Evidence for a Dinuclear Mechanism in Alkyne Hydrogenations Catalyzed by Pyrazolate-Bridged Diiridium Complexes

Francisco Torres, Eduardo Sola, Anabel Elduque, Ana P. Martínez, Fernando J. Lahoz, and Luis A. Oro*[a]

Abstract: The products obtained from the sequential reaction of $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H_3(NCCH_3)(P\textit{i}Pr_3)_2]$ (**1**) with diphenylacetylene and their subsequent reactions with hydrogen have been investigated in order to deduce the mechanisms operating in the hydrogenation reactions catalyzed by **1**. The reaction of **1** with an excess of diphenylacetylene gives *cis*-stilbene and $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}\{(Z)\text{-}C(Ph){=}CHPh\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (**2**), the structure of which has been determined by X-ray diffraction. The formation of **2** involves the intermediate species $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H_2\{(Z)\text{-}C(Ph){=}CHPh\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (**3**), $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{(Z)\text{-}C(Ph){=}CHPh\}_2(NCCH_3)(P\textit{i}Pr_3)_2]$ (**4**), and $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (**5**), which have been isolated and characterized. These three complexes react with hydrogen to give *cis*-stilbene and **1** and are possible intermediates of the diphenylacetylene hydrogenation under catalytic conditions. Nevertheless, the rate of formation of **5** is very slow compared with the rate of catalytic hydrogenation, which excludes its participation during catalysis. Compound **2** also reacts with hydrogen in benzene, but in this case the hydrogenation gives 1,2-diphenylethane as the sole organic product. The course of this reaction in acetone has been investigated, and deuteration experiments were carried out. The formation of $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(OC(CD_3)_2)(P\textit{i}Pr_3)_2]$ (**6**) and $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (**7**) was observed under these conditions. The experimental evidence obtained supports two alternative mechanisms for the alkyne hydrogenation catalyzed by **1**, one of them being dinuclear and the other mononuclear. The experimental data suggest that the former is favored.

Keywords: alkynes · cooperative effects · homogeneous catalysis · hydrogenations · iridium

Introduction

The peculiar chemical behavior that may result from the proximity of metal centers in polynuclear complexes is a challenging research topic, which can be also of technological importance in the field of homogeneous catalysis.[1] In fact, during the last decades a variety of compounds have been prepared in which intermetallic cooperation or synergetic effects lead to enhanced catalytic properties.[2] Also, intriguing examples of substrate activations simultaneously performed by two or more metal atoms have been reported.[3] Unfortunately, the complexity of these systems often precludes their detailed mechanistic study, and, therefore, the performance of such polynuclear species and the reasons for the observed catalytic enhancements remain unclear. Then, the necessary information required for a rational design of catalysts based on this kind of cooperative effects is still not available.

Recently, we reported the synthesis of the pyrazolate-bridged diiridium(III) complex $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H_3(NCCH_3)(P\textit{i}Pr_3)_2]$ (**1**), which displays noticeable substrate activation capabilities and catalyzes alkene hydrogenation.[4] This compound and its derivatives constitute rather simple and valuable models for the study of intermetallic relationships in dinuclear species; this has allowed us to recognize aspects relevant to dinuclear catalysis such as ligand migrations and the transmission of *trans* effects along the dinuclear skeletons. In the course of these investigations, we observed peculiar structures and reactivities for the intermediates of ethene hydrogenation, suggesting that this catalytic reaction could involve a novel dinuclear mechanism. Aimed at the identification of such a mechanism, we describe here a detailed study on the intermediates involved in the hydrogenation of diphenylacetylene by complex **1**. Interestingly, the dinuclear pathway followed by this reaction seems to operate even in the presence of an alternative mononuclear mechanism.

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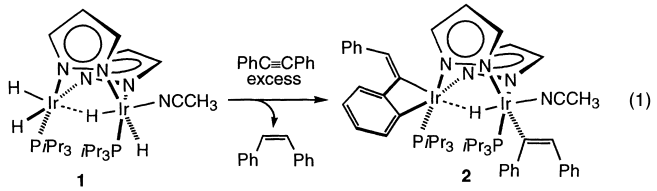
Results

Sequential reactions of complex 1 with diphenylacetylene: The reaction of complex **1** with an excess of diphenylacetylene in toluene affords, after 24 h at room temperature, $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}\{(Z)\text{-}C(Ph){=}CHPh\}(NCCH_3)(P\mathit{i}Pr_3)_2]$ (**2**) together with one equivalent of *cis*-stilbene [Eq. 1]. The molecular structure of **2** determined by



X-ray diffraction is shown in Figure 1. Important bond lengths and angles are given in Table 1.

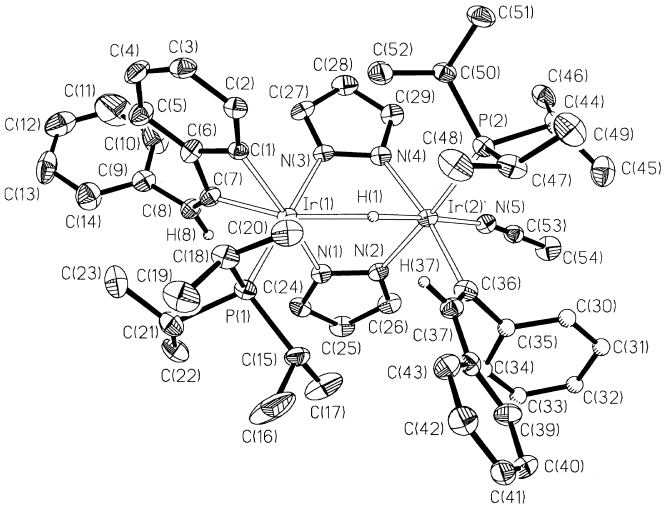


Figure 1. Molecular structure of complex **2**.

Complex **2** is an asymmetric species that contains two organic fragments derived from diphenylacetylene: a (*Z*)-diphenylvinyl ligand and its *ortho*-metallated derivative, which forms a four-membered metallacycle. The coordination environment of Ir(2) is nearly a perfect octahedron, whereas the environment of Ir(1) is strongly distorted due to the position of the bridging hydride and the geometry of the *ortho*-metallated vinyl ligand. The latter chelates the metal with a bite angle of 65.74(18)°, which is in the range found for related chelating ligands such as η^3-allyl or acetate.[5] As a result of this small bite angle, the angles around C(6), the central carbon of the chelate, strongly deviate from the sp^2 ideal values, as also found in other complexes containing related *ortho*-metallated ligands.[6]

The hydride ligand was located in the difference Fourier maps, bridging the iridium atoms with remarkably different distances of 1.52(4) and 1.99(4) Å. Although the hydride positions must be interpreted with some caution, the location of H(1) agrees with the observed NMR spectra of **2**. Thus, the hydrido bridge of **2** appears, in the ^{1}H NMR spectrum in $CDCl_3$ at 293 K, as a doublet of doublets at $\delta = -23.16$, with J(H,P) coupling constants of 13.2 and 2.1 Hz. Since the relative position of the bridging hydride with respect to both phosphane ligands is *cis*, the different coupling constants would indicate different Ir–H bond lengths, showing that the asymmetric position found in the solid state is maintained in solution. As in other cases in which an asymmetric bridging hydride has been found,[7, 8] the asymmetry can be attributed to the different *trans* influences of the ligands *trans* to the bridge, a vinyl moiety and an acetonitrile in this case.

Table 1. Selected bond lengths [Å] and angles [°] for complex **2**.

Ir(1)–H(1)	1.99(4)	Ir(2)–H(1)	1.52(4)
Ir(1)–N(1)	2.115(4)	Ir(2)–N(2)	2.095(4)
Ir(1)–N(3)	2.101(3)	Ir(2)–N(4)	2.110(4)
Ir(1)–P(1)	2.3208(12)	Ir(2)–P(2)	2.3353(12)
Ir(1)–C(1)	2.076(4)	Ir(2)–C(36)	2.093(5)
Ir(1)–C(7)	2.036(4)	Ir(2)–N(5)	2.051(4)
C(7)–C(8)	1.337(6)	C(36)–C(37)	1.345(6)
H(1)-Ir(1)-N(1)	78.7(12)	H(1)-Ir(2)-N(2)	84.2(16)
H(1)-Ir(1)-N(3)	75.3(12)	H(1)-Ir(2)-N(4)	81.1(15)
H(1)-Ir(1)-P(1)	103.2(12)	H(1)-Ir(2)-P(2)	96.3(16)
H(1)-Ir(1)-C(1)	112.0(12)	H(1)-Ir(2)-C(36)	93.7(15)
H(1)-Ir(1)-C(7)	162.3(12)	H(1)-Ir(2)-N(5)	168.3(16)
N(1)-Ir(1)-N(3)	85.57(13)	N(2)-Ir(2)-N(4)	82.66(14)
N(1)-Ir(1)-P(1)	96.43(10)	N(2)-Ir(2)-P(2)	174.82(10)
N(1)-Ir(1)-C(1)	166.10(16)	N(2)-Ir(2)-C(36)	90.65(16)
N(1)-Ir(1)-C(7)	101.31(16)	N(2)-Ir(2)-N(5)	85.30(14)
N(3)-Ir(1)-P(1)	177.28(10)	N(4)-Ir(2)-P(2)	92.33(10)
N(3)-Ir(1)-C(1)	88.57(15)	N(4)-Ir(2)-C(36)	171.90(16)
N(3)-Ir(1)-C(7)	86.99(16)	N(4)-Ir(2)-N(5)	92.37(14)
P(1)-Ir(1)-C(1)	89.87(12)	P(2)-Ir(2)-C(36)	94.44(13)
P(1)-Ir(1)-C(7)	94.41(13)	P(2)-Ir(2)-N(5)	93.62(11)
C(1)-Ir(1)-C(7)	65.74(18)	C(36)-Ir(2)-N(5)	91.62(16)
Ir(1)-C(1)-C(6)	96.1(3)	Ir(2)-C(36)-C(35)	117.3(3)/117.4(3)[a]
Ir(1)-C(7)-C(6)	95.7(3)	Ir(2)-C(36)-C(37)	122.5(4)
C(1)-C(6)-C(7)	102.5(4)	Ir(2)-N(5)-C(53)	170.4(4)
N(5)-C(53)-C(54)	177.6(5)		

[a] Atom C(35) is involved in phenyl disorder (see Experimental Section).

The Ir–N(5) bond length 2.051(4) Å is shorter than those found for other labile acetonitrile ligands *trans* to terminal hydrides (2.13–2.15 Å),[5, 9] but similar is to that found in complex **1** (2.04(2) Å) in which the dissociation of acetonitrile with low activation energies is still possible.[4] In agreement with this observation, the acetonitrile ligand of **2** is readily substituted by $[D_3]$acetonitrile in benzene at room temperature.

The formation of complex **2** requires three equivalents of diphenylacetylene and involves several individual processes, such as alkyne insertions into Ir–H bonds, C–H reductive eliminations, and C–H bond activations. The spectroscopic observation of the course of this reaction revealed the participation of at least three intermediate species, compounds **3**–**5**, which were isolated and characterized. Scheme 1 shows the structures deduced for these intermediates together with their reactions with hydrogen, which will be described in detail in the next section.

The compound $[Ir_2(\mu\text{-}H)(\mu\text{-}Pz)_2H_2\{(Z)\text{-}C(Ph){=}CHPh\}(NCCH_3)(P\mathit{i}Pr_3)_2]$ (**3**) can be isolated as a yellow solid after treatment of **1** with one equivalent of diphenylacetylene in toluene. Figure 2 shows the high-field region of the ^{1}H NMR spectrum of **3** in $[D_8]$toluene at room temperature, which

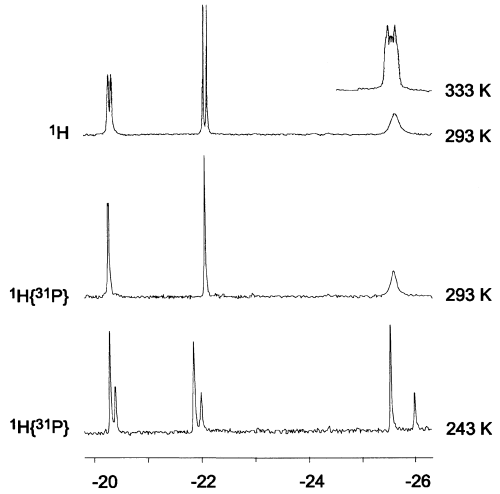


Figure 2. High-field region of the ^{1}H and ^{1}H{^{31}P} NMR spectra of complex **3** in [D_8]toluene at different temperatures.

displays three signals corresponding to three nonequivalent hydrides. The broadening observed for the hydride signal at highest field also affects the resonances corresponding to one phosphane and the vinyl moiety. Most likely, this is the result of the large steric requirements of these ligands hindering their fast rotation in solution. This interpretation is consistent with the observed low-temperature ^{1}H NMR spectra, which, below 250 K, show decoalescence of each hydride signal to give two sets of similar signals in a about 0.7:0.3 molar ratio. Each set of signals may correspond to a conformational minimum.

On raising the temperature to 333 K, the broad ^{1}H NMR hydride signal of **3** resolves into a ddd signal that displays two different J(H,P) coupling constants of 13.2 and 6.0 Hz and a J(H,H) of 4.2 Hz (Figure 2). As for **2**, the two different H–P couplings suggest an asymmetric bridging position of this hydride. The remaining J(H,H) coupling is due to the terminal hydride that gives the dd signal at lowest field. The ^{1}H NOESY spectrum shows the existence of NOE effects between the bridging hydride and both terminal ones, in agreement with the *cis* arrangement of these three hydrides. In the low-field part of the proton spectrum at 333 K, both resonances due to the hydrogens in the 4-position of the pyrazolate bridges are doublets of triplets, containing J(H,P) coupling constants of about 2 Hz. This indicates that each pyrazolate has one *trans* triisopropylphosphane ligand,[4] or, in other words, that the arrangement of the phosphanes in the dinuclear framework is *transoid*. The ^{31}P{^{1}H} NMR spectrum at 333 K displays two singlets at $\delta = 12.93$ and 3.22, which under *off resonance* conditions split into two doublets of doublets. This splitting indicates that each metal coordinates both a terminal and a bridging hydride.

The aforementioned spectroscopic data of **3** are in agreement with the structure depicted in Scheme 1 although, unfortunately, these data are not informative about the *Z* or *E* configuration of the vinyl ligand. Nevertheless, the treatment of **3** with hydrogen in C_6D_6 at room temperature and atmospheric pressure readily yields compound **1** together with *cis* stilbene; this suggests that, as for **2**, the configuration of the vinyl ligand is *Z*.

The solutions of **3** react with a second equivalent of diphenylacetylene to give the yellow dihydrido complex $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{(Z)\text{-C(Ph)=CHPh}\}_2(NCCH_3)(P\textit{i}Pr_3)_2]$ (**4**). Similarly to what happens for **3**, most of the signals of the room temperature NMR spectra of **4** are slightly broad. Nevertheless, with the exception of those corresponding to one phosphane ligand, the other signals are resolved enough to allow observation of the coupling constants in the room temperature spectra.

The high-field region of the ^{1}H NMR spectrum of **4** in C_6D_6 shows two resonances: a doublet at $\delta = -21.31$ (J(H,P) = 21.6 Hz) and a doublet of doublets at $\delta = -24.42$ (J(H,P) = 12.6 and 2.4 Hz). Again, the pattern of the latter signal points to an asymmetric hydrido bridge. The low-field part of the proton spectrum is consistent with the presence of two nonequivalent vinyl ligands and also indicates a *transoid* arrangement of the triisopropylphosphanes. The ^{13}C{^{1}H} NMR spectrum contains two doublets at $\delta = 126.80$ (J(C,P) = 7.2 Hz) and 133.35 (J(C,P) = 7.8 Hz) corresponding to the two vinylic α-carbons, which bind the iridium atoms in positions *cis* relative to the phosphanes. The ^{31}P{^{1}H} spectrum shows two singlets at $\delta = 4.74$ and -10.15. Under *off resonance* conditions the former signal shows a large J(P,H) coupling due to a terminal hydride (21.6 Hz) and a small one due to the hydrido bridge (2.4 Hz). The high-field signal splits into a doublet with a J(H,P) constant of 12.6 Hz. As for compound **1** and its derivatives **2** and **3**, the acetonitrile ligand of **4** is labile, being readily substituted by [D_3]acetonitrile in solution at room temperature. This observation strongly suggests the *trans* position of the labile acetonitrile with respect to the bridging hydride. The structure for **4** depicted in Scheme 1 is the only one that rationalizes all the above spectroscopic observations and assumes a *Z* configuration of both vinyl ligands.

Complex **4** does not react directly with diphenylacetylene, but in solution at room temperature it slowly generates *cis*-stilbene to give the new complex $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-C=CHPh}]\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (**5**). The pseudo-first-order rate constant for this **4** to **5** transformation has been determined by ^{31}P{^{1}H} NMR spectroscopy as 1.2×10^{-4} s^{-1}, in [D_8]toluene at 293 K. The spectroscopic data collected for **5** again indicate the presence of two hydrides (a terminal and an asymmetric bridging one) and two phosphanes in *transoid* arrangement. In addition, the ^{1}H and ^{13}C{^{1}H} NMR spectra show complex low-field regions, consistent with the presence of an *ortho*-metallated vinyl ligand. In the ^{13}C{^{1}H} spectrum, two signals due to quaternary carbons at $\delta = 112.12$ and 119.42 with J(C,P) couplings of 5.8 and 8.7 Hz, respectively, indicate that the carbons bonded to the iridium center are both *cis* to the phosphane ligand. Taking into account the proposed *Z* configuration of both vinyl ligands of **4**, the aromatic C–H activation leading to **5** should result in a four-membered iridacycle. Although the relative orientation of this iridacycle cannot be determined spectroscopically, the structure of **4** depicted in Scheme 1 maintains the orientation found for complex **2**, which is obtained after the treatment of **5** with a new equivalent of diphenylacetylene.

Reactions with hydrogen: As mentioned above, the reaction of **3** with hydrogen at room temperature and atmospheric

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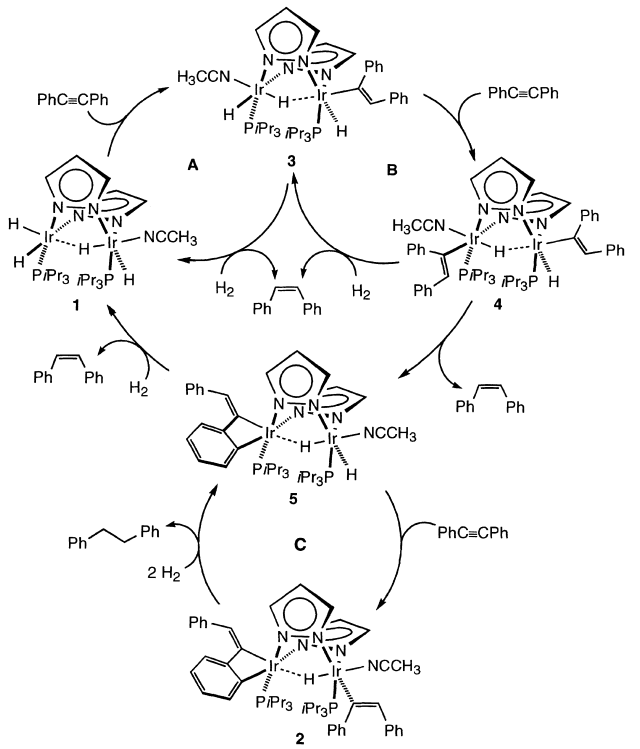
pressure gives, after few minutes, *cis*-stilbene and complex **1**. In the absence of hydrogen, the *cis*-stilbene is slowly isomerized to the *trans* isomer, which is the only detectable organic product in the mixture after 8 h at room temperature. This slow isomerization is consistent with the previously observed reactions of **1** with ethylene, in which products of alkene coordination and insertion were observed.[4] Also in agreement with the latter, in the presence of hydrogen, complex **1** hydrogenates the stilbenes to 1,2-diphenylethane, although completion of this reaction requires several hours.

Complex **4** also reacts with hydrogen at room temperature to give after few minutes *cis*-stilbene and **3**. In this respect, compounds **3** and **4** represent intermediates in the catalytic hydrogenation of diphenylacetylene by complex **1** (cycles A and B in Scheme 1). The catalytic runs for this hydrogenation

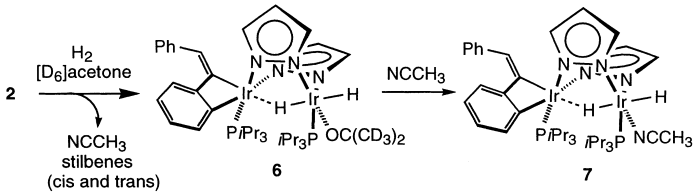


Scheme 1.

show the selective formation of *cis*-stilbene (>90%) at low conversions, although, in agreement with the stoichiometric behavior described above, significant formation of *trans*-stilbene and 1,2-diphenylethane is observed as the conversion increases.

The pseudo-first-order rate constant for the catalytic hydrogenation, in benzene at 293 K and with using **1** as catalyst precursor, has been determined as $1.7 \times 10^{-2}\ s^{-1}$. Comparison of this rate with that determined under similar conditions for the formation of compound **5** ($1.2 \times 10^{-4}\ s^{-1}$), excludes the participation of this intermediate in the catalytic transformations, since its formation is about hundred times slower than the catalytic hydrogenation. In any case, complex **5** can slowly regenerate **1** upon treatment with hydrogen, giving *cis*-stilbene as reaction product.

Although the above considerations also exclude any significant participation of complex **2** under catalytic conditions, its reaction with hydrogen allows interesting observations to be made. Bubbling of hydrogen through solutions of **2** in C_6D_6 or $CDCl_3$ at 278 K over a period of about one minute results in the formation of complex **5** together with 1,2-diphenylethane (Scheme 1). Remarkably, the expected organic product of the reaction, *cis*-stilbene, cannot be detected by NMR spectroscopy even when the reactions are performed at very low temperatures. In contrast, when the reactions are carried out in [D$_6$]acetone at 273 K, stilbenes (*cis* and *trans*) are the main reaction products, which are accompanied by the formation of a new complex **6** (Scheme 2). Along with these major products, significant amounts of **5** and 1,2-diphenylethane are formed (about 20% of the reaction products).



Scheme 2.

The intermediate **6** can be maintained in solution at low temperature for long periods, allowing its spectroscopic study. However, our attempts to isolate **6** from its acetone solutions were unsuccessful. On the basis of its NMR spectra, compound **6** can be formulated as the [D$_6$]acetone complex [Ir$_2$(μ-H)(μ-Pz)$_2$H{η^1-C$_6$H$_4$-2-[η^1-(*Z*)-C=CHPh]}(OC(CD$_3$)$_2$)(P*i*Pr$_3$)$_2$].

The most intriguing feature of **6** is the mutually *trans* arrangement of the terminal and bridging hydrides, which can be deduced from their mutual coupling constant of 13.8 Hz in the ^{1}H NMR spectrum (Figure 3). The spectroscopic data for

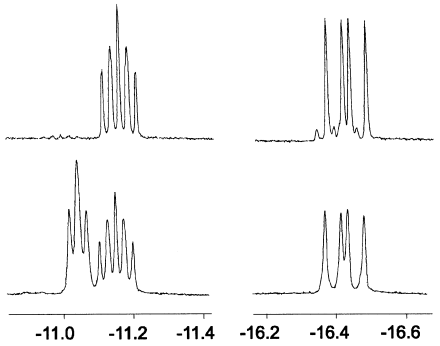


Figure 3. High-field region of the ^{1}H NMR spectrum of complex **6** (above) and the isotopomeric mixture **6**/[D]**6** (below) in [D$_6$]acetone at 263 K.

6 are also in agreement with the presence of a remaining four-membered metallacycle and with the *transoid* arrangement of the phosphanes; this leads to the structural proposal depicted in Scheme 2. The presence of a [D$_6$]acetone ligand is inferred from the ^{13}C{^{1}H} NMR spectrum at 263 K, which shows a singlet at $\delta = 224.98$ attributable to the ketonic carbon of the coordinated solvent. As in the previous compounds, the ^{1}H NMR signal of **6** corresponding to the bridging hydride displays two different J(H,P) coupling constants (13.5 and 7.2 Hz), which indicate the asymmetry of the bridge. In this case, since the expected *trans* influences of both groups *trans*

to the bridge (hydride and vinyl) are large, the assignment of a qualitative position for this bridge is not evident. The structural proposal of Scheme 2, which shows a shorter bond *trans* to hydride, is based on the magnitude of the J(H,H) coupling constant (13.8 Hz), which is rather large relative to those found in **1** (3.9 Hz[4]) and other related compounds.[7] Nevertheless, such proposal should be regarded with caution.

Treatment of **2** with D_2, also in [D_6]acetone at 253 K, produces complex **6** together with its isotopomer [D]**6**, which is selectively deuterated at the terminal hydrido position. The proportion of each isotopomer in the mixture is close to 50%. The deuteration of the terminal hydride results in down-field isotopic shifts of different magnitude in the two $^{31}P\{^1H\}$ NMR signals of [D]**6** with respect to those of **6** (the two singlets at $\delta = 17.53$ and 7.28 are shifted by 0.110 and 0.044 ppm, respectively). Also, the resonance due to the bridging hydride shifts toward lower field by 0.103 ppm (Figure 3). The magnitude of this shift is larger than those found for equivalent isotopic substitutions in related complexes.[4, 7] No H/D scrambling between the terminal and bridging position is observed, but, at temperatures above 273 K, fast H/D scrambling between the terminal hydride and the phosphane methyl groups takes place. The incorporation of deuterium to the phosphane can be observed in the ^2H NMR spectrum of a sample generated in acetone, whereas the H/D exchange at the hydride terminal position can be followed in the proton NMR spectrum.

The organic products of the reaction of **2** with D_2 are mono- and di-deuterated stilbenes (*cis* and *trans*), as can be seen in both the ^1H and ^2H NMR spectra. The formation during this reaction of two isotopomers of both the stilbenes and complex **6** strongly suggests the participation of alkyl intermediates, as will be discussed in detail below. The observed H/D scrambling between the terminal hydride and the phosphane could involve the formation of an agostic species, since precedents for such exchanges have been reported.[10]

The presumably labile acetone ligand of **6** is slowly replaced by acetonitrile when the solutions of **6** in [D_6]acetone are warmed up to room temperature. Completion of this replacement requires three hours and results in the formation of complex $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(NCCH_3)(P\mathit{i}Pr_3)_2]$ (**7**), an isomer of **5**, which retains the *trans* arrangement of the hydrides (Scheme 2). In spite of the fact that **7** is stable in solution, we could not separate it from the other components of the reaction solution in an analytically pure form.

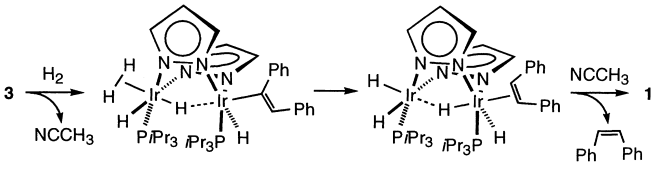
In contrast to the behavior of **5**, its isomer **7** does not react with hydrogen or diphenylacetylene. Also, the treatment of **7** with [D_3]acetonitrile does not lead to substitution of the coordinated acetonitrile. This observations suggest that the acetonitrile coordinated *trans* to a pyrazolate nitrogen is not labile enough to provide a coordination vacancy.

Discussion

In line with the last observation of the previous section, two kinds of coordination sites in these type of hydrido-bridged dimers can be distinguished: the sites *trans* to the pyrazolate bridges and those *trans* to the hydrido bridge. As illustrated by the behavior of the isomers **5** and **7**, only the sites *trans* to the bridging hydride are labilized enough to afford coordination vacancies by dissociation of a weakly coordinating ligand. This observation will be important to understand the mechanisms of the hydrogenation catalyzed by these complexes.

A second important observation arises from the analysis of the structure deduced for complex **3**. In this dinuclear species, the vinyl ligand derived from the incoming alkyne and the labile acetonitrile ligand coordinate to different metal centers. Assuming that the formation of **3** is initiated by acetonitrile dissociation from **1** and alkyne coordination (as found for other substitution reactions involving substrates such as CO or ethylene),[4] the structure of **3** implies that the coordination vacancy generated by the insertion of the alkyne into the Ir–H bond migrates from one metal center to the other before the unsaturated intermediate is stabilized by the coordination of the acetonitrile. The vacancy migration process could take place through hydride exchange between the metallic centers, as suggested by some previously reported reactions of **1**. Thus, the treatment of **1** with D_2 results in the statistical deuteration of all hydrido positions and, furthermore, the dihydrogen complex $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H_3(\eta^2\text{-}H_2)(P\mathit{i}Pr_3)_2]$ derived from **1** displays a unique ^1H NMR hydride signal at room temperature, as a result of the fast hydride exchange.[4]

The two aforementioned observations suggest that alkyne hydrogenation of complex **3** may take place through the intermediates shown in Scheme 3. Thus, hydrogen coordination to the vacancy generated by acetonitrile dissociation is followed by the reductive elimination of stilbene from the other metallic center and the rearrangement of the hydrides. The stilbene ligand so formed is bonded to a labile position and can be subsequently dissociated to regenerate **1**. This mechanism implies the efficient use of both labile positions of the dinuclear species, driven by the hydride exchange between iridium centers.



Scheme 3.

In favor of this mechanism, the treatment of **3** with D_2 in C_6D_6 results in the formation of *cis*-stilbene (non-deuterated) and deuterated isotopomers of **1**. This strongly suggests that D_2 coordination and stilbene formation occur at different metal centers, also showing that stilbene is formed before the H/D exchange reaches the second metal center. Other possible reaction sequences, such as those initiated by reductive elimination of stilbene, seem to be ruled out by the reaction leading to **4**.

The *ortho*-metallation of the diphenylvinyl ligand blocks one of the labile positions of the dinuclear compound, providing an excellent system to compare the above described dinuclear behavior with the reactivity due to a single metal

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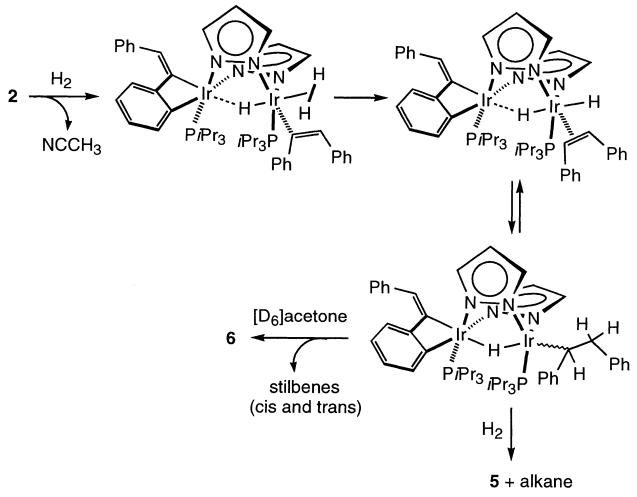
center. As shown in Scheme 1, the still available labile position of compound **5** can be used for alkyne insertion to give **2** and subsequent reaction with hydrogen. Then, the catalytic hydrogenation using a single metal center is possible, following cycle C of Scheme 1. However, this catalytic reaction in benzene produces selectively 1,2-diphenylethane, in contrast with the dinuclear cycle A which yields *cis*-stilbene. Scheme 4 describes a more detailed proposal for the reaction



Scheme 4.

of hydrogen with **2**, which rationalizes the observed selectivity, the reaction intermediates observed in acetone, and the deuteration experiments performed in this mononuclear hydrogenation.

The key proposal to explain the observed selectivity is that, after the concerted reaction between the hydrogen and the vinyl, the resulting stilbene ligand occupies a nonlabile coordination position (*trans* to pyrazolate), from which it cannot be simply released. The stilbene complex so formed would be coordinatively saturated, although it could generate a coordination vacancy by insertion, to form an unsaturated alkyl complex. This alkyl intermediate can explain a number of experimental facts. Thus, its reaction with hydrogen would give the alkane, explaining the observed selectivity. In the presence of a solvent like acetone, coordination of the solvent to a nonlabile position of the alkyl intermediate can result in the β-elimination to give complex **6** and both *cis* and *trans* stilbenes, in agreement with our experiments. Moreover, when the alkyl contains two deuterium atoms, the β-elimination can generate either the isotopomer [D]**6** or **6**,[11] and in consequence the mono- or di-deuterated stilbenes.

The occurrence of an insertion step can explain how substitution of the stilbene coordinated to a non-labile position may take place with retention of the *trans* arrangement of the hydrides. Also, such a process could account for the slow substitution of the [D_6]acetone of **6** by acetonitrile to give **7**, through the formation of an alkoxy intermediate.[12] However, at present, we have not got evidence for the formation of such intermediate, and acetone hydrogenation was also not observed.

The connection existing between cycles A and C prevents the evaluation of their individual hydrogenation rates, and, therefore, the quantitative comparison between the activities of the two catalytic mechanisms is not possible. Nevertheless, qualitative conclusions can be obtained from the behavior of complex **4**, in which the mononuclear and the dinuclear mechanism can compete. In this respect, the observation that only *cis*-stilbene is formed from the reaction between **4** and hydrogen strongly supports the conclusion that the dinuclear mechanism is favored.

The activity and selectivity of the catalytic reactions remain unaffected when any of the complexes **2** to **5** is used instead of **1** as catalyst precursor; this shows that the same active species is formed under catalytic conditions. These conditions (large excess of alkyne) are those favoring complex **4**, which is most likely the main responsible for catalysis, through cycle B. Then, the catalytic alkyne hydrogenation in a sequential way is a consequence of the preponderance of the dinuclear mechanism over the mononuclear.

Conclusion

The studies reported in this article support the formulation of a new dinuclear mechanistic route for alkyne to alkene hydrogenation, which operates in pyrazolate-bridged diiridium complexes that contain a bridging hydride. Given that each metal center of these dinuclear compounds has only one labile coordination site, the novelty of this mechanism lies in the fact that the two labile positions of the dinuclear species are used for reactant coordination and product release in a concerted way. The necessary communication between the metal centers is established by hydride migrations.

Further support for the occurrence of such dinuclear hydrogenation process is provided by the observation of an alternative mononuclear route. The latter is the only one possible after *ortho*-metallation of one diphenylvinyl ligand, which blocks one labile position of the dinuclear species. Under such conditions, alkyne hydrogenation is still possible but the release of the alkene is hindered and, in consequence, the reaction product is the alkane. For reaction intermediates where the two mechanisms can compete, the selectivity observed strongly suggests that the dinuclear pathway is favored.

Experimental Section

Physical Measurements: Infrared spectra were recorded as Nujol mulls on polyethylene sheets with a Nicolet 550 spectrometer. C, H, and N analyses were carried out with a Perkin–Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on a Varian UNITY, a Varian Gemini 2000 or a Bruker ARX 300 MHz spectrometer. ^{1}H, ^{2}H, and ^{13}C chemical shifts were measured relative to partially deuterated (or protonated) solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P 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. 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 about 30 kV, and NBA was used as the matrix.

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 complex $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H_3(NCCH_3)(P\textit{i}Pr_3)_2]$ (**1**) was prepared as described in ref. [4].

Preparation of $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}\{(Z)\text{-}C(Ph){=}CHPh\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (2): A solution of **1** (230 mg, 0.26 mmol) in toluene (5 mL) was treated with diphenylacetylene (236 mg, 1.30 mmol) and stirred for 24 h at room temperature. The solvent was removed and the residue treated with methanol to give a yellow solid. This was decanted, washed with methanol, and dried in vacuo. Yield: 279 mg (87%); IR (Nujol): $\tilde{\nu}$ = 1716 (Ir-H-Ir), 1595, 1556 cm^{-1} (C=C); ^1H NMR (300 MHz, $CDCl_3$, 293 K): $\delta = -23.16$ (dd, J(H,P) = 13.2, 2.1 Hz, 1H; IrHIr), 1.01 (dd, J(H,P) = 12.6 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.09 (dd, J(H,P) = 13.5 Hz, J(H,H) = 7.5 Hz, 9H; PCHCH_3), 1.18 (dd, J(H,P) = 13.2 Hz, J(H,H) = 7.5 Hz, 9H; PCHCH_3), 1.34 (dd, J(H,P) = 12.6 Hz, J(H,H) = 7.5 Hz, 9H; PCHCH_3), 1.76 (s, 3H; NCCH_3), 2.7 (m, 6H; PCHCH$_3$), 5.74 (dt, J(H,P) = J(H,H) = 1.5 Hz, 1H; CH), 5.94 (dt, J(H,P) = J(H,H) = 1.5 Hz, 1H; CH), 6.21 (s, 1H; CH), 6.47 (t, J(H,H) = 7.5 Hz, 1H; CH), 6.52 (d, J(H,H) = 7.5 Hz, 2H; CH), 6.70 (t, J(H,H) = 7.5 Hz, 1H; CH), 6.74 (d, J(H,H) = 7.5 Hz, 1H; CH), 6.78 (s, 1H; CH), 6.82 (d, J(H,H) = 7.5 Hz, 1H; CH), 6.92 (t, J(H,H) = 7.5 Hz, 2H; CH), 6.96 (d, J(H,H) = 1.5 Hz, 1H; CH), 7.02–7.32 (m, 11H; all CH), 7.47 (d, J(H,H) = 7.5 Hz, 2H; CH), 7.83 (m, 1H; CH); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 293 K): $\delta = -5.61$ (s), -6.85 (s); ^{13}C NMR (75 MHz, $CDCl_3$, 293 K): δ = 1.30 (s, NCCH$_3$), 19.39 (d, J(C,P) = 2.1 Hz, PCHCH$_3$), 19.65, 20.04, 20.24 (all s, PCHCH$_3$), 23.93 (d, J(C,P) = 28.0 Hz, PCHCH$_3$), 25.32 (d, J(C,P) = 27.9 Hz, PCHCH$_3$), 103.27 (d, J(C,P) = 3.0 Hz, CH), 103.35 (d, J(C,P) = 3.0 Hz, CH), 104.12 (d, J(C,P) = 6.6 Hz, C), 117.15 (s, CH), 117.47 (s, NCCH$_3$), 119.32, 119.57 (both s, CH), 119.64 (d, J(C,P) = 6.2 Hz, C), 123.50, 123.61, 124.58, 124.80, 127.28, 127.71, 127.89, 127.93 (all s, CH), 133.28 (d, J(C,P) = 7.7 Hz, C), 134.03 (d, J(C,P) = 3.0 Hz, CH), 134.88 (s, CH), 136.27 (d, J(C,P) = 2.8 Hz, CH), 136.92 (d, J(C,P) = 3.0 Hz, CH), 138.13 (d, J(C,P) = 4.1 Hz, CH), 139.61, 141.46 (both s, C), 141.58 (s, CH), 152.88 (s, C), 164.45 (d, J(C,P) = 1.0 Hz, C); elemental analysis calcd (%) for $C_{54}H_{73}N_5Ir_2P_2$ (1238.6): C 52.36, H 5.94, N 5.65; found C 52.26, H 5.84, N 5.63.

Preparation of $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H_2\{(Z)\text{-}C(Ph){=}CHPh\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (3): A solution of **1** (230 mg, 0.26 mmol) in toluene (10 mL) at 273 K was treated with diphenylacetylene (46 mg, 0.26 mmol). After 15 min, the yellow solution was evaporated to dryness and treated with diethyl ether to give a pale yellow solid, which was decanted, washed with diethyl ether, and dried in vacuo. Yield: 197 mg (71%); ^1H NMR (300 MHz, C_6D_6, 293 K): $\delta = -25.93$ (br, 1H; IrHIr), -21.93 (d, J(H,P) = 21.6 Hz, 1H; IrH), -20.38 (dd, J(H,P) = 18.0 Hz, J(H,H) = 4.2 Hz, 1H; IrH), 0.52 (br, 3H; NCCH$_3$), 0.70 (br, 9H; PCHCH_3), 0.90 (dd, J(H,P) = 13.2 Hz, J(H,H) = 7.8 Hz, 9H; PCHCH_3), 1.02 (dd, J(H,P) = 12.9 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.25 br dd, J(H,P) = 12.9 Hz, J(H,H) = 6.9 Hz, 9H; PCHCH_3), 2.13 (m, 3H; PCHCH$_3$), 2.39 (br, 3H; PCHCH$_3$), 6.11 (br, 1H; CH), 6.40 (br, 1H; CH), 6.87 (t, J(H,H) = 6.6 Hz, 1H; CH), 7.0–7.27 (m, 9H; all CH), 7.68 (br, 2H; CH), 7.70 (s, 1H; CH), 8.20 (br, 1H; CH), 8.49 (br, 1H; CH); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 293 K): δ = 12.99 (s), 3.17 (br); elemental analysis calcd (%) for $C_{40}H_{65}N_5Ir_2P_2$ (1062.3): C 45.22, H 6.16, N 6.59; found C 45.48, H 5.97, N 6.15.

Preparation of $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{(Z)\text{-}C(Ph){=}CHPh\}_2(NCCH_3)(P\textit{i}Pr_3)_2]$ (4): A solution of **3** (130 mg, 0.12 mmol) in toluene (10 mL) at 273 K was treated with diphenylacetylene (40 mg, 0.22 mmol). After 30 min, the yellow solution was evaporated to dryness and treated with hexane to give a yellow solid, which was decanted, washed with hexane, and dried in vacuo. Yield: 132 mg (87%); IR (Nujol): $\tilde{\nu}$ = 2208 (Ir–H), 1688 (Ir-H-Ir), 1593, 1549 cm^{-1} (C=C); ^1H NMR (300 MHz, C_6D_6, 293 K): $\delta = -24.42$ (dd, J(H,P) = 12.6, 2.4 Hz, 1H; IrHIr), -21.31 (d, J(H,P) = 21.6 Hz, 1H; IrH), 0.58 (s, 3H; NCCH$_3$), 0.76 (br dd, 9H; PCHCH_3), 1.09 (dd, J(H,P) = 12.3 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.14 (dd, J(H,P) = 12.6 Hz, J(H,H) = 7.5 Hz, 9H; PCHCH_3), 1.38 (br, 9H; PCHCH_3), 2.48 (m, 3H; PCHCH$_3$), 2.59 (br, 3H; PCHCH$_3$), 5.96 (dt, J(H,P) = J(H,H) = 1.8 Hz, 1H; CH), 6.35 (dt, J(H,P) = J(H,H) = 1.8 Hz, 1H; CH), 6.80–6.88 (m, 3H; CH), 6.88 (s, 1H; CH), 6.97–7.20 (m, 17H; all CH), 7.37 (m, 1H; CH), 7.68 (br, 2H; CH), 8.14 (d, J(H,H) = 1.8 Hz, 1H; CH), 8.53 (m, 1H; CH); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 293 K): δ = 4.74 (s), -10.15 (s); ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ = 1.14 (s, NCCH$_3$), 19.63, 19.75, 21.20 (all s, PCHCH$_3$), 24.04 (d, J(C,P) = 27.0 Hz, PCHCH$_3$), 24.1 (br, PCHCH$_3$), 103.19 (d, J(C,P) = 3.1 Hz, CH), 104.52 (d, J(C,P) = 2.8 Hz, CH), 119.32 (s, NCCH$_3$), 124.06, 124.15, 124.45, 125.06 (all s, CH), 126.80 (d, J(C,P) = 7.2 Hz, C), 127.91, 128.19, 128.45, 128.53, 128.63, 128.76, 130.99, 131.09, 132.71 (all s, CH), 133.35 (d, J(C,P) = 7.8 Hz, C), 136.33 (d, J(C,P) = 4.0 Hz, CH), 136.73 (d, J(C,P) = 3.2 Hz, CH), 137.04 (d, J(C,P) = 4.0 Hz, CH), 138.17 (d, J(C,P) = 2.5 Hz, CH), 140.58, 141.49 (both s, C), 141.82 (d, J(C,P) = 1.0 Hz, CH), 152.43, 157.41 (both s, C); elemental analysis calcd (%) for $C_{54}H_{75}N_5Ir_2P_2$ (1240.6): C 52.28, H 6.09, N 5.64; found C 52.17, H 5.93, N 5.55.

Preparation of $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (5): A solution of **4** (130 mg, 0.10 mmol) in toluene (5 mL) was stirred at 318 K for 2 h. The resulting solution was evaporated to dryness and treated with hexane to give a yellow solid, which was decanted, washed with hexane, and dried in vacuo. Yield: 100 mg (90%); IR (Nujol): $\tilde{\nu}$ = 2174 (Ir–H), 1726 cm^{-1} (Ir-H-Ir); ^1H NMR (300 MHz, C_6D_6, 293 K): $\delta = -24.59$ (ddd, J(H,P) = 13.5, 3.9 Hz, J(H,H) = 4.2 Hz, 1H; IrHIr), -20.04 (dd, J(H,P) = 19.8 Hz, J(H,H) = 4.2 Hz, 1H; IrH), 0.62 (s, 3H; NCCH$_3$), 0.93 (dd, J(H,P) = 13.2 Hz, J(H,H) = 6.9 Hz, 9H; PCHCH_3), 1.14 (dd, J(H,P) = 12.6 Hz, J(H,H) = 7.5 Hz, 9H; PCHCH_3), 1.15 (dd, J(H,P) = 13.2 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.31 (dd, J(H,P) = 12.9 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 2.28 (m, 6H; PCHCH$_3$), 6.01 (dt, J(H,P) = J(H,H) = 1.5 Hz, 1H; CH), 6.21 (dt, J(H,P) = J(H,H) = 1.5 Hz, 1H; CH), 6.63 (s, 1H; =CH), 6.82 (t, J(H,H) = 7.5 Hz, 1H; CH), 7.05 (t, J(H,H) = 7.5 Hz, 1H; CH), 7.15 (t, J(H,H) = 7.5 Hz, 1H; CH), 7.28 (d, J(H,H) = 7.5 Hz, 1H; CH), 7.29 (d, J(H,H) = 7.5 Hz, 1H; CH), 7.33 (t, J(H,H) = 7.5 Hz, 2H; CH), 7.63 (m, 2H; CH), 7.81 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.83 (d, J(H,H) = 7.5 Hz, 2H; CH), 7.88 (m, 1H; CH); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 293 K): δ = 12.99 (s), -4.15 (s); ^{13}C NMR (75 MHz, C_6D_6, 293 K): δ = 1.11 (s, NCCH$_3$), 18.88, 19.21, 19.55, 20.05 (all s, PCHCH$_3$), 25.58 (d, J(C,P) = 27.9 Hz, PCHCH$_3$), 26.71 (d, J(C,P) = 29.8 Hz, PCHCH$_3$), 103.32 (d, J(C,P) = 2.1 Hz, CH), 104.13 (d, J(C,P) = 2.0 Hz, CH), 112.13 (d, J(C,P) = 5.8 Hz, C), 117.95 (s, NCCH$_3$), 118.21 (s, CH), 119.42 (d, J(C,P) = 8.7 Hz, C), 120.47, 121.07, 124.99, 126.08, 128.55, 132.84 (all s, CH), 134.22 (d, J(C,P) = 2.0 Hz, CH), 135.43 (d, J(C,P) = 2.5 Hz, CH), 136.79 (d, J(C,P) = 3.3 Hz, CH), 138.07 (d, J(C,P) = 4.0 Hz, CH), 141.03, 165.82 (both s, C); elemental analysis calcd (%) for $C_{40}H_{63}N_5Ir_2P_2$ (1060.3): C 45.31, H 5.99, N 6.60; found C 45.33, H 5.86, N 6.55.

$[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(OC(CD_3)_2)(P\textit{i}Pr_3)_2]$ (6) and $[Ir_2(\mu\text{-H})(\mu\text{-Pz})_2H\{\eta^1\text{-}C_6H_4\text{-}2\text{-}[\eta^1\text{-}(Z)\text{-}C{=}CHPh]\}(NCCH_3)(P\textit{i}Pr_3)_2]$ (7): In an NMR tube, a slow stream of hydrogen was bubbled through a suspension of complex **2** (50 mg, 0.04 mmol) in [D$_6$]acetone (0.5 mL) at 273 K. After about 1 min, when the solid was completely dissolved, argon was bubbled through the solution for 2 min in order to remove the excess of dissolved hydrogen. The spectroscopic analysis of the resulting solution at 263 K shows the presence of the organic products 1,2-diphenylethane, *cis*-stilbene, and *trans*-stilbene (molar ratio: 21:42:37) and the organometallic species **5**, **6**, and **7** in molar ratio: 20:75:5 (traces of complex **3** were also observed). At room temperature, compound **6** slowly transforms into **7**, and, after 3 h, the solution contains the complexes **5** and **7** in about 20:80 molar ratio.

Data for **6**: ^1H NMR (300 MHz, [D$_6$]acetone, 263 K): $\delta = -16.42$ (dd, J(H,P) = 19.2 Hz, J(H,H) = 13.8 Hz, 1H; IrH), -11.16 (ddd, J(H,P) = 13.5, 7.2 Hz, J(H,H) = 13.8 Hz, 1H; IrHIr), 1.06 (dd, J(H,P) = 13.8 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.10 (dd, J(H,P) = 14.4 Hz, J(H,H) = 7.5 Hz, 9H; PCHCH_3), 1.26 (dd, J(H,P) = 13.8 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 1.30 (dd, J(H,P) = 14.1 Hz, J(H,H) = 6.9 Hz, 9H; PCHCH_3), 2.34, 2.47 (both m, 3H; PCHCH$_3$), 5.43 (dt, J(H,P) = 1.8 Hz, J(H,H) = 2.1 Hz, 1H; CH), 5.79 (dt, J(H,P) = J(H,H) = 1.8 Hz, 1H; CH), 6.34, 6.54 (both td, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 6.66 (dd, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 6.67 (d, J(H,H) = 1.8 Hz, 1H; CH), 6.77 (s, 1H; CH), 7.11 (m, 1H; CH), 7.16 (dd, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 7.27 (m, 3H; CH), 7.38 (d, J(H,H) = 2.1 Hz, 1H; CH), 7.52 (dd, J(H,H) = 7.5, 1.1 Hz, 2H; CH), 7.75 (m, 1H; CH); $^{31}P\{^1H\}$ NMR (121 MHz, [D$_6$]acetone, 263 K): δ = 17.53 (s), 7.28 (s); ^{13}C NMR (75 MHz, [D$_6$]acetone, 263 K): $\delta = -19.37$, 19.49, 20.18 (all s, PCHCH$_3$), 24.34 (d, J(C,P) = 29.2 Hz, PCHCH$_3$), 26.32 (d, J(C,P) = 28.9 Hz, PCHCH$_3$), 103.95 (d, J(C,P) = 2.3 Hz, CH), 105.08 (d, J(C,P) = 3.0 Hz, CH), 118.19, 119.26 (both s, CH), 121.53 (d, J(C,P) = 7.7 Hz, C), 122.50 (s, CH), 123.53 (d, J(C,P) = 6.8 Hz, C), 124.58, 124.86, 128.10 (all s, CH), 133.79 (d, J(C,P) = 3.0 Hz, CH), 134.71 (s, CH), 138.45 (d, J(C,P) = 4.5 Hz, CH), 143.12 (d, J(C,P) = 3.8 Hz, CH), 143.62 (s, C), 143.83 (d, J(C,P) = 5.0 Hz, CH), 167.09 (s, C), 224.98 (s, OC(CD$_3$)$_2$).

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Data for **7**: ^{1}H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -16.35$ (dd, J(H,P) = 18.9 Hz, J(H,H) = 14.4 Hz, 1H; IrH), −12.49 (ddd, J(H,P) = 13.8, 6.6 Hz, J(H,H) = 14.4 Hz, 1H; IrHIr), 1.11, 1.16 (both dd, J(H,P) = 14.7 Hz, J(H,H) = 6.9 Hz, 9H; PCHCH_3), 1.32, 136 (both dd, J(H,P) = 12.9 Hz, J(H,H) = 7.2 Hz, 9H; PCHCH_3), 2.33, 2.43 (both m, 3H; PCHCH$_3$), 2.56 (s, 3H; NCCH$_3$), 5.51 (dt, J(H,P) = J(H,H) = 2.1 Hz, 1H; CH), 5.83 (dt, J(H,P) = J(H,H) = 1.8 Hz, 1H; CH), 6.35, 6.51 (both td, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 6.71 (dd, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 6.75 (s, 1H; CH), 6.83 (d, J(H,H) = 1.8 Hz, 1H; CH), 7.08 (dd, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 7.15 (td, J(H,H) = 7.5, 1.2 Hz, 1H; CH), 7.16 (m, 1H; CH), 7.26 (m, 3H; CH), 7.52 (dd, J(H,H) = 7.5, 1.1 Hz, 2H; CH), 7.71 (m, 1H; CH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone, 293 K): $\delta = 20.16$ (s), 6.79 (s); ^{13}C NMR (75 MHz, [D$_6$]acetone, 293 K): $\delta = 3.30$ (s, NCCH$_3$), 19.49 (d, J(C,P) = 1.4 Hz, PCHCH$_3$), 19.69, 20.03 (both s, PCHCH$_3$), 20.54 (d, J(C,P) = 1.0 Hz, PCHCH$_3$), 24.75 (d, J(C,P) = 29.9 Hz, PCHCH$_3$), 26.53 (d, J(C,P) = 28.5 Hz, PCHCH$_3$), 104.12, 105.18 (both d, J(C,P) = 3.2 Hz, CH), 118.61 (s, CH), 119.28 (s, NCCH$_3$), 119.66 (s, CH), 121.28 (d, J(C,P) = 8.7 Hz, C), 122.14 (d, J(C,P) = 6.4 Hz, C), 122.95, 124.91, 125.25, 128.48, 128.79 (all s, CH), 134.17 (d, J(C,P) = 3.2 Hz, CH), 135.08 (s, CH), 138.50 (d, J(C,P) = 4.6 Hz, CH), 143.11 (d, J(C,P) = 3.7 Hz, CH), 143.36 (d, J(C,P) = 5.1 Hz, CH), 143.87 (s, C), 167.39 (s, C); MS (FAB$^+$): m/z (%): 1060 (45) $[M]^+$.

Catalytic reactions and kinetic analysis: The catalytic reactions were carried out in a conventional glass hydrogenation apparatus equipped with a shaker. The reaction conditions were as follows: solvent benzene (8 mL); [**1**] = 7×10^{-4} M; [PhC≡CPh] = 0.35 M; T = 293 K; $P(H_2)$ = 1 atm. The course of the catalytic reaction was followed by GC in a HP 5890 series II gas chromatograph with a HP-Innowax cross-linked polyethylenglicol column (30 m × 0.53 mm × 1.0 μm) at 493 K. The pseudo-first-order rate constants for these hydrogenations were obtained from gas-uptake measurements during the initial part of the catalytic reactions (ca. 20%). The kinetics of the transformation of **4** into **5** were measured in 0.05 M solutions of **4** in [D$_8$]toluene. The decrease of the intensity of the ^{31}P{^{1}H} NMR signals of **4** were measured automatically at intervals in a Varian Gemini 2000 spectrometer. The pseudo-first-order rate constants were obtained by fitting the data to an exponential decay function, with the routine programs of the spectrometer.

Crystal structure determination of 2: Suitable crystals for X-ray diffraction were obtained from a saturated solution in acetone stored at 273 K over a number of days. A summary of crystal data and refinement parameters is reported in Table 2. Intensity data were collected at 160 K on a CCD Bruker AXS-SMART diffractometer equipped with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$), and by using ω rotations with narrow frames (0.3°; $2.9 \le 2\theta \le 56.9°$). Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times and no decay was observed. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied (min. and max. transmission factors 0.500 and 0.603).[13] The structure was solved by standard Patterson and difference Fourier methods.[14] High thermal parameters identified the presence of static disorder in a phenyl group. The disorder was modeled with the splitting of the C(30)–C(35) atoms, and refined initially with geometrical constrains (AFIX command). Anisotropic thermal parameters were applied for all nondisordered non-hydrogen atoms. Geometric constraints were eliminated in the final steps of refinement. The bridging hydride, H(1), and the vinylic hydrogens, H(8) and H(37), were included in the refinement from observed positions and refined as free isotropic atoms. All the remaining hydrogen atoms were included from calculated positions and refined with riding positional and displacement parameters. Two molecules of acetone were detected as crystallization solvent and included in the model. Refinements were carried out by full-matrix least-squares on F^2 (SHELXL-97).[15] Residual peaks in the final difference map were 1.23 and −1.20 e Å^{-3}. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement programs. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136606. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Crystallographic data and structure refinement for **2**.

formula	$C_{54}H_{73}Ir_2N_5P_2.2(CH_3)_2CO$
M_w	1354.67
T [K]	160(2)
space group	$P\bar{1}$
a [Å]	11.9322(10)
b [Å]	15.2124(12)
c [Å]	17.4017(14)
α [°]	95.650(2)
β [°]	95.029(2)
γ [°]	111.530(2)
V [Å^3]	2897.8(4)
Z	2
ρ_{calcd} [g cm^{-3}]	1.553
μ(Mo$_{K\alpha}$) [mm^{-1}]	4.688
$R(F)$ [$F^2 > 2\sigma(F^2)$][a]	0.0337
$wR(F^2)$[b] [all data]	0.0679
S[c] [all data]	1.036

[a] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for 9962 observed reflections. [b] $wR(F^2) = (\Sigma[w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]^{1/2}$. [c] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$; ($n$ = number of reflections, p = number of parameters).

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