Synthesis, Structural Characterization, and Chemistry of a Monomeric Cationic Iridium Carbyne Complex

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The synthesis and characterization of compounds containing multiple bonds between carbon and transition metals has played an important role in fundamental organometallic chemistry, in advancing our understanding of a variety of industrially important processes and in the development of novel synthetic transformations.[1−8] While a number of terminal and bridging carbyne complexes have been prepared, terminal carbyne complexes containing a group 9 metal are very rare.[9−11] We report here the generation, isolation, structure determination, and preliminary chemistry of a stable terminal iridium carbyne complex, $[(Cp')(PMe_3)Ir\equiv CPh]^+BAr_f^-$ (**1**) ($Cp' = \eta^5\text{-}C_5Me_4Et$; $BAr_f = B[C_5H_3(3,5\text{-}CF_3)_2]_4$).

The synthetic route to **1** employed is outlined in Scheme 1. These reactions proceed cleanly with the analogous $\eta^5\text{-}C_5Me_5$ (Cp*) complexes, but because of their increased crystallinity, only the $\eta^5\text{-}C_5Me_4Et(Cp')$ complexes are presented here. This synthetic approach involves O-methylation of iridium acyl complex **2**, to afford the cationic hydrido Fischer carbene complex **3** in 89% yield. Deprotonation of **3** using LiN(TMS)₂ in THF at −40 °C affords the neutral Fischer carbene complex **4** in 62% yield. The addition of 1 equiv of trimethylsilyl triflate to **4** in pentane at −40 °C results in gradual formation of carbyne salt **5** as an off-white precipitate. Upon evacuation, the solid and solution darken to a gray-green color. Analysis of the volatile products indicates that trimethylsilyl methyl ether is the only byproduct of this reaction. We presume that this reaction proceeds by direct silylation of the oxygen atom to form a silyloxonium complex, which subsequently evolves the silyl ether byproduct. When more conventional abstraction agents such as boranes[12] are employed, a mixture of products is obtained. Analysis of these product mixtures by NMR spectroscopy indicates that the cationic carbyne is present in small quantities. Crude **5**, despite being clean by NMR, cannot be recrystallized. Therefore, the triflate counterion was metathesized using NaBAr_f to afford **1** in 84% yield. The ¹H NMR spectrum of **1** in CD_2Cl_2 exhibits a single trimethylphosphine resonance at δ 1.65 ppm (d), two ring methyl resonances at δ 2.22 and 2.25 ppm, ring ethyl resonances at δ 1.18 (t) and 2.49 ppm (q), and three phenyl resonances at δ 7.45
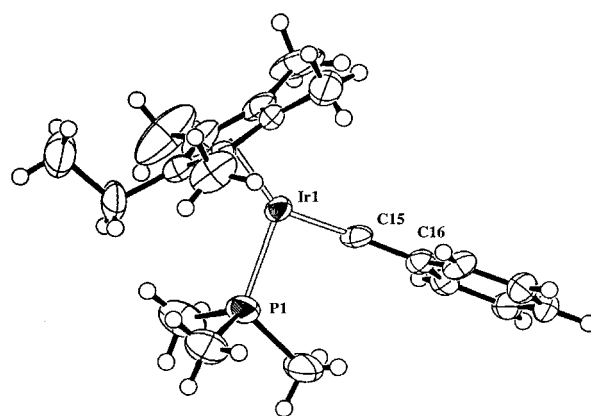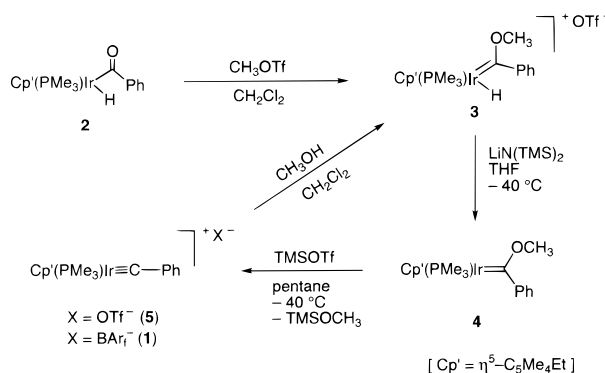

Figure 1. ORTEP diagram of the cationic portion of **1**.

Scheme 1

[Cp' = η^5–C₅Me₄Et]

(t), 7.83 (d), and 7.89 ppm (t), as well as resonances corresponding to the BAr_f anion. The ³¹P{¹H} NMR spectrum exhibits a singlet at δ −49.7 ppm. The ¹³C{¹H} NMR spectrum displays a broad singlet resonance at δ 296.9 ppm, which is within the range of chemical shifts observed for other transition metal carbyne complexes.[2,12]
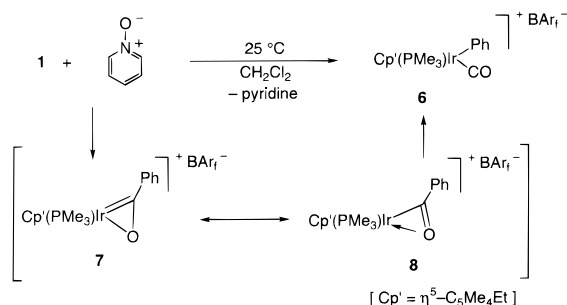
A single crystal was grown by slow vapor diffusion of Et₂O into a CH_2Cl_2 solution of **1** at −40 °C. An X-ray diffraction study was carried out on this sample and the structure solved by direct methods and refined using least-squares methods. An ORTEP diagram of the cationic portion of **1** is shown in Figure 1. The Ir−C(15) bond distance is 1.734(6) Å, the Ir−C(15)−C(16) angle is 175.7(4)°, and the iridium, phosphorus, and carbon atoms are coplanar. Additionally, there are no unusual contacts between the cation and the anion. A full description of the data collection and positional parameters is presented in the Supporting Information.

In contrast to related carbyne complexes,[9−11] the cationic benzylidyne complex **1** is exceptionally thermally stable in dry degassed CH_2Cl_2 and THF, decomposing to unknown products only at temperatures above 105 °C. The thermal stability of **1** has allowed us to explore its reactivity. The carbyne complex reacts readily with pyridine *N*-oxide to form cationic phenyl carbonyl complex **6** in 94% yield. We presume that this reaction proceeds by the mechanism outlined in Scheme 2. The initial step is oxygen atom transfer to the iridium−carbon triple bond of **1** to form an intermediate complex which can be represented by either an oxairidacyclopropene (**7**) or an η^2-acyl (**8**) resonance structure.[13] The cationic acyl complex **8** has been proposed as

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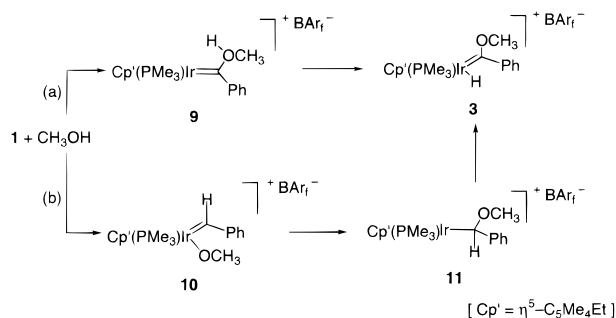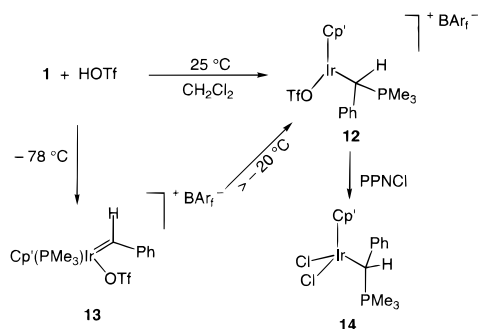
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Scheme 2

Scheme 3

Scheme 4

an intermediate in the C−H activation of benzaldehyde by (η^5-C$_5$Me$_5$)(PMe$_3$)Ir(Me)(OTf); it rapidly rearranges to form the analogous cationic phenyl carbonyl complex by migratory deinsertion.[14]

Upon exposure of **1** to dry degassed CH$_3$OH at 25 °C, the hydrido Fischer carbene complex **3** is regenerated cleanly and isolated in 95% yield. Two mechanistic extremes for the addition of CH$_3$OH to **1** are shown in Scheme 3. Pathway a involves initial nucleophilic attack of the oxygen atom at the carbyne carbon of **1** to form the oxonium complex **9**, which subsequently rearranges by a proton shift to form the observed product **3**. Pathway b involves initial proton transfer, followed by attack of methoxide at Ir to form benzylidene complex **10**, which rearranges to a methoxy benzyl complex **11** and subsequently forms **3** via α-hydrogen migration. Heating a CD$_2$Cl$_2$ solution of **3** in the presence of 4-Å molecular sieves at 95 °C for extended periods of time does not afford **1**. We therefore assume that this equilibrium greatly favors carbene complex **3**.[15]

We have also examined the reactivity of **1** with stronger protic acids. The addition of HOTf to **1** in CH$_2$Cl$_2$ at 25 °C results in rapid formation of ylide complex **12** (Scheme 4), which can be isolated in 85% crude yield. The ^{31}P{^{1}H} NMR spectrum of this

complex displays a singlet resonance at δ 25.5 ppm, which is in the range typical of phosphonium ylide complexes.[16,17] The ^{19}F{^{1}H} NMR spectrum displays normal resonances for the BAr$_f^-$ and OTf$^-$ moieties. Formation of **12** is consistent with initial generation of benzylidene complexes **13**, which is unstable with respect to phosphine migration.[18] Due to the instability of this compound in solution, it has been characterized by derivatization with PPNCl to form Cp′Ir(CH(Ph)PMe$_3$)Cl$_2$ (**14**), which has been generated independently by the addition of trimethylbenzylidenephosphorane to [Cp′IrCl$_2$]$_2$.

To obtain additional information about the protonation of carbyne complex **1**, we monitored its reaction with HOTf at −78 °C in CD$_2$Cl$_2$ by low-temperature NMR spectroscopy. The ^{1}H NMR spectrum at −30 °C displays a broad singlet at δ 18.74 ppm, broad aryl resonances, and broadened resonances for the Cp′ and PMe$_3$ ligands. The ^{31}P{^{1}H} NMR spectrum exhibits a singlet resonance at δ −45.1 ppm, indicative of an iridium-bound trimethylphosphine ligand.[19] These data are consistent with the benzylidene structure **13** shown in Scheme 4. When DOTf is used, the resonance at δ 18.74 ppm is absent, which further supports the assigned structure. Benzylidene complex **13** is stable at temperatures below −20 °C, but at higher temperatures, rearrangement to **12** is observed. Addition of the stronger acids HBF$_4$ and H(Et$_2$O)BAr$_f$ to **1** at −78 °C results in immediate decomposition. This indicates that the presence of the triflate anion is important for the stabilization of **13**, most likely by coordination to the electrophilic iridium center. Addition of NaBAr$_f$ to **12** also results in decomposition. Interestingly, the addition of styrene to **13** at −30 °C results in the formation of 1,2-diphenylcyclopropane (eq 1), isolated in 95% yield as a 2:1

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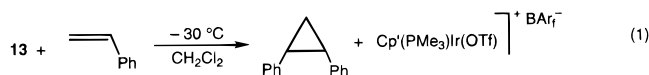
ratio of trans and cis isomers.

In summary, we have synthesized and crystallographically characterized a terminal iridium carbyne complex. Complex **1** reacts readily with protic acids and amine *N*-oxides; both processes probably occur by reaction at the α-carbon atom. This is supported by the fact that protonation of **1** at low temperature forms a highly electrophilic alkylidene complex which is capable of mediating cyclopropanation of styrene. We are currently examining the scope and mechanism of the cyclopropanation reaction and further studying the reactivity of this novel carbyne complex.

Supporting Information Available: Spectroscopic and analytical data for all new complexes and, additionally, X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional parameters, and intramolecular distances and angles) for **1** (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(19) The resonances in the ^{13}C{^{1}H} NMR spectrum of **13** are broad; therefore, we have not been able to assign a resonance to the α-carbon.