C−C Formation and C−O Cleavage Reactions on Hemilabile Arene−Phosphine Ligands in Route to η^5-Cyclohexadienyl Iridium Compounds[§]

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Received May 6, 2008

Complexes of the type [Ir{η^5-3-(CH_3COCH_2)$C_6H_5OCH_2CH_2P$*t*-Bu_2-*k*-P}(alkene)] (alkene = C_2H_4, **4**, C_3H_6, **5**) were prepared by nucleophilic addition of acetone enolate to the "*ansa*" π-arene/phosphine-type compounds [Ir(alkene)(η^6-$C_6H_5OCH_2CH_2P$*t*-Bu_2-*k*-P)][BF_4] (alkene = C_2H_4, **1**, C_3H_6, **2**) where the arene−phosphine is acting as a formal eight-electron-donor chelate ligand. On the other hand, the related [Ir{η^5-3-($C_6H_5C{\equiv}C$)$C_6H_5OCH_2CH_2P$*t*-Bu_2-*k*-P}(C_2H_4)] complex (**6**) was obtained by addition of phenylacetylide to compound **1**, but the reaction was not fully completed. Compounds **4** and **5** react with methanol with a C−O bond cleavage process, producing the vinylphosphine complexes [Ir(η^5-C_6H_5O)(alkene)(*t*-$Bu_2PCH{=}CH_2$)] (alkene = C_2H_4, **7**, C_3H_6, **8**). Compounds **7** and **8** are also obtained by treatment of **1** and **2**, respectively, with a basic solution in methanol. The vinyl group in **7** adds methanol to render an ether phosphine, which coordinates in a chelate form, and the final compound isolated was [Ir(OC_6H_5)(C_2H_4)(*t*-$Bu_2PCH_2CH_2OMe$-k^2-*O*,*P*)] (**9**). In addition, the molecular structures of complexes **4** and **7** have been determined by X-ray diffraction methods.

Introduction

Functionalized phosphines have been intensively studied,[1] as they could behave as hemilabile ligands during catalysis, either providing easily accessible coordination vacancies or protecting the active catalytic site, with a potentially dynamic "on and off" chelating effect for the metal complex. Hybrid P,O-[2] and P,N-based ligands[3] have been the most investigated since P usually binds strongly to the metal center, whereas the other donor atom (O or N) is generally only weakly bonded.

Half-sandwich metal−arene complexes are an important and widely used class of organometallic compounds, which exhibit a diverse range of coordination chemistry and show considerable potential as precursors for catalytic organic transformations.[4] To stabilize otherwise elusive or coordinatively unsaturated species, recent work on half-sandwich metal−arene complexes has mainly concentrated on arene-tethered ligands, the arene-tethered phosphine with a flexible linkage being the most popular. Thus, much attention has been paid to ligands such as $R_2P(CH_2)_nXC_6H_4R$ (n = 1, 2; X = CH_2, O), which could behave as either two-electron or (2+6)-electron donors, thus having a hemilabile character.[5] It is noticeable that η^6-arene/free arene exchange reactions have been studied in detail by Mirkin[6] with the phosphine $PhO(CH_2)_2PPh_2$. Werner[5c] has found that unsaturated monomeric species such as [$MCl(PR_3)_2$] (M = Rh, Ir) are accessible both with P*i*-Pr_3 and with the aryl-functionalized phosphines *i*-$Pr_2P(CH_2)_n$(aryl) and *t*-$Bu_2P(CH_2)_n$(aryl) (n = 2 or 3), both related in terms of size with P*i*-Pr_3. However, interesting differences in reactivity were observed with these aryl-functionalized phosphines compared with the monodentate P*i*-Pr_3, as is the case, for instance, of the reversible C−H activation of the aryl moiety,[7,8] the stabilization of a *cis*-rhodium dicarbonyl [$RhCl$(*t*-$Bu_2P(CH_2)_2C_6H_3$-2,6-Me_2)$(CO)_2$],[9] or the formation of a dinuclear rhodium(III) complex built up by two 14-electron units.[10]

[§] Dedicated to Heinrich Nöth on the occasion of his 80th birthday.

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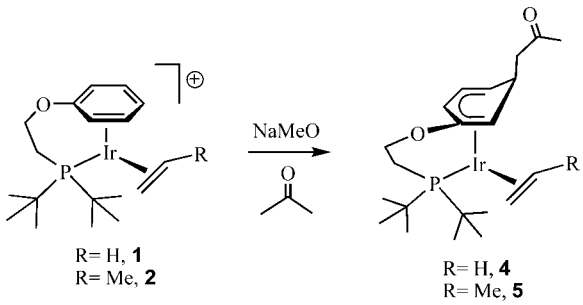
Publication on Web 07/31/2008

Scheme 1



In spite of several aryloxy-tethered bis-phosphines having found applications in the design of metallomacrocycles,[11] less attention has been paid to the reactivity of metal complexes containing aryloxy-tethered phosphines of the type R_2P-$(CH_2)_n$-OC_6H_4R.[6,8,12] Their particular reactivity concerns the *ortho*-selective functionalization of phenols,[13] as the presence of the oxygen atom can promote the activation of the aryl group, providing potentially novel reactivity.

In this paper, we report the reactivity of cationic Ir(I) and Ir(III) complexes, [Ir(alkene)(η^6-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P)][BF_4] (alkene = C_2H_4, C_3H_6) and [IrH_2(η^6-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P)][BF_4],[8] containing the phosphine *t*-$Bu_2P(CH_2)_2(OC_6H_5)$.[14] The aryloxy−alkylphosphine in these complexes is coordinated in an "*ansa*" π-arene/phosphine fashion, acting as a formal eight-electron-donor ligand. In general, the reactivity toward nucleophiles gives rise to new neutral alkoxy-η^5-cyclohexadienyl phosphine iridium compounds resulting from nucleophilic addition to the arene ring. Interestingly, along with the C−C coupling reactions, where the whole phenoxy-tethered phosphine remains coordinated to the iridium, a C−O bond cleavage has been observed in the ligand to form oxo-η^5-cyclohexadienyl−vinylphosphine iridium complexes.

Results and Discussion

Reaction of Iridium(I) Phenoxy−Phosphine Derivatives [Ir(alkene)(η^6-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P)][BF_4] (1, 2) with Nucleophiles. The alkene Ir(I) complexes [Ir(C_2H_4)(η^6-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P)][BF_4] (**1**) and [Ir(C_3H_6)(η^6-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P)][BF_4] (**2**), containing the "*ansa*" π-arene/phosphine ligand, were prepared by reaction of [IrH_2(η^6-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P)][BF_4] (**3**) with ethene or propene.[8]

Reaction of the complexes **1** and **2** with sodium methoxide in acetone gave the neutral complexes [Ir{η^5-3-(CH_3COCH_2)-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P}(C_2H_4)] (**4**) and [Ir{η^5-3-(CH_3COCH_2)-$C_6H_5O(CH_2)_2P$*t*-Bu_2-*k*-P}(C_3H_6)] (**5**), which were isolated as pale yellow solids in good yields. The formation of these complexes results from the selective nucleophilic attack of acetone enolate ($CH_3-CO-CH_2^-$) at the *meta* position of the phenyl ring, resulting in the formation of a new C−C bond (Scheme 1). It is noticeable that only the addition of acetone enolate (generated in the reaction medium) was observed, in accordance with the superior stability of the new C−C bond compared to a possible C−O bond formed through the nucleophilic addition of methoxide (MeO^-) to the arene.[15]

Compounds **4** and **5** do not behave as conductors in acetone and have been fully characterized by elemental analysis, mass spectrometry, and multinuclear NMR spectroscopy. In addition, the molecular structure of complex **4** has been determined by X-ray diffraction methods and confirms the regioselective *meta* attack of the nucleophilic addition. The 2-oxo-propyl fragment was clearly identified in the ^{1}H NMR spectrum by a complex resonance characteristic of the methylenic protons at δ 1.68 (**4**) and 1.85 (**5**) ppm as the AB part of an ABX system (X = H_3 of the alkoxy-η^5-cyclohexadienyl fragment). The carbonyl group was observed at 1710 cm^{-1}, ν(C=O) stretching, in the IR spectrum and at δ 204.49 ppm in the $^{13}C\{^1H\}$ NMR. The alkoxy-η^5-cyclohexadienyl fragment showed a characteristic set of five resonances in the ^{1}H NMR[16] for the ring very much high-field shifted compared to those of the starting complexes **1** and **2**. Full assignment of the proton and carbon resonances of the new ligand was achieved by a combination of the $^1H-^1H$ COSY and correlation $^1H-^{13}C$ HSQC NMR spectra (Figure 1, compound **4**). Interestingly, the H_3 resonance was observed as a complex pattern resulting from the coupling to the two methylenic protons of the 2-oxo-propyl fragment, the two adjacent CH protons (H_2 and H_4), and the phosphorus atom. Similarly, the C_4 resonance was observed as a doublet around 35 ppm in the $^{13}C\{^1H\}$ NMR, exhibiting a large coupling constant ($J_{C4-P} \approx 28$ Hz), in agreement with the relative *transoid* disposition to the P*t*-Bu_2 fragment observed in the molecular structure (Figure 2).

Coordination to a metal imparts significant electrophilic character to a coordinated cyclic π-hydrocarbon. Its reaction with nucleophiles could include multiple possibilities as single or double addition to the coordinated ring, substitution of a ring substituent, deprotonation of the coordinated ring or of the side chain, ligand substitution, or a single electron transfer.[17] In addition, when olefins are coordinated simultaneously together with a cyclic π-hydrocarbon, the nucleophilic attack takes place preferably at the alkene,[18] although this is not a general rule as in [$Ru(C_6H_6)(PMe_3)_2(C_2H_4)]^{2+}$, where another PR_3 (R = Me, *i*-Pr, Ph, OMe) added attacks the coordinated ethylene, but hard bases such as LiMe, NaMeO, and LiMe lead to nucleophilic addition to the arene.[19]

Concerning the observed regioselectivity in the nucleophilic attack to a η^6-phenol ring, Amouri and Harman have described the *ortho* and *para* selective addition to cathionic oxo-η^5-cyclohexadienyl complexes of iridium(III)[13c,20] and η^2-pheno-

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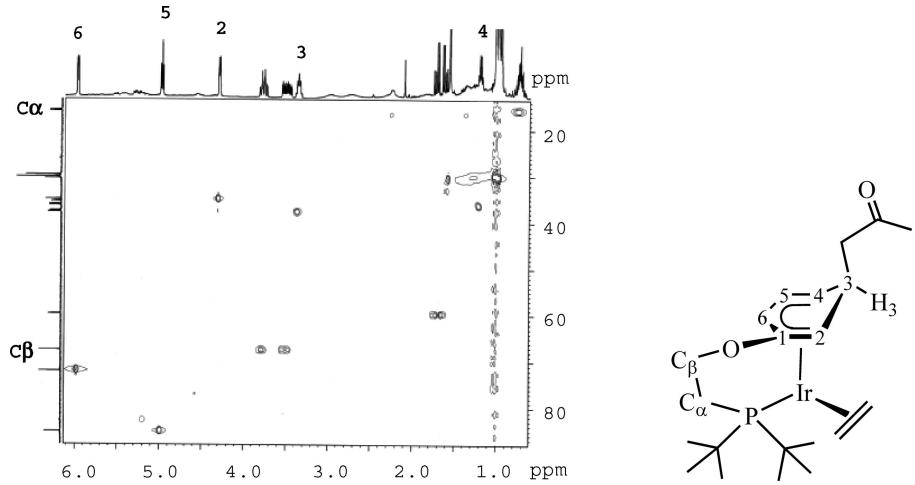

Figure 1. $^1H/^{13}C$ HSQC NMR spectrum for compound **4** showing the characteristic ^1H pattern for the alkoxy−cyclohexadienyl fragment and, in particular, the high-field shift of the protons, especially for H_4.

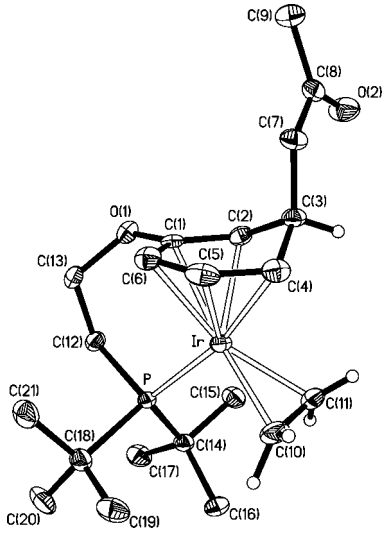

Figure 2. Molecular structure of complex **4** (hydrogen atoms are represented only for the olefinic ligand and for the asymmetric C(3) atom).

losmium(II),[21] respectively. In general, it has been found that the selectivity of the nucleophilic attack on substituted arene metal complexes is influenced by the electronic effect of the substituent on the arene.[18b,22] Electron-donating groups such as −OMe or $-NR_2$ direct *meta* addition, in contrast to electron withdrawing substituents, such as chloro, that induce mainly *ortho* addition. Thus, the regioselective *meta* addition is in good agreement with the expected electron-donating character of the alkoxy substituent in the arene.

Good quality crystals for an X-ray diffraction experiment were obtained from low concentrated solutions of **4** in diethyl ether. Bond distances and angles are given in Table 1. Coordination angles around the metal center, considering midpoints of multiply bonded ligands (η^5-ring and η^2-ethylene), reveal an ideal, slightly distorted trigonal-planar environment of ligands. The most interesting structural feature of **4** concerns the *meta* carbon atom C(3) of the alkoxy-η^5-cyclohexadienyl ring; the Ir−C(3) separation, 2.799(4) Å, is remarkably longer than the rest of the Ir−C distances (2.155−2.297(4) Å), and it could not be considered as a bond distance. The five Ir-bonded carbon atoms (C(1), C(2), C(4), C(5), and C(6)) maintain a roughly coplanar disposition, making a significant dihedral angle of 43.9(3)° with the plane defined by C(2), C(3), and C(4). These structural parameters are clearly indicative of a η^5-coordination and are comparable with other related oxo-cyclohexadienyl complexes.[23] Additionally, the C−C bond distances within the six-membered ring also reveal the different nature of the C−C bonds to C(3) and, consequently, the referred ring η^5-coordination; while the C(2)−C(3) and C(3)−C(4) bond distances are typical of single C−C bonds (mean 1.516(4) Å)—analogous, for instance, to C(3)−C(7) or C(7)−C(8) bond lengths (mean 1.519(4) Å)—the remaining C−C separations are clearly shorter, in the usual range of aromatic metal-coordinated bond distances (1.387−1.442(6) Å). As a whole, the Cromer and Pople parameters characterized the η^5-cyclohexadienyl ring conformation as a clear, highly bent envelope (θ = 57.6(5), ϕ = 125.3(6)°, and Q = 0.473(4) Å).[24]

Reaction of compound **1** with other nucleophiles such as methyllithium or butyllithium also gave addition products. However, in contrast with the precedent cases, the reactions were unselective and produced a complicated mixture of compounds (^1H NMR evidence). Interestingly, the nucleophilic addition of lithium phenylacetylide in acetone cleanly proceeds to give the compound [Ir{η^5-3-($C_6H_5C'C$)$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P}(C_2H_4)] (**6**), which is in equilibrium with **1** (Scheme 2). Using a moderate excess of LiC≡CPh, an approximately 1:1 mixture of both compounds was obtained. Attempts to isolate pure **6** from the reaction mixture were unsuccessful, and the compound has been characterized in solution.

The ^1H NMR of **6** shows the characteristic set of resonances for the alkoxy-η^5-cyclohexadienyl fragment that confirms the nucleophilic addition of phenylacetylide at the *meta* position on the phenoxy ring. The resonance for the H_3 proton is observed at δ 3.14 ppm and is masked by those of methylenic

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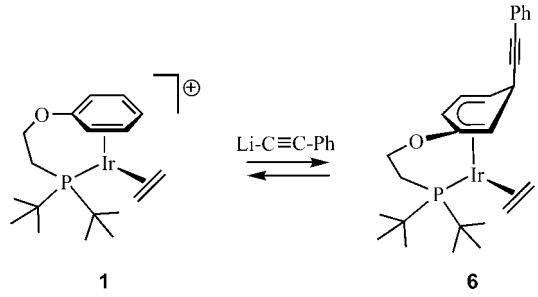
Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 4 and 7

	4	7		4	7
Ir−P	2.3188(10)	2.2834(7)	O(1)−C(1)	1.397(5)	1.267(3)
Ir/C(1)[a]	2.253(4)	2.492(3)	O(1)−C(13)	1.431(5)	
Ir−C(2)	2.297(4)	2.343(3)	O(2)−C(8)	1.216(5)	
Ir/C(3)[a]	2.799(4)	2.266(3)	C(1)−C(2)	1.387(5)	1.430(4)
Ir−C(4)	2.155(4)	2.299(3)	C(1)−C(6)	1.442(6)	1.452(4)
Ir−C(5)	2.206(4)	2.231 (3)	C(2)−C(3)	1.530(6)	1.414(4)
Ir−C(6)	2.273(4)	2.216(3)	C(3)−C(4)	1.502(6)	1.410(4)
Ir−G[b]	1.770(2)	1.8090(12)	C(3)−C(7)	1.532(6)	
Ir−C(10)	2.105(5)	2.103 (3)	C(4)−C(5)	1.424(7)	1.397(4)
Ir−C(11)	2.097(4)	2.103 (3)	C(5)−C(6)	1.418(6)	1.415(4)
P−C(12)	1.854(4)	1.820(3)	C(7)−C(8)	1.506(6)	
P−C(14)	1.900(4)	1.894(3)	C(10)−C(11)	1.437(7)	1.425(4)
P−C(18)	1.910(4)	1.897(3)	C(12)−C(13)	1.525(6)	1.308(4)
P−Ir−G[b]	124.00(7)	133.39(4)	O(1)−C(1)−C(2)	117.2(4)	123.9(2)
P−Ir−M[b]	100.73(11)	91.61(7)	O(1)−C(1)−C(6)	121.0(4)	122.2(3)
G−Ir−M[b]	135.27(12)	134.81(7)	C(2)−C(1)−C(6)	121.8(4)	113.4(2)
Ir−P−C(12)	111.01(14)	113.50(9)	C(1)−C(2)−C(3)	118.2(4)	121.1(3)
Ir−P−C(14)	117.97(13)	113.61(9)	C(2)−C(3)−C(4)	101.2(3)	122.3(3)
Ir−P−C(18)	115.81(13)	114.41(9)	C(2)−C(3)−C(7)	114.5(4)	
C(12)−P−C(14)	99.13(18)	98.58(12)	C(4)−C(3)−C(7)	114.9(3)	
C(12)−P−C(18)	102.36(19)	104.05(13)	C(3)−C(4)−C(5)	119.5(4)	117.8(3)
C(14)−P−C(18)	108.19(18)	111.23(12)	C(4)−C(5)−C(6)	118.3(4)	119.8(3)
C(1)−O(1)−C(13)	118.0(3)		C(1)−C(6)−C(5)	116.4(4)	123.0(3)
			P−C(12)−C(13)	118.2(3)	130.5(2)

[a] These distances are considered bond or interaction distances (see discussion). [b] G represents the centroid of the η^5-dienyl ligands; M that of the olefinic double bond C(10)−C(11).

Scheme 2



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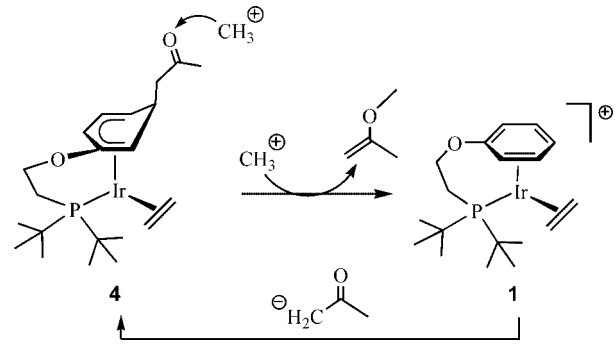
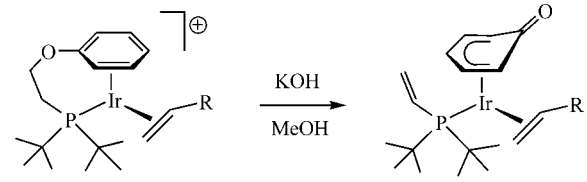
Scheme 3



4 1

Scheme 4



R= H, **1**
R= Me, **2**

R= H, **7**
R= Me, **8**

protons, although the coupling with H_2, and H_4 was clearly evidenced in the $^1H-^1H$ COSY spectrum. The ethylene ligand is seen as a very broad signal centered at δ 2.47 ppm. The Cα and Cβ of the methylenic groups were observed at δ 69.11 and 81.44 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectrum. In addition, the MALDI-TOF mass spectrum showed an ion at *m*/*z* 559.1, which corresponds to the loss of the ethylene ligand. All these spectroscopic data seem to suggest that the molecular structure of **6** is analogous to that of **4**.

C−C or C−O Bond Cleavage Reactions on the Complexes [Ir{η^5-3-(CH$_3$COCH$_2$)C$_6$H$_5$O(CH$_2$)$_2$P*t*-Bu$_2$-*k*-P}(alkene)] (4, 5). The reaction of [Ir{η^5-3-(CH$_3$COCH$_2$)C$_6$H$_5$O(CH$_2$)$_2$P*t*-Bu$_2$-*k*-P}(C$_2$H$_4$)] (**4**) with electrophiles, such as H^+ or CH_3^+, resulted in the elimination of the 2-oxo-propyl fragment (Scheme 3). Thus, addition of a stoichiometric amount of methyl triflate or triflic acid to solutions of compound **4** in dichloromethane allowed the quantitative recovery of η^6-arene starting material **1** as the triflate salt. The reaction pathway should involve the direct electrophilic attack of Me^+/H^+ to the 2-oxo-propyl fragment, as isopropenyl methyl ether, $CH_2{=}C(CH_3)(O\text{-}CH_3)$, and acetone were detected by both GC-MS and ^1H NMR.

Alkylations of enolate with triflates are among the most useful carbon−carbon bond formation reactions.[25] It is known that the reaction of the deprotonated form of acetone with bromomethane results in the formation of either ethyl methyl ketone or isopropenyl methyl ether as a consequence of the alkylation of the keto and enol tautomers, respectively.[26] In our case, as isopropenyl methyl ether is the only organic compound detected by ^1H NMR, the Me^+ should selectively attack the oxygen atom of the 2-oxo-propyl group.

Unexpectedly, the alkoxy-η^5-cyclohexadienyl compounds [Ir{η^5-3-(CH$_3$COCH$_2$)C$_6$H$_5$O(CH$_2$)$_2$P*t*-Bu$_2$-*k*-P}(alkene)] (**4**, **5**) slowly convert into new species in methanol. The monitoring of the reactions by $^{31}P\{^1H\}$ NMR evidenced a gradual decrease in the intensity of the resonances at δ 5.85 and 4.70 ppm, corresponding to compounds **4** and **5**, respectively, as new

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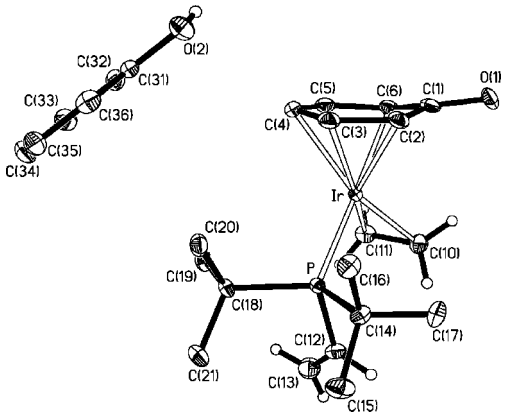

Figure 3. Molecular structure of complex **7** showing the labeling scheme used (hydrogens are shown only for the coordinated olefin and for the OH group of the phenol crystallization molecule).

downfield-shifted resonances became visible at δ 32.02 and 31.04 ppm corresponding to the new species. From these solutions, complexes [Ir(η^5-C_6H_5O)(C_2H_4)(*t*-Bu_2PCH=CH_2)] (**7**) and [Ir(η^5-C_6H_5O)(C_3H_6)(*t*-Bu_2PCH=CH_2)] (**8**) were obtained (Scheme 4) in moderate yield. The complexes have been fully characterized by elemental analysis, mass spectrometry, and multinuclear NMR spectroscopy. The presence of oxo-η^5-cyclohexadienyl and vinylphosphine ligands in the complexes has been further confirmed by an X-ray diffraction study on complex **7**.

Single crystals of **7** suitable for X-ray studies were grown from acetone solutions. Its molecular structure is depicted in Figure 3, and bond distances and angles are given in Table 1. As described for **4**, the determined geometric parameters confirm the oxo-η^5-cyclohexadienyl bonding mode, although the structural modifications of the ketonic carbon atom (C(1)) from an ideal η^6-coordination are not as intense as those observed in **4**. Thus, the Ir−C(1) separation, 2.492(3) Å, is only slightly longer than the remaining Ir−C bond distances, 2.216−2.343(3) Å; the interplanar angle between the five coplanar Ir-bonded carbons and the ketonic plane is 14.9(2)°, significantly smaller than the value observed in **4** (43.9(3)°); and the intra-ring C−C bond distances do not show serious differences between the formally single bonds to C(1) (mean 1.441(4) Å) and those of the aromatic Ir-coordinated C−C bonds (range 1.397−1.415(4) Å). The ketonic character of the C−O link is evidenced by the bond distance, 1.267(3) Å, which is quite similar to the bond lengths described in δ- or γ-lactams.[27] The breaking of the alkoxy C−O bond and formation of the unsaturated vinylphosphine substituent is also manifested from the structural analysis (C12−C(13) 1.308(4) Å).

The Ir−C separation observed for the ketonic carbon, 2.492(3) Å, compares well with other related transition metal complexes where a cyclohexadienyl ligand is described to be linked to a metal in a η^5-coordination mode (distances range 2.337−2.666 Å).[28] As usual, both η^5-dienyl ligands in **4** and **7** maintain a planar disposition almost perpendicular to the metal−ring centroid vector (γ-angle 9.4(1)° in **4** and 8.9(1)° in **7**).

The oxo-η^5-cyclohexadienyl ligand in complexes **7** and **8** was observed in the ^{1}H NMR spectra as a set of three and five resonances (4.7−6.2 ppm), respectively, as expected from the lack of symmetry of the latter. The ketonic group was observed in the ^{13}C{^{1}H} NMR spectra at δ 166.43 (**7**) and 166.19 ppm (**8**), values that are characteristic for the noncoordination of the C=O group. In addition, the infrared spectra of both complexes showed the expected ν(C=O) absorption at 1625 and 1630 cm^{-1}, respectively, in accordance with the ν(C=O) vibrations observed in deprotonated phenol derivatives.[23,29] Finally, the vinyl group of the phosphine ligand was observed as a set of three multiplets in the range 5.8−6.0 ppm, with the expected J_{HP} coupling constants (12−30 Hz).

The formation of complexes **7** and **8** is a consequence of the methanol-induced C−C and C−O bond cleavage reactions in the parent complexes [Ir{η^5-3-(CH_3COCH_2)C_6H_5O(CH_2)$_2$P*t*-Bu_2-*k*-P}(alkene)] (**4**, **5**) that result in the elimination of the 2-oxo-propyl fragment, the degradation of the "*ansa*" π-arene/phosphine ligand, and the formation of a new vinylphosphine group.

As the 2-oxo-propyl group is easily lost by reaction with electrophiles (Me^+ or H^+), the reaction is probably driven by the electrophilic attack of the alcohol-liberated proton to the oxygen atom of the 2-oxo-propyl group, resulting in the elimination of acetone and the restoration of the η^6-coordination mode of the "*ansa*" π-arene/phosphine ligand. However, the presence of the methoxide ion could induce proton abstraction on the Cα atom of the ligand side-chain, leading to the unexpected breaking of the alkyl C−O bond and the concerted formation of the new C=C bond. The formation of the final complexes requires the further tautomerization of the probably formed η^6-phenoxide ligand into the oxo-η^5-cyclohexadienyl ligand. This proposal is strongly supported by the observation that the "*ansa*" π-arene/phosphine complexes **1** and **2** react with potassium hydroxide or potassium *tert*-butoxide in methanol to give directly compounds **7** and **8**, which were isolated in moderate yield. Related MeO bond cleavage through a hydrolysis process has been observed in a metalated crown ether complex of Ir(III).[30]

The process outlined above is further complicated by the formation of phenol in the reaction media (NMR evidence), which most likely results from the protonation of the η^6-phenoxide/oxo-η^5-cyclohexadienyl ligands by the solvent and that is probably responsible for the moderate yield of the reactions. In fact, crystals of complex **7** were obtained as the phenol solvate in the same way as found in related late transition metal complexes containing oxo-η^5-cyclohexadienyl ligands.[31] In addition, complexes of iridium(III) of formula [Cp*Ir(oxo-η^5-cyclohexadienyl)][BF_4] have been obtained by Amouri[13c,20] by deprotonation of the corresponding phenol derivatives.

The oxo-η^5-cyclohexadienyl ligand in complexes **7** and **8** is not the only reactive site, as the vinyl group of the *t*-Bu_2P(CH=CH_2) ligand smoothly undergoes the addition of MeOH under the experimental conditions, leading to its transformation. Interestingly, the controlled treatment of solutions of complex **7** in toluene with methanol resulted in the formation of the compound [Ir(OC_6H_5)(C_2H_4)(*t*-Bu_2P(CH_2)$_2$OMe-k^2-*O*,*P*)] (**9**), which was isolated as a brown solid in moderate yield. Compound **9** contains the methoxiethyldi-*tert*-butylphosphine[32] ligand, which results from the anti-Markovnikoff

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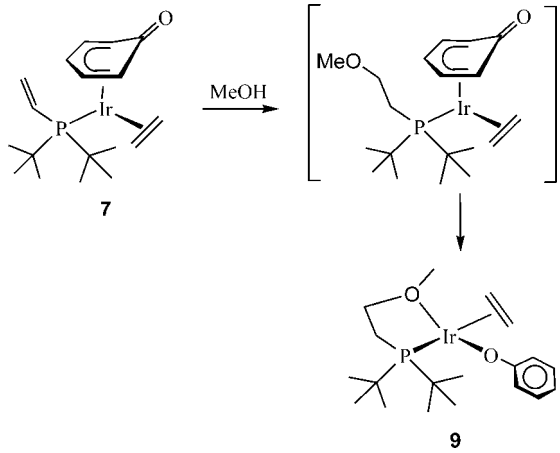
Scheme 5. Proposed Mechanism for the Formation of Compound 9

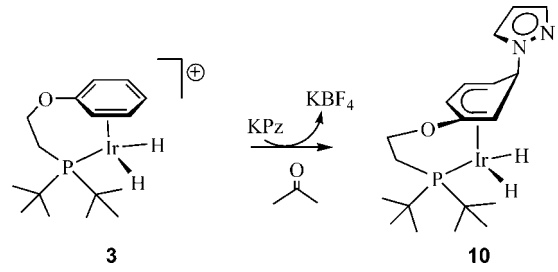


addition of MeOH to the vinyl group of the coordinated vinylphosphine ligand in **7** (Scheme 5).

The characterization of **9** as a square-planar phenoxyiridium(I)[33] complex was fairly straightforward by NMR spectroscopy. The presence of the *k*-*O*-phenoxide ligand was inferred by the set of resonances in the ranges δ 6.89−7.20 ppm and δ 111.74−118.23 ppm observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively. The ethylene ligand displayed two multiplets at δ 1.60 and 2.05 ppm in the ^{1}H NMR spectrum, as in precedent complexes. On the other hand, the ^{31}P{^{1}H} NMR showed a single resonance at δ 46.09 ppm, which is also indicative of a k^2-*O*,*P* mode of coordination for the methoxiethyldi-*tert*-butylphosphine ligand, as it has been contrasted with the spectroscopic data of related k^2-*O*,*P*-coordinated ether-functionalized phosphine ligands.[12,34] Although both methylene groups of the methoxyethyl fragment were observed as a doublet of triplets at δ 3.24 (CH_2O) and 1.51 (CH_2P), the observed J_{PH} coupling constant is larger for the former. This fact has already been noticed in phenoxyethyldi-*tert*-butylphosphine complexes coordinated in a k^2-*O*,*P* mode.[8]

Vinylphosphines play an important role in organophosphorus chemistry both as intermediates for the preparation of polyphosphines and as ligands in organometallic catalysis.[35] The base-catalyzed addition of alcohols to vinylphosphine oxide to form alkoxyethylphosphine oxides is known.[36] Although the coordination chemistry of several vinylphosphine ligands has been studied,[37] the effect of the phosphine complexation on the reactivity of the olefinic double bond has not been extensively studied. Noteworthy, Schmidbaur[38] has demonstrated that uncoordinated vinylidene groups in a gold vinylidenebis(diphenylphosphine) complex become strongly activated for the addition of methanol to form methoxiethanodiphenylphosphine through diphosphine−metal coordination. In the same way, the coordination of the *t*-$Bu_2P(CH{=}CH_2)$ ligand to iridium results in the activation of the uncoordinated vinyl fragment for the addition of MeOH to give the intermediate complex [Ir(η^5-C_6H_5O)(C_2H_4)(*t*-$Bu_2P(CH_2)_2OMe$-*k*-*P*)], which has been observed by ^{1}H NMR (δ 4.20, 5.27, and 5.42 ppm). The oxo-η^5-cyclohexadienyl ligand tautomerizes to a *k*-*O*-phenoxide ligand, facilitating the k^2-*O*,*P* mode of coordination of the methoxiethyldi-*tert*-butylphosphine ligand in compound [Ir(OC_6H_5)(C_2H_4)(*t*-$Bu_2P(CH_2)_2OMe$-k^2-*O*,*P*)] (**9**) (Scheme 5).

Scheme 6. Formation of Compound 10 in Acetone at −60 °C



Reactions of the Iridium(III) Phenoxy−Phosphine Derivative [$IrH_2(\eta^6$-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)][BF_4] (3) with Nucleophiles. The related dihydride Ir(III) complex, [$IrH_2(\eta^6$-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)][BF_4] (**3**), was prepared as previously described[8] by smooth reaction of molecular hydrogen with the chelate complex [Ir(C_8H_{12})($C_6H_5O(CH_2)_2$P*t*-Bu_2-k^2-O,P)][BF_4]. In general, this compound is more reactive than the iridium(I) complexes **1** and **2**, although the reactions with nucleophiles usually resulted in complex mixtures of products. However, the resulting product from the addition of potassium pyrazolate has been cleanly obtained and characterized in solution at low temperature.

The addition of an equimolecular amount of potassium pyrazolate to an acetone solution of complex **3** at 200 K afforded a pale yellow solution that contains a unique compound, as evidenced by the resonance at δ 39.27 ppm in the ^{31}P{^{1}H} NMR spectrum. The compound is stable below 213 K and can be maintained in solution for several hours, but on raising the temperature above 233 K, it quickly decomposes.

The new compound exhibits two doublets of doublets for the hydride ligands in the ^{1}H NMR spectrum at δ −11.25 and −17.10 ppm, with coupling constants J_{HP} and J_{HH} that indicate a mutual *cis* position.[39] The most important characteristic of this compound is the loss of aromaticity of the phenoxide fragment, as inferred from both ^{1}H and ^{13}C{^{1}H} NMR spectra. The five phenoxide signals are identified from its coupling scheme deduced from the ^{1}H/^{1}H COSY spectrum. The pyrazolate is observed at the expected positions, the H_5 proton is close to pyrazolate signals at δ 6.15 ppm, H_2 and H_6 are shifted ca. 1 ppm to high field at δ 5.20 and 5.31 ppm, and shifted to higher fields are H_4 and H_3 at 3.69 and 3.87 ppm, respectively. Their carbon atoms and those belonging to the pyrazolate ligand are assigned from the ^{1}H/^{13}C HSQC correlated spectrum (see Experimental Section). The proposed formula [IrH_2{η^5-(pz)$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P}] (**10**) is based on the spectroscopic data similarity with those of compound **4**, and there is no doubt that no enolate is coordinated to the arene because no signals for that fragment were found in either the ^{1}H or ^{13}C{^{1}H} NMR. Thus, compound **10** results from the selective nucleophilic attack of the pyrazolate to the 3-position of the arene to form an alkoxy-η^5-cyclohexadienyl ligand (Scheme 6).

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Conclusions

We have described the reactivity with nucleophiles of the "*ansa*" π-arene/phosphine complexes [Ir(alkene)(η^6-C_6H_5O-$(CH_2)_2$P*t*-Bu_2-*k*-P)][BF_4] (**1**, **2**) and [IrH_2(η^6-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)][BF_4] (**3**), where the phosphine is a formal eight-electron-donor chelate ligand. Regioselective nucleophilic addition to the arene is observed when acetone enolate, phenylacetylide, or pyrazolate are reacted with complexes **1**−**3** in acetone solvent. However, the starting materials **1** and **2** reacted with bases in methanol solution, giving rise to C−O bond splitting and formation of oxo-η^5-cyclohexadienyl vinylphosphine compounds. For the π-arene/phosphine complexes mentioned above, the arene is activated for nucleophilic addition through iridium coordination, and in determined conditions C−C bond formation is reached, but the presence of the oxygen in the backbone flexible arm is not innocent, and in basic methanol medium C−O bond breaking occurs. Coordination of the vinylphosphine to the iridium center can also induce methanol addition to the unsaturated bond.

Experimental Section

Scientific Equipment. Elemental analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Infrared spectra were recorded on a FT-Perkin-Elmer Spectrum One spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded on Bruker Avance 300 MHz and Bruker Avance 400 MHz spectrometers. ^{1}H (300.1276 MHz, 400.1625 MHz) and ^{13}C (75.4792 MHz, 100.6127 MHz) NMR chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in hertz. Spectral assignments were achieved by a combination of ^{1}H−^{1}H COSY, NOESY, ^{1}H{^{31}P}, ^{13}C DEPT, and ^{1}H−^{13}C HSQC experiments. MALDI-TOF mass spectra were obtained on a Bruker MICROFLEX spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.[40] Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formiate as reference. Conductivities were measured in ca. 5×10^{-4} M acetone solutions of the complexes using a Philips PW 9501/01 conductimeter.

Synthesis. All experiments were carried out under an argon atmosphere using Schlenk techniques, and the solvents were distilled immediately prior to use from the appropriate drying agents. Oxygen-free solvents were employed throughout. $CDCl_3$ and CD_2Cl_2 was dried using activated molecular sieves, C_6D_6 was dried using Na/K, and acetone-d_6 and methanol-d_4 (<0.02% D_2O) were purchased from Euriso-top and used as received. Complexes **1**−**3** were prepared following published methods.[8] The numbering scheme corresponds to that shown in the structures of compounds **4** and **7** depicted in Figures 2 and 3, respectively.

Preparation of [Ir{η^5-3-$(CH_3COCH_2)C_6H_5O(CH_2)_2$P*t*-$Bu_2$-*k*-P}-$(C_2H_4)$] (4). A solution of **1** (200 mg, 0.35 mmol) in acetone (10 mL) was treated with sodium methoxide (22 mg, 0.40 mmol). After 12 h of stirring, the solvent was pumped off and the residue extracted with diethyl ether. The resulting pale yellow solution was filtered, concentrated to ca. 0.5 mL, and treated with pentane. A light yellow solid precipitated and was filtered, washed twice with 2 mL portions of pentane, and dried in vacuo. Yield: 135 mg (71%). IR (Nujol, cm^{-1}): 1710 (s) ν(C═O), 1587 (w) ν(C═C). ^{1}H NMR (C_6D_6, 298 K): δ 0.73 (m, 2H, CH_2−Cα), 1.10 (d, J_{HP} = 11.8, 9H, PCCH_3), 1.10 (d, J_{HP} = 11.6, 9H, PCCH_3), 1.20 (ddd, J_{HH} = 5.6, 5.6, J_{HP} = 1.2, 1H, H_4), 1.54 (s, 3H, $COCH_3$), 1.68 (AB part of a ABX spin system, ABX, δ_A = 1.73, δ_B = 1.63, J_{AB} = 15.2, J_{AX} = J_{BX} = 6.2, 2H, CH_2CO), 2.90 (m br, 4H, C_2H_4), 3.36 (ddddd, J_{HH} = 6.2, 6.2, 5.6, 5.6, J_{HP} = 1.2, 1H, H_3), 3.50 (m 1H, CH_2−Cβ), 3.78 (m, 1H, CH_2−Cβ), 4.30 (ddd, J_{HH} = 5.6, 1.8, J_{HP} = 1.2, 1H, H_2), 4.98 (ddd, J_{HH} = 5.6, 5.6, J_{HP} = 0.8, 1H, H_5), 5.97 (ddd, J_{HH} = 5.6, 1.8, J_{HP} = 1.2, 1H, H_6). ^{31}P{^{1}H} NMR (161 MHz, C_6D_6, 298 K): δ 5.85 (s). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 15.65 (d, J_{CP} = 21.6, CH_2−Cα), 22.45 (s, CH_2CO), 29.50 (d, J_{CP} = 3.8, PCCH_3), 29.95 (d, J_{CP} = 4.7, PCCH_3), 30.31 (CO CH_3), 34.79 (C_2), 35.19 (d, J_{CP} = 16.6, PCCH_3), 36.08 (d, J_{CP} = 28.3, C_4), 37.33 (d, J_{CP} = 16.3, PCCH_3), 37.52 (d, J_{CP} = 5.9, C_3), 59.53 (d, J_{CP} = 10.0, CO CH_2), 67.29 (s, CH_2−Cβ), 71.81 (C_6), 84.94 (d, J_{CP} = 1.0, C_5), 121.20 (C_1), 204.49 (CO). Anal. Calcd (%) for $C_{21}H_{36}IrO_2P$ (543.7094): C 46.39, H 6.67. Found C 46.42, H 6.71. MS (MALDI-TOF, DCTB matrix, CH_2Cl_2): *m*/*z* 515.4 [M − C_2H_4]$^+$.

Preparation of [Ir{η^5-3-$(CH_3COCH_2)C_6H_5O(CH_2)_2$P*t*-$Bu_2$-*k*-P}($C_3H_6$)] (5). The compound was prepared following the procedure described for **4** but starting from the propene complex [Ir(C_3H_6)(η^6-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)] (**2**) (0.34 mmol). Complex **5** was isolated as a pale yellow solid. Yield: 135 mg (62%). IR (Nujol, cm^{-1}): 1711 (s) ν(C═O), 1585 (m) ν(C═C). ^{1}H NMR (acetone-d_6, 298 K): δ 1.15 (d, J_{HP} = 12.0, 9H, PCCH_3), 1.20 (d, J_{HH} = 6.1, 3H, ═CHCH_3), 1.24 (d, J_{HP} = 12.0, 9H, PCCH_3), 1.45 (m, 2H, CH_2−Cα), 1.85 (AB part of a ABX spin system, δ_A = 1.87, δ_B = 1.85, J_{AB} = 7.6, J_{AX} = J_{BX} = 3.8, 2H, CH_2CO), 2.10 (dd, J_{HH} = 5.9, 5.2, 1H, H_4), 2.28 (dd, J_{HH} = 11.7, 1.4, 1H, ═CH_2), 2.31 (s, 3H, $COCH_3$), 2.60 (ddd, J_{HP} = 3.5, J_{HH} = 8.0, 1.4, 1H, ═CH_2), 2.67 (ddq, J_{HH} = 11.7, 8.0, 6.1, 1H, ═CHCH_3), 3.24 (ddddd, J_{HH} = 5.2, 5.2, 3.8, 3.8, J_{HP} = 1.2, 1H, H_3), 3.96 (dd, J_{HH} = 5.2, 1.8, 1H, H_2), 4.21 (m, 1H, CH_2−Cβ), 3.84 (m, 1H, CH_2−Cβ), 4.87 (dd, J_{HH} = 5.9, 5.2, 1H, H_5), 6.29 (dd, J_{HH} = 5.9, 1.2, 1H, H_6). ^{31}P{^{1}H} NMR (acetone-d_6, 298 K): δ 4.70 (s). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ 16.76 (d, J_{CP} = 25.1, CH_2−Cα), 19.9 (═CH CH_3), 20.84 (═CHCH$_3$), 28.4 (═CH_2), 30.31 (s, $COCH_3$), 29.02 (d, J_{CP} = 4.3, PCCH_3), 30.89 (d, J_{CP} = 4.0, PCCH_3), 35.43 (d, J_{CP} = 27.2, C_4), 36.39 (d, J_{CP} = 16.1, PCCH_3), 36.47 (C_2), 37.32 (d, J_{CP} = 5.3, C_2), 38.84 (d, J_{CP} = 18.1, PCCH_3), 60.42 (d, J_{CP} = 10.0, $COCH_2$), 67.64 (CH_2−Cβ), 70.80 (C_6), 87.62 (C_5), 209.96 (CO). Anal. Calcd (%) for $C_{22}H_{38}IrO_2P$ (557.7363): C 47.38, H 6.87. Found: C 47.62, H 6.50. MS (MALDI-TOF, DCTB matrix, CH_2Cl_2): *m*/*z* 515.4 [M − C_3H_6]$^+$.

Reaction of [Ir(C_2H_4)(η^6-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)][BF_4] (1) with LiC≡C−Ph. A suspension of **1** (20 mg, 0.035 mmol) in acetone-d_6 (0.5 mL) was treated with lithium phenylacetylide (5.4 mg, 0.05 mmol) to give a yellow solution. The ^{1}H NMR spectrum evidenced the formation of compound [Ir{η^5-3-(C_6H_5C≡C)C_6H_5O-$(CH_2)_2$P*t*-Bu_2-*k*-P}(C_2H_4)] (**6**), which is in equilibrium with **1**. Spectroscopic data for **6**: ^{1}H NMR (acetone-d_6, 298 K): δ 1.0 (m, 1H, CH_2−Cα), 1.10 (m, 1H, H_4), 1.15 (d, J_{HP} = 8.7, 9H, PCCH_3), 1.17 (d, J_{HP} = 8.6, 9H, PCCH_3), 1.40 (m, 1H, CH_2−Cα), 2.47 (m br, 4H, C_2H_4), 3.14 (masked, 1H, H_3), 3.90 (m 1H, CH_2−Cβ), 4.03 (dd, J_{HH} = 7.1, J_{HP} = 1.0, 1H, H_2), 4.21 (m, 1H, CH_2−Cβ), 5.18 (dd, J_{HH} = 7.1, 5.8, 1H, H_5), 6.30 (ddd, J_{HH} = 7.1, 1.0, J_{HP} = 1.0, 1H, H_6). ^{31}P{^{1}H} NMR (acetone-d_6, 298 K): δ 7.04 (s). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ 16.14 (d, J_{CP} = 22.4, CH_2−Cα), 29.18 (PCCH_3), 30.40 (d, J_{CP} = 4.5, PCCH_3), 34.91 (C_2), 35.79 (d, J_{CP} = 17.1, PCCH_3), 36.22 (d, J_{CP} = 28.3, C_4), 38.05 (d, J_{CP} = 5.9, C_3), 38.25 (d, J_{CP} = 17.4, PCCH_3), 68.01 (s, CH_2−Cβ), 69.11 (C≡C−Ph), 81.44 (C≡C−Ph), 85.42 (C_6), 115.30 (C_5), 128.69 (CH), 129.05 (CH), 130.06 (C), 131.99 (CH), 138.68 (C). MS (MALDI-TOF, DCTB matrix, acetone-d_6): *m*/*z* 559.1 [M − C_2H_4]$^+$.

Reaction of [Ir{η^5-3-$(CH_3COCH_2)C_6H_5O(CH_2)_2$P*t*-$Bu_2$-*k*-P}-$(C_2H_4)$] (4) with Methyltriflate. A solution of **4** (15 mg, 0.027 mmol) in 0.5 mL of CD_2Cl_2 placed in a 5 mm NMR tube was treated with 3.12 μL of $CH_3CF_3SO_3$ (0.027 mmol). The initial signal at δ 5.65 ppm in the ^{31}P NMR corresponding to **4** was completely transformed in 30 min into a new signal at δ 6.96 ppm assigned to [Ir(C_2H_4)(η^6-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)]$^+$ (**1**). Analysis of the solu-

(40) Ulmer, L.; Mattay, J.; Torres-García, H. G.; Luftmann, H. *Eur. J. Mass Spectrom* **2000**, *6*, 49–52.

tion mixture by ^{1}H NMR showed the quantitative formation of **1** and 2-methoxypropene: ^{1}H NMR (acetone-d_6, 298 K): δ 3.85 (s, 2H, =CH_2), 3.52 (s, 3H, OCH_3), 1.82 (s, 3H, CH_3). GC-MS (CD_2Cl_2): m/z 72 $[M]^+$.

Reaction of [Ir{η^5-3-(CH_3COCH_2)$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P}(C_2H_4)] (4) with Triflic Acid. Compound **4** (0.027 mmol) was reacted with HCF_3SO_3 in CD_2Cl_2 and the reaction monitored by NMR. Analysis of the solution mixture by ^{1}H NMR and GC-MS showed the formation of **1** and acetone.

Preparation of [Ir(η^5-C_6H_5O)(C_2H_4)(*t*-Bu_2PCH=CH_2)] (7). Method A: A suspension of **4** (100 mg, 0.18 mmol) in methanol (10 mL) was stirred for 8 h, the solvent was evacuated, and the residue was treated with pentane, washed with pentane, and dried in vacuo. Yield: 64 mg (72%). Method B: A solution of **1** (200 mg, 0.35 mmol) in acetone (10 mL) was treated with potassium hydroxide in methanol (1 mmol). After 2 h of stirring, the solvent was pumped off and the residue treated with diethyl ether. The resulting brown solution was filtered, concentrated to ca. 0.5 mL, and treated with pentane. A light yellow solid precipitated, which was filtered, washed twice with 2 mL portions of pentane, and dried in vacuo. Yield: 64 mg (38%). IR (Nujol mull, cm^{-1}): 1625 (m) ν(C=O), 1540 (m) ν(C=C). ^{1}H NMR (acetone-d_6, 298 K): δ 1.30 (d, J_{HP} = 13.3, 18H, PCCH_3), 1.41 (m, 2H, *endo*-H CH_2=CH_2), 2.16 (m, 2H, *exo*-H CH_2=CH_2), 4.95 (d, J_{HH} = 6.7, 2H, H_2), 5.75 (t, J_{HH} = 5.4, 1H, H_4), 5.82 (dd, J_{HP} = 12.0, J_{HH} = 4.0, 1H, =CH_2), 5.83 (dd, J_{HP} = 10.9, J_{HH} = 11.3, 1H, =CH_2), 6.08 (ddd, J_{HP} = 30.8, J_{HH} = 11.3, J_{HH} = 4.0, 1H, =CH), 6.20 (dd, J_{HH} = 6.7, 5.4, 2H, H_3). ^{31}P{^{1}H} NMR (acetone-d_6, 298 K): δ 32.02 (s). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ 17.94 (br, CH_2=CH_2), 30.27 (d, J_{CP} = 3.6, PCCH_3), 37.93 (d, J_{CP} = 26.5, PCCH_3), 80.10 (C_2), 81.15 (C_4), 97.37 (C_3), 124.65 (d, J_{CP} = 39.8, PCH=CH_2), 130.03 (PCH=CH_2), 166.43(CO C_1). Anal. Calcd (%) for $C_{18}H_{30}$IrOP (485.6294): C 44.52, H 6.23. Found: C 44.58, H 6.29.

Preparation of [Ir(η^5-C_6H_5O)(C_3H_6)(*t*-Bu_2PCH=CH_2)] (8). Method A: The compound was prepared from [Ir{η^5-3-(CH_3COCH_2)$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P}(C_3H_6)] (**5**) following the procedure described for compound **7** and isolated as a pale yellow solid. Yield: 76 mg (45%). IR (Nujol mull, cm^{-1}): 1630 (m) ν(C=O), 1545 (m) ν(C=C). ^{1}H NMR (acetone-d_6, 298 K): δ 1.29 (d, J_{HP} = 13.2, 9H, PCCH_3), 1.32 (d, J_{HP} = 13.2, 9H, PCCH_3), 1.56 (d, J_{HP} = 6.0, 9H, =CHCH_3), 1.59 (dd, J_{HH} = 13.2, 1.5, 1H, =CH_2), 1.90 (ddd, J_{HH} = 9.6, J_{HH} = J_{HP} = 1.5, 1H, =CH_2), 2.10 (m, 1H, =CHCH$_3$), 4.71 (d, J_{HH} = 6.9, 1H, H_2 or H_6), 5.35 (d, J_{HH} = 6.9, 1H, H_2 or H_6), 5.74 (t, J_{HH} = 5.7, 1H, H_4), 5.83 (dd, J_{HP} = 12.0, J_{HH} = 2.7, 1H, =CH_2), 5.86 (dd, J_{HP} = 14.1, J_{HH} = 11.4, 1H, =CH_2), 6.07 (dd, J_{HH} = 6.9, 5.7, 1H, H_3 or H_5), 6.11 (ddd, J_{HP} = 33.0, J_{HH} = 11.4, J_{HH} = 2.7, 1H, =CH), 6.18 (dd, J_{HH} = 6.9, 5.7, 1H, H_3 or H_5). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 31.43 (s). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 14.23 (=CH CH_3), 21.64 (=CH_2), 22.68 (=CHCH$_3$), 29.78 (d, J_{CP} = 4.0, PCCH_3), 30.39 (PCCH_3), 37.61 (d, J_{CP} = 27.1, PCCH_3), 38.15 (d, J_{CP} = 26.3, PCCH_3), 77.53 (C_2), 83.45 (C_4), 98.02 (C_3), 124.00 (d, J_{CP} = 35.8, PCH=CH_2), 129.19 (PCH=CH_2), 166.19 (s, CO, C_1). Anal. Calcd (%) for $C_{19}H_{32}$IrOP (499.6562): C 45.67, H 6.45. Found: C 45.58, H 6.36.

Preparation of [Ir(OC_6H_5)(C_2H_4)(*t*-Bu_2P(CH_2)$_2$OMe-k^2-*O*,*P*)] (9). A solution of **7** (100 mg, 0.21 mmol) in toluene (5 mL) was treated with methanol (20 μL, 0.49 mmol). After 2 h of stirring, the solvent was pumped off and the residue treated with hexane at 0 °C. The resulting brown solid was washed with hexane, filtered, and dried in vacuo. Yield: 66 mg (61%). IR (Nujol mull, cm^{-1}): 1060 (m) ν(C—O), 1580 (m) ν(C=C). ^{1}H NMR (C_6D_6, 298 K): δ 1.10 (d, J_{HP} = 13.2, 18H, PCCH_3), 1.51 (dt, J_{HP} = 6.1, J_{HH} = 6.1, 2H, CH_2—C_α), 1.60 (m, 2H, *endo*-H CH_2=CH_2), 2.05 (m, 2H, *exo*-H CH_2=CH_2), 3.07 (s, 3H, MeO), 3.24 (dt, J_{HP} = 12.0, J_{HH} = 6.1, 2H, CH_2—C_β), 6.89 (t, J_{HH} = 7.7, 1H, PhO), 7.04 (dd, J_{HH} = 7.7, 7.6, 2H, PhO), 7.20 (d, J_{HH} = 7.6, 1H, PhO). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 46.09 (s). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 17.94 (CH_2—C_α, CH_2=CH_2), 27.27 (d, J_{CP} = 3.0, PCCH_3), 27.79 (d, J_{CP} = 3.8, PCCH_3), 27.91 (d, J_{CP} = 28.6, PCCH_3), 32.24 (d, J_{CP} = 27.5, PCCH_3), 52.34 (OCH_3), 62.03 (CH_2—C_β), 111.74, 113.26, 118.23 (CH-PhO), not seen (C_1). Anal. Calcd (%) for $C_{19}H_{34}$IrO$_2$P (517.6715): C 44.08, H 6.62. Found: C 43.78, H 5.98.

Preparation of [IrH_2(η^5-3-(pz)-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P}] (10). A solution of [IrH_2(η^6-$C_6H_5O(CH_2)_2$P*t*-Bu_2-*k*-P)][BF_4] (**3**) (40 mg, 0.073 mmol) in acetone-d_6 (0.5 mL) was treated with potassium pyrazolate (7.7 mg, 0.073 mmol) at −78 °C and then allowed to warm up to −60 °C. ^{1}H and ^{13} C{^{1}H} NMR evidenced the formation of compound **10**. Spectroscopic data: ^{1}H NMR (acetone-d_6, 213 K): −17.10 (dd, J_{HP} = 18.9, J_{HH} = 7.4, 1H, Ir—H), −11.25 (dd, J_{HP} = 21.4, J_{HH} = 7.4, 1H, Ir—H), 1.13 (d, J_{HP} = 13.3, 9H, PCCH_3), 1.26 (d, J_{HP} = 12.6, 9H, PCCH_3), 1.46 (m, 2H, CH_2—C_α), 3.69 (m, 1H, H_4), 3.87 (d, J_{HH} = 6.2, 1H, H_3), 4.10 (m 1H, CH_2—C_β), 4.24 (m, 1H, CH_2—C_β), 5.20 (dd, J_{HH} = 5.6, 5.6, 1H, H_2), 5.31 (m, 1H, H_6), 6.14 (m, 1H, Pz-H_4), 6.15 (m, 1H, H_5), 7.34 (d, J_{HH} = 1.0, 1H, Pz-H_5), 7.40 (d, J_{HH} = 1.0, 1H, Pz-H_3). ^{31}P{^{1}H} NMR (acetone-d_6, 213 K): δ 39.27 (s). ^{13}C{^{1}H} NMR (acetone-d_6, 213 K): δ 13.01 (d, J_{CP} = 26.3, CH_2—C_α), 28.60 (PCCH_3), 29.48 (d, J_{CP} = 4.5, PCCH_3), 34.56 (d, J_{CP} = 26.8, PCCH_3), 35.47 (d, J_{CP} = 28.5, PCCH_3), 35.67 (d, J_{CP} = 28.3, C_4), 41.98 (C_3), 60.62 (d, J_{CP} = 3.8 Hz, C_2), 69.07 (C_5), 69.79 (CH_2—C_β), 90.87 (C_6), 104.84, 126.31 (CH-Pz), 130.49 (C_1), 137.99 (CH-Pz).

X-ray Structural Determination of Compounds 4 and 7. Crystals of complex **4** suitable for the X-ray diffraction experiment were obtained by slow evaporation of diethyl ether from a concentrated solution at room temperature in the drybox. Suitable crystals of **7** were obtained by slow diffusion of diethyl ether into a concentrated solution of the compound in acetone at 0 °C. Both sets of intensity data were collected at low temperature (100(2) K) on a CCD Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using ω rotations (0.3°). Instrument and crystal stability were evaluated by measuring equivalent reflections at different times; no significant decay was observed. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied.[41] The structure was solved by Patterson and difference Fourier methods.[42] Anisotropic displacement parameters were applied for all non-hydrogen atoms. Hydrogen atoms were found in subsequent difference Fourier maps and included as free isotropic atoms. Refinements were carried out by full-matrix least-squares on F^2 (SHELXL-97).[41] The highest residuals in both structures were found in the proximity of metal centers and have no chemical sense.

Crystal data for compound 4: $C_{21}H_{36}IrO_2P$, M = 543.67; crystal size 0.252 × 0.247 × 0.041 mm^3; monoclinic, $P2_1/n$; a = 13.1600(8) Å, b = 8.4206(5) Å, c = 19.5860(12) Å; β = 105.4520(10)°; Z = 4; V = 2092.0(2) $Å^3$; D_c = 1.726 g/cm^3; μ = 6.470 mm^{-1}, minimum and maximum transmission factors 0.262 and 0.775; $2\theta_{max}$ = 55.4°; 13 531 reflections collected, 4946 unique [R(int) = 0.0339]; number of data/restrains/parameters 4946/0/370; final GoF 1.048, R_1 = 0.0301 [4427 refln $I > 2\sigma(I)$], wR_2 = 0.0706 for all data.

Crystal data for compound 7: $C_{18}H_{30}$IrOP·C_6H_6O, M = 579.72; crystal size 0.299 × 0.247 × 0.089 mm^3; monoclinic, $P2_1/n$; a = 7.9252(6) Å, b = 29.893(2) Å, c = 9.7153(7) Å; β = 102.441(1)°; Z = 4; V = 2247.6(3) $Å^3$; D_c = 1.713 g/cm^3; μ =

(41) *SAINT+ Software for CCD difractometers*; Bruker AXS: Madison, WI, 2000. (b) Sheldrick, G. M. *SADABS Program for Correction of Area Detector Data v. 2.03*; University of Göttingen: Göttingen, Germany, 2001.

(42) *SHELXTL Package v. 6.10*; Bruker AXS: Madison, WI, 2000. Sheldrick G. M. *SHELXS-86* and *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

6.028 mm^{-1}, minimum and maximum transmission factors 0.197 and 0.585; $2\theta_{max} = 54.1°$; 26 188 reflections collected, 4933 unique [R(int) = 0.0320]; number of data/restrains/parameters 4933/0/397; final GoF 1.100, $R_1 = 0.0190$ [4629 reflns $I > 2\sigma(I)$], $wR_2 = 0.0437$ for all data.

Acknowledgment. The financial support from Ministerio de Educación y Ciencia (MEC/FEDER) (Project CTQ2006-03973/BQU) and CONACYT-México for a postdoctoral fellowship to I.I.R. are gratefully acknowledged.

Supporting Information Available: X-ray crystallographic information files containing full details of the structural analysis of complexes **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800402N