C−H Bond Activation of Thiophenes by Ir Complexes of the Hydrotris(3,5-dimethylpyrazolyl)borate Ligand, Tp^{Me2}

Margarita Paneque,* Manuel L. Poveda, Verónica Salazar, Soraya Taboada, and Ernesto Carmona

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, Angeles Monge, and Caridad Ruiz*

Instituto de Ciencia de Materiales de Madrid, CSIC, Campus de Cantoblanco, 28049 Madrid, Spain

Received June 10, 1998

The bis(ethylene) derivative $Tp^{Me2}Ir(C_2H_4)_2$ (**1**) reacts with thiophene, 2-methylthiophene, and 3-methylthiophene with formation of $Tp^{Me2}Ir(2\text{-thienyl})_2(SC_4H_3R)$ (R = H, **4**; R = Me, **7**, **8**) species in which the two thienyl moieties are the result of the α-C−H bond activation of the thiophenes. PMe_3 and CO adducts of formulation $Tp^{Me2}Ir(2\text{-thienyl})_2(L)$ are readily synthesized from the corresponding *S*-bonded thiophene derivatives. The structure of the CO complex $Tp^{Me2}Ir(2\text{-}SC_4H_3)_2(CO)$ (**6**) has been confirmed by a single-crystal X-ray analysis. NMR spectroscopic studies are in accord with these adducts existing in solution as mixtures of three rotameric species that arise from restricted rotation around the Ir−thienyl bonds. Hydrogenation of complexes **4**, **7**, and **8** under relatively mild conditions gives the corresponding $Tp^{Me2}IrH_2(SC_4H_3R)$ dihydrides. These last mentioned species experience interesting Ir−H and C−H(thienyl) deuteration exchanges with C_6D_6 as well as a complex decomposition reaction that gives mainly dimeric species with an unusual $C,S\text{-}\mu^2\text{-}\eta^1\text{-}\eta^1$ bridging ligand. Mechanistic proposals for these two processes are presented. Monothienyl Ir(III) species are also accessible; for example the complex $Tp^{Me2}IrH(2\text{-}SC_4H_3)(SC_4H_4)$ (**19**) can be obtained from $Tp^{Me2}IrH_2(C_2H_4)$ and thiophene. Finally, the thermal activation of SC_4H_4, 2- and 3-SC_4H_3Me, and 2,5-$SC_4H_2Me_2$ by the 2,3-dimethylbutadiene−Ir(I) complex $Tp^{Me2}(\eta^4\text{-}CH_2C(Me)C(Me)CH_2)$ has been investigated. Thiophene and the monomethylthiophenes give the complexes **4**, **7**, and **8**, whereas for 2,5-$SC_4H_2Me_2$, the reaction takes a different course and affords a hydride-thienyl derivative along with the *E* and *Z* isomers of a thienyl-substituted olefin.

Introduction

The activation of thiophenes by transition-metal complexes continues to attract general interest. This is due to the relevance of these model studies in the industrially important hydrodesulfurization reaction of petroleum (HDS)[1,2] and also to their potential applications in organic synthesis.[3] In recent studies we have reported[4a,b] the thermal C−H bond activation of benzene by the complex $Tp^{Me2}Ir(C_2H_4)_2$ (**1**).[4c] This reaction takes place via the intermediacy of the hydride-vinyl species $Tp^{Me2}IrH(CH{=}CH_2)(C_2H_4)$ (**2**)[4c] and furnishes the bis(phenyl) derivative $Tp^{Me2}Ir(C_6H_5)_2(N_2)$ with concomitant formation of C_2H_4 and C_2H_6.[4a,b] Other $Tp^{Me2}Ir$ species are also able to activate benzene,[4b] and in particular, the dimethylbutadiene Ir(I) derivative $Tp^{Me2}Ir(\eta^4\text{-}CH_2C(Me)C(Me)CH_2)$ (**3**) affords the dimeric compound $[Tp^{Me2}IrH(C_6H_5)]_2(N_2)$.[5] Herein we describe the reactions of these and related derivatives with thiophene and the monomethylthiophenes. Part of this work has appeared in a preliminary form.[6]

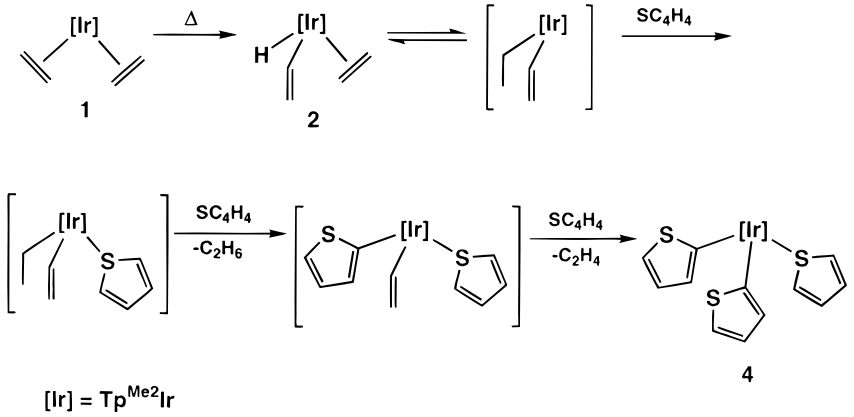
Results and Discussion

Reaction of $Tp^{Me2}Ir(C_2H_4)_2$ (1) with Thiophene. Formation of Bis(2-thienyl) Derivatives. Upon heating (60 °C) solutions of complex **1** in neat thiophene for 6 h, a yellow-brown liquor is obtained, from which a yellow-green microcrystalline solid **4**, for which analytical data are in accord with the incorporation of three thiophene units per Ir atom, precipitates upon cooling to room temperature in ca. 80% yield. NMR spectroscopy provides evidence for the slow decomposition of **4** in

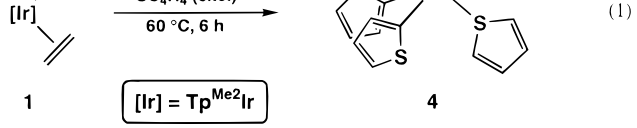
(1) Angelici, R. A. *Polyhedron* **1997**, *16*, 3073.
(2) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287.
(3) Bianchini, C.; Meli, A. *Synlett* **1997**, 643.
(4) (a) Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791. (b) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem. Eur. J.* **1998**, *4*, 2225. (c) Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.
(5) Boutry, O.; Poveda, M. L.; Carmona, E. *J. Organomet. Chem.* **1997**, *528*, 143.
(6) Paneque, M.; Poveda, M. L.; Rey, L.; Taboada, S.; Carmona, E.; Ruiz, C. *J. Organomet. Chem.* **1995**, *504*, 147.

10.1021/om9804834 CCC: $18.00
Publication on Web 12/19/1998

Scheme 1



solution (room temperature) by irreversible dissociation of thiophene. Although **4** displays much higher stability at low temperatures, the NMR spectra are so complicated that, even with the help of two-dimensional experiments, only the presence of two thienyl and one intact thiophene per $Tp^{Me2}Ir$ unit can be inferred from these studies. The complications arise mainly from the restricted rotation around the Ir−thienyl bond and the population of up to three conformational isomers, i.e., rotamers that undergo slow exchange at −40 °C. This is not surprising, as M(III)−Ar bonds (M = Rh, Ir; Ar = C_6H_5, thienyl) are known to have high rotational barriers.[4a,b,7−9] Therefore, the identification of the thienyl residues as 2-thienyl ligands rests upon the successful spectroscopic characterization of the very stable derivatives that contain a molecule of PMe_3 or CO in place of the thiophene (see below). The *S*-coordination[1,2,10] of the third thiophene fragment is based upon the ^1H chemical shifts of this entity, which are very close to those found in free thiophene. Therefore the reaction of **1** with thiophene can be represented as depicted in eq 1. As can be observed, the activation of thiophene is



(1)

similar to that of benzene;[4a,b] two aromatic rings experience the C−H breakage. The fate of the ethylene ligands of **1** has not been investigated, but it appears reasonable that they have been lost in the form of ethylene and ethane. In fact, as for the benzene reaction, the hydride−vinyl complex **2** is an active intermediate in the C−H activation process and gives exclusively complex **4** when reacted with neat thiophene. As in related studies reported recently, the activation of C−H bonds by the $Tp^{Me2}Ir$ system involves only Ir(III) intermediates.[4] A plausible mechanism for the overall process is included in Scheme 1. Even though the proposed Ir−thiophene intermediates are depicted as *S*-bound thiophene adducts (with tetrahydrothiophene the *S*-bound complex $Tp^{Me2}Ir(CH{=}CH_2)(C_2H_5)(SC_4H_8)$ is obtained; see Experimental Section), it is highly probable that the C−H activation reaction requires a prior change to the η^2-SC_4H_4 coordination mode.[11,12] It is also worthwhile to note that only the α-C−H bond of thiophene is activated. Prolonged heating of **4** in neat thiophene does not alter its composition, but it is probable that unproductive reversible C−H activation of the solvent is taking place. In accord with this assumption, complex **4** undergoes a facile reaction with C_6H_6 to give phenyl Ir species.[4a,b] Also, and since 2,5-dimethylthiophene is activated in the aromatic 3-position (see below), it appears likely that both the 2- and the 3-positions of SC_4H_4 are actually being activated, with the first being the thermodynamically favored in this system. Other C−H bond activations of thiophene end up with formation of 2-thienyl derivatives,[9,10b,12a,13,14] and at least in one case the thermodynamic preference for this regioisomer has been demonstrated.[11]

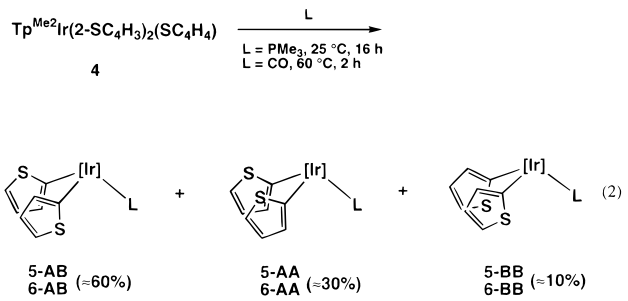
From Scheme 1 it is quite clear why **4** or the *S*-bonded intermediates do not isomerize to open forms by breakeage of the C−S bond.[1,2,14c] This will be a highly disfavored Ir(III) → Ir(V) transformation in a very crowded molecule.[15] In that respect it would be more interesting to study Ir(I) species of the type $Tp^{Me2}Ir$(thio-

(7) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583.
(8) Partridge, M. G.; Field, L. D.; Messerle, B. A. *Organometallics* **1996**, *15*, 872.
(9) Paneque, M.; Taboada, S.; Carmona, E. *Organometallics* **1996**, *15*, 2678.
(10) (a) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424. (b) White, C. J.; Angelici, R. J. *Organometallics* **1994**, *13*, 5132. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. A. *Organometallics* **1994**, *13*, 721. (d) Sánchez-Delgado, R. A.; Herrera, V.; Bianchini, C.; Masi, D.; Mealli, C. *Inorg. Chem.* **1993**, *32*, 3766.
(11) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.
(12) (a) Bianchini, C.; Casares, J. A.; Osman, R.; Pattison, D. I.; Peruzzini, M.; Perutz, R. N.; Zanobini, F. *Organometallics* **1997**, *16*, 4611. (b) Sargent, A. L.; Titus, E. P. *Organometallics* **1998**, *17*, 65.
(13) Competitive formation of 2- and 3-thienyl derivatives has been observed. See ref 8.
(14) Thiophene can afford species different from those involving a simple C−H activation process; see for example: (a) Vicic, D. A.; Jones, W. D. *Organometallics* **1997**, *16*, 1912. (b) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198. For metallathiacycle formation, see: (c) Blonski, C.; Myers, A. W.; Palmer, M.; Harris, S.; Jones, W. D. *Organometallics* **1997**, *16*, 3819, and refs 1 and 2.
(15) For some examples of Ir(V) compounds, see: (a) $(C_5Me_5)IrMe_4$, Isobe, K.; Vázquez de Miguel, A.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929. (b) $IrH_4(SiR_3)(PPh_3)_2$, Loza, M.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 2937. (c) $IrH_4(C_6H_3\text{-}2,6\text{-}(CH_2PBu^t_2)_2)$, Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (d) $Tp^{Me2}IrH_4$, Paneque, M.; Poveda, M. L.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519. (e) $Tp^{Me2}IrH_3(SiEt_3)$, Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Taboada, S.; Trujillo, M.; Carmona, E. *J. Am. Chem. Soc.*, in press.

phene)(L), but unfortunately no synthetic routes to these complexes have, as yet, been found. Specifically, compound **1**, known to react easily with soft bases such as CO and PMe_3 by associative processes that displace the ethylene ligands,[16] only reacts with thiophene through the hydrido−vinyl Ir(III) intermediate **2**.

As mentioned above, the *S*-bound thiophene ligand of **4** is quite labile in solution even at room temperature. This allows the generation of the more stable complexes $Tp^{Me2}Ir(2\text{-}SC_4H_3)_2(L)$ (L = PMe_3, **5**; CO, **6**) by treatment of **4** with an excess of the corresponding Lewis base. Even N_2 seems to form an adduct, as inferred from the observation of an IR absorption at ca. 2210 cm^{-1} when solutions of **4** are stirred under N_2 at 25 °C.[4a,b] So far we have been unable to obtain a clean product from this reaction.

Complex **5** has been characterized by one- and two-dimensional NMR techniques (these include $^1H-^1H$ COSY and NOESY and $^1H-^{13}C$, one bond, and long-range HETCOR experiments; see Experimental Section), as a thermodynamic mixture of the three rotamers represented in eq 2. Of those, the asymmetric conformer,



(2)

5-AB, is the more abundant species. The other two, **5-AA** and **5-BB**, correspond to the molecules in which the two sulfur atoms, or the 3-CH bonds, are respectively pointing toward the Tp^{Me2} ligand. A similar situation is found for the CO adduct **6**. In this case, at temperatures higher than −40 °C, broadening of the ^1H NMR spectra as a consequence of rotameric exchange becomes evident. At 70 °C (CD_2Cl_2:C_6D_6, 5:1) the fast exchange limit is reached.

Complex **6** has been subjected to a single-crystal X-ray study. Figure 1 shows an ORTEP view of the molecular structure; pertinent bond distances and angles are summarized in Table 1. As expected, complex **6** exhibits a distorted octahedral geometry in which the N atoms of the Tp^{Me2} ligand occupy three facial positions, the two thienyls and the molecule of carbon monoxide filling the remaining coordination sites. The solid-state structure corresponds to rotamer **6-AA**, in which the sulfur atoms of the two thienyl ligands are pointing to the Tp^{Me2} moiety. As a consequence, the molecule has a plane of symmetry that contains the carbonyl ligand and the pyrazolyl ring trans to it. The N−Ir−N bond angles have values close to the ideal 90° and the Ir−N bond lengths are equal within experimental error (ca. 2.11 Å, av). The Ir−C(thienyl) bond distance is 2.052(6) Å, and this compares well with the Ir−C(phenyl) distance of 2.05 Å found in $[Tp^{Me2}Ir(C_6H_5)_2]_2(\mu\text{-}N_2)$.[4a,b] Other structural data merit no further attention.

(16) 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.

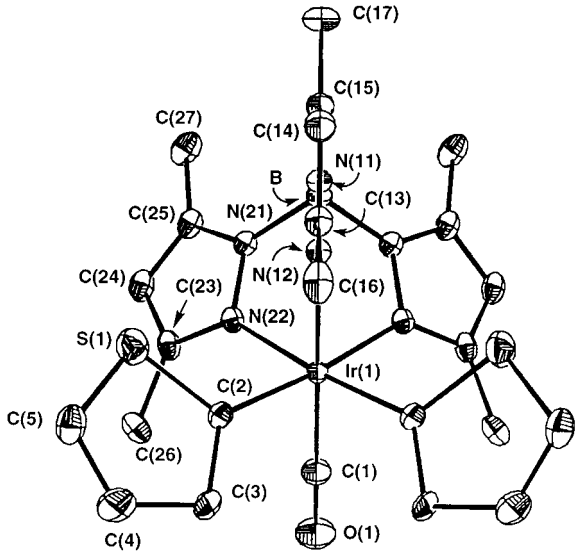


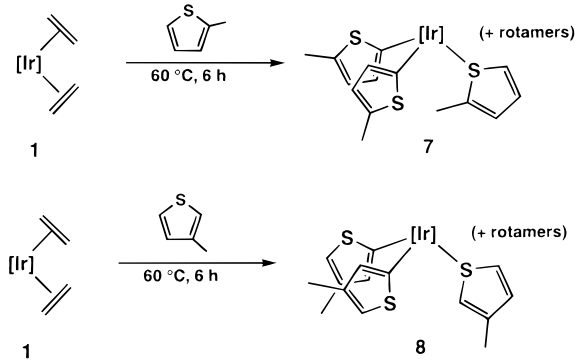
Figure 1. X-ray structure of complex **6**.

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

Ir(1)−C(2)	2.052(6)	S(1)−C(5)	1.688(9)
Ir(1)−N(12)	2.104(6)	C(2)−C(3)	1.456(9)
Ir(1)−N(22)	2.126(5)	C(3)−C(4)	1.47(1)
Ir(1)−C(1)	1.843(9)	C(4)−C(5)	1.34(1)
S(1)−C(2)	1.710(6)	C(1)−O(1)	1.12(1)

N(22)−Ir(1)−C(1)	94.1(1)	C(2)−Ir(1)−N(22′)	90.9(2)
N(12)−Ir(1)−C(1)	177.4(4)	C(2)−Ir(1)−N(12)	89.0(2)
N(12)−Ir(1)−N(22)	87.6(1)	N(22)−Ir(1)−N(22′)	85.3(2)
C(2)−Ir(1)−C(1)	89.4(2)	C(2)−Ir(1)−C(2′)	92.7(3)
C(2)−Ir(1)−N(22)	175.0(2)		

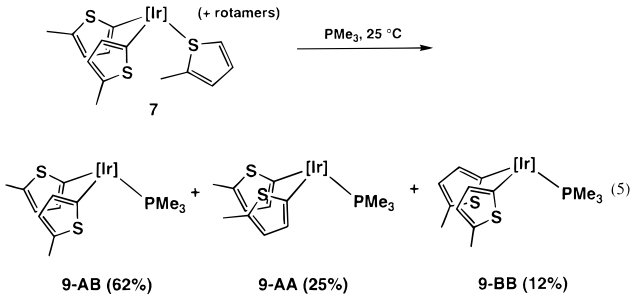
Reactions of $Tp^{Me2}Ir(C_2H_4)_2$ (1) with 2- and 3-Methylthiophene. Under the same experimental conditions described above for the interaction with SC_4H_4, complex **1** reacts with the monomethylated thiophene isomers (eqs 3 and 4) to afford the related bis(thienyl)



(3)
(4)

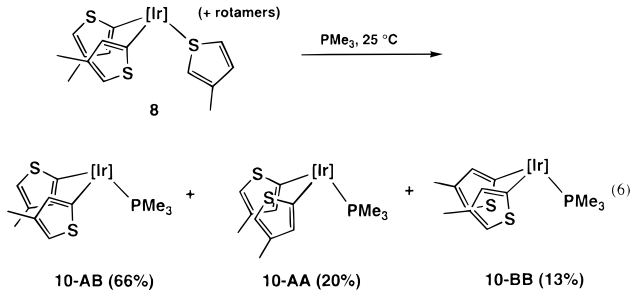
species **7** (2-methylthiophene adduct) and **8** (3-methylthiophene). Only 2-thienyl derivatives are obtained, and in the reaction involving 3-methylthiophene, the α-CH bond of the unsubstituted double bond is regiospecifically activated. This selectivity is not unexpected, being moreover in accord with previous studies carried out with the $(C_5Me_5)Rh(PMe_3)$ system.[11] The thiophene adducts **7** and **8** exist in solution as mixtures of rotamers. As for the reaction leading to **4**, the activation sites of the Me−thiophene substrates have been inferred from the analysis of the PMe_3 derivatives. For 2-methylthiophene the corresponding PMe_3 adduct **9** exists as a mixture of the **AB**:**AA**:**BB** rotamers in a

ratio of 5:2:1 at 25 °C (eq 5), while for complex **10**,



(5)

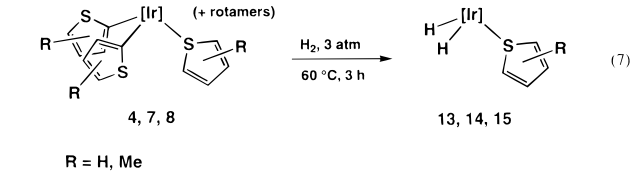
isolated from the reaction of **8** with an excess of trimethylphosphine, this ratio is 5:1.5:1 at 25 °C (eq 6).



(6)

Carbon monoxide also affords similar adducts, **11** and **12**, and these have been characterized only by high-temperature NMR spectroscopy under conditions where the exchange of rotamers is fast compared to the NMR time scale.

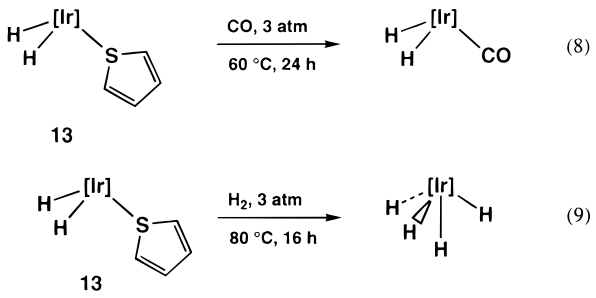
Hydrogenation of the Thiophene−Ir(III) Adducts 4, 7, and 8. When cyclohexane suspensions of complexes **4**, **7**, and **8** are heated at 60 °C under 2 atm of H_2, the new dihydrides $Tp^{Me2}IrH_2(SC_4H_3R)$ (R = H, **13**; 2-Me, **14**; 3-Me, **15**) are formed in >80% yield (eq 7). An analysis of the volatiles produced in the reaction



(7)

leading to **13** revealed the presence of free thiophene, in accord with these hydrides being generated by hydrogenolysis of the Ir−2-thienyl σ bonds. Compounds **13**−**15** have been fully characterized by spectroscopy. The ^1H and $^{13}C\{^1H\}$ NMR spectra, as well as the NOESY experiments, are in accord with the presence of an *S*-bound thiophene ligand in all the cases. As it is evident from the comparative higher thermal stabiliy of these dihydrides, the thiophene ligand of these complexes is more tightly bound than in the parent thienyls. Related thiophene adducts of Ir(III) hydrides have been described in the literature.[10c,d]

Chemical Properties of $Tp^{Me2}IrH_2(SC_4H_4)$ (13). Complex **13** exhibits an interesting reactivity pattern. Dissociation of the thiophene ligand requires heating in solution at 60 °C for ca. 3 h, but decomposition only proceeds to a small extent under these conditions. Upon prolonged heating under CO (60 °C, 3 atm, 24 h) or H_2 (80 °C, 3 atm, 16 h), the SC_4H_4 ligand is irreversibly extruded and the very stable known compounds $Tp^{Me2}IrH_2(CO)$[15d,e,16] and $Tp^{Me2}IrH_4$[15d,e] are obtained in high yields (eqs 8 and 9). Even N_2 can replace the thiophene

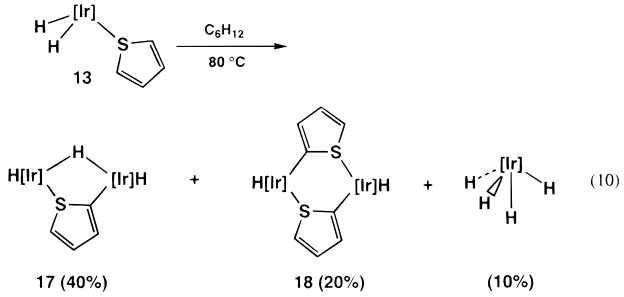


(8)

(9)

ligand of **13** to yield the new dinitrogen species $Tp^{Me2}IrH_2(N_2)$ (**16**). However, the formation of **16** is accompanied by partial decomposition of **13** (see below), and the yields for **16** are usually below 70% (60 °C, 3 atm N_2, 24 h). As we are unable to purify this complex, its characterization relies only in ^1H NMR and IR data ($\nu(N{\equiv}N)$ at ca. 2165 cm^{-1}).[4a,b]

These substitution reactions seem to proceed by the formation of a common 16e "$Tp^{Me2}IrH_2$" intermediate which is eventually trapped either irreversibly (PMe_3 and CO) or reversibly (N_2 and thiophene). Additionally, this proposed Ir(III) unsaturated species seems to play an important role in the photochemistry of $Tp^{Me2}IrH_2$(coe) (coe = cyclooctene).[17] In the absence of an efficient trapping reagent $Tp^{Me2}IrH_2$ appears to be responsible for the thermal decomposition of **13**. Monitoring this transformation by ^1H NMR spectroscopy (C_6D_{12}, 80 °C) reveals that three main species are formed at the expense of **13**. After 8 h only ca. 10% of the starting material remains unaltered, while the two new binuclear species, **17** and **18**, reach concentrations of ca. 40 and 20%, respectively. $Tp^{Me2}IrH_4$ (10%) is also observed along with other minor uncharacterized species (eq 10). Complex **17** has been fully characterized



(10)

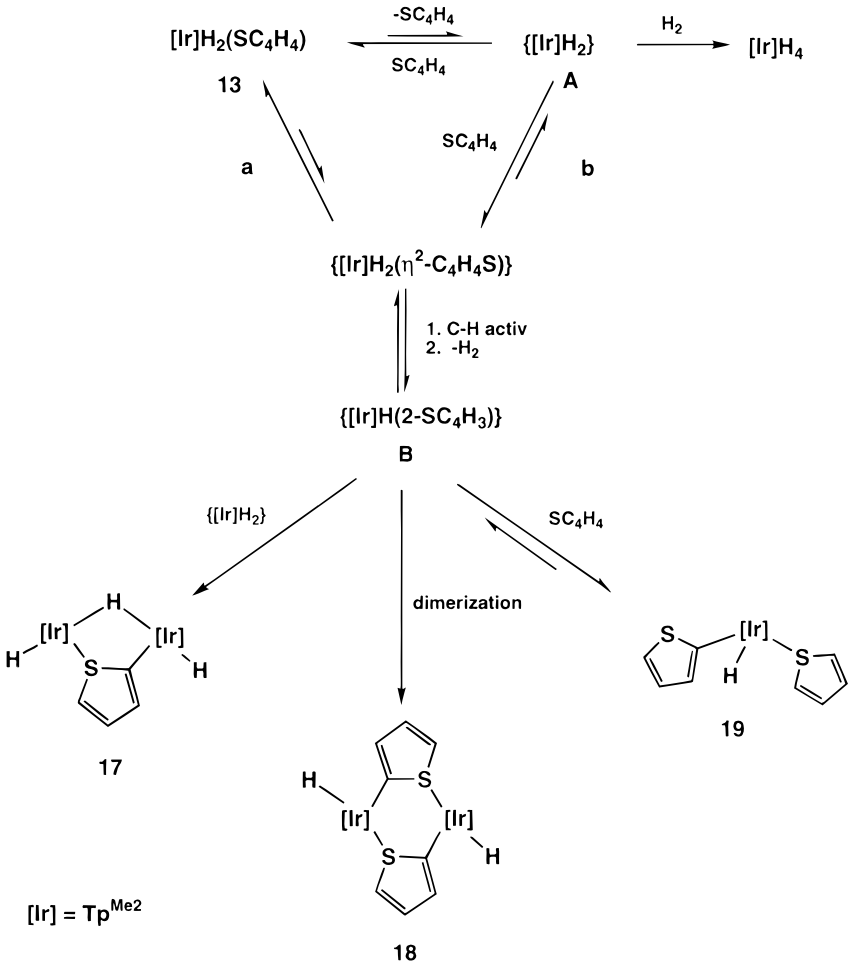
by NMR spectroscopy and by single-crystal X-ray studies to be discussed below. It represents a very rare example of a *C,S*-μ^2-η^1-η^1-thienyl ligand[18] and adds to an interesting series of Cp′-containing dimeric species of iridium that contain a bridging hydride ligand.[19] As for **18**, spectroscopic data are in accord with the symmetric structure shown in eq 10. However despite our efforts we have been unable to prepare it in an analytically pure form.

Scheme 2 presents a plausible mechanism for the thermal decomposition of **13**. An unsaturated species

(17) Ferrari, A.; Polo, E.; Rüegger, H.; Sostero, S.; Venanzi, L. M. *Inorg. Chem.* **1996**, *35*, 1602.

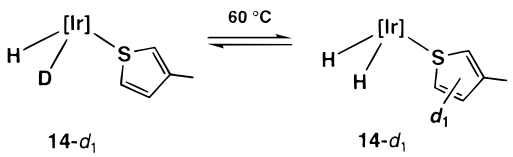
(18) For a different bridging mode of a thienyl ligand see: Waldbach, T. A.; van Eldik, R.; van Rooyen, P. H.; Lotz, S. *Organometallics* **1997**, *16*, 4056.

Scheme 2



B is suggested as an important intermediate in the formation of the binuclear compounds **17** and **18**. If the assumption is made that the C−H activation of thiophene requires π-olefin coordination,[11,12] this purported isomer of **13** could be generated intra- or intermolecularly (routes **a** and **b**, respectively). According to additional experimental data to be presented below, **a** seems to be a lower energy route than **b**. Following C−H activation to give the Ir(V) species $Tp^{Me2}IrH_3(2\text{-}SC_4H_3)$ (**C**), intermediate **B** would form by reductive elimination of H_2, this extruded molecule being seemingly involved in the production of the small amounts of $Tp^{Me2}IrH_4$ detected in this process. It is pertinent to mention in this respect that even when this tetrahydride[15d] is obtained by reacting **13** with H_2, small amounts of the binuclear complex **17** are invariably produced. Recently, a phenyl analogue of **B**, i.e., $Tp^{Me2}IrH(C_6H_5)$, has been proposed to form similarly from $Tp^{Me2}IrH_2$ and C_6H_6.[17] Even though Scheme 2 postulates the reversible formation of the hydride−thienyl complex **19** (vide infra for an alternative generation procedure), it has escaped detection by spectroscopic means even at low conversions.

There is an interesting chemical reaction of **13** that, at variance with those already described, does not apparently involve any unsaturated intermediate. This is the H → D exchange[1] that takes place upon heating this complex in C_6D_6 at 60 °C and that eventually affords $Tp^{Me2}IrD_2(SC_4D_4)$ (**13**-d_6). Interestingly, all the Ir−H and C−H sites become deuterated with approximately the same rate. Quantitative studies carried out with the 3-methylthiophene complex **14**, in which the three C−H bonds of the thiophene ligand are unequivalent in the ^{1}H NMR spectrum, show that at 60 °C the half-lives, $t_{1/2}$, for the exchange are ca. 30 and 40 min for the Ir−H and each of the C−H bonds, respectively. This probably indicates that once a specific H site is occupied by D, a thermodynamic equilibrium, of the type exemplified in eq 11 for the **14**-d_1 species, is



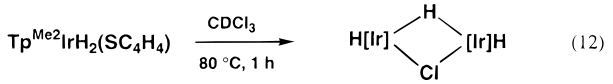
(11)

quickly attained. All the aromatic C−H bonds participate in this exchange reaction that probably occurs through the Ir(V) species $Tp^{Me2}IrH_3(2\text{-}SC_4H_2Me)$ (**C**-Me). By careful integration of the ^{1}H NMR spectra at low and medium conversions, and after correcting for the statistics, the experimental deuterium fractionation factor found for this system is $K_{eq} = 1.5$ with the

(19) See for example: (a) Gomes, T. M.; Matt, D.; Braunstein, P. *Coord. Chem. Rev.* **1989**, *96*, 49. (b) McGhee, W. D.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8428. (c) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502. (d) Fernández, M. J.; Maitlis, P. M. *Organometallics* **1983**, *2*, 164. (e) Maitlis, P. M. *Coord. Chem. Rev.* **1982**, *43*, 377. (f) Burns, C. J.; Rutherford, N. M.; Berg, D. J. *Acta Crystallogr.* **1987**, *C43*, 229. (g) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1977**, *16*, 1488. (h) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

expected preferential occupation of the aromatic sites by the deuterium atoms.[20] As the intramolecular D exchange is faster than the intermolecular one with C_6D_6, no information is available regarding which H site is activated first by C_6D_6, nor about the individual intramolecular exchange rates. The deuteration rate for **14** measured at 60 °C does not change appreciably by the addition of 4 equiv of SC_4H_3-3-Me, and moreover the free thiophene does not participate in any exchange process under these experimental conditions (both these facts are against the participation of the unsaturated species $Tp^{Me2}IrH_2$, **A** in the H → D exchange at 60 °C). Only at 80−90 °C do the bound and the free thiophene start exchanging at a measurable rate, with **A** as the proposed intermediate. As a result, complex **14** acts as a catalyst for the deuterium exchange between C_6D_6 and SC_4H_3-3-Me. Under these forcing conditions even the Me group of the thiophene slowly deuterates. Unfortunately, the slow decomposition of complexes **13** and **14** at the temperatures needed for the thiophene exchange reduces greatly the practical use of these catalysts. With respect to the intermolecular mechanism of the deuteration reaction we believe that the Ir(V) species $Tp^{Me2}IrH_3$(*σ*-thienyl) is the actual species undergoing the exchange with C_6D_6, as it is known that $Tp^{Me2}IrH_4$ also experiences a similar process.[15e] No other evidence is however available to support this contention. If this hypothesis is correct, it follows that species of the type $Tp^{Me2}IrH_3R$ are able to exchange its hydrides by the D of C_6D_6 only when R = H and Ar but not when R is the more electron-releasing $SiEt_3$ group.[15e]

Finally in what concerns this chemistry a different binuclear species **20** is formed in high yields when complex **13** is allowed to decompose in $CDCl_3$ at 80 °C (eq 12). We propose that its formation is the result of



(12)

13 **20**

the collapse of the unsaturated fragments $Tp^{Me2}IrHCl$ and $Tp^{Me2}IrH_2$, and this is in agreement with the known chlorination of $Tp^{Me2}IrH_2(PR_3)$ to $Tp^{Me2}IrHCl(PR_3)$ species in $CDCl_3$.[16] As the reaction shown in eq 12 is very clean, the proposed $Tp^{Me2}IrHCl$ must be a very good trapping reagent for $Tp^{Me2}IrH_2$ and consequently supresses the formation of intermediate **B** of Scheme 2.

The structure of the binuclear, hydride-bridged complex **17** has been solved by X-ray crystallography. Figure 2 shows an ORTEP view of its molecules. Table 2 compiles the more important bond distances and angles. As can be seen, the two $Tp^{Me2}Ir(H)$ moieties are bridged by a hydride and by a 2-thienyl fragment, the latter acting as an η^2-ligand, *C*- and *S*-bound, respectively, to the two Ir atoms. To our knowledge this is an unprecedented coordination for a 2-thienyl ligand. Due to the positional disorder that involves the activated thiophene ring, the refinement of the structure has been carried out in the *C*2/*c* group, with constrained populations

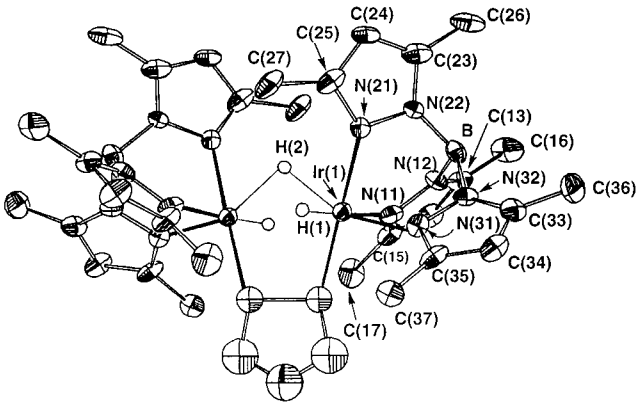


Figure 2. X-ray structure of complex **17**.

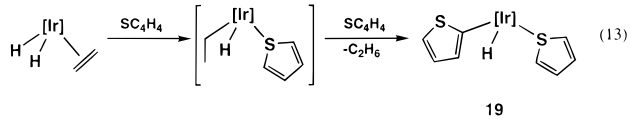
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 17

Ir(1)−S(1)	2.281(9)	H(1)−Ir(1)	1.70(0)
Ir(1)−N(11)	2.24(1)	H(2)−Ir(1)	1.91(17)
Ir(1)−N(21)	2.06(1)	Ir(1)−Ir(1′)	3.066(1)
Ir(1)−N(31)	2.05(1)		

H(1)−Ir(1)−H(2)	84.94(4)	S(1)−Ir(1)−N(31)	100.6(4)
H(2)−Ir(1)−N(31)	154.6(3)	S(1)−Ir(1)−N(21)	171.7(4)
H(2)−Ir(1)−N(21)	69.3(3)	Ir(1)−H(2)−Ir(1′)	106(13)
H(2)−Ir(1)−N(11)	95.0(3)	Ir(1)−N(21)−C(25)	135(1)
H(2)−Ir(1)−S(1)	104.8(2)	Ir(1)−N(21)−N(22)	119.0(8)
H(1)−Ir(1)−N(31)	93.3(3)	S(1)−Ir(1)−N(11)	84.2(4)
H(1)−Ir(1)−N(21)	89.5(3)	Ir(1)−S(1)−C(1)	133(1)
H(1)−Ir(1)−N(11)	179.9(3)	Ir(1)−N(11)−C(15)	141(1)
H(1)−Ir(1)−S(1)	95.9(2)	Ir(1)−N(11)−N(12)	113.0(8)
N(21)−Ir(1)−N(31)	85.4(5)	Ir(1)−N(31)−C(35)	133(1)
N(11)−Ir(1)−N(31)	86.8(5)	Ir(1)−N(31)−N(32)	118.3(8)
N(11)−Ir(1)−N(21)	90.5(5)		

factors of 0.5 for the C(4) and the S(1) atoms both in the same position. For this reason, an analysis of the bond lengths of this fragment does not seem appropriate. The bridging hydride atom was located in a final Fourier difference synthesis at a distance of 1.91(17) Å from each Ir center. The complex is best described as an Ir(III)−Ir(III) system, and it is characterized by an Ir−Ir distance of 3.066(1) Å. This compares well with the corresponding distances found in other Ir(*μ*-H)Ir complexes.[19] For example, in the compound {[Cp*IrCl]$_2$(*μ*-H)(*μ*-Cl)},[19g] which has also a single hydride bridge, the Ir−Ir separation amounts to 2.903(1) Å. As in the latter compound, the IrHIr moiety of **20** forms a two-electron three-center bond that involves significant Ir−Ir bonding interaction.[19h]

Reaction of $Tp^{Me2}IrH_2(C_2H_4)$ with Thiophene. Recent work from our group has shown that the complex $Tp^{Me2}IrH_2(C_2H_4)$[16] is able to activate a variety of C−H bonds through the intermediacy of the 16e Ir(III) species $Tp^{Me2}IrH(CH_2CH_3)$.[4b] Thiophene can be activated similarly at temperatures close to 80 °C to give the new species **19** in almost quantitative yield (eq 13). As



(13)

19

observed for other *σ*-thienyl derivatives described in this work, at 25 °C complex **19** also exhibits restricted rotation around the Ir−C bond, on the NMR time scale. However NMR spectroscopic studies in the fast ex-

(20) (a) Rashidi, M.; Puddephat, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 7111. (b) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246. (c) Casey, C. P.; Hallenbeck, S. L.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4607.

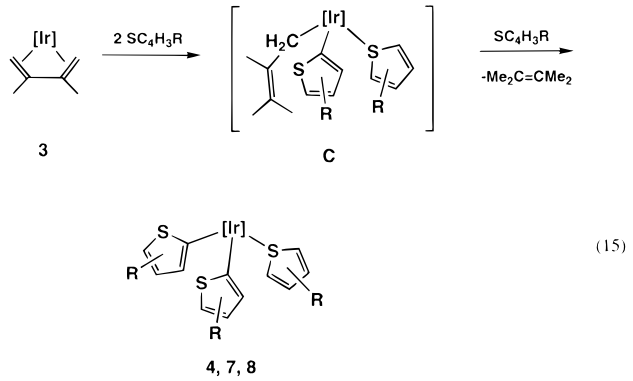
change regime (>50 °C) are severely limited by the fast dissociation of the coordinated thiophene and also by the conversion of this compound (≥70%) into the binuclear species **18**. It is clear from our data that the facility of thiophene dissociation in the series of $Tp^{Me2}IrR_2$(thiophene) complexes (R = H, 2-thienyl) increases in the order **4** > **19** > **13**, i.e., with the steric crowding around the Ir center.

Complex **19** reacts also with Lewis bases (PMe_3, CH_3CN) with formation of the corresponding adducts **21** (PMe_3) and **22** (CH_3CN) (eq 14). Interestingly,

(14)

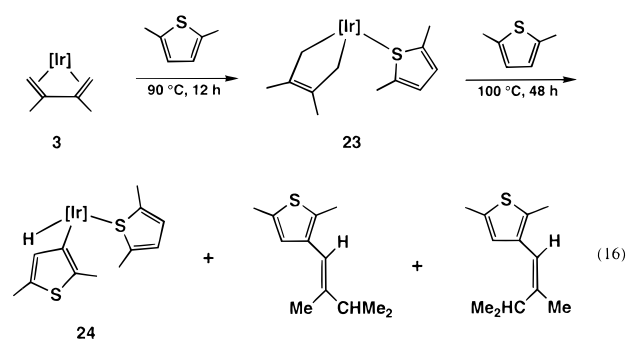
compound **21** is very thermally stable and does not rearrange (170 °C) to the isomeric compound $Tp^{Me2}Ir$(SCHCHCHCH)(PMe_3), resulting from thiophene C−S bond breaking. Whether this is due to thermodynamic or kinetic effects remains unknown.

Reaction of $Tp^{Me2}(\eta^4$-$CH_2C(Me)C(Me)CH_2)$ (3) with Thiophene and Monomethylthiophenes. Complex **3** reacts with thiophene substrates at 60−80 °C with clean formation of the already described bis(thienyl) complexes **4**, **7**, and **8** (eq 15). This behavior



(15)

contrasts with the reported thermal activation (120 °C) of C_6H_6 by **3** that gives the Ir(III) hydride species $[Tp^{Me2}IrH(C_6H_5)]_2(N_2)$.[5] It may be suggested that for these thiophenes two consecutive α-C−H activations take place, as shown in eq 15. Why C_6H_6 behaves differently in its reaction with **3** is not clear at the present stage. The bulkier 2,5-dimethylthiophene affords (100 °C, 48 h) a related hydride−thienyl complex **24** with concomitant formation of thienyl-substituted olefins (eq 16). In this case, a thiophene adduct intermediate **23** can be detected and shown to possess an unusual 2e donor σ,σ-bonded butadienyl ligand.[21] Complex **23** is formed almost selectively under less drastic experimental conditions (90 °C, 12 h). A careful reexamination of the reaction of **3** with C_6H_6 has now revealed the formation of related phenyl−olefins (rather than dimethylbutadiene as erroneously stated in ref 5), but the mechanism of these reactions is presently unknown.



(16)

Experimental Section

General Procedures. Microanalyses were by the Microanalytical Service of the University of Sevilla. Within series of similar complexes only one representative example has been subjected to microanalysis. Infrared spectra were obtained from Perkin-Elmer spectrometers, models 577 and 684. The NMR instruments were Bruker AMX-500, Bruker DRX-400, and Bruker AMX-300 spectrometers. Spectra are referenced to external $SiMe_4$ ($\delta = 0$ ppm) using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). For $^{31}P\{^1H\}$ NMR spectroscopy, 85% PO_4H_3 is used as the reference. Spectra 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 $Tp^{Me2}Ir(C_2H_4)_2$,[4c] $Tp^{Me2}IrH(CH{=}CH_2)(C_2H_4)$,[4c] $Tp^{Me2}Ir(CH_2C(Me)C(Me)CH_2)$,[5] and $Tp^{Me2}IrH_2(C_2H_4)$[16] were obtained by published procedures. The thiophenes were freshly distilled and degassed before use.

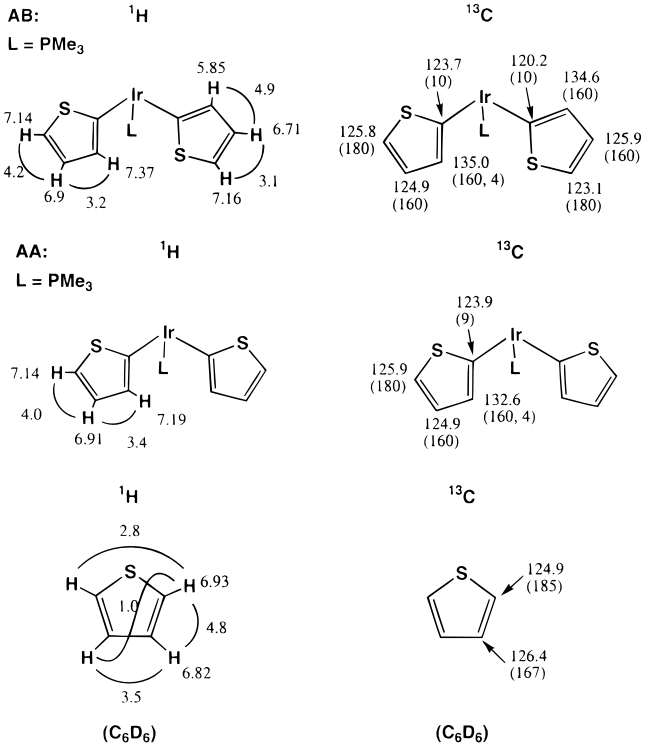
$Tp^{Me2}Ir(2\text{-}SC_4H_3)_2(SC_4H_4)$ (4). A stirred suspension of complex **1** (0.65 g, 1.2 mmol) in thiophene (13 mL) was heated at 60 °C in a Teflon-sealed ampule for 5 h. The resulting yellow-brown solution was slowly cooled to room temperature and left aside for 2 days; 0.21 g of big, well formed, yellow-green crystals were obtained. The filtrate was concentrated and cooled to −20 °C to provide another crop (0.32 g) of complex **4** as a microcrystalline solid. Total yield: 80%. Anal. Calcd for **4**: C, 43.8; H, 4.4; N, 11.4. Found: C, 44.6; H, 4.5; N, 11.0. This complex could not be recrystallized without decomposition and was used in subsequent reactions in this crude form.

Reaction of 1 with Tetrahydrothiophene. When complex **1** (0.21 g, 0.4 mmol) is heated in 2 mL of C_6H_{12} containing 0.2 mL of SC_4H_8 (24 h, 60 °C), the adduct $Tp^{Me2}Ir(CH{=}CH_2)(C_2H_5)(SC_4H_8)$ could be obtained in 50% yield after crystallization from petroleum ether/CH_2Cl_2 (5:1). ^1H NMR (C_6D_6, 25 °C): δ 8.69 (dd, 1 H, $^3J_{AC} = 18.0$, $^3J_{AB} = 10.3$ Hz, H_A), 6.26 (dd, 1 H, $^2J_{BC} = 3.2$ Hz, H_B), 5.74, 5.68, 5.56 (s, 1 H each, 3 CH_{pz}), 5.08 (dd, 1 H, H_C), 2.94, 2.70 (dq, 1 H each, $^2J_{HH} = 12.1$, $^3J_{HMe} = 7.3$ Hz, $IrCH_2$), 2.59, 2.49, 2.28, 2.22, 2.20, 2.07 (s, 3 H each, 6 Me_{pz}), 2.55, 2.20 (m, 4 H each, $S[CH_2CH_2]_2$), 0.96 (t, 3 H, $IrCH_2\mathit{Me}$).$^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 151.2, 150.4, 149.6, 142.9, 142.9, 142.4 (C_{qpz}), 136.6 ($IrCH_A$), 118.7 ($IrCH{=}\mathit{C}H_2$), 107.7, 107.1, 106.6 (CH_{pz}), 32.9, 27.9 (SCH_2CH_2), 16.1 ($IrCH_2\mathit{Me}$), 14.4, 14.2, 13.2, 12.8, 12.5, 12.4 (Me_{pz}), −12.8 ($IrCH_2$). Anal. Calcd for $C_{23}H_{38}BN_6SIr$: C, 42.4; H, 5.8; N, 12.7. Found: C, 42.2; H, 5.8; N, 12.7.

$Tp^{Me2}Ir(2\text{-}SC_4H_3)_2(PMe_3)$ (5). Complex **4** (0.52 g, 0.7 mmol) was suspended in benzene (25 mL) and an excess of PMe_3 added via syringe (5 mL of a 1 M solution in C_6H_{12}). The resulting mixture was stirred at room temperature for 16 h

(21) (a) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.*, in press. (b) Barker, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1839. (c) Gausing, W.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 186. (d) Bleeke, J. R.; Behm, R. *J. Am. Chem. Soc.* **1997**, *119*, 8503.

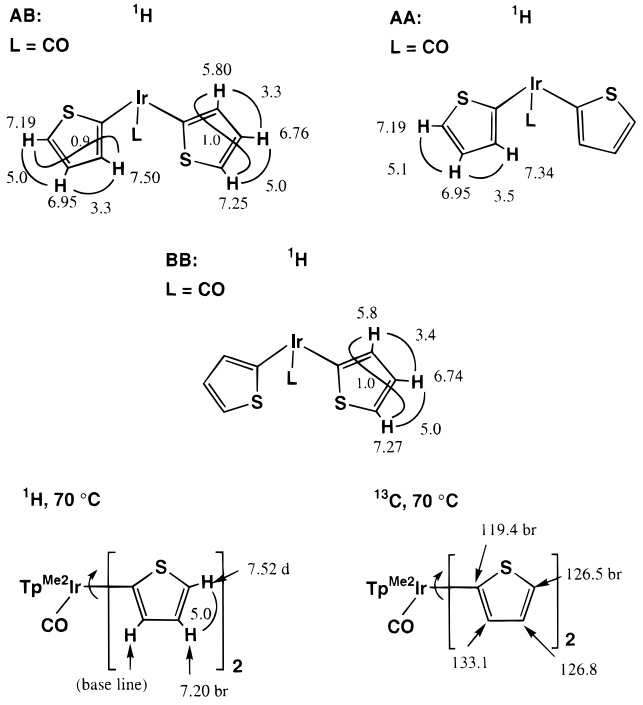
and evaporated to dryness. Crystallization of the residue from Et_2O/petroleum ether afforded the title compound in 75% yield. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ −52.0 (s), −52.1 (s), −52.3 (s) in a 4:2:1 ratio. Anal. Calcd for **5**: C, 42.7; H, 5.1; N, 11.5. Found: C, 42.4; H, 5.4; N, 11.1. The ^1H and $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) data for the thienyl ligands in the two main rotamers are presented below in a schematic form along with the corresponding data for free thiophene (C_6D_6). The values in parentheses that accompany the ^{13}C chemical shift data are the $^1J_{CH}$ and/or J_{CP} coupling constants.



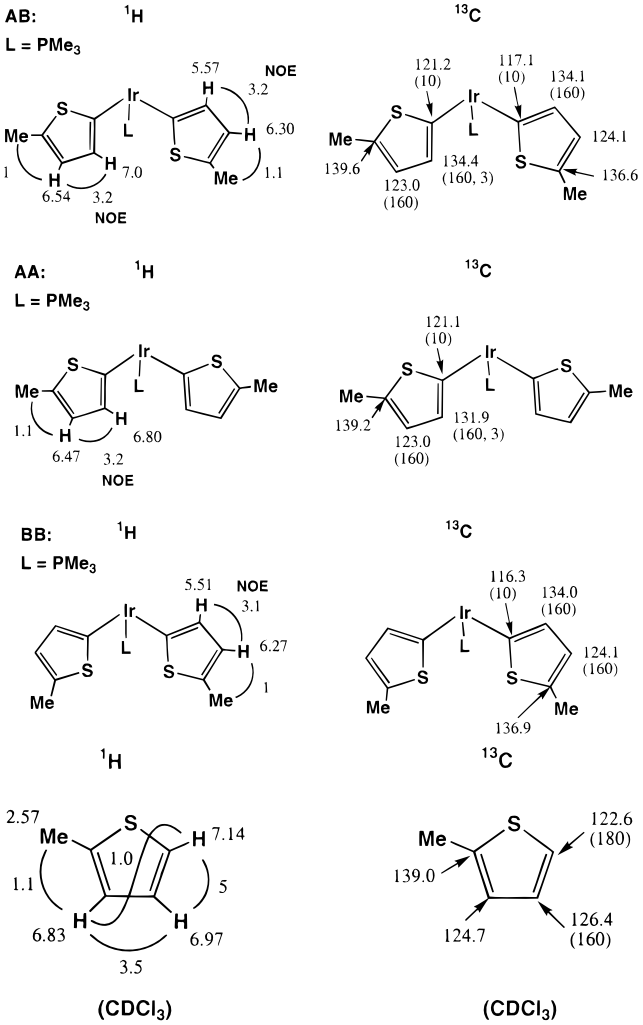
$Tp^{Me2}Ir(2\text{-}SC_4H_3)_2(CO)$ (6). A suspension of complex **4** (0.37 g, 0.5 mmol) in cyclohexane (50 mL) was placed in a Fisher-Porter vessel. The stirred mixture was heated under 3 atm of CO at 60 °C for 2 h. The volatiles were evaporated under vacuum and the pale blue residue crystallized from petroleum ether to produce compound **6** in ca. 90% yield. Monocrystals of **6** suitable for X-ray studies were obtained from the slow evaporation of benzene solutions at 25 °C. IR (Nujol): ν(CO) 2045 cm^{-1}. Anal. Calcd for **6**: C, 42.2; H, 4.1; N, 12.3. Found: C, 42.5; H, 3.9; N, 12.6. ^1H NMR (CD_2Cl_2, −40 °C): Three rotamers in a 4:2:0.5 ratio. A schematic representation of the data corresponding to the thienyl ligands of these species is shown below. Also represented are the data for **6** obtained at 70 °C (CD_2Cl_2/C_6D_6, 5:1). Other resonances recorded also at this temperature are as follows. ^1H NMR: δ 6.05 (s, 2 H, 2 CH_{pz}), 6.04 (s, 1 H, CH_{pz}), 2.71 (s, 3 H, Me), 2.69 (s, 6 H, 2 Me), 2.02 (s, 6 H, 2 Me), 1.48 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR: 166.1 (CO), 154.6 152.4, 144.6, 144.3 (1:2:2:1 ratio, C_{qpz}), 108.5, 107.6 (1:2 ratio, CH_{pz}), 14.5, 13.5, 12.7, 12.4 (1:2:1:2 ratio, 6 Me).

$Tp^{Me2}Ir(2\text{-}SC_4H_2Me)_2(SC_4H_3Me)$ (7 and 8). These complexes were obtained following a procedure similar to that described above for **4**. Yield: >80%.

$Tp^{Me2}Ir(2\text{-}SC_4H_2\text{-}5\text{-}Me)_2(PMe_3)$ (9). Complex **7** was reacted with PMe_3 in the manner described above for the synthesis of **5**. Yield: 50−60%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ −54.0 (s), −54.1 (s), −54.1 (s) in a 5:2:1 ratio. The ^1H and ^{13}C NMR ($CDCl_3$, 25 °C) for the thienyl ligands in the three rotamers are presented below in a schematic form along with the corresponding data for free 2-SC_4H_3Me ($CDCl_3$). The values

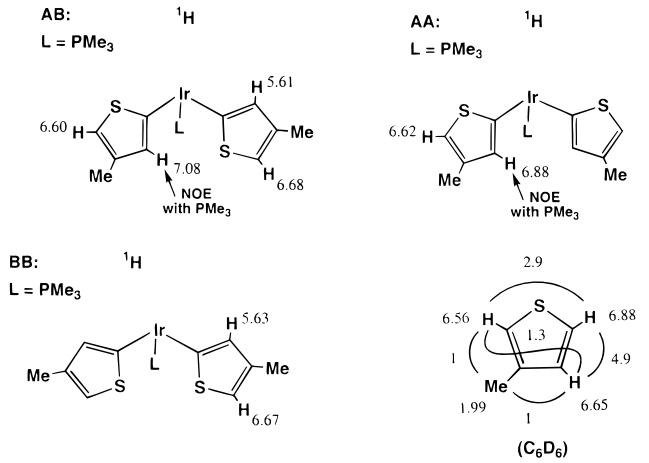


in parentheses that accompany the ^{13}C chemical shift data are the $^1J_{CH}$ and/or J_{CP} coupling constants.

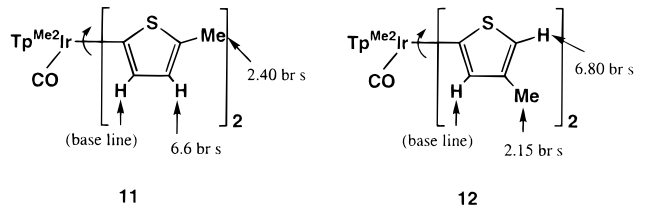


$Tp^{Me2}Ir(2\text{-}SC_4H_2\text{-}4\text{-}Me)_2(PMe_3)$ (10). This complex was obtained from **8** and PMe_3 in ca. 60% yield. $^{31}P\{^1H\}$ NMR

($CDCl_3$, 25 °C): δ −54.0 (s), −54.7 (s), −53.6 (s) in a 5:1.5:1 ratio. The ^{1}H NMR ($CDCl_3$, 25 °C) for the thienyl ligands in the three rotamers are presented below in a schematic form along with the corresponding data for free 3-SC_4H_3Me (C_6D_6).



$Tp^{Me2}Ir(2\text{-}SC_4H_2Me)_2(CO)$ (11 and 12). These complexes were obtained from **7** and **8**, respectively, by treatment with CO (3 atm) at 60 °C. Data for **11**: IR (Nujol): ν(CO) 2040 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 95 °C): δ 5.59 (s, 1 H, CH_{pz}), 5.55 (s, 2 H, 2 CH_{pz}), 2.23, 2.22, 1.84, 1.49 (s, 1:2:2:1 ratio, 6 Me_{pz}). The data corresponding to the thienyl ligands are shown schematically below. Data for **12**: IR (Nujol): ν(CO) 2044 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 95 °C): δ 5.60 (s, 1 H, CH_{pz}), 5.55 (s, 2 H, 2 CH_{pz}), 2.21, 1.81, 1.44 (s, 3:2:1 ratio, 6 Me_{pz}). The data corresponding to the thienyl ligands are shown schematically below.



$Tp^{Me2}IrH_2(SC_4H_3R)$ (R = H, 13; 2-Me, 14; 3-Me, 15). All these complexes were obtained in a similar manner. A representative procedure follows: Complex **4** (0.95 g, 1.3 mmol) was suspended in C_6H_{12} (70 mL), transferred to a Fischer−Porter bottle, and pressurized with H_2 (3 atm). After heating with stirring (60 °C, 3 h) the volatiles were removed in vacuo and the residue washed with cold (0 °C) petroleum ether and dried. This crude material (85% yield) is sufficiently pure for most purposes. A microcrystalline sample can be obtained by recrystallization from Et_2O/petroleum ether mixtures. Data for **13**: IR (Nujol): ν(IrH) 2141, 2123 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 7.08, 6.55 (AA′XX′ spin system, 2 H, 2 H, SC_4H_4), 5.72 (s, 2 H, 2 CH_{pz}), 5.64 (s, 1 H, CH_{pz}), 2.37, 2.29, 2.13, 2.04 (s, 2:1:1:2 ratio, 6 Me), −20.41 (s, 2 H, 2 IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 150.9, 150.6, 143.1, 142.5 (2:1:2:1 ratio, C_q), 136.9, 128.2 (1:1 ratio, SC_4H_4), 105.4, 105.2 (2:1 ratio, CH_{pz}), 17.8, 14.2, 12.4, 12.1 (1:2:1:2 ratio, Me). Anal. Calcd for $C_{19}H_{28}BN_6SIr$: C, 39.6; H, 4.9; N, 14.6. Found: C, 40.0; H, 4.8; N, 14.7.

Data for 14. IR (Nujol): ν(IrH) 2122 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 6.96, 6.50, 6.42 (br, dd, br, 1 H each, J_{HH} = 5.2, 3.8 Hz, SC_4H_3Me), 5.69 (s, 2 H, 2 CH_{pz}), 5.47 (s, 1 H, CH_{pz}), 2.37, 2.29, 2.13, 2.04 (s, 1:2:1:2 ratio, 6 Me_{pz}), 1.39 (br s, 3 H, SC_4H_3*Me*), −20.51 (s, 2 H, 2 IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 150.8, 150.5, 143.0, 142.5 (2:1:2:1 ratio, C_{qpz}), 149.9 (C_{qth}), 128.8, 128.8 (CH_{th}), 105.3, 105.1 (2:1 ratio, CH_{pz}), 26.9 (Me_{th}), 17.8, 14.1, 12.4, 12.2 (1:2:1:2 ratio, 6 Me_{pz}).

Data for 15. IR (Nujol): ν(IrH) 2124, 2104 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 7.08 (dd, 1 H, J_{HH} = 5.1, 2.7 Hz, $H^4{}_{th}$), 6.60 (m, dd upon {Me_{th}} decoupling, 1 H, J_{HH} = 2.7, 1.1 Hz, $H^2{}_{th}$), 6.41 (dd, 1 H, J_{HH} = 5.1, 1.1 Hz, $H^3{}_{th}$), 5.74 (s, 2 H, 2 CH_{pz}), 5.47 (s, 1 H, CH_{pz}), 2.39, 2.30, 2.13, 2.10 (s, 1:2:1:2 ratio, 6 Me_{pz}), 1.66 (d, 3 H, J_{HH} = 0.9 Hz, SC_4H_3*Me*), −20.52 (s, 2 H, 2 IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 150.9, 150.6, 143.1, 142.4 (2:1:2:1 ratio, C_{qpz}), 139.5 (C_{qth}), 138.4, 131.9, 127.5 (3 CH_{th}), 105.4, 105.1 (2:1 ratio, CH_{pz}), 18.8 (Me_{th}), 15.7, 14.3, 12.4, 12.1 (1:2:1:2 ratio, 6 Me_{pz}).

Reactions of $Tp^{Me2}IrH_2(SC_4H_4)$ (13) with CO or H_2. A solution of complex **13** in C_6H_{12} was pressurized (3 atm) with CO or H_2. After heating (60 °C, 20 h, CO; 80 °C, 16 h, H_2), the resulting mixture was taken to dryness. NMR analysis of the corresponding residues showed almost quantitative formation of the known $Tp^{Me2}IrH_2(CO)$ or $Tp^{Me2}IrH_4$ derivatives, respectively.[15d,e,16]

$Tp^{Me2}IrH_2(N_2)$ (16). A solution of complex **13** (0.09 gr, 0.15 mmol) was dissolved in C_6H_{12} (20 mL) and pressurized with N_2 (3 atm). After heating at 60 °C for 20 h, the volatiles were removed in vacuo. A ^{1}H NMR spectrum of the residue revealed ca. 60% conversion into **16**. IR (Nujol) ν(N≡N) 2165 cm^{-1}, ν(IrH) 2140, 2127 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.83 (s, 2 H, 2 CH_{pz}), 5.70 (s, 1 H, CH_{pz}), 2.38, 2.29, 2.28, 2.13 (s, 2:2:1:1 ratio, 6 Me), −18.76 (s, 2 H, 2 IrH). This complex could not be obtained spectroscopically pure.

$[Tp^{Me2}IrH]_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-}C,S\text{-}SC_4H_3)$ (17) and $[Tp^{Me2}IrH]_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-}C,S\text{-}SC_4H_3)_2$ (18). The dihydride **13** (0.90 g, 1.5 mmol) in C_6H_{12} (45 mL) was heated at 80 °C for 8 h. ^{1}H NMR analysis of an aliquot revealed 40% of unreacted **13** along with 40% of **17** and 15% of **18**. Further heating showed a significant growing of other unidentified products. A sample of pure, red, crystalline **17** was obtained as a byproduct in the reaction of **13** with H_2 (see above). After extraction of the crude $Tp^{Me2}IrH_4$ with cold methanol a red solution resulted from which complex **17** could be crystallized from Et_2O in <10% yield.

Data for 17. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.07 (d, 1 H, J_{HH} = 5.1 Hz, CH_{th}), 7.02 (dd, 1 H, J_{HH} = 4.9, 3.1 Hz, CH_{th}), 6.59 (d, 1 H, J_{HH} = 3.1 Hz, CH_{th}), 5.86, 5.72, 5.69, 5.68, 5.55, 5.45 (s, 1 H each, CH_{pz}), 3.11, 2.47, 2.36, 2.34, 2.33, 2.31, 2.22, 2.13, 2.05, 1.25, 1.01 (s, 12 Me), −23.23 (d, 1 H, J_{HH} = 4.1 Hz, IrH), −24.94 (d, 1 H, IrH), −30.76 (t, 1 H, IrHIr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 153.7−142.5 (12 C_{qpz}), 132.7 (C_{qpz}), 135.5, 132.4, 131.1 (CH_{th}), 107.8−105.0 (6 CH_{pz}), 16.3−12.4 (12 Me), IrC not observed. Anal. Calcd for **17**: C, 38.3; H, 4.7; N, 15.8. Found: C, 37.9; H, 4.8; N, 15.3.

Data for 18. ^{1}H NMR (C_6D_6, 25 °C): δ 6.70 (d, 1 H, J_{HH} = 5.3 Hz, CH_{th}), 6.56 (dd, 1 H, J_{HH} = 5.3, 3.5 Hz, CH_{th}), 6.41 (d, 1 H, J_{HH} = 3.5 Hz, CH_{th}), 5.83, 5.72, 5.50 (s, 1 H each, 3 CH_{pz}), 2.84, 2.36, 2.23, 2.13, 1.96, 1.53 (s, 6 Me).

$Tp^{Me2}IrH(2\text{-}SC_4H_3)(SC_4H_4)$ (19). A solution of $Tp^{Me2}IrH_2(C_2H_4)$ (0.4 g, 0.77 mmol) in thiophene (7 mL) was heated, with stirring, at 60 °C for 18 h. The solvent was evaporated in vacuo to afford complex **19** in almost quantitative yield. IR (Nujol): ν(IrH) 2150 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 7.42, 7.09, 6.70 (m, m, m, 1 H each, CH_{th}), 7.19, 6.54 (AA′XX′ spin system, 2 H each, SC_4H_4), 5.78, 5.55, 5.43 (s, 1 H each, CH_{pz}), 2.29, 2.19, 2.07, 1.94, 1.89, 1.58 (s, 6 Me), −19.72 (s, 1 H, IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 152.2, 151.7, 151.6, 143.5, 143.1, 142.9 (6 C_{qpz}), 135.0, 129.9 (SC_4H_4), 126.9, 126.6, 126.0 (CH_{th}), 106.9, 106.5, 105.4 (CH_{pz}), 15.1, 14.1, 13.5, 12.4, 12.2, 12.1 (6 Me). Anal. Calcd for $C_{23}H_{30}BIrS_2N_6$: C, 42.0; H, 4.6; N, 12.8. Found: C, 41.8; H, 4.8; N, 12.7.

$[Tp^{Me2}IrH]_2(\mu\text{-}H)(\mu\text{-}Cl)$ (20). Complex **13** (0.14 g, 0.24 mmol) was dissolved in $CDCl_3$ (0.8 mL) and heated at 80 °C for 30 min. NMR monitoring indicated complete transformation into **20**. A signal due to $CDHCl_2$ was also apparent. The solvent was evaporated and the oily residue crystallized from pentane at −20 °C. Yield of brown microcrystals: 47%. IR (Nujol): ν(IrH) 2308, 2260 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.75, 5.72, 5.69 (s, 1 H each, CH_{pz}), 2.76, 2.42, 2.41, 2.36, 2.25, 1.55 (s, 6 Me), −27.34 (d, 2 H, J_{HH} = 4.3 Hz, 2 IrH), −28.65 (t, 1 H, IrHIr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 153.1, 152.5, 151.5, 143.4, 142.9, 142.8 (C_{qpz}), 107.8, 105.8, 105.5 (CH_{pz}), 16.8, 15.7, 13.5, 12.8, 12.7, 12.6 (6 Me). Anal. Calcd for $C_{30}H_{47}B_2ClN_{12}Ir_2\cdot 0.5C_5H_{12}$: C, 37.0; H, 4.5; N, 16.0. Found: C, 37.5; H, 4.8; N, 16.1.

Table 3. Crystal and Structure Refinement Data for Complexes 6 and 17

compound	**6**	**17**
formula	$C_{24}H_{28}BN_6OS_2Ir\cdot C_6H_6$	$C_{34}H_{50}B_2N_{12}SIr_2$
mol wt	761.8	1064.9
cryst syst	monoclinic	monoclinic
space group	$P2_1/m$	$C2/c$
a (Å)	10.432(3)	19.955(6)
b (Å)	19.033(2)	13.310(3)
c (Å)	8.159(3)	15.677(3)
β (deg)	104.21(2)	107.42(2)
Z	2	4
V (Å^3)	1570.4(8)	3972(2)
ρ_{calcd} (g cm^{-3})	1.61	1.78
$F(000)$	756	2064
temp (°C)	22	−100
diffractometer	Enraf-Nonius	Enraf-Nonius
radiation	graphite-monochromated Mo $K\alpha$	
wavelength (Å)	0.710 69	0.710 69
linear abs coeff μ (cm^{-1})	43.9	67.6
cryst size (mm)	0.20 × 0.25 × 0.15	0.5 × 0.2 × 0.15
θ limits (deg)	1−28	1−28
scan technique	$\omega/2\theta$	$\omega/2\theta$
octants collected	(−13, 0, 0) to (13, 25, 10)	(−26, 0, 0) to (26, 17, 20)
no. of unique data	3906	4783
no. of obsd data, (I) $2\sigma(I)$	3223	2623
R_{int}(%)	5.0	5.5
decay	≤6%	≤1%
standard reflns	3/128	2/58
weighting scheme	unit	unit
$R = \sum\|\Delta F/\sum\|F_0\|$	3.6	5.2
$R_w = (\sum w\Delta^2 F/\sum w\|F_0\|^2)^{1/2}$	4.1	6.0
goodness of fit	0.98	1.01
max shift/error	0.04	0.05
abs corr range	0.98−1.02	0.82−1.26

Tp^{Me2}IrH(2-SC$_4$H$_3$)(PMe$_3$) (21) and Tp^{Me2}IrH(2-SC$_4$H$_3$)(CH$_3$CN) (22). Complex **19** (0.15 g, 0.23 mmol) was dissolved in CH_3CN (10 mL) and heated at 60 °C for 3 h. The solvent was evaporated, and upon addition of pentane, a pale green sample of analytically pure **22** precipitated. Cooling the mother liquors provided another crop of material. Yield: 80%. Complex **21** was prepared following a similar procedure, using an excess of PMe_3 as reagent (0.2 mL, 2 mmol) in cyclohexane (10 mL). Yield: 60%.

Data for 21. IR (Nujol): ν(IrH) 2183 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.59 (d, 9 H, J_{HP} = 9.6 Hz, PMe_3), −21.74 (d, 1 H, J_{HP} = 75.7 Hz, IrH). Other resonances are broad, due to rotameric exchange, and not reported. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 132.7, 126.5, 124.4 (br, CH_{th}), 17.7 (d, J_{CP} = 38 Hz, PMe_3); IrC not observed. Anal. Calcd for **21**: C, 40.7; H, 5.4; N, 12.9. Found: C, 40.7; H, 5.2; N, 12.1.

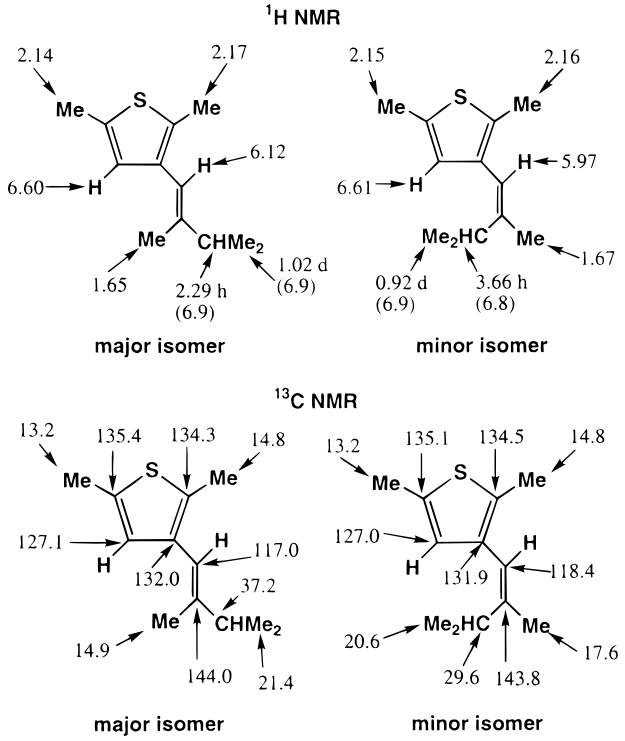
Data for 22. IR (Nujol): ν(C≡N) 2285, ν(IrH) 2183 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 7.51, 7.50, 7.18 (br, 1 H each, CH_{th}), 5.82, 5.71, 5.49 (s, 1 H each, CH_{pz}), 2.36, 2.28, 2.22, 2.12, 2.00. 1.99 (2, 3 H each, 6 Me), 0.76 (s, 3 H, CH_3CN), −19.42 (s, 1 H, IrH). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 162.4 (CH_3CN), 152.2, 150.5, 150.4, 143.7, 143.1, 143.0 (C_{qpz}), 130.9, 126.8, 124.1 (CH_{th}), 106.6, 106.2, 105.9 (CH_{pz}), 16.1, 15.6, 13.9, 13.7, 13.3, 13.2 (6 Me), 4.65 (CH_3CN); IrC not observed. Anal. Calcd for **22**: C, 41.0; H, 4.7; N, 15.9. Found: C, 41.3; H, 4.9; N, 15.2.

Tp^{Me2}IrH(3-SC$_4$H-1,4-Me$_2$)(2,5-SC$_4$H$_2$Me$_2$) (24). To complex **3** (0.21 g, 0.38 mmol) was added 2,5-$SC_4H_2Me_2$ (2 mL) and the mixture stirred for 48 h at 100 °C. The solvent was evaporated, and a NMR analysis of the residue showed quantitative transformation into complex **24**, with concomitant formation of aryl−olefin species. Complex **24** was purified by precipitation with pentane (yield 70%). The decanted solution obtained was cromatographed through a silica gel column to yield a pure mixture of the organic compounds. Complex **24** can also be prepared, in very high yield, by the reaction of the derivative Tp^{Me2}IrH$_2$(C_2H_4) with 2,5-$SC_4H_2Me_2$ (60 °C, 15 h).

Data for 24. IR (Nujol): ν(IrH) 2135 cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 7.37 (s, 1 H, CH_{th}), 6.40, 6.20 (dd, dd, 1 H, 1 H, J_{HH} = 3.4, 1.0 Hz, $SC_4H_2Me_2$), 5.68, 5.52, 5.45 (s, 1 H each, CH_{pz}), 2.68, 2.58, 2.28, 2.20, 2.11, 2.11, 2.04, 1.56, 1.35, 1.27 (s, 3 H each, 10 Me), −19.45 (s, 1 H, IrH). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 152.5, 151.8, 151.3, 143.1, 142.9, 142.5 (C_{qpz}), 147.1, 146.8, 132.0, 129.9 (C_{qth}), 143.1 (IrC*C*H), 127.0, 126.5 (CH_{th}), 114.4 (IrC), 106.2, 105.9, 105.2 (CH_{pz}), 15.5, 15.4, 15.3, 14.3, 13.6, 13.3, 13.0, 12.4, 12.2, 12.2 (10 Me). Anal. Calcd for **22**: C, 45.4; H, 5.3; N, 11.8. Found: C, 45.7; H, 5.5; N, 12.0.

As stated in the text, the complex Tp^{Me2}Ir(η^1,η^1-CH_2C(Me)C(Me)CH_2)(2,5-$SC_4H_2Me_2$) (**23**) can be detected as an intermediate. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.66 (br, 1 H, 1 CH_{th}), 6.54 (br, 1 H, 1 CH_{th}), 5.70 (s, 2 H, 2 CH_{pz}), 5.63 (s, 1 H, 1 CH_{pz}), 3.42 (d, 2 H, J_{HH} = 13.3 Hz, 2 IrCH_AH$_B$), 2.94 (d, 2 H, J_{HH} = 13.3 Hz, 2 IrCH$_A$$H_B$), 2.39, 2.31, 2.21, 2.05, 1.98, 1.72, 0.80 (s, 2:1:1:1:2:2:1 ratio, 10 Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 151.4, 151.3, 142.6, 141.2 (2:1:1:2 ratio, C_{qpz}), 146.1 (C_{qth}), 128.5, 126.7 (1:1 ratio, CH_{th}), 108.8, 106.8 (1:2 ratio, CH_{pz}), 18.1, 15.3, 13.6, 13.5, 12.6, 12.2, 11.4 (2:1:1:2:2:1:1 ratio, 10 Me), 4.2 (IrCH$_2$).

The aryl−olefins that accompanied the formation of **24** have been characterized by the following NMR data:



X-ray Structure Determination of 6·C$_6$H$_6$ and 17. A summary of the fundamental crystal data is given in Table 3.

A colorless (**6**) and a red crystal (**17**) of prismatic shape, coated with an epoxy resin, were mounted in a Kappa diffractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir were taken from the literature.[22] The structure was solved by Patterson and Fourier methods. An empirical absorption correction[23] was applied at the end of the isotropic refinement. For **6**, a final refinement was undertaken with unit weights and fixed isotropic factors and coordinates for all H atoms. A final difference synthesis showed no significant electron density. For **17**, a final refinement was done with unit weights and anisotropic thermal motion for all atoms except S(1), C(4), C(1), C(2) and hydrogen atoms that have been refined isotropically. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions, except the H(2) hydride atom that was located in a final Fourier difference synthesis, and their coordinates were subsequently refined. Most of the calculations were carried out with the *X-ray 80 system*.[24]

Acknowledgment. The DGES (Projects PB96-0824 and PB94-1445) 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 of atomic coordinates, thermal parameters, hydrogen coordinates, bond lengths, and bond angles for complexes **6** and **17** (12 pages). Ordering information is given on any current masthead page.

OM9804834

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.
(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(24) Stewart, J. M. *The X-ray 80 System*; Computer Science Center, University of Maryland: College Park, MD, 1985.