Synthesis and Reactivity of $[Ir(C_2H_4)_2Tpm^{Me2}]PF_6$ (Tpm^{Me2} = Tris(3,5-dimethylpyrazolyl)methane): Comparison with the Analogous Tp^{Me2} Derivatives (Tp^{Me2} = Hydrotris(3,5-dimethylpyrazolyl)borate)

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Received July 3, 2001

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on December 6, 2001 on http://pubs.acs.org | doi: 10.1021/om010594u

A series of cationic Ir complexes of the neutral Tpm^{Me2} ligand (Tpm^{Me2} = tris(3,5-dimethylpyrazolyl)methane) have been investigated and compared, chemically and structurally, with the analogous derivatives of the monoanionic Tp^{Me2} (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate). The bis(ethene) compound $[Ir(C_2H_4)_2Tpm^{Me2}]PF_6$ (**1**) undergoes olefinic C−H activation under very mild conditions to give first $[Ir(H)(CH{=}CH_2)(C_2H_4)Tpm^{Me2}]^+$ (**2**) (all cationic species described have been isolated in the form of PF_6^- salts) and subsequently hydride−crotyl products derived from C−C coupling of the hydrocarbon ligands of **2**. A different bond-forming reaction has been encountered during the solid-state thermal activation of **1** (suspended in C_6H_{12}), leading to the hydride−α,ω-butenyl derivative **4**. X-ray studies on the latter compound show close structural analogies with related complexes of the Tp^{Me2} ligand and, specifically, a striking similarity of the structural parameters of the $IrTpm^{Me2}$ and $IrTp^{Me2}$ moieties. Compound **4** reacts with hard donors, giving $[Ir(CH_2CH_2CH_2CH_2)(L)Tpm^{Me2}]^+$ adducts (**9**; L = py, NCMe), whereas the soft donors PR_3 (R = Me, Et) and CN^- allow the isolation of complexes derived from the attack of the soft nucleophile at the internal coordinated olefinic carbon (complexes **10a**−**c**). Hydrogenation of **1** under different experimental conditions permits the production of different hydride products, e.g. $[Ir(H)_2(C_2H_4)Tpm^{Me2}]^+$ (**13**) and $[Ir(H)(C_2H_5)(C_2H_4)Tpm^{Me2}]^+$ (**12**). Carbene derivatives resulting from the regioselective double C−H bond activation of THF (compounds **11** and **16**) have been produced using **4** and **13** as the reactants.

Introduction

Alkenes are very important substrates for the chemical industry and are central to many organometallic transformations.[1] Of the characteristic reactions of these molecules, the cleavage of olefinic C−H bonds by transition-metal compounds has aroused considerable interest, due to its relevance to the general field of C−H bond activation.[2,3]

Even though the conversion of an M−ethylene fragment into the M(H)(vinyl) isomeric unit is usually thermodynamically unfavorable for mononuclear systems,[4] iridium complexes of the tris(pyrazolyl)borate

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(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. (b) *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Hermann, W. A., Eds.; VCH: Cambridge, U.K., 1996.

(2) For some recent reviews on C−H bond activation see: (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (b) Arndsten, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (c) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125. (d) Junk, T.; Catallo, W. J. *Chem. Soc. Rev.* **1997**, *26*, 401. (e) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2184. (f) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.

(3) For some recent examples see: (a) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995. (b) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992. (c) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (d) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831. (e) González-Herrero, P.; Weberndörfer, K. I.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3266. (f) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. *J. Am. Chem. Soc.* **2000**, *122*, 7414. (g) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252. (h) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063. (i) Maury, O.; Lefort, L.; Vidal, Y.; Cazat-Thivolle, J.; Basset, J.-M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1952. (j) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (k) Rybtchinski, B.; Milstein, D. *J. Am. Chem. Soc.* **1999**, *121*, 4528. (l) Martin, R. L. *J. Am. Chem. Soc.* **1999**, *121*, 9459. (m) Gross, C. L.; Girolami, G. S. *J. Am. Chem. Soc.* **1998**, *120*, 6605.

(4) (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.

10.1021/om010594u CCC: $22.00 © 2002 American Chemical Society
Publication on Web 12/06/2001

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ligands[5,6] (Tp′) exhibit the opposite order of stability,[7,8] so that the $Ir^{I}-C_2H_4$ moiety of these compounds converts readily into the corresponding $Ir^{III}(H)(CH{=}CH_2)$ species. Thus, it appears that an Ir(NNN) coordination environment provides an appropriate electronic situation for this transformation to occur. Nonetheless, comparative studies of vinylic activations for series of related [Ir(Tp′)(C_2H_4)] compounds have demonstrated that, within the Ir(NNN) framework, the Ir(C_2H_4) to Ir(H)($CH{=}CH_2$) rearrangement becomes more facile with an increase of the steric effects of the Tp′ ligand. Accordingly, compounds of the 3,5-Me_2-substituted Tp^{Me2} group are more susceptible to C−H oxidative addition than those of the unsubstituted Tp;[8] furthermore, for the even bulkier Tp^{Ph} group, the corresponding Ir(C_2H_4)$_2$ complex cannot be isolated.[9] Ab initio quantum-mechanical calculations give theoretical support to these experimental observations.[10]

Since changing the nature of the 3-substituent (R) of the pyrazolyl ring (for example, using $Tp^{R,R'}$ ligands for R = H, Me, Ph) causes a significant variation of the ligand steric characteristics without simultaneously inducing an important modification of its electron-donating properties,[11] it may be assumed that steric effects modulate the Ir−ethene to Ir(H)($CH{=}CH_2$) isomerization process.[10] To get further insight into this interesting problem, we have investigated the effect of a formal positive charge on the iridium atom by preparing a cationic $[Ir(C_2H_4)_2(L)]^+$ complex, with steric properties very similar to those of $IrTp^{Me2}(C_2H_4)_2$.[8] As the L ligand, we have chosen the neutral, potentially tridentate tris(3,5-dimethylpyrazolyl)methane (Tpm^{Me2}), which is isosteric and isoelectronic with the anionic Tp^{Me2} group. Despite the similarity between the two families of ligands, and the widespread use of the tris(pyrazolyl)-borates,[5] the tris(pyrazolyl)methanes (Tpm′) have received comparatively little attention, although in the last few years they have been employed more frequently in coordination and organometallic chemistry.[12,13] In accord with studies in the literature,[12,13c] we have encountered many similarities in the structural and chemical properties of the $IrTp^{Me2}$ and $IrTpm^{Me2}$ compounds.

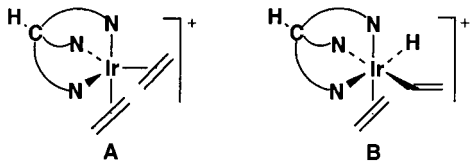
Results and Discussion

The Bis(ethene) Compound $[Ir(C_2H_4)_2Tpm^{Me2}]PF_6$ (1) and the Products of Its Thermal and Photochemical Rearrangement.

By a procedure similar to that used for the synthesis of the neutral $IrTp^{Me2}(C_2H_4)_2$,[8] the low-temperature reaction of [Ir(μ-Cl)(coe)$_2$]$_2$ (coe = cyclooctene, C_8H_{14}) with C_2H_4 and Tpm^{Me2} in THF, and subsequent addition of NH_4PF_6, allows the isolation of $[Ir(C_2H_4)_2Tpm^{Me2}]PF_6$ (**1**) in ca. 80% yield, in the form of a yellow microcrystalline solid (eq 1).

$$[Ir(\mu\text{-}Cl)(coe)_2]_2 \xrightarrow[\text{2. } NH_4PF_6]{\text{1. } C_2H_4,\ Tpm^{Me2},\ (-20\ ^\circ C)} \underset{\mathbf{1}}{[Ir(C_2H_4)_2Tpm^{Me2}]PF_6} \quad (1)$$

In accord with its ionic formulation, compound **1** is insoluble in hydrocarbon solvents but exhibits good solubility properties in CH_2Cl_2, $CHCl_3$, THF, acetone, and other polar organic solvents. Like the analogous $IrTp^{Me2}(C_2H_4)_2$ derivative, **1** is highly fluxional in solution; the ^1H NMR spectrum (20 °C, $CDCl_3$) shows only two singlets for the Tpm^{Me2} methyl groups at δ 2.57 and 2.49. In the $^{13}C\{^1H\}$ NMR spectrum these groups appear at 15.2 and 11.3 ppm, whereas the olefinic carbons give rise to one signal at δ 28 ($^1J_{CH}$ = 156 Hz). These data are in good correspondence with those of $IrTp^{Me2}(C_2H_4)_2$ and suggest the structures of the two compounds are alike (**A**). The comparable reactivity of [Ir(C_2H_4)$_2$-



$Tpm^{Me2}]^+$ (**1**) and $IrTp^{Me2}(C_2H_4)_2$, to be described below, can be taken as additional support for this proposal.

Heating a CD_2Cl_2 solution of **1** at 60 °C gives a kinetic mixture of the hydride−crotyl isomers [Ir(H)(η^3-C_4H_7)-$Tpm^{Me2}]PF_6$ (**3**). No intermediates can be observed, but this reaction probably occurs through the intermediacy of the hydride−vinyl compound [Ir(H)($CH{=}CH_2$)(C_2H_4)-$Tpm^{Me2}]PF_6$ (**2**). In fact, compound **2**, which can be cleanly generated by photochemical activation of a suspension of **1** in C_6H_{12} (eq 2), undergoes a clean

(5) (a) Trofimenko, S. *Scorpionates-The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (c) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (d) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 418.

(6) The abbreviations used in this paper for the tris(pyrazolyl)-borates are those proposed by Trofimenko in ref 5a. Tp′ stands for any ligand of this type. By analogy Tpm′ and Tpm^{Me2} denote a general tris-(pyrazolyl)methane and the particular 3,5-Me_2-substituted derivative, respectively.

(7) Ghosh, C. K.; Hoyano, J. K.; Kreutz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480.

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

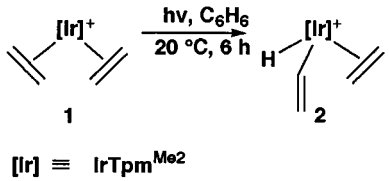
(9) (a) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Chem. Commun.* **2000**, 121. (b) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. Submitted for publication.

(10) Jiménez-Cataño, R.; Niu, S.; Hall, M. B. *Organometallics* **1997**, *16*, 1962.

(11) Slugovc, C.; Padilla-Martínez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129 and references therein.

(12) See for example: (a) Kläui, W.; Berghahn, M.; Rhünwald, G.; Lang, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2464. (b) Dhawan, I. K.; Bruck, M. A.; Schilling, B.; Grittini, C.; Enemark, J. H. *Inorg. Chem.* **1995**, *34*, 3801. (c) Byers, P. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 305. (d) Fernández-Baeza, J.; Jalón, F. A.; Otero, A.; Rodrigo-Blanco, M. E. *J. Chem. Soc., Dalton Trans.* **1995**, 1015. (e) Jalón, F. A.; Manzano, B. R.; Otero, A.; Rodríguez-Pérez, M. C. *J. Organomet. Chem.* **1995**, *494*, 179. (f) Bhambri, S.; Tocher, D. A. *Polyhedron* **1996**, *15*, 2763. (g) Shiu, K.-B.; Ling, S.-T.; Fung, D.-W.; Chan, T.-J.; Peng, S.-M.; Cheng, M.-Ch.; Chou, J. L. *Inorg. Chem.* **1995**, *34*, 854. (h) Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Concolino, T.; Mohan, A.; Long, G. J. *Inorg. Chem.* **2000**, *39*, 4674. (i) Lawrence, S. C.; Skinner, M. E. G.; Green, J. C.; Mountford, P. *Chem. Commun.* **2001**, 705.

(13) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118. (b) For the synthesis of the ligands see: Julia, S.; del Mazo, J.; Ávila, L.; Elguero, J. *Org. Prep. Proced. Int.* **1984**, *16*(5), 299. (c) While this paper was in preparation, an improved synthesis of Tpm^{Me2} was reported: Reger, D. L.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, *607*, 120. (d) For a review of complexes of some Tpm′ ligands and some group 11−14 metals see: Reger, D. L. *Comments Inorg. Chem.* **1999**, *21*, 1. For a comparison of Tp^{Me2}− and Tpm^{Me2}−Cd complexes see: (e) Reger, D. L.; Collins, J. E.; Myers, S. M.; Rheingold, A. L.; Liable-Sands, L. M. *Inorg. Chem.* **1996**, *35*, 4904. (f) Reger, D. L.; Collins, J. E.; Rheingold, A. L.; Liable-Sands, L. M. *Inorg. Chem.* **1999**, *38*, 3235.



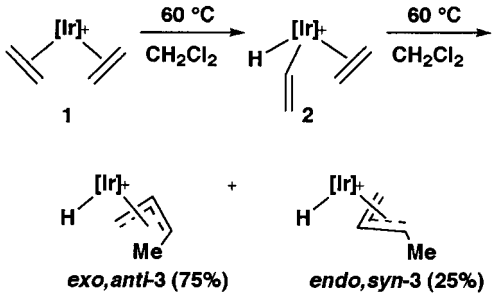
(2)

thermal activation in CD_2Cl_2 to give the same kinetic mixture of complexes **3**. The hydride functionality of **2** is responsible for an IR absorption at ca. 2210 cm^{-1} and for a high-field ^1H NMR resonance at −17.73 ppm. These and other spectroscopic data are very close to those reported for $Ir(H)(CH{=}CH_2)Tp^{Me2}(C_2H_4)$, thereby suggesting analogous coordination environments for the Ir(III) centers of the two compounds (structure **B**). It is worth pointing out that the **1** → **2** conversion appears to be irreversible; hence, for this cationic system the $Ir^{III}(H)(CH{=}CH_2)$ isomer is also thermodynamically more stable than the $Ir^{I}(C_2H_4)$ species. Since steric effects for complexes of the Tp^{Me2} and Tpm^{Me2} ancillary ligands are closely similar, it can be concluded that the presence of a positive charge on the complex does not alter significantly the relative stability between iridium−ethene complexes and their hydride−vinyl isomers. This is in line with previous comparative studies on related complexes of the Tp′ and Tpm′ ligands, which have found a number of similarities in the binding and other properties of the two families of compounds.[13c]

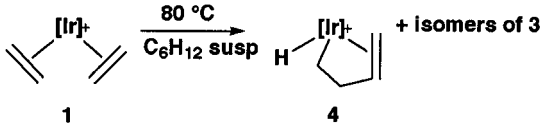
As already mentioned, the thermal (60 °C, CH_2Cl_2) activation of **1** gives a kinetically controlled (see below) mixture of hydride−allyl compounds **3**. Additionally, pure **2** converts into the same mixture of isomers of **3**, suggesting that **2** is an active intermediate in the **1** → **3** transformation (Scheme 1). As for the neutral Ir(H)-(η^3-C_4H_7)Tp^{Me2} analogues, the ^1H NMR resonance of the hydride functionality appears at fairly high field (in the proximity of δ −30). Also analogously to these Tp^{Me2} compounds, the anti and syn distribution of the allylic Me substituent of **3** can be determined from the values of the J_{HH} couplings and from NOESY experiments, which permit us, in addition, to assign the exo or endo configuration of the allyl moiety with respect to the tridentate Tpm^{Me2} group. NMR data for compounds **3** (see Experimental Section) are in agreement with those reported in the literature for analogous complexes.[8,14,15] It is likely that the $[Ir(H)(CH{=}CH_2)(C_2H_4)Tpm^{Me2}]^+$ → $[Ir(H)(C_4H_7)Tpm^{Me2}]^+$ transformation follows the mechanistic pathway already suggested for the Tp^{Me2} system.[8]

Interestingly, whereas the thermal, solid-state activation of the neutral $IrTp^{Me2}(C_2H_4)_2$ gives a combination of hydride−allyl species,[8] via the hydride−vinyl complex, that of **1** provides a mixture of the crotyl isomers **3**, plus a new compound, characterized as the hydride−α,ω-butenyl derivative **4**. The reaction requires prolonged heating at temperatures near 100 °C, which causes partial decomposition of the reaction mixture. Nevertheless, compound **4** can be generated in ca. 80% yields by heating at 80 °C, for 24 h, a finely divided suspension of **1** in cyclohexane. Under these conditions,

Scheme 1



small amounts of the *exo-syn*-**3** are also produced, along with the other two isomers of **3** (eq 3).



(3)

The formation of **4** is stereoselective; only one of the two possible stereomers has been obtained and characterized. Since isomerization by a change of the olefin coordination face seems to be a facile process in complexes of this kind,[16] we assume that the observed structure is that of the thermodynamic isomer.

Upon heating (60 °C, CH_2Cl_2), compound **4** converts exclusively into the hydride−allyl *exo-anti*-**3**. This species can then isomerize at higher temperatures (C_6H_{12}, 120 °C, 3 days) to produce a 3:2:1 mixture of *exo-anti*-, *endo-syn*-, and *exo-syn*-**3**, respectively. Thermal decomposition prevents achievement of the thermodynamic mixture of these compounds. Since no additional experimental evidence on the **4** → **3** transformation has been gained, discussion of its mechanistic aspects is not justified.

The solid-state thermal activation of **1** (C_6H_{12} suspension) was periodically monitored by ^1H NMR spectroscopy. Only small amounts of the hydride−vinyl species **2** are formed at the earlier stages of the reaction, which then disappear by transformation into the crotyl compounds **3**. Monitoring of the thermal activation of **2** under identical conditions reveals that the major products are the crotyl derivatives **3**, conversion into **4** being at a level of around 30% or below. Thus, whereas partial transformation of **2** into **4** may occur, the major route for the solid-state conversion of **1** into **4** seems to involve an alternative reaction pathway. In the absence of conclusive experimental evidence in this regard, we speculate on the possibility of oxidative coupling of the ethene molecules to an iridacyclopentane species, followed by β-H elimination.

Compound **4** has been fully characterized by spectroscopic and X-ray methods. In accord with the nonsymmetrical coordination environment of the iridium center, the three 3,5-Me_2pz rings of the Tpm^{Me2} ligand are inequivalent and give rise to separate, well-resolved resonances, in both the ^1H and $^{13}C\{^1H\}$ NMR spectra. Of structural diagnostic value are a high-field ^1H signal at −19.5 ppm, due to the hydride ligand, and also a

(14) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.

(15) Fryzuk, M. D.; Gao, X.; Rettig, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 3106.

(16) (a) Penag, T.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174. (b) Casey, C. P.; Underiner, T. L.; Vosejpka, P. C.; Slough, G. A.; Cavney, J. A.; Hayashi, R. K. *Organometallics* **1997**, *16*, 2189. (c) Alías, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *Organometallics* **1998**, *17*, 4124.

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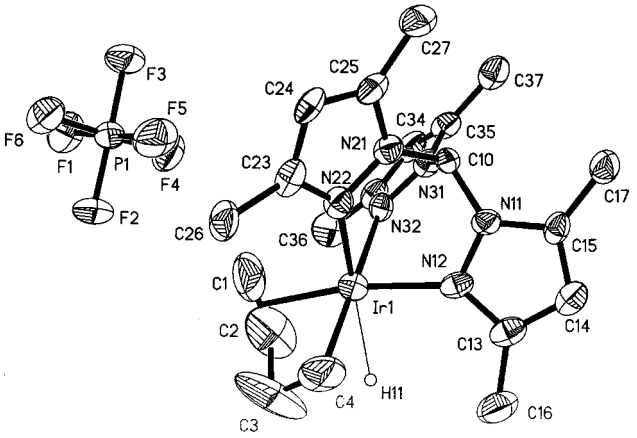


Figure 1. ORTEP view of complex **4**.

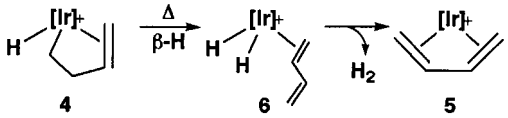
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Ir(1)−C(1)	2.171(10)	Ir(1)−N(12)	2.104(5)
Ir(1)−C(2)	2.142(11)	Ir(1)−N(22)	2.235(5)
Ir(1)−C(4)	2.047(8)	Ir(1)−N(32)	2.152(5)
C(1)−C(2)	1.30(2)	Ir(1)−H(11)	1.82(7)
N(12)−Ir(1)−N(22)	84.6(2)	C(4)−Ir(1)−N(12)	98.2(3)
N(22)−Ir(1)−N(32)	84.1(2)	C(4)−Ir(1)−N(22)	99.7(3)
N(12)−Ir(1)−N(32)	84.5(2)	C(4)−Ir(1)−N(32)	175.5(4)
C(1)−C(2)−C(3)	119.3(14)	C(3)−C(4)−Ir(1)	94.3(6)

high-field ^{13}C resonance at δ −50.1 ($^1J_{C,H}$ = 136 Hz), which can be assigned to the iridium-bound methylene group of the α,ω-butenyl group. The coordinated olefinic carbons give separate signals in the vicinity of 50 ppm, with normal $^1J_{CH}$ couplings of about 160 Hz.

Figure 1 gives an ORTEP view of the molecules of **4**. The complex has the expected distorted-octahedral structure consisting of three pyrazolyl nitrogen atoms in one of the faces of the octahedron and the hydride and the chelating α,ω-butenyl ligands in the remaining coordination sites. Comparison with somewhat related neutral or cationic complexes of Ir(III) and Tp^{Me2} seems appropriate. The Ir−CH_2 distance in **4** (2.047(8) Å) is very similar to the Ir−C(vinyl) separation of 2.030(9) Å found in Ir(H)(CH═CH_2)Tp^{Me2}(PMe_2Ph).[17] In turn, the Ir−olefin bond of **4** is characterized by Ir−C(1) and Ir−C(2) bond lengths of 2.171(10) and 2.142(11) Å, respectively, which is once more in close analogy with corresponding distances in related, structurally characterized[18] cationic species (e.g. [Ir(H)Tp^{Me2}(Me(H)C═$CHCH_2$CH═NH)]$^+$; 2.21(2) and 2.23(2) Å). Bond lengths and angles (Table 1) within the IrTpm^{Me2} moiety of **4** show striking similarity to the corresponding parameters of analogous IrTp^{Me2} complexes. For example, in the cationic Tp^{Me2} derivative mentioned above[18] the Ir−N distances span the interval 2.02−2.24 Å, while the N−Ir−N angles cluster around 86°. Similarly, in the cationic species [Ir(H)Tp^{Me2}(═C(Me)C(H)MeC(Me)═NH)]$^+$, the IrTp^{Me2} fragment has Ir−N separations of 2.05(2)−2.15(2) Å[16c] and N−Ir−N bond angles close to 86°. In **4**, the three Ir−N bond lengths are equal to 2.104(5) Å (Ir−N12), 2.152(5) Å (Ir−N32), and 2.235(5) Å (Ir−N22), the longest Ir−N bond being that trans with respect to the hydride, whereas the three N−Ir−N angles are equal to 84.5°.

Scheme 2



It can therefore be concluded that the Tp^{Me2} and Tpm^{Me2} ligands coordinate to Ir(III) in a very similar fashion.[13d]

The thermal transformation of compound **4** into the allyls **3** also gives small amounts of the η^4-butadiene compound [Ir(η^4-C_4H_6)Tpm^{Me2}]$^+$ (**5**) (less than 10% conversion after heating at 150 °C for 2 days). A likely intermediate for this conversion is the dihydride compound **6** (Scheme 2), which would yield **5** by reductive elimination of H_2. This assumption has been confirmed by the independent generation of the dihydride complex **6** and its conversion into **5**. Photolysis of a cyclohexane suspension of **4** induces β-H elimination and formation of **6**, characterized by two distinct ^1H NMR hydride resonances at δ −17.32 and −26.46. Compound **6** is very labile in solution and loses H_2 spontaneously, to afford **5**. This lability has precluded its isolation in an analytically pure form. An alternative, high-yield route to **5** is that of eq 1, using C_4H_6 in place of C_2H_4.[19] Compound **5** is fluxional in solution and exhibits ^{13}C NMR resonances at δ 6.7 (CH_2; $^1J_{CH}$ = 152 Hz) and δ 71.4 (olefinic CH; $^1J_{CH}$ = 173 Hz). These data resemble those reported for IrTp^{Me2}(η^4-C_4H_6)[19] and suggest therefore a comparable 18-electron formulation, with a κ^3N,N',N''-Tpm^{Me2} ligand.

In the NMR spectra of each of the Tpm^{Me2} complexes, a low-field signal is observed in the vicinity of δ 8.0 ppm. This signal, and the associated ^{13}C resonance near 70 ppm, are assigned to the central CH unit of the tridentate ligand. Upon treatment of some of these complexes with $KOBu^t$ (e.g. **4** and **6**), these resonances disappear, suggesting deprotonation of the acidic methine proton[12a,i] and formation of the corresponding zwitterionic derivatives. The resulting solutions are, however, exceedingly sensitive to traces of water (or any other adventitious source of protons), and this has precluded full characterization of these compounds.

Reactions with Lewis Bases. In contrast with the neutral IrTp^{Me2}(C_2H_4)$_2$, which reacts with hard donors such as NCMe, DMSO, and pyridine with formation of Ir(CH═CH_2)(C_2H_5)Tp^{Me2}(L), via the hydride−vinyl isomer, interaction of the cationic species [Ir(C_2H_4)$_2$-Tpm^{Me2}]$^+$ (**1**) with these Lewis bases leads only to extensive decomposition, probably due to displacement of the chelating Tpm^{Me2} ligand. Not unexpectedly, however, the anticipated Ir(III) adducts may be obtained by the room-temperature reaction of the hydride−vinyl species **2** and the Lewis base (vide infra).

At variance with this result, carbon monoxide reacts smoothly with **1**, with successive generation of the mono- and disubstituted derivatives [Ir(CO)(C_2H_4)-Tpm^{Me2}]$^+$ and [Ir(CO)$_2$$Tpm^{Me2}$]$^+$ (NMR evidence) and then of the hydride−metallocarboxylic compound **7a** (Scheme 3). IrTp^{Me2}(C_2H_4)$_2$ exhibits the same behavior toward CO.[17] The formation of the latter compound is doubtless due to the action of adventitious water. In line with this observation, addition of MeOH and EtOH

(17) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.

(18) Alías, F. M. Ph.D. Thesis, University of Seville, 1997.

(19) Boutry, O.; Poveda, M. L.; Carmona, E. *J. Organomet. Chem.* **1997**, *528*, 143.

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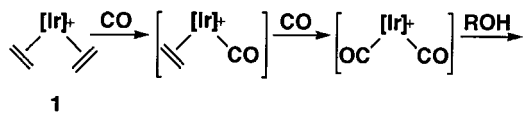
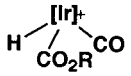
Scheme 3



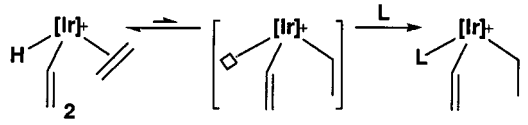
1



7a-c

R = H, 7a; Me, 7b; Et, 7c

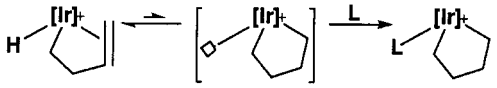
Scheme 4



2

L = py, 8a; NCMe, 8b

Scheme 5



4

L = py, 9a; NCMe, 9b

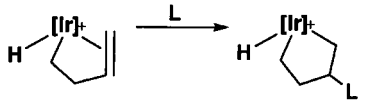
allows the isolation of the hydride−metallocarboxylic ester derivatives **7b** and **7c**. Spectroscopic data for compounds **7** are similar to those reported for Ir(H)-$(CO_2H)Tp'(CO)$.[17,20] Characteristic IR features for **7** include ν(Ir−H) at about 2190 cm^{-1}, a terminal carbonyl C−O stretching in the proximity of 2060 cm^{-1}, and ν-(CO_2R) at 1625 cm^{-1} (R = H) or 1660 cm^{-1} (R = Me, Et). These bands are somewhat shifted toward higher energy, in comparison with the corresponding absorptions in $Ir(H)(CO_2H)Tp^{Me2}(CO)$ (for instance, ν(CO) for the carbonyl ligand of the latter complex appears at 2040 cm^{-1}), in accord with the existence in complexes **7** of a formal positive charge on the metal center.

As briefly mentioned above, the hydride−vinyl compound **2** reacts readily with acetonitrile and pyridine to give the vinyl−ethyl adducts **8**. Kinetic studies, effected in acetonitrile-d_3 and pyridine-d_5, show that both reactions exhibit pseudo-first-order kinetics and are characterized by half-lives of ca. 56 min (NCMe) and 19 min (pyridine), in agreement with the mechanistic proposal of Scheme 4.

An interesting behavior was found during the course of studies aimed at ascertaining the reactivity of the hydride−α,ω-butenyl complex **4** with different Lewis bases. Treatment of this complex with an excess of pyridine produces a darkening of the solution and, as revealed by ^1H NMR monitoring in C_5D_5N, formation of **9a** as the only reaction product (Scheme 5).

A similar, albeit somewhat slower, transformation occurs when **4** is dissolved in acetonitrile. The elemental analysis and the spectroscopic data (IR; ^1H and $^{13}C\{^1H\}$ NMR) obtained for these compounds are in full agreement with their formulation as cationic iridacyclopentane complexes, thereby resulting from the Lewis base-induced migratory insertion of the coordinated olefin into the Ir−H bond. Compounds **9a**,**b** show characteristic high-field $^{13}C\{^1H\}$ resonances associated with the iridium-bound methylene groups (δ 1.2 and −2.0 for **9a** and **9b**, respectively; $^1J_{CH} \approx 125$ Hz).

Whereas the hard Lewis bases py and NCMe attack preferentially at the vacant coordination site created by the migration of the hydride onto the coordinated alkene moiety of **4**, the soft bases PMe_3 and PEt_3 lead instead to selective nucleophilic attack at the internal olefinic carbon,[21−23] generating single diastereomeric products, **10a**,**b** (eq 4). In each case, the product is that resulting



4 (4)

L = PMe_3, 10a; PEt_3, 10b; CN^-, 10c

from the Markonikoff addition[22] and precipitates gradually in 85−90% yield as a yellow microcrystalline solid, over the course of the reaction (ca. 24 h). A similar reaction using $(n\text{-Bu})_4NCN$ as a source of the soft carbon nuclephile CN^- produces the related compound **10c**. Due to the complexity of the ^1H NMR spectra, NOESY experiments have proved to be of little use for the assignment of the stereochemistry of these complexes.

In contrast to the case for adducts **9a**,**b**, complexes **10a**−**c** show characteristic IR (ca. 2115−2140 cm^{-1}) and ^1H NMR (ca. δ −24 ppm) absorbances, indicative of the presence of an Ir−H functionality. Moreover, the phosphonium ylides **10a**,**b** display typical NMR features associated with this kind of compound.[25] A low-field singlet appears in their $^{31}P\{^1H\}$ NMR spectra (δ 18.9, **10a**; δ 31.0, **10b**), whereas large $^1J_{PC}$ (for the *C*$HPMe_3$ carbon nucleus) and $^2J_{PH}$ (for the PMe_3 group) couplings are found in their $^{13}C\{^1H\}$ and ^1H NMR spectra (for example, 28 and 13 Hz, respectively, for the trimethylphosphonium ylide **10a**). As for product **10c**, an IR band at 2210 cm^{-1} and a ^{13}C resonance at δ 128.4 are assigned to the cyanide substituent[24] within the metallacyclic unit.

The iridacyclopentane protons of **10a**−**c** give complex multiplets due to their coupling with different ^1H nuclei (and in **10a**,**b** with the ^{31}P nucleus). ^1H and $^{13}C\{^1H\}$ chemical shifts for this moiety have been assigned from NOESY and $^1H-^{13}C$ correlation spectra.

The results discussed in the preceding paragraphs show that the reaction of the hydride−α,ω-butenyl compound **4** with nucleophilic reagents may progress along two alternative reaction pathways, namely migratory insertion of the olefin terminus onto the Ir−H bond and stereoselective nucleophilic attack at the internal olefinic carbon. Since the soft P- or C-based nucleophiles appear to induce the latter transformation, we have studied the interaction of **4** with some Grignard reagents, Mg(R)X, for R = Me, Et, *i*-Pr, $CH_2C_6H_5$. Unfortunately, C−C bond formation does not seem to occur

(20) Fernández, M. J.; Rodríguez, M. J.; Oro, L. A. *J. Organomet. Chem.* **1992**, *438*, 337.

(21) Bäckvall, J.-E. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, Chapter 11.

(22) Cameron, A. D.; Smith, V. H., Jr.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1988**, 1037.

(23) Bosch, M.; Laubender, M.; Weberndörfer, B.; Werner, H. *Chem. Eur. J.* **1999**, *5*, 2203.

(24) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S.; Concolino, T. E.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5381.

(25) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem. Eur. J.* **1998**, *4*, 2225.

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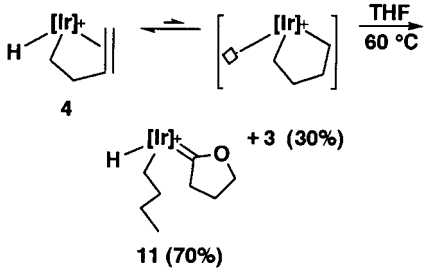
Scheme 6

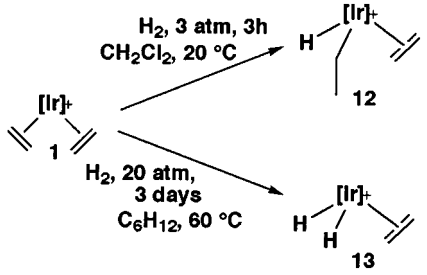


and we were only able to isolate products from side decomposition reactions.

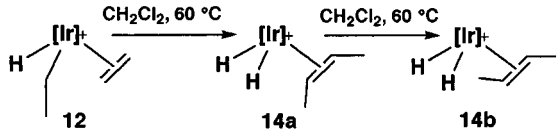
With respect to the hard donors, as represented in Scheme 5, an unsaturated iridacyclopentane species (possibly stabilized by means of an agostic interaction[25,26]) seems to be a likely intermediate that would give the products in the last trapping step. Our previous observation[25] in the $IrTp^{Me2}$ system, that compounds able to generate $Ir(R)(R')Tp^{Me2}$ fragments and have in addition a vacant or readily accessible coordination site are able to activate THF, together with the chemical similarity discussed in this contribution between the $IrTp^{Me2}$ and $[IrTpm^{Me2}]^+$ compounds, prompted us to investigate this double C−H bond activation.[27] In accord with our suspicions, a mixture of the hydride−allyl derivatives **3** and of the new product **11** was generated in THF at 60 °C (Scheme 6), from which the Fischer carbene complex **11** may be isolated, following its chromatographic separation from the allyl coproducts. No significant isotope effect can be found when the reaction is effected in THF-d_8, but under these circumstances deuterium incorporation into the hydride site and partial labeling of the α- and β-butyl carbons takes place.[25] Although extensive ^1H and ^{13}C, 1D and 2D NMR experiments are needed to fully characterize this compound, its close analogy with the related $IrTp^{Me2}$ species[25] makes this process straightforward. As a matter of fact, the most characteristic spectroscopic features of both compounds (Ir−H, Ir−CH_2, and Ir=C< resonances) exhibit remarkable similarities. For example, the hydride ligand of **11** resonates at −17.17 ppm (−17.90 in the analogous Tp^{Me2} derivatives) and the carbene carbon resonance appears at δ 260.5 and 258.8 in **11** and the Tp^{Me2} analogue, respectively.

Hydrogenation and Related Reactions. The homogeneous hydrogenation of **1** (CH_2Cl_2 solution, 3 atm of H_2, 3 h) yields almost exclusively the hydride−ethyl−ethene derivative **12** of Scheme 7. In contrast, the hydrogenation of **1** in a suspension in C_6H_{12} needs more forcing conditions and the bis(hydride) species **13** is formed, in ca. 80% yield (20 atm of H_2, 60 °C, 3 days). Minor hydride components of this complex reaction mixture are **12** and its 2-butene−Ir(III) thermal degradation products **14a**,**b** (see below). Additionally, the 1-butene−Ir(III) species **14c** and the allyl *exo-anti*-**3**, both derived from complex **4** (**1** partially transforms into **4** under these reaction conditions), are also formed.

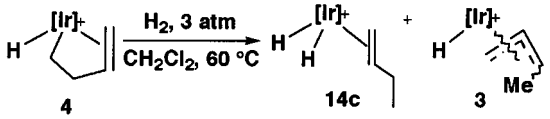
Scheme 7



Scheme 8



Scheme 9



The following observations support the above reactivity (Scheme 8). Complex **12** transforms cleanly into the *trans*-2-butene species **14b** upon heating its CH_2Cl_2 solutions for 3 days at 60 °C. NMR monitoring of this reaction shows the intermediacy of the thermodynamically less favored *cis*-2-butene isomer **14a** (Scheme 8).

Moreover, even though the hydrogenation of the hydride−α,ω-butenyl complex **4** does not occur at 25 °C at an observable rate, under somewhat more forcing conditions (60 °C, 3 atm, 1 day), complex **14c** is produced along with the allyl *exo-anti*-**3**, as a result of the thermal activation of **4** (ca. 1:1 ratio, Scheme 9). The same result is observed upon hydrogenation of a suspension of **4** in C_6H_{12}, although with low (ca. 35%) conversion into products, after heating at 80 °C for 3 days under 3 atm of H_2. Complex **14c** appears to be a kinetically robust species and does not transform into the 2-butene isomers upon heating in CH_2Cl_2 at 60 °C for 3 days. Interestingly, complex **14c** can also be prepared (see Experimental Section) by the direct reaction of **4** with an excess of $Li[BH(C_2H_5)_3]$.

As can be foreseen, the coordinated ethylene of the above compounds rotates freely (for **14b** this rotation is detected by EXSY NMR at 25 °C), on the NMR time scale at room temperature. Thus, only one proton and one carbon-13 resonance are detected for the C_2H_4 molecule of **13** in the ^1H (δ 3.39) and $^{13}C\{^1H\}$ NMR spectra (δ 38.3; $^1J_{CH}$ = 163 Hz). The chemical behavior of these compounds is also consistent with this assumption. For example, facile migratory insertion is observed when **12** is dissolved in pyridine or acetonitrile, while double C−H activation of THF[25] occurs when the bis(hydride)−ethylene complex **13** is heated at 60 °C in THF (Scheme 10).

Some final comments on the formation of these hydride products appear appropriate at this stage. Whereas it is reasonable to assume that the 1-butene compound **14c** results from the direct hydrogenation of the unsaturated intermediate, originating from the straightforward migratory insertion chemistry of **4**

(26) (a) Brookhart, M.; Green, M. L.; Wong, L.-L. *Prog. Inorg. Chem.* **1998**, *36*, 1. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

(27) For other recent double or triple C−H activation reactions see: (a) Petrovic-Ristic, D.; Torkelson, J. R.; Hilts, R. W.; McDonald, R.; Cowie, M. *Organometallics* **2000**, *19*, 4432. (b) Kickham, J. E.; Guérin, F.; Stewart, J. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3263.

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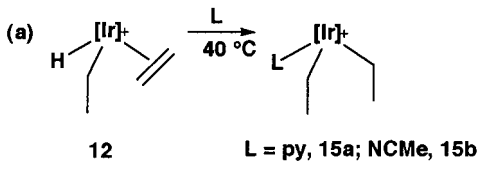
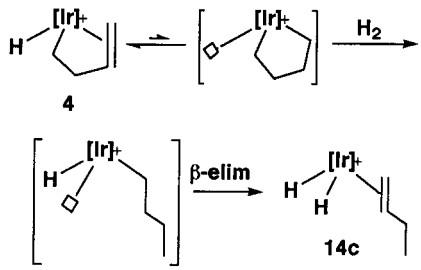
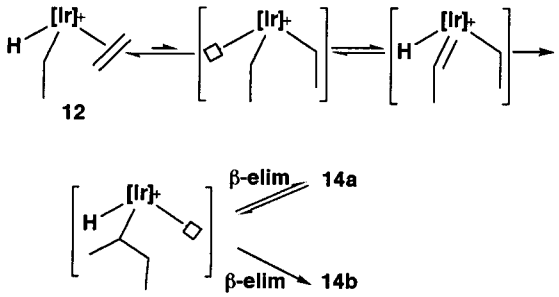
Scheme 10



Scheme 11



Scheme 12



(Scheme 11), the production of complexes **14a**,**b** is better understood through the sequence of events proposed in Scheme 12. Notice that neither the insertion of C_2H_4 into the Ir−C_2H_5 bond of **12** or β-H elimination from the −CHMe group of the proposed alkyl intermediate can be of importance, since they would generate complex **14c**. The suggested α-H elimination finds support in the behavior of closely related, well-characterized cationic ethyl−ethylidene Ir(III) compounds[18,28] and in the mechanistic pathway proposed for the conversion of $IrTp^{Me2}$-(H)(CH=CH_2)(C_2H_4) into the corresponding hydride−crotyl products.[8,29] Partial dissociation of the weakly bonded C_2H_4 ligand of **12** can occur, explaining the formation of the minor amounts of the dihydride **13** that always accompany complexes **14a**,**b**.

In summary, the neutral Tpm^{Me2} ligand has been found to bind to Ir(I) and Ir(III) centers, as does the isosteric and isoelectronic, but formally monoanionic, Tp^{Me2}. The resulting cationic Tpm^{Me2} complexes display structural properties closely reminiscent of those of the neutral $IrTp^{Me2}$ analogues. Some differences in chemical reactivity between the two systems have been found, and these may be highlighted by the isolation in the Tpm^{Me2} series of compounds of the hydride−α,ω-butenyl complex **4**. Nevertheless, and despite their cationic nature, analogously to the Tp^{Me2} system, the $[Ir^{III}(H)(CH{=}CH_2)(C_2H_4)Tpm^{Me2}]^+$ complex is thermodynamically more stable than its $[Ir^{I}(C_2H_4)_2Tpm^{Me2}]^+$ isomer. These observations support the notion that, in the systems based on Ir(NNN) fragments, the energetics of the olefinic C−H bond activation reactions are modulated by the steric properties of the Ir−ancillary ligand moiety.[8−10]

Experimental Section

General Procedures. Microanalyses were by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained from Perkin-Elmer spectrometers, Models 577 and 684. The NMR Instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 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). For ^{31}P-{^{1}H} NMR spectroscopy, 85% H_3PO_4 was used as the reference. 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, following conventional Schlenk techniques. The compound $[IrCl(coe)_2]_2$[30] was obtained by the published procedure, whereas the ligand Tpm^{Me2} was synthesized following Elguero's reported method.[13b] A detailed, multigram-scale, slightly modified procedure is as follows: 2,3-dimethylpyrazole (18.46 g, 0.194 mol), K_2CO_3 (132.7 g), and $[CH_3(CH_2)_3]_4NHSO_4$ (3.0 g, 8.84 mmol) were placed in a mortar. The solid mixture was homogenized, transferred to a 250 mL reaction flask, and suspended in 100 mL of $CHCl_3$. The mixture was refluxed for 12 h with vigorous stirring. After the mixture was cooled at room temperature, the liquid phase was decanted and 50 mL of $CHCl_3$ was added to the solid left behind. The described operations were repeated twice, and finally the remaining solid was washed with two 100 mL portions of chloroform. The chloroform phases were combined, and the solvent was evaporated to give a brown viscous solid that was extracted with three 50 mL portions of petroleum ether. The volatiles were removed under vacuum, and to the remaining brown sticky solid were added 600 mL of hexanes and 3 g of activated charcoal; the mixture was then refluxed. After filtration, the hexane phase was concentrated to cloudiness and cooled to obtain, after filtering and drying, 13.0 g of a raw product. After repeated recrystallizations from hexane, 10.5 g (54% yield) of pure tris(2,3-dimethylpyrazolyl)methane was obtained.[13c] Due to the strong tendency of these ionic complexes to retain crystallization solvent, for some of the compounds reported carbon analyses deviate ca. 0.6−0.8% from calculated values.

$[Ir(C_2H_4)_2Tpm^{Me2}]PF_6$ (1). Ethylene was bubbled through a suspension of 2.0 g (2.2 mmol) of $[IrCl(C_8H_{14})_2]_2$ in 100 mL of THF at −20 °C to give a colorless solution (ca. 20 min). A solution of 1.330 g (4.5 mmol) of tris(3,5-dimethylpyrazolyl)-methane in 50 mL of THF was then added. The color of the reaction mixture changed from orange to red, following stirring for 5 h at the same temperature. After this time, 0.740 g (4.5 mmol) of NH_4PF_6 dissolved in 25 mL of THF was added, creating a yellow precipitate. The volatiles were then removed under vacuum, the residue was dissolved in 50 mL of CH_2Cl_2, and the resulting solution was filtered. The filtrate was

(28) Alías, F. M.; Poveda, M. L.; Sellin, M.; Carmona, E. *J. Am. Chem. Soc.* **1998**, *120*, 5816.

(29) For some examples of α-H elimination in transition-metal alkyls see: (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942. (c) Fryzuk, M. D.; Joshi, K. *J. Am. Chem. Soc.* **1989**, *111*, 4498. (d) Belderraín, T. R.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Paneque, M.; Poveda, M. L.; Carmona, E. *Organometallics* **1993**, *12*, 4431.

(30) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 19.

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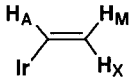
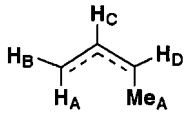
evaporated to dryness and then washed several times with 10 mL portions of a 2:1 mixture of Et_2O and CH_2Cl_2 at 0 °C. The reddish supernatant was discarded and the remaining yellow powder dried under vacuum to yield 2.6 g (80%) of **1**. ^{1}H NMR ($CDCl_3$): δ 7.72 (s, 1 H, CH(pz)$_3$), 6.06 (s, 3 H, 3 CH), 2.57, 2.49 (s, 9 H each, 3 Me), 2.29 (s, 8 H, 2 C_2H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.3, 143.2 (C_q), 110.7 (CH), 69.9 (CH(pz)$_3$), 28.0 (C_2H_4, $^1J_{CH}$ = 156 Hz), 15.2, 11.3 (Me). Anal. Calcd for $C_{20}H_{30}F_6N_6PIr$: C, 34.7; H, 4.4; N, 12.2. Found: C, 34.4; H, 4.3; N, 12.2.

[IrH(CH=CH$_2$)(C$_2$H$_4$)Tpm^{Me2}]PF$_6$ (2). A suspension of 0.150 g (0.217 mmol) of the bis(ethylene) complex **1** in 70 mL of cyclohexane was photolyzed for 6 h with an UV lamp (Hg, 125 W) through a Pyrex photoreactor cooled with running water. Cyclohexane was decanted, and the remaining solid was washed several times with Et_2O and then dried under vacuum to give **2** as a pale yellow powder in almost quantitative yield.

vinyl nomenclature: 

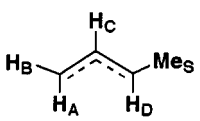
^{1}H NMR ($CDCl_3$): δ 7.99 (s, 1 H, CH(pz)$_3$), 6.46, 5.05, 4.34 (dd, 1 H each, H_A, H_M, H_X, respectively, $^3J_{AM}$ = 10.2, $^3J_{AX}$ = 17.7, $^2J_{MX}$ = 2 Hz), 6.19, 6.16, 5.96 (s, 1 H each, 3 CHpz), 3.82, 3.16 (m, AA′XX′ spin system, 2 H each, C_2H_4), 2.71, 2.64, 2.62, 2.38, 2.34, 2.06 (s, 3 H each, 6 Mepz), −17.73 (s, 1 H, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.3, 155.4, 154.8, 142.5, 142.3, 142.1 (C_q pz), 120.8 (CH=*C*H$_2$, $^1J_{CH}$ = 153 Hz), 120.1 (*C*H=CH$_2$, $^1J_{CH}$ = 143 Hz), 110.5, 109.9, 109.4 (CHpz), 69.5 (CH(pz)$_3$, $^1J_{CH}$ = 153 Hz), 45.5 (C_2H_4, $^1J_{CH}$ = 163 Hz), 16.3, 15.1, 14.2, 11.1, 10.9, 10.9 (Mepz). IR (KBr): ν(Ir−H) 2208, 2100 cm^{-1}. Anal. Calcd for $C_{20}H_{30}F_6N_6PIr$: C, 34.7; H, 4.4; N, 12.2. Found: C, 34.4; H, 4.1; N, 12.0.

***exo,anti*-[IrH(η^3-CH$_2$CHCHMe)Tpm^{Me2}]PF$_6$ (3a).** A solution of 0.1 g (0.145 mmol) of the α,ω-butenyl complex **4** (see below), in 10 mL of CH_2Cl_2, was heated at 60 °C for 24 h. The solution was concentrated to approximately 2 mL, and then Et_2O was added until precipitation of a pale yellow solid. After filtering, the solid was dried under vacuum to give 0.090 g of the *exo,anti*-methylallyl complex in 90% yield. Monitoring of the reaction by ^{1}H NMR in CD_2Cl_2 shows that the methylallyl species was the only compound formed.



^{1}H NMR (CD_2Cl_2): δ 7.78 (s, 1 H, CH(pz)$_3$), 6.21, 5.98 (s, 2:1 ratio, 3 CHpz), 5.00 (dt, 1 H, H_C, $^3J_{CA}$= 10.8, $^3J_{CB} \approx {}^3J_{CD}$ = 7.2 Hz), 4.39 (dq, 1 H, H_D, $^3J_{DMe(A)}$ = 6.3 Hz), 3.37 (dd, 1 H, H_B, $^2J_{BA}$= 1.7 Hz), 2.67 (m, 1 H, H_A), 2.58, 2.57, 2.56, 2.36, 2.32, 2.30 (s, 3 H each, 6 Mepz), 1.35 (d, 3 H, Me_A), −29.97 (s, 1 H, Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.5, 156.2, 142.0, 141.4, 141.3 (2:1:1:1:1 ratio, C_q pz), 111.2, 108.8, 108.8 (CHpz), 81.3 (CH_C, $^1J_{CH}$ = 156 Hz), 69.2 (CH(pz)$_3$), 34.5 (*C*HMe$_A$, $^1J_{CH}$ = 150 Hz), 20.0 (Me_A), 17.8 (CH_AH_B, $^1J_{CH}$ = 157 Hz), 16.6, 16.3, 15.1, 11.3, 11.2, 11.1 (Mepz). IR (KBr): ν(Ir−H) 2242 cm^{-1}. Anal. Calcd for $C_{20}H_{30}F_6N_6PIr$: C, 34.7; H, 4.4; N, 12.2. Found: C, 34.8; H, 4.3; N, 12.0.

A 1:3 mixture of the endo-syn and exo-anti hydride−crotyl isomers (**3b** and **3a**, respectively) was generated by heating a solution of 0.05 g (0.073 mmol) of the bis(ethylene) complex **1** in CD_2Cl_2 at 60 °C for 24 h in a NMR tube. From this mixture the spectroscopic characterization of **3b** was effected.

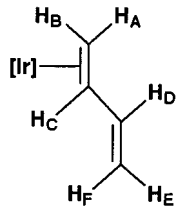


^{1}H NMR (CD_2Cl_2): δ 7.96 (s, 1 H, CH(pz)$_3$), 6.08, 6.04, 6.01 (s, 1 H each, 3 CHpz), 4.98 (td, 1 H, H_C, $^3J_{CA} \approx {}^3J_{CD}$ = 10.0, $^3J_{CB}$ = 6.8 Hz), 3.44 (dd, 1 H, H_B, $^2J_{BA}$ = 2.9 Hz), 3.37 (dq, 1 H, H_D, $^3J_{DMe(S)}$ = 6.0 Hz), 2.66, 2.64, 2.60, 2.17, 2.12, 2.06 (s, 3 H each, 6 Mepz), 2.35 (m, 1 H, H_A), 1.5 (d, 3 H, Me_S), −28.92 (s, 1 H, Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 155.4, 155.0, 154.9, 142.4, 142.1 (1:1:1:1:2 ratio, C_q pz), 110.8, 108.8, 108.3 (CHpz), 84.5 (CH_C, $^1J_{CH}$ = 158 Hz), 69.4 (CH(pz)$_3$), 40.3 (*C*HMe$_S$, $^1J_{CH}$ = 149 Hz), 22.7 (Me_S), 19.7 (CH_AH_B, $^1J_{CH}$ = 157 Hz), 15.8, 15.4, 14.4, 14.2, 11.1 (1:1:1:1:2 ratio, Mepz).

The exo-syn isomer **3c** was produced by thermolysis of **4** in C_6H_{12} at 120 °C and was characterized by NMR methods from its mixtures with **3a**,**b** and **5**. ^{1}H NMR (CD_2Cl_2): δ 7.81 (s, 1 H, CH(pz)$_3$), 6.18, 6.15 (s, 1:2 ratio, 3 CHpz), 4.75 (td, 1 H, H_C, $^3J_{CA} \approx {}^3J_{CD}$ = 10, $^3J_{CB}$ = 7.2 Hz), 3.33 (dq, 1 H, H_D, $^3J_{DMeS}$ = 5.9 Hz), 3.21 (m, 1 H, H_A), 2.8 (m, 1 H, H_B), 2.64, 2.58, 2.54, 2.44, 2.39, 2.19 (s, 3 H each, 6 Mepz), 1.32 (d, 3 H, Me_S), −30.01 (s, 1 H, Ir−H).

[IrH(CH$_2$CH$_2$CH=CH$_2$)Tpm^{Me2}]PF$_6$ (4). A suspension of 0.3 g (0.434 mmol) of the bis(ethylene) complex **1** in 60 mL of cyclohexane was heated at 80 °C with stirring for 24 h. The solvent was filtered off and the solid dried under vacuum. ^{1}H NMR spectroscopy showed this solid consisted of **4** (ca. 80%) and **3a** (ca. 15%), with only very small amounts of **3b** and **3c**. A crude material, useful for most synthetic purposes, can be obtained from this solid by dissolving it in CH_2Cl_2 (10 mL), adding Et_2O (5 mL), and stirring for 5 min with activated charcoal. Filtration, evaporation of the solvent, and addition of Et_2O gives the desired material. Analytically pure samples of **4** were obtained by crystallization from CH_2Cl_2:Et_2O mixtures. ^{1}H NMR ($CDCl_3$): δ 7.91 (s, 1 H, CH(pz)$_3$), 6.20, 6.12, 5.96 (s, 1 H each, 3 CHpz), 5.07 (m, 1 H, C*H*=CH$_2$), 3.86 (d, 1 H, CH=C*H*H, $^3J_{HH}$ = 11.1 Hz), 3.83, 2.97 (m, 1 H each, Ir−CH$_2$C*H*$_2$), 2.68, 2.59, 2.52, 2.50, 1.76 (s, 1:2:1:1:1, 6 Mepz), 2.49 (d, 1 H, CH=CH*H*, $^3J_{HH}$ = 8 Hz), 1.37, 0.42 (m, 1 H, each, Ir−CH$_2$), −19.5 (s, 1 H, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.0, 155.6, 154.1, 142.3, 142.2, 141.3 (C_q pz), 110.6, 109.4, 108.7 (CHpz), 69.7 (CH(pz)$_3$), 48.6 (*C*H$_2$=CH, $^1J_{CH}$ = 158 Hz), 46.0 (CH$_2$=*C*H, $^1J_{CH}$ = 168 Hz), 32.1 (Ir−CH$_2$*C*H$_2$, $^1J_{CH}$ = 132 Hz), 15.7, 14.4, 12.9, 11.3, 11.2, 10.9 (Mepz), −50.1 (Ir−CH$_2$, $^1J_{CH}$ = 136 Hz). IR (KBr): ν(Ir−H) 2210, 2100 cm^{-1}. Anal. Calcd for $C_{20}H_{30}F_6N_6PIr$: C, 34.7; H, 4.4; N, 12.2. Found: C, 34.5; H, 4.0; N, 12.0.

[Ir(η^4-C$_4$H$_6$)Tpm^{Me2}]PF$_6$ (5) and [IrH$_2$(η^2-C$_4$H$_6$)Tpm^{Me2}]PF$_6$ (6). A suspension of 0.1 g (0.145 mmol) of the α,ω-butenyl complex **4** in 60 mL of cyclohexane was photolyzed with an UV lamp (Hg, 125 W) for 8 h. Cyclohexane was filtered off, and the remaining solid was washed several times with Et_2O and dried under vacuum to give a beige powder. The solid was shown by ^{1}H NMR to consist mostly of **6** (80%) and **5** (ca. 15%). Attempts to obtain pure **6** failed, due to its fast conversion into the butadiene complex **5**; hence, its spectroscopic characterization was effected from these mixtures.



^{1}H NMR (CD_2Cl_2, −10 °C): δ 7.80 (s, 1 H, CH(pz)$_3$), 6.27, 6.13, 6.08 (s, 1 H each, 3 CHpz), 5.42 (dt, 1 H, H_D, $^3J_{DC} \approx {}^3J_{DE}$ = 10.0, $^3J_{DF}$ = 16.9 Hz), 5.20 (dd, 1 H, H_F, $^2J_{FE}$ = 1.3 Hz), 5.05 (pseudo q, 1 H, H_C, $^3J_{CA}$ = 11.5, $^3J_{CB}$ = 8.2 Hz), 4.79 (dd, 1 H, H_E), 3.61 (d, 1 H, H_A), 3.35 (d, 1 H, H_B), 2.64, 2.61, 2.53, 2.38, 2.19, 2.18 (s, 3 H each, 6 Mepz), −17.32, −26.46 (d, 1 H each, 2 Ir−H, $^2J_{HH}$ = 7.1 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, −10 °C): δ 156.0, 155.3, 155.2, 143.0, 142.1, 141.8 (C_q pz), 142.2 (CH_D,

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$^1J_{CH}$ = 156 Hz), 114.3 (CH_EH_F, $^1J_{CH}$ = 155 Hz), 109.7 109.6, 108.3 (3 CHpz), 69.9 ($CH(pz)_3$), 59.2 (CH_C, $^1J_{CH}$ = 156 Hz), 40.1 (CH_AH_B, $^1J_{CH}$ = 161 Hz), 17.1, 15.9, 14.8, 12.3, 11.2, 11.1 (Mepz). IR (KBr): ν(Ir−H) 2035 cm^{-1}.

A 0.1 g amount of the mixture obtained as described above was dissolved in 5 mL of THF and heated to 60 °C for 6 h. The solvent was pumped off, and the remaining solid was washed several times with a 2:1 mixture of Et_2O and CH_2Cl_2 and dried to obtain 0.065 g of **5** (65% yield). NMR monitoring in CD_2Cl_2 shows that the butadiene complex is the only product formed. ^{1}H NMR (CD_2Cl_2): δ 7.80 (s, 1 H, $CH(pz)_3$), 6.22, 6.00 (s, 1:2 ratio, 3 CHpz), 5.50, 0.12 (m, 2 H each, CH_2═CH), 2.63 (m, 2 H, CH_2═C*H*), 2.60, 2.53, 2.28, 2.19 (s, 1:2:1:2 ratio, 6 Mepz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 157.4, 155.4, 141.1, 140.8 (1:2:1:2 ratio, C_q pz), 109.8 109.1 (2:1 ratio, CHpz), 71.4 (CH_2═*C*H, $^1J_{CH}$ = 173 Hz), 68.8 ($CH(pz)_3$), 14.5, 13.9, 11.3, 11.1 (1:2:2:1 ratio, Mepz), 6.7 (*C*H_2═CH, $^1J_{CH}$ = 152 Hz). Anal. Calcd for $C_{20}H_{28}F_6N_6Ir$: C, 34.8; H, 4.1; N, 12.2. Found: C, 34.5; H, 3.9; N, 12.0.

Reaction of 1 with CO. In a glass pressure reactor, 0.50 g of the bis(ethene) compound **1**, suspended in 10 mL of C_6H_{12}, was stirred at 20 °C under 1 atm of CO for 2 h. A mixture of the monocarbonyl− and dicarbonyl−Ir^I adducts, along with the metallocarboxylic derivative **7a**, of which $[Ir(C_2H_4)(CO)\text{-}Tpm^{Me2}]^+$ is the main component, is produced in this way. ^{1}H NMR ($CDCl_3$): δ 7.94 (s, 1 H, $CH(pz)_3$), 6.21, 6.18 (s, 1:2 ratio, 3 CHpz), 2.64, 2.55, 2.42, 2.40 (s, 1:2:2:1 ratio, 6 Mepz), 2.40, 2.01 (m, 2 H each, AA′BB′ spin system, C_2H_4).

If the reaction above is effected at 60 °C for 6 h, $[Ir\text{-}(CO)_2Tpm^{Me2}]^+$ forms, along with minor amounts of **7a**. ^{1}H NMR ($CDCl_3$): δ 7.90 (s, 1 H, $CH(pz)_3$), 6.23 (s, 3 H, 3 CHpz), 2.50, 2.45 (s, 1:1 ratio, 6 Mepz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.0 (CO), 143.7 (C_q pz), 109.4 (CHpz), 71.4 ($CH(pz)_3$), 15.4, 11.0 (1:1 ratio, Mepz).

The metallocarboxylic complexes **7a**−**c** are obtained as the single reaction products when mixtures of **1** and ROH (ca. 0.5 mL, an excess; R = H (**7a**), Me (**7b**), Et (**7c**)) are stirred at room temperature for about 9 h, under 1 atm of carbon monoxide.

7a: ^{1}H NMR (CD_2Cl_2) δ 10.31 (br, 1 H, COOH), 7.95 (s, 1 H, $CH(pz)_3$), 6.31, 6.25, 6.22 (s, 3 H, 3 CHpz), 2.67, 2.63, 2.34, 2.29 (s, 1:2:2:1 ratio, 6 Mepz), −16.33 (s, 1 H, Ir−H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 165.4 (COOH), 162.8 (CO, $^2J_{CH}$ = 7 Hz), 156.5, 156.1, 155.5, 143.7, 143.4, 143.0 (C_q pz), 109.4, 109.3, 109.0 (CHpz), 69.7 ($CH(pz)_3$), 16.1, 15.4, 14.6, 11.2, 11.1, 11.0 (Mepz); IR (KBr) ν(Ir−H) 2188, ν(CO) 2064, ν(COO) 1625 cm^{-1}. Anal. Calcd for $C_{18}H_{28}O_3F_6N_6PIr$: C, 30.5; H, 3.41; N, 11.8. Found: C, 30.4; H, 3.5; N, 10.9.

7b: ^{1}H NMR ($CDCl_3$) δ 8.00 (s, 1 H, $CH(pz)_3$), 6.25, 6.20 (s, 1:2 ratio, 3 CHpz), 3.62 (s, 3 H, OMe), 2.66, 2.62, 2.29, 2.24, 2.19 (s, 1:2:1:1:1 ratio, 6 Mepz), −16.50 (s, 1 H, Ir−H); ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 162.7 (CO, $^2J_{CH}$ = 7 Hz), 158.7 (*C*OOMe), 155.9, 155.5, 154.8, 143.8, 143.4, 143.1 (C_q pz), 109.2, 109.2, 109.0 (CHpz), 69.6 ($CH(pz)_3$), 51.7 (OMe, $^1J_{CH}$ = 146 Hz) 15.2, 14.3, 10.9, 10.7, 10.7 (1:1:1:1:2 ratio, Mepz); IR (KBr) ν(Ir−H) 2188, ν(CO) 2060, ν(COO) 1660 cm^{-1}. Anal. Calcd for $C_{19}H_{26}O_3\text{-}F_6N_6PIr$: C, 31.5; H, 3.6; N, 11.6. Found: C, 31.3; H, 3.6; N 11.3.

7c: ^{1}H NMR ($CDCl_3$) δ 8.01 (s, 1 H, $CH(pz)_3$), 6.24, 6.20 (s, 1:2 ratio, 3 CHpz), 4.15, 4.14 (q, 1 H each, OCH_2CH$_3$, $^3J_{HH}$ = 7.0 Hz), 2.67, 2.63, 2.30, 2.26, 2.22 (s, 1:2:1:1:1 ratio, 6 Mepz), 1.24 (t, 3 H, OCH$_2$CH_3), −16.5 (s, 1 H, Ir−H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 163.1 (CO), 158.7 (*C*OOEt), 156.2, 155.6, 155.0, 144.0, 143.7, 143.3 (C_q pz), 109.4, 109.2 (CHpz, 2:1 ratio), 69.8 ($CH(pz)_3$), 60.5 (O*C*H$_2$CH$_3$, $^1J_{CH}$ = 146 Hz), 16.1, 15.5, 14.6, 11.2, 11.0 (1:1:1:1:2 ratio, Mepz), 15.1 (OCH$_2$*C*H$_3$, $^1J_{CH}$ = 127 Hz); IR (KBr) ν(Ir−H) 2189, ν(CO) 2060, ν(COO) 1655 cm^{-1}. Anal. Calcd for $C_{20}H_{28}O_3F_6N_6PIr$: C, 32.6; H, 3.8; N, 11.4. Found: C, 32.5; H, 3.6; N, 11.4.

$[Ir(C_2H_3)(C_2H_5)(L)Tpm^{Me2}]PF_6$ (L = py, 8a; NCMe, 8b). A solution of 0.1 g of the hydride−vinyl **2** in 2 mL of the appropriate solvent was stirred at room temperature for 24 h. Evaporation of the solvent in vacuo and washing of the residue with 5 mL of a 4:1 mixture of Et_2O and CH_2Cl_2 afforded pure **8a** and **8b** in 50−70% isolated yield. The reactions were shown by ^{1}H NMR to proceed with quantitative conversion.

8a: ^{1}H NMR ($CDCl_3$) δ 7.91, (s, 1 H, $CH(pz)_3$), 7.77, 7.23, 6.05 (t, br, br, 1:2:2 ratio, NC_5H_5), 7.58, 5.36, 4.39 (1 H each, H_A, H_X, H_M respectively, $^3J_{AX}$ = 17.8, $^3J_{AM}$ = 10.5, $^2J_{MX}$ = 2.5 Hz), 6.09, 6.06, 6.00 (s, 1 H each, 3 CHpz), 2.67, 2.65, 2.64, 2.28, 1.58, 1.44 (s, 3 H each, 6 Mepz), 2.22, 1.83 (m, 1 H each, CH_2Me), 0.36 (t, 3 H, CH_2*Me*, $^3J_{HH}$ = 7.5 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.3, 153.5, 153.1, 141.8, 141.1, 141.0 (C_q pz), 155.5, 136.8. 125.0 (br, s, br, 2:1:2 ratio, NC_5H_5), 135.5 (*C*H═CH_2, $^1J_{CH}$ = 136 Hz), 121.3 (CH═*C*H_2, $^1J_{CH}$ = 152 Hz), 110.0, 109.8 (1:2 ratio, CHpz), 69.9 ($CH(pz)_3$), 16.6 (CH_2*Me*, $^1J_{CH}$ = 123 Hz), 15.4, 14.1, 12.5, 11.7, 11.2, 11.1 (Mepz), −6.7 (*C*H_2Me, $^1J_{CH}$ = 124 Hz). For unknown reasons, we have obtained no satisfactory analysis for this complex.

8b: ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 1 H, $CH(pz)_3$), 7.69, 5.49, 4.66 (1 H each, H_A, H_X, H_M respectively, $^3J_{AX}$ = 17.5, $^3J_{AM}$ = 10.0, $^2J_{MX}$ = 2.5 Hz), 6.10, 6.03, 5.99 (s, 1 H each, 3 CHpz), 2.61, 2.60, 2.59, 2.57, 2.37, 2.26 (s, 3 H each, 6 Mepz), 2.32, 2.13 (m, 1 H each, CH_2Me), 2.20 (s, 3 H, MeCN), 0.43 (t, 3 H, CH_2*Me*, $^3J_{HH}$ = 7.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.3, 154.3, 154.0, 141.5, 141.4, 140.8 (C_q pz), 130.5 (*C*H═CH_2, $^1J_{CH}$ = 140 Hz), 118.7 (CH═*C*H_2, $^1J_{CH}$ = 152 Hz), 115.2 (Me*C*N, $^2J_{CH}$ = 10 Hz), 109.9, 109.5, 109.2 (CHpz), 69.7 ($CH(pz)_3$), 16.3 (CH_2*Me*, $^1J_{CH}$ = 123 Hz), 14.2, 13.7, 13.2, 11.6, 11.1, 11.0 (Mepz), 3.9 (*Me*CN, $^1J_{CH}$ = 138 Hz), −11.6 (*C*H_2Me, ^{1}J(C,H) = 129 Hz); IR (KBr) ν(CN) 2294 cm^{-1}. Anal. Calcd for $C_{21}H_{33}F_6N_7\text{-}PIr$: C, 35.0; H, 4.6; N, 13.6. Found: C, 35.7; H, 4.3; N, 12.7.

Reactions of 4 with Hard and Soft Lewis Bases. (a) Pyridine and Acetonitrile. The two compounds **9a** (pyridine) and **9b** (acetonitrile) were prepared as described above for **8a**,**b** but with complex **4** as starting material. The reactions were quantitative by NMR analysis and provided the desired adducts **9** as brown or beige powders in ca. 60−80% isolated yields.

9a: ^{1}H NMR ($CDCl_3$) δ 8.34, 7.6, 7.18 (d, t, t, 2:1:2 ratio, NC_5H_5, $^3J_{HoHm}$ = 8.3, $^3J_{HmHp}$ = 7.2 Hz), 7.85 (s, 1 H, $CH(pz)_3$), 6.04, 6.01 (s, 2:1 ratio, 3 CHpz), 2.88, 2.42 (m, 2 H each, 2 IrCH_2CH$_2$), 1.90, 1.61 (m, 2 H each, 2 Ir−CH$_2$CH_2), 2.64, 2.61, 2.42, 1.53 (s, 2:1:1:2 ratio, 6 Mepz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.1, 153.4, 141.9, 141.3 (1:2:1:2 ratio, C_q pz),155.3, 135.8. 125.9 (2:1:2 ratio, NC_5H_5, $^1J_{CH}$ = 183, 166, 167 Hz), 110.6, 110.0 (1:2 ratio, CHpz), 69.9 ($CH(pz)_3$), 31.7 (Ir−CH$_2$*C*H$_2$, $^1J_{CH}$ = 122 Hz) 15.0, 13.1, 11.8, 11.1 (1:2:1:2 ratio, Mepz), 1.2 (Ir*C*H$_2$CH$_2$, $^1J_{CH}$ = 124 Hz). Anal. Calcd for $C_{25}H_{35}F_6N_7PIr$: C, 39.0; H, 4.6; N, 12.7. Found: C, 39.8; H, 4.6; N, 11.7.

9b: ^{1}H NMR ($CDCl_3$) δ 7.73 (s, 1 H, $CH(pz)_3$), 6.05, 6.00 (s, 2:1 ratio, 3 CHpz), 2.59, 2.55, 2.42, 2.34 (s, 1:2:1:2 ratio, 6 Mepz), 2.55 (s, 3 H, MeCN), 2.40, 2.33 (m, 2 H each, 2 IrCH_2-CH$_2$), 1.31, 1.29 (m, 2 H each, 2 Ir−CH$_2$CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.4, 154.1, 141.7, 140.6 (1:2:1:2 ratio, C_q pz), 116.2 (Me*C*N), 110.1, 109.6 (1:2 ratio, CHpz), 69.6 ($CH(pz)_3$), 33.1 (Ir−CH$_2$*C*H$_2$, $^1J_{CH}$ = 126 Hz), 15.1, 13.7, 11.7, 11.0 (1:2:1:2 ratio, Mepz), 4.1 (*Me*CN, $^1J_{CH}$ = 138 Hz), −2.0 (Ir*C*H$_2$CH$_2$, $^1J_{CH}$ = 126 Hz). Anal. Calcd for $C_{21}H_{33}F_6N_7PIr$: C, 35.0; H, 4.6; N, 13.6. Found: C, 35.8; H, 4.3; N, 12.8.

(b) PMe_3 and PEt_3. An excess of the phosphine (5 mL of a 1 M solution in THF) was added to 0.106 g (ca. 0.145 mmol) of **4** and the resulting THF solution stirred at room temperature for 24 h, during which time a yellow solid formed. The solvent was evaporated, and the remnant solid (PMe_3, **10a**; PEt_3, **10b**) was washed with 2 mL of cold THF (−20 °C) and then with Et_2O.

10a: ^{1}H NMR (CD_2Cl_2) δ 7.61 (s, 1 H, $CH(pz)_3$), 6.04, 6.02, 5.95 (s, 1 H each, 3 CHpz), 3.20, 2.16, 1.91 (m, 1:2:1 ratio, 2 Ir−CH_2), 2.51, 2.45, 2.42, 2.32, 2.27, 2.22 (s, 3 H each, 6 Mepz), 2.35 (m, 1 H, C*H*PMe_3), 1.85, 1.50 (m, 1 H each, CH_2CH_2CH-(PMe_3)CH_2), 1.72 (d, 9 H, PMe_3, $^2J_{HP}$ = 13 Hz), −24.08 (d, 1

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H, Ir−H, $^4J_{HP}$ = 5.3 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 153.9, 153.7, 152.7, 139.7, 139.0, 138.8 (C_q pz), 109.1, 108.3, 108.2 (CHpz), 69.9 ($CH(pz)_3$), 48.0 ($CH_2CH_2CH(PMe_3)CH_2$, $^1J_{CP}$ = 28, $^1J_{CH}$ = 129 Hz), 33.8 ($CH_2CH_2CH(PMe_3)CH_2$, $^1J_{CH}$ = 121 Hz), 14.8, 14.7, 14.0, 11.3, 11.3 (1:1:1:1:2 ratio), 7.5 (PMe_3, $^1J_{CP}$ = 52 Hz), −15.2 ($CH_2CH_2CH(PMe_3)CH_2$, $^3J_{CP}$ = 28, $^1J_{CH}$ = 125 Hz), −15.7 ($CH_2CH_2CH(PMe_3)CH_2$, $^2J_{CP}$ = 10, $^1J_{CH}$ = 130 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 18.9; IR (KBr) ν(Ir−H) 2116 cm^{-1}. Anal. Calcd for $C_{23}H_{36}F_6N_6IrP_2$: C, 36.1; H, 4.7; N, 11.0. Found: C, 35.5; H, 4.7; N, 10.5.

10b: ^1H NMR (CD_2Cl_2) δ 7.61 (s, 1 H, $CH(pz)_3$), 6.04, 6.02, 5.95 (s, 1 H each, 3 CHpz), 3.20, 2.15, 1.82 (m, 1:2:1 ratio, 2 Ir−CH_2), 2.52, 2.46, 2.42, 2.33, 2.28, 2.21 (s, 3 H each, 6 Mepz), 2.44 (m, 1 H, $CH_2CH_2CH(PEt_3)CH_2$), 2.08, 1.29 (m, dt, 15 H, PEt_3, $^3J_{HH}$ = 7.8, $^3J_{HP}$ = 16 Hz), 1.80 (m, 2 H, $CH_2CH_2CH(PEt_3)CH_2$), −24.16 (d, 1 H, Ir−H, $^4J_{HP}$ = 5.2 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 153.8, 153.5, 152.7, 139.8, 139.1, 138.9 (C_q pz), 109.1, 108.3, 108.2 (CHpz), 69.9 ($CH(pz)_3$), 44.9 ($CH_2CH_2CH(PEt_3)CH_2$, $^1J_{CP}$ = 22, $^1J_{CH}$ = 131 Hz), 34.1 ($CH_2CH_2CH(PEt_3)CH_2$, $^1J_{CH}$ = 126 Hz), 14.9, 14.7, 14.0, 11.3, 11.3 (1:1:1:1:2 ratio, Mepz), 11.3 ($P(CH_2Me)_3$, $^1J_{CP}$ = 47 Hz), 6.4 ($P(CH_2Me)_3$, $^2J_{CP}$ = 5 Hz), −14.5 ($CH_2CH_2CH(PEt_3)CH_2$, $^1J_{CH}$ = 121 Hz), −14.6 ($CH_2CH_2CH(PEt_3)CH_2$, $^3J_{CP}$ = 38, $^1J_{CH}$ = 122 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 31.0; IR (KBr) ν(Ir−H) 2139 cm^{-1}. Anal. Calcd for $C_{26}H_{45}N_6IrP_2F_6$: C, 38.6; H, 5.6; N, 10.4. Found: C, 38.5; H, 5.4; N, 10.2.

(c) CN^-. A 0.525 g portion (0.725 mmol) of the α,ω-butenyl complex **4** and 0.20 g of $(n\text{-Bu})_4NCN$ were dissolved in 50 mL of THF, and the mixture was stirred for 24 h at room temperature. The solvent was removed by evaporation under vacuum, and the resulting solid was washed with several 2 mL portions of acetone, cooled to −20 °C. Recrystallization from acetone gave 0.30 g of a yellow solid in 73% yield. ^1H NMR (acetone-d_6): δ 7.77 (s, 1 H, $CH(pz)_3$), 6.07, 6.02, 5.97 (s, 1 H each, 3 CHpz), 3.00, 1.77 (m, 1 H each, Ir−CH_2), 2.64, 2.57, 2.54, 2.38, 2.24, 2.15 (s, 3 H each, 6 Mepz), 2.45 (m, 1 H, CHCN), 2.44, 2.09 (m, 1 H each, Ir−CH_2), 1.74 (m, 2 H, CH_2-CHCN), −24.10 (s, 1 H, Ir−H). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 153.4, 152.7, 140.9, 140.1, 140.0 (2:1:1:1:1 ratio, C_q pz), 128.4 (CN), 109.1, 108.2, 108.1 (CHpz), 70.6 ($CH(pz)_3$), 42.6 (CHCN, $^1J_{CH}$ = 137 Hz), 40.1 (CH_2CHCN, $^1J_{CH}$ = 120 Hz), 14.9, 14.6, 14.0, 11.1 (1:1:1:3 ratio, Mepz), −4.5 (Ir−CH_2, $^1J_{CH}$ = 123 Hz), −15.8 (Ir−CH_2, $^1J_{CH}$ = 123 Hz). IR (KBr): ν(CN) 2211, ν(Ir−H) 2121 cm^{-1}. Anal. Calcd for $C_{21}H_{30}N_7Ir$: C, 44.0; H, 5.3; N, 17.1. Found: C, 44.4; H, 5.3; N, 16.8.

Reaction of 4 with Tetrahydrofuran. A 0.1 g portion of the hydride−α,ω-butenyl complex **4** were dissolved in 20 mL of THF and heated to 60 °C overnight. Following removal of the volatiles under vacuum, the resulting solid was shown by ^1H NMR to be composed of the carbene complex **11** (ca. 70%) plus the hydride−crotyl isomers **3** (30%). Upon chromatographic separation on silica gel, using a 2:1 mixture of THF and CH_2Cl_2 as eluent, 0.032 g of analytically pure **11** was obtained in 30% isolated yield. ^1H NMR ($CDCl_3$): δ 7.91 (s, 1 H, $CH(pz)_3$), 6.11, 6.09, 6.00 (s, 1 H each, 3 CHpz), 4.59 (m, 2 H, $CH_2CH_2CH_2O$), 2.68, 1.39 (m, 1 H each, Ir−CH_2Pr), 2.65 (m, 2 H, Ir=CCH_2), 2.66, 2.62, 2.57, 2.49, 2.0, 1.82 (s, 3 H each, 6 Mepz), 2.08 (m, 2 H, OCH_2CH_2), 1.18 (m, 2 H, $MeCH_2CH_2$-CH_2), 0.84 (m, 2 H, $EtCH_2CH_2$), 0.76 (t, 3 H, $Me(CH_2)_3$, $^3J_{HH}$ = 7.4 Hz), −17.17 (s, 1 H, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 260.5 (Ir=C), 156.4, 153.4, 152.5, 142.4, 141.5, 141.3 (C_q pz), 109.0 108.2 (2:1 ratio, CHpz), 81.3 (OCH_2, $^1J_{CH}$ = 152 Hz), 70.0 ($CH(pz)_3$), 57.8 (Ir=CCH_2, $^1J_{CH}$ = 134 Hz), 36.4 ($EtCH_2CH_2$, $^1J_{CH}$ = 124 Hz), 27.1 ($MeCH_2CH_2CH_2$, $^1J_{CH}$ = 124 Hz), 23.2 (OCH_2CH_2, $^1J_{CH}$ = 135 Hz), 15.1, 14.7, 13.7, 11.2, 11.2, 11.2 (Mepz), 14.3 ($Me(CH_2)_3$, $^1J_{CH}$ = 124 Hz), −11.9 (Ir−CH_2, $^1J_{CH}$ = 124 Hz). IR (KBr): ν(Ir−H) 2162.3 cm^{-1}. Anal. Calcd for $C_{24}H_{38}OF_6N_6PIr$: C, 37.7; H, 5.0; N, 11.0. Found: C, 37.4; H, 4.8; N, 10.8.

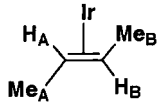
Reactions of 1 with H_2. (a) Synthesis of $[IrH(C_2H_5)(C_2H_4)Tpm^{Me2}]PF_6$ (12). In a glass reactor, 0.5 g (0.725 mmol) of the bis(ethylene) complex was dissolved in 25 mL of CH_2Cl_2, and the solution was subjected to 3 atm of H_2. After the mixture was stirred for 24 h at 20 °C, removal of the solvent under vacuum gave complex **12** in analytically pure form and quantitative yield. ^1H NMR ($CDCl_3$): δ 7.87 (s, 1 H, $CH(pz)_3$), 6.25, 5.94 (s, 2:1 ratio, 3 CHpz), 3.64, 2.92 (AA′BB′ system, 2 H each, CH_2=CH_2), 2.67, 2.60, 2.55, 2.48, 2.43, 1.95 (s, 3 H each, 6 Mepz), 2.00, 0.22 (dt, 1 H each, CH_2CH_3, $^2J_{HH}$ = 7.6, $^3J_{HH}$ = 6.9 Hz), 0.28 (t, 3 H, CH_2CH_3), −18.10 (s, 1 H, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.6, 155.4, 154.5, 141.9, 141.8, 141.1 (C_q pz), 110.5, 109.6, 109.5 (CHpz), 69.6 ($CH(pz)_3$), 43.6 (C_2H_4, $^1J_{CH}$ = 162 Hz), 15.9, 15.0, 13.6, 11.47, 11.2, 11.1 (Mepz), 14.6 (CH_2Me, $^1J_{CH}$ = 124 Hz), −17.9 (CH_2Me, $^1J_{CH}$ = 127 Hz). IR (KBr): ν(Ir−H) 2206 cm^{-1}. Anal. Calcd for $C_{20}H_{32}F_6N_6PIr$: C, 34.6; H, 4.7; N, 12.1. Found: C, 34.7; H, 4.5; N, 12.3.

(b) $[IrH_2(C_2H_4)Tpm^{Me2}]PF_6$ (13). A 0.2 g amount of the bis(ethene) compound **1** was suspended in 15 mL of C_6H_{12} and reacted in an autoclave with 20 atm of H_2, at 60 °C, for 24 h. The resulting solid was separated by filtration and crystallized from a mixture of CH_2Cl_2 and Et_2O (0.17 g, 90% yield). ^1H NMR ($CDCl_3$): δ 7.92 (s, 1 H, $CH(pz)_3$), 6.13, 5.11 (s, 1:2 ratio, 3 CHpz), 3.39 (s, 4 H, CH_2=CH_2), 2.63, 2.56, 2.19, 2.07 (s, 2:1:1:2 ratio, 6 Mepz), −22.09 (s, 2 H, 2 Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.7, 155.2, 142.6, 142.3 (2:1:2:1 ratio, C_q pz), 109.5, 108.5 (2:1 ratio, CHpz), 68.2 ($CH(pz)_3$), 38.3 (CH_2=CH_2, $^1J_{CH}$ = 163 Hz), 15.9, 14.6, 11.2, 11.0 (1:2:1:2 ratio, Mepz). IR (KBr): ν(Ir−H) 2186, 2027 cm^{-1}. Anal. Calcd for $C_{18}H_{28}F_6N_6PIr$: C, 32.5; H, 4.2; N, 12.6. Found: C, 32.8; H, 4.3; N, 12.0.

At higher temperature, but lower pressure (90 °C, 3 atm), two hydride−η^2-butene isomeric complexes are formed as minor products of the reaction. They are best prepared by starting from complex **12**, as detailed below.

(c) $[IrH_2(\eta^2\text{-}C_4H_8)Tpm^{Me2}]PF_6$ (14a,b). A 0.3 g portion of $[IrH(C_2H_5)(C_2H_4)Tpm^{Me2}]PF_6$ (**12**), dissolved in 5 mL of CH_2Cl_2, was heated at 40 °C for 5 days. ^1H NMR studies of the products of the reaction revealed ca. 70% conversion of the starting material into a mixture of products consisting mainly of the 2-butene cis and trans isomers **14a**,**b**, from which the cis isomer was identified by ^1H and $^{13}C\{^1H\}$ NMR. Conducting the reaction in a C_6H_{12} suspension at 90 °C for 3 days allows the isolation from CH_2Cl_2−Et_2O solvent mixtures of the trans isomer **14b** in ca. 55% yield.

14a: ^1H NMR (CD_2Cl_2, 25 °C) δ 7.77 (s, 1 H, $CH(pz)_3$), 6.25, 6.18, 6.10 (s, 1 H each, 3 CHpz), 4.30 (AA′ part of $AA'M_3M_3'$ spin system, 2 H, CH_3CH=$CHCH_3$, coupling constants calculated by simulation: $^3J_{AA'}$ = 8.9, $^3J_{AX_3}$ = 6.2, $^3J_{AX'_3}$ = −0.88 Hz), 2.65, 2.64, 2.61, 2.56, 2.31 (s, 1:1:1:2:1 ratio, 6 Mepz), 1.97 (m, X_3X_3' part of an $AA'X_3X_3'$ spin system, 6 H, CH_3CH=$CHCH_3$), −22.84 (s, 2 H, 2 Ir−H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ 158.6, 156.7, 156.5, 143.0, 142.7, 141.4 (C_q pz), 110.5, 110.1, 109.6 (CHpz), 69.4 ($CH(pz)_3$), 58.3 (CH_3CH, $^1J_{CH}$ = 158 Hz), 19.7 (CH_3CH, $^1J_{CH}$ = 126 Hz), 15.5, 13.8, 11.4, 11.3 (1:1:1:3 ratio, Mepz).



14b: ^1H NMR ($CDCl_3$, 25 °C) δ 7.86 (s, 1 H, $CH(pz)_3$), 6.24, 6.05, 6.02 (s, 3 H, 3 CHpz), 4.46 (br, 1 H, H_A), 4.00 (br, 1 H, H_B), 2.68, 2.62, 2.53, 2.40, 2.24, 2.14 (s, 3 H each, 6 Mepz), 2.22 (br, 3 H, Me_A), 0.93 (br, 3 H, Me_B), −17.70, −27.10 (d, 1 H each, 2 Ir−H, $^2J_{HH}$ = 6.2 Hz). ^1H NMR (CD_2Cl_2, −30 °C): δ 7.34, (s, 1 H $CH(pz)_3$), 6.26, 6.07, 6.03 (s, 1 H each, 3 CHpz), 4.48 (dq, 1 H, H_A, $^3J_{AB}$ = 11.0, $^3J_{AMe_A}$ = 5.5 Hz), 3.99 (dq, 1 H, H_B, $^3J_{BMe_B}$ = 5.5 Hz), 2.63, 2.57, 2.48, 2.39, 2.24, 2.13 (s, 3 H each, 6 Mepz), 2.21 (d, 3 H, Me_A), 0.89 (d, 3 H, Me_B), −17.59 (d, 1 H, Ir−H, $^3J_{HH}$ = 6.1 Hz), −26.95 (d, 1 H, Ir−H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 156.6, 155.0, 154.5, 143.3, 142.8, 141.9

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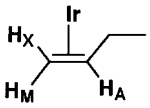
Published on December 6, 2001 on http://pubs.acs.org | doi: 10.1021/om010594u

(C_q pz), 109.6, 109.4, 107.9 (CHpz), 69.8 ($CH(pz)_3$), 62.8 (br, CH_A, $^1J_{CH}$ = 151 Hz), 55.1 (br, CH_B, $^1J_{CH}$ = 164 Hz), 28.4 (br, Me_A, $^1J_{CH}$ = 125 Hz), 18.1 (br, Me_B, $^1J_{CH}$ = 126 Hz), 17.0, 15.7, 15.5, 11.0, 11.0, 10.9 (Mepz); IR (KBr) ν(Ir−H) 2179 cm^{-1}. Anal. Calcd for $C_{20}H_{32}N_6F_6PIr$: C, 34.6; H, 4.7; N, 12.1. Found: C, 34.9; H, 4.2; N, 12.

14c: A 0.10 g portion (0.14 mmol) of the α,ω-butenyl complex **4** was dissolved in 15 mL of THF and reacted with 0.5 mL of a 1 M solution of $LiBH(C_2H_5)_3$ in THF (0.500 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 1 h and then at room temperature overnight and finally heated to 60 °C for 1 h. The solvent was pumped off, and the remaining solid was stirred for 15 min in a mixture of 3 mL of CH_2Cl_2 and 10 μL of distilled water. The salts were filtered, and the solvent was pumped off. The solid was washed twice with 0.5 mL of THF at −20 °C and dried under reduced pressure to give 50 mg of a crystalline white solid in 54% yield.



^{1}H NMR (acetone-d_6): δ 8.13 (s, 1 H, $CH(pz)_3$), 6.40, 6.31, 6.20 (s, 1 H each, 3 CHpz), 4.85, 3.37, 2.73 (m, d, d, 1 H each, H_A, H_M, H_X respectively, $^3J_{AX}$ = 11.7, $^3J_{AM}$ = 8.3, $^3J_{ACH_2}$ = 7.6 Hz), 2.81, 2.76, 2.72, 2.34, 2.24, 2.07 (s, 3 H each, 6 Mepz), 2.25, 2.02 (m, 1 H each, $MeCH_2$), 1.21 (t, 3 H, $MeCH_2$, $^3J_{HH}$ = 7.2 Hz), −17.71, −26.65 (d, 1 H each, 2 Ir−H, $^2J_{HH}$ = 7.4 Hz). ^{13}C{^{1}H} NMR (acetone-d_6): δ 156.6, 155.3, 144.7, 143.9, 143.7 (1:2:1:1:1 ratio, C_q pz), 109.6, 109.5, 108.4 (CHpz), 70.7 ($CH(pz)_3$), 67.6 ($MeCH_2CH{=}CH_2$, $^1J_{CH}$ = 151 Hz), 40.5 ($MeCH_2CH{=}CH_2$, $^1J_{CH}$ = 158 Hz), 18.5 ($MeCH_2CH{=}CH_2$, $^1J_{CH}$ = 126 Hz), 17.1, 15.7, 11.2, 11.1, 11.0 (1:1:1:1:2 ratio, Mepz), 13.8 ($MeCH_2CH{=}CH_2$). Anal. Calcd for $C_{20}H_{32}F_6N_6PIr$: C, 34.6; H, 4.7; N, 12.1. Found: C, 34.3; H, 4.6; N, 11.4.

[Ir(C$_2$H$_5$)$_2$Tpm^{Me2}(L)]PF$_6$ (L = py (15a), NCMe (15b)). To a CH_2Cl_2 solution of complex **12** (0.1 g, 0.145 mmol; 5 mL) was added 1 mL of pyridine (**15a**) or acetonitrile (**15b**), and the reaction mixture was heated at 40 °C for a period of 24 h. Removal of the volatiles under vacuum and successive washing with 5 mL of Et_2O gave compounds **15** in yields higher than 90%.

15a: ^{1}H NMR (CD_2Cl_2) δ 8.09, 7.89, 7.83, 7.41, 7.06 (d, d, m, t, t, 1 H each, C_5H_5N, $J_{HoHm} = J_{HmHp}$ = 6.3 Hz), 7.83 (s, 1 H, $CH(pz)_3$), 6.13, 6.11 (s, 2:1 ratio, 3 CHpz), 2.63, 2.48, 1.57 (s, 3:1:2 ratio, 6 Mepz), 2.15, 1.64 (m, 2 H each, 2 CH_2CH_3), 0.41 (t, 6 H, 2 CH_2CH_3, $^3J_{HH}$ = 7.4 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 156.4, 153.1, 140.9, 140.8 (1:2:1:2 ratio, C_q pz), 155.2, 154.3, 136.4, 126.9, 124.7 (C_5H_5N), 110.0 109.6 (1:2 ratio, CHpz), 69.8 ($CH(pz)_3$), 16.8 (CH_2Me, $^1J_{CH}$ = 123 Hz), 13.1, 12.5, 11.6, 11.1 (1:2:1:2 ratio, Mepz), −5.1 (CH_2Me, $^1J_{CH}$ = 123 Hz). Anal. Calcd for $C_{25}H_{37}F_6N_7PIr$: C, 38.9; H, 4.8; N, 12.7. Found: C, 38.4; H, 4.7; N, 12.4.

15b: ^{1}H NMR ($CDCl_3$) δ 7.76, (s, 1 H, $CH(pz)_3$), 6.05, 5.96 (s, 2:1 ratio, 3 CHpz), 2.60, 2.58, 2.41, 2.30 (s, 1:2:1:2 ratio, 6 Mepz), 2.58 (s, 3 H, NCMe), 2.10, 1.97 (m, 2 H each, 2 CH_2CH_3), 0.51 (t, 6 H, 2 CH_2CH_3, $^3J_{HH}$ = 7.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.9, 153.3, 141.2, 140.8 (1:2:1:2 ratio, C_q pz), 115.1 (NCMe), 110.2, 109.3 (1:2 ratio, CHpz), 69.6 ($CH(pz)_3$), 15.9 (CH_2Me, $^1J_{CH}$ = 123 Hz), 13.6, 13.2, 11.7, 11.1 (1:2:1:2 ratio, Mepz), 4.1 ($CNMe$, $^1J_{CH}$ = 138 Hz), −12.9 (CH_2Me, $^1J_{CH}$ = 124 Hz); IR (KBr) ν(CN) 2294 cm^{-1}. Anal. Calcd for $C_{22}H_{35}F_6N_7PIr$: C, 36.0; H, 4.8; N, 13.3. Found: C, 35.6; H, 4.7; N, 13.0.

[Ir(H)$_2$(=C(CH$_2$)$_3$O)Tpm^{Me2}]PF$_6$ (16). A 0.1 g amount (0.144 mmol) of the $[Ir(H)_2(C_2H_4)Tpm^{Me2}]PF_6$ complex **13** was dissolved in 20 mL of THF and heated to 80 °C overnight. After evaporation of the solvent, the resulting solid was washed twice with 0.5 mL of $CHCl_3$ at −20 °C to give 0.082 g of an analytically pure, white microcrystalline powder in 80% yield.

Table 2. Crystal Data and Structure Refinement Details for 4

empirical formula	$C_{20}H_{30}F_6IrN_6P$
fw	691.66
temp	296(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	a = 11.5844(8) Å b = 15.9549(11) Å c = 16.7246(12) Å β = 128.3820(10)°
vol, Z	2423.1(3) Å^3, 4
density (calcd)	1.893 mg/m^3
abs coeff	5.643 mm^{-1}
F(000)	1348
cryst size	0.1 × 0.1 × 0.26 mm
θ range for data collection	2.77−32.06°
limiting indices	$-15 \le h \le 17$, $-22 \le k \le 14$, $-24 \le l \le 8$
no. of colld rflns	11 903
no. of indep rflns	6853 (R_{int} = 0.0433)
abs cor	none
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	6853/0/316
goodness of fit on F^2	0.934
final R indices ($I > 2\sigma(I)$)	R1 = 0.0503, wR2 = 0.1125
R indices (all data)	R1 = 0.1113, wR2 = 0.1316
largest diff peak and hole	2.438 and −2.094 e Å^{-3}

^{1}H NMR (CD_2Cl_2): δ 7.87 (s, 1 H, $CH(pz)_3$), 6.15, 6.12 (s, 2:1 ratio, 3 CHpz), 4.58 (t, 2 H, $CH_2CH_2CH_2O$, $^3J_{HH}$ = 7.3 Hz), 2.77 (t, 2 H, Ir=CCH_2, $^3J_{HH}$ = 7.7 Hz), 2.61, 2.56, 2.40, 1.96 (s, 2:1:1:2 ratio, 6 Mepz), 2.01 (m, 2 H, OCH_2CH_2), −18.33 (s, 2 H, 2 Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 260.2 (Ir=C), 156.4, 153.8, 141.8, 141.3 (1:2:1:2 ratio, C_q pz), 108.1, 108.1 (2:1 ratio, CHpz), 81.4 (OCH_2, $^1J_{CH}$ = 153 Hz), 69.9 ($CH(pz)_3$), 63.5 (Ir=CCH_2, $^1J_{CH}$ = 137 Hz), 23.4 (OCH_2CH_2, $^1J_{CH}$ = 135 Hz), 16.7, 15.0, 11.0 (1:2:3 ratio, Mepz). IR (KBr): ν(Ir−H) 2150, 2020 cm^{-1}. Anal. Calcd for $C_{20}H_{30}OF_6N_6PIr$: C, 33.9; H, 4.3; N, 11.9. Found: C, 33.6; H, 4.1; N, 11.7.

X-ray Structure Determination of 4. A summary of the fundamental crystal data is given in Table 2. A crystal showing well-defined faces was mounted on a Bruker-Siemens CCD diffractometer equipped with a low-temperature device and a normal-focus, 2.4 kW sealed-tube X-ray source (molybdenum radiation, λ = 0.710 67 Å) operating at 50 kV and 20 mA. Data were collected over a quadrant of the reciprocal space by a combination of three exposure sets. Each exposure of 10 s covered 0.3° in ω. The unit cell dimensions were determined by a least-squares refinement using reflections with $I > 20\sigma$ and $6° < 2\theta < 60°$. The crystal to detector distance was 6.05 cm. Coverage of the unique set was over 92% complete to at least 23° in θ. The first 50 frames were were re-collected at the end of the data collection to monitor crystal decay. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir and P were taken from ref 31[31]. The structure was solved by Multan and Fourier methods. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. Some nonresolvable disorder from the thermal motion involved C3 and C1 atoms. The H11 atom was located in a difference synthesis map and isotropically refined. The highest peak of the residual electron density is situated on the Ir atom. Refinement was on F^2, and conventional R factors (R) are based on F. Most of the calculations were carried out with SMART[32] software for data collection and reduction and SHELXTL[32] for structure solution and refinements.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.
(32) SMART and SHELXTL; Siemens Energy and Automation Inc., Analytical Instrumentation, Madison, WI, 1996.

Acknowledgment. The DGESIC (Project PB97-0733) and the Junta de Andalucía are thanked for financial support. I.I.P.-M. thanks the CONACYT and COTEPABEIPN (México) for a research grant.

Supporting Information Available: Tables giving all crystallographic data, bond lengths, and bond angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010594U

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on December 6, 2001 on http://pubs.acs.org | doi: 10.1021/om010594u