3120 *Organometallics* **2000,** *19,* 3120−3126

# Synthesis of $\eta^2$:$\sigma^2$-Diene Complexes of Iridium(III) by the Reaction of $\eta^4$:$\pi^2$-Diene Iridium(I) Species with Lewis Bases

Margarita Paneque,* Manuel L. Poveda,* and Verónica Salazar[†]

*Instituto de Investigaciones Químicas-Departamento de Química Inorgánica, Consejo Superior de Investigaciones Científicas-Universidad de Sevilla, Avda. Américo Vespucio s/n, Isla de la Cartuja, 41092 Sevilla, Spain*

Enrique Gutiérrez-Puebla and Angeles Monge

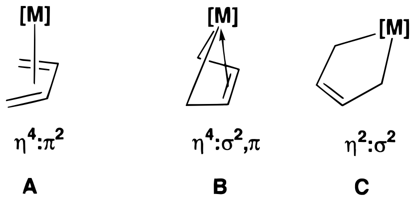
*Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Campus de Cantoblanco, 28049 Madrid, Spain*

*Received May 5, 2000*

Treatment of the $\eta^4$-diene complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (**1**) with a variety of soft and hard Lewis bases induces an unprecedented change in the binding mode of the diene ligand from $\eta^4$:$\pi^2$ to $\eta^2$:$\sigma^2$ and formation of Ir(III) derivatives of composition $Tp^{Me2}Ir(\eta^2\text{:}\sigma^2\text{-}CH_2C(Me){=}C(Me)CH_2)(L)$ (**4**) (L = CO, $PMe_3$, MeCN, $C_5H_5N$, etc.). Similar reactivity is exhibited by the analogous compounds $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)CH{=}CH_2)$ (**2**) and $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$ (**3**); the facility with which the transformation occurs follows the sequence **1** > **2** > **3**. The study of these processes under kinetic and thermodynamic control suggests that metal-based Lewis acid centers of composition $Tp^{Me2}Ir(R)(R')$ (R and R′ = alkyl groups) are of intermediate soft−hard nature.

## Introduction

Butadiene and its simple derivatives commonly bind to middle and late transition elements in the $\eta^4$:$\pi^2$ form **A**.[1] Of the other less frequent structural variations, the $\eta^4$:$\sigma^2$,$\pi$ coordination **B** has been encountered in numerous compounds of the more electropositive early transition and actinide metals.[2,3] In this coordination mode the hydrocarbon ligand exhibits considerable $\sigma^2$-diyl character, but there is always some additional bonding interaction with the central carbon−carbon double bond. Bonding of type **C** can be viewed as an extreme variation of **B**. It is frequently invoked to explain the fluxional NMR behavior and other properties of compounds with ground-state geometry **B**. Despite this, it is very rare in transition metal complexes. To our knowledge, only three such compounds[4] with simple $\eta^2$:$\sigma^2$-butadiene moieties have been reported to date.[5] These are $Pt(\eta^1\text{:}\eta^1\text{-}CH_2C(R){=}C(R)CH_2)(L_2)$ (R = Me, $L_2$ = cod, $(NCBu^t)_2$; R = Ph, $L_2$ = cod),[6] $(Li(tmeda)_2)_2M(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)_2(\eta^1\text{:}\eta^1\text{-}CH_2CH{=}CHCH_2)$ (M = Mo, W),[7] and the recently X-ray characterized Ir(III) complex $[\overline{Ir(CH_2C(Me){=}CH}CHMe)(CO)(PMe_3)_3](O_3SCF_3)$.[8]



Even though the addition of a Lewis base to an $\eta^4$-diene complex could result in the conversion of structures **A** or **B** into **C**,[9] none of the above-mentioned

---

[†] Present address: Centro de Investigaciones Químicas de la Universidad Autónoma del Estado de Hidalgo, Car. Pachuca-Tulanango, Km. 4.5, Pachuca, Hidalgo, México.

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. (b) For a recent example of a $\sigma^2$,$\pi$ butadiene complex, see: Mashima, K.; Kaidzu, M.; Nakayama, Y.; Nakamura, A. *Organometallics* **1997**, *16*, 1345.

(3) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

(4) Benzoannelated butadiene complexes, i.e., *o*-xylylenes and heterobutadiene species such as perfluorobutadiene complexes, are more prone electronically, although for different reasons, to stabilize coordination mode **C**. See: (a) Bennet, M. A.; Bown, M.; Hockless, D. C. R.; McGrady, J. E.; Schranz, H. W.; Stranger, R.; Willis, A. C. *Organometallics* **1998**, *17*, 3784. (b) Hitchcock, P. B.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1967**, 242. For 1,4-diiminocobaltacyclopentenes with structure **C** see: (c) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1986**, 1193.

(5) $\eta^2$:$\sigma^2$ butadiene ligands are frequently found in the chemistry of main group metals. (a) Barrau, J.; Rima, G.; El Amraoui, T. *Organometallics* **1998**, *17*, 607. (b) Mashima, K.; Sugiyama, H.; Kanehisa, N.; Kai, Y.; Yasuda, H.; Nakamura, A. *J. Am. Chem. Soc.* **1994**, *116*, 6977. (c) Schulman, J. M.; Disch, R. L.; Schleyer, P. v. R.; Bühl, M.; Bremer, M.; Koch, W. *J. Am. Chem. Soc.* **1992**, *114*, 7897, and references therein.

(6) (a) Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1839. $Pt(C_4H_8)(PPh_3)_2$ has been formulated as a Pt(0) complex having a monodentate $\eta^2$,$\pi$-butadiene ligand. See: (b) Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073.

(7) Gausing, W.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 186

(8) Bleeke, J. R.; Behm, R. *J. Am. Chem. Soc.* **1997**, *119*, 8503.

(9) For some examples of Lewis bases addition to 14 $e^-$ and 16 $e^-$ $\eta^4$-diene complexes, see: (a) Blenkers, J.; Hessen, B.; van Bolhouis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459. (b) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *358*, 135. (c) Beatty, R. P.; Datta, S.; Wreford, S. S. *Inorg. Chem.* **1979**, *18*, 3139. In none of these cases does the $\eta^4$-coordination mode of the diene change, i.e., these are 14 $e^-$ → 16 $e^-$ and 16 $e^-$ → 18 $e^-$ transformations.

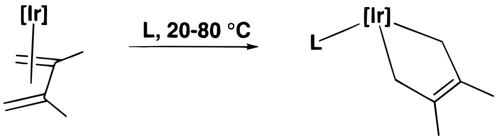
10.1021/om000382h CCC: $19.00

compounds have been produced following this synthetic methodology (some $\eta^4$-1,4-diiminobutadiene complexes of cobalt undergo this transformation,[4c] but they cannot actually be considered as simple $\eta^4$-diene transition metal complexes). Moreover, this preparative approach often gives rise to the displacement of the diene[10] or to other different transformations.[10b,11]

In the course of studies on the reactivity of the iridium complex Tp$^{Me2}$Ir($\eta^4$-CH$_2$=C(Me)C(Me)=CH$_2$)[12] (Tp$^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borate[13]) with aldehydes[14] and substituted thiophenes[15] we have observed the temporary formation of Ir(III) intermediates of composition Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-CH$_2$C(Me)=C(Me)CH$_2$)(L). With the aim of gaining additional information on this interesting transformation we have investigated the reactions of the Ir(I)-diene derivatives Tp$^{Me2}$Ir($\eta^4$-CH$_2$=C(R)C(R′)=CH$_2$) (R = R′ = Me, **1**; R = H, R′ = Me, **2**; R = R′ = H, **3**) with different Lewis bases. Here we report the results of these studies that include the structural characterization by X-ray methods of one of the resulting adducts, Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-CH$_2$CH=CHCH$_2$)(PMe$_3$) (**6a**), as well as the analysis of the relative strength of the Ir−L bond of the compounds Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-CH$_2$C(R)=C(R′)CH$_2$)(L).

## Results

The Ir(I) complex Tp$^{Me2}$Ir($\eta^4$-CH$_2$=C(Me)C(Me)=CH$_2$) (**1**), which contains 2,3-dimethyl-1,3-butadiene coordinated in the $\eta^4$:$\pi^2$ mode, reacts readily (eq 1) with a variety of Lewis bases (cyclohexane, 20−80 °C) to afford 18e-Ir(III) adducts of composition Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-CH$_2$C(Me)=C(Me)CH$_2$)(L) (**4**) in good to excellent isolated yields (all the reactions are quantitative by NMR). Both soft and hard Lewis bases are able to participate in this transformation (L = PMe$_3$, **4a**; CO, **4b**; SC$_4$H$_8$ (tetrahydrothiophene), **4c**; C$_2$H$_4$, **4d**; NCMe, **4e**; NC$_5$H$_5$ (pyridine), **4f**; and N(Me)=C(H)C$_6$H$_5$ (*N*-benzyliden-methylamine), **4g**). In most cases a large excess of L (usually greater than 10-fold) causes the formation of adducts **4** to occur rapidly at room temperature. C$_2$H$_4$ reacts rather slowly ($t_{1/2}$ = 12 h; C$_6$H$_6$, 4 atm, 25 °C), and *N*-benzylidenemethylamine is by far the least reactive of the Lewis bases we have investigated (the synthesis of **4g** requires prolonged heating of **1** in the neat imine at 60−80 °C). From these and other data obtained in a series of competition experiments under strict kinetic control (**1** was allowed to react with appropriate mixtures of Lewis bases under the mildest conditions, see Experimental Section) the following order of reactivity has been determined: (CO?) > PMe$_3$ > C$_5$H$_5$N > SC$_4$H$_8$ > MeCN > C$_2$H$_4$ > MeC(O)H[14] > ArC(O)H[14] > C$_6$H$_5$C(H)=NMe. The position of carbon monoxide in the sequence of these neutral donors has not been determined experimentally, and it is only estimated from the stability studies that will be described below.



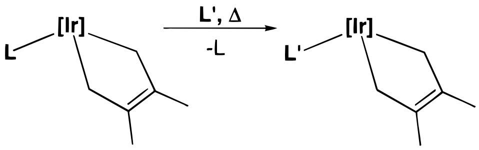
(1)

**1** **4**

**a: L = PMe$_3$**
**b: L = CO**
**c: L = SC$_4$H$_8$**
**d: L = C$_2$H$_4$**
**e: L = NCMe**
**f: L = C$_5$H$_5$N**
**g: L = C$_6$H$_5$C(H)=NMe**

The proposed $\eta^2$:$\sigma^2$ coordination mode of the unsaturated hydrocarbon ligand becomes apparent from the analysis of the NMR data. Most informative in this regard is the observation of a high-field $^{13}$C resonance in the range 15−5 ppm, which is due to the two equivalent iridium-bound methylene groups. The value of ca. 125 Hz found for the one-bond C−H coupling constant is in accord with a sp$^3$ hybridization of these carbon atoms. Moreover, both the $\delta$ and the $^1J_{CH}$ values are similar to those observed for Tp$^{Me2}$Ir(III)−alkyl functionalities.[16] Interestingly, the corresponding carbon nuclei of the $\eta^4$-diene complex **3** also resonate at high fields (3.9 ppm), but they exhibit higher C−H couplings (154 Hz). The $^{13}$C resonance of the central olefinic carbons, >C=, appears at ca. 140 ppm, in accord with their free, noncoordinated olefinic character (68.4 ppm for compound **3**).

For SC$_4$H$_8$, NCMe, and C$_6$H$_5$C(H)=NMe, adduct formation is reversible and complex **1** may be recovered when solutions of the respective compounds **4c**, **4e**, and **4g** are heated at sufficiently high temperatures (80 °C for **4c** and **4g**; 120 °C in the case of **4e**) in the absence of the free base. The lability of the Ir−L bond of compounds **4** is also manifested by the facility with which they undergo substitution chemistry by L′ to give the corresponding Ir−L′ derivatives (eq 2). For example, the acetonitrile compound **4e** converts quantitatively into **4e**-$d_3$ when heated at 80 °C in CD$_3$CN for 6 h. The pyridine derivative **4f** is less labile ($t_{1/2}$ = 16 h, 125 °C, neat C$_5$D$_5$N), but even the PMe$_3$ adduct **4a** undergoes slow conversion into **4f** upon prolonged heating in neat pyridine (after 12 h at 150 °C the conversion is only 5%). The carbonyl ligand of **4b** does not undergo exchange under any attempted conditions, the superior stability of this compound being evinced by its quantitative



(2)

---

[10] (a) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z. *J. Chem. Soc., Chem. Commun.* **1996**, 1. (b) Erker, G.; Engel, K.; Krüger, C.; Müller, G. *Organometallics* **1984**, *3*, 128.

[11] (a) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 2809. (b) Erker, G.; Mühlenberd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 402. (c) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (d) Gemel, C.; Kalt, D.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *17*, 427.

[12] Boutry, O.; Poveda, M. L.; Carmona, E. *J. Organomet. Chem.* **1997**, *528*, 143.

[13] (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 418.

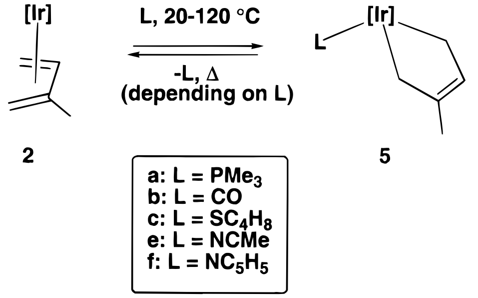
[14] Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248.

[15] Paneque, M.; Poveda, M. L.; Salazar, V.; Taboada, S.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Ruiz, C. *Organometallics* **1999**, *18*, 139.

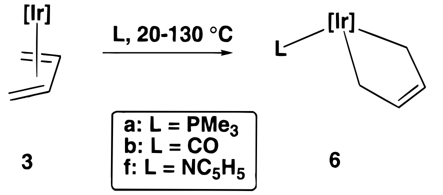
[16] (a) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem. Eur. J.* **1998**, *4*, 2225. (b) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.

formation by reaction of the py adduct with CO at 130 °C. From these and other competition experiments effected under thermodynamic control (**1** and the appropriate L and L′ mixtures were heated at temperatures high enough to ensure complete equilibration between the adducts; the course of the reactions was monitored by NMR spectroscopy), the relative stabilities of adducts **4** have been found to follow the order CO > $\mathrm{PMe_3}$ > $\mathrm{C_5H_5N}$ > $\mathrm{CH_3CN}$ ≈ $\mathrm{SC_4H_8}$ > $\mathrm{C_6H_5C(H){=}NMe}$.

The 2-methyl-1,3-butadiene (isoprene) complex $\mathrm{Tp^{Me2}}$-$\mathrm{Ir}(\eta^4\text{-}\mathrm{CH_2{=}CHC(Me){=}CH_2})$ (**2**) and the analogous 1,3-butadiene derivative $\mathrm{Tp^{Me2}Ir}(\eta^4\text{-}\mathrm{CH_2{=}CHCH{=}CH_2})$ (**3**) also experience this transformation, albeit with increasing difficulty (eqs 3 and 4). Thus whereas adducts **5a**–**f** can be obtained, somewhat harsher conditions than those necessitated for their **4** analogues are needed (for example **5c**,**e**,**f** require heating at 80–90 °C in neat L as the solvent, while under similar conditions **4c**,**e**,**f** form at room temperature). $\mathrm{PMe_3}$ and CO still add rapidly to **2** at 25 °C, but the reaction of **3** with CO (eq 4) demands heating at 40 °C overnight for completion. The inertness of **3** toward these transformations explains our failure to generate the acetonitrile adduct even at high temperatures (ca. 150 °C). Under the same conditions, however, the py adduct **6f** is actually formed. Compounds **5** and **6** are best characterized by $^{13}$C NMR spectroscopy. As an illustrative example, the carbonyl adduct **6b** exhibits $^{13}$C resonances at $\delta$ 6.0 ($^1J_{\mathrm{CH}} = 127$ Hz) and 142.3 ($^1J_{\mathrm{CH}} = 154$ Hz) for the $-C\mathrm{H_2CH}{=}$ and $-\mathrm{CH_2}C\mathrm{H}{=}$ nuclei, respectively.



(3)



(4)

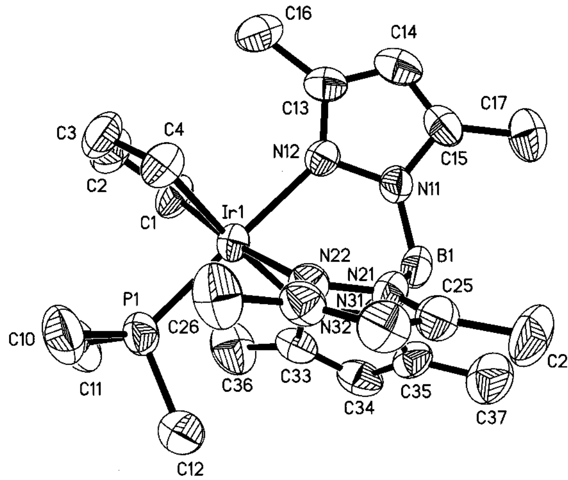


**Figure 1.** ORTEP view of complex **6a**.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 6a**

| | | | |
|---|---|---|---|
| Ir(1)–C(1) | 2.090(13) | Ir(1)–N(12) | 2.163(9) |
| Ir(1)–C(4) | 2.087(13) | Ir(1)–N(22) | 2.250(10) |
| C(1)–C(2) | 1.51(2) | Ir(1)–N(32) | 2.215(9) |
| C(2)–C(3) | 1.27(2) | Ir(1)–P(1) | 2.234(3) |
| C(3)–C(4) | 1.49(2) | | |
| C(4)–Ir(1)–C(1) | 82.3(5) | C(4)–Ir(1)–P(1) | 89.8(4) |
| C(1)–Ir(1)–P(1) | 89.0(5) | | |

The proposed $\eta^2{:}\sigma^2$ coordination mode of the diene ligand in complexes **4**–**6** has been unambiguously demonstrated by a single-crystal X-ray study carried out with the $\mathrm{PMe_3}$ adduct **6a**. Figure 1 shows an ORTEP view of the structure of this molecule, while selected bond distances and angles are presented in Table 1. As it can be observed, the metallacyclic unit presents almost perfect planarity; the maximum deviation from the mean quadratic plane corresponds to C(4) and amounts only to 0.089(9) Å. This fact and the short C(2)–C(3) bond length of 1.27(2) Å (compare with 1.33 Å in $\mathrm{C_2H_4}$)[17] indicate an undisturbed, noncoordinated C=C bond. Finally, the Ir–$\mathrm{CH_2}$ bond distance of 2.09(1) Å (av) compares well with those found in somewhat related Ir(III) alkyls (e.g., 2.10 Å in $\mathrm{Tp^{Me2}}$-$\overline{\mathrm{Ir}(=\mathrm{CCH_2CH_2CH_2O}}\mathrm{)(H)(CH_2CH_2CH_2CH_3)}$).[16a]

## Discussion

The unprecedented transformation of the Ir(I) compounds **1**–**3**, which contain $\eta^4{:}\pi^2$ butadiene-type ligands, into the Ir(III) species **4**–**6** with an $\eta^2{:}\sigma^2$ hydrocarbyl functionality may be attributed to the particular spatial and electronic properties of the $\mathrm{Tp^{Me2}}$ ligand. As for other unusual transformations found during the investigation of the $\mathrm{Tp^{Me2}Ir}$ system,[14,16,18] two factors should be invoked to account for the observed reactivity. These are the hard nature of the tris(pyrazolyl)borate ligands, Tp′, as compared with the softer cyclopentadienyls, Cp′, which favors conversion to the Ir(III) oxidation state, and their well-known tendency to enforce octahedral coordination of the metal,[19] a stereochemistry that is especially favorable for the d$^6$ electronic configuration of Ir(III). It is worth recalling that the formation of the Ir(III) adduct takes place even with CO, a ligand that strongly favors low oxidation states.

As shown in Scheme 1 two routes may be envisaged for the formation of compounds **4**–**6**. In the first (route **a**) the starting diene is postulated to be in fast equilibrium with small amounts of an unsaturated enediyl Ir(III) species that would then react with the Lewis base. The alternative path **b** implies an associative

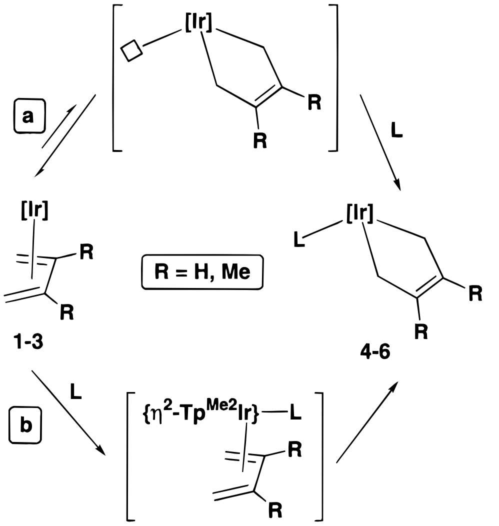
---

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

(18) 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.

(19) (a) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. Curtis, M. D.; Shiu, K. B.; Butler, W. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3335. See also: Reger, D. L.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 579.

**Scheme 1**



interaction of L with the diene complex, followed by fast conversion to the final compounds **4**−**6**. A kinetic study on the formation of the acetonitrile adduct **4e** leads to $k_{obs} = k$[NCMe], with $k = 1.4 \times 10^{-4}$ s$^{-1}$·mol$^{-1}$ ($CD_2Cl_2$, 30 °C; [NCMe] up to 2 M) and therefore does not distinguish between the two. However the reactivity studies described in the Results section and other reported studies on Tp$^{Me2}$Ir(I)−olefin systems cannot be easily reconciled with a single general path, **a** or **b**, for all the reactions studied. For instance on the basis of steric and electronic arguments the **1** > **2** > **3** experimental order of reactivity would seem to be in favor of route **a**, because the unsaturated intermediate will be increasingly disfavored in that order, but it is difficult to understand why the soft bases CO and $PMe_3$ will trap these intermediates much faster than pyridine and acetonitrile.

On the other hand, the associative route **b** seems very likely for CO and $PMe_3$ adduct formation, as this is similar to the reactions of Tp$^{Me2}$Ir($C_2H_4$)$_2$ with these bases, which appear to proceed through an associative mechanism.[16b,20] However, the bis(ethylene) compound reacts quite differently, and always under more forcing conditions, with hard N-donors (e.g., NCMe, py) in processes that involve Ir(III) intermediates.[16b,18] Therefore it is reasonable to suggest that CO and $PMe_3$ prefer route **b**, whereas for $SC_4H_8$, py, and other N-donors the sequence of events depicted in **a** constitutes the more facile reaction path.

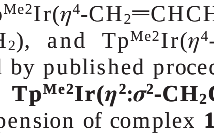
An additional important result of these studies is the observation for the first time in this kind of system of a Tp′Ir(III) → Tp′Ir(I) reduction process. Many Tp′Ir(III) compounds we have investigated are extremely reluctant to evolve through Ir(I) intermediates or to give Ir(I) reaction products. In the compounds under investigation, the reversibility of the reaction that leads to the $\eta^2$:$\sigma^2$-enediyl complexes **4**−**6** could be related with the stability expected for the Ir(I)−$\eta^4$-diene moiety, the reversion being most facile for the compounds of the unsubstituted 1,3-butadiene ligand. In what concerns the nature of L, the higher stability of the CO and $PMe_3$ adducts as compared to those of the N-donors is a clear reflection of the strength of the Ir(III)−CO and −$PMe_3$ bonds. Finally, since $K_{eq}$ for **4**−NCMe $\rightleftharpoons$ **4**−$SC_4H_8$ is equal to 1 at 80 °C, it may be concluded that Lewis acid centers of the kind Tp$^{Me2}$Ir(R)(R′) (R, R′ = hydrocarbyl) are of intermediate hard−soft character. In accord with this proposal, both hard (py) and soft (CO, $PMe_3$) bases form Tp$^{Me2}$Ir(R)(R′)L complexes of high stability.

In summary, the stereoelectronic properties of the Ir(I) center of Tp$^{Me2}$Ir($\eta^4$-$CH_2$=C(R)C(R)=$CH_2$) compounds allow the observation of a very unusual Lewis base-induced rearrangement to the corresponding Ir(III) species Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-$CH_2$C(R)=C(R)$CH_2$)(L). Comparative studies of this transformation under different experimental conditions indicate an intermediate soft−hard Lewis acid character of Ir(III) in these species.

## Experimental Section

**General Procedures.** Microanalyses were by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). Infrarred 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 $SiMe_4$ ($\delta = 0$ ppm) using the residual protio solvent peaks as internal standards ($^1$H NMR experiments) or the characteristic resonances of the solvent nuclei ($^{13}$C NMR experiments). 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 by following conventional Schlenk techniques. The complexes Tp$^{Me2}$Ir($\eta^4$-$CH_2$=CHCH=$CH_2$), Tp$^{Me2}$Ir($\eta^4$-$CH_2$=CHC(Me)=$CH_2$), and Tp$^{Me2}$Ir($\eta^4$-$CH_2$=C(Me)C(Me)=$CH_2$), were obtained by published procedures.[12]

**Preparation of Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-$CH_2$C(Me)=C(Me)$CH_2$)($PMe_3$) (4a)**. A suspension of complex **1** (0.30 g, 0.54 mmol) in $C_6H_{12}$ (1 mL) was treated with a solution of $PMe_3$ in THF (2 mL, 1 M, 2 mmol). After stirring for 1 h at room temperature, the volatiles were removed under vacuo and the residue stirred vigorously with 5 mL of pentane for 5 min. The white precipitate was filtered off and dissolved in a mixture of petroleum ether/$CH_2Cl_2$ (8 mL, 5:3). After filtration and cooling at −20 °C, complex **4a** was obtained as white crystals (0.22 g, 65%). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.70, 5.62 (s, 2:1, 3 $CH_{pz}$), 2.64, 2.61 (br d, ABX spin system, 4 H, $^2J_{AB} = 15.0$ Hz, 2 Ir$CH_2$, the coupling of A with the $^{31}$P nucleus is not resolved in $CDCl_3$, but the $^3J_{AX}$ data of 7.7 Hz can be obtained in $C_6D_6$), 2.36, 2.35, 2.25, 2.02 (s, 2:2:1:1, 6 $Me_{pz}$), 1.64 (br s, 6 H, 2 $Me_C$), 1.28 (d, 9 H, $^2J_{HP} = 9.4$ Hz, $PMe_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C) $\delta$ 150.3, 150.1, 143.0, 142.4 (1:2:2:1, $C_{qpz}$), 140.5 ($C^2$), 107.9, 107.3 (1:2, $CH_{pz}$), 18.3 ($Me_C$), 15.6, 13.1, 10.8 (2:3:1, $Me_{pz}$), 14.8 (d, $^1J_{CP} = 37$ Hz, $PMe_3$), 6.5 (d, $^2J_{CP} = 8$, Ir$C^1$, $^1J_{CH} = 124$ Hz). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ −47.0. Anal. Calcd for $C_{24}H_{41}BN_6PIr$: C, 44.5; H, 6.3; N, 12.9. Found: C, 44.9; H, 6.5; N, 12.8.



**Preparation of Tp$^{Me2}$Ir($\eta^2$:$\sigma^2$-$CH_2$C(Me)=C(Me)$CH_2$)(CO) (4b)**. A suspension of complex **1** (0.10 g, 0.17 mmol) in $C_6H_{12}$ (15 mL) was tranferred into a Fischer−Porter vessel. The mixture was stirred under 2 atm of CO at room temperature for 1 h. The resulting solution was taken to dryness and the pale yellow residue washed with 10 mL of pentane. The yield of complex **4b** is almost quantitative. IR (Nujol): $\nu$(CO)

---

[20] Oldham, W. J.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467.

2000 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.79, 5.73 (s, 2:1, 3 $CH_{pz}$), 3.05, 2.46 (br d, 4 H, $^2J_{AB}$ = 13.3 Hz, 2 $IrCH_2$), 2.38, 2.34, 2.33, 2.06 (s, 2:2:1:1, 6 $Me_{pz}$), 1.70 (brs, 6 H, $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 169.2 (CO), 152.0, 150.7, 143.5, 143.2 (1:2:1:2, $C_{qpz}$), 139.0 ($C^2$), 108.9, 106.7 (1:2, $CH_{pz}$), 18.3 ($Me_C$), 14.3, 13.1, 12.6, 10.8 (2:1:2:1, $Me_{pz}$), 10.4 ($IrC^1$). Anal. Calcd for $C_{22}H_{32}BN_6OIr$: C, 44.0; H, 5.3; N, 14.0. Found: C, 44.2; H, 5.4; N, 13.9.

**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2C(Me){=}C(Me)CH_2)(SC_4H_8)$ (4c).** Complex **1** (0.10 g, 0.17 mmol) was suspended in 1 mL of $C_6H_{12}$ and treated with recently distilled tetrahydrothiophene (0.04 mL, 0.34 mmol). The suspension was stirred for 1 h at room temperature, and the volatiles were removed in vacuo. The residue was stirred vigorously with 5 mL of pentane for 5 min and the yellow precipitate separated by filtration. Extraction with a mixture of petroleum ether/$Et_2O$ (8 mL, 3:1), filtration, and cooling at −20 °C furnished complex **4c** as colorless crystals (0.07 g, 60%). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.71, 5.64 (s, 2:1, 3 H, 3 $CH_{pz}$), 2.89, 2.85 (br d, 4 H, $^2J_{AB}$ = 15.0 Hz, 2 $IrCH_2$), 2.54 (br s, 4 H, 2 $SCH_2$), 2.41, 2.36, 2.29, 2.01 (s, 2:2:1:1, 6 $Me_{pz}$), 1.94 (br s, 4 H, 2 $SCH_2CH_2$), 1.68 (br s, 6 H, 2 $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 151.2, 150.3, 142.8, 142.6 (1:2:1:2, $C_{qpz}$), 140.6 ($C^2$), 108.1, 106.9 (1:2, $CH_{pz}$), 31.0 ($SCH_2$), 28.2 ($SCH_2CH_2$), 18.4 ($Me_C$), 14.2, 13.3, 12.9, 10.7 (2:1:2:1, $Me_{pz}$), 7.3 ($IrC^1$, $^1J_{CH}$ = 123 Hz). Anal. Calcd for $C_{25}H_{40}BN_6SIr\cdot0.5Et_2O$: C, 46.6; H, 6.3; N, 12.0. Found: C, 46.5; H, 6.0; N, 12.4.

**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2C(Me){=}C(Me)CH_2)(C_2H_4)$ (4d).** In a Fischer−Porter vessel a suspension of complex **1** (0.10 g, 0.17 mmol) in $C_6H_{12}$ (15 mL) was reacted with $C_2H_4$ (2 atm) at room temperature for 1 h. The resulting solution was taken to dryness and the pale brown residue extracted with a mixture of $Et_2O$/pentane (10 mL, 1:1). After filtration and cooling at −20 °C, complex **4d** was obtained as pale brown crystals (0.09 g, 85%). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.71, 5.68 (s, 2:1, 3 $CH_{pz}$), 3.37 (s, 4 H, $C_2H_4$), 2.61, 2.39 (br d, 4 H, $^2J_{AB}$ = 12.9 Hz, 2 $IrCH_2$), 2.38, 2.30, 2.19, 2.01 (s, 2:1:2:1, 6 $Me_{pz}$), 1.67 (s, 6 H, 2 $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) $\delta$ 150.8, 150.7, 143.2, 143.0 (2:1:1:2, $C_{qpz}$), 138.9 ($C^2$), 108.8, 108.0 (1:2, $CH_{pz}$), 58.7 ($C_2H_4$), 18.1 ($Me_C$), 14.0, 13.4, 12.6, 11.4 (2:1:2:1, $Me_{pz}$), 13.1 ($IrC^1$). Anal. Calcd for $C_{23}H_{36}BN_6Ir$: C, 46.0; H, 6.0; N, 14.0. Found: C, 46.2; H, 5.8; N, 14.3.

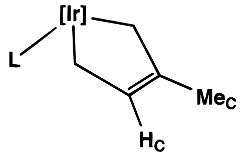
**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2C(Me){=}C(Me)CH_2)(NCMe)$ (4e).** A suspension of complex **1** (0.10 g, 0.17 mmol) in NCMe (6 mL) was stirred at room temperature for 1 h. The volatiles were removed under vacuo, and the residue was vigorously stirred with 5 mL of petroleum ether. The resulting amber precipitate was allowed to settle, decanted, and dried under vacuo. The yield of complex **4e** was almost quantitative. IR (Nujol): $\nu$(CN) 2273 cm$^{-1}$.$^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.72, 5.60 (s, 2:1, 3 $CH_{pz}$), 2.87, 2.69 (br d, 4 H, $^2J_{AB}$ = 13.3 Hz, 2 $IrCH_2$), 2.39, 2.34, 2.33, 2.29 (s, 1:2:2:1, 6 $Me_{pz}$), 1.94 (s, 3 H, NCMe), 1.70 (br s, 6 H, 2 $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 151.8, 150.0, 143.0, 142.5 (1:2:1:2 $C_{qpz}$), 138.8 ($C^2$), 111.8 (N*C*Me), 108.1, 106.6 (1:2, $CH_{pz}$), 18.6 ($Me_C$), 13.8, 13.4, 12.5, 10.9 (2:1:2:1, $Me_{pz}$), 7.5 ($IrC^1$), 4.5 (NC*Me*). Anal. Calcd for $C_{23}H_{35}BN_7Ir$: C, 46.0; H, 6.1; N, 15.0. Found: C, 46.1; H, 5.6; N, 15.2.

**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2C(Me){=}C(Me)CH_2)(NC_5H_5)$ (4f).** Complex **1** (0.10 g, 0.17 mmol) was suspended in $C_6H_{12}$ (0.5 mL) and 0.03 mL of dry pyridine (2 mmol) added. After stirring for 1 h at room temperature, the resulting solution was taken to dryness. The residue was triturated with 5 mL of pentane and the green precipitate isolated by filtration. Complex **4f** (0.08 g, 70%) was obtained as a green solid by crystallization, at −20 °C, from a mixture of $Et_2O/CH_2Cl_2$/petroleum ether (2:0.5:1). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 8.36, 7.87 (br d, 1 H each, $^3J_{HH}$ = 5.7 Hz, 2 $H_o$), 7.52 (t, 1 H, $^3J_{HH}$ = 7.5 Hz, $H_p$), 7.12, 6.67 (br t, 1 H each, 2 $H_m$), 5.70, 5.65 (s, 2:1, 3 $CH_{pz}$), 3.27, 2.46 (br d, 2 H, $^2J_{AB}$ = 13.7 Hz, 2 $IrCH_2$), 2.45, 2.36, 2.03, 1.45 (s, 2:1:1:2, 6 $Me_{pz}$), 1.61 (brs, 6 H, 2 $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 156.2, 154.1, 132.7, 125.9, 123.4 ($CH_{py}$), 151.9, 150.4, 143.4, 142.4 (1:2:1:2, $C_{qpz}$), 140.0 ($C^2$), 108.3, 106.8 (1:2, $CH_{pz}$), 18.9 ($Me_C$), 13.6, 13.0, 12.7, 11.9 (1:2:2:1, $Me_{pz}$), 11.5 ($IrC^1$). Anal. Calcd for $C_{26}H_{37}BN_7Ir$: C, 47.9; H, 5.7; N, 15.0. Found: C, 48.0; H, 5.4; N, 14.2.

**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2C(Me){=}C(Me)CH_2)(N(Me){=}CHPh)$ (4g).** This complex was obtained by the procedure described above for the pyridine adduct, but its formation needed heating at 80 °C for 6 h. Starting from **1** (0.40 g, 0.70 mmol) and N(Me)=CHPh (0.13 mL, 1.05 mmol), complex **4g** was isolated as orange needles (0.41 g, 85%) from $CH_2Cl_2$/pentane (0.8:2). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 8.90 (br s, 1 H, C*H*Ph), 7.03 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, $H_p$), 6.79 (t, 2 H, $^3J_{HH}$ = 7.4 Hz, 2 $H_m$), 6.08 (d, 2 H, 2 $H_o$), 5.57, 5.38 (s, 1:2, 3 $CH_{pz}$), 3.87 (d, 3 H, $^4J_{HH}$ = 1.1 Hz, NMe), 3.01 (br s, 4 H, 2 $IrCH_2$), 2.38, 2.29, 2.06, 2.05 (s, 2:1:2:1, 6 $Me_{pz}$), 1.77 (br s, 6 H, 2 $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 171.9 (*C*HPh), 151.7, 150.2, 142.7, 142.7 (1:2:1:2, $C_{qpz}$), 140.5 ($C^2$), 135.3 ($C_{qph}$), 127.9, 127.1, 127.0 ($CH_{ph}$), 108.9, 106.8 (1:2, $CH_{pz}$), 55.4 (NMe), 21.7 ($Me_C$), 14.1, 13.5, 12.4, 12.0 (2:1:2:1, $Me_{pz}$), 9.7 ($IrC^1$). Anal. Calcd for $C_{29}H_{41}BN_7Ir$: C, 50.4; H, 5.9; N, 14.1. Found: C, 49.9; H, 5.9; N, 13.7.

**Competition Experiments**. To determine the relative reactivity of the different Lewis bases that react at room temperature, on a typical experiment, to a solution of complex **1** in cyclohexane was added a 1:1 mixture of the corresponding L and L′ Lewis bases (total amount ca. 100 equiv with respect to Ir). After 15 min. stirring at room temperature, the solution was taken to dryness and the composition of the mixture analyzed by $^1$H NMR ($CDCl_3$).

**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2CH{=}C(Me)CH_2)(PMe_3)$ (5a).** This complex was obtained, starting from **2** and $PMe_3$, as described above for the related species **4a**. White needles resulted from petroleum ether/$CH_2Cl_2$ (6:2) at −20 °C (yield: 55%). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.75, 5.74, 5.69 (s, 1 H each, 3 $CH_{pz}$), 5.13 (br s, 1 H, $H_C$), 2.63 (m, 4 H, 2 $IrCH_2$), 2.40, 2.30, 2.26 (s, 4:1:1, 6 $Me_{pz}$), 1.87 (br s, 3 H, $Me_C$), 1.36 (d, 9 H, $^2J_{HP}$ = 9.4 Hz, $PMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) $\delta$ 151.1 ($CMe_C$), 150.9−142.6 ($C_{qpz}$), 137.8 ($CH_C$), 108.0, 107.5 (d, 1:2, $J_{CP}$ = 3 y 7 Hz, respectively, $CH_{pz}$), 19.5 ($Me_C$) 15.7, 13.2, 11.7 (2:3:1, $Me_{pz}$), 14.8 (d, $^1J_{CP}$ = 37 Hz, $PMe_3$), 4.7, −1.7 (d, $^2J_{CP}$ = 8 Hz, $IrCH_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ −48.0. Anal. Calcd for $C_{23}H_{39}BN_6PIr$: C, 43.6; H, 6.1; N, 13.2. Found: C, 43.1; H, 6.2; N, 12.7.



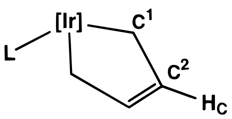
**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2CH{=}C(Me)CH_2)(CO)$ (5b).** Starting from complex **2** (0.05 g, 0.09 mmol), compound **5b** was obtained by the procedure described for the related compound **4b**. A white solid was obtained in almost quantitative yield. IR (Nujol): $\nu$(C−O) 2001 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.79, 5.75 (s, 2:1, 3 $CH_{pz}$), 5.27 (br s, 1 H, $H_C$), 3.07, 2.52 (br d, 2 H, $^2J_{AB}$ = 15 Hz, $IrCH_2$), 2.96, 2.47 (br d, 2 H, $^2J_{AB}$ = 15.3 Hz, $IrCH_2$), 2.39, 2.36, 2.34, 2.33, 2.21 (s, 1:1:2:1:1, 6 $Me_{pz}$), 1.88 (br s, 3 H, $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 169.2 (CO), 152.1, 149.5, 143.6, 143.3 (1:2:1:2, $C_{qpz}$), 150.8 ($CMe_C$), 135.9 ($CH_C$), 108.6, 106.9, 106.8 ($CH_{pz}$), 19.4 ($Me_C$), 14.3, 13.1, 12.6, 11.7 (2:1:2:1, $Me_{pz}$), 9.0, 2.9 ($IrCH_2$). Anal. Calcd for $C_{21}H_{30}BN_6OIr$: C, 43.0; H, 5.1; N, 14.3. Found: C, 43.1; H, 5.1; N, 13.8.

**Preparation of $Tp^{Me2}Ir(\eta^2{:}\sigma^2\text{-}CH_2CH{=}C(Me)CH_2)(SC_4H_8)$ (5c).** Starting from complex **2** (0.30 g, 0.55 mmol) and $SC_4H_8$ (1 mL, 8.4 mmol), complex **5c** was obtained by the procedure described for the related compound **4c**; however, heating at 80 °C was needed in this case. White needles resulted from toluene/petroleum ether/$CH_2Cl_2$ (1:4:3) at −20 °C (yield: 45%). $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.70, 5.69, 5.64 (s, 1 H each, 3 $CH_{pz}$), 5.04 (br s, 1 H, $H_C$), 2.92, 2.73 (br d, 2 H, $^2J_{AB}$ = 15.4 Hz, $IrCH_2$), 2.87 (br s, 2 H, $IrCH_2$), 2.55 (br s, 4 H, 2 $SCH_2$), 2.39, 2.34, 2.28, 2.14 (s, 2:2:1:1, 6 $Me_{pz}$), 1.93 (br s, 4 H, 2 $SCH_2CH_2$), 1.83 (br s, 3 H, $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 151.5-($CMe_C$), 150.4, 150.2, 142.8, 142.7, 142.6 ($C_{qpz}$), 137.8 ($CH_C$), 108.0, 107.0, 106.8 ($CH_{pz}$), 31.3 ($SCH_2$), 28.2 ($SCH_2CH_2$), 19.5 ($Me_C$), 14.3, 14.0, 13.3, 12.8, 11.7 (1:1:1:2:1, $Me_{pz}$), 5.4, −1.1 ($IrCH_2$). Anal. Calcd for $C_{24}H_{38}BN_6SIr{\cdot}0.5CH_2Cl_2$: C, 42.8; H, 5.7; N, 12.2. Found: C, 43.6; H, 5.9; N, 12.4.

**Preparation of $Tp^{Me2}Ir(\eta^2:\sigma^2\text{-}CH_2CH{=}C(Me)CH_2)(NCMe)$ (5e).** Starting from **2** (0.05 g, 0.09 mmol), complex **5e** was obtained by the procedure described for the related compound **4e**, but heating at 80−90 °C was needed in this case. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.97, 5.87 (s, 2:1, 3 $CH_{pz}$), 5.33 (br s, 1 H, $H_C$), 3.10, 2.96 (br d, 1 H cada, $^2J_{AB}$ = 14.3 Hz, $IrCH_2$), 3.00 (br s, 2 H, $IrCH_2$), 2.65, 2.58, 2.57, 2.54 (s, 1:1:3:1, 6 $Me_{pz}$), 2.36 (br s, 3 H, $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 152.3, 150.3, 143.4, 142.9 (1:2:1:2, $C_{qpz}$), 150.4 ($CMe_C$), 136.1 ($CH_C$), 112.4 (NCMe), 108.3, 107.1, 107.0 ($CH_{pz}$), 20.0 ($Me_C$), 14.1, 13.7, 12.8, 12.0 (2:1:2:1, $Me_{pz}$), 5.9, −0.6 ($IrCH_2$), 4.6 (NC*Me*). Anal. Calcd for $C_{22}H_{33}BN_7Ir$: C, 44.1; H, 5.5; N, 16.3. Found: C, 44.7; H, 5.5; N, 15.7.

**Preparation of $Tp^{Me2}Ir(\eta^2:\sigma^2\text{-}CH_2CH{=}C(Me)CH_2)(NC_5H_5)$ (5f).** Complex **2** (0.05 g, 0.09 mmol) suspended in pyridine (2 mL) was heated at 90 °C for 12 h. The solvent was evaporated in vacuo and the residue vigorously stirred with pentane, to yield compound **5f** as a pale green solid, which was isolated, by filtration, in almost quantitative yield. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 8.59, 7.82 (br d, 1 H each, $^3J_{HH}$ = 5.1 Hz, 2 $H_o$), 7.53 (t, 1 H, $^3J_{HH}$ = 7.5 Hz, $H_p$), 7.14, 6.68 (br t, 1 H each, 2 $H_m$), 5.69, 5.65 (s, 2:1, 3 $CH_{pz}$), 5.24 (br s, 1 H, $H_C$), 3.28, 3.25, 2.47, 2.43 (d, 1 H each, $^2J_{AB}$ = 14.6 Hz, 2 $IrCH_2$), 2.40, 2.36, 2.18, 1.43, 1.42 (s, 2:1:1:1:1, 6 $Me_{pz}$), 1.97 (br s, 3 H, $Me_C$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 156.2, 154.3, 132.9, 125.8, 123.4 ($CH_{py}$), 152.0, 149.4, 149.4, 143.5, 142.5 (1:1:1:1:2, $C_{qpz}$), 150.5 ($CMe_C$), 137.5 ($CH_C$, $^1J_{CH}$ = 145 Hz), 108.3, 106.9, 106.9 ($CH_{pz}$), 19.8 ($Me_C$), 13.5, 13.0, 13.0, 12.6 (1:2:1:2, $Me_{pz}$), 9.5 ($IrCH_2$, $^1J_{CH}$ = 121 Hz), 2.7 ($IrCH_2$, $^1J_{CH}$ = 124 Hz). Anal. Calcd for $C_{25}H_{35}BN_7Ir$: C, 47.1; H, 5.5; N, 15.4. Found: C, 47.4; H, 5.6; N, 14.8.

**Preparation of $Tp^{Me2}Ir(\eta^2:\sigma^2\text{-}CH_2CH{=}CHCH_2)(PMe_3)$ (6a).** This complex was obtained, starting from **3** and $PMe_3$, by the method described above for **4a** and **5a**. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.63, 5.17 (s, 2:1, 3 $CH_{pz}$), 5.34 (br s, 2 H, 2 $H_C$), 2.8 (m, ABX spin system, 4 H, $^2J_{AB}$ = 13.5, $^3J_{AP}$ = 7.6 Hz, 2 $IrCH_2$), 2.36, 2.25, 2.17 (s, 4:1:1, 6 $Me_{pz}$), 1.32 (d, 9 H, $^2J_{HP}$ = 8.9 Hz, $PMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 150.3, 143.2, 142.6 (3:2:1, $C_{qpz}$), 144.1 ($C^2$), 107.8, 107.5 (1:2, $CH_{pz}$), 15.7, 13.2, 12.4 (2:3:1, $Me_{pz}$), 14.9 (d, $^1J_{CP}$ = 37 Hz, $PMe_3$), 1.2 (d, $^2J_{CP}$ = 9 Hz, $IrC^1$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C) $\delta$ −48.4. Anal. Calcd for $C_{22}H_{37}BN_6PIr$: C, 42.6; H, 5.9; N, 13.5. Found: C, 42.5; H, 6.0; N, 13.4.



**Preparation of $Tp^{Me2}Ir(\eta^2:\sigma^2\text{-}CH_2CH{=}CHCH_2)(CO)$ (6b).** This compound was obtained from **3** and CO as described above for the synthesis of **4b** and **5b**. The reaction needed in this case heating at 40 °C for 12 h for completion. A pale yellow solid is obtained in almost quantitative yield. IR (Nujol): $\nu$(CO) 1999 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 5.80, 5.75 (s, 2:1, 3 $CH_{pz}$), 5.55 (br s, 2 H, 2 $H_C$), 3.19, 2.65 (br d, 4 H, $^2J_{AB}$ = 13.9 Hz, 2 $IrCH_2$), 2.38, 2.35, 2.34, 2.23 (s, 2:2:1:1, 6 $Me_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 168.8 (CO), 152.2, 150.9, 143.6, 143.4 (1:2:1:2, $C_{qpz}$), 142.3 ($C^2$, $^1J_{CH}$ = 154 Hz), 108.6, 106.9 (1:2, $CH_{pz}$), 14.3, 13.1, 12.6, 12.4 (2:1:2:1, $Me_{pz}$), 6.0 ($IrC^1$, $^1J_{CH}$ = 127 Hz). Anal. Calcd for $C_{20}H_{28}BN_6OIr$: C, 42.0; H, 4.9; N, 14.7. Found: C, 42.3; H, 4.8; N, 14.5.

**Table 2. Crystal Data and Structure Refinement for 6a**

| | |
|---|---|
| empirical form | $C_{22}H_{37}BIrN_6P$ |
| fw | 619.56 |
| temp | 296(2) K |
| wavelength | 0.710 73 Å |
| cryst syst | triclinic |
| space group | $P\bar{1}$ |
| unit cell dimens | $a$ = 8.2435(7) Å<br>$b$ = 10.9707(9) Å<br>$c$ = 17.1091(14) Å<br>$\alpha$ = 104.7190(10)°<br>$\beta$ = 98.7730(10)°<br>$\gamma$ = 104.3936(10)° |
| vol, $Z$ | 1410.6(2) Å$^{3,}$ 2 |
| density (calcd) | 1.459 mg/m$^3$ |
| abs coeff | 4.808 mm$^{-1}$ |
| $F$(000) | 616 |
| crystal size | 0.2 × 0.1 × 0.1 mm |
| $\theta$ range for data collection | 2.01−23.27° |
| limiting indices | $-9 \le h \le 6$, $-9 \le k \le 12$,<br>$-18 \le l \le 18$ |
| no. of colld reflns | 5315 |
| no. of indep reflns | 3817 ($R_{int}$ = 0.0220) |
| abs corr | none |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 3817/0/329 |
| goodness-of-fit on $F^2$ | 1.191 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0488, wR2 = 0.1485 |
| $R$ indices (all data) | R1 = 0.0561, wR2 = 0.1530 |
| absolute structure param | 0.02(3) |
| largest diff peak and hole | 3.098 and −0.739 e Å$^{-3}$ |

**Preparation of $Tp^{Me2}Ir(\eta^2:\sigma^2\text{-}CH_2CH{=}CHCH_2)(NC_5H_5)$ (6f).** This complex was obtained, starting from **3** and $NC_5H_5$, by the method described above for **5f**, although heating at 150 °C for 12 h was required for completion. A green solid was obtained in almost quantitative yield. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 8.58, 7.78 (br d, 1 H each, $^3J_{HH}$ = 5.7 Hz, 2 $H_o$), 7.52 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, $H_p$), 7.12, 6.68 (br d, 1 H each, 2 $H_m$), 5.64, 5.53 (s, 1:2, 3 $CH_{pz}$), 3.45, 2.65 (br d, 4 H, $^2J_{AB}$ = 13.9 Hz, 2 $IrCH_2$), 2.41, 2.35, 2.18, 1.42 (s, 2:1:1:2, 6 $Me_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 156.4, 154.6, 133.4, 125.9, 123.8 ($CH_{py}$), 152.2, 149.7, 143.8, 142.8, (1:2:1:2, $C_{qpz}$), 144.1 ($C^2$, $^1J_{CH}$ = 152 Hz) 108.5, 107.3 (1:2, $CH_{pz}$), 14.5, 13.8, 13.3, 12.9 (1:1:2:2, $Me_{pz}$), 6.3 ($IrC^1$, $^1J_{CH}$ = 123 Hz). Anal. Calcd for $C_{24}H_{33}BN_7Ir$: C, 46.2; H, 5.3; N, 15.7. Found: C, 46.7; H, 5.4; N, 15.2.

**X-ray Structure Determination of 6a**. A summary of the fundamental crystal data is given in Table 2. A white crystal of prismatic shape was coated with an epoxy resin and mounted in a CCD detector diffractometer. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir and P were taken from the *International Tables for X-ray Crystallography*.[21] The structure was solved by Patterson and Fourier methods. A final mixed refinement was undertaken.[22] Hydrogen atoms were included as fixed contributions at their calculated positions, except those involved in the $C_6H_4$ group, which were located in a difference synthesis and their coordinates and isotropic thermal parameters were refined. Refinement was effected on $F^2$ for all reflections. Weighted $R$ factors ($R_w$) and goodness of fit $S$ are based on $F^2$, and conventional $R$ factors ($R$) are based on $F$. The observed criterion of $F^2 > 2\sigma F^2$ is used only for calculating the $R$ factor obs, and it is not relevant to the choice of reflections for refinement. $R$ factors based on $F^2$ are statistically about twice as large than those based on $F$, and $R$ factors based on all data would be even larger.

---

(21) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

(22) Sheldrick, G. M. Programs *SADABS*, *SHELXS-97*, and *SHELXL-97*; Göttingen, 1997.

**Geometry Special Details**. All esds are estimated using the full covariance matrix. The cell esd's are taken into account individually. In the estimation of esd's in distances and angles correlations between esd's in cell paremeters are only used when they are defined by crystal symmetry.

Final difference synthesis shows a maximum of 3.09 e Å$^{-3}$ corresponding to a Cl atom, with a population factor of 0.25, which is involved in the very disordered 1/2 $CH_2Cl_2$ solvent molecule existent per unit cell.

**Acknowledgment.** The DGESIC (Projects PB96-0824 and PB97-0733) and the Junta de Andalucía are thanked for financial support. V.S. thanks the Instituto Nacional de Cooperación Iberoamericana (ICI), the Universidad Autónoma del Estado de Hidalgo (UAEH), and the Secretaría de Educación Pública (SEP, México) for research grants.

**Supporting Information Available:** Tables giving X-ray crystallographic data for **6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000382H