

Combined Experimental and Computational Studies on Carbon–Carbon Reductive Elimination from Bis(hydrocarbyl) Complexes of (PCP)Ir

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Abstract: The reductive elimination of carbon–carbon bonds is one of the most fundamentally and synthetically important reaction steps in organometallic chemistry, yet relatively little is understood about the factors that govern the kinetics of this reaction. C–C elimination from complexes with the common d^6 six-coordinate configuration generally proceeds via prior ligand loss, which greatly complicates any attempt to directly measure the rates of the specific elimination step. We report the synthesis of a series of five-coordinate d^6 iridium complexes, $(^t\text{BuPCP})\text{Ir}(\text{R})(\text{R}')$, where R and R' are Me, Ph, and (phenyl-substituted) vinyl and alkynyl groups. For several of these complexes (R/R' = Ph/Vi, Me/Me, Me/Vi, Me/CCPh, and Vi/CCPh, where Vi = *trans*-CH=CHPh) we have measured the absolute rate of C–C elimination. For R/R' = Ph/Ph, Ph/Me, and Ph/CCPh, we obtain upper limits to the elimination rate; and for R/R' = CCPh/CCPh, a lower limit. In general, the rates decrease (activation barriers increase) according to the following order: acetylide < vinyl \sim Me < Ph. Density functional theory (DFT) calculations offer significant insight into the factors behind this order, in particular the slow rates for elimination of the vinyl and, especially, phenyl complexes. The transition states are calculated to involve rotation of the aryl or vinyl group around the Ir–C bond, prior to C–C elimination, such that the group to which it couples can add to the face of the aryl or vinyl group. This rotation is severely hindered by the presence of the phosphino-*t*-butyl groups that lie above and below the plane of the aryl/vinyl group in the ground state. Accordingly, calculations predict dramatically different relative rates of elimination from the much less sterically hindered complexes $(^t\text{HPCP})\text{Ir}(\text{R})(\text{R}')$. For example, the barrier to elimination from $(^t\text{HPCP})\text{Ir}(\text{Me})_2$ is 20 kcal/mol, which is 2 kcal/mol greater than from the $(^t\text{BuPCP})\text{Ir}$ analogue. In contrast, the activation enthalpies calculated for vinyl–vinyl and phenyl–phenyl elimination from $(^t\text{HPCP})\text{Ir}$ are remarkably low, only 2 and 9 kcal/mol, respectively; these values are 16 and 22 kcal/mol less than those of the corresponding $(^t\text{BuPCP})\text{Ir}$ complexes. Moreover, since these eliminations are very nearly thermoneutral, the barriers are calculated to be equally low for the reverse reactions [C–C oxidative addition to $(^t\text{HPCP})\text{Ir}$]. The absence of differences in intraligand C=C bond lengths in the transition states relative to the ground states, combined with a comparison of calculated “face-on” and “planar” transition states for C–C coupling, suggests that the critical importance of the aryl/vinyl rotation is based on geometric or steric factors rather than electronic ones. Thus there is no evidence for participation of the π or π^* orbitals of the aryl or vinyl groups in the formation of the C–C bond, although a small π effect cannot be rigorously excluded. Likewise, the results do not support the hypothesis that the degree of directionality of the carbon-based orbital used for bonding to iridium ($sp^3 > sp^2 > sp$) plays an important role in this system in determining the barrier to reductive elimination.

Introduction

The carbon–carbon bond is the fundamental linkage of organic chemistry. Direct formation of C–C bonds by the reductive elimination of two hydrocarbyl ligands (e.g., alkyl, vinyl, or aryl) from a transition metal complex is, accordingly, one of the most important reaction steps in organometallic chemistry as applied to organic synthesis. C–C reductive elimination is the critical bond-forming step in cross-coupling reactions,^{1–14} most notably, but in other important transition-metal-based approaches to C–C bond formation as well.¹⁵ Yet, in spite of the importance of this reaction step in organic

synthesis and its very fundamental nature in the context of organometallic chemistry, the factors that govern its kinetics

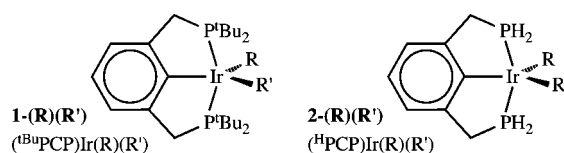
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(or the kinetics of the microscopic reverse, C–C oxidative addition) still remain poorly understood.^{16–23}

Recently Ananikov, Musaev, and Morokuma^{24,25} (AMM) conducted “the first detailed theoretical study of carbon–carbon bond formation through the reductive elimination process involving unsaturated organic ligands”. Specifically, these authors focused on complexes of the type $(\text{PH}_3)_2\text{M}(\text{R})(\text{R}')$ (where $\text{M} = \text{Pd}, \text{Pt}$ and $\text{R}, \text{R}' = \text{methyl, vinyl, phenyl, and ethynyl}$). It was concluded that the barriers to C–C bond formation are dependent on (i) the thermodynamics of elimination and (ii) the directionality of the M–C bond, as determined by hybridization of the bond-forming C atoms, according to the order $\text{sp} > \text{sp}^2 > \text{sp}^3$. The explanation for the calculated differences between species of different hybridization is intuitively appealing as an extension of the directionality principle used by Goddard and co-workers²⁶ to rationalize the more facile addition/elimination of C–H versus C–C bonds.

Mechanistically, one of the very few well-established tenets concerning C–C elimination is that it is kinetically much more facile from five-coordinate d^6 metal centers than from the corresponding six-coordinate (18-electron) complexes.^{21,27–41}

Thus, elimination from the much more common saturated species generally occurs via ligand loss, and this introduces a complicating variable into any potential mechanistic study of such eliminations. We have recently discovered a route to an unusual class of stable five-coordinate d^6 bis(hydrocarbyl) complexes, specifically, pincer-ligated iridium acetylide vinyl complexes.⁴² One such complex was found to undergo C–C elimination, thus offering an example of direct observation of this reaction without the requirement of prior ligand loss.⁴² Prompted by this result, we set out to synthesize a range of analogous bis(hydrocarbyl) complexes with the aim of elucidating the factors that determine the relative kinetics of elimination of various hydrocarbyl pairs. In particular we report complexes with methyl, vinyl, aryl, and acetylide ligands. We have been able to generate nine of the 10 possible permutations of bis(hydrocarbyl) complexes with these four ligand types, 1-(R)(R') , and determine their kinetics of C–C elimination or at least the relevant upper or lower limits.

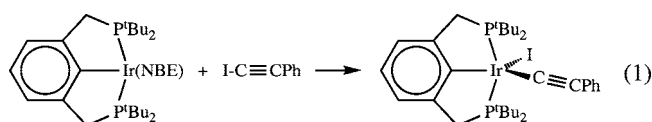


In combination with electronic structure calculations (density functional theory, DFT) of these elimination reactions, in which both the full 1-(R)(R') and truncated model compounds such as 2-(R)(R') are investigated, this study has yielded significant and unanticipated conclusions concerning the factors governing the kinetics of this important reaction class.

Results

Synthesis of Bis(hydrocarbyl) Complexes. The bis(hydrocarbyl) complexes were synthesized via corresponding hydrocarbyl–halide complexes. Detailed information on the syntheses and characterizations of the hydrocarbyl halides and the bis(hydrocarbyl) complexes is given in Supporting Information; in this section we summarize the synthetic pathways. Single-crystal structures (primarily of the six-coordinate CO adducts) and selected metric data are given in Figure 1 and Table 1, respectively.

$(^t\text{BuPCP})\text{Ir}(\text{CCPh})\text{I}$ [1-(CCPh)(I)]; $^t\text{BuPCP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2$] was synthesized by reaction of the $(^t\text{BuPCP})\text{Ir}$ precursor $(^t\text{BuPCP})\text{Ir}(\text{NBE})$ (where NBE = norbornene) with PhCCl (eq 1). 1-(CCPh)(I) was treated with MeLi or PhLi to afford 1-(CCPh)(Me) and 1-(CCPh)(Ph) , respectively; these species were characterized by ^1H and ^{31}P NMR and by single-crystal X-ray diffraction of the six-coordinate products formed by addition of CO. The attempt to synthesize 1-(CCPh)_2 by reaction of 1-(CCPh)(I) with LiCCPh led to the formation of $[(^t\text{BuPCP})\text{Ir}(\text{CCPh})_2]\text{Li}$ (Scheme 1). The six-coordinate anionic complex, like its five-coordinate neutral analogues, was characterized by ^1H and ^{31}P NMR and by its reaction with CO to give the neutral CO complex (Scheme 1).



Precursors to vinyl complexes were prepared from the complex 1-(Vi)(Cl) ($\text{Vi} = \text{trans-PhCH=CH-}$), which in turn was synthesized by the insertion reaction of $(^t\text{BuPCP})\text{IrHCl}$ with

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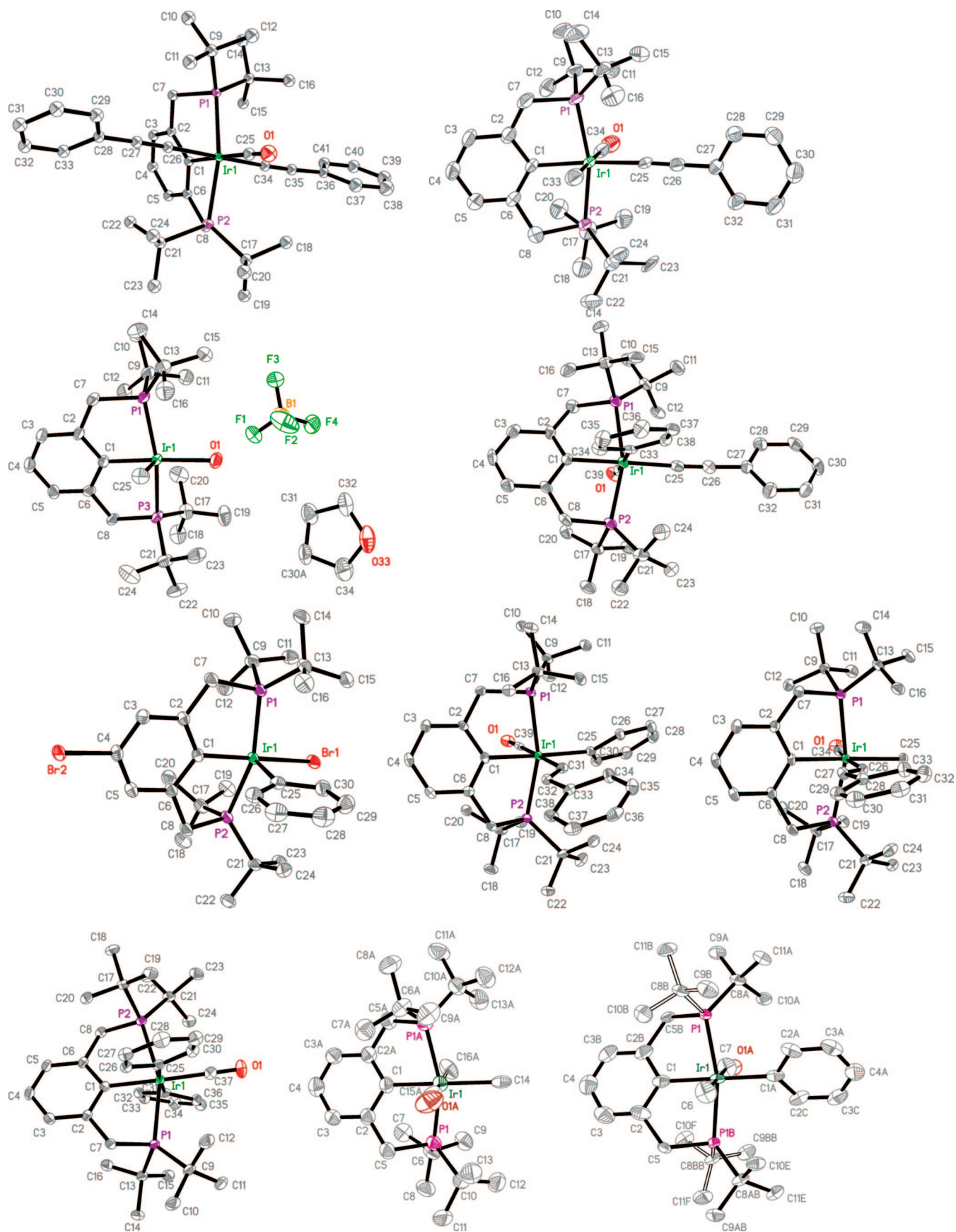
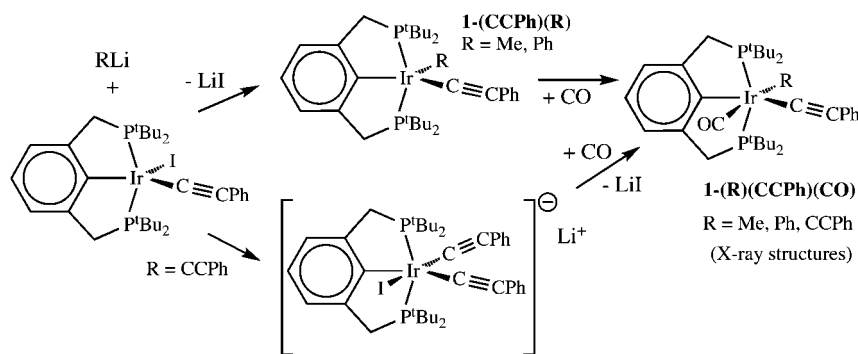


Figure 1. ORTEP diagrams (from top left to bottom right) for complexes 1-(CCPh)₂(CO), 1-(Me)(CCPh)(CO), [(^tBuPCP)Ir(Me)(H₂O)][BF₄]·THF, 1-(CO)(CCPh)(Ph), (Br-PCP)Ir(Ph)Br, 1-(CH=CHPh)(Ph)(CO), 1-(Me)(CH=CHPh)(CO), *trans*-1-(Ph)₂(CO), *cis*-1-(Me)₂(CO), and 1-(CO)(Me)(Ph).

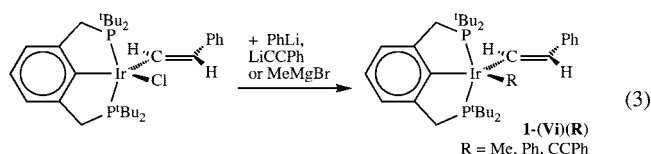
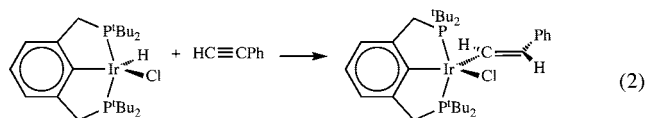
Table 1. Selected Bond Distances and Angles

complex	Ir–C(PCP)	Ir–P(avg)	Ir–C(CO)	Ir–C(R1)	Ir–C(R2)	P–Ir–P	C(PCP)–Ir–C(R1)	C(PCP)–Ir–C(R2)	C(R1)–Ir–C(R2)
(PCP)Ir(CCPH) ₂ (CO)	2.085(2)	2.4017(6)	1.924(3)	2.049(2) ^a	2.050(3) ^a	159.87(2)	88.11(10)	88.38(9)	176.44(9)
(PCP)Ir(CCPH)(Me)(CO)	2.088(6)	2.3587(14)	1.896(6)	2.062(6) ^a	2.162(7) ^b	164.43(6)	166.1(2)	77.5(3)	88.7(3)
(PCP)Ir(CO)(Ph) ₂	2.081(2)	2.4135(5)	1.906(3)	2.183(2) ^c	2.159(2) ^c	157.76(2)	90.68(9)	93.51(9)	175.81(9)
(PCP)Ir(CO)(CH=CHPh)(Ph)	2.107(4)	2.3945(11)	1.887(5)	2.160(5) ^c	2.101(4) ^d	160.81(4)	177.14(17)	90.11(17)	89.08(18)
(PCP)Ir(Me)(CO)(CH=CHPh)	2.115(2)	2.3774(6)	1.884(2)	2.194(2) ^b	2.103(2) ^d	163.30(2)	170.32(9)	82.79(9)	87.55(9)
(PCP)Ir(CO)(Ph)(CCPh)	2.102(6)	2.3874(17)	1.896(7)	2.056(7) ^a	2.142(6) ^c	161.28(6)	179.1(2)	92.2(2)	88.2(2)
(PCP)Ir(CO)(Me) ₂	2.085(12)	2.370(3)	1.888(9)	2.303(14) ^b	2.138(9) ^b	159.87(12)	180.0(4)	89(3)	91(3)
(PCP)Ir(CO)(Me)(Ph)	2.110(5)	2.3714(14)	1.916(7)	2.110(5) ^c	2.113(8) ^b	165.75(6)	180.00(2)	90.00(2)	90.00(3)
(PCP)Ir(I)(CCPh)	2.0417(17)	2.3520(4)		1.9236(18) ^a	2.7417(2) ^e	161.48(2)	85.29(7)	176.07(5)	96.97(5)
(Br-PCP)Ir(CO)(Ph)(Br)	2.029(2)	2.3431(6)		2.030(3) ^c	2.5947(3) ^f	162.37(2)	87.67(10)	171.28(7)	100.47(8)
[(PCP)Ir(H ₂ O)(Me)] ⁺ [BF ₄] [–]	2.002(3)	2.337(1)		2.065(3) ^b	2.223(2) ^g	163.20(4)	86.53(13)	176.97(10)	90.80(12)

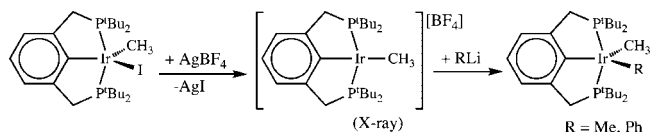
^a R group = CCPh. ^b R group = Me. ^c R group = Ph. ^d R group = CH=CHPh. ^e R group = I. ^f R group = Br. ^g R group = OH₂.

Scheme 1

phenylacetylene (eq 2).⁴² The iridium(vinyl)chloride reacted with PhLi, LiCCPh, or MeMgBr to give the respective iridium(vinyl)hydrocarbyl complex (eq 3).



1-(Me)(I) was synthesized, analogously to the acetylide iodide, by the reaction of (^tBuPCP)Ir(NBE) with methyl iodide. Attempts to convert **1-(Me)(I)** to the methyl hydrocarbyl complexes by reaction with Grignard or hydrocarbyllithium reagents were unsuccessful. However, reaction with AgBF₄ gave [(^tBuPCP)Ir(Me)](BF₄) (characterized by ¹H and ³¹P NMR as well as X-ray crystallography of its H₂O adduct), which was successfully treated with methyllithium and phenyllithium.



Phenyl iodide or phenyl bromide did not react with (^tBuPCP)Ir(NBE). Upon treatment of (^tBuPCP)Ir(NBE) with Br₂, a mixture of (^tBuPCP)IrBr₂ and its para-brominated-ligand analogue, (Br-PCP)IrBr₂, was obtained (Scheme 2). Subsequent treatment of this mixture with PhLi gave a mixture of (^tBuPCP)Ir(Ph)Br and

(Br-PCP)Ir(Ph)Br, (characterized by ¹H and ³¹P NMR and by X-ray crystallography of a single crystal of the two species in a 1:3 ratio). Analogously to **1-(Me)(I)**, this mixture reacted with organolithium reagents only after treatment with AgBF₄, to afford **1-Ph₂** and **1-(Ph)(Vi)** and their *p*-brominated derivatives (Scheme 2).

Kinetics of Elimination. Of the nine synthesized complexes of the form **1-(R)(R')**, some underwent clean C–C elimination upon warming at various temperatures (monitored by ³¹P NMR). Others decomposed through different pathways upon heating, thereby allowing us to infer an upper limit to the rate of C–C elimination (or, equivalently, a lower limit to the free energy of activation ΔG[‡]).

Upon thermolysis, acetylide complexes **1-(R)(CCPh)** (R = Me, Vi) underwent C–C elimination (Table 2) to give the π-(triple-bond)-coordinated (^tBuPCP)Ir adducts of the resulting acetylenes (characterized by ¹H, ¹³C, and ³¹P NMR, and X-ray crystallography for (^tBuPCP)Ir(η²-PhC≡C^{Vi})). In the case of [(^tBuPCP)Ir(CCPH)₂][Li], the reaction with AgBF₄ resulted in the formation of (^tBuPCP)Ir(η²-PhC≡C–C≡CPh) (¹H, ¹³C, and ³¹P NMR spectroscopy and X-ray crystallography), presumably via loss of iodide anion and rapid C–C reductive elimination from **1-(CCPh)₂** (Scheme 3). The bis-acetylide was not directly observed,

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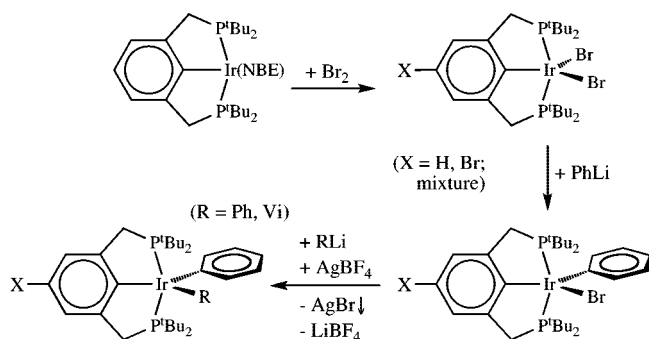
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Scheme 2



and we infer in this case a lower limit to the rate constant of ca. 0.098 s^{-1} for C–C elimination at 50°C (Table 2).

The behavior of the vinyl complex **1**-(Vi)(Me) was similar to that of the acetylide complexes in that C–C elimination affords the $(^t\text{BuPCP})\text{Ir}$ complex of the coupled organic product (methyl styrene). **1**-(Vi)(Ph) gave free *trans*-stilbene (25% yield) and hydrogenated product [ca. 70% yield diphenylethane; the hydrogen source is believed to be residual dibutyl ether from the synthesis of **1**-(Vi)(Ph)]. The iridium-containing product was not identified.

The dimethyl complex **1**-Me₂ was generated by the addition of 20 equiv of MeLi in diethyl ether to $[(^t\text{BuPCP})\text{Ir}(\text{Me})\text{BF}_4]$ in toluene (this solution also has tetrahydrofuran, THF, remaining from the synthesis of $[(^t\text{BuPCP})\text{Ir}(\text{Me})(\text{BF}_4)]$). Upon warming to 15°C , **1**-Me₂ disappears. Although the Ir-containing products (apparently a mixture of products of the reaction with Et₂O, THF, and toluene) were not identified, ethane was quantified (>90% yield) by gas chromatography (GC) after the reaction progress was monitored by ^{31}P NMR.

1-(Ph)(Me) and **1**-Ph₂ underwent decomposition upon heating (45 and 80°C , respectively) to give unidentified iridium-containing products and benzene, presumably resulting from cyclometalation of the phosphino-*t*-butyl groups and C–H elimination. Likewise, **1**-(Ph)(CCPh) afforded no diphenylacetylene but only unidentified decomposition products. These results allow us to place upper limits on the rates of C–C elimination from these complexes (Table 2).

Computational Studies. DFT calculations [Perdew–Burke–Ernzerhof (PBE) functionals with effective-core potential on Ir and basis sets of split-valence or better quality on all atoms] were carried out for the C–C elimination reactions of the full experimental systems (i.e., including *t*-Bu groups on P as well as phenyl on the vinyl and acetylide ligands) and truncated models, where the phosphine *t*-Bu and the phenyl substituents on the vinyl or acetylide groups were replaced by H. The calculations generally show good agreement with experimentally determined C–C rates (or limits) of elimination from the bis-hydrocarbyl complexes. In all cases, the computed free energies of activation for C–C elimination, calculated at $T = 25^\circ\text{C}$ and reagent concentrations equal to 1 M, were found to be slightly lower than the experimental values (see Table 2). The difference was typically ca. 2–5 kcal/mol [except for **1**-(CCPh)(Me), for which the difference was 8 kcal/mol].⁴³ Given the consistent

direction of the difference between experimental and calculated values, the trends are in even better agreement than the absolute values.

We note that for the two cases where the enthalpic and entropic contributions to the barrier energy have been determined experimentally [**1**-(Vi)(Ph) and **1**-(Me)₂], the differences between computed and experimental activation free energies are 2–3 kcal/mol [2.0 kcal/mol in the case of **1**-(Vi)(Ph); 2.6 kcal/mol for **1**-(Me)₂], but the differences in activation enthalpies are less than 1 kcal/mol. For **1**-(Vi)(Ph), the experimentally derived value for ΔH^\ddagger is $19.4(\pm 0.1)$ kcal/mol and the computed value is 18.6 kcal/mol; for **1**-(Me)₂, the corresponding activation enthalpies are $18.4(\pm 0.1)$ kcal/mol and 18.4 kcal/mol (!). The differences between measured and computed rates may hence, at least in these two particular cases, be attributed to differential activation entropy contributions. For **1**-(Vi)(Ph), the experimentally derived and computed values for ΔS^\ddagger are $-10.9(\pm 1)$ and -7.0 cal/mol·K, respectively; for **1**-(Me)₂, the corresponding ΔS^\ddagger values are $-8.5(\pm 1)$ and $+0.7$ cal/mol·K. If the data are taken at face value, the computed activation entropies appear to be insufficiently negative, for reasons that are not clear to us. It is, however, plausible that the major part of the experimental/theoretical disagreements in the magnitudes of ΔG^\ddagger arises from entropic contributions.

A significant advantage of calculations, vis-à-vis experiments, is that calculations can also yield the kinetic and thermodynamic parameters for C–C addition for the systems of interest. These values potentially reveal how much of the barrier to elimination (if any) may be attributed to the thermodynamics of the process. We find that elimination from all four acetylide complexes is endothermic; the other six permutations are exothermic. Thus, although the kinetic barriers to elimination of the acetylide complexes are substantial, they are largely attributable to the thermodynamic barrier.²⁴ Indeed, the *intrinsic* kinetic barriers (the barriers in the exothermic direction, that is, addition in the case of the acetylides) are quite small. In two cases, **1**-(CCPh)₂ and **1**-(CCPh)(Vi), the computed transition states (TS) appear to be of lower energy than free $(^t\text{BuPCP})\text{Ir}$ plus the appropriate coupling product. Intrinsic reaction coordinate (IRC) calculations show this result to be attributable to the formation of $(^t\text{BuPCP})\text{Ir}$ complexes of the C–C coupled organic products. The TS located for C–C coupling for **1**-(CCPh)₂ leads to a symmetric $(^t\text{BuPCP})\text{Ir}(\text{PhCC-CCPh})$ complex that is, at least formally, a C–C σ -complex intermediate,⁴⁴ bonding through the central C–C bond of the diacetylene coupling product. This complex is 3.3 kcal/mol above **1**-(CCPh)₂ in enthalpy and 4.0 kcal/mol below the TS (Scheme 4). However, a second diacetylene complex, in which one of the acetylene units engages in conventional π -type bonding with Ir, is 16.9 kcal/mol lower in enthalpy [$\Delta G = -12.5$ kcal/mol relative to **1**-(CCPh)₂].⁴⁵

To summarize, the computed data collected in Table 2 show that the *intrinsic* kinetic barriers to addition/elimination increase in the order acetylide < vinyl ~ Me < Ph. For both addition and elimination, the barriers increase as vinyl ~ Me < Ph. These trends are in good agreement with the experimental results.

Discussion

The observed and computed order noted above for barriers to elimination of the various hydrocarbyl groups (acetylide <

(43) The ground-state geometry for **1**-(CCPh)(Me) is a distorted square pyramid with Me apical (CCPh trans to PCP ipso-carbon). A second conformer, a distorted square pyramid with CCPh apical, is found to be 10.3 kcal/mol higher in energy. We have no particular rationalization for the larger discrepancy between observed and calculated activation barriers for C–C elimination from **1**-(CCPh)(Me).

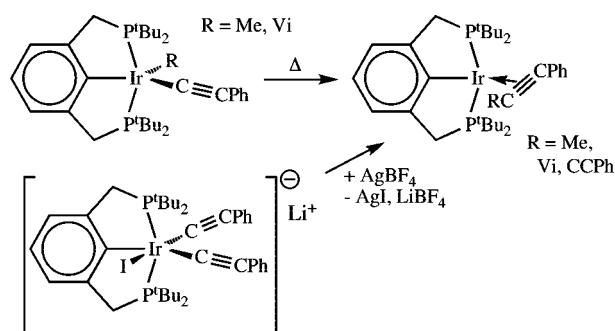
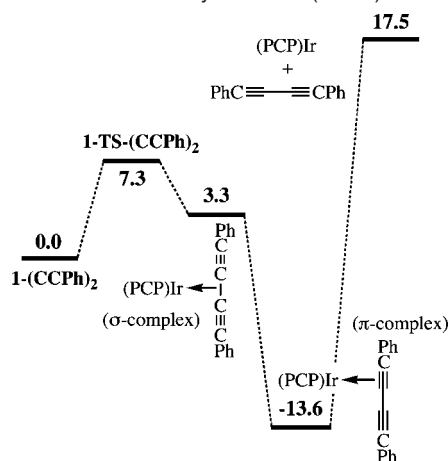
(44) For a rare example of a C–C σ -bond complex and a discussion of such complexes and C–C bond addition, see Weller, A. S.; Brayshaw, S. K.; Sceats, E. L.; Green, J. C. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6921.

Table 2. Experimental Rate Constants and Activation Parameters for C–C Elimination, Calculated Activation and Thermodynamics Parameters for C–C Elimination, and Calculated Activation Enthalpy for C–C Addition^a

R	R'	experimental				calculated				
		rate constant [temp] ^b	activation			activation		thermo		addition
			ΔS	ΔH	ΔG	ΔH	ΔG	ΔH	ΔG	
Me	Me	9.94×10^{-4} [15]	–8.5	18.4	20.8	18.4	18.2	–15.7	–27.3	34.1
Me	Ph	$<9 \times 10^{-4}$ [45] ^c			>23.1	26.1	27.1	–9.6	–24.1	35.7
Me	Vi	3.15×10^{-4} [7]			20.9	15.3	17.7	–3.9	–15.7	19.3
Me	CCPh	2.69×10^{-4} [45]			23.9	15.2	16.0	8.9	–2.7	6.2
Ph	Ph	$<1.27 \times 10^{-4}$ [80] ^c			>27.1	31.2	32.4	–12.2	–25.9	43.4
Ph	Vi	7.35×10^{-4} [40]	–10.9	19.4	22.7	18.6	20.7	–8.3	–23.1	26.9
Ph	CCPh	no elimination ^d			>34	27.2	30.4	13.8	3.7	13.3
Vi	CCPh	3.13×10^{-4} [40]			23.4	15.4	18.1	15.8	6.1	–0.5
CCPh	CCPh	>0.098 [50]			<20.5	7.3	7.0	17.5	6.4	–10.2

^a ΔH and ΔG values are given in kilocalories per mole; ΔS values are given in calories per mole per kelvin. The standard state for the theoretical free energies is $T = 25^\circ\text{C}$ and reagent concentrations of 1 M. Estimated experimental error limits are 0.1 kcal/mol for ΔH^\ddagger and 1.0 cal/mol·K for ΔS^\ddagger .

^b Rate constants are given per second; temperatures (in brackets) are given in degrees Celsius. ^c Does not eliminate as RR' ; RH and $\text{R}'\text{H}$ are formed, possibly via cyclometalation of the phosphino-*t*-butyl groups. ^d No elimination observed even at 95°C ; lower limit of ΔG^\ddagger was calculated with the assumption of $<2\%$ decrease after 48 h.

Scheme 3**Scheme 4.** Elimination of Dialkyne from **1**-(CCPh)₂^a

^a Enthalpies are shown in kilocalories per mole.

vinyl $\sim \text{Me} < \text{Ph}$) contrasts with that obtained in the only other systematic study of this type that has been reported to our knowledge. In AMM's purely computational investigation of elimination from $(\text{PH}_3)_2\text{MRR}'$ ($\text{M} = \text{Pd}, \text{Pt}$) it was found, in particular, that the barriers to eliminations of alkyl groups are much greater than those for phenyl groups, which in turn are greater than for vinyl groups.²⁴ By contrast, in the present (^tBuPCP)Ir systems, the elimination barriers of the sp^2 -bound groups, particularly phenyl, are relatively much greater.

Insight into the origin of the high calculated and experimentally determined barriers for phenyl and (to a lesser extent) vinyl groups may be obtained by inspection of the transition-state

geometries. Most significantly, in all cases calculated, the vinyl and/or phenyl group has undergone a rotation in the TS of ca. 90° around the Ir–C single bond relative to the reactant [the bis(hydrocarbyl) complex], as we have previously noted in the specific case of vinyl–acetylide coupling.^{42,46} Note that, in both the reactant complex (Figure 2) and the coupled organic product (e.g., toluene), the carbon atom of the partner group undergoing elimination is located in the plane of the aryl or vinyl group. In the TS, however, the incipient C–C bond is approximately perpendicular to the aryl or vinyl planes: there is a “face-on” orientation of this group with the hydrocarbyl group to which it is coupling (Figure 3).

The bulky phosphino-*t*-butyl groups impose a very large steric barrier to the rotation of the sp^2 -bound hydrocarbyl groups. For example, the activation parameters for rotation of the phenyl group around the Ir–C bond in **1**-(H)(Ph)(CO) have previously been determined to be $\Delta H^\ddagger = 16.6$ kcal/mol and $\Delta S^\ddagger = -1.2$ eu.⁴² Figure 4 shows some selected close H–H contacts resulting from rotation of phenyl and vinyl (or phenylvinyl) groups. Even rotation of the smallest such group, vinyl, results in numerous short interligand contacts involving the H atoms at both C1 and C2 (cis to iridium only) positions of the vinyl groups. In addition, the crowding at the site of the rotation is also reflected in close contacts remote from that site, as the phosphino-*t*-butyl groups are forced away from the rotating groups.

In order to quantitate the steric contribution to the barrier to elimination in complexes **1**-(R)(R'), we calculated the elimination barriers for the analogous truncated species, in which the *t*-butyl groups were replaced with hydrogen atoms, **2**-(R)(R'). It has been well demonstrated, for several transition metal systems, that increased ancillary ligand bulk tends to favor the kinetics of reductive elimination reactions.^{17,47–49} However,

(45) In the case of **1**-(CCPh)(Vi), the TS leads to a π -complex with Ir bonded to the hydrocarbon product through the vinyl double bond. This complex has $\Delta G = 3.4$ kcal/mol relative to **1**-(CCPh)(Vi) and $\Delta G = -14.7$ kcal/mol relative to the TS.

(46) This rotation is not specifically noted in the work of AMM because their $\text{L}_2\text{MRR}'$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{L} = \text{PH}_3$) species are sterically unhindered. Hence the ground states already feature the vinyl and phenyl groups rotated by approximately 90° .

(47) Jones, W. D.; Kuykendall, V. L. *Inorg. Chem.* **1991**, *30*, 2615–2622.

(48) Hartwig, J. F.; Richards, S.; Baranano, D.; Paul, F. J. *Am. Chem. Soc.* **1996**, *118*, 3626–3633.

(49) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 3694–3703.

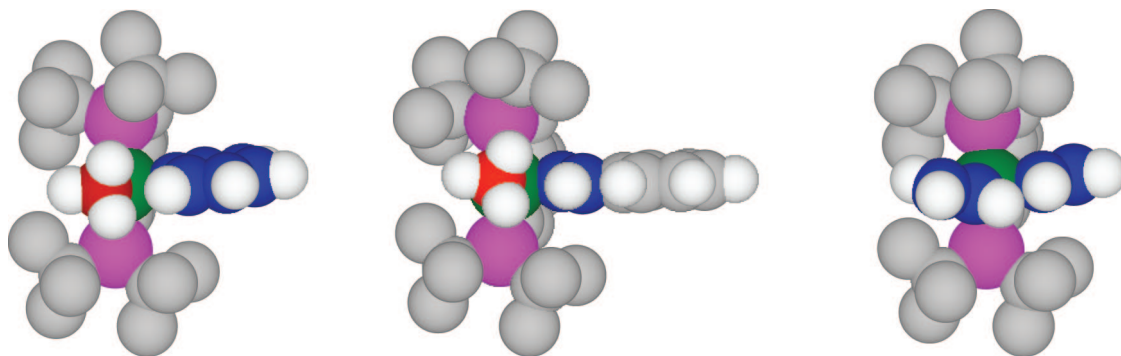


Figure 2. Ground-state structures for **1**-(Me)(Ph), **1**-(Me)(Vi), and **1**-(C₂H₃)₂. Three-dimensional models are shown with H atoms omitted (other than those on hydrocarbyl ligands). Atoms are depicted at 75% van der Waals radii.

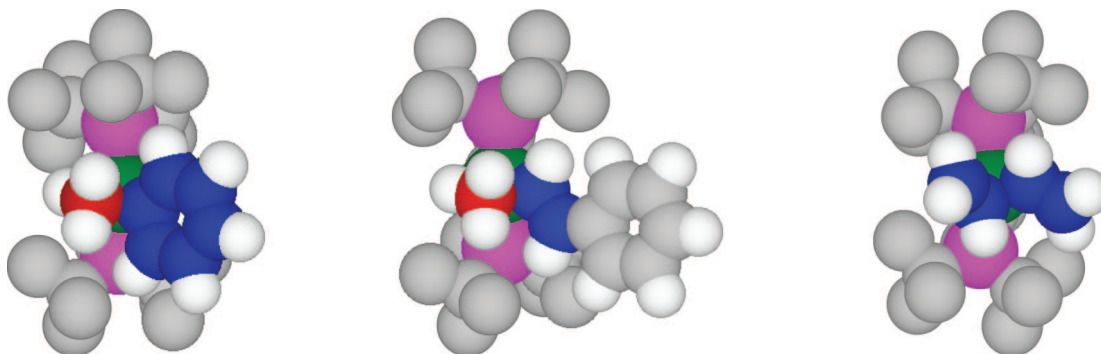


Figure 3. Transition-state structures for **1**-(Me)(Ph), **1**-(Me)(Vi), and **1**-(C₂H₃)₂. Graphical details are as in Figure 2.

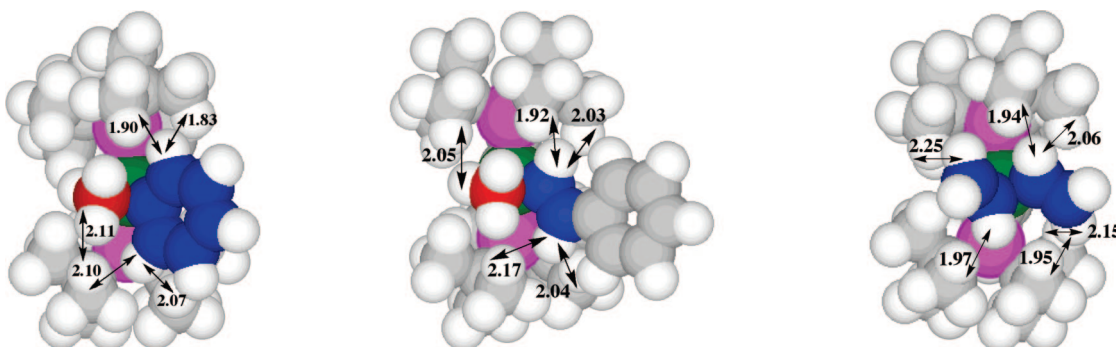


Figure 4. Transition-state structures for **1**-(Me)(Ph), **1**-(Me)(Vi), and **1**-(C₂H₃)₂. Three-dimensional models are shown with H atoms, and selected close H–H contacts are indicated. Atoms are depicted at 75% van der Waals radii.

Table 3. Calculated Activation Enthalpies for C–C Elimination from (PH₃)₂MRR', ^tBuPCP)IrRR', and (^HPCP)IrRR'

R	R'	calcd activation enthalpy (kcal/mol)							
		(PH ₃) ₂ Pt		(PH ₃) ₂ Pd		(^t BuPCP)Ir		(^H PCP)Ir	
		ΔH [‡]	ΔH [‡]	ΔH [‡]	ΔH [‡]	ΔH [‡]	ΔH [‡]	ΔH [‡]	ΔH [‡]
Ph	Ph	27	–16	11	–31	31	–12	9	1
Ph	Me	36	–15	18	–30	26	–10	15	2
Me	Me	45	–15	24	–30	18	–16	20	–4
vinyl ^b	vinyl ^b	18	–18	6	–33	18	–6	2	0
vinyl ^b	Ph	23	–16	9	–31	21	–8	5	1
vinyl ^b	Me	32	–15	16	–29	14	–10	10	1

^a From ref 24. ^b Vinyl = C₂H₃.

substitution of the *t*-butyl groups of **1**-(R)(R') by hydrogen atoms should greatly reduce or eliminate barriers to rotation. For **2**-(R)(R'), the relative values of the barriers to elimination (Table 3) involving phenyl or vinyl groups were indeed calculated to be remarkably different from those of the full (^tBuPCP)Ir complexes. For example, the activation enthalpy for elimination

from **1**-Me₂ is predicted to be 18 kcal/mol; the barrier is slightly greater, 20 kcal/mol, for the truncated analogue **2**-Me₂. In contrast, the respective activation enthalpies calculated for vinyl–vinyl and phenyl–phenyl elimination from (^HPCP)Ir are remarkably low, only 2 and 9 kcal/mol, respectively. These barriers are 16 and 22 kcal/mol less than for the corresponding

Table 4. Calculated Activation and Reaction Enthalpies for C–X Elimination from (^tBuPCP)Ir(R)(X) and (^hPCP)Ir(R)(X) and Activation Enthalpies of the Corresponding Addition Reaction^a

	calculated enthalpy (kcal/mol)					
	(^t BuPCP)Ir(Me)(X)			(^h PCP)Ir(Me)(X)		
	$\Delta H^\ddagger_{\text{elim}}$	ΔH_{elim}	$\Delta H^\ddagger_{\text{addn}}$	$\Delta H^\ddagger_{\text{elim}}$	ΔH_{elim}	$\Delta H^\ddagger_{\text{addn}}$
Me	18	–16	34	20	–4	23
Ph	26	–10	36	15	2	13
NH ₂	31	7	24	36	22	14
OH	38	16	18	38	24	14

^a X = Me, Ph, OH, and NH₂.

(^tBuPCP)Ir complexes. This very large kinetic effect of reducing the steric demands of the pincer ligand is in the direction opposite that of the thermodynamics; eliminations from **2**-(vinyl)₂ and **2**-Ph₂ are 6 and 13 kcal/mol less favorable, respectively, than from the **1**-R₂ analogues. Indeed, the eliminations from **2**-(vinyl)₂ and **2**-Ph₂ are approximately thermoneutral (versus the very exothermic eliminations from **1**-R₂) and thus the barriers are equally low for the (hypothetical) reverse reaction, C–C addition to (^hPCP)Ir.

Why does rotation of the hydrocarbyl groups so dramatically affect the barrier to elimination? A priori, perhaps the most obvious answer to this question involves accessibility of the aryl or vinyl π systems in the TS for C–C bond formation. Participation of either filled π or empty π^* orbitals would be expected to result in an increase in the intraligand C=C bond distances in the TS relative to the hydrocarbyl minimum; however, virtually no such change is calculated. There is a very minor elongation of the vinyl C=C distances in **1**-TS-(C₂H₃)₂: the calculated C=C distances are both 1.364 Å in this TS versus 1.352 and 1.360 Å in the (approximately square pyramidal) **1**-(C₂H₃)₂ ground state (apical and basal vinyl groups). However, even this very minor elongation is essentially absent in a sterically unhindered analogue. In the case of **2**-TS-(C₂H₃)₂, the C=C distances (1.361 Å) fall in between the C=C bond lengths calculated in the ground state **2**-(C₂H₃)₂ (1.350 and 1.362 Å). Note also that the C=C bond lengths in the transition states are effectively equal to that of the elimination product (free 1,3-butadiene), 1.354 Å.

An additional argument against the significance of any participation of the hydrocarbyl π -orbitals is suggested by calculations on elimination of Me-NH₂ and Me-OH from (^tBuPCP)Ir and (^hPCP)Ir complexes. The availability of the lone-pair electrons on the heteroatoms appears to offer no assistance in these eliminations; indeed, they have barriers significantly greater than either Ph–Me or Me–Me elimination (Table 4). The C–O and C–N eliminations are thermodynamically much less favorable than C–C elimination, which presumably contributes to the higher elimination barriers. However, in spite of the much more favorable thermodynamics of addition, the barriers to addition are only moderately lower than that of Me–Me addition and no greater than that of Ph–Me addition in the absence of the phosphino-*t*-butyl groups (Table 4).

Additional calculations on elimination from **1**-(Ph)(Me) were conducted in which the Ph group was held fixed in the horizontal plane during C–C elimination [i.e., the plane defined by Ir, Ph, and C(Me); Figure 5]. The resulting approximate TS for C–C coupling, **1**-TS-(Ph-planar)(Me), is calculated to be 17 kcal/mol higher in energy than **1**-TS-(Ph)(Me) in which the Ph group is essentially perpendicular to the horizontal plane (ΔE^\ddagger = 43.4 kcal/mol for the “planar elimination” versus 26.4 kcal/mol). Interestingly, in both planar and unconstrained transition states

the Ir–C(Me) and C(Ph)–C(Me) distances are computed to be nearly identical: ca. 2.31 Å (Ir–C) and 1.93 Å (C–C), respectively, for both species. However, the two transition states show a very significant difference in the Ir–C(Ph) distances: in **1**-TS-(Ph)(Me), the Ir–C(Ph) distance is 2.11 Å [elongated only slightly from 2.03 Å in **1**-(Ph)(Me)], whereas in **1**-TS-(Ph-planar)(Me) it is 2.54 Å.

Further arguing against the participation of the π -system in bond formation, the effective hybridization of C(Ph) in the C–C bond orbital being formed is essentially the same in both the planar and actual (unconstrained) transition states for elimination from **1**-(Ph)(Me). In fact there is slightly *less* p-character in the unconstrained TS; the respective hybridization of C(Ph) in the actual TS is sp^{2.97}, versus sp^{3.08} in **1**-TS-Ph(planar)(Me). Moreover, the net natural charges on C(Ph) and C(Me) are effectively the same in the two transition states. In **1**-TS-(Ph)(Me) the net charges are –0.06 and –0.81, respectively; in **1**-TS-(Ph-planar)(Me) the analogous net charges are –0.05 and –0.79.

Thus, in contrast to the actual TS, very significant disruption of the Ir–C(Ph) bond is required to reach the TS for the planar elimination. The Ir–C(Ph) bond not only must lengthen [2.54 Å in **1**-TS-(Ph-planar)(Me) versus 2.11 Å in **1**-TS-(Ph)(Me)] but also must bend such that one of the ortho C–H units is now quite close to Ir [Ir–C2 = 2.85 Å, Ir–C2(H) = 2.42 Å; Figure 5], while there are still significant H–H contacts between the other ortho hydrogen and the methyl hydrogens (H–H ~ 2.1–2.2 Å). In the absence of reorientation and lengthening of the Ir–C(Ph) bond, the steric barrier would be much more severe. Attempts to model a planar transition state in which the Ir–C(Ph) distance was held at 2.11 Å [the value in nonplanar **1**-TS-(Ph)(Me)] failed to converge to a stationary point. These constrained geometry optimizations appeared to be headed toward a species with a short C(Ph)–C(Me) distance of 1.66 Å [Ir–C(Me) = 2.20 Å] (**3**, Figure 6) situated ca. 23 kcal/mol above **1**-TS-(Ph-planar)(Me) [40 kcal above **1**-TS-(Ph)(Me)]. Severe interactions between the ortho hydrogen and the methyl group [H(Ph)–H(Me) = 1.92 Å] are calculated, along with commensurate distortions of the methyl group (an H–C–H angle of 98.9°) and an extremely short Ir–H(Me) nonbonding distance of 1.90 Å.

Rotation of the Ph group to give the actual TS [**1**-TS-(Ph)(Me)] eliminates this otherwise severe steric strain [seen both in **3** and in **1**-TS-(Ph-planar)(Me)] and the energy of bond disruption necessary to minimize it. Thus, although we cannot rule out the possibility of π -system participation in C–C bond formation, the simple steric-based argument appears sufficient to explain the critical requirement for aryl or vinyl rotation in the C–C elimination transition states.

Analogously, elimination from the truncated vinyl complex **2**-(C₂H₃)(Me) was calculated with the vinyl group held coplanar with the C(vinyl)–Ir–C(Me) elimination plane. The approximate planar TS for C–C coupling, **2**-TS-(C₂H₃-planar)(Me) (ΔE^\ddagger = 38.1 kcal/mol) is 28.1 kcal/mol in energy above that of unconstrained **2**-TS-(C₂H₃)(Me). Significant crowding is manifest in the planar TS, particularly a short H(vinyl)–C(Me) distance of 2.12 Å (the sum of the van der Waals radii of methyl and H is ca. 3.2 Å)⁵⁰ and an Ir–C(Me)–H angle of 68° (Figure 7). As in **1**-TS-(Ph)(Me), the eliminating sp²-C–Ir bond is greatly elongated [0.33 Å longer in **2**-TS-(C₂H₃-planar)(Me) than

(50) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

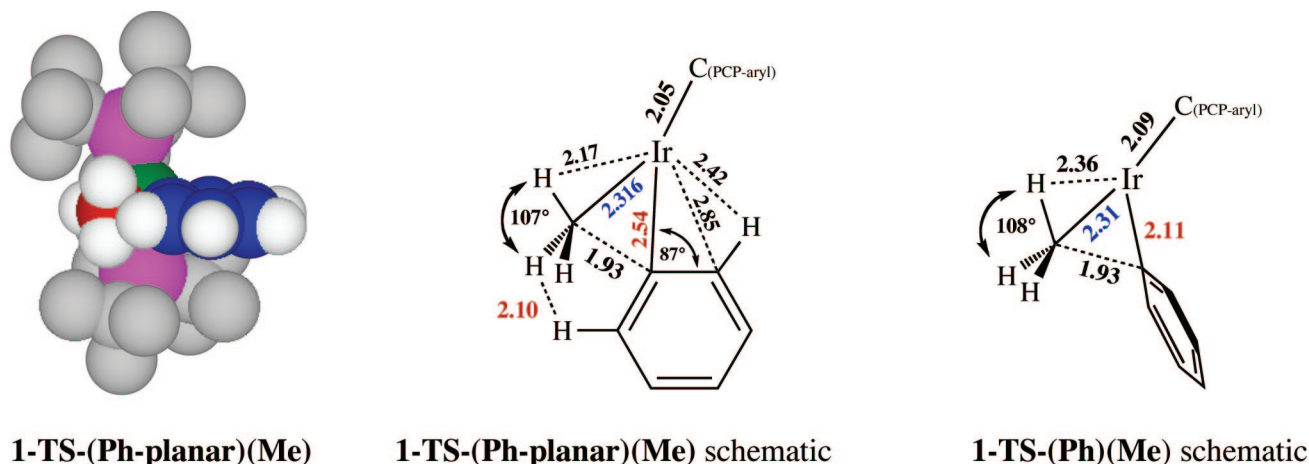


Figure 5. Three-dimensional model of 1-TS-(Ph-planar)(Me), with H atoms omitted (other than those on eliminating hydrocarbonyl groups), and schematic diagrams of Ir–C–C planes in the constrained, approximate TS [1-TS-(Ph-planar)(Me)] and in the actual, unconstrained TS [1-TS-(Ph)(Me)] (rotated 90° relative to the 3D models in this figure and Figures 3 and 4). Bond distances are shown in angstroms.

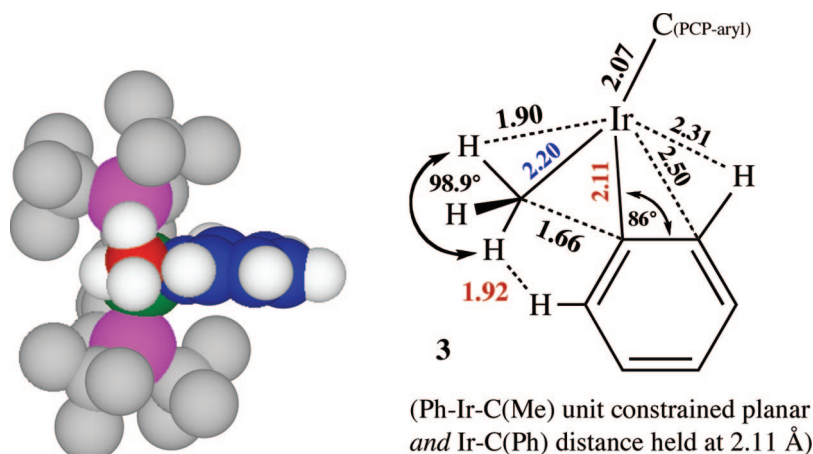


Figure 6. Three-dimensional model of **3**, with H atoms omitted (other than those on eliminating hydrocarbyl groups), and schematic diagram of Ir–C–C plane with bond distances shown in angstroms. Structure **3** resulted from a search for an approximate C–C elimination TS from **1**-(Ph)(Me) in which Ir, C(Me), and the phenyl group were constrained to lie in the same plane and the Ir–C(Ph) distance was held fixed at 2.11 Å, its value in nonplanar **1**-TS-(Ph)(Me). **3** does not represent a stationary point on the potential energy surface.

in 2-TS-(C₂H₃)(Me)], apparently in order to mitigate the steric repulsion between the vinyl and methyl groups.

The above results strongly suggest that it is unnecessary to invoke the varying degrees of directionality of the carbon-based bonding orbitals in order to explain the differences in elimination rates observed between sp^3 , sp^2 , and sp -bound hydrocarbonyl groups.^{24,25} For example, the very low barrier calculated for vinyl–vinyl elimination from **2**-(vinyl)₂ (2.2 kcal/mol) indicates that the substantial p-character of the sp^2 -hybridized carbon orbitals does not significantly retard elimination (relative to sp -carbon). Conversely, the lesser p-character of the sp^2 -hybridized carbon orbital, vis-à-vis the sp^3 orbital of a methyl group, *does not confer any advantage in the absence of ligand rotation*. Indeed, the barriers to “planar” Me–Ph or Me–Vi elimination [**1**-TS-(Ph-planar)(Me), $\Delta E^\ddagger = 43$ kcal/mol; **2**-TS-(vinyl-planar)(Me), $\Delta E^\ddagger = 38$ kcal/mol] are substantially *greater* than that for Me–Me elimination [**1**-TS-(Me)₂, $\Delta E^\ddagger = 20$ kcal/mol].

Thus the major advantage enjoyed by sp^2 -carbon-bound groups in reductive elimination (versus sp^3) is apparently *not due to any intrinsic property of the sp^2 orbitals such as directionality*. Rather, it is a result of the simple fact that such hydrocarbyl groups are planar. Therefore, when—and only when—they are appropriately rotated, the group to which they

are coupling encounters no steric resistance from the atoms bound to the sp^2 -carbon. In contrast, sp^3 -C-bound groups obviously cannot be oriented in such a favorable fashion. On the other hand, sp -C-bound groups are obviously not required to undergo rotation, but in the present system there is a significant thermodynamic barrier to the eliminations of the sp -C-bound groups.

Our results also seem to shed light on the relative ease of C–C elimination of different carbon-bound groups from different metal centers. Factors elucidated in this work may, for example, contribute to the utility of Pd complexes for bond formation involving sp^2 -carbon-bound groups.^{1–11} Note that the presence of bulky ligands generally *favors* C–C elimination from L_2PdR_2 complexes,^{17,25,48,49} the opposite of the effect seen for elimination from $(^R\text{PCP})Ir$. This is easily explained in terms of the direction of the steric effects in question in each case. In the case of $(^R\text{PCP})IrR_2$, increased bulk (above and below the “M–C–C plane” defined by the metal and the eliminating groups) enforces coplanarity of the R groups. In the case of L_2PdR_2 (or even $LPdR_2$ ^{51,52}) the effect is opposite: increased bulk of the ancillary ligands can only *favor* rotation of these hydrocarbyl groups outside the C–M–C plane (Figure 8).

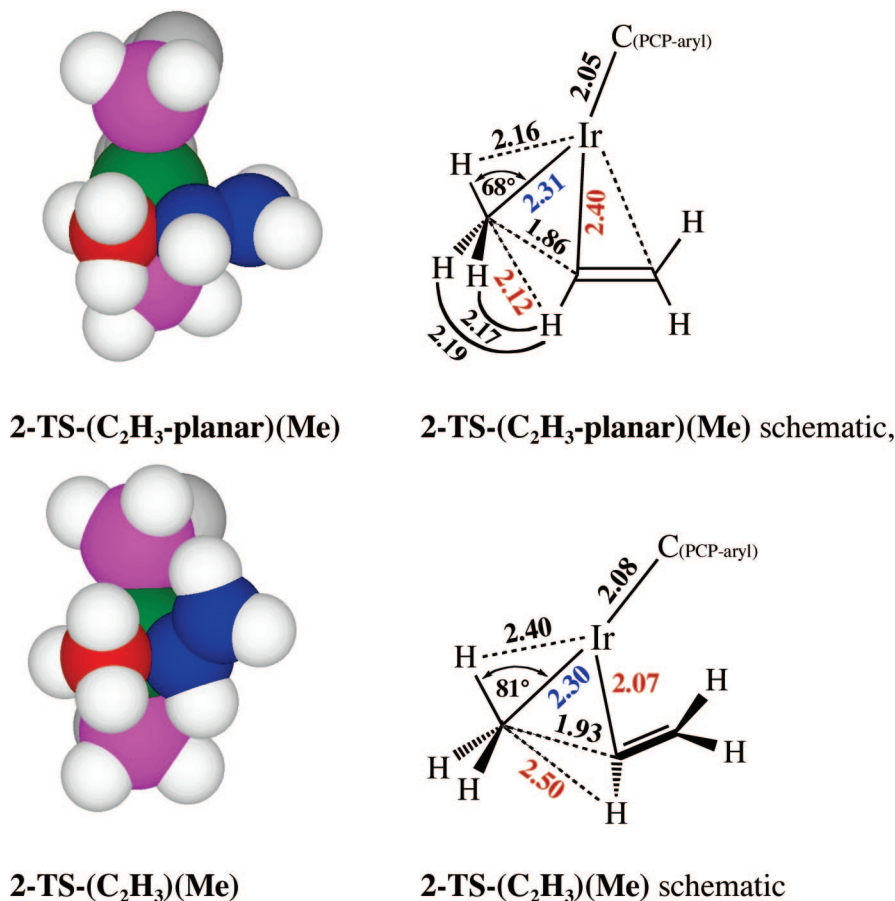


Figure 7. Three-dimensional models of **2-TS-(C₂H₃-planar)(Me)** and **2-TS-(C₂H₃)(Me)**, with H atoms omitted (other than those on eliminating hydrocarbyl groups and P), and schematic diagrams of the respective Ir-C-C planes (rotated 90° relative to the 3-D models in this figure). Bond distances are shown in angstroms.

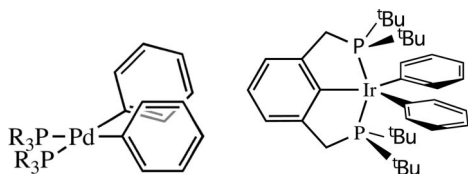


Figure 8. Schematic illustrating how the presence of phosphine ligands favors a conformation in which the phenyl ligands “face each other” in the case of (R₃P)₂PdPh₂. In the case of (tBuPCP)IrPh₂, bulky phosphino groups favor a coplanar conformation of the phenyl ligands.

The dominance of group 10 and later metals (Ni and Pd^{1–11,14} but also Cu^{12,13}) in transition-metal-catalyzed coupling may stem in part from the lack of steric bulk typically present outside the C–M–C plane in such species. The results herein suggest the possibility that complexes with higher coordination numbers (i.e., typical configurations of complexes of iridium or any other metals in groups 9 or earlier) may be of greater value in coupling reactions if an ancillary ligand sphere is appropriately designed to favor a “face-on” orientation of hydrocarbyl groups.

General Experimental Methods and Computational Details

General Experimental Methods. All reactions, recrystallizations, and routine manipulations were performed at ambient

temperature in an argon-filled glovebox or under argon via standard Schlenk techniques. Benzene and *p*-xylene were distilled from sodium/potassium alloy and vacuum-transferred under argon. Deuterated solvents for use in NMR experiments were dried as their protiated analogues. (PCP)IrH₂ was synthesized according to published methods. All other chemicals were used as received from commercial suppliers. ¹H and ³¹P{¹H} NMR spectra were obtained on a 400-MHz Varian Inova-400 or a 300-MHz Varian Mercury-300 spectrometer. ¹H chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to residual protiated (¹H) or deuterated solvent. ³¹P NMR chemical shifts were referenced to 85% H₃PO₄. Mesitylene was employed as an internal standard when yields were determined by NMR spectroscopy. 1-Iodo-2-phenylacetylene (PhCCI)⁵³ was synthesized by literature procedure.

Computational Details. All electronic structure calculations employed the DFT method⁵⁴ and the PBE⁵⁵ exchange and correlation functionals. The relativistic, small-core ECP and corresponding basis set (6s5p3d) of Dolg et al.⁵⁶ were used for the Ir atom (SDD model); all-electron basis sets of at least split-valence quality were applied to all P, C, and H atoms. C, N, O, and P atoms in the immediate Ir coordination sphere were covered with

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6-31+G(d) basis sets,⁵⁷ whereas other C atoms in the hydrocarbyl ligands and the principal PCP unit received a 6-31G basis set. A 3-21G basis set was placed on the 12 C atoms in the phosphine *t*-Bu groups as well as on all H atoms.⁵⁸

Calculations were made in which the (PCP)Ir [PCP = κ^3 -2,6-(R₂PCH₂)₂C₆H₃] species was modeled including the *t*-Bu groups actually used in the experiments, that is, PR₂ = P(*t*-Bu)₂, and on truncated models where PR₂ = PH₂. Reactant, transition-state, and product geometries were fully optimized and the stationary points were characterized further by normal-mode analysis. The (unscaled) vibrational frequencies formed the basis for the calculation of vibrational zero-point energy (ZPE) corrections. Standard thermodynamic corrections (based on the harmonic oscillator/rigid rotor approximations and ideal gas behavior) were made to convert from purely electronic (reaction or activation) energies (ΔE and ΔE^\ddagger ; no ΔZPE) to (standard) enthalpies (ΔH and ΔH^\ddagger ; ΔZPE included) and free energies (ΔG and ΔG^\ddagger ; $T = 298$ K, $P = 1$ atm).⁵⁹ Tabulated enthalpies and free energies refer to a standard state of $T = 298$ K and 1 M, unless otherwise noted.

In some instances, the intrinsic reaction coordinate method was used to follow the reaction coordinate from a particular C–C

elimination TS toward the hydrocarbon products.⁶⁰ Electronic population analyses employed the NBO scheme of Weinhold and co-workers.⁶¹

All calculations were executed with the *Gaussian 03* series of computer programs.⁶²

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Supporting Information Available: Experimental details and procedures; spectroscopic characterization of all complexes; geometries and energies for all molecular species relevant to Table 2; crystallographic details (CIF files) for complexes **1**-(CCPh)₂(CO), **1**-(Me)(CCPh)(CO), [(^tBuPCP)Ir(Me)(H₂O)]-[BF₄]·THF, (Br-PCP)Ir(Ph)Br, **1**-(CH=CHPh)(Ph)(CO), **1**-(CO)(C-CPh)(Ph), **1**-(Me)(CH=CHPh)(CO), *trans*-**1**-(Ph)₂(CO), *cis*-**1**-(Me)₂(CO), **1**-(CO)(Me)(Ph), and **1**-(I)(CCPh); and complete ref 62. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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