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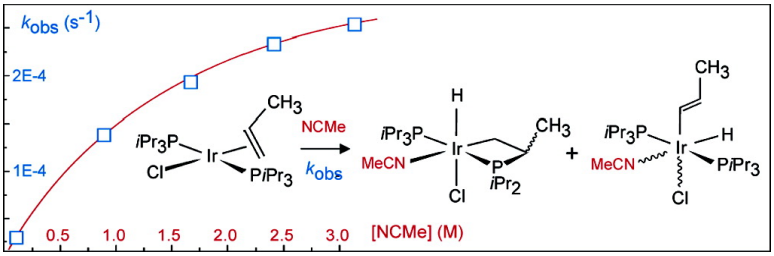


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# C−H Activations at Iridium(I) Square-Planar Complexes Promoted by a Fifth Ligand

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***Abstract:*** In the presence of ligands such as acetonitrile, ethylene, or propylene, the Ir(I) complex [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)(NCMe)($PMe_3$)]$BF_4$ (**1**) transforms into the Ir(III) derivatives [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$)(NCMe)(L)($PMe_3$)]-$BF_4$ (L = NCMe, **2**; $\eta^2$-$C_2H_4$, **3**; $\eta^2$-$C_3H_6$, **4**), respectively, through a sequence of C−H oxidative addition and insertion elementary steps. The rate of this transformation depends on the nature of L and, in the case of NCMe, the pseudo-first-order rate constants display a dependence upon ligand concentration suggesting the formation of five-coordinate reaction intermediates. A similar reaction between **1** and vinyl acetate affords the Ir(III) complex [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$){$\kappa$-*O*-$\eta^2$-OC(Me)$OC_2H_3$}($PMe_3$)]$BF_4$ (**7**) via the isolable five-coordinate Ir(I) compound [Ir(1,2,5,6-$\eta$-$C_8H_{12}$){$\kappa$-*O*-$\eta^2$-OC(Me)$OC_2H_3$}($PMe_3$)]$BF_4$ (**6**). DFT (B3LYP) calculations in model complexes show that reactions initiated by acetonitrile or ethylene five-coordinate adducts involve C−H oxidative addition transition states of lower energy than that found in the absence of these ligands. Key species in these ligand-assisted transformations are the distorted (nonsquare-planar) intermediates preceding the intramolecular C−H oxidative addition step, which are generated after release of one cyclooctadiene double bond from the five-coordinate species. The feasibility of this mechanism is also investigated for complexes [IrCl(L)(P*i*Pr$_3$)$_2$] (L = $\eta^2$-$C_2H_4$, **27**; $\eta^2$-$C_3H_6$, **28**). In the presence of NCMe, these complexes afford the C−H activation products [IrClH(CH═CHR)(NCMe)(P*i*Pr$_3$)$_2$] (R = H, **29**; Me, **30**) via the common cyclometalated intermediate [IrClH{$\kappa$-*P,C*-P(*i*Pr)$_2$CH($CH_3$)$CH_2$}(NCMe)(P*i*Pr$_3$)] (**31**). The most effective C−H oxidative addition mechanism seems to involve three-coordinate intermediates generated by photochemical release of the alkene ligand. However, in the absence of light, the reaction rates display dependences upon NCMe concentration again indicating the intermediacy of five-coordinate acetonitrile adducts.

## Introduction

The need for sustainable industrial chemical processes has boosted the research on functionalization methods involving C−H activations at metal complexes, since they may lead to atom-economic catalytic transformations of readily available hydrocarbon substrates. This intense research has already afforded various well-established functionalization strategies,[1] together with a wealth of well-characterized C−H activating metal systems.[2] A substantial part of such findings is based on the solution chemistry of rhodium and iridium complexes, although a noticeably minor role is attributed within this context to the very common unsaturated $d^8$ square-planar compounds. In fact, the most effective Rh(I) and Ir(I) precursors for C−H oxidative addition hitherto reported are five-coordinate complexes bearing Cp-type ligands,[3] while the success of other saturated or unsaturated $d^8$ C−H activating systems seems to rely on the generation of very reactive three-coordinate intermediates via ligand dissociations.[4] Even though thermodynamics are obviously crucial to determine whether the corresponding $d^6$ C−H activation products can be observed, the relative inadequacy of $d^8$ square-planar species in these activations might have a kinetic origin.

The currently accepted mechanistic rationalization of C−H oxidative additions to metal complexes indicates the availability of empty metal orbitals allowing side-on C−H coordination to be a requisite.[5] As indicated by the theoretical work of Saillard and Hoffmann,[6] the generation of such suitable empty orbitals from unsaturated Rh and Ir $d^8$ complexes involves a significant distortion of their square-planar ground-state geometry, which

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(6) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006−2026.


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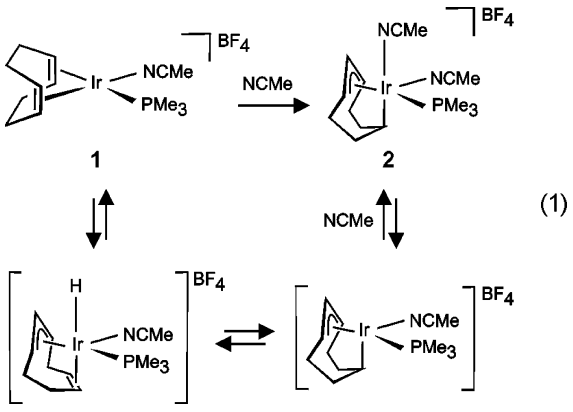
is likely associated with significant activation energies and short lifetimes of the reactive intermediates. While these latter features may still allow facile oxidative additions of reactive substrates such as dihydrogen,[7] they seemingly render this C−H activation pathway unfavorable against other routes based on ligand dissociation.[4]

Alternatively, the postulated electronic and geometric requisites for C−H oxidative addition can be easily fulfilled by unsaturated intermediates generated after ligand dissociation from five-coordinate complexes, although such intermediates are expected to readily evolve inactive square-planar states in the absence of restraints.[6,8] With regard to the experimental evidence, the rigid, fac-coordinating and strong Cp-type ligands effectively restrict such undesirable evolution, rendering the lifetime of the distorted intermediates long enough to allow for intermolecular activations of a variety of substrates, alkanes included.[3] Unfortunately, such advantageous features of the Cp ligands become disadvantages for the subsequent functionalization of the activated substrate, since any further generation of vacancies at the activation product is hindered by the strong Cp ligand coordination. In this context, the following pages will illustrate that such strong and rigid polydentate ligands are not strictly necessary for the success of C−H oxidative additions initiated by Ir(I) five-coordinate compounds, by showing that distorted four-coordinate intermediates exclusively bearing monodentate ligands can live long enough to accomplish intramolecular C−H activations. Furthermore, the five-coordinate precursors of such activations are not required to be thermodynamically stable species, whenever significant amounts of them could be generated in situ from square-planar compounds in the presence of weak ligands or coordinating solvents. This leads to intramolecular C−H activation reactions at square-planar complexes promoted by weakly coordinating ligands which afford labile Ir(III) compounds capable of undergoing further reaction.

## Results and Discussion

**Studies in Complex [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)(NCMe)($PMe_3$)]$BF_4$.** In a recent paper on the reactivity of cationic cyclooctadiene iridium complexes,[9] we described the transformation of the Ir(I) complex [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)(NCMe)($PMe_3$)]$BF_4$ (**1**) into the Ir(III) derivative [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$)(NCMe)$_2$($PMe_3$)]$BF_4$ (**2**). The reaction was found to slowly take place in chlorinated solvents in the presence of acetonitrile excess. Our rationalization of this process assumed a reversible sequence of C−H activation and insertion elementary steps (eq 1), since



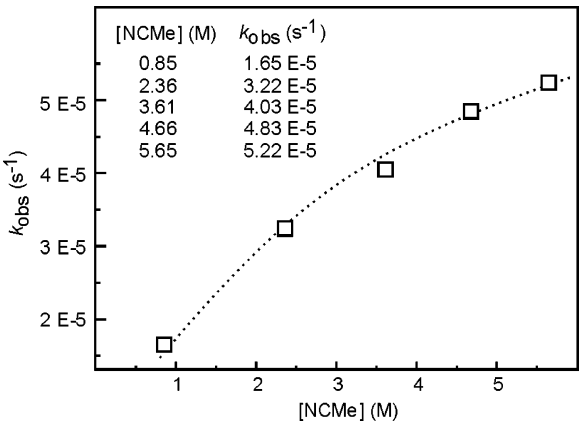
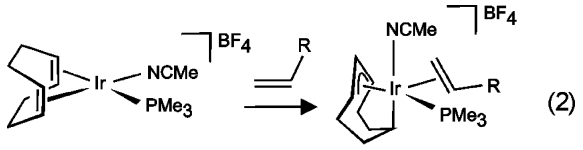




***Figure 1.*** Pseudo-first-order rate constants obtained by $^{31}P$ NMR for the transformation of **1** into **2** at various acetonitrile concentrations. Solvent: 1,2-dichloroethane; $[\mathbf{1}]_0 = 6.3 \times 10^{-2}$ M; $T = 343$ K.

indirect experimental evidence for the proposed hydride intermediate was obtained in the form of alkenyl complexes resulting from its intermolecular reaction with added alkynes.

The need for acetonitrile in this reaction was rationalized in thermodynamic terms, just as a requisite to turn the final product into a stable octahedral species, thus shifting the equilibria in eq 1 toward complex **2**. However, in a further investigation of this transformation, we have found the reaction rate to be directly dependent upon acetonitrile concentration. This new observation indicates that, in addition to the proposed thermodynamic contribution, the acetonitrile plays a kinetic role during the transformation. The plot of the pseudo-first-order reaction rates ($k_{obs}$), obtained by $^{31}P\{^1H\}$ NMR in 1,2-dichloroethane as solvent, versus acetonitrile concentration resembles those common for saturation kinetics (Figure 1), suggesting an involvement of acetonitrile in the reaction mechanism beyond possible solvent effects.

Acetonitrile is not the only ligand accelerating this reaction. In fact, upon treatment with an excess of simple alkenes such as ethylene or propylene, complex **1** has been found to afford analogues of **2** containing an $\eta^2$-alkene ligand (eq 2). The rates




**1** **3**, R = H; **4**, R = Me

of these latter transformations, in 1,2-dichloroethane solutions of **1** saturated in the corresponding alkenes, are about 2 orders of magnitude faster than those obtained with acetonitrile as additive. This kinetic dependence upon the nature of the additive further suggests the involvement of the added ligands in the reaction mechanism.

The spectroscopic data collected for the complexes [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$)(NCMe)($\eta^2$-$C_2H_4$)($PMe_3$)]$BF_4$ (**3**) and [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$)(NCMe)($\eta^2$-$C_3H_6$)($PMe_3$)]$BF_4$ (**4**) agree with the

(7) See, for example: Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148−3160.
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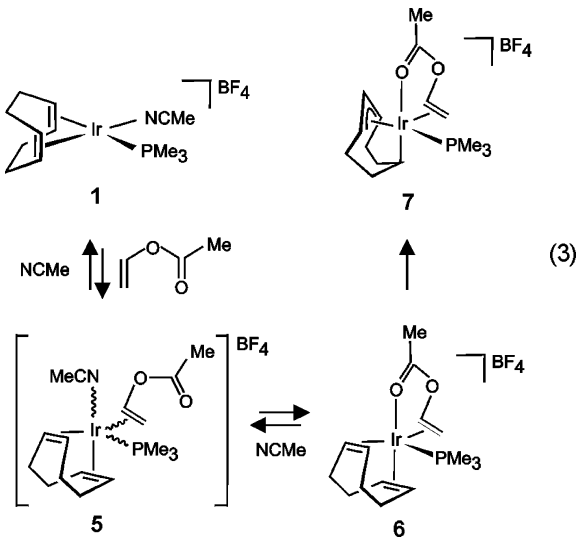
structures proposed in eq 2. They also confirm that, despite the use of additives susceptible to C−H activation, this process remains restricted to the cyclooctadiene ligand. The $^1$H NMR signals corresponding to the $\eta^2$-ethylene of **3** are two multiplets at $\delta$ 2.83 and 3.59 which indicate the fast rotation of this ligand in the NMR time scale. The coordination position of the alkene ligands, cis to the phosphine, the $\sigma$-carbon, and one side of the allyl moiety, has been deduced from the $^1$H NOESY NMR spectra.

The potentially chelating vinyl acetate has provided further insight into the possible mechanistic role of the additional ligand in this metal-mediated isomerization of the cyclooctadiene ligand. The $CD_2Cl_2$ solutions obtained by treatment of **1** with 1 equiv of vinyl acetate have been observed by NMR to contain the five-coordinate compound [Ir(1,2,5,6-$\eta$-$C_8H_{12}$){$\kappa$-*O*-$\eta^2$-OC(Me)$OC_2H_3$}($PMe_3$)]$BF_4$ (**6**) together with the precursor complex in fast equilibrium with two other species. The low-temperature NMR spectra (see the Experimental Section and the Supporting Information) indicate these two new species to coordinate both an acetonitrile and an $\eta^2$-bonded molecule of the additive, thus allowing their tentative formulation as two isomers of the five-coordinate complex [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)-(NCMe)($\eta^2$-$C_2H_3OC(O)CH_3$}($PMe_3$)]$BF_4$ (**5** in eq 3, assuming trigonal bipyramidal structures). These isomers have been




observed to be the major components of the solutions when using 1 equiv of vinyl acetate, although they disappear under a ca. 10-fold excess of added ligand allowing quantitative formation of **6**. Crystals suitable for an X-ray diffraction experiment have been obtained for the analogue of **6** with the $BPh_4^-$ anion (**6-BPh$_4$**). The cation of this complex is shown in Figure 2, and its relevant distances and angles are collected in Table 1.

The preparation of **6** has been found to require either low temperature or fast reaction manipulation, since the complex has been observed to transform into its Ir(III) isomer [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$){$\kappa$-*O*-$\eta^2$-OC(Me)$OC_2H_3$}($PMe_3$)]$BF_4$ (**7**) (eq 3). The X-ray structure of this analogue of complexes **2**−**4** is depicted in Figure 2, and its main distances and angles are listed in Table 1.

The pseudo-first-order rates for the transformation of **1** into **7** in the presence of 10 equiv of vinyl acetate have been found

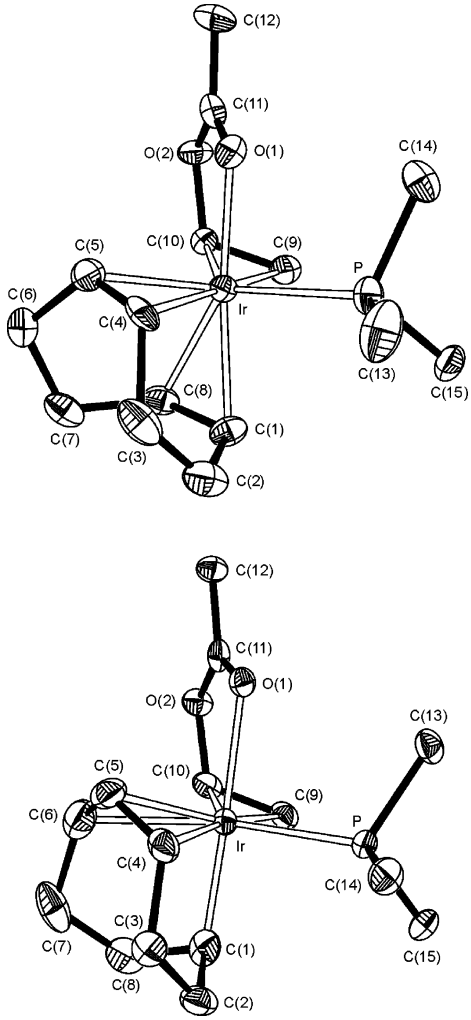



***Figure 2.*** Molecular structure of the cations of complexes **6-BPh$_4$** (above) and **7** (below).

***Table 1.*** Selected Bond Distances (angstrom) and Angles (deg) for Complexes **6-BPh$_4$** and **7**

| | 6-BPh4 | 7 |
|---|---|---|
| Ir−P | 2.3813(16) | 2.3215(14) |
| Ir−C(1) | 2.155(7) | 2.043(5) |
| Ir−C(4) | 2.132(7) | 2.196(5) |
| Ir−C(5) | 2.140(7) | 2.168(6) |
| Ir−C(6) | | 2.289(6) |
| Ir−C(8) | 2.156(7) | |
| Ir−C(9) | 2.102(8) | 2.156(6) |
| Ir−C(10) | 2.063(6) | 2.128(5) |
| Ir−O(1) | 2.081(4) | 2.238(3) |
| C(10)−O(2) | 1.457(7) | 1.443(6) |
| C(11)−O(2) | 1.311(7) | 1.320(6) |
| C(11)−O(1) | 1.267(7) | 1.236(6) |
| P−Ir−C(1) | 85.55(19) | 91.49(16) |
| P−Ir−C(4) | 93.74(18) | 91.01(17) |
| P−Ir−C(5) | 129.39(19) | 124.55(18) |
| P−Ir−C(6) | | 156.95(16) |
| P−Ir−C(8) | 122.7(2) | |
| P−Ir−C(9) | 90.0(2) | 84.56(16) |
| P−Ir−C(10) | 125.48(18) | 121.37(16) |
| P−Ir−O(1) | 85.77(11) | 91.77(9) |
| O(1)−Ir−C(1) | 169.8(2) | 175.41(18) |

similar in magnitude to those of the aforementioned reactions with ethylene or propene excess ($k_{obs} = 4.5 \times 10^{-3}$ s$^{-1}$ at 323 K in 1,2-dichloroethane). Interestingly, the same rate constant has been obtained either under larger vinyl acetate excess or

by using **6** as precursor of **7** without ligand addition. These latter observations strongly suggest that acceleration of the 1,2,5,6-$\eta$-$C_8H_{12}$ to 1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$ isomerization in the presence of added ligands is related to the formation of five-coordinate species from the square-planar precursor **1**. This is expected to result into reaction rates independent upon the concentration of those additives affording thermodynamically stable five-coordinate adducts but, in general, should lead to rate dependences reflecting adduct formation preequilibria. Under this interpretation, the analysis of the rates determined at 343 K with acetonitrile as the additive (Figure 1), using the equation for saturation kinetics ($k_{obs} = k_2$[NCMe]/{[NCMe] + ($k_{-1} + k_2$)/$k_1$}), leads to an estimated equilibrium constant for five-coordinate acetonitrile adduct formation ($k_1/k_{-1}$) of 0.2 ± 0.1 $mol^{-1}$ L (assuming $k_{-1} \gg k_2$) and a first-order rate constant for the 1,2,5,6-$\eta$-$C_8H_{12}$ to 1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$ isomerization at this adduct ($k_2$) of $1.0 \times 10^{-4} \pm 2 \times 10^{-5}$ $s^{-1}$.

The proposed acetonitrile adducts of **1** could not be detected by NMR, although the dynamic behavior of the complex in solutions containing added acetonitrile has provided indirect evidence for the formation of five-coordinate intermediates. In fact, **1** has been observed to undergo a rearrangement in solution that eventually averages, inter alia, the two $^1$H NMR resonances due to nonequivalent COD olefinic protons. Pseudo-first-order rate constants for this dynamic process have been obtained by line-shape analysis of the $CD_2Cl_2$ $^1$H NMR spectra of **1** at various temperatures and different acetonitrile concentrations (see the Supporting Information). This study has concluded a first-order dependence of the observed rate constants upon acetonitrile concentration, in agreement with a process driven by acetonitrile coordination. Moreover, the activation parameters obtained for the dynamic process, $\Delta H^{\ddagger} = 4.3 \pm 0.5$ kcal $mol^{-1}$, $\Delta S^{\ddagger} = -13 \pm 1$ cal $K^{-1}$ $mol^{-1}$, are consistent with an associative transition state, also indicating the energetic barrier for the proposed acetonitrile coordination to be very low.

**Theoretical Calculations.** The consequences to the C−H activation mechanism of the postulated five-coordination have been examined in the model cation [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)(NCMe)-($PH_3$)]$^+$ (**1′**) by use of DFT (B3LYP) calculations. Initially, for comparison purposes, the best possible reaction sequence for the transformation of **1′** into an unsaturated analogue of **2**, the model cation [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$)(NCMe)($PH_3$)]$^+$ (**11′**), has been investigated. The calculations indicate this transformation to be thermodynamically disfavored in the absence of added ligands. The calculated potential energy surface (Figure 3) features two elementary steps of allylic C−H oxidative addition and insertion, respectively, mediated by an unsaturated hydride species, **9′**, coordinating a 1-$\kappa$-5,6-$\eta$-cyclooctadienyl ligand. The highest point of the computed reaction coordinate corresponds to the C−H oxidative addition transition state, **TS8**, the free energy of which under standard conditions being as large as 45.6 kcal $mol^{-1}$.

In the presence of acetonitrile, the model cation **1′** has been found to form two five-coordinate adducts of formula [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)(NCMe)$_2$($PH_3$)]$^+$, **12a′** and **12b′** (Figure 4). These adducts display trigonal bipyramidal structures, with one or two acetonitrile ligands in equatorial positions, respectively. Formation of the adducts is exothermic by ca. 5 kcal $mol^{-1}$ although, due to the unfavorable entropy, both isomers of **12′** are thermodynamically disfavored against separate **1′** and aceto-

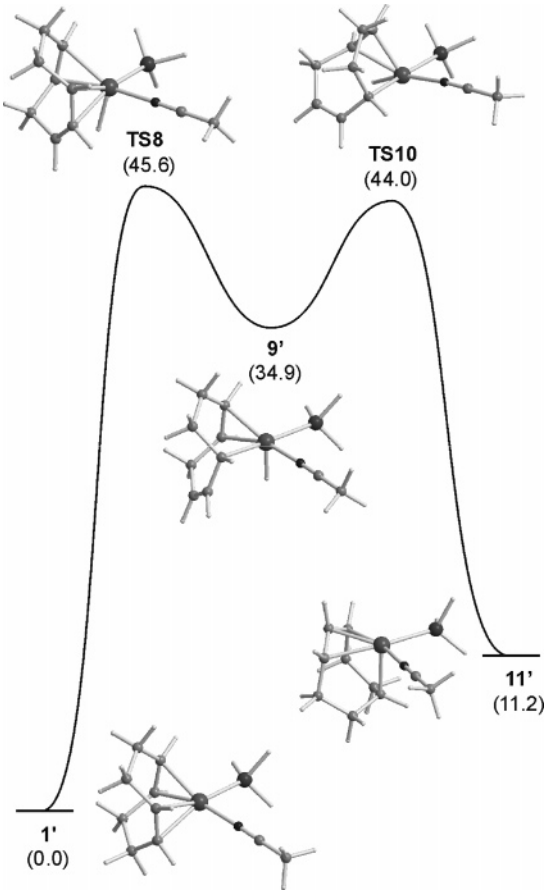



***Figure 3.*** DFT (B3LYP)-computed reaction coordinate for the 1,2,5,6-$\eta$-$C_8H_{12}$ to 1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$ isomerization of the cyclooctadiene ligand at the model cation **1′**. Values in parentheses are relative free energies (kcal $mol^{-1}$) in standard conditions.

nitrile, in agreement with the experimental observations. The geometric optimization of the various possible four-coordinate species generated after release of one COD alkene moiety from compounds **12′** has been found to afford the square-planar compounds **13′**−**15′** but also a high-energy isomer adopting a nonplanar structure, **16′**. This latter species results from the most stable adduct **12b′**, after decoordination of the C═C trans to phosphine. Such a process is likely to be kinetically preferred over the release of the equatorial C═C, which with regard to the shorter Ir−C distances (2.11 vs 2.29 and 2.32 Å) and the longer C═C bond length (1.46 vs 1.39 Å) seems to coordinate stronger.

The species **16′** nearly retains the ligand arrangement of its tbp precursor **12b′** without the participation of agostic interactions. Nevertheless, an agostic interaction can be readily developed within such a distorted structure, to eventually afford a product of allylic C−H oxidative addition, [IrH(1,2,3-$\eta$-$C_8H_{11}$)(NCMe)$_2$($PH_3$)]$^+$ (**19′**) (Figure 5). The transition state for this C−H oxidative addition, **TS18**, lies 11.7 kcal $mol^{-1}$ above the ground state of **16′**, and only 6 kcal $mol^{-1}$ above **TS17**, that required to restore the five-coordinate precursor **12b′**. This is in contrast to the behavior of the square-planar isomers **13′**−**15′**, for which our attempts to find a low-energy C−H activation pathway have been unsuccessful.

The calculations on the hydride-$\eta^3$-allyl C−H oxidative addition product **19′** have found a more stable coordination isomer, **20′**, which displays a cyclooctadienyl ligand coordinated

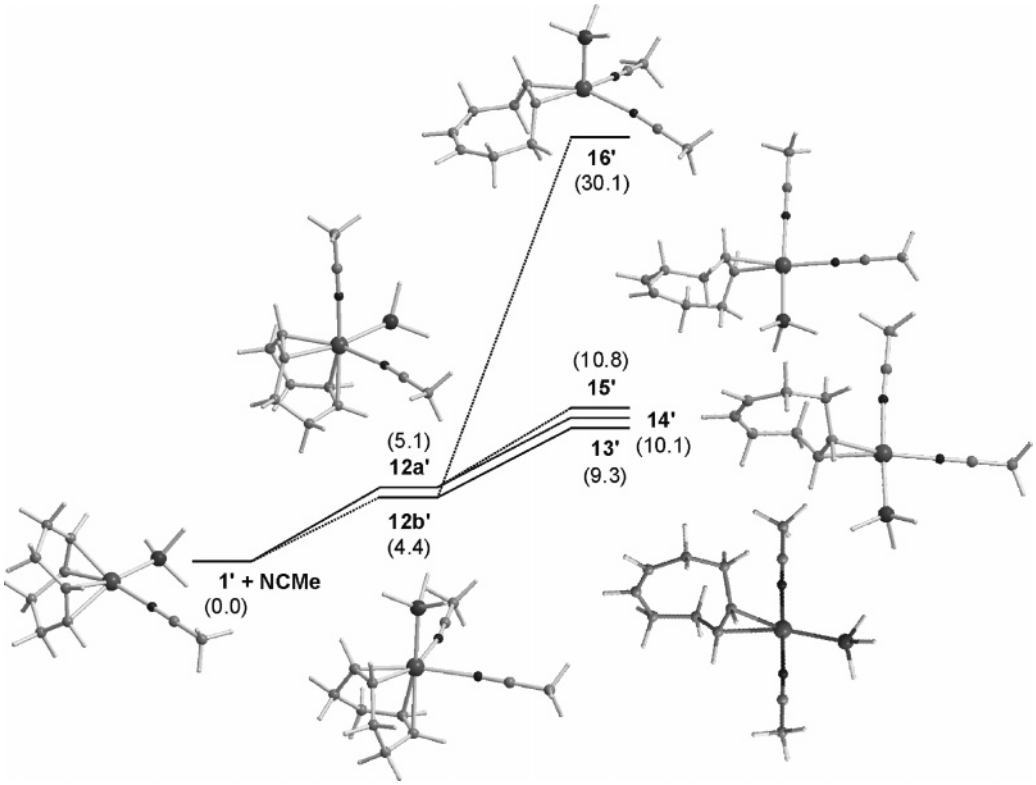



***Figure 4.*** DFT (B3LYP)-calculated five- and four-coordinate complexes formed from the model cation **1′** and acetonitrile. Values in parentheses are relative free energies (kcal mol$^{-1}$) in standard conditions.

in the 1-$\kappa$-5,6-$\eta$- fashion. This latter isomer can undergo an insertion elementary step to afford the model final product [Ir(1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$)(NCMe)$_2$($PH_3$)]$^+$ (**2′**), thus completing the experimentally observed transformation. The relative free energies, intermediates, and transition states involved in this calculated transformation are depicted in Figure 5. Assuming the isomerization of **19′** into **20′** to be kinetically facile, the highest point of the reaction coordinate (37.4 kcal mol$^{-1}$) is significantly lower than that calculated for cation **1′**, thus providing a possible rationalization for the accelerating effect exhibited by acetonitrile. An analogous reaction coordinate can be started from the five-coordinate ethylene adduct [Ir(1,2,5,6-$\eta$-$C_8H_{12}$)(NCMe)($\eta^2$-$C_2H_4$)($PH_3$)]$^+$ (**22b′**). This model compound has been found to behave similarly to **12b′**, leading to a C−H oxidative addition activation energy 4 kcal mol$^{-1}$ below that of the acetonitrile-promoted reaction. This calculated result is also in qualitative agreement with the experimental observation of faster reactions in the presence of ethylene. Further energetic details for all these calculated transformations and detailed geometric parameters of their intermediates and transition states are included as Supporting Information.

The calculations in this section indicate that, in the presence of potential ligands or coordinating solvents, square-planar iridium(I) compounds can undergo sequences of ligand coordination/dissociation affording distorted intermediates capable of activating intramolecular C−H bonds. As in the calculated examples, this ligand-assisted distortion of the ground-state square-planar geometry can result in C−H oxidative additions which are faster than those involving simpler nonassisted distortions, thus rationalizing the experimentally observed reaction acceleration upon addition of ligands.

**Studies in Complexes [IrCl($\eta^2$-$C_2H_3R$)(P*i*Pr$_3$)$_2$].** Due to their chelating and relatively rigid cyclooctadiene ligands, the complexes studied in the previous sections could be regarded as peculiar, and the deduced C−H activation mechanism might be considered just a particular consequence of the restraints introduced by the COD ligand. To check the feasibility of this mechanism in a more general ligand environment, we have investigated the behavior of the neutral square-planar Ir(I) complex [IrCl($\eta^2$-$C_2H_4$)(P*i*Pr$_3$)$_2$] (**27**). This compound was previously reported to activate the ethylene ligand under UV irradiation, to afford an unsaturated hydride−vinyl Ir(III) derivative.[10] The addition of ligands such as pyridine or CO was found necessary to obtain thermodynamically stable octahedral complexes from the activation product, although possible kinetic effects of these added ligands were not considered.

In agreement with the previously reported results, we have observed that addition of acetonitrile excess to solutions of **27** or its $\eta^2$-propylene analogue [IrCl($\eta^2$-$C_3H_6$)(P*i*Pr$_3$)$_2$] (**28**) affords hydride compounds. Nevertheless, the composition of the reaction outcome has been found to depend on the reaction conditions. The expected ethylene C−H activation product, [IrClH(CH═$CH_2$)(NCMe)(P*i*Pr$_3$)$_2$] (**29**), has been obtained by treatment of **27** with 2 equiv of acetonitrile at room temperature. Its solution $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra at temperatures above 303 K are consistent with a single reaction product, but the signals in the spectra broaden upon decreasing the temperature, eventually splitting into two sets of signals of approximately equal intensity. Even though the low-temperature signals (183 K) do not resolve enough to permit the identification of each component in the mixture, the observed behavior

(10) Schulz, M.; Werner, H. *Organometallics* **1992**, *11*, 2790−2795.

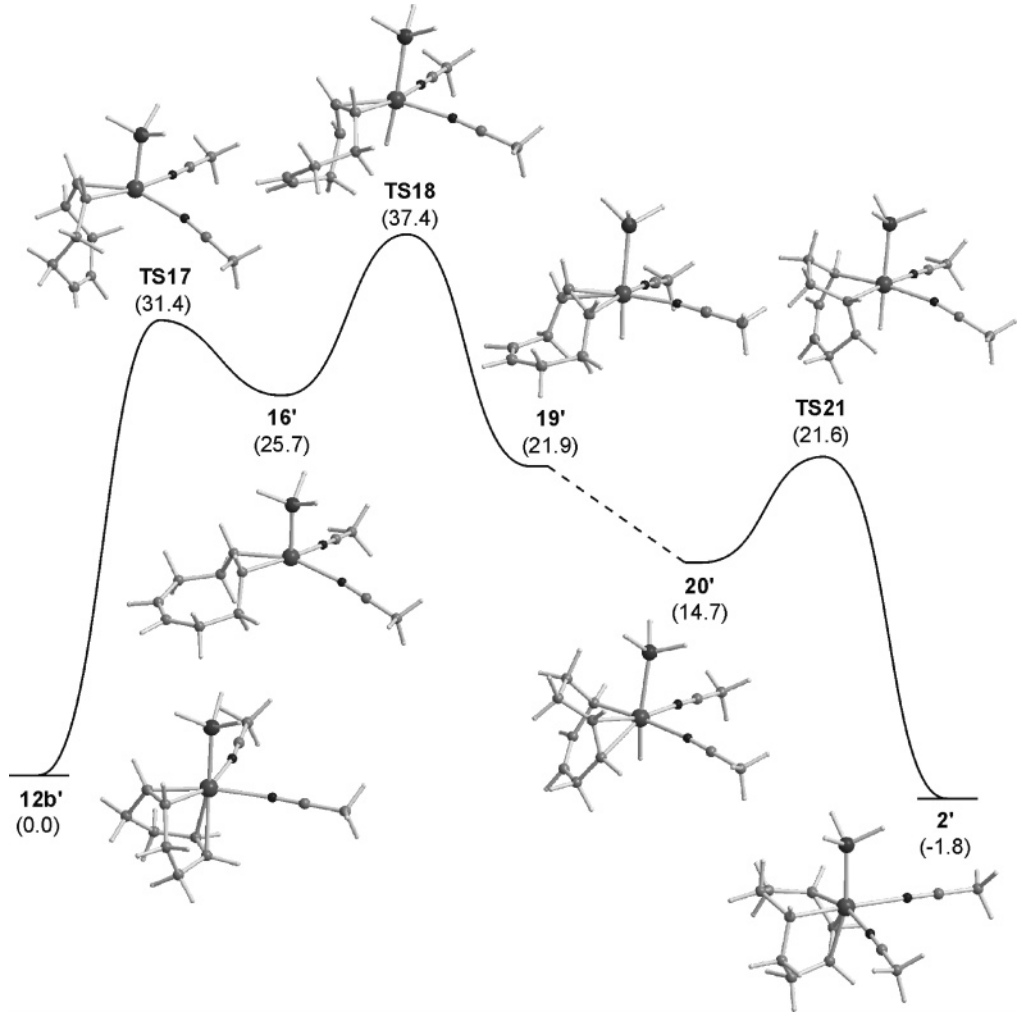
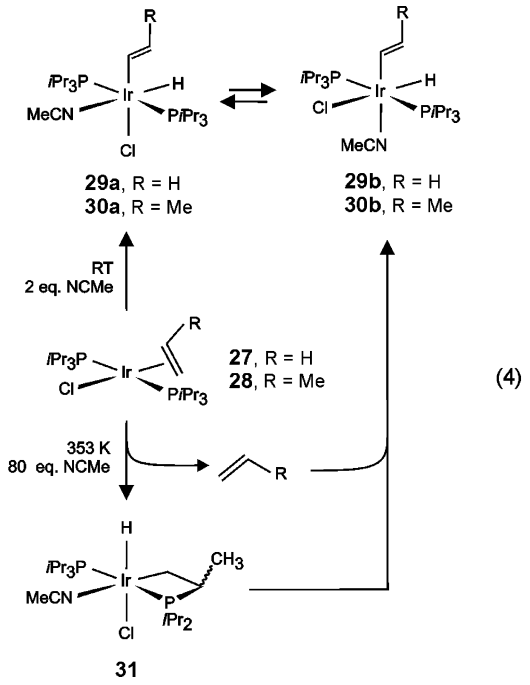



***Figure 5.*** DFT (B3LYP)-computed reaction coordinate for the 1,2,5,6-$\eta$-$C_8H_{12}$ to 1-$\kappa$-4,5,6-$\eta$-$C_8H_{12}$ isomerization of the cyclooctadiene ligand at the model five-coordinate acetonitrile adduct **12b′**. Values in parentheses are relative free energies (kcal mol$^{-1}$) in standard conditions.

is consistent with a fast exchange in the NMR time scale between two isomers of **29** (eq 4), as previously observed for the analogous reaction with pyridine.[10] The crystals obtained from solutions of **29** have allowed the X-ray characterization of one of the isomers, **29b**, the structure of which is shown in Figure 6. The most noticeable feature in this structure is the very long Ir−N bond distance (2.102(4) Å, Table 2), which should correspond to a readily dissociable acetonitrile ligand.[11,12] Since the other expected isomer, **29a**, is proposed to coordinate acetonitrile trans to the also trans-labilizing hydride ligand,[13] the observed fast exchange between isomers of **29** is likely to result from facile acetonitrile dissociations in both isomers.




(4)

Under similar reaction conditions, the propylene compound **28** has been found to afford the hydride−alkenyl complex [IrClH(*E*-CH=$CH_2CH_3$)(NCMe)(P*i*$Pr_3$)$_2$] (**30**) (eq 4). With regard to the variable temperature NMR data, the solutions of this compound also consist of a mixture of the two expected labile isomers in fast exchange. In this case, the crystals obtained from the mixture correspond to the isomer with acetonitrile trans to hydride, **30a**, the structure of which is shown in Figure 6. In agreement with the reasons given to rationalize the fast exchange between isomers, the Ir−N bond distance in this structure is indeed very long (2.122(3) Å, Table 2). The selectivity of this

(11) Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534−3546.
(12) Navarro, J.; Sola, E.; Martín, M.; Dobrinovitch, I. T.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2004**, *23*, 1908−1917.
(13) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5−80.

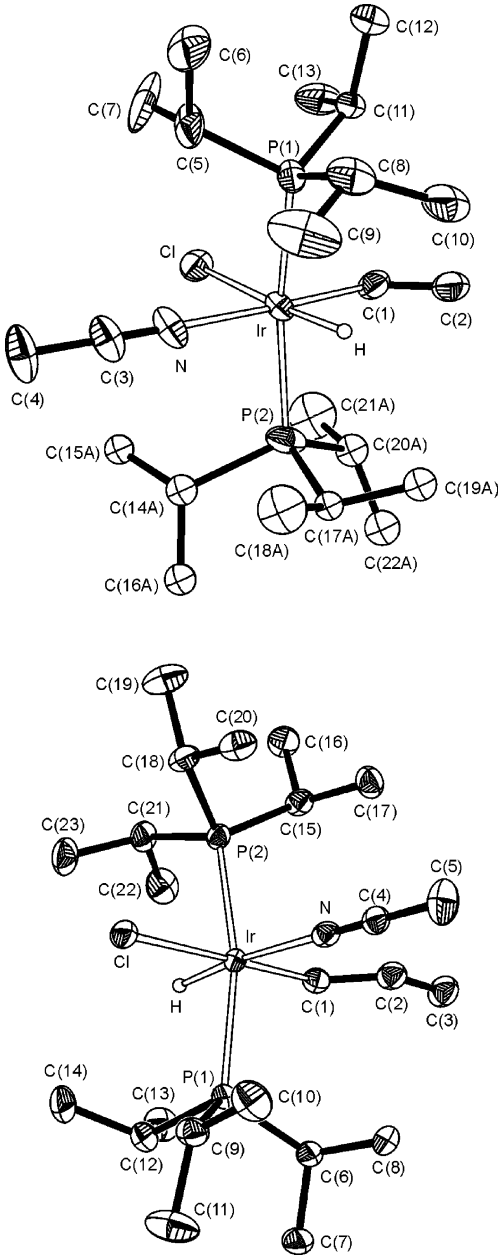



***Figure 6.*** Molecular structures of complexes **29b** (above) and **30a** (below).

C−H oxidative addition is noticeable, since isomeric compounds resulting from the activation of the methyl group or other alkene protons have not been observed. This is in contrast with the cases examined in the previous sections, in which allylic activations are those kinetically favored, and against the thermodynamic selectivity found in related propylene activations, which also favors hydride-$\eta^3$-allyl compounds.[11,14]

Higher reaction temperatures and/or the use of larger acetonitrile excess during the synthesis of **29** and **30** has been observed to result into the partial formation of two new hydride products. With regard to their NMR data and the previously reported result of a similar reaction with ammonia as additive,[15] these new complexes can be formulated as two isomers of the cyclometalated complex [IrClH{$\kappa$-*P*,*C*-P($i$Pr)$_2$CH(CH$_3$)CH$_2$}-(NCMe)(P$i$Pr$_3$)] (**31**). This mixture of isomers has been prepared in analytically pure form either by using a large acetonitrile excess (ca. 80 equiv) at 353 K or, more conveniently, by reacting the cyclooctene dimer [Ir($\mu$-Cl)(coe)$_2$]$_2$ with 4 equiv of phosphine and acetonitrile. Contrarily to the thermodynamic mixtures of fast exchanging isomers observed for **29** and **30**, the mixture **31** seems to consist of two kinetic isomers in ca. 7:3 molar ratio. The isomers do not convert each other in the NMR time scale despite the lability of their acetonitrile ligands, which show characteristic broad signals in the RT NMR spectra due to their fast dissociation. This observation suggests the isomers differ from each other in the syn or anti orientation of the activated isopropyl group relative to the hydride, rather than in the acetonitrile coordination position (eq 4). Unfortunately, further structural assignments have been found impossible due to the absence of measurable NOE effects among the $^1$H NMR signals of hydrides and those due to relevant protons of the activated isopropyl group. The structure of **31** depicted in eq 4 also assumes the trans relative position between hydride and chloride ligands previously proposed for the analogue of this complex with ammonia.[15]

***Table 2.*** Selected Bond Distances (angstrom) and Angles (deg) for Complexes **29b** and **30a**

| | 29b | 30a |
|---|---|---|
| Ir−Cl | 2.5239(13) | 2.4988(8) |
| Ir−P(1) | 2.3424(14) | 2.3405(8) |
| Ir−P(2) | 2.3383(15) | 2.3357(8) |
| Ir−N | 2.102(4) | 2.122(3) |
| Ir−C(1) | 2.020(5) | 2.047(3) |
| C(1)−C(2) | 1.310(7) | 1.334(5) |
| C(2)−C(3) | | 1.504(4) |
| P(1)−Ir−P(2) | 166.88(5) | 164.37(3) |
| N−Ir−C(1) | 176.5(2) | 91.51(12) |
| Cl−Ir−H | 173.5(15) | 96.6(13) |
| Cl−Ir−C(1) | 88.21(16) | 178.92(10) |
| Cl−Ir−N | 88.28(12) | 89.55(7) |
| Ir−C(1)−C(2) | 134.1(5) | 127.7(3) |
| C(1)−C(2)−C(3) | | 125.7(3) |

The mixture of isomers **31** has been observed to react with ethylene or propylene affording compound **29** or **30**, respectively (eq 4). These reactions are complete after few seconds at room temperature, seemly being much faster than those forming the same compounds from the starting complexes **27** and **28**. This observation strongly suggests that isomers **31** constitute intermediates in the formation of the alkene activation compounds, being the final reaction products only under experimental conditions diminishing alkene concentration in solution and disfavoring alkene coordination (high temperature and large acetonitrile excess, respectively). This suggested mechanism would imply that alkene activation takes place at unsaturated Ir(III)[16] centers generated after acetonitrile dissociation from the kinetic C−H activation products **31**, rather than at any Ir(I) species.

The rates of transformation of **27** and **28** into any of their C−H activation products have been observed to strongly depend on the presence or absence of light. In agreement with the previously reported photochemical character of these activations,[10] the reactions exposed to daylight have been found to

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(15) Schulz, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1993**, 318−319.
(16) For recent work on C−H activation by Ir(III) complexes with leading references, see: (a) Klei, S. R.; Golden, J. T.; Burger, P.; Bergman, R. G. *J. Mol. Catal. A: Chem.* **2002**, *189*, 79−94. (b) Wong-Foy, A. G.; Bhalla, G.; Lui, X. Y.; Periana, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 14292−14293.

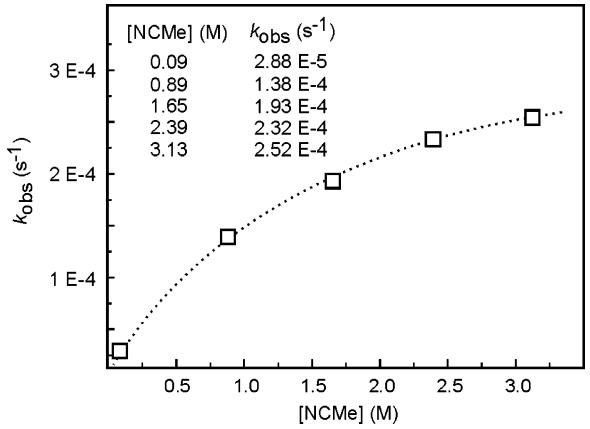


***Figure 7.*** Pseudo-first-order rate constants obtained by $^{31}P$ NMR for the transformation of **28** into mixtures of the C−H activation products **30** and **31**, at various acetonitrile concentrations. Solvent: toluene-$d_8$; $[\mathbf{28}]_0 = 4.2 \times 10^{-2}$ M; $T = 303$ K.

occur at relatively fast rates. Nevertheless, the C−H oxidative additions have also been observed to take place under strict absence of light, although at slower rates. Under the latter conditions, the rates estimated by $^{31}P$ NMR depend on the nature of the alkene ligand in the starting compound (even when the final product is the common mixture of isomers **31**), being faster for the propylene derivative **28**. Furthermore, the pseudo-first-order rate constants measured in toluene-$d_8$ solutions of **28** display a direct dependence upon acetonitrile concentration (Figure 7), with a diagnostic saturation profile similar to that obtained for the cationic cyclooctadiene complex **1**. The analysis of these kinetic data affords an estimated value of $0.7 \pm 0.1$ $mol^{-1}$ L for the equilibrium constant of five-coordinate acetonitrile adduct formation from **28** and a first-order rate constant for C−H oxidative addition at this adduct of $3.7 \times 10^{-4} \pm 2 \times 10^{-5}$ $s^{-1}$.

The above qualitative and quantitative kinetic observations suggest the feasibility of two possible C−H activation mechanisms in the square-planar complexes **27** and **28**. The most effective one seems to be that initiated by a photochemical release of the alkene ligand, whereas in the absence of light, alkene dissociation requires the previous coordination of acetonitrile. With regard to reported results and the conclusions of the previous sections, such activation steps would afford three-coordinate[17] or distorted four-coordinate intermediates, respectively, both capable of undergoing intramolecular C−H activation of the phosphine ligand and, depending on the reaction conditions, subsequent intermolecular reaction with the previously dissociated alkene.

## Conclusion

The counterintuitive observation that ligands such as acetonitrile, ethylene, or propylene accelerate the isomerization of cyclooctadiene ligands at iridium centers has led to the recognition of a mechanism for the activation of Ir(I) square-planar compounds toward C−H oxidative additions. This mechanism affords distorted (nonsquare-planar) four-coordinate intermediates through a sequence of ligand coordination/dissociation steps mediated by five-coordinate species. In the examples examined in this work, the C−H activations preceded by such a sequence have been found to be faster than those involving simpler, nonassisted, distortions of the square-planar geometry. Even though the distorted intermediates generated in this way seem only capable of activating intramolecular C−H bonds, the weakly coordinating nature of the ligands promoting this mechanism permit subsequent reactions on the activation products, such as intermolecular C−H oxidative additions of alkenes. This characteristic suggests the possible exploitation of this fifth ligand effect in new C−H activation/functionalization strategies using seemly nonreactive $d^8$ square-planar complexes.

## Experimental Section

**Equipment.** Infrared spectra were recorded in KBr in a Bruker Equinox 55 (4000−400 $cm^{-1}$) spectrometer. C, H, and N elemental analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on Bruker Avance 400 or 300 MHz spectrometers. $^1H$ (400 or 300 MHz) and $^{13}C$ (100.6 or 75.5 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. $^{31}P$ (162.0 or 121.5 MHz) NMR chemical shifts were measured relative to $H_3PO_4$ (85%). Coupling constants ($J$ and $N$) are given in hertz. Spectral assignments were achieved through $^1H$-COSY, $^1H$-NOESY, $^{13}C$-DEPT, and $^1H$,$^{13}C$-HSQC experiments. The sample temperature was calibrated using the temperature dependence of the chemical shifts of MeOH. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the $Cs^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

**Synthesis.** All experiments were carried out under argon atmosphere by Schlenk techniques. Solvents were dried by known procedures and distilled under argon before use. The complexes $[Ir(\mu\text{-Cl})(coe)_2]_2$,[18] $[Ir(1,2,5,6\text{-}\eta\text{-}C_8H_{12})(NCMe)(PMe_3)]BF_4$ (**1**), $[Ir(1\text{-}\kappa\text{-}4,5,6\text{-}\eta\text{-}C_8H_{12})(NCMe)_2(PMe_3)]BF_4$ (**2**),[9] and $[IrCl(\eta^2\text{-}C_2H_4)(P\mathit{i}Pr_3)_2]$ (**27**),[10] were prepared as previously reported. The analogue of **1** with tetraphenylborate as anion, $[Ir(1,2,5,6\text{-}\eta\text{-}C_8H_{12})(NCMe)(PMe_3)]BPh_4$, was prepared as described for **1** starting from $[Ir(\mu\text{-OMe})(cod)]_2$[19] (150.0 mg, 0.22 mmol) and $[HPMe_3]BPh_4$ (68.0 mg, 0.44 mmol, prepared by anion exchange from $[HPMe_3]BF_4$ and $NaBPh_4$ in methanol): yield 231.0 mg (71%). Anal. Calcd for $C_{37}H_{44}NBIrP$: C, 60.32; H, 6.02; N, 1.90. Found: C, 60.32; H, 5.62; N, 1.83. $^1H$ NMR ($CD_2Cl_2$, 293 K): $\delta$ 1.36 (d, $J_{HP} = 9.6$, 9H, $PCH_3$), 1.85 (s, 3H, $NCCH_3$), 1.99, 2.25 (both m, 4H each, $CH_2$), 4.30 (br, 4H, CH), 6.92 (m, 4H, CH), 7.05 (m, 8H, CH), 7.36 (br, 8H, CH). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 293 K): $\delta$ −19.82 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 183 K): $\delta$ 2.01 (s, $NCCH_3$), 12.13 (d, $J_{CP} = 35.4$, $PCH_3$), 28.56, 32.25 (both br, $CH_2$), 64.73, 91.93, 121.49, 125.48 (all br, CH), 126.08 (s, $NCCH_3$), 134.86 (br, CH), 163.13 (m, $J_{CB} = 49.0$, C). All other reagents were obtained from commercial sources and used as received. The new compounds described below are air-sensitive in solution.

**Preparation of $[Ir(1\text{-}\kappa\text{-}4,5,6\text{-}\eta\text{-}C_8H_{12})(NCMe)(\eta^2\text{-}C_2H_4)(PMe_3)]BF_4$ (3).** Method A: Ethylene was bubbled during 1 min through a solution of **1** (20 mg, 0.04 mmol) in 1,2-dichloroethane (0.5 mL) contained in an NMR tube. The tube was introduced in the NMR spectrometer at 333 K, and the reaction was monitored by $^{31}P\{^1H\}$ NMR. Quantitative transformation into **3** was complete after 15 min. Method B: A solution of **2** (100 mg, 0.18 mmol) in $CH_2Cl_2$ (8 mL) was stirred under ethylene atmosphere (1 bar) for 1 h at room temperature. The resulting solution was concentrated to 0.5 mL, cooled at 233 K, and treated with diethyl ether to give a pale yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 53.5 mg (55%). Anal. Calcd for $C_{15}H_{28}$-

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(19) Usón, R.; Oro, L. A.; Cabeza, J. *Inorg. Synth.* **1985**, *23*, 126−130.

$NBF_4IrP$: C, 33.84; H, 5.30; N, 2.63. Found: C, 33.44; H, 5.30; N, 2.63. MS (FAB+, *m*/*z* (%)): 405 (96) [$M^+$−NCMe]. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ 0.77 (m, 1H, IrCH), 0.89, 1.16 (both m, 1H each, $CH_2$), 1.54 (m, 4H, $CH_2$), 1.83 (d, $J_{HP}$ = 10.1, 9H, $PCH_3$), 2.07 (m, 2H, $CH_2$), 2.19 (br, 3H, $NCCH_3$), 2.83, 3.59 (both m, 2H each, $\eta^2$-$CH_2$=$CH_2$), 4.72, 5.69, 6.31 (all m, 1H each, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta$ −41.33 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta$ 2.82 (s, NC*C*$H_3$), 15.75 (d, $J_{CP}$ = 38.1, $PCH_3$), 21.84 (br, IrCH), 23.44 (d, $J_{CP}$ = 2.2, $CH_2$), 25.06 (s, $CH_2$), 48.45 (s, $\eta^2$-$CH_2$=$CH_2$), 48.84 (d, $J_{CP}$ = 7.6, $CH_2$), 50.16 (d, $J_{CP}$ = 6.3, $CH_2$), 77.33 (s, CH), 88.08 (d, $J_{CP}$ = 19.6, CH), 98.36 (s, CH), 117.89 (br, N*C*$CH_3$).

**Preparation of [Ir(1-κ-4,5,6-η-$C_8H_{12}$)(NCMe)(η²-$C_3H_6$)($PMe_3$)]$BF_4$ (4).** The compound was prepared through any of the two methods described for **3** by using propylene instead of ethylene. Method B gave **4** as a pale yellow solid in 73% yield. Anal. Calcd for $C_{16}H_{30}NBF_4IrP$: C, 35.17; H, 5.53; N, 2.56. Found: C, 34.78; H, 5.23; N, 2.35. MS (FAB+, *m*/*z* (%)): 459 (12) [$M^+$], 418 (16) [$M^+$−NCMe]. $^1H$ NMR ($CD_2Cl_2$, 233 K): $\delta$ 0.69 (m, 1H, IrCH), 0.87, 1.14, 1.51, 1.56, 1.58 (all m, 1H each, $CH_2$), 1.68 (d, $J_{HH}$ = 3.3, 3H, $\eta^2$-$CH_2$=CHC$H_3$), 1.72 (m, 1H, $CH_2$), 1.77 (d, $J_{HP}$ = 9.9, 9H, $PCH_3$), 2.07, 2.12 (both m, 1H each, $CH_2$), 2.16 (s, 3H, $NCCH_3$), 2.85 (dd, $J_{HH}$ = 9.0, 7.8, 1H, $\eta^2$-C$H_2$=CHCH$_3$), 3.02 (dd, $J_{HH}$ = 11.7, 7.8, 1H, $\eta^2$-C$H_2$=CHCH$_3$), 4.64 (m, 1H, CH), 4.98 (m, 1H, $\eta^2$-$CH_2$=C*H*$CH_3$), 5.32, 5.75 (both m, 1H each, CH). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 233 K): $\delta$ −41.23 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 233 K): $\delta$ 3.28 (s, NC*C*$H_3$), 15.44 (d, $J_{CP}$ = 37.9, $PCH_3$), 21.17 (s, $\eta^2$-$CH_2$=CH*C*$H_3$), 22.72 (d, $J_{CP}$ = 4.0, IrCH), 24.14 (d, $J_{CP}$ = 2.6, $CH_2$), 25.02 (s, $CH_2$), 48.47 (d, $J_{CP}$ = 7.4, $CH_2$), 50.01 (d, $J_{CP}$ = 6.6, $CH_2$), 53.44 (d, $J_{CP}$ = 5.1, $\eta^2$-*C*$H_2$=CHCH$_3$), 64.56 (s, $\eta^2$-$CH_2$=*C*HCH$_3$), 74.29 (s, CH), 94.33 (d, $J_{CP}$ = 21.7, CH), 98.71 (s, CH), 117.72 (s, N*C*$CH_3$).

**Reaction of 1 with Vinyl Acetate.** A solution of **1** (60.82 mg, 0.12 mmol) in $CD_2Cl_2$ (0.45 mL) contained in an NMR tube was treated with vinyl acetate (11 μL, 0.12 mmol) and introduced in the NMR spectrometer at 293 K. The $^{31}P\{^1H\}$ NMR spectrum displayed a singlet attributable to complex [Ir(1,2,5,6-η-$C_8H_{12}$){κ-*O*-η²-OC(Me)$OC_2H_3$}-($PMe_3$)]$BF_4$ (**6**) together with a broad signal at ca. $\delta$ −19. Upon decreasing the temperature this latter signal was found to progressively shift to higher field and simultaneously broaden. After decoalescence, the signal gave rise in the 193 K NMR spectrum to two major compounds in 2:1 molar ratio, identified as the isomers [Ir(1,2,5,6-η-$C_8H_{12}$)(NCMe)(η²-$C_2H_3OC(O)CH_3$}($PMe_3$)]$BF_4$ (**5**). A more detailed evolution of the $^{31}P\{^1H\}$ NMR spectrum with the temperature can be found as Supporting Information. Data for the major isomer of **5** is as follows. $^1H$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 1.19 (m, 1H, $\eta^2$-C$H_2$=CHOC-(O)$CH_3$), 1.55 (m, 1H, $CH_2$), 1.72 (d, $J_{HP}$ = 9.6, 9H, $PCH_3$), 1.82 (m, 1H, $CH_2$), 2.09 (s, 3H, $\eta^2$-$CH_2$=CHOC(O)C*H*$_3$), 2.14 (m, 1H, CH), 2.19 (m, 1H, $CH_2$), 2.20 (m, 1H, $\eta^2$-C*H*$_2$=CHOC(O)$CH_3$), 2.27, 2.51, 2.55, 2.62, 3.13 (all m, 1H each, $CH_2$), 3.13, 3.45, 3.75 (all m, 1H each, CH), 6.87 (m, 1H, $\eta^2$-$CH_2$=C*H*OC(O)$CH_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 193 K): $\delta$ −47.94 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 4.08 (s, NC*C*$H_3$), 15.16 (d, $J_{CP}$ = 30.4, $PCH_3$), 20.83 (d, $J_{CP}$ = 6.7, $\eta^2$-*C*$H_2$=CHOC(O)$CH_3$), 21.37 (s, $\eta^2$-$CH_2$=CHOC(O)*C*$H_3$), 27.24, 30.69, 36.00, 36.46 (all s, $CH_2$), 63.85 (d, $J_{CP}$ = 5.3, CH), 68.96 (d, $J_{CP}$ = 11.5, CH), 71.78 (s, CH), 75.36 (d, $J_{CP}$ = 20.3, CH), 84.81 (s, $\eta^2$-$CH_2$=*C*HOC(O)$CH_3$), 117.25 (s, N*C*$CH_3$), 169.94 (s, $\eta^2$-$CH_2$=CHO*C*(O)$CH_3$). Data for the minor isomer of **5** is as follows. $^1H$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 1.36, 1.60 (both m, 1H each, $CH_2$), 1.72 (d, $J_{HP}$ = 9.6, 9H, $PCH_3$), 1.85 (s, 3H, $\eta^2$-$CH_2$=CHOC(O)C*H*$_3$), 2.22, 2.38, 2.62 (all m, 1H each, $CH_2$), 2.67 (m, 1H, $\eta^2$-C*H*$_2$=CHOC(O)$CH_3$), 2.90 (m, 1H, $CH_2$), 2.99 (m, 1H, CH), 3.00, 3.13 (both m, 1H each, $CH_2$), 3.33 (m, 1H, CH), 3.34 (m, 1H, $\eta^2$-C*H*$_2$=CHOC(O)$CH_3$=$CH_2$), 3.40, 3.93 (both m, 1H each, CH), 5.63 (m, 1H, $\eta^2$-$CH_2$=C*H*OC(O)$CH_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 193 K): $\delta$ −47.73 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 193 K): $\delta$ 4.60 (s, NC*C*$H_3$), 14.66 (d, $J_{CP}$ = 31.4, $PCH_3$), 21.13 (s, $\eta^2$-$CH_2$=CHOC(O)*C*$H_3$), 24.65 (d, $J_{CP}$ = 16.4, $\eta^2$-*C*$H_2$=CHOC(O)$CH_3$), 25.57, 28.59, 36.00, 37.90 (all s, $CH_2$), 64.16 (d, $J_{CP}$ = 5.0, CH), 71.60 (s, CH), 72.17, (d, $J_{CP}$ = 10.2, CH), 73.83 (d, $J_{CP}$ = 8.2, CH), 83.24 (s, $\eta^2$-$CH_2$=*C*HOC(O)$CH_3$), 118.50 (s, N*C*$CH_3$), 171.07 (s, $\eta^2$-$CH_2$=CHO*C*(O)$CH_3$).

**Preparation of [Ir(1,2,5,6-η-$C_8H_{12}$){κ-*O*-η²-OC(Me)$OC_2H_3$}-($PMe_3$)]$BF_4$ (6).** A solution of **1** (200 mg, 0.41 mmol) in $CH_2Cl_2$ (8 mL) was reacted with vinyl acetate (2.3 mL, 24.6 mmol) and rapidly concentrated to ca. 0.5 mL under reduced pressure. The addition of diethyl ether produced the precipitation of a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 180.9 mg (83%). Anal. Calcd for $C_{15}H_{27}BF_4IrO_2P$: C, 32.80; H, 4.95. Found: C, 32.38; H, 4.82. MS (FAB+, *m*/*z* (%)) 463 (57) [$M^+$]. IR ($cm^{-1}$): 1760, 1647, 1596 ν(CO). $^1H$ NMR ($CD_2Cl_2$, 253 K): $\delta$ 1.58 (m, 1H, $CH_2$), 1.61 (m, 1H, κ-*O*-η²-C*H*$_2$=CHOC(O)-$CH_3$), 1.76 (d, $J_{HP}$ = 10.1, 9H, $PCH_3$), 1.82 (m, 1H, κ-*O*-η²-C*H*$_2$=CHOC(O)$CH_3$), 1.86, 2.09 (both m, 1H each, $CH_2$), 2.24 (s, 3H, κ-*O*-η²-$CH_2$=CHOC(O)C*H*$_3$), 2.32, 2.37, 2.40 (all m, 1H each, $CH_2$), 2.43 (m, 1H, CH), 2.59, 2.96 (both m, 1H each, $CH_2$), 3.02, 3.65, 3.82 (all m, 1H each, CH), 7.26 (m, 1H, κ-*O*-η²-$CH_2$=C*H*OC(O)$CH_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 253 K): $\delta$ −39.63 (s). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 253 K): $\delta$ 15.01 (d, $J_{CP}$ = 31.8, $PCH_3$), 18.42 (s, κ-*O*-η²-$CH_2$=CHOC-(O)*C*$H_3$), 19.79 (d, $J_{CP}$ = 6.4, κ-*O*-η²-*C*$H_2$=CHOC(O)$CH_3$), 26.02 (d, $J_{CP}$ = 4.1, $CH_2$), 31.57, 33.87 (both s, $CH_2$), 35.79 (d, $J_{CP}$ = 2.4, $CH_2$), 62.38 (d, $J_{CP}$ = 3.2, CH), 68.37 (d, $J_{CP}$ = 6.0, CH), 73.63 (s, CH), 75.76 (d, $J_{CP}$ = 9.1, CH), 90.91 (d, $J_{CP}$ = 22.9, κ-*O*-η²-$CH_2$=*C*HOC-(O)$CH_3$), 187.74 (d, $J_{CP}$ = 10.2, κ-*O*-η²-$CH_2$=CHO*C*(O)$CH_3$).

**Preparation of [Ir(1,2,5,6-η-$C_8H_{12}$){κ-*O*-η²-OC(Me)$OC_2H_3$}-($PMe_3$)]$BPh_4$ (6-$BPh_4$).** The compound was prepared as described for **6** but starting from [Ir(1,2,5,6-η-$C_8H_{12}$)(NCMe)($PMe_3$)]$BPh_4$ (200 mg, 0.27 mmol) and vinyl acetate (1.50 mL, 16.29 mmol): yield 186.8 mg (88%). Anal. Calcd for $C_{39}H_{47}BIrO_2P$: C, 59.92; H, 6.06. Found: C, 59.47; H, 5.69. The crystals used in the X-ray diffraction experiment were obtained by slow diffusion of hexane into a saturated solution of **6**-$BPh_4$ in $CH_2Cl_2$ at 253 K.

**Preparation of [Ir(1-κ-4,5,6-η-$C_8H_{12}$){κ-*O*-η²-OC(Me)$OC_2H_3$}-($PMe_3$)]$BF_4$ (7).** A solution of **1** (100 mg, 0.20 mmol) in $CH_2Cl_2$ (8 mL) was treated with vinyl acetate (56 μL, 0.60 mmol) and allowed to react at the reflux temperature for 8 h. The resulting solution was filtered through Celite, concentrated to ca. 0.5 mL, and cooled at 233 K. Addition of diethyl ether produced the precipitation of a pale yellow solid, which was separated by decantation, washed with diethyl ether, and dried in vacuo: yield 81.3 mg (74%). Anal. Calcd for $C_{15}H_{27}BF_4IrO_2P$: C, 32.79; H, 4.69. Found: C, 32.59; H, 4.69. MS (FAB+, *m*/*z* (%)): 463 (100) [$M^+$]. IR ($cm^{-1}$): 1740, 1654, 1597 ν(CO). $^1H$ NMR (acetone-$d_6$, 293 K): $\delta$ 0.88 (m, 2H, $CH_2$), 1.33 (m, 2H, $CH_2$ + CH), 1.49 (m, 1H, $CH_2$), 1.69 (m, 2H, $CH_2$), 1.95 (d, $J_{HP}$ = 10.8, 9H, $PCH_3$), 2.04 (s, 3H, κ-*O*-η²-$CH_2$=CHOC(O)C*H*$_3$), 2.20 (m, 2H, $CH_2$), 2.92 (ddd, $J_{HH}$ = 5.5, 4.2, $J_{HP}$ = 4.6, 1H, κ-*O*-η²-C*H*$_2$=CHOC(O)$CH_3$), 3.28 (ddd, $J_{HP}$ = 10.9, $J_{HH}$ = 7.2, 4.2, 1H, κ-*O*-η²-C*H*$_2$=CHOC(O)*CH*$_3$), 4.58, 5.93, 6.67 (all m, 1H each, CH), 7.95 (ddd, $J_{HH}$ = 7.2, 5.5, $J_{HP}$ = 4.3, 1H, κ-*O*-η²-$CH_2$=C*H*OC(O)$CH_3$). $^{31}P\{^1H\}$ NMR (acetone-$d_6$, 293 K): $\delta$ −34.41 (s). $^{13}C\{^1H\}$ NMR (acetone-$d_6$, 293 K): $\delta$ 14.64 (d, $J_{CP}$ = 39.0, $PCH_3$), 18.61 (s, κ-*O*-η²-$CH_2$=CHOC(O)*C*$H_3$), 22.89 (d, $J_{CP}$ = 2.7, $CH_2$), 24.48 (s, $CH_2$), 24.91 (d, $J_{CP}$ = 3.6, CH), 37.36 (d, $J_{CP}$ = 6.7, κ-*O*-η²-*C*$H_2$=CHOC(O)$CH_3$), 48.14 (d, $J_{CP}$ = 6.4, $CH_2$), 49.78 (d, $J_{CP}$ = 7.2, $CH_2$), 79.21 (s, CH), 85.58 (d, $J_{CP}$ = 6.1, κ-*O*-η²-$CH_2$=*C*HOC(O)$CH_3$), 94.40 (d, $J_{CP}$ = 17.7, CH), 102.41 (d, $J_{CP}$ = 0.8, CH), 183.24 (d, $J_{CP}$ = 3.4, κ-*O*-η²-$CH_2$=CHO*C*(O)$CH_3$). The crystals used in the X-ray determination were obtained by slow diffusion of diethyl ether into a saturated solution of **7** in $CH_2Cl_2$ at 253 K.

**Preparation of [IrCl(η²-$C_3H_6$)(*Pi*$Pr_3$)$_2$] (28).** A suspension of [Ir(μ-Cl)(coe)$_2$]$_2$ (679.4 mg, 0.75 mmol) in pentane (15 mL) was treated with P*i*$Pr_3$ (637 μL, 3.34 mmol) at 273 K. After 10 min of reaction, the resulting suspension was protected from the light, treated with propylene at atmospheric pressure, and then cooled at 233 K. The resulting solution was concentrated to ca. 0.5 mL to give an orange solid, which was separated by decantation, washed with pentane at 233 K, and dried in

vacuo: yield 239 mg (27%). Anal. Calcd for $C_{21}H_{48}ClIrP_2$: C, 42.73; H, 8.20. Found: C, 42.55; H, 8.38. $^1$H NMR ($CD_2Cl_2$, 263 K): $\delta$ 1.21 (d, $J_{HH}$ = 6.21, 3H, $\eta^2$-$CH_2$=CHC$H_3$), 1.26−1.39 (m, 36H, PCHC$H_3$), 1.55, 1.75 (both m, 1H each, $\eta^2$-C$H_2$=CHCH$_3$), 2.47, 2.66 (both m, 3H each, PC$H$CH$_3$), 2.71 (m, 1H, $\eta^2$-$CH_2$=C$H$CH$_3$). $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 263 K): $\delta$ 13.37, 17.55 (both d, $J_{PP}$ = 360.7). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 263 K): $\delta$ 18.83 (br, $\eta^2$-$C$H$_2$=CHCH$_3$), 19.60, 19.70, 20.08, 20.36 (all s, PCH$C$H$_3$), 22.58 (br, $\eta^2$-CH$_2$=$C$HCH$_3$), 22.18 (d, $J_{CP}$ = 17.0, P$C$HCH$_3$), 23.24 (d, $J_{CP}$ = 17.7, P$C$HCH$_3$), 33.27 (s, $\eta^2$-CH$_2$=CH$C$H$_3$).

**Preparation of [IrClH(CH=CH$_2$)(NCMe)(P*i*Pr$_3$)$_2$] (29).** A solution of **27** (143.6 mg, 0.25 mmol) in benzene (3 mL) was treated with acetonitrile (2.6 $\mu$L, 0.50 mmol) and stirred for 1 h while exposed to the daylight. The resulting solution was concentrated to ca. 0.5 mL and treated with hexane to give a white solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 98.6 mg (64%). Anal. Calcd for $C_{22}H_{49}NClIrP_2$: C, 42.81; H, 8.00; N, 2.27. Found: C, 43.02; H, 7.96; N, 2.05. IR (cm$^{-1}$): 2285, 2256 $\nu$(IrH). $^1$H NMR (toluene-$d_8$, 308 K): $\delta$ −21.05 (t, $J_{HP}$ = 15.9, 1H, IrH), 0.79 (s, 3H, NCCH$_3$), 1.22 (dvt, $J_{HH}$ = 7.2, $N$ = 12.8, 18H, PCHC$H_3$), 1.23 (dvt, $J_{HH}$ = 7.2, $N$ = 12.0, 18H, PCHC$H_3$), 2.82 (m, 6H, PC$H$CH$_3$), 5.26 (ddt, $J_{HH}$ = 18.0, 3.6, $J_{HP}$ = 1.6, 1H, IrCH=C$H_2$), 5.98 (ddt, $J_{HH}$ = 10.4, 3.6, $J_{HP}$ = 1.6, 1H, IrCH=C$H_2$), 7.89 (dd, $J_{HH}$ = 18.0, 10.4, 1H, IrC$H$=CH$_2$). $^{31}$P{$^1$H} NMR (toluene-$d_8$, 308 K): $\delta$ 11.41 (br). $^{13}$C{$^1$H} NMR (toluene-$d_8$, 308 K): $\delta$ 0.15 (s, NC$C$H$_3$), 18.86 (s, PCH$C$H$_3$), 22.97 (vt, $N$ = 26.5, P$C$HCH$_3$), 115.68 (s, N$C$CH$_3$), 116.76 (s, IrCH=$C$H$_2$), 127.87 (s, Ir$C$H=CH$_2$). The crystals used in the X-ray structural determination were obtained by cooling at 253 K a saturated solution of **29** in toluene.

**Preparation of [IrClH(*E*-CH=CH$_2$CH$_3$)(NCMe)(P*i*Pr$_3$)$_2$] (30).** A solution of **28** (100.0 mg, 0.17 mmol) in benzene (5 mL) was treated with acetonitrile (9 $\mu$L, 0.18 mmol) and stirred for 15 min while exposed to the daylight. The resulting solution was concentrated to 0.5 mL and treated with hexane to give a white solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 77.3 mg (72%). Anal. Calcd for $C_{23}H_{51}NClIrP_2$: C, 43.76; H, 8.08; N, 2.22. Found: C, 43.80; H, 8.30; N, 2.21. $^1$H NMR ($C_6D_6$, 293 K): $\delta$ −20.89 (br, 1H, IrH), 1.00 (s, 3H, NCCH$_3$), 1.44 (dvt, $J_{HH}$ = 6.2, $N$ = 12.8, 18H, PCHC$H_3$), 1.45 (dvt, $J_{HH}$ = 6.3, $N$ = 13.0, 18H, PCHC$H_3$), 2.04 (dt, $J_{HH}$ = 6.0, $J_{HP}$ = 1.7, 3H, IrCH=CHC$H_3$), 3.00 (m, 6H, PC$H$CH$_3$), 5.54 (dq, $J_{HH}$ = 15.6, 6.0, 1H, IrCH=C$H$CH$_3$), 7.31 (brd, $J_{HH}$ = 15.6, 1H, IrC$H$=CHCH$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$, 293 K): $\delta$ 12.28 (s). $^{13}$C{$^1$H} NMR ($C_6D_6$, 293 K): $\delta$ 1.66 (s, NC$C$H$_3$), 19.17 (s, PCH$C$H$_3$), 23.61 (vt, $N$ = 26.3, P$C$HCH$_3$), 24.83 (s, IrCH=CH$C$H$_3$), 115.02 (br, Ir$C$H=CHCH$_3$), 118.20 (s, N$C$CH$_3$), 124.77 (br, IrCH=$C$HCH$_3$). The crystals used in the X-ray structural determination were obtained by cooling at 253 K a saturated solution of **30** in toluene.

**Preparation of [IrClH{κ-*P,C*-P(*i*Pr)$_2$CH(CH$_3$)CH$_2$}(NCMe)-(P*i*Pr$_3$)] (31).** Method A: A solution of **27** (96.5 mg, 0.17 mmol) in benzene (2 mL) was treated with acetonitrile (704 $\mu$L, 13.39 mmol) and stirred for 2 h at 353 K. The resulting solution was concentrated to ca. 0.5 mL, and hexane was slowly added to give a white solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 42.4 mg (43%). Method B: A suspension of [Ir($\mu$-Cl)-(coe)$_2$]$_2$ (226.8 mg, 0.25 mmol) in pentane (15 mL) was treated with P*i*Pr$_3$ (212 $\mu$L, 1.11 mmol). After 15 min at room temperature, 4 equiv of acetonitrile (53 $\mu$L, 1.01 mmol) was added. The resulting yellow solution was stirred during 10 min, concentrated to ca. 0.5 mL, and treated with hexane to give a white solid. The solid was separated by decantation, washed with hexane, and dried in vacuo: yield 198.8 mg (67%). Anal. Calcd for $C_{20}H_{45}NClIrP_2$: C, 40.77; H, 7.70; N, 2.38. Found: C, 40.60; H, 7.40; N, 2.26. MS (FAB+, $m/z$ (%)): 548 (32) [M$^+$−NCCH$_3$]. IR (cm$^{-1}$): 2271, 2207 $\nu$(IrH). The compound was observed by NMR to consist of two isomers in molar ratio of 7:3. Data for the major isomer is as follows. $^1$H NMR (toluene-$d_8$, 253 K): $\delta$ −21.86 (dd, $J_{HP}$ = 16.2, 11.7, 1H, IrH), 0.96 (s, 3H, NCCH$_3$), 1.15 (m, 1H, IrCH$_2$), 1.17 (m, 3H, PCHC$H_3$), 1.26−1.67 (m, 15H, PCHC$H_3$), 1.80 (m, 1H, IrCH$_2$), 1.92 (m, 1H, PC$H$CH$_3$), 2.22 (m, 3H, PC$H$CH$_3$), 3.14, 3.70 (both m, 1H each, PC$H$CH$_3$). $^{31}$P{$^1$H} NMR (toluene-$d_8$, 253 K): $\delta$ −25.75, 15.13 (both d, $J_{PP}$ = 361.8). $^{13}$C{$^1$H} NMR (toluene-$d_8$, 253 K): $\delta$ −22.95 (dd, $J_{CP}$ = 22.9, 3.2, IrCH$_2$), 1.23 (s, NC$C$H$_3$), 19.07, 20.39, 20.43, 21.97, 22.04 (all s, PCH$C$H$_3$), 22.35 (d, $J_{CP}$ = 21.1, P$C$HCH$_3$), 23.82 (d, $J_{CP}$ = 21.5, P$C$HCH$_3$), 24.26 (d, $J_{CP}$ = 22.4, P$C$HCH$_3$), 44.25 (d, $J_{CP}$ = 31.2, P$C$HCH$_3$), 116.48 (s, N$C$CH$_3$). Data for the minor isomer is as follows. $^1$H NMR (toluene-$d_8$, 253 K): $\delta$ −21.63 (dd, $J_{HP}$ = 14.0, 14.4, 1H, IrH), 0.96 (s, 3H, NCCH$_3$), 1.17 (m, 3H, PCHC$H_3$), 1.26−1.40 (m, 15H, PCHC$H_3$), 1.46, 1.86 (both m, 1H each, IrCH$_2$), 1.92 (m, 1H, PC$H$CH$_3$), 2.22 (m, 3H, PC$H$CH$_3$), 3.25, 3.34 (both m, 1H each, PC$H$CH$_3$). $^{31}$P{$^1$H} NMR (toluene-$d_8$, 253 K): $\delta$ −32.04, 13.43 (both d, $J_{PP}$ = 362.5). $^{13}$C{$^1$H} NMR (toluene-$d_8$, 253 K): $\delta$ −24.17 (d, $J_{CP}$ = 24.5, IrCH$_2$), 1.13 (s, NC$C$H$_3$), 18.85 (s, PCH$C$H$_3$), 19.05 (d, $J_{CP}$ = 19.3, P$C$HCH$_3$), 20.25, (s, PCH$C$H$_3$), 21.13 (d, $J_{CP}$ = 19.0, P$C$HCH$_3$), 21.84 (s, PCH$C$H$_3$), 24.26 (d, $J_{CP}$ = 22.4, P$C$HCH$_3$), 44.48 (d, $J_{CP}$ = 30.5, P$C$HCH$_3$), 116.67 (s, N$C$CH$_3$).

**Kinetics.** The transformations of **1** and **28** into any of their products were followed by registering the intensity decrease of their $^{31}$P{$^1$H} NMR signals as a function of time, in 1,2-dichloroethane or toluene-$d_8$ solutions, respectively. The lock and field homogenization of the NMR samples in 1,2-dichloroethane were achieved by introducing a capillary tube containing toluene-$d_8$. For the studies under acetonitrile excess, solutions of known concentration were prepared by mixing exact volumes of previously prepared concentrated solutions of the starting complex and acetonitrile and subsequent adjustment of the sample total volume to 0.5 mL using the corresponding solvent. These manipulations were done avoiding exposition to daylight in the case of **28**. Pseudo-first-order rate constants were obtained either directly, from the adjustment of the entire reaction to an exponential decay function, or indirectly from the initial zero-order rates. The $CDCl_3$ solutions of **1** used in the variable temperature studies under acetonitrile excess were also prepared as described above. The line-shape analysis of the $^1$H NMR spectra was performed with the g-NMR program. Errors in the activation parameters obtained from the Eyring regression were estimated through conventional error propagation formulas,[20] assuming 1K error in the temperature and a 10% error in the rate constant.

**X-ray Structure Analysis of 6-BPh$_4$, 7, 29b, and 30a.** X-ray data were collected for all complexes on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) using $\omega$ scans (0.3°). Data were collected over the complete sphere by a combination of four sets and corrected for absorption using a multiscan method applied with the SADABS program.[21] The structures were solved by the Patterson method. Refinement, by full-matrix least-squares on $F^2$ using SHELXL97,[22] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. Hydrogen atoms were included in calculated positions and refined riding on carbon atoms with the thermal parameter related to bonded atoms or in observed positions and refined freely. Particular details concerning the presence of solvent, static disorder, and hydride ligand refinement are listed below.

**Crystal Data for 6-BPh$_4$.** $C_{39}H_{47}BIrO_2P\cdot CH_2Cl_2$, $M$ = 866.67; colorless plate prism, 0.18 × 0.08 × 0.04 mm$^3$; monoclinic, $P2_1/c$; $a$ = 12.976(3), $b$ = 12.175(3), $c$ = 23.421(6) Å, $\beta$ = 91.686(5); $Z$ = 4; $V$ = 3698.4(16) Å$^3$; $D_c$ = 1.557 g/cm$^3$; $\mu$ = 3.832 mm$^{-1}$, minimum and maximum transmission factors 0.600 and 0.756; $2\theta_{max}$ = 56.9°; temperature 100.0(2) K; 29 752 reflections collected, 8688 unique [$R$(int) = 0.076]; number of data/restrains/parameters 8688/0/431; final GOF 0.848, R1 = 0.0468 [5554 reflections $I > 2\sigma(I)$], wR2 = 0.0713

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for all data; largest difference peak 1.87 e·Å$^{-3}$. A dichloromethane was observed disordered in two positions. Both dichloromethane molecules share the same carbon atom with a turn angle of 49.7° and were refined with occupancy factors 0.54 and 0.46, respectively. The highest electronic residuals were observed close to the solvent.

**Crystal Data for 7.** $C_{15}H_{27}BF_4IrO_2P$, $M = 549.35$; irregular block pale yellow, 0.10 × 0.010 × 0.06 mm$^3$; monoclinic, $P2_1/c$; $a = 12.4262(10)$, $b = 10.0804(8)$, $c = 15.6876(12)$ Å, $\beta = 113.1280(10)$; $Z = 4$; $V = 1807.1(2)$ Å$^3$; $D_c = 2.019$ g/cm$^3$; $\mu = 7.521$ mm$^{-1}$, minimum and maximum transmission factors 0.463 and 0.625; $2\theta_{max} = 57.0°$; temperature 100.0(2) K; 21 415 reflections collected, 4331 unique [$R$(int) = 0.050]; number of data/restrains/parameters 4331/1/242; final GOF 0.900, R1 = 0.0307 [3248 reflections $I > 2\sigma(I)$], wR2 = 0.0568 for all data; largest difference peak 2.08 e·Å$^{-3}$. The highest electronic residual was observed close to the Ir atom and has no chemical sense.

**Crystal Data for 29b.** $C_{22}H_{49}ClIrNP_2 \cdot 0.50(C_{14}H_{16})$, $M = 709.35$; colorless prism, 0.10 × 0.08 × 0.08 mm$^3$; triclinic, $P-1$; $a = 8.4587(19)$, $b = 11.443(3)$, $c = 17.379(4)$ Å, $\alpha = 78.694(6)$, $\beta = 78.537(7)$, $\gamma = 87.473(6)$; $Z = 2$; $V = 1616.6(6)$ Å$^3$; $D_c = 1.457$ g/cm$^3$; $\mu = 4.328$ mm$^{-1}$, minimum and maximum transmission factors 0.714 and 0.759; $2\theta_{max} = 58.0°$; temperature 100.0(2) K; 20 500 reflections collected, 7777 unique [$R$(int) = 0.041]; number of data/restrains/parameters 7777/48/298; final GOF 0.919, R1 = 0.0418 [6435 reflections $I > 2\sigma(I)$], wR2 = 0.0692 for all data; largest difference peak 1.80 e·Å$^{-3}$. In the last cycles of the refinement a phosphine ligand was observed disordered in two positions, due to a turn on the P−Ir bond of about 21°. This ligand was refined with restrained geometry and thermal parameters. Two toluene molecules were also observed disordered over symmetry centers. The hydride ligand was refined with fixed Ir−H bond length. The highest electronic residual was observed close to the Ir atom and has no chemical sense.

**Crystal Data for 30a.** $C_{23}H_{51}ClIrP_2 \cdot 1.5C_6H_6$, $M = 748.40$; colorless irregular block, 0.24 × 0.14 × 0.08 mm$^3$; triclinic, $P-1$; $a = 8.9291(4)$, $b = 11.4598(5)$, $c = 18.4112(8)$ Å, $\alpha = 84.5070(10)$, $\beta = 82.5280(10)$, $\gamma = 70.6030(10)$; $Z = 2$; $V = 1759.14(13)$ Å$^3$; $D_c = 1.413$ g/cm$^3$; $\mu = 3.982$ mm$^{-1}$, minimum and maximum transmission factors 0.522 and 0.643; $2\theta_{max} = 57.8°$; temperature 100.0(2) K; 22 169 reflections collected, 8437 unique [$R$(int) = 0.031]; number of data/restrains/parameters 8437/1/357; final GOF 0.901, R1 = 0.0266 [7447 reflections $I > 2\sigma(I)$], wR2 = 0.0528 for all data; largest difference peak 1.69 e·Å$^{-3}$. This compound crystallizes with two molecules of benzene, one of them located over a symmetry center and shared by two asymmetric units. The hydride ligand was refined with fixed Ir−H bond length and thermal parameter. The highest electronic residual was observed close to the Ir atom and has no chemical sense.

**Computation.** All calculations were carried out with the Gaussian 98 package of programs[23] using the density functional theory (DFT)[24] with the B3LYP functional.[25] An effective core potential operator was used to replace the innermost electrons of Ir and P.[26] The basis set for the metal was that associated with the pseudopotential,[26] with a standard valence double-ξ LANL2DZ contraction.[23] A 6-31G(d) basis was used for all the ethylene and diene C atoms.[27a] The nitrogen N atoms were also described with a 6-31G(d) basis. The rest of the atoms were described with a 6-31G basis set.[27] The transition states found have been confirmed by frequency calculations, and the connection between the starting and final reactants has been checked by slightly perturbing the TS geometry toward the minima geometries and reoptimizing.

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**Supporting Information Available:** Complete ref 23; VT NMR experiments and simulations; electronic energies and Cartesian coordinates for the computed species; X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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