

C–H Oxidative Addition with a (PCP)Ir(III)-Pincer Complex

Hani A. Y. Mohammad,[†] Jost C. Grimm,[†] Klaus Eichele,[†] Hans-Georg Mack,[‡] Bernd Speiser,[§] Filip Novak,[§] M. Gloria Quintanilla,[⊥] William C. Kaska,^{||} and Hermann A. Mayer^{*,†}

Institut für Anorganische Chemie and Institut für Organische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany, Institut für Physikalische und Theoretische Chemie, Auf der Morgenstelle 8, 72076 Tübingen, Germany, and Department of Chemistry, University of Santa Barbara, Santa Barbara, California 93106

Received July 31, 2002

Treatment of 4-MeO-C₆H₃-2,6-(CH₂P^tBu₂)₂ with IrCl₃·nH₂O in *i*-PrOH/H₂O gives a cyclometalated pincer chlorohydrido iridium complex. A second intramolecular oxidative addition reaction of one of the *tert*-butyl C–H bonds to the Ir(III) center followed by the reductive elimination of H₂ gives a novel doubly metalated compound that is stable to air and water. X-ray crystallographic analysis revealed a chelated square-pyramidal iridium compound with two cyclometalated five-membered rings in the basal plane and the iridium bound methylene group of the four-membered ring in the apical position. The free coordination site is protected by an agostic C–H bond. While a phosphorus–phosphorus coupling constant of 351.1 Hz establishes the *trans* position of the phosphorus groups there is no indication of a hydridic or weakly bound hydrogen. Electrochemical studies establish an equilibrium between the pincer chlorohydrido compound and the doubly metalated complex and H₂. A square scheme can be used to describe the relationship between the redox couples and solution equilibria. The unusual stability of the doubly metalated complex was supported by DFT calculations at different levels of theory on model compounds. They show the coordination of two hydrogen atoms best described as η²-coordinated dihydrogen and suggest an Ir(V) oxidation state as intermediate.

Introduction

Homogeneous catalytic dehydrogenation of saturated hydrocarbons is just one part of a concerted effort to develop and broaden the scope of transition metal catalyzed carbon–hydrogen bond reactivity.^{1–9} The chemistry of iridium^{10,11} has played a central role in the expansion of this challenging field.¹² For example, the

multifaceted complex Cp*(PMe₃)IrMeOTf can activate alkanes by a “σ-bond metathesis” pathway, by an oxidative addition–reductive elimination pathway, or by electrophilic activation.^{13–16}

Similar pathways can be expected for the interaction of (PCP)IrH₂ pincer complexes with alkanes.¹⁷ Consequently, there is considerable interest in determining which of these mechanistic pathways are important in catalytic dehydrogenation and other C–H interactions so that more efficient complexes can be designed to facilitate the reaction. Experimental observations¹⁸ in some instances seem to support reductive elimination of H₂ from Ir(III)H₂ to generate a reactive 14e Ir(I) species. This coordinatively unsaturated fragment oxidatively adds RH to give an Ir(III)R(H) complex, which results in an olefin complex by β-H transfer. Release of olefin is the last step to re-form the starting material.^{19–21}

[†] Institut für Anorganische Chemie. E-mail: hermann.mayer@uni-tuebingen.de.

[‡] Institut für Physikalische und Theoretische Chemie.

[§] Institut für Organische Chemie.

[⊥] Permanent address: Dpto. Química Organica, Edificio de Farmacia, Universidad de Alcalá, Carretera Barcelona Km 33.600, 28871 Alcalá de Henares-Madrid, Spain.

^{||} Department of Chemistry, University of Santa Barbara.

(1) Shilov, A. E.; Shul'pin, G. B. In *Catalysis by Metal Complexes*; James, B. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000; p 162.

(2) Johnson, J. A.; Sames, D. *J. Am. Chem. Soc.* **2000**, *122*, 6321.

(3) Six, C.; Gabor, B.; Görls, H.; Mynott, R.; Philipps, P.; Leitner, W. *Organometallics* **1999**, *18*, 3316.

(4) Braunstein, P.; Chauvin, Y.; Nähring, J.; DeCian, A.; Fischer, J.; Tiripicchio, A.; Ugozzoli, F. *Organometallics* **1996**, *15*, 5551.

(5) Kakiuchi, F.; Murai, S. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Springer-Verlag: New York, 1999; p 47.

(6) Tellers, D. M.; Bergman, R. G. *Organometallics* **2001**, *20*, 4819.

(7) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047.

(8) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068.

(9) Miller, J. A.; Knox, J. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1449.

(10) Cotton, S. A. *Chemistry of Precious Metals*; Chapman and Hall: London, 1997; p 78.

(11) Dickson, R. S. *Organometallic Chemistry of Rhodium and Iridium*; Academic Press: New York, 1983.

(12) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025.

(13) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

(14) Tellers, D. M.; Yung, C. M.; Arndtsen, B. A.; Adamson, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 1400.

(15) Bach, I.; Goddard, R.; Kopske, C.; Seevogel, K.; Porschke, K. R. *Organometallics* **1999**, *18*, 10.

(16) Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1998**, *120*, 6169.

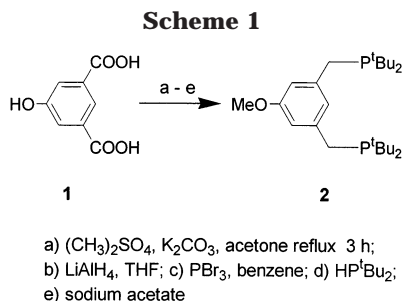
(17) Jensen, C. M.; Nemeh, S.; Kaska, W. C. Presented at the 1980 Biennial Inorganic Chemistry Symposium, Guelph, Ontario, Canada.

(18) Jensen, C. M. *Chem. Commun.* **1999**, 2443.

(19) Kanzelberger, M.; Singh, B.; Czerw, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 11017.

(20) Liu, F. C.; Goldman, A. S. *Chem. Commun.* **1999**, 655.

(21) Krogh-Jespersen, K.; Czerw, M.; Kanzelberger, M.; Goldman, A. S. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 56.

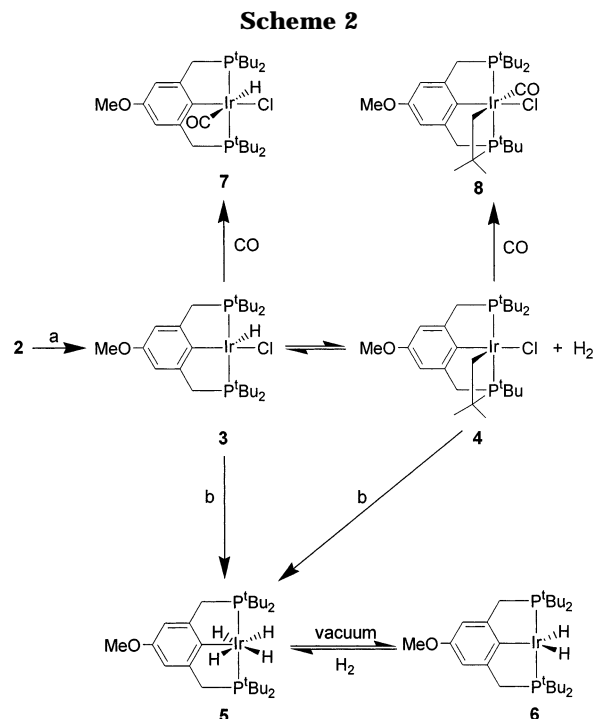


Recent calculations suggest a more prominent role for an oxidative addition pathway from Ir(III) to Ir(V) in catalytic C–H activation reactions.^{21–23} Experimental observations appear to support this pathway,^{24,25} including the reactions of novel high-temperature systems.²⁶ Examples which involve catalytic systems are sparse. The PCP pincer complexes of iridium may present the opportunity for a breakthrough in this area because they can interact with alkanes via dehydrogenation pathways to give olefins at 200 °C and above.^{18,26–28}

This broad temperature range of stability and interaction suggests that functionalization of the PCP pincer complexes for immobilization to enable easy separation of the catalyst from the products is promising.²⁹ Very often the incorporation of a functional group into the ligand backbone is accompanied by changes in reactivity of the corresponding metal complex. Therefore, investigations of model compounds which are closely related, electronically and structurally, to the supported catalysts need to be performed. Here we report on the synthesis and characterization of the methoxy functionalized PCP iridium complex **3**. In contrast to its non-functionalized congener, **3** is kinetically unstable and undergoes a second intramolecular C–H activation to form complex **4**. Interestingly, this is a low-temperature C–H activation by a 16e Ir(III) species.

Results

Ligand Synthesis. The pincer ligand 3,5-(di-*tert*-butylphosphinomethyl)anisole (**2**) can be prepared in a series of steps which have been described in the literature starting from 5-hydroxy-1,3-benzenedicarboxylic acid (**1**) (Scheme 1).^{30–33} Ligand **2** was characterized by NMR and mass spectroscopy as well as by elemental analysis. Characteristic features are a singlet



in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 33.9, and one set of resonances each in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for the di-*tert*-butylphosphinomethyl functions. The signals due to the aromatic ring and the methoxy group complete the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra and are compatible with the structure shown in Scheme 1.

Intramolecular C–H Oxidative Addition to Ir(III). Over the years many research groups have exploited the synthesis and chemistry of various (PCP)-[M] pincer metal complexes ([M] = Rh, Ir, Ru, Pt fragments)³⁴ first described by Shaw.^{35–37} The complexation of C_6H_4 -1,3-($\text{CH}_2\text{P}^t\text{Bu}_2$)₂ to a metal fragment generates two five-membered metallacycles and in the case of a d^6 Ir(III) metal center a square-pyramidal coordination geometry.

However, the treatment of the methoxy functionalized ligand **2** with $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ in 2-propanol/water gave a reaction mixture from which deep red crystals were isolated and identified as the doubly cyclometalated Ir(III) complex **4** (Scheme 2). In addition, **3** was also present in the reaction mixture. Changing to a nonpolar reaction medium by treating **2** with stoichiometric amounts of $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ in toluene also leads to reaction mixtures which contain both **3** and **4**. The ratio of **3**:**4** varies with reaction time and temperature and the amount of hydrogen present in the system. Thus, if hydrogen is allowed to escape from the reaction mixture, only **4** is observed. On the other hand, if **4** is treated with hydrogen, **3** is formed exclusively. Figure 1 displays a series of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded for a typical reaction of **2** with $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ in toluene. The chlorohydrido complex **3** already arises when the solution is stirred at room temperature for 4 h. The $^{31}\text{P}\{^1\text{H}\}$ NMR

(22) Strout, D. L.; Zaric, S.; Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6086.

(23) Niu, S. Q.; Hall, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 3992.

(24) Toner, A. J.; Gründemann, S.; Clot, E.; Limbach, H. H.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2000**, *122*, 6777.

(25) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816.

(26) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596.

(27) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083.

(28) Morales-Morales, D.; Lee, D. W.; Wang, Z. H.; Jensen, C. M. *Organometallics* **2001**, *20*, 1144.

(29) Lindner, E.; Schneller, T.; Auer, F.; Mayer, H. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2154.

(30) Bolt, P.; Bruhnke, D. *J. Prakt. Chem./Chem.-Ztg.* **1994**, 110.

(31) Boekelheide, V.; Griffin, R. W. *J. Org. Chem.* **1969**, *34*, 1960.

(32) Zimmerman, H. E.; Jones, G. *J. Am. Chem. Soc.* **1970**, *92*, 2753.

(33) Grimm, J. C.; Nachtigal, C.; Mack, H.-G.; Kaska, W. C.; Mayer, H. A. *Inorg. Chem. Commun.* **2000**, *3*, 511.

(34) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

(35) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(36) Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307.

(37) Rybtchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786.

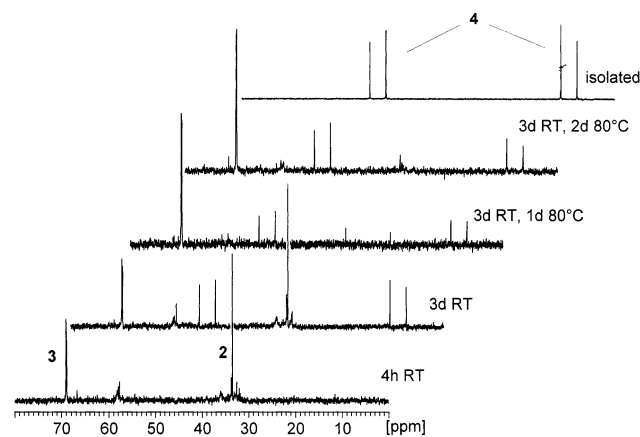


Figure 1. Time- and temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of ligand **2** with $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ in toluene.

spectrum taken after the reaction mixture was stirred for 3 d shows appreciable amounts of **4**. Additional heating of the solution at 80 °C for another day leads to the consumption of **2** to form **3**, which is gradually converted into **4**. The spectra demonstrate that the cyclometalated chlorohydrido complex **3** is generated first. In a second step a *tert*-butyl C–H bond is intramolecularly oxidatively added to the Ir(III) complex followed by the reductive elimination of H_2 to give **4**. The deep red complex **4** can be handled and stored under air for weeks and melts at 200 °C without decomposition.

The NMR spectra of **3** are comparable with those of previously reported square-pyramidal pincer ligand chlorohydrido complexes where the hydride occupies the apical site.^{33,35} Thus, the plane of symmetry perpendicular to the aromatic ring and the metal carbon bond is responsible for the equivalence of the aromatic CH, the ring- CH_2 , and two of the *tert*-butyl groups. The two $[\text{A}_9\text{X}]_2$ patterns in the ^1H and the two AXX' multiplets in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra as well as the singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (δ 69.1) are consistent with the $\text{Bu}_2\text{P}-\text{Ir}(\text{H},\text{Cl})-\text{P}^t\text{Bu}_2$ fragment in the molecule of **3**. This is also supported by the hydride triplet observed in the ^1H NMR spectrum at -43.21 ppm ($^2J(\text{P},\text{H}) = 12.8$ Hz). The spectroscopic data reveal a square-pyramidal arrangement around iridium with the hydride ligand positioned at the apical site that is in agreement with the X-ray structure analysis of the analogous nitro compound $\{4\text{-NO}_2\text{-C}_6\text{H}_4\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2\}\text{Ir}(\text{H})\text{Cl}$.³³

On the other hand, the oxidative addition of one *tert*-butyl C–H bond to iridium causes the formation of an additional four-membered ring and the loss of any symmetry in the molecule. This is reflected by an increased number of resonances in the NMR spectra of **4**. Thus the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** displays two doublets at δ 50.8 and 9.8 which are assigned to P^tBu_2 and P^tBu , respectively.³⁸ The large phosphorus–phosphorus coupling of 351.1 Hz agrees with the mutual trans position of the two phosphine groups. Three resonances, which are split by the interaction with the corresponding adjacent phosphorus nucleus, are observed for the intact *tert*-butyl groups in the ^1H and ^{13}C -

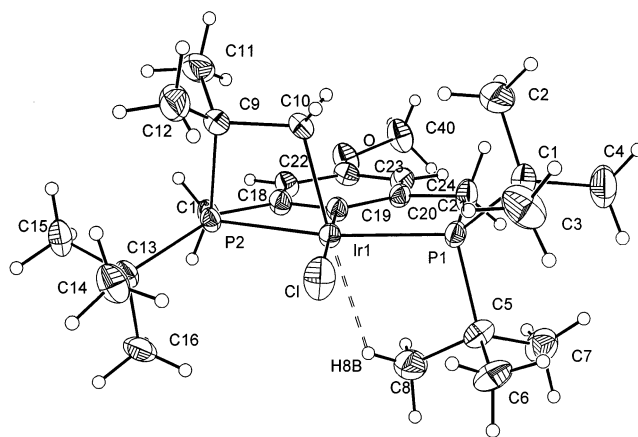


Figure 2. Molecular structure of complex **4** in the solid state (ORTEF plot).

Table 1. Relevant Structural Parameters of **4 As Obtained by X-ray Diffraction and Density Functional Calculations (Bond Lengths in [Å], Angles in [deg])**

	X-ray	B3LYP/ LACVP*	SVWN/ LACVP*
Ir(1)–C(19)	2.042(4)	2.053	2.025
Ir(1)–C(10)	2.064(4)	2.086	2.057
Ir(1)–P(2)	2.2702(11)	2.304	2.267
Ir(1)–P(1)	2.3217(11)	2.365	2.275
Ir(1)–Cl	2.4643(11)	2.505	2.430
Ir(1)⋯C(8)	3.022	3.260	3.462
Ir(1)⋯(H8B)	2.34	2.827	2.699
P(2)–C(9)	1.872(5)	1.915	1.881
C(9)–C(10)	1.559(6)	1.558	1.538
C(19)–Ir(1)–C(10)	88.37(18)	88.0	83.8
C(19)–Ir(1)–P(2)	82.49(11)	83.0	82.6
C(10)–Ir(1)–P(2)	70.85(12)	71.2	71.1
C(19)–Ir(1)–P(1)	83.29(11)	83.2	82.1
C(10)–Ir(1)–P(1)	104.23(12)	103.3	103.9
P(2)–Ir(1)–P(1)	165.06(4)	165.2	164.2
C(19)–Ir(1)–Cl	177.38(12)	171.2	177.2
C(10)–Ir(1)–Cl	94.16(14)	100.7	93.5
P(2)–Ir(1)–Cl	97.70(4)	98.0	97.0
P(1)–Ir(1)–Cl	96.72(4)	96.4	98.4
C(9)–P(2)–Ir(1)	88.71(15)	87.6	87.8
C(10)–C(9)–P(2)	94.0(3)	94.6	94.4
C(9)–C(10)–Ir(1)	106.0(3)	106.4	106.1

$\{^1\text{H}\}$ NMR spectra. Special features are generated by the nuclei of the four-membered ring. Thus, in the ^1H NMR spectrum the two diastereotopic protons of the ring methylene group give rise to doublets of doublets due to coupling to each other and the two inequivalent phosphorus nuclei. The resonance of the metal-bound CH_2 group is shifted to δ -6.7 in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum and is split into a doublet of doublets by a large and a small phosphorus carbon interaction. The two geminal methyl groups are observed as doublets each. There is no indication of either hydridic or weakly bound hydrogen to iridium in the ^1H NMR spectra at different temperatures.

X-ray Structure Analysis of **4.** The stereochemistry of **4**, which was deduced by NMR spectroscopy in solution, is compatible with the geometry found by an X-ray structure analysis in the solid state. Figure 2 presents the molecular structure of **4** in the solid state; bond lengths and angles are collected in Table 1. Single crystals were obtained by slowly precipitating **4** from a solution of 2-propanol/water. Complex **4** crystallizes in the monoclinic space group $P2_1/n$. The coordination

(38) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

geometry around iridium is best described as distorted square-pyramidal. The iridium atom deviates only by 0.016 Å from the basal plane composed of the two phosphorus atoms P(1) and P(2), the carbon atom C(19), and the chlorine. Interestingly, the bond lengths and angles involving the atoms in this plane are comparable to those found for the dihydrido complex $\{C_6H_3-2,6-(CH_2P^tBu_2)_2\}IrH_2$,³⁹ the dinitrogen compound $[\{C_6H_3-2,6-(CH_2P^tBu_2)_2\}Ir]_2(\mu-N_2)$,⁴⁰ the hydrido hydroxy complex $\{C_6H_3-2,6-(CH_2P^tBu_2)_2\}IrH(OH)$,²⁸ and the nitro functionalized hydrochloro compound $\{4-NO_2-C_6H_2-2,6-(CH_2P^tBu_2)_2\}Ir(H)Cl$.³³ Variations are observed for the two Ir–P distances in **4**, the Ir–P(2) bond being shorter by 0.052 Å than the Ir–P(1) bond. Thus, the formation of the four-membered ring pulls P(2) closer to the metal. The Ir–C(10) bond is slightly longer (2.064(4) Å) than the Ir–C(19) distance (2.042(4) Å). The metalated CH₂ group in the apical position is shifted toward the four-membered ring as indicated by the small C(10)–Ir–P(2), 70.85°, and large C(10)–Ir–P(1), 104.23°, angles. A nearly perpendicular arrangement is obvious by the dihedral angle (89.46°) between the planes consisting of the atoms Ir, P(2), C(9), C(10) and Cl, P(2), C(19), P(1), Ir. From the positions of Ir and C(8) it is concluded that there is an agostic interaction⁴¹ between the metal and the C(8)–H(8B) bond. The Ir–C(8) distance amounts to 3.022 Å, from which the Ir–H(8B) bond length of 2.34 Å is obtained.^{42,43} An asymmetric cavity at the free coordination site of iridium is generated as the C(13)–P(2)–Ir and C(5)–P(1)–Ir angles differ by 28.6°.

Reactivity of Complexes 3 and 4. Reactions of complexes **3** and **4** are presented in Scheme 2. Treatment of solutions of either **3** or **4** in THF with NaH under a hydrogen atmosphere gives iridium tetrahydride **5** in nearly quantitative yield. If the solvent is removed under vacuum or by a stream of argon the iridium dihydride **6** is obtained exclusively. Reaction of **4** with NaH in THF under an argon atmosphere gives mixtures of **5** and **6**, and according to ³¹P{¹H} NMR spectroscopy, one additional product that has not yet been identified. The hydrides **5** and **6** were characterized by their NMR spectra which are fully compatible with those of analogous PCP pincer complexes.^{39,44} In the ¹H NMR spectra of **5** and **6** the equivalence of all four *tert*-butyl groups indicates a higher symmetry (*C*_{2v}) of the molecules as compared to **3** and **4**. The triplets observed at –9.12 (²*J*(P,H) = 9.66 Hz) or –19.75 (²*J*(P,H) = 9.14 Hz) agree well with the tetrahydride **5** and the dihydride **6**, respectively. This is supported by the singlets in the ³¹P{¹H} NMR spectra at δ 74.5 (**5**) and 87.4 (**6**), which split into a quintet and a triplet upon decoupling of the protons with the exception of the hydride region.

Different products are observed when the deep red solutions of **3** and **4** in benzene are treated with carbon monoxide. In both cases colorless solutions are formed

(39) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840.

(40) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1.

(41) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(42) Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242.

(43) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

(44) Nemeš, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.

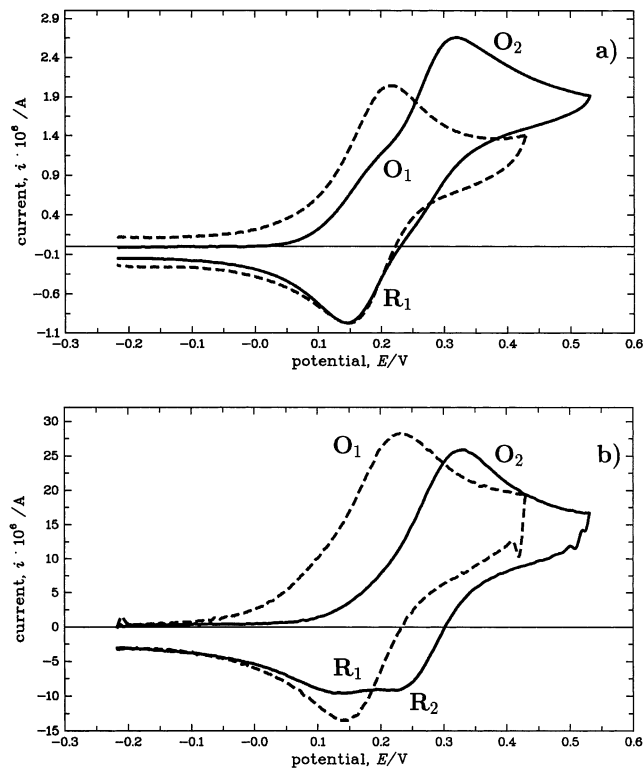


Figure 3. Cyclic voltammograms of complexes **3** (full lines) and **4** (dashed lines) in CH₂Cl₂/0.1 M TBAHFP; *c*(**3**) = 0.2 mM, *c*(**4**) = 0.2 mM; (a) *v* = 50 mV/s, (b) *v* = 5 V/s.

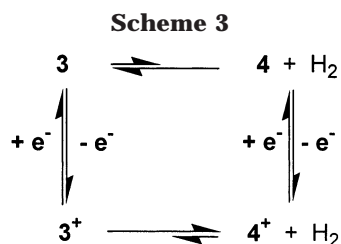
immediately. The spectroscopic data of the carbonyl complex **7** agree with the structure displayed in Scheme 2 and are compatible with those reported for $\{C_6H_3-2,6-(CH_2P^tBu_2)_2\}Ir(CO)(H)Cl$.³⁵ The AB pattern in the ³¹P{¹H} NMR spectrum, the number of resonances, and their multiplicities in the ¹H and ¹³C{¹H} NMR spectra of the carbonyl complex **8** are comparable with those of the educt **4** and demonstrate that the four-membered ring is maintained. The reduced electron density at the metal center of **8** as compared to **4** has a pronounced effect on the nuclei of the four-membered ring. For this reason, P(2) experiences a high field shift by 32.6 ppm. A high field shift of 1.36 and 1.44 ppm, respectively, is also observed for the protons of the IrCH₂ group. In contrast to this, the carbon resonance of the IrCH₂ group is shifted downfield by 20.96 ppm. Characteristic absorptions in the infrared are observed at 1987 (**7**) and 1990 cm⁻¹ (**8**) for the CO stretching vibration.

Electrochemical Studies. The redox properties of **3** and **4** were investigated by cyclic voltammetric experiments in a dichloromethane/tetra-*n*-butylammonium hexafluorophosphate electrolyte at a Pt electrode. Both compounds are oxidized at potentials only a few hundred millivolts positive of the ferrocene standard potential (Figure 3). Here, we give a qualitative description of the electron transfer behavior. A more detailed, quantitative account including simulation studies will be published elsewhere.⁴⁵

Complex **4** exhibits a peak couple that indicates a simple one-electron oxidation from the starting Ir(III) form to the Ir(IV) oxidation state **4**⁺ (Figure 3, dashed curves, *E*^o ~ +180 mV vs the ferrocene standard⁴⁶). It

(45) Novak, F.; Mayer, H. A.; Speiser, B. Manuscript in preparation.

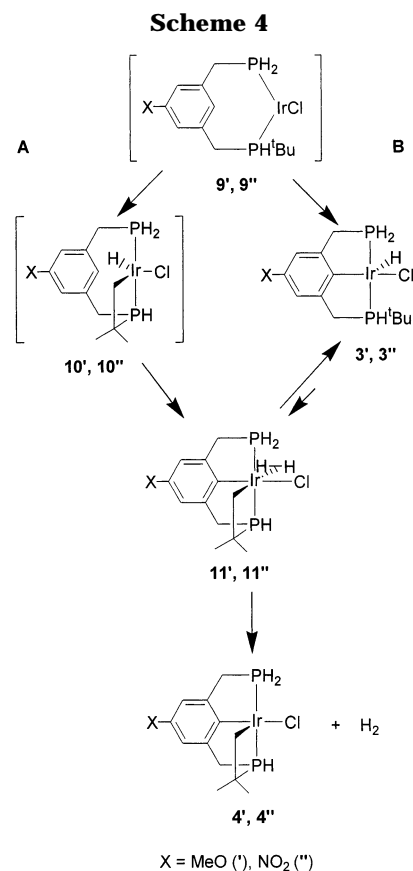
(46) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.



is important to note that the electrochemical studies of **4** were performed in the absence of molecular hydrogen. Slow follow-up reactions of the oxidized complex may become important only at very slow scan rates. In contrast, complex **3** shows a more complicated voltammetric signal (Figure 3, full lines). At slow scan rates (see Figure 3a for the example of $\nu = 50$ mV/s), the oxidation signal is composed of two waves O_1 and O_2 , which are strongly superimposed. Only one reverse peak (R_1) for the first wave at less positive potentials is observed under such conditions. At higher scan rates (see Figure 3b for $\nu = 5$ V/s), oxidation wave O_2 becomes dominant. However, at these faster time scales, the reverse (reduction) signal splits into two peaks, R_1 and R_2 . The position of R_2 indicates that this peak corresponds to O_2 ($E^\circ \sim +270$ mV), while R_1 is identical to the reduction peak at slow ν (Figure 3a). Furthermore, the superimposition of the cyclic voltammograms of compounds **3** and **4** in Figure 3 clearly suggests that the shoulder O_1 and the reduction signal R_1 in voltammograms of **3** result from the redox couple $\mathbf{4} \rightleftharpoons \mathbf{4}^+ + e^-$. This voltammetric behavior indicates a “square scheme”^{47,48} electrode reaction mechanism with solution equilibria between two redox active complexes on both the Ir(III) and the Ir(IV) oxidation states (Scheme 3). At the beginning of the experiment starting with complex **3**, the reaction between **3** and **4** + H_2 is in equilibrium, with **4** being formed from **3**. As the voltammogram at $\nu = 5$ V/s shows (Figure 3b), only a small amount of **4** is present, and the oxidation signal O_1 is almost totally absent under such equilibrium conditions. At $\nu = 50$ mV/s, however, **4** is replenished partially from **3** by the kinetic process in the Ir(III) state. Hence, the oxidation signal of **4** becomes visible. After passage of the oxidation peaks, $\mathbf{4}^+$ and $\mathbf{3}^+$ are present and can be observed (by their reduction peaks, R_1 and R_2 , respectively) on the fast time scale ($\nu = 5$ V/s). If the system is allowed to reach equilibrium in the Ir(IV) state ($\nu = 50$ mV/s), only R_1 remains. We conclude that the equilibrium between the Ir(IV) complexes is shifted strongly to the side of $\mathbf{4}^+$.

A change in the oxidation state of complexes **3** and **4** thus reverses the relative stability of the ring open and closed forms: The electrochemical oxidation induces ring formation to generate **4**. Furthermore, the time scale dependence of signal O_1 clearly indicates the presence of an equilibrium reaction between **3** and **4** + H_2 in the Ir(III) state.

Quantum Mechanical Calculations. The unusual finding of the stable complex **4** prompted us to perform density functional calculations at various levels of theory for the model compounds shown in Scheme 4 (X



= OCH₃ (prime) and NO₂ (double prime)) as well as for complex **4** presented in Figure 2. The nitro functionalized complex was taken into consideration, because an X-ray structure of the square-pyramidal {4-NO₂-C₆H₂-2,6-(CH₂P^tBu)₂}Ir(H)Cl together with DFT calculations on {4-NO₂-C₆H₂-2,6-(CH₂PH₂)₂}Ir(H)Cl have been reported.³³ Thus, experimental and theoretical data for the two types of structures represented by **3** and **4** can be compared. In the case of the model complexes only one *tert*-butyl group was retained during the calculations, the other three groups were replaced by hydrogen atoms in order to reduce the computational effort. The geometric structures of **3'**, **11'**, **4'**, **9'**, and **10'** and of their nitro functionalized analogues were optimized in the local density approximation (SVWN⁴⁹) as well as with the gradient-corrected B3LYP⁵⁰ hybrid functional. For this purpose, the effective core potential SDD⁵¹ (augmented with one set of f-functions on Ir, exponent $\alpha_f = 0.938^{52}$) and LACVP⁵³ basis sets were applied using the programs Gaussian 98,⁵⁴ Jaguar 3.5,⁵⁵ and Titan 1.0.5.⁵⁶ In the case of **4**, structure optimizations were performed at the SVWN/LACVP* and B3LYP/LACVP* levels of approximation.

The relative thermodynamical stabilities of the model complexes are presented in Table 2. Almost parallel trends in the theoretical energy differences are obtained

(49) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(50) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(51) Wedig, U.; Dolg, M.; Stoll, H.; Preuss, H. *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*; Reidel: Dordrecht, The Netherlands, 1968; p 79.

(52) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(53) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(47) Evans, D. H. *Chem. Rev.* **1990**, *90*, 739.

(48) Valat, A.; Person, M.; Roullier, L.; Laviron, E. *Inorg. Chem.* **1987**, *26*, 332.

Table 2. Relative Thermodynamical Stabilities [kcal/mol] of the Complexes Given in Scheme 3 As Obtained by the Various Computational Procedures

	B3LYP/ SDD(f)	SVWN/ SDD(f)	B3LYP/ LACVP*	SVWN/ LACVP*
(a) X = OCH ₃				
3'	0.0	0.0	0.0	0.0
11'	+28.5	+16.3	+30.1	19.7
4' + H ₂	+34.6	+38.4	+31.9	36.8
9' ^a	—	—	—	—
10' ^a	—	—	—	—
(b) X = NO ₂				
3''	0.0	0.0	0.0	0.0
11''	+29.1	+16.7	+30.1	21.4
4'' + H ₂	+34.9	+38.5	+33.7	37.9
9'' ^b	—	—	—	—
10'' ^b	—	—	—	—

^a **9'** and **10'** represent no stable structures (see text) ^b **9''** and **10''** represent no stable structures (see text)

for the methoxy and the nitro compounds. All computational procedures predict the square-pyramidal chlorohydrido complexes **3'**, **3''** to be most stable. The structures **11'**, **11''** are higher in energy by ca. 16 to 30 kcal/mol, depending on whether the SVWN or the B3LYP approach is applied. Therefore, the B3LYP method leads to pronounced larger energy differences (Table 2). The doubly cyclometalated **4'** and **4''** (+H₂) are predicted to be highest in energy: they are energetically less stable than **3'**, **3''** by about 32 (**4'**, B3LYP/LACVP*) to 39 kcal/mol (**4''**, SVWN/SDD(f)). In this case, higher relative energies are obtained in the SVWN approximation. The postulated intermediates **9'**, **9''** and **10'**, **10''** represent no stable structures on the energy hypersurface. On geometry optimizations they converge to the structures **3'**, **3''** at all applied levels of theory.

Bond distances for the model complexes **3'**, **3''**, **11'**, **11''**, **4'**, and **4''** as obtained by the various computational procedures are listed in Table 3. In the case of **11'**, **11''** the bonding of the two hydrogen atoms to iridium may be best described as η²-coordinated H₂. The calculated H–H and Ir···H_{av} distances in these complexes drastically depend on the computational approach. At the SVWN level of theory longer H–H bonds (0.883 to 0.902 Å) and shorter Ir···H_{av} distances (1.769 to 1.807 Å) are obtained as compared to the B3LYP calculations (H–H = 0.789 to 0.799 Å, Ir···H_{av} = 1.905 to 1.930 Å). In any case, the H–H distances in **11'**, **11''** are longer than the theoretical bond length predicted for the H₂ molecule (0.743 (B3LYP/LACVP*) and 0.763 Å (SVWN/LACVP*), respectively). Likewise, the Ir···H_{av} distances in these complexes are much longer than the Ir–H bonds in **3'**,

Table 3. Calculated Bond Distances [Å] in the Ir Moiety for the Model Complexes **3', **3''**, **11'**, **11''**, **4'**, and **4''** (Same Atom Numbering as in Figure 2)**

		B3LYP/ SDD(f)	SVWN/ SDD(f)	B3LYP/ LACVP*	SVWN/ LACVP*
(a) X = OCH ₃					
3'	Ir–H	1.555	1.566	1.558	1.582
	Ir–Cl	2.477	2.403	2.432	2.363
	Ir–P(1)	2.349	2.300	2.292	2.243
	Ir–P(2)	2.356	2.307	2.324	2.288
	Ir–C(19)	2.041	2.003	2.062	2.017
	11'	H–H	0.799	0.902	0.789
	Ir···H _{av}	1.905	1.769	1.927	1.796
	Ir–Cl	2.540	2.480	2.513	2.439
	Ir–P(1)	2.349	2.292	2.316	2.257
	Ir–P(2)	2.341	2.307	2.294	2.257
	Ir–C(19)	2.076	2.045	2.080	2.055
	Ir–C(10)	2.105	2.084	2.110	2.087
	4'	Ir–Cl	2.493	2.425	2.454
	Ir–P(1)	2.345	2.287	2.301	2.246
	Ir–P(2)	2.330	2.290	2.288	2.251
	Ir–C(19)	2.056	2.105	2.071	2.012
	Ir–C(10)	2.087	2.051	2.098	2.059
(b) X = NO ₂					
3''	Ir–H	1.557	1.569	1.579	1.587
	Ir–Cl	2.461	2.394	2.419	2.351
	Ir–P(1)	2.356	2.305	2.312	2.264
	Ir–P(2)	2.364	2.314	2.328	2.278
	Ir–C(19)	2.021	1.980	2.029	1.991
	11''	H–H	0.795	0.894	0.797
	Ir···H _{av}	1.921	1.783	1.930	1.807
	Ir–Cl	2.527	2.458	2.484	2.428
	Ir–P(1)	2.354	2.309	2.315	2.225
	Ir–P(2)	2.343	2.306	2.298	2.261
	Ir–C(19)	2.058	2.011	2.066	2.023
	Ir–C(10)	2.107	2.089	2.114	2.075
	4''	Ir–Cl	2.475	2.411	2.441
	Ir–P(1)	2.352	2.296	2.300	2.253
	Ir–P(2)	2.333	2.294	2.290	2.255
	Ir–C(19)	2.038	1.995	2.058	2.015
	Ir–C(10)	2.093	2.056	2.102	2.064

3'' (1.555 (B3LYP/SDD(f), **3'**) to 1.587 Å (SVWN/LACVP*, **3''**), see Table 3). These remarkable differences in structural features for **11'**, **11''** as obtained by the SVWN and B3LYP methods, respectively, correspond to the trends in the relative energies (see Table 2). The SVWN approximations predict **11'**, **11''** to be closer in energy to **3'**, **3''** as compared to the B3LYP results. On the other hand, the B3LYP energies are closer to those obtained for complexes **4'**, **4''** (+H₂) than the energies calculated at the SVWN level of theory (Table 2).

Relevant structural parameters of **4** as obtained by X-ray diffraction and density functional calculations (B3LYP/LACVP*, SVWN/LACVP*) are compared in Table 1. The same distorted square-pyramidal coordination geometry around iridium as observed in the experiment is predicted by the computational procedures. In most cases, the B3LYP bond lengths are too long and the SVWN distances are too short in comparison to the experimental values. Remarkable exceptions are the nonbonded Ir(1)···C(8) and Ir(1)···(H8B) distances, which are predicted to be longer than the experimentally observed ones in both cases. The variation in the two Ir–P bond lengths as well as the difference between the Ir(1)–C(19) and the Ir–C(10) distance are well reproduced by the theoretical approaches. The calculated bond angles are in nearly perfect agreement with the experiment (within the experimental error limits). Exceptions represent the C(19)–Ir(1)–C(10) angle (too small by ca. 4°, SVWN), the C(19)–Ir(1)–Cl angle (too

(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. A.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(55) *Jaguar 3.5*; Schrödinger, Inc.: Portland, OR, 1998.

(56) *Titan 1.0.5*; Wavefunction, Inc.: Irvine, CA, and Schrödinger, Inc.: Portland, OR, 2000.

small by ca. 6°, B3LYP), and the C(10)–Ir(1)–Cl angle (too large by ca. 6°, B3LYP). The overall agreement between the experimental crystal structure and the gas-phase structures as predicted for **4** by both theoretical procedures is very good.

Discussion

Complex **4** is the result of two consecutive intramolecular C–H bond activations (Schemes 2 and 4).^{57,58} The highly reactive 14-electron intermediate **9'**, **9''** is formed after coordination of the two phosphine groups either to IrCl₃ followed by reduction or to the IrCl(COE)₂ fragment accompanied by loss of COE. Although, according to our calculations, structures **9'**, **9''** are not found to be stable, intermediates such as **9'**, **9''** have been observed for ruthenium^{59–61} and platinum⁶² and were proposed for rhodium.⁶³ Thus, there are two possible pathways from **9'**, **9''** to **4'**, **4''**. In pathway A one of the 36 methyl C–H bonds is oxidatively added to iridium followed by the C–H activation of the aromatic C–H bond, while in pathway B the reaction of the aromatic C–H bond is preferred over that of the methyl C–H bonds. All experimental and theoretical data are in favor of pathway B, where the bis-chelate with two thermodynamically stable internal five-membered rings is generated first. The analogy to the Thorpe–Ingold effect, where geminal dialkyl groups enhance ring closure, was emphasized by Shaw.^{36,64} Indeed the sterically encumbered *tert*-butyl groups at the ligated phosphorus atoms, which mimic the effect of geminal dialkyl groups, kinetically facilitate the intramolecular metalation of the aromatic C–H bond. In contrast to this, we had previously shown that in the case of the PCP pincer complex {^tBu₂PCH₂CH₂CHCH₂–CH₂P^tBu₂}IrH₂ there is an equal ease with which *tert*-butyl and the ligand backbone C–H bonds can be activated.⁶⁵ Thus, one must consider here kinetic vs thermodynamic selectivity. The formation of the phenyl iridium bond occurs first, in spite of the greater number of methyl C–H bonds, because this bond is stronger than the cyclo alkyl iridium bond from the *tert*-butyl group. Jones and Feher consistently pointed out that it is the product M–C bond strength that determines hydrocarbon metalation equilibria.⁶⁶

Bruice and Lightstone have postulated that thermodynamic control of intramolecular cyclization reactions is dominated by enthalpy.⁶⁷ They conclude that intramolecular cyclization is driven by an accumulation of NAC (near attack conformations) molecules, which define the required conformations for juxtaposed reac-

tants in the ground state leading to exact conformations in the transition state and to a kinetic selectivity for cyclometalation. In the case of pincer ligands, this most likely involves an η^2 arene intermediate, so there is no direct insertion into the aromatic C–H bond.^{68–70} Since **3** is stable to reductive elimination under the conditions of the reaction, the lowest energy pathway for reductive elimination must be the lowest energy pathway for oxidative addition. Thus, calculations sustain the observation that **3'**, **3''** are thermodynamically the most stable complexes and that structures **9'**, **9''** and **10'**, **10''** are not observed.

Interestingly enough, although numerous complexes of type **3** have been synthesized and a broad chemistry with these complexes has been developed, the oxidative addition of a C–H bond of one of the *tert*-butyl groups to the metal center to form an isolable complex has not been reported before. For this reason, it is more difficult to explain why **4**, with two cyclometalated bonds and easily melting at 200 °C, forms at all, since the calculations show that it is thermodynamically less stable than **3** and **11'**, **11''**. The most likely attack of a *tert*-butyl methyl C–H bond is at the free coordination site opposite the hydride ligand in **3**. This will generate a seven-coordinate Ir(V) dihydride chloride complex, which rearranges to give the Ir(III) dihydrogen complexes **11'**, **11''**. Although **11'**, **11''** were not observed spectroscopically, their theoretical existence was demonstrated by quantum chemical calculations (Table 2). Comparable η^2 -H₂ complexes are well established.⁷¹ As demonstrated by the electrochemical studies, complex **4** + H₂ is in fast equilibrium with **3**, the equilibrium being on the side of the chlorohydrido complex **3**. This explains why there was no indication of an η^2 -H₂ complex in the ¹H NMR spectra. The loss of H₂ from **11'**, **11''** leads to the thermodynamically least stable product **4**. This is only achieved if H₂ is allowed to escape from the reaction mixture, which renders the overall process irreversible. Moreover, this is consistent with the observation that the presence or absence of hydrogen in the reaction mixture regulates the amounts of **3** and **4** regardless of different solvents and temperatures during the reaction. Thus, if H₂ is added to pure **4**, the hydrochloride complex **3** is formed exclusively. In this case the attack of hydrogen will occur at the empty coordination site, which is *trans* to the iridium-bound CH₂ group, and the η^2 -H₂ complex **11'**, **11''** will be formed. To reductively eliminate the *tert*-butyl C–H bond, the dihydrogen complex has to rearrange to give a Ir(V) dihydride intermediate with at least one hydride ligand *cis* to the CH₂ group bound to iridium. This is the microscopic reverse of the *tert*-butyl C–H activation (*vide infra*). That the empty coordination site *trans* to the CH₂ group is easily accessible to donor ligands was demonstrated by the reaction of **4** with CO, which gave the carbonyl complex **8**.

Finally, it is interesting to note that evidence from the electrochemical experiments shows that the stability of **3** and **4** in their respective oxidized Ir(IV) states is

(57) van der Boom, M. E.; Liou, S. Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 2562.

(58) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(59) Dani, P.; Toorneman, M. A. M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2000**, *19*, 5287.

(60) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317.

(61) Dani, P.; Albrecht, M.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2000**, *19*, 4468.

(62) van der Boom, M. E.; Gozin, M.; Ben-David, Y.; Shimon, L. J. W.; Frolow, F.; Kraatz, H.-B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 7068.

(63) Liou, S.-Y.; Milko, E.; Milstein, D. *Chem. Commun.* **1998**, 687.

(64) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856.

(65) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816.

(66) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(67) Bruice, T. C.; Lightstone, F. C. *Acc. Chem. Res.* **1999**, *32*, 127.

(68) Vignalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.

(69) Vignalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 895.

(70) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233.

(71) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

reversed as compared to the Ir(III) states (Scheme 3). The redox process appears to be facile and both **3** as well as **4** are easily oxidizable compounds. Consequently, redox processes should certainly be taken into account when considering both the transformation of **3** to **4** and the catalytic activity of pincer complexes of the type discussed here. Indeed, one-electron oxidation has been shown to favor the reductive elimination of hydrocarbons from hydridoalkyl Ir species,⁷² which is the reverse reaction of a C–H bond activation process.

The possibility of electron-transfer catalysis (ETC) in the C–H activation reaction of the (PCP)Ir complexes can be revealed by comparison of their electrochemical behavior with the electrochemistry⁷³ of Cp*Ir(L)Me₂ (L = phosphine).⁷⁴ The oxidized form of Cp*Ir(L)Me₂ irreversibly eliminates CH₄, and subsequently adds an aromatic hydrocarbon. The resulting 17-electron species Cp*Ir(L)MeAr* is able to oxidize the starting material and is itself reduced to the closed shell product Cp*Ir(L)MeAr. This is only possible if the formal potentials of the two redox couples account for favorable thermodynamics of the cross redox reaction. In the case of our pincer complexes, the Diversi et al. mechanism would require that the equilibrium $\mathbf{3} + \mathbf{4}^+ \rightleftharpoons \mathbf{3}^+ + \mathbf{4}$ is shifted to the right-hand side. An inspection of the redox potentials $E^\circ(\mathbf{3}/\mathbf{3}^+)$ and $E^\circ(\mathbf{4}/\mathbf{4}^+)$ as estimated in the present work, however, shows that the equilibrium constant of this reaction is smaller than unity and that this homogeneous redox process is not in favor of ETC, i.e., $\mathbf{4}^+$ is not able to oxidize **3** to a large extent. Indeed, simulation shows that the redox equilibrium cannot be detected in the cyclic voltammograms.⁴⁵

Conclusion

The isolation and X-ray crystal structure of **4** show that pincer complexes with pendant P-*t*-Bu₂ groups can form thermally stable multiple C–H insertion reactions by consecutive cyclometalations. The experimental data reveal that in solution there is an equilibrium between **3** and **4** + H₂ that implies C–H oxidative addition via an Ir(V) oxidation state. Loss of hydrogen is the thermodynamic driving force for the isolation of **4**. Electrochemical oxidation accelerates the C–H activation via an Ir(IV) state. Moreover, the isolation of **4** including its air and temperature stability suggests that it will be an excellent immobilization candidate for catalytic preparations.

Experimental Section

General. All experiments were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried with appropriate reagents, distilled, degassed, and stored under argon.

5-Hydroxy-1,3-benzenedicarboxylic acid was purchased from Aldrich. Di-*tert*-butylphosphine^{75,76} and [Ir(COE)₂Cl]₂⁷⁷ were

(72) Pedersen, A.; Tilsted, M. *Organometallics* **1994**, *13*, 4887.

(73) Diversi, P.; Iaconi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 351.

(74) Diversi, P.; Iaconi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Pinzino, G.; Uccello-Barretta, G.; Zanello, P. *Organometallics* **1995**, *14*, 3275.

(75) Timmer, K.; Thewissen, D. H. M. W.; Marsmann, J. W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 248.

(76) Voskuil, W.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 302.

prepared according to literature procedures. IrCl₃·*n*H₂O was a gift from DEGUSSA AG.

Elemental analyses were performed with an Elemental Vario EL analyzer. FAB/MS mass spectra were taken on a Finnigan MAT 711 A instrument, modified by AMD, and reported as mass/charge (*m/z*). The high-resolution ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded with a Bruker DRX 250 spectrometer at 298 K. Frequencies and standards were as follows: ³¹P{¹H} NMR 101.25 MHz and ¹³C{¹H} 62.90 MHz. The ¹H and ¹³C chemical shifts were calibrated to deuterated solvent peaks, which were reported relative to TMS. All assignments were supported by ¹H{³¹P} decoupling and ¹³C 135DEPT experiments. ³¹P chemical shifts were measured relative to 85% H₃PO₄ (δ = 0). In all cases the number of hydrogen atoms bound to iridium was obtained by the multiplicity of selectively decoupled ³¹P NMR spectra (only the alkane region was decoupled).

Cyclic Voltammetric Studies. Dichloromethane was used as a solvent with tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte (*c* = 0.1 M). Dichloromethane (Fluka) was distilled first and then dried by standing for 10–12 h over activated α-Al₂O₃. TBAHFP was prepared by the procedure described before.⁷⁸ The electrolyte (dichloromethane + TBAHFP) was degassed by 3 freeze–pump–thaw cycles before transferring it into the electrochemical cell under argon. Concentrations of the complexes **3** and **4** were in the range of 1 × 10^{−4} to 6 × 10^{−4} M.

Cyclic voltammograms were recorded with a BAS 100 B/W electrochemical workstation (Bioanalytical Systems, West Lafayette, IN) controlled by a standard 80486 personal computer (BAS control program version 2.0). All electrochemical experiments were carried out at room temperature under argon with a gastight full-glass three-electrode cell. The working electrode was a Pt-disk electrode (Metrohm, A = 0.064 cm²). The Pt disk was polished before each experiment with α-Al₂O₃ (Buehler, 0.05 μm). The counter electrode was a platinum wire (∅ 1 mm) spiral with diameter 7 mm. As the reference electrode, a Haber-Luggin double reference electrode⁷⁹ was used. The resulting potentials refer to the Ag/Ag⁺ redox system (0.01 M in CH₃CN with 0.1 M TBAHFP). All potentials in this paper are reported to an external *fc*/*fc*⁺ standard⁴⁶ and were rescaled to $E^\circ(\text{fc}/\text{fc}^+) = 0.218 \text{ V vs Ag}/\text{Ag}^+$.

3,5-(Di-*tert*-butylphosphinomethyl)anisole (2). Di-*tert*-butylphosphine (4.74 g, 32.4 mmol) was added to a solution of 3,5-di(bromomethyl)anisole (4.76 g, 16.2 mmol) in 30 mL of acetone. The mixture was stirred for a few minutes and then refluxed for 45 min, whereupon a white precipitate is formed. The suspension was allowed to cool to room temperature, and the precipitate was collected on a sintered glass frit, washed once with 5 mL of dry acetone, and dried under vacuum. Yield (6.10 g, 88%). A solution of sodium acetate (2.7 g, 32.9 mmol) in 10 mL of water was added to a solution of the phosphonium salt (2.0 g, 4.7 mmol) in 20 mL of water. After the solution was stirred for 30 min, the aqueous phase was extracted with 20 mL of diethyl ether (3–5 times). The diethyl ether was removed from the combined organic layers, and the white gel residue obtained was vacuum dried. Yield (0.97 g, 50%). Elemental analysis (%) calcd for C₂₅H₄₆OP₂ (424.3): C 70.72, H 10.92. Found: C 70.27, H 10.52. MS (EI): *m/z* (%) 424.3 (80) [M]⁺, 368.3 (100) [M – *t*Bu]⁺, 311.2 (50) [M – 2*t*Bu]⁺, 255.1 (30) [M – 3*t*Bu]⁺, 199.1 (10) [M – 4*t*Bu]⁺. ³¹P{¹H} NMR (CDCl₃, 25°C, H₃PO₄): δ 33.9 (s). ¹H NMR (CDCl₃, 25°C, TMS): δ 6.80 (s, 1H; CH), 6.62 (s, 2H; CH), 3.65 (s, 3H; OCH₃), 2.69 (br, 4H; CH₂), 1.02 (d, ³J(P,H) = 11.06 Hz, 36H; CH₃). ¹³C{¹H} NMR

(77) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorganic Synthesis* **1974**, *73*, 18.

(78) Dümmling, S.; Eichhorn, E.; Schneider, S.; Speiser, B.; Würde, M. *Curr. Sep.* **1996**, *15*, 53.

(79) Gollas, B.; Krauß, B.; Speiser, B.; Stahl, H. *Curr. Sep.* **1994**, *13*, 42.

(CDCl₃, 25 °C, TMS): δ 159.2 (s, COCH₃), 142.2 (d, $^2J(\text{P,C}) = 12.58$ Hz, CCH₂), 123.1 (t, $^3J(\text{P,C}) = 9.43$ Hz, CH₂CCH), 112.0 (d, $^3J(\text{P,C}) = 12.58$ Hz, CH₃OCH), 54.8 (s, OCH₃), 31.4 (d, $^1J(\text{P,C}) = 25.16$ Hz, CCH₃), 29.6 (d, $^2J(\text{P,C}) = 18.87$ Hz, CCH₃), 28.3 (d, $^1J(\text{P,C}) = 25.16$ Hz, CH₂).

3 and 4. A suspension of **2** (2.53 g, 5.96 mmol) and IrCl₃·*n*H₂O (1.00 g, 3.01 mmol) in 24 mL of 2-propanol/water (7:1) was stirred at room temperature for 12 h and then heated at 85 °C for 24 h. The reaction mixture was allowed to cool slowly to room temperature with continuous stirring, and then cooled in ice/salt for 24 h. Supernatant solution was withdrawn by pipet, and the precipitate was washed two times with 2-propanol/water (7:3), with stirring, and dried under vacuum. A mixture of **3** and **4** is always observed.

3: Mp >200 °C dec. Elemental analysis (%) calcd for C₂₅H₄₆O₂IrCl (652.0): C 46.04, H 7.10, Cl 5.44. Found: C 45.92, H 6.92, Cl 5.22. MS (FD): *m/z* (%) 652.0 (100) [M]⁺. IR (KBr, cm⁻¹): $\nu = 2866, 2899, 2940$ (m, C–H), 2004 (w, Ir–H), 1585 (s, C=C). $^{31}\text{P}\{^1\text{H}\}$ NMR [D₈]toluene, 25 °C, H₃PO₄): δ 69.1 (s). ^1H NMR ([D₈]toluene, 25 °C, TMS): δ -43.21 (t, $^2J(\text{P,H}) = 12.8$ Hz, 1H; Ir–H), 1.23 (m, $^{80a}N = 12.80$ Hz, 18H; CCH₃), 1.28 (m, $^{80a}N = 12.80$ Hz, 18H; CCH₃), 2.99 (m, $^{80b}N = 2.99$ Hz, CH₂H₂P), 3.03 (m, $^{80b}N = 2.99$ Hz, CH₂H₂P), 3.56 (s, 3H; OCH₃), 6.70 (s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR ([D₈]toluene, 25 °C, TMS): δ 29.21 (m, $^{81a}N = 4.7$ Hz, C(CH₃)₃), 29.97 (m, $^{81a}N = 4.7$ Hz, C(CH₃)₃), 34.74 (m, $^{81b}N = 22.20$ Hz, CP), 35.93 (m, $^{81b}N = 27.80$ Hz, CH₂P), 37.54 (m, $^{81}N = 19.60$ Hz, CP), 54.65 (s, OCH₃), 107.83 (m, $^{81c}N = 16.17$ Hz, CHCCH₂P), 135.33 (s, COCH₃), 152.18 (t, $^2J(\text{P,C}) = 8.4$ Hz, ClIr), 157.34 (m, $^{81a}N = 3.4$ Hz, CH₂CCH).

4: Mp 200 °C. Elemental analysis (%) calcd for C₂₅H₄₄P₂OIrCl (650.4): C 46.18, H 6.82, Cl 5.45. Found: C 45.81, H 6.25, Cl 6.23. MS (FAB, 3-NBA): *m/z* (%) 650 (30) [M]⁺, 615 (100) [M – Cl]⁺, 557 (40) [M – Cl – ^tBu]⁺, 501 (55) [M – Cl – ^tBu]⁺. IR (KBr, cm⁻¹): ν 2939, 2864, 2907 (m, C–H), 1584 (C=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, H₃PO₄): δ 9.8 (d, $^2J(\text{P,P}) = 351.1$ Hz; P₂). ^1H NMR (C₆D₆, 25 °C, TMS): δ 0.72 (d, $^3J(\text{P}_2, \text{H}) = 12.79$ Hz, 3H; C(CH₃)₂), 1.11 (d, $^3J(\text{P}_1, \text{H}) = 12.79$ Hz, 9H; C(CH₃)₃), 1.27 (d, $^3J(\text{P}_1, \text{H}) = 12.79$ Hz, 9H; C(CH₃)₃), 1.35 (d, $^3J(\text{P}_2, \text{H}) = 13.71$ Hz, 9H; C(CH₃)₃), 1.50 (d, $^3J(\text{P}_2, \text{H}) = 13.71$ Hz, 3H; C(CH₃)₂), 2.19 (ddd, $^2J(\text{H,H}) = 4.68$ Hz, $^3J(\text{P}_2, \text{H}) = 5.37$ Hz, $^3J(\text{P}_1, \text{H}) = 2.40$ Hz, 1H; CH₂H₂Ir), 3.08 (m, 4H; PCH₂), 3.55 (ddd, $^2J(\text{H,H}) = 4.68$ Hz, $^3J(\text{P}_2, \text{H}) = 9.25$ Hz, $^3J(\text{P}_1, \text{H}) = 2.17$ Hz, 1H; CH₂H₂Ir), 3.61 (s, 3H; OCH₃), 6.88 (d, $^4J(\text{H,H}) = 2.28$ Hz, 1H; CH), 6.94 (d, $^4J(\text{H,H}) = 2.28$ Hz, 1H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, TMS): δ -6.71 (dd, $^2J(\text{P,C}) = 23.9$ Hz, $^2J(\text{P,C}) = 1.0$ Hz, CH₂–Ir), 26.23 (s, CH₃CP₂), 27.34 (d, $^2J(\text{P,C}) = 4.0$ Hz, CH₃CP₂), 29.23, 29.38, 30.70 (dd, $^2J(\text{P,C}) = 4.1$ Hz, $^2J(\text{P,C}) = 1.3$ Hz, CH₃CP), 34.52 (d, $^1J(\text{P,C}) = 3.4$ Hz, CH₂P), 34.92 (s, CH₂P), 35.19 (dd, $^1J(\text{P,C}) = 14.5$ Hz, $^3J(\text{P,C}) = 5.1$ Hz, CP), 36.86 (dd, $^1J(\text{P,C}) = 3.0$ Hz, CP), 55.14 (s, OCH₃), 59.67 (dd, $^1J(\text{P,C}) = 20.6$ Hz, $^3J(\text{P,C}) = 2.4$ Hz, CP), 108.37 (d, $^3J(\text{P,C}) = 16.8$ Hz, CH), 109.33 (d, $^3J(\text{P,C}) = 16.8$ Hz, CH), 140.76 (s, CH₃OC), 150.00 (dd, $^2J(\text{P,C}) = 11.1$ Hz, $^3J(\text{P,C}) = 3.7$ Hz, CCH₂P), 153.16 (dd, $^2J(\text{P,C}) = 14.12$ Hz, $^3J(\text{P,C}) = 5.4$ Hz, CCH₂P), 158.0 (dd, $^2J(\text{P,C}) = 1.7$ Hz, ClIr).

5. Complexes **3** and **4** (10 mg, 0.015 mmol) were treated in THF (3 mL) with a 100% excess of NaH. After the reddish mixtures were stirred at room temperature for 1 h under a H₂ atmosphere, they were sonicated for another 6 h with intermittent cooling and vigorous stirring. With continued stirring at room temperature for 24 h the mixtures changed color to pale brown. The solutions were filtered, and THF was removed by a stream of H₂. The residue left was dissolved in C₆D₆ and spectra were recorded. $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C,

H₃PO₄): δ 74.5 (s). ^1H NMR (C₆D₆, 25 °C, TMS): δ -9.12 (t, $^2J(\text{P,H}) = 9.66$ Hz, 4H; Ir–H), 1.19 (m, $^{80a}N = 12.8$ Hz, 36H; C(CH₃)₃), 3.25 (m, $^{80b}N = 7.46$ Hz, 4H; 2CH₂), 3.59 (s, 3H; OCH₃), 6.82 (s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, TMS): δ 25.7 (s, C(CH₃)₃), 29.7 (d, $^1J(\text{P,C}) = 2.5$ Hz, CP), 30.3 (s, CP), 41.9 (m, $^{81b}N = 30.3$ Hz, CH₂), 55.1 (s, OCH₃), 107.3 (m, $^{81c}N = 15.2$ Hz, CH), 141.5 (s, C–Ir), 149.3 (m, $^{81a}N = 15.3$ Hz, CHCCH₂).

6. If in the reaction mixture of **5** the solvent is removed by a stream of argon, **6** is formed exclusively. $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, H₃PO₄): δ 87.4 (s). ^1H NMR (C₆D₆, 25 °C, TMS): δ -19.75 (t, $^2J(\text{P,H}) = 9.14$ Hz, 2H; Ir–H), 1.35 (m, $^{80a}N = 13.24$ Hz, 36H; C(CH₃)₃), 3.24 (m, 2CH₂), 3.58 (s, 3H; OCH₃), 7.02 (s, 2H; CH).

7. CO gas was bubbled into a solution of **3** (30 mg, 0.046 mmol) in benzene in a Schlenk tube. The solution becomes colorless immediately. Evaporation of the solvent under vacuum resulted in the colorless solid **7** in quantitative yield. Mp 212–214 °C. Elemental analysis (%) calcd for C₂₆H₄₆O₂P₂IrCl (680): C 45.90, H 6.82, Cl 5.21. Found: C 46.15, H 6.90, Cl 4.86. MS (FD): *m/z* (%) 680.1 (100) [M]⁺, 643.1 (43) [M – Cl]⁺. IR (KBr, cm⁻¹): ν 2946, 2987 (C–H), 2154 (w, Ir–H), 1987, 1976 (s, CO), 1586 (m, C=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, H₃PO₄): δ 57.0 (s). ^1H NMR (C₆D₆, 25 °C, TMS): δ -7.59 (t, $^2J(\text{P,H}) = 15.38$ Hz, 1H; Ir–H), 1.27 (m, $^{80a}N = 13.50$ Hz, 18H; C(CH₃)₃), 1.38 (m, $^{80a}N = 13.81$ Hz, 18H; C(CH₃)₃), 2.88 (m, 4H; CH₂), 3.51 (s, 3H; OCH₃), 6.61 (s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, TMS): δ 29.1 (m, $^{81a}N = 4.1$ Hz, C(CH₃)₃), 29.9 (m, $^{81a}N = 4.1$ Hz, C(CH₃)₃), 36.47 (m, $^{81b}N = 20.2$ Hz, CP), 36.81 (m, $^{81b}N = 26.27$ Hz, CP), 38.3 (m, $^{81b}N = 28.29$ Hz, CH₂P), 54.77 (s, OCH₃), 108.3 (m, $^{81c}N = 15.49$ Hz, CH), 147.02 (m, $^{81a}N = 12.13$ Hz, CCH₂P), 127.3 (s, COCH₃), 157.70 (t, $^2J(\text{P,C}) = 1.4$ Hz, ClIr), 182.4 (t, $^2J(\text{P,C}) = 5.03$ Hz, CO).

8. CO gas was bubbled into a solution of **4** (30 mg, 0.046 mmol) in benzene in a Schlenk tube. The solution immediately becomes colorless. Evaporation of the solvent under vacuum gave the colorless solid **8** in quantitative yield. Mp 214–216 °C. Elemental analysis (%) calcd for C₂₆H₄₄O₂P₂IrCl (678): C 46.04, H 6.54, Cl 5.23. Found: C 46.49, H 5.89, Cl 6.01. MS (FAB, 3-NBA): *m/z* (%) 679.2 (3) [M + 1]⁺, 650.2 (30) [M – CO]⁺, 643.3 (45) [M – Cl]⁺. IR (KBr, cm⁻¹): ν 2950 (m, C–H), 1990 (s, CO), 1587 (m, C=C). $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, H₃PO₄): δ -22.8 (d, $^2J(\text{P,P}) = 317.2$ Hz; P₂), 42.1 (d, $^2J(\text{P,P}) = 317.2$ Hz; P₁). ^1H NMR (C₆D₆, 25 °C, TMS): δ 0.75 (ddd, $^2J(\text{H,H}) = 8.54$ Hz, $^3J(\text{P}_2, \text{H}) = 7.69$ Hz, $^3J(\text{P}_1, \text{H}) = 4.08$ Hz, 1H; CH₂H₂–Ir), 0.94 (d, $^3J(\text{P,H}) = 15.38$ Hz, 3H; C(CH₃)₂), 1.22 (d, $^3J(\text{P,H}) = 12.87$ Hz, 9H; C(CH₃)₃), 1.29 (d, $^3J(\text{P,H}) = 13.5$ Hz, 9H; C(CH₃)₃), 1.32 (d, $^3J(\text{P,H}) = 12.56$ Hz, 9H; C(CH₃)₃), 1.77 (d, $^2J(\text{P,H}) = 16.01$ Hz, 3H; C(CH₃)₂), 2.29 (ddd, $^2J(\text{H,H}) = 8.54$ Hz, $^3J(\text{P}_2, \text{H}) = 13.58$ Hz, $^3J(\text{P}_1, \text{H}) = 2.43$ Hz, 1H; CH₂H₂Ir), 2.89 and 3.01 (AB part of an ABMX spin system, $^2J(\text{H}_a, \text{H}_b) = 16.64$ Hz, $^2J(\text{P,H}_a) = 9.73$ Hz, $^2J(\text{P,H}_b) = 9.42$ Hz, $^3J(\text{P,H}_b) = 2.0$ Hz, 2H; CH₂P), 3.23 (m, 2H; CH₂P₂), 3.63 (s, 3H; OCH₃), 6.80 (s, 2H; CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 25 °C, TMS): δ 14.25 (dd, $^2J(\text{P,C}) = 30.65$ Hz, $^2J(\text{P,C}) = 3.03$ Hz, CH₂Ir), 28.35 (s, C(CH₃)₂), 30.00 (s, C(CH₃)₂), 30.28 (d, $^2J(\text{P,C}) = 2.69$ Hz, C(CH₃)₃), 30.4 (s, C(CH₃)₃), 33.66 (dd, $^2J(\text{P,C}) = 3.37$ Hz, $^4J(\text{P,C}) = 0.67$ Hz, C(CH₃)₃), 34.35 (dd, $^1J(\text{P,C}) = 8.42$ Hz, $^3J(\text{P,C}) = 8.42$ Hz, CP), 35.84 (d, $^1J(\text{P,C}) = 28.97$ Hz, CH₂P), 36.95 (d, $^1J(\text{P,C}) = 26.95$ Hz, CH₂P), 37.27 (dd, $^1J(\text{P,C}) = 16.17$ Hz, $^3J(\text{P,C}) = 2.02$ Hz, CP), 38.27 (dd, $^1J(\text{P,C}) = 15.16$ Hz, $^3J(\text{P,C}) = 6.40$ Hz, CP), 55.22 (s, OCH₃), 55.55 (dd, $^1J(\text{P,C}) = 27.96$ Hz, $^3J(\text{P,C}) = 5.05$ Hz, CP), 108.76 (d, $^3J(\text{P,C}) = 14.82$ Hz, CH), 109.72 (d, $^3J(\text{P,C}) = 15.50$ Hz, CH), 132.1 (s, COCH₃), 146.14 (dd, $^2J(\text{P,C}) = 8.08$ Hz, $^3J(\text{P,C}) = 2.69$ Hz, CHCCH₂P), 148.0 (dd, $^2J(\text{P,C}) = 11.45$ Hz, $^3J(\text{P,C}) = 3.37$ Hz, CHCCH₂P), 158.1 (dd, $^2J(\text{P,C}) = 1.01$ Hz, $^2J(\text{P,C}) = 1.01$ Hz, ClIr), 177.53 (d, $^2J(\text{P,C}) = 6.06$ Hz, CO).

X-ray Crystal Structure Analysis of 4. A dark red crystallite measuring approximately 0.5 × 0.5 × 0.5 mm³ was cut from larger crystals grown from a solution of **4** in

(80) (a) m: [A₃X]₂ pattern, $N = |^3J_{\text{PH}} + ^5J_{\text{PH}}|$. (b) m: [ABX]₂ pattern, $N = |^2J_{\text{PH}} + ^4J_{\text{PH}}|$.

(81) (a) m: AXX' pattern, $N = |^2J_{\text{PC}} + ^4J_{\text{PC}}|$. (b) m: AXX' pattern, $N = |^1J_{\text{PC}} + ^3J_{\text{PC}}|$. (c) m: AXX' pattern, $N = |^3J_{\text{PC}} + ^5J_{\text{PC}}|$.

Table 4. Crystal Data and Collection Parameters

formula	C ₂₅ H ₄₄ ClIrOP ₂
<i>M</i> [g mol ⁻¹]	650.19
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.344(2)
<i>b</i> [Å]	22.033(5)
<i>c</i> [Å]	15.031(3)
β [deg]	104.04(2)
volume [Å ³]	2680.8(11)
<i>Z</i>	4
ρ _{calcd} [g cm ⁻³]	1.611
radiation	Mo Kα (λ = 0.71073 Å)
μ [mm ⁻¹]	5.214
θ _{max} [deg]	27.5
index ranges	-1 ≤ <i>h</i> ≤ 10; -28 ≤ <i>k</i> ≤ 1; -19 ≤ <i>l</i> ≤ 19
no. of measd reflns	7764
no. of unique reflns	6141
no. of obsd reflns	5559 [<i>I</i> ≥ 2σ(<i>I</i>)]
no. of parameters	284
refinement method	full-matrix least-squares on <i>F</i> ²
GoF	1.087
<i>wR</i> 2 ^a	0.0805 (obsd data), 0.0827 (all data)
<i>R</i> 1 ^b	0.0328 (obsd data), 0.0373 (all data)
final diff Fourier map	min, -1.685; max, 2.361
[e Å ⁻³]	

^a $wR2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(w(F_o^2)^2)]^{0.5}$; $w = [\exp(5 \sin^2\theta) / (\sigma^2(F_o^2) + 6.3966P + (0.039P)^2)]$; $P = [F_o^2 + 2F_c^2] / 3$. ^b $R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$.

2-propanol/water. X-ray diffraction data were collected using a Siemens P4 four-circle diffractometer operating at 173 K in the ω-scan mode. Details of data collection and structure refinement are summarized in Table 4. Measured intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using φ-scans was applied.

(82) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(83) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

Structure solution and refinement was carried out with the Bruker XShell 4.01 suite of programs, incorporating SHELXS-97⁸² for structure solution and SHELXL-97⁸³ for structure refinement. The structure was solved by direct methods, and most of the non-hydrogen atoms were located in the initial electron density map and the rest of them in subsequent difference Fourier maps. All hydrogen atoms were geometrically placed and allowed to ride on the atom to which they are connected. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168728. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. The support of this research by the Deutsche Forschungsgemeinschaft (Forschergruppe, Grant FOR 184/3-1 and Graduiertenkolleg, Grant GK-GRK 441/1-00), Bonn/Bad Godesberg, and by the Fonds der Chemischen Industrie, Frankfurt/Main, is gratefully acknowledged. W.C.K. acknowledges the University of California Energy Institute, the University of California Santa Barbara, and the NSF. H.G.M. thanks the HLRS, University of Stuttgart, for access to substantial computer time. M.G.Q. thanks the Consejo Social of the Universidad de Alcalá for financial support of her stay at the University of Tübingen.

Supporting Information Available: Tables of crystal and structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles for **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020621W