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Reactivity of cyclopentadienyl transition metal(II) complexes with borate ligands: structural characterization of the toluene-activated molybdenum complex [$Cp^*Mo(CO)_2(\eta^3\text{-}CH_2C_6H_5)$]

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Reactions of cyclopentadienyl transition-metal halide complexes [$Cp^*Mo(CO)_3Cl$], **1**, and [$CpFe(CO)_2I$], **2**, ($Cp = C_5H_5$; $Cp^* = \eta^5\text{-}C_5Me_5$) with borate ligands are reported. Treatment of **1** with [$NaBt_2$] (Bt_2 = dihydrobis(2-mercapto-benzothiazolyl)borate) in toluene yielded [$Cp^*Mo(CO)_2(C_7H_4S_2N)$], **3**, and [$Cp^*Mo(CO)_2(\eta^3\text{-}CH_2C_6H_5)$], **4**, with a selective binding of toluene through C–H activation followed by orthometallation. Note that compound **4** is structurally characterized toluene-activated molecule in which the metal is in η^3-coordination mode. Under similar reaction conditions, [$NaPy_2$] (Py_2 = dihydrobis(2-mercaptopyridyl)borate) produced only the mercaptopyridyl molybdenum complex [$Cp^*Mo(CO)_2(C_5H_4SN)$], **5**, in good yield. On the other hand, when compound **2** was treated individually with [NaBt] (Bt = trihydro(2-mercapto-benzothiazolyl)borate) and [$NaPy_2$] in THF, formation of the η^1-coordinated complexes [$CpFe(CO)_2(C_7H_4S_2N)$], **6**, and [$CpFe(CO)_2(C_5H_4SN)$], **7**, was observed. The solid-state molecular structures of compounds **3**, **4**, **6**, and **7** have been established by single-crystal X-ray crystallographic analyses.

Introduction

Direct and selective C-H bond activation of unactivated hydrocarbons by transition-metal complexes continues to be an attractive goal due to its versatility in organic synthesis and natural gas conversions.[1] Transition-metal complexes have always played a major role in site selective C-H activation of substituted arenes in which the competition appears between benzylic (sp^3) and aromatic (sp^2) C-H bonds.[2] The mechanistic pathway of these reactions have been the subject of several investigations.[3] During the last two decades, there have been several reports on arene activation by transition-metal complexes especially platinum and iridium (Chart 1, I-IV).[2-5] Recent reports revealed that metallation of arenes was also achieved by tungsten η^3-allyl complexes,[6] mixed iron–tin metal clusters (V),[7] sterically encumbered cyclopentadienyl yttrium (VI), gadolinium,[8] and cerium complexes.[9a] Although all the reports describe the isolation of η^1-coordination mode of the arenes, a couple of reports support the formation of η^3-coordination.[9b-g] Thus, the synthesis of η^3-coordination by crystallographic characterization is of interest as this might constitute a milestone in this domain.

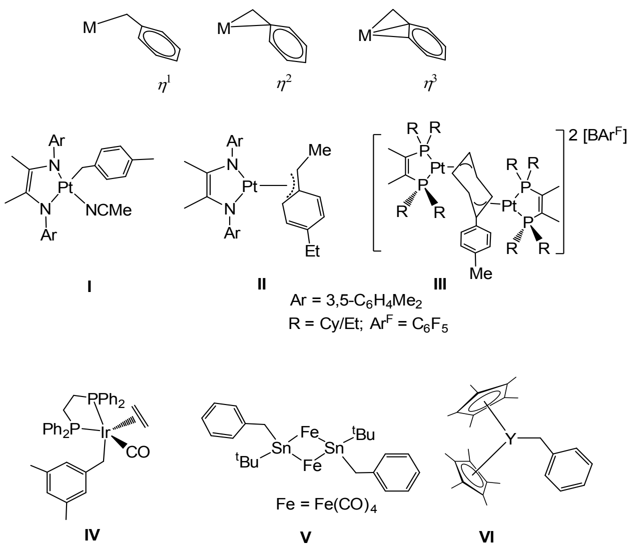

Chart 1 Different coordination modes of arene and arene-activated transition-metal complexes (I–VI)

As part of our ongoing studies on the synthesis of metallaboranes[10-12] and their derivatives,[13,14] we have recently reported the C-H activation of arene and heteroarenes by early

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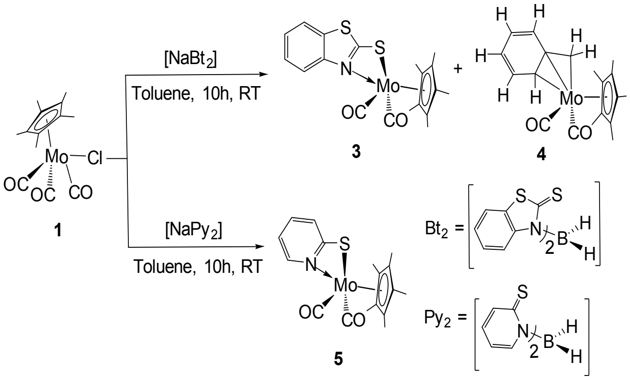
Electronic Supplementary Information (ESI) available: **3**, **4**, **6** and **7** had deposited with CCDC numbers 1451372(**3**), 1451371(**4**), 1451373(**6**), 1451374(**7**) and a MOL file of the Cartesian coordinates of calculated geometry **4** are provided as supporting information.For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x transition metallaboranes, such as $[(Cp^*Ta)_2B_5H_{11}]$.[15] In our continuing emphasis laid on late transition metals, we have recently demonstrated that $[(Cp^*Ru)_2B_3H_9]$, $[(Cp^*Rh)_2B_3H_7]$ and $[Cp^*MCl_2]_2$ (M = Ru, Rh, Ir) are good precursors for the synthesis of σ-borane/borate complexes.[16] We have also reported the synthesis of borate complexes from the reaction of $[Cp^*Mo(CO)_3Me]$ with $[BH_3EPh]Li$ (E = S, Se, Te).[17] As part of our on-going synthesis of σ-borane/borate complexes, we have extended our studies to other metal precursors such as $[Cp^*Mo(CO)_3Cl]$ (**1**) and $[CpFe(CO)_2I]$ (**2**). Herein, we report the synthesis and structural characterization of novel complexes including toluene-activated monometallic molybdenum complex.

Results and discussion

Reactivity of $[Cp^*Mo(CO)_3Cl]$ (1) with $[NaBt_2]$ and $[NaPy_2]$.

As shown in Scheme 1, reaction of $[Cp^*Mo(CO)_3Cl]$, **1**, with one equivalent of $[NaBt_2]$ (Bt_2 = dihydrobis(2-mercaptobenzothiazolyl)borate) yielded $[Cp^*Mo(CO)_2(C_7H_4S_2N)]$, **3**, and a C-H activated product $[Cp^*Mo(CO)_2(\eta^3\text{-}CH_2C_6H_5)]$, **4**, in moderate yields. Being motivated by our preliminary results, we were encouraged to explore the feasibility of the same reaction under different solvents. Although similar reaction conditions were followed, only complex **3** was obtained regardless of the solvents, such as xylene, anisole or cyclohexane. Thus, orthometallated C-H activation was not observed. The same reaction was explored with the heavier congener of the group 6 metal precursor $[Cp^*W(CO)_3Cl]$ that gave several less yield products. However, due to instability and insufficient amount of compounds their isolation and characterization was not possible. On the basis of mass spectrometric and spectroscopic data, complexes **3** and **4** formulated as shown in Scheme 1.



Scheme 1 Reactions of $[Cp^*Mo(CO)_3Cl]$ with borate ligands.

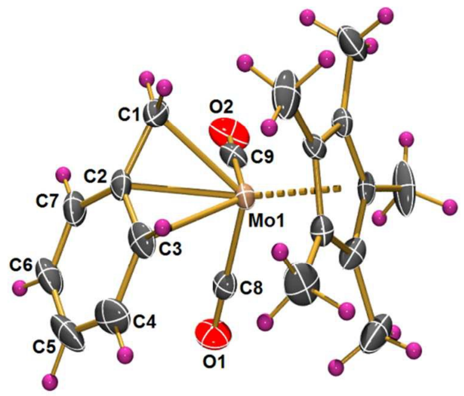
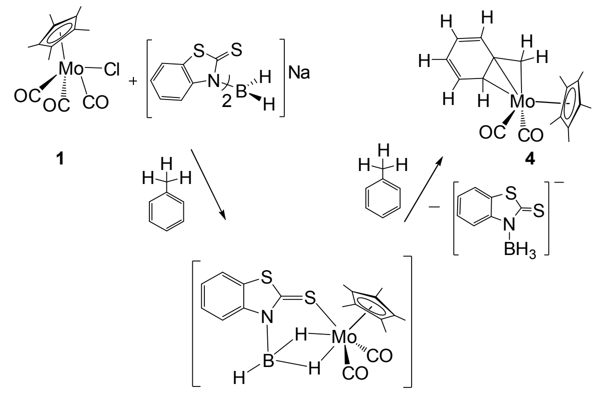


Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and bond angles (°): Mo1–C1 2.262(4), Mo1–C2 2.367(4), Mo1–C3 2.449(4), C1–C2 1.424(6), C2–C3 1.400(7), C2–C7 1.420(7), C3–C4 1.427(7), Mo1–C8 1.960(5), C8–O1 1.153(6), Mo1–C9 1.926(5), C9–O2 1.168(6); Mo1–C1–C2 76.1(2), Mo1–C2–C3 76.3(2), Mo1–C3–C2 69.9(2), Mo1–C2–C1 68.1(2), Mo1–C8–O1 178.6(4). Mo1–C9–O2 177.9(4).

The ^1H NMR spectrum of **4** reveals the presence of one type of Cp* signal at δ = 1.73 ppm along with characteristic phenyl peaks in the aromatic region. In addition, resonance associated with benzylic protons is observed at δ = 1.99 ppm. Compound **4** crystallizes in the triclinic crystal system with *P*-1 space group. The ORTEP diagram of **4** accompanied with selected bond parameters are shown in Fig. 1. The structure reveals that a benzylic group has been coordinated to molybdenum in a η^3-fashion, acting as a formal allyl-like three-electron donor allowing the metal center to satisfy 18-electron rule. In general, η^3-allyl-transition metal complexes are often key intermediates in many of the organic reactions.[18] Transition-metal benzyl complexes are usually synthesized by salt metathesis having a framework relatively similar to **4**, such as, $[Cp^*Mo(NO)(\eta^2\text{-}CH_2C_6H_5)Cl]$,[19] $[Cp^*Mo(NO)(\eta^2\text{-}CH_2C_6H_5)(CH_2SiMe_3)]$,[20] $[Cr(N^tBu)_2(\eta^2\text{-}CH_2C_6H_5)\text{-}(\eta^1\text{-}CH_2C_6H_5)]$[21] and $[Zr(\eta^1{:}\eta^2\text{-}CH_2C_6H_5)_4]$.[22] However, the benzyl group of these complexes is bound to the metal either in η^1 or η^2 fashion. Interestingly, in compound **4**, the molybdenum center binds to a solvent toluene in a η^3-fashion.

A thorough search at Cambridge Structural Data base indicates that the bond angles $M\text{-}C(H_2)\text{-}C_6H_5$ in the benzyl η^x-coordinated complexes (x = 1-3) span in the range of 80-100°, such as 81.10(4)° in $[Cp^*Mo(NO)(\eta^2\text{-}CH_2C_6H_5)Cl]$,[19] or 82.97(12)° in $[Cp^*Mo(NO)(\eta^2\text{-}CH_2C_6H_5)(CH_2SiMe_3)]$.[20] That measured in **4**, (76.2(2)°) is significantly smaller, reflecting a stronger interaction between molybdenum and the η^3-benzyl group. The other pertinent bond parameters involving Mo-Cp*, Mo-CO and $Mo\text{-}CH_2C_6H_5$ are comparable to those of related complexes (Table S1, Supporting Information).[19,20]

As shown in Scheme 2, complex $[Cp^*Mo(CO)_3Cl]$, **1** is capable of activating toluene only in the presence of an additional $[NaBt_2]$ moiety by releasing $[Bt]^-$ (Bt = trihydro(2-mercaptobenzthiazolyl)borate). A complex ^1H NMR spectrum was obtained for the reaction mixtures of $[Cp^*Mo(CO)_3Cl]$, **1** with $[NaBt_2]$. However, we were unable to isolate and characterize any intermediate species, preventing us to describe the role of diborate in the C-H activation of toluene.



Scheme 2 Plausible mechanism for the selective orthometallated benzylic C–H activation of toluene.

Nevertheless, an intermediate compound [Cp*Mo(CO)$_2$BH$_3$-(C$_7$H$_4$S$_2$N)] can be proposed that is related to recently isolated [Cp*Mo(CO)$_2$BH$_3$(1-benzothiazol-2-ylidene)].[17]

In order to understand the bonding properties of **4**, density functional theory (DFT) calculations were carried out on **4'** (Cp analogue of **4**) at the B3LYP level of theory. The optimized geometry compares relatively well with that of **4**. Mo-C1 distance is well reproduced, but Mo-C2 and Mo-C3 are little overestimated (Fig. S18, Supporting Information). The computed C-C separations in the η^3-benzyl group (C1-C2 = 1.44 and C2-C3 = 1.42 Å) are in a reasonably good agreement with the experimental values. They anticipate partial double bonds, suggesting some delocalization of π-electron density over C1-C2-C3 backbone. The rather acute Mo-C1-C2 angle measured in **4** (76.1(2)°) is well reproduced in **4'** (78.3°). An energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of about 3 eV is computed for **4'**, which indicates that **4** is thermodynamically stable (Fig. S19, Supporting Information). Further, we have observed that HOMO-5 and HOMO-6 show some bonding Mo-C interaction (Fig. S20, Supporting Information).

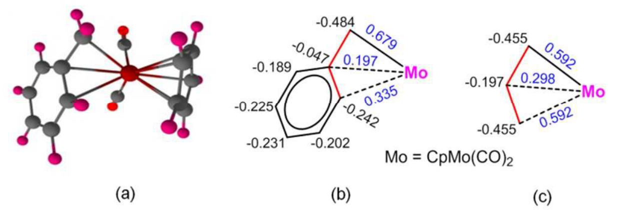


Fig. 2 Optimized geometry of **4'** (a), NBO atomic charges (black) and WBI's (in blue) in **4'** (b), and [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] (c).

The η^3-benzyl group in **4** can be considered as an allyl-like system, which is asymmetrically bonded to the molybdenum atom. Therefore, it is interesting to compare **4** with Davison's η^3-allyl complex [CpMo(CO)$_2$(η^3-C$_3$H$_5$)].[23] Strong interaction between the Mo fragment and η^3-benzyl group is confirmed by a natural bond orbital (NBO)[41] analysis of **4'** (Fig. S21, Supporting Information). Atomic charges on C1, C2 and C3 are -0.484, -0.047 and -0.242, respectively, which are comparable to those of the carbon atoms of the allyl group in [CpMo(CO)$_2$(η^3-C$_3$H$_5$)] (Fig. 2). This further indicates that the electron π-density of the benzyl ligand is mainly localized on C1 and the *ortho* carbon C3. On the other hand, a slight amount localized on other carbon atoms of the benzyl ring (-0.23 in total). The substantial Wiberg bond indices (WBI) of 0.679, 0.197 and 0.335 further confirm the strong bonding interaction between Mo and C1 and to a lesser extent between Mo1 and C2 and C3.

The other main product obtained from the reaction of **1** with one equivalent of [NaBt$_2$] is [Cp*Mo(CO)$_2$(C$_7$H$_4$S$_2$N)], **3** (Scheme 1). It adopts a four-legged piano-stool structure (Fig. 3) considering two carbonyls and a η^2-coordinated mercaptobenzothiazolyl ligand as four legs and it obeys the 18-elctron rule.[24]

Further, we have extended our experiments to different borate ligand with the same metal precursor. As shown in Scheme 1, one equivalent of [NaPy$_2$] (Py$_2$ = dihydrobis(2-mercapto-pyridyl)borate) with **1** yielded only the molybdenum mercaptopyridyl adduct [Cp*Mo(CO)$_2$(C$_5$H$_4$SN)], **5**, in good yield. Very recently, this compound which also adopts a four-legged piano-stool geometry was reported by another synthetic route and was structurally characterized.[25] The Cp analogues of both **3** and **5** are reported in literature.[26,27] Single crystal X-ray structures of **3** and **5**[25] reveal that they both crystallize in an *endo* conformation, whereas their Cp analogues show an *exo* geometry, differing in the orientation of the chelate ligand with respect to the Cp*/Cp unit (Fig. S17, Supporting Information). Table S2 (Supporting Information) provides a comparison of pertinent bond and torsion angles of **3** and **5** and their Cp analogues. Bond angles and bond parameters associated with Mo-S, Mo-N, Mo-C and Mo-Cp* are within the range of the values reported for related compounds.[26-28]

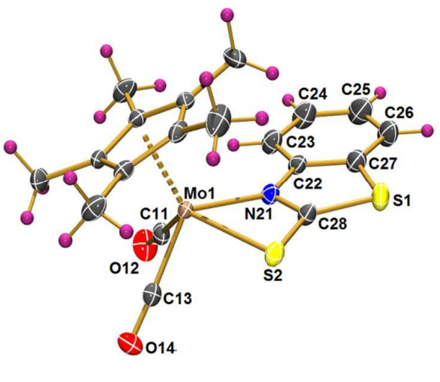
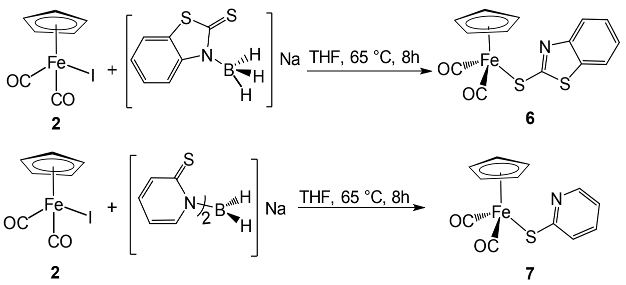


Fig. 3 Molecular structure of **3**. Selected bond lengths (Å) and bond angles (°): Mo1–S2 2.5564(7), Mo1–N21 2.190(2), Mo1–C11 1.972(3), Mo1–C13 1.965(3), S1–C28 1.752(3), S2–C28 1.710(3), C28–N21 1.321(3), C13–O14 1.153(3); S2–Mo1–N21 64.59(6), S2–Mo1–C13 84.47(7), C13–Mo1–C11 76.52(10), C11–Mo1–N21 86.28(9), N21–C28–S2 114.31(19).

Reactivity of [CpFe(CO)$_2$I] (2) with [NaBt] and [NaPy$_2$].

Further, we have extended this chemistry to group 8 metal precursor, [CpFe(CO)$_2$I], **2**, and it was observed that no clear



Scheme 3 Reaction of [CpFe(CO)$_2$I] with borate ligands.

reaction with [NaBt$_2$] in toluene. On the other hand, it independently reacts with [NaBt] (Bt = trihydro(2-mercaptobenzothiazolyl)borate) and [NaPy$_2$] in THF forming the 18-electron mercapto-benzothiazolyl and mercaptopyridyl iron adducts [CpFe(CO)$_2$-(C$_7$H$_4$S$_2$N)], **6**, and [CpFe(CO)$_2$(C$_5$H$_4$SN], **7**, respectively, in moderate yields.

The ^{1}H NMR spectra of **6** and **7** show the presence of one singlet for the cyclopentadienyl protons along with resonances associated with respective mercaptobenzothiazolyl and mercaptopyridyl aromatic protons. The IR spectra show intense bands in the region 2036 to 1988 cm^{-1}, characteristics of terminal carbonyl groups. Needle-shaped crystals of **6** and **7**, which were subjected to X-ray analysis, were grown from a hexane/DCM mixture. Their ORTEP diagrams along with selected metrical parameters are shown in Fig. 4 and Fig. 5, respectively. The molecular structures depict the well-known three-legged piano-stool geometry, in which the η^1-mercaptobenzothiazolyl or η^1-mercaptopyridyl ligand occupies one of the three legs. The structural similarity between **6** and **7** mainly concern the η^1-coordination of the mercapto-benzothiazolyl and mercaptopyridyl moieties. The Fe-S bond distances differ in these complexes (2.265 Å for **6** and 2.35 Å for **7**) but are in the range of those reported in related organo iron sulphur complexes.[29] In compound **7** the pyridyl unit lies 1.659 Å below the ‘basal’ plane made by S2-O3-O4, whereas the benzothiazolyl group in compound **6** lies 0.169 Å above the ‘basal’ plane S11-O42-O44. The Fe2–S11–C51 bond angle in **6** (107.7°) and the Fe1-S2-C11 bond angle (110.34°) in **7** are slightly smaller than that in the related dithiolate complex [Fe(C$_5$H$_5$)(CO)$_2$(C$_3$S$_5$)]$_2$ (111.5(1)°).[30]

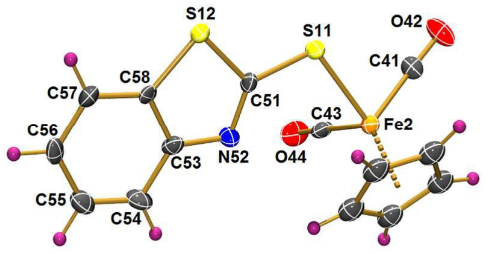


Fig. 4 Molecular structure of **6**. Selected bond lengths (Å) and bond angles (°): Fe2–S11 2.278(3), Fe2–C41 1.779(9), Fe2–C43 1.789(10), S11–C51 1.735(9), N52–C51 1.297(12), S12–C51 1.776(10), S12–C58 1.739(9); Fe2–S11–C51 107.7(3), S11–C51–N52 129.0(8), S11–C51–S12 115.3(5), S11–Fe2–C41 88.7(4), S11–Fe2–C43 90.6(4), C41–Fe2–C43 95.5(5), Fe2–C41–O42 176.7(10), Fe2–C43–O44 177.2(11).

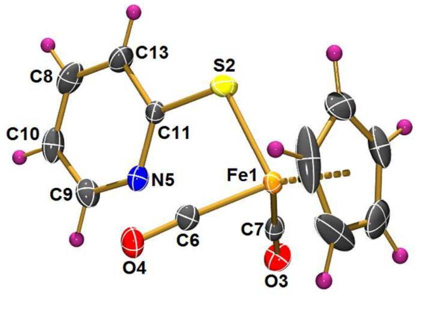


Fig. 5 Molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): Fe1–S2 2.2651(18), Fe1–C6 1.772(6), Fe1–C7 1.778(6), S2–C11 1.752(6), N5–C11 1.330(8), N5–C9 1.353(8); Fe1–S2–C11 110.3(2), S2–C11–N5 121.2(5), S2–C11–C13 116.2(5), S2–Fe1–C6 91.9(2), S2–Fe1–C7 91.9(2), C6–Fe1–C7 94.7(3), Fe1–C6–O4 176.8(6), Fe1–C7–O3 177.4(6).

Conclusions

In this contribution, synthesis and characterization of new 18-electron mercaptobenzothiazolyl and mercaptopyridyl molybdenum and iron adducts have been reported, obtained from the reactions of [Cp*Mo(CO)$_3$Cl] and [CpFe(CO)$_2$I] with borate ligands. Interestingly, the reaction of the former with [NaBt$_2$] in toluene yielded orthometallated product [Cp*Mo(CO)$_2$(η^3-CH$_2$C$_6$H$_5$)]. Attractively, in this complex the molybdenum centre is bound to a solvent toluene molecule in η^3-coordination fashion. Our current investigations are centered on similar reactions with other metal precursors.

Experimental details

All the syntheses were carried out under an argon atmosphere with standard Schlenk and glove box techniques. Compounds [NaBt][31], [NaBt$_2$],[32] [NaPy$_2$],[33] [CpFe(CO)$_2$I],[34] and [Cp*Mo(CO)$_3$Cl][35] were prepared according to literature methods and other chemicals were obtained commercially and used as received. The external reference for the ^{11}B NMR [Bu$_4$N][B$_3$H$_8$], was synthesized according to the literature method.[36] Thin-layer chromatography was carried on 250 mm dia aluminum supported silica gel TLC plates. NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometers. Residual solvent protons were used as reference (δ, CDCl$_3$, 7.26 and C$_6$D$_6$, 7.16), while a sealed tube containing [Bu$_4$N][B$_3$H$_8$] in benzene-d$_6$ (δ_B, ppm, –30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet iS10 spectrometer. Mass spectra were recorded on a BrukerMicroTOF-II mass spectrometer in ESI ionization mode.

Synthesis of 3 and 4. In a flame-dried Schlenk tube, [Cp*Mo(CO)$_3$Cl] (0.100 g, 0.28 mmol) was taken in 15 mL of toluene followed by the addition of [NaBt$_2$] (0.103 g, 0.28 mmol) at 0 °C and stirred for additional 10h at room temperature. The color of reaction mixture changes from orange to dark red. The solvent was evaporated in vacuo, the residue was extracted into hexane and passed through Celite. After removal of solvent from filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/DCM (80:20 v/v) yielded orange **3** (0.056 g, 43%) and yellow **4** (0.022 g, 20%).

3: HRMS (ESI$^+$): *m/z* calculated for [$C_{19}H_{19}MoNO_2S_2$ + H]$^+$ 455.9989, found 455.9998; ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C): δ = 7.64-7.17 (m, 4H, Ph), 1.86 (s, 15H, Cp*); ^{13}C NMR (125 MHz, $CDCl_3$, 22 °C): δ = 261.6, 258.8 (CO), 176.6 (C=S), 150.4 (CN), 131.1 (CS), 126.0, 123.1, 121.8, 115.7 (Ph), 107.4 (C_5Me_5), 11.0 (C_5Me_5); IR (hexane, cm^{-1}): ῡ = 2034, 1934 (CO).

4: HRMS (ESI$^+$, additive: KI): *m/z* calculated for [$C_{19}H_{22}MoO_2$ + K]$^+$ 419.0310, found 419.0323; ^{1}H NMR (500 MHz, C_6D_6, 22 °C): δ = 7.55-7.04 (m, 5H, Ph), 1.73 (s, 15H, Cp*), 1.99 (m, 2H, CH_2); ^{13}C NMR (125 MHz, C_6D_6, 22 °C): δ = 205.8 (CO), 127.4, 127.3, 125.5, 122.6, 121.2 (s, $C_6H_5CH_2$), 107.1(C_5Me_5), 30.0 (s, $C_6H_5CH_2$), 10.2 (C_5Me_5); ^{13}C –DEPT NMR (125 MHz, C_6D_6, 22 °C): δ = 125.5, 122.6, 121.2, 115.2, 30.0, 10.2; IR (hexane, cm^{-1}): ῡ = 1941, 1845 (CO).

Synthesis of 5. In a flame-dried Schlenk tube, [Cp*Mo(CO)$_3$Cl] (0.100 g, 0.28 mmol) was taken in 15 mL of toluene followed by the addition of [NaPy$_2$] (0.071 g, 0.28 mmol) stirred for 10h at room temperature. The color of reaction mixture was changes from orange to dark red. The solvent was evaporated in vacuo, residue was extracted into hexane and passed through Celite. After removal of solvent from filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/DCM(80:20 v/v) yielded yellow **5** (0.063 g, 55%).

Note that compound **5** has been confirmed by comparing its X-ray structure along with spectroscopic data reported earlier.[25]

Synthesis of 6. In a flame-dried Schlenk tube, [CpFe(CO)$_2$I] (0.100 g, 0.33 mmol) was taken in 12 mL of THF followed by the addition of [NaBt] (0.067 g, 0.33 mmol) and stirred for additional 8h at 65 °C. The color of reaction mixture was changes from chocolate brown to orange red. The solvent was evaporated in vacuo, residue was extracted into hexane and passed through Celite. After removal of solvent from filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/DCM (50:50 v/v) yielded orange **6** (0.036 g, 32%) and brown, [CpFe(CO)$_2$]$_2$ (0.03 g, 26%).

6: HRMS (ESI$^+$): *m/z* calculated for [$C_{14}H_9FeNO_2S_2$ + H]$^+$ 343.9502, found 343.9524;^{1}H NMR (400 MHz, $CDCl_3$,22 °C): δ = 7.70-7.14 (m, 4H, Ph), 5.14 (s, 5H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 211.9 (CO), 175.5, 154.3 (CS), 137.3 (CN), 125.2, 123.0, 120.2, 120.1 (Ph), 85.6 (s, Cp); IR (DCM, cm^{-1}): ῡ = 2036, 1988 (CO).

Synthesis of 7. Complex **7** was synthesized from [CpFe(CO)$_2$I] (0.100 g, 0.33 mmol) and [Na(py)$_2$] (0.084 g, 0.33 mmol) following similar reaction conditions of **6** (0.039 g, 41%).

7: HRMS (ESI$^+$): *m/z* calculated for [$C_{12}H_9FeNO_2S$ + H]$^+$ 287.9781, found 287.9765; ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 8.23-7.13 (m, 4H, Py), 5.02 (s, 5H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 213.1 (CO), 158.8 (CS), 149.5 (CN), 137.4, 121.1, 119.6, (Py), 85.4 (s, Cp); IR (DCM, cm^{-1}): ῡ = 2031, 1988 (CO).

Computational details

Density-functional theory (DFT) calculations were carried out on model compound **4'** (Cp analogue of **4**) using the Gaussian09 program package.[37] Geometry optimization was performed in gas phase (no solvent effect) using the hybrid functional B3LYP[38] and a combination of SDD[39] basis set for Mo and 6-31G(d) basis set for rest of the atoms using the X-ray structure of **4** as starting geometry. In order to assess the nature of the stationary point on the potential energy surface, harmonic frequency calculations were performed at the same level of theory on the optimized geometry. Molecular structures and molecular orbitals were plotted with the GaussView program. The Wiberg bond indices (WBI)[40] were obtained from a natural bond orbital (NBO) analysis.[41]

X-ray structure determination

Crystallographic information for compounds **3**, **4**, **6** and **7** is given in Table 1. Crystal diffraction data of **3** and **4** were collected and integrated using a Bruker AXS Kappa APEXII diffractometer, with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at room temperature. Crystal diffraction data of **6** and **7** were collected and integrated using a D8 VENTURE Bruker AXS diffractometer, with multilayers monochromated Mo-Kα (λ = 0.71073 Å) radiation at 150 K. The structures were solved by direct methods using SIR92[42] or SIR97[43] and refined using SHELXL-97.[44]

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Notes and references

‡The authors declare no competing financial interest.

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Table 1. Crystallographic data and structure refinement information for **3, 4, 6** and **7**.

	3	**4**	**6**	**7**
CCDC no.	1451372	1451371	1451373	1451374
Empirical formula	$C_{19}H_{19}MoNO_2S_2$	$C_{19}H_{22}MoO_2$	$C_{42}H_{27}Fe_3N_3O_6S_6$	$C_{12}H_9FeNO_2S$
Formula weight	453.41	378.30	1029.57	287.11
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	*P*-1	*P*-1	$Pna2_1$	*P*-1
a (Å)	7.6144(3)	9.1583(9)	54.393(3)	7.3073(10)
b (Å)	8.3214(4)	10.0150(8)	8.1444(4)	7.4344(12)
c (Å)	16.6856(7)	10.7858(5)	9.4966(4)	11.3494(17)
α (°)	77.412(2)	66.836(6)	90.00	96.919(5)
β (°)	88.615(2)	73.262(7)	90.00	98.640(5)
γ (°)	66.580(2)	72.681(8)	90.00	100.293(5)
V (Å^3)	944.52(7)	851.67(13)	4207.0(3)	592.84(15)
Z	2	2	4	2
D_{calc}(g/cm^3)	1.594	1.475	1.626	1.608
F (000)	460	388	2088	292
μ (mm^{-1})	0.927	0.774	1.371	1.434
ϑ Range (°)	2.922-27.479	3.977-25.000	2.915-27.484	3.122-27.509
no. of reflections collected	4307	2974	8608	2689
no. of unique reflns [$I > 2\sigma(I)$]	3774	2561	8185	2399
goodness-of-fit on F^2	1.052	1.018	1.133	1.283
R1, *w*R2 [$I > 2\sigma(I)$]	0.0342, 0.0705	0.0437, 0.1004	0.0717, 0.1761	0.0698, 0.2165
R1, *w*R2 (all data)	0.0410, 0.0732	0.0526, 0.1095	0.0747, 0.1777	0.0771, 0.2198

Table of Content Entry Only

Reactivity of cyclopentadienyl transition metal(II) complexes with borate ligands: structural characterization of the toluene-activated molybdenum complex [Cp*Mo(CO)$_2$(η^3-CH$_2$C$_6$H$_5$)]

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Unprecedented formation of toluene activated molybdenum complex, [Cp*Mo(CO)$_2$(CH$_2$C$_6$H$_5$)] in η^3-fashion was elucidated by the reaction of [Cp*Mo(CO)$_3$Cl] with [NaBt$_2$] (Bt = dihydrobis(2-mercaptobenzothiazolyl)borate).