Unusual 1-Alkyne Dimerization/Hydrogenation Sequences Catalyzed by $[Ir(H)_2(NCCH_3)_3(P\text{-}i\text{-}Pr_3)]BF_4$: Evidence for Homogeneous-Like Mechanism in Imidazolium Salts

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Abstract: The reaction of complex $[Ir(H)_2(NCCH_3)_3(P\text{-}i\text{-}Pr_3)]BF_4$ (**1**) with excess of 1-alkynes such as *t*-BuC≡CH and PhC≡CH gave the butadiene compounds $Ir[\eta^4\text{-}(R)_2C_4H_4](NCCH_3)_2(P\text{-}i\text{-}Pr_3)]BF_4$ (R = *t*-Bu, **5**; R = Ph, **6**). Compound **5** was obtained as a single isomer containing a 1,3-disubstituted butadiene ligand, whereas **6** was formed as a 7:1 mixture of isomers containing 1,3- and 1,4-disubstituted butadienes, respectively. Spectroscopic observations showed alkenyl hydride reaction intermediates, consistent with a double insertion/C-C coupling sequence. Complexes **5** and **6** were found to react with dihydrogen to give **1** and alkenes resulting from the partial hydrogenation of the butadiene moieties. This dimerization/hydrogenation sequence has been found to be the major reaction of *t*-BuC≡CH under conditions of homogeneous hydrogenation whereas that of PhC≡CH produced styrene and ethylbenzene as major products. Similar selectivity was observed for these hydrogenations using organic/ionic liquid biphasic conditions with toluene/$BMIM\cdot BF_4$, suggesting reaction mechanisms similar to those operating under homogeneous conditions. This conclusion is also supported by the spectroscopic observation of alkenyl hydride intermediates during the formation of **6** in $BMIM\cdot BF_4$ as solvent.

Keywords: alkynes; biphasic catalysis; homogeneous catalysis; hydrogenation; ionic liquids, iridium

Introduction

The investigation of biphasic catalytic systems based on ionic liquids has demonstrated that most homogeneous catalytic reactions can be transferred to such biphasic media without requiring substantial modification of the catalyst precursors or the reaction conditions.[1] This lack of special requirements enhances the attractiveness of using ionic liquids as immobilizing agents allowing facile catalyst recycling whilst maintaining the characteristic selectivity of molecular catalysts. In addition, it has been observed that the ligand effects typical of some homogeneous processes remain operative under such biphasic conditions,[2] suggesting the occurrence of similar reaction mechanisms in both media, and indicating that our current understanding of structure/function relationships in solution could also be used for catalyst improvement in ionic liquids. Nevertheless, other studies have found reaction selectivities strongly dependent on the features of the ionic liquid,[3] evidencing possible non-innocent roles of these immobilizing media during catalysis.[4] Due to the latter traits and the lack of mechanistic studies on these biphasic systems, whether or not the catalytic mechanisms in solution can be extrapolated to ionic liquids remains open to discussion.

In this paper, we present experimental evidence indicating that similar mechanisms are operating in both organic solvents and in 1,3-dialkylimidazolium-based ionic liquids, during the hydrogenation of 1-alkynes catalyzed by the compound $[Ir(H)_2(NCCH_3)_3(P\text{-}i\text{-}Pr_3)]BF_4$ (**1**). This hydrogenation system has been found to be highly diagnostic, due to the spectroscopic accessibility of its reaction intermediates and to the occurrence of an unusual hydrogenative dimerization reaction, which is competitive with alkyne hydrogenation, and strongly dependent upon the alkyne's features.

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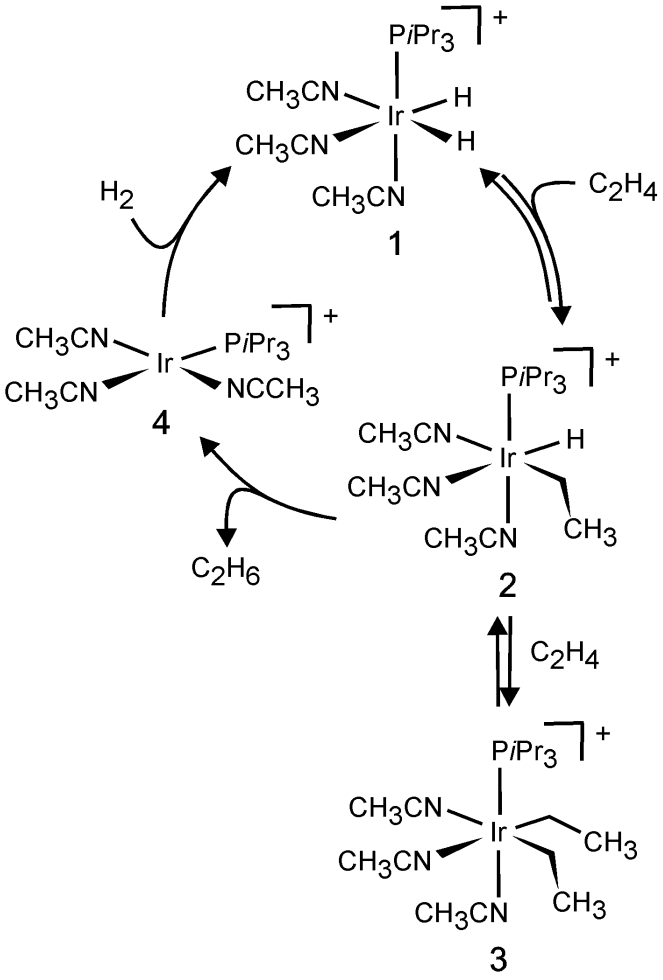
Results and Discussion

Recently, we have reported on the catalytic activity of complex **1** in alkene hydrogenation reactions.[5] This compound has also been found to facilitate the spectroscopic observation and characterization of labile species likely involved in the catalytic cycles, as illustrated by the intermediates of ethene hydrogenation depicted in Scheme 1. A noticeable feature of this cycle is the formation of the bis-ethyl compound **3**, which results from an unusual double insertion of ethene into the two Ir-H bonds of **1**. The reaction pathway opened by this double insertion was found to be non-productive given that the hydrogen β-elimination from **3** to reform **2** seems to be kinetically favored over the reductive elimination of butane.

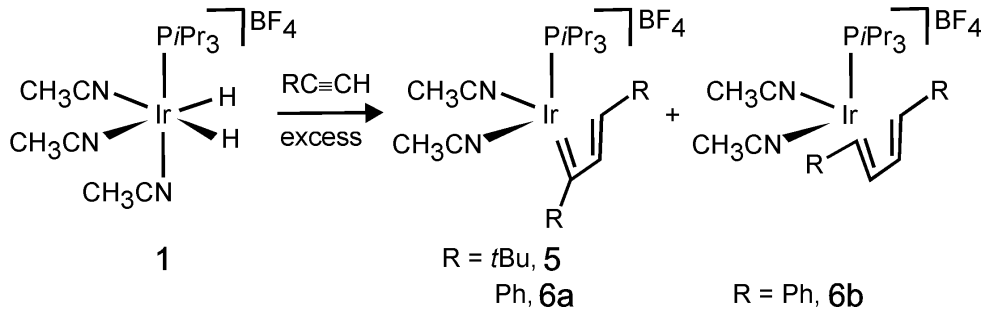


Scheme 1.

In an attempt at exploiting the potential of these double insertions in C-C coupling reactions, we have explored the reactivity of **1** towards alkynes. In reference to well-established trends in organometallic reactivity, such substrates are likely to provide favorable relationships between β-elimination and C-C reductive elimination rates. In fact, to the best of our knowledge, the facile β-elimination of hydrogen from an alkenyl ligand has never been reported, and the reductive coupling of two sp^2 carbons has been found to be favored over that of sp^3 ones.[6] In agreement with these expectations, the reaction of **1** with an excess of 1-alkynes such as PhC≡CH or *t*-BuC≡CH has been found to afford butadiene complexes (Scheme 2).

The stereoselectivity of these reactions has been found to be dependent on the 1-alkyne substrate. Thus, the reaction with *t*-BuC≡CH selectively gave compound $\{Ir[\eta^4\text{-}1,3\text{-}(t\text{-}Bu)_2C_4H_4](NCCH_3)_2(P\text{-}i\text{-}Pr_3)\}BF_4$ (**5**) in quantitative yield. The structure of **5** determined by X-ray diffraction is shown in Figure 1.[7] Under the same conditions, the reaction with PhC≡CH was less selective, leading to the compound $\{Ir[(\eta^4\text{-}(Ph)_2C_4H_4](NCCH_3)_2(P\text{-}i\text{-}Pr_3)\}BF_4$ (**6**) as a 7:1 mixture of isomers which contain 1,3- (**6a**) and 1,4-diphenylbutadiene (**6b**) ligands, respectively. The major isomer was isolated in an analytically pure state by crystallization of the product mixture in CH_2Cl_2/diethyl ether.

The NMR investigation of the course of these reactions in $CDCl_3$ at low temperature allowed observation of alkenyl hydride intermediates which are consistent with the expected double insertion/C-C coupling reaction sequence.[8] Thus, the treatment of **1** with one equivalent of PhC≡CH at 253 K readily afforded an equimolar mixture of two isomeric alkenyl hydride complexes, **7a** and **7b**, which have α- and β-(*Z*)-alkenyl ligands, respectively (Scheme 3). Both isomers were found to be stable towards the reductive elimination of styrene at room temperature. The reactivity of these two isomers towards a second equivalent of the alkyne was found to be different. Thus, **7b** readily



Scheme 2.

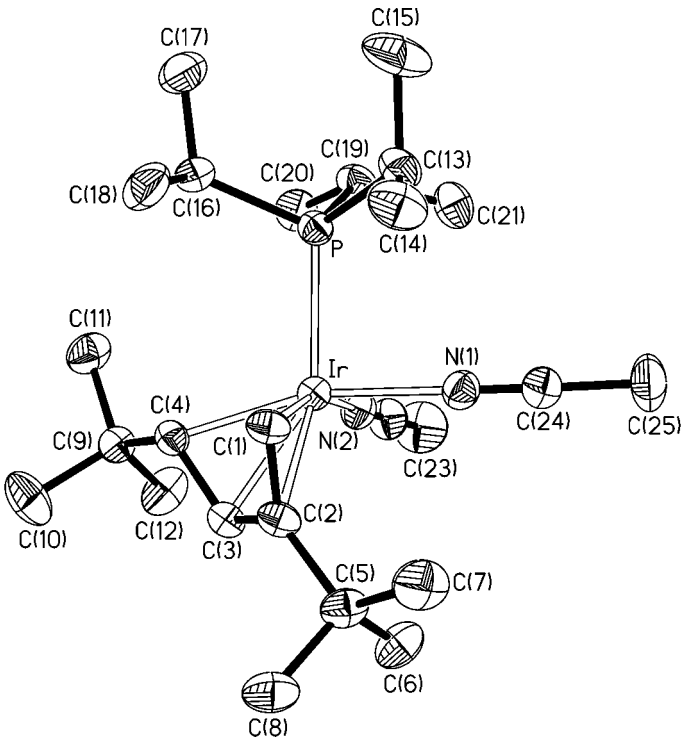
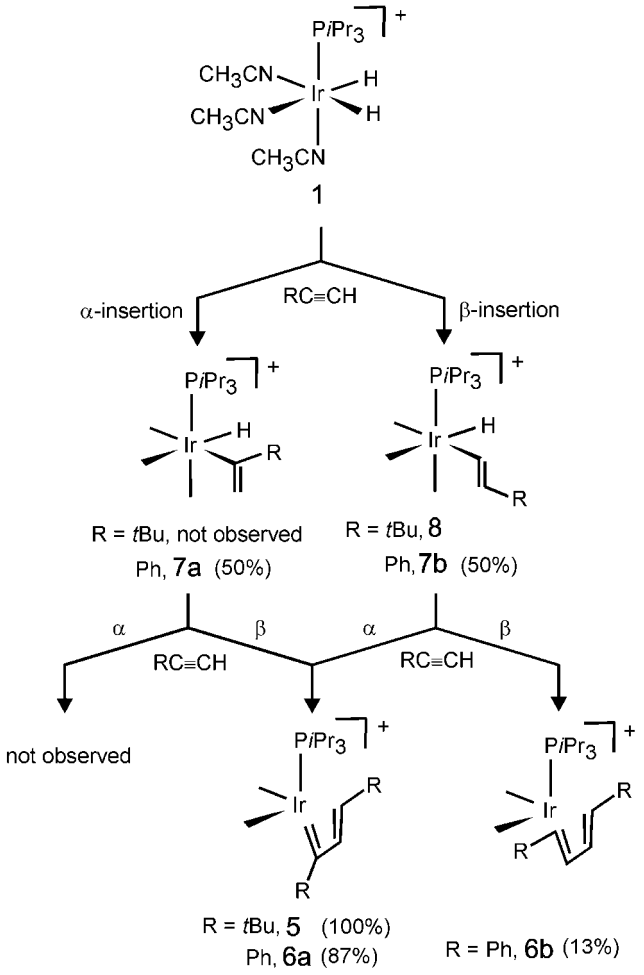


Figure 1. Molecular structure of the cation of complex **5** (ORTEP). Selected bond distances [Å] and angles [°]: Ir–P 2.3559(12), I–N1 2.1000(4), Ir–N2 2.090(4), Ir–C1 2.111(4), Ir–C2 2.193(4), Ir–C3 2.179(4), Ir–C4 2.151(4); C1–C2–C3 113.3(4), C2–C3–C4 118.6(4), C3–C4–C9 118.1(4).

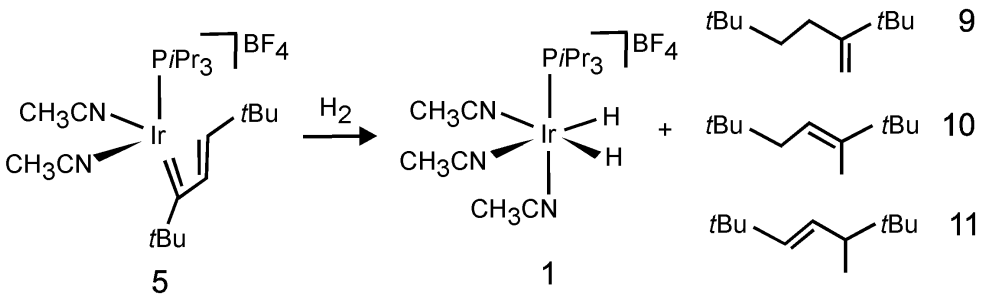


Scheme 3.

reacted with an excess of the alkyne at 253 K giving **6**, whereas the disappearance of the α-alkenyl hydride **7a** was slow even at temperatures above 273 K. In both cases, the spectroscopic observations did not allow the detection of additional intermediates of this second reaction step. This suggests that once the second insertion takes place, the subsequent C-C reductive coupling is fast.

The isomeric distribution of **6** resulting from the evolution of each alkenyl hydride intermediate revealed interesting stereochemical features. Thus, **7b** afforded **6a** and **6b** in a 3:1 molar ratio respectively, indicating that for the second alkyne insertion step, α-stereochemistry is preferred. On the contrary, the intermediate **7a** exclusively produced the isomer **6a**, most likely through a selective second insertion step of β-(*Z*)-stereochemistry. In the latter case, both the relative inertness of **7a** and its proclivity to undergo selective β-(*Z*)-insertions could be rationalized on the basis of the steric hindrance introduced by the α-alkenyl ligand. However, we still cannot offer a plausible rationale for the preferential α-stereochemistry of the second alkyne insertion in the β-(*Z*)-alkenyl hydride **7b.** Moreover, the use of *t*-BuC≡CH seems to enhance this latter stereochemical preference. Only one alkenyl hydride intermediate of β-(*Z*)-stereochemistry (**8**) could be detected along with the selective formation of the 1,3-disubstituted butadiene complex **5**, suggesting a sequence of two completely stereoselective insertions of β-(*Z*)- and α-stereochemistry, respectively. In this case, the formation of the butadiene complex could not be carried out stepwise since the first and second insertion steps seem to have comparable rates. In consequence, intermediate **8** was detected only as a minor component in the reaction mixture (10%).

The reaction of the butadiene compounds **5** and **6** with dihydrogen, in $CDCl_3$ and in excess of acetonitrile, has been found to give alkenes thus regenerating the starting complex **1** (Scheme 4). This reaction closes a possible cycle for hydrogenative dimerization of terminal alkynes which may operate at room temperature in dihydrogen at atmospheric pressure. The alkenes formed from hydrogenation of complex **5** were those shown in Scheme 4 and have been identified by mass spectrometry and NMR spectroscopy. Isomer **9** was found to be the main kinetic product of the reaction, although, at room temperature and in the presence of stoichiometric amounts of **1**, it was readily isomerized to **10** (major) and **11** (minor). The subsequent hydro-



Scheme 4.

genation of these alkenes to the alkane was not observed under such mild conditions. The hydrogenation of isomers **6** under the same conditions also produced **1** together with a complicated mixture of organic products which was not analyzed in detail.

Interestingly, the reaction sequence leading to products **9** – **11** was found to be the major reaction path when *t*-BuC≡CH and dihydrogen were treated with catalytic amounts of complex **1** in 1,2-dichloroethane (Figure 2a). As a contrast and under the same catalytic conditions, phenylacetylene mostly afforded simple hydrogenation products: styrene and ethylbenzene, amounting to 90% of all products at 90% conversion. With regard to the aforementioned experimental observations and mechanistic proposals, this dependence on the alkyne of the selectivity may arise from the competition of substrates for the alkenyl hydride reaction intermediates. Thus, under the actual catalytic conditions, the second insertion of *t*-BuC≡CH in intermediate **8** seems to be kinetically favored over its reaction with dihydrogen, whereas for intermediates **7** this latter reaction seems to be faster than the second PhC≡CH insertion. Such rationalization based on substrate competition, would imply a dependence of the reaction selectivity upon the relative concentration of the reactants. In agreement with this, the proportion of *t*-BuCH=CH_2 and *t*-$BuCH_2CH_3$ hydrogenation products was found to increase at low alkyne concentrations (Figure 2b). Under the latter conditions, the lower substrate/catalyst ratio led to a faster isomerization of the kinetic product **9** into its internal isomers **10** and **11**, and a faster hydrogenation of *t*-BuCH=CH_2 to *t*-$BuCH_2CH_3$. The decrease in the initial alkyne concentration also resulted in higher initial hydrogenation rates. A similar substrate inhibition effect has been observed with PhC≡CH, revealing a complex dependence of the hydrogenation rate upon the alkyne concentration and is currently under study.

To the best of our knowledge, a catalytic hydrogenative dimerization such as that leading to **9** – **11** has not been previously reported. With regard to this lack of precedent and the aforementioned mechanistic observations, the occurrence of such a transformation in the presence of iridium catalyst precursors could be considered as a sound indication for the participation of dihydride species and double insertion/C-C coupling sequences. In addition, considering that both the extent of this reaction under catalytic conditions and the stereochemistry of its products are strongly dependent on the alkyne features, it seems likely that small changes in the steric or electronic properties of the active species would lead to changes in the reaction outcome.

Despite the likely sensitivity of this hydrogenation system, the selectivity of the catalytic reactions remained essentially the same when the processes were carried out in toluene/1-butyl-3-methylimidazolium tetrafluoroborate (BMIM · BF_4) biphasic solvent mixtures. Thus, as in homogeneous conditions, PhC≡CH produced styrene and ethylbenzene (with C-C coupled products less than 4%), whereas *t*-BuC≡CH was transformed into a mixture of products similar to that obtained in 1,2-dichloroethane at low alkyne concentrations (Figure 2c). This would indicate that the changes in the active species provoked by variations of the reaction media are if any, very minor.

The minor differences in rate and selectivity of these latter reactions with respect to those in the homogeneous phase can be readily rationalized as a consequence of the expected low solubility of the substrates in the ionic liquid and mass transfer limitations. Thus, we observed that the increase of the initial alkyne concentration in the biphasic system had little effect on the reaction rate; a likely consequence of the limited solubility of this substrate in the ionic liquid. Similarly, the low solubility of the reaction products in the ionic liquid is expected to diminish the extent of isomerization of **9** and the hydrogenation of *t*-BuCH=CH_2, as was observed under biphasic conditions. In this way the partition of the primary (kinetic) products and the catalyst into their respective organic and ionic liquid phases, provides protection against further reduction or isomerization and this may be a useful feature for selective syntheses.

The similarity of the active species suggested by the above catalytic experiments is also in agreement with the conclusions of our spectroscopic observations on stoichiometric reactions of **1** with PhC≡CH and *t*-BuC≡CH in BMIM · BF_4 as solvent. In fact, the ^{31}P NMR spectra under *off resonance* conditions (allow-

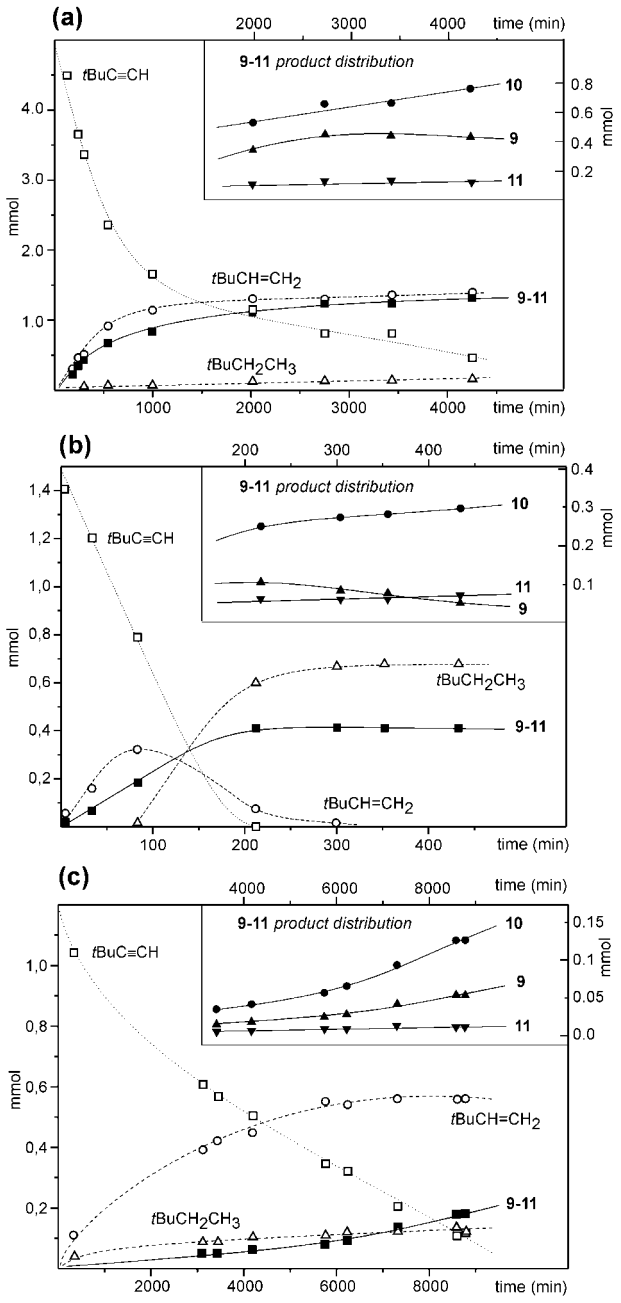


Figure 2. Reaction profiles for *t*-BuC≡CH hydrogenations catalyzed by **1**. Conditions: (**a**) 1,2-dichloroethane (8 mL), 293 K, $[\mathbf{1}]_o = 0.010$ mmol, $[t\text{-BuC}{\equiv}\text{CH}]_o = 5.0$ mmol, $P(H_2) = 1.1$ bar; (**b**) 1,2-dichloroethane (8 mL), 293 K, $[\mathbf{1}]_o = 0.015$ mmol, $[t\text{-BuC}{\equiv}\text{CH}]_o = 1.5$ mmol, $P(H_2) = 1.1$ bar; (**c**) toluene (6 mL), BMIM · BF_4 (2 mL), 293 K, **1** = 0.019 mmol, $[t\text{-BuC}{\equiv}\text{CH}]_o = 1.19$ mmol, $P(H_2) = 1.1$ bar.

ing hydride coupling) are indicative of the sequential formation of the alkenyl hydrides **7** and the butadiene complexes **6** on treatment of BMIM · BF_4 solutions of **1** with PhC≡CH at room temperature (Figure 3). Interestingly, the isomeric distributions of **6** and **7** obtained in this solvent were similar to those observed in $CDCl_3$, suggesting that the factors governing alkyne coordination and insertion remain unaltered despite the significant change in the solvent properties.

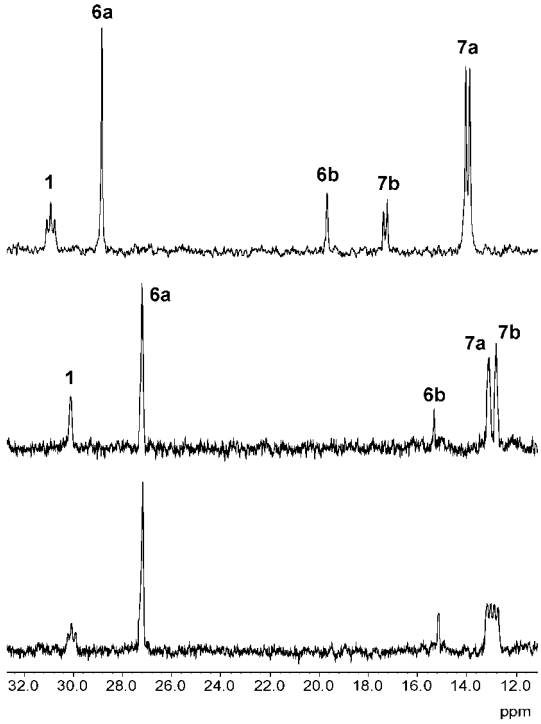


Figure 3. ^{31}P NMR spectra of compound mixtures obtained by treatment of **1** with PhC≡CH at room temperature: (above) ^{31}P *off resonance* spectrum in $CDCl_3$; (center) $^{31}P\{^1H\}$ spectrum in BMIM · BF_4; (below) ^{31}P *off resonance* spectrum in BMIM · BF_4.

Attempted recycling of the catalyst in the ionic liquid phase was met with fair success. In the case of *t*-BuC≡CH, the selectivity has been found to be maintained, although each recycling step brought about a progressive decrease in the activity (*ca.* 30%). When PhC≡CH was hydrogenated in toluene/BMIM · BF_4 (293 K, substrate/catalyst = 100), the total conversion of the substrate in 2 hours first reached 57% (styrene/ethylbenzene = 6:1), but then decreased to 25, 20 and 11% in the subsequent 2 hour runs, respectively, with an increase in the proportion of styrene over the fully hydrogenated product (10:1 ratio in the fourth run). In some cases, the catalyst-containing ionic liquid phase was washed with toluene between successive runs but this was found detrimental to the catalytic activity. It is conceivable that acetonitrile originating from the facile dissociation of the catalyst is removed as a result of the repeated removal of the organic phase (especially when the ionic liquid phase is washed with toluene between the runs), nevertheless, simple addition of acetonitrile to the toluene phase did not restore the catalytic activity. Although these latter findings show the limits of the use of $[Ir(H)_2(NCCH_3)_3(P\text{-}i\text{-}Pr_3)]BF_4$ (**1**) in toluene/BMIM · BF_4 biphasic systems, the unchanged selectivity of the hydrogenations together with the spectroscopic

observations reveal that no major changes in the hydrogenation mechanisms are brought about by the presence of the ionic liquid. This gives space to catalyst design. According to our preliminary results, the compound $[Ir(H)_2(C_6H_6)(P\text{-}i\text{-}Pr_3)]BF_4$[9] shows similar activity and selectivity but is substantially more robust than **1** under the same biphasic conditions.

Conclusions

Under hydrogenation conditions, the dihydride complex $[Ir(H)_2(NCCH_3)_3(P\text{-}i\text{-}Pr_3)]BF_4$ catalyzes unprecedented hydrogenative dimerizations of terminal alkynes. Such catalytic reactions involve butadiene iridium(I) intermediates, which are most likely formed through a reaction sequence comprising double insertion and C-C reductive coupling steps. The extent of this reaction under homogeneous catalytic conditions is strongly dependent on the alkyne features and the concentrations of the substrates. Despite this sensitivity, the selectivity of the catalytic reactions remains essentially the same for homogeneous (1,2-dichloroethane) or biphasic (toluene/$BMIM\cdot BF_4$) systems, suggesting a common mechanism under both experimental conditions. This conclusion is supported by the spectroscopic observation of similar alkenyl hydride and butadiene complexes, likely catalytic intermediates, in both 1,2-dichloroethane and $BMIM\cdot BF_4$ solutions.

Experimental Section

General Remarks

Reactions were carried out under exclusion of air by using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon just prior to use. PhC≡CH (Aldrich), was distilled under argon and stored over molecular sieves. *t*-BuC≡CH (Lancaster) was used as received without further purification. 1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIM\cdot BF_4$),[10] and the complex $[Ir(H)_2(NCCH_3)_3(P\text{-}i\text{-}Pr_3)]BF_4$ (**1**),[5] were prepared as previously reported. $BMIM\cdot BF_4$ was dried by azeotropic distillation with benzene several times, followed by prolonged evacuation. NMR spectra were recorded on Varian UNITY, Varian GEMINI 2000, or Bruker ARX, 7.04 T spectrometers, operating at 300 MHz (^1H), 121 MHz (^{31}P), and 75.2 MHz (^{13}C). ^1H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{31}P NMR chemical shifts were measured relative to H_3PO_4 (85%). The samples dissolved in $BMIM\cdot BF_4$ were examined without the addition of any deuterated compound or TMS. A capillary containing acetone-d_6 was added to provide a lock signal and an approximate reference. As a result of this referencing method, the chemical shifts are subject to a significant error due to susceptibility effects.[4a] ^{31}P *off resonance* spectra were recorded under continuous decoupling of the P-*i*-Pr_3 protons. Under these conditions, the large $J(H,P)$ coupling constants (19–21 Hz) due to hydride coupling were clearly observed, whereas smaller ones (2–3 Hz) due to possible couplings with alkenyl protons were not resolved. Spectral assignments were achieved by ^1H COSY, NOESY, and ^{13}C DEPT experiments. Infrared spectra were recorded as Nujol mulls on polyethylene sheets with use of a Bruker Equinox 55 spectrometer. IR frequencies are reported in cm^{-1}. C, H, N analyses were carried out using a Perkin-Elmer 2400B CHNS/O analyzer. MS data were recorded on a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^+ gun at *ca.* 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Conductivities were measured in *ca.* 3×10^{-4} M solutions with a Philips PW 9501/01 conductivity meter. GC analyses were preformed either on an Agilent 6890 Series gas chromatograph equipped with an Agilent 5973 mass selective detector and a 30 m (0.25 mm i. d.; 0.25 μm FT) HP-5MS column, or on a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with a flame ionization detector and a 25 m (0.32 mm i. d., 0.17 μm FT) HP Ultra 1 column. Calibration of the detector response to the substrates and products was made by comparing the GC integrals with those obtained in the same samples by $^{13}C\{^1H\}$ NMR, setting the relaxation delay between pulses to 30 s.

Synthesis of $\{Ir[\eta^4\text{-}1,3\text{-}(t\text{-}Bu)_2C_4H_4](NCCH_3)_2(P\text{-}i\text{-}Pr_3)\}BF_4$ (5)

A solution of **1** (100 mg, 0.18 mmol) in acetone (5 mL) at 273 K was treated with *t*-BuC≡CH (43.4 μL, 0.35 mmol), and allowed to react for 2 h at room temperature. The resulting red solution was concentrated to *ca.* 0.5 mL, layered with diethyl ether, and stored at 273 K for 24 h to yield pale yellow crystals. The crystals were separated by decantation and washed with diethyl ether; yield: 111 mg (90%). Anal. calcd. for $C_{25}H_{49}N_2BF_4IrP$: C 43.67, H 7.18, N 4.07%; found: C, 43.63; H, 7.49; N, 4.36%; IR: $\tilde{\nu}=1629$ (C=C), 1054 cm^{-1} (BF_4); ^1H NMR ($CDCl_3$, 293 K): $\delta=0.16$ [ddd, $J(H,H)=5.4$, 0.9 Hz, $J(H,P)=6.9$ Hz, 1H, CH_2=C(*t*-Bu)CH=CH(*t*-Bu)], 0.52 [dd, $J(H,H)=7.2$ Hz, $J(H,P)=5.7$ Hz, 1H, CH_2=C(*t*-Bu)CH=C*H*(*t*-Bu)], 0.95 [s, 9H, C(CH_3)$_3$], 1.25 [dd, $J(H,P)=13.5$ Hz, $J(H,H)=7.5$ Hz, 9H, PCHCH_3], 1.26 [s, 9H, C(CH_3)$_3$], 1.27 [dd, $J(H,P)=13.5$ Hz, $J(H,H)=7.8$ Hz, 9H, PCHCH_3], 2.42, (s, 3H, NCCH_3), 2.43 [d, $J(H,H)=5.4$ Hz, 1H, CH_2=C(*t*-Bu)CH=CH(*t*-Bu)], 2.49 (s, 3H, NCCH_3), 2.69 (m, 3H, PC*H*CH_3), 5.12 [ddd, $J(H,H)=7.2$, 0.9 Hz, $J(H,P)=3.0$ Hz, 1H, CH_2=C(*t*-Bu)C*H*=CH(*t*-Bu)]; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta=27.77$ (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta=3.09$, 3.36 (both s, NC*C*H$_3$), 11.64 [br, *C*H$_2$=C(*t*-Bu)CH=CH(*t*-Bu)], 18.76, 19.51 (both s, PCH*C*H$_3$), 27.13 [d, $J(C,P)=24.8$ Hz, P*C*HCH$_3$], 30.08 [s, CH_2=C(*t*-Bu)CH=*C*H(*t*-Bu)], 30.10, 30.90 [both s, C(*C*H$_3$)$_3$], 33.38, 34.18 [both s, *C*(CH$_3$)$_3$], 82.77 [d, $J(C,P)=4.6$ Hz, CH_2=C(*t*-Bu)*C*H=CH(*t*-Bu)], 110.62 [d, $J(C,P)=6.0$ Hz, CH_2=*C*(*t*-Bu)CH=CH(*t*-Bu)], 121.76, 124.11 (both s, N*C*CH$_3$); MS (FAB+): *m/z* (%) = 599 (5) [M^+], 560 (15) [M^+ – NCCH$_3$], 517 (100) [M^+ – CH_2=C(*t*Bu)]; Λ_M (4.8×10^{-5}, acetone) = 114 Ω^{-1} cm^2 mol^{-1} (1:1).

Synthesis of {Ir[η⁴-(Ph)$_2$C$_4$H$_4$](NCCH$_3$)$_2$(P-*i*-Pr$_3$)}BF$_4$ (6)

The same procedure described for **5** but starting from PhC≡CH (48.6 μL, 0.44 mmol) led to a pale yellow microcrystalline solid; Yield: 104 mg (80%). The NMR analysis of this solid revealed a mixture of complexes {Ir[η⁴-1,3-(Ph)$_2$C$_4$H$_4$](NCCH$_3$)$_2$(P-*i*-Pr$_3$)}BF$_4$ (**6a**) and {Ir[η⁴-1,4-(Ph)$_2$C$_4$H$_4$](NCCH$_3$)$_2$(P-*i*-Pr$_3$)}BF$_4$ (**6b**) in a 7:1 molar ratio. The solid was dissolved in *ca.* 1 mL of CH_2Cl_2, layered with diethyl ether, and stored at room temperature for 24 h. The yellow solid formed was separated by decantation, washed with diethyl ether and dried under vacuum. This solid was found to be 6a in purity >98% (NMR). The yield of the recrystallization step was 31%.

Data for **6a**: Anal. calcd. for $C_{29}H_{41}N_2BF_4IrP$: C 47.87, H 5.68, N 3.85%; found: C 47.71, H 6.04, N 3.94%; IR: $\tilde{\nu}$ = 1604 (C=C), 1064 cm^{-1} (BF_4); ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.73 [ddd, *J*(H,H) = 4.5, 0.8 Hz, *J*(H,P) = 5.1 Hz, 1H, C*H*$_2$=C(Ph)CH=CH(Ph)], 1.08, 1.10 [both dd, *J*(H,P) = 14.1 Hz, *J*(H,H) = 7.2 Hz, 9H each, PCHC*H*$_3$], 1.93, (br, 3H, NCCH$_3$), 2.00 [dd, *J*(H,H) = 6.6 Hz, *J*(H,P) = 5.1 Hz, 1H, CH$_2$=C(Ph)CH=C*H*(Ph)], 2.44 (m, 3H, PC*H*CH$_3$), 2.45 (s, 3H, NCCH$_3$), 2.61 [d, *J*(H,H) = 4.5 Hz, 1H, C*H*$_2$=C(Ph)CH=CH(Ph)], 6.21 [ddd, *J*(H,H) = 6.6, 0.8 Hz, *J*(H,P) = 3.0 Hz, 1H, CH$_2$=C(Ph)C*H*=CH(Ph)], 7.13–7.19 (m, 5H, Ph), 7.36–7.44 (m, 3H, Ph), 7.66 (m, 2H, Ph); ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 28.87 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 2.38 (br, NC*C*H$_3$), 3.48 (s, NC*C*H$_3$), 13.64 [d, *J*(C,P) = 2.3 Hz, *C*H$_2$=C(Ph)CH=CH(Ph)], 18.67, 18.78 (both s, PCH*C*H$_3$), 26.37 [d, *J*(C,P) = 26.3 Hz, P*C*HCH$_3$], 29.05 [d, *J*(C,P) = 1.4 Hz, CH$_2$=C(Ph)CH=*C*H(Ph)], 85.68 [d, *J*(C,P) = 6.0 Hz, CH$_2$=C(Ph)*C*H=CH(Ph)], 100.20 [d, *J*(C,P) = 5.1 Hz, CH$_2$=*C*(Ph)CH=CH(Ph)], 121.22 (br, N*C*CH$_3$), 121.62 (s, N*C*CH$_3$), 125.08, 126.73, 128.53, 128.64, 128.65, 129.03 (all CH), 136.41 [d, *J*(C,P) = 1.8 Hz, C], 143.66 (s, C); MS (FAB +): *m/z* (%) = 557 (100) [M$^+$ – Ph]; Λ_M (4.8 × 10^{-5}, acetone) = 109 Ω^{-1} cm^2 mol^{-1} (1:1).

Partial data for **6b** (from the **6a/6b** mixture): ^{1}H NMR ($CDCl_3$, 293 K): δ = 1.26 [dd, *J*(H,P) = 12.3 Hz, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.30 [dd, *J*(H,P) = 13.8 Hz, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 2.26 [m, 5H, PC*H*CH$_3$ + C*H*(Ph)=CH-CH=C*H*(Ph)], 2.33 (s, 6H, NCCH$_3$), 4.00 [dd, *J*(H,H) = 8.8 Hz, *J*(H,P) = 3.7 Hz, 2H, CH(Ph)=C*H*-C*H*=CH(Ph)]; ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 19.71 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 2.80 (s, NC*C*H$_3$), 19.15 (s, PCH*C*H$_3$), 24.65 [d, *J*(C,P) = 24.6 Hz, P*C*HCH$_3$], 48.66 [d, *J*(C,P) = 2.2 Hz, *C*H(Ph)=CH-CH=*C*H(Ph)], 80.42 [d, *J*(C,P) = 26.1 Hz, CH(Ph)=*C*H-*C*H=CH(Ph)], 112.96 (s, N*C*CH$_3$), 125.58, 127.66, 128.62 (all CH), 135.92 (s, C).

{Ir(H)[C(Ph)=CH$_2$](NCCH$_3$)$_3$(P-*i*-Pr$_3$)}BF$_4$ (7a) and [Ir(H)(*Z*-CH=CHPh)(NCCH$_3$)$_3$(P-*i*-Pr$_3$)]BF$_4$ (7b)

PhC≡CH (40 μL, 0.36 mmol) was slowly added to a stirred solution of complex **1** (200 mg, 0.36 mmol) in $CDCl_3$ (2 mL) at 253 K. 0.5 mL of this solution was transferred under argon to an NMR tube also cooled at 253 K. The NMR spectra of the solution recorded at 253 K revealed the formation of complexes **7a** and **7b** in equimolar amounts, together with minor amounts of complex 6a and traces of styrene. The sample was heated to 293 K and the stability of the reaction mixture was monitored for 4 hours during which periodic recordings of ^{1}H NMR spectra were made. Even though the sample decomposed partially (*ca.* 20%) throughout this period to give several unidentified products, such decomposition reactions did not produce styrene.

Partial data for **7a**: ^{1}H NMR ($CDCl_3$, 293 K): δ = – 22.29 [d, *J*(H,P) = 22.2 Hz, 1H, Ir-H], 0.87 [dd, *J*(H,P) = 13.8 Hz, *J*(H,H) = 7.2 Hz, 9H, PCHC*H*$_3$], 1.08 [dd, *J*(H,P) = 13.8 Hz, *J*(H,H) = 6.9 Hz, 9H, PCHC*H*$_3$], 1.91 (br, 3H, NCCH$_3$), 2.17 (m, 3H, PC*H*CH$_3$), 2.36 (s, 3H, NCCH$_3$), 2.42 (br, 3H, NCCH$_3$), 5.10, 5.45 [both d, *J*(H,H) = 2.4 Hz, 1H each, Ir-C(Ph)=C*H*$_2$]; ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 13.98 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 1.91 (br, NC*C*H$_3$), 3.04, 3.66 (both s, NC*C*H$_3$), 18.51, 19.30 (both s, PCH*C*H$_3$), 24.22 [d, *J*(C,P) = 33.0 Hz, P*C*HCH$_3$], 117.54 [d, *J*(C,P) = 16.5 Hz, N*C*CH$_3$], 119.76 (s, N*C*CH$_3$), 121.20 (s, Ir-C(Ph)=*C*H$_2$), 125.41, 127.71, 127.82 (all CH), 135.35 [d, *J*(C,P) = 8.2 Hz, Ir-*C*(Ph)=CH$_2$], 156.11 (s, C).

Partial data for **7b**: ^{1}H NMR ($CDCl_3$, 293 K): δ = – 22.20 [d, *J*(H,P) = 21.0 Hz, 1H, Ir-H], 6.43 [d, *J*(H,H) = 16.2 Hz, 1H, Ir-CH=C*H*Ph], 7.75 [dd, *J*(H,H) = 16.2 Hz, *J*(H,P) = 2.7 Hz, 1H, Ir-C*H*=CHPh]; ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 17.30 (s); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 137.65 [d, *J*(C,P) = 6.9 Hz, Ir-*C*H=CHPh].

{Ir(H)[*Z*-CH=CH(*t*-Bu)](NCCH$_3$)$_3$(P-*i*-Pr$_3$)}BF$_4$ (8)

The procedure described for the observation of isomers **7**, but using *t*-BuC≡CH (44 μL, 0.36 mmol), led to mixtures containing complexes **1**, **5**, and **8** in a 9:9:1 molar ratio, respectively.

Partial data for **8**: ^{1}H NMR ($CDCl_3$, 293 K): δ = – 22.01 [d, *J*(H,P) = 21.0 Hz, 1H, Ir-H], 5.26 [d, *J*(H,H) = 16.0 Hz, 1H, Ir-CH=C*H*(*t*-Bu)], 6.18 [dd, *J*(H,H) = 16.0 Hz, *J*(H,P) = 3.0 Hz, 1H, Ir-C*H*=CH(*t*-Bu)]; ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): δ = 14.88 (s).

Catalytic Reactions

The equipment consisted of a 25 mL two-necked flask fitted with a septum (to allow sampling without opening the system), and connected through a condenser to a conventional Schlenk manifold that used dihydrogen instead of inert gas. Magnetic stirring (1000 rpm) was used during the reactions. The progress of the reactions was followed by GC. Dry solvents should be used throughout. In a typical procedure for homogeneous reactions, complex **1** and octane (10 μL for internal reference) were dissolved in 8 mL of 1,2-dichloroethane. The solution was degassed and the system was refilled with dihydrogen at 1.1 bar, to exclude the penetration of air during sampling. Then, the substrate was injected through the septum. In the biphasic reactions, the catalyst was previously dissolved in 2 mL of BMIM·BF_4 under argon. Then, 6 mL of toluene containing the internal reference was added. The reaction mixture was degassed, put under dihydrogen and the substrate was added as in the homogeneous case. After completion of the reaction, the ionic liquid was separated by decantation. For recycling experiments, the products and the unreacted substrate were removed in the toluene phase through a cannula by applying a positive pressure of dihydrogen, and then reduced

pressure was used to introduce a new toluene solution prepared under dihydrogen. The pressure of the system was reset to 1.1 bar and the magnetic stirring started.

Isolation of 2-*tert*-Butyl-5,5-dimethyl-1-hexene (9), 2,2,3,6,6-Pentamethyl-*E*-3-heptene (10), and 2,2,5,6,6-Pentamethyl-*E*-3-heptene (11)

After completion of the catalytic reactions with *t*-BuC ≡ CH in 1,2-dichloroethane described above, the solvent and the volatile products were removed by distillation at 356 K. The remaining residue was distilled under reduced pressure to give a mixture of compounds **9 – 11.** Each individual product was separated from the mixture by column chromatography on silica gel (70 – 230 mesh) with hexane. The yields based on the reaction of Figure 2a (410 mg of *t*-BuC ≡ CH) were: 39 mg of **9** (9%), 129 mg of **10** (31%), 12 mg of **11** (3%). Purity of the compounds were confirmed by GC-MS. Mass spectra indicated the empirical formula $C_{12}H_{24}$ for all compounds.

NMR data for **9**: ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.89, 1.05 [both s, 9H each, $C(CH_3)_3$], 1.30, 1.96 (both m, 2H each, CH_2), 4.65 [dt, *J*(H,H) = 1.2, 1.2 Hz, 1H, =CH_2], 4.81 (m, 1H, =CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 25.98 (CH_2), 30.35, 36.24 [$C(CH_3)_3$], 30.25, 32.77 [$C(CH_3)_3$], 44.27 (CH_2), 105.87 (=CH_2), 159.24 (=C).

NMR data for **10**: ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.85, 1.01 [both s, 9H each, $C(CH_3)_3$], 1.56 [dt, *J*(H,H) = 1.2, 0.6 Hz, 3H, CH_3], 1.85 [brd, *J*(H,H) = 7.7 Hz, 2H, CH_2], 5.26 [tq, *J*(H,H) = 7.7, 1.2 Hz, 1H, =CH]; ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 25.43 [$C(CH_3)_3$], 27.38 (CH_3), 29.13, 29.19 [$C(CH_3)_3$], 31.69 [$C(CH_3)_3$], 41.79 (CH_2), 44.24 [$C(CH_3)_3$], 118.22 (=CH), 144.24 (=C); The *E*-stereochemistry has been confirmed by ^{1}H NOE measurements.

NMR data for **11**: ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.81 [s, 9H, $C(CH_3)_3$], 0.88 [d, *J*(H,H) = 6.9 Hz, 3H, CH_3], 0.97 [s, 9H, $C(CH_3)_3$], 1.80 [dq, *J*(H,H) = 8.7, 6.9 Hz, 1H, CH], 5.21 [dd, *J*(H,H) = 15.6, 8.7 Hz, 1H, =CH], 5.36 [d, *J*(H,H) = 15.6 Hz, 1H, =CH]; ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ = 15.68 (CH_3), 29.35, 29.81 [$C(CH_3)_3$], 36.73, 44.39 [$C(CH_3)_3$[, 47.01 (CH), 127.98, 141.22 (=CH).

X-Ray Crystallographic Study

Crystals of **5** suitable for a crystallographic study were obtained from solutions in acetone layered with diethyl ether. X-ray data were collected on a four-circle Siemens P4 diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω/2θ scan. Data were corrected for absorption by using a psi-scan method at 10° ψ-intervals.[11] The structure was solved by direct methods with SHELXS-97.[12] Refinement, by full-matrix least-squares on F^2 with SHELXL-97, included anisotropic displacement parameters for all non-hydrogen atoms. A solvation acetone molecule was included in the refinement without hydrogen atoms. Hydrogen atoms for the metal complex were found from difference Fourier maps and refined as isotropic atoms with coordinates riding on carbon atoms. Crystal data for $5.(CH_3)_2CO$: $C_{25}H_{49}BF_4IrN_2P.(CH_3)_2CO$; *M* = 745.72; colorless prismatic block, 0.44 × 0.40 × 0.28 mm; monoclinic, $P2_1/c$; *a* = 18.360(3), *b* = 14.714(1), *c* = 13.176(2) Å, β = 108.83(1)°; *Z* = 4; *V* = 3369.0(8) Å^3; *d* = 1.470; μ = 4.055 mm^{-1}; minimum and maximum transmission factors 0.1682 and 0.3211; $2\theta_{max} = 52.0°$; temperature 173(1) K; 8094 reflections measured, 6607 unique [*R*(int) = 0.0276]; number of data/restrains/parameters 6607/0/393; final $R_1(F)$ ($F^2 \geq 4\sigma(F^2)$) = 0.0324, w$R(F^2)$ (all data) = 0.0848; final GoF 1.045; largest diff. peak 1.029 e.Å^{-3}; extinction coefficient 0.00081(11).

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-186454. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-(1223)-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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