Nucleophilic Attack in Methoxy–carbenes: Heterolytic Cleavage of the Carbon(sp^3)–Oxygen Bond Versus Aminolysis.

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KEYWORDS. Alkoxy–carbene • Aminolysis • Heterolytic cleavage • Allenylidene • Iridium

ABSTRACT: The iridium methoxycarbene [IrCp*Cl{=C(OMe)CH=CPh$_2$}(PPh$_2$Me)]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, 2) a nucleophilic attack of the ammonia at the carbenic carbon, which forms a primary amino–carbene.

INTRODUCTION

Reactivity of alkoxy–carbenes is well known,[1] especially with metals of the 6–8 groups. Alkoxy–carbene 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 alkoxy–carbenes 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, electron–pair donor. On 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 alkoxy–carbene complexes is the heterolytic cleavage of the Carbon(sp^3)–Oxygen bond. Thus, it occurs when the nucleophiles are metal carbonyl anions,[4] when the nucleophiles are strong (for example I^-)[5] or when the cationic alkoxy–carbene 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 the 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 alkoxy–carbenes. In order to do that we present: i) the synthesis of an iridium methoxy–carbene complex by nucleophilic attack of methanol to an iridium allenylidene complex, ii) the reactivity of the iridium methoxy–carbene complex with different amines and aqueous ammonia solution.

RESULTS AND DISCUSSION

Synthesis and Reactivity with Strong Bases of a (Methoxy)alkenylcarbeneiridium Complex.

Reaction of the half–sandwich acetonitrileiridium (III) complex [IrCp*Cl(NCMe)(PPh$_2$Me)]PF$_6$ (**2**) (which was obtained by reacting the complex [IrCp*Cl$_2$(PPh$_2$Me)] (**1**)[8] with TlPF$_6$ in acetonitrile, see experimental) 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$_2$Me)]PF$_6$ (**3**) (Scheme 1). Complex **3** was isolated in 80% yield. The NMR spectra supported the proposed formulation, which was further confirmed by the X–ray crystal structure determination of complex **3**, Figure 1. For the carbene ligand (Ir=C(OCH$_3$)CH=CPh$_2$) of **3**, $^{13}C\{^1H\}$ NMR spectrum exhibits a characteristic low–field resonance at δ 263.3 (s br) ppm for the α–carbon, and at 148.6 (s) and 136.6 (s) ppm for the γ–carbon and the β–carbon, respectively. The signal corresponding to C$_\beta$–*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, the nucleophilic attack by the oxygen atom of methanol on the C$_\alpha$ of the allenylidene followed by the proton transfer at C$_\beta$ gives the final (methoxy)alkenylcarbeneiridium complex **3**, (Scheme 1). Nucleophilic attack by alcohols on the C$_\alpha$ atom of the allenylidene ligand has previously been reported for other metal complexes[9] but no for iridium complexes, being compound **3** the first half–sandwich (methoxy)alkenylcarbeneiridium 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$_2$Me)]PF$_6$ (**A**). Complex **3** is obtained when methanol is added to this solution, which confirms our hypothesis. The compound **A** is the first half–sandwich iridium allenylidene complex known, but unfortunately this product begin to decompose at the same time it is formed.[10] We were able to fully characterized the intermediate **A** at low temperature (243 K) by multinuclear (^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$), multidimensional ($\{^1H,^1H\}$ COSY, $\{^1H, ^{13}C\}$ HSQC and $\{^1H, ^{13}C\}$ HMBC) NMR experiments and, in 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$_\alpha$), 175.3 (s, C$_\gamma$) and 169.4 (s, C$_\beta$) 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 $[IrCp^*\{=C(OMe)CH_2Ph\}][PPh_2(C_6H_3(OMe)_2-\kappa-P,O]PF_6$,[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 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]

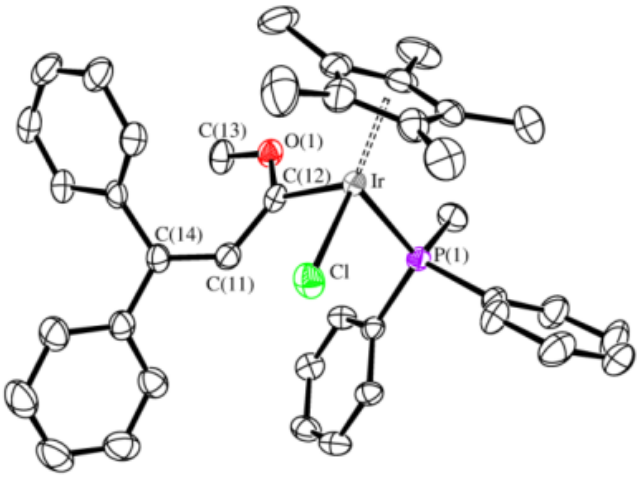


Figure 1. The Cation Complex $[IrCp^*Cl\{=C(OMe)CH=CPh_2\}(PPh_2Me)]^+$ **(3)**

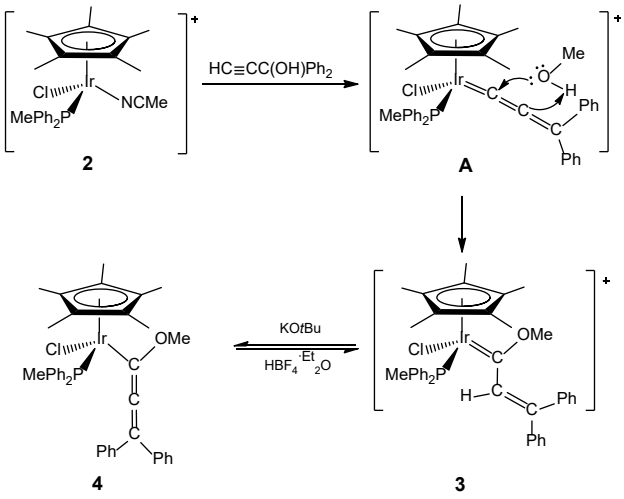
Table 1. Selected Bond Lengths [Å] and Angles [°] for 4

Ir–[a]CT01	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(14)	1.355(6)	C(11)–C(12)	1.464(7)
O(1)–C(12)	1.317(6)	O(1)–C(13)	1.471(6)
[a]CT01–Ir–C(12)	128.18(14)	[a]CT01–Ir–Cl	120.73(3)
[a]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.

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 the complex **3** can be regenerated by addition of one equivalent of $HBF_4 \cdot Et_2O$ to a dichloromethane solution of **4** (Scheme 1).

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

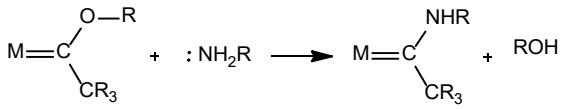


In the ^1H NMR spectrum of **4** the most noticeable feature is the absence of the C*H*=CPh_2 resonance. In the $^{13}C\{^1H\}$ NMR spectrum the resonance of the α–carbon atom of the allenyl ligand is observed as a doublet at 123.0 ppm with a C–P coupling constant of 17.7 Hz, the β–carbon and γ–carbon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

Heterolytic Cleavage of the Carbon(sp^3)–Oxygen Bond of the (Methoxy)alkenylcarbeneiridium Complex by Amines.

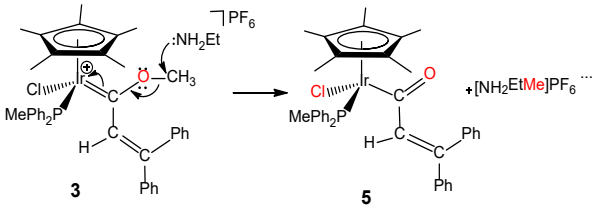
The analogue of a metal alkoxy–carbene complex in organic chemistry is an ester. This analogy is very useful to explain the development of metal alkoxy–carbene reactions. For example, the reaction of an ester with primary or secondary amines results in an amide, which is an aminolysis reaction. The same reaction appears in organometallic chemistry.[3] It is usually assumed that the reaction of a primary or a secondary amine with an alkoxy–carbene is through the attack at the carbene carbon, producing an amino–carbene, Scheme 2.

Scheme 2. Reaction of Aminolysis of a Metal Alkoxy–carbene.



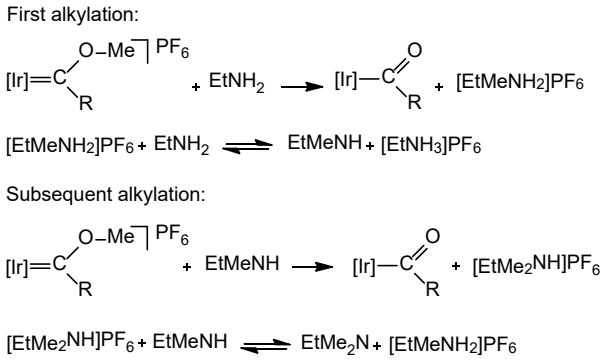
Unexpectedly, when a dichloromethane solution of the methoxy–carbene compound **3** was reacted with a wide variety of amines ($MeNH_2$, $EtNH_2$, Et_2NH, $PrNH_2$, Pr_2NH, $PhNH_2$, $CyNH_2$, Cy_2NH, piperidine, NEt_3) we have observed in all cases the formation of the acyl complex $[IrCp^*Cl\{C(O)CH=CPh_2\}(PPh_2Me)]$ **(5)**. As it is well known, the Fischer–type carbenes react with water to give hydroxy–carbenes by nucleophilic substitution of the alkoxy group (eliminated as alcohol)[13] and the hydroxy–carbenes (generally unstable) may degrade to give acyl derivatives.[13c,14] To rule out this possibility we treated compound **3** with water but the compound **3** remains 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.

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

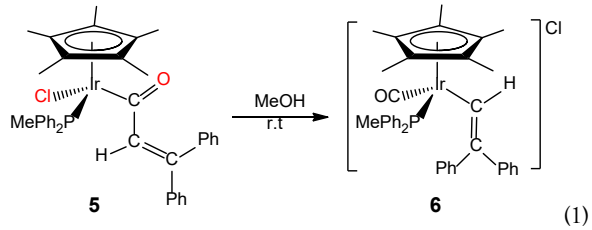


Additionally, we have observed that the formation of acyliridium complex **5** comes always with a mixture of ammonium salts with different degrees of methylation. This finding indicates that the methoxycarbene **3** behaves as a methylating agent of amines, in a similar way to well–known methylhalides reacting with nitrogen nucleophiles in an organic reaction,[15] Scheme 4. Another finding supporting this proposal occurs when the reaction is carried out with the tertiary amine Et_3N, in this case only the ammonium salt $[Et_3MeN]PF_6$ is accompanying the formation of complex **5**.

Scheme 4. Methylation of Amines by Metal Methoxy–carbene.



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 the $CHCPh_2$. 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 the 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 the complex **5** shows a band at 1577cm^{-1} due to the $\nu_{(CO)}$ of the acyl ligand. The 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 were found in literature.[13c,14b]



(1)

The presence of a terminal carbonyl ligand in complex **6** is confirmed by a strong IR band at 2035 cm^{-1} $\nu_{(CO)}$, 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. Besides, 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 in 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.

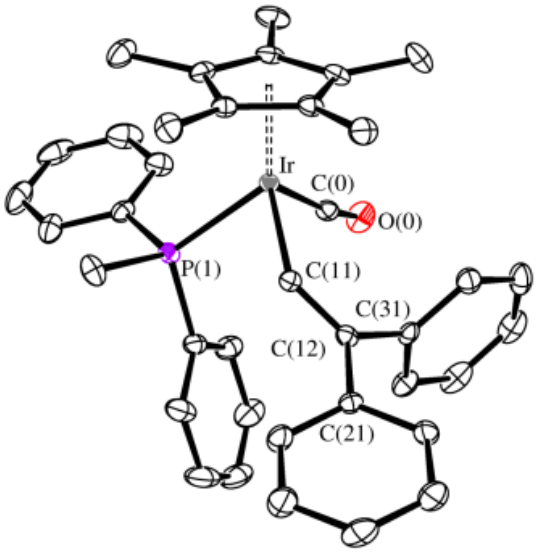


Figure 2. The Cation Complex $[IrCp^*(CH{=}CPh_2)(CO)(PPh_2Me)]^+$ (**6**)

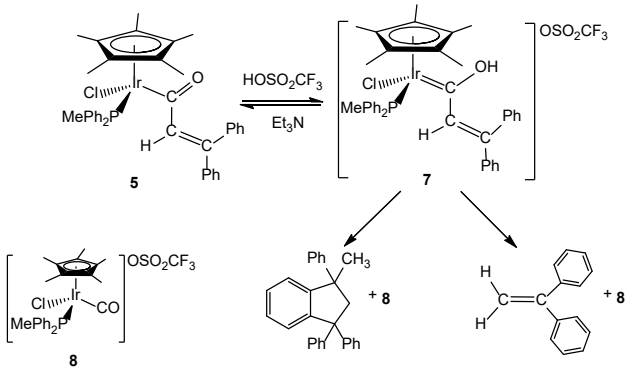
Table 1. Selected Bond Lengths [Å] and Angles [°] for 4

Ir–C(0)	1.869(3)	Ir–[a]CT01	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–[a]CT01	125.36(9)
[a]CT01–Ir–C(11)	118.48(8)	[a]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.

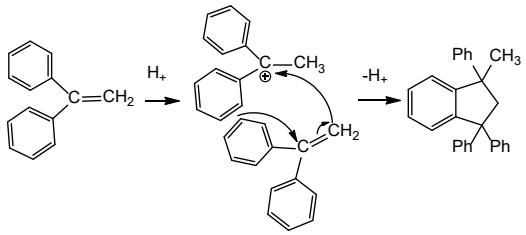
When 1.1 equivalents of a strong acid ($HBF_4{\cdot}Et_2O$ or $HOSO_2CF_3$) were added to **5** in a solution of dichloromethane the hydroxycarbene $[IrCp^*Cl\{{=}C(OH)CH{=}CPh_2\}PPh_2Me]X$ (**7**) (X = BF_4 or OSO_2CF_3) was isolated as a red solid in 87% yield. This reaction is reversible by addition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

Scheme 5. Formation of Hydroxycarbene and its Evolution to 1,1–Diphenylethene and 3–Methyl–1,1,3–triphenylindane.



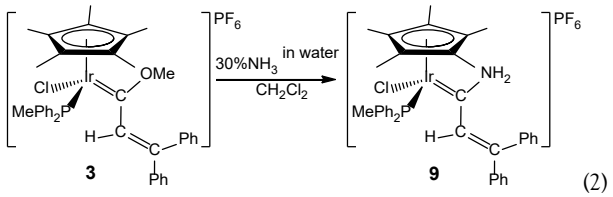
The hydroxycarbene **7** was unambiguously characterized by NMR spectroscopy ({^{1}H, ^{13}C} HMBC, {^{1}H, ^{13}C} HSQC, ^{13}C{^{1}H}) and confirmed by refluxing complex **2** with water and 1,1–diphenyl–2–propyn–1–ol for 30 minutes.[16] If the reaction mixture of **5** and trifluoromethanesulfonic acid is set aside for two hours the carbonyl complex **8**[17] and 1,1–diphenylethene[18] were formed. Moreover, when the same reaction is performed with four equivalents of acid and set aside overnight the 1,1–diphenylethene transforms into 3–methyl–1,1,3–triphenylindane.[19] A plausible mechanism (Scheme 6) may involve the reaction of 1,1–diphenylethene with the excess of acid. A similar reaction was found in literature[20] but the mechanism was not reported.

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



Aminolysis *via* Aqueous Ammonia Solution.

Surprisingly and contrary 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$_2$)CH=CPh$_2$}PPh$_2$Me]PF$_6$ (**9**) was obtained as an orange solid in a 82% yield (eq. 2).



(2)

The ^{1}H NMR spectrum of **9** shows a singlet at 6.8 ppm for C$_\beta$–*H*, and two broad singlets at 8.3 and 9.7 ppm corresponding to the N*H*$_2$ group.[21] Its ^{13}C{^{1}H} 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 coupling constant C–P of 11.9 Hz. All the proton and carbon resonances of **9** were unambiguously assigned by means of {^{1}H, ^{13}C} HSQC, {^{1}H, ^{13}C} HMBC and {^{1}H,^{1}H} COSY experiments.

CONCLUSION

In this paper we have reported the formation of the first half–sandwich allenylidene complex of iridium by Selegue reaction and the first methoxyalkenyliridium carbene *via* allenylidene complex. In addition, we have studied the behavior of this iridium carbene complex with amines and we have observed an unusual nucleophilic attack of the amine at the Carbon(sp^3)–Oxygen bond, which gives an acyl complex and amine alkylation. By contrast, the ammonia forms a primary amino–carbene 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 to a nucleophilic one because ammonia nucleophilicity 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$_2$Me)] (**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 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, ^{19}F{^{1}H} is referred to CFCl$_3$ and those of ^{31}P{^{1}H} to 85% H$_3$PO$_4$; 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 in 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 polarisation effects. The software SMART[23] was used for collecting frames of data, 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 a 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.

Details of crystal data and structural refinement for complex **3** and **6** are given in Table 3.

Table 3. Crystal Data and Structure Refinement for Complex 3 and 6.

Empirical formula	$C_{39}H_{42}ClF_6IrOP_2$	$C_{62}H_{59}BIrOP$
Formula weight	930.32	1054.07
Temperature (K)	183(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*–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(°)	90	73.8360(10)
β(°)	101.3580(10)	87.8390(10)
γ(°)	90	72.0190(10)
Volume (Å^3)	7552.2(10)	2530.7(3)
Z	8	2
Density (Mg/m^3)	1.636	1.383
Absorption coefficient (mm^{-1})	3.751	2.711
F(000)	3696	1072
Crystal size (mm)	0.48 x 0.37 x 0.05	0.43 x 0.31 x 0.29
Theta range for data collection (°)	1.66 to 28.03	1.79 to 28.01
Index ranges	–53≤h≤52;	–15≤h≤14;
	–15≤k≤16;	–12≤k≤16;
	–19≤l≤18	–23≤l≤24
Reflections collected	24349	17026
Independent reflections	8969	11736
	[R(int) = 0.0456]	[R(int) = 0.0247]
Reflections observed (>2σ)	6308	10081
Data Completeness	0.979	0.959
Absorption correction	Semi–empirical from equivalents	Semi–empirical 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	Full–matrix least–squares on F^2
Data / restraints / parameters	8969 / 0 / 460	11736 / 0 / 601
Goodness-of-fit on F^2	1.044	1.003
R_1/wR_2 [I>2σ(I)]	R_1 = 0.0348	R_1 = 0.0294
	wR_2 = 0.0727	wR_2 = 0.0600
R indices (all data)	R_1 = 0.0703	R_1 = 0.0401
	wR_2 = 0.0883	wR_2 = 0.0647
Largest diff. peak and hole (e. Å^{-3})	1.619 and –0.979	1.098 and –0.735

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. Solvent was vacuum removed and the solid obtained was redissolved in dichloromethane. The solution was filtered through Celite® again and the solvent was vacuum removed to yield a yellow solid that was washed with diethyl ether (3 x 2 mL). Finally it was dried in vacuum. Yield: 600 mg (96%). ^{1}H NMR (CD_2Cl_2): δ 7.45–7.70 (m, 10H, P*Ph*$_2$CH$_3$); 2.39 (s br, 3H, NCC*H*$_3$); 2.31 (d, 3H, $^2J_{H-P}$ = 10.8 Hz, PPh$_2$C*H*$_3$); 1.54 (d, 15H, $^4J_{H-P}$ = 2.4 Hz, C$_5$(C*H*$_3$)$_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –9.75 (s, *P*Ph$_2$CH$_3$); –144.10 (sept, $^1J_{P-F}$ = 710.8 Hz, *P*F$_6$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 128.6–133.9 (C P*Ph*$_2$Me); 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$_2$CH$_3$); 8.7 (s, C$_5$(CH$_3$)$_5$); 4.0 (s, NCCH$_3$) ppm. IR (cm^{-1}): ν(CN) 2324 (w), 2296 (w); (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 of colour 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, 243K): δ 7.22–7.97 (m, *Ph*); 2.29 (d, 3H, $^2J_{H-P}$ = 11.5 Hz, PPh$_2$C*H*$_3$); 1.63 (s, 15H, C$_5$(C*H*$_3$)$_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2, 243K): δ –3.93 (s, *P*Ph$_2$CH$_3$); –144.27 (sept, $^1J_{P-F}$ = 711.5 Hz, *P*F$_6$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 243K): δ 238.7 (d, $^2J_{C-P}$ = 16.3 Hz, Cα); 175.3 (s, Cγ); 169.4 (s, Cβ); 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$_2$CH$_3$); 8.7 (s, C$_5$(CH$_3$)$_5$); ppm. IR (cm^{-1}): ν(=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 in 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 x 8 mL) and dried in vacuum. Recrystallization of this complex from a mixture of CH_2Cl_2/MeOH (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, P*Ph*$_2$CH$_3$); 7.45–7.54 (m, 5H, C*Ph*$_2$ + P*Ph*$_2$CH$_3$); 7.35–7.44 (m, 3H, C*Ph*$_2$); 7.21–7.29 (m, 2H, C*Ph*$_2$); 6.93–7.00 (m, 2H, C*Ph*$_2$); 6.68–6.76 (m, 2H, C*Ph*$_2$); 5.37 (s, 1H, Cβ–*H*); 3.91 (s br, 3H, OC*H*$_3$); 2.41 (d, 3H, $^2J_{H-P}$ = 10.5 Hz, PPh$_2$C*H*$_3$); 1.53 (d, 15H, $^4J_{H-P}$ = 2.0 Hz, C$_5$(C*H*$_3$)$_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –14.97 (s, *P*Ph$_2$CH$_3$); –144.11 (sept, $^1J_{P-F}$ = 710.6 Hz, *P*F$_6$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 263.3 (s br, Cα); 148.6 (s, Cγ); 139.8 (s, C_{ipso}–Ph); 139.5 (s, C_{ipso}–Ph); 136.6 (s, Cβ–H); 133.3 (d, $^2J_{C-P}$ = 9.4 Hz, C P*Ph*$_2$Me); 132.8 (d, $^2J_{C-P}$ = 9.4 Hz, C P*Ph*$_2$Me); 132.3 (d, $^3J_{C-P}$ = 2.8 Hz, C P*Ph*$_2$Me); 132.2 (d, $^3J_{C-P}$ = 2.8 Hz, C P*Ph*$_2$Me); 131.1 (d, $^1J_{C-P}$ = 32.6 Hz, P–C_{ipso}); 130.8 (s, 1C C*Ph*$_2$); 130.6 (s, 1C C*Ph*$_2$); 130.5 (d, $^1J_{C-P}$ = 31.9 Hz, P–C_{ipso}); 129.6 (s, 1C C*Ph*$_2$); 129.5 (s, 1C C*Ph*$_2$); 129.5 (s, 2C C*Ph*$_2$); 129.5 (s, 1C C*Ph*$_2$); 129.4 (s, C P*Ph*$_2$Me); 129.4 (s, C P*Ph*$_2$Me); 129.4 (s, 1C C*Ph*$_2$); 128.81 (s, 2C C*Ph*$_2$); 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$_2$CH$_3$);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): m/z: 785 [M]$^+$. Anal. Calcd for $C_{39}H_{42}OClF_6IrP_2$ (930.37 g/mol): C 50.35, H 4.55; found: C, 50.43; H, 4.59.

Preparation of [IrCp*Cl{C(OMe)=C=CPh_2}(PPh_2Me)] (4). KtBuO (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 to vacuum giving an oil, which was treated with diethyl ether. The brown solid formed was separated by decantation, washed with diethyl ether (3 x 2 mL) and dried in vacuum. Yield: 51 mg (60%). ^{1}H NMR (CD_2Cl_2): δ6.94–7.81 (m, 20H, *Ph*); 3.59 (s br, 3H, OC*H*$_3$); 2.18 (d, 3H, $^2J_{H-P}$ = 9.8 Hz, PPh$_2$C*H*$_3$);1.38 (d, 15H, $^4J_{H-P}$ = 2.1 Hz, C$_5$(C*H*$_3$)$_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –8.88 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 197.0 (s, Cβ); 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 P*Ph*$_2$Me); 133.9 (d, $^1J_{C-P}$ = 52.2 Hz P–C_{ipso}); 133.3 (d, $^2J_{C-P}$ = 9.5 Hz, C P*Ph*$_2$Me); 130.2 (d, $^3J_{C-P}$ = 2.5 Hz, C P*Ph*$_2$Me); 130.1 (d, $^3J_{C-P}$ = 2.5 Hz, C P*Ph*$_2$Me); 128.9 (s, C C*Ph*$_2$); 128.7 (s, C C*Ph*$_2$); 128.1 (s, C P*Ph*$_2$Me); 128.0 (s, C C*Ph*$_2$); 127.9 (s, C P*Ph*$_2$Me); 127.8 (s, C C*Ph*$_2$); 126.1 (s, C C*Ph*$_2$); 125.6 (s, C C*Ph*$_2$); 123.0 (d, $^2J_{C-P}$ = 17.7 Hz, Cα); 112.5 (s, Cγ); 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}): ν (C=C=C) 1889 (w). MS (m/z, referred to the most abundant isotopes): m/z: 785 $[M+1]^+$. Anal. Calcd for $C_{39}H_{41}OClIrP$ (784.4 g/mol): 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 five minutes at room temperature, and then the solvent was vacuum removed obtaining 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 being the acyl complex **5** 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 vacuum removed giving a yellow solid that was washed with methanol (3 x 6 mL) and dried under vacuum. Yield: 350 mg (47%). ^{1}H NMR (C_6D_6): δ 7.67 (s, 1H, Cβ–*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, Cα); 144.9 (s, C_{ipso}–Ph); 143.2 (d,$^3J_{C-P}$ = 2.6 Hz, Cβ); 141.1 (s, C_{ipso}–Ph); 136.5 (s, Cγ); 134.6 (d, $^1J_{C-P}$ = 53.4 Hz,P–C_{ipso}); 134.5 (d, $^2J_{C-P}$ = 9.8 Hz, C P*Ph*$_2$Me); 133.1 (d, $^2J_{C-P}$ = 9.5 Hz, C P*Ph*$_2$Me); 132.9 (d, $^1J_{C-P}$ = 54.1 Hz, P–C_{ipso}); 131.8 (s, C P*Ph*$_2$Me); 130.2 (d, $^3J_{C-P}$ = 2.4 Hz, C P*Ph*$_2$Me); 129.9 (d, $^3J_{C-P}$ = 2.4 Hz, C P*Ph*$_2$Me); 129.5 (s, C P*Ph*$_2$Me); 128.4 (s, C C*Ph*$_2$); 127.6–128.4 (some signals are overlapped with solvent's signal); 127.3 (s, C C*Ph*$_2$); 127.2 (s, C C*Ph*$_2$); 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): m/z: 771 $[M+1]^+$, 735 $[M–Cl]^+$. Anal. Calcd for $C_{38}H_{39}OClIrP$ (770.37g/mol): 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 24h. Then, the solvent was vacuum removed yielding a white precipitate which was washed with pentane (3 x 3 mL) and, finally dried in 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. **[IrCp*(CH=CPh$_2$)(CO)(PPh$_2$Me)]PF$_6$**: ^{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_2CH_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_2CH_3); –143.94 (sept, $^1J_{P-F}$ = 710.4 Hz, *P*F_6) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 165.3 (d, $^2J_{C-P}$=13.7 Hz, CO); 152.1 (s, CH=CPh$_2$); 146.0 (s, Ph–C_{ipso}); 144.3 (s, Ph–C_{ipso}); 133.4 (d, $^3J_{C-P}$ = 2.8 Hz, C P*Ph*$_2$Me); 132.7 (d, $^3J_{C-P}$ = 2.8 Hz, C P*Ph*$_2$Me); 132.4 (d, $^2J_{C-P}$ = 10.0 Hz, C P*Ph*$_2$Me); 132.2 (d, $^2J_{C-P}$ = 10.0 Hz, C P*Ph*$_2$Me); 130.1 (s, C C*Ph*$_2$); 130.0 (d, $^2J_{C-P}$ = 11.3 Hz, C P*Ph*$_2$Me); 129.5 (d, $^2J_{C-P}$ = 11.4 Hz, C P*Ph*$_2$Me); 128.9 (s, C C*Ph*$_2$); 128.7 (s, C C*Ph*$_2$); 128.1 (s, C C*Ph*$_2$); 127.8 (s, P–C_{ipso}); 127.2 (s, C C*Ph*$_2$); 127.1 (s, P–C_{ipso}); 126.9 (s, C C*Ph*$_2$); 115.1 (d, $^2J_{C-P}$ = 13.9 Hz, CH=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_2CH_3); 9.0 (s, $C_5(CH_3)_5$) ppm. IR (cm^{-1}): ν (CO) 2035 (s); (PF_6) 840 (s). MS (m/z, referred to the most abundant isotopes): m/z: 735 $[M]^+$. Anal. Calcd for $C_{38}H_{39}OF_6IrP_2$ (880g/mol): 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), trifluoromethanesulfonic acid (17 µL, 0.19 mmol) was added 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 x 4 mL). Finally, the red solid obtained was dried in 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, Cβ–*H*); 7.03–7.10 (m, 2H, C*Ph*$_2$); 2.26 (d, 3H, $^2J_{H-P}$ = 10.2 Hz, PPh_2CH_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_2CH_3) ppm. ^{19}F{^{1}H} NMR (CD_2Cl_2): δ –78.92 (s, *C*F_3SO_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 159.5 (s, Cγ); 133.7 (s, Cβ); 99.5 (s, $C_5(CH_3)_5$); 13.8 (d, $^1J_{C-P}$ = 39.6 Hz, PPh_2CH_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): m/z: 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 two hours, a new organometallic compound and an organic substrate. The NMR data indicate that the organometallic complex is $[IrCp^*Cl(CO)(PPh_2Me)](OSO_2CF_3)$ (**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 obtaining a brown solution. After the solvent was removed under reduced pressure, brown oil was obtained. This oil was treated with diethylether giving a precipitate, which was filtrated and washed with pentane (2 x 2 mL). This solid was characterized as complex **8**. On the other hand, the diethylether solution was passed through a silica column giving a brown oil that was identified as 3–methyl–1,1,3–triphenylindane.

8·OSO$_2$CF$_3$: ^{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_2CH_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_2CH_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{^{1}H} NMR (CD_2Cl_2) (not previously reported): δ 166.1 (d, $^2J_{C-P}$ = 14.3 Hz, CO); 132.6–133.3 (C P*Ph*$_2$Me); 129.4–129.8 (C P*Ph*$_2$Me); 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. **1,1–Diphenylethene:** ^{1}H NMR (CD_2Cl_2): δ 7.31–7.36 (m, 10H, *Ph*$_2$); 5.47 (s, 2H, CH_2) ppm. ^{13}C{^{1}H} 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. **3–Methyl–1,1,3–triphenylindane:** ^{1}H NMR (CD_2Cl_2): δ 7.00–7.36 (m, 19H, *Ph*); 3.39 (d, 1H$_B$, system AB, $^{2}J_{H-H}$ = 13.4 Hz CH_2); 3.13 (d, 1H$_A$, system AB, $^{2}J_{H-H}$ = 13.4 Hz CH_2); 1.56 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} 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, CPh_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 minutes, and then the solvent was vacuum removed obtaining an orange oil that was precipitated and washed with pentane (3 x 6mL). Finally it was dried in vacuum. Yield: 362 mg (82 %). ^{1}H 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$_\beta$–*H*); 2.19 (d, 3H, $^{2}J_{H-P}$=10.1 Hz, PPh$_2$CH_3); 1.61 (d, 15H, $^{4}J_{H-P}$=2.2 Hz, C$_5$(CH_3)$_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –13.39 (s, PPh_2CH$_3$); –144.15 (sept, $^{1}J_{P-F}$=710.6 Hz, PF_6) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 209.9 (d, $^{2}J_{C-P}$ = 11.9 Hz, C$_\alpha$); 150.4 (s, C$_\gamma$); 139.3 (s, C$_{ipso}$–*Ph*); 136.7 (s, C$_{ipso}$–*Ph*); 133.0 (d, $^{2}J_{C-P}$ = 9.9 Hz, C PPh_2Me); 132.6 (d, $^{2}J_{C-P}$ = 9.7 Hz, C PPh_2Me); 132.1 (d, $^{3}J_{C-P}$ = 2.7 Hz, C$_\beta$–H); 132.0 (d, J_{C-P} = 2.2 Hz, C PPh_2Me); 131.9 (d, $^{3}J_{C-P}$ = 2.8 Hz, C PPh_2Me); 131.4 (s, C CPh_2); 130.7 (d, $^{1}J_{C-P}$ = 43.1 Hz, P–C$_{ipso}$); 130.6 (s, C CPh_2); 130.4 (s, C CPh_2); 130.1 (d, $^{1}J_{C-P}$ = 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, $^{2}J_{C-P}$ = 2.2 Hz, C$_5$(CH$_3$)$_5$); 13.9 (d, $^{1}J_{C-P}$ = 41.8 Hz, PPh$_2$CH$_3$); 8.9 (s, C$_5$(CH$_3$)$_5$) ppm. IR (cm^{-1}): ν(N–H) 3370 (m); (PF_6) 840 (s). MS (m/z, referred to the most abundant isotopes): m/z: 770 [M]$^+$. Anal. Calcd for $C_{38}H_{41}ClF_6IrNP_2$ (915.36 g/mol): C 49.86, H 4.51; N 1.53; found: C 49.98; H 4.57; N 1.57.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data for compounds **3** and **6** (cif) and computational details. 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.

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Nucleophilic Attack in Methoxy–carbenes: Heterolytic Cleavage of the Carbon(sp^3)–Oxygen Bond Versus Aminolysis.

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