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Communication

Molybdenum-Mediated Coupling of Carbon Monoxide to a C_3 Product on a Single Metal Site

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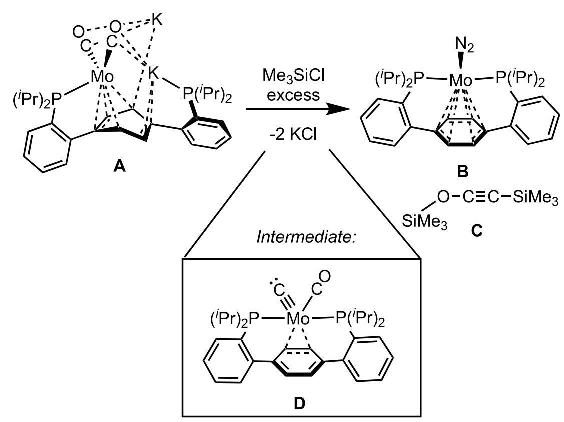
ABSTRACT: The synthesis and characterization of a series of naphthalenediyl-diphosphine molybdenum complexes are reported. A novel dicarbonyl−Mo complex (**3**) converts to a bis(siloxy)acetylene complex (**5**) upon reduction and treatment with a silyl electrophile, Me_3SiCl. This process shows exclusive C−C coupling distinct from the previously reported phenylene-linked analogue that undergoes C−O cleavage. Further CO catenation can be engendered from **5** under mild conditions providing metallacyclobutenone complex **6**, with a C_3O_3 organic motif derived from CO. Differences in reactivity are assigned to the nature of the arene linker, where the naphthalenediyl fragment shows a propensity for η^4 binding previously not observed for phenylene. Consistent with this hypothesis, a Mo precursor with a 1,3-cyclohexadienediyl-based linker was prepared which also showed exclusive formation of a bis(siloxy)acetylene complex and subsequent coupling of a third CO molecule.

Synthesis gas, if renewably sourced from CO_2 and water, could provide an alternative to petroleum for the synthesis of reduced and energy-rich multicarbon chemical precursors and liquid fuels via the Fisher−Tropsch (F−T) process.[1,2] Increasing the selectivity of F−T, which traditionally generates a Schultz-Flory distribution of hydrocarbons, is of significant interest; an appealing approach has been the development of homogeneous organometallic systems with tunable ligands.[3,4] The selective generation of C_2 products from CO has been reported with several organometallic complexes.[5−10] The generation of higher homologues is more desirable as their properties better resemble fuels employed in the current energy infrastructure, but complexes capable of such chemistry are scarce.[11] Moreover, besides the F−T process,[3,4,12] CO electroreduction on Cu electrodes[13] and CO reduction by nitrogenases[14] all result in product distributions that include $C_{>2}$ species. Molecular insight into the nature of intermediates capable of enchainment of more than two carbons is of interest for future catalyst design.[15−34] Despite that, there have been limited examples of sequential catenation of CO to a C_2 product and then to C_{2+} products that can provide mechanistic information and structure−reactivity relationships.[35] A system employing cooperative reactivity of $W(CO)_6$ and an Al(I) reductant elegantly demonstrates the stepwise carbon chain growth from CO.[36]

Previous work in our group has demonstrated that single-site Mo complexes (**A**, **D**) supported by a *para*-terphenyl diphosphine ligand are capable of reductive coupling of CO via two distinct pathways, with (Scheme 1) or without C−O bond cleavage preceding C−C bond formation, depending on temperature.[37−39] However, catenation of the C_2 products at these complexes has not been observed. As four (deoxygenative) vs two (non-deoxygenative) electron reductive coupling of CO resulted in different ligand binding modes, we hypothesized that changing the supporting ligand may enable new pathways of CO catenation. Herein, we report CO coupling chemistry with Mo complexes supported by two diphosphine ligands, either with a naphthlenediyl or a 1,3-cyclohexadienediyl linker, that promote the formation of C_3 products, informing structure/function relationships in reductive CO catenation.

Scheme 1. Previous Work Demonstrating Four-Electron Deoxygenative C−C Coupling of Metal-Coordinated CO



Extension of polyarene ligands (benzene to naphthalene or anthracene) in metal−arene complexes can significantly increase the lability of the arene and alter the reactivity at the metal center.[40,41] Chromium bis(naphthalene) has been

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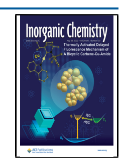

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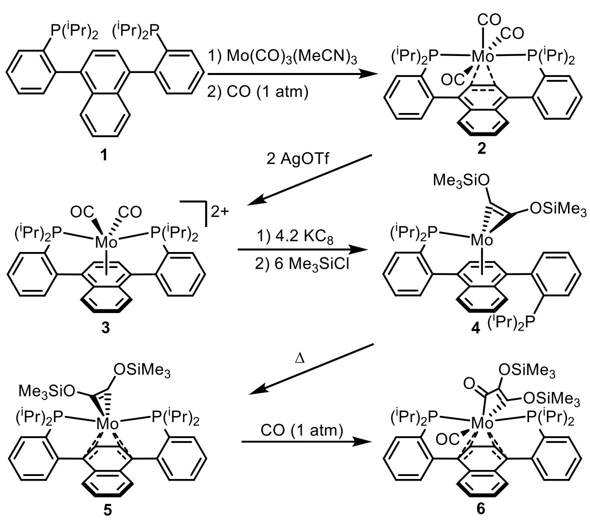
shown to display much higher substitutional lability compared to its benzene analogue.[42,43] In a series of (η^6-arene)Mo-$(PMe_3)_3$ complexes (arene = benzene, naphthalene, or anthracene), only with anthracene was oxidative addition of H_2 at the metal center observed, accompanied by a η^6-to-η^4 ring slip.[44] Additional computational studies in that report suggest that this increased propensity for ring slippage stems from the increasingly favorable η^4- vs η^6-arene interaction with lengthening of the aromatic system. To seek out novel CO catenation pathways and/or products that may result from hapticity changes at the basal arene, we tartgeted a diphosphine ligand with a naphthalene-based arene donor.

Naphthalenediyl-linked diphosphine **1** was synthesized in an analogous manner to the previously reported phenylene-linked variant starting from 1,4-diiodonaphthalene.[45] Metalation of **1** with $Mo(CO)_3(MeCN)_3$ under an atmosphere of CO provided tricarbonyl complex **2** (Scheme 2). Single crystal X-ray diffraction (XRD) analysis of **2** confirmed η^2-binding to the edge carbons of the naphthalenediyl linker (Figure 1). Mild disruption of the central arene aromaticity is observed, with shortening of the C2−C3 bond and lengthening of the C1−C2 and C3−C4 bonds compared to those in free naphthalene (Figure 1), a sign of partial localization of single and double C−C bond character.[46]

Scheme 2. Synthesis and Reactivity of Naphthalenediyl-Linked Diphosphine Molybdenum Complexes



Oxidative decarbonylation by reaction of **2** with 2 equiv of silver trifluoromethanesulfonate yielded dicationic dicarbonyl complex **3** as orange microcrystals. The solid-state structure of **3** displays η^6-binding to the central arene, maintaining an 18-electron count at the metal center. Significant changes in the C−C bond lengths of the outer ring of the naphthylene, such as localized double-bond character in C6−C7 and C8−C9, suggest disruption of aromaticity. In contrast, aromaticity is mostly maintained in the core Mo-bound ring.

Four-electron reduction of **3** with 4.2 equiv of KC_8 in THF provided an asymmetric species spectroscopically (displaying two peaks in the ^{31}P NMR spectrum indicating a loss of mirror plane related the two phosphines), analogous to the previously reported dianionic phenylene-linked complex **A** and consistent with dissociation of one of the *trans*-spanning phosphines.[38]

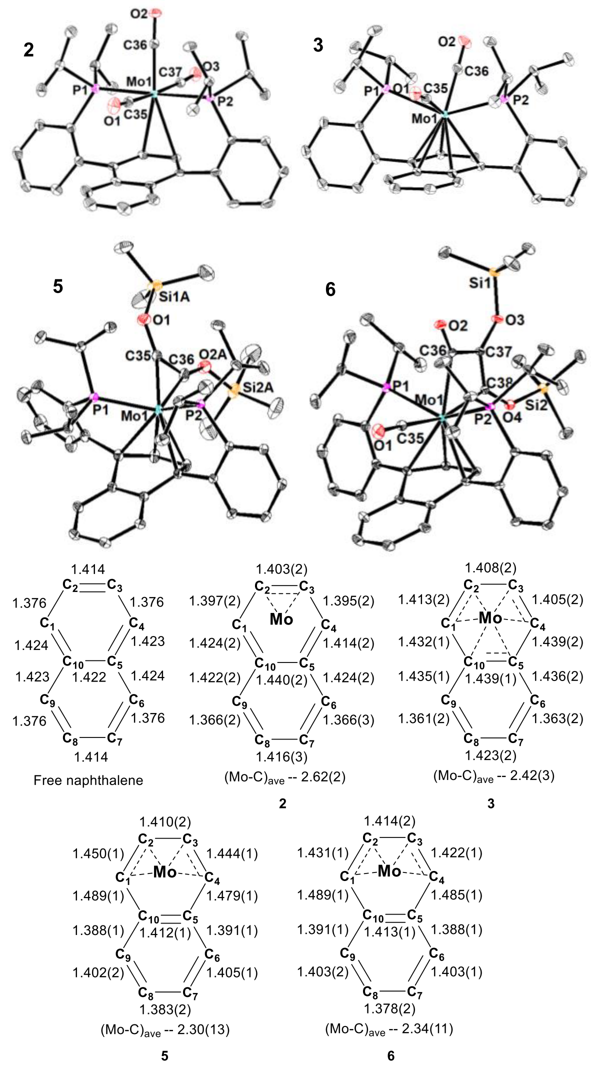


Figure 1. Solid-state structures of **2**, **3**, **5**, and **6** with thermal ellipsoids shown at 50% probability. Solvent molecules, counterions, and hydrogen atoms omitted for clarity. Relevant bond metrics for naphthalene and naphthalenediyl linker complexes **2**, **3**, **5**, and **6** shown.

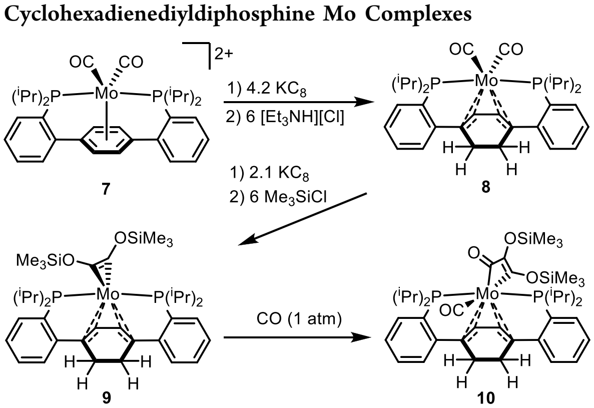
Infrared (IR) spectroscopy shows C−O stretches at 1678 and 1580 cm^{-1} similar to those observed for **A** (1657 and 1570 cm^{-1}), which has been structurally characterized,[38] supporting its assignment as a dicarbonyl species with substantial backbonding. Expecting the naphthalenediyl linker to be more readily reduced than the phenylene-linked analogue,[47] the use of milder reductants was investigated. Compared to the phenylene-linked complex which required the use of potassium naphthalenide (−3.05 V vs Fc) to access a dianionc redox state, it was found that **3** could be reduced with potassium anthracenide (−2.47 V vs Fc).[48]

Treatment of the putative dianionic species with chlorotrimethylsilane (Me_3SiCl) afforded asymmetric species **4**. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **4** are consistent with a complex possessing a free phosphine arm and a bis(siloxy)acetylene ligand formed from C−C coupling of the two carbonyl ligands (Figure S13). In contrast with the phenylene-linked system wherein C−O bond cleavage occurred prior to C−C bond formation, exclusive C−C coupling without C−O bond cleavage was observed in this instance.[38] This difference in selectivity upon electrophile addition may be due to (1) the less electron-rich (less reducing) nature of the dianionic naphthalenediyl-linked species vs phenylene and/or (2) more accessible η^4-arene bound transition states or intermediates in the naphthalenediyl-linked system. These differences may result in the C−O cleavage step becoming inaccessible, leading to the selective C−C bond formation observed.

Because **4** converts to a new symmetric complex **5** (displaying a single peak in the ^{31}P{^{1}H} NMR spectrum) even at −35 °C, over days, or at 90 °C in about an hour, solid-state characterization of **4** was not obtained. Solid-state characterization confirmed the identity of **5** as a bis(siloxy)-acetylene complex with molybdenum bound to both phosphines with an η^4 metal−arene interaction. Significant deviation of the naphthalenediyl linker from planarity is observed (41° angle between the C1C2C3C4 and C1C4C5C10 planes), consistent with previously reported η^4-bound naphthalene complexes.[49,50] C1−C10 and C4−C5 distances are indicative of single bond character while aromaticity is maintained in the outer ring, with relatively similar C−C bond distances (Figure 1). Compared to the phenylene linker that does not show similar reactivity, the conversion of **4** to **5** is likely facilitated by the increased propensity for η^4-arene binding in the naphthalenediyl linker.

To further investigate if the origin of selectivity toward exclusive C−C coupling vs C−O cleavage preceding C−C coupling was a result of coordination hapticity of the bridging ligand, the synthesis of complexes supported by a 1,4-cyclohexadienediyl-linked diphosphine was targeted. Conveniently, the synthesis of neutral dicarbonyl complex **8** can be achieved by reduction of dication **7** followed by the addition of a Brønsted acid (Scheme 3). ^{31}P{^{1}H} NMR spectroscopy

Scheme 3. Synthesis and Reactivity of Cyclohexadienediyldiphosphine Mo Complexes



reveals a singlet at 82.4 ppm, while the ^{1}H NMR spectrum shows two multiplets at 2.77 and 2.29 ppm, corresponding to coupled nuclei integrating to two protons each, consistent with both the cyclohexadiene methylene protons and formal arene hydrogenation at adjacent carbons. When complex **8** was sequentially reduced by two electrons and functionalized with Me_3SiCl, a bis(siloxy)acetylene complex (**9**) was formed on the basis of NMR and XRD characterization (see Figure S32). Since the electron richness of the reduced phenylene linker is between that of the naphthalenediyl and the cyclohexadienediyl linkers, the observed selectivity more likely originates from the ability of the central ligand to support an η^4-binding mode during reaction with an electrophile, a feature both the naphthalenediyl and the cyclohexadienediyl share.

The reactivity of bis(siloxy)acetylene complex **5**, bearing a metal-bound C_2 fragments, was pursued for the generation of C_{2+} products through further CO catenation. Stirring a benzene solution of **5** under 1 atm of CO at room temperature for 12 h resulted in a color change from brown to red-brown. ^{31}P{^{1}H} NMR spectroscopy showed the clean formation of a new species, **6**, with a chemical shift at 56.1 ppm. To further probe the identity of this species, **5** was treated with ^{13}CO. Two enhanced resonances were observed in the ^{13}C{^{1}H} NMR spectrum at 232.93 and 225.15 ppm (see Figure S20). Their triplet of doublets splitting pattern, alongside the observation of a doublet of doublets splitting pattern of the ^{31}P resonance indicated the incorporation of two isotopically enriched CO molecules into **6-^{13}C**. The solid-state structure of **6** (Figure 1) confirmed the incorporation of two CO molecules, one of which is part of a metallacyclobutenone motif, consistent with the NMR data. The insertion of CO relieves steric strain near the metal center by shifting the Me_3Si group further away, resulting in a pseudo-C_s symmetric structure. This represents a rare example of CO insertion into a CO-derived C_2 fragment to generate a C_3 motif at a single metal site.

With the similar coordination environment at Mo between **5** and **9**, further CO catenation with **9** was explored. Using ^{13}CO-derived bis(siloxy)acetylene complex **9-^{13}C**, treatment with ^{13}CO results in the formation of CO inserted complex **10-^{13}C** showing rich coupling information in both the ^{13}C{^{1}H} and ^{31}P{^{1}H} spectra (Figure S30), resulting from scalar coupling between the four $S = 1/2$ ^{13}C atoms derived from CO and the two $S = 1/2$ phosphine ligands. The solubility of **10** prohibited growth of high-quality single crystals but allowed for the collection of a data set that supports its structural assignment (see Figure S33), corroborating the spectroscopic data and confirming the metallacyclobutenone formation. The formation of metallacyclobutenone sourced solely from CO provides a new, well-defined pathway for C_3 product formation from CO.

In summary, the synthesis of two new Mo diphosphine complexes capable of the stepwise enchainment of three CO molecules is reported. Reduction of Mo(II) dicarbonyl complexes (**3** and **7**) by four electrons, followed by silyl electrophile addition, resulted in chemoselective two-electron reductive CO coupling to bis(siloxy)acetylene complexes (**5** and **9**). This selectivity is proposed to be related to the ability of the diphosphine linker to support η^4-binding modes not readily accessible on the phenylene-linked system. Exposure of the bis(siloxy)acetylene complexes (**5** and **9**) to CO resulted in further CO catenation to give metallacyclobutenone complexes (**6** and **10**) featuring a functional-group-rich C_3 fragment fully derived from CO.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c00266.

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Experimental procedures for the synthesis of compounds **1−10**, detailed characterization data, supplementary figures (PDF)

Accession Codes

CCDC 1495764, 1909081−1909084, and 2117715−2117716 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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