A Case of C−H Activation (Ortho Metalation) Which Is Reversible at 25 °C

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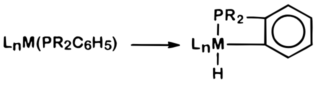
The reaction of LiC_2Ph with $Ir(H)_2ClL_2$ ($L = P^tBu_2Ph$) gives $Ir(H)_2(C_2Ph)L_2$, which readily loses H_2 to form the ortho-metalated species $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(C_2Ph)L$. This molecule is unique in showing $(sp^2)C/H$ reductive elimination/oxidative addition, which is thermally reversible at 25 °C. Line shape analysis of the $^{31}P\{^1H\}$ NMR spectra yield $\Delta H^‡ = 12.3\ (\pm 0.4)$ kcal mol^{-1} and $\Delta S^‡ = -2.0\ (\pm 1.1)$ cal deg^{-1} mol^{-1} for this process. This implicates the 14-electron species $Ir(C_2Ph)L_2$ as highly reactive, yet more easily accessible, than $IrClL_2$ (which ortho metallates essentially irreversibly). The strained four-membered ring in $IrH(\eta^2\text{-}C_6H_4P\text{-}{}^tBu_2)(C_2Ph)L$ reacts readily with PhC_2H to give $IrH(C_2Ph)_2L_2$, another unsaturated molecule essentially devoid of π-stabilization. The structure of this molecule, a square pyramid with apical hydride (proton NMR chemical shift −44 ppm), minimizes the Lewis acidity of such a species. Crystal data (−181 °C): $a = 9.616(1)$ Å, $b = 23.032(2)$ Å, $c = 8.886(1)$ Å, $\alpha = 95.18(1)°$, $\beta = 99.03(1)$, $\gamma = 98.16(1)$, with $Z = 2$ in space group $P\bar{1}$.

Introduction

Ortho metalation of the aryl ring of a phosphine attached to a metal (eq 1) is a widely occurring reaction.[1] It was one of the earliest examples of metal activation of (i.e., attack on) a C−H bond. Generally, this reaction



(1)

lies to one side: $\Delta G°$ is either strongly positive or negative (depending upon the L_nM moiety). Thus, even the unsaturated molecule $RuHCl(PPh_3)_3$ shows no detectable equilibrium population of the metalated alternative, although deuterium in $RuDCl[P(C_6H_5)_3]_3$ is readily exchanged into the phenyl rings by a mechanism involving an ortho-metalated species.[2] Such isotope exchange is one way to implicate the existence of a reversible equilibrium involving an otherwise unobservable species.

In the work presented here, we report a situation where the equilibrium lies toward the ortho-metalated species, yet the equilibrium is detected by the presence of two alternative phenyl rings, one on each phosphine. Because of this, and since this demetalation (C−H reductive elimination) occurs with an exceptionally low activation energy, NMR spectroscopy becomes a method for detecting its occurrence, as well as determination of activation parameters for the process.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under argon. Toluene was dried and deoxygenated over sodium benzophenone and distilled under argon. 1-Hexene and decane were distilled under argon before storage over activated 4 Å molecular sieves. Deuterated solvents (C_6D_6 and C_7D_8) were dried over sodium metal and vacuum distilled before use in the glovebox. ^1H NMR (referenced to residual solvent impurity) spectra were collected on a Varian XL-300 spectrometer. ^{31}P NMR (referenced to external 85% H_3PO_4) spectra were collected on Nicolet NT-360 and Varian VXR-400 spectrometers operating at 146 and 162 MHz, respectively. Deuterium NMR was run on a Varian Unity 500 spectrometer. Lithium phenylacetylide was prepared by the reaction of freshly distilled phenylacetylene with ^nBuLi (−78 °C, pentane). $Ir(H)_2Cl(P^tBu_2Ph)_2$ has been prepared previously.[3] The presence of P^tBu_2Ph makes $Ir(H)_2(CCPh)(P^tBu_2Ph)_2$ extremely soluble and unwilling to crystallize, even after column chromatography on neutral alumina or silica. The elemental analysis of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$, because it differs by only 2 H in ~800 amu, is not as diagnostic of purity as is NMR spectroscopy. Elemental analysis was therefore not accomplished.

$Ir(H)_2(CCPh)(P^tBu_2Ph)_2$. To a flask containing lithium phenylacetylide (300 mg, 2.8 mmol) was added a solution of $Ir(H)_2Cl(P^tBu_2Ph)_2$ (300 mg, 0.44 mmol) in 30 mL of toluene with stirring. This solution was stirred until the color had changed from orange to pale yellow (ca. 2 h). The solution was filtered through a 25-micron Teflon filter tip (Centaur Chemical Company) attached to a cannula, and the toluene was removed *in vacuo* to yield a sticky yellow solid (yield: 79%). ^1H NMR (C_6D_6, 25 °C): δ 8.68 (m), 7.25−6.91 (overlapping m), 1.64 (vt, $J_{PH} = 6.3$ Hz), −14.0 (t, $J_{PH} = 18$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, only sp carbons of acetylide ligand): δ 139.4 (t, $J_{PC} = 14$ Hz), 112.1 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 49.6 (s).

$IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$. In 15 mL of 1-hexene was dissolved $Ir(H)_2(CCPh)(P^tBu_2Ph)_2$ (150 mg, 0.20 mmol), with stirring. This solution was refluxed under argon for 12 h, causing a gradual color change of the solution from pale yellow to dark red. The solvent was removed *in vacuo*, yielding a dark red solid (yield: 82%). ^1H NMR (C_6D_6, 25 °C): δ 7.57 (d), 7.28−6.86 (overlapping m), 1.46 (br apparent d).

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

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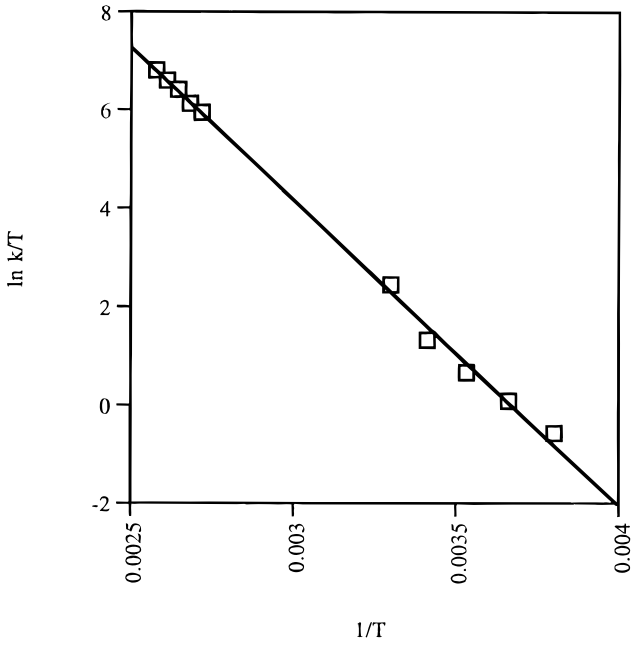


Figure 1. Eyring plot for the reversible ortho metalation, from line shape analysis of the ^{31}P NMR spectra.

Table 1. Crystallographic Data for $IrH(CCPh)_2(P^tBu_2Ph)_2$

formula: $C_{44}H_{57}P_2Ir$	fw = 840.10
$a = 9.616(1)$ Å	space group $P\bar{1}$
$b = 23.032(2)$ Å	$T = -181$ °C
$c = 8.886(1)$ Å	$\lambda = 0.710\ 69$ Å[a]
$\alpha = 95.18(1)°$	$\rho_{calcd} = 1.460$ g cm^{-3}
$\beta = 99.03(1)°$	$\mu = 35.9$ cm^{-1}
$\gamma = 98.16(1)°$	$R(F_o)^b = 0.0242$
$V = 1911.18$ Å^3	$R_w(F_o)^c = 0.0215$
$Z = 2$	

[a] Graphite monochromator. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

^1H NMR (C_7D_8, −40 °C): δ −42.6 (apparent t, $J_{PH} = 11$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, only sp carbons of acetylide ligand): δ 115.3 (apparent t, $J_{PC} = 10$ Hz), 108.7 (s). $^{31}P\{^1H\}$ NMR (C_7D_8, −40 °C, with decoupling of non-hydridic protons): δ 57.6 (dd, $J_{PP} = 328.5$ Hz, $J_{PH} = 10.1$ Hz), −15.9 (dd, $J_{PP} = 328.5$ Hz, $J_{PH} = 10.5$ Hz).

Variable-Temperature $^{31}P\{^1H\}$ NMR Measurement of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$ Exchange. The $^{31}P\{^1H\}$ NMR spectra of a sample of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$ (ca. 80 mg in 0.7 mL of decane) were recorded on a Varian VXR-400 spectrometer. Data was collected by increasing the temperature in 5° or 10° intervals from −20 to +130 °C (with an accuracy of ±0.1 °C) and obtaining 256 scans at each temperature. The data was transferred to an Apple Macintosh computer and processed using an NMR data processing program (MacFID; Tecmag, Inc.). Approximate line widths of the decoalesced AX pattern for $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$ (from −10 to 30 °C) and the coalesced signal (from 100 to 115 °C) were obtained by a Lorentzian fit of the appropriate signals. Using an NMR simulation program (DNMR5) and starting from the calculated line widths, the direct comparison of actual and simulated NMR spectra was used to refine the exchange rate at each temperature. The least-squares linear fit of a plot of 1n k/T *vs.* 1/T (Eyring plot, Figure 1) gave the slope and intercept values necessary for the calculation of $\Delta H^{\ddagger}$ and °$S^{\ddagger}$.

$IrH(C_2Ph)_2(P^tBu_2Ph)$. Freshly distilled PhCCH (14.3 μL, 0.13 mmol) and $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$ (80 mg, 0.11 mmol) were stirred together in 10 mL of benzene for 1 h at 25 °C. After vacuum removal of benzene, the resulting brown solid was dissolved in 5 mL of pentane and cooled to −40 °C overnight to yield dark brown crystals. These were separated from the solution, washed with cold pentane (0 °C, 2 × 2 mL), and dried *in vacuo* (yield: 76%). ^1H NMR (C_6D_6, 25 °C): 7.95 (br, s), 7.22−7.10 (overlapping m), 1.56 (CH_3, vt, $J_{PH} = 6.6$ Hz), −43.9 (IrH, t, $J_{PH} = 11$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 52.7 (s).

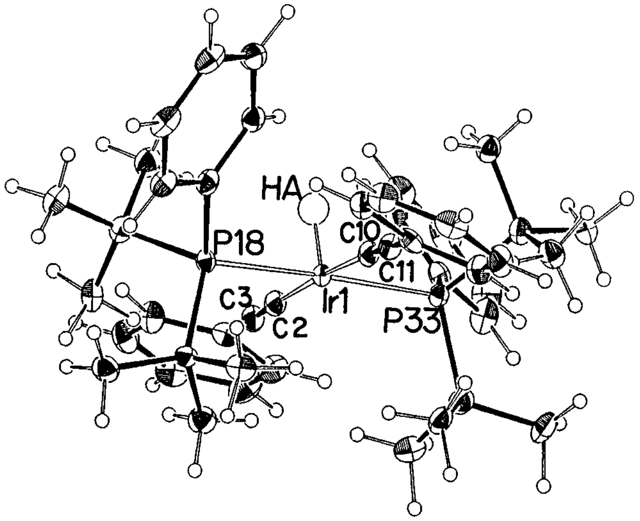


Figure 2. ORTEP view of $IrH(CCPh)_2(P^tBu_2Ph)_2$, showing selected atom numbering.

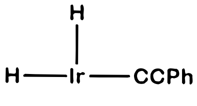
Table 2. Selected Bond Distances (Å) and Angles (deg) for $IrH(CCPh)_2(P^tBu_2Ph)_2$

Ir(1)−P(18)	2.3524(12)	C(3)−C(4)	1.437(6)
Ir(1)−P(33)	2.3603(12)	C(10)−C(11)	1.216(6)
Ir(1)−C(2)	2.017(5)	C(11)−C(12)	1.443(6)
Ir(1)−C(10)	2.027(5)	Ir(1)−H(A)	1.21(4)
C(2)−C(3)	1.224(6)		
P(18)−Ir(1)−P(33)	177.24(4)	C(10)−Ir(1)−H(A)	100.2(18)
P(18)−Ir(1)−C(2)	86.73(13)	C(2)−C(3)−C(4)	178.5(5)
P(18)−Ir(1)−C(10)	93.29(13)	Ir(1)−C(10)−C(11)	172.0(4)
P(33)−Ir(1)−C(2)	93.96(13)	C(10)−C(11)−C(12)	176.1(5)
P(33)−Ir(1)−C(10)	85.87(13)	P(18)−Ir(1)−H(A)	95.4(18)
C(2)−Ir(1)−C(10)	176.62(19)	P(33)−Ir(1)−H(A)	87.4(18)
Ir(1)−C(2)−C(3)	174.1(4)	C(2)−Ir(1)−H(A)	83.2(18)

X-ray Structure Determination of $IrH(CCPh)_2(P^tBu_2Ph)_2$. A nearly equidimensional crystal was selected and affixed to the end of a glass fiber using silicone grease. The mounted sample was then transferred to the goniostat where it was cooled to −181 °C for characterization (Table 1) and data collection (6° < 2θ < 45°). Standard inert atmosphere handling techniques were used throughout the investigation. A systematic search of a limited hemisphere of reciprocal space located no symmetry or systematic absences, indicating a triclinic space group. Subsequent solution and refinement of the structure confirmed the proper space group to be $P\bar{1}$. Data were collected using a standard moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms and for absorption, based on the measured distances to the well-defined faces. The structure was solved by Patterson and Fourier techniques. A difference Fourier map phased on the non-hydrogen atoms clearly located all hydrogen atoms, and these were included in the subsequent least-squares refinement. Examination of the difference Fourier clearly located the hydride as the second largest peak (the largest is at the metal site). In the final cycles, all atoms were varied, including the hydride. A final difference Fourier map was essentially featureless, the largest peak lying at the site of the Ir atom. Results of the structure determination are shown in Figure 2 and Table 2.

Results

Synthesis and Characterization of $Ir(H)_2(C_2Ph)(P^tBu_2Ph)_2$, 1. Reaction of $Ir(H)_2Cl(P^tBu_2Ph)_2$ with PhC_2Li in toluene gives clean conversion to $Ir(H)_2(C_2Ph)(P^tBu_2Ph)_2$. This molecule shows one ^{31}P NMR chemical shift and a ^1H NMR ^tBu virtual triplet, consistent with *trans* phosphines. The α-carbon of the acetylide shows triplet splitting by two equivalent phosphorus nuclei, as does the hydride signal. The hydride chemical shift (−14 ppm) is inconsistent with a hydride *trans* to an open site in a square pyramid (**I**), and we therefore assign it the "Y"-shaped structure, **II**.



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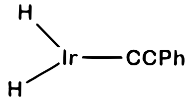
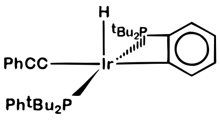


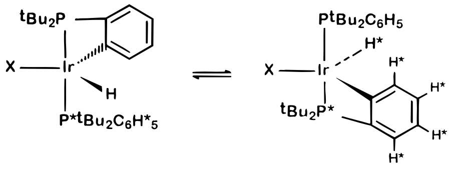
II

This molecule is remarkable in being metastable, losing H_2 upon vacuum filtration through Celite or (oven-dried) filter paper attached to one end of a cannula. Prolonged exposure of **1** in solution and in the solid state to a vacuum also causes partial conversion to the metalated **2**. This conversion is, however, difficult to drive to completion to give pure product. Vacuum also produces significant amounts of free phosphine and uncharacterized metal complexes. We have therefore devised the following conversion.

Synthesis and Characterization of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$, 2. Generation of $Ir(H)_2(CCPh)(P^tBu_2Ph)_2$, followed by pressure filtering with a cannula fitted with a Teflon filter tip, caused only limited (5%) conversion of **1**. Removal of toluene *in vacuo* and refluxing in 1-hexene for 12 h caused a color change from yellow to the dark red of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$. Both the ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** are broad at 25 °C, so its structure is best determined at low temperature. At −40 °C, the $^{31}P\{^1H\}$ NMR spectrum shows one resonance within 8 ppm of that of **1** and a second signal shifted 73.5 ppm to higher field. Such a large upfield shift is diagnostic of *ortho* metalation.[4] The P−P coupling constant, 329 Hz, indicates *trans* positioning of the phosphorus nuclei. The hydride chemical shift, −42.6 ppm, is so very far upfield that it signifies a position *trans* to *no* ligand: that is, a square pyramidal structure (**III**). Both acetylide carbons were detected in the $^{13}C\{^1H\}$ NMR spectrum, with the α-carbon showing coupling to two ^{31}P spins. The spectra simplify at higher temperatures. The hydride signal is too broad to observe at 25 °C. The ^tBu ^1H NMR signal simplified to one (broad) apparent doublet at 25 °C. Most diagnostic, however, is the ^{31}P NMR spectrum, which coalesces from the AX pattern at −40 °C to one broad line at ca. 60 °C and which further sharpens in the range 80−115 °C. In contrast, the ^{31}P NMR spectrum of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)Cl(P^tBu_2Ph)$ shows a sharp AX pattern at 25 °C.[5] This is consistent with interconversion of the phosphines by reversible metalation/demetalation of *ortho*-hydrogens on the two different phosphines (eq 2). These spectra were simulated, and the resulting rate constants yield the Eyring plot shown in Figure 1. The unusually large temperature range over which rate constants can be measured is beneficial to the accuracy of the derived activation parameters: $\Delta H^\ddagger = 12.3\ (\pm 0.4)$ kcal mol^{-1} and $\Delta S^\ddagger = -2.0\ (\pm 1.1)$ cal deg^{-1} mol^{-1}.



III



(2)

Reactivity of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$. (a) With H_2. Reaction with 1 atm of H_2 in C_6D_6 caused a rapid color change of the solution from the deep red of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$ to a lighter red color. ^{31}P and ^1H NMR confirmed a quantitative reaction of the metalated species to give two products in ca. 4:1 ratio. The identity of the minor product is assigned to the polyhydride complex $Ir(H)_5(P^tBu_2Ph)_2$.[6] The major product has a ^{31}P NMR resonance at 68.3 ppm (s) and a ^1H NMR hydride signal at −26.9 ppm (t, J_{PH} = 14.1 Hz) with coupling to two equivalent ^{31}P NMR nuclei. The ^1H NMR spectrum also shows that free phenylacetylene liberated by the reaction of $IrH(\eta^2\text{-}C_6H_4P^tBu_2)(CCPh)(P^tBu_2Ph)$ with H_2 is hydrogenated to styrene.

(b) With HCCPh: Synthesis of $IrH(CCPh)_2(P^tBu_2Ph)_2$. Addition of 1.2 equiv of phenylacetylene to a solution of $IrH(\eta^2\text{-}P^tBu_2C_6H_4)(CCPh)(P^tBu_2Ph)$ in C_6H_6 did not produce a noticeable color change, yet, after stirring for 1 h at room temperature, ^1H NMR assay showed the conversion of **2** to one major product with small (*ca.* 5%) amounts of uncharacterized impurities. The benzene was removed *in vacuo*, and the brown solid was dissolved in a minimum amount of pentane. Cooling this solution to −40 °C overnight caused the formation of dark brown crystals. The crystalline solid was characterized as $IrH(CCPh)_2(P^tBu_2Ph)_2$ by ^1H and ^{31}P NMR spectroscopies and X-ray crystal structure determination.

The structure determination, in which the hydride was located (Figure 2), shows a square pyramidal geometry with apical hydride. The *trans* phosphines adopt a conformation in which one ^tBu group from each phosphine lies to the same side of the IrP_2C_2 plane. This leaves the opposite side of the coordination plane open, and it is on this side that the hydride is located. There are no agostic interactions involving the open side of Ir; Ir/H distances to methyl hydrogens are all longer than 2.78 Å. The Ir/C and the acetylide C/C bonds are

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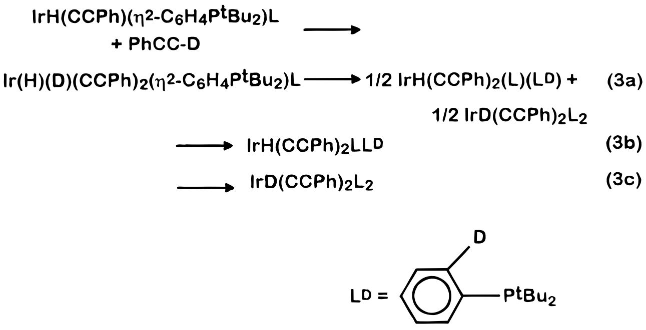
(4) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(5) Caulton, K. G.; Cooper, A. C. *Inorg. Chim. Acta*, submitted for publication.

(6) $Ir(H)_5(P^tBu_2Ph)_2$ has been prepared independently by the reaction of $Ir(H)_2X(P^tBu_2Ph)_2$ (X = F, OCH_2CF_3, OH) with excess H_2. $^{31}P\{1H\}$ NMR (C_6D_6, 25 °C): 67.1 (s). ^1H NMR (C_6D_6, 25 °C): 8.65 (m), 7.22−6.89 (overlapping m), 1.46 (vt, J_{PH} = 6.3 Hz), −9.75 (t, J_{PH} = 11.8 Hz).

both short. A complex with an analogous structure, $RhH(CCC(^iPr)_2OH)_2(P^iPr_2C_2H_4OMe)_2$, was recently reported.[7]

There are several plausible mechanisms for the reaction in eq 3, and isotope labeling can distinguish certain of these. The mechanism shown in eq 3a is primary oxidative addition (forming Ir(V)), followed by H-C(*ortho*) reductive elimination. Assuming rapid hydride site exchange fluxionality in the seven-coordinate intermediate, the isotope will be scrambled between metal and *ortho* carbon sites. The mechanism shown in eq 3b involves direct delivery of the acidic acetylene deuteron to the Ir−C bond and thus to the *ortho* carbon. This could involve four center σ-bond metathesis or a nearly ionic proton transfer mechanism or anything between these extremes. The mechanism shown in eq 3c involves the incoming acetylene triggering or inducing[8] the reductive elimination of the pre-existing Ir−C and Ir−H bonds. Reductive elimination has been shown in other systems to be triggered by either nucleophilic attack or oxidation. In reality, the ^2D NMR spectrum of the product of the reaction of PhC_2D with **2** shows only $IrD(C_2Ph)_2L_2$, with any deuterium at a phosphine *ortho* phenyl site being less than our detection limits (76.8 MHz, 1024 scans) of 5% of the Ir−D peak height. This same sample was also assayed by ^1H NMR spectroscopy; the integration of the *ortho* hydrogen signal at 7.95 ppm was undiminished from that expected for 0% D. The mechanism is thus that of eq 3c.

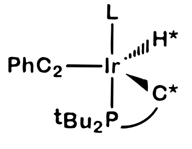


Discussion

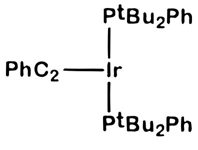
Why does $Ir(H)_2(CCPh)(P^tBu_2Ph)_2$ lose H_2 so readily? For comparison, the chloride analog shows no tendency to lose H_2 after 20 days at 65 °C in a solution with high olefin concentration (1.6 M allylbenzene in C_6D_6).[5] We suggest that there is a stabilization of the H_2 reductive elimination transition state by formation of a H−C(*ortho*) agostic interaction. This would be less likely to occur in an $Ir(H)_2X(P^tBu_2Ph)_2$ species for a π-donor because $X \rightarrow Ir$ π donation makes the agostic interaction less necessary. In other words, $IrX(P^tBu_2Ph)_2$ is much more reactive at Ir when X is acetylide than when it is a halide or pseudohalide. Although we have also studied the species IrHX(P-C)L for X = F, Cl, Br, I and OR and P-C = η^2-$C_6H_4P^tBu_2$, the case with X = C_2Ph is the only one to show reversibility of the metalation by NMR spectroscopy (i.e., phosphorus site exchange as low as 25 °C). What might be the reason for this? Certainly the transition state might have a reduced coordination number and valence electron count (14 e^-?). Moreover, it is the only one with a hydrocarbyl ligand X and, thus, minimal $X \rightarrow Ir$ π-donation: in fact, we have ranked the composite ($\sigma + \pi$) donor ability of C_2Ph as comparable to that of Br.[9] As such, the electrophilicity of iridium in the transition state may be exceptionally high when X = C_2Ph. For comparison, there is no evidence of exchange among ortho-metalated and pendant phenyl rings in $Re(H)_2(\eta^2\text{-}C_6H_4PPh_2)(PEt_3)_3$ by ^1H NMR spin-saturation transfer at 85 °C. Other dynamic processes in the molecule occur with $\Delta G^{\ddagger}_{38}$ °C of 15.1 kcal mol^{-1}.[10]

We have considered three (intramolecular) mechanisms for the site exchange (eq 2). Full oxidative addition of a new *ortho* C−H bond prior to reductive elimination of the former H and C(*ortho*), via $Ir(H)_2(CCPh)(\eta^2\text{-}C_6H_4P^tBu_2)_2$, should have a quite negative $\Delta S^{\ddagger}$ and can thus be excluded. Full reductive elimination of H and C(*ortho*) to form $Ir(CCPh)(P^tBu_2Ph)_2$ should have a quite positive $\Delta S^{\ddagger}$ and can thus be excluded.[11] An "internal displacement", wherein an agostic H-C(*ortho*) donates to unsaturated Ir(III) and facilitates the reductive elimination without the necessity of the 14-electron species $Ir(CCPh)(P^tBu_2Ph)_2$, should have compensating ordering and disordering and thus be in accord with the observed $\Delta S^{\ddagger}$ of −2 entropy units. These arguments require that there be no agostic Ir/H−C(*ortho*) interaction in the ground state of $Ir(H)_2(CCPh)(\eta^2\text{-}C_6H_4P^tBu_2)L$, where the hydride is *trans* to an empty coordination site. This is in accord with the observed far upfield chemical shift of the hydride ligand.

Both ground state and transition state structures may in fact be different from **IV** and **V**. An alternative to five-coordinate **IV** (because of the absence of a more effective π-donor halide) is a structure with an agostic *ortho*-phenyl hydrogen from L. This could immediately furnish compensating stability to the species as reductive elimination of C* and H* begins in **IV**. Equally well, species **V** could be stabilized (thus lowering $\Delta G^{\ddagger}$) if it retains two agostic *ortho* C−H bonds, one from each P^tBu_2Ph ligand (i.e., trigonal bipyramidal structure). In each case postulated here, this effect would be more fully developed for the weakly π-donating acetylide (via an acetylide filled π-orbital) than for halide or OR_f. In summary, this reaction formally resembles an (intramolecular) displacement (S_N2) process and the transition state thereby avoids full loss of the energy of two Ir−ligand homolytic bond dissociation energies (compensated by formation of one C−H bond). It is thus analogous to the mechanism of eq 3c.



IV



V

The reversibility observed here is strong evidence for the high reactivity of the species of formula $Ir(C_2Ph)$-

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[11] Solvent coordination to this three-coordinate transition state, which could make $\Delta S^{\ddagger}$ less positive, is unlikely because the coalescence behavior is similar in toluene and in decane.

$(P^tBu_2Ph)_2$: even when it is produced at a rate of 10^2 s^{-1} (i.e., the fluxional process), it does not persist. The thermodynamically-preferred form is a redox product (Ir(III)). Dimerization by acetylide bridging,[12] which is the observed form for many M(halide)L_2 species, is apparently precluded by the presence of two bulky phosphines per metal. In summary, a 14-electron Ir(I) species, Ir(hydrocarbyl)L_2, finds an alternative lower energy (redox) isomeric form, in spite of the strain energy involved in forming a four-membered IrPCC ring.

Conclusions

The strain in the ortho-metalated ring is evident in its willingness to reductively eliminate in the reversible eq 2. Strain is also evident in its ready “acidolysis” (σ-bond metathesis?) with the carbon acid PhCC−H, to form a new Ir−C bond in an otherwise very unsaturated molecule, $IrH(CCPh)_2(P^tBu_2Ph)_2$. The deuterium isotope study with PhC_2D in fact shows that this reaction is neither acidolysis nor σ-bond metathesis but is instead C−H reductive elimination triggered by the interaction of Ir with incoming alkyne, either at its π-cloud or its C−D bond. $IrH(CCPh)_2(P^tBu_2Ph)_2$, a 16-electron species, devoid of π-donor ligands, achieves metastability by adopting a structure (Figure 2) with the strong σ-donor hydride ligand *trans* to the empty coordination site. The very high hydride chemical shift is diagnostic of such an environment. With an atom of very low electronegativity (i.e., a strong σ-donor) *trans* to the empty site, the unoccupied orbital (LUMO) has minimum metal character and is thus poorly adapted to binding another ligand in that site. Thus, this hydride site, by monopolizing the metal orbitals for its own binding, minimizes the Lewis acidity (unsaturation) of the ground state structure. All molecules adopt a structure which maximizes their “stability”. In the case of a Lewis acid, this can mean maximizing the HOMO/LUMO gap and/or making the LUMO the least well-adapted for binding a Lewis base. In the case at hand, putting the strongest σ-donor ligand *trans* to the sterically empty (open) site accomplishes this by minimizing the spatial extension of the LUMO into the open site.

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Supporting Information Available: Tables of crystallographic data, positional parameters, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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