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Formation and Reactivity of a Transient Cationic Alkyl Phosphinidene Complex

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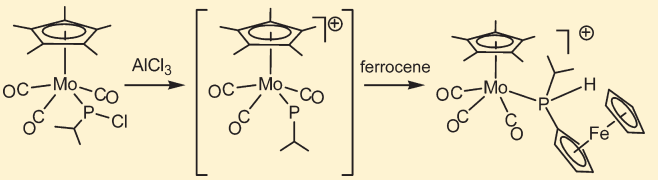
Supporting Information

ABSTRACT: Reaction of the chloroisopropylphosphido complex [Cp*Mo(CO)$_3${P(Cl)*i*-Pr}] (**1**) with $AlCl_3$ generates the transient cationic alkylphosphinidene complex [Cp*Mo(CO)$_3${P(*i*-Pr)}][$AlCl_4$] (**2**). If it is generated in the presence of diphenylacetylene, **2** undergoes a (1 + 2) cycloaddition to form the phosphirene complex [Cp*Mo(CO)$_3${P(*i*-Pr)C(Ph)C(Ph)}][$AlCl_4$] (**3**). Reaction of **2** with PPh_3 forms the phosphine-coordinated phosphinidene complex [Cp*Mo(CO)$_3${P(PPh_3)(*i*-Pr)}][$AlCl_4$] (**4**). Compound **2** reacts with Ph_2SiH_2 to insert the phosphinidene phosphorus atom into the Si−H bond, forming the secondary silylphosphine complex [Cp*Mo(CO)$_3${P(H)($SiHPh_2$)(*i*-Pr)}][$AlCl_4$] (**5**). Similarly, **2** reacts with ferrocene to activate a C−H bond, resulting in the formation of [Cp*Mo(CO)$_3${P(H)(*i*-Pr)($C_5H_4FeC_5H_5$)}][$AlCl_4$] (**6**).



INTRODUCTION

Terminal phosphinidene complexes can be considered phosphorus analogues of carbene complexes. Like carbenes, their reactivity ranges between nucleophilic and electrophilic extremes. Lappert and co-workers reported the first stable nucleophilic phosphinidenes in 1987,[1] and the reactivity of nucleophilic phosphinidene complexes has been well studied.[2] The first electrophilic phosphinidenes were transient species, generated in situ by the thermal decomposition of 7-phosphanorbornadiene complexes, and their reactivity has been well studied by trapping reactions with different substrates.[3] Several alternate routes to transient electophilic phosphinidene complexes have since been described.[4−6] Characteristic reactions of electrophilic phosphinidenes include (1 + 2) cycloaddition, nucleophilic attack at phosphorus, and bond insertions. The (1 + 2) cycloaddition reactions of electrophilic phosphinidenes are exemplified by addition of alkenes and alkynes to phosphinidene complexes to form phosphirane and phosphirene rings.[5,7−9] Nucleophilic attack at terminal phosphinidene is illustrated by their reactions with phosphines, which result in P−P bond formation.[10,11] Depending on the nature of the phosphinidene, phosphine coordination to the phosphinidene P atom can be weak and reversible[11] or strong.[6,10] Insertion reactions of electrophilic phosphinidenes into O−H and N−H bonds,[9] strained C−N and C−O bonds,[12] carbon−transition-metal bonds,[13] and carbon−halogen bonds[14] have been described. A few isolated examples of phosphinidene insertion into C−H bonds have also been observed.[15−17]

Stable electrophilic terminal phosphinidene complexes of Mo, W, and Ru were first reported in 2001.[18] They were formed via chloride abstraction from chloroaminophosphido complexes (Scheme 1) and are stabilized by π donation from N to P. Although the electrophilicity on the phosphinidene phosphorus is reduced by the π donation from N, these phosphinidenes still react as electrophiles.[6,7,11,19] Since that initial paper, analogous complexes of Fe, Os, Co, and Re have also been reported.[6,7,20]

We were interested in extending this methodology to the formation of cationic terminal phosphinidene complexes with alkyl or aryl substituents, with the expectation that replacement of the π-donor amino substituent with an alkyl substituent would increase the electrophilicity of the resulting phosphinidene complex. Unfortunately, this methodology is much less versatile in the formation of alkylphosphinidene compelxes, as many candidate metal anions simply reduce dichloroalkylphosphines, rather than substituting chloride to form the targeted chlorophosphido complexes.[21] Although an alkylchlorophosphido complex of iron has been described, attempts to form a phosphinidene via chloride abstraction were not successful.[22] Senturk and Carty showed that the phosphido complex [Cp*Mo(CO)$_3${P(Cl)(*i*-Pr)}] (**1**) can be formed by this methodology.[23] Here we report the formation and reactivity of the cationic alkylphosphinidene complex [Cp*Mo(CO)$_3$(P-*i*-Pr)][$AlCl_4$] (**2**), derived from **1** via chloride abstraction. We will also compare the reactivity of **2** with that of the aminophosphinidene analogue [Cp*Mo(CO)$_3$(PN-*i*-Pr_2)][$AlCl_4$] and show that the alkylphosphinidene is more electrophilic, as expected.

RESULTS AND COMPOUND CHARACTERIZATION

The phosphido precursor [Cp*Mo(CO)$_3${P(Cl)(*i*-Pr)}] (**1**) can be formed via reaction of Cp*Mo(CO)$_3^-$ with *i*-$PrPCl_2$, as shown in Scheme 2. An alternate route to **1** developed in our

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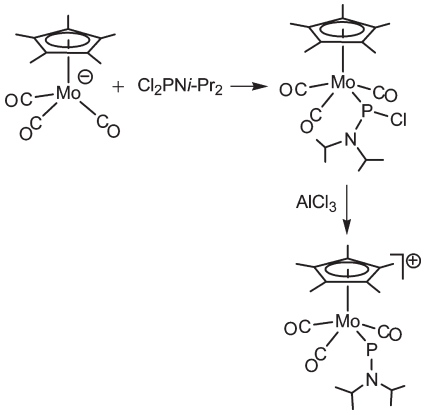
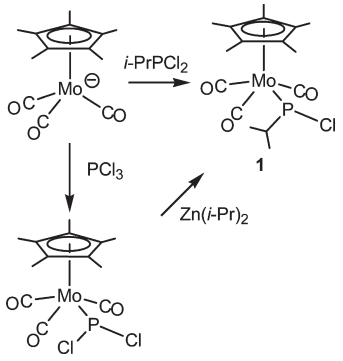
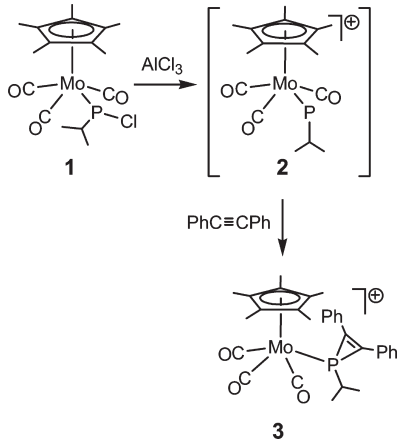
Scheme 1



Scheme 2



Scheme 3



laboratory avoids the use of the costly reagent *i*-PrPCl$_2$ by forming **1** via reaction of the known dichlorophosphido complex [Cp*Mo(CO)$_3$PCl$_2$][24] with Zn(*i*-Pr)$_2$. This is the method we now routinely use to synthesize **1**.

The chloride group on the chloroisopropylphosphido ligand of complex **1** can be readily abstracted using the Lewis acid AlCl$_3$. Chloride abstraction, however, does not generate a stable phosphinidene complex. The ^{31}P NMR spectrum of the reaction solution shows a complex mixture of products and no characteristic low-field signal for a phosphinidene complex. This is not surprising, given the absence of heteroatom stabilization. Attempts to observe a phosphinidene complex at low temperature were not successful. At temperatures below 0 °C, the chloride abstraction reaction from **1** was effectively suppressed. Above this temperature, decomposition of the phosphinidene is rapid, and only the decomposition products were observed.

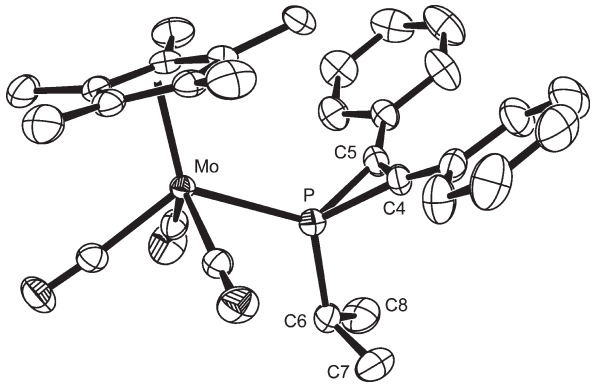


Figure 1. ORTEP diagram of [Cp*Mo(CO)$_3${P(*i*-Pr)C(Ph)C(Ph)}][AlCl$_4$] (**3**). Hydrogen atoms and the counterion have been omitted. Selected distances (Å) and angles (deg): Mo−P = 2.5090(5), P−C4 = 1.779(2), P−C5 = 1.784(2), C4−C5 = 1.329(3); P−C5−C4 = 67.9(1), P−C4−C5 = 68.3(1), C4−P−C5 = 43.78(9).

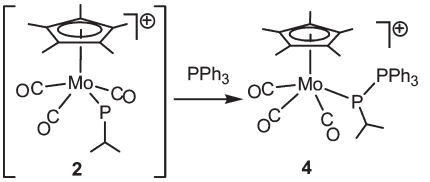
In order to demonstrate that a phosphinidene complex is being generated, the chloride abstraction reaction was carried out in the presence of diphenylacetylene (Scheme 3). The reaction occurs readily at room temperature and results in the formation of the expected phosphirene complex [Cp*Mo(CO)$_3${P(*i*-Pr)-C(Ph)C(Ph)}][AlCl$_4$] (**3**) as the only observed product. The ^{31}P NMR spectrum of **3** shows a singlet at δ −106.9, in the high-field region expected for a phosphirene complex.[25]

The structure of **3** was confirmed by X-ray crystallography (Figure 1). The cationic metal complex shows a four-legged piano-stool geometry, with three legs occupied by carbonyl ligands and the fourth by the phosphirene P atom. The isopropyl group is oriented away from the Cp* ring, and the methyl groups of the *i*-Pr group are oriented away from the metal. The Mo−P bond length of 2.509 Å is typical for an Mo−P single bond, and the structural parameters of the phosphinidene ring are as expected.[25] Reaction with alkynes to form phosphirenes is considered a characteristic reaction of terminal electrophilic phosphinidene complexes, and the observed product is strong supporting evidence for a transient phosphinidene.[26]

The electrophilicity of the isopropylphosphinidine **2** toward the moderately nucleophilic phosphine PPh$_3$ was examined. Generation of **2** in the presence of PPh$_3$ led to the phosphine-coordinated phosphinidene complex [Cp*Mo(CO)$_3${P(PPh$_3$)(*i*-Pr)}][AlCl$_4$] (**4**) (Scheme 4). This reactivity contrasts with that of the analogous aminophosphinidene complex, which does not react with triphenylphosphine, although it reacts with more basic phosphines.[11] The ^{31}P NMR spectrum of **4** shows doublets at δ 36.3 and −19 with a common coupling constant of 459 Hz. This large coupling constant indicates a direct P−P bond and falls in the middle of the range of P−P couplings observed in other phosphine-coordinated phosphinidene complexes (361−607 Hz).[10,11]

Compound **4** has been structurally characterized, and the ORTEP diagram is shown in Figure 2. The geometry at the metal

Scheme 4



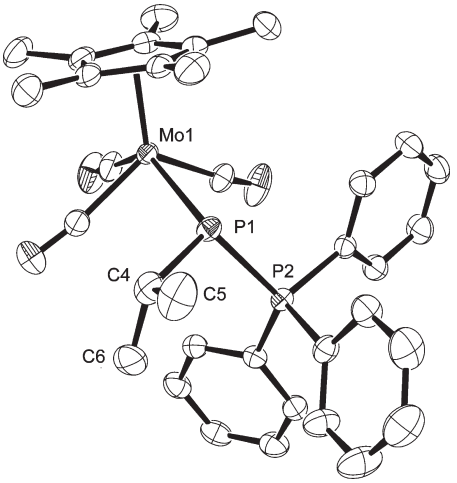
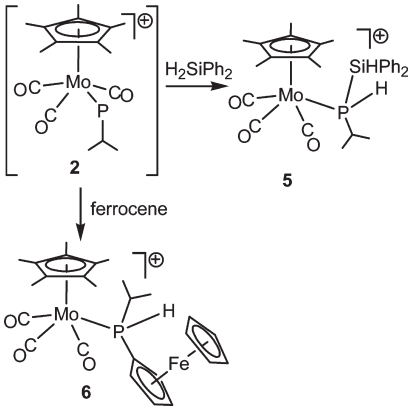


Figure 2. ORTEP diagram of $[Cp^*Mo(CO)_3\{P(PPh_3)\text{-}i\text{-}Pr\}][AlCl_4]$ (**4**). Hydrogen atoms and the counterion have been omitted. Selected distances (Å) and angles (deg): Mo1−P1 = 2.5826(5), P1−P2 = 2.1630(6), P1−C4 = 1.890(2); Mo1−P1−P2 = 116.35(2), Mo1−P1−C4 = 115.04(6), C4−P1−P2 = 103.47(6).

center is again a four-legged piano stool with carbonyl ligands on the three legs and the phosphine-coordinated phosphinidene ligand on the other leg. The geometry at P1 is pyramidal, indicating the presence of a stereoactive lone pair. The lone pair is directed toward the Cp* ring, allowing the isopropyl group and the triphenylphosphine moiety to point away from the Cp* ring. The geometry at P2 is tetrahedral, and the P1−P2 bond distance is 2.163 Å. This distance is closer to a P−P single bond (typically 2.21 Å)[27] than a P═P double bond (1.985−2.050 Å in diphosphenes).[28] However, it is significantly shorter than the P−P bond lengths observed in the analogous phosphine-coordinated *amino*phosphinidenes (2.215−2.266 Å)[6,11] but is comparable in length to the P−P bond (2.156 Å) in $[W(CO)_4\{P(PEt_3)C(O)OEt\}]$, formed by trapping the transient phosphinidene $[W(CO)_4\{PC(O)OEt\}]$ with triethylphosphine.[10]

The reactivity of the transient phosphinidene **2** toward bond activation reactions was investigated by generating it in the presence of diphenylsilane. The reaction results in insertion of the phosphinidene P atom into the Si−H bond, forming the silyl isopropyl secondary phosphine complex $[Cp^*Mo(CO)_3\{P(H)(SiHPh_2)(i\text{-}Pr)\}]$ (**5**) (Scheme 5). Analogous reactivity has been described for stable aminophosphinindene complexes.[29] The ^{31}P NMR of **5** shows a singlet at δ −64.5 with ^{29}Si satellites and a $^1J_{PSi}$ value of 26 Hz. The presence of the electron-donating isopropyl group and the relatively electropositive silyl and PH groups shifts the P resonance to high field.[30] The ^1H NMR spectrum shows a doublet of doublets at δ 4.35 that corresponds to the P−H. The large J_{PH} coupling of 326 Hz confirms the

Scheme 5



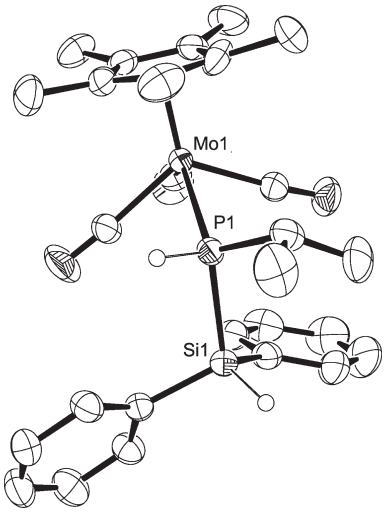


Figure 3. ORTEP diagram of $[Cp^*Mo(CO)_3\{P(H)(SiHPh_2)(i\text{-}Pr)\}]$ (**5**). Hydrogen atoms, other than Si−H and P−H, and the counterion have been omitted. Selected distances (Å) and angles (deg): Mo1−P1 = 2.533(1), P1−Si1 = 2.296(2); Mo1−P1−C4 = 118.7(2), Mo1−P1−Si1 = 117.70(7), Si1−P1−C4 = 105.9(2).

formation of a P−H bond. The resonance is further split by small couplings of 4 Hz to SiH. The Si−H resonance appears at δ 5.5 as a doublet of doublet of doublets, with a 29 Hz coupling to P, 4 Hz coupling to P−H, and a 2 Hz coupling to the isopropyl CH. Coupling of the Si−H with PH and P and ^{29}Si satellites in the ^{31}P spectrum confirm the formation of a P−Si bond.

The ORTEP diagram for the X-ray crystal structure of **5** is shown in Figure 3. The metal geometry is again a four-legged piano stool with three carbonyl ligands and one isopropyl silyl secondary phosphine. The Mo−P bond length is 2.534 Å, which is close to the Mo−P distance observed in the acetylene (**3**) and phosphine (**4**) trapped complexes. The P−Si bond length is 2.296 Å, which is typical for a P−Si single bond.[31] Both P and Si are tetrahedral, and the substituents are staggered, with the two hydrogen substituents in relative gauche positions (dihedral angle 79.6°). The groups on P are oriented such that the large $SiHPh_2$ group is directed away from Cp*.

The transient phosphinidene **2** was also found to be sufficiently electrophilic to activate C−H bonds. Generation of **2** in

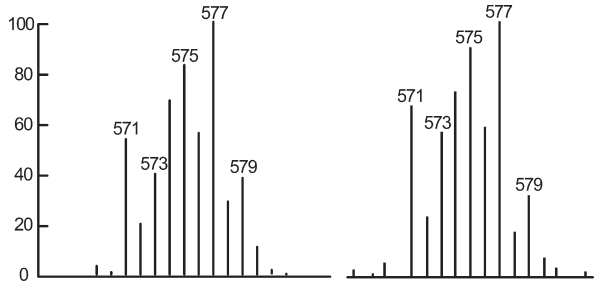


Figure 4. Calculated and experimental isotope patterns for the molecular ion peak of **6**.

the presence of 1 equiv of ferrocene resulted in insertion of the phosphinidene phosphorus into the C−H bond of the ferrocene to form the ferrocenylisopropylphosphine complex $[Cp^*Mo(CO)_3\{P(H)(i\text{-}Pr)(C_5H_4FeCp)\}][AlCl_4]$ (**6**) (Scheme 5). Although **6** could not structurally characterized, as the crystals did not diffract, spectroscopic evidence strongly supports the proposed structure. The ^{31}P NMR spectrum shows a sharp singlet at δ 17. The ^{1}H NMR spectrum shows a doublet at δ 5.73 that corresponds to the P−H. The large coupling of 378 Hz indicates the direct P−H bond. The five H atoms of the free Cp moiety of ferrocene give a sharp singlet at δ 4.3, while the phosphine-bound cyclopentadienyl ring shows broad singlets at δ 4.56 (1H), 4.54 (2H), and 4.26 (1H). The ^{13}C NMR spectrum shows five chemically inequivalent Cp carbons for the phosphine-bound Cp ring, all of which show phosphorus coupling with J values ranging from 8 to 46 Hz, clearly demonstrating the addition of the phosphinidene to the Cp ring. Further evidence for the proposed structure comes from the electrospay mass spectrum, which shows an isotope pattern centered at m/z 575 that corresponds to the predicted masses for the cation of the product (Figure 4).

DISCUSSION

The bonding in electrophilic phosphinidene complexes is best conceptualized by considering them to be derived from the singlet state of free phosphinidene, which contains two lone pairs and an empty p_z orbital. One lone pair forms a σ-donor interaction to the transition metal, while the second lone pair remains stereoactive, leading to the bent geometry at phosphorus. The electrophilicity at P results from the empty p_z orbital. In aminophosphinidene complexes, this empty p_z orbital is stabilized by π donation from the heteroatom substituent and from filled metal d orbitals (Figure 5). The heteroatom stabilization of terminal electrophilic phosphinidene complexes is analogous to the heteroatom stabilization of Fischer carbenes and accounts for the fact that the only known stable terminal electrophilic phosphinidene complexes are aminophosphinidenes. In contrast, the empty p orbital in electrophilic alkylphosphinidene complexes is only stabilized by metal-to-phosphorus back-donation. Since the $Cp^*Mo(CO)_3$ fragment is cationic and relatively electron poor, the alkylphosphinidene complex described here is expected to be strongly electrophilic because there is little electronic stabilization of the empty p_z orbital.

In the phosphine trapping experiments, the transient alkylphosphinidene is significantly more reactive than its aminophosphinidene analogue. Unlike the aminophosphinidene, the alkylphosphinidene reacts with triphenylphosphine. The greater reactivity of **2** can be attributed to the greater electrophilicity that

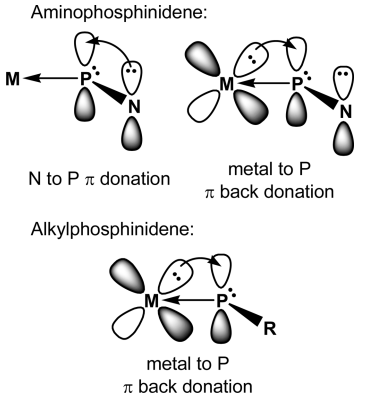


Figure 5

results from the lack of a π-donor substituent, although the smaller steric size of the isopropyl group on P may also influence the reactivity. The greater electrophilicity of the alkylphosphinidene is also evident in the structure of the adduct, which has a significantly shorter and stronger P−P bond than any of the structurally characterized phosphine-coordinated aminophosphinidene complexes.[6,11]

X−H bond activation reactions are characteristic reactions of terminal electrophilic phosphinidene complexes. These reactions occur either by initial coordination to P followed by proton transfer or by a concerted mechanism. Here, we have shown that the Si−H bond can be activated by the transient alkylphosphinidene complex, resulting in insertion of the phosphinidene P atom into the Si−H bond. The same reactivity has previously been demonstrated with aminophosphinidenes and was expected for the alkylphosphinidene.

In contrast to the case for aminophosphinidenes, the alkylphosphinidene is also capable of activating the C−H bond of ferrocene. The greater reactivity toward C−H bonds reflects the alkylphosphinidene's greater electrophilicity. However, this cationic phosphinidene is still not sufficiently electrophilic to activate C−H bonds other than those of ferrocene. For example, it is unreactive toward activated aromatic C−H bonds. The reactivity of the cationic alkylphosphinidene complex **2** toward ferrocene suggests that its electrophilicity is similar to that of the well-studied transient phosphinindene complexes $[W(CO)_4(PR)]$, which behave similarly toward ferrocene and also fail to activate other C−H bonds.[16] Thus, the donor ability of the Cp* ligand in **2**, which is expected to decrease electrophilicity at P, is offset by the positive charge on the complex, which increases electrophilicity.

Direct C−H activation by electrophilic phosphinidene complexes has potential as a synthetic tool for P−C bond formation. Intramolecular C−H activation has been described.[15] However, examples of direct intermolecular C−H activation are limited to activation of the C−H bonds in ferrocene. In order to develop C−H activation by terminal electrophilic phosphinidene complexes into a useful synthetic tool, the electrophilicity of the phosphinidene must be further increased to extend the range of potential substrates. This might be achieved by replacing the $Cp^*Mo(CO)_3^+$ fragment with a more electron-poor metal fragment such as $Re(CO)_5^+$. Synthetic routes to such complexes are being developed in our group.

In summary, we have shown that a transient cationic alkyl phosphinidene complex can be generated by chloride abstraction

from a chloroalkylphosphido complex. This is the first cationic alkylphosphinidene complex to be described. As expected, it reacts as an electrophilic phosphinidene, and we have demonstrated examples of three characteristic reactions of electrophilic phosphinidenes: (1 + 2) cycloaddition, coordination by nucleophiles, and bond insertion reactions. The ability of the alkylphosphinidene to activate the C−H bond in ferrocene clearly demonstrates that alkylphosphinidenes are more electrophilic than the corresponding aminophosphinidenes.

EXPERIMENTAL SECTION

General Comments. All procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in an inert-atmosphere glovebox. THF was distilled from Na/benzophenone. Dichloromethane and hexane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper catalyst (hexane). Deuterated chloroform was distilled from P_2O_5. The NMR spectra were recorded in $CDCl_3$ using a Varian Mercury 300 spectrometer operating at 300.179 MHz (^{1}H) and 121.515 MHz (^{31}P{^{1}H}). Infrared spectra were recorded in solution in hexane or CH_2Cl_2. Mass spectra were recorded using a Finnigan-Matt TSQ-700 mass spectrometer equipped with electrospray ionization and a Harvard syringe pump.

Synthesis of [Cp*Mo(CO)$_3${P(Cl)*i*-Pr}] (1). This compound was prepared using a modification of the method developed by Senturk et al.[23] To pentamethylcyclopentadiene (0.52 g, 3.8 mmol, 0.60 mL) in 50 mL of THF was added *n*-butyllithium (1.5 mL of 2.5 M solution in hexane, 3.8 mmol). Molybdenum hexacarbonyl (1.00 g, 3.78 mmol) was then added, and the resulting suspension was heated under reflux for 12 h, resulting in a orange solution of Li[Cp*Mo(CO)$_3$]. This solution was added in small portions to a solution of dichloroisopropylphosphine (0.93 mL, 7.5 mmol) in 50 mL of THF at −80 °C. The reaction mixture was stirred for 30 min at −80 °C and then warmed to 0 °C. The solvent was removed under vacuum at 0 °C. The red-orange residue obtained was extracted into pentane (25 mL). The pentane was removed under vacuum at 0 °C, and the orange oil obtained was dissolved in a minimum amount of hexane. The hexane solution was then cooled to −35 °C for 24 h, resulting in the formation of large orange crystals. At room temperature, these crystals revert to an oil; thus, they were stored at −35 °C. Yield: 0.89 mg, 56%. IR (hexane solution, cm^{-1}, ν(CO)): 2007, 1945, 1916. ^{31}P NMR: δ 268.7. ^{1}H NMR: δ 2.31 (d sept, 1H, $^2J_{HP}$ = 27.9 Hz, $^3J_{HH}$ = 7 Hz, C*H*(CH$_3$)$_2$), 1.96 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.37 (dd, 3H, $^3J_{HP}$ = 23.4 Hz, $^3J_{HH}$ = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.36 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR: δ 236.8 (d, $^2J_{CP}$ = 9 Hz, MoCO), 229.1 (s, MoCO), 225.0 (s, MoCO), 106.6 (s, *C*$_5$(CH$_3$)$_5$), 36.4 (d, $^1J_{CP}$ = 47 Hz, PCH(CH$_3$)$_2$), 22.7 (d, $^2J_{CP}$ = 18 Hz, PCH(CH$_3$)$_2$), 21.3 (d, $^2J_{CP}$ = 3 Hz, PCH(*C*H$_3$)$_2$), 10.6 (d, J_{PC} = 6 Hz, C$_5$(*C*H$_3$)$_5$). Anal. Calcd for $C_{16}H_{22}O_3PClMo$: C, 45.25; H, 5.22. Found: C, 45.06; H, 5.34.

Synthesis of [Cp*Mo(CO)$_3${P(*i*-Pr)C(Ph)C(Ph)}][AlCl$_4$] (3). [Cp*Mo(CO)$_3${P(*i*-Pr)Cl] (**1**; 20 mg, 0.047 mmol) and diphenylacetylene (17 mg, 0.017 mmol) were dissolved in CH_2Cl_2 (0.5 mL). The resulting solution was added to $AlCl_3$ (12.6 mg, 0.094 mmol), resulting in a color change from pale yellow to dark red. The solvent was removed in vacuo, and the residue was extracted into CH_2Cl_2 (0.5 mL) and crystallized as orange crystals by slow diffusion of diethyl ether into the CH_2Cl_2 solution. Yield: 21 mg, 63%. IR (cast, cm^{-1}, ν(CO)): 2035, 1970, 1944. ^{31}P{^{1}H} NMR: δ −106.9. ^{1}H NMR: δ 7.9−7.3 (multiplets, Ph), 2.28 (septet, 1H, $^2J_{HH}$ = 7.2 Hz, C*H*(CH$_3$)$_2$), 1.66 (s, 15H, Cp*), 0.93 (dd, 6H, $^2J_{HP}$ = 21.0 Hz, $^3J_{HH}$ = 7.2 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR: δ 229.3 (d, $^2J_{CP}$ = 3 Hz, MoCO), 229.2 (d, $^2J_{CP}$ = 36 Hz, MoCO), 132.5 (s, Ph), 131.7 (s, Ph), 130.7 (d, $^3J_{PC}$ = 6 Hz, *o*-Ph), 130.3 (s, Ph), 128.6 (d, $^3J_{PC}$ = 5 Hz, *o*-Ph), 126.5 (d, $^2J_{PC}$ = 6 Hz, *ipso*-Ph), 125.7 (d, $^1J_{PC}$ = 14 Hz, phosphirene ring C), 109.4 (s, *C*$_5$(CH$_3$)$_5$), 39.8 (d, $^1J_{PC}$ = 8 Hz, PCH(CH$_3$)$_2$), 20.3 (d, $^2J_{PC}$ = 2 Hz, PCH(*C*H$_3$)$_2$), 10.9 (s, C$_5$(*C*H$_3$)$_5$). MS (electrospray, CH_2Cl_2 solution): m/z 569 (M^+). Anal. Calcd for $C_{30}H_{32}O_3PAlCl_4Mo$: C, 48.94; H, 4.38. Found: C, 48.59; H, 4.42.

Synthesis of [Cp*Mo(CO)$_3${P(PPh$_3$)*i*-Pr}][AlCl$_4$] (4). [Cp*Mo(CO)$_3${P(*i*-Pr)Cl] (**1**; 20 mg, 0.047 mmol) and PPh$_3$ (19 mg, 0.071 mmol) were dissolved in CH_2Cl_2 (0.5 mL). The resulting solution was added to $AlCl_3$ (9 mg, 0.071 mmol), resulting in an immediate color change from yellow to dark red. The solvent was removed in vacuo, and the residue was extracted into CH_2Cl_2 (0.5 mL) and crystallized as dark red crystals by slow diffusion of hexane into the CH_2Cl_2 solution. Yield: 30 mg, 77%. IR (CH_2Cl_2 solution, cm^{-1}, ν(CO)): 2036, 1970 sh, 1946 cm^{-1}. ^{31}P{^{1}H} NMR: δ 36.4 (d, $^1J_{PP}$ = 459.3 Hz, MoP*P*), −19.9 (d, $^1J_{PP}$ = 459.3 Hz, Mo*P*P). ^{1}H NMR: δ 7.85−7.60 (multiplets, Ph), 2.17 (m, C*H*(CH$_3$)$_2$), 1.93 (s, 15H, Cp*), 1.083 (dd, 3H, $^3J_{HP}$ = 15.4 Hz. $^3J_{HH}$ = 7.2 Hz, C*H*$_3$), 1.081 (dd, 3H, $^3J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$). ^{13}C NMR: δ 228.3 (d, $^2J_{CP}$ = 26 Hz, MoCO), 226.6 (s, MoCO), 225.4 (s, MoCO), 134.1 (dd, J_{PC} = 9 Hz, J_{PC} = 3 Hz, Ph), 133.9 (s, Ph), 130.0 (d, J_{PC} = 12 Hz, Ph), 123.7 (dd, $^1J_{PC}$ = 67 Hz, $^2J_{PC}$ = 8 Hz, *ipso*-Ph), 109.4 (s, *C*$_5$(CH$_3$)$_5$), 28.6 (dd, $^1J_{CP}$ = 28 Hz, $^2J_{CP}$ = 2 Hz, PCH(CH$_3$)$_2$), 25.1 (d, $^2J_{PC}$ = 8 Hz, PCH(*C*H$_3$)$_2$), 25.0 (d, $^2J_{PC}$ = 8 Hz, PCH(*C*H$_3$)$_2$), 10.8 (d, J_{PC} = 6 Hz, C$_5$(*C*H$_3$)$_5$). Anal. Calcd for $C_{34}H_{32}O_3P_2AlCl_4Mo$: C, 49.78; H, 4.55. Found: C, 49.51; H, 4.75.

Synthesis of [Cp*Mo(CO)$_3${P(H)(SiHPh$_2$)(*i*-Pr)}][AlCl$_4$] (5). [Cp*Mo(CO)$_3${P(*i*-Pr)Cl] (**1**; 20 mg, 0.047 mmol) was dissolved in CH_2Cl_2 (0.5 mL), and SiH_2Ph_2 (17 μL, 0.094 mmol) was added. The resulting solution was mixed well and added to $AlCl_3$ (9 mg, 0.071 mmol), resulting a color change from yellow to dark red. The solvent was removed in vacuo, and the residue was extracted into CH_2Cl_2 (0.5 mL) and crystallized as pale yellow crystals by slow diffusion of hexane into the CH_2Cl_2 solution. Yield: 29 mg, 82%. IR (CH_2Cl_2 solution, cm^{-1}): ν(CO) 2051, 1988, 1966, ν(SiH) 2171. ^{31}P{^{1}H} NMR: δ −64.5. ^{1}H NMR: 7.80−7.44 (m, Ph), δ 5.54 (dd, 1H, $^2J_{PH}$ = 28 Hz, $^3J_{HH}$ = 4 Hz, Si−H), 4.35 (dd, $^1J_{PH}$ = 327 Hz, $^3J_{HH}$ = 4 Hz, PH), 2.48 (m, C*H*(CH$_3$)$_2$), 2.04 (s, 15H, Cp*), 1.29 (dd, 3H, $^3J_{PH}$ = 9.9 Hz, $^3J_{HH}$ = 7.4 Hz, C*H*$_3$), 1.22 (dd, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 7.2 Hz, C*H*$_3$). ^{13}C NMR: δ 231.5 (s, MoCO), 228.4 (d, $^2J_{CP}$ = 26 Hz, MoCO), 227.3 (d, $^2J_{CP}$ = 24 Hz, MoCO), 136.3 (d, J_{CP} = 2 Hz, Ph), 136.1 (d, J_{CP} = 2 Hz, Ph), 135.8 (s, Ph), 134.7 (s, Ph), 132.43 (s, Ph), 132.39 (s, Ph), 131.4 (s, Ph), 130.1 (s, Ph), 129.5 (s, Ph), 129.4 (s, Ph), 128.5 (s, Ph), 128.3 (s, Ph), 108.6 (s, *C*$_5$(CH$_3$)$_5$), 26.4 (d, $^1J_{CP}$ = 18 Hz, PCH(CH$_3$)$_2$), 25.5 (d, $^2J_{CP}$ = 6 Hz, PCH(CH$_3$)$_2$), 20.3 (d, $^2J_{CP}$ = 2 Hz, PCH(*C*H$_3$)$_2$), 11.0 (s, C$_5$(*C*H$_3$)$_5$). Note: the silyl phosphine complex is extremely sensitive to Si−P bond cleavage. As a result, satisfactory elemental analysis for **5** could not be obtained, as bulk samples always contain decomposition products (see ref 29 for a discussion of the Si−P cleavage mechanism in related silylphosphines).

Synthesis of [Cp*Mo(CO)$_3${P(H)(*i*-Pr)(C$_{10}$H$_9$Fe)}][AlCl$_4$] (6). [Cp*Mo(CO)$_3${P(*i*-Pr)Cl] (**1**; 20 mg, 0.047 mmol) and ferrocene (8.8 mg, 0.047 mmol) were dissolved in CH_2Cl_2 (0.5 mL). The resulting solution was added to $AlCl_3$ (9.5 mg, 0.071 mmol), resulting in an immediate color change from yellow to dark red. The solvent was removed in vacuo, and the residue was extracted into CH_2Cl_2 (0.5 mL) and crystallized as orange crystals by slow diffusion of diethyl ether into the CH_2Cl_2 solution. Yield: 30 mg, 85%. IR (cast, cm^{-1}, ν(CO)): 2035, 1965 sh, 1948. ^{31}P{^{1}H} NMR: δ 17.2 (s). ^{1}H NMR: δ 5.73 (d, 1H, $^1J_{PH}$ = 378 Hz, P−H), 4.58 (s, 1H, Cp), 4.55 (s, 2H, Cp), 4.31 (s, 5H, Cp), 4.27 (s, 1H, Cp), 3.17 (septet, 1H, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 9 Hz), 1.87 (s, 15H, Cp*), 1.37 (dd, 3H, $^3J_{PH}$ = 12 Hz, $^3J_{HH}$ = 9 Hz, C*H*$_3$), 1.30 (dd, $^3J_{PH}$ = 12 Hz, $^3J_{HH}$ = 9 Hz, C*H*$_3$). ^{13}C NMR: δ 231.1 (s, MoCO), 229.1 (d, $^2J_{CP}$ = 27 Hz, MoCO), 228.3 (s, MoCO), 108.6 (s, *C*$_5$(CH$_3$)$_5$), 74.1 (d, J_{CP} = 8.8 Hz, *C*$_5$H$_4$P), 73.1 (d, $^1J_{CP}$ = 46 Hz, *C*$_5$H$_4$P), 73.0 (d, J_{CP} = 8.3 Hz, *C*$_5$H$_4$P), 71.7 (d, J_{CP} = 14.8 Hz, *C*$_5$H$_4$P), 71.3 (d, J_{CP} = 8.3 Hz, *C*$_5$H$_4$P), 70.6 (s, Fe*C*$_5$H$_5$), 33.3 (d, $^1J_{CP}$ = 31 Hz, PCH(CH$_3$)$_2$), 20.8 (d,

$^2J_{CP}$ = 26 Hz, $PCH(CH_3)_2$), 16.1 (d, $^2J_{PC}$ = 14 Hz, $PCH(CH_3)_2$), 10.9 (s, $C_5(CH_3)_5$). MS (electrospray, CH_2Cl_2 solution): *m/z* 569−582 (M^+ isotope pattern, see Figure 5). Anal. Calcd for $C_{26}H_{32}O_3AlCl_4FePMo$: C, 41.97; H, 4.33. Found: C, 41.48; H, 4.36.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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