Labile Hydrido Complexes of Iridium(III): Synthesis, Dynamic Behavior in Solution, and Reactivity toward Alkenes

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The trisacetonitrile complexes $[IrClH(P^iPr_3)(NCCH_3)_3]BF_4$ (**1**) and $[IrH_2(P^iPr_3)(NCCH_3)_3]BF_4$ (**2**) have been prepared in one-pot reactions with high yields by reaction of the iridium(I) dimers $[Ir(\mu\text{-}Cl)(coe)_2]_2$ and $[Ir(\mu\text{-}OMe)(cod)_2]_2$ with the phosphonium salt $[HP^iPr_3]BF_4$. The rates of exchange between free acetonitrile and the labile acetonitrile ligands of complexes **1** and **2** have been measured by NMR spectroscopy. This kinetic study has shown that both complexes readily dissociate one acetonitrile ligand trans to hydride, giving rise to fluxional five-coordinate intermediates. Substitution products **3**−**7** have been obtained by treatment of complexes **1** and **2** with CO and PMe_3. The structures determined for **3**−**7** can be rationalized on the basis of the steric requirements of the ligands, indicating that the products are formed by thermodynamic control. Ethene inserts reversibly into the Ir−H bond of **1** to give the compound $[IrCl(Et)(P^iPr_3)(NCCH_3)_3]BF_4$ (**8**), which has been used for the preparation of the stable ethyliridium(III) complexes $[IrCl(Et)(P^iPr_3)(Py)_2(NCCH_3)]BF_4$ (**9**) and $[Ir(\eta^2\text{-}O_2CCH_3)Cl(Et)(P^iPr_3)(NCCH_3)_3]$ (**10**), respectively. The molecular structure of **10** has been determined by X-ray crystallography. The reaction of **2** with ethene, at low temperature, results in the sequential formation of the ethene complex $[IrH_2(\eta^2\text{-}C_2H_4)(P^iPr_3)(NCCH_3)_2]BF_4$ (**11**) and the diethyl derivative $[Ir(Et)_2(P^iPr_3)(NCCH_3)_3]BF_4$ (**14**). At room temperature in solution, **14** undergoes reductive elimination of ethane to form the iridium(I) species $[Ir(P^iPr_3)(NCCH_3)_3]BF_4$ (**15**) and $[Ir(P^iPr_3)(\eta^2\text{-}C_2H_4)(NCCH_3)_2]BF_4$ (**16**). These cations readily react with H_2 to regenerate **2**, closing a cycle for ethene hydrogenation in which several participating species have been identified. The reaction of **2** with propene in solution also allows the characterization of products of propene coordination (**17**) and insertion (**18**). In this case, the species obtained after elimination of propane are products of allylic C−H activation: $[IrH(\eta^3\text{-}C_3H_5)(P^iPr_3)(NCCH_3)_2]BF_4$ (**19**) and $[IrH(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)(P^iPr_3)(NCCH_3)]BF_4$ (**20**). The structure of complex **19** has been determined by X-ray diffraction, and the kinetics of dissociation of its two labile acetonitrile ligands have been studied by NMR spectroscopy. Complex **19** undergoes electrophilic activation of H_2 to give propene and reform the starting complex **2**.

Introduction

The organometallic chemistry of iridium(III) is dominated by compounds containing six-electron donor ligands such as cyclopentadienyl, indenyl, trispyrazolyl, or triphosphines and by complexes coordinating various monodentate phosphine ligands, generally two or more.[1] Some of these species, or their related Ir(I) derivatives, provide striking examples for activation reactions of small molecules, including the activation of C−H bonds under mild conditions.[2−10] However, despite this remarkable ability of substrate activation, the subsequent conversion of the activated substrates into functionalized organic products has been achieved in just a few cases,[11] and the incorporation of such activation steps into catalytic cycles remains to be solved.[12] This problem has been extensively discussed[2,4] and attributed to the inability of the products obtained in the activation step to generate new coordination vacancies, thus preventing further reaction with other substrates.

A feasible strategy to overcome this problem may involve the use of reactive complexes with weakly

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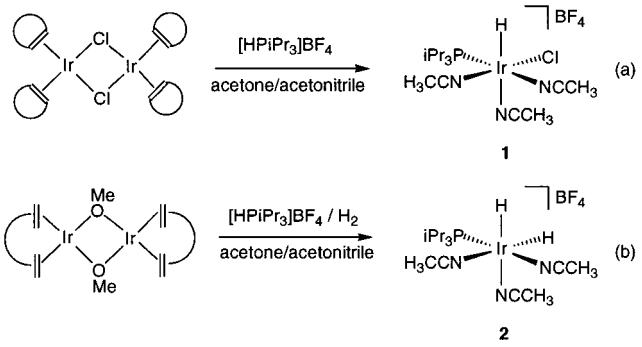
coordinated ligands, which can generate free coordination sites under mild conditions. An excellent example of this strategy can be found in the work by Crabtree and others on cationic solvato complexes of the general composition $[IrP_2H_2S_2]^+$.[13] These complexes contain two trans-disposed bulky phosphines (P), together with two cis-disposed hydrido and solvent ligands (S) such as water, acetone, or acetonitrile. Such compounds are good starting materials for the synthesis of several other d^6 iridium(III) complexes and are also active in a variety of catalytic transformations.[11b,13b,14]

Following and extending the aforementioned strategy, we report here on the synthesis and reactivity of the solvato complexes $[IrClH(P^iPr_3)(NCCH_3)_3]BF_4$ (**1**) and $[IrH_2(P^iPr_3)(NCCH_3)_3]BF_4$ (**2**), which coordinate three acetonitrile molecules and only one phosphine ligand. These compounds have been conceived to provide as many coordination and reaction sites as possible, minimizing the number of coordination positions occupied by strong unreactive ligands. As an initial step in the investigation of these compounds, the kinetics of dissociation of the acetonitrile ligands and the course of some substitution reactions have been studied. In the second part of the paper, the reactivity of these complexes toward simple alkenes such as ethene and propene is described.

Scheme 1



Results

1. Preparation and Characterization of Complexes 1 and 2. Apart from derivatives coordinating cyclopentadienyl or other tridentate ligands in a fac coordination mode, most d^6 metal complexes containing bulky phosphines possess a trans P−M−P skeleton. The enhanced stability provided by this arrangement imposes a synthetic difficulty in the preparation of monophosphine metal complexes, especially if the aim is to coordinate at the same metal center a single phosphine and several weakly coordinating ligands. In the case of iridium, the previously reported synthesis of the complex $[IrH_2(P^iPr_3)(NCCH_3)_3]BF_4$ (**2**) illustrates a feasible way to obtain such complexes: via iridium(I) derivatives of formula $[Ir(cod)(S)(PR_3)]^+$, provided that the cyclooctadiene ligand can be removed by hydrogenation.[15] As a more general procedure, we have found that such complexes can be readily prepared by the use of phosphonium salts of basic phosphines as oxidative addition reactants to iridium(I) complexes.

The compound $[IrClH(P^iPr_3)(NCCH_3)_3]BF_4$ (**1**) can be prepared by refluxing a solution of $[Ir(\mu\text{-Cl})(coe)_2]_2$ and $[HP^iPr_3]BF_4$ in acetone/acetonitrile (20:1) (Scheme 1a). In a similar way, complex **2** is obtained in good yield, in a one-pot synthesis, by treatment of the complex $[Ir(\mu\text{-OMe})(cod)]_2$ with the phosphonium salt in acetone/acetonitrile (20:1) and subsequent reaction with H_2 (Scheme 1b).

The solution of **1** in $CDCl_3$ at room temperature displays a doublet at δ −23.43 with a H−P coupling constant of 18.4 Hz in the ^1H NMR spectrum, which is characteristic of a hydride in cis position to a phosphine ligand. In agreement with the proposed fac arrangement of the acetonitrile units, three signals assigned to these ligands are observed, a singlet at δ 2.63, a doublet at δ 2.50 (J_{HP} = 0.5 Hz), and a broad signal at δ 2.46. These

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Table 1. Rate Constants for Acetonitrile Exchange in Complex 1[c]

T (K)	[NCCH$_3$]	k_1	k_{2obs}	$(k_1/k_{-1})k_2$
263	0.15	0.40[a]		
268	0.15	0.94[a]		
273	0.15	1.7[a]		
280	0.15	3.8[a]		
280	0.40	3.9[a]		
280	0.80	3.9[a]		
289	0.15	10[b]		
293	0.15	19[b]	0.06[a]	0.009
298	0.15	32[b]	0.13[a]	0.019
303	0.15	53[b]	0.43[a]	0.064
303	0.40	50[b]	0.18[a]	0.072
303	0.80	50[b]	0.09[a]	0.072
307	0.15	84[b]	0.74[a]	0.11
313	0.15	129[b]	1.9[a]	0.28
318	0.15	236[b]	4.6[a]	0.69
323	0.15		6.4[a]	0.96

[a] By spin-saturation transfer. [b] By line-width analysis. [c] [**1**] = 0.10 M in $CDCl_3$.

three signals correlate with those observed for the quaternary carbons of the acetonitrile ligands in the $^{13}C\{^1H\}$ NMR spectrum: a singlet at δ 117.28, a doublet at δ 117.60 (J_{CP} = 17.0 Hz), and a broad signal at δ 119.45. On cooling to 273 K, the latter broad resonance transforms into a singlet which, under *off-resonance* conditions, splits into a doublet (J_{CH} = 10.1 Hz) due to hydride coupling. This allows the assignment of the broad signals observed in both the ^1H and $^{13}C\{^1H\}$ NMR spectra to the acetonitrile ligand trans to hydride. Moreover, the signals showing phosphorus coupling can be assigned to the acetonitrile trans to phosphine, and therefore the singlets of both spectra must correspond to the CH_3CN ligand trans to chloride.

The above-mentioned temperature dependence of the NMR signals of **1** corresponding to the acetonitrile ligand trans to hydride results from an exchange between this ligand and free acetonitrile, as can be deduced from spin saturation transfer experiments. Table 1 summarizes the rate constants for this exchange (k_1) measured by ^1H NMR spectroscopy in $CDCl_3$. The values of k_1 are independent of the concentration of acetonitrile, indicating that they correspond to the rates of acetonitrile dissociation from **1**. The activation parameters obtained from the Eyring plot of Figure 1, $\Delta H^{\ddagger}$ = 18.5 ± 1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 10 ± 2 eu, are consistent with a dissociative process.

At temperatures above 293 K, the spin saturation transfer experiments show that the acetonitrile ligand trans to phosphine also participates in the exchange with the free acetonitrile. The pseudo-first-order rate constants for this second exchange (k_{2obs}) display an inverse dependence on the concentration of free acetonitrile. The logarithmic representation of k_{2obs} vs [$NCCH_3$] of the three experimental values obtained at 303 K (Table 1) reveals a reaction order close to −1 (−0.93). This indicates that the exchange of the acetonitrile trans to P^iPr_3 requires the formation of a five-coordinate intermediate by acetonitrile dissociation. Most likely, this dissociation step is followed by the isomerization of the five-coordinate intermediate, as shown in Scheme 2. In light of this mechanistic proposal, and assuming that acetonitrile coordination to the proposed five-coordinate intermediates is much faster than dissociation, k_{2obs} is equal to $(k_1/k_{-1})k_2[NCCH_3]^{-1}$. The values

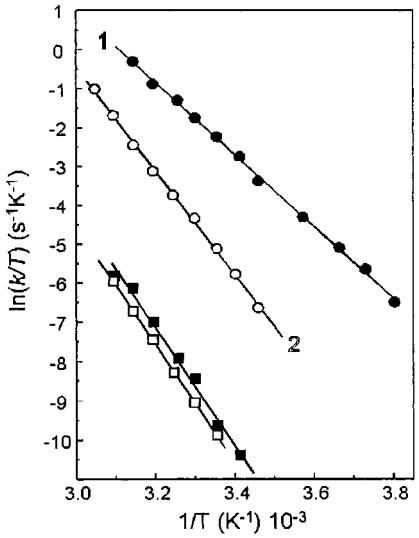
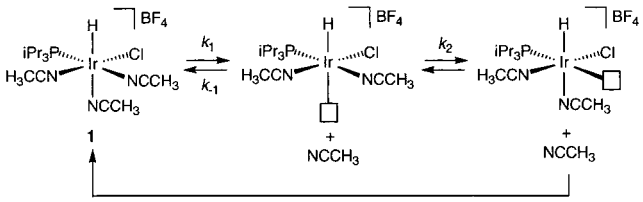


Figure 1. Eyring plots of the rate constants for the exchange between free acetonitrile and acetonitrile coordinated to complexes **1** (black) and **2** (white). Circles represent values corresponding to k_1 (trans to hydride); squares correspond to $(k_1/k_{-1})k_2$ (trans to phosphine).

Scheme 2



of these first-order rate constants for the overall process, $(k_1/k_{-1})k_2$, have been used to estimate the activation parameters for the generation of a vacant site trans to phosphine as $\Delta H^{\ddagger}$ = 30 ± 3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 34 ± 4 eu (Figure 1). The activation entropy increment is compatible with the mechanism shown in Scheme 2, in which the expected main contribution to the activation entropy is that related to the dissociation of acetonitrile (absolute entropy 34.5 eu[16]).

The acetonitrile ligand occupying the position trans to chloride does not exchange with free acetonitrile even at higher temperatures. In fact, solutions of **1** in CD_3CN maintain the nondeuterated ligand trans to chloride even after a period of several weeks.

The kinetic behavior of the acetonitrile ligands of complex **2** is similar to that described for **1**. Dissociation of any of the two equivalent acetonitriles trans to hydride follows first-order kinetics (k_1), whereas the rates of exchange for the acetonitrile trans to phosphine (k_{2obs}) are inversely dependent on the free acetonitrile concentration (Table 2). The kinetic data allow the evaluation of the activation parameters for acetonitrile dissociation from **2** as $\Delta H^{\ddagger}$ = 26.6 ± 1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 32 ± 2 eu (Figure 1). The activation parameters for the generation of a vacant site trans to phosphine can also be estimated as $\Delta H^{\ddagger}$ = 30 ± 3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 34 ± 4 eu. The calculated activation enthalpy for acetonitrile dissociation in **2** is slightly higher than that observed for the same process in related bisphos-

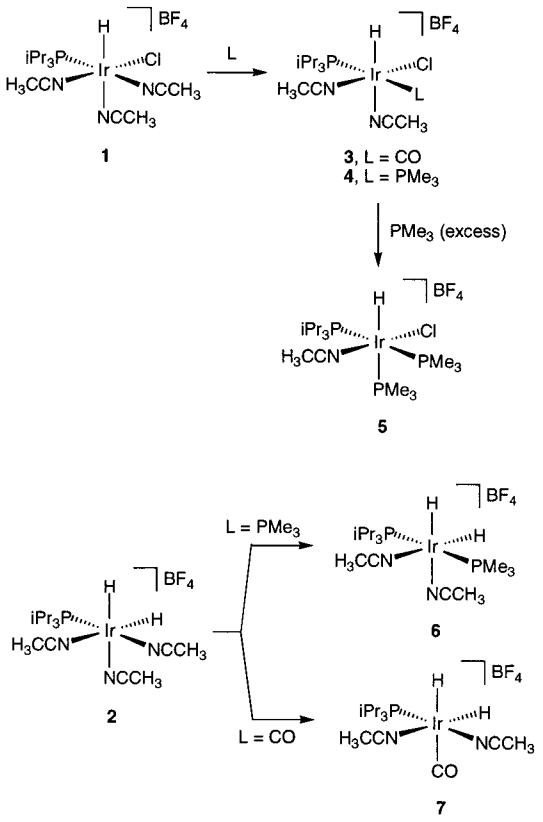
(16) *Handbook of Chemistry and Physics*, 66th ed.; Chemical Rubber Co.: Boca Raton, FL, 1985.

Table 2. Rate Constants for Acetonitrile Exchange in Complex 2[c]

T (K)	[$NCCH_3$]	k_1	k_{2obs}	$(k_1/k_{-1})k_2$
289	0.1	0.38[a]		
294	0.1	0.92[a]		
294	1.0	0.95[a]		
294	1.9	1.0[a]		
298	0.1	1.8[a]	0.15[a]	0.015
303	0.1	4.0 [a]	0.35[a]	0.035
308	0.1	7.4[a]	0.76[a]	0.076
313	0.1	14[b]	1.8[a]	0.18
318	0.1	28[b]	3.8[a]	0.38
323	0.1	60[b]	8.3[a]	0.83
326	0.1		9.3[a]	0.93
326	1.0		0.83[a]	0.83
326	1.9		0.56[a]	1.06
328	0.1	122[b]		

[a] By spin-saturation transfer. [b] By line-width analysis. [c] [**2**] = 0.10 M in $CDCl_3$.

Scheme 3

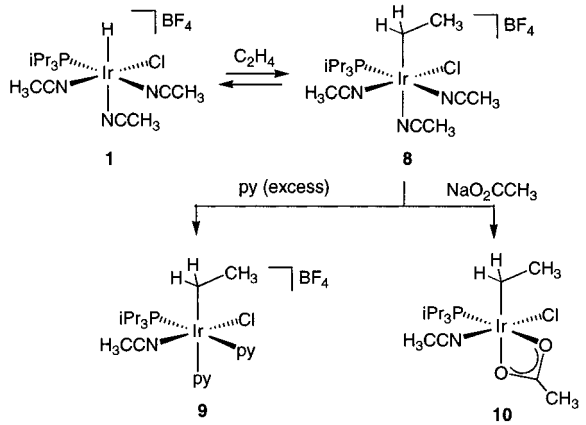


phinedihydrido derivatives[14a] as well as in the tris-acetonitrile dication $[CpIr(NCCH_3)_3]^{2+}$.[17]

2. Substitution Reactions of Complexes 1 and 2. Although the most labile acetonitrile ligand of **1** coordinates trans to hydride, treatment of **1** with CO or 1 equiv of PMe_3 leads to the formation of substitution products in which the new ligand is trans-disposed to the phosphine: $[IrClH(P^iPr_3)(CO)(NCCH_3)_2]BF_4$ (**3**) and $[IrClH(P^iPr_3)(PMe_3)(NCCH_3)_2]BF_4$ (**4**), respectively (Scheme 3). In agreement with the proposed structure, the $^{13}C\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ displays a doublet for the carbonyl ligand at δ 160.87, with a C−P coupling constant of 125.2 Hz. Similarly, the $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits an AB spin system with a

(17) Cusanelli, A.; Nicula-Dadci, L.; Frey, U.; Merbach, A. E. *Inorg. Chem.* **1997**, *36*, 2211.

Scheme 4



J_{PP} = 359.0 Hz, in agreement with a trans arrangement of the phosphine ligands. Treatment of **4** with an excess of PMe_3 results in the substitution of a second acetonitrile ligand to yield the complex $[IrClH(P^iPr_3)(PMe_3)_2(NCCH_3)]BF_4$ (**5**). However, the acetonitrile trans to chloride cannot be replaced by PMe_3 even in refluxing $CHCl_3$. The structure of **5** shown in Scheme 3 is supported by the pattern of the hydride signal in the ^1H NMR spectrum, which consists of a doublet of triplets at δ −11.95 with H−P coupling constants of 165.6 and 17.2 Hz, respectively.

Similar to **1**, complex **2** reacts with 1 equiv of PMe_3 to give the complex $[IrH_2(P^iPr_3)(PMe_3)(NCCH_3)_2]BF_4$ (**6**), for which a trans arrangement of the phosphines is assumed. In contrast, passing a stream of CO through a solution of **2** in $CDCl_3$ leads to the formation of complex **7**, in which the incoming ligand coordinates trans to the hydride. The structure proposed for **7** is supported by the observation of two different hydride resonances in the ^1H NMR spectrum, at δ −20.28 and −8.11, both showing H−P and H−H coupling constants of 18 and 3.6 Hz, respectively. Compound **7** can be maintained in solution for long periods of time, but any attempt to isolate it gave only a rather insoluble solid. The analytical data of this solid, its conductivity, and its NMR spectra in nitromethane-d_3 suggest that, most probably, it is a trinuclear iridium cluster similar to others formed from related mononuclear fragments.[13b] However, the available data do not allow us to give a tentative structural proposal.

3. Reactions of Complex 1 with Ethene. In solution, ethene inserts into the Ir−H bond of **1** to give the cationic ethyl complex $[IrCl(Et)(P^iPr_3)(NCCH_3)_3]BF_4$ (**8**). In the $^{13}C\{^1H\}$ NMR spectrum, the carbon atoms of the ethyl moiety give rise to a doublet at δ −13.38 (J_{CP} = 5.0 Hz) and a singlet at δ 13.95, in agreement with the structure shown in Scheme 4. In the ^1H NMR spectrum at room temperature, two of the three signals for the CH_3CN protons are broad, resolving into singlets at δ 2.45 and 2.51 upon cooling to 223 K. Again, this indicates that two of the acetonitrile ligands of **8** readily exchange with free acetonitrile.

The insertion reaction leading to complex **8** is reversible, precluding the isolation of the compound in analytically pure form. However, solutions of **8** allow the preparation of other stable ethyliridium(III) complexes by addition of good donor ligands such as pyridine or of anionic ligands such as acetate (Scheme 4). The struc-

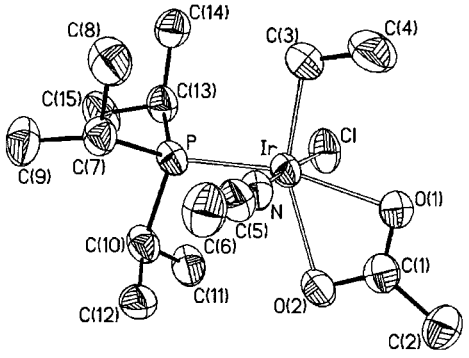


Figure 2. Molecular structure of the complex **10**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Ir(η^2-O_2CCH_3)Cl(Et)(P^iPr_3)($NCCH_3$)] (10)

Ir−Cl	2.356(2)	Ir−P	2.276(3)
Ir−O(1)	2.170(7)	Ir−O(2)	2.326(7)
Ir−N	2.000(8)	Ir−C(3)	2.086(11)
O(1)−C(1)	1.274(12)	O(2)−C(1)	1.258(12)
C(3)−C(4)	1.534(17)	N−C(5)	1.123(12)
C(5)−C(6)	1.488(14)		
Cl−Ir−P	92.73(9)	Cl−Ir−O(1)	86.12(19)
Cl−Ir−O(2)	87.21(19)	Cl−Ir−N	175.2(2)
Cl−Ir−C(3)	90.1(3)	P−Ir−O(1)	166.21(19)
P−Ir−O(2)	108.21(17)	P−Ir−N	92.1(2)
P−Ir−C(3)	97.0(3)	O(1)−Ir−O(2)	58.0(2)
O(1)−Ir−N	89.2(3)	O(1)−Ir−C(3)	96.7(4)
O(2)−Ir−N	91.2(3)	O(2)−Ir−C(3)	154.7(4)
N−Ir−C(3)	89.4(4)	Ir−C(3)−C(4)	109.3(8)
Ir−O(1)−C(1)	94.6(6)	Ir−O(2)−C(1)	87.9(6)
O(1)−C(1)−O(2)	119.3(9)		

ture proposed for the pyridine complex [IrCl(Et)(P^iPr_3)-$(Py)_2(NCCH_3)$]BF_4 (**9**) takes into account the previously observed inertness against substitution of the acetonitrile ligand trans to chloride and is also supported by the structure of the neutral complex [Ir(η^2-O_2CCH_3)-Cl(Et)(P^iPr_3)$(NCCH_3)_3$] (**10**), which has been confirmed by X-ray crystallography (Figure 2). Selected bond distances and angles are presented in Table 3.

The cation of compound **10** has a nearly octahedral geometry, significantly distorted by the small bite angle of the chelating acetate ligand (58.0(2)°). The acetate binds the metal via two different Ir−O distances: Ir−O(1) 2.170(7) and Ir−O(2) 2.326(7) Å. The shorter bond length, trans to phosphine, compares well with those found in the related benzoate complexes such as [IrH-(η^2-$O_2CC_6H_5$)$(PMe_3)_3]^+$ (2.198(8) and 2.244(8) Å) and [Ir(η^2-$O_2CC_6H_5$){C(CO_2Me)=C(H)(CO_2Me)}$(PMe_3)_3]^+$ (2.183(5) and 2.197(5) Å).[18] The longer Ir−O distance, trans to ethyl, reflects the large trans influence of the alkyl ligand. Despite the asymmetry in the Ir−O bonds, both C−O distances are nearly identical (1.274 and 1.258(12) Å), confirming the η^2 coordination mode of the acetate unit. The Ir−C(3) bond length (2.086(11) Å) is slightly shorter than those observed for other Ir^{III}−Et bonds such as in [$IrBr_2$(Et)$(PMe_3)_3$] (2.123(5) Å) and [IrH(Et)$(Et_2In)(PMe_3)_3$] (2.192(7) Å).[19] In agreement with the reactivity studies and the kinetic measurements discussed in the previous sections, the acetonitrile ligand remaining from complex **1** lies trans to chloride, showing a short Ir−N bond distance (2.000(8) Å).

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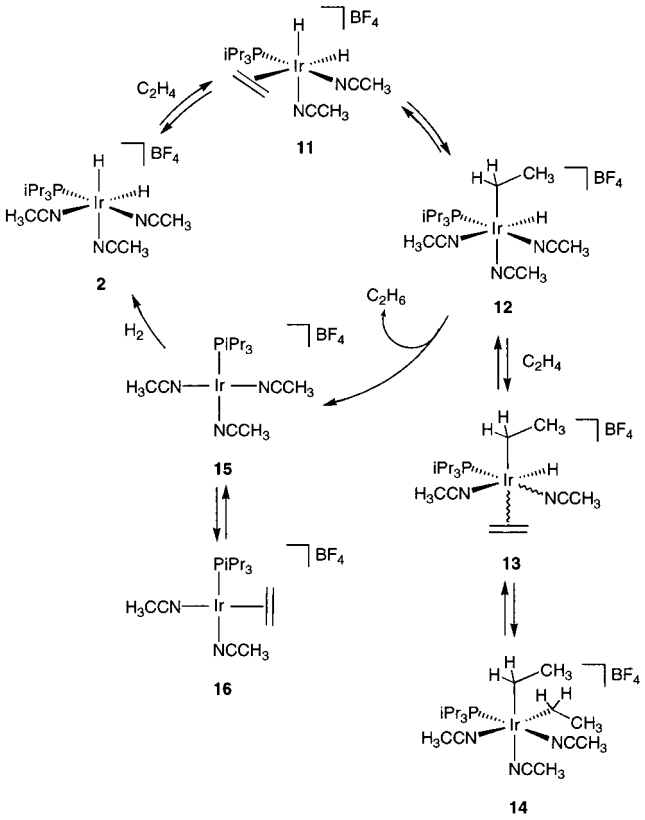
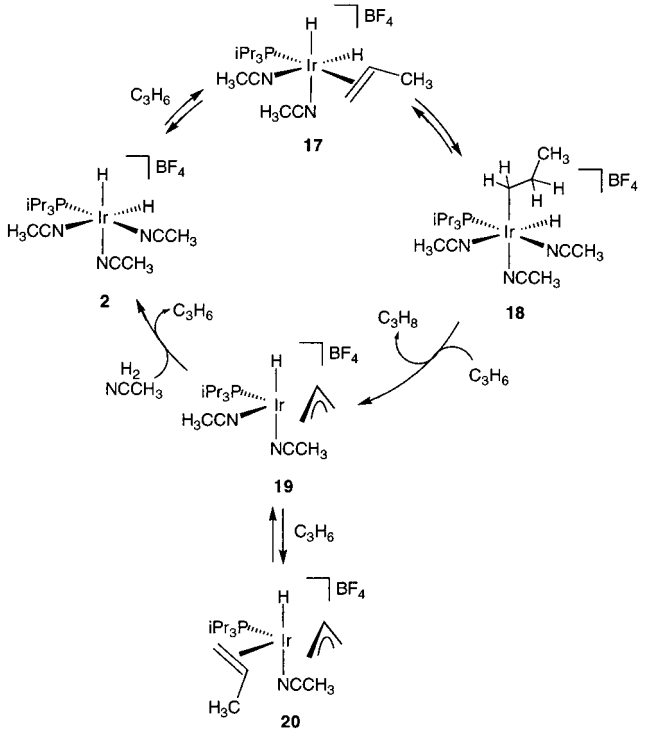
Scheme 5



4. Reactions of Complex 2 with Ethene. The reaction of complex **2** with ethene results in the consecutive formation of several products, as illustrated in Scheme 5. The complex [IrH_2(η^2-C_2H_4)(P^iPr_3)$(NCCH_3)_2$]-BF_4 (**11**) is observed after a slow stream of ethene is passed through a solution of **2** in $CDCl_3$ at 233 K. In agreement with the proposed structure, the high-field region of the ^1H NMR spectrum of **11** shows two different hydride resonances: two doublets of doublets at δ −19.89 and −9.89 with a H−H coupling constant of 1.4 Hz and H−P coupling constants of 18.6 and 19.5 Hz, respectively. In the low-field region of the spectrum, the resonance for the ethene ligand appears as an AA′BB′ spin system centered at δ 3.71, indicating a fast rotation of the olefin around the Ir−C_2H_4 axis.

On raising the temperature to 273 K, and in the presence of an excess of dissolved ethene, complex **11** is converted into the diethyl complex [Ir(Et)$_2$(P^iPr_3)-$(NCCH_3)_3$]BF_4 (**14**), as a result of the insertions of two ethylene molecules into the two Ir−H bonds. The spectroscopic control of this reaction reveals the appearance and subsequent disappearance of two intermediates, which can be tentatively identified as compounds **12** and **13** (Scheme 5). Both intermediates exhibit in the high-field region of the ^1H NMR spectrum signals that are assigned to hydride ligands cis to phosphine: doublets at δ −19.00 (J_{HP} = 18.2) and −23.03 (J_{HP} = 19.0), respectively. Since the coordination of an alkene trans to hydride (as in **11**) usually results in a pronounced downfield shift of the hydride resonance, the chemical shifts of the two doublets are consistent with a trans disposition of the hydrido and acetonitrile ligands. The $^{31}P\{^1H\}$ NMR spectra of both **12** and **13** display singlets (δ 17.04 and 20.98, respectively) which under *off-resonance* conditions split into

Scheme 6



doublets due to P−H coupling. This indicates that both species are monohydrido complexes. When the conversion of compound **11** into **14** takes place in the presence of an excess of acetonitrile, only the signals assigned to complex **12** can be observed, which supports our mechanistic scheme.

The formation of complex **14** from **2** is a reversible process. Thus, if argon is bubbled through a solution of **14** at 273 K, a quantitative formation of **2** occurs. However, if solutions of **14** are warmed to room temperature, the diethyl complex disappears and the elimination of ethane is observed. Since the formation of butane cannot be detected, we conclude that **14** does not undergo C−C reductive coupling of the mutually cis-disposed ethyl ligands.

In the presence of an excess of ethene, the NMR spectra of the white solution resulting upon the reductive elimination of ethane display several broad signals. After removal of the excess of ethene, the color of the solution changes to orange and the observed spectra become more simple. We assume that under these conditions, the solution contains a mixture of the two complexes $[Ir(P^iPr_3)(NCCH_3)_3]BF_4$ (**15**) and $[Ir(P^iPr_3)(\eta^2\text{-}C_2H_4)(NCCH_3)_2]BF_4$ (**16**) in a ratio that depends on the time employed for the removal of ethene. The lifetime of these complexes in $CDCl_3$ is short, and decomposition to unidentified species takes place even at temperatures below 230 K. However, the same mixture generated in CD_2Cl_2 is stable enough to allow the spectroscopic characterization of compounds **15** and **16** at low temperature (233 K). The ^1H NMR spectrum of **15** shows two resonances assigned to acetonitrile ligands: a singlet at δ 2.19 with the relative intensity of 6H and a doublet at δ 2.29 with a H−P coupling of 0.9 Hz and a relative intensity of 3H. On the other hand, the protons and carbon atoms of the ethene ligand of **16** give rise to four separate resonances in the 233 K

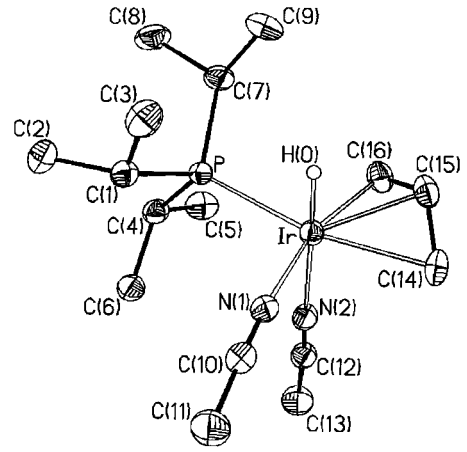


Figure 3. Molecular structure of the cation of complex **19**.

^1H NMR spectrum and to two singlets (δ 27.52 and 33.24) in the $^{13}C\{^1H\}$ NMR spectrum. These data are in agreement with the presence of a nonrotating C_2H_4 ligand which is cis-disposed to the phosphine.

As is shown in Scheme 5, solutions containing **15** and **16** readily react with H_2 to regenerate the starting complex **2**. This reaction closes a cycle for ethene hydrogenation in which most of the participating species have been spectroscopically characterized.

5. Reactions of Complex 2 with Propene. The reaction of complex **2** with propene reveals some noticeable differences compared to the process involving ethene as the substrate. As shown in Scheme 6, the initial step consists of the formation of the complex $[IrH_2(\eta^2\text{-}C_3H_6)(P^iPr_3)(NCCH_3)_2]BF_4$ (**17**), which is observed upon treatment of **2** with propene at 233 K. In **17**, the alkene ligand coordinates trans to the phosphine, in contrast to the analogous ethene complex **11**. The structure proposed for **17** relies on the similar chemical shifts observed for both hydride resonances (δ −23.05 and −23.10) and on the C−P coupling constants of 9.4 and 10.8 Hz for the signals of the olefinic carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum.

On raising the temperature to 273 K, the propene ligand inserts into one of the Ir−H bonds to yield the complex $[IrH(^nPr)(P^iPr_3)(NCCH_3)_3]BF_4$ (**18**), which does not undergo any observable reaction at this temperature. It appears that the regioselectivity of this insertion is very high, since a species containing the isomeric 2-propenyl ligand cannot be detected. On warming to room temperature, compound **18** eliminates propane; however, the expected iridium(I) species resulting from this abstraction cannot be observed. Instead, a mixture of allylic C−H activation[3a,5a,20] products is formed, namely, the allylhydrido derivatives $[IrH(\eta^3\text{-}C_3H_5)(P^iPr_3)(NCCH_3)_2]BF_4$ (**19**) and $[IrH(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)(P^iPr_3)(NCCH_3)]BF_4$ (**20**), respectively. Both complexes **19** and **20** have been isolated and fully characterized by analytic and spectroscopic methods. In addition, the structure of **19** has been determined by X-ray diffraction. Figure 3 shows the molecular structure of the

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for [IrH(η^3-C_3H_5)(P^iPr_3)($NCCH_3$)$_2$]BF_4 (19)

Ir−P	2.3087(8)	Ir−N(1)	2.055(2)
Ir−N(2)	2.147(3)	Ir−C(14)	2.262(3)
Ir−C(15)	2.163(3)	Ir−C(16)	2.144(3)
Ir−H(0)	1.34(4)	N(1)−C(10)	1.142(4)
C(10)−C(11)	1.458(5)	N(2)−C(12)	1.144(4)
C(12)−C(13)	1.457(4)	C(14)−C(15)	1.409(5)
C(15)−C(16)	1.420(5)		
P−Ir−N(1)	95.60(7)	P−Ir−N(2)	98.92(7)
P−Ir−C(14)	165.47(10)	P−Ir−C(16)	98.77(9)
P−Ir−H(0)	77.9(15)	N(1)−Ir−N(2)	88.79(10)
N(1)−Ir−C(14)	98.52(12)	N(1)−Ir−C(16)	165.54(11)
N(1)−Ir−H(0)	93.7(15)	N(2)−Ir−C(14)	84.84(12)
N(2)−Ir−C(16)	87.36(12)	N(2)−Ir−H(0)	176.1(15)
C(14)−Ir−C(16)	67.26(13)	C(14)−Ir−H(0)	97.7(15)
C(16)−Ir−H(0)	90.9(15)	Ir−N(1)−C(10)	175.5(2)
Ir−N(2)−C(12)	175.4(3)	Ir−C(14)−C(15)	67.64(18)
Ir−C(16)−C(15)	70.01(18)	C(14)−C(15)−C(16)	119.3(3)

cation of **19**, and Table 4 summarizes the important bond distances and angles.

Assuming that the allyl ligand occupies two cis-disposed coordination sites, the cation of **19** has a distorted octahedral geometry. The binding to the allyl ligand is asymmetric, giving rise to Ir−C bond lengths of 2.144(3), 2.163(3), and 2.262(3) Å. In contrast, the C−C distances of the ligand are equal within experimental error (1.409(5) and 1.420(5) Å). The mutually cis-disposed acetonitrile ligands were found to have different Ir−N bond lengths, the longer corresponding to the ligand trans to hydride (2.147(3) Å). This distance is similar to those found for the cation $[IrH_2(MeCN)_2(P^iPr_3)_2]^+$ (2.127(9) and 2.147(9) Å), in which the acetonitrile and hydride ligands are also trans-coordinated.[21] The shorter Ir−N bond, 2.055(2) Å, is still longer than that of compound **10**, 2.000(8) Å, but in the range for related compounds such as $[(cod)Ir(\mu\text{-form})_2Ir(MeCN)_2]^+$ and $[Ir_2(\mu\text{-form})_2(MeCN)_6]^+$ (form = *N*,*N*′-di-*p*-tolylformamidinate).[22] The Ir−H distance found in this crystallographic study is unrealistically short (see Experimental Section). It should lie in the range 1.48−1.63 Å, as determined for the terminal hydrides of nine iridium complexes studied by neutron diffraction.[23] Despite this short distance, the bond angles around iridium involving the hydride ligand are in good agreement with an octahedral coordination.

The NMR spectra of complex **19** in solution are consistent with the structure in the solid state. The protons of the two acetonitrile ligands of **19** give rise to two singlets at δ 2.52 and 2.42 in the ^{1}H NMR spectrum in $CDCl_3$ at 293 K. The latter signal is slightly broad due to the exchange between this acetonitrile ligand and free acetonitrile, similar to the situation described above for complexes **1** and **2**. The resonances for the quaternary carbons atoms of coordinated CH_3CN appear in the $^{13}C\{^1H\}$ NMR spectrum as a singlet at δ 122.57 and a broad peak at δ 122.09. The latter splits into a doublet (J_{HH} = 11.2 Hz) under *off-resonance* conditions, indicating that the broad signal corresponds to the acetonitrile trans to the hydride ligand. The rate constants for this ligand exchange (k_1) obtained by ^{1}H NMR spectroscopy in $CDCl_3$ solutions, which are listed in Table 5, agree with a first-order dissociative process. The activation parameters for this dissociation, evaluated on the basis of the Eyring equation, are $\Delta H^‡ = 18.4 \pm 1$ kcal mol^{-1} and $\Delta S^‡ = 8 \pm 2$ eu.

Table 5. Rate Constants for Acetonitrile Exchange in Complex 19[d]

T (K)	[$NCCH_3$]	k_1	k_2
279	0.8	1.1[a]	
283	0.8	1.8[a]	
293	0.8		7.0×10^{-4} [c]
298	0.8		1.3×10^{-3} [c]
303	0.8	17[b]	
308	0.4	30[b]	4.7×10^{-3} [c]
308	0.8	32[b]	4.4×10^{-3} [c]
308	1.6	30[b]	5.0×10^{-3} [c]
313	0.8	46[b]	1.0×10^{-2} [c]
323	0.8	122[b]	
328	0.8	176[b]	

[a] By spin-saturation transfer. [b] By line-width analysis. [c] By $NCCH_3/NCCD_3$ exchange. [d] [**19**] = 0.04 M in $CDCl_3$.

The acetonitrile ligand trans to the allyl ligand also exchanges with free acetonitrile, although at a slower rate. This rate can be measured by ^{1}H NMR spectroscopy, using acetonitrile-d_3 as the substrate. The rate constants obtained for this exchange (k_2, Table 5) at various concentrations of added CD_3CN reveal that this is also a zero-order reaction in acetonitrile. This indicates that, in contrast to the situation for **1** and **2**, the exchange of the second acetonitrile ligand in **19** is the result of a simple dissociation. The activation parameters estimated for this process are $\Delta H^‡ = 23 \pm 3$ kcal mol^{-1} and $\Delta S^‡ = 8 \pm 4$ eu.

As expected from the low energy of activation, **19** readily reacts with propene to give compound **20**. The replacement by propene of the remaining acetonitrile ligand of **20** is not observed at atmospheric pressure. The structure of **20** depicted in Scheme 6 is supported by the chemical shift of the hydride ligand resonance in the ^{1}H NMR spectrum, which appears as a doublet at δ −29.19. Moreover, the ^{1}H NOESY spectrum shows an NOE effect between the hydride signal and the resonances corresponding to protons which are located close to it in the proposed structure. These are (i) the methyl protons and the proton trans to the CH_3 group of propene, (ii) the methyl protons of the phosphine, and (iii) the *meso* proton of the allyl ligand.

The cycle for the hydrogenation of C_3H_6 outlined in Scheme 6 is closed by the reaction of complex **19** with hydrogen in the presence of 1 equiv of acetonitrile. At room temperature and 1 atm of hydrogen, the formation of complex **2** goes to completion within a few minutes. The NMR spectra of the reaction mixtures formed with substoichiometric amounts of hydrogen indicate that the formation of **2** occurs with the simultaneous release of propene (not propane). Under the same experimental conditions, the reaction with deuterium leads to the formation of [IrHD(P^iPr_3)($NCCH_3$)$_3$]BF_4 (**2-*d***) as the major product (Scheme 7), together with minor quantities of complexes **2** and **2-*d*$_2$**, the latter deuterated at both hydride positions.

A similar isotopomeric distribution is observed if a stream of D_2 is passed through a solution of complex **2** in $CDCl_3$. The isotopomer **2-*d*** shows characteristic downfield isotopic shifts in the hydride ^{1}H NMR ($\Delta\delta$ = 0.025 ppm) and $^{31}P\{^1H\}$ NMR ($\Delta\delta$ = 0.12 ppm) signals.

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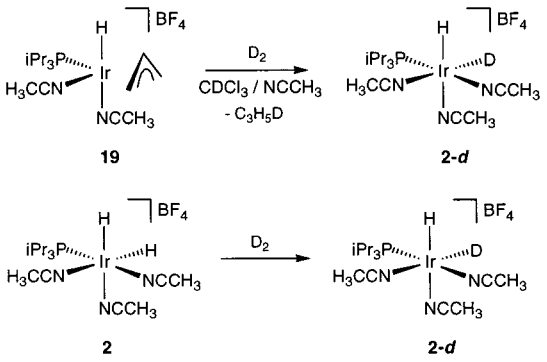
(22) Dunbar, K. R.; Majors, S. O.; Sun, J.-S. *Inorg. Chim. Acta* **1995**, *229*, 373.

Scheme 7



The $^{31}P\{^1H\}$ NMR resonance of **2-*d*$_2$** also exhibits a $\Delta\delta$ of 0.12 ppm with respect to that of **2-*d***. We note that similar deuterium isotopic shifts have been reported for other iridium hydrido derivatives as well.[15a,24]

Discussion

Lability of the Starting Materials. As expected from the trend of trans effects, the trisacetonitrile complexes **1** and **2** are transformed into activated species by dissociation of the acetonitrile ligand trans to hydride. The energy required for this dissociation is lower for the chlorohydrido complex **1** ($\Delta H^{\ddagger} = 18.5 \pm 1$ kcal mol^{-1}) than for the dihydrido derivative **2** ($\Delta H^{\ddagger} = 26.6 \pm 1$ kcal mol^{-1}). This difference in energy can be attributed to the ability of halides to assist the dissociation process via X→Ir π-bonding, which has been well established for related compounds.[25] The occurrence of this π-bonding assistance may also be supported by the entropy increments associated with the dissociation of acetonitrile. Thus, the value of $\Delta S^{\ddagger}$ obtained for the ligand exchange of complex **2**, 32 ± 2 eu, is close to that expected for the complete release of the acetonitrile ligand (see Results). This suggests that the free energy increases if a lengthening of the Ir−N bond distance takes place, reaching the maximum when the cleavage of the bond is nearly complete. However, dissociation from **1** occurs with a much lower $\Delta S^{\ddagger}$, 10 ± 2 eu, indicating that some additional degrees of freedom will be thermally populated along the reaction coordinate after the energy decreases again. This may be due to the fact that, as soon as the Ir−N bonding becomes less efficient, the metal orbitals involved in this bond can be stabilized by π-interaction with the cis chloro ligand.

The five-coordinate species generated by acetonitrile dissociation from **1** and **2** are fluxional. This fluxionality provides an alternative trajectory of attack (trans to phosphine) for the incoming acetonitrile to regenerate the starting material and finally leads to the exchange between free acetonitrile and CH_3CN coordinated trans to phosphine. The energy required for this fluxional process ($\Delta H^{\ddagger} = 30 \pm 3$ kcal mol^{-1}) is the same for both five-coordinate species generated from **1** and **2**. This coincidence suggests that, during the fluxional process, the changes affecting one of the hydrides of compound **2** and the chloro ligand of compound **1** are small. In the context of the commonly operating mechanism for such dynamic processes,[25] this observation may be rationalized if we assume that chloride and hydride occupy axial positions in the corresponding five-coordinate intermediates. These species could interconvert between square-pyramidal and distorted trigonal-bipyramidal configurations. This interpretation is also in agreement with the observed inertness to substitution of the acetonitrile ligand trans to chloride, which would maintain the linear arrangement $CH_3CN-Ir-Cl$ even in the fluxional five-coordinate intermediate.

The allylhydrido complex **19** also undergoes activation via dissociation of the acetonitrile ligand trans to hydride ($\Delta H^{\ddagger} = 18.4 \pm 1$ kcal mol^{-1}). However, in this case, the subsequent isomerization of the five-coordinate intermediate generated after this dissociation is not observed. This can be attributed to the fact that the moderate trans effect of the allyl ligand reduces the energy for the dissociation of the trans-disposed acetonitrile ($\Delta H^{\ddagger} = 23 \pm 3$ kcal mol^{-1}) below the barrier required for the isomerization of the five-coordinate intermediate (30 kcal mol^{-1} in the case of complexes **1** and **2**). Moreover, the rigidity imposed by the presence of a chelating η^3-C_3H_5 ligand in the five-coordinate intermediate could, at first sight, raise the energy required for the fluxional process or, possibly, inhibit it.

Substitution Reactions. The lability of two of the acetonitrile ligands in the complexes described above allows facile substitution reactions. These processes may involve ligands such as CO or PMe_3 but also weaker donors such as alkenes. The use of alkenes can promote the observation of labile reaction intermediates, as shown in Schemes 5 and 6, which represent catalytic cycles for the hydrogenation of ethene and propene, respectively.

The proposed structure for the derivatives obtained from compounds **1** and **2** reveals that, despite the larger lability of the acetonitrile ligand trans to hydride, substitution mainly occurs at the position trans to the phosphine. Therefore, it appears that the substitution products are the result of thermodynamic control. The conclusion that the size of the ligands plays a key role in determining the structure of the products is supported by the composition of the products of the reaction of complex **2** with alkenes. While ethylene coordinates to the metal at the position trans to hydride (**11**), propene prefers the position trans to phosphine (**17**).

Reactions with Alkenes. The series of reactions outlined in Schemes 5 and 6 illustrate that ethene as well as propene can be hydrogenated with complex **2** as the catalyst. In agreement with this proposal it has been found that **2** also catalyzes the hydrogenation of cyclohexene under very mild conditions. At 298 K and 1 atm of hydrogen, turnover frequencies of about 1 min^{-1} are obtained in acetone as solvent.

In addition to the catalytic hydrogenations, the reactive intermediates shown in Schemes 5 and 6 provide

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the opportunity not only for the unusual double insertion of ethene into a cis-IrH_2 moiety but also for the oxidative addition of C−H bonds and the electrophilic activation of hydrogen. The occurrence of these various *side reactions* allows a direct comparison with some processes that are of fundamental importance in homogeneous catalysis.

The slowest reactions among those described above involve reductive elimination processes. In fact, the reductive elimination of ethane is the rate-determining step in the catalytic hydrogenation of ethene (Scheme 5), since it is the only reaction that requires temperatures above 273 K to proceed. Nevertheless, this C−H reductive elimination is faster than the corresponding C−C and H−H eliminations from isostructural complexes. This follows from the observation that solutions containing complex **14** eliminate ethane instead of butane and equally from the high thermal stability of complex **2**. The same trend in the relative rates of C−H and C−C reductive eliminations has been found for other related systems.[26] Moreover, recent work by Bergman et al. has shown that compounds containing a M(H)R fragment thermally eliminate alkanes, while the corresponding dihydrido analogues are remarkably stable.[27] However, when competing C−H and H−H eliminations can take place at the same metal center, elimination of H_2 has been found to be kinetically favored.[28]

The reductive elimination of alkanes is also slow with regard to the allylic C−H activation of propene, as can be deduced from the fact that reduced iridium(I) species cannot be detected in the reactions involving propene (Scheme 6). In agreement with this observation, bubbling of propene through solutions containing the complexes **15** and **16** at 243 K readily results in the formation of compounds **19** and **20**. Previous studies on related d^8-metal intermediates of osmium which are able to activate C−H bonds have also shown that although the allylic activation of substituted propenes requires energies higher than those necessary for the activation of arene or alkene C−H bonds, it leads to more stable complexes.[29] This result suggests that the activation of C−H bonds of ethene or other alkenes by the iridium(I) intermediates generated from **2** could be kinetically feasible and that the lack of detection of the respective iridium(III) products is probably due to their thermodynamic instability.

The reductive elimination of propene from the allylhydrido complex **19** is not observed at temperatures below 330 K. However, the release of propene is relatively fast at room temperature upon treatment of **19** with hydrogen. This reaction, which most likely involves a σ-bond metathesis process in a transient dihydrogen complex,[30] represents a lower energy pathway for slow reductive eliminations.[31] In agreement with this observation, the thermally stable dihydrido complex **2** reacts readily with D_2 at room temperature to generate HD (Scheme 7).

Concluding Remarks

The labile trisacetonitrileiridium(III) complexes **1** and **2**, which contain one triisopropylphosphine and one or two hydrido ligands, have been prepared in high-yield one-pot reactions by oxidative addition of the phosphonium salt $[HP^iPr_3]BF_4$ to readily accessible iridium(I) precursors. This method can presumably be extended to other basic phosphines and other iridium(I) starting materials. The compounds prepared via this route create free coordination sites under mild conditions, which allows the characterization and investigation of intermediates as well as reaction steps relevant to homogeneous catalytic hydrogenation. Moreover, the labile species generated in the reaction cycle are convenient precursors for the formation of iridium(I) complexes, which are active in the oxidative addition of C−H bonds. Interestingly, the products resulting from these C−H activation reactions are still capable of generating new coordination vacancies with low kinetic barriers. This capability points to the potential use of such compounds in the activation and subsequent functionalization of alkenes. Further studies in order to develop this methodology are in progress.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. C, H, N analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer. Conductivities were measured in ca. 3×10^{-4} M solutions using a Philips PW 9501/01 conductometer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000, and a Bruker ARX 300 MHz instrument. The temperature was calibrated by ^{1}H NMR with a standard methanol sample. ^{1}H (300 MHz) and ^{13}C (75.19 MHz) NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P NMR (121 MHz) chemical shifts were measured relative to H_3PO_4 (85%). Coupling constants are given in hertz. Generally, spectral assignments were achieved by ^{1}H COSY and NOESY and ^{13}C DEPT experiments. The relaxation times T_1 were obtained by a conventional inversion−recovery method. The calculations of the relaxation times were made using the fitting routine of the Varian spectrometers. A 5% experimental error for T_1 measurements follows from the reproducibility of the relaxation experiments.

Synthesis. All reactions were carried out with exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complexes $[Ir(\mu\text{-Cl})(coe)_2]_2$[32] and $[Ir(\mu\text{-OMe})(cod)]_2$[33] were prepared by published methods. $[HP^iPr_3]BF_4$ was prepared in quantitative yields by slow addition of a solution of HBF_4 (54% in diethyl ether) to a diethyl ether solution of P^iPr_3. The white solid obtained was filtered, washed with ether, and dried in vacuo: ^{1}H NMR ($CDCl_3$, 293 K) δ 1.41 (dd, $J_{HP} = 17.6$, $J_{HH} = 7.2$, 18H, $PCHCH_3$), 2.75 (m. 3H, $PCHCH_3$), 5.71 (dq, $J_{HP} = 468.4$, $J_{HH} = 4.2$, 1H, PH); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K) δ 42.37 (s).

Preparation of $[IrClH(P^iPr_3)(NCCH_3)_3]BF_4$ (1). A suspension of $[Ir(\mu\text{-Cl})(coe)_2]_2$ (300 mg, 0.33 mmol) in acetone (10 mL) was treated with acetonitrile (0.5 mL) and $[HP^iPr_3]BF_4$

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(166.2 mg, 0.67 mmol). The resulting mixture was refluxed for 3 h, and the resulting pale yellow solution was filtered through Celite and concentrated to ca. 0.5 mL in vacuo. Slow addition of diethyl ether gave a white solid, which was filtered, washed with ether, and dried in vacuo: yield 349 mg (88%); IR (Nujol mull, cm^{-1}) 2250 ν(IrH), 1050 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −23.43 (d, J_{HP} = 18.4, 1H, IrH), 1.20 (dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHCH_3), 1.21 (dd, J_{HP} = 14.0, J_{HH} = 7.3, 9H, PCHCH_3), 2.39 (m, 3H, PCHCH$_3$), 2.46 (br s, 3H, NCCH$_3$), 2.50 (d, J_{HP} = 0.5, 3H, NCCH$_3$), 2.63 (s, 3H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 13.28 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 3.40 (br, NCCH$_3$), 3.70, 3.92 (both s, NCCH$_3$), 17.89, 18.01 (both s, PCHCH$_3$), 22.72 (d, J_{CP} = 33.4, PCHCH$_3$), 117.28 (s, NCCH$_3$), 117.60 (d, J_{CP} = 17.0, NCCH$_3$), 119.45 (br, NCCH$_3$). Anal. Calcd. for $C_{15}H_{31}N_3BClF_4IrP$: C, 30.09; H, 5.21; N, 7.02. Found: C, 29.77; H, 5.36; N, 6.99. Λ_M (CH_3NO_2): 86 Ω^{1-} cm^2 mol^{-1}.

Preparation of [IrH$_2$(P^{i}Pr$_3$)(NCCH$_3$)$_3$]BF$_4$ (2). A suspension of [Ir(μ-OMe)(cod)]$_2$ (300 mg, 0.45 mmol) in acetone (10 mL) was treated with acetonitrile (0.5 mL) and [HP^{i}Pr$_3$]BF_4 (223 mg, 0.90 mmol). The resulting orange solution was stirred under hydrogen atmosphere (P = 1 atm) for 3 h, and the resulting pale yellow solution was filtered through Celite and concentrated to ca. 0.5 mL in vacuo. After diethyl ether was added, a white solid precipitated, which was filtered, washed with ether, and dried in vacuo: yield 432 mg (85%). The spectroscopic data of the compound were identical to those previously reported for complex **2** in ref 15a.

Preparation of [IrClH(P^{i}Pr$_3$)(CO)(NCCH$_3$)$_2$]BF$_4$ (3). A slow stream of CO was passed through a solution of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) for 2 min. The resulting yellow solution was concentrated to ca. 0.5 mL in vacuo and worked up as described for **2**. A white solid was obtained: yield 85 mg (87%); IR (Nujol mull, cm^{-1}) 2080 ν(CO), 1050 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −20.89 (d, J_{HP} = 15.3, 1H, IrH), 1.28, 1.30 (both dd, J_{HP} = 14.5, J_{HH} = 8.6, 9H, PCHCH_3), 2.44 (m, 3H, PCHCH$_3$), 2.53 (s, 3H, NCCH$_3$), 2.67 (s, 3H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 16.52 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 3.14, 3.68 (both s, NCCH$_3$), 18.08, 18.23 (both d, J_{CP} = 1.5, PCHCH$_3$), 22.19 (d, J_{CP} = 29.2, PCHCH$_3$), 121.43, 122.31 (both s, NCCH$_3$), 160.87 (d, J_{CP} = 125.2, CO). Anal. Calcd for $C_{14}H_{28}N_2BClF_4IrOP$: C, 28.70; H, 4.81; N, 4.78. Found: C, 28.48; H, 5.08; N, 4.70. Λ_M (acetone): 128 Ω^{-1} cm^2 mol^{-1}.

Preparation of [IrClH(P^{i}Pr$_3$)(PMe$_3$)(NCCH$_3$)$_2$]BF$_4$ (4). A solution of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) was treated with PMe_3 (17.4 μL, 0.16 mmol) and stirred for 10 min at room temperature. The resulting pale yellow solution was concentrated to ca. 0.5 mL in vacuo and worked up as described for **2**. A white solid was obtained: yield 76 mg (75%); IR (Nujol mull, cm^{-1}) 2110 ν(IrH), 1070 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −22.78 (dd, J_{HP} = $J_{HP'}$ = 13.6, 1H, IrH), 1.25, 1.26 (both dd, J_{HP} = 13.7, J_{HH} = 7.1, 9H, PCHCH_3), 1.65 (dd, J_{HP} = 10.8, $J_{HP'}$ = 2.6, 9H, PCH$_3$), 2.47 (s, 3H, NCCH$_3$), 2.50 (m, 3H, PCHCH$_3$), 2.60 (s, 3H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) AB system, δ_A 15.57, δ_B −35.92, J_{AB} = 359.0. Anal. Calcd for $C_{16}H_{37}N_2BClF_4IrP_2$: C, 30.31; H, 5.88; N, 4.42. Found: C, 29.88; H, 5.96; N, 3.97. Λ_M (CH_3NO_2): 90 Ω^{-1} cm^2 mol^{-1}.

Preparation of [IrClH(P^{i}Pr$_3$)(PMe$_3$)$_2$(NCCH$_3$)]BF$_4$ (5). A solution of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) was treated with PMe_3 (87 μL, 0.8 mmol) and stirred for 2 h at room temperature. The resulting colorless solution was concentrated to ca. 0.5 mL in vacuo and worked up as described for **2**. A white solid was obtained: yield 96 mg (90%); IR (Nujol mull, cm^{-1}) 2070 ν(IrH), 1070 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −11.95 (ddd, J_{HP} = 16.6, $J_{HP'}$ = $J_{HP''}$ = 17.2, 1H, IrH), 1.18 (dd, J_{HP} = 12.0, J_{HH} = 7.5, 9H, PCHCH_3), 1.24 (dd, J_{HP} = 13.2, J_{HH} = 6.6, 9H, PCHCH_3), 1.55 (d, J_{HP} = 8.0, 9H, PCH$_3$), 1.67 (dd, J_{HP} = 10.5, $J_{HP'}$ = 2.2, 9H, PCH$_3$), 2.50 (m, 3H, PCHCH$_3$), 2.64 (s, 3H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) ABX system, δ_A 10.85, δ_B −45.10, δ_X −59.00, J_{AB} = 339.0; J_{AX} = 18.0, J_{BX} = 16.2. Anal. Calcd for $C_{17}H_{43}NBClF_4IrP_3$: C, 30.52; H, 6.48; N, 2.09. Found: C, 30.96; H, 6.22; N, 2.21. Λ_M (CH_3NO_3): 88 Ω^{-1} cm^2 mol^{-1}.

Preparation of [IrH$_2$(P^{i}Pr$_3$)(PMe$_3$)(NCCH$_3$)$_2$]BF$_4$ (6). A solution of **2** (100 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was treated with PMe_3 (18.4 μL, 0.186 mmol) and stirred for 15 min at room temperature. The resulting colorless solution was concentrated to ca. 0.5 mL in vacuo and worked up as described for **2**. A white solid was obtained: yield 96 mg (90%); IR (Nujol mull, cm^{-1}) 2175 (br, ν(IrH)), 1100 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −22.26 (dd, J_{HP} = $J_{HP'}$ = 17.0, 2H, IrH), 1.11 (dd, J_{HP} = 13.6, J_{HH} = 6.8, 18H, PCHCH_3), 1.57 (dd, J_{HP} = 10.0, $J_{HP'}$ = 2.4, 9H, PCH$_3$), 2.20 (m, 3H, PCHCH$_3$), 2.34 (s, 6H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) AB system, δ_A 33.58, δ_B −38.02, J_{AB} = 322.4. Anal. Calcd for $C_{16}H_{38}N_2BF_4IrP_2$: C, 32.06; H, 6.39; N, 4.67. Found: C, 31.65; H, 6.49; N, 4.61.

[IrH$_2$(P^{i}Pr$_3$)(CO)(NCCH$_3$)$_2$]BF$_4$ (7). A slow stream of CO was passed through a solution of **2** (ca. 30 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) for 2 min. Spectroscopic analysis of the resulting solution revealed the formation of compound **7** as the single reaction product. ^1H NMR ($CDCl_3$, 293 K) δ −20.28 (dd, J_{HP} = 18.2, J_{HH} = 3.6, 1H, IrH), −8.11 (dd, J_{HP} = 18.1, J_{HH} = 3.6, 1H, IrH), 1.14, 1.16 (both dd, J_{HP} = 15.2, J_{HH} = 7.3, 9H, PCHCH_3), 2.15 (m, 3H, PCHCH$_3$), 2.49 (s, 3H, NCCH$_3$), 2.52 (s, 3H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 35.32 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 2.85, 3.10 (both s, NCCH$_3$), 18.92 (d, J_{CP} = 2.1, PCHCH$_3$), 19.11 (d, J_{CP} = 1.5, PCHCH$_3$), 25.82 (d, J_{CP} = 35.4, PCHCH$_3$), 121.70, 121.94 (both s, NCCH$_3$), 173.01 (d, J_{CP} = 10.6, CO); IR (CH_2Cl_2, cm^{-1}) 2115 (br, ν(IrH)), 2015 ν(CO).

[IrCl(Et)(P^{i}Pr$_3$)(NCCH$_3$)$_3$]BF$_4$ (8). A stream of ethene was passed through a solution of **1** (ca. 28 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) for 2 min. The spectroscopic analysis of the resulting solution revealed that, in the presence of dissolved ethylene, compound **7** is the only species in solution: ^1H NMR ($CDCl_3$, 293 K) δ 0.84 (t, X part of an ABMX$_3$ spin system (M = ^{31}P), J_{AX} = J_{BX} = 7.5, 3H, IrCH$_2$CH_3), 1.25, 1.28 (both dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, PCHCH_3), 2.01 (br, 6H, NCCH$_3$), 2.24 (m, A part of an ABMX$_3$ spin system (M = ^{31}P), J_{AB} = 11.1, J_{AX} = 7.5, J_{AM} = 4.5, 1H, IrCH_2CH$_3$), 2.46 (m, B part of an ABMX$_3$ spin system (M = ^{31}P), J_{AB} = 11.1, J_{BX} = 7.5, J_{BM} = 0, 1H, IrCH_2CH$_3$), 2.56 (m, 3H, PCHCH$_3$), 2.68 (s, 3H, NCCH$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −9.43 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −13.38 (d, J_{CP} = 5.0, IrCH$_2$CH$_3$), 3.04 (br, NCCH$_3$), 3.78 (s, NCCH$_3$), 13.95 (s, IrCH$_2$$CH_3$), 18.94, 19.04 (both d, J_{CP} = 1.8, PCHCH$_3$), 23.53 (d, J_{CP} = 32.0, PCHCH$_3$), 118.09 (s, NCCH$_3$), 120.18 (br, NCCH$_3$).

Preparation of [IrCl(Et)(P^{i}Pr$_3$)(Py)$_2$(NCCH$_3$)]BF$_4$ (9). A solution of **1** (206 mg, 0.39 mmol) in CH_2Cl_2 (5 mL) was stirred under ethene atmosphere (P = 1 atm) for 30 min at room temperature and then cooled to 273 K. Pyridine (100 μL, 1.23 mmol) was then added to the solution, and the mixture was stirred at 273 K for 15 min. The solution was then concentrated to ca. 0.5 mL in vacuo and treated with diethyl ether to give a white solid, which was worked up as described for **2**: yield 206 mg (75%);^1H NMR ($CDCl_3$, 293 K) δ 0.24 (t, X part of an ABX$_3$ spin system, J_{AX} = J_{BX} = 7.2, 3H, IrCH$_2$CH_3), 1.16, 1.30 (both dd, J_{HP} = 12.6, J_{HH} = 7.2, 9H, PCHCH_3), 2.37 (m, A part of an ABX$_3$ spin system, J_{AB} = 11.7, J_{AX} = 7.2, 1H, IrCH_2CH$_3$), 2.50 (m, B part of an ABX$_3$ spin system, J_{AB} = 11.7, J_{BX} = 7.2, 1H, IrCH_2CH$_3$), 2.57 (m, 3H, PCHCH$_3$), 2.85 (s, 3H, NCCH$_3$), 7.34 (d, J_{HH} = 7.2, 2H, CH), 7.36 (d, J_{HH} = 7.2, 2H, CH), 7.77 (t, J_{HH} = 7.2, 1H, CH), 7.79 (J_{HH} = 7.2, 1H, CH), 8.58 (m, 2H, CH), 9.02 (br, 2H, CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −16.28 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −14.71 (d, J_{CP} = 4.2, IrCH$_2$CH$_3$), 4.80 (s, NCCH$_3$), 16.15 (s, IrCH$_2$$CH_3$), 19.47 (d, J_{CP} = 2.0, PCHCH$_3$), 19.63 (d, J_{CP} = 2.5, PCHCH$_3$), 24.63 (d, J_{CP} = 29.9, PCHCH$_3$), 118.84 (s, NCCH$_3$), 125.68, 125.71, 138.27, 138.36, 150.15 (all s, CH). Anal. Calcd for $C_{23}H_{39}N_3BClF_4IrP$: C, 39.30; H, 5.59; N, 5.98. Found: C, 39.08; H, 5.29; N, 5.71.

Preparation of [Ir(η^2-O_2CCH_3)Cl(Et)(P^iPr_3)($NCCH_3$)] (10). A solution of **1** (206 mg, 0.39 mmol) in CH_2Cl_2 (5 mL) was stirred under ethene atmosphere (P = 1 atm) for 30 min at room temperature and then cooled to 273 K. An excess of anhydrous sodium acetate (ca. 200 mg) was added to the solution, and the mixture was then stirred at 273 K for 3 h. After this period of time, the resulting suspension was brought to dryness in vacuo. The residue was treated with 5 mL of toluene, and the solution was filtered through Celite. The pale yellow filtrate was concentrated to ca. 0.5 mL, layered with methanol, and stored at 273 K for 24 h to yield pale yellow crystals: yield 100 mg (50%); IR (Nujol mull, cm^{-1}) 1545 ν_{asym}(OCO); ^1H NMR ($CDCl_3$, 293 K) δ 0.59 (dd, J_{HH} = 7.1, 7.5, 3H, $IrCH_2CH_3$), 1.22, 1.27 (both dd, J_{HP} = 14.0, J_{HH} = 7.2, 9H, $PCHCH_3$), 2.06 (s, 3H, O_2CCH_3), 2.55 (s, 3H, $NCCH_3$), 2.56 (m, 3H, $PCHCH_3$), 2.72 (ddq, J_{HH} = 9.2, J_{HP} = 3.1, J_{HH} = 7.5, 1H, $IrCH_2CH_3$), 3.01 (ddq, J_{HH} = 9.2, J_{HP} = 2.0, J_{HH} = 7.1, 1H, $IrCH_2CH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −4.97 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ −16.47 (d, J_{CP} = 5.5, $IrCH_2CH_3$), 4.21 (s, $NCCH_3$), 16.29 (s, $IrCH_2CH_3$), 18.77, 18.79 (both s, $PCHCH_3$), 23.24 (d, J_{CP} = 32.6, $PCHCH_3$), 29.00 (s, O_2CCH_3), 116.49 (s, $NCCH_3$), 187.25 (d, J_{CP} = 3.7, O_2CCH_3). Anal. Calcd for $C_{15}H_{32}NClIrO_2P$: C, 34.84; H, 6.24; N, 2.71. Found: C, 34.85; H, 6.22; N, 2.84.

[IrH_2(η^2-C_2H_4)(P^iPr_3)($NCCH_3$)$_2$]BF_4 (11). A stream of ethene was passed through a solution of **2** (ca. 25 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 233 K for 2 min. The resulting solution was subsequently found to contain a mixture of complexes **2** and **11** in a 3:2 molar ratio. Data for **11**: ^1H NMR ($CDCl_3$, 233 K) δ −19.89 (dd, J_{HP} = 18.6, J_{HH} = 1.4, 1H, IrH), −9.89 (dd, J_{HP} = 19.5, J_{HH} = 1.4, 1H, IrH), 1.03, 1.08 (both dd, J_{HP} = 13.8, J_{HH} = 7.2, 9H, $PCHCH_3$), 1.81 (m, 3H, $PCHCH_3$), 2.37 (s, 3H, $NCCH_3$), 2.52 (s, 3H, $NCCH_3$), 3.71 (AA′BB′ spin system, δ_A = 3.65, δ_B = 3.77, J_{AB} = $J_{A'B'}$ = 9.0, $J_{AA'}$ = $J_{BB'}$ = 13.5, 4H, η^2-C_2H_4); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K) δ 22.28 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K) δ 3.22, 3.50 (both s, $NCCH_3$), 18.22 (d, J_{CP} = 2.7, $PCHCH_3$), 19.40 (s, $PCHCH_3$), 23.31 (d, J_{CP} = 34.9, $PCHCH_3$), 68.19 (s, C_2H_4), 118.91 (s, $NCCH_3$), 119.09 (d, J_{CP} = 16.6, $NCCH_3$).

[Ir(Et)$_2$(P^iPr_3)($NCCH_3$)$_3$]BF_4 (14). A stream of ethylene was passed through a solution of **2** (ca. 25 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 233 K for 2 min. The resulting solution was then warmed to 273 K. A spectroscopic analysis of the solution revealed the quantitative formation of complex **14**: ^1H NMR ($CDCl_3$, 273 K) δ 0.78 (t, J_{HH} = 7.3, 6H, $IrCH_2CH_3$), 1.01 (m, partially covered by the phosphine resonances, 2H, $IrCH_2CH_3$), 1.09 (dd, J_{HP} = 12.9, J_{HH} = 7.4, 18H, $PCHCH_3$), 1.50 (ddq, J_{HH} = 11.9, J_{HP} = 5.3, J_{HH} = 7.3, 2H, $IrCH_2CH_3$), 2.34 (s, 6H, $NCCH_3$), 2.35 (m, 3H, $PCHCH_3$), 2.43 (s, 3H, $NCCH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 273 K) δ −6.07 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K) δ −16.38 (d, J_{CP} = 7.3, $IrCH_2CH_3$), 3.20, 3.25 (both s, $NCCH_3$), 17.58 (s, $IrCH_2CH_3$), 18.89 (s, $PCHCH_3$), 22.40 (d, J_{CP} = 31.1, $PCHCH_3$), 114.50 (d, J_{CP} = 18.4, $NCCH_3$), 118.26 (s, $NCCH_3$).

[Ir(P^iPr_3)($NCCH_3$)$_3$]BF_4 (15) and [Ir(P^iPr_3)(η^2-C_2H_4)($NCCH_3$)$_2$]BF_4 (16). A stream of ethene was passed through a solution of **2** (ca. 25 mg, 0.5 mmol) in CD_2Cl_2 (0.5 mL) at room temperature for 2 min. The solution was stirred for 5 min, and then the dissolved ethene was removed by slow bubbling of argon through the solution, at 273 K, for 1 min. The resulting solution was found to contain complexes **15** and **16** in a 1:2 molar ratio. Data for **15**: ^1H NMR (CD_2Cl_2, 233 K) δ 1.19 (dd, J_{HP} = 13.5, J_{HH} = 7.2, 18H, $PCHCH_3$), 1.92 (m, 3H, $PCHCH_3$), 2.19 (s, 6H, $NCCH_3$), 2.29 (d, J_{HP} = 0.9, 3H, $NCCH_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K) δ 15.63 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K) δ 2.54, 3.53 (both s, $NCCH_3$), 19.02 (s, $PCHCH_3$), 22.04 (d, J_{CP} = 32.5, $PCHCH_3$), 117.90 (d, J_{CP} = 16.4, $NCCH_3$), 125.86 (s, $NCCH_3$). Data for **16**: ^1H NMR (CD_2Cl_2, 233 K) δ 1.10 (dd, J_{HP} = 13.2, J_{HH} = 6.9, 18H, $PCHCH_3$), 1.95 (m, 3H, $PCHCH_3$), 2.28 (d, J_{HP} = 0.6, 3H, $NCCH_3$), 2.34 (dd, J_{HH} = 9.8, 7.5, 1H, η^2-C_2H_4), 2.57 (s, 3H, $NCCH_3$), 2.44 (dd, J_{HH} = 11.3, 6.8, 1H, η^2-C_2H_4), 2.72 (ddd, J_{HH} = 11.3, 7.5, 1.0, 1H, η^2-C_2H_4), 3.42 (ddd, J_{HH} = 9.8, 6.8, 1.0, 1H, η^2-C_2H_4); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 233 K) δ −11.35 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 233 K) δ 3.29, 3.80 (both s, $NCCH_3$), 18.52 (s, $PCHCH_3$), 21.63 (d, J_{CP} = 29.0, $PCHCH_3$), 27.52, 33.24 (both s, C_2H_4), 115.01 (d, J_{CP} = 17.6, $NCCH_3$), 119.35 (s, $NCCH_3$).

[IrH_2(η^2-C_3H_6)(P^iPr_3)($NCCH_3$)$_2$]BF_4 (17). A stream of propene was passed through a solution of **2** (ca. 25 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 233 K for 2 min. The resulting solution was found to contain a mixture of complexes **2** and **17** in a 3:7 molar ratio. Data for **17**: ^1H NMR ($CDCl_3$, 233 K) δ −23.08 (AB part of an ABX system (X = ^{31}P), δ_A = −23.10, δ_B = −23.05, J_{AB} = 7.2, J_{AX} = J_{BX} = 18.0, 2H, IrH), 1.11 (dd, J_{HP} = 13.8, J_{HH} = 6.9, 9H, $PCHCH_3$), 1.14 (dd, J_{HP} = 14.4, J_{HH} = 7.2, 9H, $PCHCH_3$), 2.00 (dd, J_{HH} = 5.7, 2.1, 3H, CH_2=$CHCH_3$), 2.02 (m, 3H, $PCHCH_3$), 2.37 (s, 6H, $NCCH_3$), 3.75 (dd, J_{HH} = 8.1, J_{HP} = 3.6, 1H, CH_2=$CHCH_3$), 3.79 (m, 1H, CH_2=$CHCH_3$), 4.79 (dddq, J_{HH} = 8.1, 5.1, J_{HP} = 3.0, J_{HH} = 5.7, 1H, CH_2=$CHCH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K) δ 38.26 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K) δ 3.20 (s, $NCCH_3$), 19.01, 19.11 (both s, $PCHCH_3$), 23.48 (s, CH_2=$CHCH_3$), 24.72 (d, J_{CP} = 30.9, $PCHCH_3$), 65.89 (d, J_{CP} = 10.8, CH_2=$CHCH_3$), 84.26 (d, J_{CP} = 9.4, CH_2=$CHCH_3$), 117.99, 118.06 (both s, $NCCH_3$).

[IrH(^{n}Pr)(P^iPr_3)($NCCH_3$)$_3$]BF_4 (18). A stream of propene was passed through a solution of **2** (ca. 25 mg, 0.5 mmol) in $CDCl_3$ (0.5 mL) at 233 K for 2 min, which was then warmed to 273 K. The spectroscopic analysis of the solution revealed the quantitative formation of complex **18**: ^1H NMR ($CDCl_3$, 273 K) δ −22.73 (d, J_{HP} = 22.5, 1H, IrH), 0.75 (t, J_{HH} = 6.9, 3H, $IrCH_2CH_2CH_3$), 1.12 (dd, J_{HP} = 13.2, J_{HH} = 7.2, 9H, $PCHCH_3$), 1.14 (dd, J_{HP} = 13.5, J_{HH} = 7.2, 9H, $PCHCH_3$), 1.18−1.25 (m, 4H, $IrCH_2CH_2CH_3$), 2.19 (m, 3H, $PCHCH_3$), 2.32, 2.38 (both s, 3H, $NCCH_3$), 2.43 (d, J_{HP} = 0.9, 3H, $NCCH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 273 K) δ 16.66 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 273 K) δ −8.64 (d, J_{CP} = 6.6, $IrCH_2CH_2CH_3$), 3.09, 3.14, 3.33 (all s, $NCCH_3$), 18.16, 18.42 (both d, J_{CP} = 1.0, $PCHCH_3$), 19.29 (s, $IrCH_2CH_2CH_3$), 23.36 (d, J_{CP} = 33.2, $PCHCH_3$), 28.49 (s, $IrCH_2CH_2CH_3$), 117.01 (d, J_{CP} = 17.8, $NCCH_3$), 118.06, 118.63 (both s, $NCCH_3$).

Preparation of [IrH(η^3-C_3H_5)(P^iPr_3)($NCCH_3$)$_2$]BF_4 (19). A solution of **2** (200 mg, 0.36 mmol) in CH_2Cl_2 (10 mL) was stirred under propene atmosphere (P = 1 atm) for 2 h. The resulting solution was filtered through Celite and evaporated to dryness. The residue was treated with diethyl ether to give a white solid, which was worked up as described for **2**: yield 143 mg (70%); IR (Nujol mull, cm^{-1}) 2235 ν(IrH), 1064 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −25.77 (d, J_{HP} = 16.5, 1H, IrH), 1.11, 1.16 (both dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, $PCHCH_3$), 1.39 (dd, J_{HH} = 10.3, 1.9, 1H, η^3-CH_2CHCH_2), 2.30 (m, 3H, $PCHCH_3$), 2.35 (dd, J_{HH} = 7.0, 1.9, 1H, η^3-CH_2CHCH_2), 2.41 (dd, J_{HH} = 6.4, 2.3, 1H, η^3-CH_2CHCH_2), 2.42 (br, 3H, $NCCH_3$), 2.52 (s, 3H, $NCCH_3$), 3.72 (ddd, J_{HH} = 7.1, 2.3, J_{HP} = 4.1, 1H, η^3-CH_2CHCH_2), 4.99 (ddddd, J_{HH} = 10.3, 7.1, 7.0, 6.4, J_{HP} = 3.3, 1H, η^3-CH_2CHCH_2); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 30.73 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ 3.06, 3.59 (both s, $NCCH_3$), 18.91, 19.10 (both s, $PCHCH_3$), 23.71 (d, J_{CP} = 2.3, η^3-CH_2CHCH_2), 25.57 (d, J_{CP} = 28.0, $PCHCH_3$), 53.16 (d, J_{CP} = 24.9, η^3-CH_2CHCH_2), 89.78 (s, η^3-CH_2CHCH_2), 122.09 (br, $NCCH_3$), 122.57 (s, $NCCH_3$). Anal. Calcd for $C_{16}H_{33}N_2BF_4IrP$: C, 34.10; H, 5.90; N, 4.97. Found: C, 34.12; H, 5.88; N, 4.99.

Preparation of [IrH(η^3-C_3H_5)(η^2-C_3H_6)(P^iPr_3)($NCCH_3$)]BF_4 (20). A solution of **19** (100 mg, 0.18 mmol) in CH_2Cl_2 (0.5 mL) was stirred under propene atmosphere (P = 1 atm) for 20 min. Upon addition of diethyl ether (10 mL) a white solid was worked up as described for **2**: yield 80 mg (80%); IR (Nujol mull, cm^{-1}) 2257 ν(IrH), 1061 (BF_4); ^1H NMR ($CDCl_3$, 293 K) δ −29.19 (d, J_{HP} = 16.5, 1H, IrH), 1.14, 1.15 (both dd, J_{HP} = 14.1, J_{HH} = 7.2, 9H, $PCHCH_3$), 1.73 (dd, J_{HH} = 5.7, J_{HP} = 1.8, 3H, CH_2=$CHCH_3$), 2.31 (s, 3H, $NCCH_3$), 2.38 (d, J_{HH} = 10.5, 1H, η^3-CH_2CHCH_2), 2.58 (m, 3H, $PCHCH_3$), 2.79 (dd, J_{HH} =

12.2, J_{HP} = 5.1, 1H, CH_2=CHCH$_3$), 3.01 (dd, J_{HH} = 8.4, J_{HP} = 6.0, 1H, CH_2=CHCH$_3$), 3.10 (dd, J_{HH} = 11.6, J_{HP} = 5.7, 1H, η^3-CH_2CHCH$_2$), 3.35 (m, 1H, η^3-CH$_2$CHCH_2), 4.04 (ddd, J_{HH} = 6.6, 3.2, J_{HP} = 3.0, 1H, η^3-CH$_2$CHCH_2), 4.82 (m, 1H, CH$_2$=CHCH$_3$), 4.95 (m, 1H, η^3-CH$_2$CHCH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K) δ 17.35 (s); ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K) δ 2.79 (s, NCCH$_3$), 18.54, 18.63 (both s, PCHCH$_3$), 24.44 (s, CH$_2$=CHCH$_3$), 26.98 (d, J_{CP} = 28.3, PCHCH$_3$), 42.83 (d, J_{CP} = 1.0, η^3-CH$_2$CHCH$_2$), 50.52 (d, J_{CP} = 5.0, CH$_2$=CHCH$_3$), 62.61 (d, J_{CP} = 3.0, CH$_2$=CHCH$_3$), 64.41 (d, J_{CP} = 17.8, η^3-CH$_2$CHCH$_2$), 90.79 (s, η^3-CH$_2$$CHCH_2$), 120.95 (s, N$CCH_3$). Anal. Calcd for $C_{17}H_{36}NBF_4IrP$: C, 36.17; H, 6.42; N, 2.48. Found: C, 35.85; H, 6.56; N, 2.67.

Kinetic Analysis. The kinetics of the exchange between the acetonitrile ligands of **1** and **2** and free acetonitrile were measured in 0.10 M solutions of the complexes in $CDCl_3$. Rate constants were obtained either by spin saturation transfer methods or by line-width measurements. Spin saturation transfer measurements were performed according to the Forsén−Hoffman method[34] by irradiating the resonance of the free acetonitrile and measuring the integral of the resonance of the coordinated acetonitrile. The exchange rates k_1 or k_{2obs} were calculated from the equation $k = (1/T_1)((I/I') - 1)$, where I' and I are the integrals for the resonance of coordinated acetonitrile with and without saturation of the resonance of free acetonitrile. T_1 is the spin−lattice relaxation time of the signal of coordinated acetonitrile obtained by the inversion−recovery method in the presence of the saturating field at the free acetonitrile signal.[35] Values of k_1 were obtained at higher temperatures by measuring the line-width (T_2^{obs}) of the ^{1}H signal corresponding to the acetonitrile ligand trans to hydride, through the equation[36] $1/\pi T_2^{obs} - 1/\pi T_2^* = 1/\pi\tau$, where $k = 1/\tau$. The reference line-width (T_2^*) was obtained from the signal of the acetonitrile ligand trans to chloride for **1** and from the signals of the phosphine methyl groups for **2**. At higher temperatures, when the broad signal of the exchanging acetonitrile ligands are partially obscured by other resonances, T_2^{obs} can be obtained from the resonance corresponding to the free acetonitrile, taking into account the relative concentrations of complex and free acetonitrile.

The first exchange process affecting complex **19** was studied in 0.04 M solutions of **19** in $CDCl_3$ also by spin saturation transfer and line-width measurements, following the same procedures as described above. The rates corresponding to the second exchange process of **19** (k_2) were measured by replacement of coordinated acetonitrile by acetonitrile-d_3. The decrease of the intensity of the signal corresponding to the acetonitrile ligand trans to allyl was measured automatically at intervals in a Varian Gemini 2000 spectrometer. The rate constants were obtained by fitting the data to an exponential decay function, using the routine programs of the spectrometer.

In all cases, the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were obtained from a linear least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Errors were computed by published methods.[37] The error in temperature was assumed to be 1 K; error in k_{obs} was estimated as 10%.

Hydrogenation of Cyclohexene with Compound 2 as Catalyst. The reactions were carried out in a conventional glass hydrogenation apparatus equipped with a shaker. The reaction conditions were as follows: solvent acetone (8 mL); [**2**] = 0.12 M; [cyclohexene] = 35.0 M; T = 298 K. Turnover frequencies were obtained from gas uptake measurements during the initial part of the catalytic reaction (ca. 20%). Under these conditions, the turnover frequencies gave constant values of 1.1 ± 0.2 min^{-1}.

Table 6. Crystallographic Data for [Ir(η^2-O$_2$CCH$_3$)Cl(Et)(P^{i}Pr$_3$)(NCCH$_3$)] (10) and [IrH(η^3-C$_3$H$_5$)(P^{i}Pr$_3$)(NCCH$_3$)$_2$]BF$_4$ (19)

formula	$C_{15}H_{32}ClIrNO_2P$	$C_{16}H_{33}BF_4IrN_2P$
M	517.04	563.42
T (K)	173(2)	150(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	8.927(3)	8.5164(13)
b, Å	14.778(4)	8.7603(12)
c, Å	15.571(6)	14.591(2)
α, deg		99.475(12)
β, deg	103.82(3)	90.412(14)
γ, deg		96.096(11)
V, Å^3	1994.7(12)	1067.3(3)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.722	1.753
μ, mm^{-1}	6.911	6.365
θ range data collec (deg)	1.9−25.0	2.3−30.0
no. of measd reflns	6046	8842
no. of unique reflns	3501 (R_{int} = 0.0636)	6207 (R_{int} = 0.0195)
no. of data/restraints/params	3501/0/199	6207/0/358
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.0477	0.0233
$wR(F^2)$ [all data][b]	0.1338	0.0524

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$, for 3096 and 5621 observed reflections. [b] $wR(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$.

Determination of the Crystal Structures of [Ir(η^2-O$_2$CCH$_3$)Cl(Et)(P^{i}Pr$_3$)(NCCH$_3$)] (10) and [IrH(η^3-C$_3$H$_5$)(P^{i}Pr$_3$)(NCCH$_3$)$_2$]BF$_4$ (19). A summary of crystal data and refinement parameters is listed in Table 6. Data were collected on a Siemens P4 (**10**) or a Siemens-Stoe AED2 (**19**) diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), using the $\omega/2\theta$ scan method. Three standard reflections were monitored every 100 measurements (**10**) or 55 min (**19**) throughout data collection; no important variations were observed. Both data were corrected for Lorentz and polarization effects and for absorption using the ψ-scan method (minimum and maximum transmission factors 0.0040 and 0.0267 for (**10**), 0.1549 and 0.2061 for (**19**)).[38] Both structures were solved by direct methods (SIR92)[39] and Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97).[40] Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

Data for (10). Pale yellow prismatic crystals were obtained by diffusion of methanol into a solution of **10** in CH_2Cl_2; a crystal of approximate dimensions 0.62 × 0.45 × 0.43 mm was used for data collection. Cell constants were obtained from the least-squares fit on the setting angles of 60 reflections in the range 27° ≤ 2θ ≤ 45°. Data were collected at 173 K in the range 3.8° ≤ 2θ ≤ 50° (−2 ≤ h ≤ 10, −17 ≤ k ≤ 1, −18 ≤ l ≤ 18); 6046 measured reflections, 3501 unique (R_{int} = 0.0636). Anisotropic displacement parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined riding

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on the corresponding carbon atoms. The calculated weighting scheme was $1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $x = 0.0668$, $y = 18.9465$, and $P = (F_o^2 + 2F_c^2)/3$. Final agreement factors were $R(F) = 0.0477$ (3096 observed reflections, $F_o^2 \geq 2\sigma(F_o^2)$) and $wR(F^2) = 0.1338$. Largest peak and hole in the difference map were 2.558 (close to the iridium atom) and -1.272 e Å^{-3}.

Data for (19). Suitable crystals were obtained from a saturated solution in CH_2Cl_2/diethyl ether stored at 273 K during various days; a colorless irregular block (0.15 × 0.18 × 0.22 mm) was selected for the data collection. Cell constants were obtained from the least-squares fit on the setting angles of 62 reflections in the range $25° \leq 2\theta \leq 36°$. Data were collected at 150 K in the range $4.6° \leq 2\theta \leq 60°$ ($-11 \leq h \leq 3$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$); 8842 measured reflections, 6207 unique ($R_{int} = 0.0195$). Anisotropic displacement parameters were used in the last cycles of refinement for all non-hydrogen atoms. The high quality and extended range of the diffraction data allows location of all hydrogen atoms, including the hydride ligand, in difference Fourier maps; they were introduced in the refinement as free isotropic atoms. We have tried to confirm the validity of our assignment and improve the metal−hydride bond distance analyzing several difference Fourier maps containing data with different cuts of low-angle reflections;[41] the results confirm that the peak assigned to the hydride is not an electronic residue but does not significantly alter the final bond length. The short Ir−H bond distance observed (1.34(4) Å) may be due to a well-known behavior of the X-ray diffraction experiments that usually shows shorter M−H distances than those based on neutron diffraction, a radiation much more appropriate for the precise localization of lighter elements. A weighting scheme analogous to that used for **10** was applied, with $x = 0.0269$ and $y = 0.2355$. Final agreements factors were $R(F) = 0.0233$ (5621 observed reflections, $F_o^2 \geq 2\sigma(F_o^2)$) and $wR(F^2) = 0.0524$. Largest peak and hole in the difference map were 0.940 and -1.465 e Å^{-3}.

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Supporting Information Available: Full listings of crystallographic data, complete atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for complexes **10** and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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