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Vinylic C−H Bond Activation and Hydrogenation Reactions of Tp′Ir(C_2H_4)(L) Complexes

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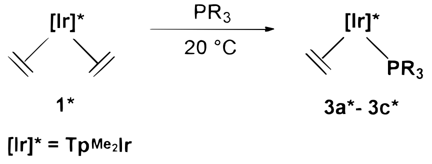
The substitution of one of the ethylene ligands of the complexes Tp′Ir(C_2H_4)$_2$ (Tp′ = Tp^{Me_2}, **1***; Tp′ = Tp, **1**) by soft donors such as tertiary phosphines or carbon monoxide is a facile reaction that gives the corresponding Tp′Ir(C_2H_4)(L) adducts. Spectroscopic studies support their formulation as five-coordinate, 18-electron species that possess a distorted trigonal bipyramidal geometry. This proposal has been confirmed by a single-crystal X-ray study carried out with the PMe$_2$Ph complex Tp^{Me_2}Ir(C_2H_4)(PMe$_2$Ph) (**3b***). Related hydride derivatives of Ir(III) can be obtained either by hydrogenation of the Ir(I) adducts (in general, this gives Tp′IrH$_2$(L) compounds) or by thermal activation of one of the C−H bonds of the coordinated C_2H_4 ligand of the Tp^{Me_2}Ir(C_2H_4)(L) compounds. All these reactions can be understood by invoking the participation of transient, 16-electron (η^2-Tp′)Ir intermediates, but the thermodynamics of the [Ir](C_2H_4) to [Ir]H(CH=CH$_2$) conversion does not require an overall change in the coordination mode of the Tp′ ligand.

Introduction

The transformation of transition metal−ethylene complexes into their hydride−vinyl isomers is, in general, thermodynamically uphill for mononuclear systems.[1−3] Up to now, the only exceptions to this rule which are known involve Tp′Ir systems (Tp′ = hydrotris(1-pyrazolyl)borate ligand[4]). Thus, the Ir(III) hydride−vinyl derivative $Tp^{CF_3,Me}$IrH(CH=CH$_2$)(CO)[5] and the somewhat analogous Tp^{Me_2}IrH(CH=CH$_2$)(C_2H_4) complex and others closely related to it[6] were found to be the products of the thermal activation of the corresponding Ir(I)−olefin species Tp′Ir(C_2H_4)(L). In Graham's system,[5] namely $Tp^{CF_3,Me}$Ir(C_2H_4)(CO),[5] a change in the coordination mode of the Tp′ ligand from η^2 to η^3 was suggested to accompany the activation of the C−H bond of the C_2H_4 ligand, and it was further assumed that the extra coordination of the free pyrazolyl arm provided the thermodynamic driving force needed for the activation reaction to take place. We have demonstrated, however, that Tp^{Me_2}Ir(C_2H_4)$_2$ has a five-coordinate, 18-electron structure, both in solution and in the solid state.[6] Hence, in our case, the above transformation occurs without a change in the net electron count at the Ir center and in the coordination mode of the Tp^{Me_2} ligand. In this contribution, we extend previous studies on olefinic C−H activation to a series of Tp′Ir(C_2H_4)(L) complexes (Tp′ = Tp, Tp^{Me_2}; L = PR$_3$, CO) and investigate in addition the hydrogenation of these compounds.

Results and Discussion

Synthesis and Characterization of Tp′Ir(C_2H_4)(L) Complexes. We showed recently that the compound Tp^{Me_2}Ir(C_2H_4)$_2$ (**1***) reacts with hard donors such as MeCN and DMSO with formation of Tp^{Me_2}Ir(CH=CH$_2$)(C_2H_5)(L). These reactions require heating at 60 °C, with the participation of Tp^{Me_2}IrH(CH=CH$_2$)(C_2H_4) (**2***) as an active intermediate.[6] In marked contrast, soft bases such as tertiary phosphines and CO readily substitute one of the C_2H_4 ligands in **1*** and give the corresponding Tp^{Me_2}Ir(C_2H_4)(L) adducts, as illustrated in eq 1



(1)

1* **3a*- 3c***

[Ir]* = Tp^{Me_2}Ir

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(1) (a) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212. (b) Bell, T. W.; Brough S.-A.; Partridge, M. G.; Perutz, R. N.; Rooney, A. D. *Organometallics* **1993**, *12*, 2933. (c) Bianchini, C.; Barbaro, P.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1993**, *12*, 2505.

(2) Hydride−vinyl species however can be active in the evolution of M−ethylene complexes. See for example: (a) Desrosiers, P. J.; Cai, L.; Halpern, J. *J. Am. Chem. Soc.* **1989**, *111*, 8513. (b) Burger, P.; Bergman R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462. (c) Pérez, P. J.; Poveda, M. L.; Carmona, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 231.

(3) For some recent reviews on C−H bond activation see: (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(4) Abreviations used in this paper: Tp = HB(pz)$_3$, Tp^{Me_2} = HB(3,5-Me$_2$pz)$_3$, Tp′ = any tris(pyrazolyl)borate ligand. For recent, general reviews on Tp′ ligands see: (a) Trofimenko, S. *Chem Rev.* **1993**, *93*, 943. (b) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 418. In these references, the values of the cone angles for the Tp and Tp^{Me_2} ligands are somewhat different. The numbers given in the text are taken from ref 4c.

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(6) Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Pérez, P. J.; Ruíz, C.; Bianchini, C.; Carmona, E. *Chem.−Eur. J.* **1997**, *3*, 860.

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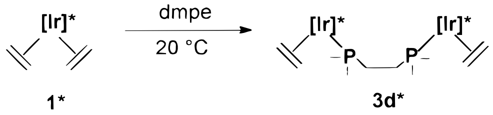
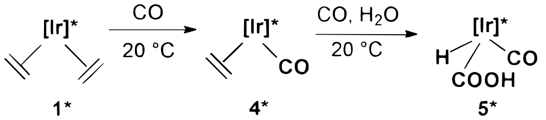
for the monodentate phosphines PMe_3 (**3a***), PMe_2Ph (**3b***), and PEt_3 (**3c***). Interestingly, the chelating phosphine $Me_2PCH_2CH_2PMe_2$, dmpe, affords, under similar conditions, the binuclear species **3d***, in which the diphosphine ligand bridges the two equivalent metallic centers (eq 2).



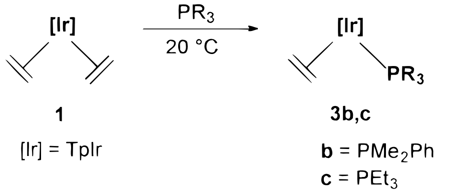
(2)

Carbon monoxide also induces a fast substitution reaction in THF to give first the mixed adduct $Tp^{Me_2}Ir(C_2H_4)(CO)$ (**4***) (NMR evidence) and then the hydride-metallocarboxylic compound **5*** (eq 3), which has been fully characterized by IR and NMR spectroscopy and microanalysis. We presume that complex **5*** is formed by the action of adventitious water on the undetected dicarbonyl $Tp^{Me_2}Ir(CO)_2$, a compound previously reported in preliminary form.[7] During the progress of our work, compound **5*** was isolated by Venanzi et al.[8] The analogous, albeit slower, reaction of the $TpIr(CO)_2$ derivative with H_2O has been investigated by Oro and co-workers.[9] As stated by these authors, the very high reactivity of the $Tp'Ir(CO)_2$ complexes toward H_2O is remarkable.[8,9] We will briefly come back later to this point. For the time being, it should be mentioned that, on a practical basis, the mixed C_2H_4-CO adduct **4*** is best obtained by action of KTp^{Me_2} on $[IrCl(coe)(CO)]_2$ (coe = cyclooctene) in the presence of C_2H_4.



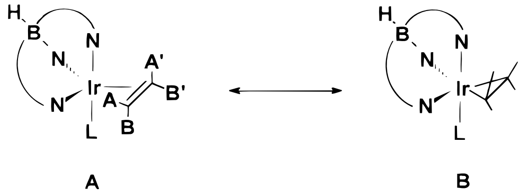
(3)

As expected, the bis(ethylene) derivative of the unsubstituted Tp ligand, $TpIr(C_2H_4)_2$ (**1**),[10] is also prone to undergo a similar $C_2H_4-PR_3$ substitution, the analogous complexes **3b,c** being formed readily according to eq 4. The similar PPh_3 adduct has been obtained recently by Heinekey et al.[11]



(4)

All the compounds of composition Tp′Ir(C_2H_4)(L) exhibit spectroscopic properties in agreement with a common, trigonal bipyramidal geometry **A**. This structure is closely related to that found for **1** and **1***[6] and results from the replacement of the axial C_2H_4 ligand of the latter compounds by the L group. Theoretical calculations by Eisenstein and Caulton show that in this way back-donation to the π^* orbital of the remaining C_2H_4 group is maximized while keeping at a minimum the overall molecular electronic energy.[12] This type of structure has also been suggested for $TpIr(C_2H_4)(CO)$ and $TpIr(C_2H_4)(PPh_3)$.[11,13] As discussed below, the structure proposed for these complexes on spectroscopic grounds has been confirmed by an X-ray study carried out with the PMe_2Ph complex **3b***.



At variance with the parent bis(ethylene) compounds **1** and **1***, all the Tp′Ir(C_2H_4)(L) derivatives reported in this paper are rigid at room temperature on the NMR time scale. This is evidenced by the observation of two sets of resonances (2:1 intensity ratio) for the pyrazolyl groups of the Tp′ ligand. In fact, of the members of this Tp′Ir(C_2H_4)(PR_3) family of compounds, only $TpIr(C_2H_4)(PPh_3)$ has been found to be fluxional in solution.[11] The dynamic behavior of this complex could be ascribed to the steric pressure exerted by the bulky PPh_3 ligand, which would facilitate the fast dissociation of one of the pyrazolyl arms. It is worth noting that even the coordinated C_2H_4 group of these mixed C_2H_4-L adducts has a static orientation, no rotation around the $Ir-C_2H_4$ axis taking place on the NMR time scale (an AA′BB′ spin pattern is observed for the ethylene protons under ^{31}P-decoupling conditions). The mirror symmetry plane of these molecules is also manifested in the observation of only one resonance for the olefinic ^{13}C nuclei. It is remarkable that this signal appears at rather high field, as compared with those of other related $M-C_2H_4$ complexes. For the Tp^{Me_2} series, the shielding increases with the donor capability of the L ligand: 0.6 (CO); −7.2 (PMe_2Ph); −8.1 (PMe_3); −9.1 (dmpe); −10.9 ppm (PEt_3). These signals are observed at somewhat lower field for the analogous compounds of the less-donating, unsubstituted Tp group (e.g., 0.5 ppm in the $TpIr(C_2H_4)(PMe_2Ph)$ derivative) but seem to maintain the same dependence on the donicity of the L ligand (a chemical shift of 2 ppm has been reported for $TpIr(C_2H_4)(PPh_3)$[11]).

The one-bond $^{13}C-^{1}H$ coupling constant found for the C_2H_4 ligand in these complexes has a relatively low value of ca. 145 Hz. On the basis of this and of the above chemical shift data, it is tempting to speculate on the possibility that the metallacyclopropane resonance form **B** has an important contribution to the ground-state electronic structure of these compounds.[14] Comparison with the data reported for other compounds that appear to behave chemically as metallacyclopropanes seems appropriate. For example, $(C_5H_5)_2Ti(C_2H_4)$,[15a] $(ArO)_2Ti(C_2H_4)(PMe_3)$,[15b] and $(C_5H_5)(Me_2PCH_2CR_2O)Ti(C_2H_4)$[15c] exhibit $\delta(C_2H_4)$ at 105, 72 (average), and 57 (average) ppm, respectively, and are further characterized by $^{1}J_{CH}$ values in the proximity of 145−150 Hz.[15] The above $\delta(^{13}C)$ values highlight the difficulties that arise when the attempt is made to compare the chemical shifts of a certain functionality bound to very

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Table 1. Crystal and Refinement Data for **3b*** and **13b***

	3b*	**13b***
formula	$C_{25}H_{37}N_6BPIr$	$C_{25}H_{37}N_6BIr$
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$ (N° 2)
a, Å	26.104(3)	11.287(3)
b, Å	16.767(5)	11.404(3)
c, Å	16.967(2)	12.516(3)
α, deg		99.56(2)
β, deg	128.551(9)	100.73(2)
γ, deg		117.90(2)
V, Å^3	5808(2)	1338.0(7)
Z	8	1
F(000)	2608	652
D_{calcd}, g cm^{-1}	1.5	1.63
temp, °C	22	22
μ(Mo Kα), cm^{-1}	46.6	50.5
cryst dimens, mm	0.4 × 0.2 × 0.2	0.1 × 0.2 × 0.3
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	graphite-monochromated Mo Kα ($\lambda = 0.710\ 69$ Å)	graphite-monochromated Mo Kα ($\lambda = 0.710\ 69$ Å)
scan technique	$\omega/2\theta$	$\omega/2\theta$
2θ, range, deg		1−60
data collcd	(−31,0,0) to (31,19,20)	(−15,−16,0) to (15,16,17)
no. of reflns collcd	5269	
no. of unique data	5111	5674
no. of obsd reflns	3210 ($I \geq 2\sigma_I$)	3273 ($I \geq 2\sigma_I$)
R_{int}, %	3.5	5.8
std reflns	3/233	3/92
R1[a]	4.3	4.7
wR2[a]	5.2	5.1
av shift/error	0.18	0.06

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o{}^2)^2]]^{1/2}$.

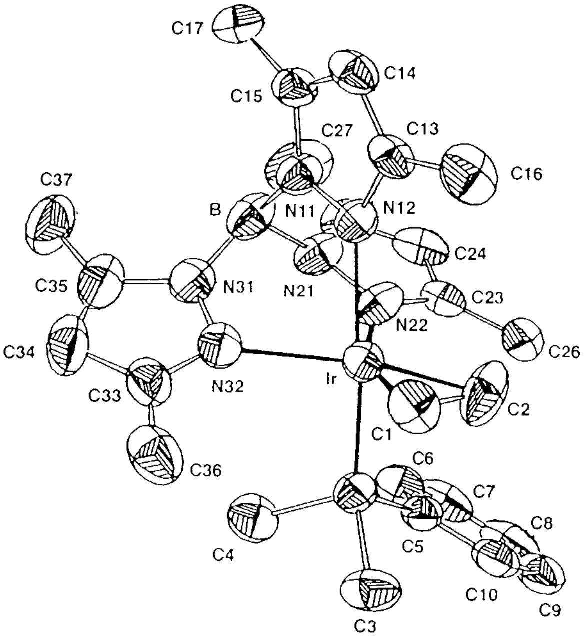

Figure 1. Molecular structure of **3b***. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths and Angles for **3b***

Bond Distances (Å)			
Ir−P	2.207(4)	Ir−C2	2.06(2)
Ir−N12	2.17(1)	P−C3	1.82(2)
Ir−N22	2.16(1)	P−C4	1.83(2)
Ir−N32	2.18(2)	P−C5	1.82(1)
Ir−C1	2.10(2)	C1−C2	1.44(2)
Bond Angles (deg)			
C1−Ir−C2	40.6(7)	P−Ir−C1	93.3(4)
N32−Ir−C2	153.6(5)	P−Ir−N32	92.1(3)
N32−Ir−C1	113.0(5)	P−Ir−N22	94.7(3)
N22−Ir−C2	112.9(7)	P−Ir−N12	171.3(3)
N22−Ir−C1	152.3(6)	Ir−P−C5	117.8(4)
N22−Ir−N32	93.2(5)	Ir−P−C4	114.9(7)
N12−Ir−C2	98.3	Ir−P−C3	119.8(5)
N12−Ir−C1	94.6(5)	C4−P−C5	100.7(7)
N12−Ir−N32	81.6(5)	C3−P−C5	101.6(8)
N12−Ir−N22	79.7(4)	C3−P−C4	98.8(7)
P−Ir−C2	90.0(6)		

different metal environments. However, the coupling constants are very similar to those of our Ir compounds and may be considered in support of the metallacyclopropane formulation. Caution should nonetheless be taken, and we would rather stress that the chemical behavior of our Tp′Ir(C_2H_4)(L) complexes is that expected for Ir(I)−olefin species. It should also be mentioned that the somewhat related Cp′Ir(C_2H_4)(PMe_3) compounds, which contain as well a static C_2H_4 ligand, are characterized by similar NMR parameters (Cp′ = C_5Me_5, δ 10.5, $^1J_{CH}$ = 151 Hz;[16] Cp = C_5H_5, δ 4.1[1a]). We conclude that retrodonation from the electron-rich Ir(I) center to the C_2H_4 ligand must be important in these compounds and suggest that this explanation should suffice to account for their NMR properties.

As indicated above, a single-crystal X-ray study of $Tp^{Me_2}Ir(C_2H_4)(PMe_2Ph)$ (**3b***), has been undertaken. Figure 1 shows an ORTEP view of the molecules of this compound; a summary of the crystal data is given in Table 1, and pertinent bond distances and angles are summarized in Table 2. The Ir atom lies in the center of a severely distorted trigonal-bipyramidal (tbp) environment, similar to that found for the parent compound **1***, except, naturally, for the presence of a molecule of PMe_2Ph in place of the axial ethylene group of the latter complex. As in **1***, the equatorial plane contains two of the N atoms of the Tp^{Me_2} group (which, as discussed below, form an almost

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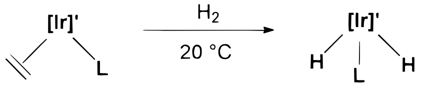
(16) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

right N22−Ir−N32 angle of 93.2(5)°, far from the ideal value of 120° expected for a regular tbp geometry) as well as the carbon atoms C1 and C2 of the ethylene ligand. Within experimental error, the Ir−C1 and Ir−C2 separations are identical to the corresponding distances in **1*** (2.08(2) Å (average) vs 2.06(2) Å in (**1***)[6]). The C1−C2 bond length, 1.44(2) Å, is intermediate between a single (1.54 Å) and a double (1.34 Å) carbon−carbon bond. It is interesting to note that this bond has a length identical to that of the equatorial C_2H_4 group in **1***, which shows that the substitution of the axial C_2H_4 bond by the stronger donor PMe_2Ph ligand has no apparent effect on this bonding parameter. A similar situation holds for the Ir−N12 bond, i.e. that trans to the PMe_2Ph ligand, which is identical, within the limits of the standard deviation, to the other two (2.17(1), 2.16(1), and 2.18(1) Å). As mentioned above, the equatorial N−Ir−N angle deviates considerably from the ideal 120° value. This important distortion within the equatorial plane is also manifested by the very large N22−Ir−C2 and N32−Ir−C1 angles of 152.3 and 152.6°, respectively. The other two N−Ir−N bond angles also have values close to 90°, albeit slightly smaller (79.7(4) and 81.6(5)°), well in the range generally encountered in complexes that contain trihapto-bonded hydrotris(pyrazolyl)borate ligands.[10a,17a] We believe that this geometrical constraint imposed by the Tp′ ligands is largely responsible for the high tendency of these ligands to enforce six-coordination to the metal center.[18]

The structural data just discussed confirm the identity of the solution and solid-state structures of this compound and, by extension, of the other related compounds reported in this paper. Further confirmation comes from $^{13}C\{^1H\}$ CPMAS studies carried out with **3b*** which show the C_2H_4 resonance at δ −8, i.e. very close to the solution value of −7.2 ppm.

Before we conclude this section, some brief comments regarding the facility with which compounds **1** and **1*** undergo substitution reactions in the presence of soft bases appear appropriate. Although both ethylene derivatives have a five-coordinate, trigonal bipyramidal ground-state structure,[6] four-coordinate intermediates resulting from the disengagement of one of the pyrazolyl rings are probably sufficiently close in energy to become accessible at normal temperatures. These intermediates probably have a high affinity for the soft ligands whereas in the case of the harder donors (e.g. acetonitrile) an alternative reaction pathway, namely that involving vinylic C−H activation and formation of the hydride−vinyl species **2** and **2***, appears to be kinetically favored. The easy formation of the 16-electron intermediates is a characteristic of these $Tp'Ir^I$ systems that makes them much more reactive, in particular in associative processes, than the corresponding $Cp'Ir^I$ derivatives. This same conclusion has been independently reached by Heinekey and associates.[11]

Hydrogenation of Tp′Ir(C_2H_4)(L) Complexes. A characteristic chemical feature of the ethylene complexes of the $Tp'Ir^I$ fragment is their ability to interact with H_2 under very mild conditions. All the Tp′Ir(C_2H_4)(PR_3) compounds tested react with H_2 at 20 °C, under 1−2 atm of this gas, to yield quantitatively (by NMR monitoring) the new Ir(III) dihydrides $Tp'IrH_2(PR_3)$ ($Tp' = Tp^{Me_2}$, $PR_3 = PMe_3$ (**6a***), PMe_2Ph (**6b***), $^1/_2$ dmpe (**6d***); Tp′ = Tp, $PR_3 = PMe_2Ph$ (**6b**)). As shown in eq 5, a related dihydride, **7*** (L = CO), is formed by starting



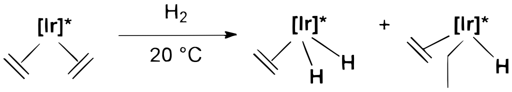
(5)

3, 3*, 4* 6, 6*, 7*

with the monocarbonyl complex **4***. The structure proposed for these derivatives is in agreement with their spectroscopic data, which are collected in the Experimental Section. Compound **6a*** was obtained recently by Heinekey et al. using a different synthetic method.[19]

The dihydride complexes exhibit good thermal stability, but they decompose slowly in $CDCl_3$. For example, solutions of compounds **6a*** and **6b*** in this solvent, when heated at 60−70 °C, convert slowly into the monohydrides $Tp^{Me_2}Ir(H)Cl(PR_3)$ ($PR_3 = PMe_3$ (**8a***), PMe_2Ph (**8b***)) with concomitant production of $CHDCl_2$. For synthetic purposes, it proves more convenient to heat the dihydrides in a mixture of $CHCl_3$−CCl_4 until complete transformation (NMR monitoring).

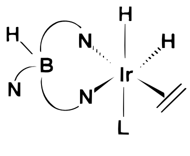
A somewhat more complex behavior is found upon hydrogenation (1−2 atm) of the bis(ethylene) complex **1***, a mixture of two compounds being now formed (eq 6). One of them is the dihydride species $Tp^{Me_2}IrH_2(C_2H_4)$ (**9***), related to those previously discussed and reported independently by Venanzi and co-workers.[17] The second is the hydride ethyl compound **10***, whose formation is favored with respect to that of **9*** upon lowering the temperature. Thus the **9***:**10*** ratio varies from 1:1.5 at 20 °C to 1:2.5 at 0 °C and 1:4 at −60 °C. These proportions are kinetic in origin since compound **10*** does not react with H_2 at the above temperatures (vide infra) and are in accord with the expected influence of the entropy term in the rates of the two competitive reactions, that involving the extrusion of one of the C_2H_4 ligands becoming more favorable at higher temperatures. At variance with a previous observation,[10b] the unsubstituted Tp complex **1** can also be hydrogenated at room temperature. In this case, however, only the ethyl complex $TpIrH(C_2H_5)(C_2H_4)$ (**10**) appears to form.



(6)

1* 9* 10*

In accord with studies by Heinekey and co-workers,[11] we propose that these hydrogenations proceed through an associative process in which 16-electron reactive intermediates are trapped by H_2 to give species of type **C**, from which C_2H_4 may be easily extruded. For reasons that remain to be fully understood, when L = C_2H_4 the insertion of C_2H_4 into the Ir−H bond becomes kinetically competitive with the dissociation of the C_2H_4 ligand and ethyl products are obtained.



C

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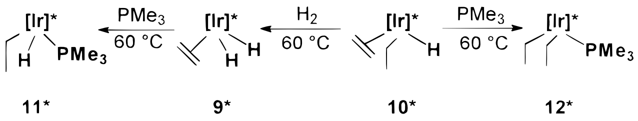
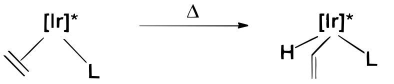
Scheme 1



Compounds **9*** and **10*** are, in our opinion, interesting examples of Ir(III)–hydride–ethylene complexes that deserve further comment. As expected for an Ir(III)–ethylene linkage,[1a,6] the coordinated olefin udergoes fast rotation on the NMR time scale around the $Ir-C_2H_4$ bond axis. The lower back-donation from the metal center, as compared to that of the analogous Ir(I) derivatives, is also manifested in the values of the chemical shift $\delta(C_2H_4)$ and of the coupling constants $^1J_{CH}$ (ca. 40 ppm and 160 Hz, respectively). The weakness of the $Ir-C_2H_4$ bond may also account for the facility with which insertion reactions take place. As shown in Scheme 1, treatment of **9*** and **10*** with PMe_3, at 60 °C, produces the expected ethyl complexes **11*** and **12***, respectively, as the result of the migratory insertion of ethylene into the Ir–H bond. In the case of the **10*** to **12*** conversion, this observation clearly implies that migration of the hydride group is more favorable than that of the ethyl fragment. Although this appears to be a general observation, not only for these $\mathrm{Tp^{Me_2}Ir^{III}}$ complexes[6] but also for many organometallic compounds, we have found that the migratory insertion of C_2H_4 into an Ir–C bond can indeed take place under mild conditions.[20]

Scheme 1 also shows that at 60 °C the hydride–ethyl complex **10*** reacts with H_2 to produce the dihydride compound **9***. Further hydrogenation gives the known tetrahydride $\mathrm{Tp^{Me_2}IrH_4}$.[21] Interestingly, this transformation can be reversed; treatment of **9*** with C_2H_4, at the same temperature, yields **10***. However, under these conditions, the latter compound undergoes formally a rapid σ-bond metathesis with C_2H_4 that gives first the hydride–vinyl complex $\mathrm{Tp^{Me_2}IrH(CH{=}CH_2)(C_2H_4)}$ (**2***) and then, in a fast sequence of events, the products previously reported as resulting from the interaction of **2*** with C_2H_4.[6]

Olefinic C–H Bond Activation in $\mathbf{Tp'Ir(C_2H_4)(L)}$ Complexes. As already mentioned, compounds **1** and **1*** and other related species undergo thermal C–H vinylic activation, under mild conditions, to yield the corresponding hydride–alkenyl derivatives.[6] We have now extended these studies to the related $\mathrm{Tp'Ir(C_2H_4)(L)}$ complexes and have found that in the $\mathrm{Tp^{Me_2}}$ series clean conversion to the hydride–vinyl species $\mathrm{Tp^{Me_2}IrH(CH{=}CH_2)(L)}$ takes place when L = PMe_3 or PMe_2Ph, upon heating at 60–70 °C (C_6D_6, NMR monitoring). This conversion (eq 7) is about 1 order of magnitude faster for the PMe_3 complex as compared with the PMe_2Ph analogue.[22] For carbon monoxide, the transformation is somewhat disfavored; heating at 130 °C (cyclohexane) is needed for the reaction to proceed at a practical rate. The unsubstituted Tp ligand has also a negative effect; no clean product can be obtained when the complexes $\mathrm{TpIr(C_2H_4)(PR_3)}$ (**3b,c**) are heated in C_6D_6 at 60–80 °C. An analogous behavior was also encountered for the parent $\mathrm{TpIr(C_2H_4)_2}$ derivative.[6] We have not attempted the photochemical activation of **3b,c**.



(7)

3a*,b*, 4* L = PMe_3, PMe_2Ph, **13a*,b***; L = CO, **14***

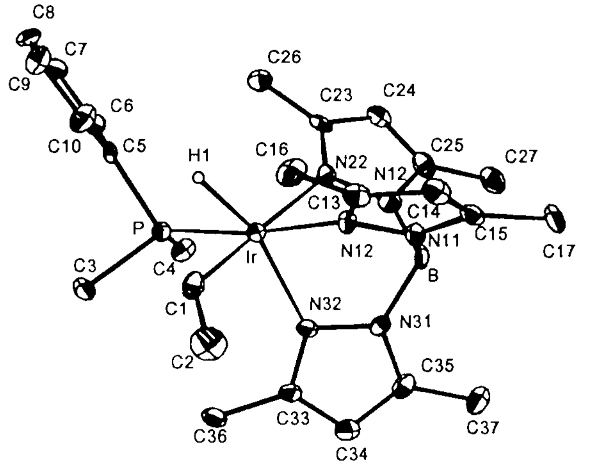


Figure 2. Molecular structure of **13b***. Hydrogen atoms are omitted for clarity, except for H1 on iridium which is represented by a sphere of arbitrary radius.

Table 3. Selected Bond Lengths and Angles for **13b***

Bond Distances (Å)			
Ir–P	2.242(3)	Ir–N32	2.215(9)
Ir–C1	2.030(9)	Ir–H1	1.6(2)
Ir–N12	2.105(9)	C1–C2	1.27(2)
Ir–N22	2.201(9)		
Bond Angles (deg)			
N22–Ir–N32	87.7(4)	P–Ir–N12	174.1(3)
N12–Ir–N32	86.2(4)	P–Ir–C1	89.3(4)
N12–Ir–N22	83.5(5)	H1–Ir–N32	163(6)
C1–Ir–N32	93.2(5)	H1–Ir–N22	10(7)
C1–Ir–N22	173.7(5)	H1–Ir–N12	103(6)
C1–Ir–N12	90.3(5)	H1–Ir–C1	73(8)
P–Ir–N32	99.7(2)	H1–Ir–P	71(6)
P–Ir–N22	96.7(3)		

In view of the scarcity of X-ray structures reported for hydride–vinyl complexes, we have carried a single-crystal X-ray analysis of the PMe_2Ph derivative **13b***. This study appears further justified by the information it may provide on the intriguing reactivity of these alkenyl complexes of iridium, a topic which is under intense scrutiny in our laboratories.[23] The structure (Figure 2) shows the expected distorted octahedral geometry, in which the N atoms of the $\mathrm{Tp^{Me_2}}$ ligand occupy three facial positions and the vinyl, hydride, and phosphine ligands occupy the others. Bond angles around the metal center (Table 3) have values close to those expected for octahedral geometry, except those involving the hydride ligand. However, due to the difficulties in locating this atom with sufficient precision, these deviations should be taken with caution. As in the parent compound **3b***, the N–Ir–N bond angles have values close to the ideal 90°; nevertheless, in **13b***, they are slightly acute (83.5(5), 86.2(4), and 87.7(4)°). The Ir–H distance of 1.6(2) Å is in the range reported for these bonds.[6,10a,16,17,24]

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(20) (a) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288. (b) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem. Eur. J.*, in press.

(21) (a) Paneque, M.; Poveda, M. L.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519. (b) Paneque et al., submitted.

(22) Surprisingly, these reactions are considerably slower when crude, noncrystallized, starting materials are used. We do not know the nature of the inhibitor, but a series of experiments indicates that it is not O_2, H_2O, PMe_3, or adventitious acid or base.

(23) (a) Alvarado, Y.; Daff, P. J.; Pérez, P. J.; Poveda, M. L.; Sánchez-Delgado, R.; Carmona, E. *Organometallics* **1996**, *15*, 2192. (b) Alías, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *J. Am. Chem. Soc.* **1998**, *120*, 5816. (c) Alías, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A. *Organometallics*, in press.

The Ir−P bond (2.242(3) Å) is longer than that in **3b*** (2.207(4) Å). This is the opposite trend expected for the increase in the oxidation state of the Ir center, and whereas it might be attributed to a π-acceptor role[25] of the PMe_2Ph ligand in the Ir(I) complex **3b***, we would rather ascribe the lengthening of this bond in **13b*** to its being trans with respect to the shortest Ir−N bonds (Ir−N12, 2.105(9) Å). As can be seen in Figure 2, the vinyl fragment lies almost in the plane defined by Ir−H1−N22−N32. It is actually slightly above that plane, almost eclipsing the H1−Ir−N32 vector, with Cα facing the hydride ligand. This conformation is similar to that found in Cp*IrH($CH{=}CH_2$)(PMe_3),[16] but rotated by 180°. The Ir−C1 distance of 2.030(9) Å is however shorter than in the latter compound (2.054(4) Å), although this value can be considered normal. Finally, the length of the C=C bond in the vinyl group (1.270(2) Å) is somewhat shorter than that of a typical double bond but identical to that found in the Cp* complex mentioned above.

It is pertinent to address again[6] the C−H bond activation reaction that converts the Ir−C_2H_4 fragment into an isomeric IrH($CH{=}CH_2$) structure. The characterization of the Tp^{Me_2}Ir(C_2H_4)(L) complexes as five-coordinate, 18-electron species leaves no doubt that the C−H activation occurs between electronically saturated, i.e. 18-electron, iridium centers. Hence, and at variance with Graham's proposal for a somewhat related system,[5] no thermodynamic driving force associated with the electronic and coordination unsaturation of the starting Ir(I) center can be invoked to explain the olefinic C−H activation reaction. In the related C_5R_5Ir−PMe_3 system, the Ir−C_2H_4 and IrH($CH{=}CH_2$) structures exhibit opposite thermodynamics; i.e., the Ir−C_2H_4 complex is more stable than the hydride−vinyl isomer. Tp′ and Cp′ ligands have relatively similar electron-donor properties[26a,b] although some differences appear to exist and the following order of donor ability was recently proposed:[26c,d] $Tp^{Me_2} \leq C_5H_5 < C_5Me_5$. For the Ir(III) compounds (A)-IrH($CH{=}CH_2$)(CO) (A = Tp^{Me_2} (**14***), C_5H_5[1a]), almost identical ν(CO) frequencies have been identified (2020 and 2022 cm^{-1}, respectively). A similar situation is encountered in Ir(I) compounds: 1990 cm^{-1} for Tp^{Me_2}Ir(C_2H_4)(CO) (**4***) and 1979 cm^{-1} for (C_5H_5)Ir(C_2H_4)(CO).[1a] The above data for the Tp^{Me_2} system show that an increase in ν(CO) of ca. 30 cm^{-1} accompanies the **4*** to **14*** transformation, and in this regard, it should be noted that a similar $\Delta\nu$(CO) of ca. 32 cm^{-1} is associated with the conversion of the $Tp^{CF_3,Me}$Ir(C_2H_4)(CO) (2030 cm^{-1}) into $Tp^{CF_3,Me}$IrH($CH{=}CH_2$)(CO) (2062 cm^{-1}). This and the close resemblance of the ^1H NMR data reported for $Tp^{CF_3,Me}$Ir(C_2H_4)(CO) with those of **4*** may be taken as suggestive of analogous ground-state structures. Since, in TpIr(C_2H_4)(CO),[13] ν(CO) appears at 2000 cm^{-1}, the electron-donating power of these hydrotris(pyrazolyl)borate ligands varies in the order $Tp^{Me_2} > Tp \gg Tp^{CF_3,Me}$.[26e]

The Cp′ and Tp′ ligands differ considerably in size and therefore exert dissimilar steric pressure; cone angles of 236 (Tp^{Me_2}), 199 (Tp), 182 (C_5Me_5), and 150° (C_5H_5) have been reported for these groups (Tp′;[4c] Cp′[27]). Even though these differences could be invoked to account for the above order of thermodynamic stability, i.e. [Ir]′H($CH{=}CH_2$) > [Ir]′(C_2H_4), we would rather emphasize two additional factors which we believe play an important role in helping the Tp′Ir system to overcome the otherwise unfavorable thermodynamics of the Ir(C_2H_4) to IrH($CH{=}CH_2$) transformation: (a) the harder nature of the Tp′ ligands as compared to the Cp′, which makes them bind preferentially to the also harder Ir(III) centers, and (b) their well-known propensity to impose six-coordination at the metal center,[18] a situation that is highly favorable for d^6 Ir(III). We presume that these factors are of importance to understand the somewhat anomalous chemistry exhibited in this respect by the Tp′Ir complexes.[6,17b,28] In the present case, these arguments can be additionally used to explain the exceedingly high reactivity of the dicarbonyl compounds Tp′Ir$(CO)_2$ toward water.

Since unsaturated species derived from the Tp^{Me_2}Ir(C_2H_4)(L) compounds by dissociation of either the C_2H_4 or the L ligand are very active in reactions that involve aromatic C−H bond activation,[29] such dissociation processes cannot take place during the vinylic C−H activations discussed above. A simple, concerted oxidative addition reaction would be in accord with all the experimental data accumulated during the progress of this work. However, a recent theoretical analysis by Hall et al.[30] suggests the process could be more complex and require as a previous step the rupture of one of the Ir−N bonds within the Tp^{Me_2}Ir fragment. A detailed study of these mechanistics aspects has not been undertaken, but nonetheless we have gathered enough qualitative evidence regarding the influence of the steric and electronic effects in the C−H bond activation reaction that may be in accord with this proposal. It appears reasonable to assume that an increase of the steric hindrance and/or the electron density at the metal center should favor the temporary disengagement of one of the pyrazolyl rings. When one compares the Tp^{Me_2} and the Tp systems, the bulkier and somewhat better donor Tp^{Me_2} favors the C−H activation,[6] and the same can be said for the bulkier terminal olefins propene and 1-butene when they are compared with ethylene. Within the Tp^{Me_2} system, the reactivity increases in the order CO < PMe_2Ph < PMe_3 < C_2H_4, which clearly includes both electronic and steric effects. Finally, the latter seem predominant when a comparison of the reactivities of $Tp^{CF_3,Me}$Ir(C_2H_4)(CO)[5] (the C−H activation occurs at 100 °C) and Tp^{Me_2}Ir(C_2H_4)(CO) (**4***) (120−140 °C) complexes is made.

Conclusions

Several complexes of the general composition Tp′Ir(C_2H_4)(L), for Tp′ = Tp or Tp^{Me_2} and L = tertiary phosphine or CO, have been isolated and characterized structurally as five-coordinate, 18-electron species. Similar to other Tp′-C_2H_4 derivatives,[5,6] *but at variance with the related Cp′* compounds, they are thermodynamically unstable with respect to their hydride−vinyl isomers. We propose that this behavior may be associated with the hard nature of the Tp′ ligands and with their strong tendency to impose six-coordination at the metal center, a situation which is particularly favorable for the d^6 Ir(III) systems. The Ir(I) mixed C_2H_4−L adducts also undergo easy ligand exchange (with soft bases) and hydrogenation reactions,

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(25) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339.

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(27) These values have been taken from ref 4e.

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(29) Unpublished results from this laboratory.

(30) Jiménez-Castaño, R.; Niu, S.; Hall, M. B. *Organometallics* **1997**, *16*, 1962. See also: Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260.

which are best explained by the accessibility of low-energy, albeit undetected, 16-electron intermediates, formed by momentary unanchoring of one of the pyrazolyl arms. The same type of species may be the key intermediates in the vinylic C−H activation experienced by the $Tp^{Me_2}Ir(C_2H_4)(L)$ derivatives.

Experimental Section

Microanalyses were performed by the Analytical Service of the Universidad de Sevilla. Infrared spectra were obtained from Perkin-Elmer spectrometers, models 577 and 684. The NMR instruments were Varian XL-200, Bruker AMX-500, and Bruker AMX-300 spectrometers. Spectra were referenced to external $SiMe_4$ ($\delta = 0$ ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen by following conventional Schlenk techniques. The complexes $Tp^{Me_2}Ir(C_2H_4)_2$,[6] $TpIr(C_2H_4)_2$,[10] and $[IrCl(coe)(CO)]_2$[31] (coe = cyclooctene) were obtained by published procedures.

$Tp^{Me_2}Ir(C_2H_4)(PMe_3)$ (3a*). The bis(ethylene) complex **1*** (0.2 g, 0.37 mmol) was dissolved in THF (20 mL), and PMe_3 was added (0.40 mL, 1 M solution in THF). The mixture was stirred for 2 h at ambient temperature, and the solvent was evaporated to dryness. The oily residue was treated with petroleum ether (10 mL), and the volatiles were removed in vacuo. The resulting powder was then redissolved in acetone (10 mL), and the solution was filtered. Concentration and cooling at −20 °C afforded the product as a white-cream-colored powder in ca. 50−70% yield. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 5.78 (s, 2 H, 2 CH_{pyr}), 5.10 (s, 1 H, CH_{pyr}), 2.68 (m, 2 H, 2 CH_{olef}), 2.43 (s, 6 H, 2 Me), 2.35 (s, 6 H, 2 Me), 2.22 (s, 3 H, Me), 2.04 (s, 3 H, Me), 1.56 (m, $^3J_{PH} = 5.9$ Hz, 2 H, 2 CH_{olef}), 0.76 (d, $^2J_{PH} = 9.6$ Hz, 9 H, PMe_3). ^{1}H{^{31}P} NMR: the C_2H_4 protons appear as an AA′BB′ spin system with δ_A 2.68 (pseudoquartet, $J_{app} = 4$ Hz) and δ_B 1.56 (pseudoquartet). ^{31}P{^{1}H} NMR (88 MHz, C_6D_6, 298 K): δ −45.6 (s). ^{13}C{^{1}H} (50 MHz, C_6D_6, 298 K): δ 151.4 (2 *C*Me), 151.1 (d, $^3J_{PC} = 6$ Hz, *C*Me), 144.2 (2 *C*Me), 141.9 (*C*Me), 107.7 (d, $^4J_{PC} = 4$ Hz, CH_{pyr}), 105.7 (2 CH_{pyr}), 17.0, 13.5, 13.1, 11.7 (s, 2:2:1:1 ratio, C*Me*), 12.7 (d, $^1J_{PC} = 10$ Hz, PMe_3), −8.1 (d, $^2J_{PC} = 4$ Hz, $^1J_{CH} = 145$ Hz, C_2H_4). Anal. Calcd for $C_{20}H_{35}N_6BPIr$: C, 42.5; H, 6.3; N, 13.5. Found: C, 41.9; H, 6.7; N, 13.2.

$Tp^{Me_2}Ir(C_2H_4)(PMe_2Ph)$ (3b*). This compound was obtained as pale yellow crystals from acetone in approximately the same yield by following a procedure similar to that described for complex **3a***. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 6.8 (m, 5 H, C_6H_5), 5.63, 5.09 (s, 2 H, 1 H, 2 CH_{pyr}), 2.78, 1.73 (m, 2 H, 2 H, C_2H_4), 2.38, 2.25, 2.17, 2.03 (s, 2:1:2:1 ratio, 6 Me), 1.09 (d, $^1J_{PH} = 9.2$ Hz, 6 H, 2 PMe). ^{31}P{^{1}H} NMR (132 MHz, C_6D_6, 298 K): δ −40.7 (s). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ 152.1 (2 *C*Me), 151.3 (d, $^3J_{PC} = 4$ Hz, *C*Me), 144.4 (2 *C*Me), 142.2 (*C*Me), 137.7 (d, $^1J_{PC} = 52$ Hz, $C_{ar}P$), 130−127 (CH, Ph), 108.1 (d, $^4J_{PC} = 4$ Hz, CH_{pyr}), 106.0 (2 CH_{pyr}), 16.5, 13.4, 12.8, 11.3 (2:1:2:1 ratio, C*Me*), 11.9 (d, $^1J_{PC} = 16$ Hz, 2 PMe), −7.2 (d, $^2J_{PC} = 4$ Hz, C_2H_4). Anal. Calcd for $C_{25}H_{37}N_6BPIr$: C, 45.8; H, 5.6; N, 12.8. Found: C, 45.9; H, 5.7; N, 12.9.

$Tp^{Me_2}Ir(C_2H_4)(PEt_3)$ (3c*). By the same general method, complex **3c*** was obtained in ca. 70% yield, from Et_2O, as pale yellow needles. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 5.83 (s, 2 H, 2 CH_{pyr}), 5.30 (s, 1 H, CH_{pyr}), 2.44 (s, 6 H, 2 Me), 2.42 (s, 6 H, 2 Me), 2.22 (m, 2 H, 2 CH_{olef}), 2.16 (s, 3 H, Me), 2.14 (s, 3 H, Me), 1.57 (m, 2 H, 2 CH_{olef}), 1.54 (m, 6 H, 3 PCH_2CH_3), 0.67 (m, 9 H, 3 PCH_2CH_3). ^{31}P{^{1}H} NMR (132 MHz, $CDCl_3$, 298 K): δ −31.9 (s). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 151.5, 150.7 (2:1 ratio, *C*Me), 144.4, 142.0 (2:1 ratio, *C*Me), 107.5 (d, $^4J_{PC} = 4$ Hz, CH_{pyr}), 105.5 (2 CH_{pyr}), 16.9, 13.3, 12.7, 11,7 (2:1:2:1 ratio, C*Me*), 14.9 (d, $^1J_{PC} = 34$ Hz, PCH_2), 6.9 (d, $^2J_{PC} = 4$ Hz, PCH_2CH_3), −10.9 (d, $^2J_{PC} = 4$ Hz, $^1J_{CH} = 145$ Hz, C_2H_4). Anal. Calcd for $C_{23}H_{41}N_6BPIr$: C, 43.4; H, 6.5; N, 13.2. Found: C, 43.5; H, 6.6; N, 13.3.

$[Tp^{Me_2}Ir(C_2H_4)]_2(dmpe)$ (3d*). From complex **1*** and dmpe, complex **3d*** was obtained in ca. 45% yield in the form of small yellow needles ($Et_2O-CH_2Cl_2$; −20 °C). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.77 (s, 2 H, 2 CH_{pyr}), 5.27 (s, 1 H, CH_{pyr}), 2.34 (s, 6 H, 2 Me), 2.20 (s, 6 H, 2 Me), 2.09 (s, 3 H, Me), 2.07 (m, 2 H, 2 CH_{olef}), 2.06 (s, 3 H, Me), 1.00 (m, 2 H, 2 CH_{olef}), 0.66 (pseudot, $J_{PHapp} = 4.4$ Hz, 6 H, 2 PMe), 0.10 (d, $J_{PH} = 2.3$ Hz, 2 H, PCH_2). ^{31}P{^{1}H} NMR (220 MHz, $CDCl_3$, 298 K): δ −38.7 (s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ 151.2, 150.9 (2:1 ratio, *C*Me), 143.9, 142.9 (2:1 ratio, *C*Me), 107.5, 105.9 (1:2 ratio, CH_{pyr}), 20.9 (pseudot, $J_{PCapp} = 18$ Hz, PCH_2), 16.8, 13.3, 12.5, 11.7 (2:1:2:1 ratio, C*Me*), 10.9 (pseudot, $J_{PCapp} = 18$ Hz, PMe), −9.1 ($^1J_{CH} = 146$ Hz, C_2H_4).

$TpIr(C_2H_4)(PMe_2Ph)$ (3b). According to the same general procedure, complex **3b** was obtained in ca. 85% yield as yellow crystals from acetone. ^{1}H NMR (500 MHz, C_6D_6, 296 K): δ 7.8−5.7 (m, 5 H, C_6H_5, m, 2:1 pattern, 9 H, CH_{pyr}), 1.7−1.62 (m, 4 H, C_2H_4), 1.26 (d, $^2J_{PH} = 9.3$ Hz, 6 H, 2 PMe). ^{31}P{^{1}H} NMR (220 MHz, C_6D_6, 296 K): δ −29.0 (s). ^{13}C{^{1}H} NMR (120 MHz, C_6D_6, 296 K): δ 143−104 (C_6H_5 and CH_{pyr},), 13.5 (d, $^1J_{PC} = 37$ Hz, PMe), 0.5 (d, $^2J_{PC} = 3$ Hz, C_2H_4). Anal. Calcd for $C_{19}H_{25}N_6BPIr$: C, 39.9; H, 4.4; N, 14.7. Found: C, 39.5; H, 4.3; N, 13.9.

$TpIr(C_2H_4)(PEt_3)$ (3c). The product was obtained as pale yellow crystals from acetone (yield 50%). ^{1}H NMR (300 MHz, $CDCl_3$, 296 K): 7.9−6.0 (m, 9 H, 2:1 pattern, CH_{pyr}), 1.65 (m, 6 H, 3 PCH_2), 1.18 (m, 2 H, 2 CH_{olef}), 1.00 (m, 2 H, 2 CH_{olef}), 0.83 (m, 9 H, 3 PCH_2CH_3). ^{31}P{^{1}H} NMR (132 MHz, $CDCl_3$, 296 K): δ −16.4 (s). ^{13}C{^{1}H} NMR (132 MHz, $CDCl_3$, 296 K): δ 144−104 (2:1 pattern, CH_{pyr},), 15.3 (d, $^1J_{PC} = 34$ Hz, PCH_2), 7.8 (PCH_2CH_3), −2.8 (C_2H_4). Anal. Calcd for $C_{17}H_{29}N_6BPIr$: C, 37.0; H, 5.3; N, 15.2. Found: C, 37.0; H, 5.3; N, 15.2.

$Tp^{Me_2}Ir(C_2H_4)(CO)$ (4*). $[IrCl(coe)(CO)]_2$ (0.3 g, 0.41 mmol) was suspended in 30 mL of THF at 0 °C. Ethylene was bubbled through the mixture for 10 min to give a colorless solution to which KTp* (0.28 g, 0.82 mmol) was added. The reaction mixture became orange and gradually evolved to a final pale reddish color after 4 h of stirring at room temperature. Volatiles were pumped off under vacuum, and the residue was extracted with 30 mL of a 1:1 mixture of Et_2O and CH_2Cl_2. The resulting suspension was filtered through Celite to eliminate the potassium chloride, and the solution was partially evaporated until cloudiness. Cooling at −20 °C afforded **4*** as a white material in 70% yield. IR (Nujol): ν(CO) 1990 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.85 (s, 2 H, 2 CH_{pyr}), 5.50 (s, 1 H, CH_{pyr}), 2.37 (s, 12 H, 4 Me), 2.32 (pseudoquartet, $J_{app} = 4.5$ Hz, 2 H, 2 CH_{olef}), 2.25 (s, 3 H, Me), 2.24 (s, 3 H, Me), 1.76 (pseudoquartet, 2 H, 2 CH_{olef}). The AA′BB′ spin system of the C_2H_4 ligand has been successfully simulated: $J_{AB} = 9.2$, $J_{AA'} = J_{BB'} = -7.4$, $J_{A'B} = J_{AB'} = -4.3$ Hz. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 165.3 (CO), 152.4, 150.2 (1:2 ratio, *C*Me), 143.6, 143.2 (1:2 ratio, *C*Me), 109.4, 105.5 (1:2 ratio, CH_{pyr}), 15.3, 13.3, 12.4, 12.2 (2:1:1:2 ratio, C*Me*), 0.6 (C_2H_4).

$Tp^{Me_2}IrH(CO)(COOH)$ (5*). Through a solution of complex **4*** (0.1 g, 0.2 mmol) in THF (20 mL) was bubbled carbon monoxide for ca. 10 min. The solvent was evaporated and the residue taken up in CH_2Cl_2. After centrifugation, the dicloromethane was evaporated to give a white residue of spectroscopically pure **5*** (yield 70%). IR (Nujol): ν(Ir−H) 2170; ν(CO) 2040; ν(COOH) 1630 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 296 K): δ 8.85 (br, 1 H, COOH), 5.78, 5.72, 5.69 (s, 1 H, 1 H, 1 H, CH_{pyr}), 2.28, 2.24, 2.23, 2.16, 2.15, 2.12 (s, 3 H each, 6 Me), −15.81 (s, 1 H, Ir−H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 296 K): δ 168.3 (CO), 166.0 ($^2J_{CH} = 7$ Hz, Ir−COOH), 151.5, 151.0, 150.8, 144.4, 144.3, 144.1 (*C*Me), 106.6, 106.5, 105.9 (CH_{pyr}), 16.0, 15.4, 14.5, 12.7, 12.3, 12.3 (6 Me). Anal. Calcd for $C_{17}H_{24}N_6BO_3Ir$: C, 36.2; H, 4.3; N, 14.9. Found: C, 35.2; H, 4.2; N, 14.0.

$Tp^{Me_2}IrH_2(PMe_3)$ (6a*). Complex **3a*** (0.12 g, 0.2 mmol) was dissolved in THF (10 mL) and transferred to a Fisher-Porter bottle. The solution was pressurized with 2 atm of H_2. After 2 h of stirring at room temperature, excess H_2 was vented and replaced by an atmosphere of N_2. The volatiles were removed in vacuo, and an ^{1}H NMR spectrum of the residue revealed a quantitative conversion to the dihydride. A crystalline solid was obtained in 70% yield by cooling a concentrated Et_2O solution at −20 °C. IR (Nujol): ν(Ir−H) 2150, 2135 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 5.76 (s, 2 H, 2

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CH$_{pyr}$), 5.47 (s, 1 H, CH$_{pyr}$), 2.40, 2.30, 2.27, 2.10 (s, 1:2:2:1 ratio, 6 Me), 1.40 (d, $^2J_{PH}$ = 9.6 Hz, 9 H, PMe$_3$), −21.21 (d, $^2J_{PH}$ = 26.1 Hz, 2 H, Ir−H). ^{31}P{^{1}H} NMR (132 MHz, C$_6$D$_6$, 298 K): δ −53.2 (s). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K): δ 150.2, 149.5 (s, d, 2:1 ratio, $^3J_{PC}$ = 4 Hz, *C*Me), 143.7, 142.0 (s, s, 2:1 ratio, 2 *C*Me), 105.6 (2 CH$_{pyr}$), 104, 6 (d, $^4J_{PC}$ = 3 Hz, CH$_{pyr}$), 23.2 (d, $^1J_{PC}$ = 37 Hz, PMe$_3$), 17.3, 17.2, 12.6, 12.3 (s, 1:2:2:1 ratio, C*Me*). Anal. Calcd for C$_{18}$H$_{33}$N$_6$BPIr: C, 38.1; H, 5.8; N, 14.8. Found: C, 38.4; H, 6.0; N, 14.4.

Tp^{Me_2}IrH$_2$(PMe$_2$Ph) (6b*). This complex was obtained by following the method described for the previous dihydride. Colorless crystals (70% yield) were obtained from Et$_2$O. IR (Nujol): ν(Ir−H) 2160, 2145 cm^{-1}. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 7.5−6.8 (m, 5 H, C$_6$H$_5$), 5.66 (s, 2 H, 2 CH$_{pyr}$), 5.53 (s, 1 H, CH$_{pyr}$), 2.47, 2.31, 2.14, 1.95 (s, 1:2:1:2 ratio, 6 Me), 1.88 (d, $^2J_{PH}$ = 9.0 Hz, 6 H, 2 PMe), −21.16 (d, $^2J_{PH}$ = 26.8 Hz, 2 H, Ir−H). ^{31}P{^{1}H} NMR (220 MHz, C$_6$D$_6$, 298 K): δ −38.3 (s). ^{13}C{^{1}H} NMR (120 MHz, C$_6$D$_6$, 298 K): δ 150.6, 149.7 (2:1 ratio, *C*Me), 143.5, 142.0 (2:1 ratio, *C*Me), 139.3 (d, $^1J_{PC}$ = 45 Hz, C$_{ar}$P), 131−127 (CH, Ph), 105.7, 104.8 (2:1 ratio, CH$_{pyr}$), 25.7 (d, $^1J_{PC}$ = 41 Hz, PMe), 17.5, 16.6, 12.7, 12.2 (1:2:2:1 ratio, C*Me*). Anal. Calcd for C$_{23}$H$_{35}$N$_6$BPIr: C, 43.9; H, 5.6; N, 13.3. Found: C, 44.1; H, 5.8; N, 13.3.

[Tp^{Me_2}IrH$_2$]$_2$(dmpe) (6d*). According to the already described general method, this complex was obtained in 70% yield as white crystals from Et$_2$O−CH$_2$Cl$_2$. IR (Nujol): ν(Ir−H) 2165, 2130, 2110 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 5.75 (s, 2 H, 2 CH$_{pyr}$), 5.57 (s, 1 H, CH$_{pyr}$), 2.37 (s, 6 H, 2 Me), 2.19 (s, 3 H, Me), 2.10 (s, 6 H, 2 Me), 2.07 (s, 3 H, Me), 1.25 (pseudot, J_{PHapp} = 3.7 Hz, 6 H, 2 PMe), 0.76 (s, 2 H, PCH$_2$), −21.87 (filled-in d, J_{PHapp} = 24.5 Hz, 2 H, Ir−H). ^{31}P{^{1}H} NMR (220 MHz, CDCl$_3$, 298 K): δ −40.0 (s). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): δ 150.2, 149.2 (2:1 ratio, *C*Me), 143.8, 142.6 (2:1 ratio, *C*Me), 105.5, 104.1 (2:1 ratio, CH$_{pyr}$), 25.7 (pseudot, J_{PCapp} = 16 Hz, PCH$_2$), 22.7 (pseudot, J_{PCapp} = 19 Hz, PMe), 17.2, 17.0, 12.7, 12.6 (1:2:1:2 ratio, C*Me*). Anal. Calcd for C$_{36}$H$_{64}$N$_{12}$B$_2$P$_2$Ir$_2$: C, 38.2; H, 5.6; N, 14.8. Found: C, 38.6; H, 5.6; N, 14.3.

TpIrH$_2$(PMe$_2$Ph) (6b). The above procedure gave crude white material with a quantitative yield. Colorless crystals may be obtained from Et$_2$O at −20 °C. IR (Nujol): ν(Ir−H) 2138 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 8.0−7.0 (m, 11 H, C$_6$H$_5$ and 3,5-CH$_{pyr}$), 5.84 (m, 2 H, 4-CH$_{pyr}$), 5.70 (m, 1 H, 4-CH$_{pyr}$), 1.69 (d, $^2J_{PH}$ = 9.8 Hz, 6 H, 2 PMe), −20.34 (d, $^2J_{PH}$ = 25.2 Hz, 2 H, Ir−H). ^{31}P {^{1}H} NMR (220 MHz, CDCl$_3$, 298 K): δ −31.0 (s). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): δ 146.1, 143.5 (d, s, $^3J_{PC}$ = 3 Hz, 1:2 ratio, 3-CH$_{pyr}$), 138.2 (d, $^1J_{PC}$ = 51 Hz, C$_{ar}$P), 134.0, 133.1 (s, s, 2:1 ratio, 5-CH$_{pyr}$), 131−127 (C$_6$H$_5$), 105.4, 104.9 (s, s, 1:2 ratio, 4-CH$_{pyr}$), 21.0 (d, $^1J_{PC}$ = 40 Hz, PMe). Anal. Calcd for C$_{17}$H$_{23}$N$_6$BPIr·$^1/_2$Et$_2$O: C, 39.2; H, 4.8; N, 14.4. Found: C, 40.0; H, 5.3; N, 13.9.

Tp^{Me_2}IrH$_2$(CO) (7*). This complex was obtained similarly to the above dihydrides. The yield was quantitative by NMR. IR (Nujol): ν(CO) 2008; ν(Ir−H) 2150, 2120 cm^{-1}. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 5.54 (s, 2 H, 2 CH$_{pyr}$), 5.42 (s, 1 H, CH$_{pyr}$), 2.25, 2.24, 2.14, 2.02 (s, 2:1:2:1 ratio, 6 Me), −16.50 (s, 2 H, Ir−H). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 298 K): δ 170.0 (CO), 151.0, 150.4 (1:2 ratio, *C*Me), 143.4, 143.3 (1:2 ratio, CH$_{pyr}$), 105.5, 105.4 (2:1 ratio, CH$_{pyr}$), 17.0, 15.3, 12.0, 11.9 (1:2:1:2 ratio, C*Me*).

Tp^{Me_2}IrHCl(PMe$_3$) (8a*). A 0.02 g sample of complex **6a*** was dissolved in a mixture of CDCl$_3$ (0.5 mL) and CCl$_4$ (0.2 mL), and the resulting solution was transferred to an NMR tube. Heating at 80−90 °C, with continuous monitoring of the reaction by ^{1}H NMR spectroscopy, afforded the title compound. The solvent was evaporated to dryness to give the product as a white powder. IR (Nujol): ν(Ir−H) 2200 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 5.79, 5,72, 5,65 (s, 1 H, 1H, 1 H, CH$_{pyr}$), 2.58, 2.43, 2.41, 2.37, 2.23, 2,19 (s, 3 H each, 6 Me), 1.55 (d, $^2J_{PH}$ = 9.5 Hz, 9 H, PMe$_3$), −23.43 (d, $^2J_{PH}$ = 21.8 Hz, 2 H, Ir−H). ^{31}P{^{1}H} NMR (220 MHz, CDCl$_3$, 298 K): δ −50.8 (s). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): δ 152.4, 151.6, 151.1, 145.1, 143.4, 142.6 (*C*Me), 107.8, 106.7, 106.0 (CH$_{pyr}$), 18.1, 17.8, 17.5, 13.1, 12.6, 12.4 (C*Me*), 14.9 (d, $^1J_{PC}$ = 46 Hz, PMe$_3$). Anal. Calcd for C$_{18}$H$_{32}$N$_6$BClPIr: C, 35.9; H, 5.3; N, 14.0. Found: C, 35.7; H, 5.5; N, 11.6.

Tp^{Me_2}IrHCl(PMe$_2$Ph) (8b*). This compound was obtained in the same fashion as the monochloride described above. The crude sample can be crystallized from Et$_2$O at −20 °C. IR (Nujol): ν(Ir−H) 2225 cm^{-1}. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 7.3−6.9 (m, 5 H, C$_6$H$_5$), 5.71, 5.48, 5.24 (s, 1 H, 1 H, 1 H, CH$_{pyr}$) 2.7−1.4 (s, 3 H each, 6 Me), 1.96 (d, $^2J_{PH}$ = 10.1 Hz, 3 H, PMe), 1.44 (d, $^2J_{PH}$ = 10.0 Hz, 3 H, PMe), −22.93 (d, $^2J_{PH}$ = 21.3 Hz, 1 H, Ir−H). ^{31}P{^{1}H} NMR (220 MHz, C$_6$D$_6$, 298 K): δ −39.0 (s). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 298 K): δ 153.1, 151.8, 151.6, 143.9, 143.3, 142.1 (s, s, d, s, s, s, $^3J_{PC}$ = 3 Hz, *C*Me), 137.6 (d, $^1J_{PC}$ = 52 Hz, C$_{ar}$P), 130−127 (CH, Ph), 108.0, 106.3, 106.2 (CH$_{pyr}$), 18.5 (d, $^1J_{PC}$ = 42 Hz, PMe), 16.0 (d, $^1J_{PC}$ = 37 Hz, PMe), 16.2, 15.1, 15.1, 12.8, 12.6, 12.2 (C*Me*). Anal. Calcd for C$_{23}$H$_{34}$N$_6$BClPIr: C, 41.6; H, 5.1; N, 12.7. Found: C, 42.0; H, 5.2; N, 12.3.

Tp^{Me_2}IrH$_2$(C$_2$H$_4$) (9*). A solution of complex **1*** (0.3 g, 0.55 mmol) in THF (30 mL) was pressurized with H$_2$ (2 atm). After 1 h of stirring at room temperature, the H$_2$ atmosphere was replaced by N$_2$, and the solvent was evaporated. ^{1}H NMR analysis of the crude material was in accord with its being a 1:1.5 mixture of complexes **9*** and **10***. Column cromatography (silica gel as support; petroleum ether as eluent) allowed the separation of the two compounds with the ethyl derivative being the first to drain down the column. The individual compounds were obtained as colorless crystals by crystallization from petroleum ether. IR (Nujol): ν(Ir−H) 2190, 2170 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 298 K): δ 5.61 (s, 2 H, 2 CH$_{pyr}$), 5.48 (s, 1 H, CH$_{pyr}$), 3.46 (s, 4 H, C$_2$H$_4$), 2.35 (s, 3 H, Me), 2.23 (s, 6 H, 2 Me), 2.09 (s, 3 H, Me), 1.92 (s, 6 H, 2 Me), −20.77 (s, 2 H, Ir−H).^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$, 298 K): δ 150.6, 150.2 (2:1 ratio, *C*Me), 143.2, 142.8 (2:1 ratio, *C*Me), 106.1, 105.2 (2:1 ratio, CH$_{pyr}$), 35.6 (C$_2$H$_4$), 17.5, 13.9, 12.3, 12.2 (1:2:1:2 ratio, C*Me*). Anal. Calcd for C$_{17}$H$_{28}$N$_6$BIr: C, 39.2; H, 5.4; N, 16.1. Found: C, 39.5; H, 5.6; N, 16.3.

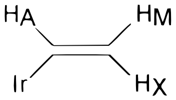
Tp^{Me_2}IrH(CH$_2$CH$_3$)(C$_2$H$_4$) (10*). IR (Nujol): ν(Ir−H) 2195 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 298 K): 5,74, 5.62, 5.39 (s, 1 H, 1 H, 1 H, CH$_{pyr}$), 3.65 (m, AA′ part of an AA′XX′ spin system, 2 H, 2 CH$_{olef}$), 2.80 (m, XX′ part of an AA′XX′ spin system, 2 H, 2 CH$_{olef}$), 2.49, 2.30, 2.22, 2.13, 2.08, 1.72 (s, 3 H each, 6 Me), 2.43 (dq, $^2J_{AB}$ = 9.8, $^3J_{HH}$ = 7.0 Hz, 1 H, CH_AH$_B$CH$_3$), 0.68 (t, 3 H, CH$_2$CH_3), 0.50 (dq, 1 H, CH$_A$CH_BCH$_3$), −17.52 (s, 1 H, IrH). ^{13}C{^{1}H} NMR (50 MHz, THF-*d*$_8$, 298 K): δ 155−140 (6 *C*Me), 109.0, 107.7, 107.4 (CH$_{pyr}$), 43.6 (C$_2$H$_4$), 16.4 (IrCH$_2$*C*H$_3$), 15.4, 15.0, 14.3, 13.4, 13.1 (1:1:1:2 ratio, C*Me*), −17.9 (Ir*C*H$_2$CH$_3$). Anal. Calcd for C$_{19}$H$_{32}$N$_6$BIr: C, 41.7; H, 5.8; N, 15.3. Found: C, 41.8; H, 6.0; N, 14.9.

TpIrH(CH$_2$CH$_3$)(C$_2$H$_4$) (10). Under the same experimental conditions described above, complex **1** was hydrogenated to give complex **10** as the sole product. Pale yellow crystals were obtained from concentrated solutions in petroleum ether−Et$_2$O (2:1). IR (Nujol): ν(Ir−H) 2200 cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 298 K): δ 7.90, 7.50, 7.38, 7.32, 7.30, 6.80 (d, $^3J_{HH}$ = 2.5 Hz, 1 H each, 3,5-CH$_{pyr}$), 5.9, 5.76, 5.74 (t, 1 H each, 4-CH$_{pyr}$), 3.0 (m, 4 H, C$_2$H$_4$), 1.41, 1.17 (m, m, 1 H each, CH_2CH$_3$), 1.23 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, CH$_2$CH_3), −16.2 (s, 1 H, IrH). ^{13}C{^{1}H} NMR (50 MHz, C$_6$D$_6$, 298 K): δ 142.7, 140.8, 137.8, 134.1, 105.9, 105.8, 105.2 (CH$_{pyr}$), 43.6 (C$_2$H$_4$), 19.7 (IrCH$_2$*C*H$_3$), −13.9 (Ir*C*H$_2$CH$_3$).

Tp^{Me_2}IrH(CH$_2$CH$_3$)(PMe$_3$) (11*). Complex **9*** (0.3 g, 0.55 mmol) was dissolved in neat PMe$_3$ (1 mL), and the resulting mixture was heated at 60 °C for 8 h (sealed ampule). The volatiles were removed in vacuo, and the residue was extracted with petroleum ether. Concentration and cooling at −20 °C afforded white crystals in 70% yield. IR (Nujol): ν(Ir−H) 2170 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 5.75, 5.63, 5.57 (s, 1 H, 1 H, 1 H, CH$_{pyr}$), 2.58 (m, 2 H, 2 IrCH$_2$), 2.53, 2.38, 2.27, 2.20, 2.14, 2.10 (s, 3 H each, 6 Me), 1.45 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, IrCH$_2$CH_3), 1.34 (d, $^2J_{PH}$ = 9.1 Hz, 9 H, PMe$_3$), −23.19 (d, $^2J_{PH}$ = 25.9 Hz, 1 H, IrH). ^{31}P{^{1}H} NMR (132 MHz, C$_6$D$_6$, 298 K): δ −51.6 (s). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K): δ 107.1, 105.8 (1:2 ratio, CH$_{pyr}$), 21.9 (IrCH$_2$*C*H$_3$), 19.5 (d, $^1J_{PC}$ = 36 Hz, PMe$_3$), 17.0, 15.2, 15.0, 12.8, 12.7, 12.5 (C*Me*), −24.2 (d, $^2J_{PC}$ = 6 Hz, Ir*C*H$_2$CH$_3$).

Tp^{Me_2}Ir(CH$_2$CH$_3$)$_2$(PMe$_3$) (12*). According to an analogous procedure, but starting with **10*** (0.1 g, 0.18 mmol), white crystals of the bis(ethyl) complex were obtained from petroleum ether (90% yield). ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 5.68 (s, 2 H, 2 CH$_{pyr}$), 5.61 (s, 1 H, CH$_{pyr}$), 2.62 (s, 3 H, Me), 2.51 (dq, $^2J_{AB} = 12.6$, $^3J_{HH} = 7.5$ Hz, 2 H, 2 CH_AH$_B$CH$_3$), 2.35 (dquint, $^3J_{PH} = 7.5$ Hz, 2 H, 2 CH$_A$$H_BCH_3$), 2.26 (s, 6 H, 2 Me), 2.18 (s, 6 H, 2 Me), 2.09 (s, 3 H, Me), 1.17 (d, $^2J_{PH} = 8.7$ Hz, 9 H, PMe$_3$), 0.92 (t, 6 H, 2 CH$_2$CH_3). ^{31}P{^{1}H} NMR (88 MHz, C$_6$D$_6$, 298 K): δ −49.8 (s). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 298 K): δ 150.2, 148.9 (d, s, 1:2 ratio, $^3J_{PC} = 4$ Hz, *C*Me), 142.8, 142.1, (2:1 ratio, Me), 107.6, 107.4 (d, s, 1:2 ratio, $^4J_{PC} = 3$ Hz), 16.3 (d, $^3J_{PC} = 1$ Hz, IrCH$_2$*C*H$_3$), 15.7, 13.7, 12.9, 12.8 (2:1:2:1 ratio, C*Me*), 15.6 (d, $^1J_{PC} = 36$ Hz, PMe$_3$), −19.5 (d, $^2J_{PC} = 7$ Hz, Ir*C*H$_2$CH$_3$). Anal. Calcd for $C_{22}H_{41}N_6BPIr$: C, 42.3; H, 6.6; N, 13.5. Found: C, 42.5; H, 6.7; N, 13.5.

Tp^{Me_2}IrH(CH=CH$_2$)(PMe$_3$) (13a*). Complex **3a*** was dissolved in 0.5 mL of C$_6$D$_6$ and the resulting solution transferred to a NMR tube. Heating at 60 °C was monitored periodically until the transformation was completed. The solvent was removed in vacuo to give complex **13a*** in quantitative yield. This white material was pure enough for most purposes. It can be recrystallized from acetone at −20 °C but with appreciable losses. IR (Nujol): ν(Ir−H) 2170 cm^{-1}. ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 8.51 (ddd, $^3J_{AX} = 18.2$, $^3J_{AM} = 10.6$, $^3J_{PA} = 2.0$ Hz, 1 H, H$_A$), 6.42 (dd, $^2J_{MX} = 3.8$ Hz, 1 H, H$_M$), 5,78, 5.65, 5.50 (s, 1 H, 1 H, 1 H, CH$_{pyr}$), 5.52 (dd, 1 H, H$_X$), 2.56, 2.38, 2.30, 2.23, 2.16, 2.08 (s, 3 H each, 6 Me), 1.33 (d, $^2J_{PH} = 9.4$ Hz, 9 H, PMe$_3$), −21.60 (d, $^2J_{PH} = 25.7$ Hz, 1 H, Ir−H). ^{31}P{^{1}H} NMR (132 MHz, C$_6$D$_6$, 298 K): δ −49.7 (s). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K): δ 150.7, 150.4, 150.1, 143.9, 143.4, 142.1 (*C*Me), 130.3 (d, $^2J_{PC} = 10$ Hz, Ir*C*H=CH$_2$), 121.1 (d, $^3J_{PC} = 3$ Hz, IrCH=*C*H$_2$), 107.0, 106.0, 105.9 (3 CH$_{pyr}$), 18.9 (d, $^1J_{PC} = 37$ Hz, PMe$_3$), 16.9, 16.2, 15.7, 12.7, 12.6, 12.4 (6 C*Me*).



Vinyl nomenclature

Tp^{Me_2}IrH(CH=CH$_2$)(PMe$_2$Ph) (13b*). In the same way as described above for the PMe$_3$ analogue, complex **13b*** was obtained in quantitative yield. The analytical sample, white crystals, was recrystallized from acetone. IR (Nujol): ν(Ir−H) 2195 cm^{-1}. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ 8.61 (ddd, $^3J_{AX} = 18.2$, $^3J_{AM} = 10.6$, $^3J_{PA} = 3.3$ Hz, 1 H, H$_A$), 7.4−6.8 (m, 5 H, C$_6$H$_5$), 6.39 (dd, $^2J_{MX} = 3.6$ Hz, 1 H, H$_M$), 5,80, 5.56, 5.41 (s, 1 H, 1 H, 1 H, CH$_{pyr}$), 5.55 (dd, 1 H, H$_X$), 2.60, 2.34, 2.33, 2.23, 2.11, 1.63 (s, 3 H each, 6 Me), 1.98, 1.52 (d, $^2J_{PH} = 9.3$ Hz, 3 H each, 2 PMe), −21.38 (d, $^2J_{PH} = 25.1$ Hz, 1 H, IrH). ^{31}P{^{1}H} NMR (132 MHz, C$_6$D$_6$, 298 K): δ −36.1 (s). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$, 298 K): δ 150.8, 150.6, 150.5, 143.4, 142.1 (*C*Me), 138.5 (d, $^1J_{PC} = 49$ Hz, C$_{ar}$P), 130−127 (CH, Ph), 130.3 (d, $^2J_{PC} = 10$ Hz, Ir*C*H=CH$_2$), 121.0 (IrCH=*C*H$_2$), 107.1, 106.0, 105.8 (3 CH$_{pyr}$), 21.8 (d, $^1J_{PC} = 42$ Hz, PMe), 16.9 (d, $^1J_{PC} = 36$ Hz, PMe), 16.5, 15.9, 15.8, 12.8, 12.7, 12.4 (C*Me*). Anal. Calcd for $C_{25}H_{37}N_6BPIr$: C, 45.8; H, 5.7; N, 12.8. Found: C, 45.5; H, 5.8; N, 12.2.

Tp^{Me_2}IrH(CH=CH$_2$)(CO) (14*). Complex **4*** was dissolved in C$_6$H$_{12}$, and the mixture was heated at 120 °C (sealed ampule) until complete disappearance of the starting material (NMR monitoring). The hydride−vinyl complex was obtained in ca. 70% yield along with some unidentified material. IR (petroleum ether): ν(CO) 2020 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K): δ 7.14 (dd, $^3J_{AX} = 18.1$, $^3J_{AM} = 10.4$ Hz, 1 H, H$_A$), 5.98 (dd, $^3J_{MX} = 2.7$ Hz, 1 H, H$_M$), 5.81, 5.78, 5.77 (s, 1 H, 1 H, 1 H, CH$_{pyr}$), 5.37 (dd, 1 H, H$_X$), 2.4−2.2 (6 s, 3 H each, 6 Me), −16.62 (s, 1 H, IrH). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 298 K): δ 169.1 (CO), 151.3, 151.1, 150.4, 143.8, 143.7, 143.4 (*C*Me), 123.7, 123.6 (IrCH=CH$_2$), 106.4, 106.3, 105.5 (CH$_{pyr}$), 16−12 (6 Me).

X-ray Structure Determination of 3b*. A summary of the fundamental crystal data is given in Table 1. A yellow crystal of prismatic shape was coated with an epoxy resin and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir and P were taken from ref 32. The structure was solved by Patterson and Fourier methods. The compound crystallizes with $^1/_4$ of CH$_3$COCH$_3$ per formula unit. An empirical absorption correction[33] was applied at the end of the isotropic refinement. Some nonresolvable disorder from the thermal motion was found around the CH$_3$COCH$_3$ molecule of crystallization, and because of this, the atoms of this molecule were refined only isotropically. No trend in ΔF vs F_o or (sin θ)/λ was observed. Final refinement with fixed isotropic temperature factors and coordinates for hydrogen atoms gave $R = 0.43$. Final difference calculations were carried out with the X-ray 80 system.[34]

X-ray Structure Determination of 13b*. A summary of the fundamental crystal data is given in Table 1. A colorless crystal of prismatic shape was coated with an epoxy resin and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting of the values of 25 reflections with a 2θ range of 12−28°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir and P were taken from ref 32. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[33] was applied at the end of the isotropic refinement. To prevent bias on ΔF vs F_o or (sin θ)/λ, weights were assigned as $w = 1/(a + bF_o)^2$, with the following coefficients: for $F_o < 45$, $a = 10.2$ and $b = -0.22$; for $F_o > 45$, $a = 1.05$ and $b = 0.01$. A final mixed refinement was undertaken. Hydrogen atoms were included with fixed isotropic contributions at their calculated positions, except the H1 atom, which was located in a difference Fourier map and whose coordinates were refined. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-ray 80 system.[34]

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Supporting Information Available: For **3b*** and **13b***, tables of positional and thermal parameters, fractional coordinates, and bond lengths and angles (20 pages). Ordering information is given on any current masthead page.

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