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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[η³-C₆H₄CH₂C₆H₅]]

Rongala Ramalakshmi,¹ K. Maheswari,¹ Dudekula Sharmila,¹ Anamika Paul,¹ Thierry Roisnel,² Jean-François Halet,³,⁴ and Sundargopal Ghosh*¹

Reactions of cyclopentadienyl transition-metal halide complexes [Cp*Mo(CO)₂Cl], 1, and [CpFe(CO)₂]₂, 2, (Cp = C₅H₅, Cp* = η³-C₅Me₅) with borate ligands are reported. Treatment of 1 with [NaBt₂] (Bt₂ = dihydrobis(2-mercapto-benzothiazolyl)borate) in toluene yielded [Cp*Mo(CO)₂(C₆H₄S₂N)], 3, and [Cp*Mo(CO)₂(η³-C₆H₄CH₂C₆H₅)], 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 η³-coordination mode. Under similar reaction conditions, [NaPy₂] (Py = dihydrobis(2-mercapto-pyridyl)borate) produced only the mercaptopyridyl molybdenum complex [Cp*Mo(CO)₂(C₆H₄SN)], 5, in good yield. On the other hand, when compound 2 was treated individually with [NaBt] (Bt = trihydro(2-mercapto-benzothiazolyl)borate) and [NaPy₂] in THF, formation of the η¹-coordinated complexes [CpFe(CO)₂(C₆H₄S₂N)], 6, and [CpFe(CO)₂(C₆H₄CH₂C₆H₅)], 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 (sp³) and aromatic (sp²) 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).³⁻⁵ Recent reports revealed that metallation of arenes was also achieved by tungsten η³-allyl complexes,⁶ mixed iron–tin metal clusters (V),⁷ sterically encumbered cyclopentadienyl yttrium (VI), gadolinium,⁸ and cerium complexes.⁹,¹⁰ Although all the reports describe the isolation of η³-coordination mode of the arenes, a couple of reports support the formation of η¹-coordination.⁹b,⁹g Thus, the synthesis of η¹-coordination by crystallographic characterization is of interest as this might constitute a milestone in this domain.

As part of our ongoing studies on the synthesis of metalloboranes¹⁰⁻¹² and their derivatives,¹³,¹⁴ we have recently reported the C-H activation of arene and heteroarenes by early...
Results and discussion

Reactivity of [Cp*Mo(CO)Cl] (1) with [NaBt$_2$] and [NaPy$_2$]

As shown in Scheme 1, reaction of [Cp*Mo(CO)$_2$Cl]$_2$ with one equivalent of [NaB$_2$T] (B$_2$T = dihydrobis(2-mercaptobenzothiazolyl)borate) yielded [Cp*Mo(CO)$_2$(C$_9$H$_7$S$_3$N)], 3, and a C-H activated product [Cp*Mo(OCl)$_2$($\eta^5$-C$_8$H$_4$CH$_2$)$_2$], 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)$_2$Cl] 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.

The $^1$H NMR spectrum of 4 reveals the presence of one type of Cp* signal at $\delta = 1.73$ ppm along with characteristic phenyl peaks in the aromatic region. In addition, resonance associated with benzylic protons is observed at $\delta = 1.99$ 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 $\eta^1$-fashion, acting as a formal allyl-like three-electron donor allowing the metal center to satisfy 18-electron rule. In general, $\eta^1$-allyl-transition metal complexes are often key intermediates in many of the organic reactions. Transition-metal benzyl complexes are usually synthesized by salt metathesis having a framework relatively similar to 4, such as, [Cp*Mo(NO)($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$], [Cp*Mo(NO)($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$][Cr(N$\eta^2$Bu)$_3$($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$], [Cr(N$\eta^2$Bu)$_3$($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$] and [Zr($\eta^1$-$\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$]$_2$. However, the benzyl group of these complexes is bound to the metal either in $\eta^1$ or $\eta^2$ fashion. Interestingly, in compound 4, the molybdenum center binds to a solvent toluene in a $\eta^1$-fashion.

A thorough search at Cambridge Structural Data base indicates that the bond angles M-C(H$_5$)$_3$C$_9$H$_7$ in the benzyl $\eta^1$-coordinated complexes ($x$ = 1-3) span in the range of 80-100$^\circ$, such as 81.10(4)$^\circ$ in [Cp*Mo(NO)($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$], or 82.97(12)$^\circ$ in [Cp*Mo(NO)($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$][Cr(N$\eta^2$Bu)$_3$($\eta^2$-C$_{8}$H$_4$CH$_2$)$_3$]. That measured in 4, (76.2(2)$^\circ$) is significantly smaller, reflecting a stronger interaction between molybdenum and the $\eta^1$-benzyl group. The other pertinent bond parameters involving Mo-Cp*, Mo-CO and Mo-C$_8$H$_7$ are comparable to those of related complexes (Table S1, Supporting Information).

As shown in Scheme 2, complex [Cp*Mo(CO)$_2$Cl], 1 is capable of activating toluene only in the presence of an additional [NaB$_2$T] moiety by releasing [Bt]$^+$ (Bt = trihydrobis(2-mercaptop benzothiazolyl)borate). A complex $^1$H NMR spectrum was obtained for the reaction mixtures of [Cp*Mo(CO)$_2$Cl], 1 with [NaB$_2$T]. 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.
Nevertheless, an intermediate compound \([\text{Cp}^*\text{Mo}(\text{CO})_2\text{BH}_3\eta^3-(\text{C}_2\text{H}_5\text{S}N)]\) can be proposed that is related to recently isolated \([\text{Cp}^*\text{Mo}(\text{CO})_2\text{BH}_3(1\text{-benzothiazol}-2\text{-ylidene})]\).\(^{17}\)

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 other main product obtained from the reaction of 1 with one equivalent of [NaPy] is \([\text{Cp}^*\text{Mo}(\text{CO})_2(\text{C}_2\text{H}_5\text{S}N)]\), 3 (Scheme 1). It adopts a four-legged piano-stool structure (Fig. 3) considering two carbonyls and a \(\eta^2\)-coordinated mercaptobenzothiazolyl ligand as four legs and it obeys the 18-electron rule.\(^{23}\)

Further, we have extended our experiments to different borate ligand with the same metal precursor. As shown in Scheme 1, one equivalent of [NaPy] \((\text{Py}_2 = \text{dihydrobis(2-mercapto-pyridyl)borate})\) with 1 yielded only the molybdenum mercaptopyridyl adduct \([\text{Cp}^*\text{Mo}(\text{CO})_2(\text{C}_2\text{H}_5\text{S})\text{N}]\), 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 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.\(^{26-28}\)

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The \(\eta^3\)-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 \(\eta^1\)-allyl complex \([\text{CpMo}(\text{CO})_2(\eta^3-C_2H_5)]\).\(^{23}\) Strong interaction between the Mo fragment and \(\eta^3\)-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 \([\text{CpMo}(\text{CO})_2(\eta^3-C_2H_5)]\) (Fig. 2). This further indicates that the electron \(\pi\)-density of the benzyl ligand is mainly localized on C1 and the \textit{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] is \([\text{Cp}^*\text{Mo}(\text{CO})_2(\text{C}_2\text{H}_5\text{S}N)]\), 3 (Scheme 1). It adopts a four-legged piano-stool structure (Fig. 3) considering two carbonyls and a \(\eta^2\)-coordinated mercaptobenzothiazolyl ligand as four legs and it obeys the 18-electron rule.\(^{23}\)

**Reactivity of \([\text{CpFe}(\text{CO})_2]\) (2) with [NaBt] and [NaPy].**

Further, we have extended this chemistry to group 8 metal precursor, \([\text{CpFe}(\text{CO})_2]\), 2, and it was observed that no clear...
reaction with [NaBt] in toluene. On the other hand, it independently reacts with [NaBt] (Bt = trihydro(2-mercaptobenzothiazolyl)borate) and [NaPy] in THF forming the 18-electron mercapto-benzothiazolyl and mercaptopyridyl iron adducts [CpFe(CO)₂{(C₅H₅S₂)N}], 6, and [CpFe(CO)₂{(C₅H₅S₂)N}], 7, respectively, in moderate yields.

The '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 η¹-mercaptobenzothiazolyl or η¹-mercaptopridyl ligand occupies one of the three legs. The structural similarity between 6 and 7 mainly concern the η¹-coordination of the mercaptobenzothiazolyl 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 Fe2–S11–C11 bond angle (110.34°) in 7 are slightly smaller than that in the related dithiolate complex [Fe(C₅H₅)(CO)₂(C₅H₅S₂)] (111.5(1)°).³⁰

**Conclusions**

In this contribution, synthesis and characterization of new 18-electron mercapto-benzothiazolyl and mercaptopyridyl molybdenum and iron adducts have been reported, obtained from the reactions of [Cp*Mo(CO)₂Cl] and [CpFe(CO)₂] with borate ligands. Interestingly, the reaction of the former with [NaBt] in toluene yielded orthometallated product [Cp*Mo(CO)₂(η¹-CH₂CH₂S₂)]. Attractively, in this complex the molybdenum centre is bound to a solvent toluene molecule in η¹-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]³², [NaPy]³³, [CpFe(CO)₂]³⁴ and [Cp*Mo(CO)₂Cl]³⁵ were prepared according to literature methods and other chemicals were obtained commercially and used as received. The external reference for the ¹¹B NMR [Bu₄N][B₄H₆], 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, CDCl₃, 7.26 and C₆D₆, 7.16), while a sealed tube containing [Bu₄N][B₄H₆] in benzene-d₆ (δₖ, ppm, -30.07) was used as an external reference for the ¹¹B NMR. Infrared spectra were recorded on a Nicolet 10Sx spectrometer. Mass spectra were recorded on a Bruker MicroTOF-II mass spectrometer in ESI ionization mode.

**Synthesis of 3 and 4.** In a flame-dried Schlenk tube, [Cp*Mo(CO)₂Cl] (0.100 g, 0.28 mmol) was taken in 15 mL of toluene followed by the addition of [NaBt] (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
the addition of [NaPy](s, Cp); IR (DCM, cm−1): δ = 7.64-7.17 (m, 4H, Ph), 8.16 (s, 15H, Cp*). 13C NMR (125 MHz, CDCl3, 22 °C): δ = 122.6, 121.2 (s, 5Cp), 107.1 (C5Mes), 30.0 (s, 5C6Mes). DFT calculations were carried out on the program package. 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 APEX II 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 or SIR92† and refined using SHELXL-97.‡

Acknowledgements

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Notes and references

†The authors declare no competing financial interest.


Computational details

Density-functional theory (DFT) calculations were carried out on model compound 4 (Cp analogue of 4) using the Gaussian09 program package. Geometry optimization was performed in gas phase (no solvent effect) using the hybrid functional B3LYP† and a combination of SDD† 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 molecular structures and molecular orbitals were plotted with the GaussView program. The Wiberg bond indices (WBI)† were obtained from a natural bond orbital (NBO) analysis.41

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

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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)$_2$(η$^3$-C$_6$H$_5$)]

Rongala Ramalakshmi,$^{1,4}$ K. Maheswari,$^1$ Dudekula Sharmila,$^1$ Anamika Paul,$^1$ Thierry Roisnel,$^4$ Jean-François Halet,$^{*,4}$ and Sundargopal Ghosh$^{*,1}$

$^1$Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

$^4$Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de, Rennes 1, F-35042 Rennes Cedex, France

E-mail: sghosh@iitm.ac.in; Fax: (+91) 44 2257 4202; Tel: (+91) 44 2257 4230; halet@univ-rennes1.fr.

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).