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Nucleophilicity and P–C Bond Formation Reactions of a Terminal Phosphanido Iridium Complex

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Supporting Information

ABSTRACT: The diiridium complex [Ir(ABPN2)(CO)2(μ-CO)]1 (Ir[ABPN2]− = [(allyl)B(Pz)2(CH2PPh2)]) reacts with diphenylphosphane affording [Ir(ABPN2)(CO)(H)(PPh3)]2 (2), the product of the oxidative addition of the P–H bond to the metal. DFT studies revealed a large contribution of the terminal phosphanido lone pair to the HOMO of 2, indicating nucleophilic character of this ligand, which is evidenced by reactions of 2 with typical electrophiles such as H+, Me+, and O2. Products from the reaction of 2 with methyl chloroacetate were found to be either [Ir(ABPN2)(CO)(H)(PPh3)(CH2CO2Me)]22 or [Ir(ABPN2)(CO)(Cl)(H)]23 (7) and the free phosphane (PPh3(CH2CO2Me)), both involving P–C bond formation, depending on the reaction conditions. New complexes having iridacyclophosphapentenone and iridacyclophosphapentenone moieties result from reactions of 2 with dimethyl acetylenedicarboxylate and dimethyl maleate, respectively, as a consequence of a further incorporation of the carboxyl ligand. In this line, the terminal alkyne methyl propiolate gave a mixture of a similar iridacyclophosphapentanone complex and [Ir(ABPN2){CH=C(CO2Me)−CO}{PPh3−CH=CH(CO2Me)}]24 (10), which bears the functionalized phosphane PPh3−CH=CH(CO2Me) and an iridacyclobutenone fragment. Related model reactions aimed to confirm mechanistic proposals are also studied.

INTRODUCTION

Transition metal phosphanido complexes [M−PR2] are valuable species proposed to be actively involved in modern catalytic transformations.1 Among them, metal-mediated dehydrocoupling (DHC) of phosphane-boranes or primary and secondary phosphanes is providing an easy synthetic access to new inorganic materials, such as high molecular weight polyphosphanoboranes or phosphaneborane rings and chains.2 Furthermore, [M−PR2] species are highly relevant in both stoichiometric and catalytic P–E (E = B, C, Si, Ge) bond formation processes,3 which usually afford P-containing products that are otherwise difficult to prepare by conventional methods.4 As a matter of fact, phosphanido complexes of late transition metals have been recognized as active intermediates in catalytic hydrophosphonation (or hydrophosphorylation) of unsaturated substrates,5 especially with palladium-5 and platinum-based catalysts.6 Some studies involving rhodium-catalyzed DHC of phosphanes indicate that they occur through P−H bond activation processes, that is, by insertion of the metal into the P−H bonds of the substrates.7 However, despite the relevance of this activation step, which should render terminal hydrido phosphanido species in the first stage, it is difficult to find isolated mononuclear hydrido organophosphano metal complexes. Just a few complexes of rhodium,7a platinum,8 nickel,9 tantalum,10 molybdenum, and tungsten,11 coming from such a type of reaction, have been reported. The scarcity of terminal [M−PR2] species is among other reasons due to their marked tendency to form phosphanido bridges. Indeed, the vast majority of these complexes (Co triad and after) are di- or polyynuclear with bridging phosphanido moieties. Thus, a wide range of di12, and trinuclear13 complexes of platinum and palladium have been reported; some of them promote interesting stoichiometric P–C,14 P–N,15 and P–O16 bond formation reactions. Dinitrogen rhodium and iridium phosphanido complexes have also been widely studied,17 uncovering unusual coordination environments and bonding schemes, such as tetrahedral geometries for d8-M configurations (M = Rh, Ir),18 or square-planar in edge-sharing coplanar d5-Rh compounds.19

On the contrary, terminal phosphanido compounds of iridium are very scarce. Isolated complexes include [Ir{N(SiMe3)2CH2PPh2}(CH3)(PR3)]20 (R = Ph, m-tolyl), [Ir(CO)-(H)(L2X2(PH3))]21 (L = PEt3, 1/2 dppe; X = Br, Cl), [IrCl2(PMe2Ph)(PH3)]22 and two recent examples with fac-L1-iridium(I)23 and mer-L2-iridium(III)24 scaffolds in which the phosphanido functionality is embedded within a tripodal ligand.

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Herein, we report the P–H bond activation of a secondary organophosphane by an iridium complex, which affords a terminal phosphanido hydrido compound involving direct oxidative addition of the $R_3P–H$ bond to iridium. The new complex incorporates the original anionic hybrid scorpionate ligand $\left[\text{allyl}\right]B(Pz)_2(CH_1PPh_2)$ [$\text{[ABPN}_2$]--$^{-}$, $Pz$ = pyrazolate] that displays three different arms suitable for coordination. Some reactions involving the new Ir–PPh$_2$ bond as well as the molecular and electronic structure of the complex are also reported.

**RESULTS AND DISCUSSION**

Addition of diphenylphosphane (PPh$_2$) to the carbonyl-bridged dinuclear iridium(I) complex $\text{[Ir(ABPN}_2$)(CO)]$_2(\mu$-CO)]$^{25\text{a}}$ (1) produces an immediate reaction to give the mononuclear hydrido phosphanido iridium(III) complex $\text{[Ir(ABPN}_2$](CO)(H)(PPh$_2$)] (2) (Scheme 1), isolated as a pale-yellow microcrystalline solid in 92% yield after workup.

**Scheme 1. Synthesis of the Hydrido-phosphanido Iridium(III) Complex (2)**

\[
\text{[Ir(ABPN}_2$](CO)]$_2(\mu$-CO)] + 2 \text{PPh}_2 \rightarrow \text{[Ir(ABPN}_2$](CO)(H)(PPh}_2$)] (2) (92%)
\]

Complex 2 crystallized in a centrosymmetric space group $P2(1)/n$, so that the crystal contains the racemic mixture. The enantiomer OC-6-25-C is shown in Figure 1. In the complex, the iridium atom lies at the center of a slightly distorted octahedron, bound to the scorpionate ligand in a $\kappa^2N_1^\prime\kappa^2P$-mode, the hydride, the carbonyl, and the phosphanido ligands. Both phosphorus atoms are mutually trans, while the carbonyl and hydrido ligands are located trans to the nitrogen atoms of the pyrazolyl rings. The strong trans influence of the hydride ligand is reflected in a longer Ir–N3 bond distance when compared to the Ir–N1 distance, trans to the carbonyl ligand (Figure 1). Simultaneously, the phosphanido Ir–P2 bond distance is also clearly longer than the corresponding Ir–P1 bond distance of the phosphane arm of the tripod ligand. This short/long bonding scheme for trans-$R_3P–M–PR_3$ moieties in square-planar/octahedral complexes is quite common, and has been attributed to the stronger trans influence of the phosphane ligand.

Electronic repulsion between the phosphanido lone pair and the filled iridium $d_{3z^2}$, $d_{xz}$, and $d_{yz}$ orbitals might also play a role.

Figure 2 shows two views of the molecule along the P2–Ir–P1 axis highlighting the eclipsed conformation of the P1–C7 with P2–C29 bonds and P1–C13 with P2–C23 bonds. The lone-pair on phosphorus is placed between both pyrazolate rings. Accordingly, quite different torsion angles C23–P2–Ir–N1 and C29–P2–Ir–N3 (Figure 1) were observed.

The stereochemistry of 2 in solution was assessed through a combination of NMR multinuclear experiments. Two well-separated doublets ($\overline{J}_{EP} = 97$ Hz) observed in the $^{31}$P$\{^1$H$\}$ NMR spectrum reveal that both phosphorus atoms are located in mutual trans positions. However, the value of the coupling constant was found to be considerably smaller than that typically observed for trans-phosphane ligands (ca. 300–400 Hz), which can be attributed to a substantial reduction in the s-orbital character of the Ir–PR$_2$ bond as compared to Ir–PR$_3$. Moreover, the NMR data (see the Supporting Information) reflect a restricted rotational motion around the Ir–P2 bond and a structure close to that observed in the solid state. The relatively static nature of the molecule observed in solution contrasts with the typical dynamic behavior observed for M–PR$_2$ complexes, for which both phosphorus inversion and rotation around the M–PR$_2$ bond have been reported to be low-energy processes.

The geometry of complex $\text{[Ir(ABPN}_2$](CO)(H)(PPh$_2$)] (2) was also optimized with DFT (b3-lyp, def2-TZVP, see the Supporting Information). Apart from somewhat longer Ir–L distances (which is common in DFT), the main difference between the optimized geometry and the X-ray structure is a slight reorientation of the phosphanido ligand, rotated somewhat around the Ir–P2 bond in the DFT optimized geometry.

The phosphanido lone pair has a large contribution to the HOMO of complex 2, thus indicating nucleophilic character of this ligand. Interestingly, the LUMO of 2 is not located at the metal, but is centered at one of the phenyl groups of the neutral phosphane ligand (Figure 3). As can be expected, both the total atomic 3s-orbital population (1.48) and the total atomic 3p-orbital population (3.02) of the anionic phosphanido ligand P

![Figure 1. Molecular structure (ORTEP at the 50% level) of complex 2. H atoms and the solvent of crystallization have been removed, and only the C$_{phen}$ atoms of the phenyl groups are shown for clarity. Selected bond distances (Å) and angles (deg): Ir–P1, 2.348(1); Ir–P2, 2.436(1); Ir–N1, 2.094(3); Ir–N3, 2.161(3); Ir–C35, 1.838(5); Ir–H, 1.54(4); C23–O, 1.139(5); P1–Ir–P2, 174.21(4); N1–Ir–C35, 175.0(2); N3–Ir–H, 176.2(16); C23–P2–Ir–N1, 104.4(2); C29–P2–Ir–N3, −61.8(2).](image1)

![Figure 2. Two views of complex 2 along the P1–Ir–P2 axis.](image2)

![Figure 3.](image3)
atom are larger than those of the neutral phosphane ligand P atom (3s 1.20; 3p 2.63). The DFT calculated Ir−P bond order (Wiberg) of the phosphanido donor (0.86) is stronger than that of the neutral phosphane donor (0.67), despite the longer (calculated and experimental) Ir−P bond as compared to the Ir−P1 bond. The Wiberg Bond Index (WBI) is a density-matrix-based quantum chemical descriptors of the bond order, and reflects both the strength and the covalency/polarity of a bond. WBI bond orders of 1 are typically only observed for nonpolarized σ-bonds, with substantially smaller values for polarized σ-bonds.

Because metal–ligand bonds are intrinsically polarized toward the ligand, metal–ligand WBI values between 0 and 1 are expected for M−L bonds with σ-donating ligands such as the phosphanido and phosphane donors under consideration. The increased WBI of the Ir−P bond for the phosphanido donor as compared to the phosphane donor reflects a stronger covalency and stronger Ir−P σ-bond.

The overall reaction leading to complex 2 involves the cleavage of the dinuclear complex 1 by coordination of the secondary phosphate and the oxidative-addition of the P−H bond to the iridium centers. Monitoring the reaction by NMR, cleavage of the dinuclear complex 1 into 2 was readily observed, but no intermediates were detected. Nonetheless, the origin of the hydrido ligand in 2 was confirmed in a straightforward manner by monitoring the reaction of 1 with PDPh2 by 2H NMR, which gave [Ir(ABPN2)(CO)(D)(PPh2)] (2-d1). This information confirms the iridium-mediated scission of the P−H bond and rules out any other considerations about the origin of the hydrido ligand.

The product from the first step of the reaction of [Ir(ABPN2)(CO)(μ-CO)] (1) with PHPh2 would be the mononuclear complex [Ir(ABPN2)(CO)(PHPh2)] (A), similar to the previously reported phosphane counterpart [Ir(ABPN2)−(CO)(PPh3)].

The latter was found to exist as a mixture of two isomers in solution in equilibrium, involving the trigonal bipyramidal (TBPY) species, with one of the pyrazolyl groups and the carbonyl at the axial positions, and the square-planar (SP) with the two phosphorus atoms in a trans disposition. Such type of equilibrium has also been observed for related complexes with hybrid scorpionate ligands decorated with allyl groups.

Consequently, a similar equilibrium can be expected for complex [Ir(ABPN2)(CO)(PHPh2)] (A, Scheme 2).

Both isomers, A-TBPY and A-SP, were optimized with DFT (b3-lyp, def2-TZVP), and their structures are shown in Figure 4. For A, the energy difference between the SP and TBPY isomers turned out to be quite big. The A-SP geometrical isomer is 14.3 kcal mol−1 more stable than A-TBPY, and accordingly (in contrast to [Ir(ABPN2)(CO)(PPh3)]) only A-SP should be present in appreciable amounts for [Ir(ABPN2)−(CO)(PHPh2)] species A. This is likely a reflection of the stronger donor capacity of the PHPh2 ligand as compared to PPh3.

The subsequent oxidative addition of the P−H bond from A-SP via TS1 to form the hydride complex 2 was also computationally investigated (b3-lyp, def2-TZVP), revealing a moderate transition state barrier (TS1) of ΔG‡ = +22.1 kcal mol−1 (relative to A-SP). The structure of TS-1 (Figure 5) shows the hydrogen between phosphorus and iridium (P−H distance, 1.486 Å; Ir−H distance, 2.053 Å; corresponding distances in A-SP; P−H distance, 1.413 Å; Ir−H distance, 3.182 Å). The free pyrazole donor approaches to iridium from 2.871 Å in A-SP to 2.623 Å in TS-1, showing partial oxidation from IrII to IrIII in TS-1, and partial coordination of the pyrazole donor, which likely plays a role in stabilization of the transition state (anomERIC effect).

In principle, an intermediate with a σ-coordinated P−H bond could also be considered as being the precursor complex to TS1 (instead of A-SP). However, all attempts to optimize complexes with a σ-coordinated P−H bond to iridium converged back to geometries with a P-coordinated phosphate PPh2PH ligand without any interaction between the hydrogen...
atom and iridium. Furthermore, following the intrinsic reaction coordinate of TS1 in two directions showed that the transition state is directly connected with the complexes A-SP and 2.

**Reactions of 2 with Electrophiles.** The nucleophilic character of the phosphanido ligand of complex 2 was evidenced from its reactions with electrophiles, such as H⁺ and Me⁺, in good agreement with the HOMO of complex 2 being essentially the phosphanido lone-pair (Figure 3). Both reactions were found to occur immediately to produce the white cationic complexes \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{PEPh}_2)]^+ (E = \text{H}, [3]^+; \text{Me}, [4]^+) \] (Scheme 3). Quaternization of the parent phosphanido ligand in 2 results in a considerable enlargement of the \(^1J_{P,P}\) coupling constant, from 97 Hz in 2 to ca. 310 Hz in complexes [3]^+ and [4]^+. This behavior has been systematically observed for the rest of the complexes reported here.

Oxygen also reacts with complex 2, although the reaction was found to be slow, requiring around 12 h to reach completion. The product was identified as \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{POPh}_2)] \] (5), where some reduction of the electronic density on the iridium atom in 5 was detected by an increase of the \(\nu(\text{CO})\) frequency from 2023 cm\(^{-1}\) in complex 2 to 2053 cm\(^{-1}\) in 5.

Organic chlorides such as methyl chloroacetate (\(\text{ClCH}_2\text{CO}_2\text{Me}\)) also react with the phosphanido ligand at \(\text{P}_2\) in complex 2 (Scheme 4), and the outcome of the reaction was found to be very sensitive to the reaction conditions. Thus, if the reaction is carried out in acetone in the presence of stoichiometric amounts of KPF\(_6\), the cationic complex \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{PPh}_2\text{CH}_2\text{CO}_2\text{Me})][\text{PF}_6] \] ([6][PF\(_6\)]) was isolated after workup. Formation of the new \(\text{P}−\text{C}\) bond was confirmed through an \(^1\text{H},^{31}\text{P}\)-hmbc NMR experiment where the expected correlation peaks between the \(\text{CH}_2\) protons of the coordinated phosphane, \(\text{Ir}−\text{P}^3\text{Ph}_2\text{CH}_2\text{CO}_2\text{Me}\), and \(\text{P}^2\) were observed.

If the reaction is performed in less polar solvents such as benzene or toluene and in the absence of KPF\(_6\) the products were found to be the neutral hydride chloride complex \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{Cl})(\text{H})][\text{PF}_6] \] ([7][PF\(_6\)]) and the free phosphane, \(\text{PPh}_2\text{CH}_2\text{CO}_2\text{Me}\). In this case, the overall reaction involves the formal replacement of the functionalized phosphane by the chloride, an unexpected reaction because phosphanes are typically strongly bound to iridium. Moreover, dissociation of the phosphane is clearly evidenced by the observation of the hydride ligand in 7 as a doublet instead of a doublet of doublets (as observed for [6]^+). Furthermore, the free phosphane \(\text{PPh}_2\text{CH}_2\text{CO}_2\text{Me}\) was easily identified from a singlet at \(\delta = -16.5\) ppm in the \(^{31}\text{P}\)\{\(^1\text{H}\}\) NMR spectrum.\(^{31}\) In addition, and according to its formula, complex 7 was independently prepared by reacting complex 2 with dry HCl in a 1:2 molar ratio. Its molecular structure is shown in Figure 6. The iridium atom in 7 shows an octahedral environment bound to the tripodal ligand and to the carbonyl, hydride, and chloride ligands, the latter being placed \(\text{trans}\) to the phosphorus atom. As expected, the strong \(\text{trans}\) influence of the hydride ligand is reflected in a longer \(\text{Ir}−\text{N}\) bond distance as compared to the \(\text{Ir}−\text{N}\) bond (Figure 6).

The cationic complex \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{PPh}_2\text{CH}_2\text{CO}_2\text{Me})][\text{PF}_6] \] ([6][PF\(_6\)]) remains unaltered in solution, but in the presence of PPNCl (PPN = bis(triphenylphosphane)iminium) evolves cleanly and quantitatively to \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{Cl})(\text{H})][\text{PF}_6] \] (7) and \(\text{PPh}_2\text{CH}_2\text{CO}_2\text{Me}\). As such, we could assume that the first intermediate in the reaction of 2 with \(\text{ClCH}_2\text{CO}_2\text{Me}\) in benzene is \[ \text{[Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{PPh}_2\text{CH}_2\text{CO}_2\text{Me})][\text{PF}_6] \] ([6][PF\(_6\)])

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**Scheme 3. Reactions of \([\text{Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{PPh}_2)]\) (2) with HBF\(_4\), MeOTf, and O\(_2\)**

**Scheme 4. Reaction of \([\text{Ir}(\text{ABPN}_2)(\text{CO})(\text{H})(\text{PPh}_2)]\) (2) with Methyl Chloroacetate To Give Either Complex [6][PF\(_6\)] or Complex 7 and the Free Phosphane**
The new iridacyclophosphapentenone fragment shown in the tripodal ligand is coordinated in a facial hydride ligand and the octahedral arrangement around iridium is completed by the phosphane and species was found to be in a chemical equilibrium with the free phosphane instead (see the Supporting Information). Moreover, this only the Cipso atoms of the phenyl groups are shown for clarity. 

Reactions of 2 with Alkynes and Alkenes. The high functionality of the phosphanido group also promotes the close a hypothetical catalytic cycle for the synthesis of iridium through P2 (trans to the phosphane arm of the scorpionate) and the ketonic carbonyl group.

The P2 atom displays the typical tetrahedral geometry expected for a phosphane type ligand, and, accordingly, a significant decrease in the Ir–P2 bond length is observed on going from 2 to 8, which is expected on going from a (formal) covalent P→Ir bond to a dative P→Ir bond (vide infra). The five-membered iridacycle “Ir→P2-C37-C36-C35” is strictly planar, with the maximum deviation from the best plane being 0.028 Å. The C23–C37 and C37–C38 bond distances are appropriate for single and double carbon–carbon bonds, respectively (Figure 7), and comparable to related metal-lacyclophosphapentenone complexes of iron, molybdenum, or tungsten. In good agreement, the angles around C37 and C38 of the incorporated alkyne fit with that expected for a sp3 hybridization, reflecting clearly the formation of an olefin as a result of the formal cycloaddition process. Spectroscopic data of complex 8 in solution reflect accurately the structure observed in the solid state. Thus, the ketonic carbonyl group in the iridacycle was detected in the IR spectrum by a strong band at 1729 cm⁻¹, and, accordingly, it was low-field shifted from 170.4 (in 2) to 207.0 ppm (in 8) in the 13C{1H} NMR spectrum.

The most plausible mechanism involves a two-step process with the initial formation of the zwitterion B formed by nucleophilic attack of the phosphanido lone pair of 2 to the C=C triple bond (Scheme 6), followed by attack on the

**Scheme 5. Reaction of [Ir(ABPN2)(CO)(H)(PPh2)] (2) with dmad (MeO2CC≡CSCO2Me) To Give Complex 8**
resulting carbanion to the terminal carbonyl group, as previously suggested for carbonyl complexes with terminal phosphanide,

\[ \text{[Ir]} \] \rightarrow \text{[Ir(ABPN \_2)]}. \] Path ii was not observed.

**Scheme 6. Plausible Mechanism for the Synthesis of Complex 8 from the Reaction of 2 with dmad**

**Scheme 7. Reaction of [Ir(ABPN \_2)(CO)(H)(PPh \_2)] (2) with Methyl Propiolate (HC=CCO \_2Me) To Give Complexes 9 and 10**

The related monosubstituted alkyne methyl propiolate (HC=CCO2Me) also reacts with the phosphanide complex 2 leading to a mixture of complexes 9 and 10 (Scheme 7) in a variable ratio depending on the amount of the alkyne added. Thus, addition of 1.5 mol equiv of HC=CCO2Me to 2 produces an almost equimolar mixture of both products, while a ratio of 32:67 9:10 can be obtained by adding the alkyne in excess (5 mol equiv).

Complex 9 was identified as the iridacyclopentadienone compound [Ir(ABPN \_2)(H){PPh \_2−CH=CH(CO \_2Me)−CO}] by its spectroscopic data, similar to those corresponding to complex 8 (see the Supporting Information). Moreover, complex 9 is indeed the isomer expected for a Michael-type nucleophilic attack of the phosphanide to the alkyne.

The second product from the reaction was identified as [Ir(ABPN \_2){CH=CH(CO \_2Me)−CO}{PPh \_2−CH=CH−(CO \_2Me)}] (10), having an iridacyclobutenone fragment and the functionalized phosphane Ph2P−CH=CH(CO2Me) (Scheme 7) according to its spectroscopic data (see the Supporting Information). The iridacyclobutenone fragment was supported by the observation of the Ir−C3H \_\_ proton at very low field (\( \delta = 9.46 \text{ ppm} \)) in the \(^1H\) NMR spectrum, while the high field shift of the ketonic Ir−CO carbon up to to \( \delta = 177.3 \text{ ppm} \) can be attributed to the four-membered nature of the iridacycle in complex 10.

According to Scheme 6, complex 9 is the expected result from path i, while formation of complex 10 would require path ii, to give [Ir(ABPN \_2)(CO){PPh \_2−CH=CH(CO \_2Me)}] in this case, followed by alkyne coordination and CO insertion into the metallacyclopropene ring. While a concerted [2+2] cycloaddition reaction cannot be fully disregarded, it seems less likely considering the product mixture obtained in the reaction described in Scheme 7. Furthermore, we were thus far unable to locate such a concerted transition state with DFT.

In any case, this was a quite unexpected reaction because isolated mononuclear metallocyclobutenone complexes are very rare, despite the interest of such type of complexes in metal-centered alkyne–carbonyl coupling reactions.37 Reported examples include complexes of ruthenium,38 iron,39 rhodium,40 and iridium41 obtained from reactions of carbonyl compounds with activated alkynes and of platinum42 and cobalt43 coming from metal insertion into cyclopropenones.

To verify the participation of the iridium(I) species [Ir(ABPN \_2)(CO){PPh \_2−CH=CH(CO \_2Me)}] in the formation of complex 10, a model reaction between [{[Ir(ABPN \_2)−(CO)} \_2(\( \mu\)-CO)] (1) and PPh \_2Me (to generate the mononuclear complex [Ir(ABPN \_2)(CO)(PPh \_2Me)] followed by the addition of 1 mol equiv of HC=CCO2Me was carried out. The overall reaction produces clean and quantitatively complex
[Ir(ABPN2)(CO)(H)(PPh2)] (11), which was isolated as a white crystalline solid in 94% yield (Scheme 8). Spectroscopic data of 11 were those expected for a complex having an iridacyclobutenone fragment (see the Supporting Information). The related alkynes HC≡CH, HC≡CPh, and PhC≡CPh, having less electrophilic carbons than HC≡CCO2Me and MeO2CC≡CCO2Me, do not react with complex 2, which supports the mechanism depicted in Scheme 6 starting with the nucleophilic attack of the phosphanido ligand.

Activated olefins such as dimethyl maleate (cis-MeO2CCH=CHCO2Me) also react with the phosphane complex [Ir(ABPN2)(CO)(H)(PPh2)] (2) to give the complex [Ir(ABPN2)(H){PPh2−CH(CO2Me)−CH(CO2Me)−CO}] (12, Scheme 9), the aliphatic version of the iridacycle above-described for complexes 8 and 9. Because complex 12 contains three stereogenic centers, the iridium atom and the two carbons of the iridacycle, four pairs of enantiomers could be expected a priori to result. Indeed, if the reaction is carried out at −30 °C, some of them can be observed, but they evolve to the thermodynamic pair of enantiomers on raising the temperature, which corresponds to the isolated product.

The methylene protons of the new formed iridacyclopophenapentanone were observed at δ = 4.98 (J_H,H = 13.2 Hz, J_H,P = 1.4 Hz) and 4.69 (J_H,H = 13.2 Hz, J_H,P = 10.9 Hz) ppm (in red and green, respectively, in Scheme 9). The different values for the J_H,P coupling constants allowed the assignment of both protons because J_H,P is expected to be larger than J_H,P. Moreover, the large J_H,H coupling constant suggests both protons to be in an antiperiplanar conformation (torsion angle around 180°), while selective selnOe experiments allowed one to unambiguously establish the stereochemistry of 12 (see the Supporting Information).

Complex 12 was also the product from the reaction between 2 and dimethyl fumarate (trans-MeO2CCH=CHCO2Me) as observed by “in situ” NMR experiments, which otherwise confirm the thermodynamic control of both reactions. In this case, monitoring the reaction by NMR revealed a more complicated mechanism than that expected from the stepwise pathway exemplified in Scheme 6 for the alkynes case. Four major compounds were observed: complex 12 and one of its isomers (12′), the free phosphane, PPh2CH(CO2Me)−CH2(CO2Me), and a new species having broad resonances that have been attributed to the iridium(I) complex [Ir(ABPN2)(CO)(PPh2R)] (R = CH(CO2Me)CH2(CO2Me), D) (Figure 8). This mixture cleanly evolves to complex 12, along with small amounts of the free phosphane, PPh2CH(CO2Me)−CH2(CO2Me), overnight (see the Supporting Information).

Participation of the iridium(I) complex [Ir(ABPN2)(CO)(PPh2R)] (R = CH(CO2Me)CH2(CO2Me), D) in the course of the reaction was confirmed by the reaction between the dinuclear complex [[Ir(ABPN2)(CO)]_2(μ-CO)] (1) and the phosphane PPh2CH(CO2Me)CH2(CO2Me), which produces a 31P{1H} NMR spectrum after 5 min of reaction (see the Supporting Information), similar to that observed in the...
reaction of 2 with dimethyl fumarate. This mixture evolved to complex 12 as expected.

Understanding the overall reactions is not obvious. Assuming a two-step mechanism similar to that shown in Scheme 6 for the alkynes case, complexes 12 and 12’ would come from the nucleophilic attack of the phosphanido in 2 to one face (or the other) of dimethyl fumarate to give the carbanion C (Scheme 10) followed by the attack of the resulting carbanion to the terminal carbonyl group (path i). The alternative proton migration from the iridium to the carbanion (path ii) would produce the iridium(I) complex D. Starting from D, the formation of 12 and 12’ would require the concurrence of an oxidative-addition reaction of one the methylenic protons in the −CH2(CO2Me) group and the migratory insertion of the carbonyl group into the Ir−C bond (Scheme 10). This migration generates a more favorable, less strained five-membered metallacycle and has been previously observed in iridium chemistry.44

Isomerization of complex 12’ into 12 could take place through the participation of the enol-type intermediates E1 and E2 (Scheme 10). Indeed, on heating (40 °C) a solution of complex 12 in the presence of a small amount of D2O, deuteration of both methylenic protons was observed. Figure 9 shows a couple of spectra at the beginning of the reaction (bottom trace) and after 17 h at 40 °C in the presence of 5 mol equiv of D2O (top trace), where a similar decrease in the intensity of the signal corresponding to the methylenic protons is clearly observed. The remaining resonances correspond to the complexes [Ir(ABPN2)(X){PPh2−CX(CO2Me)−CY(CO2Me)−CO}] (X = H, Y = D; X= D, Y = D). Although enols from esters are quite uncommon, its participation provides the simplest explanation to account for the experimental observations.

Moreover, Figure 9 also shows deuteration at the hydride position suggesting that the equilibrium between 12 and D or, alternatively, between 12 and 2 and MeO2CH=CHCO2Me is also operative (Scheme 10). The latter possibility has been confirmed from the reaction between 2 and dimethyl maleate in a ratio 1:5, which produces complex 12 and dimethyl fumarate after 3 days. This olefin isomerization gives support to the proposed double retro-fragmentation reaction in 12, associated with the decoordination of the olefin. Such type of isomerizations through metallacyclopentanones has been previously observed in cyclopentamethyl iron complexes.32b Finally, considering the values of the integrals in Figure 9, it is clear that the equilibria involving the methylenic protons show a lower activation barrier than the equilibria involving the hydride ligand.

**SUMMARY AND CONCLUSIONS**

In this Article, we showcase the ability of an iridium complex to react with a secondary phosphane to afford an iridium(III) compound (2) with a terminal phosphano ligand. This rare compound results formally from the oxidative addition of a P−H bond to iridium(I). The reactivity of the phosphano complex is governed by the nucleophilicity of the phosphano phosphorus atom. Thus, simple electrophiles (H+, Me+, O2)
directly attack the phosphorus atom leading to the formation of P–H, P–C, and P=O bonds, respectively. In the same fashion, the reaction with ethyl chloroacetate in the presence of KPF6 gives the cation with a functionalized phosphine [Ir(ABPN2)−(CO)(H)(PPh2CH2CO2Me)]+ by a P–C coupling reaction, while in the absence of the salt the free phosphine PPh2CH2CO2Me results along with the hydrido complex [Ir(ABPN2)(CO)(Cl)(H)]. The terminal phosphanido complex is appropriate to undergo P–C coupling reactions with activated unsaturated hydrocarbons. Nonetheless, the presence of a nucleophilic phosphorus atom and a terminal carbonyl ligand in the complex induces cycloaddition processes that involve the concomitant formation of P–C and C=C bonds, as illustrated by the synthesis of iridacyclopentanepentene complexes [Ir(ABPN2)(H){PPh2−CR−C=(C=O)Me}−CO)] (R = CO2Me, H) from reactions of 2 with dimethyl acetylenedicarboxylate and methyl propiolate, respectively. A parallel reaction in the second case also affords a rare iridacyclobutene complex [Ir(ABPN2)(H=CC=O)(CO)]{PPh2−CH=CH(C=O)Me}) by alkyne coordination and CO insertion into the metallacyclopentene ring. Activated alkenes such as dimethyl maleate and dimethyl fumarate also reacted with 2 to form eventually the same iridacyclopentane complex [Ir(ABPN2)(H){PPh2−CH=CH(C=O)Me}−CH(C=O)Me−CO)], the thermodynamic product of both reactions. Deuterium exchange of the methylene and hydride protons in the presence of D2O as well as isomerization of dimethyl maleate into dimethyl fumarate suggest that several equilibria involving enol-type species and double-retrofragmentation steps are involved in the mechanism.

**Experimental Section**

**General Methods.** All procedures were performed under an argon atmosphere, using standard Schlenk techniques. Solvents were dried and distilled under argon before use by standard methods.14 Carbon, hydrogen, and nitrogen analyses were carried out with a PerkinElmer 2400 CHNS/O microanalyzer. High-resolution electrospray mass spectra were acquired on a Bruker Microtof-Q (ESI+). NMR spectra were recorded on Bruker AV 300, AV 400, and AV 500 spectrometers operating at 300.13, 400.13, and 500.13 MHz, respectively, for ′H. Chemical shifts are reported in ppm and referenced to SiMe4 using the internal signal of the deuterated solvent (H and 13C) and external H2PO4−(18P). IR spectra in solution were recorded with a Nicolet 550 spectrophotometer using NaCl cells, while IR spectra of solid samples were recorded with a PerkinElmer 100 FT-IR spectrometer (4000–400 cm−1) equipped with an ATR (attenuated total reflectance). Conductivities were measured in acetonitrile solutions (5.0 × 10−4 M) using a Philips PW 9501/01 conductivity cell. Recrystallizations were performed from a 5.0% (v/v) solution of methanol.

**Synthesis of the Complexes:** [Ir(ABPN2)(CO)(H)(PPh2)]2+ (2). Diphenylphosphine (28.1 mL, 0.16 mmol) was added via microsyringe to a yellow solution of 1 (100.4 mg, 0.08 mmol) in THF (5 mL). Evolution of gaseous carbon monoxide was observed. After 30 min of stirring, the solution was concentrated to ca. 0.5 mL, and then hexane (5 mL) was added. The pale-yellow solid that precipitated was filtered out, washed with hexane (2 × 5 mL), and dried under vacuum. Colorless microcrystals suitable for X-ray diffraction studies were obtained by layering a solution of 2 in THF with hexane. Yield: 117.4 mg (92%). IR (ATR): ν (IR−H)/cm−1 2233 (w), ν (CO)/cm−1 2023 (s). MS (MALDI-TOF−): m/z (%) 793.4 (100) [M+H]+, 765.4 (40) [M]+ + H−CO). Anal. Calc. for C35H34BF3IrN4O2P2: C, 69.69; H, 4.70; N, 7.08. Found: C, 69.92; H, 4.56; N, 6.88. For NMR data, see the Supporting Information.

[Ir(ABPN2)(CO)(D)(PPh2)]2− (2d). A NMR tube was loaded with 1 (15 mg, 0.01 mmol) and dissolved in benzene (0.5 mL). Deuterated diphenylphosphine (D-PPh2, 4 μL, 0.02 mmol) was then added to the solution. 1D NMR (400 MHz, C6H6, 25 °C): δ = 15.09 (br, 1H; Ir−D). IR (ATR−D): ν (IR−H)/cm−1 2081 (w), ν (CO)/cm−1 2063 (s). MS (MALDI-TOF−): m/z (%) 793.2 (100) [M+H]+, 607.2 (25) [M−H−HPPh2]+, 577.0 (20) [M−2H−HPPh2−CO]+. Anal. Calc. for C34H33BF3IrN4O2P2: C, 50.52; H, 3.99; N, 6.97. Found: C, 50.52; H, 3.99; N, 6.97. For NMR data, see the Supporting Information.

[Ir(ABPN2)(CO)(PMePh2)]2− (3). A solution of 2 (80.0 mg, 0.10 mmol) in THF (4 mL) was shaken under an oxygen atmosphere for 12 h. The solvent was removed and the residue was stirred with hexane (5 mL) to render a white solid, which was filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield: 78.2 mg (95%). IR (ATR−D): ν (IR−H)/cm−1 2184 (w), ν (CO)/cm−1 2062 (s). MS (MALDI-TOF−): m/z (%) 807.2 (30) [M]+, 779.2 (35) [M−CO]+, 607.2 (100) [M−CH2PPh2]+. Anal. Calc. for C36H38BF3IrN4O3P3: C, 52.05; H, 4.39; N, 6.97. Found: C, 52.58; H, 4.55; N, 6.72. Analytical: 57.9 Ω−1 cm2 mol−1 (acetone, 5.0 × 10−4 M). For NMR data, see the Supporting Information.

[Ir(ABPN2)(CO)(PPhMe2)]2− (4). A solution of 2 (107.6 mg, 0.14 mmol) in acetonitrile (8 mL) was added methyl chloroacetate (131.1 μL, 0.14 mmol) via microsyringe. The mixture was stirred for 30 min, and then KPF6 (25.0 mg, 0.14 mmol) was added. The cloudy solution was stirred overnight at room temperature. The solvent was removed by vacuum, and dichloromethane (10 mL) was added. The cloudy solution was filtered out to eliminate the precipitated KCl, and the reaction was evaporated to ca. 0.5 mL. Addition of diethyl ether (5 mL) yielded a white solid, which was filtered off, and then it was vacuum-dried. Yield: 127.8 mg (93%). IR (ATR−D): ν (IR−H)/cm−1 2183 (w), ν (CO)/cm−1 2050 (s), ν (CO)/cm−1 1729 (s, br), ν (CO)/cm−1 1100 and 1072 (s, ν(PF3)/cm−1 832 and 741. MS (MALDI-TOF−): m/z (%) 865.2 (95%) [M]+. Anal. Calc. for C36H38BF3IrN4O6P2: C, 51.74; H, 4.13; N, 6.98. For NMR data, see the Supporting Information.

[Ir(ABPN2)(CO)(Cl)(H)]2+ (7). Method A: To a colorless solution of 2 (103.6 mg, 0.13 mmol) in toluene (4 mL) was added methyl chloroacetate (13.8 μL, 0.16 mmol) in a slight excess (1:1.2) via microsyringe. The reaction mixture was stirred for 2 h at 50 °C, and the solution was then dried under vacuum, yielding an oily residue. Hexanes (5 mL) were added, affording a whitish solid that was isolated by filtration and dried by vacuum. The washing solution was collected and filtered through a pad of silica, and upon removal of the solvents the phosphine PPh2CH2CO2Me was obtained as an oily material (see below). Yield: 73.9 mg (88%). Method B: Complex 1 (97.0 mg, 0.08 mmol) was dissolved in diethyl ether (4 mL), and a solution of dry HCl in Et2O (0.68 M, 0.23 mL) was added via microsyringe inducing the immediate precipitation of a white solid. Upon 30 min of stirring,
the solid was isolated by filtration and then vacuum dried. Yield: 92.5 mg (92%). IR (toluene): v (IR−H)/cm⁻¹ 2189 (w), ν(C=O)/cm⁻¹ 2057 (s). MS (MALDI-TOPF): m/z (%) 681.2 (25) [M+ K]⁺, 607.2 (100) [M+ Cl]. Anal. Calcld for C₁₈H₁₂BCl₂N₂O₅P: C, 43.03; H, 3.77; N, 8.73. Found: C, 43.40; H, 4.02; N, 8.40. For NMR data, see the Supporting Information.

P₂H₅CH₂CO₂Me was obtained as a byproduct from the formation of 7 as a colorless oil (method A). Yield: 26.9 mg (80%). ¹H NMR (500 MHz, CDCl₃, δ 7.40 (m, 4H, H₂PPh₂), 7.04 (m, 6H, H°-ν PPh₂), 3.19 (s, 3H, OCH₃), 2.94 (m, 2H, CH₂P), 3.19 (p) [H] NMR (202 MHz, CDCl₃, δ −16.5 (br). ¹³C{¹H} NMR (125 MHz, CDCl₃, δ 170.4 (d, J_{C,P} = 60 Hz; C°-PPh₂), 136.3 (d, J_{C,P} = 60 Hz; C° PPh₂), 133.1 (d, J_{C,P} = 20 Hz, 2C°; C° PPh₂), 129.1 (2C°; C° PPh₂), 128.8 (m, 2C°; C° PPh₂), 51.4 (OCH₃), 35.2 (d, J_{C,P} = 21 Hz, CH₂P).

Detection of [Ir((ABPN2)Cl(H)[PPh₂CH₂CO₂Me]) (B)] as a yellow solution of 8 after 28 h showed quantative conversion to complex 12. IR (CD₂Cl₂): ν (IR−H)/cm⁻¹ 2173 (w), ν(C=O)/cm⁻¹ 1741 (s, br), ν(C=O)/cm⁻¹ 1209 (m, br). MS (MALDI-TOPF): m/z (%) 937.3, 935.3 (M+ − C₂H₅O₂), 932.2 (M+ − C₂H₅N), 817.3 (45) [M+ − H₂O], 931.2 (38) [M+ − Na], 891.0 (38) [M+ − H₂O], 889.0 (42) [M+ − H].

Spectroscopic measurements revealed complete conversion of 2, and formation in solution of 6, Ph₅PC₅H₅MeCO₂HMe, in room temperature for 2 h. Spectroscopic measurements revealed consumption of 2, and formation in solution of complex 7 after 28 h showed complete conversion to complex 12. IR (CD₂Cl₂): ν (IR−H)/cm⁻¹ 2173 (w), ν(C=O)/cm⁻¹ 1741 (s, br), ν(C=O)/cm⁻¹ 1209 (m, br). MS (MALDI-TOPF): m/z (%) 937.3, 935.3 (M+ − C₂H₅O₂), 932.2 (M+ − C₂H₅N), 817.3 (45) [M+ − H₂O], 931.2 (38) [M+ − Na], 891.0 (38) [M+ − H₂O], 889.0 (42) [M+ − H].

Inorganic Chemistry

Spectroscopic measurements revealed complete conversion of 2 and formation in solution of complex 7 after 28 h showed complete conversion to complex 12. IR (CD₂Cl₂): ν (IR−H)/cm⁻¹ 2173 (w), ν(C=O)/cm⁻¹ 1741 (s, br), ν(C=O)/cm⁻¹ 1209 (m, br). MS (MALDI-TOPF): m/z (%) 937.3, 935.3 (M+ − C₂H₅O₂), 932.2 (M+ − C₂H₅N), 817.3 (45) [M+ − H₂O], 931.2 (38) [M+ − Na], 891.0 (38) [M+ − H₂O], 889.0 (42) [M+ − H].

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