Synthesis and Reactivity of Molybdenum(0) Complexes Containing Sterically Expanded Arene Ligands

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Abstract

Synthesis of a series of sterically expanded arenes, containing one or more 1,2,3,4-tetrahydro-1,1,4,4-tetramethyl substituents, was accomplished in high yield utilizing classic Friedel-Crafts alkylation conditions. Metallation of these arenes with molybdenum was accomplished via reflux of Mo(CO)₆ in a mixed solvent combination in the presence of the ligand. The (η⁶-arene)Mo(CO)₃ complexes were isolated in reasonable yields (45-60%) and characterized through a combination of ¹H and ¹³C NMR spectroscopy, X-ray crystallography, IR spectroscopy, elemental analysis, and mass spectrometry. The crystallographic data reveal the ability to tune the steric profile of the arene through judicious ligand choice. Ligand electronics can also be modified to some

degree, though to a lesser extent than the steric congestion about the metal center. Computational analysis of the arene complexes corroborate the observed trend of increasing electron donation by the arene as the steric bulk increases. Reactivity of selected Mo complexes highlight the dramatic change in stability substitution imparts on the compounds, as the least sterically congested complex undergoes fastest arene exchange while the bulkiest ligand results in a compound indefinitely stable in neat arene under identical conditions. Attempts at determining whether this substitution chemistry is driven by thermodynamic or kinetic factors were explored computationally and align with systems that have been examined previously. These studies introduce a family of tunable, sterically congested arene ligands that may find value as new supports in the preparation of a range of metal-arene complexes.

Graphical Abstract

Synopsis

A series of sterically expanded arenes have been prepared. Metallation with molybdenum was achieved and provides access to $(\eta^6\text{-arene})\text{Mo(CO)}_3$ complexes, demonstrating the first use of these ligands as supports for transition metals. Significant steric modulation is accomplished through careful arene choice, as demonstrated by the ligand effect upon benzene exchange.

Keywords arene exchange, metal carbonyls, molybdenum, sterically expanded arenes, X-ray crystallography

1. Introduction

Since the pioneering synthesis and X-ray structural characterization of bis(benzene) chromium [1], π -complexes of arenes and related ligands have been central to the development of organometallic chemistry. Use of aromatic supports for transition metals now impact a range of diverse fields, including materials science, medicinal chemistry, organic synthesis, among others [2-4]. Within the organometallic community, arene complexes continue to serve as key platforms for the investigation of the stoichiometric and catalytic activation and subsequent functionalization of small molecules [5].

Our initial interest in arene complexes stems from use of the triple decker sandwich compound $[(\text{Cp}^*\text{Co})_2-\mu-(\eta^4:\eta^4\text{-toluene})]$, originally developed by Schneider and coworkers [6], in catalytic and stoichiometric C-H bond activation [7-10] and to access the isolable 16 electron complex $\text{Cp}^*\text{Co}(\text{NHC})$ (NHC = N-heterocyclic carbene) [10]. Based on mechanistic studies by Schneider and coworkers involving arene exchange of $[(\text{Cp}^*\text{Co})_2-\mu-(\eta^4:\eta^4\text{-toluene})]$ with benzene, ready dissociation of a $\text{Cp}^*\text{Co}(\text{I})$ equivalent occurs at ambient temperature and results in formation of $\text{Cp}^*\text{Co}(\eta^6\text{-toluene})$, as observed by ^1H NMR spectroscopy [11]. This fragmentation likely results from the strong driving force to re-establish planarity in the toluene ligand, which is severely distorted from aromaticity in the triple decker complex. As we ultimately desire to destabilize the monomeric intermediate, this led us to attempt to access readily tunable, yet sterically encumbering arenes. Furthermore, given the demonstrated value of rationally altering the symmetry, sterics, and electronics of cyclopentadienyl (Cp) and related ligands to modulate polymer structure in Group 4 catalyzed olefin polymerization

[12,13], we envisioned a series of related arene ligands could provide value for use with a range of transition metals.

The target ligand scaffold relies on the sterically encumbering 1,2,3,4-tetrahydro-1,1,4,4-tetramethyl substituent. This particular pattern of substitution was chosen both because of the ease of synthetic access to a range of substitutions on the arene using a modular Friedel-Crafts alkylation protocol, and due to the prior demonstrated success in the substituent's use in the development of bulky fluorenyl ligands as supports for Zr catalyzed olefin polymerization [14]. Somewhat surprisingly, these types of arenes had received little attention to date as potential ligand supports for transition metals.

Given the rich chemistry of Group 6 arene complexes, serving as synthons in organic synthesis [15], platforms for small molecule activation [16], and building blocks for materials science [17], we initially targeted the synthesis and study of the fundamental coordination chemistry of a series of (η^6 -arene)Mo(CO)₃ derivatives using the sterically expanded arenes [18]. With this family of complexes in hand, we intend to explore their use in a range of stoichiometric and catalytic transformations.

Here, we present the initial studies of the synthesis of these sterically expanded arenes and their use as ligand supports for molybdenum(0). A combination of physical characterization and computational studies establish that the rational tuning of sterics and electronics can be accomplished using the family of alkyl substituted arenes. A greater variance in steric rather than electronic tuning appears possible, resulting in dramatic differences in the exchange of benzene with the (η^6 -arene)Mo(CO)₃ complexes. The new ligand series accomplishes our desired goal of providing a diverse range of reactivity in organometallic complexes as a function of steric bulk of the arene.

2. Experimental

2.1 General Considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures [19]. Benzene- d_6 for NMR spectroscopy was purchased from Cambridge Isotope Labs and distilled from sodium metal under an atmosphere of nitrogen and stored over 4 Å molecular sieves or sodium metal. Dichloromethane was purchased from Fisher Chemical and dried over calcium hydride and distilled prior to use. Dioxane heptane, toluene, and para-xylene were purchased from Fisher Chemical and dried over 4 Å molecular sieves prior to use. Celite was purchased from Acros and dried at 160 °C overnight under vacuum prior to storage and use in a glovebox. Anhydrous magnesium sulfate was purchased from Fisher Chemical and used as received. 2-chloro-2-methylpropane was purchased from Alfa Aesar and used as received. Tetralin was purchased from EMD Millipore and used as received. Molybdenum hexacarbonyl was purchased from Acros and used as received. Anhydrous aluminum chloride was purchased from Acros, stored inside a glovebox, and used as received. Ferrocene was purchased from Aldrich, sublimed, and stored in a glovebox prior to use. 2,5-Dichloro-2,5-dimethylhexane was prepared from 2,5-dimethyl-2,5-hexanediol (purchased from Aldrich and used as received) based on a literature procedure [14]. Ligand **1** was purchased from Acros and used as received. Ligands **2-4** [20] and **5** [21] were prepared

according to modified literature procedures. A representative procedure for synthesis of **2** is provided below.

^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz Spectrometer. Initial ^1H NMR experiments were conducted on site at Mount St. Mary's University on an Anasazi 90 MHz NMR spectrometer. All chemical shifts are reported relative to SiMe_4 using ^1H (residual) or ^{13}C NMR chemical shifts of the solvent as a secondary standard. Fourier-Transform Infrared (FT-IR) Spectroscopy was performed on a Shimadzu IRAffinity-1 spectrometer using a liquid cell purchased from Pike Technologies. LIFDI Spectrometry [22] was performed by the High Resolution Mass Spectrometry Facility at the University of California, Riverside. Elemental Analysis was performed at the Texas Tech University Molecular Characterization Facility.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Bruker Apex II detector system equipped with a molybdenum X-ray tube ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 150 K. Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker AXS SHELXTL software and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier transformation and refinement by full-matrix least-squares procedures. Initial crystallographic determinations were collected on site at Mount St. Mary's University at 170 K on a Rigaku XtaLAB mini.

Preparation of 1,2,3,4-tetrahydro-1,1,4,4,6-pentamethyl-naphthalene (2). A 1 L three neck flask, equipped with a reflux condenser and solid addition funnel, was charged with 20.0 g (0.217 mol) of toluene. Approximately 400 mL of dichloromethane was added via cannula transfer under nitrogen on a Schlenk line in a fume hood. 2,5-Dichloro-2,5-dimethylhexane (26.50 g, 0.145 mol) was then added to the reaction mixture. The solution was cooled in an ice bath, an oil bubbler was attached to the system, and 0.967 g (7.25 mmol) of aluminum chloride was charged in the solid addition funnel and slowly added to the reaction mixture over the course of an hour. *Caution: tremendous amounts of HCl gas are liberated throughout the course of the reaction. The solid should be added slowly to control the rate of HCl formation. The procedure should only be performed in a fume hood.* The deep red reaction was allowed to stir overnight at ambient temperature. Ice was then slowly added to the reaction mixture until it turned a pale yellow. Additional deionized water (~300 mL) and brine (~100 mL) was added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 250 mL portions). The combined organic layers were dried with MgSO_4 , filtered, and subsequent solvent removal *in vacuo* afforded 17.30 g (59%) of **2** as an oil which crystalized upon cooling to give a white solid upon rinsing with cold pentane. Comparison of spectral data matched previous literature reports [20].

Preparation of η^6 -1,2,3,4-tetrahydro-1,1,4,4-tetramethyl-naphthalene molybdenum tricarbonyl (1-Mo(CO)₃). A one piece, 100 mL round-bottomed flask equipped with a built in reflux condenser (Supplementary Material) was charged with 0.734 g (3.90 mmol) of **1** and 1.03 g (3.90 mmol) of Mo(CO)_6 . Approximately 20 mL of heptane and

40 mL of 1,4-dioxane was added and the apparatus was placed under a dynamic stream of nitrogen for 15 minutes. The reaction mixture was then refluxed for 48 hours under nitrogen during which time the reaction turned a deep green color. ***Caution: the reaction liberates carbon monoxide and should be performed in a fume hood near a carbon monoxide detector.*** The reaction was cooled and solvent was removed *in vacuo* on a Schlenk line. The condenser setup was transferred inside a glovebox where the resulting green solid was rinsed with pentane (50 mL) and filtered through Celite to remove any unreacted **1**. This wash was discarded and the remaining solid was extracted with ~75 mL of ether. Solvent removal *in vacuo* provided 0.933 g (65%) of **1-Mo(CO)₃** as a yellow solid. Recrystallization in ether at -30 °C affords analytically pure **2** and samples amenable to single crystal analysis. Alternatively, **1-Mo(CO)₃** can be prepared by reaction of Mo(CO)₃(CH₃CN)₃ [23] (1.210 g, 4.00 mmol) with **1** (0.750 g, 3.99 mmol) in refluxing toluene [24], affording improved yield (1.130 g, 75%). LIFDI mass spectrum for C₁₇H₂₀O₃Mo: calcd. 370 *m/z*; found 370 *m/z*. Anal. Calcd for C₁₇H₂₀O₃Mo: C, 55.44; H, 5.47. Found: C, 55.19; H, 5.53. ¹H NMR (benzene-*d*₆): δ = 0.82 (s, 6H, *Me*), 1.09 (s, 6H, *Me*), 1.18 (m, 2H, CH₂), 1.37 (m, 2H, CH₂), 4.74 (d, 2H, 4 Hz, arene CH), and 4.91 (d, 2H, 4Hz, arene CH). ¹³C NMR (benzene-*d*₆): δ = 32.10, 33.31, 34.17 (CH₂/CMe₂), 92.75, 93.57, 126.52 (arene), and 222.77 (Mo-CO). IR (ether, cm⁻¹): 1888, 1966 (CO).

Preparation of η⁶-1,2,3,4-tetrahydro-1,1,4,4,6-pentamethyl-naphthalene molybdenum tricarbonyl (2-Mo(CO)₃). A similar procedure as used in the synthesis of **1-Mo(CO)₃** was employed, using 0.763 g (3.77 mmol) of **2** and 0.996 g (3.77 mmol) of Mo(CO)₆. Analogous workup resulted in isolation of 0.750 g (52%) of **2-Mo(CO)₃** as a

yellow solid. Recrystallization in ether at -30 °C affords analytically pure **2-Mo(CO)₃** and samples amenable to single crystal analysis. Anal. Calcd for C₁₈H₂₂O₃Mo: C, 56.55; H, 5.80. Found: C, 56.32; H, 5.73. ¹H NMR (benzene-*d*₆): δ = 0.85 (s, 3H, *Me*), 0.88 (s, 3H, *Me*), 1.05 (s, 3H, *Me*), 1.19 (s, 3H, *Me*), 1.26 (m, 3H, CH₂), 1.50 (m, 1H, CH₂), 1.69 (s, 3H, tolyl CH₃), 4.66 (d, 1H, 4 Hz, arene CH), 5.06 (s, 1H, arene CH), and 5.14 (d, 1H, 4Hz, arene CH). ¹³C NMR (benzene-*d*₆): δ = 20.39, 32.11, 32.21, 32.76, 32.81, 33.63, 34.20, 34.34, 35.85 (CH₂/CMe₂), 92.47, 92.97, 95.07, 112.42, 122.60 (arene), and 223.40 (Mo-CO). One arene resonance not located. IR (ether, cm⁻¹): 1885, 1963 (CO).

Preparation of η⁶-1,2,3,4-tetrahydro-1,1,4,4,6,7-hexamethyl-naphthalene molybdenum tricarbonyl (3-Mo(CO)₃). A similar procedure as used in the synthesis of **1-Mo(CO)₃** was employed, using 0.860 g (3.98 mmol) of **3** and 1.05 g (3.98 mmol) of Mo(CO)₆. Analogous workup resulted in isolation of 0.710 g (45%) of **3-Mo(CO)₃** as a yellow solid. Recrystallization in ether at -30 °C affords analytically pure **3-Mo(CO)₃**. Anal. Calcd for C₁₉H₂₄O₃Mo: C, 57.58; H, 6.10. Found: C, 57.49; H, 6.08. ¹H NMR (benzene-*d*₆): δ = 0.93 (s, 6H, *Me*), 1.19 (s, 6H, *Me*), 1.24 (m, 2H, CH₂), 1.42 (m, 2H, CH₂), 1.68 (s, 3H, xylyl CH₃), and 5.32 (s, 2H, arene CH). ¹³C NMR (benzene-*d*₆): δ = 18.56 (Me), 32.13, 33.10, 34.35, 34.49 (CH₂/CMe₂), 95.84, 110.04, 125.49 (arene), and 224.10 (Mo-CO). IR (ether, cm⁻¹): 1880, 1960 (CO).

Preparation of η⁶-1,2,3,4,5,6,7,8-octahydro-1,1,4,4-tetramethyl-anthracene molybdenum tricarbonyl (4-Mo(CO)₃). A similar procedure as used in the synthesis of

1-Mo(CO)₃ was employed, using 0.982 g (4.05 mmol) of **4** and 1.07 g (4.05 mmol) of Mo(CO)₆. Analogous workup resulted in isolation of 1.04 g (61%) of **4-Mo(CO)₃** as a yellow solid. Recrystallization in ether at -30 °C affords analytically pure **4-Mo(CO)₃**. Anal. Calcd for C₂₁H₂₆O₃Mo: C, 59.72; H, 6.20. Found: C, 60.11; H, 6.39. ¹H NMR (benzene-*d*₆): δ = 0.95 (s, 6H, *Me*), 1.13 (s, 6H, *Me*), 1.19 (m, 2H, *CH*₂), 1.28 (m, 2H, *CH*₂), 1.46 (m, 4H, *CH*₂), 2.05 (m, 2H, *CH*₂), 2.37 (m, 2H, *CH*₂), and 5.34 (s, 2H, arene *CH*). ¹³C NMR (benzene-*d*₆): δ = 22.30, 28.06, 32.45, 33.13, 34.36, 34.46 (*CH*₂/*CMe*₂), 94.61, 112.28, 125.54 (arene), and 224.37 (Mo-CO). IR (ether, cm⁻¹): 1878, 1958 (CO).

Preparation of η⁶-1,2,3,4,5,6,7,8-octahydro-1,1,4,4,5,5,8,8-octamethyl-anthracene molybdenum tricarbonyl (5-Mo(CO)₃). A similar procedure as used in the synthesis of **1-Mo(CO)₃** was employed, using 1.13 g (3.77 mmol) of **5** and 0.995 g (3.77 mmol) of Mo(CO)₆. The reaction mixture was refluxed for a total of 72 hours. Analogous workup resulted in isolation of 0.848 g (47%) of **5-Mo(CO)₃** as a yellow solid. Recrystallization in ether at -30 °C affords analytically pure **5-Mo(CO)₃**. Anal. Calcd for C₂₅H₃₄O₃Mo: C, 62.76; H, 7.16. Found: C, 63.07; H, 7.38. ¹H NMR (benzene-*d*₆): δ = 0.95 (s, 12H, *Me*), 1.24 (s, 12H, *Me*), 1.25 (m, 4H, *CH*₂), 1.46 (m, 4H, *CH*₂), 5.58 (s, 2H, arene *CH*). ¹³C NMR (benzene-*d*₆): δ = 32.38, 33.37, 34.10, 34.29 (*CH*₂/*CMe*₂), 91.36, 124.94 (arene), and 223.99 (Mo-CO). One aromatic resonance not located. IR (ether, cm⁻¹): 1877, 1957 (CO).

Arene exchange experiments with 1-Mo(CO)₃, 2-Mo(CO)₃, and 5-Mo(CO)₃. Stock solutions were prepared using 0.009 g (0.024 mmol) of **1-Mo(CO)₃**, 0.009 g (0.024 mmol) of **2-Mo(CO)₃**, and 0.011 g (0.023 mmol) of **5-Mo(CO)₃** in 4 mL of benzene-*d*₆.

to provide ~6 mM solutions. 0.003 g (0.016 mmol) of ferrocene was added as a reference to each stock solution as an internal integration standard. A portion of the stock solutions (0.4 mL of each) were transferred to a J. Young NMR tube and heated at 70 °C and monitored by ^1H NMR spectroscopy until complete conversion was observed to ($\eta^6\text{-C}_6\text{D}_6$)Mo(CO) $_3$, except in the case of **5-Mo(CO) $_3$** . Each reaction was performed in duplicate to determine the $t_{1/2}$ for arene exchange, based on integration of starting material and free ligand liberated during the reaction versus the internal standard.

Decomposition experiments with 1-Mo(CO) $_3$, 2-Mo(CO) $_3$, and 5-Mo(CO) $_3$. Stock solutions were prepared using 0.009 g (0.024 mmol) of **1-Mo(CO) $_3$** , 0.009 g (0.024 mmol) of **2-Mo(CO) $_3$** , and 0.011 g (0.023 mmol) of **5-Mo(CO) $_3$** in 4 mL of benzene- d_6 to provide ~6 mM solutions. 0.003 g (0.016 mmol) of ferrocene was added as a reference to each stock solution as an internal integration standard. A portion of the stock solutions (0.4 mL of each) were transferred to a J. Young NMR tube, where 20 μL (0.25 mmol) of THF was then added, and the tubes were heated at 45 °C and monitored by ^1H NMR spectroscopy until complete loss of starting material and formation of free ligand was observed. During the course of the reaction, black Mo(0) was observed to form on the walls of the tubes. Each reaction was performed in duplicate to determine the $t_{1/2}$ for decomposition, based on integration of starting material and free ligand liberated during the reaction versus the internal standard.

2.2 Computational details.

All DFT calculations were performed using a hybrid functional, the three-parameter exchange functional of Becke (B3) [25] and the correlation functional of Lee, Yang, and Parr (LYP) (B3LYP) [26] as implemented in Gaussian 09 [27]. The molybdenum atom uses the effective core potential and associated basis set of Hay and Wadt (LANL2DZ) [28] in which the two outermost p functions were replaced by reoptimized $4p$ functions as suggested by Couty and Hall [29], and an f polarization function was added [30]. All other atoms use the 6-31G(d',p') basis set [31]. Unless otherwise noted, all geometries are fully optimized and confirmed as minima or n -order saddle points by analytical frequency calculations at the same level. Coordinates for the geometry minimizations were taken from the X-ray coordinates of **1-Mo(CO)₃**, **2-Mo(CO)₃**, and **5-Mo(CO)₃** or created *in silico* in Molden using these structures as a starting point (in the case of **3-Mo(CO)₃** and **4-Mo(CO)₃**).

3. Results and Discussion

Aside from **1**, which was purchased commercially, arenes **2-5** were prepared in a series of Friedel-Crafts alkylations based on slightly modified literature procedures [20, 21]. Synthesis of arenes **2-4** were accomplished by AlCl₃ mediated reaction of the parent arene (toluene, para-xylene, or tetralin) with 2,5-dichloro-2,5-dimethylhexane in dichloromethane (Scheme 1). Though this procedure also permits access to arene **5**, in our hands alkylation of benzene with tert-butyl chloride and subsequent carbocation rearrangement provides **5** in much improved yield (Scheme 1) [21]. The arenes can all be isolated as white, crystalline solids in reasonable yields (45-65%) upon workup.

Scheme 1. Synthesis of arenes **2-5** by Friedel-Crafts alkylation of arene a) with 2,5-dichloro-2,5-dimethylhexane or b) tert-butyl chloride.

The target arene complexes were all prepared in a similar manner, by refluxing $\text{Mo}(\text{CO})_6$ and one equivalent of the ligand of choice in a 1,4-dioxane:heptane (2:1) solvent mixture (Eq. 1). This versatile procedure was based on modifications of syntheses of related molybdenum arene complexes [32a] and improves upon typical $(\eta^6\text{-arene})\text{Mo}(\text{CO})_3$ preparations which utilize a large excess of the arene, making product isolation more challenging [18]. Note in the case of **5-Mo(CO)₃**, perhaps as might be expected for the most sterically encumbering ligand, additional reflux (72 versus 48 hours) is necessary to ensure reasonable yields of the desired product. The arene complexes can also be prepared using other Mo(0) sources, as refluxing $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ [23] with **1** in toluene provides **1-Mo(CO)₃** in 75% yield [24].

The molybdenum carbonyls were characterized by a variety of spectroscopic methods and physical techniques. Aside from combustion analysis data for each of the complexes consistent with the proposed structures, a LIFDI mass spectrum [22] of **1-Mo(CO)₃** displays the expected parent ion peak at $m/z = 370$ (Supplementary Material). ^1H and ^{13}C NMR spectra of the complexes further indicate successful complexation of arene in each of the compounds. Representative ^1H and ^{13}C NMR spectra of **1-Mo(CO)₃** recorded in benzene- d_6 are shown in Figure 1. In general, the expected symmetries are observed for each complex, with **2-Mo(CO)₃** displaying the most resonances due to the positional substitution of the arene methyl group (Supplementary Material). Of note in both the ^1H and ^{13}C NMR spectra of the complexes are significant upfield shifting of the carbon and hydrogen resonances, consistent with coordination of the ligand to molybdenum [32a]. The ^{13}C NMR spectra of the complexes also display the expected downfield carbon resonance attributed to the molybdenum carbonyl.

Figure 1. a) ¹H and b) ¹³C NMR spectra of **1-Mo(CO)₃** recorded in benzene-*d*₆.

Three of the molybdenum complexes (**1-Mo(CO)₃**, **2-Mo(CO)₃**, and **5-Mo(CO)₃**) were characterized by single crystal X-ray crystallography, using crystals grown from

ether at -30 °C. ORTEP representations of the three structures are shown in Figure 2 along with metric data compiled in Table 1. The structures clearly establish η^6 arene coordination, based on comparison of Mo-C and arene C-C bond distances to those in known (η^6 -arene)Mo(CO)₃ complexes [32]. Though bond distances are comparable in all three structures, the increasing steric presence imparted by **2** and **5** are best manifested by the OC-Mo-CO angles in the three complexes (Table 2), as the carbonyls compress towards one another, on average, by approximately 0.5 and 2.4° in **2-Mo(CO)₃** and **5-Mo(CO)₃** respectively. This reduction in angle is likely a direct result of the greater steric pressure brought about by the larger arenes in **2-Mo(CO)₃**, and **5-Mo(CO)₃**. The crystallographic data, coupled with dramatic differences observed in arene exchange of the three complexes (*vide infra*) establish the readily tunable nature of the sterically expanded arenes.

Figure 2. Molecular structures of a) **1-Mo(CO)₃**, b) **2-Mo(CO)₃**, and c) **5-Mo(CO)₃** with 30% probability ellipsoids. Hydrogen atoms omitted for clarity.

Table 1. Structural Parameters for the Sterically Expanded (η^6 -arene)Mo(CO)₃ Complexes

	1-Mo(CO)₃	2-Mo(CO)₃	5-Mo(CO)₃
Bond Distances (in Å)			
Mo(1)-C(1)	2.373(2)	2.350(4)	2.346(5)
Mo(1)-C(2)	2.392(2)	2.380(5)	2.459(5)
Mo(1)-C(3)	2.417(2)	2.385(5)	2.456(5)
Mo(1)-C(4)	2.356(2)	2.382(4)	2.374(5)
Mo(1)-C(5)	2.382(2)	2.408(3)	2.397(5)
Mo(1)-C(6)	2.370(2)	2.433(4)	2.423(5)
Average Mo-C Bond Length	2.382(2)	2.390(4)	2.413(5)
Arene C-C Bond Ranges	1.39-1.44	1.39-1.43	1.40-1.43
Angles (in °)			
₁ OC-Mo-CO ₂	86.29(8)	85.6(2)	84.8(3)
₂ OC-Mo-CO ₃	87.09(9)	86.0(3)	84.8(3)
₁ OC-Mo-CO ₃	89.05(9)	89.3(2)	85.8(3)
Average Angle	87.48(9)	87.0(2)	85.1(3)

Infrared spectra of the complexes provide insight into the electronic effects engendered by the series of ligands. The carbonyl stretching region of the IR spectrum of **4-Mo(CO)₃**, recorded in ether, is shown in Figure 3. Two bands are observed in each case, in the range of 1877-1888 and 1957-1966 cm⁻¹, respectively [33] (Table 2). Comparison of the individual stretches or the average of the bands, methods previously used to compare ligands electronics in metal carbonyls [34], both indicate the expected moderate increase in electron donation with the addition of successive alkyl substituents on the arene core (Table 2).

Figure 3. Infrared spectrum of the carbonyl region of **4-Mo(CO)₃** recorded in ether.

Table 2. Carbonyl Stretching Frequencies of the Sterically Expanded Arene (η^6 -arene)Mo(CO)₃ Complexes^a

Compound	$\nu(\text{CO})_1$ (cm ⁻¹)	$\nu(\text{CO})_2$ (cm ⁻¹)	$\nu(\text{CO})_{\text{avg}}$ (cm ⁻¹)
1-Mo(CO)₃	1966	1888	1927
2-Mo(CO)₃	1963	1885	1924
3-Mo(CO)₃	1960	1880	1920
4-Mo(CO)₃	1958	1878	1918
5-Mo(CO)₃	1957	1877	1917

^a Spectra record in ether.

Ligand electronics were probed further by computational methods. Geometry optimizations of all five complexes and (η^6 -benzene)Mo(CO)₃ were performed using either the coordinates provided by the X-ray crystal structures for three of the compounds (**1-Mo(CO)₃**, **2-Mo(CO)₃**, **5-Mo(CO)₃**) or from *in silico* generated structures based on modifications of the X-ray structures. Experimental and calculated metrics for **1-Mo(CO)₃**, **2-Mo(CO)₃**, **5-Mo(CO)₃** are in good agreement. The carbonyl stretching frequencies computed for each of the compounds are shown in Table 3. Three bands are calculated for each structure with comparable intensities, suggesting the two stretches observed experimentally are a result of overlap. Though there is a noticeable shifting of the calculated frequencies relative to the experimentally determined stretches, this is a

discrepancy not uncommon with DFT calculations when calculating spectral bands for both organic [35] and inorganic molecules [36]. The scaling factor (0.9615), calculated by plotting the observed versus calculated C-O stretching bands and determining the slope of the subsequent line generated by the data points, provides a standard value for the parameter [36] (Supplementary Material). Qualitatively, the average calculated stretches track well with the trend observed in the solution phase data.

Table 3. Calculated Carbonyl Stretching Frequencies of the Sterically Expanded (η^6 -arene)Mo(CO)₃ Molybdenum Complexes^a

Compound	$\nu(\text{CO})_1$ (cm ⁻¹)	$\nu(\text{CO})_2$ (cm ⁻¹)	$\nu(\text{CO})_3$ (cm ⁻¹)	$\nu(\text{CO})_{\text{avg}}$ (cm ⁻¹)
(η^6 -benzene)Mo(CO) ₃	2055	1996	1995	2015
1-Mo(CO)₃	2038	1984	1964	1995
2-Mo(CO)₃	2034	1979	1961	1991
3-Mo(CO)₃	2029	1973	1958	1987
4-Mo(CO)₃	2026	1968	1955	1983
5-Mo(CO)₃	2020	1973	1958	1977

^a Computational details: Gaussian 09, B3LYP exchange/correlation functionals with LANL2TZ+ on Mo and 6-31g(d',p') on all other atoms.

After fully characterizing the series of complexes and establishing perturbations in the steric and electronic profiles of the ligands, we sought evidence of arene influence on metal reactivity in the family of compounds. As a result, we examined arene exchange of **1**-, **2**-, and **5-Mo(CO)₃** with benzene-*d*₆ at 70 °C (Eq. 2), a reaction known to occur readily with substituted coordinated arenes [37]. Following the reactions *in situ* by ¹H and ²H NMR spectroscopy, the complexes proceed cleanly to generate (η^6 -C₆D₆)Mo(CO)₃ and extrude arene (Figure 4), except in the case of **5-Mo(CO)₃**. No molybdenum black is observed visually during the course of the reactions.

Figure 4. Stack plot of the arene exchange reaction of **1-Mo(CO)₃** with benzene-*d*₆ at various times.

Using an internal integration standard, the $t_{1/2}$ values for arene exchange were measured for each of the three complexes, and are shown in Table 4. A dramatic trend in the stability of the complexes is noted, as the least sterically hindered metal center

undergoes fastest exchange while the metal supported by the bulkiest ligand does not react at all, even after prolonged reaction times (> 1 month). Addition of a single methyl group to the sterically expanded ligand core also notably provides an approximate 3-fold increase in stability of the complex.

Table 4. $t_{1/2}$ Values for Benzene Exchange with the $(\eta^6\text{-arene})\text{Mo}(\text{CO})_3$ Complexes^a

Complex	$t_{1/2}$ (hours)
1-Mo(CO)₃	23
2-Mo(CO)₃	84
5-Mo(CO)₃	No reaction

^aReaction conditions: 70 °C, 0.024 mmol of complex, 0.4 mL in benzene- d_6 , 0.016 mmol ferrocene standard.

Stability of the three complexes was also studied in the presence of THF at 45 °C (Table 5). Unlike in the absence of polar solvent, where clean conversion to $(\eta^6\text{-C}_6\text{D}_6)\text{Mo}(\text{CO})_3$ is observed, only free arene and plating of molybdenum metal are seen. Control experiments with $(\eta^6\text{-C}_6\text{D}_6)\text{Mo}(\text{CO})_3$ at 45 °C in the presence of THF confirm the instability of the arene exchange product under these reaction conditions, likely due to the formation of reactive $(\text{THF})_3\text{Mo}(\text{CO})_3$ or related intermediates [38]. Despite decomposition, it is notable that stability of the complexes supported by the sterically expanded arenes parallel the studies in the absence of polar solvent.

Table 5. $t_{1/2}$ Values for Benzene Exchange of the $(\eta^6\text{-arene})\text{Mo}(\text{CO})_3$ Complexes^a

Complex	$t_{1/2}$ (hours)
1-Mo(CO)₃	8
2-Mo(CO)₃	16
5-Mo(CO)₃	48

^aReaction conditions: 45 °C, 0.024 mmol of complex, 0.4 mL in benzene-*d*₆, 0.25 mmol of THF, and 0.016 mmol ferrocene standard.

To investigate if the dramatic changes in reactivity of the arene complexes were dictated by thermodynamic or kinetic factors, we turned to computational analysis to model arene dissociation from the $(\eta^6\text{-arene})\text{Mo}(\text{CO})_3$ complexes. The thermodynamics (ΔH and ΔG) of arene loss from the five complexes and $(\eta^6\text{-benzene})\text{Mo}(\text{CO})_3$, to give free arene and the singlet $[\text{Mo}(\text{CO})_3]$ fragment, were calculated using DFT methods from the geometry optimized structures and are shown in Table 6.

Table 6. Calculated Thermodynamic Parameters for Arene Dissociation in $(\eta^6\text{-arene})\text{Mo}(\text{CO})_3$ Complexes^a

Compound	ΔH (kcal/mol)	ΔG (kcal/mol)
$(\eta^6\text{-benzene})\text{Mo}(\text{CO})_3$	40.8	30.5
1-Mo(CO)₃	40.6	27.7
2-Mo(CO)₃	41.8	28.3
3-Mo(CO)₃	41.3	28.4
4-Mo(CO)₃	42.4	28.7
5-Mo(CO)₃	40.3	25.9

^a Computational details: Gaussian 09, B3LYP exchange/correlation functionals with LANL2TZ+ on Mo and 6-31g(d',p') on all other atoms.

The collected data indicate kinetic factors likely play a more significant role in the arene exchange, given the most favorable arene loss involves the bulkiest ligand, which is contradictory to the observed lack of arene substitution in **5-Mo(CO)₃**. As prior studies of arene exchange in Group 6 systems implicate either an associative mechanism or simultaneous mechanisms at work, it perhaps is not surprising the observed $t_{1/2}$ values do not correlate well with the enthalpies (and free energies) for arene dissociation [38,39]. Furthermore, the experimental data corroborates prior assertions that entropy factors may play a greater role with bulkier arenes upon metal coordination, due to the more restricted motion of substituents in the (η^6 -arene)Mo(CO)₃ complexes [38].

4. Conclusions

Our studies have established the first demonstrated coordination of a series of sterically expanded arenes to transition metals and their influence on the reactivity of the corresponding molybdenum complexes. Steric alterations in particular give rise to a range of reactivity changes in the exchange of arenes with the complexes. With the (η^6 -arene)Mo(CO)₃ complexes in hand, we now intend to investigate the stoichiometric reactivity and catalytic applications of the compounds. In addition, we hope to explore the sterically expanded arenes as ligand supports for a range of transition metal complexes. These studies are currently underway.

5. Acknowledgements

The authors gratefully recognize Mount St. Mary's University (CAB, start-up), the National Science Foundation (Grants: 1431522 (IUSE), 1300508 (RUI), and 1337428 (X-ray)), the Robert A. Welch Foundation (Grant number D1707) and the Marion I & Henry J. Knott Foundation (IR spectrometer) for financial support of this research. JWT

acknowledges the Centre for Computational Nanoscience at Ball State University for computational time. Tim Funk (Gettysburg College) is thanked for access to a 400 MHz NMR spectrometer for high field studies.

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