ORGANOMETALLICS

Note

A Cationic Terminal Methylene Complex of Ir(I) Supported by a Pincer Ligand

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Supporting Information

ABSTRACT: A rare example of a cationic methylene complex of Ir(I), [(PONOP)-Ir(CH₂)]⁺, **2** (PONOP = 2,6-bis(di-*tert*-butylphosphinito)pyridine), has been prepared by α -hydride abstraction from the previously described neutral methyl complex [(PONOP)Ir(CH₃)]. The intrinsic high reactivity of the compound prevented both the isolation of a pure solid and its full characterization in the solid state. Nevertheless, the proposed molecular structure finds unequivocal support in multinuclear NMR spectroscopy and in reactivity studies that include reactions with Lewis bases, dihydrogen, and ethyl diazoacetate. An ylide compound, 3, resulted from



the reaction between $[(PONOP)Ir(CH_2)]^+$ and PMe₃, while the η^2 -alkene complex 5 formed in a C=C coupling reaction involving the methylene ligand of 2 and ethyl diazoacetate. Hydrogenolysis of the Ir=CH₂ linkage of 2 led to several, previously known, hydride and dihydrogen iridium complexes.

S ince the original report by Fischer and Maasböl of the first heteroatom carbene complex,¹ transition metal carbenes have become one of the most prominent families of organometallic compounds.^{2,3} The past 15 years have witnessed remarkable advances in the chemistry of carbene complexes of rhodium and iridium, both with and without stabilizing heteroatoms,³⁻¹² including the accessibility of O- and Nsubstituted carbenes by double C–H bond activation reactions.^{4,5,8-11}

It was early recognized that metal alkylidene compounds, that is, carbene complexes that possess only hydrogen or hydrocarbyl substituents, were of special interest due to their higher reactivity compared to heteroatom-stabilized carbene complexes.¹³ Schrock's discovery of an isolable nucleophilic $Ta = CH_2$ complex¹⁴ called attention to the simple methylene ligand, in both mononuclear and binuclear systems.^{15,16} Terminal methylene ligands may exhibit nucleophilic or electrophilic reactivity at the carbene carbon atom.13-15 Whereas, as already indicated, a wealth of experimental and theoretical information has accumulated concerning Rh and Ir carbene complexes over the years, only a few examples of their methylene derivatives are known to date. Following initial studies by Thorn and Tulip¹⁷ and by Roper and co-workers, ^{13b,15a,18} a major advance in this field was the structural characterization by Fryzuk's group of an isolable Ir(I)methylene complex.¹⁹ In all these early examples the Ir= CH₂ moiety featured electrophilic reactivity, whereas the complex $(\eta^5 - C_5 Me_5) Ir(CH_2)(PMe_3)$ described in 1989 by Bergman and Klein exhibited nucleophilic character.²⁰

Rhodium and iridium complexes bearing the ancillary tridentate pincer ligand 2,6-bis(di-*tert*-butylphosphinito)-pyridine (PONOP, in shorthand notation) have recently

demonstrated utility in stabilizing elusive species such as σ -CH₄²¹ complexes or related σ -H₂ derivatives.²² Moreover, they have provided relevant mechanistic information regarding C–H bond activation, metal–carbon bond hydrogenolysis, and other important organometallic transformations.²³ The high level of steric protection provided by this ligand is believed to be responsible for the kinetic stabilization of its complexes, which allows detecting and studying reactive intermediates often invoked as key participants in catalytic and stoichiometric reactions.

We have recently discussed the generation of electrophilic cationic alkylidene complexes of $Ir(III)^{24a}$ and $Pt(II)^{24b}$ by α -hydride abstraction reactions from the appropriate metalacyclic precursor. The alkylidene functionality of these complexes was part of a sterically protected five-membered ring originally derived from the facile metalation of a xylyl phosphine, PMeXyl₂^{24a} and PiPr₂Xyl,^{24b} respectively (Xyl = 2,6-dimethyl-phenyl). Accordingly, we envisaged that the bulky PONOP ligand might stabilize a fleeting cationic Ir(I) methylene species, [(PONOP)Ir(CH₂)]⁺, obtained by α -hydride abstraction from the methyl terminus of (PONOP)Ir(CH₃).^{23a}

In agreement with expectations, we found that treatment of a C_6D_5Br solution of 1 with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ at -20 °C resulted in a rapid color change from orange to dark green. Investigation of the reaction by NMR spectroscopy showed the selective formation of the desired complex (Scheme 1) and concomitant disappearance of its precursor 1. No other products were detected. In the ${}^{31}P\{{}^{1}H\}$ NMR spectrum of 2, the singlet at 186.4 ppm corresponding to the starting methyl

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complex was replaced by a new, also sharp singlet at 180.2 ppm, suggesting that the integrity of the [(PONOP)Ir]⁺ moiety was maintained in the new compound **2**. At the same time, the ¹H and ¹³C{¹H} NMR signals due to the iridium-bound methyl group in **1** experienced a remarkable shift to higher frequencies, from 2.1 (¹H) and -24.8 (¹³C) in **1**, to 18.6 and 252.2 ppm (¹J_{CH} = 138 Hz) in **2**, respectively, in agreement with the formation of [(PONOP)Ir(CH₂)]⁺. These NMR data compare well with those reported²⁵ for the few cationic alkylidenes of iridium known to date.

The dark green solutions of the iridium methylene complex 2 were thermally stable at -20 °C but slowly decomposed at room temperature with a half-life of ca. 4 days (C_6D_5Br). In addition, they exhibited high reactivity toward oxygen and water, which, along with the presence of the triphenylmethane reaction byproduct and of small amounts of unidentified impurities resulting from partial thermal decomposition, precluded isolation of 2 with analytical purity. Evaporation of the solvent or precipitation by addition of hexane led invariably to a dark oily material. It is worth mentioning in this regard that attempts to produce a cationic $Rh=CH_2$ analogue starting from (PONOP) $Rh(CH_3)^{21a}$ proved unsuccessful. NMR studies of the reaction of the latter compound with $[Ph_3C][B(C_6F_5)_4]$ at -80 °C indicated the formation of a complex mixture of products, among them the quinoid dimer of the triphenylmethyl radical,²⁶ probably as a result of a radical reaction pathway.

To provide additional support for the formulation of **2** as a cationic methylene complex, we investigated its reactivity. The first indication of its electrophilic character was a result of serendipity, since performing the reaction of complex **1** and $[Ph_3C][B(C_6F_5)_4]$ in tetrahydrofuran produced a viscous solution interpreted as originating from the cationic polymerization of THF.²⁷ However, the alkylidene nature of **2** was unequivocally demonstrated by its reaction with PMe₃ (Scheme 2) that afforded an orange crystalline solid characterized by

Scheme 2. Synthesis of the Ylide 3 and Its Conversion into the Trimethyl Phosphine Adduct 4



NMR spectroscopy and X-ray crystallography as the ylide $[(PONOP)Ir(CH_2PMe_3)][B(C_6F_5)_4]$, 3. On the basis of detailed low-temperature NMR studies on the analogous reaction of the neutral methylene complex $Ir(CH_2)[N-(SiMe_2CH_2PPh_2)_2]$, Fryzuk and co-workers¹⁹ identified the corresponding ylide, $Ir(CH_2PMe_3)[N(SiMe_2CH_2PPh_2)_2]$, as a low-temperature intermediate in a process ultimately yielding the corresponding phosphine adduct, $Ir(PMe_3)[N-(SiMe_2CH_2PPh_2)_2]$. Indeed, as shown in Scheme 2, the use of an excess of PMe₃ furnished the cationic adduct 4, which was

independently prepared by treatment of (PONOP)IrCl with NaBAr_{F} and $\text{PMe}_{3}.$ The fate of the ylide ligand of 3 was not investigated. In the ¹H NMR spectrum of the latter complex, a doublet of triplet resonance centered at 2.56 ppm and featuring two- and three-bond ¹H-³¹P couplings of 17.0 and 5.8 Hz, respectively, replaced the deshielded triplet at 18.6 ppm characteristic of the Ir=CH₂ unit of 2. In accordance with expectations, the ³¹P{¹H} NMR spectrum of 3 consisted of two singlets at δ 182.0 (PONOP) and 32.5 ppm (PMe₃). The methylene carbon atom of 2 resonating at 252.2 ppm undergoes, upon ylide formation, a remarkable shift to lower frequencies, appearing in 3 as a doublet of triplets centered at -27.9 ppm, with corresponding ${}^{13}C-{}^{31}P$ coupling constants of 27 and 5 Hz. The NMR spectra of the cationic adduct 4 are unexceptional. As expected, its ³¹P{¹H} NMR spectrum consists of a doublet and a triplet centered at 194.6 and -46.2 ppm, due respectively to the PONOP and the PMe₃ ³¹P nuclei, with a two-bond J_{PP} value of 16 Hz.

The molecular structures of the two PMe₃ complexes, 3 and 4, were unequivocally confirmed by X-ray crystallography, with the results represented in Figure 1. For the two compounds, the coordination environment around the Ir center presents little distortion from an ideal square-planar geometry. In the ylide complex 3, the Ir(1)–C(22) bond distance of 2.135(2) Å is only slightly longer than the 2.091(4) Å value reported for the cationic methyl hydride^{23a} [(PONOP)Ir(CH₃)(H)]⁺ and comparable to that in other pincer methyl derivatives of Ir(III).²⁸ The ylidic carbon has a distorted tetrahedral environment, with an Ir(1)–C(22)–P(3) angle of 125.2(1) °.

We also studied the reactivity of **2** toward ethyl diazoacetate, N₂CHCO₂Et (EDA). A smooth C–C coupling reaction occurred at -20 °C, accompanied by a marked color change from dark green to intense red. From the resulting solutions, red crystals of an also cationic alkene complex, **5**, that contains a coordinated molecule of ethyl acrylate, were isolated (Scheme 3). In addition to resonances due to the ester terminus, -CO₂Et, the ¹H and ³¹C NMR spectra of **5** contained signals revealing η^2 -coordination of a CH₂==CH— fragment. In particular, the coordinated ¹³C nuclei resonate at δ 39.9 (CH₂; ¹J_{CH} = 162 Hz) and 34.7 ppm (CH; ¹J_{CH} = 157 Hz).

The solid state molecular structure of **5** was also determined by X-ray crystallography, and it is shown in Figure 2. Suitable crystals were grown by slow diffusion of pentane into Et_2O solutions of **5**. Whereas the pincer ligand was well-refined to its specific positions, the ethyl acrylate ligand presented a substitutional disorder between two equivalent, symmetryrelated orientations (ca. 85:15 ratio). As expected, the acrylate ester skeleton has a nearly orthogonal orientation with respect to the (PONOP)Ir backbone and exhibits a C(22)-C(23)bond length of 1.394(8) Å, typical for a coordinated alkene.

Recent studies on the hydrogenation of square-planar hydrocarbyl complexes of Ir(I) have provided interesting results.^{23b,29} In particular, Brookhart's group analyzed the reactivity of the methyl complex 1 toward H₂, leading to a methyl bis(hydride) species (PONOP)Ir(CH₃)(H)₂. This compound, which possesses *trans* hydride ligands, formed in a proton catalyzed reaction that proceeded through the intermediacy of the previously characterized [(PONOP)Ir(CH₃)(H)]⁺ cation, **6**.^{23a} In view of the obvious formal connection that exists between the Ir(I) methylene complex **2** and the latter Ir(III) hydride methyl cation by means of H₂ interplay, we set out to probe it experimentally. The hydrogenation of **2** was performed at low temperatures (from



Figure 1. ORTEP view of the cationic complexes 3 (left) and 4 (right) with ellipsoids set at 50% probability. Counteranions, solvent molecules, and hydrogen atoms have been omitted for clarity. Only the major disordered components of compound 4 are shown in the displacement ellipsoid plot.





Figure 2. ORTEP view of the cationic complex 5 with ellipsoids set at 50% probability. Only the major disordered components are shown in the displacement ellipsoid plot. Counteranion and hydrogen atoms have been omitted for clarity.

-120 to -60 °C) using 3 equiv of H₂ and CDCl₂F as the solvent (Scheme 4). Monitoring of the process by ¹H and ³¹P{¹H} NMR spectroscopy evinced no reaction until -60 °C, when the [(PONOP)Ir(CH₃)(H)]⁺ cation formed selectively, albeit with a conversion of only ca. 10% (Scheme 4). Since this low reaction yield was most probably due to slow hydrogen diffusion into the Freon solvent, H₂ was then bubbled through this solution maintained at -60 °C, with frequent shaking of the NMR tube. Under these conditions full consumption of **2** was observed, with two other, previously known complexes, 7 and **8**, adding to this reaction manifold, in agreement with previous studies.^{21c,23a}

In short, the cationic methylene complex [(PONOP)Ir- (CH_2)]⁺, **2**, produced by α -hydride abstraction from the neutral methyl derivative (PONOP)Ir(CH_3), **1**, exhibits the expected high electrophilicity and undergoes facile C–C coupling and hydrogenolysis reactions, as well as ylide formation by action of PMe₃.

Scheme 4. Reactions of 2 with Dihydrogen at Low Temperature^a

Note



^aSpectroscopic molar yields based on 2 are indicated in parentheses.

ASSOCIATED CONTENT

Supporting Information

Experimental details and procedures, NMR data, and crystallographic data for complexes **3**, **4**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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