ORGANOMETALLICS

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Nucleophilic Attack in Methoxycarbenes: Heterolytic Cleavage of the Carbon (sp^3)−Oxygen Bond versus Aminolysis

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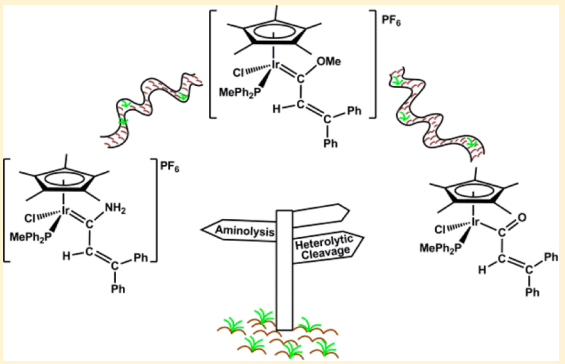
Supporting Information

ABSTRACT: The iridium methoxycarbene [IrCp*Cl{=C(OMe)-CH=CPh_2}(PPh_2Me)]PF_6 (**3**) can undergo a clean attack by nucleophiles at least by two different pathways: (1) an unusual nucleophilic attack of primary, secondary, and tertiary amines at the sp^3 carbon−oxygen bond, which gives an acyl complex and amine alkylation and (2) a nucleophilic attack of the ammonia at the carbenic carbon, which forms a primary aminocarbene.



INTRODUCTION

The reactivity of alkoxycarbenes is well known,[1] especially with metals of groups 6−8. Alkoxycarbene complexes undergo a nucleophilic attack at the carbene carbon[2] to form other carbene complexes. A well-known example of this behavior is aminolysis of alkoxycarbenes by amines.[2,3] This reaction can be envisioned as a Lewis acid−base reaction, in which the carbene carbon atom is the Lewis acid, the electron-pair acceptor, and the amine is the Lewis base, the electron-pair donor. In this process, primary or secondary amines attack the carbenic carbon and the proton of the amine leads to the displacement of the alkoxy group as an alcohol. Another example of nucleophilic attack in alkoxycarbene complexes is the heterolytic cleavage of the carbon (sp^3)−oxygen bond. Thus, this occurs when the nucleophiles are metal carbonyl anions,[4] when the nucleophiles are strong (for example I^-),[5] or when the cationic alkoxycarbene complex has π-acceptor ligands in the first coordination sphere (for example, CO and P-$(OMe)_3$).[5a,6] However, to the best of our knowledge there are only two examples where heterolytic cleavage appears with amines, and so far there is not a clear explanation for this reactivity.[7] It may be due to electronic or to steric hindrance reasons, which favor the heterolytic cleavage of the carbon (sp^3)−oxygen bond above the acid−base reaction. The aim of this work is to show that the heterolytic cleavage reaction plays a relevant role in the reactivity of alkoxycarbenes. In order to do that, we present (i) the synthesis of an iridium methoxycarbene complex by nucleophilic attack of methanol at an iridium allenylidene complex and (ii) the reactivity of the iridium methoxycarbene complex with different amines and aqueous ammonia solution.

RESULTS AND DISCUSSION

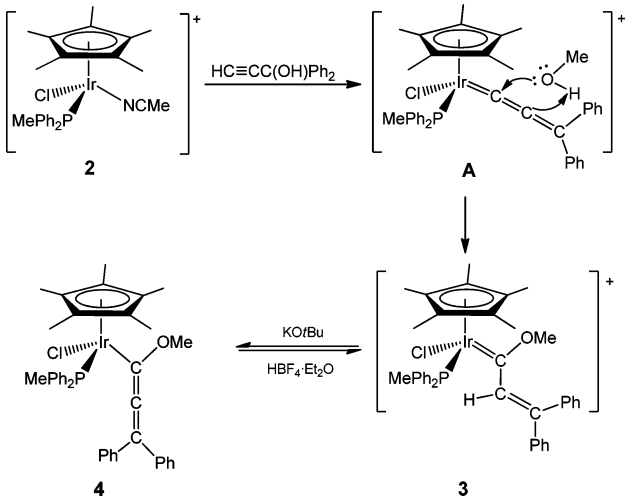
Synthesis and Reactivity with Strong Bases of a (Methoxyalkenylcarbene)iridium Complex. The reaction of the half-sandwich (acetonitrile)iridium(III) complex [IrCp*Cl(NCMe)(PPh_2Me)]PF_6 (**2**) (which was obtained by reacting the complex [IrCp*Cl_2(PPh_2Me)] (**1**)[8] with $TlPF_6$ in acetonitrile; see the Experimental Section) with 1,1-diphenyl-2-propyn-1-ol in methanol gave a yellow solution which immediately turned purple, and finally an orange solid was obtained, [IrCp*Cl{=C(OMe)CH=CPh_2}(PPh_2Me)]PF_6 (**3**) (Scheme 1). Complex **3** was isolated in 80% yield. The NMR spectra supported the proposed formulation, which was further confirmed by an X-ray crystal structure determination of complex **3** (Figure 1). For the carbene ligand (Ir=C(OCH_3)-CH=CPh_2) of **3**, the $^{13}C\{^1H\}$ NMR spectrum exhibits a characteristic low-field resonance at δ 263.3 (s br) ppm for the α-carbon and resonances at 148.6 (s) and 136.6 (s) ppm for the γ- and β-carbons, respectively. The signal corresponding to C_β-H in the ^1H NMR spectrum appears as a broad singlet at 5.37 ppm.

The formation of **3** may be explained according to the initial formation of an allenylidene complex as an intermediate (**A**). After that, nucleophilic attack by the oxygen atom of methanol on the C_α of the allenylidene followed by proton transfer at C_β gives the final (methoxyalkenylcarbene)iridium complex **3** (Scheme 1). Nucleophilic attack by alcohols on the C_α atom of the allenylidene ligand has previously been reported for other metal complexes[9] but not for iridium complexes, compound **3** being the first half-sandwich

Received: June 17, 2013

   dx.doi.org/10.1021/om400565c | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 1. Formation of Allenylidene (A), Methoxyalkenylcarbene (3), and Methoxyallenyl (4) Complexes of Iridium



(methoxyalkenylcarbene)iridium complex known. In order to confirm our hypothesis about the mechanism of the reaction, the compound **2** was treated with an excess of 1,1-diphenyl-2-propyn-1-ol in dichloromethane-d_2, which gave a purple solution due to the formation of $[IrCp^*Cl(=C=C=CPh_2)(PPh_2Me)]PF_6$ (**A**). Complex **3** was obtained when methanol was added to this solution, which confirmed our hypothesis. Compound **A** is the first half-sandwich iridium allenylidene complex known, but unfortunately this product began to decompose at the same time it was formed.[10] We were able to fully characterize the intermediate **A** at low temperature (243 K) by multinuclear (^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$) and multidimensional ($\{^1H,^1H\}$ COSY, $\{^1H, ^{13}C\}$ HSQC, and $\{^1H, ^{13}C\}$ HMBC) NMR experiments and, in the solid state, by IR. Confirmatory evidence of the presence of the allenylidene moiety comes from both the IR spectrum ($\nu_{C=C=C}$ weak band at 1989 cm^{-1}) and the $^{13}C\{^1H\}$ spectrum with resonances at 238.7 (d, $^2J_{C-P}$ = 16.3 Hz, C_α), 175.3 (s, C_γ), and 169.4 (s, C_β) ppm.

The ORTEP representation of **3** is given in Figure 1 with the ellipsoids drawn at a probability level of 50%, while selected bond and angle parameters for **3** are given in Table 1. The complex cation **3** is formed by a pentamethylcyclopentadienyl ligand (Cp*) η^5-coordinated to an iridium atom, which is also coordinated to other three donor atoms, leading to the formation of a "three-legged piano stool" structure with pseudooctahedral geometry. These ligands are a Fisher-type carbene ligand (1-methoxy-3,3-diphenylprop-2-en-1-ylidene), a chlorine ligand, and a diphenylmethylphosphane ligand. The carbene Ir−C bond length in complex **3** and in the complex $[IrCp^*\{=C(OMe)CH_2Ph\}\{PPh_2(C_6H_3\text{-}2\text{-}(OMe)\text{-}6\text{-}O)\}]PF_6$[11] has the same value, 1.973(5) Å. This bond length is shorter than the Ir−C σ-bond length for other complexes,[11] showing the presence of some multiple-bond character in the Ir−C carbene bond. However, this value is slightly longer than that found in the Fischer-type iridium carbenes of formula Ir=C(H)OR.[12]

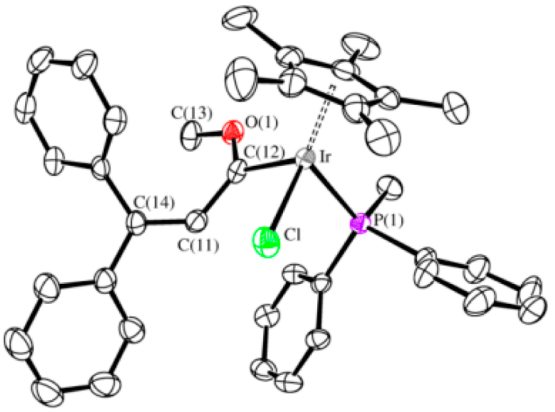


Figure 1. Cationic complex $[IrCp^*Cl\{=C(OMe)CH=CPh_2\}(PPh_2Me)]^+$ (**3**).

The complex **3** can be deprotonated with a strong base. The addition of 5 equiv of KO*t*Bu to a dichloromethane solution of **3** leads to the neutral methoxyallenyl derivative $[IrCp^*Cl\{C(OMe)=C=CPh_2\}(PPh_2Me)]$ (**4**) as a result of the abstraction of the hydrogen atom bonded to the β-carbon of **3**, which is isolated as a brown solid in 60% yield. This reaction is reversible, and complex **3** can be regenerated by addition of 1 equiv of $HBF_4{\cdot}Et_2O$ to a dichloromethane solution of **4** (Scheme 1).

In the ^1H NMR spectrum of **4** the most noticeable feature is the absence of the C*H*=CPh_2 resonance. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the α-carbon atom of the allenyl ligand is observed as a doublet at 123.0 ppm with a C−P coupling constant of 17.7 Hz; the β- and γ-carbon resonances are observed as singlets at 197.0 and 112.5 ppm, respectively. The IR spectrum shows a weak band at 1889 cm^{-1} due to the $\nu_{C=C=C}$ band of the allenyl ligand.

Heterolytic Cleavage of the Carbon (sp^3)−Oxygen Bond of the (Methoxyalkenylcarbene)iridium Complex by Amines. The analogue of a metal alkoxycarbene complex in organic chemistry is an ester. This analogy is very useful to explain the development of metal alkoxycarbene reactions. For example, the reaction of an ester with primary or secondary amines results in an amide, which is an aminolysis reaction. The same reaction appears in organometallic chemistry.[3] It is usually assumed that the reaction of a primary or a secondary amine with an alkoxycarbene is through attack at the carbene carbon, producing an aminocarbene (Scheme 2).

Unexpectedly, when a dichloromethane solution of the methoxycarbene compound **3** was reacted with a wide variety of amines ($MeNH_2$, $EtNH_2$, Et_2NH, $PrNH_2$, Pr_2NH, $PhNH_2$, $CyNH_2$, Cy_2NH, piperidine, NEt_3), we observed in all cases the formation of the acyl complex $[IrCp^*Cl\{C(O)CH=CPh_2\}(PPh_2Me)]$ (**5**). As is well known, the Fischer-type carbenes react with water to give hydroxycarbenes by nucleophilic substitution of the alkoxy group (eliminated as alcohol)[13] and the hydroxycarbenes (generally unstable) may degrade to give acyl derivatives.[13c,14] To rule out this possibility, we treated compound **3** with water, but compound **3** remained stable and we did not detect the formation of the acyl derivative. Therefore, **5** is a consequence of the attack of the amine at the carbon (sp^3)−oxygen bond (Scheme 3).

Additionally, we have observed that the formation of acyliridium complex **5** comes always with a mixture of ammonium salts with different degrees of methylation. This finding indicates that the methoxycarbene **3** behaves as a methylating agent of amines, in a way similar to that for well-known methyl halides reacting with nitrogen nucleophiles in an organic reaction[15] (Scheme 4). Another finding supporting this

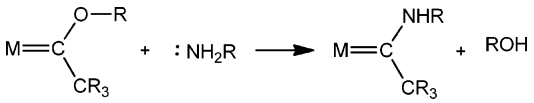
dx.doi.org/10.1021/om400565c | *Organometallics* XXXX, XXX, XXX−XXX

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

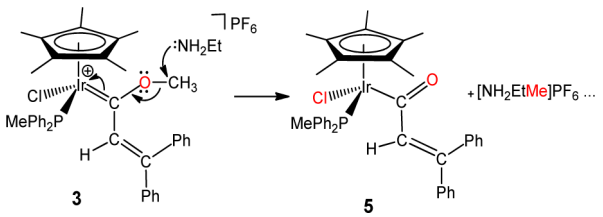
Ir–CT01[a]	1.8835(2)	Ir–C(12)	1.973(5)
Ir–P(1)	2.3063(12)	Ir–Cl	2.4147(12)
Ir–C(1)	2.247(5)	Ir–C(2)	2.190(5)
Ir–C(3)	2.264(5)	Ir–C(4)	2.250(5)
Ir–C(5)	2.239(5)	C(11)–C(12)	1.464(7)
C(11)–C(14)	1.355(6)	O(1)–C(13)	1.471(6)
O(1)–C(12)	1.317(6)		
CT01–Ir–C(12)	128.18(14)	CT01–Ir–Cl	120.73(3)
CT01–Ir–P(1)	125.24(3)	C(12)–Ir–P(1)	89.93(14)
P(1)–Ir–Cl	92.45(4)	C(12)–Ir–Cl	89.87(14)
C(14)–C(11)–C(12)	130.8(4)	O(1)–C(12)–C(11)	120.7(4)
O(1)–C(12)–Ir	115.8(3)	C(11)–C(12)–Ir	123.5(3)

[a]CT01 refers to the centroid of the Cp* ligand.

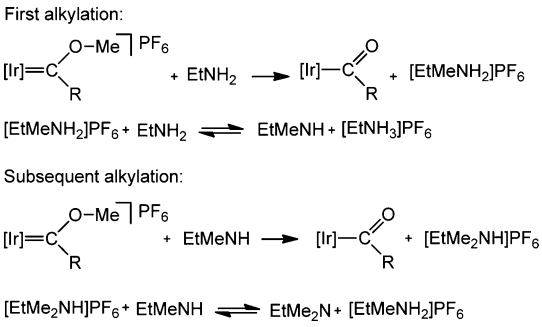
Scheme 2. Reaction of Aminolysis of a Metal Alkoxycarbene



Scheme 3. Reaction of Heterolytic Cleavage of the Carbon (sp^3)–Oxygen Bond by Amines

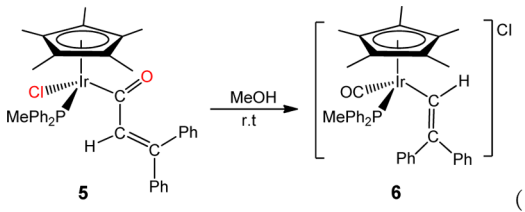


Scheme 4. Methylation of Amines by Metal Methoxycarbene



proposal occurs when the reaction is carried out with the tertiary amine Et_3N; in this case only the ammonium salt $[Et_3MeN]PF_6$ accompanies the formation of complex **5**.

The spectral data confirmed the formulation of **5** as $[IrCp^*Cl\{C(O)CH{=}CPh_2\}(PPh_2Me)]$. The most noteworthy facts in these data are the disappearance of the OCH_3 and C_β-*H* signals in the ^1H NMR experiment and the presence of a new signal at 7.7 ppm corresponding to $CHCPh_2$. Moreover, a signal in the $^{13}C\{^1H\}$ NMR experiment appearing at 219.0 ppm as a doublet with a C–P coupling constant of 13.0 Hz corresponds to η^1-$C(O)CHCPh_2$. All of this confirms the presence of the acyl ligand, η^1-$C(O)CHCPh_2$. The IR spectrum of complex **5** shows a band at 1577 cm^{-1} due to the ν_{CO} band of the acyl ligand. Compound **5** is thermodynamically unstable in methanol solution at room temperature and spontaneously converts to $[IrCp^*(CH{=}CPh_2)(CO)(PPh_2Me)]Cl$ (**6·Cl**) by CO deinsertion of the acyl ligand and concurrent displacement of the Cl^- ligand (eq 1). Similar reactions can be found in the literature.[13c,14b]



The presence of a terminal carbonyl ligand in complex **6** is confirmed by a strong IR band at 2035 cm^{-1} for ν_{CO}, as well as by a doublet signal at δ 165.3 ppm with a C–P coupling constant of 13.7 Hz in the $^{13}C\{^1H\}$ NMR spectrum. In addition, a doublet at 115.1 ppm with a C–P coupling constant of 13.9 Hz and a broad singlet at 152.1 ppm can be assigned to the C_α and C_β nuclei of the vinyl ligand, respectively. The ^1H NMR spectrum of **6** shows a doublet at 7.0 ppm with a C–P coupling constant of 8.8 Hz, which corresponds to the hydrogen on the α-carbon of the vinyl ligand. All resonance assignments were confirmed by $\{^1H,^{13}C\}$ HSQC and $\{^1H,^{13}C\}$ HMBC experiments.

The structure of the cation complex **6** consists of a pentamethylcyclopentadienyl ligand (Cp*) η^5-coordinated to an iridium atom, which is also coordinated to three donor atoms, leading to the formation of a "three-legged piano stool" structure with pseudooctahedral geometry. These ligands are a 2,2-diphenylethenyl ligand, a carbonyl ligand, and a diphenylmethylphosphane ligand. The ORTEP representation of **6** is given in Figure 2 with the ellipsoids drawn at a probability level of 30%, while selected bond and angle parameters for **6** are given in Table 2.

When 1.1 equiv of a strong acid ($HBF_4{\cdot}Et_2O$ or $HOSO_2CF_3$) was added to **5** in a solution of dichloromethane, the hydroxycarbene $[IrCp^*Cl\{{=}C(OH)CH{=}CPh_2\}PPh_2Me]X$ (**7**; X = BF_4, OSO_2CF_3) was isolated as a red solid in 87% yield. This reaction is reversible by addition of Et_3N (Scheme 5).

The hydroxycarbene **7** was unambiguously characterized by NMR spectroscopy ($\{^1H,^{13}C\}$ HMBC, $\{^1H,^{13}C\}$ HSQC, $^{13}C\{^1H\}$) and confirmed by refluxing complex **2** with water and 1,1-diphenyl-2-propyn-1-ol for 30 min.[16] When the reaction mixture of **5** and trifluoromethanesulfonic acid was set aside for 2 h, the carbonyl complex **8**[17] and 1,1-diphenylethene[18] were formed. Moreover, when the same reaction was performed with 4 equiv of acid and set aside overnight, the 1,1-diphenylethene

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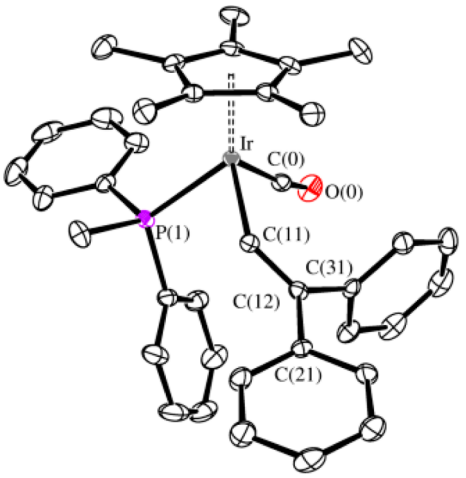
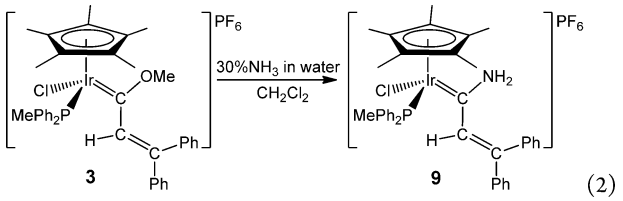


Figure 2. Cationic complex $[IrCp^*(CH{=}CPh_2)(CO)(PPh_2Me)]^+$ (**6**).

transformed into 3-methyl-1,1,3-triphenylindane.[19] A plausible mechanism (Scheme 6) may involve the reaction of 1,1-diphenylethene with excess acid. A similar reaction was found in the literature,[20] but the mechanism was not reported.

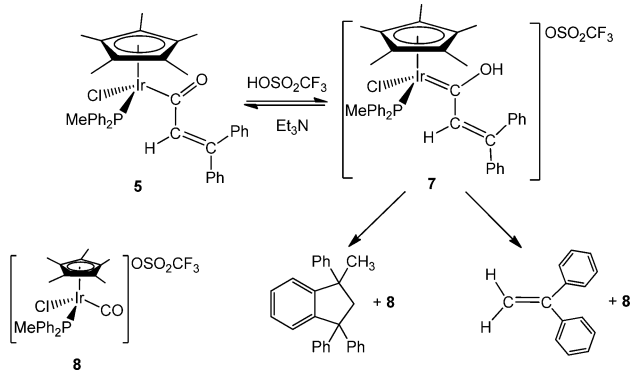
Aminolysis via Aqueous Ammonia Solution. Surprisingly, and in contrast to what was observed with amines, when an aqueous ammonia solution (30%) was added to a dichloromethane solution of **3** a typical aminolysis reaction occurred and the primary aminocarbene $[IrCp^*Cl\{{=}C(NH_2)\text{-}CH{=}CPh_2\}PPh_2Me]PF_6$ (**9**) was obtained as an orange solid in 82% yield (eq 2).



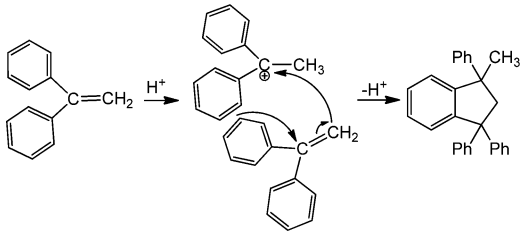
(2)

The ^1H NMR spectrum of **9** shows a singlet at 6.8 ppm for C_β-*H* and two broad singlets at 8.3 and 9.7 ppm corresponding to the NH_2 group.[21] Its $^{13}C\{^1H\}$ NMR spectrum confirms the presence of a carbene ligand. The carbene carbon appears as a doublet with a chemical shift of 209.9 ppm and a C−P coupling constant of 11.9 Hz. All of the proton and carbon resonances of **9** were unambiguously assigned by means of $\{^1H,^{13}C\}$ HSQC, $\{^1H,^{13}C\}$ HMBC, and $\{^1H,^1H\}$ COSY experiments.

Scheme 5. Formation of Hydroxycarbene and Its Evolution to 1,1-Diphenylethene and 3-Methyl-1,1,3-triphenylindane



Scheme 6. Formation of 3-Methyl-1,1,3-triphenylindane by Diphenylethene in Acid Media



CONCLUSION

In this paper we have reported the formation of the first half-sandwich allenylidene complex of iridium by a Selegue reaction and the first (methoxyalkenylcarbene)iridium complex via an allenylidene complex. In addition, we have studied the behavior of this iridium carbene complex with amines and have observed an unusual nucleophilic attack of the amine at the carbon (sp^3)−oxygen bond, which gives an acyl complex and amine alkylation. In contrast, ammonia forms a primary aminocarbene by a typical aminolysis reaction.

Experimental results suggest that a competitive process occurs between aminolysis and heterolytic cleavage of the carbon (sp^3)−oxygen bond. This process is likely due to a steric effect and not a nucleophilic effect, because the nucleophilicity

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

Ir−C(0)	1.869(3)	Ir−CT01[a]	1.90114(14)
Ir−C(11)	2.072(3)	Ir−P(1)	2.3022(8)
Ir−C(1)	2.266(3)	Ir−C(2)	2.255(3)
Ir−C(3)	2.259(3)	Ir−C(4)	2.234(3)
Ir−C(5)	2.277(3)	C(0)−O(0)	1.144(4)
C(11)−C(12)	1.342(4)	C(12)−C(21)	1.494(4)
C(12)−C(31)	1.498(4)		
C(11)−Ir−P(1)	83.64(8)	C(0)−Ir−P(1)	91.61(10)
C(0)−Ir−C(11)	98.14(12)	C(0)−Ir−CT01	125.36(9)
CT01−Ir−C(11)	118.48(8)	CT01−Ir−P(1)	129.01(2)
O(0)−C(0)−Ir	171.1(3)	C(12)−C(11)−Ir	132.8(2)
C(11)−C(12)−C(21)	119.4(3)	C(11)−C(12)−C(31)	122.8(3)
C(21)−C(12)−C(31)	117.7(3)		

[a]CT01 refers to the centroid of the Cp* ligand.

dx.doi.org/10.1021/om400565c | *Organometallics* XXXX, XXX, XXX−XXX

of ammonia is intermediate among the other amines used in this work.

EXPERIMENTAL SECTION

General Procedures, Methods, and Materials. All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures[22] and, prior to use, distilled under argon. The starting material [IrCp*Cl_2(PPh_2Me)] (**1**) was prepared as described in the literature.[8] All reagents were obtained from commercial sources. Unless stated, NMR spectra were recorded at room temperature on a Bruker ARX-400 instrument, with resonating frequencies of 400 MHz (^{1}H), 161 MHz (^{31}P{^{1}H}), 376 MHz (^{19}F{^{1}H}), and 100 MHz (^{13}C{^{1}H}) using the solvent as the internal lock. ^{1}H and ^{13}C{^{1}H} signals are referred to internal TMS, those of ^{19}F{^{1}H} to $CFCl_3$, and those of ^{31}P{^{1}H} to 85% H_3PO_4; downfield shifts (expressed in ppm) are considered positive. ^{1}H and ^{13}C{^{1}H} NMR (or JMOD) signal assignments were confirmed by {^{1}H,^{1}H} COSY, {^{1}H,^{13}C} HSQC, {^{1}H,^{13}C} HMBC, and DEPT experiments. Coupling constants are given in hertz. Infrared spectra were run on a Jasco FT/IR-6100 spectrometer using KBr pellets. C, H, and N analyses were carried out with a Carlo Erba 1108 analyzer. High-resolution electrospray mass spectra were acquired using an apex-Qe spectrometer.

X-ray Diffraction Analysis. Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarization effects. The software SMART[23] was used for collecting frames of data and indexing reflections and the determination of lattice parameters, SAINT[24] for integration of intensity of reflections and scaling, and SADABS[25] for empirical absorption correction.

The crystallographic treatment of the compounds was performed with the Oscail program.[26] The structure was solved by direct methods and refined by full-matrix least squares based on F^2.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters.

Crystal data and structure refinement details for complexes **3** and **6** are given in Table 3.

Synthesis and Characterization of New Complexes. *Preparation of [IrCp*Cl(NCMe)(PPh_2Me)]PF_6 (**2**).* An orange solution of [IrCp*Cl_2(PPh_2Me)] (500 mg, 0.83 mmol) in acetonitrile (25 mL) was treated with thallium(I) hexafluorophosphate (385.6 mg, 1.105 mmol). The reaction mixture was stirred for 50 min at room temperature and then was filtered through Celite to give a yellow solution. The solvent was removed by vacuum, and the solid obtained was redissolved in dichloromethane. The solution was filtered through Celite again, and the solvent was removed by vacuum to yield a yellow solid that was washed with diethyl ether (3 × 2 mL). Finally it was dried under vacuum. Yield: 600 mg (96%). ^{1}H NMR (CD_2Cl_2): δ 7.45−7.70 (m, 10H, PPh_2CH_3); 2.39 (s br, 3H, NCCH_3); 2.31 (d, 3H, $^2J_{H-P}$ = 10.8 Hz, PPh_2CH_3); 1.54 (d, 15H, $^4J_{H-P}$ = 2.4 Hz, $C_5(CH_3)_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −9.75 (s, PPh_2CH_3); −144.10 (sept, $^1J_{P-F}$ = 710.8 Hz, PF_6) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 128.6−133.9 (C PPh_2Me); 121.2 (s, NCCH$_3$); 95.4 (d, $^2J_{C-P}$ = 2.4, $C_5(CH_3)_5$); 13.2 (d, $^1J_{C-P}$ = 40.8 Hz, PPh_2CH_3); 8.7 (s, $C_5(CH_3)_5$); 4.0 (s, NCCH$_3$) ppm. IR (cm^{-1}): ν_{CN} 2324 (w), 2296 (w); ν_{PF_6} 841 (s).

*In Situ NMR Formation of [IrCp*Cl(=C=C=CPh_2)(PPh_2Me)]PF_6 (**A**).* A yellow solution of **2** (31.1 mg, 0.042 mmol) in dichloromethane-d_2 (600 μL) was placed in an NMR tube, and a solution of 1,1-diphenyl-2-propyn-1-ol (34.6 mg, 0.168 mmol) in dichloromethane-d_2 (50 μL) was added through the serum cap via a microsyringe at 243 K; immediately a change in color to purple was observed. Once the NMR study was completed, the solvent was removed and the residue was used to prepare the KBr pellet to record the IR spectrum. ^{1}H NMR (CD_2Cl_2, 243 K): δ 7.22−7.97 (m, *Ph*); 2.29 (d, 3H, $^2J_{H-P}$ = 11.5 Hz, PPh_2CH_3); 1.63 (s, 15H, $C_5(CH_3)_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 243 K): δ −3.93 (s, PPh_2CH_3); −144.27 (sept, $^1J_{P-F}$ = 711.5 Hz, PF_6) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 243 K): δ 238.7 (d, $^2J_{C-P}$ = 16.3 Hz, C_α); 175.3 (s, C_γ); 169.4 (s, C_β); 124.7−135.6 (*C Ph*); 103.9 (d, $^2J_{C-P}$ = 2.0 Hz, $C_5(CH_3)_5$); 15.7 (d, $^1J_{C-P}$ = 42.0 Hz, PPh_2CH_3); 8.7 (s, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): $\nu_{C=C=C}$ 1989 (w).

*Preparation of [IrCp*Cl{=C(OMe)CH=CPh_2}(PPh_2Me)]PF_6 (**3**).* When 1,1-diphenyl-2-propyn-1-ol (93 mg, 0.44 mmol) was added to a yellow solution of **2** (294 mg, 0.39 mmol) in methanol (10 mL), the mixture immediately turned purple. After 20 min of stirring an orange suspension was obtained. This suspension was concentrated to ca. 4 mL, yielding an orange solid that was separated by decantation, washed with pentane (5 × 8 mL), and dried under vacuum. Recrystallization of this complex from a CH_2Cl_2/MeOH mixture (1/1 v/v) yielded red monocrystals adequate for X-ray diffraction analysis. Yield: 292 mg (80%). ^{1}H NMR (CD_2Cl_2): δ 7.54−7.67 (m, 6H, PPh_2CH_3); 7.45−7.54 (m, 5H, CPh_2 + PPh_2CH_3); 7.35−7.44 (m, 3H, CPh_2); 7.21−7.29 (m, 2H, CPh_2); 6.93−7.00 (m, 2H, CPh_2); 6.68−6.76 (m, 2H, CPh_2); 5.37 (s, 1H, C_β-*H*); 3.91 (s br, 3H, OCH_3); 2.41 (d, 3H, $^2J_{H-P}$ = 10.5 Hz, PPh_2CH_3); 1.53 (d, 15H, $^4J_{H-P}$ = 2.0 Hz, $C_5(CH_3)_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −14.97 (s, PPh_2CH_3); −144.11 (sept, $^1J_{P-F}$ = 710.6 Hz, PF_6) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 263.3 (s br, C_α); 148.6 (s, C_γ); 139.8 (s, C_{ipso}-Ph); 139.5 (s, C_{ipso}-Ph); 136.6 (s, C_β-H); 133.3 (d, $^2J_{C-P}$ = 9.4 Hz, C PPh_2Me); 132.8 (d, $^2J_{C-P}$

Table 3. Crystal Data and Structure Refinement Details for Complexes 3 and 6

	3	6
empirical formula	$C_{39}H_{42}ClF_6IrOP_2$	$C_{62}H_{59}BIrOP$
formula wt	930.32	1054.07
temp (K)	183(2)	173(2)
wavelength (Å)	0.71073	
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
a (Å)	40.922(3)	11.9619(8)
b (Å)	12.8637(10)	12.5140(8)
c (Å)	14.6334(12)	18.5316(12)
α (deg)	90	73.8360(10)
β (deg)	101.3580(10)	87.8390(10)
γ (deg)	90	72.0190(10)
V (Å^3)	7552.2(10)	2530.7(3)
Z	8	2
density (Mg/m^3)	1.636	1.383
abs coeff (mm^{-1})	3.751	2.711
F(000)	3696	1072
cryst size (mm)	0.48 × 0.37 × 0.05	0.43 × 0.31 × 0.29
θ range for data collection (deg)	1.66−28.03	1.79_28.01
index ranges	$-53 \le h \le 52$	$-15 \le h \le 14$
	$-15 \le k \le 16$	$-12 \le k \le 16$
	$-19 \le l \le 18$	$-23 \le l \le 24$
no. of rflns collected	24349	17026
no. of indep rflns	8969 (*R*(int) = 0.0456)	11736 (*R*(int) = 0.0247)
no. of rflns obsd (>2σ)	6308	10081
data completeness	0.979	0.959
abs cor	semiempirical from equivalents	
max and min transmission	0.7456 and 0.4464	0.7456 and 0.6256
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	8969/0/460	11736/0/601
goodness of fit on F^2	1.044	1.003
R indices ($I > 2\sigma(I)$)	R1 = 0.0348, wR2 = 0.0727	R1 = 0.0294, wR2 = 0.0600
R indices (all data)	R1 = 0.0703, wR2 = 0.0883	R1 = 0.0401, wR2 = 0.0647
largest diff peak and hole (e Å^{-3})	1.619 and −0.979	1.098 and −0.735

dx.doi.org/10.1021/om400565c | *Organometallics* XXXX, XXX, XXX−XXX

= 9.4 Hz, *C* PPh_2Me); 132.3 (d, $^3J_{C-P}$ = 2.8 Hz, *C* PPh_2Me); 132.2 (d, $^3J_{C-P}$ = 2.8 Hz, *C* PPh_2Me); 131.1 (d, $^1J_{C-P}$ = 32.6 Hz, P-C_{ipso}); 130.8 (s, 1*C* CPh_2); 130.6 (s, 1*C* CPh_2); 130.5 (d, $^1J_{C-P}$ = 31.9 Hz, P-C_{ipso}); 129.6 (s, 1*C* CPh_2); 129.5 (s, 1*C* CPh_2); 129.5 (s, 2*C* CPh_2); 129.5 (s, 1*C* CPh_2); 129.4 (s, *C* PPh_2Me); 129.4 (s, *C* PPh_2Me); 129.4 (s, 1*C* CPh_2); 128.8 (s, 2*C* CPh_2); 101.2 (d, $^2J_{C-P}$ = 1.9 Hz, $C_5(CH_3)_5$); 69.6 (s, OCH_3); 13.6 (d, $^1J_{C-P}$ = 43.2 Hz, PPh_2CH_3); 8.9 (d, $^3J_{C-P}$ = 0.9 Hz, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): ν_{PF_6} 845 (s). MS (*m*/*z*, referred to the most abundant isotopes): 785 [M]$^+$. Anal. Calcd for $C_{39}H_{42}OClF_6IrP_2$ (930.37): C, 50.35; H, 4.55. Found: C, 50.43; H, 4.59.

*Preparation of [IrCp*Cl{C(OMe)=C=CPh$_2$}(PPh$_2$Me)] (**4**).* K*t*BuO (63 mg, 0.54 mmol) was added to an orange solution of **3** (100 mg, 0.11 mmol) in dichloromethane (15 mL). The reaction mixture was stirred for 30 min at room temperature, and then it was filtered through Celite. The solvent of the brown filtrate was removed by vacuum, giving an oil, which was treated with diethyl ether. The brown solid that formed was separated by decantation, washed with diethyl ether (3 × 2 mL), and dried under vacuum. Yield: 51 mg (60%). ^{1}H NMR (CD_2Cl_2): δ 6.94−7.81 (m, 20H, *Ph*); 3.59 (s br, 3H, OCH_3); 2.18 (d, 3H, $^2J_{H-P}$ = 9.8 Hz, PPh_2CH_3); 1.38 (d, 15H, $^4J_{H-P}$ = 2.1 Hz, $C_5(CH_3)_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −8.88 (s, *P*Ph_2CH_3) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 197.0 (s, C_β); 142.6 (s, C_{ipso}-Ph); 140.8 (s, C_{ipso}-Ph); 135.3 (d, $^1J_{C-P}$ = 52.2 Hz P-C_{ipso}); 134.4 (d, $^2J_{C-P}$ = 10.0 Hz, *C* PPh_2Me); 133.9 (d, $^1J_{C-P}$ = 52.2 Hz P-C_{ipso}); 133.3 (d, $^2J_{C-P}$ = 9.5 Hz, *C* PPh_2Me); 130.2 (d, $^3J_{C-P}$ = 2.5 Hz, *C* PPh_2Me); 130.1 (d, $^3J_{C-P}$ = 2.5 Hz, *C* PPh_2Me); 128.9 (s, *C* CPh_2); 128.7 (s, *C* CPh_2); 128.1 (s, *C* PPh_2Me); 128.0 (s, *C* CPh_2); 127.9 (s, *C* PPh_2Me); 127.8 (s, *C* CPh_2); 126.1 (s, *C* CPh_2); 125.6 (s, *C* CPh_2); 123.0 (d, $^2J_{C-P}$ = 17.7 Hz, C_α); 112.5 (s, C_γ); 94.8 (d, $^2J_{C-P}$ = 2.6 Hz, $C_5(CH_3)_5$); 59.1 (s, OCH_3); 15.1 (d, $^1J_{C-P}$ = 39.5 Hz, PPh_2CH_3); 8.7 (s, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): $\nu_{C=C=C}$ 1889 (w). MS (*m*/*z*, referred to the most abundant isotopes): 785 [M + 1]$^+$. Anal. Calcd for $C_{39}H_{41}OClIrP$ (784.4): C, 59.72; H, 5.27. Found: C, 59.89; H, 5.35.

*Preparation of [IrCp*Cl{C(O)CH=CPh$_2$}(PPh$_2$Me)] (**5**).* An orange solution of **3** (900 mg, 0.97 mmol) in dichloromethane (20 mL) was treated with amine (1.16 mmol). The solution was stirred for 5 min at room temperature, and then the solvent was removed by vacuum to give an orange oil. This oil was treated with C_6H_6 to extract the ammonium salts obtained in this reaction. The ammonium salts are insoluble in this media, and the acyl complex **5** is totally soluble. The ^{1}H NMR experiment of the isolated solid (the ammonium salts) in dichloromethane shows different groups of signals, in agreement with the presence of a mixture of ammonium salts. Thus, when Et_3N was used, the formation of [Et_3NMe]PF_6 was observed. ^{1}H NMR (CD_2Cl_2): 3.25 (q, 6H, $^3J_{H-H}$ = 7.3 Hz, CH_2); 2.89 (s, 3H, CH_3); 1.32 (t, 9H, $^3J_{H-H}$ = 7.3 Hz, CH_3) ppm. When Et_2NH was used, a mixture (60/40) of [Et_2NH(CH_3)]PF_6 and [Et_2N(CH_3)$_2$]PF_6 was observed. ^{1}H NMR (CD_2Cl_2) for [Et_2NH(CH_3)]PF_6: 6.37 (s br, 1H, N-*H*); 2.81 (q, 4H, $^3J_{H-H}$ = 7.1 Hz, CH_2), 2.34 (s, 3H, N−CH_3); 1.21 (t, 6H, $^3J_{H-H}$ = 7.2 Hz, CH_3) ppm and for [Et_2N(CH_3)$_2$]PF_6: 3.25 (q, 4H, $^3J_{H-H}$ = 7.3 Hz, CH_2), 2.94 (s, 6H, N-CH_3); 1.30 (t, 6H, $^3J_{H-H}$ = 7.3 Hz, CH_3) ppm. The solvent of the orange solution was removed by vacuum, giving a yellow solid that was washed with methanol (3 × 6 mL) and dried under vacuum. Yield: 350 mg (47%). ^{1}H NMR (C_6D_6): δ 7.67 (s, 1H, C_β-*H*); 7.54−7.73 (m, 8H, *Ph*); 7.19−7.24 (m, 2H, *Ph*); 6.95−7.10 (m, 10H, *Ph*); 1.88 (d, 3H, $^2J_{H-P}$ = 10.4 Hz, PPh_2CH_3); 1.27 (d, 15H, $^4J_{H-P}$ = 1.9 Hz, $C_5(CH_3)_5$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −10.88 (s, *P*Ph_2CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 219.0 (d, $^2J_{C-P}$ = 13.0 Hz, C_α); 144.9 (s, C_{ipso}-Ph); 143.2 (d, $^3J_{C-P}$ = 2.6 Hz, C_β); 141.1 (s, C_{ipso}-Ph); 136.5 (s, C_γ); 134.6 (d, $^1J_{C-P}$ = 53.4 Hz, P-C_{ipso}); 134.5 (d, $^2J_{C-P}$ = 9.8 Hz, *C* PPh_2Me); 133.1 (d, $^2J_{C-P}$ = 9.5 Hz, *C* PPh_2Me); 132.9 (d, $^1J_{C-P}$ = 54.1 Hz, P-C_{ipso}); 131.8 (s, *C* PPh_2Me); 130.2 (d, $^3J_{C-P}$ = 2.4 Hz, *C* PPh_2Me); 129.9 (d, $^3J_{C-P}$ = 2.4 Hz, *C* PPh_2Me); 129.5 (s, *C* PPh_2Me); 128.4 (s, *C* CPh_2); 127.6−128.4 (some signals are overlapped with the solvent signal); 127.3 (s, *C* CPh_2); 127.2 (s, *C* CPh_2); 95.3 (d, $^2J_{C-P}$ = 2.8 Hz, $C_5(CH_3)_5$); 14.0 (d, $^1J_{C-P}$ = 39.2 Hz, PPh_2CH_3); 8.4 (s, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): ν_{CO} 1577 (s). MS (*m*/*z*, referred to the most abundant isotopes): 771 [M + 1]$^+$, 735 [M − Cl]$^+$. Anal. Calcd for $C_{38}H_{39}OClIrP$ (770.37): C, 59.25; H, 5.10. Found: C, 59.44; H, 5.20.

Preparation of [IrCp(CH=CPh$_2$)(CO)(PPh$_2$Me)]Cl (**6**).* An orange solution of **5** (100 mg, 0.13 mmol) in methanol (5 mL) was stirred for 24 h. Then, the solvent was removed by vacuum, yielding a white precipitate which was washed with pentane (3 × 3 mL) and finally dried under vacuum. Yield: 97 mg (85%). Treating complex **6** with $NaPF_6$ or $NaBPh_4$ in methanol produced the corresponding anion interchange. In the case of BPh_4^- monocrystals of [IrCp*(CH=CPh_2)(CO)(PPh_2Me)]BPh_4 adequate for X-ray diffraction analysis were obtained. The PF_6^- derivative was employed for characterization. Data for [IrCp*(CH=CPh_2)(CO)(PPh_2Me)]PF_6 are as follows. ^{1}H NMR (CD_2Cl_2): δ 7.62−7.73 (m, 3H, P*Ph*$_2$CH$_3$); 7.42−7.58 (m, 5H, P*Ph*$_2$CH$_3$); 7.18−7.32 (m, 8H, C*Ph*$_2$ + P*Ph*$_2$CH$_3$); 7.09−7.14 (m, 2H, C*Ph*$_2$); 7.02 (d, 1H, $^3J_{H-P}$ = 8.8 Hz, C*H*=CPh$_2$); 6.55−6.61 (m, 2H, C*Ph*$_2$); 2.33 (d, 3H, $^2J_{H-P}$ = 10.5 Hz, PPh$_2$C*H*$_3$); 1.83 (d, 15H, $^4J_{H-P}$ = 2.3 Hz, $C_5(CH_3)_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −13.84 (s, *P*Ph$_2$CH$_3$); −143.94 (sept, $^1J_{P-F}$ = 710.4 Hz, PF_6) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 165.3 (d, $^2J_{C-P}$ = 13.7 Hz, *C*O); 152.1 (s, CH=*C*Ph$_2$); 146.0 (s, Ph-C_{ipso}); 144.3 (s, Ph-C_{ipso}); 133.4 (d, $^3J_{C-P}$ = 2.8 Hz, *C* PPh$_2$Me); 132.7 (d, $^3J_{C-P}$ = 2.8 Hz, *C* PPh$_2$Me); 132.4 (d, $^2J_{C-P}$ = 10.0 Hz, *C* PPh$_2$Me); 132.2 (d, $^2J_{C-P}$ = 10.0 Hz, *C* PPh$_2$Me); 130.1 (s, *C* CPh$_2$); 130.0 (d, $^2J_{C-P}$ = 11.3 Hz, *C* PPh$_2$Me); 129.5 (d, $^2J_{C-P}$ = 11.4 Hz, *C* PPh$_2$Me); 128.9 (s, *C* CPh$_2$); 128.7 (s, *C* CPh$_2$); 128.1 (s, *C* CPh$_2$); 127.8 (s, P-C_{ipso}); 127.2 (s, *C* CPh$_2$); 127.1 (s, P-C_{ipso}); 126.9 (s, *C* CPh$_2$); 115.1 (d, $^2J_{C-P}$ = 13.9 Hz, *C*H=CPh$_2$); 103.8 (d, $^2J_{C-P}$ = 1.7 Hz, $C_5(CH_3)_5$); 14.1 (d, $^1J_{C-P}$ = 44.5 Hz, PPh$_2$CH$_3$); 9.0 (s, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): ν_{CO} 2035 (s); ν_{PF_6} 840 (s). MS (*m*/*z*, referred to the most abundant isotopes): 735 [M]$^+$. Anal. Calcd for $C_{38}H_{39}OF_6IrP_2$ (880): C, 51.87; H, 4.47. Found: C, 51.92; H, 4.50.

*Preparation of [IrCp*Cl{=C(OH)CH=CPh$_2$}(PPh$_2$Me)]OCF$_3$SO$_3$ (**7**).* To an orange solution of **5** (120 mg, 0.16 mmol) in dichloromethane (5 mL) was added trifluoromethanesulfonic acid (17 μL, 0.19 mmol), and the mixture was stirred for 5 min. The red solution obtained was concentrated, yielding a red oil that was washed and precipitated with pentane (4 × 4 mL). Finally, the red solid that was obtained was dried under vacuum. Yield: 128 mg (87%). ^{1}H NMR (CD_2Cl_2): δ 7.27−7.68 (m, 18H, P*Ph*$_2$CH$_3$ + C*Ph*$_2$); 7.16 (s br, 1H, C_β-*H*); 7.03−7.10 (m, 2H, C*Ph*$_2$); 2.26 (d, 3H, $^2J_{H-P}$ = 10.2 Hz, PPh$_2$C*H*$_3$); 1.66 (d, 15H, $^4J_{H-P}$ = 1.9 Hz, $C_5(CH_3)_5$); ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.43 (s, *P*Ph$_2$CH$_3$) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ −78.92 (s, C*F*$_3$SO$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 159.5 (s, C_γ); 133.7 (s, C_β); 99.5 (s, $C_5(CH_3)_5$); 13.8 (d, $^1J_{C-P}$ = 39.6 Hz, PPh$_2$CH$_3$); 8.8 (s, $C_5(CH_3)_5$) ppm, the other resonances were not assigned because of the instability of the compound. IR (cm^{-1}): ν_{OH} 3443 (w br). MS (*m*/*z*, referred to the most abundant isotopes): 771 [M]$^+$, 735 [M − Cl]$^+$.

In Situ Formation of 1,1-Diphenylethene and 3-Methyl-1,1,3−triphenylindane. 1,1-Diphenylethene. To an orange solution of **5** (70 mg, 0.092 mmol) in dichloromethane-d_2 (0.5 mL) was added trifluoromethanesulfonic acid (9.4 μL, 0.10 mmol). In the ^{1}H and ^{31}P{^{1}H} NMR experiments was observed the formation of **7**, which in this acid media yielded, after 2 h, a new organometallic compound and an organic substrate. The NMR data indicate that the organometallic complex is [IrCp*Cl(CO)(PPh$_2$Me)](OSO_2CF_3) (**8**) and the organic compound is 1,1-diphenylethene.

3-Methyl-1,1,3-triphenylindane. Trifluoromethanesulfonic acid (34 μL, 0.36 mmol) was added to an orange solution of **5** (70 mg, 0.092 mmol) in dichloromethane (4 mL), and the mixture was stirred overnight to give a brown solution. After the solvent was removed under reduced pressure, a brown oil was obtained. This oil was treated with diethyl ether, giving a precipitate, which was filtrated and washed with pentane (2 × 2 mL). This solid was characterized as complex **8**. On the other hand, the diethyl ether solution was passed through a silica column, giving a brown oil that was identified as 3-methyl-1,1,3-triphenylindane.

Data for **8**·OSO_2CF_3 are as follows. ^{1}H NMR (CD_2Cl_2): δ 7.50−7.70 (m, 10H, P*Ph*$_2$CH$_3$); 2.40 (d, 3H, $^2J_{H-P}$ = 11.2 Hz, PPh$_2$C*H*$_3$); 1.80 (d, 15H, $^4J_{H-P}$ = 2.5 Hz, $C_5(CH_3)_5$); ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.08 (s, *P*Ph$_2$CH$_3$) ppm. The nature of **8** was

confirmed by comparing its NMR data with those of the [IrCp*Cl(CO)(PPh_2Me)]BPh_4 complex recently reported[17] and after a metathesis reaction of **8** with an excess of $NaBPh_4$ in methanol. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) (not previously reported): δ 166.1 (d, $^2J_{C-P}$ = 14.3 Hz, CO); 132.6−133.3 (C PPh_2Me); 129.4−129.8 (C PPh_2Me); 129.0 (d, $^1J_{C-P}$ = 61.7 Hz, C_{ipso}); 127.6 (d, $^1J_{C-P}$ = 61.8 Hz, C_{ipso}); 105.6 (s, $C_5(CH_3)_5$); 15.1 (d, $^1J_{C-P}$ = 42.6 Hz, PPh_2CH_3); 9.4 (s, $C_5(CH_3)_5$) ppm.

Data for 1,1-diphenylethene are as follows. ^1H NMR (CD_2Cl_2): δ 7.31−7.36 (m, 10H, Ph_2); 5.47 (s, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 150.6 (s, C_{ipso}-*Ph*); 141.9 (s, C_{ipso}-*Ph*); 128.6 (s, *C Ph*); 128.5 (s, *C Ph*); 128.1 (s, *C Ph*); 114.5 (s, CH_2) ppm.

Data for 3-methyl-1,1,3-triphenylindane are as follows. ^1H NMR (CD_2Cl_2): δ 7.00−7.36 (m, 19H, *Ph*); 3.39 (d, $1H_B$, system AB, $^2J_{H-H}$ = 13.4 Hz CH_2); 3.13 (d, $1H_A$, system AB, $^2J_{H-H}$ = 13.4 Hz, CH_2); 1.56 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 150.9 (s, CPh_2); 149.8 (s, C_{ipso}-*Ph*); 149.2 (s, CPhMe); 149.0 (s, C_{ipso}-*Ph*); 148.0 (s, C_{ipso}-*Ph*); 125.4, 125.9, 126.0, 126.4, 127.3, 127.9, 128.2, 128.3, 129.0, 129.1 (all s, *C Ph*); 61.4 (s, CH_2); 61.3 (s, $CCPh_2$); 51.5 (s, CCPhMe); 29.2 (s, CH_3) ppm.

*Preparation of [IrCp*Cl{=C(NH$_2$)CH=CPh$_2$}(PPh$_2$Me)]PF$_6$ (**9**).* An orange solution of **3** (450 mg, 0.48 mmol) in dichloromethane (10 mL) was treated with ammonia (30%; 38 μL, 0.53 mmol). The solution was stirred for 90 min, and then the solvent was removed by vacuum to give an orange oil that was precipitated and washed with pentane (3 × 6 mL). Finally it was dried under vacuum. Yield: 362 mg (82%). ^1H NMR (CD_2Cl_2): δ 9.71 (s br, 1H, NH_2); 8.26 (s br, 1H, NH_2); 7.37−7.62 (m, 16H, CPh_2 + PPh_2CH_3); 7.13−7.18 (m, 2H, CPh_2); 7.07−7.12 (m, 2H, CPh_2); 6.85 (s, 1H, C_β-*H*); 2.19 (d, 3H, $^2J_{H-P}$ = 10.1 Hz, PPh_2CH_3); 1.61 (d, 15H, $^4J_{H-P}$ = 2.2 Hz, $C_5(CH_3)_5$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −13.39 (s, PPh_2CH_3); −144.15 (sept, $^1J_{P-F}$ = 710.6 Hz, PF_6) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 209.9 (d, $^2J_{C-P}$ = 11.9 Hz, C_α); 150.4 (s, C_γ); 139.3 (s, C_{ipso}-*Ph*); 136.7 (s, C_{ipso}-*Ph*); 133.0 (d, $^2J_{C-P}$ = 9.9 Hz, *C* PPh_2Me); 132.6 (d, $^2J_{C-P}$ = 9.7 Hz, *C* PPh_2Me); 132.1 (d, $^3J_{C-P}$ = 2.7 Hz, C_β-H); 132.0 (d, J_{C-P} = 2.2 Hz, *C* PPh_2Me); 131.9 (d, $^3J_{C-P}$ = 2.8 Hz, *C* PPh_2Me); 131.4 (s, *C* CPh_2); 130.7 (d, $^1J_{C-P}$ = 43.1 Hz, P-C_{ipso}); 130.6 (s, *C* CPh_2); 130.4 (s, *C* CPh_2); 130.1 (d, $^1J_{C-P}$ = 43.7 Hz, P-C_{ipso}); 129.6 (s, *C* CPh_2); 129.4 (d, J_{C-P} = 10.8 Hz, *C* PPh_2Me); 128.9 (d, J_{C-P} = 10.8 Hz, *C* PPh_2Me); 128.5 (s, *C* CPh_2); 128.2 (s, *C* CPh_2); 98.1 (d, $^2J_{C-P}$ = 2.2 Hz, $C_5(CH_3)_5$); 13.9 (d, $^1J_{C-P}$ = 41.8 Hz, PPh_2CH_3); 8.9 (s, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): ν_{NH} 3370 (m); ν_{PF_6} 840 (s). MS (*m*/*z*, referred to the most abundant isotopes): 770 $[M]^+$. Anal. Calcd for $C_{38}H_{41}ClF_6IrNP_2$ (915.36): C, 49.86; H, 4.51; N, 1.53. Found: C, 49.98; H, 4.57; N, 1.57.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for compounds **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

■ ACKNOWLEDGMENTS

We thank the University of Vigo CACTI services for collecting X-ray data. S.B. thanks M. A. Esteruelas for fruitful discussions.

■ REFERENCES

(1) Dötz, K. H.; Stendel, J., Jr. *Chem. Rev.* **2009**, *109*, 3227−3274.

(2) Fischer, H. *Mechanistic Aspects of Carbene Complex Reactions in Transition Metal Carbene Complexes*; Seyferth, D., Ed.; Verlag Chemie: Deerfield Beach, FL, 1983; pp 248−259.

(3) (a) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545−574. (b) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441−443. (c) Ulrich, K.; Porhiel, E.; Péron, V.; Ferrand, V.; Bozec, H. L. *J. Organomet. Chem.* **2000**, *601*, 78−86. (d) Andrada, D. M.; Jiménez-Halla, J. O. C.; Sola, N. *J. Org. Chem.* **2010**, *75*, 5821−5836 and references therein. (e) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall: Upper Saddle River, NJ, 1997; pp 323−326.

(4) (a) Toomey, L. M.; Atwood, J. D. *Organometallics* **1997**, *16*, 490−493.

(5) (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237−9238. (b) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604−606. (c) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. Pl.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688−7705.

(6) (a) Treichel, P. M.; Wagner, K. P. *J. Organomet. Chem.* **1975**, *88*, 199−206. (b) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794−797.

(7) (a) Chisholm, M. H.; Clark, H. C.; Johns, W. S.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* **1975**, *14*, 900−905. (b) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2060−2062. (c) Ching, C. S.; Kim, M.; Lee, M. K.; Lee, H. *Organometallics* **2003**, *22*, 3239−3244.

(8) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479−1486.

(9) Cadierno, V.; Gimeno, J. *Chem. Rev.* **2009**, *109*, 3512−3560.

(10) The intermediate **A** evolved to **6**. The allenylidene ligand in **A** reacts with the water (1 equiv) released along the Selegue reaction. This released water assembles the metallacumulene species **A** to produce **6**: Selegue, J. P. *Organometallics* **1982**, *1*, 217−218.

(11) Yamamoto, Y.; Sugawara, K.; Han, X. H. *Dalton Trans.* **2002**, 195−211.

(12) Álvarez, E.; Paneque, M.; Petronilho, A. G.; Poveda, M. L.; Santos, L. L.; Carmona, E.; Mereiter, K. *Organometallics* **2007**, *26*, 1231−1240.

(13) (a) Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875−4880. (b) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145−149. (c) O'Connor, J. M.; Hiibner, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1209−1210.

(14) (a) Albertin, G.; Antoniutti, S.; Castro, J. *Organometallics* **2011**, *30*, 1558−1568. (b) Bianchini, C.; Casares, J. A.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Am. Chem. Soc.* **1996**, *118*, 4585−4594. (c) Grundy, K. R.; Jenkins, J. *J. Organomet. Chem.* **1984**, *265*, 77−85.

(15) Fox, M. A.; Whitesell, J. K. *Organic Chemistry*, 2nd ed.; Jones and Bartlett: Sudbury, MA, 1994.

(16) This reaction gave a mixture of several compounds that were identified by $^{31}P\{^1H\}$ NMR experiments as **5**, **6**, **A**, and **7** (signal at −12.4 ppm).

(17) Talavera, M.; Bolaño, S.; Bravo, J.; Castro, J.; García-Fontán, S. *J. Organomet. Chem.* **2012**, *715*, 113−118.

(18) (a) Eisch, J. J.; Quian, Y.; Singh, M. *J. Organomet. Chem.* **1996**, *512*, 207−217. (b) Li, J. H.; Li, J. L.; Wang, D.-P.; Pi, S.-F.; Xie, Y.-X.; Zhang, M.-B.; Hu, X.-C. *J. Org. Chem.* **2007**, *72*, 2053−2057.

(19) Basavaiah, D.; Reddy, K. R. *Org. Lett.* **2007**, *9*, 57−60.

(20) Barzaghi, M.; Beltrame, P. L.; Gamba, A.; Simonetta, M. *J. Am. Chem. Soc.* **1978**, *100*, 251−259.

(21) Bianchini, C.; Dante, M.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Organometallics* **1999**, *18*, 2376−2386.

(22) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Butterworth/ Heinemann: London/Oxford, 1988.

(23) *SMART Version 5.054, Instrument control and data collection software*; Bruker Analytical X-ray Systems: Madison, WI, 1997.

(24) *SAINT Version 6.01, Data Integration software package*; Bruker Analytical X-ray Systems: Madison, WI, 1997.

(25) Sheldrick, G. M. *SADABS. A Computer Program for Absorption Corrections*; University of Göttingen, Göttingen, Germany, 1996.

(26) McArdle, P. *J. Appl. Crystallogr.* **1995**, *28*, 65.

(27) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.