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CO Coupling Chemistry of a Terminal Mo Carbide: Sequential Addition of Proton, Hydride, and CO Releases Ethenone

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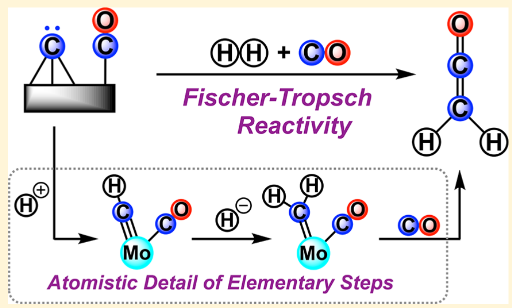
Supporting Information

ABSTRACT: The mechanism originally proposed by Fischer and Tropsch for carbon monoxide (CO) hydrogenative catenation involves C−C coupling from a carbide-derived surface methylidene. A single molecular system capable of capturing these complex chemical steps is hitherto unknown. Herein, we demonstrate the sequential addition of proton and hydride to a terminal Mo carbide derived from CO. The resulting anionic methylidene couples with CO (1 atm) at low temperature (−78 °C) to release ethenone. Importantly, the synchronized delivery of two reducing equivalents and an electrophile, in the form of a hydride ($H^- = 2e^- + H^+$), promotes alkylidene formation from the carbyne precursor and enables coupling chemistry, under conditions milder than those previously described with strong one-electron reductants and electrophiles. Thermodynamic measurements bracket the hydricity and acidity requirements for promoting methylidene formation from carbide as energetically viable relative to the heterolytic cleavage of H_2. Methylidene formation prior to C−C coupling proves critical for organic product release, as evidenced by direct carbide carbonylation experiments. Spectroscopic studies, a monosilylated model system, and Quantum Mechanics computations provide insight into the mechanistic details of this reaction sequence, which serves as a rare model of the initial stages of the Fischer−Tropsch synthesis.



INTRODUCTION

The Fischer−Tropsch (FT) synthesis is a well-established industrial-scale process that uses synthesis gas, a mixture of CO and H_2, as a feedstock for the generation of a broad range of catenated products.[1−5] While the variation in outputs can be versatile, it is often cost prohibitive in regards to petroleum substitution.[1,2] As efforts increase to synthesize biodiesels from renewably sourced synthesis gas,[6,7] shifting FT catalysis toward specific desirable products becomes ever more important.[7] Understanding the operative mechanism(s) of FT provides potential for rational catalyst design and, in turn, improved selectivity.[1,2,8]

While there is little consensus as to the operative mechanism(s) of FT,[9,10] all proposals share two fundamental commonalities: CO reduction (via C−H bond formation and/or C−O cleavage) and C−C coupling. The elementary step of C−C coupling between CO and surface hydrocarbons has been studied extensively in model systems.[1,11−14] In contrast, the investigation of carbide/CO coupling remains largely underexplored. In seminal studies of carbonyl-bridged metal carbide ensembles,[15] more exposed carbides demonstrated enhanced reactivity, including C/CO coupling in the Fe_3 cluster.[16] Additional examples of C≡O cleavage and coupling have been reported, likely via carbide intermediacy, with oxophilic metals.[17−19] To our knowledge, CO coupling has yet to be demonstrated from a terminal carbide precursor, likely due to the paucity of reactive yet well-characterized examples of such motifs.[20−24]

Previous work in our group has focused on reductive C−O catenation chemistry employing one-electron reductants (KC_8) and silyl electrophiles, demonstrating the deoxygenation of bound CO to a terminal carbide (**1**, Scheme 1).[25] This reactivity models the early steps proposed for FT, achieving the six-electron cleavage of CO using reducing equivalents stored in a redox noninnocent supporting ligand. C−C coupling was achieved via an isolated silyl alkylidyne complex, which, upon addition of 2 equiv of strong reductant (KC_8 or naphthalenide) followed by strong electrophiles (silyl chlorides), afforded disilylketene (Scheme 1, top).[25,26]

In contrast to these relatively harsh reducing conditions, several molecular FT models have employed proton and hydride equivalents, the products of heterolytic cleavage of H_2.[27−29] Herein, we revisit CO coupling chemistry from terminal carbide **1**, the first reported example of a terminal group VI carbide bearing d-electrons. While C−C bond formation from this species is facile, it ultimately results in deleterious ligand functionalization. Sequential proton and

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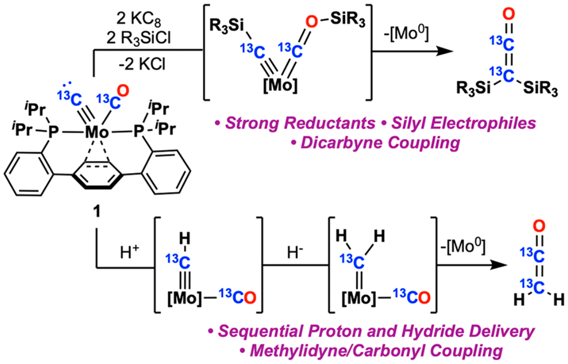
Scheme 1. Mechanistically Distinct Modes of C/CO Coupling to Free Ketene Fragments[30]

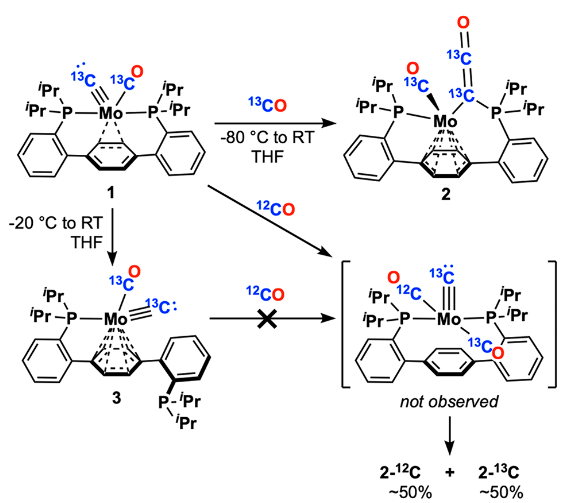


hydride delivery convert complex **1** to a terminal methylidene via an isolated terminal methylidyne (Scheme 1, bottom). Importantly, thermochemical experiments with $NaBPh_3H$ and $[Ar_2PhPMe]Cl$ (Ar = 2,4,6-trimethoxyphenyl) provide a formal demonstration that, thermodynamically, H_2 can promote reduction and protonation of complex **1**, illustrating the feasibility of using proton and hydride as H_2 surrogates in carbide conversion chemistry. Addition of exogenous CO to the formed methylidene releases ketene, realizing the sequential formation of two C−H bonds and C/CO coupling, to yield a silicon-free, metal-free C_2O_1 organic.

■ RESULTS AND DISCUSSION

Carbide/CO Coupling Reactivity. Direct carbide carbonylation represents an early bifurcation in the mechanistically complicated FT process; surface C_2 formation via carbide/CO coupling has been proposed for syngas conversion on iron foils.[31] To explore carbide/CO coupling in a well-defined system, complex **1** was treated with CO (Scheme 2).[30,32]

Scheme 2. CO Coupling Chemistry of Terminal Molybdenum Carbides[a]



[a]Carbide **1** was synthesized cleanly in situ via deprotonation of P2Mo(CH)(CO)(Cl) **4** with benzyl potassium. For more details, see the Supporting Information.

Admission of 1 atm of ^{13}CO to a THF solution of **1** at −80 °C showed no effect; however, upon warming to 25 °C, new spectral features were observed. A peculiar high-field doublet of doublets (−32.14 ppm, ^1J(P,C) = 118 and ^1J(C,C) = 103 Hz) was present in the $^{13}C\{^1H\}$ NMR spectrum, in addition to two downfield resonances. Concomitantly, two new features were observed in the $^{31}P\{^1H\}$ NMR spectrum, including a doublet of doublet of doublets (37.64 ppm, ^1J(P,C) = 118.1 Hz, ^2J(P,C) = 33.2 Hz, and ^3J(P,P) = 4.2 Hz) displaying strong scalar coupling to the high-field carbon. The large P−C and C−C spin−spin coupling constants, in addition to the broken symmetry of the terphenyl diphosphine (**P2**) ligand, are most consistent with formation of a Mo-bound phosphoranylideneketene, **2**.

A single-crystal X-ray diffraction (XRD) study of **2** confirmed the proposed assignment (Figure 1). The short

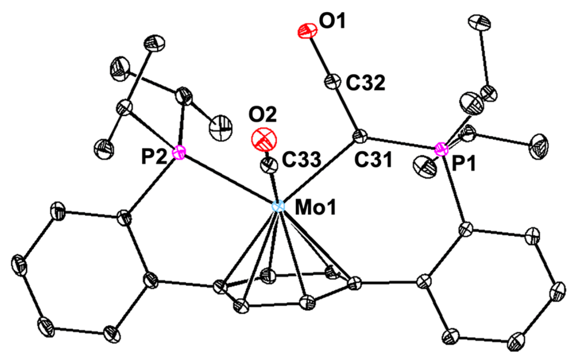


Figure 1. Solid-state structure of **2**. Thermal anisotropic displacement ellipsoids are shown at the 50% probability level. H atoms are omitted. Selected bond distances [Å] and angles [deg]: P1−C31 1.7144(11), C31−C32 1.2885(11), C32−O1 1.1865(10), Mo1−C31 2.2899(16), Mo1−C33 1.9563(12), C33−O2 1.1693(10), C31−C32−O1 179.01(8), P1−C31−Mo1 130.73(5).

C31−C32 bond length and wide C31−C32−O1 angle (1.2885(11) Å and 179.01°, respectively) support assignment of the η^1-C(P)=C=O bonding motif.[33] Mo engages the central arene in an η^6 fashion, to stabilize the low-valent metal center resulting from C−C coupling. Transition metal-bound phosphoranylidene ketenes, relatively rare motifs, are generally prepared via reaction of a metal precursor with preformed ketene, R_3PCCO.[34] In one example, the P−C linkage was formed at the metal center, from cleavage of carbon suboxide.[35] Complex **2** therefore represents the first example of such a motif in which both the P−C and the C−C bonds were formed at the metal center.

We hypothesized that CO binding could induce C−C bond formation[36,37] in **1** via a putative dicarbonyl carbide intermediate (Scheme 2). Labeling experiments were conducted to explore this process. Addition of ^{12}CO to **1** results in a 50:50 mixture of isotopes at the phosphoranylideneketene α-carbon (Figure 2). Likewise, the $^{31}P\{^1H\}$ NMR spectrum displays a broad resonance for the Mo-bound phosphine arm comprised of an overlapping doublet of doublets and doublet, the former split by partial (ca. 50%) ^{13}C enrichment at the carbonyl carbon. Taken together, these data are consistent with an intramolecular coupling pathway from a proposed dicarbonyl carbide complex. This process contrasts the ostensibly similar cleavage and coupling of CO by $Ta(silox)_3$,[38]

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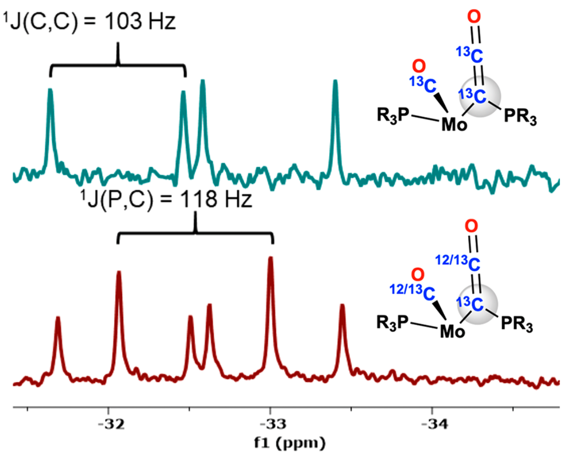


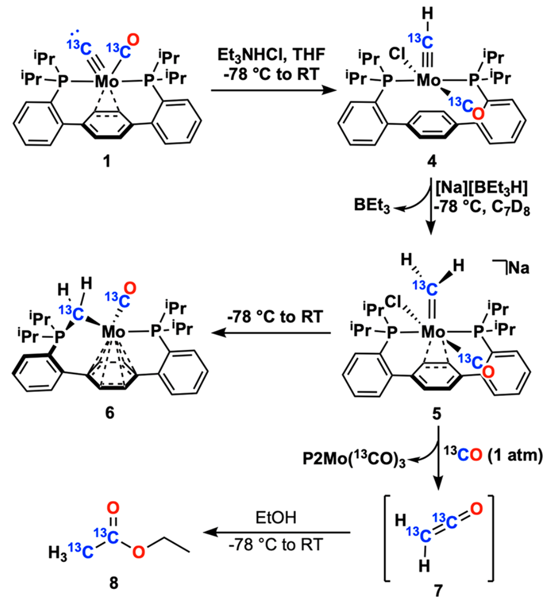
Figure 2. High-field partial $^{13}C\{^1H\}$ NMR spectra of **2** generated under ^{13}CO (top) and ^{12}CO (bottom) showing splittings for the phosphoranylidene ^{13}C nucleus circled in gray.

which, through a series of detailed mechanistic studies, was shown to form the C−C bond prior to the first deoxygenation event, en route to a ditantalum dicarbide ((silox)$_3$Ta≡CC≡Ta(silox)$_3$).[39] Related transformations starting from alkylidyne carbonyl complexes, namely addition of phosphines leading to the assembly of neutral PC(R)═C═O ligands, have also been reported.[40−43] Combined, these molecular systems represent complementary precedents for potential elementary steps in the early stages of the FT synthesis.

Recognizing that carbide **1** need not bind an additional molecule of CO to form a ketenylidene, it was slowly warmed to rt. While this results in a composite mixture of largely intractable species,[25] one of these complexes proved highly soluble. Extraction of the crude residue with hexamethyldisiloxane afforded a deep purple solution, which, upon standing at −35 °C, precipitated **3** as a purple powder. While single crystals of **3** have proven elusive, the structure can be confidently inferred from multinuclear NMR spectroscopy. A diagnostic carbidic $^{13}C\{^1H\}$ resonance is observed at 569.92 ppm, further downfield shifted from that of **1**. Two distinct features in the $^{31}P\{^1H\}$ NMR spectrum at 91.48 and −4.08 ppm support an arm-on arm-off binding mode for the **P2** ligand, and four upfield aromatic ^1H shifts corroborate an η^6 metal−arene interaction. Addition of 1 atm of CO to solutions of **3** likewise did not afford the coupled product **2**, however. Instead, an intractable mixture is formed, together with free **P2**, reflecting additional, deleterious pathways that are enabled by dissociation of the second phosphine arm.

Carbide Protonation, Hydride Transfer, and Methylidene/CO Coupling. Toward modeling the proposed role of surface hydrides in FT, and ultimately forming C−H bonds, carbide protonation was targeted.[21,44] Addition of Et$_3$NHCl to a −78 °C THF solution of **1** results in formation of a new compound upon warming to room temperature. A single resonance between 3.5 and 6.5 ppm is observed in the ^1H NMR spectrum, a doublet of triplets centered at 5.06 ppm (^1J(C,H) = 147.8 Hz, ^3J(P,H) = 3.1 Hz), with a relative integration of one. This suggests both a terminal methylidyne[20,24,45−51] and a five-coordinate pseudo-square pyramidal structure, as in **4**, without metal−arene interactions (vide infra; Scheme 3). The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data further

Scheme 3. Sequential Proton and Hydride Addition En Route to Ketene Formation[a]



[a]Carbide **1** was synthesized cleanly in situ via deprotonation of P2Mo(CH)(CO)(Cl) **4** with benzyl potassium. For more details, see the Supporting Information.

corroborate the proposed assignment of **4**, with a doublet of doublets at δ_P 40.21 ppm (^2J(C,P) = 18.6 and 10.2 Hz) and a characteristic methylidyne resonance at δ_C 281.19 ppm, respectively.[45,51]

Gratifyingly, **4** is thermally stable, both facilitating its use for reaction chemistry and permitting growth of single crystals. A single-crystal XRD study corroborates the structure inferred from spectroscopy (Figure 3). The Mo center sits above the central arene ring at a distance of 2.749 Å, suggesting negligible metal arene interaction. The Mo≡CH distance is appropriately short (1.764(2) Å) but slightly longer than that in a

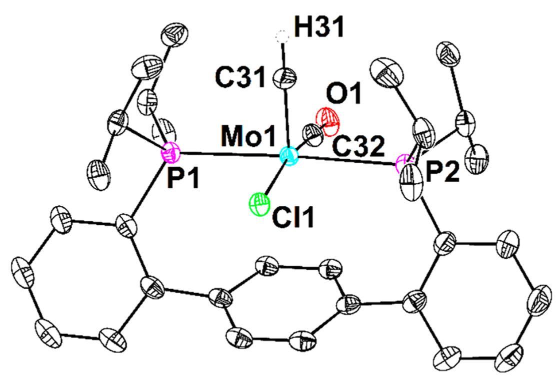


Figure 3. Solid-state structure of **4**. Thermal anisotropic displacement ellipsoids are shown at the 50% probability level. H atoms are omitted, except for the methylidyne proton, which was refined freely. Selected bond distances [Å]: Mo1−C31 1.764(2), Mo1−C32 1.930(4), O1−C32 1.197(6).

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structurally characterized Mo(VI) methylidyne (1.702(5) Å),[44] likely a manifestation of the more-reduced metal center.

Hydride addition to both terminal[21] and bridging[52] methylidyne ligands has precedent, and we sought to target this reactivity, considering proton and hydride as a crude surrogate for H_2 (vide infra). $NaBEt_3H$ was added to a C_7D_8 solution of **4** at −78 °C. Mixing the reagents immediately resulted in a color change to dark brown, and VT NMR spectroscopy showed signals in the $^{31}P\{^1H\}$ (s, 52.07 ppm), $^{13}C\{^1H\}$ (br s, 296.91 and br s, 237.52 ppm), and ^1H (15.03, d, $^1J(C,H)$ = 114.90 Hz and 13.27, d, $^1J(C,H)$ = 142.7 Hz) spectra, in line with formation of methylidene **5** (Scheme 3).[21] Warming the sample to 0 °C showed quantitative conversion to a new asymmetric complex with a triplet of doublets (84.68 ppm, $^2J(P,C_{CO})$ = 15.5 and $^2J(P,C_{CH2})$ = 6.0 Hz) and doublet of doublets (47.41 ppm, $^1J(P,C_{CH2})$ = 21.9 ppm and $^2J(P,C_{CO})$ = 17.0 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The $^{13}C\{^1H\}$ NMR spectrum likewise showed two signals, a broad doublet of triplets centered at 251.88 ppm ($^2J(C_{CO},P)$ = 15.3 and $^2J(C_{CO},C_{CH2})$ = 2.2 Hz) and an extremely high-field resonance at −34.87 ppm (ddd, $^1J(C_{CH2},P)$ = 21.8, $^2J(C_{CH2},P)$ = 6.2 Hz, and $^2J(C_{CH2},C_{CO})$ = 2.2 Hz). The high-field chemical shift in the $^{13}C\{^1H\}$ NMR spectrum[49] and the C_1 symmetry are consistent with P−C bond formation, giving **6**,[53,54] unexpectedly suggesting some electrophilic carbene character in electron-rich, anion **5**.[53−55] The small $^1J(P,C_{CH2})$ spin−spin coupling[56] observed for **6** is consistent with phosphonium ylide complexation to transition metal centers; ligation results in rehybridization, C(sp^2) to C(sp^3), which is reflected in the smaller one-bond scalar coupling constant.[57] The structure of **6** was confirmed in a single-crystal XRD study, which corroborated the assignment of the η^1-C-bound ylide moiety (see the Supporting Information).

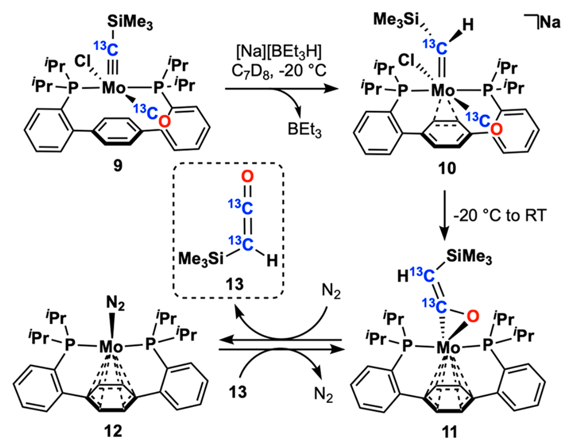
We hypothesized that similarly to the effect observed for carbide/CO coupling, methylidene/CO coupling may be favored by addition of exogenous CO, either via direct CO attack[58] or via coordination to Mo. Placing a −78 °C solution of in situ generated **5** under a ^{13}CO atmosphere resulted in a gradual color change to bright orange, as the gas diffused down the sample (Scheme 3). The $^{13}C\{^1H\}$ NMR spectrum at −78 °C showed both free ^{13}CO and three resonances in the metal-bound region, the CO signals of previously characterized $P2Mo(^{13}CO)_3$.[59]

Anticipating that zerovalent Mo was indicative of a C−C coupling process, identification of ethenone by $^{13}C\{^1H\}$ NMR spectroscopy was attempted. The diagnostic signals for free ketene (^{13}C δ = 193.7 and 2.7 ppm)[60] were absent, but coupling doublets at 154.69 and 83.90 ppm ($^1J(C,C)$ = 76.1 Hz) were observed, attributed to a putative ethenone-triethyl borane adduct.[61] While further efforts to detect free ethenone (**7**) were unsuccessful, ketene trapping with ethanol has precedent, giving stable and easily detectable ethyl acetate (EtOAc).[60,62] Forming **5** at low temperature, adding ^{13}CO, and condensing EtOH into the reaction tube afforded EtOAc-$^{13}C_2$, **8**, unequivocally demonstrating the generation and ejection of parent ketene (Scheme 3). Alkylidene carbonylation has been demonstrated on a variety of molecular scaffolds,[13] but often requires CO overpressures,[58,63−65] proceeds from activated Fischer carbene complexes,[13,66−68] or occurs at bridging alkylidene ligands.[69,70] Rarely is this coupling achieved at monometallic complexes with carbene fragments derived from CO.[67,71−73]

Isotopic labeling studies were conducted in which ^{12}CO was added to **5**. Mixed isotopolog $P2Mo(^{12/13}CO)_3$ was formed, consistent with either (i) rapid exchange of the ^{13}CO ligand in **5** with free ^{12}CO and on-metal C−C bond formation or (ii) ^{12}CO binding and C−C coupling proceeding from a methylidene dicarbonyl complex. We favor the latter, given that coordination to Mo facilitates C−C coupling chemistry in the related carbide/CO chemistry described above.

Reactivity of a Silylcarbyne Model System. Expecting that similar C/CO coupling chemistry would be achieved from silyl carbyne **9**, affording a more stable organic product, a related reactivity sequence was explored with this silyl model system (Scheme 4). Low-temperature addition of $NaBEt_3H$ to

Scheme 4. Hydride-Initiated C−C Coupling



a C_7D_8 solution of alkylidyne **9** and subsequent warming to −20 °C resulted in the gradual formation of a new species demarcated by a $^{31}P\{^1H\}$ resonance at 48.53 ppm and low-field doublet in the ^1H NMR spectrum (δ = 15.79 ppm, $^1J(C,H)$ = 121.7 Hz). Such a signal could be consistent with either formyl generation,[74−77] via CO insertion into an intermediate Mo hydride (a process that is facilitated by borane Lewis acids),[29,78−80] or hydride attack at the carbyne to give a silyl alkylidene. The ^{13}C NMR spectrum was more informative, displaying a broad doublet at 315.09 ppm ($^1J(C,H)$ = 121.7 Hz) and a broad singlet at 251.83 ppm (Figure S32). C−H coupling to the more downfield resonance is suggestive of a carbene/carbonyl isomer rather than the alternative carbyne/formyl complex. 2D $^1H/^{13}C$ correlation experiments further disambiguated the structure (Figure S33), with strong HMBC cross peaks between the H-bound carbon atom and the $SiMe_3$ methyl protons. These data point to hydrogen transfer to the alkylidyne carbon,[21,81−83] affording silyl carbene **10**, in analogy to the reactivity observed for parent methylidyne **4** (vide supra).

While **10** was the major species observed at −20 °C, it proved transient, slowly reacting further to give a mixture of two Mo complexes with a doublet and singlet in the ^{31}P NMR spectrum at 58.38 and 76.24 ppm, respectively. The latter corresponds to previously characterized $Mo^0−N_2$ adduct **12**,[59,84] demonstrating loss of the carbon-based ligands, presumably via C−C coupling. The isotopically enriched ^{13}C signals at 84.76 and 191.35 ppm showed strong scalar coupling ($^1J(C,C)$ = 69.7 Hz); the latter split into a doublet of triplets ($^2J(C,P)$ = 26.3 Hz) by the trans-spanning phosphines of the

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P2 ancillary ligand. This spectral signature is consistent with C−C bond formation affording the trimethylsilyl ketene complex **11**. Interestingly, in this case, CO addition is not requisite for C−C coupling.

The assignment of **11** was further supported via independent synthesis.[85] Anticipating that the observed mixture of **11** and **12** resulted from a ligand substitution equilibrium between the isoelectronic Mo^0 adducts, a C_6D_6 solution of **12** was treated with trimethylsilyl ketene.[86] While only starting material was observed under an N_2 atmosphere, degassing the reaction mixture resulted in significant conversion to **11**, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. The N_2/ketene exchange was borne out in the hydride-initiated C−C coupling chemistry; in addition to the coupling doublets of the bound ketene, a pair of doublets at 192.48 and 60.28 ppm (^1J(C,C) = 73.5 Hz) were observed in the ^{13}C NMR spectrum, corresponding to the metal-free C_2 fragment.[61]

An XRD study of single crystals of **11** grown from slow evaporation of liquid butane confirmed the inferred η^2-CO ketene assignment (Figure 4), with comparable O1−C31 (1.2799(12) Å) and C31−C32 (1.3536(14) Å) distances.[87−89] η^2-CC ketene adducts are known,[90−92] but the O-bound form is often thermodynamically favored.[90] Contrasting the structure of **9**,[25] as in the structure of **2** above, the central arene is engaged in η^6 coordination to Mo, consistent with the more reduced Mo center formed on C−C coupling.

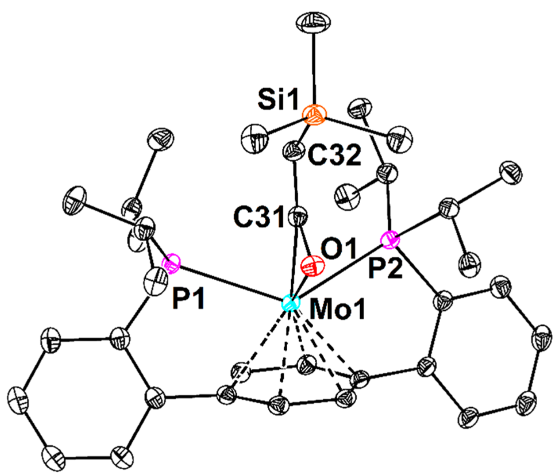

Figure 4. Solid-state structure of **11**. Thermal anisotropic displacement ellipsoids are shown at the 50% probability level. H-atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Mo1−O1 2.1858(7), Mo1−C31 2.1629(10), Mo1−C_{arene} (av) 2.2599(9), O1−C31 1.2799(12), C31−C32 1.3536(14), ∠O1−C31−C32 132.32(9).

Quantum Mechanics Computations. Akin to the sequential addition of potassium graphite and silyl electrophile to alkylidyne **9**,[25,26] $NaBEt_3H$ proved proficient for enacting the reductive coupling of silyl carbyne with CO. The latter reactivity manifold, proceeding through a carbene intermediate (**10**) rather than a dicarbyne complex, is accessible under much milder conditions and shows equal efficacy in C−C coupling. Given the facility with which the catenation proceeds, Quantum Mechanics computation (using the M06-2X flavor of Density Functional Theory)[93] was employed to interrogate the electronic structure requirements in the critical bond-forming step. The optimized structure following hydride addition to **9** resembles silyl alkylidene **10**,[94] in agreement with experiment; however, a close contact between Na^+ and the Cl ligand is observed in addition to borane binding to the carbonyl (Figure S46).[95] The HOMO of this complex, with d_{xz} parentage, is dominated by a π-bonding interaction with CO (**10**·BEt_3, Figure 5, inset). As the C−C distance contracts, the alkylidene ligand rotates, directing the Mo−CSi π-system toward CO (^{1}**X**, Figure 5). This geometry has a d_{yz} HOMO stabilized by M−arene backbonding. With further C−C shortening, the ground state crosses to a triplet, resulting from electron promotion from the d_{yz} (Mo−arene π) to the d_{xz} (Mo−CSi π^*) and representing cleavage of the Mo−C π-bond (^{1}**X** to ^{3}**X**, Figure 5, right insets). This alkylidene activation process, with significant electron density localization on the carbon, is facilitated by the proximal Na^+ ion, without which a low-energy pathway could not be identified. Bond formation is additionally assisted by borane coordination, stabilizing the oxygen lone pair as electron density is transferred to CO.[95] The direct impact of the Lewis acids Na^+ and BEt_3 on this C−C coupling process is particularly notable. While BEt_3 has no direct relevance to FT, there is precedent for both Lewis acidic promoters in FT catalysis[10] and selectivity perturbations resulting from alkali metal cation addition in electrochemical CO reduction.[96,97] Our computations highlight in a well-defined molecular system the necessity of these interactions for coupling chemistry to ketene.

Thermochemistry of Proton and Hydride Transfer to Carbide 1. Thus far, a moderate acid (Et_3NHCl, pK_a = 14.9 in THF[98]) and a strong hydride donor ($NaBEt_3H$, $\Delta G°_{H-}$ = 26 kcal/mol in MeCN[99]) have been described in the reaction chemistry for the formation of ethenone from **1**. These reagents are only a crude surrogate for H_2, as the free energy of hydrogen formation is favorable by ca. 25 kcal/mol, considering the reaction free energy of H_2 heterolysis in MeCN.[100] Given the basicity of related Mo(VI) and W(VI) carbide complexes (Mo(≡CH)$(NRAr)_3$, pK_a ≈ 30 kcal/mol in THF;[20] W(≡CH)$(CO)_2$(Tp*), pK_a = 28.7 kcal/mol in THF[21]), we anticipated that weaker acids could be employed to access methylidyne **4**.

Further protonation studies assessed the basicity of carbide **1** and supported a pK_a (Cl) for methylidyne **4** of ≥33.[101] Treatment of carbide **1** with the phosphazene base P2Et·HCl (Scheme 5; pK_a 26.6 in THF[102]) resulted in quantitative conversion to methylidyne **4**, with observation of the expected conjugate base P_2Et at 15.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Reaction with the weaker acid $[Ar_2PhPMe]Cl$ (Ar = 2,4,6-trimethoxyphenyl; pK_a 33.5 in THF[102]) likewise furnished methylidyne **4**, along with a new species, **4′**, whose NMR signature mirrored that of **4**, suggesting a closely related isomer. Most diagnostic was the singlet observed in the $^{31}P\{^1H\}$ NMR spectrum at 41.81 ppm , only ca. 1.5 ppm downfield from that of **4**, and the triplet observed in the $^{13}C\{^1H\}$ NMR spectrum at 267.76 ppm (^3J(C,P) = 18.3 Hz), which correlated by HMQC analysis to a triplet in the ^1H NMR spectrum at 2.64 ppm for the methylidyne proton (^3J(H,P) = 3.8 Hz). Independent synthesis, together with a single-crystal XRD study, confirmed **4′** to be an isomer of **4** in which the methylidyne is oriented *cis* with respect to the central arene (Figure 6; for details, see the Supporting Information). As in the previously reported *cis* silylcarbyne isomer,[26] the *cis* methylidyne isomer adopts a pseudo-octahedral geometry with a clear η^2-arene interaction *trans* to

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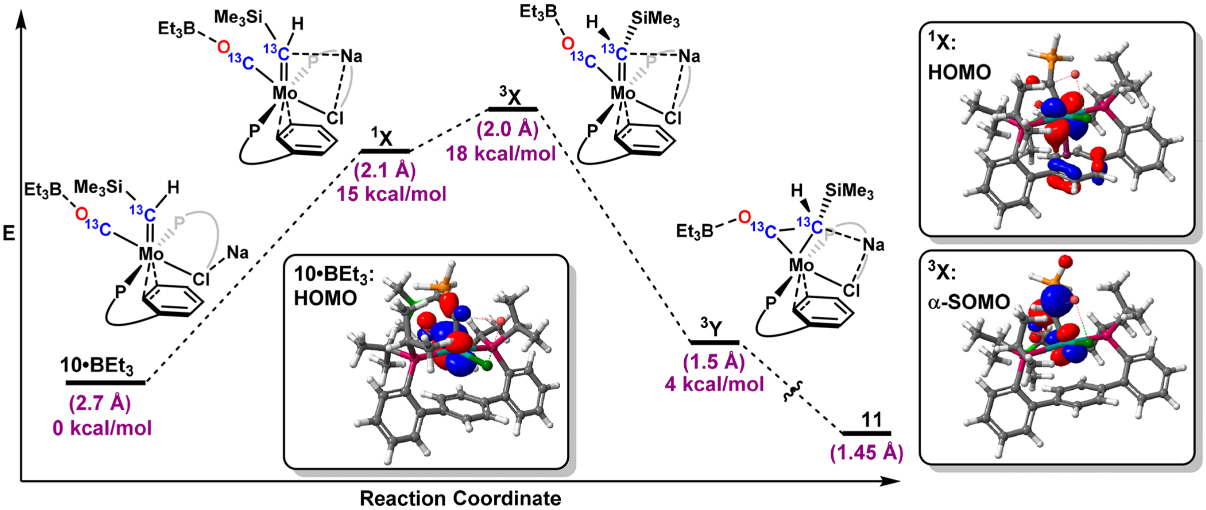
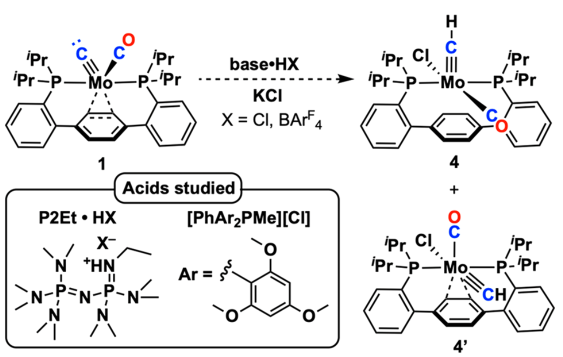


Figure 5. Potential energy landscape for C−C bond formation. Truncated transition state structures, computed C−C bond distances, and energies (relative to **10**·BEt_3) are provided. The insets depict key molecular orbitals (0.05 e $Å^{-3}$ isosurfaces) involved in bond-breaking and -making steps.

Scheme 5. Protonation Studies of Carbide 1[a]



[a]pK_a values of HCl salts in THF: P2Et·HCl, 26.6;[98] [PhAr_2PMe][Cl], 33.5.[102] Carbide **1** was synthesized cleanly in situ via deprotonation of P2Mo(CH)(CO)(Cl) **4** with benzyl potassium. For more details, see the Supporting Information.

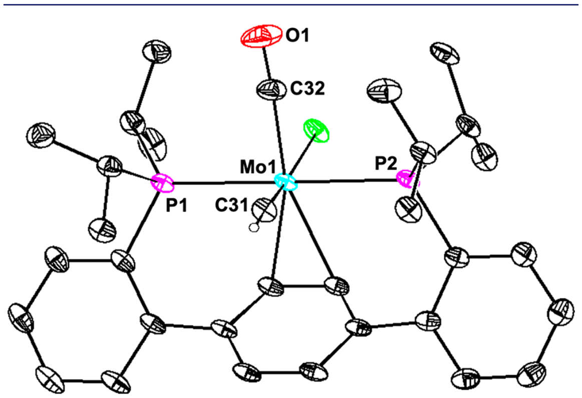


Figure 6. Solid-state structure of **4′**. Thermal anisotropic displacement ellipsoids are shown at the 50% probability level. H-atoms are omitted for clarity, except the methylidyne proton. Selected bond distances [Å]: Mo1−C31 1.781(2), Mo1−C32 1.972(2), O1−C32 1.155(2).

CO. The Mo−C31 distances are similar between the two isomers (*cis*/*trans* 1.781(2) vs 1.764(2) Å, respectively), both being consistent with a Mo−C triple bond.

The conjugate ylide $Ar_2PhP{=}CH_2$ was not detected, however (δ_P 7.00 ppm). Instead, a new peak in the $^{31}P\{^1H\}$ NMR spectrum at 7.90 ppm was observed, together with free **P2** (δ_P −3.45 ppm), suggesting displacement of **P2** by ylide in the formed methylidyne complex. Competing decomposition of the carbide complex by other pathways, however, cannot be strictly ruled out. Taken together, these protonation studies suggest a lower limit of 33 for the pK_a (Cl) of methylidyne **4**, roughly 3 orders of magnitude higher than that of the closest previously reported comparator, Mo(≡CH)($NRAr)_3$.[20] The higher effective basicity of carbide **1** may reflect diminished π-donation from the carbide ligand in this more electron-rich, formally Mo(IV), complex, and/or the favored energetics of chloride binding to Mo.

To gain insight into the hydride affinity of methylidyne **4**, weaker hydride sources were employed. Hydride transfer was complete using $NaBPh_3H$ ($\Delta G°_{H-}$ = 36 in MeCN[99]), as judged by the quantitative formation of **6** upon warming the reaction to RT. However, in a variable-temperature NMR study, methylidene **5** was not observed on maintaining the reaction at −78 °C. Instead, observation of **5** necessitated warming to ca. −30 °C, consistent with a higher activation energy of hydride transfer from the bulkier borohydride. Up to equal proportions of **5** and **4** were observed at −20 °C, suggesting that the hydride affinity of methylidyne **4** is at least comparable to that of $NaBPh_3H$. Competing conversion of **5** to **6** occurred at these temperatures, however, preventing extraction of the exact thermodynamic parameters.

Addition of $NaBPh_3H$ at −78 °C, followed by reaction with CO (1 atm), likewise furnished P2Mo$(CO)_3$ on warming to rt, as expected on the basis of the thermodynamic favorability of conversion from **5** described above. A small peak assigned to **5** was apparent only at intermediate temperatures (0 °C), again consistent with the higher activation barrier using $NaBPh_3H$.

Reconsidering the relevance to H_2 splitting, the pK_a of [Ar_2PhPMe]Cl and hydricity of $NaBPh_3H$ suggest that a reaction between carbide **1** and H_2 is thermodynamically

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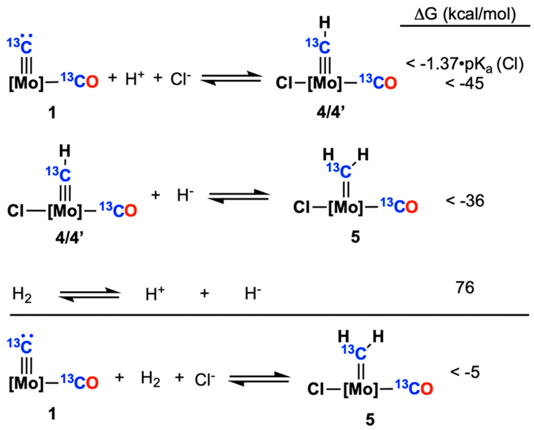
downhill by at least 5 kcal/mol (Scheme 6).[103] These experiments therefore constitute a thermochemical demon-

Scheme 6. Thermochemical Cycle Evaluating Relevance to Syngas Chemistry



stration that H_2 is a suitable source of protons and hydrides in the studied system. However, warming a THF solution of **1** under 1 atm H_2 showed only slight conversion to **3**. Direct reaction of carbides with H_2 therefore appears to be kinetically disfavored.[104] Cleavage of H_2, either heterolytically or on a surface, may be important to reaction with carbide and subsequent enabling of C−C coupling reactivity. This is in contrast to the reactivity of transition metal imides and carbenes, for which direct activation of R−H bonds (R = C, H) is kinetically allowed.[105−107]

CONCLUSION

In summary, a terminal Mo carbide complex has been demonstrated to undergo direct carbonylation, in conjunction with ligand functionalization, affording a phosphoranylidene-ketene complex. Carbide protonation provides a thermally stable methylidyne carbonyl complex, which, upon sequential treatment with hydride and CO, induces C−C coupling. Experimental and Quantum Mechanics computational interrogation of reactions between the silyl alkylidyne congener and hydride suggests that this C−C bond formation differs from the mechanism established for stepwise reduction/electrophile addition, proceeding through carbene carbonyl intermediates rather than dicarbynes.

Notably, this reaction sequence models, with high fidelity, the proposed mechanism of FT: surrogates of H_2 react with a terminal carbide (**1**) to afford a reactive methylidene (**5**) (cf., **B**−**F**, Figure 7). This methylidene is the precursor to C−C bond formation, coupling with CO to give ketene. These steps provide valuable precedent for the reactivity proposed for the heterogeneous FT process, mimicking the multielectron C−C coupling reactivity postulated following C−O scission at a well-defined monometallic Mo carbide complex. Critically, the use of hydride as a FT relevant two-electron reductant provides an efficient strategy to accomplish C−C coupling and C−H bond formation. The reaction of **1** with weak acid and hydride sources (the products of formal H_2 heterolytic cleavage) to access a methylidene contrasts the lack of reactivity observed when treated with H_2 directly, highlighting the need for preactivation to achieve productive carbide

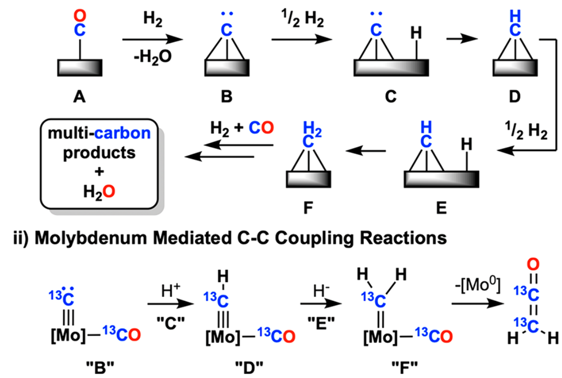


Figure 7. (i) Schematic representation of the early steps of Fischer−Tropsch synthesis. (ii) Molecular Mo complexes modeling C/CO coupling to metal-free organics.

hydrogenation either in the present molecular model system or via cleavage on the catalyst surface in FT.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b07743.

Detailed experimental procedures, full characterization, and spectroscopic data (PDF)

X-ray crystallographic details (CIF)

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Notes

The authors declare no competing financial interest.

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