:9). Yield: 1.0 g (4.0 mmol, 80%). Pale yellow oil. Anal. Calc. for C₁₉H₁₄O₃: C: 53.47; H: 3.63. Found: C: 52.29; H: 3.80.

Synthesis of 3-(MeOCH₂CH₂OOC)C₆H₇ (3)

3-(HOCOC)C₆H₇ (0.80 g; 5.0 mmol) was dissolved in the excess of thionyl chloride (5 mL) and stirred at room temperature for 1 h and then heated at 60 °C for 10 min. The volatiles were vacuum evaporated. The sticky solid was treated with the excess of MeOCH₂CH₂OH (3.8 g, 50 mmol) and stirred for 2 h. The reaction mixture was diluted with diethyl ether and the reaction was quenched with addition of aqueous solution sodium carbonate. The organic phase was separated and the water phase was washed with an additional portion of diethyl ether. The combined organic phases were washed with water, dried with magnesium sulfate. The volatiles were vacuum evaporated on a rotavapor and the crude product was purified by column chromatography on silica (diethyl ether/hexane = 1:9). Yield: 0.84 g (3.8 mmol, 77%). Pale yellow oil. Anal. Calc. for C₁₃H₁₂O₃: C: 71.54; H: 6.47. Found: C: 71.59; H: 6.45.

Synthesis of 3-[MeOCH₂CH₂OOC]C₆H₇ (3)

3-(HOCOC)C₆H₇ (0.80 g; 5.0 mmol) was dissolved with 30 mL of THF, cooled at 0 °C and treated dropwise with 3.1 mL of BuLi (1.6 mol L⁻¹). The reaction mixture was stirred for 1 h and then added dropwise to the THF solution of [[η⁴-C₅H₅]Mo(CO)₅] (NCMe)₂Cl [6; 1.55 g, 5 mmol) precooled to −80 °C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The solid residue was washed with cold hexane (10 mL) and extracted several times with hot hexane. The volatiles were vacuum evaporated and product was vacuum dried. Yield: 1.24 g (3.4 mmol, 68%). Yellow powder. Mp = 89 °C. Anal. Calc. for C₁₇H₁₄O₃: C: 52.47; H: 3.85. Found: C: 52.29; H: 3.80. ¹H NMR (CDCl₃; 100 MHz; δ ppm): 8.08 (d, J(¹H,¹H) = 7.7 Hz, 1H, C₆H₆), 7.67 (t, J(¹H,¹H) = 2.0 Hz, 1H, C₆H₆), 7.25 (td, J(¹H,¹H) = 7.5 Hz, J(¹H,¹H) = 1.2 Hz, 1H, C₆H₆), 4.45 (t, J(¹H,¹H) = 4.7 Hz, 2H, CH₂), 3.72 (t, J(¹H,¹H) = 4.7 Hz, 2H, CH₂), 3.51 (d, J(¹H,¹H) = 2.0 Hz, 2H, C₆H₆), 3.42 (s, 3H, OCH₃). ¹³C{¹H} NMR (CDCl₃; 101 MHz; δ ppm): 164.2 (1C, C₆H₆), 145.0 (1C, CH, C₆H₆), 143.5, 140.9, 136.2 (3 × 1C, C₆H₆), 126.9, 125.7, 124.0, 122.7 (4 × 1C, CH, C₆H₆), 70.8, 63.7 (2 × 1C, CH₂CH₃), 59.2 (1C, CH₃, OCH₃), 38.6 (1C, CH₂, C₆H₆). IR (ATR, cm⁻¹): 1713s [v(=C(=O))]. Raman (capillary, cm⁻¹): 1717(3) [v(=C(=O))].
Synthesis of [(η^3-C_5H_5)[η^5-1-(MeOCH_2CH_2OCO)C_9H_8]Mo(CO)_3] (8)

The steps of the synthesis followed the procedure for compound 7. Reagents: 3-(MeOCH_2CH_2OCO)C_9H_8 (0.12 mmol), C_5H_5Mo(CO)_2 (63.2 mg, 0.12 mmol), Mo(CO)_5 (1.0 mL of THF). The mixture was stirred for 1 h and then added dropwise to the THF solution of [(η^3-Ind)Mo(CO)_3] (11; 0.3 mmol) precooled to –80 °C. The reaction mixture was stirred at room temperature overnight and then vacuum evaporated to dryness. The solid residue was washed with cold hexane (10 mL) and extracted several times with diethyl ether. The volatile were vacuum evaporated and product was vacuum dried. Yield: 0.19 g (43 mmol, 43%). Pale yellow solid.Mp = 120 °C (dec). Anal. Calc. for C_{46}H_{32}MoO_{12}: C: 59.74; H: 4.10. Found: C: 59.87; H: 4.03. 1H NMR (CDCl_3; 400 MHz; δ ppm): 7.52–6.65 (m, 9H, C_9H_8), 4.73 (s, 3H, C_9O), 3.94 (s, 3H, C_9O), 3.70 (s, 3H, C_9O), 3.35 (s, 3H, C_9O), 2.15 (d, J(H,H) = 7.7 Hz, 1H, C_9H_8), 1.70 (t, J(H,H) = 7.7 Hz, 1H, C_9H_8), 0.90 (d, J(H,H) = 7.7 Hz, 1H, C_9H_8).IR (ATR, cm⁻¹): 1963 vs [ν(C=O)CO] = 1865 vs [ν(C=O)CO] = 1862 vs [ν(C=O)CO] = 1714 (ν(C=O)).

Synthesis of (η^3-C_5H_5)[η^5-1-(MeOCH_2CH_2OCO)C_9H_8]Mo(CO)_3] (12)

The steps of the synthesis followed the procedure for compound 2. Reagents: indene (1; 11.7 mL, 0.10 mol), sodium hydride (2.4 g, 0.10 mol), ethyl acetate (9.8 mL, 0.10 mol). The crude product was vacuum distilled (90 °C, 660 Pa). Yield: 6.0 g (38 mmol, 38%). Pale yellow solid. Mp = 58 °C (CaH_2MoO); C: 83.52; H: 6.37. Found: C: 83.44; H: 6.31. 1H NMR (CDCl_3; 400 MHz; δ ppm): 8.19 (d, J(H,H) = 7.7 Hz, 1H, C_9H_8), 7.41 (d, J(H,H) = 7.4 Hz, 1H, C_9H_8), 7.30 (t, J(H,H) = 7.4 Hz, 1H, C_9H_8), 7.27 (t, J(H,H) = 1.8 Hz, 1H, C_9H_8), 7.22 (t, J(H,H) = 1.8 Hz, 1H, C_9H_8), 3.47 (d, J(H,H) = 1.8 Hz, 2H, CH_2), 2.46 (s, 3H, COCH_3). 11C NMR (CDCl_3; 101 MHz; δ ppm): 196.2 (1C, CH, C_9H_8), 143.5, 143.2, 140.8
Synthesis of [(η⁵-C₅H₅)η³-1-(MeCO)C₆H₄]Mo(CO)₃(14)

The steps of synthesis followed the procedure for compound 7. Reagents: 3-(MeCO)C₆H₄ (13; 0.79 g, 5 mmol), 3.1 mL of BuLi (1.6 mol L⁻¹), [(η⁵-C₅H₅)Mo(CO)₃][NEt₃]Cl (0.03 mL, 1.55 g, 5 mmol).

Yellow powder. Mp = 124 °C. Anal. Calc. for C₁₄H₁₇NO: C: 78.10; H: 7.96; N: 6.51. Found: C: 78.22; H: 8.04; N: 6.67. 1H NMR (CDCl₃, 400 MHz; δ ppm): 7.98 (d, 2J(H-H') = 2.0 Hz, 1H of H', 2H of C₆H₅), 7.48 (d, 2J(H-H') = 7.4 Hz, 1H of C₆H₅), 7.37–7.32 (m, 1H of C₆H₅), and 2H of C₆H₅, 7.27 (td, 2J(H-H') = 7.4 Hz, 2J(H-H') = 1.2 Hz, 1H of C₆H₅), 7.13 (tt, 2J(H-H') = 7.5 Hz, 2J(H-H') = 1.0 Hz, 1H of C₆H₅), 7.06 (t, 2J(H-H') = 2.0 Hz, 1H of C₆H₅). 13C{¹H} NMR (CDCl₃; 101 MHz; δ ppm): 163.1 (C, C₆H₅), 143.7, 141.2, 140.9, 137.9 (4 × C, C₆H₅ and C₆H₄), 137.0 (1C, CH₃C₆H₅), 129.3 (2C, CH₂C₆H₅), 127.0, 126.0 (2 × C, CH₂C₆H₅), 124.7 (2C, CH₂C₆H₅), 124.1, 122.2 (1 × C, CH₂C₆H₅), 120.3 (2C, CH₃C₆H₅), 38.6 (1C, CH₃C₆H₅). IR (ATR, cm⁻¹): 3284 vs [ν(NH)], 1648 s [ν(CO)] cm⁻¹.

Reaction of 1-Na with PhNCO

Lithium indene (1-Li), freshly prepared from indene (1; 11.7 mL, 0.10 mol) and 62.5 mL of BuLi (1.6 mol L⁻¹) in THF (150 mL), was cooled at ~80 °C, treated with PhNCO (10.9 mL, 0.10 mol), slowly warmed at room temperature and stirred overnight. The reaction mixture was poured on an ice/water mixture, treated with CH₄Cl₂ and neutralized with hydrochloric acid. The aqueous phase was separated and disposed. The organic phase was filtered on a glass frit. The collected solid was recrystallized from acetone to give colorless crystals of 18 (yield: 2.9 g, 8.2 mmol, 8%). The volatiles from the filtrate were vacuum evaporated and the product was washed with diethyl ether to give 9 g of a mixture of 16 and 17 in a molar ratio of 1:5 (according to ¹H NMR).

Analytically pure samples of 16 and 17 were obtained by column chromatography on silica (hexane/ethyl acetate = 7:3). 1,3-(PhNHCO)₂C₆H₆ (18): white solid. Mp = 240 °C (dec). Anal. Calc. for C₂₁H₂₀N₂O₂: C: 77.95; H: 5.12; N: 7.90. Found: C: 77.90; H: 5.04; N: 7.96. ¹H NMR (acetone-d₆; 400 MHz; δ ppm): 9.66 (s, 1H, NHPh), 9.14 (1s, 1H, NHPh), 8.03 (d, 2J(H-H') = 7.6 Hz, 1H, C₆H₄), 7.85 (d, 2J(H-H') = 8.2 Hz, 2H, C₆H₄), 7.68–7.63 (m, 1H of C₆H₄ and 2H of C₆H₅), 7.42–7.27 (m, 3H of C₆H₄ and 4H of C₆H₅), 7.12 (tt, 2J(H-H') = 7.3 Hz, 2J(H-H') = 1.1 Hz, 1H, C₆H₄), 7.08 (tt, 2J(H-H') = 7.3 Hz, 2J(H-H') = 1.1 Hz, 1H, C₆H₄), 4.71 (d, 2J(H-H') = 2.1 Hz, H, C₆H₄). IR (ATR, cm⁻¹): 3286 vs [ν(NH)], 1662 s [ν(CO)] cm⁻¹, 1646 s [ν(CO)] cm⁻¹. Raman (capillary, cm⁻¹): 1647 [ν(CO)] cm⁻¹, 3-PH(NH)CONPH(C₆H₅) (17): colorless crystals. Mp = 116 °C. Rₜ(TLC; hexane/ethyl acetate = 7:3) = 0.53. Anal. Calc. for C₂₃H₂₄N₂O₄: C: 77.95; H: 5.12; N: 7.90. Found: C: 77.84; H: 5.18; N: 7.79. ¹H NMR (CDCl₃; 400 MHz; δ ppm): 16.5 (s, 1H, NHPh), 7.75 (d, 2J(H-H') = 7.7 Hz, 1H, C₆H₄), 6.52 (d, 2J(H-H') = 1.4 Hz, 2H, C₆H₄), 7.18 (tt, 2J(H-H') = 7.3 Hz, 2J(H-H') = 1.1 Hz, 1H, C₆H₄), 6.70 (tt, 2J(H-H') = 7.3 Hz, 2J(H-H') = 1.1 Hz, 1H, C₆H₄), 3.25 (d, 2J(H-H') = 2.1 Hz, 2H, C₆H₄).
Synthesis of [(n-2-C3H5)Mo(CO)2(NCMe)2Cl] (21)

The steps of synthesis followed the procedure for compound 7.

Reagents: 3-(PhNHCO)C9H7 (0.80 g, 5.0 mmol), 4-ClC6H4NH2 (2.6 g, 20 mmol). The crude product was washed with ether and purified by column chromatography on silica (hexane/ethyl acetate = 7:3). Yield: 0.60 g (2.2 mmol, 44%). Colorless crystals. Mp = 172 °C. Rf (TLC; hexane/ethyl acetate = 7:3) = 0.42. Anal. Calc. for C16H13CINO: C 71.25; H: 4.48; N: 5.19. Found: C 71.35; H: 4.46; N: 5.12. 1H NMR (CDCl3; 400 MHz; δ ppm): 7.91 (d, J(1H,1H) = 7.5 Hz, 1H, C9H7), 7.80 (s, 1H, NHPh), 7.57 (d, J(1H,1H) = 8.8 Hz, 2H, C9H7), 7.48 (d, J(1H,1H) = 7.4 Hz, 1H, C9H7), 7.34 (t, J(1H,1H) = 7.5 Hz, 1H, C9H7), 7.29 (d, J(1H,1H) = 8.8 Hz, 2H, C9H7), 7.27 (d, J(1H,1H) = 7.4 Hz, 1H, C9H7), 1.11 Hz, 1H, C9H7), 0.76 (t, J(1H,1H) = 2.0 Hz, 1H, C9H7), 3.50 (d, J(1H,1H) = 2.0 Hz, 2H, C9H7). 13C NMR (CDCl3; 100 MHz; δ ppm): 163.2 (1C, Cq, CONH), 143.7, 141.1, 140.7, 136.5, 127.9 (5 × 1C, Cq, C=C and C-H, C9H7), 137.5 (1C, CH, CH, C9H7), 129.3 (2C, CH, C=C), 127.0, 126.2, 122.1, (4 × 1C, CH, CH, C9H7), 121.6 (2C, CH, C9H7), 38.6 (1C, CH2, C9H7). IR (ATR, cm⁻¹): 3284m [v(NH)], 1655s [v(CO)=O]. Raman (capillary, cm⁻¹): 1657(10) [v(CO)=O].

Synthesis of [(n-2-C3H5)[n-1-(4-C3H6NHCO)C9H7]Mo(CO)3] (22)

The steps of synthesis followed the procedure for compound 7.

Reagents: 3-(4-C3H6NHCO)C9H7 (15; 0.43 g, 2 mmol), 1.3 mL of 2BuLi (1.6 mol L⁻¹), [(n-2-C3H5)Mo(CO)2(NCMe)2Cl] (6; 0.62 g, 2 mmol). Yield: 0.50 g (1.23 mmol, 61%). Yellow powder. Mp = 185 °C (dec.). Anal. Calc. for C20H19ClMoNO3: C 54.62; H: 3.49; N: 3.03. Found: C: 54.70; H: 3.52; N: 3.08. 1H NMR (CDCl3, 400 MHz; δ ppm; 3:1 mixture of 23a (exo-C9H7) and 23b (endo-C9H7)): 8.00–7.91 (1H, a and 1H of b, H7 of C9H7), 7.21–6.98 (1H, a and 3H of b, H7 of C9H7, 5.98 (d, J(1H,1H) = 3.0 Hz, 1H of a, H7 of C9H7), 5.91 (d, J(1H,1H) = 2.5 Hz, 1H of b, H7 of C9H7), 5.86 (d, J(1H,1H) = 3.0 Hz, 1H of b, H7 of C9H7), 5.79 (d, J(1H,1H) = 2.5 Hz, 1H of b, H7 of C9H7, 5.68 (s, 1H of a, NH), 5.62 (s, 1H of b, NH), 5.34 (s, 1H, of b, C9H7), 3.33 (s, 1H, of b, C9H7), 3.24 (d, J(1H,1H) = 6.7 Hz, 1H of a, syn of C9H7), 2.11 (d, J(1H,1H) = 6.6 Hz, 1H of a, syn of C9H7), 1.48 (s, 9H of a and 9H of b, C(CH3)3), 1.06 (d, J(1H,1H) = 10.7 Hz, 1H of a, ant of C9H7), 0.85 (d, J(1H,1H) = 10.8 Hz, 1H of a, ant of C9H7), 0.78 (m, 1H, of a, mes of C9H7), –0.06 (d, J(1H,1H) = 9.6 Hz, 1H, of b, ant of C9H7), –1.09 (d, J(1H,1H) = 9.7 Hz, 1H, of b, ant of C9H7). IR (ATR, cm⁻¹): 3273m [v(NH)], 1932vs [v(CO)=O], 1848vs [v(CO)=O], 1635s [v(CO)=O]. Raman (capillary, cm⁻¹): 1931(6) [v(CO)=O], 1850(10) [v(CO)=O], 1637(4) [v(CO)=O]. Single crystals of 20 suitable to X-ray diffraction analysis were prepared by slow evaporation of MeOH solution.
low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Data reductions were performed using DENZO-SMN. and refined by full-matrix least squares based on F² and hydrogen atoms in aromatic rings or the allyl 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. The structure of 7 contains a disorder of the allyl group which, is positionally disordered on one of the carbon atoms (C13) and splits into two positions with an occupancy of about 7:3; this disorder was treated using SHELXL software.

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