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Benz[e]indenyl and benz[f]indenyl molybdenum compounds: evidence of the η^3 -coordination mode†

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This study reports the synthesis and characterization of new molybdenum compounds bearing benz[e]-indenyl and benz[f]indenyl ligands. The capability of the ligands to undergo η^5 -to- η^3 haptotropic rearrangement was evidenced on reactions with tris(pyrazolyl)methane. Appearance of the η^3 -coordination mode was determined by NMR spectroscopy and X-ray structure analysis on a single crystal.

Introduction

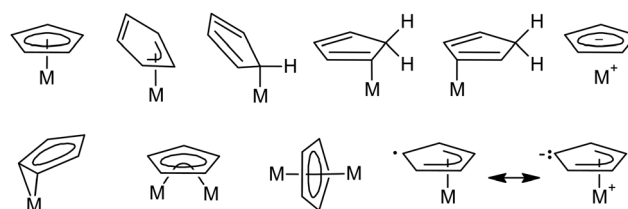
Cyclopentadienyl compounds of transition metals have attracted considerable attention since ferrocene, (η^5 -Cp)₂Fe (Cp = C₅H₅), was discovered in the early 1950s.¹ Variations in the cyclopentadienyl ligand periphery often result in dramatic changes in the physical, chemical, and biological properties of the corresponding compounds.² These changes can be attributed to the electronic and steric effects caused by the partial or full replacement of the hydrogen atoms by other groups. The extraordinary diversity of cyclopentadienyl compounds has been documented on many bonding modes described for the Cp ligand (Scheme 1).³

The ability of the cyclopentadienyl ligand to adjust its hapticity, *i.e.*, the number of contiguous carbon atoms involved in bonding to the central metal, gives rise to processes known as “haptotropic shifts”. These rearrangements have been investigated on Cp and few congeners with annulated benzene rings (Cp'), mainly on indenyl (Ind = C₉H₇)^{4–12} and fluorenyl (Flu = C₁₃H₉).^{12–14} Electronically saturated transition metal complexes with η^5 -bonded extended aromatic systems exhibit a substantial increase in the reaction rates of substitution reactions, when compared to their η^5 -Cp counterpart that has given rise to the term “indenyl effect”.^{15–18} It is usually interpreted in

terms of the M–Cp' bond strength in the two relevant hapticity modes. For instance, the η^5 -bond is stronger for the cyclopentadienyl ligand providing ground-state stabilization for complexes with η^5 -Cp, when compared to their indenyl and fluorenyl analogues. In contrast, the η^3 - and η^1 -bonds are stronger for ligands with annulated benzene ring stabilizing the corresponding η^3 - and η^1 -intermediates and transition states that result in increased rates of substitution reactions^{19,20} and activation of coordinated ligands.^{21–23}

Although haptotropic shifts of cyclopentadienyl, indenyl and fluorenyl ligands have been deeply investigated, revealing various distinct coordination modes, rearrangements of congeners with larger conjugated π -systems stay almost unexplored even though they are of particular importance due to the consequent implications for the design of catalytic systems.^{18,24} To the best of our knowledge, only η^1 - and η^5 -bonds are reported for transition metal compounds of indenyl and fluorenyl linearly or angularly annulated with benzene rings.^{25,26}

The first occurrence of transition metal complexes bearing indenyl/fluorenyl ligands with extended conjugated π -systems appears in the literature in 1992,²⁷ but the systematic work in this area has been started by Brintzinger *et al.* a few years later²⁸ within development of metallocene-based catalysts for olefin polymerization.^{29,30} Later contributions have brought novel



Scheme 1 The most pronounced bonding modes of Cp.

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transition metal-based catalysts for polymer tailoring^{31,32} and ruthenium compounds suitable for catalytic racemization of secondary alcohols.³³

Although the assembly of the first transition metal compounds bearing benzannulated indenyl and fluorenyl ligands started more than three decades ago, a deeper insight into their physical and chemical properties is dated much later. In 2006, Beckhaus *et al.* have pointed out a large helical twist of the tetrabenz[*a,c,g,i*]fluorenyl ligand in titanium complexes and their increased stability when compared with fluorenyl analogues.³⁴ A similar behavior was observed for yttrium complexes.³⁵ Contributions of Thiel *et al.* on various dibenz[*c,g*]fluorenyl compounds have proven a partial loss of aromaticity in the angularly annulated fluorenyl ligands that finally led to revision of the concept of aromaticity in metallocene compounds with extended π -systems.^{36–39}

The aim of this study is to synthesize new benz[*e*]indenyl (*e*-Bind) and benz[*f*]indenyl (*f*-Bind) compounds capable of η^5 – η^3 rearrangement. The attention will be given to 18e molybdenum(II) compounds which adjust the hapticity of the π -ligand upon coordination of an additional 2e donor.

Results and discussion

Benz[*e*]indene (**1**) and benz[*f*]indene (**2**) were prepared according literature procedures starting from benz[*e*]indanone²⁸ and benz[*f*]indanone,^{40,41} respectively (for details see the ESI†). Labeling of **1** with deuterium in 1- and 3-positions was done following the standard H/D exchange protocol using the repeated lithiation/deuterolysis protocol (Scheme 2).^{8,42}

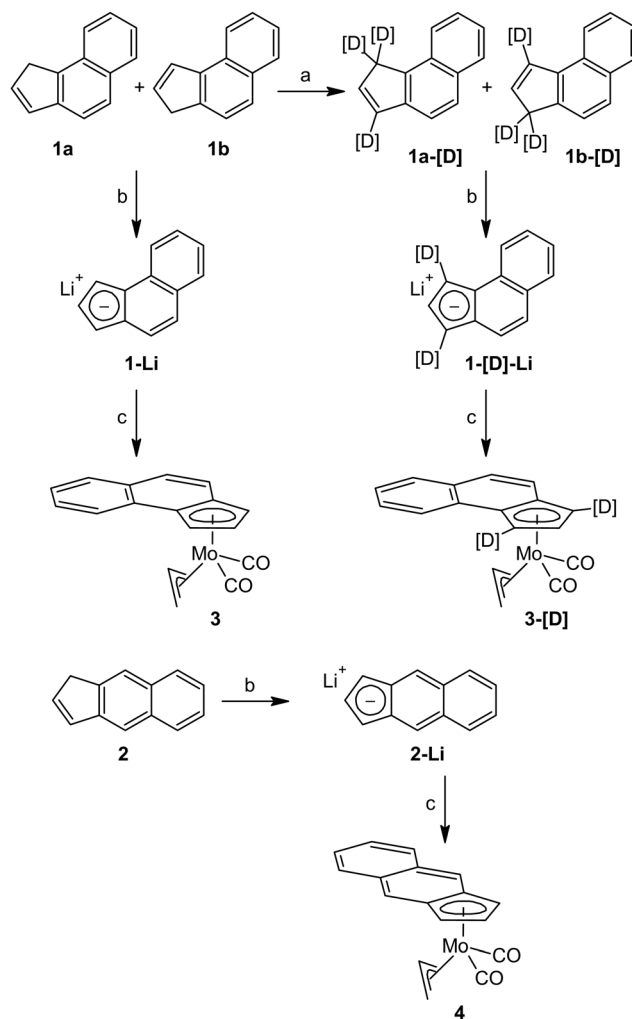
Lithiated compounds **1-Li** and **2-Li**, accessible by deprotonation with *n*-butyllithium, were isolated and characterized by multinuclear NMR spectroscopy. The patterns of ¹H and ¹³C APT NMR spectra verified aromatization of the five membered ring.

The values of ⁷Li chemical shifts, measured in thf-d⁸, are considerably lower than those reported for CpLi, IndLi and FluLi (Table 1).⁴³ This is attributed to the higher electron density on the lithium atom probably caused by the higher covalency of metal–carbon bonds or the difference in the coordination sphere of the lithium atom.

Lithiated benz[*e*]indene (**1-Li**) reacts with the chloride complex [(η^3 -C₃H₅)Mo(CO)₂(NCMe)₂Cl] to give the benz[*e*]indenyl complex [(η^3 -C₃H₅)(η^5 -*e*-Bind)Mo(CO)₂] (**3**) in medium yield; see Scheme 2. The isotopically labeled derivative [(η^3 -C₃H₅)(η^5 -*e*-1,3-[D]₂-Bind)Mo(CO)₂] (**3-[D]**) and benz[*f*]indenyl analogue [(η^3 -C₃H₅)(η^5 -*f*-Bind)Mo(CO)₂] (**4**) were prepared accordingly starting from the compounds **1-[D]** and **2**, respectively.

Infrared spectra of the compounds **3** and **4** show CO stretching bands in the range typical for terminal carbonyl ligands. In the case of **3**, the antisymmetric vibration mode is split on doublet due to the effects of the solid state.

¹H NMR spectra of the compounds **3** and **4** show formation of two conformers arising from a different orientation of the η^3 -bonded allyl ligand. Signals of the allyl ligand were assigned to



Scheme 2 Synthesis of allyl molybdenum compounds. Reagents: (a) *n*-BuLi/THF, D₂O, work-up (repeated three times); (b) *n*-BuLi/THF; and (c) [(η^3 -C₃H₅)Mo(CO)₂(NCMe)₂Cl].

Table 1 Effect of benzannulation on the ⁷Li chemical shift^a

	δ (ppm)	Ref.
1-Li	−4.88	This work
2-Li	−2.35	This work
CpLi	8.37	43
IndLi	6.12	43
FluLi	2.08	43

^a Measured in thf-d⁸.

the *exo*-isomer (allyl ligand eclipsed with OC–Mo–CO) and the *endo*-isomer according to the data published for the indenyl analogue.⁴⁴ At room temperature, the molar ratios (*exo/endo*) in **3** and **4** were found to be 3 : 1 and 2 : 1, respectively. This reveals a higher thermodynamic stability of the *exo*-isomer, which is in line with the data reported for [(η^3 -C₃H₅)(η^5 -Ind)Mo(CO)₂]⁴⁴ and its ring-substituted derivatives.^{45–47}

Solid-state structures of the compounds **3** and **4** were determined by single-crystal X-ray diffraction analysis. Both



molecules have a distorted tetrahedral structure with allyl, *e*-Bind/*f*-Bind and two carbonyl ligands around molybdenum in the formal oxidation state II (Fig. 1 and 2). Geometric parameters describing the coordination sphere of molybdenum are listed in Table 2. The η^3 -coordinated allyl ligand is positionally disordered and was split into *exo* and *endo* conformations with occupancies 85:15 and 80:20 for **3** and **4**, respectively. The *e*-Bind as well as *f*-Bind are η^5 -coordinated as evidenced by the small envelope fold angle [**3**: $\Omega = 2.9(3)^\circ$; **4**: $\Omega = 5.53(18)^\circ$] and low $\Delta(\text{M}-\text{C})$ parameter [**3**: $0.089(3) \text{ \AA}$; **4**: $0.1219(17) \text{ \AA}$] nearing the values calculated for the indenyl analogue [$(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2$] from the X-ray data [$\Omega = 3.3(3)^\circ$, $\Delta(\text{M}-\text{C}) = 0.115(3) \text{ \AA}$].⁴⁸

Our attempt to reach reactive species, which can undergo haptotropic rearrangement under mild conditions, led us to compounds of the formula $[(\eta^5\text{-Cp}')\text{Mo}(\text{CO})_2(\text{NCMe})_2][\text{BF}_4]$ (**5**: $\text{Cp}' = e\text{-Bind}$; **6**: $\text{Cp}' = f\text{-Bind}$). They were prepared *in situ* by reaction of **3** and **4** with HBF_4 in line with a protocol developed for the cyclopentadienyl analogues.⁴⁹ Although synthetic difficulties preclude their isolation in the pure form, they appear as intermediates upon synthesis of cationic molybdenum compounds bearing *e*-Bind and *f*-Bind shown in Schemes 3 and 4.

Stable compounds bearing η^5 -bonded *e*-Bind were prepared by reaction with bpy (**7**) and phen (**8**). ^1H NMR spectra proved coordination of the bidentate ligands. They give eight signals due to lowering of the molecular symmetry. The coordination mode of the *e*-Bind ligand was estimated from the chemical shifts of H^1/H^3 of the ligand. In both compounds, the signal of H^2 appears at a considerably higher (~ 5.9 ppm) field than the signals of H^1 (~ 6.9 ppm) and H^3 (7.1 ppm). Such a pattern is typical for species bearing η^5 -bonded ligands derived from indenyl.^{10,50} We note that the initial assignment, based on the assumption that $^3J(\text{H}^1, \text{H}^2) \approx ^3J(\text{H}^2, \text{H}^3) > ^4J(\text{H}^3, \text{H}^1)$, was verified on deuterium labeled species **7**-[D] and **8**-[D]. The cationic character of the compounds **7** and **8** is in line with a strong B-F stretching band observed in the infrared spectra at 1054 cm^{-1} . Appearance of two CO stretching bands in the infrared spectra at frequencies close to cyclopentadienyl and

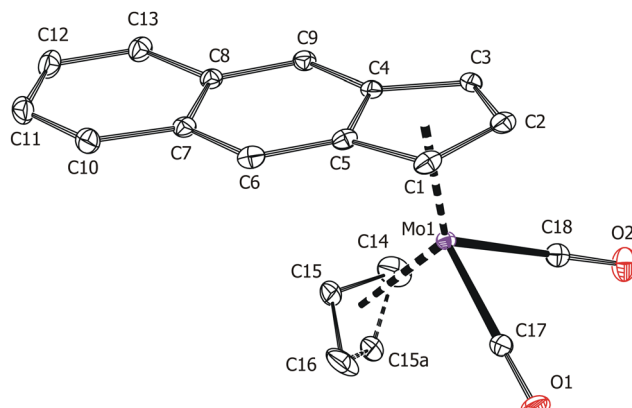


Fig. 2 ORTEP drawing of the molecule $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-f-Bind})\text{Mo}(\text{CO})_2]$ present in the crystal structure of **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (in \AA) and angles (in $^\circ$) determined by X-ray analysis

	3	4	10
Mo–C(CO)	1.939(3) 1.955(3)	1.942(2) 1.947(2)	1.958(3) 1.961(3)
Mo–Cg ^a	2.0269(11)	2.0355(8)	2.107(3)
Mo–N1	—	—	2.201(2)
Mo–N3	—	—	2.265(2)
Mo–N5	—	—	2.263(2)
C(CO)–Mo–C(CO)	80.64(11)	80.27(7)	80.30(12)
Ω^b	2.9(3)	5.53(18)	21.6(3)
$\Delta(\text{M}-\text{C})^c$	0.089(3)	0.1219(17)	0.804(3)

^a Cg is the center of gravity (C1–C5 for **3** and **4**; C1–C3 for **10**).

^b Envelope fold angle. ^c Difference in metal-carbon bonds defined as the difference between the averages of the metal-carbon distances Mo–C1, Mo–C2, and Mo–C3 and those of Mo–C4 and Mo–C5.

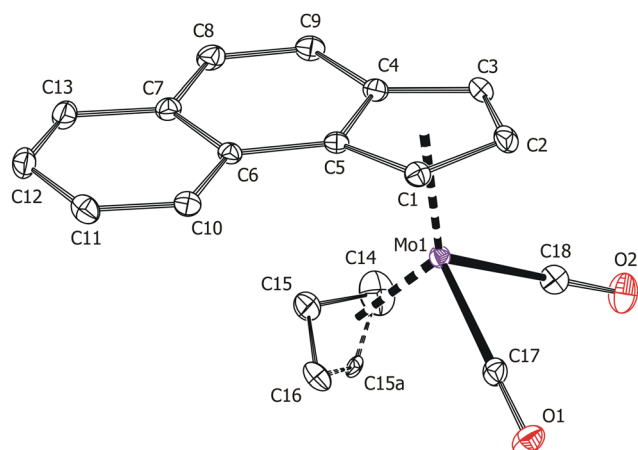
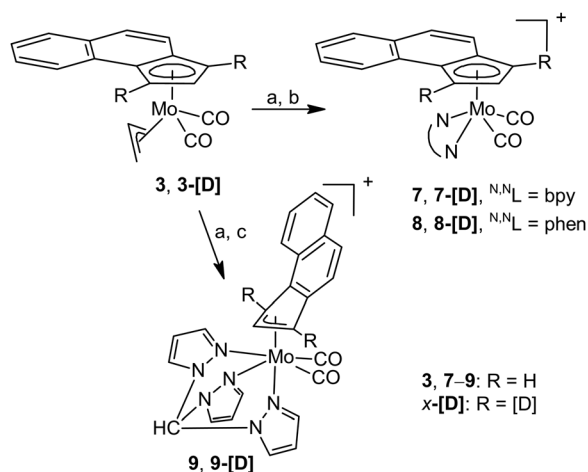


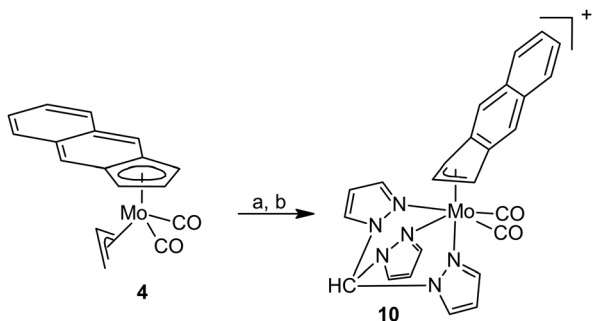
Fig. 1 ORTEP drawing of the molecule $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-e-Bind})\text{Mo}(\text{CO})_2]$ present in the crystal structure of **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



Scheme 3 Synthesis of cationic *e*-Bind compounds. Reagents: (a) $\text{HBF}_4 \cdot \text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$, MeCN; (b) $\text{N,N'L}/\text{CH}_2\text{Cl}_2$; and (c) $\text{tpm}/\text{CH}_2\text{Cl}_2$.

indenyl analogues^{51,52} implies formation of square-pyramidal complexes which obey the 18-electron rule.





Scheme 4 Synthesis of the compound **10**. Reagents: (a) $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ / CH_2Cl_2 , MeCN and (b) tmp.

Compound **9** bearing η^3 -coordinated *e*-Bind is accessible from **3** and tris(pyrazolyl)methane (tpm) using a similar synthetic protocol as in the case of bidentate ligands. The κ^3 -coordination of such a tripodal tridentate ligand enables induction of η^5 - η^3 haptotropic rearrangement of the *e*-Bind, which maintains 18 electrons in the valence sphere of molybdenum. Hapticity of the *e*-Bind ligand was estimated by ^1H NMR spectroscopy. The problems with assignment of diagnostic NMR signals led us to synthesize deuterium labelled products **9**-[D], which enabled distinguishing unambiguously H^2 (7.90 ppm) from $\text{H}^{1/3}$ (6.04 and 6.63 ppm). The appearance of H^2 at a considerably lower field than H^1 and H^3 is typical for η^3 -molybdenum complexes bearing indenyl ligands.^{10,50} The infrared spectrum shows CO stretching modes at 1955 and 1874 cm^{-1} .

Our attempts to synthesize cationic η^5 -*f*-Bind compounds, analogous to **7** and **8**, were not successful. The suggested species were not isolated in sufficient purity probably owing to a lower stability of the intermediate **6**. Nevertheless, a modified protocol enables isolation of η^3 -*f*-Bind compound **10** bearing the κ^3 -coordinated tpm ligand (Scheme 4).

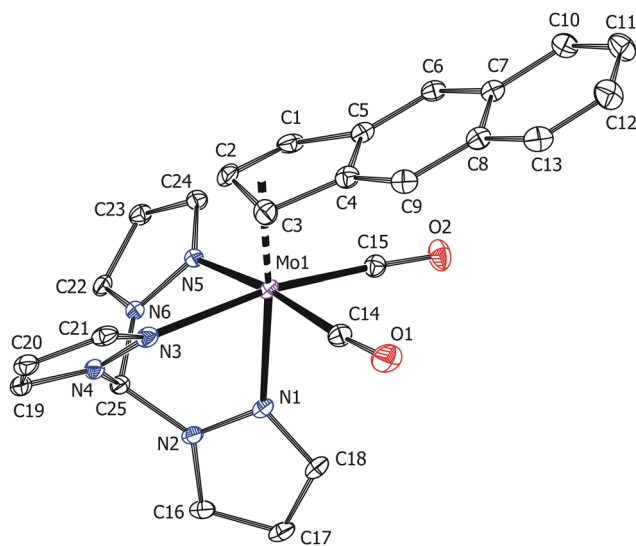


Fig. 3 ORTEP drawing of the cation $[(\eta^3\text{-f-Bind})\text{Mo}(\text{CO})_2(\kappa^3\text{-tpm})]^+$ present in the crystal structure of **10**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

^1H and ^{13}C APT NMR spectra of **10** show a pattern typical for C_s molecular symmetry. Full assignment of the appeared signals was done using 2D correlation techniques (^1H - ^1H COSY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC). The η^3 -coordination mode of *f*-Bind is evident from the chemical shift of the hydrogen atom H^2 and the appearance of carbon atoms C^{3a} and C^{9a} at a low field (145.0 ppm).

The X-ray crystallographic data proved the suggested molecular structure in the solid state (Fig. 3). The coordination sphere of the complex cation forms a distorted octahedron with one face occupied by nitrogen donor atoms of the tripodal tpm ligand. The opposite face of the distorted octahedron is occupied by η^3 -*f*-Bind and two carbonyl ligands. The coordination mode of *f*-Bind was elucidated from the high values of the envelope fold angle [$\Omega = 21.6(3)^\circ$] and $\Delta(\text{M-C})$ parameter [$0.804(3) \text{ \AA}$] (Table 2).¹⁰ These values are close to those reported for indenyl compounds $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-tpm})][\text{BF}_4]$ [$\Omega = 21.9(2)^\circ$, $\Delta(\text{M-C}) = 0.815(2) \text{ \AA}$]²⁰ and $[(\eta^3\text{-Ind})\text{Mo}(\text{CO})_2(\kappa^3\text{-Tp})][\text{BF}_4]$ [$\Omega = 21.4(2)^\circ$, $\Delta(\text{M-C}) = 0.819(3) \text{ \AA}$]¹⁰, implying a similarly strong indenyl effect. The Mo-N bond lengths vary in a wide range of 2.201(2)-2.265(2) \AA . This is due to a strong *trans* effect of carbonyl ligands which weakens the bonds Mo-N3 and Mo-N5.^{10,20}

Conclusions

This study documented the appearance of stable molybdenum compounds with two distinct coordination modes (η^3 and η^5) for both *e*-Bind and *f*-Bind. The properties of both ligands resemble rather the indenyl ligand than cyclopentadienyl. Although compounds with η^5 -bonds (**3**, **4**, **7** and **8**) have their cyclopentadienyl and indenyl analogues $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-Cp'})\text{Mo}(\text{CO})_2]$,⁴⁴ $[(\eta^5\text{-Cp'})\text{Mo}(\text{CO})_2(\kappa^2\text{-bpy})][\text{BF}_4]$ ⁵¹ and $[(\eta^5\text{-Cp'})\text{Mo}(\text{CO})_2(\kappa^2\text{-phen})][\text{BF}_4]$,⁵¹ the η^3 -species analogous to **9** and **10** was reported only for the indenyl ligand.^{10,20} The Cp analogue of **9** and **10** is not available due to a considerably lower tendency to undergo η^5 -to- η^3 rearrangement.²⁰ We note that the synthesized *f*-Bind compounds seem to be less stable than their *e*-Bind analogues, which is in line with previously reported experiments on half-sandwich titanium compounds.⁵³

Our contribution to the understanding of the coordination ability of *e*-Bind and *f*-Bind ligands could be helpful in tuning the catalytic properties of the indenyl ligand by benzannulation, as this type of modification not only increases the ligand bulkiness but also affects its electronic properties.

Experimental

Materials

Synthesis of the organometallic compounds was done under an argon atmosphere using conventional Schlenk-line techniques. The solvents were dried using standard methods.⁵⁴ The reagents were purchased from commercial sources (Acros Organics) or prepared according to literature procedures: $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{NCMe})_2\text{Cl}]$ ⁴⁴ and tris(pyrazolyl)methane (tpm).⁵⁵ Synthetic details for benz[e]indene and benz[f]indene are given in the ESI.†



Measurements

Infrared spectra were recorded on a Nicolet iS50 FTIR spectrometer in the 4000–400 cm^{-1} region (resolution: 1 cm^{-1}) using a Diamond Smart Orbit ATR. The ^1H , ^7Li , and ^{13}C -APT NMR spectra were recorded on Bruker Avance 400 and Bruker Avance 500 spectrometers at 300 K in thf-d^8 , CDCl_3 , acetone- d^6 , benzene- d^6 and dmsO-d^6 .

Synthesis of benz[e]indenyl lithium (1-Li)

Benz[e]indene (**1**; 0.33 g, 2.0 mmol) was dissolved in Et_2O (12 mL), cooled at -70°C , and treated with $n\text{-BuLi}$ (1.6 mol L^{-1} , 1.24 mL, 2.0 mmol) dropwise. The reaction mixture was stirred at room temperature for 2 h and volatiles were vacuum-evaporated. Yield: 0.21 g (1.2 mmol, 61%). Yellow powder. ^1H NMR (500.2 MHz, thf-d^8): δ = 8.04 (d, $^3J(^1\text{H}, ^1\text{H})$ = 8.0 Hz, 1H, $\text{H}^{6/9}$), 7.50 (d, $^3J(^1\text{H}, ^1\text{H})$ = 7.9 Hz, 1H, $\text{H}^{6/9}$), 7.45 (d, $^3J(^1\text{H}, ^1\text{H})$ = 8.4 Hz, 1H, $\text{H}^{4/5}$), 7.08, 6.92 ($2 \times$ dd, $^3J(^1\text{H}, ^1\text{H})$ = 6.3 Hz, $^4J(^1\text{H}, ^1\text{H})$ = 8.0 Hz, 2H, $\text{H}^{7,8}$), 6.77 (d, $^3J(^1\text{H}, ^1\text{H})$ = 8.5 Hz, 1H, $\text{H}^{4/5}$), 6.60 (s, 1H, $\text{H}^{1/3}$), 6.46 (t, $^3J(^1\text{H}, ^1\text{H})$ = 3.3 Hz, 1H, H^2), 6.10 (s, 1H, $\text{H}^{1/3}$). ^{13}C APT NMR (125.8 MHz, thf-d^8): δ = 131.5, 129.6, 125.4, 123.4 (4C, $\text{C}^{1a,3a,5a,9a}$), 128.0 (1C, $\text{C}^{6/9}$), 123.5 (1C, $\text{C}^{4/5}$), 122.8 (1C, $\text{C}^{7/8}$), 122.4 (1C, $\text{C}^{6/9}$), 119.3 (1C, $\text{C}^{7/8}$), 113.8 (1C, $\text{C}^{4/5}$), 112.9 (1C, C^2), 96.7 (1C, $\text{C}^{1/3}$), 94.1 (1C, $\text{C}^{1/3}$). ^7Li NMR (194.4 MHz, thf-d^8): δ = -4.88 .

Synthesis of benz[f]indenyl lithium (2-Li)

The reaction was performed as described for compound **1-Li** but with benz[f]indene. Yield: 0.24 g (1.4 mmol, 70%). Light orange powder. ^1H NMR (500.2 MHz, thf-d^8): δ = 7.69 (s, 2H, $\text{H}^{4,9}$), 7.53 (dd, $^3J(^1\text{H}, ^1\text{H})$ = 6.4 Hz, $^4J(^1\text{H}, ^1\text{H})$ = 3.3 Hz, 2H, $\text{H}^{5,8}$), 7.05 (t, 1H, $^3J(^1\text{H}, ^1\text{H})$ = 3.4 Hz, H^2), 6.70 (dd, $^3J(^1\text{H}, ^1\text{H})$ = 6.6 Hz, $^4J(^1\text{H}, ^1\text{H})$ = 3.2 Hz, 2H, $\text{H}^{6,7}$), 6.06 (d, 2H, $^3J(^1\text{H}, ^1\text{H})$ = 3.4 Hz, $\text{H}^{1,3}$). ^{13}C APT NMR (125.8 MHz, thf-d^8): δ = 134.3, 125.7 ($2 \times$ 2C, $\text{C}^{1a,3a,4a,8a}$), 128.2 (2C, $\text{C}^{5,8}$), 125.6 (1C, C^2), 117.4 (2C, $\text{C}^{6,7}$), 113.2 (2C, $\text{C}^{4,9}$), 90.4 (2C, $\text{C}^{1,3}$). ^7Li NMR (194.4 MHz, thf-d^8): δ = -2.35 .

Synthesis of $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-e-Bind})\text{Mo}(\text{CO})_2]$ (**3**)

A solution of benz[e]indene (**1**; 1.66 g, 10.0 mmol) in THF (30 mL) was cooled to 0°C , treated dropwise with a solution of $n\text{-BuLi}$ in hexane (1.6 M, 6.25 mL, 10.0 mmol), and stirred for 2 h at room temperature. The mixture was cooled to -80°C and treated dropwise with a solution of $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\text{-}(\text{NCMe})_2\text{Cl}]$ (3.11 g, 10.0 mmol) in THF (30 mL). The mixture was stirred at room temperature overnight. The volatiles were evaporated under reduced pressure, and the crude product was extracted with hexane (5×70 mL) at 60°C . The solvent was evaporated under reduced pressure. The product was recrystallized from hexane/ Et_2O at -80°C and vacuum-dried. Yield: 2.82 g (7.87 mmol, 78.7%). Yellow powder. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{MoO}_2$: C, 60.35; H, 3.94. Found: C, 60.58; H, 3.77. Mp: $145\text{--}150^\circ\text{C}$ (dec). ^1H NMR (400.1 MHz, CDCl_3 , 3:1 mixture of isomers **3a** and **3b**): δ = 7.78–7.68 (m, 2H of **3a** and 2H of **3b**, H^{6-9} , C_{13}H_9), 7.55–7.43 (m, 2H of **3a** and 2H of **3b**, H^{6-9} , C_{13}H_9), 7.34 [d, $^3J(^1\text{H}, ^1\text{H})$ = 9.0 Hz, 1H of **3a**, $\text{H}^{4,5}$, C_{13}H_9], 7.27 [d, $^3J(^1\text{H}, ^1\text{H})$ = 9.0 Hz, 1H of **3b**, $\text{H}^{4,5}$, C_{13}H_9], 7.02 [d, $^3J(^1\text{H}, ^1\text{H})$ =

9.0 Hz, 1H of **3b**, $\text{H}^{4,5}$, C_{13}H_9], 6.98 [d, $^3J(^1\text{H}, ^1\text{H})$ = 9.0 Hz, 1H of **3a**, $\text{H}^{4,5}$, C_{13}H_9], 6.36 [dd, $^3J(^1\text{H}, ^1\text{H})$ = 2.8 Hz, $^4J(^1\text{H}, ^1\text{H})$ = 1.5 Hz, 1H of **3a**, $\text{H}^{1,3}$, C_{13}H_9], 6.32 (br. s, 1H of **3b**, $\text{H}^{1,3}$, C_{13}H_9), 5.96 [dd, $^3J(^1\text{H}, ^1\text{H})$ = 2.8 Hz, $^4J(^1\text{H}, ^1\text{H})$ = 1.5 Hz, 1H of **3a**, $\text{H}^{1,3}$, C_{13}H_9], 5.88 (br. s, 1H of **3b**, $\text{H}^{1,3}$, C_{13}H_9), 5.68 [t, $^3J(^1\text{H}, ^1\text{H})$ = 2.8 Hz, 1H of **3a**, H^2 , C_{13}H_9], 5.65 (br. s, 1H of **3b**, H^2 , C_{13}H_9), 3.27 (br. s, 2H of **3b**, H^{syn} , C_3H_5), 3.07 (br. s, 1H of **3b**, H^{meso} , C_3H_5), 2.17 [d, $^3J(^1\text{H}, ^1\text{H})$ = 7.5 Hz, 1H of **3a**, H^{syn} , C_3H_5], 1.88 [d, $^3J(^1\text{H}, ^1\text{H})$ = 7.3 Hz, 1H of **3a**, H^{syn} , C_3H_5], 0.84 [d, $^3J(^1\text{H}, ^1\text{H})$ = 11.0 Hz, 1H of **3a**, H^{anti} , C_3H_5], 0.81 [d, $^3J(^1\text{H}, ^1\text{H})$ = 11.0 Hz, 1H of **3a**, H^{anti} , C_3H_5], 0.29 [tt, $^3J(^1\text{H}, ^1\text{H})$ = 11.0 Hz, $^3J(^1\text{H}, ^1\text{H})$ = 7.4 Hz, 1H of **3a**, H^{meso} , C_3H_5], -0.85 [d, $^3J(^1\text{H}, ^1\text{H})$ = 9.8 Hz, 1H of **3b**, H^{anti} , C_3H_5], -0.88 [d, $^3J(^1\text{H}, ^1\text{H})$ = 9.8 Hz, 1H of **3b**, H^{anti} , C_3H_5]. IR(ATR-C; cm^{-1}): 1952 s [$\nu_a(\text{C}\equiv\text{O})$]; 1927 s [$\nu_a(\text{C}\equiv\text{O})$]; 1831 vs. [$\nu_s(\text{C}\equiv\text{O})$]. Single crystals of **3** suitable for X-ray diffraction analysis were prepared by sublimation in a vacuum sealed ampoule (110°C ; 1 Pa). When the synthesis was carried out from **1-D**, **3-D** was obtained, for which the signals at 6.36, 6.32, 5.96 and 5.88 ppm in the ^1H NMR spectrum decreased in intensity and those at 5.68 and 5.65 ppm were seen as a broadened singlet.

Synthesis of $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-f-Bind})\text{Mo}(\text{CO})_2]$ (**4**)

The reaction was performed as described for compound **3** but with benz[f]indene (**2**; 1.66 g; 10 mmol). Yield: 2.63 g (7.34 mmol, 73.4%). Yellow powder. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{MoO}_2$: C, 60.35; H, 3.94. Found: C, 60.06; H, 3.72. Mp: $140\text{--}145^\circ\text{C}$ (dec). ^1H NMR (400.1 MHz, benzene- d_6 , 2:1 mixture of isomers **4a** and **4b**): δ = 7.33–7.26 (m, 2H of **4a** and 2H of **4b**, H^{5-8} , C_{13}H_9), 6.99 (s, 2H of **4a** and 2H of **4b**, $\text{H}^{4,9}$, C_{13}H_9), 6.96–6.93 (m, 2H of **4a**, H^{5-8} , C_{13}H_9), 6.90–6.88 (m, 2H of **4b**, H^{5-8} , C_{13}H_9), 5.75 (d, $^3J(^1\text{H}, ^1\text{H})$ = 1.9 Hz, 2H of **4b**, $\text{H}^{1,3}$, C_{13}H_9), 5.67 [d, $^3J(^1\text{H}, ^1\text{H})$ = 2.2 Hz, 2H of **4a**, $\text{H}^{1,3}$, C_{13}H_9], 5.33 [t, $^3J(^1\text{H}, ^1\text{H})$ = 2.2 Hz, 1H of **4a**, H^2 , C_{13}H_9], 5.20 [t, $^3J(^1\text{H}, ^1\text{H})$ = 1.9 Hz, H^2 , 1H of **4b**, C_{13}H_9], 3.34 [d, $^3J(^1\text{H}, ^1\text{H})$ = 6.5 Hz, H^{syn} , 2H of **4b**, C_3H_5], 2.91 [tt, $^3J(^1\text{H}, ^1\text{H})$ = 11.1 Hz, $^3J(^1\text{H}, ^1\text{H})$ = 6.5 Hz, H^{meso} , 1H of **4b**, C_3H_5], 2.09 [d, $^3J(^1\text{H}, ^1\text{H})$ = 7.4 Hz, H^{syn} , 2H of **4a**, C_3H_5], 0.77 [d, $^3J(^1\text{H}, ^1\text{H})$ = 11.2 Hz, H^{anti} , 2H of **4a**, C_3H_5], -0.18 [tt, $^3J(^1\text{H}, ^1\text{H})$ = 11.2 Hz, $^3J(^1\text{H}, ^1\text{H})$ = 7.4 Hz, H^{meso} , 1H of **4a**, C_3H_5], -0.85 [d, $^3J(^1\text{H}, ^1\text{H})$ = 11.1 Hz, H^{anti} , 2H of **4b**, C_3H_5]. IR(ATR-C; cm^{-1}): 1916 vs. [$\nu_a(\text{C}\equiv\text{O})$]; 1870 vs. [$\nu_s(\text{C}\equiv\text{O})$]. Single crystals of **4** suitable for X-ray diffraction analysis were prepared by sublimation in a vacuum sealed ampoule (120°C ; 1 Pa).

Synthesis of $[(\eta^5\text{-e-Bind})\text{Mo}(\text{CO})_2(\kappa^2\text{-bpy})][\text{BF}_4]$ (**7**)

A solution of **3** (460 mg, 1.28 mmol) in CH_2Cl_2 (30 mL) was treated with MeCN (2 mL), cooled to 0°C and treated with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (176 μL , 1.28 mmol). The reaction mixture was stirred for 2 h at room temperature. Solvents were vacuum-evaporated and the crude intermediate was washed with Et_2O (3×20 mL) and recrystallized from an acetone/ Et_2O mixture at -80°C . The purified intermediate was dissolved in CH_2Cl_2 (20 mL), treated with 2,2'-bipyridine (200 mg, 1.28 mmol) and stirred at room temperature for 18 h. Solvents were vacuum-evaporated and the crude product was washed with Et_2O (3×20 mL), recrystallized from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture and vacuum-dried. Yield: 650 mg (1.16 mmol, 90.7%). Dark red powder.



Anal. Calcd for $C_{25}H_{17}BF_4MoN_2O_2$: C, 53.60; H, 3.06; N, 5.00. Found: C, 53.32; H, 3.11; N, 5.25. Mp: 160–165 °C (dec). 1H NMR (400.1 MHz, acetone- d_6): δ = 9.51 [ddd, $^3J(^1H, ^1H)$ = 5.8 Hz, $^4J(^1H, ^1H)$ = 1.4 Hz, $^5J(^1H, ^1H)$ = 0.7 Hz, 1H, $H^{2,9}$, bpy], 9.20 [ddd, $^3J(^1H, ^1H)$ = 5.7 Hz, $^4J(^1H, ^1H)$ = 1.5 Hz, $^5J(^1H, ^1H)$ = 0.7 Hz, 1H, $H^{2,9}$, bpy], 8.50 [d, $^3J(^1H, ^1H)$ = 8.3 Hz, 1H, $H^{5,6}$, bpy], 8.24 [td, $^3J(^1H, ^1H)$ = 7.7 Hz, $^4J(^1H, ^1H)$ = 1.5 Hz, 1H, $H^{4,7}$, bpy], 8.19 [d, $^3J(^1H, ^1H)$ = 8.2 Hz, 1H, $H^{5,6}$, bpy], 8.06–8.03 (m, 1H, $H^{6,9}$, $C_{13}H_9$), 7.91 [td, $^3J(^1H, ^1H)$ = 7.7 Hz, $^4J(^1H, ^1H)$ = 1.4 Hz, 1H, $H^{4,7}$, bpy], 7.76 [ddd, $^3J(^1H, ^1H)$ = 7.5 Hz, $^3J(^1H, ^1H)$ = 5.8 Hz, $^4J(^1H, ^1H)$ = 1.4 Hz, 1H, $H^{3,8}$, bpy], 7.49 [ddd, $^3J(^1H, ^1H)$ = 7.5 Hz, $^3J(^1H, ^1H)$ = 5.8 Hz, $^4J(^1H, ^1H)$ = 1.3 Hz, 1H, $H^{3,8}$, bpy], 7.48–7.42 (m, 2H, $H^{7,8}$, $C_{13}H_9$), 7.15 [d, $^3J(^1H, ^1H)$ = 9.0 Hz, 1H, H^5 , $C_{13}H_9$], 7.08 [ddd, $^3J(^1H, ^1H)$ = 2.8 Hz, $^4J(^1H, ^1H)$ = 2.5 Hz, $^4J(^1H, ^1H)$ = 0.5 Hz, 1H, H^3 , $C_{13}H_9$], 6.97 [dd, $^3J(^1H, ^1H)$ = 9.0 Hz, $^4J(^1H, ^1H)$ = 0.5 Hz, 1H, H^4 , $C_{13}H_9$], 6.82 [dd, $^3J(^1H, ^1H)$ = 2.8 Hz, $^4J(^1H, ^1H)$ = 1.5 Hz, 1H, H^1 , $C_{13}H_9$], 5.88 [t, $^3J(^1H, ^1H)$ = 2.8 Hz, 1H, H^2 , $C_{13}H_9$]. IR(ATR-C; cm^{-1}): 1966 vs. [$\nu_a(C\equiv O)$]; 1887 vs. [$\nu_s(C\equiv O)$]; 1054 s [$\nu(B-F)$]. When the synthesis was carried out from 3-[D], 7-[D] was obtained, for which the signals at 7.08 and 6.82 ppm in the 1H NMR spectrum decreased in intensity and that at 5.88 ppm was seen as a broadened singlet.

Synthesis of $[(\eta^5\text{-}e\text{-Bind})Mo(CO)_2(\kappa^2\text{-phen})][BF_4]$ (8)

The reaction was performed as described for compound 7 but with 1,10-phenanthroline (230 mg; 1.28 mmol). Yield: 660 mg (1.13 mmol, 88.3%). Dark red powder. Anal. Calcd for $C_{27}H_{17}BF_4MoN_2O_2$: C, 55.51; H, 2.93; N, 4.80. Found: C, 55.78; H, 3.04; N, 5.01. Mp: 160–165 °C (dec). 1H NMR (400.1 MHz, acetone- d_6): δ = 9.88 [dd, $^3J(^1H, ^1H)$ = 5.4 Hz, $^4J(^1H, ^1H)$ = 1.2 Hz, 1H, $H^{2,9}$, phen], 9.59 [dd, $^3J(^1H, ^1H)$ = 5.4 Hz, $^4J(^1H, ^1H)$ = 1.3 Hz, 1H, $H^{2,9}$, phen], 8.85 [dd, $^3J(^1H, ^1H)$ = 8.1 Hz, $^4J(^1H, ^1H)$ = 1.2 Hz, 1H, $H^{4,7}$, phen], 8.52 [dd, $^3J(^1H, ^1H)$ = 8.2 Hz, $^4J(^1H, ^1H)$ = 1.2 Hz, 1H, $H^{4,7}$, phen], 8.15 [dd, $^3J(^1H, ^1H)$ = 8.1 Hz, $^3J(^1H, ^1H)$ = 5.4 Hz, 1H, $H^{3,8}$, phen], 8.13 [d, $^3J(^1H, ^1H)$ = 8.8 Hz, 1H, $H^{5,6}$, phen], 8.00 [d, $^3J(^1H, ^1H)$ = 8.9 Hz, 1H, $H^{5,6}$, phen], 7.99 [d, $^3J(^1H, ^1H)$ = 8.1 Hz, 1H, $H^{6,9}$, $C_{13}H_9$], 7.86 [dd, $^3J(^1H, ^1H)$ = 8.2 Hz, $^3J(^1H, ^1H)$ = 5.4 Hz, 1H, $H^{3,8}$, phen], 7.37 [ddd, $^3J(^1H, ^1H)$ = 7.9 Hz, $^3J(^1H, ^1H)$ = 7.3 Hz, $^4J(^1H, ^1H)$ = 1.3 Hz, 1H, $H^{7,8}$, $C_{13}H_9$], 7.24 [ddd, $^3J(^1H, ^1H)$ = 7.9 Hz, $^3J(^1H, ^1H)$ = 7.3 Hz, $^3J(^1H, ^1H)$ = 1.3 Hz, 1H, $H^{7,8}$, $C_{13}H_9$], 7.13 [ddd, $^3J(^1H, ^1H)$ = 2.7 Hz, $^4J(^1H, ^1H)$ = 1.4 Hz, $^4J(^1H, ^1H)$ = 0.8 Hz, 1H, H^3 , $C_{13}H_9$], 7.04 [d, $^3J(^1H, ^1H)$ = 8.9 Hz, 1H, $H^{6,9}$, $C_{13}H_9$], 6.90 [dd, $^3J(^1H, ^1H)$ = 2.7 Hz, $^4J(^1H, ^1H)$ = 1.4 Hz, 1H, H^1 , $C_{13}H_9$], 6.83 [dd, $^3J(^1H, ^1H)$ = 9.0 Hz, $^4J(^1H, ^1H)$ = 0.8 Hz, 1H, H^4 , $C_{13}H_9$], 6.67 [d, $^3J(^1H, ^1H)$ = 9.0 Hz, 1H, H^5 , $C_{13}H_9$], 5.92 [t, $^3J(^1H, ^1H)$ = 2.7 Hz, 1H, H^2 , $C_{13}H_9$]. IR(ATR-C; cm^{-1}): 1966 vs. [$\nu_a(C\equiv O)$]; 1889 vs. [$\nu_s(C\equiv O)$]; 1054 s [$\nu(B-F)$]. When the synthesis was carried out from 3-[D], 8-[D] was obtained, for which the signals at 7.13 and 6.90 ppm in the 1H NMR spectrum decreased in intensity and that at 5.92 ppm was seen as a broadened singlet.

Synthesis of $[(\eta^3\text{-}e\text{-Bind})Mo(CO)_2(\kappa^3\text{-tpm})][BF_4]$ (9)

The reaction was performed as described for compound 7 but with tris(pyrazolyl)methane (275 mg; 1.28 mmol). Yield: 575 mg (0.93 mmol, 72.7%). Dark red powder. Anal. Calcd for $C_{25}H_{19}BF_4MoN_6O_2$: C, 48.57; H, 3.10; N, 13.59. Found: C, 48.22;

H, 3.14; N, 13.73. Mp: 155–160 °C (dec). 1H NMR (400.1 MHz, acetone- d_6): δ = 9.35 [d, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^3 , pz], 9.29 (s, 1H, pz_3CH), 8.67 [d, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^3 , pz], 8.48 [d, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^3 , pz], 8.43 [d, $^3J(^1H, ^1H)$ = 2.5 Hz, 1H, H^5 , pz], 8.41 [d, $^3J(^1H, ^1H)$ = 2.5 Hz, 1H, H^5 , pz], 8.40 [d, $^3J(^1H, ^1H)$ = 2.5 Hz, 1H, H^5 , pz], 8.02 [d, $^3J(^1H, ^1H)$ = 8.2 Hz, 1H, $H^{6,9}$, $C_{13}H_9$], 7.90 [t, $^3J(^1H, ^1H)$ = 3.1 Hz, 1H, H^2 , $C_{13}H_9$], 7.54 [d, $^3J(^1H, ^1H)$ = 8.3 Hz, 1H, $H^{6,9}$, $C_{13}H_9$], 7.23 [ddd, $^3J(^1H, ^1H)$ = 8.4 Hz, $^3J(^1H, ^1H)$ = 6.7 Hz, $^4J(^1H, ^1H)$ = 1.2 Hz, 1H, $H^{7,8}$, $C_{13}H_9$], 7.14 [ddd, $^3J(^1H, ^1H)$ = 8.2 Hz, $^3J(^1H, ^1H)$ = 6.9 Hz, $^4J(^1H, ^1H)$ = 1.2 Hz, 1H, $H^{7,8}$, $C_{13}H_9$], 7.13 [d, $^3J(^1H, ^1H)$ = 8.0 Hz, 1H, $H^{4,5}$, $C_{13}H_9$], 7.03 [d, $^3J(^1H, ^1H)$ = 8.0 Hz, 1H, $H^{4,5}$, $C_{13}H_9$], 6.91 [dd, $^3J(^1H, ^1H)$ = 2.5 Hz, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^4 , pz], 6.72 [dd, $^3J(^1H, ^1H)$ = 2.5 Hz, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^4 , pz], 6.70 [dd, $^3J(^1H, ^1H)$ = 2.5 Hz, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^4 , pz], 6.63 [dd, $^3J(^1H, ^1H)$ = 3.1 Hz, $^4J(^1H, ^1H)$ = 3.1 Hz, 1H, $H^{1,3}$, $C_{13}H_9$], 6.04 [dd, $^3J(^1H, ^1H)$ = 3.1 Hz, $^4J(^1H, ^1H)$ = 3.1 Hz, 1H, $H^{1,3}$, $C_{13}H_9$]. IR(ATR-C; cm^{-1}): 1955 vs. [$\nu_a(C\equiv O)$]; 1874 vs. [$\nu_s(C\equiv O)$]; 1047 s [$\nu(B-F)$]. When the synthesis was carried out from 3-[D], 9-[D] was obtained, for which the signals at 6.63 and 6.04 ppm in the 1H NMR spectrum decreased in intensity and that at 7.90 ppm was seen as a broadened singlet.

Synthesis of $[(\eta^3\text{-}f\text{-Bind})Mo(CO)_2(\kappa^3\text{-tpm})][BF_4]$ (10)

A solution of 4 (52.1 mg, 145 μ mol) in CH_2Cl_2 (5 mL) was treated with MeCN (0.1 mL), cooled at 0 °C and treated with $HBF_4 \cdot Et_2O$ (20 μ L, 145 μ mol). The reaction mixture was treated with tris(1-pyrazolyl)methane (31.1 mg, 145 μ mol), stirred for 30 min at room temperature, then overlaid with Et_2O (50 mL) and kept for 18 h to give crystals of 10 suitable for X-ray analysis. The sample for analyses was washed with Et_2O (20 mL) and CH_2Cl_2 (20 mL) and vacuum-dried. Yield: 55 mg (89 μ mol, 61.4%). Orange-red crystals. Anal. calcd for $C_{25}H_{19}BF_4MoN_6O_2$: C, 48.57; H, 3.10; N, 13.59. Found: C, 48.26; H, 3.26; N, 13.77. Mp: 155–160 °C (dec). 1H NMR (500.2 MHz, $dmsO-d_6$): δ = 9.51 (s, 1H, pz_3CH), 9.19 [d, 1H, $^3J(^1H, ^1H)$ = 2.2 Hz, H^3 , pz], 8.54 [d, 2H, $^3J(^1H, ^1H)$ = 2.2 Hz, H^3 , pz], 8.42 [d, 1H, $^3J(^1H, ^1H)$ = 2.5 Hz, H^5 , pz], 8.37 [d, 2H, $^3J(^1H, ^1H)$ = 2.5 Hz, H^5 , pz], 7.51 (m, 2H, $H^{5,8}$, $C_{13}H_9$), 7.20 (m, 2H, $H^{6,7}$, $C_{13}H_9$), 7.06 (s, 2H, $H^{4,9}$, $C_{13}H_9$), 6.84 [dd, $^3J(^1H, ^1H)$ = 2.5 Hz, $^3J(^1H, ^1H)$ = 2.2 Hz, 1H, H^4 , pz], 6.71 [dd, $^3J(^1H, ^1H)$ = 2.5 Hz, $^3J(^1H, ^1H)$ = 2.2 Hz, 2H, H^4 , pz], 6.52 [t, 1H, $^3J(^1H, ^1H)$ = 3.6 Hz, H^2 , $C_{13}H_9$], 5.97 [d, 2H, $^3J(^1H, ^1H)$ = 3.6 Hz, $H^{1,3}$, $C_{13}H_9$]. ^{13}C APT NMR (125.8 MHz, $dmsO-d_6$): δ = 225.6 (2C, CO), 152.0 (1C, C^3 , pz), 146.5 (2C, C^3 , pz), 145.0 (2C, $C^{3a,9a}$, $C_{13}H_9$), 135.5 (2C, C^5 , pz), 134.8 (1C, C^5 , pz), 132.0 (2C, $C^{4a,8a}$, $C_{13}H_9$), 127.4 (2C, $C^{5,8}$, $C_{13}H_9$), 125.1 (2C, $C^{6,7}$, $C_{13}H_9$), 114.9 (2C, $C^{4,9}$, $C_{13}H_9$), 109.5 (1C, C^4 , pz), 108.2 (2C, C^4 , pz), 95.0 (1C, C^2 , $C_{13}H_9$), 74.7 (2C, $C^{1,3}$, $C_{13}H_9$), 74.4 (1C, pz_3CH). IR(ATR-C; cm^{-1}): 1951 vs. [$\nu_a(C\equiv O)$]; 1867 vs. [$\nu_s(C\equiv O)$]; 1024 s [$\nu(B-F)$].

X-ray crystallography

Crystallographic data for the single crystals of the compounds 3, 4 and 10 were collected on a Bruker D8 VENTURE Kappa Duo PHOTON100 using an $I\mu S$ micro-focus sealed tube with $MoK\alpha$ radiation (λ = 0.71073 Å) at a temperature of 150 K. The



structures were solved by direct methods (SHELXT39a)⁵⁶ and refined by full matrix least squares based on F^2 (SHELXL201439b).⁵⁷ The hydrogen atoms on carbon were fixed into idealized positions (riding model) or found on the difference Fourier map and all refined under rigid body assumption with assigned temperature factors $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$. The allyl ligands in **3** and **4** crystals are disordered over two positions.

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2295997–2295999 for **3**, **4** and **10**, respectively, and can be obtained free of charge from the centre via its website (<https://www.ccdc.cam.ac.uk/structures/>).

Author contributions

The authors contributed equally.

Conflicts of interest

There are no conflicts to declare.

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