Synthesis and Reactivity of the Coordinatively Unsaturated Methylene Complex $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$

Michael D. Fryzuk,* Xiaoliang Gao, Kiran Joshi, Patricia A. MacNeil, and Roberta L. Massey

Contribution from the Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1

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Abstract: The reactions of the coordinatively unsaturated iridium methylene complex $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ are described. This methylene complex is prepared by the reaction of 2 equiv of $KOBu^t$ with the methyl iodide derivative $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ in toluene; the extra equivalent of $KOBu^t$ serves to coordinate the $HOBu^t$ that is produced as the precipitate $KOBu^t{\cdot}HOBu^t$. The reaction of H_2 with the methylene complex generates the trihydride amine $IrH_3[HN(SiMe_2CH_2PPh_2)_2]$ via a series of oxidative addition and migratory insertion steps; the trihydride derivative loses H_2 upon workup to generate the iridium(III) dihydride $IrH_2[N(SiMe_2CH_2PPh_2)_2]$. The reaction of the methylene complex with PMe_3 produces the square planar PMe_3 derivative $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$ and ethylene (0.5 equiv); monitoring this reaction at low temperatures shows the presence of a number of intermediates that suggest the mechanism involves the generation of free $H_2C{=}PMe_3$ which reacts with the methylene complex to ultimately give the observed products. The reaction of the methylene complex with CO results in the formation of $Ir(CO)[(CH_2PPh_2CH_2SiMe_2NSiMe_2CH_2PPh_2)]$, in which the methylene unit has inserted into one of the iridium–phosphine bonds of the ancillary tridentate ligand. Also produced in this reaction is a small and variable amount ($\leq$15%) of the iridium(I) carbonyl complex $Ir(CO)[N(SiMe_2CH_2PPh_2)_2]$; the fate of the coordinated methylene unit for this side reaction could not be determined. Oxidative addition reactions were also examined; addition of Al_2Me_6 to the methylene derivative resulted in the formation of the hydride–aluminum complex $Ir(\mu\text{-}AlMe_2)H[N(SiMe_2CH_2PPh_2)_2]$; this heterobimetallic species has the $AlMe_2$ unit directly bound to iridium and bridged by the amide donor of the backbone. A mechanism is proposed that involves oxidative addition of $AlMe_3$ to the iridium center followed by migratory insertion of the methylene unit and the methyl to generate an ethyl ligand which β-eliminates and releases ethylene to generate the hydride. The methylene complex also reacts with methyl iodide to generate the ethylene hydride iodide complex $Ir(\eta^2\text{-}C_2H_4)H(I)[N(SiMe_2CH_2PPh_2)_2]$; the proposed mechanism also involves oxidative addition as the first step followed by migratory insertion to generate an ethyl moiety; however, rather than simple β-elimination to the iridium center, the amide unit abstracts the β-hydrogen to form an amine–olefin complex that subsequently inverts at nitrogen and then oxidatively adds the N–H unit to generate the hydride complex. Deuterium-labeling experiments show that the abstraction of the β-hydrogen is reversible since there is scrambling of the label equally into both the α and β positions of the coordinated ethylene.

Introduction

Transition-metal complexes with metal–carbon double bonds, $L_nM{=}CR_2$, are implicated in a variety of catalytic and stoichiometric processes, such as olefin metathesis,[1] ring-opening metathesis polymerization (ROMP),[2-7] and cyclopropanation.[8-10] Although there are a large number of such species in the literature, mononuclear complexes having R = H, transition-metal methylidene or methylene derivatives, are relatively few in number. This is somewhat surprising given that the first such complex, $(\eta^5\text{-}C_5H_5)_2Ta{=}CH_2(CH_3)$,[11,12] was the forerunner to a whole class of nucleophilic carbene derivatives. Chart I shows a variety of known transition-metal methylene complexes.

Although the particular group of methylene complexes shown in Chart I is not comprehensive, the indicated examples do provide a fair assessment of the range of metals and ligand types available. While a number of methylene complexes are stable at room temperature and can be isolated, many are quite reactive and have been only characterized spectroscopically; for example, the cationic derivatives **D** and **F** are generated[9,13-20] at low temperatures by the reaction of the corresponding methyl ethers with a Lewis acid whereas the neutral iridium methylene **H** is detected below −40 °C by photoextrusion of acetone from $(\eta^5\text{-}C_5Me)$Ir-

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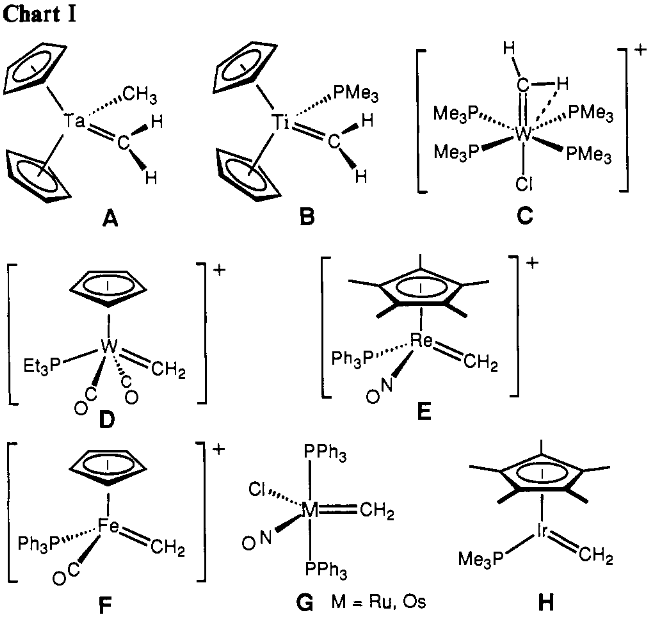
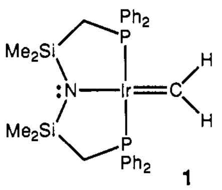
Chart I



$(OCMe_2CH_2)PMe_3$.[21] All of the methylene complexes shown in Chart I do share one common feature, and that is they are all 18-electron complexes; compound **C** *without* its agostic C–H interaction would be a 16-electron species and is therefore the only possible exception.[22]

Some time ago we reported[23] the synthesis and X-ray structure of the iridium methylene complex $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (**1**). This complex is remarkable for a number of reasons; of the



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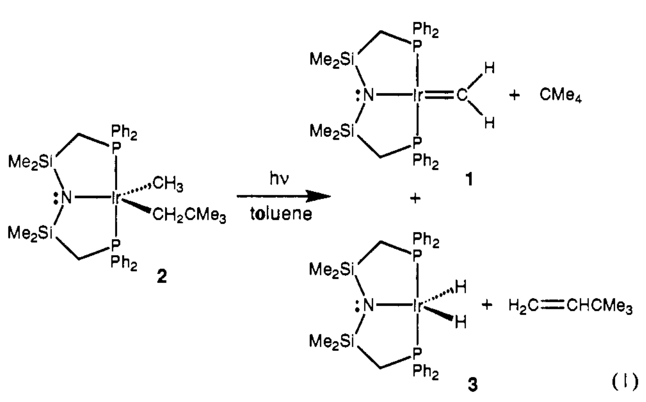
three known methylene complexes of iridium, this is the only one to be structurally characterized; as mentioned above, $(\eta^5\text{-}C_5Me)\text{-}Ir{=}CH_2(PMe_3)$ (**H**) is only stable below −40 °C[21] and $Ir{=}CH_2(CO)I(PPh_3)_2$, while isolable,[24] rearranges in solution. More importantly, complex **1** is a 16-electron derivative and is therefore coordinatively unsaturated. This latter feature is of particular interest since one can anticipate that reactivity patterns for this iridium methylene complex will be quite different as compared to those for the 18-electron species mentioned above. In this paper we report the reactions of a number of small molecules with the iridium methylene complex **1** that take advantage of its coordinative unsaturation and result in ligand binding followed by migratory insertion, as well as oxidative addition processes followed by migratory insertion. The range of reaction types that emerge show clearly that the iridium methylene complex **1** is truly in a class by itself.

Results and Discussion

Preparation of $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (1). The deep purple iridium methylene complex **1** was originally prepared[23] by photolysis of the bis(hydrocarbyl) derivative $Ir(CH_3)(CH_2CMe_3)[N(SiMe_2CH_2PPh_2)_2]$ (**2**), a reaction that also gave the dihydride $IrH_2[N(SiMe_2CH_2PPh_2)_2]$ (**3**) as a side product (eq 1). Separation of complex **1** from the dihydride derivative **3** was



(1)

tedious and resulted in at best 20-30% isolated yields of **1**. Given the fact that the bis(hydrocarbyl) complexes must be prepared[25] first from the readily available methyl iodide complex $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (**4**),[26] we examined the reaction of **4** with a variety of sterically-hindered bases in an effort to remove the elements of "HI"; such a procedure would obviate isolation of the bis(hydrocarbyl) complex and eliminate the separation problems of the photochemical reaction.

A number of bases were examined. For example, reactions of the methyl iodide complex **4** with $H_2C{=}PMe_3$, $KN(SiMe_3)_2$, and $LiBu^t$ all resulted in decomposition or unidentified products. The reaction of $LiNHBu^t$ with **4** generated the cyclometalated amine hydride derivative *fac*-$Ir(\eta^2\text{-}CH_2NBu^t)H[N(SiMe_2CH_2PPh_2)_2]$ in analogy to other work from our laboratory.[27] Fortunately, the use of $KOBu^t$ in toluene was found to be successful.

The yield of the methylene complex $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (**1**) from the reaction of the methyl iodide derivative $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (**4**) with $KOBu^t$ in toluene was observed to be rather sensitive to both reaction time and stoichiometry. When an excess of $KOBu^t$ (3–5 equiv) was used, the product was generated in 30–60% isolated yield, depending on how fast the workup procedure was performed. When exactly 1 equiv was utilized, the maximum yield observed was 46%, and even after a reaction time of approximately 12 h, there was still unreacted starting material present. Prolonged reaction times led to the decomposition of the product, which is attributed to the presence of $KOBu^t$ and $HOBu^t$. Indeed, following the reaction by NMR spectroscopy showed that $KOBu^t$ completely decomposed compound **1** in 3 h while $HOBu^t$ required 12 h. The ideal conditions were discovered by using exactly 2 equiv of $KOBu^t$. It was shown by NMR spectroscopy that the reaction took about 1 h to quantitatively convert $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ to the methylene complex **1**; under these conditions, **1** was observed to be stable in the reaction mixture. Surprisingly, the ^1H NMR spectrum of the reaction mixture after 1 h (i.e., at the end of the reaction) showed no resonances due to the excess $KOBu^t$ and the byproduct $HOBu^t$. In fact, some white precipitate was observed at the bottom and on the walls of the NMR tube. The precipitate was then proven to be a mixture of KI and $KOBu^t{\cdot}HOBu^t$ by mixing an equimolar amount of $KOBu^t$ and $HOBu^t$ in toluene or ether, which instantly reacted to give a white precipitate; by weight, this precipitate corresponds to $KOBu^t{\cdot}HOBu^t$.[28] Therefore, the presence of the extra equivalent of $KOBu^t$ helps drive the reaction to completion by precipitating the byproduct $HOBu^t$; moreover, by acting as a scavenger for $HOBu^t$, further decom-

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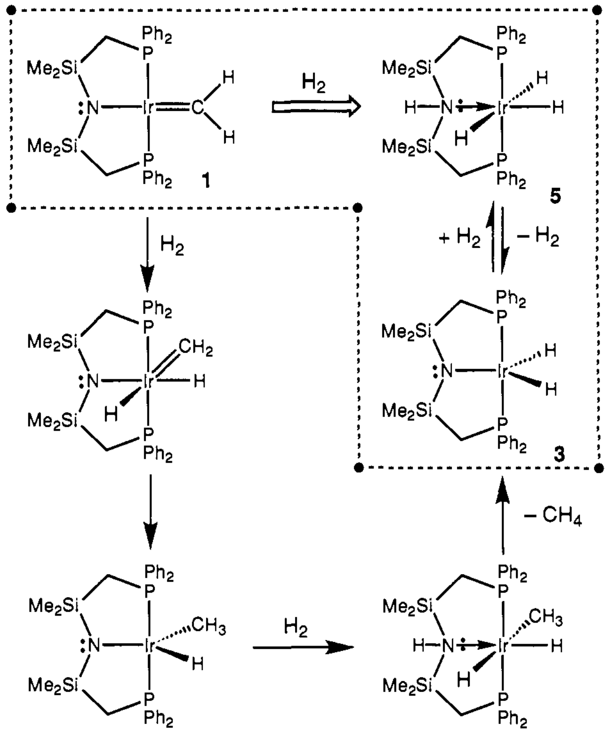
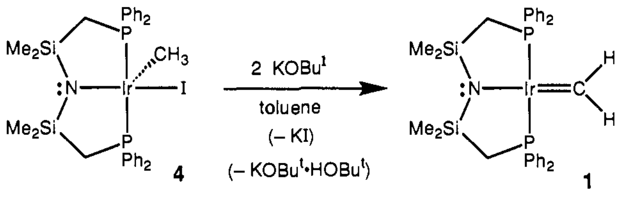
Scheme I



position of the methylene complex is avoided (eq 2). In preparative scale reactions, the methylene complex was isolated in 85–90% yield.

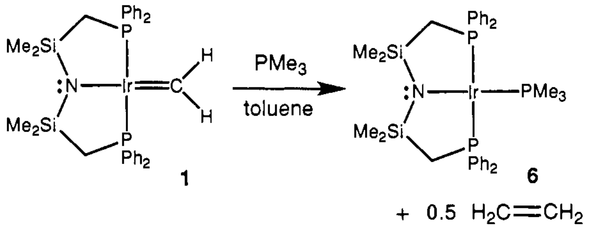


(2)

Other methylene complexes in the literature have been prepared via a variety of methods. As already mentioned,[9,13-20] the reaction of Lewis acids with methyl ether derivatives such as (η^5-C_5H_5)Fe(CH_2OMe)CO(PPh_3) at low temperatures leads to the cationic methylene $[(\eta^5\text{-}C_5H_5)Fe{=}CH_2(CO)PPh_3]^+$ (i.e., **F** in Chart I) whereas $Ph_3C^+BF_4^-$ reacts with the rhenium methyl complex (η^5-C_5Me_5)Re(CH_3)NO(PPh_3) to give $[(\eta^5\text{-}C_5Me_5)Re{=}CH_2(NO)PPh_3]^+$ (i.e., **E** in Chart I).[29,30] The reaction of $[(\eta^5\text{-}C_5H_5)Ta(CH_3)_2]^+$ with the phosphorane base $H_2C{=}PMe_3$ generates the tantalum methylene complex (η^5-C_5H_5)Ta=CH_2(CH_3) (i.e., **A** in Chart I).[11] Diazomethane can also be used to introduce the methylene unit into transition-metal complexes as evidenced by the preparation[24,31,32] of the iridium complex Ir=CH_2(I)CO(PPh_3)$_2$ and the analogous group 8 derivatives M=CH_2(Cl)NO(PPh_3)$_2$ (M = Ru, Os).[32,33] Attempts to use the diazomethane route to generate the methylene complex **1** failed; thus, reaction of CH_2N_2 with the iridium(I) cyclooctene complex Ir(η^2-C_8H_{14})[N($SiMe_2CH_2PPh_2$)$_2$] resulted in decomposition of the starting material.

Reaction of Ir=CH_2[N($SiMe_2CH_2PPh_2$)$_2$] with H_2. The reaction of the methylene complex **1** with H_2 at 1 atm proceeds rapidly even at −80 °C to generate the iridium amine trihydride complex IrH_3[NH($SiMe_2CH_2PPh_2$)$_2$] (**5**); upon workup by removal of excess H_2 and the solvent, the trihydride loses 1 equiv of H_2 to give the dihydride complex IrH_2[N($SiMe_2CH_2PPh_2$)$_2$] (**3**). The preparation and characterization of these two compounds have already been reported.[34] Although no intermediates were detected in this sequence, it is likely that the formation of the trihydride in the present system proceeds by successive oxidative additions of H_2 to the iridium center and migratory insertion. One possible sequence is shown in Scheme I and involves oxidative addition of the first equivalent of H_2 to generate a dihydride methylene species that then undergoes migratory insertion to produce a methyl hydride species; further addition of H_2 leads to an amine dihydride methyl intermediate which subsequently reductively eliminates CH_4 and adds more H_2 to generate the amine trihydride.

Reaction of Ir=CH_2[N($SiMe_2CH_2PPh_2$)$_2$] with PMe_3. Addition of PMe_3 to a solution of the methylene complex **1** in benzene or toluene at room temperature results in an instantaneous reaction as evidenced by a change in color of the solution from purple to yellow; by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, the products are Ir(PMe_3)[N($SiMe_2CH_2PPh_2$)$_2$][26] (**6**) and ethylene (0.5 equiv), both of which are formed quantitatively (eq 3). Spectroscopic monitoring of this reaction as a function of temperature provided some information on the mechanism. At −78 °C, the addition of PMe_3 (1–2 equiv) results in the formation of an orange solution consisting of three detectable intermediates and a variable amount (5–15%) of the final product **6**. There are apparently two "low-temperature" intermediates that are thermally labile and gradually transform into the third intermediate that persists at higher temperatures until it is finally consumed. On the basis of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, the "low-temperature" intermediates are the methylene phosphorane $Ir^-CH_2P^+Me_3$[N($SiMe_2CH_2PPh_2$)$_2$] (**7**) and the PMe_3 adduct of **7**, $Ir^-CH_2P^+Me_3$(PMe_3)[N($SiMe_2CH_2PPh_2$)$_2$] (**8**).



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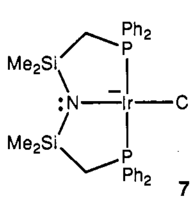

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Characterization of **7** was based on a shift in the ^1H NMR spectrum for the methylene protons ($IrCH_2$) from 16.3 ppm in the starting methylene (**1**) to 11.35 ppm with additional coupling to PMe_3 ($^2J_{PMe_3}$ = 17.1 Hz, $^3J_{PPh_2}$ = 12.0 Hz). When the methylene carbon was labeled with ^{13}C, this overlapping doublet of triplets was further split into a larger doublet with a coupling constant of $^1J_{CH}$ = 139.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum at −78 °C shows a singlet at 14.8 ppm for the PPh_2 groups of the tridentate ligand while the CH_2PMe_3 phosphorus is also a singlet at −34.6 ppm; when the methylene carbon was ^{13}C-labeled, this latter resonance was observed as a doublet with a coupling of

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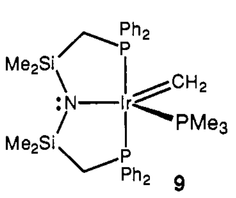
58.6 Hz ($^1J_{PC}$). The methylenephosphorane intermediate **7** could also be formulated as **9**, the isomeric five-coordinated PMe_3 adduct of the methylene complex. However, the spectroscopic evidence, particularly the $^{31}P\{^1H\}$ NMR spectral data, favors the former structure (**7**) since no coupling is observed between the different phosphorus-31 nuclei (separated by Ir–CH_2 in a square planar geometry) and, upon labeling the methylene with ^{13}C, only the directly attached PMe_3 is split into a doublet. While the five-coordinate methylene derivative **9** was not detected, it will be invoked as a first step in the formation of **7**, as there is considerable precedent for migratory insertion of a methylene unit into a coordinated phosphine ligand.[24,35,36]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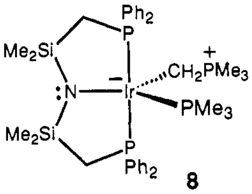
The structure of the PMe_3 adduct **8** is mainly based on the $^{31}P\{^1H\}$ NMR spectrum at −70 °C which shows a doublet of doublets at 4.9 ppm ($^2J_{PP}$ = 182.1 Hz, $^3J_{PP}$ = 30.3 Hz) due to the PPh_2 donors on the tridentate ligand, a doublet of triplets at −51.0 ppm due to the iridium-bound PMe_3, and a broad singlet at −45.2 ppm due to the coordinated methylene phosphorane, CH_2PMe_3. The rather large two-bond phosphorus–phosphorus coupling of 182.1 Hz is unusual for cis-disposed phosphorus nuclei in a structure like **8** in which the tridentate ligand spans trans diaxial sites in a trigonal bipyramidal geometry (see below). A better proposal has an alternative structure in which the tridentate ligand is in a cis geometry and all the directly-bound phosphine donors are arranged in the equatorial plane of a trigonal bipyramid as shown in **8′**; this places the inequivalent phosphorus nuclei in a more transoid relationship which should enhance coupling.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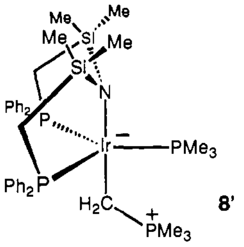
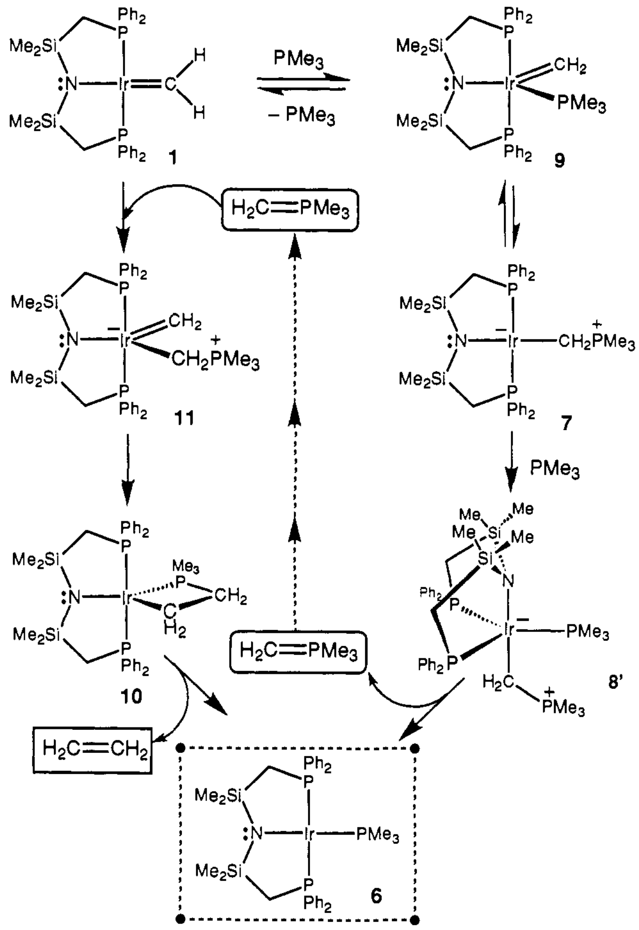
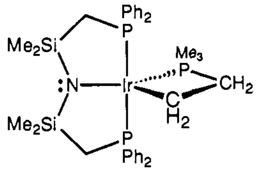

8′

The alternative geometry as represented by **8′** is also consistent with our unsuccessful attempts to independently prepare this species by addition of $H_2C{=}PMe_3$ to the PMe_3 complex **6**; we observed no reaction between $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$ and excess $H_2C{=}PMe_3$ from −70 °C to +20 °C. The large structural reorganization required to access **8′** from the square planar phosphine complex **6** is consistent with this last result; the fact that **8′** forms by addition of PMe_3 to the methylene phosphorane intermediate **7** is perhaps easier since approach of the PMe_3 to the square planar intermediate **7** could be accompanied by a bending of the phosphine arms of the tridentate ligand while maintaining a trans arrangement of the amide and methylene phosphorane donors.

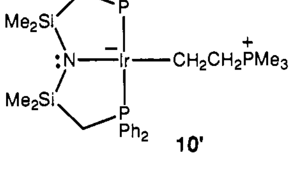
The nature of the third observable intermediate is somewhat speculative; its $^{31}P\{^1H\}$ NMR spectrum resembles that of the methylene phosphorane derivative **7** in that one observes two broad singlets in the ratio of 2:1 at 0.15 and −48.0 ppm; this latter peak broadens considerably when the methylene carbon is ^{13}C-labeled, although no splitting can be discerned. As compared to the other intermediates, **7** and **8′**, this third species is quite thermally stable since it is observable even at 20 °C as it transforms into the PMe_3 adduct **6**. We suggest that this intermediate has the structure **10**.

Scheme II




10

The main evidence supporting this structure is that a small coupling of 15.8 Hz can be observed between the phosphorus-31 nuclei when the NMR instrument is well tuned; thus the peak at 0.15 ppm is a doublet ($IrPPh_2$), and the triplet is at −48.0 ppm ($IrPMe_3$). Because of the complexity and broadness of the ^1H NMR spectrum at low temperatures, we were unable to assign resonances for the ethylene linkage ($IrCH_2CH_2P$) in intermediate **10**. One other possible structure for **10** is the phosphonium zwitterion shown as **10′**; as will be discussed in Scheme II, this kind of geometry might be more reasonable except that it is hard to reconcile the observed coupling between the phosphorus nuclei since in **10′** one might expect $^4J_{PP}$ to be negligible.


10′

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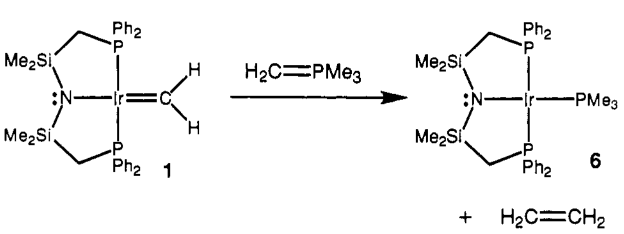
A mechanism that is consistent with these proposed intermediates is shown in Scheme II. What becomes apparent in this mechanism is that the addition of PMe_3 to the methylene complex is not a simple process. There are two pathways that lead to the final PMe_3 complex **6**. The first involves addition of PMe_3 to the methylene to generate PMe_3 adduct **9**, which subsequently rearranges to the observable intermediate **7**; further addition of PMe_3 to **7** generates the adduct **8′**. This second observable intermediate **8′** releases $H_2C{=}PMe_3$ to give the product **6**. Since $H_2C{=}PMe_3$ is not a product of this reaction nor is it detected during the reaction, it must be consumed as soon as it is formed. This is satisfied by having the $H_2C{=}PMe_3$ react with the methylene complex to form the adduct **11** which subsequently rearranges to the observable intermediate **10**. This last intermediate extrudes ethylene and generates the PMe_3 complex **6**.

The rearrangement of **11** to **10** deserves some comment. Migratory insertion of the methylene unit of **11** into the coordinated methylene phosphorane ligand would generate the phosphonium zwitterionic intermediate **10′**, which is intuitively more appealing than the indicated structure of this intermediate, **10**. However, while the spectroscopic evidence favors structure **10**, it should be pointed out that if **10′** forms initially and then closes to produce the cyclophosphorane **10**, the mechanistic and spectroscopic data are more aligned.

To provide further support for this proposed mechanism, the reaction of $H_2C{=}PMe_3$ with the methylene complex **1** was examined in an effort to mimic the left side of Scheme II. The addition of 1–1.5 equiv of $H_2C{=}PMe_3$ to **1** generates a quantitative yield of the PMe_3 complex **6** and 1 equiv of $H_2C{=}CH_2$ (eq 4). Monitoring this reaction at low temperatures shows only one intermediate being formed, and on the basis of $^{31}P\{^1H\}$ NMR spectroscopy, it is identical to that proposed as intermediate **10** for the reaction of PMe_3 with the methylene complex. Thus, this experiment confirms the viability of the left side of Scheme II involving the consumption of $H_2C{=}PMe_3$ after it is produced from the right side pathway.

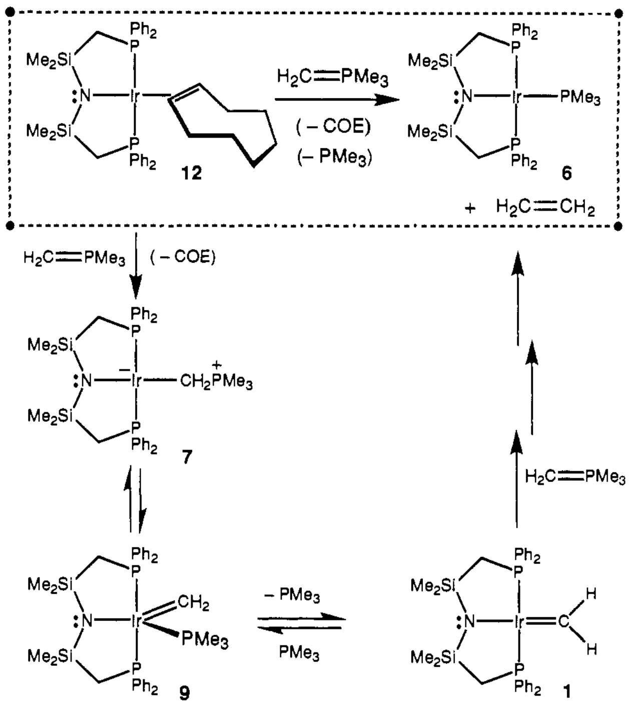


(4)

Further mechanistic evidence is obtained from the reaction of the deuterated methylene complex, $Ir{=}CD_2[N(SiMe_2CH_2PPh_2)_2]$ (**1**-d_2), with unlabeled $H_2C{=}PMe_3$ for which $D_2C{=}CH_2$ was the only gaseous product isolated and identified by GC-MS.[37] This experiment supports an intermediate like **10** since there is no observed scrambling or loss of the deuterium label of the starting methylene complex **1**-d_2.

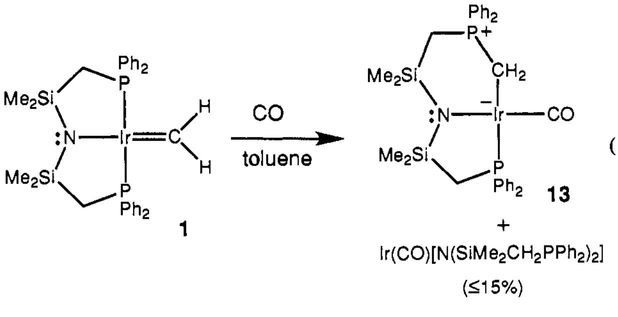
One additional point in the mechanism in Scheme II requires clarification. On the basis of simple stoichiometry, since 0.5 equiv of $H_2C{=}CH_2$ is produced and the phosphine complex **6** is the only iridium-containing product, half of the methylene complex must react via the left side of Scheme II while the other half is consumed by the right side. Yet, at low temperatures, only the intermediates **7**, **8′**, and **10** are detected along with some of the final product **6**; at −78 °C, none of the methylene complex **1** is observed. What is difficult to reconcile at this point is the fact that the "low-temperature" intermediates **7** and **8′** appear to decrease over time to produce both the final product **6** and the intermediate **10**, which must form from the methylene complex. Therefore, there must be a way of converting either of the intermediates **7** or **8′** back to the methylene complex. The following experiment does shed some light on this point. If 10 equiv of $H_2C{=}PMe_3$ is added to the iridium cyclooctene complex **12**, a very slow reaction takes place to generate the PMe_3 complex **6** and free ethylene (Scheme III).

Scheme III



Although no intermediates were detected, a reasonable scenario is that $H_2C{=}PMe_3$ displaces cyclooctene in a slow step to generate the methylene phosphorane intermediate **7** and this complex reversibly decomposes via a retro migratory insertion to give **9**;[35] loss of PMe_3 generates the methylene complex which reacts with the excess $H_2C{=}PMe_3$ present to give the final product **6** in analogy to that shown on the left side of Scheme II.

Reaction of $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ with CO. The reaction of the methylene complex **1** with 1 equiv of CO gives $Ir^-(CO)[(CH_2P^+Ph_2CH_2SiMe_2NSiMe_2CH_2PPh_2)]$ (**13**), a compound that has the methylene inserted into one of the iridium–phosphine bonds of the tridentate ligand; if excess CO is used, the reaction was found to produce variable amounts of the iridium(I) carbonyl complex $Ir(CO)[N(SiMe_2CH_2PPh_2)_2]$ up to a maximum of 15% in addition to the major product **13** (eq 5). The $^{31}P\{^1H\}$ NMR spectrum of complex **13** consists of two doublets at 26.7 and 22.5 ppm ($^3J_{PP}$ = 9.0 Hz). The ^1H NMR spectrum of **13** shows that the resonance due to the inserted methylene protons appears as a doublet of doublets at 2.37 ppm ($^2J_{PH}$ = 12.33 Hz, $^3J_{PH}$ = 7.21 Hz), and the ligand backbone methylene protons show up as two doublets at 1.68 ppm ($^2J_{PH}$ = 12.21 Hz) and 1.40 ppm ($^2J_{PH}$ = 16.06 Hz). When the methylene carbon was labeled with ^{13}C, the $^{31}P\{^1H\}$ NMR spectrum became two doublets of doublets. The resonance at 22.5 ppm, which is trans



(5)

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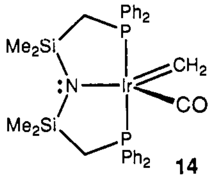
[37] Kenndler, E. *Anal. Chim. Acta* **1985**, *173*, 239.

to the ^{13}C, has a coupling constant of $^2J_{PC} = 71.7$ Hz, and the other phosphorus nucleus at 26.7 ppm has a coupling constant of $^1J_{PC} = 31.4$ Hz. The proton resonance of the inserted methylene now is a doublet of doublets of doublets with an additional coupling constant of $^1J_{CH} = 132.33$ Hz. The resonance for ligand backbone methylene protons at 1.40 ppm becomes a doublet of doublets ($^3J_{CH} = 2.69$ Hz, $^2J_{PH} = 16.09$ Hz), since these protons are three bonds away from the inserted methylene carbon. The ^{13}C NMR spectrum of the inserted methylene is a doublet of doublets at 0.075 ppm ($^1J_{PC} = 31.4$ Hz, $^2J_{PC(trans)} = 71.7$ Hz). Furthermore, when the CO is labeled with ^{13}C, the resonance at 22.5 ppm due to the phosphorus nucleus which is trans to the inserted methylene and is two bonds away from the ^{13}CO becomes an overlapping doublet of doublets ($^2J_{PC} = 9.5$ Hz, $^2J_{PP} = 8.9$ Hz) that appears as a triplet. The resonance of the other phosphorus nucleus which is three bonds away from the ^{13}CO remains unchanged; in fact, it was this particular complex that allowed us to unequivocably assign the ^{31}P{^{1}H} NMR spectrum, since only the coordinated phosphine showed the additional coupling to the ^{13}CO. The ^{13}C{^{1}H} NMR spectrum of the ^{13}CO ligand of **13** is a doublet at 173.88 ppm ($^2J_{CP} = 10.0$ Hz). The spectroscopic data for the side product $Ir(CO)[N(SiMe_2CH_2PPh_2)_2]$ are consistent with the literature values.[26] For completeness, in the ^{13}C-labeled complex $Ir(^{13}CO)[N(SiMe_2CH_2PPh_2)_2]$, the ^{31}P{^{1}H} NMR resonance is observed as a doublet at 25.02 ppm ($^2J_{PC} = 11.20$ Hz) and, in the ^{13}C{^{1}H} NMR spectrum, the coordinated ^{13}CO resonance is a triplet at 173.74 ppm ($^2J_{PC} = 11.20$ Hz).

Monitoring the reaction of the methylene complex **1** with carbon monoxide by variable-temperature NMR spectroscopy shows that, at −78 °C, there is an immediate reaction and only one species is detected; it is proposed to be the CO adduct $Ir{=}CH_2(CO)[N(SiMe_2CH_2PPh_2)_2]$ (**14**), an intermediate that is similar to complex **9** proposed in Scheme II, although the latter was not detected. The carbonyl adduct **14** was detectable up to 0 °C although, at −30 °C, it does begin to rearrange to the final inserted product **13** (eq 5). The proposed five-coordinate structure is supported by an upfield shift of the triplet in the ^{1}H NMR spectrum due to the methylene ($Ir{=}CH_2$) protons from 16.3 to 12.07 ppm ($^3J_{PH} = 17.25$ Hz). When the methylene was labeled with ^{13}C, this triplet was further split into a doublet with a coupling constant of $^1J_{CH} = 141.1$ Hz. Also consistent with this structure is the change in symmetry of the ancillary ligand from the starting methylene complex; in **14**, the ligand backbone CH$_2$'s appear as two triplets at 2.06 and 1.94 ppm ($^2J_{PH} = 5.5$ Hz) and there are two singlets at 0.35 and 0.34 ppm due to the protons on the inequivalent silyl methyl groups. In the ^{31}P{^{1}H} NMR spectrum, the adduct **14** displays a singlet at 13.3 ppm, which becomes a doublet when the methylene carbon is labeled with ^{13}C ($^2J_{PC} = 11.3$ Hz).



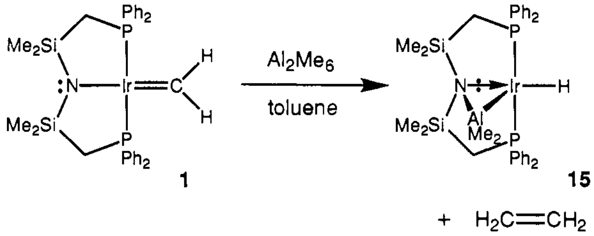
14

The binding of CO to complex **1** is reversible. When excess CO was removed from a toluene solution of the adduct **14** at low temperatures, the coordinated CO was lost and the starting methylene complex **1** was regenerated quantitatively.

Increasing the temperature to −30 °C under excess CO rearranges the adduct **14** to compound **13**, with the concomitant formation of a small amount of $Ir(CO)[N(SiMe_2CH_2PPh_2)_2]$. The mechanism for the formation of compound **13** must involve either migration of one of the coordinated phosphines of the tridentate ligand to the methylene carbon of the five-coordinate intermediate **14** followed by rearrangement to give the square planar geometry of the final product or insertion of the methylene directly into one of the iridium–phosphorus bonds of the ligand.[24,36]

As already mentioned, the formation of square planar carbonyl complex $Ir(CO)[N(SiMe_2CH_2PPh_2)_2]$ appears to require excess CO; so far we have been unable to shed any light on the origin of this side product. One reasonable process is the insertion of CH$_2$ into the Ir–CO bond to form a ketene complex, $Ir(\eta^2\text{-}H_2C{=}C{=}O)[N(SiMe_2CH_2PPh_2)_2]$, in analogy to other work;[15,32] in the presence of excess CO, the ketene is presumably displaced to generate the carbonyl complex. However, due to the small amount of this side product, all attempts to detect free ketene or any other CH$_2$ sink were decidedly unsuccessful.

Reaction with Al$_2$Me$_6$. Addition of 0.5 equiv of Al_2Me_6 to a toluene solution of the iridium methylene complex **1** at −78 °C resulted in the immediate loss of the purple color and the formation of a yellow-orange solution. Recrystallization from hexanes at −30 °C afforded a new complex with the formula $Ir(AlMe_2)H[N(SiMe_2CH_2PPh_2)_2]$ (**15**) in ≈70% yield. On the basis of related chemistry regarding the reaction of Al_2Me_6 with the iridium vinylidene complex $Ir{=}C{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$,[38] the structure of the product is probably similar to that shown in eq 6.



(6)

The ^{1}H NMR spectrum of the product **15** shows the silyl methyl protons as two singlets. The methylene protons resonate as two broad multiplets at 2.47 and 2.65 ppm. One set of the ortho phenyl protons is also a broad resonance (8.15 ppm). The equivalent methyl protons in the AlMe$_2$ ligand are observed as a singlet at 0.78 ppm. The iridium hydride ligand resonance is observed as a triplet at −13.47 ppm ($^2J_{PH} = 16.3$ Hz). Free ethylene was detected in the ^{1}H NMR spectrum (5.48 ppm, s, C_6D_6) on conducting the reaction in a sealed NMR tube. The proposal that the AlMe$_2$ ligand is bridged between the Ir–N bond is based upon the above mentioned results obtained from the reactivity of the iridium vinylidene complex, $Ir{=}C{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$, with Al_2R_6 (R = Me, Et).[38]

A mechanism proposed for the formation of complex **15** is shown in Scheme IV. Unfortunately, attempts to monitor this reaction at low temperatures under a variety of conditions failed to indicate the presence of any intermediates; only resonances due to starting material and the final product were observed. To keep in line with the vinylidene chemistry,[38] it is proposed that the reaction is likely to involve initial coordination of an AlMe$_3$ unit to the amide lone pair of the tridentate ligand followed by the oxidative addition of AlMe$_3$ at iridium to generate a transient species **A′** having an AlMe$_2$ ligand, a methyl group, and the methylene unit. Given that the oxidative addition of AlMe$_3$ reagent at the iridium center proceeds in a cis manner, and is assisted by prior coordination to the amide, then the stereochemistry would necessarily put the methyl group and the methylene ligand cis to one another. The next step involves migratory insertion of the methyl group and the iridium methylene moiety to form the ethyl ligand as shown in **B′**. Insertion reactions of carbene ligands into alkyl ligands are known[35,39–43] and are

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(38) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979.

(39) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

(40) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46.

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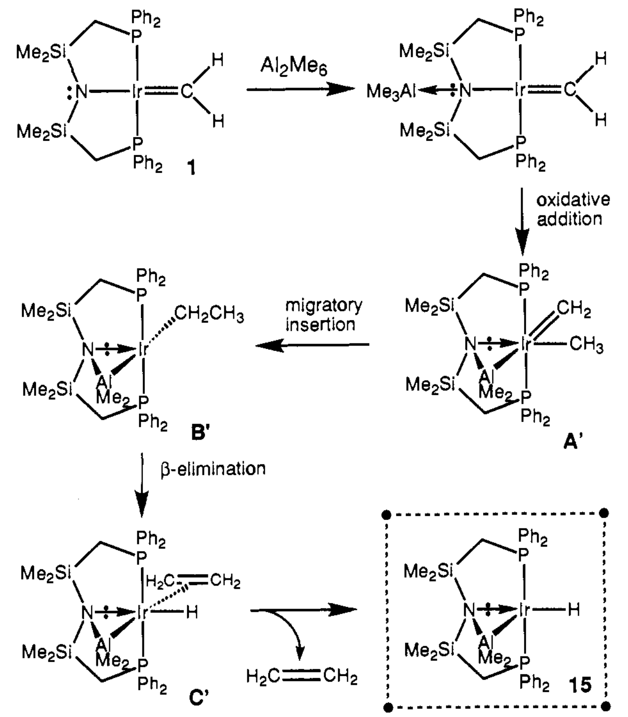
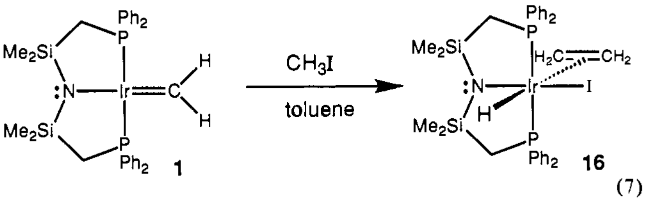
Scheme IV



considered to be analogous to the migratory insertion reactions of carbonyl complexes. The next step involves the β-hydride elimination from the ethyl ligand in **B′** to generate the iridium ethylene hydride intermediate **C′**. The elimination of the ethylene moiety from **C′** yields the final product **15**.

The iridium–aluminum adduct **15** is extremely moisture-sensitive in solution. Trace amounts of water from the glassware or the solvents were enough to convert it to IrH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (**3**) (as observed by ^{1}H NMR spectroscopy) and presumably some oligomer of "HOAlMe$_2$".

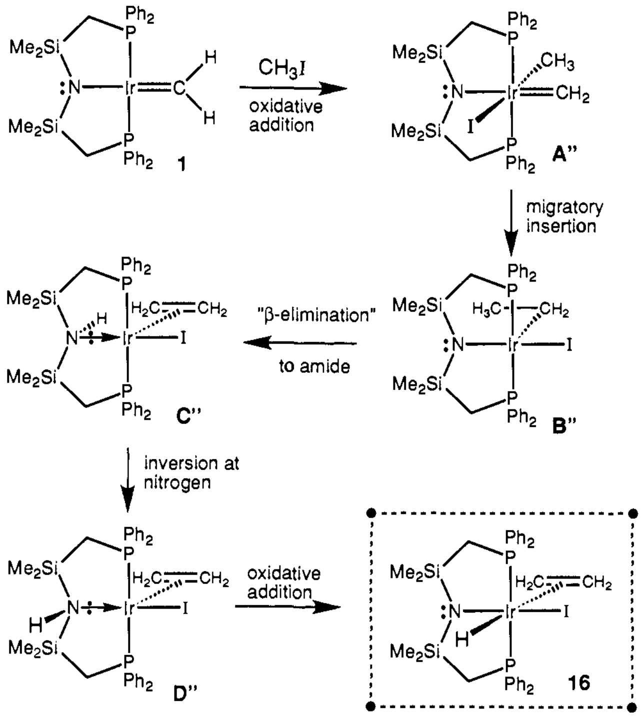
Reaction of Ir=CH$_2$[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] with Methyl Iodide. The reaction of the methylene complex **1** with excess MeI resulted in the formation of the octahedral iridium(III) ethylene hydrido iodide complex Ir(η^2-C$_2$H$_4$)(H)I[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (**16**) (eq 7). The ^{1}H NMR spectrum of this product provides an excellent



(7)

handle on the identity and the stereochemistry of this hydride complex. The resonances of the ligand backbone methylene protons are observed as an AB quartet of virtual triplets and thus are indicative of the meridional arrangement of the tridentate ligand. The resonance for the ethylene protons is a triplet centered at 2.26 ppm due to coupling to the equivalent phosphine donors of the tridentate ligand ($^3J_{PH}$ = 3.6 Hz). A triplet at −13.14 ppm ($^2J_{PH}$ = 8.7 Hz) is due to the Ir–H ligand; the fact that there is only one isomer formed is remarkable since there are three possible stereoisomers with the tridentate ligand meridionally disposed on an octahedron: (i) the hydride trans to the amide, (ii) the hydride trans to the iodide, and (iii) the hydride trans to the ethylene ligand. We have observed a consistent correlation in the chemical shift in the hydride resonance in the ^{1}H NMR spectrum and the trans ligand in an octahedral geometry, so much so that we use this as a diagnostic in determining stereochemistry. Thus the first two possible stereoisomers can be ruled out since resonances of iridium hydrides trans to an amide ligand or an iodide are typically in the range −19.0 to −24.5 ppm.[27,34,44] On the basis of the fact that the hydride resonance is downfield at −13.17 ppm, then by default, the hydride is strongly suggested to be trans to the ethylene ligand. The stability of the ethylene hydride complex **16** is undoubtedly enhanced because the hydride and ethylene ligands are trans disposed.[45-50]

Scheme V



To account for the formation of complex **16**, a mechanism is proposed in Scheme V which involves the oxidative addition of methyl iodide at the metal center (to form **A″**), followed by migratory insertion of the methylene ligand into the iridium-methyl bond, thus yielding the iridium(III) ethyl iodide intermediate (**B″**). Direct β-hydride elimination from the ethyl ligand in **B″** to iridium via a four-membered transition state would result in an ethylene hydride complex except that the ethylene and the hydride ligand should be cis-oriented to each other. Therefore, hydride abstraction from the ethyl ligand by the amide donor is invoked[38] (to afford **C″**), which, following inversion at the amine (**C″** to **D″** via amine dissociation, inversion, and then reassociation) and N–H oxidative addition to the iridium, gives the desired complex **16**.

In the presence of excess methyl iodide and with long reaction times, there is a further reaction to give the methyl diiodo amine complex *mer-cis*-Ir(CH$_3$)(I)$_2$[HN(SiMe$_2$CH$_2$PPh$_2$)$_2$] and free ethylene. The same species has also been observed in the reaction of the aforementioned iridium vinylidene complex with excess methyl iodide.[38]

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(42) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

(43) Davey, C. E.; Osborn, V. A.; Winter, M. J.; Woodward, S. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1989; Vol. 269, p 159.

(44) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803.

(45) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

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(47) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

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(49) Roe, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 7770.

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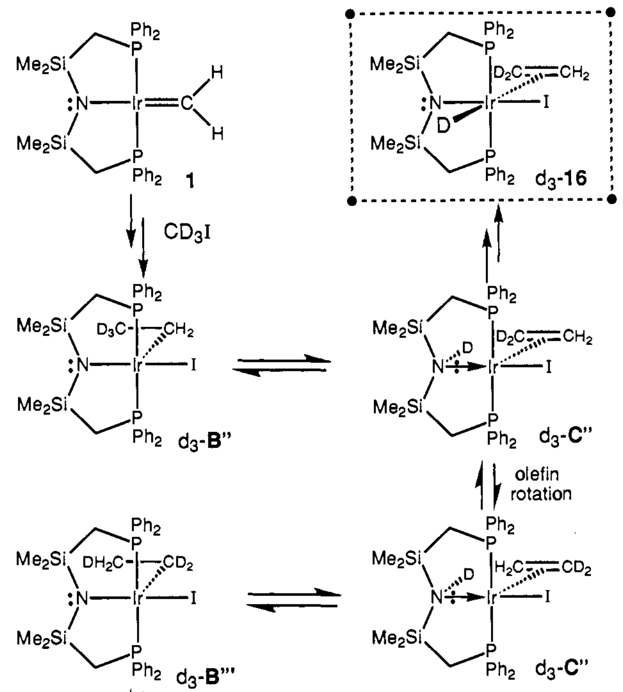
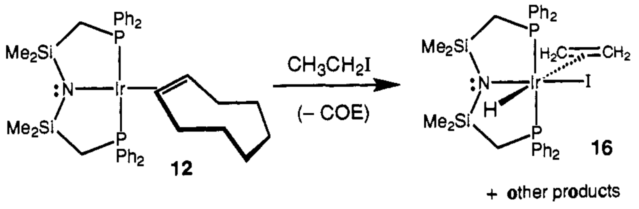
Scheme VI



Further evidence that the mechanism in Scheme V is reasonable comes from the reaction of the iridium(I) cyclooctene complex **12** with ethyl iodide (eq 8) for which the ethylene hydride complex **16** is generated as the main component of a mixture of products (due to further reaction of **16** with EtI). Since oxidative addition to the iridium(I) complex **12** is well-known,[26] the ethyl iodide reaction must also go through the proposed intermediate **B''**; this is evidence supporting the migratory insertion part of Scheme V since it generates the same intermediate **B''** (Scheme V).



(8)

Additional mechanistic information comes from the reaction of CD_3I (99.5% deuterium) with the methylene complex **1**; the product is not all $Ir(\eta^2\text{-}C_2H_2D_2)(D)I[N(SiMe_2CH_2PPh_2)_2]$ (**16**-d_3) as one might predict from the mechanistic proposal in Scheme V. The ^1H NMR spectrum of the product of this reaction shows a hydride resonance that integrates to 0.5 ± 0.1 H, and the coordinated ethylene peak corresponds to 1.5 ± 0.2 H's, thus consistent with the product existing as an approximately equal mixture of the two isotopomers $Ir(\eta^2\text{-}C_2H_2D_2)(D)I[N(SiMe_2CH_2PPh_2)_2]$ (**16**-d_3) and $Ir(\eta^2\text{-}C_2HD_3)(H)I[N(SiMe_2CH_2PPh_2)_2]$ (**16'**-d_3); Scheme VI outlines the mechanism by which these two isotopomers could arise. The formation of **16**-d_3, the iridium deuteride, is straightforward; however, to account for the formation of the hydride derivative **16'**-d_3, the abstraction of the β-deuterium/hydrogen of the ethyl ligand by the amide must be reversible and slow compared to olefin rotation. In this way, the proposed **B''**-d_3 intermediate can scramble the deuterium from the β-carbon of the ethyl group to the α-carbon to generate **B'''**-d_3. Subsequent amide abstraction of hydrogen will generate **C'''**-d_3, which upon amine inversion and N–H oxidative addition leads to the isotopomer **16'**-d_3.

Conclusions

In this report we have detailed a new synthesis of the iridium methylene complex $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (**1**). Rather than rely on the previously reported preparation that involves photolysis of the preformed iridium(III) dialkyl complex $Ir(CH_3)CH_2CMe_3[N(SiMeCH_2PPh_2)_2]$ and ultimately renders a low yield due to separation problems, we have developed an alternate procedure that involves reaction of the hindered base $KOBu^t$ with the readily prepared methyl iodide complex $Ir(CH_3)I[N(SiMeCH_2PPh_2)_2]$. We assume that this process involves formation of the methyl *tert*-butoxide complex $Ir(CH_3)OBu^t[N(SiMeCH_2PPh_2)_2]$, although this has not been detected. Of course, the other possibility is that the *tert*-butoxide deprotonates the methyl ligand directly before elimination of the iodide. Whatever the mechanism, the stoichiometry is important since 2 equiv of $KOBu^t$ are required; the second equivalent serves to remove the $HOBu^t$ that is produced in the reaction, thereby preventing decomposition of the methylene complex.

The iridium methylene complex **1** is a 16-electron complex. It is best to consider this derivative as a square planar Ir(I) species whereby the methylene unit is a neutral, two-electron donor. This particular formalism implies that this complex should be unsaturated and therefore susceptible to ligand addition, and because it is an Ir(I), d^8 complex, and isoelectronic to Vaska's complex, it should also undergo oxidative addition reactions. All of the other methylene complexes in the literature are 18-electron species, with one possible exception (see C in Chart I). However, being a formally 18-electron complex does not mean that methylene complexes are unreactive, since the $M{=}CH_2$ unit itself is unsaturated, much the same way a carbon–carbon double bond is unsaturated. But what this means is that the reactivity of most methylene complexes involves reactions directly at the methylene carbon. The focus of this work has shown that the unsaturated nature of the iridium center in the methylene complex **1** is reflected in its reactivity patterns, since ligand addition of PMe_3 and CO occurs at the iridium center; subsequent migratory insertion and ligand substitution can then take over depending on the particular reaction. Similarly, oxidative addition type processes can be used with the methylene complex **1**, as evidenced by the reactions of Al_2Me_6 and CH_3I with **1**. In both of these reactions, an oxidative addition step serves to generate a metal–carbon bond that then undergoes a C–C-bond-forming migratory insertion to ultimately result in the formation of ethylene.

These prototype reactions set the stage for further studies with this methylene complex, in particular those with olefins where both ligand addition to the unsaturated iridium center and migratory insertion reactions to form carbon–carbon bonds will be important. This work will be reported in due course.

Experimental Section

General Procedures. All manipulations were performed under purified nitrogen in a Vacuum Atmospheres HE-553-2 workstation equipped with an MO-40-2H purification system or in Schlenk-type glassware. Toluene was predried over calcium hydride and distilled over sodium under argon. Hexanes and pentane were also predried over calcium hydride and distilled over sodium–benzophenone ketyl under argon. Deuterated benzene (C_6D_6, 99.6%) and deuterated toluene (C_7D_8, 99.6%) were dried over activated 4-Å molecular sieves, vacuum transferred, and subjected to three freeze–pump–thaw cycles before use. Deuterated methyl iodide (CD_3I, 99.5%) and ^{13}C-labeled methyl iodide ($^{13}CH_3I$, 99.7%) were purchased from MSD Isotopes. They were degassed and stored over molecular sieves and a small amount of copper powder in the dark. $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$, $Ir(CH)_3I[N(SiMe_2CH_2PPh_2)_2]$, $Ir(CD_3)I[N(SiMe_2CH_2PPh_2)_2]$, and $Ir(^{13}C\ H_3)I[N(SiMe_2CH_2PPh_2)_2]$ were prepared according to the published procedures.[26] $H_2C{=}PMe_3$ was prepared by the reaction of $(CH_3)_4PBr$ and $NaNH_2$ in THF.[51] $KOBu^t$ was prepared from the reaction of potassium and $HOBu^t$ and was sublimed twice at 100 °C under dynamic vacuum (0.005 mmHg). ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker-200, Varian-300, and Bruker-400 spectrometers. ^1H NMR spectra were referenced to the residual protons of the deuterated solvents. $^{31}P\{^1H\}$ NMR spectra were referenced to external $P(OMe)_3$ set at 141.0 ppm relative to 85% H_3PO_4. C, H, N, and halogen analyses were performed by Mr. P. Borda in this department. GC-MS spectra were recorded on a Varian VISTA 6000 gas chromatograph equipped with a NERMAG R10-10C quadrupole mass spectrometer.

Preparation of $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (1). NMR Scale Reaction. $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (30 mg, 0.035 mmol) and $KOBu^t$ (8 mg, 0.071 mmol) were loaded into a NMR tube, and C_7D_8 (0.7 mL) was added. The solution was frozen in a liquid nitrogen bath, and the tube was flame-sealed. Within 10 min of the solution warming to room temperature, 15% of the Ir starting material was already converted to the product, as evidenced by the integration ratio of the two singlets at 18.1 ppm (the methylene complex **1**) and 11.2 ppm ($Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$) in the $^{31}P\{^1H\}$ NMR spectrum. After 1 h, the signals due to $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ disappeared and the methylene complex **1** was quantitatively generated. The ^1H NMR spectrum showed that all the resonances were due to $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (**1**); no resonances due to $HOBu^t$ and the excess $KOBu^t$ were observed. At the bottom of the NMR tube, a white precipitate was observed. The product was stable in the solution for another hour.

(b) Reaction of $KOBu^t$ and $HOBu^t$. $KOBu^t$ (1.04 g, 6.269 mmol) was dissolved in toluene (50 mL), and $HOBu^t$ (0.687 g, 6.269 mmol) was added from a syringe while the solution was vigorously stirred. The colorless solution immediately became cloudy and a thick gel-like precipitate formed. The mixture was stirred for 1 h, diluted with hexanes (20 mL), and filtered through a fine frit. The white solid above the frit was washed with hexanes (20 mL) and then pentane (10 mL) and was briefly dried in vacuo. The compound $KOBu^t{\cdot}HOBu^t$ was obtained as a white powder (1.60 g, 93%). Satisfactory elemental analysis on this compound was not obtained because of the facile loss of $HOBu^t$.

(c) Preparative Scale Reaction. $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (250 mg, 0.2897 mmol) and $KOBu^t$ (65 mg, 0.5794 mmol) were weighed into a vial (10 mL), and toluene (5 mL) was added. The vial was capped, and the solution was vigorously stirred. The green solution gradually became dark green, and after 40 min, it became thicker, and a gel-like precipitate was observed on the glass walls. The solution continually became darker and thicker, and after 50 min, it turned to purple. The mixture was stirred for another 10 min and was filtered through Celite. The Celite was thoroughly washed with toluene (3 × 5 mL) and hexanes (3 × 5 mL) so that the purple compound was completely transferred into a receiver flask. The filtrate was then vacuum-pumped slowly to reduce the volume to about 2 mL, and the flask was put into a freezer (–30 °C) for 5 h. The crystals thus produced were rinsed with cold hexanes (–30 °C) and dried in vacuo. The mother liquor was further reduced in volume to about 0.5 mL, and hexanes (2 mL) were added. A repeat of the crystallization process gave a second crop of crystals. The combined yield was ≈85%. NMR data: $^{31}P\{^1H\}$ (C_6D_6) δ 17.1 (s, PPh_2); ^1H (C_6D_6) δ 16.31 (t, $^3J_{PH}$ = 14.5 Hz, $Ir{=}CH_2$), 7.85 (m, ortho Ph), 7.10 (m, meta/para Ph), 2.12 (virtual triplet, N = 4.98 Hz, $SiCH_2P$), 0.18 (s, SiMe). Anal. Calcd for $C_{31}H_{38}IrNP_2Si_2{\cdot}C_7H_8$: C, 55.20; H, 5.57; N, 1.70. Found: C, 55.08; H, 5.51; N, 2.00.

The compounds $Ir{=}^{13}CH_2[N(SiMe_2CH_2PPh_2)_2]$ and $Ir{=}CD_2[N(SiMe_2CH_2PPh_2)_2]$ were prepared by the reactions of $Ir(^{13}CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ and $Ir(CD_3)I[N(SiMe_2CH_2PPh_2)_2]$ with 2 molar equiv of $KOBu^t$, respectively. NMR data for $Ir{=}^{13}CH_2[N(SiMe_2CH_2PPh_2)_2]$: $^{31}P\{^1H\}$ (C_6D_6) δ 17.11 (d, $^2J_{PC}$ = 10.2 Hz); $^{13}C\{^1H\}$ (C_6D_6) δ 194.71 (t, $^2J_{PC}$ = 10.3 Hz, $Ir{=}^{13}CH_2$); ^1H (C_6D_6) δ 16.32 (td, J_{CH} = 135.84 Hz, J_{PH} = 14.5 Hz, $Ir{=}^{13}CH_2$). Other resonances are the same as those of the unlabeled compound.

Reaction of $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ with H_2. Formation of $IrH_2[N(SiMe_2CH_2PPh_2)_2]$. The methylene complex **1** (68 mg, 0.093 mmol) was weighed into a bomb, and toluene (5 mL) was added. The solution was frozen, the N_2 in the head space was removed, and H_2 (1 atm, 60 mL) was then introduced. The solution was allowed to warm to room temperature while vigorously stirred. The solution gradually changed from purple to brownish yellow, and after 20 min, a bright yellow solution formed. The solution was stirred for another 20 min and vacuum-pumped to dryness. Both ^1H and ^{31}P NMR spectra were the same as previously reported for $IrH_2[N(SiMe_2CH_2PPh_2)_2]$.[34] The yield was virtually quantitative. When the reaction was performed in a sealed NMR tube using excess H_2, the product of the reaction was the amine trihydride complex $IrH_3[HN(SiMe_2CH_2PPh_2)_2]$; CH_4 was also detected in the ^1H NMR spectrum as the only organic byproduct.

Reaction of $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (1) with $H_2C{=}PMe_3$. Formation of $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$ and C_2H_4. The methylene complex **1** (30 mg, 0.0408 mmol) was loaded into a sealable NMR tube, and C_6D_6 (0.3 mL) was added. The solution was frozen in a liquid N_2 bath, and $H_2C{=}PMe_3$ [0.0408 mmol in 0.3 mL of C_6D_6, i.e. $^1/_3$ of a 0.9 mL C_6D_6 solution of $H_2C{=}PMe_3$ (11 mg)] was added via syringe under N_2. The tube was flame-sealed, and the mixture was warmed. Immediately after the mixture melted, the color changed from purple to orange with some gas bubbles. $^{31}P\{^1H\}$ NMR [(C_6D_6) δ 24.52 (d, $^2J_{PP}$ = 25.1 Hz), –50.15 (t, $^2J_{PP}$ = 25.0 Hz)] and ^1H NMR indicated that the product is $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$; C_2H_4 was detected by ^1H NMR spectroscopy.

Reaction of $Ir{=}CD_2[N(SiMe_2CH_2PPh_2)_2]$ with $H_2C{=}PMe_3$. $Ir{=}CD_2[N(SiMe_2CH_2PPh_2)_2]$ (31 mg, 0.042 mmol) was dissolved in 2.5 mL of toluene in a 5 mL Schlenk tube. The solution was cooled in an acetone/CO_2 bath, and 4.5 mg of $H_2C{=}PMe_3$ was added to **1** via syringe. Toluene (2 mL) was added from a syringe. The head-space gas thus produced was immediately collected in a gas-tight syringe and was introduced into a GC-MS spectrometer. The gas was shown to be $H_2C{=}CD_2$. MS data, peak (relative intensity): m/z 30 (100), 29 (44.8), 28 (36.2), 27 (37.7), 26 (14.7), 25 (4.0). The data match the literature values.[37]

Formation of $Ir(PMe_3CH_2CH_2)[N(SiMe_2CH_2PPh_2)_2]$ (10). The methylene complex **1** (22 mg, 0.029 92 mmol) was weighed into a sealable NMR tube, and C_7D_8 (0.6 mL) was added. The solution was degassed to remove any dissolved nitrogen, and was then frozen in a liquid N_2 bath. $H_2C{=}PMe_3$ (0.09 mL in C_7D_8 with a concentration of 31 mg/mL) was syringed onto the frozen solution under N_2. The NMR tube was quickly transferred into an acetone/CO_2 bath, and the reactants were mixed. A dark orange solution formed. The NMR tube was refrozen in liquid N_2 and was transferred into the NMR machine probe which was already maintained at –78 °C. The spectra were recorded from –78 to +20 °C. In this temperature range, three species, intermediate **10**, $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$, and ethylene, were observed. The concentration of the intermediate **10** decreased with an increase of temperature, and those of $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$ and ethylene increased with temperature. NMR data for intermediate **10**: $^{31}P\{^1H\}$ (C_7D_8) δ 0.15 (d, $^2J_{PP}$ = 15.8 Hz, Ph_2P–Ir), –48.0 (t, $^2J_{PP}$ = 15.8 Hz, Ir–PMe_3–); ^1H (C_7D_8) δ 7.8–7.4 (m, ortho Ph), 6.7–7.3 (m, meta/para Ph), 2.39 (m, Ir–CH_2–), 2.36 (m, $SiCH_2P$), 0.58 (s, $SiMe_2$), 0.57 (m, Ir–PMe_3–CH_2–), 0.29 (d, J_{PH} = 9.3 Hz, Ir–P*Me*$_3$), –0.11 (s, $SiMe_2$). A parallel reaction between $Ir{=}^{13}CH_2[N(SiMe_2CH_2PPh_2)_2]$ and $H_2C{=}PMe_3$ showed the liberation of $H_2C{=}^{13}CH_2$ and the splitting of the multiplet at 2.39 ppm into two with a coupling constant of 140 Hz.

Reaction of $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ with Excess $H_2C{=}PMe_3$. To a C_6D_6 solution of $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ (30 mg, 0.036 mmol) in a NMR tube was added $H_2C{=}PMe_3$ (3.3 mg in C_6D_6, 0.36 mmol). The tube was flame-sealed, and the reaction was monitored by NMR at room temperature. The reaction slowly gave $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$, ethylene, and free cyclooctene. No intermediates were observed. In a separate experiment, $H_2C{=}PMe_3$ did not react with $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$ from –70 to +20 °C.

Reaction of $Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]$ (1) with Me_3P. Formation of $Ir^-(CH_2P^+Me_3)[N(SiMe_2CH_2PPh_2)_2]$, $Ir(PMe_3)[N(SiMe_2CH_2PPh_2)_2]$, and C_2H_4. The methylene complex **1** (10 mg) was weighed into a NMR tube, and C_7D_8 (0.7 mL) was added. The solution was degassed and frozen in a liquid N_2 bath. A slight excess of Me_3P was vacuum-transferred into the NMR tube from a constant-volume bulb. The reaction was monitored by NMR from –78 °C to room temperature. The reaction first produced intermediates **7** and **8**, whose concentrations diminished with an increase of temperature and then disappeared at about –40 °C. Meanwhile, intermediate **10** formed, and its concentration increased with an increase of temperature. After intermediate **7** disappeared, the process was exactly the same as the reaction of methylene complex **1** with $H_2C{=}PMe_3$. NMR data for intermediate **7**: $^{31}P\{^1H\}$ (C_7D_8) δ 14.8 (s,

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[51] Koster, R.; Simic, D.; Grassberger, M. A. *Justus Liebigs Ann. Chem.* **1970**, *211*, 739.

$\mathrm{SiCH_2P}$), −34.6 (s, $\mathrm{IrPMe_3}$); ^{1}H ($\mathrm{C_7D_8}$) δ 11.35 (dt, $^3J_{\mathrm{PH}} = 17.1$ Hz, $^3J_{\mathrm{PH}} = 12.0$ Hz, $\mathrm{Ir{=}CH_2}$), 8.2–7.8 (m, ortho Ph), 7.2–6.9 (m, meta/para Ph), 2.08 (m, $\mathrm{SiCH_2P}$), 1.85 (m, $\mathrm{SiCH_2P}$), 0.86 (d, $^2J_{\mathrm{PH}} = 9.3$ Hz, $\mathrm{Ir{-}PMe_3}$), 0.41 (s, SiMe), 0.23 (s, SiMe).

Preparation of $\mathrm{Ir(CO)[(CH_2PPh_2CH_2SiMe_2NSiMe_2CH_2PPh_2)]}$. A constant-volume bulb (1.78 mL) was charged with CO at 734 mmHg (0.0707 mmol), which was then opened to a pre-evacuated glass bomb containing a solution of **1** (52 mg, 0.0707 mmol) in toluene. The solution became brownish yellow within 30 min and was further stirred for 2 h to produce a bright yellow solution. The solution was vacuum-pumped to dryness, and the residue was dissolved in hexanes (10 mL). Slow evaporation of the solvent to almost dryness gave yellow crystals of compound **13**; the crystals were rinsed with cold hexanes (−30 °C, 3 × 1 mL) and dried under vacuum. Yield: 49 mg, 91%. Anal. Calcd for $\mathrm{C_{32}H_{38}IrNOP_2Si_2}$: C, 50.37; H, 5.01; N, 1.83. Found: C, 50.16; H, 5.13; N, 1.76. NMR data: ^{1}H ($\mathrm{C_7D_8}$) δ 8.1–7.9 (m, ortho Ph), 7.6–7.5 (m, ortho Ph), 6.9–7.4 (m, meta/para Ph), 2.37 (dd, $^2J_{\mathrm{PH}} = 12.33$ Hz, $^3J_{\mathrm{PH}} = 7.21$ Hz, $\mathrm{PC}H_2\mathrm{Ir}$), 1.68 (d, $^2J_{\mathrm{PH}} = 12.21$ Hz, $\mathrm{SiCH_2PIr}$), 1.40 (d, $^2J_{\mathrm{PH}} = 16.06$ Hz, $\mathrm{SiC}H_2\mathrm{PCH_2Ir}$), 040 (s, SiMe), 0.040 (s, SiMe); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 26.7 (d, $^3J_{\mathrm{PP}} = 8.9$ Hz, $\mathrm{PCH_2Ir}$), 22.5 (d, IrP).

NMR data for $\mathrm{Ir(^{13}CO)[(CH_2PPh_2CH_2SiMe_2NSiMe_2CH_2PPh_2)]}$: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 26.25 (d, $^3J_{\mathrm{PP}} = 8.9$ Hz, $\mathrm{PCH_2Ir}$), 22.5 (dd, $^3J_{\mathrm{PC}} = 9.5$ Hz, $^3J_{\mathrm{PP}} = 8.9$ Hz, IrP); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 173.88 (d, $^2J_{\mathrm{CP}} = 10.11$ Hz).

NMR data for $\mathrm{Ir(CO)[(^{13}CH_2PPh_2CH_2SiMe_2NSiMe_2CH_2PPh_2)]}$: ^{1}H ($\mathrm{C_7D_8}$) δ 8.1–7.9 (m, ortho Ph), 7.6–7.5 (m, ortho Ph), 6.9–7.4 (m, meta/para Ph), 2.40 (ddd, $^1J_{\mathrm{CH}} = 132.33$ Hz, $^2J_{\mathrm{PH}} = 12.24$ Hz, $^3J_{\mathrm{PH}} = 7.30$ Hz, $\mathrm{PC}H_2\mathrm{Ir}$), 1.68 (d, $^2J_{\mathrm{PH}} = 12.32$ Hz, $\mathrm{SiCH_2PIr}$), 1.42 (dd, $^3J_{\mathrm{CH}} = 2.69$ Hz, $^2J_{\mathrm{PH}} = 16.09$ Hz, $\mathrm{SiC}H_2\mathrm{PCH_2Ir}$), 0.39 (s, SiMe), 0.04 (s, SiMe); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 26.81 (dd, $^3J_{\mathrm{PP}} = 8.25$ Hz, $^1J_{\mathrm{PC}} = 31.4$ Hz, $\mathrm{PCH_2Ir}$), 22.5 (dd, $^2J_{\mathrm{PC}} = 71.7$ Hz, IrP); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 0.0075 (dd, $^1J_{\mathrm{PC}} = 31.4$ Hz, $^2J_{\mathrm{PC}} = 71.7$ Hz).

Isolation of $\mathrm{Ir(CO)[N(SiMe_2CH_2PPh_2)_2]}$. A toluene solution (20 mL) of compound **1** (100 mg, 0.1360 mmol) cooled in an acetone/$\mathrm{CO_2}$ bath was charged with CO (1 atm, 50 mL). An instantaneous reaction took place to give a yellow solution. The bath was allowed to warm naturally for 7 h. After the bath reached room temperature, the yellow solution was continually stirred for 5 min and vacuum-pumped to dryness. A yellow solid was obtained, and NMR showed that it was a mixture of compound **13** and $\mathrm{Ir(CO)[N(SiMe_2CH_2PPh_2)_2]}$ in a ratio of 85:15. The solid was redissolved in toluene, and a small amount of hexanes was added. Yellow crystals of $\mathrm{Ir(CO)[N(SiMe_2CH_2PPh_2)_2]}$ deposited at −30 °C. Anal. Calcd for $\mathrm{C_{31}H_{36}IrNOP_2Si_2}$: C, 49.71; H, 4.84; N, 1.87. Found: C, 49.70; H, 5.08; N, 1.64. The spectroscopic data for these crystals are the same as the literature values.[26]

Formation of $\mathrm{Ir{=}CH_2(CO)[N(SiMe_2CH_2PPh_2)_2]}$. A $\mathrm{C_7D_8}$ solution (0.6 mL) of $\mathrm{Ir{=}CH_2[N(SiMe_2CH_2PPh_2)_2]}$ (17 mg, 0.023 12 mmol) in a NMR tube was degassed, and the head space was evacuated. CO at 1 atm was charged into the tube while the solution was maintained in an acetone/$\mathrm{CO_2}$ bath. The tube was flame-sealed, and the solution was shaken at −78 °C to mix the two reactants. An orange-yellow solution formed. The solution was frozen in liquid nitrogen, and the NMR tube was quickly put into the NMR machine probe. The reaction was monitored from −78 °C to room temperature. At −78 °C, the two species present in the solution were intermediate **14** and unreacted methylene complex **1**. At −50 °C, the methylene complex **1** disappeared and complex **14** was the only species remaining. As the temperature increased, the concentration of complex **14** decreased and two other species, complex **13** and $\mathrm{Ir(CO)[N(SiMe_2CH_2PPh_2)_2]}$, began to form at −30 °C. The adduct **14** persisted up to 10 °C and disappeared when the temperature was further increased to 20 °C. The final products were complex **13** and $\mathrm{Ir(CO)[N(SiMe_2CH_2PPh_2)_2]}$ with a ratio of about 85:15.

The reactions of compound **1** with $\mathrm{^{13}CO}$ and $\mathrm{Ir{=}^{13}CH_2[N(SiMe_2CH_2PPh_2)_2]}$ with CO were also carried out under similar conditions.

In another experiment, the reaction was allowed to warm naturally in an acetone/$\mathrm{CO_2}$ bath to 10 °C and the CO was removed from the reaction system. The bright yellow solution became brown. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ and ^{1}H NMR showed that the mixture contained the two products and the starting methylene complex.

NMR data for the intermediate **14**: ^{1}H ($\mathrm{C_7D_8}$, −20 °C) δ 12.07 (t, $^3J_{\mathrm{PH}} = 17.25$ Hz, $\mathrm{Ir{=}CH_2}$), 7.9–7.8 (m, ortho Ph), 7.65–7.75 (m, ortho Ph), 6.9–7.4 (m, meta/para Ph), 2.06 (t, $^2J_{\mathrm{PH}} = 5.5$ Hz, $\mathrm{SiCH_2P}$), 1.94 (t, $^2J_{\mathrm{PH}} = 5.5$ Hz, $\mathrm{SiCH_2P}$), 0.353 (s, SiMe), 0.344 (s, SiMe); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 13.3 (s).

NMR data for $\mathrm{Ir{=}^{13}CH_2(CO)[N(SiMe_2CH_2PPh_2)_2]}$: ^{1}H ($\mathrm{C_7D_8}$) δ 12.06 (dt, $^1J_{\mathrm{CH}} = 141.4$ Hz, $^3J_{\mathrm{PH}} = 17.28$ Hz, $\mathrm{Ir{=}CH_2}$), 7.9–7.8 (m, ortho Ph), 7.65–7.75 (m, ortho Ph), 6.9–7.4 (m, meta/para Ph), 2.05 (t, $^2J_{\mathrm{PH}} = 5.7$ Hz, $\mathrm{SiCH_2P}$), 1.93 (t, $^2J_{\mathrm{PH}} = 5.6$ Hz, $\mathrm{SiCH_2P}$), 0.34 (s, SiMe), 0.35 (s, SiMe); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_7D_8}$) δ 12.96 (d, $^2J_{\mathrm{PC}} = 11.3$ Hz).

Preparation of $\mathrm{Ir(\mu\text{-}AlMe_2)H[N(SiMe_2CH_2PPh_2)_2]}$ (15). A toluene solution (1 mL) of $\mathrm{AlMe_3}$ (100 μL, 0.20 mmol) was added dropwise to a cooled toluene solution (10 mL, −78 °C) of the methylene complex **1** (100 mg, 0.14 mmol). The reaction was instantaneous as the purple color changed to orange. The reaction mixture was warmed to room temperature and stirred for 1 h. The removal of excess solvent from the reaction mixture afforded a yellow oil which was crystallized from minimum hexanes (1/2 mL) at −30 °C. Yield: 70%. Anal. Calcd for $\mathrm{C_{32}H_{42}NAlP_2Si_2Ir}$: C, 49.34; H, 5.56; N, 1.80. Found: C, 49.20; H, 5.72; N, 1.69. NMR data: ^{1}H (300 MHz, $\mathrm{C_6D_6}$) δ 0.00 (s, SiMe), 0.31 (s, SiMe), 2.47 (br, m, $\mathrm{PCH_2Si}$), 2.65 (br, m, $\mathrm{PCH_2Si}$), 0.78 (s, $\mathrm{AlMe_2}$), 7.40 (m, para/meta, $\mathrm{PPh_2}$), 8.15 (br), 8.50 (m, ortho, $\mathrm{PPh_2}$), −13.47 (t, $^2J_{\mathrm{P,H}} = 16.3$ Hz, Ir–H); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$) δ 31.20 (s, $\mathrm{PPh_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$) δ 4.07 (s, SiMe), 5.55 (s, SiMe), 24.46 (t, $^1J_{\mathrm{C,P}} = 6.8$ Hz, $\mathrm{PCH_2Si}$), −3.66 (s, $\mathrm{Al{-}(CH_3)}$), 128–140 (m, $\mathrm{PPh_2}$).

Preparation of $\mathrm{Ir(\eta^2\text{-}C_2H_4)H(I)[N(SiMe_2CH_2PPh_2)_2]}$ (16). To a toluene solution (10 mL) of the methylene complex **1** (50 mg, 0.07 mmol) cooled at −78 °C was transferred by vacuum excess MeI ($\approx$5 equiv, −10 °C). The reaction mixture was warmed slowly to room temperature. Within 10 min, the purple solution turned green and then faded to light yellow. The excess MeI and toluene were pumped immediately under vacuum to avoid the production of the side product $\mathrm{Ir(CH_3)(I_2)\text{-}[HN(SiMe_2CH_2PPh_2)_2]}$. The yellow residue was crystallized from toluene/hexanes (1/2 mL) at room temperature to give complex **16** in 70% yield. Anal. Calcd for $\mathrm{C_{32}H_{45}NP_2Si_2IIr}$: C, 43.83; H, 5.17; N, 1.60. Found: C, 43.80; H, 5.11; N, 1.40. NMR data: ^{1}H ($\mathrm{C_6D_6}$) δ −13.14 (t, $^3J_{\mathrm{P,H}} = 3.6$ Hz, Ir–H), −0.65 (s, SiMe), 0.51 (s, SiMe), 1.55 (dt, $J = 14.6$ Hz, $J = 6.6$ Hz, $\mathrm{SiCH_2P}$), 2.56 (t, $^3J_{\mathrm{P,H}} = 3.6$ Hz, $\mathrm{C_2H_4}$), 2.88 (dt, $J = 14.6$ Hz, $J = 6.6$ Hz, $\mathrm{SiCH_2P}$), 7.00 (m, meta/para Ph), 7.25, 7.85 (m, ortho); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$) δ 6.01 (s, $\mathrm{PPh_2}$).

The reaction of the methylene complex **1** with $\mathrm{CD_3I}$ was carried out under the same conditions as those for the reaction with $\mathrm{CH_3I}$. ^{1}H NMR showed that there was a triplet at −13.16 ppm with an integration of 0.5 ± 0.1 H and the triplet at 2.56 ppm was only 1.5 ± 0.2 H's.

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