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DOI
10.1021/acs.inorgchem.5b02301

Publication date
2016

Document Version
Final published version

Published in
Inorganic Chemistry

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

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ABSTRACT: The diiridium complex \([\text{Ir(ABPN}_2\text{(CO)}_2\text{(μ-CO)}_2}\text{]}_\text{2}^{\text{−}}\) reacts with diphenylphosphane affording \([\text{Ir(ABPN}_2\text{(CO)(H)}\text{(PPh}_2\text{)}\text{]}_\text{2}\) (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 O\(_2\). Products from the reaction of 2 with methyl chloroacetate were found to be either \([\text{Ir(ABPN}_2\text{(CO)(H)}\text{(PPh}_2\text{CH}_2\text{CO}_2\text{Me)}\text{]}\text{2}^\text{−}\) or \([\text{Ir(ABPN}_2\text{(CO)(Cl)(H)}\text{]}_\text{2}\) (7) and the free phosphane (PPh\(_2\)CH\(_2\)CO\(_2\)Me), both involving P–C bond formation, depending on the reaction conditions. New complexes having iridacyclophosphapentenone and iridacyclophosphapentanone moieties result from reactions of 2 with dimethyl acetylenedicarboxylate and dimethyl maleate, respectively, as a consequence of a further incorporation of the carbonyl ligand. In this line, the terminal alkyne methyl propionate gave a mixture of a similar iridacyclophosphapentanone complex and \([\text{Ir(ABPN}_2\text{]}_\text{2}^\text{−}\text{(CH=C(CO}_2\text{Me)}\text{−CO)}_\text{2}\text{(PPh}_2\text{−CH=CH(CO}_2\text{Me)}\text{]}_\text{2}\) (10), which bears the functionalized phosphane PPh\(_2\)−CH=CH(CO\(_2\)Me) and an iridacyclobutenone fragment. Related model reactions aimed to confirm mechanistic proposals are also studied.

INTRODUCTION

Transition metal phosphanido complexes \([\text{M−PR}_2\text{]}_\text{a}\) are valuable species proposed to be actively involved in modern catalytic transformations.\(^\text{3}\) Among them, metal-mediated dehydrocoupling (DHC) of phosphone-boranes or phosphane-boranes or phosphaneboranes and phosphaneborane rings and chains.\(^\text{4}\) Furthermore, \([\text{M−PR}_2\text{]}_\text{a}\) species are highly relevant in both stoichiometric and catalytic P–E (E = B, C, Si, Ge) bond formation processes,\(^\text{5}\) which usually afford P-containing products that are otherwise difficult to prepare by conventional methods.\(^\text{6}\) 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, especially with palladium-\(^\text{5}\) and platinum-based catalysts.\(^\text{6}\) 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.\(^\text{7}\) 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 organophosphino metal complexes. Just a few complexes of rhodium,\(^\text{7a}\) platinum,\(^\text{8}\) nickel,\(^\text{9}\) tantalum,\(^\text{10}\) molybdenum, and tungsten,\(^\text{11}\) coming from such a type of reaction, have been reported. The scarcity of terminal \([\text{M−PR}_2\text{]}_\text{a}\) species is among other reasons due to their marked tendency to form phosphino bridges. Indeed, the vast majority of these complexes (Co triad and after) are di- or polynuclear with bridging phosphano moieties. Thus, a wide range of di-\(^\text{12}\) and trinuclear\(^\text{13}\) complexes of platinum and palladium have been reported; some of them promote interesting stoichiometric P–C,\(^\text{14}\) P–N,\(^\text{15}\) and P–O\(^\text{16}\) bond formation reactions. Dinuclear rhodium and iridium phosphanido complexes have also been widely studied,\(^\text{17}\) uncovering unusual coordination environments and bonding schemes, such as tetrahedral geometries for d\(^\text{8}\)-M configurations (M = Rh, Ir)\(^\text{18}\) or square-planar in edge-sharing coplanar d\(^\text{7}\)-Rh compounds.\(^\text{19}\)

On the contrary, terminal phosphano compounds of iridium are very scarce. Isolated complexes include \([\text{Ir(N(SiMe}_3\text{CH}_2\text{PPh}_2\text{)}_2\text{(CH}_2\text{)}_2\text{(PR}_2\text{)}_2}\text{]}_\text{2}\) \(\text{R = Ph, m-tolyl, [Ir(CO)-(H)(L)_2X(PH}_2\text{)]_2}\) \((L = P\text{Et}_3, 1/2 \text{ dppe; X = Br, Cl, [IrCl}_3\text{(PMe}_2\text{Ph)}_2\text{(PH}_2\text{)}_2}\) and two recent examples with fac-L\(_1\)-iridium(III) \(^\text{20}\) and mer-L\(_2\)-iridium(III) \(^\text{21}\) scaffolds in which the phosphano functionality is embedded within a tripodal ligand.

Received: October 6, 2015
Published: December 22, 2015

DOI: 10.1021/acs.inorgchem.5b02301
Inorg. Chem. 2016, 55, 828−839
Herein, we report the P–H bond activation of a secondary organophosphine by an iridium complex, which affords a terminal phosphanido hydrido compound involving direct oxidative addition of the R3P–H bond to iridium. The new complex incorporates the original anionic hybrid scorpionate ligand [(allyl)B(Pz2)(CH3PPh2)]− ([ABPN2]−, Pz = pyrazolate) that displays three different arms suitable for coordination.25 Some reactions involving the new Ir–PPh3 bond as well as the molecular and electronic structure of the complex are also reported.

RESULTS AND DISCUSSION

Addition of diphenylphosphane (PPh2) to the carbonyl-bridged dinuclear iridium(I) complex [(Ir(ABPN2)(CO))2(μ-CO)]25a (1) produces an immediate reaction to give the mononuclear hydrido phosphanido iridium(III) complex [Ir(ABPN2)(CO)(H)(PPh2)] (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)

![Diagram of complex 2](image1.png)

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 κ3N,A,KP-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 tripodal ligand. This short/long bonding scheme for trans-R3P–M–PR3 moieties in square-planar/octahedral complexes is quite common,26 and has been attributed to the stronger trans influence of the phosphane ligand.22 Electronic repulsion between the phosphanido lone pair and the filled iridium d3z2 or dz2 or dxy 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 (J IrP = 97 Hz) observed in the 31P{1H} 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–PR3 bond as compared to Ir–PR523,26d,27 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–PR3 complexes, for which both phosphorus inversion and rotation around the M–PR3 bond have been reported to be low-energy processes.28

The geometry of complex [Ir(ABPN2)(CO)(H)(PPh2)] (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
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 descriptor 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 phosphane and phosphanido 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 phosphane and the oxidative-addition of the P−H bond to the iridium centers. Monitoring the reaction by NMR showed no changes below 20 °C; above this temperature, a gradual transformation of 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)]2(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)].25 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.30 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 geometric 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 to 2.623 Å in TS-1, showing partial oxidation from IrI to IrII in TS-1, and partial coordination of the pyrazole donor, which likely plays a role in stabilization of the transition state (anchimeric 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 PH3 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 [Ir(ABPN\(_2\))(CO)(H)(PEPh\(_2\))]\(^+\) (E = H, [3]\(^+\); Me, [4]\(^+\), Scheme 3). Quaternization of the parent phosphanido ligand in 2 results in a considerable enlargement of the \(^1\)J\(_{P,P}\) 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 [Ir(ABPN\(_2\))(CO)(H)(POPh\(_2\))] (5), where some reduction of the electronic density on the iridium atom in 5 was detected by an increase of the \(\nu\)(CO) frequency from 2023 cm\(^{-1}\) in complex 2 to 2053 cm\(^{-1}\) in 5.

Organic chlorides such as methyl chloroacetate (ClCH\(_2\)CO\(_2\)Me) also react with the phosphanido ligand at 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 [Ir(ABPN\(_2\))(CO)(H)(PPh\(_2\)CH\(_2\)CO\(_2\)Me)][PF\(_6\)] ([6]PF\(_6\)) was isolated after workup. Formation of the new P–C bond was confirmed through an \(^1\)H,\(^{31}\)P-hmbc NMR experiment where the expected correlation peaks between the CH\(_2\) protons of the coordinated phosphane, Ir–P\(^3\)P\(_2\)CH\(_2\)CO\(_2\)Me, and 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 [Ir(ABPN\(_2\))(CO)(Cl)(H)] (7) and the free phosphane, PPh\(_2\)CH\(_2\)CO\(_2\)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 PPh\(_2\)CH\(_2\)CO\(_2\)Me was easily identified from a singlet at \(\delta = -16.5\) ppm in the \(^{31}\)P\{\(^1\)H\} NMR spectrum. 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 tripospical ligand and to the carbonyl, hydride, and chloride ligands, the latter being placed \textit{trans} to the phosphorus atom. As expected, the strong \textit{trans} influence of the hydride ligand is reflected in a longer Ir–N\(_3\) bond distance as compared to the Ir–N\(_1\) bond (Figure 6).

The cationic complex [Ir(ABPN\(_2\))(CO)(H)-PPh\(_2\)CH\(_2\)CO\(_2\)Me)][PF\(_6\)] ([6]PF\(_6\)) remains unaltered in solution, but in the presence of PPNCl (PPN = bis(triphenylphosphane)iminium) evolves cleanly and quantitatively to [Ir(ABPN\(_2\))(CO)(Cl)(H)] (7) and PPh\(_2\)CH\(_2\)CO\(_2\)Me. As such, we could assume that the first intermediate in the reaction of 2 with CICH\(_2\)CO\(_2\)Me in benzene is [Ir(ABPN\(_2\))...
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 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–P 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 sp2 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.

Scheme 5. Reaction of [Ir(ABPN2)(CO)(H)(PPh2)] (2) with dmad (MeO2CC≡CCO2Me) To Give Complex 8

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resulting carbanion to the terminal carbonyl group, as previously suggested for carbonyl complexes with terminal phosphanide, thiolate, iminophosphorane, hydroxo, or amido ligands. Moreover, because complex 2 also contains a hydride ligand, abstraction of this hydrogen by the carbanion to give the iridium(I) derivative [Ir(ABPN 2)(CO){PPh2–CH=CH(CO2Me)}] could also be considered (path ii, Scheme 6), but no evidence for such a complex was obtained when monitoring the reaction by NMR. The alternative pathway involving a concerted cycloaddition process could be also considered, but we were thus far unable to locate such a concerted transition state with DFT. Furthermore, the products obtained upon reaction of 2 with a monosubstituted alkyne are indicative of a stepwise process (see discussion below and Scheme 7).

The related monosubstituted alkyne methyl propiolate (HC≡COCO2Me) 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≡COCO2Me 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 iridacyclopentapentenone compound [Ir(ABPN 2)(H){PPh2–CH=CH(CO2Me)=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(CO2Me)=CO}{PPh2–CH=CH(CO2Me)}] (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–C=H proton at very low field (δ = 9.46 ppm) in the 1H NMR spectrum, while the high field shift of the ketonic Ir–CO carbon up to to δ = 177.3 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){PPh2–CH=CH(CO2Me)}] 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. Reported examples include complexes of ruthenium, iron, rhenium, and iridium obtained from reactions of carbonyl compounds with activated alkynes and of platinum and cobalt coming from metal insertion into cyclopropenones.

To verify the participation of the iridium(I) species [Ir(ABPN 2)(CO){PPh2–CH=CH(CO2Me)}] in the formation of complex 10, a model reaction between [[Ir(ABPN 2)–(CO)]2(μ-CO)] (1) and PPh2Me (to generate the mononuclear complex [Ir(ABPN 2)(CO)(PPh2Me)]) followed by the addition of 1 mol equiv of HC≡COCO2Me was carried out. The overall reaction produces clean and quantitatively complex...
[Ir(ABPN2){CH≡C(CO2Me)−CO}(PPh2Me)] (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 phosphanide 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 iridacyclophepantane 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,H. Moreover, the large J_H,H coupling constant suggests both protons to be in an anti-periplanar 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 of 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.

Scheme 10. Transformation of [Ir(ABPN2)(CO)(PPh2R)] (R = CH(CO2Me)CH2(CO2Me), D) in Complex 12 and a Plausible Way for the Isomerization of 12′ into 12 through the Enol Intermediates E1 and E2

**Figure 9.** Selected regions of the 1H NMR spectra of complex 12 (bottom) and after 17 h at 40 °C in the presence of 5 mol equiv of D2O (top).

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**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 phosphanido ligand. This rare compound results formally from the oxidative addition of a P−H bond to iridium(I). The reactivity of the phosphanido complex is governed by the nucleophilicity of the phosphanido 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 KPF$_6$ gives the cation with a functionalized phosphane [Ir(ABPN)$_2$](CO)(H)(PPh$_2$CH$_2$CO$_2$Me)]$^+$ by a P–C coupling reaction, while in the absence of the salt the free phosphane PPh$_2$CH$_2$CO$_2$Me results along with the hydrido complex [Ir(ABPN)$_2$)(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 iridacyclopentenone complexes [Ir(ABPN)$_2$)(H)PPh$_2$–CR=C(CO$_2$Me)=CO)] (R = CO$_2$Me, H) from reactions of 2 with dimethyl acetylenedicarboxylate and methyl propionate, respectively. A parallel reaction in the second case also affords a rare iridacyclobutene complex [Ir(ABPN)$_2$)(CH$_2$=C(CO$_2$Me)=CO)] by allyne coordination and CO insertion into the metallacyclopentene ring. Activated allenes such as dimethyl maleate and dimethyl fumarate also reacted with 2 to form eventually the same iridacyclopentanone complex [Ir(ABPN)$_2$)(H)PPh$_2$–CH=CH(CO$_2$Me)=CO)], the thermodynamic product of both reactions. Deuteration exchange of the methylenic and hydride protons in the presence of D$_2$O 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.$^{15}$ Carbon, hydrogen, and nitrogen analyses were carried out with a PerkinElmer 2400 CHNS/O microanalyzer. High-resolution electro spray mass spectra were acquired on a Bruker Microtuf-Q (ESI$^+$. NMR spectra were recorded on Bruker AV 500, AV 400, and AV 500 spectrometers operating at 300.13, 400.13, and 500.13 MHz, respectively, for $^1$H. Chemical shifts are reported in ppm and referenced to SiMe$_4$ using the internal signal of the deuterated solvent ($^1$H and $^13$C) and external H$_2$PO$_4^-$ ($^31$P). 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 conductimeter. Recorded values for complexes [3][BF$_4$]$^-$[OTf], and [6][PF$_6$] were found to be in agreement with 1:1 electrolytes (54–79 1 cm$^2$ mol$^{-1}$). The complex [Ir(ABPN)$_2$)(CO)]($^\mu$-CO)]$^{15a}$ (1) was prepared according to the literature description. All other chemicals are commercially available and were used without further purification.

**Synthesis of the Complexes: [Ir(ABPN)$_2$)(CO)(H)(PPh$_2$H)] (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): $\nu$(Ir–H)/cm$^{-1}$ 2323 (w), $\nu$(CO)/cm$^{-1}$ 2023 (s). MS (MALDI-TOF$^-$$^-$): $m/z$ (%) 793 (100) [M$^+$ + H$^-$], 765 (40) [M$^+$ + H$^-$ + CO]. Anal. Calcd for C$_{37}$H$_{37}$BF$_3$IrN$_4$O$_5$P$_2$: C, 45.73; H, 3.85; N, 5.77. Found: C, 45.43; H, 3.84; N, 5.70. $\Lambda_{d}$= 57.9 1 cm$^2$ mol$^{-1}$ (acetone, 5.0 × 10$^{-4}$ M). For NMR data, see the Supporting Information.


DOI: 10.1021/acs.inorgchem.5b02301
the solid was isolated by filtration and then vacuum dried. Yield: 92.5 mg (92%). IR (toluene): ν (1R–H)/cm⁻¹ 2189 (w), ν (C=O)/cm⁻¹ 1704 (s, br), MS (MALDI-TOF+): m/z (%) 653.1 (100) [M⁺ – H]. Anal. Calcd for C₁₂H₂₀Br₂IrN₄O₃P₂: C, 41.13; H, 3.31; Br, 16.56; P, 14.55. Found: C, 41.33; H, 3.30; Br, 16.25; P, 14.34.

**Supporting Information**

**DFT Geometry Optimizations.** Geometry optimizations were carried out with the Turbomole program package⁶⁶ coupled to the PQR Baker optimizer⁴⁷ via the Bopt package,⁴⁸ at the DFT/b3-lyp⁴⁹ level. We used the de2-TZVP basis set⁵⁰ (small-core pseudopotentials on Ir⁵¹) for the geometry optimizations. Scalar relativistic effects were included implicitly through the use of the Ir ECPs. Minima (no imaginary frequencies) and the transition state (one imaginary frequency) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The nature of the transition state was confirmed by IRC calculations. The optimized geometries of all species are supplied as separate files in .pdb and .xyz format. Mayer bond orders were calculated from the Turbomole output files using the AOMix program.⁵²

**X-ray Diffraction Studies on Complexes 2-0.5(C₄H₄), 0.4(C₄H₄), and 8(C₄H₄).** Intensity measurements were collected with a Smart Apex diffractometer, with graphite-monochromated Mo Kα radiation. A semiempirical absorption correction was applied to each data set, with the multiscan⁵³ methods. Selected crystallographic data can be found in the Supporting Information. The structures were solved by the Patterson method and refined by full-matrix least-squares, with the program SHELXL2013⁵⁴ in the WINGX⁶ package. The hydride ligands were found in residual electron density maps and refined free but with a restrained distance to the metal atom, with free isotropic displacement parameters for 2 and 8, and a riding one for complex 7.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02301.

Selected crystallographic data, and selected NMR spectra for the complexes (PDF)

X-ray data for compounds 2-0.5(C₄H₄), 0.4(C₄H₄), and 8(C₄H₄) (CIF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The generous financial support from MICINN/FEDER (Project CTQ2011-22516) and MINECO/FEDER (Projects CTQ2012-35665 and CTQ2014-53033-P), Gobierno de Aragón/FSE (GA/FSE, Inorganic Molecular Architecture Group, E70), and NWO-CW (VICI project 016.122.613; B.D.B.) is gratefully acknowledged. A.L.S. thanks MEC for a fellowship.

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