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Remarkable transformations of thiophene ligands in their pentamethylcyclopentadienyl iridium (Cp*Ir) complexes

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Contents

Abstract

The cationic η^5-2,5-dimethylthiophene complex Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**) is the entry point for the synthesis of a variety of complexes resulting from nucleophilic attack on or

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reduction of **1**. Reduction gives Cp*Ir(η^4-2,5-Me_2T) (**4**), in which the thiophene ligand is coordinated through only the four carbon atoms, and its isomer Cp*Ir(C,S-2,5-Me_2T) (**5**) in which there is a six-membered aromatic ring incorporating the original thiophene and iridium. These isomers undergo a range of reactions with Lewis acids, bases, and mono- and polynuclear transition metal complexes. Analogous studies of benzo[b]thiophene and dibenzothiophene complexes are also reviewed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Thiophene ligands; Pentamethylcyclopentadienyl iridium complexes; Dibenzothiophene complexes

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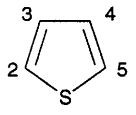
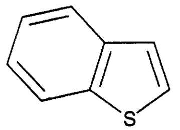
1. Introduction

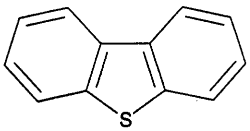
In the course of studies of the commercial process for the catalytic hydrodesulfurization (HDS) of petroleum feedstocks, many organometallic complexes of thiophenes, benzothiophene (BT) and dibenzothiophene (DBT) were prepared in order to elucidate the various ways in which these organosulfur compounds bind to metal centers [1–3].



thiophene
T



benzothiophene
BT



dibenzothiophene
DBT

Further investigations of these complexes revealed reactions of the thiophene ligands that lead to C–S cleavage and even complete desulfurization [4,5]. Although these investigations focused primarily on HDS and yielded many new insights into the heterogeneously-catalyzed HDS process [6–10], several fundamental organometallic novelties were also uncovered. One system that yielded an abundance of unexpected thiophene ligand reactivity was that with the pentamethylcyclopentadienyliridium (Cp*Ir) unit at its core. These complexes revealed new modes of thiophene ligand bonding and reactivity, which depends greatly on the oxidation state of the iridium. In this review, we describe this remarkable reactivity of thiophenes that occurs on the Cp*Ir core.

2. Syntheses of Cp*Ir(thiophenes)

2.1. Syntheses of Cp*Ir(η^5-2,5-Me_2T)$^{2+}$, Cp*Ir(η^6-BT)$^{2+}$ and Cp*Ir(η^6-DBT)$^{2+}$

The η^5-bound 2,5-dimethylthiophene complex of iridium, [Cp*Ir(η^5-2,5-Me_2T)]$(BF_4)_2$ (**1**), where Cp* is η^5-C_5Me_5 and 2,5-Me_2T is 2,5-dimethylthiophene, was prepared in high yield from $[Cp^*IrCl_2]_2$, $AgBF_4$ and 2,5-Me_2T in acetone as shown in Eq. (1) [11].

$$[\mathrm{Cp^*IrCl_2}]_2 + 4\mathrm{AgBF_4} \xrightarrow[\text{excess 2,5 Me}_2\text{T}]{\text{actone}} 2\underset{\mathbf{1}}{[\mathrm{Cp^*Ir}(\eta^5\text{-2,5-Me}_2\mathrm{T})](\mathrm{BF_4})_2} + 4\mathrm{AgCl} \quad (1)$$

The reaction of $[Cp^*IrCl_2]_2$ and $AgBF_4$ yields $[Cp^*Ir(acetone)_3](BF_4)_2$, which has been used by Maitlis and co-workers to synthesize other iridium arene dications [12]. The η^5-bound thiophene and other methyl-substituted thiophene complexes, $[Cp^*Ir(\eta^5\text{-Ts})]X_2$ ($X = BF_4$, Ts = T (thiophene) [13], 2-MeT (2-methylthiophene) [11], 3-MeT(3-methylthiophene) [11]; $X = PF_6$, Ts = Me_4T (tetramethylthiophene) [14], were synthesized in a similar manner. The $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2)^{2+}$ complex was chosen for most of the subsequent studies because the simplicity of the ^1H-NMR spectrum of the 2,5-Me_2T ligand facilitated making structural assignments to the new complexes formed in the reactions.

The η^6-bound benzo[b]thiophene (BT) complex $Cp^*Ir(\eta^6\text{-BT})^{2+}$ (**2a**) [12,15] was prepared (Eq. (2)) from $[Cp^*IrCl_2]_2$, $AgBF_4$ and BT in acetone in a manner similar to that (Eq. (1)) for the preparation of $Cp^*Ir(\eta^5\text{-Ts})^{2+}$.

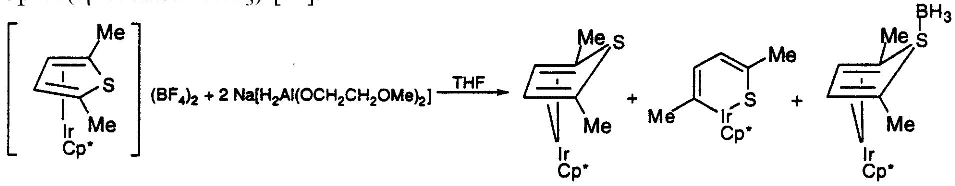
$$[Cp^*IrCl_2]_2 + 4AgBF_4 \xrightarrow[\text{excess BT}]{\text{actone}} 2\underset{\mathbf{2a}}{[Cp^*Ir(\eta^6\text{-BT})](BF_4)_2} + 4AgCl \tag{2}$$

The methyl-substituted benzo[b]thiophene complexes $Cp^*Ir(\eta^6\text{-BTs})^{2+}$ (**2b**, BTs = 2-MeBT; **2c**, BTs = 3-MeBT; **2d**, BTs = 2,3-Me_2BT) were prepared similarly [12,15]. The η^6-bound dibenzothiophene complex $Cp^*Ir(\eta^6\text{-DBT})^{2+}$ (**3**) [16], where DBT = dibenzothiophene, was synthesized (Eq. (3)) in the same manner as that for $Cp^*Ir(\eta^6\text{-BT})^{2+}$.

$$[Cp^*IrCl_2]_2 + 4AgBF_4 \xrightarrow[\text{excess DBT}]{\text{actone}} 2\underset{\mathbf{3}}{[Cp^*Ir(\eta^6\text{-DBT})](BF_4)_2} + 4AgCl \tag{3}$$

2.2. Reduction of $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$, $Cp^*Ir(\eta^6\text{-BT})^{2+}$ and $Cp^*Ir(\eta^6\text{-DBT})^{2+}$

The η^5-2,5-dimethylthiophene complex, $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ (**1**), reacts with 2 mol of $Na[H_2Al(OCH_2CH_2OMe)_2]$ ('Red-Al') at room temperature (r.t.) for 5 to 6 h according to Eq. (4). Up to three products, $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**4**), $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (**5**) and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T \cdot BH_3)$ (**6**), were isolated from the product mixtures [11]. The reaction of $[Cp^*Ir(\eta^5\text{-}2\text{-MeT})](BF_4)_2$ with 'Red-Al' also gives three types of analogous products, $Cp^*Ir(\eta^4\text{-}2\text{-MeT})$, $Cp^*Ir(C,S\text{-}2\text{-MeT})$ and $Cp^*Ir(\eta^4\text{-}2\text{-MeT} \cdot BH_3)$ [11].



1 **4** **5** **6** (4)

However, the η^5 thiophene and other methyl-substituted thiophene complexes, $[Cp^*Ir(\eta^5\text{-T})](BF_4)_2$, $[Cp^*Ir(\eta^5\text{-}3\text{-MeT})](BF_4)_2$ and $[Cp^*Ir(\eta^5\text{-}Me_4T)[(BF_4)_2$, give only one type of isolated product, $Cp^*Ir(\eta^4\text{-Ts})$ [11]. Reduction of the related $[Cp^*Rh(\eta^5\text{-}Me_4\text{-T})](OTf)_2$ with Cp_2Co gave only $Cp^*Rh(\eta^4\text{-}Me_4T)$ [17].

Complex **4** presumably forms by a two-electron reduction of **1**, whereas the BH_3 group in **6** presumably forms as a result of the conversion of the BF_4^- anions of **1** to BH_3 upon reaction with $Na[H_2Al(OCH_2CH_2OMe)_2]$. The formation of the BH_3

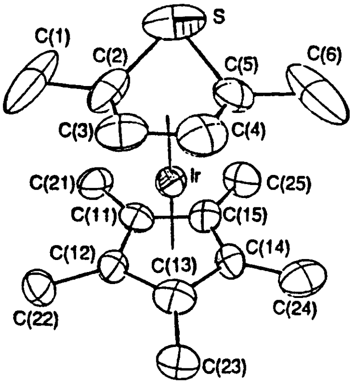
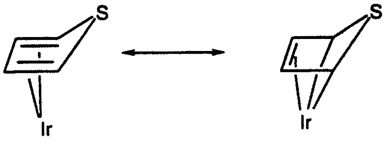


Fig. 1. Molecular structure of Cp*Ir(η^4-2,5-Me_2T) (**4**).

adduct **6** demonstrates the unusually high basicity of the sulfur in **4**, as discussed in Section 4. It is not clear by what pathway complex **5** forms in reaction (4); it appears not to form via complex **4** since **4** is not converted to **5** in the presence of $Na[H_2Al(OCH_2CH_2OMe)_2]$ under the conditions of reaction (4). The structures of representative examples of all three types of complexes have been determined by X-ray diffraction studies. Type **4** complexes, Cp*Ir(η^4-Ts), have structures (Fig. 1) in which the thiophene ligand is η^4-coordinated to the metal through the four carbon atoms at an average distance of 2.11 ± 0.01 Å [18]. The three C–C distances (1.43(2), 1.39(2) and 1.46(2) Å) in the η^4-ligand are nearly the same with the possibility that C(3)–C(4) is slightly shorter than the other two distances. Thus, the bonding of the η^4-2,5-Me_2T ligand to the metal may be represented by the two resonance forms, which both contribute about equally (Scheme 1). The C–S bond distances (1.76(2) and 1.79(2) Å) indicate that they are essentially single bonds by comparison with standard C(sp^2)–S (1.76 Å) [19] and C(sp^3)–S (1.81 Å) [19] single bonds. These bonds are lengthened from the C–S distances (1.72 Å) [20] in free thiophene. Thus, this type of coordination weakens the C–S bonds and perhaps promotes C–S bond cleavage if it were to occur on an HDS catalyst. The long C–S bond distances in **4** suggest that the two-electron pairs on the S atom do not interact with the diene system, which would leave these electron pairs, as in sulfides (R_2S), available for donation to Lewis acids. In fact, it appears that the sulfur in **4** is even more basic than it is in Me_2S, because the reaction of **4** with $Me_2S \cdot BH_3$ gives **6**.



Scheme 1.

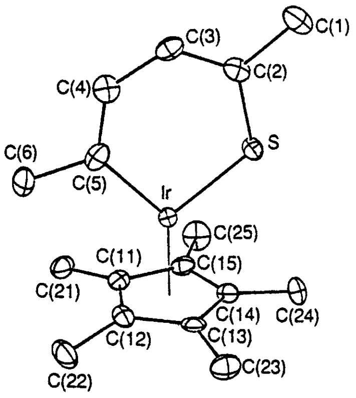
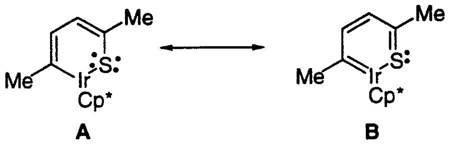


Fig. 2. Molecular structure of Cp*Ir(C,S-2,5-Me$_2$T) (**5**).

Type **5** complexes, isomers of **4**, contain a thiophene in which the Ir atom has inserted into a C–S bond. The structure of **5** (Fig. 2) consists of two planar rings that are perpendicular to each other. The plane defined by Ir, S and C(1) through C(6) is a six-membered ring that is slightly distorted toward a boat conformation. The interior angles are 94.3(2)° at Ir, 117.2(2)° at S and 122.6(5) to 130.2(6)° at the four carbon atoms. The bond distances in the six-membered ring indicate that the ring is best represented by a combination of the two resonance forms, **A** and **B** in Scheme 2. In **A**, the Ir atom is a 16-electron center; however, there may be π-donation from S to Ir which would make the Ir an 18-electron center. In resonance form **B**, the Ir has 18 electrons. The contributions of both forms to the structure of **5** are supported by the very similar C–C distances in the ring: C(2)–C(3), 1.375(9) Å; C(3)–C(4), 1.41(1) Å; C(4)–C(5), 1.394(9) Å. Also, the C(2)–S distance (1.713(6) Å) is intermediate between a C(sp^2)–S single bond distance (1.77 Å) [19] and a C(sp^2)=S double bond distance (1.61 Å) [21]. The Ir–C(5) distance (1.986(6) Å) is also intermediate between Ir–C single and Ir=C double bond distances [11], as expected for delocalized π-bonding.

The features in the NMR spectra of **5** also support a delocalized π-system in the six-membered ring. The chemical shift (180.99 ppm) of C(5) in the ^{13}C-NMR spectrum of **5** is intermediate between those of Ir=CH$_2$ (200.1 ppm) in (PPh$_2$CH$_2$SiMe$_2$)$_2$N–Ir=CH$_2$ [22] and Ir–CH=CH$_2$ (129.2 ppm) in Cp*IrH(PMe$_3$)-(CH=CH$_2$) [23]. In the ^{1}H-NMR spectrum of **5**, H(3) and H(4) occur downfield (δ 7.43 and 7.47) in the region characteristic of delocalized or aromatic six-membered,

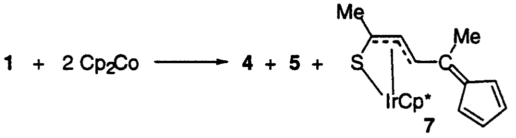


Scheme 2.

benzene-type ring systems. Considering the planar, delocalized bonding indicated by the X-ray results and the aromatic characteristics of the NMR spectrum, complex **5** may best be described as an 'iridathiabenzene'.

Type **6** complexes, $Cp^*Ir(\eta^4\text{-}Ts \cdot BH_3)$, contain an η^4-thiophene as in **4**, but the BH_3 Lewis acid is coordinated to the sulfur. In fact, the structure of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T \cdot BH_3)$ (**6**) is very similar to that of **4**, except for the BH_3 group on the sulfur [11]. Many structural features of **6** are essentially the same as those in **4**: the angle between the ligand planes C(2) through C(5) and C(11) through C(15), the four Ir–C distances to the 2,5-Me_2T ligand, the interior angles at the four carbon atoms (C(2) through C(5)) and the S atom, and the three C–C distances in the 2,5-Me_2T ligand. An apparent difference in the structures of **4** and **6** is the longer C–S bond in **6** (1.81(1) and 1.80(1) Å) as compared to **4** (1.76(2) and 1.79(2) Å). Thus, the BH_3 lengthens the C–S bonds even further from the C–S distance (1.72 Å) [20] in free thiophene; these distances in **6** are essentially the same as a normal C(sp^3)–S single bond length (1.81 Å) [19].

Cp_2Co can also be used as the reducing agent, instead of 'Red-Al', for the reaction with **1**. This reaction (Eq. (5)) yields complexes **4** and **5**, as well as the unexpected $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T \cdot C_5H_4)$ (**7**) [18,24] (Fig. 3). The latter can also be prepared [24] by reacting **1** with Cp^-.



(5)

Interestingly, complex **4** can be isomerized to **5** when catalyzed by basic Al_2O_3 or Et_3N. When the yellow **4** in benzene solvent was passed through a column of basic

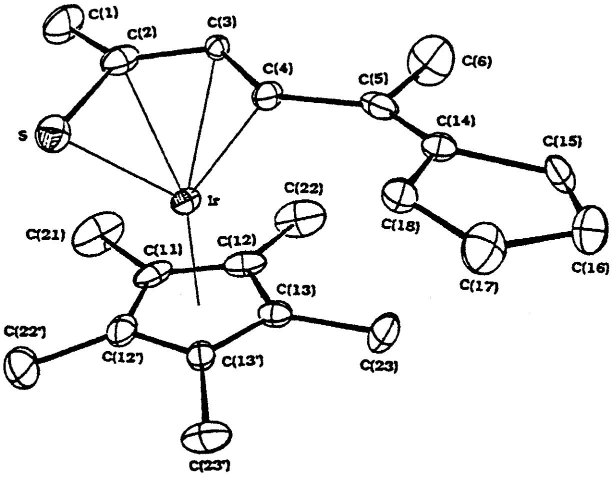
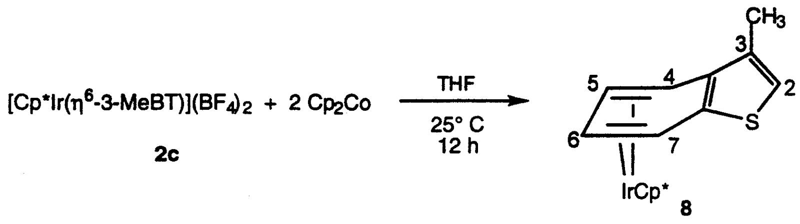


Fig. 3. ORTEP drawing of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T \cdot C_5H_4)$ (7).

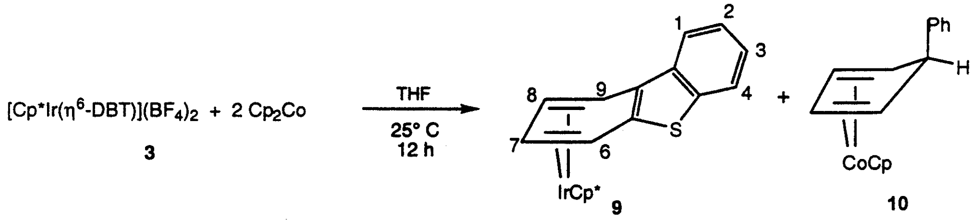
alumina, the red, more thermodynamically stable ring-opened isomer **5** was isolated in high yield (90%) [11]. The conversion of **4** to **5** in the presence of Et_3N requires a longer reaction time. The most convenient and effective method for converting **4** to **5** is ultraviolet photolysis of **4** in THF solution with a 450 W mercury lamp for 1–2 h; complex **5** is produced in nearly quantitative yield [25]. The η^4-thiophene complex Cp*Ir(η^4-2-MeT) is also converted to the ring-opened isomer Cp*Ir(C,S-2-MeT) by basic Al_2O_3 or Et_3N.

Complex **4** is quickly oxidized by two equivalents of Cp_2Fe^+ at 0°C to the cationic complex **1** in 98% isolated yield [11]. This is an expected reaction in the sense that a two-electron oxidation of the 18-electron **4** would leave the metal with only 16 electrons; coordination of the sulfur would allow it to return to 18 electrons. Surprisingly, the C,S-2,5-Me_2T complex **5** is also oxidized to give the same product **1** in 98% yield [11]. The somewhat greater reactivity of **5** means that **4** cannot be an intermediate in the conversion of **5** to **1**. Thus, oxidation of **5** promotes the reformation of the C–S bond to regenerate the η^5-2,5-Me_2T complex **1**.

A two-electron reduction of the η^6 methyl-substituted benzo[b]thiophene complex of iridium, [Cp*Ir(η^6-3-MeBT)]$(BF_4)_2$ (**2c**) with 2 mol of Cp_2Co produces (Eq. (6)) the η^4-arene complex Cp*Ir(η^4-3-MeBT) (**8**). Also, the η^6 dibenzothiophene complex Cp*Ir(η^6-DBT)$^{2+}$ (**3**) reacts (Eq. (7)) to give the analogous η^4-arene complex Cp*Ir(η^4-DBT) (**9**) [16]. In these reductions, in contrast to those involving Cp*Ir(η^5-Ts)$^{2+}$, no C–S cleavage of the thiophene ring was observed. Interestingly, Cp_2Co reduction of η^6-benzothiophene in (η^6-BT)$Mn(CO)_3^+$ in the presence of CO gives a product resulting from the insertion of Mn into a C–S bond [26].



(6)

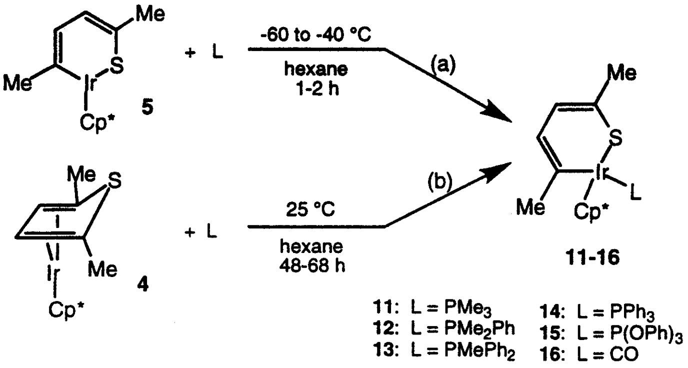


(7)

3. Reactions of Cp*Ir(η^4-2,5-Me_2T) (4) and Cp*Ir(C,S-2,5-Me_2T) (5) with Lewis bases

As mentioned above in Section 2, the structure of **5** may be represented by two resonance forms **A** and **B**. In form **A**, the Ir is a 16 electron center and might be expected to add two-electron donating ligands. In form **B**, the Ir has 18 electrons but the carbene carbon is expected to be electrophilic and susceptible to attack by two-electron donating nucleophiles. In order to determine whether the Ir or the carbene carbon is the center of reactivity, **5** was allowed to react with phosphines, CO and H_2. Indeed, complex **5** reacts readily, even at low temperature (− 60°C), with phosphorus-donor ligands (L) to give [27] the 18-electron adducts Cp*Ir(C,S-2,5-Me_2T)(PR_3) (**11**–**15**) (Eq. (8a)) in high isolated yields (> 86%). Analogous complexes Cp*Rh(C,S-thiophenes)(PMe_3) were prepared by insertion of the Cp*Rh(PMe_3) fragment into C–S bonds of a variety of thiophenes, BT and DBT [28].

Unexpectedly, the 18-electron complex **4** also reacts with L to give the same products **11**–**15** [27]. However, **4** is much less reactive than **5**, requiring a higher reaction temperature (25°C) and longer reaction times (48–68 h) (Eq. (8b)), and the yields (55-78%) are somewhat lower.



(8)

The mechanism for the reaction of **4** with L is likely to involve initial isomerization of **4** to **5**, catalyzed by the basic L ligand.

The structures of **12** (Fig. 4) and **13** are that of a piano stool with the P, S and C(5) 'legs' at roughly right angles (86–93°) to each other. The most interesting structural feature of these complexes is the C,S-2,5-Me_2T ligand. In **5**, the six-membered ring is planar and aromatic as determined from bond distances (Scheme 3) and NMR data, suggesting a delocalized π-system, which is described by resonance forms **A** and **B** (Scheme 2) and termed an 'iridathiabenzene'. But in phosphine adducts **12** and **13**, the six-membered ring is no longer planar and the C–C bond distances in the six-membered ring indicate more localized single and double bonds.

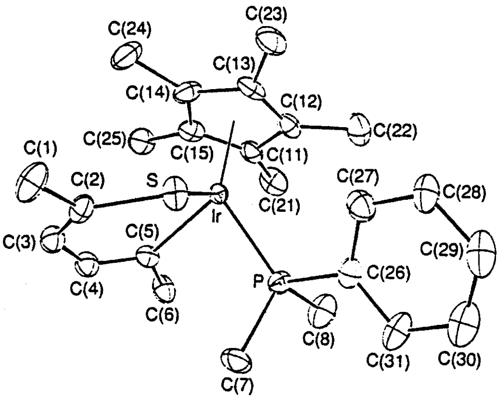
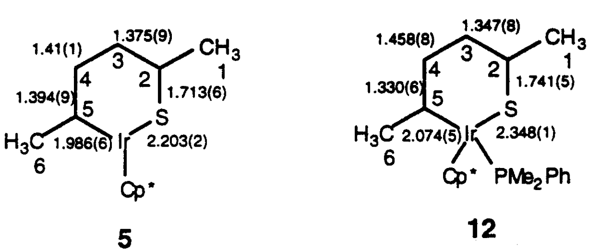


Fig. 4. ORTEP drawing of $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(PMe_2Ph)$ (**12**).

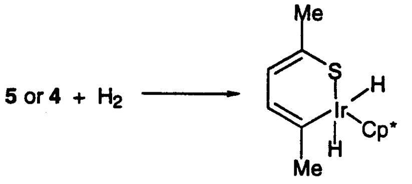
Thus, the ring is most appropriately represented by resonance form **A**, which makes the C,S-2,5-Me_2T ligand a formal two-electron donor, and the two electrons from the phosphine ligand brings the Ir to an 18-electron count. In contrast to the C–S distance in **5**, the C(2)-S distance (1.741(40 Å) in **12** is primarily a single bond since it is close to that (1.77 Å) of normal C(sp^2)-S single bonds [18] and substantially longer than C(sp^2) = S double bonds (1.61 Å) [21]. Especially interesting is the Ir-C(5) distance which is 0.088 Å longer than in **5** and corresponds to an Ir-C(sp^2) single bond as in compound $Cp^*IrH(PMe_3)(CH{=}CH_2)$ [23]. Considering all of the bond distances, **12** fits very well the localized bonding represented by resonance form **A**.

Like the phosphorus-donors, CO reacts (Eq. (8a)) with **5** under mild conditions (−30°C, 2 h) to give adduct $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)$ (**16**) [27] in 89% yield. The structure of **16** has been established by an X-ray diffraction study [29]. Complex **4** also reacts (Eq. (8b)) with CO to give the same adduct **16** but more vigorous conditions (25° C, 10 h) are required.

As complex **5** is able to add two-electron donor ligands, it can also undergo oxidative-addition with H_2 to give the dihydride **17** (Eq. (9)) in 68% yield [27]. Compound **17** is also obtained in lower yield (47%) from the reaction of **4** with H_2. A by-product of this reaction is **5**, which suggests that **5** may be an intermediate in the reaction of **4** with H_2. It appears that H_2 catalyzes the isomerization of **4** to **5**.



Scheme 3. Comparison of the six-membered rings in **5** and **12**.

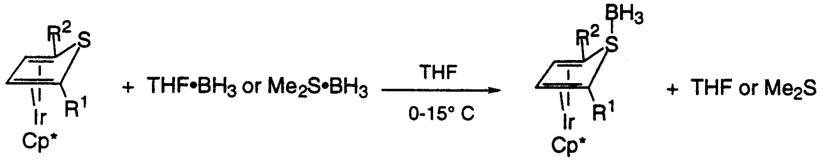


17

(9)

4. Reactions of Cp*Ir(η^4-2,5-Me_2T) (4) and Cp*Ir(C,S-2,5-Me_2T) (5) with Lewis acids

Both THF · BF_3 and $Me_2S \cdot BH_3$ react with complex Cp*Ir(η^4-2,5-Me_2T) (**4**) to give the BH_3 adduct Cp*Ir(η^4-2,5-Me_2T · BH_3) (**6**) [18,30] in high yield (Eq. (10)). The 2-methylthiophene analog of Cp*Ir(η^4-2-MeT) reacts similarly to give the BH_3 adduct Cp*Ir(η^4-2-MeT · BH_3) (**18**), whose structure was established by X-ray diffraction studies [30].

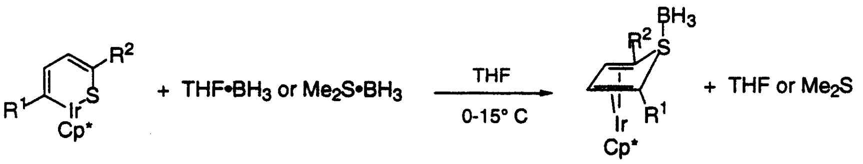


(10)

4: R^1=R^2=Me

6: R^1=R^2=Me
18: R^1=H, R^2=Me

Surprisingly, the ring-opened isomers Cp*Ir(C,S-2,5-Me_2T) (**5**) and Cp*Ir(C,S-2-MeT) also react with THF · BH_3 and $Me_2S \cdot BH_3$ to give the same BH_3 adducts, **6** and **18**, in high isolated yields (Eq. (11)) [30].

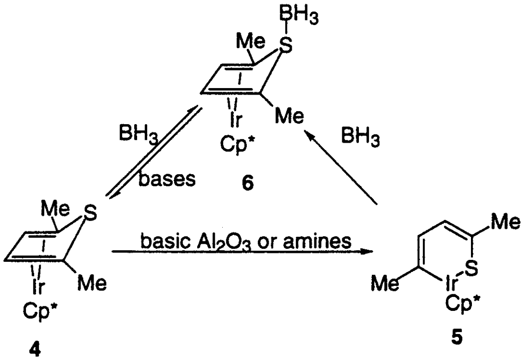


(11)

5: R^1=R^2=Me

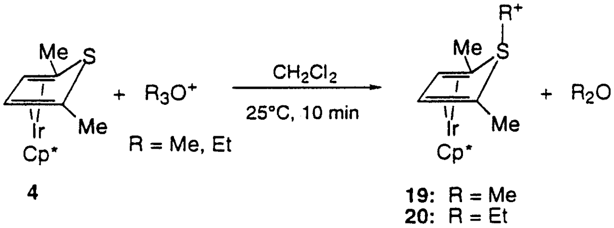
6: R^1=R^2=Me
18: R^1=H, R^2=Me

The mechanism for ring closure in reaction (11) may involve BH_3 addition at the sulfur in **5** followed by ring closure. MO calculations [31] on **5** suggest that the sulfur is electron rich. The BH_3 addition reactions indicate that the sulfur of the η^4-thiophene ligands in the Cp*Ir(η^4-thiophene) complexes is not only much more basic than the sulfur in free thiophene but also than that in organic sulfides such as Me_2S. Interestingly, basic Al_2O_3 and Et_3N easily remove the BH_3 group from the BH_3 adducts **6** to give ring-opened complex **5**, while the amine bases morpholine



Scheme 4.

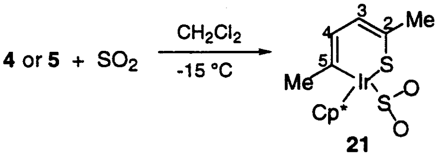
and $(CH_3)_2N(CH_2C{\equiv}CH)$ give complex **4** [30]. The remarkable ring-opening and ring-closing reactions that characterize this system are summarized in Scheme 4. As in its reaction with BH_3, complex **4** also reacts rapidly with the alkylating agents $(R_3O)BF_4$ (R = Me, Et) to yield the S-alkyl sulfonium complexes **19** and **20** (Eq. (12)) [30] in high yields.



(12)

Unlike the BH_3 reaction (Eq. (11)), the ring-opened complex **5** does not give **19** or **20** upon reaction with Me_3O^+ or Et_3O^+. Only decomposition to uncharacterized products occurs.

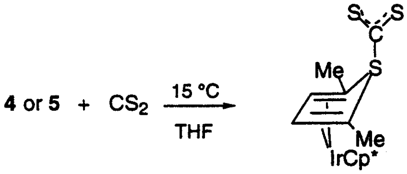
Complexes **4** and **5** also react with the small SO_2 and CS_2 molecules that often behave as Lewis acids. Both isomers **4** and **5** react (Eq. (13)) with sulfur dioxide to give the same adduct Cp*Ir(C,S-2,5-Me_2T)(SO_2) (**21**) [32].



(13)

The structure proposed in Eq. (13) was based on its ^{1}H-NMR spectrum and is related to the SO_2 adduct $Ir(Cl)(CO)(PPh_3)_2(SO_2)$ [33] in which the SO_2 is coordinated to the Ir through the sulfur. In **21**, SO_2 acts as a two-electron donor, and Ir follows the 18-electron rule.

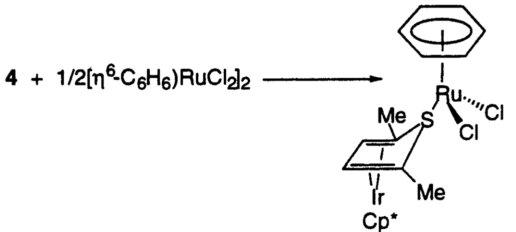
Carbon disulfide reacts (Eq. (14)) with both **4** and **5** to give the CS_2 adduct $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)(CS_2)$ (**22**) [30], whose structure is supported by comparison of its ^1H-NMR spectrum with that of the BH_3 adduct **6**.



(14)

These reactions illustrate the versatile reactivity of $Cp^*Ir(2,5\text{-}Me_2T)$, which acts as a Lewis acid with SO_2 and as a base with BH_3, R_3O^+ and CS_2.

Because the sulfur in **4** is an excellent donor toward Lewis acid centers, it also forms adducts with a variety of metal complexes (see Section 6). Complex **4** reacts (Eq. (15)) with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in benzene at 35°C to give a high yield (80%) of the crystalline $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T \cdot Ru(\eta^6\text{-}C_6H_6)RuCl_2)$ (**23**) [34]. Similar cleavage reactions of $[(\eta^6\text{-}arene)RuCl_2]_2$ complexes with a variety of L ligands to form $(\eta^6\text{-}C_6H_6Ru(Cl)_2(L)$ are well-known [35,36].



23

(15)

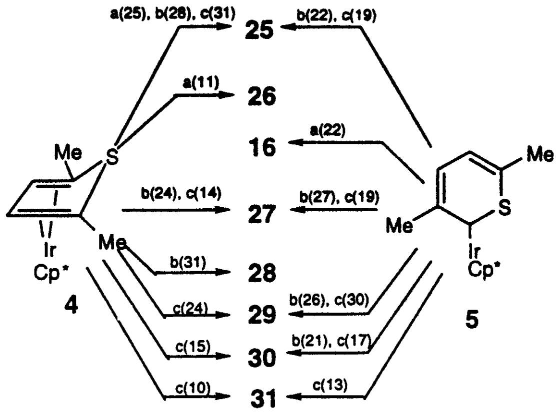
The reaction of **5** with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ under the same conditions as reaction (15) yields (69%) the dark red product $Cp^*Ir(2,5\text{-}Me_2T)[(\eta^6\text{-}C_6H_6)RuCl_2]$ (**24**) [34]. While the compositions of **23** and **24** are the same, the structure of **24** must be quite different from that of **23**, since the two methyl groups in the 2,5-Me_2T ligand of **24** are inequivalent in the ^1H-NMR spectrum. The original H(3) and H(4) protons in the 2,5-Me_2T ligand are also inequivalent, suggesting the presence of a ring-opened 2,5-Me_2T ligand of the type in **5**. However, it is not possible to assign an unequivocal structure to **24** on the basis of present evidence.

The **4** and **5** isomers of $Cp^*Ir(2,5\text{-}Me_2T)$ react at r.t. or below with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ to give a total of eight isolated and characterized organometallic products **16** and **25**–**31** (Scheme 5) [37]; their structures are shown in Scheme 6. Each iron carbonyl yields its own distribution of products, but many of the same products are formed starting with the different iron carbonyl reactants. Likewise, many of the same products are formed starting with either **4** or **5**.

In an approach to the preparation of Ir–Fe-thiophene complexes, which is quite different from those in Scheme 5, the $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ (**1**) cation was reacted with the anion $Fe_2(CO)_8^{2-}$ (Eq. (16)) to give a mixture of the same products [37] that were obtained from **4** and **5** with the neutral iron carbonyls.

$$\begin{array}{llllllll} \mathbf{1} + Fe_2(CO)_8^{2-} \longrightarrow & \mathbf{25} & + & \mathbf{28} & + & \mathbf{29} & + & \mathbf{30} \\ & (51) & & (6.4) & & (4.5) & & (6.7) \end{array} \qquad (16)$$

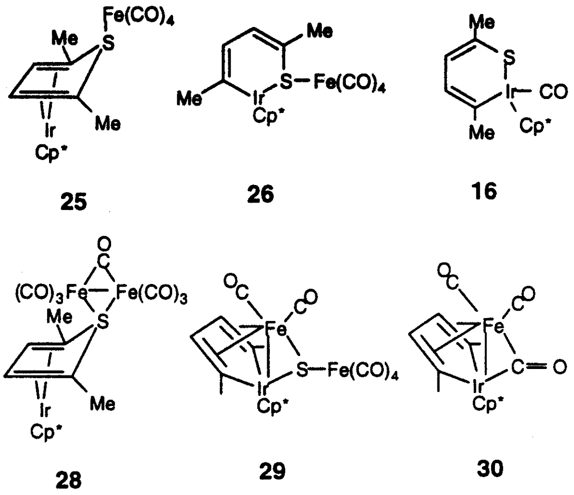
percent yields in parentheses



Scheme 5.

While the mechanism of the reaction in Eq. (16) is not known, it is possible that it proceeds via **4** and/or **5** and iron carbonyl fragments resulting from initial electron transfer from the $Fe_2(CO)_8^{2-}$ anion to the cation.

Of special interest are the structures of the products. Complex **25** is formed in five of the six reactions (Scheme 5) in relatively high yields (19–31%). Its structure (Fig. 5) contains a bridging 2,5-Me$_2$T which is η^4-coordinated through the diene portion of the thiophene to the Cp*Ir and S-bonded to the Fe(CO)$_4$; this structure is very similar to those of the BH$_3$ adduct **6** and other η^4-thiophene complexes [1]. Complex **26**, which can also be obtained [37] by the reaction of **25** with CO (1 atm) at r.t., was only characterized by its elemental analyses, IR, ^{1}H-NMR and mass spectra. Complex **16** was previously prepared [27] from the reaction of **4** or **5** with



Scheme 6.

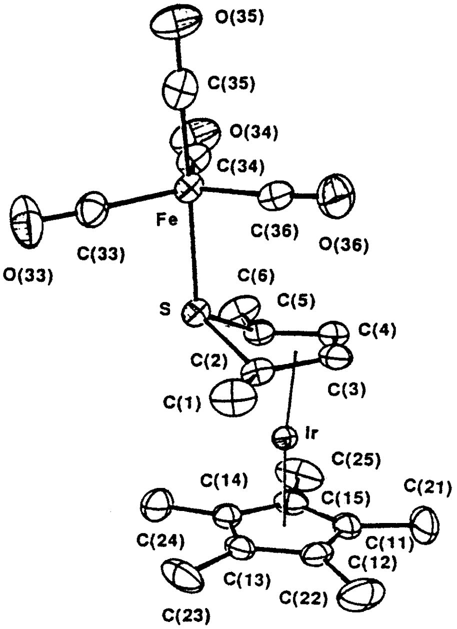


Fig. 5. Molecular structure of **25**.

CO. **16** can also be isolated [37] from the reactions of **25** or **28** with CO under the same conditions as the reaction of **25** with CO. The composition of product **27**, based on elemental analyses and the mass spectrum, is $Cp^*Ir(C,S\text{-}Me_2T)[Fe_2(CO)_8]$. The thiophene appears to be ring-opened as in **5** because of the presence of two H and two CH_3 signals in the ^1H-NMR spectrum.

Complex **28** has the structure (Fig. 6) in which the thiophene is η^4-coordinated to the Ir and $\eta^1(S)$-coordinated to the two Fe atoms. The other complexes in which thiophene is coordinated as in **28** are $Cp^*Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)[M_2(CO)_4Cp_2]$ where M = Mo, W [25,38].

In complex **29**, all of the elements of the 2,5-Me_2T ligand are present, but the S is completely removed from the thiophene ring and bridges the three metal atoms. An X-ray diffraction study shows **29** to have a structure (Fig. 7) with an iridacyclopentadiene ring η^4-bonded to the $Fe(CO)_2$ unit and the S of the S–$Fe(CO)_4$ group bridging the Ir–Fe bond. Although it is not known how **29** forms in these reaction mixtures, one can imagine that C–S cleavage in **4**, promoted by $Fe(CO)_4$ coordination to the S, Ir, or diene, would lead to **29**. A possible pathway initiated by $Fe(CO)_4$ coordination to the Ir or S is shown in Scheme 7.

The structure (Fig. 8) of **30** is nearly identical with that of **29** except the bridging S–$Fe(CO)_4$ group in **29** is replaced by a bridging CO in **30**. In fact, **30** is formed [37] (16% yield) from the reaction of **29** with CO (1 atm) at r.t.; presumably FeS or $Fe_aS_b(CO)_c$ clusters are the other Fe-containing products of this reaction.

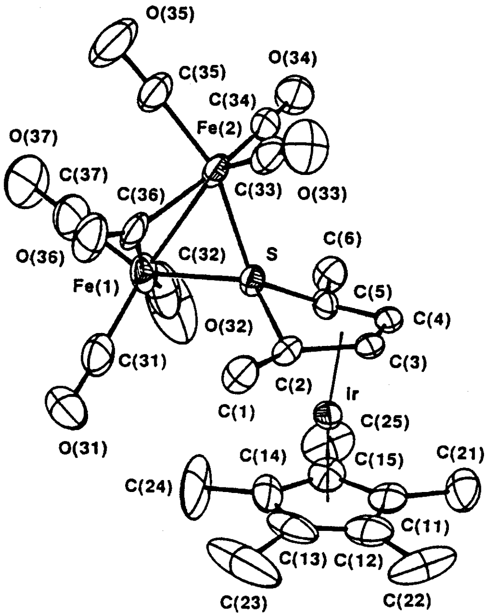


Fig. 6. Molecular structure of **28**.

As noted above, the sulfur in Cp*Ir(η^4-2,5-Me_2T) (**4**) is a stronger donor than that in thiophene itself or Me_2S toward Lewis acids such as BH_3 and $Fe(CO)_4$. The sulfur in **4** is also able to donate to two metal centers, as in **28** (Scheme 6), in its reactions with $Cp(CO)_2M{\equiv}M(CO)_2Cp$ (M = Mo, W) (Eq. (17)) to give [25,38] 38–40% yields of complexes **32** (M = Mo) and **33** (M = W), in which the thiophene is coordinated to three metals.

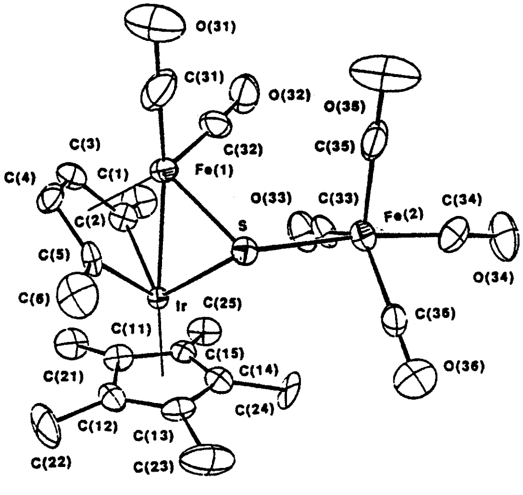
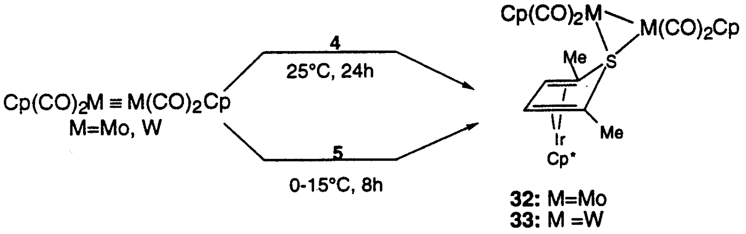


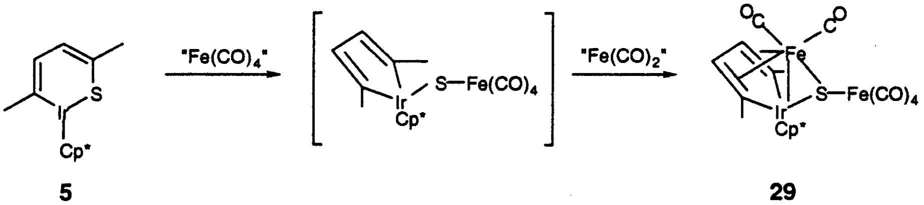
Fig. 7. Structure of **29**.



(17)

The reaction appears to be related to the known reaction [39] of $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ with tetrahydrothiophene $[S(CH_2)_4]$ to give the S-bridged analog $(S\text{-}\mu_2\text{-}S(CH_2)_4)[Mo(CO)_2Cp]_2$ of **32**. It is interesting that the ring-opened complex **5** also reacts with $Cp(CO)_2M{\equiv}M(CO)_2Cp$ (M = Mo, W) to form (Eq. (17)) the same products **32** and **33** (44–47% yield). Moreover, the conditions for the reactions of **5** with $Cp(CO)_2M{\equiv}M(CO)_2Cp$ are milder than those of **4**.

An X-ray study of the **32** establishes (Fig. 9) the structure shown in Eq. (17). The structural features of the $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ portion of **32** are very similar to those



Scheme 7.

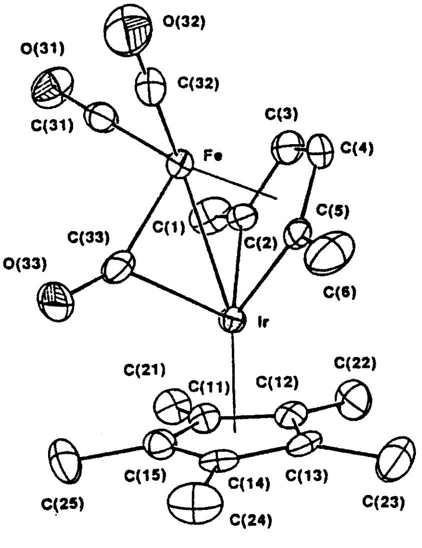


Fig. 8. Structure of **30**.

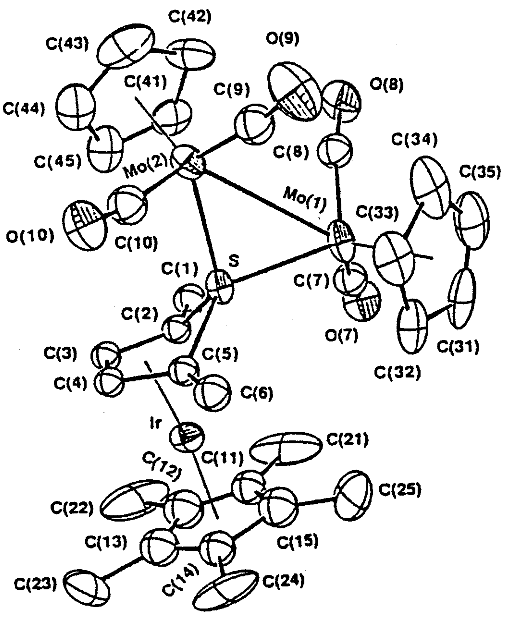
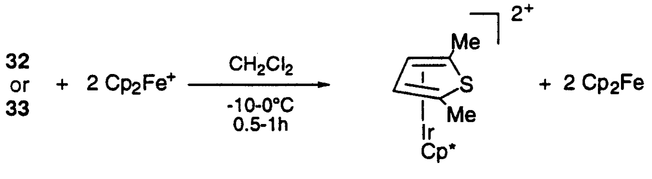


Fig. 9. Structure of **32**.

in **4**, except the C–S bond distances are slightly longer than the corresponding distances in **4**. The Mo(1)–Mo(2) distance (3.144(2) Å) is much longer than that (2.448(1) Å) [40,41] in $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$, but is slightly shorter than the Mo–Mo distance (3.235(1) Å) [42] in $Cp(CO)_3Mo–Mo(CO)_3Cp$. The structure of the $Cp(CO)_2Mo(\mu\text{-}S)Mo(CO)_2Cp$ portion of **32** is very similar to that [39] in $(S\text{-}\mu_2\text{-}S(CH_2)_6)[Mo(CO)_2Cp_2]_2$, which has a Mo–Mo distance of 3.211(2) Å.

The trimetal complexes, **32** and **33**, are oxidized rapidly by two equivalents of Cp_2Fe^+ to release (Eq. (18)) the dimers $[CpM(CO)_2]_2$ (M = Mo, W) and form the dication complex $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ (**1**) [25].



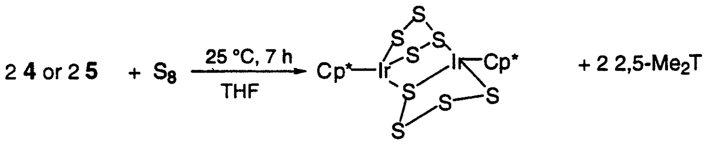
1

(18)

A related reaction is that of **4** with Cp_2Fe^+, which also rapidly gives **1** [11]. Another way by which the Mo and W dimers are displaced from the sulfur in **32** and **33** is by reaction with CO [25]. Although the studies discussed above emphasize the unusually strong donor ability of the sulfur in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**4**) a variety of other η^4-thiophene complexes, including $Cp^*Rh(\eta^4\text{-}Me_4T)$ [43], also form adducts with metal and non-metal Lewis acids [1,3,9].

5. Reactions of Cp*Ir(η^4-2,5-Me_2T) (4) and Cp*Ir(C,S-2,5-Me_2T) (5) with non-metal compounds

Complexes **4** and **5** also react with the small molecules S_8 and O_2, which may be considered to be Lewis acids and/or Lewis bases. Both isomers **4** and **5** react (Eq. (19)) with S_8 at r.t. to give the brick-red dimer $(Cp^*Ir)_2S_8$ (34) in 62–64% yield [32].

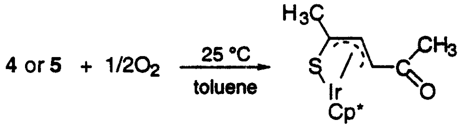


34

(19)

TheX-ray-determined structure of **34** shows the two Cp*Ir units to be linked by two S_4 ligands. The bond lengths, bond angles, and overall structure of **34** are essentially identical to those in $(Cp^*Rh)_2S_8$ [44] which was prepared by the reaction of $[Cp^*Rh(CO)]_2$ with equimolar S_8.

In contrast to the reaction of Cp*Rh(η^4-Me_4T) with O_2 to give Cp*Rh(η^4-Me_4T-1-O) [45], **4** reacts with O_2 at r.t. to give (Eq. (20)) a 77% yield of the acylthiolate complex Cp*Ir(η^4-SC_3H_2MeC(=O)Me) (**35**) [32]. The analogous reaction of **5** (Eq. (20)) was somewhat slower under the same conditions and the yield (58%) of **35** was lower.



35

(20)

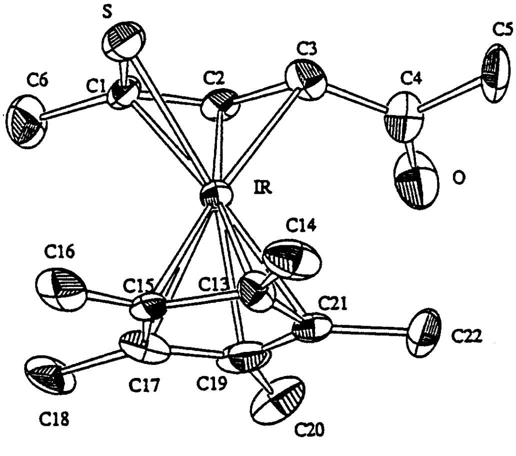
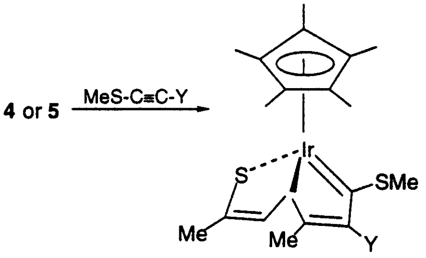


Fig. 10. ORTEP drawing of **35**.

The X-ray structure (Fig. 10) [46] of **35** is very similar to that of Cp*Rh(η^4-$SC_3Me_3C(=O)Me$) [47,48], which was prepared by reaction of Cp*Rh(η^5-$Me_4T)^{2+}$ with OH^-. The allyl portion of the acylthiolate ligand in **35** is delocalized, as indicated by the equivalent C(1)–C(2) and C(2)–C(3) distances (1.43(2) Å). The C(1)–S bond length (1.74(1) Å) is slightly shorter than that of a typical C(sp^2)–S single bond (1.77Å) [19a] suggesting that there is some π-delocalization into the C–S bond.

The ability of complex **5** to form Cp*Ir(C,S-2,5-Me_2T)(L) (L = phosphines, CO) complexes suggests that it may also react with acetylenes and olefins to form adducts which may then react with the ring-opened C,S-2,5-Me_2T ligand to give new types of organosulfur complexes. Indeed, complex **5** reacts with 2,5-dithiahex-3-yne, MeSC≡CSMe, in THF at 0–15°C for 6–7 h to give the novel chelated bicyclocarbene complex (**36**) (Eq. (21)) in 19% isolated yield [49].



36: (Y=SMe)
37: (Y=Me)

(21)

Unexpectedly, the η^4-complex **4** also reacts with MeSC≡CSMe to give the same bicyclocarbene complex **36** (Eq. (21)) [49]. However, **4** is much less reactive than **5**, requiring a higher reaction temperature (25°C) and longer reaction time (30 h), and the yield (14%) is somewhat lower. The 2-thiapent-3-yne acetylene (MeSC≡CMe) also reacts with **4** and **5** to give the analogous bicyclocarbene **37**. However, other acetylenes, such as phenylacetylene, diphenylacetylene and 3-hexyne do not react similarly. Thus, the SMe groups are important for these reactions; they probably promote this reaction by forming the MeS-stabilized carbene. The alkenes, 1-hexene, 1,3-cyclohexadiene and 1,3-cyclooctadiene, also do not react with complexes **4** and **5**. An X-ray diffraction study of **36** establishes the unexpected geometry shown in Fig. 11. Product **36** appears to result from MeSC≡CSMe acetylene insertion into the Ir–C(5) bond of **5** (Fig. 2).

The assignment of C(9) as having carbene character is supported by its planarity, as indicated by the 360° sum of the angles around C(9), and the Ir–C(9) bond distance (1.95 Å) which is shorter than the Ir–C(sp^2) single-bond distance (2.054(4) Å) [23] in Cp*(PMe_3)(H)Ir($CH=CH_2$).

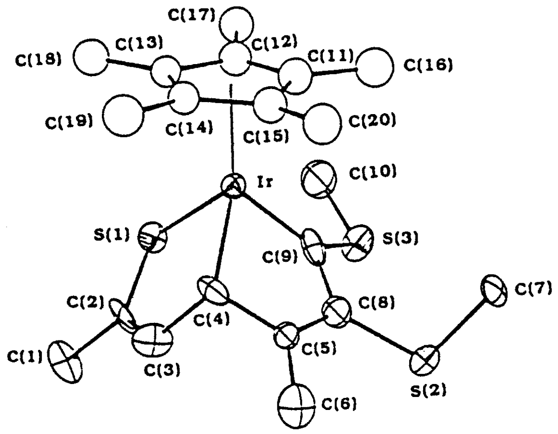
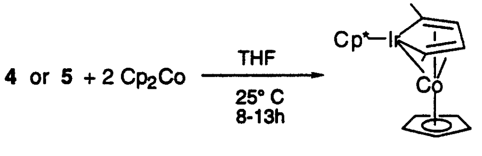


Fig. 11. ORTEP drawing of **36**.

6. Reactions of Cp*Ir(η^4-2,5-Me_2T) (4) and Cp*Ir(C,S-2,5-Me_2T) (5) with transition metal complexes

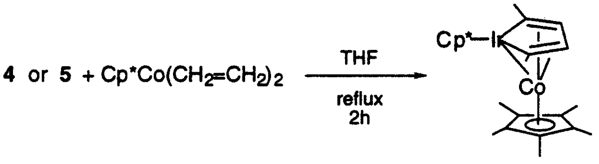
Both complexes **4** and **5**, which are obtained by reducing **1** with Cp_2Co (Eq. (5)), react further with 2 mol of Cp_2Co in THF at r.t. to give a ferrole-type product $Cp^*[\overline{IrC((Me)=CHCH=C}(Me)]CoCp$ (**38**) [24] (Eq. (22)), in which the planar iridacyclopentadiene ring is π-bonded to the Co atom.



38

(22)

The reaction of **5** occurs somewhat more rapidly (8 h) than that of **4** (13 h) and gives a slightly higher yield (42 versus 36%). Also, in the reaction of **4** with Cp_2Co, a small amount of **5** was produced, which suggests that the reaction of **4** with Cp_2Co occurs by initial isomerization to the more stable **5**. The latter reacts with Cp_2Co to give **38**. The Cp* analog **39** of **38** is prepared by the reactions of **4** and **5** with $Cp^*Co(CH_2{=}CH_2)_2$ (Eq. (23)) [24] in approximately the same yield (35–39%).



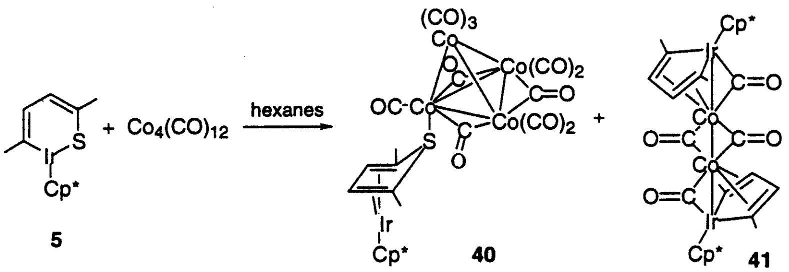
39

(23)

These reactions demonstrate that cobaltocene and $Cp^*Co(CH_2{=}CH_2)_2$ readily desulfurize the 2,5-Me_2T ligand in **4** and **5** to give metallacyclopentadiene complexes.

The structure of **38** (Fig. 12) consists of a planar iridacyclopentadiene (IrC_4) unit π-bonded to Co. Within the iridacyclopentadiene ring, the Ir–C(2) distance (2.011(7) Å) is somewhat shorter than that of an Ir–C(sp^2) single bond (2.054(4) Å), as occurs in the vinyl complex $Cp^*(PMe_3)(H)Ir(CH{=}CH_2)$ [23], but is significantly longer than the Ir=C double bond (1.868(9) Å) in $[N(SiMe_2CH_2PPh_2)_2]Ir{=}CH_2$ [22]. This suggests that there is some π-bonding between Ir and C(2) but not as much as there is in **5** for which the Ir–C distance is 1.986(6) Å. The C(2)–C(3) distance (1.39(1) Å in **38** is shorter than C(3)–C(3′) (1.46(1) Å), which indicates that the IrC_4 ligand has primarily diene character.

Complex **5** also reacts with $Co_4(CO)_{12}$ and $Co_2(CO)_8$ to give products ranging from those in which **5** and **4** are coordinated to the Co_4 cluster to those in which the iridathiabenzene ring has been desulfurized. Thus, **5** and $Co_4(CO)_{12}$ react (Eq. (24)) in hexanes to give two clusters, **40** and **41**, in varying amounts depending on the reaction temperature and reaction time [50].



(24)

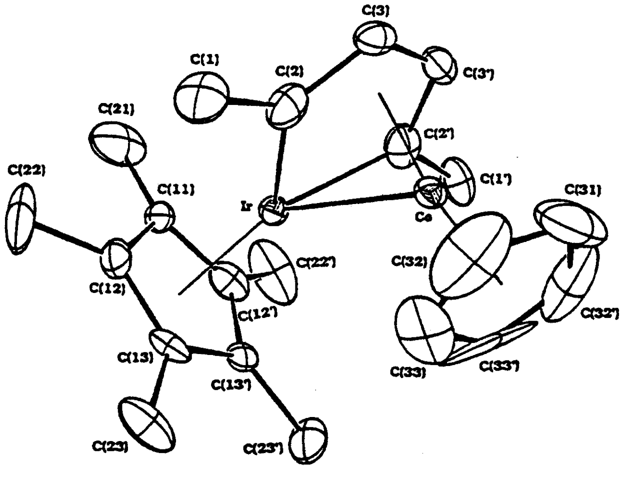


Fig. 12. ORTEP drawing of **38**.

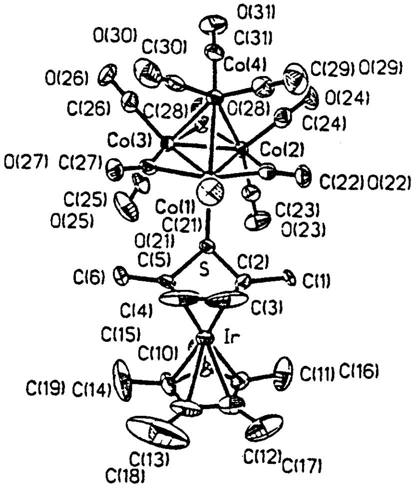


Fig. 13. ORTEP drawing of **40**.

As the reaction conditions become more rigorous, the amount of **40** decreases and **41** increases, which suggests that **41** is formed from **40**. Indeed, **40** is converted to **41** in 75% yield in refluxing hexanes for 10 h [50].

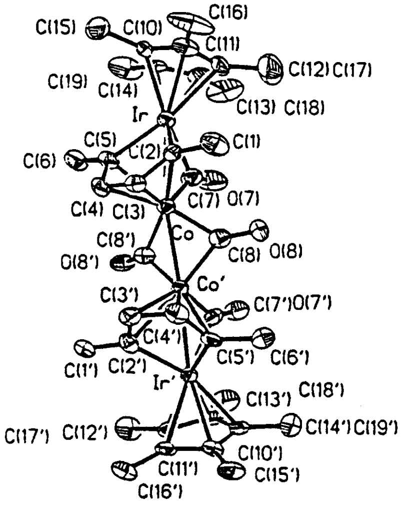
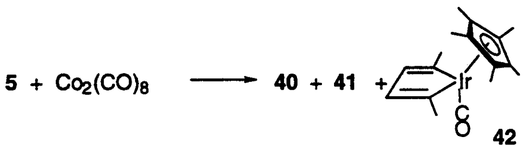


Fig. 14. ORTEP drawing of **41**.

The molecular structures of **40** and **41**, established by X-ray diffraction studies, are shown in Figs. 13 and 14. In **40**, the Cp*Ir(η^4-2,5-Me$_2$T) portion of the molecule is very similar to that of **4** itself, except the Ir–S distance (2.869(2) Å) in **40** is shorter than it is in **4** (2.969(4) Å). The $Co_4(CO)_{11}$ portion of **40** has a structure which is generally the same as that in $(PMe_3)Co_4(CO)_{11}$ [51]. The structure of **41** may be viewed as consisting of the $\mathrm{Cp^*\overline{Ir(C(Me){=}CHCH{=}C}(Me))(CO)}$ (**42**, below) and $Co_2(\mu\text{-}CO)_2$ fragments. Indeed, **41** can be prepared by reacting **42** with $Co_2(CO)_8$; formally, **42** acts as a six-electron donor ligand by displacing three CO groups from each Co to give **41**.

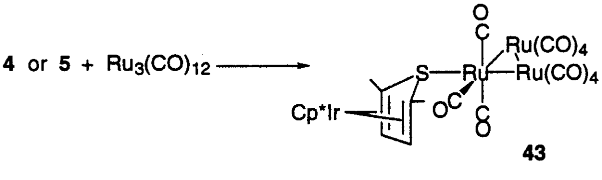
Like the reaction of **5** with $Co_4(CO)_{12}$, **5** combines with $Co_2(CO)_8$ to give **40** and **41** (Eq. (25)) in varying amounts depending on the reaction temperature and reaction time [50]. When reaction (25) is conducted in refluxing hexanes for 10 h, the new product $\mathrm{Cp^*\overline{Ir(C(Me){=}CHCH{=}C}(Me))(CO)}$ (**42**) (Eq. (25)) is also isolated in 20% yield. The structure of **42** has been established by X-ray crystallography [50].



(25)

The formation of **42** may occur by the reaction of **41** with CO that is liberated during the formation of **40** and **41**. Complex **41** does indeed react with CO even at r.t. to give **42**.

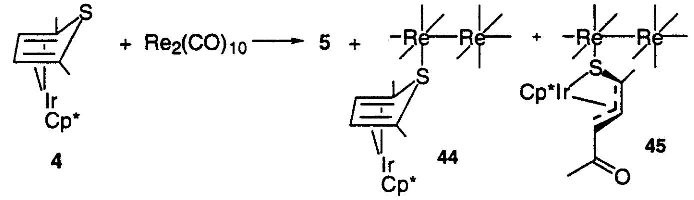
In view of the reactions of **4** and **5** with the iron carbonyls to form Cp*Ir(η^4,S-μ_2-2,5-Me$_2$T)Fe(CO)$_4$ and Cp*Ir(η^4,S-μ_3-2,5-Me$_2$T)Fe$_2$(CO)$_7$ and related complexes (Schemes 5 and 6), we explored the reactions of **4** and **5** with the di- and trinuclear metal carbonyl compounds $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$ and $Ru_3(CO)_{12}$ in order to determine whether or not they follow the same patterns of reactivity as the iron carbonyls. Thus, when $Ru_3(CO)_{12}$ reacted with **4** at r.t. for 24 h, **43** (Eq. (26)) was isolated in 45% yield [34].



(26)

The structure (Fig. 15) of **43** contains a triangular $Ru_3(CO)_{11}$ core very similar to that of $Ru_3(CO)_{12}$ and its monosubstituted products $Ru_3(CO)_{11}(L)$ [52]. The sulfur donor atom of the Cp*Ir(η^4-2,5-Me$_2$T) (**4**) ligand occupies an equatorial position in the plane of the Ru$_3$ triangle. Structural features of the Cp*Ir(η^4-2,5-Me$_2$T) (**4**) part of **43** are very similar to those in Cp*Ir(η^4,S-μ_2-2,5-Me$_2$T)Fe(CO)$_4$(**25**). The reaction (Eq. (26)) of **5** with $Ru_3(CO)_{12}$ under the same conditions as the reaction of **4** gives **43** in 32% yield. In addition, a significant amount (27%) of Cp*Ir(2,5-Me_2T)(CO) (**16**) is formed [34].

Complex **4** reacts with $Re_2(CO)_{10}$ in THF at r.t. to give (Eq. (27)) isomer **5** (18%) in addition to the two dinuclear Re compounds Cp*Ir(η^4-2,5-$Me_2T \cdot Re_2(CO)_9$) (**44**) and Cp*Ir(η^4-SC_3H_2MeC(=O)Me)[$Re_2(CO)_9$] (**45**), isolated in 34 and 31% yields, respectively [34].



(27)

Isomer **5** also reacts with $Re_2(CO)_{10}$ under the same conditions as reaction (27) to give only product **45** in 66% yield. The origin of the oxygen atom in the acyl group is not clear, but the most probable sources are the solvent THF and the CO in $Re_2(CO)_{12}$.

The structure (Fig. 16) of **44** shows that it is a CO-substituted product of $Re_2(CO)_{10}$ with the S-coordinated Cp*Ir(η^4-2,5-Me_2T) (**4**) ligand in an equatorial position. Compound **45** has a structure (Fig. 17) in which one of the CO groups in $Re_2(CO)_{10}$ is substituted by the sulfur of the acylthiolate ligand in Cp*Ir(η^4-SC_3H_2MeC(=O)Me) (**35**). The $Re_2(CO)_9$ portion of **45** is very similar to that in **44**. The equatorial ligands on the two Re atoms are staggered with respect to each other.

Like $Re_2(CO)_{12}$, $Mn_2(CO)_{10}$ also reacts with **4** and **5**; however, the products are quite different. The reaction of **4** with $Mn_2(CO)_{10}$ in THF at r.t. for 24 h yields only products Cp*Ir(C,S-2,5-Me_2T)(CO) (**16**) (53%) and Cp*$Ir(CO)_2$ (**31**) (42%), resulting from the transfer of CO from Mn to Ir. The reaction (Eq. (28)) of **5** with

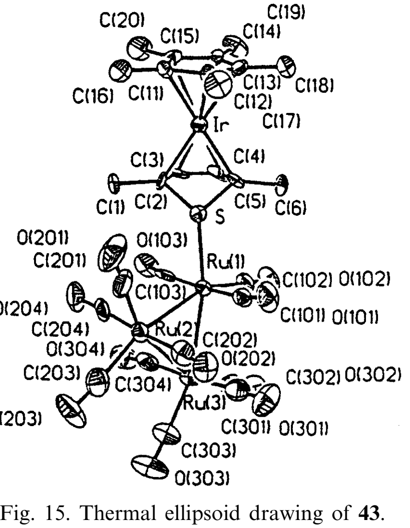


Fig. 15. Thermal ellipsoid drawing of **43**.

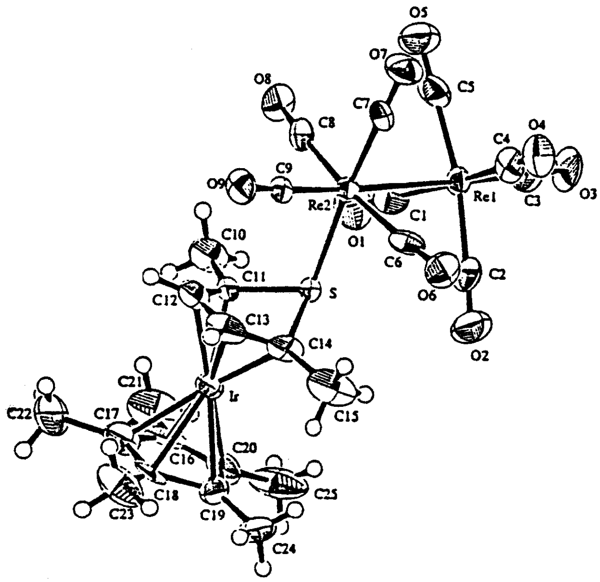
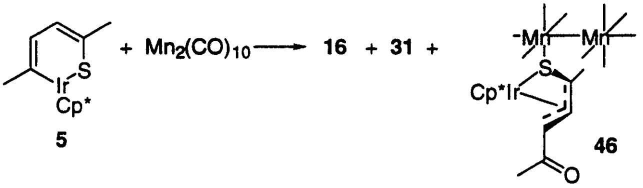


Fig. 16. ORTEP drawing of **44**.

$Mn_2(CO)_{10}$ under the same conditions also gives **16** (44%) and **31** (31%) [34]; the structure of **31** has been determined by an X-ray diffraction study [53]. In addition, a smaller yield (23%) of crystalline Cp*Ir(η^4-$SC_3H_2MeC(=O)Me$)[$Mn_2(CO)_9$] (**46**), the Mn analog of the Re complex **45**, was isolated [34].



(28)

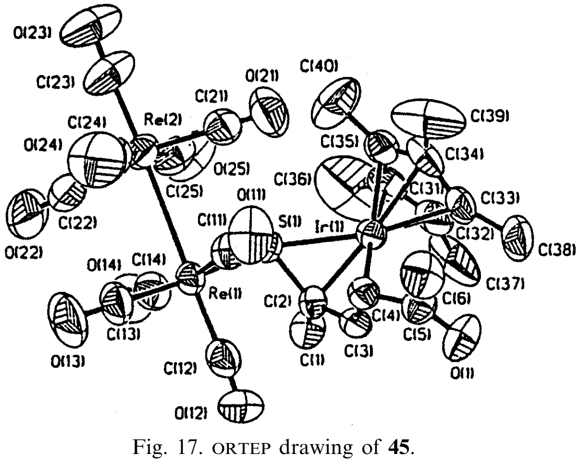
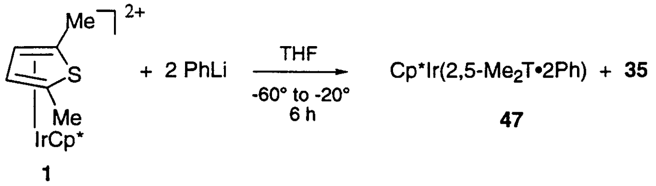


Fig. 17. ORTEP drawing of **45**.

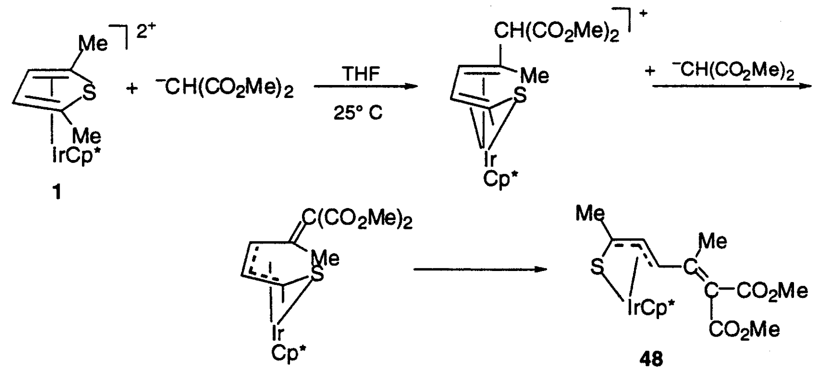
7. Reactions of Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ (1), Cp*Ir(η^6-BT)$^{2+}$ (2) and Cp*Ir(η^6-DBT)$^{2+}$ (3) with nucleophiles

In principle, dicationic η^5-thiophene complexes Cp*Ir(η^5-Ts)$^{2+}$ should be highly reactive toward nucleophiles, which is indeed the case. The reaction of dicationic complex **1** with PhLi in THF gives the products Cp*Ir(2,5-$Me_2T \cdot 2Ph$) (**47**) and Cp*Ir(η^4-$SC_3H_2MeC(=O)Me$) (**35**) (Eq. (29)) in 25 and 28% yields, respectively [46].

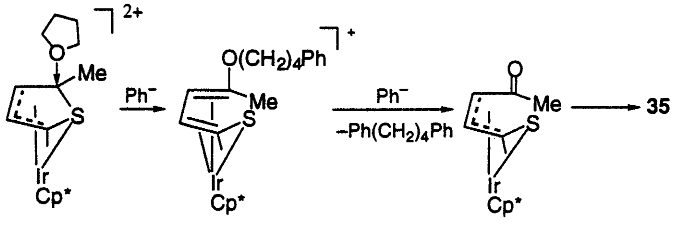


(29)

The formation of **35** is unexpected since the source of the oxygen is not obvious. We have shown (Eq. (20)) that compound **35** was formed by the reaction of **4** or **5** with O_2; however, these reactions required several hours at r.t. In contrast, reaction (29) occurs rapidly in an inert N_2 atmosphere at -60 to -20°C. The only other source of oxygen in this reaction is the solvent THF. In the reaction [54] of $Mo_3S_7Br_4$ with $(^nBu)_3P$, the solvent THF provides the oxygen for the formation of $Mo_2O_2S_2Br_4^{2-}$, whose counter cation is $(^nBu)_3P(CH_2)_4P(^nBu)_3^{2+}$. In reaction (29), the transfer of oxygen to the 2,5-Me_2T ligand could occur by a pathway as shown in Scheme 8, where the Ph^- anion acts as the nucleophile. The composition of **47**, Cp*Ir(2,5-$Me_2T \cdot 2Ph$), corresponds to that in which two Ph^- anions have added to the starting Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ cation. Its structure is not known.



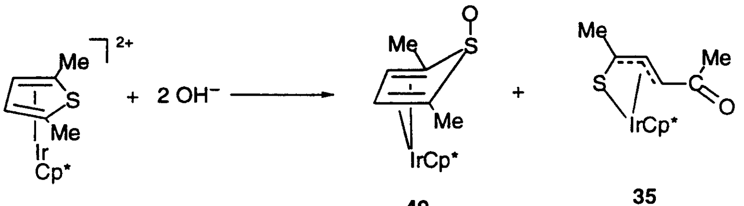
(30)



Scheme 8.

The reaction of **1** with the malonate anion $^{-}CH(CO_2Me)_2$ gives the compound $Cp^*Ir(\eta^4$-2,5-$Me_2T \cdot C(CO_2Me)_2)$ (**48**) in 43% yield [46] presumably according to the pathway shown in Eq. (30). The first step involves $^{-}CH(CO_2Me)_2$ addition at C(2) of **1**, which is accompanied by C–S cleavage. Another mole of malonate anion removes the relatively acidic proton alpha to the ester groups. Then the resulting intermediate isomerizes to **48**. The structure of **48** shown in Eq. (30) is supported by an X-ray diffraction study [55] that gave an *R* value of only 12%. However, elemental analyses along with mass and ^{1}H-NMR spectra are all consistent with this geometry.

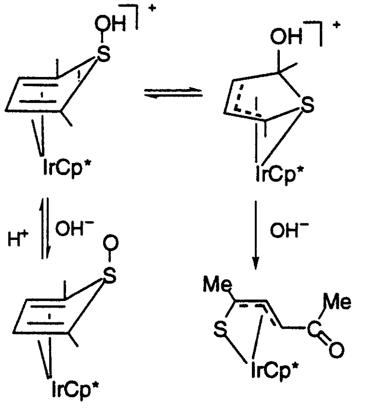
Complex **1** reacts with two equivalents of $(^nBu)_4N^+OH^-$ in CH_3CN–CH_3OH solvent to give $Cp^*Ir(\eta^4$-2,5-$Me_2T \cdot O)$ (**49**) and $Cp^*Ir(\eta^4$-$SC_3H_2MeC({=}O)Me)$ (**35**) (Eq. (31)) in 23 and 37% yields, respectively [46]. The IR and ^{1}H-NMR spectra of **49** are very similar to those of the reported Rh analog $(\eta^5$-$C_5Me_4Et)Rh(\eta^4$-$Me_4T \cdot O)$ [47], which was characterized by crystallography [45]. The mechanism (Scheme 9) for reaction (31) was proposed to follow that for the analogous reaction of $Cp'Rh(\eta^5$-$Me_4T)^{2+}$ with OH^- [45,47].



1 **49** **35** (31)

Compound **49** is not converted to **35** under the conditions of reaction (31) but is deoxygenated upon reaction with acid (HBF_4) to give the starting dication **1** in high yield (88%) [46].

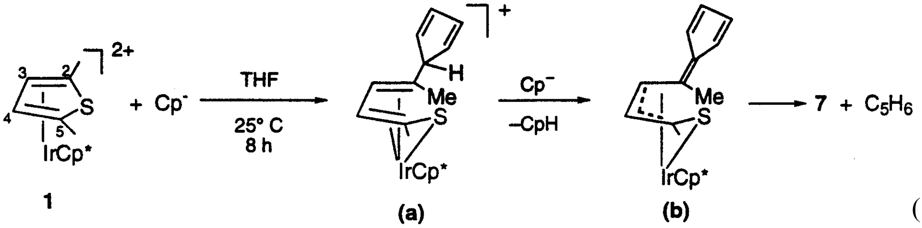
In reaction (5), the product $Cp^*Ir(\eta^4$-2,5-$Me_2T \cdot C_5H_4)$ (**7**) presumably results from the transfer of Cp^- from Cp_2Co to cation complex **1**. Indeed, **7** can also be prepared in relatively high yield (45%) from the reaction of **1** with 2 mol of KCp (Eq. (32)) [24]. This reaction presumably occurs by nucleophilic addition of Cp^- on



49 **35**

Scheme 9.

C(2) of **1** to give an intermediate **a**, in which the C(2)–S bond is cleaved as shown in Eq. (32). Deprotonation of the relatively acidic cyclopentadiene hydrogen in **a** by another Cp^- gives intermediate **b**, which isomerizes to the final product **7**.

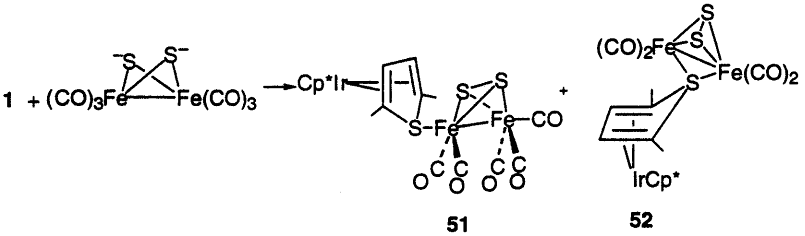


(32)

Unlike KCp, the allyl Grignard reagent $CH_2{=}CHCH_2MgBr$ does not add at C(2) to give an intermediate which undergoes deprotonation to yield a 1,3-diene product analogous to **7**. Instead (Eq. (33)) the entire η^5-2,5-Me_2T ligand is displaced by the allyl group to give $Cp^*Ir(\eta^3\text{-}C_3H_5)Br$ (**50**) [24].

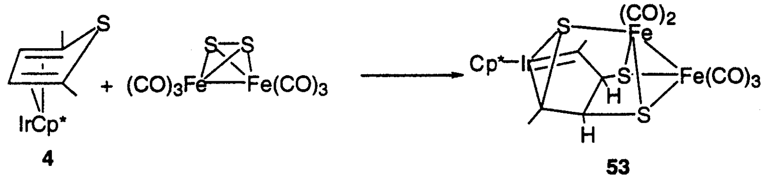
(33)

Dicationic complex **1** reacts with the iron-carbonyl-sulfide dimer anions $(\mu\text{-}S)_2Fe_2(CO)_6^{2-}$ and $(\mu\text{-}CO)(\mu\text{-}{}^nBuS)Fe_2(CO)_6^-$ [56]. The reaction of **1** with $(\mu\text{-}S)_2Fe_2(CO)_6^{2-}$ in THF at low temperature (−60 to −40°C) gives two products $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot Fe_2(CO)_5(\mu\text{-}S_2))$ (**51**) and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot Fe_2(CO)_4(\mu\text{-}S_2))$ (**52**) (Eq. (34)) in 44 and 15% yield, respectively.



(34)

The molecular structure (Fig. 18) of **51** shows that it is a derivative of $(\mu\text{-}S)_2\text{-}Fe_2(CO)_6$ in which one of the CO ligands is substituted by the S-donor $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**4**). Crystals of **52** were not suitable for X-ray study; however, its ^{1}H-NMR spectrum is very similar to those of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T\cdot Fe_2(CO)_7)$ (**28**) and $Cp^*Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)[Mo_2(CO)_4Cp_2]$ (**32**). In order to explore the possibility that reaction (34) proceeds via $(\mu\text{-}S)_2Fe_2(CO)_6$ and $Cp^*Ir(2,5\text{-}Me_2T)$ (**4** or **5**) as intermediates, $(\mu\text{-}S)_2Fe_2(CO)_6$ was allowed to react with **4** and **5**. The reaction (Eq. (35)) with **4** run at −60°C in THF gave a new compound $Cp^*Ir(C(Me){=}CHCH{=}C(Me))(\mu\text{-}S_2)Fe_2(CO)_5$ (**53**) in 48% yield [56].



(35)

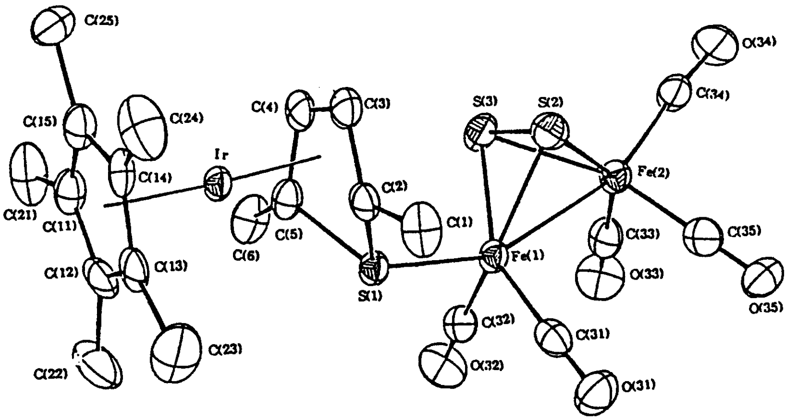


Fig. 18. Molecular structure of **51**.

The ring-opened isomer **5** reacts with $(\mu\text{-}S)_2Fe_2(CO)_6$ under the same conditions to give **53** in 24% yield. The structure (Fig. 19) of **53** is completely different from **51** although their chemical compositions are the same. In **53**, the Ir is part of a

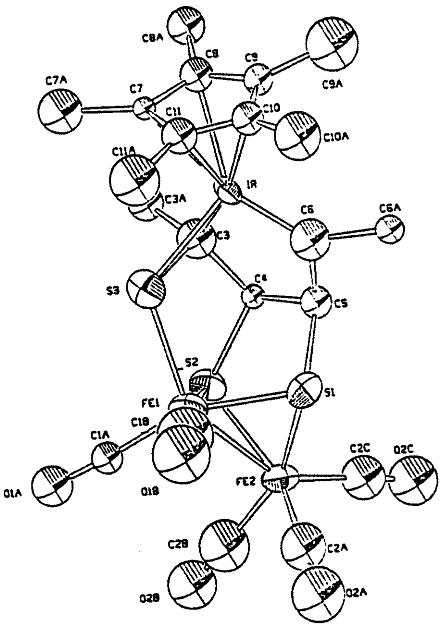


Fig. 19. Molecular structure of **53**.

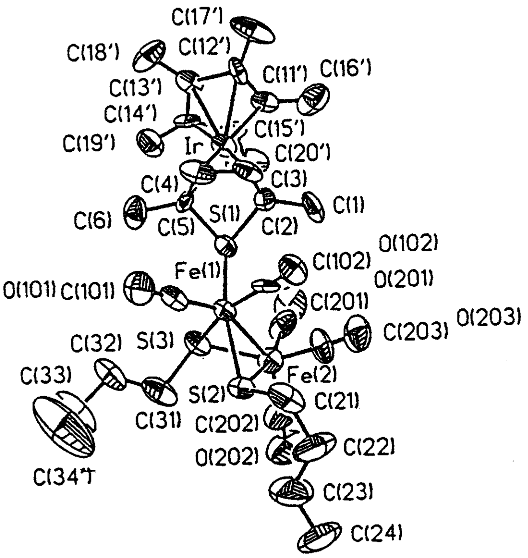
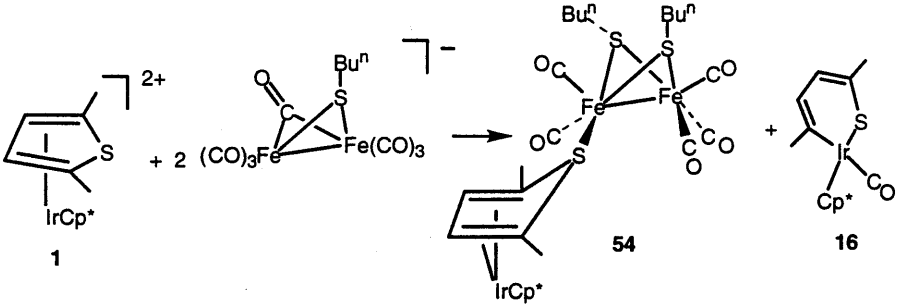


Fig. 20. Molecular structure of **54**.

five-membered ring including C(3), C(4), C(5) and C(6). All of the carbons in this ring are saturated except C(6), which is planar as indicated by the sum (360°) of the three angles around it. The short Ir=C(6) bond distance (1.77(5) Å) suggests that C(6) is a carbene carbon. The S(3) atom, which was presumably part of the 2,5-Me_2T ligand in reactant **4**, bridges the Ir–C(3) bond like an episulfide but also coordinates to Fe(1). The S(1) and S(2) atoms, assumed to be part of $(\mu\text{-}S)_2Fe_2(CO)_6$ originally, are attached at C(4) and C(5).

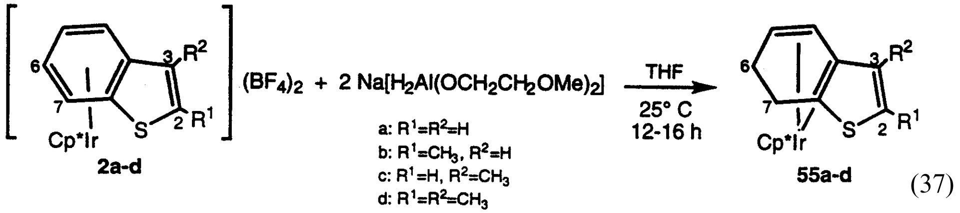
Dicationic complex **1** also reacts (Eq. (36)) with $(\mu\text{-}CO)(\mu\text{-}^{n}BuS)Fe_2(CO)_6^-$. However, the products are not those expected from nucleophilic attack by the anion on the 2,5-Me_2T ring of **1**.



(36)

Instead, the products are $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T \cdot Fe_2(CO)_5(\mu\text{-}S^nBu)_2)$ (**54**) (65%) and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)$ (**16**) (20%) [56]. The molecular structure (Fig. 20) of **54** shows that it is a derivative of $(\mu\text{-}^nBuS)_2Fe_2(CO)_6$ in which one of the four equivalent CO groups is substituted by a S-bound $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**4**) ligand. The structure of the $(\mu\text{-}^nBuS)_2Fe_2(CO)_5$ part of **54** is very similar to that of $(\mu\text{-}EtS)_2Fe_2(CO)_6$ [57]. The structure of the $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**4**) portion of **54** is very similar to that in **51**.

The cationic $Cp^*Ir(\eta^6\text{-}BT)^{2+}$ (**2a**) reacts with BH_4^- to give an inseparable mixture of four isomers of $Cp^*Ir(\eta^5\text{-}BT \cdot H)^+$. This mixture reacts further with the more reactive hydride source 'Red-Al', $Na[H_2Al(OCH_2CH_2OMe)_2]$ to give an incompletely characterized mixture of isomers of the formula $Cp^*Ir(\eta^5\text{-}BT \cdot 2H)$ [15]. The η^6-bound benzo[b]thiophene and methyl-substituted benzo[b]thiophene complexes of iridium, $[Cp^*Ir(\eta^6\text{-}BTs)](BF_4)_2$ (**2a–d**) react with 2 mol of 'Red-Al' to add two H^- to the coordinated arene ring of BTs according to (Eq. (37)) to give the cyclohexadiene complexes $Cp^*Ir(\eta^4\text{-}BTs \cdot 2H)$ (**55a–d**) in moderate yields [16]. Also, the η^6-bound dibenzothiophene complex $Cp^*(\eta^6\text{-}DBT)^{2+}$ (**3**) reacts similarly to give $Cp^*(\eta^4\text{-}DBT \cdot 2H)$ (**56**) (Eq. (38)) [16]. Complexes **55c** (Fig. 21) and **56** (Fig. 22) were established by X-ray diffraction studies to have structures in which the two added hydrides (H^-) are at positions 6 and 7, and the Ir is coordinated to the diene portion of the resulting cyclohexadiene ring. The structures of both **55c** and **56** are generally similar to those of other cyclohexadiene complexes [58].



(37)

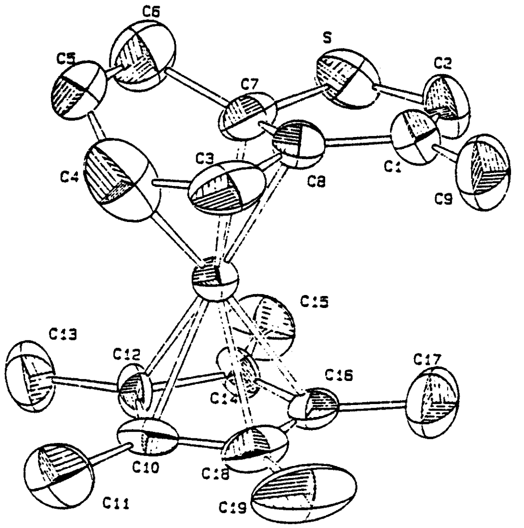


Fig. 21. ORTEP drawing of **55c**.

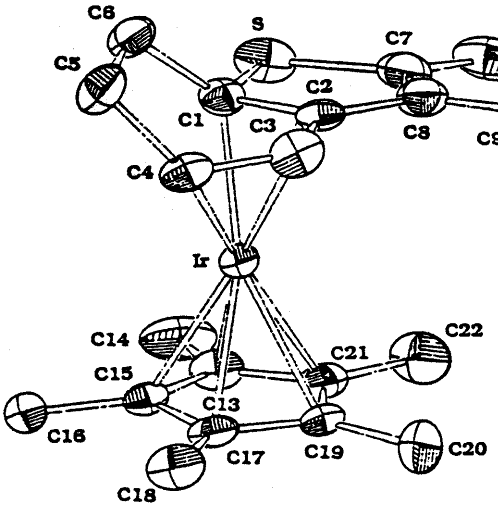
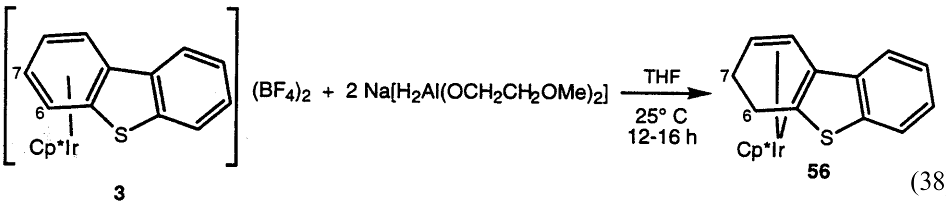
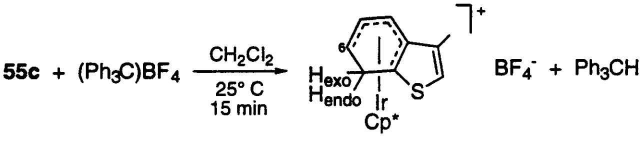


Fig. 22. ORTEP drawing of **56**.



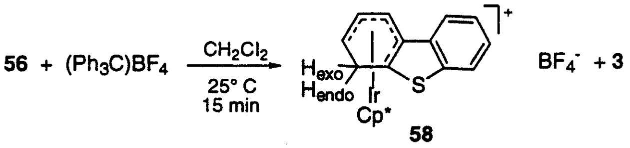
(38)

One hydride (H^-) is abstracted (Eq. (39)) from **55c** when reacted with equimolar $(Ph_3C)BF_4$ in CH_2Cl_2 to give complex $Cp^*Ir(\eta^5\text{-}3\text{-}MeBT \cdot H)^+$ (**57**) in high yield (83%) [16]. However, when **55c** reacts with two equivalents of $(Ph_3C)BF_4$ under the same conditions, two hydrides are removed from the cyclohexadiene portion of the η^4-3-MeBT · 2H ligand to give $Cp^*Ir(\eta^6\text{-}3\text{-}MeBT)^{2+}$ (**2c**) [16].



(39)

As for the reaction of **55c**, **56** reacts (Eq. (40)) with one equivalent of $(Ph_3C)BF_4$ to give the monohydride abstraction product $Cp^*Ir(\eta^5\text{-}DBT \cdot H)^+$ (**58**) (55%) but also some **3** (30% yield). The reaction of **56** with 2 equivalents of $(Ph_3C)BF_4$ removes both hydrides to give $Cp^*Ir(\eta^6\text{-}DBT)^{2+}$ (**3**) in 90% yield [16].

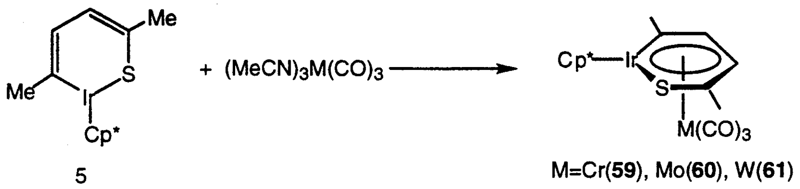


(40)

8. η^6-Iridathiabenzene complexes of Cp*Ir(C,S-2,5-Me$_2$T) (5)

As discussed in Section 2.2, **5** was described as an iridathiabenzene, a derivative of benzene in which two CH units are replaced by S and Cp*Ir. This delocalized description is supported by a recent MO calculation [31]. In previous sections of this review, many reactions of **5** were described; they all resulted in products in which the π-system was disrupted. In this section we demonstrate that the six-membered ring in **5** is capable of forming η^6-complexes that are analogs of well-known η^6-arene complexes. Moreover, **5** is a more strongly coordinating ligand than arenes.

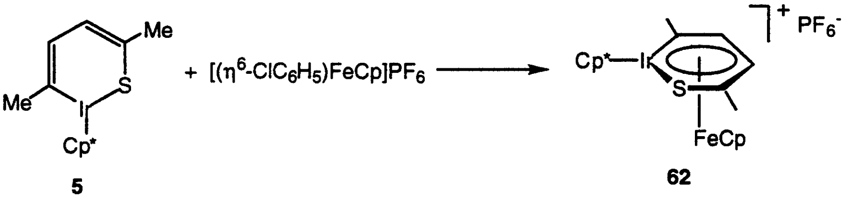
The series of purple complexes [η^6-Cp*Ir(C,S-2,5-Me$_2$T)]M(CO)$_3$ (**59**, M = Cr; **60**, M = Mo; **61**, M = W), containing **5** as an η^6-coordinated ligand, were prepared in > 92% yield according to Eq. (41) [59].



(41)

Complex **60** was also prepared [59] by reaction of the η^6-toluene complex (η^6-C$_6$H$_5$CH$_3$)Mo(CO)$_3$ with **5** in hexane at r.t. for 6 h; the 94% isolated yield of **60** demonstrates that the six-membered ring of **5** is more strongly coordinating than toluene. The greater donor ability of the iridathiabenzene as compared with toluene is also indicated by the lower ν(CO) values (in hexane) for **60** (1957 vs, 1894 vs, 1880 s) than for (η^6-C$_6$H$_5$CH$_3$)Mo(CO)$_3$ (1985 vs, 1914 vs).

The notable tendency of **5** to give η^6 complexes is further demonstrated by its formation (Eq. (42)) of the cationic complex [η^6-Cp*Ir(C,S-2,5-Me$_2$T)]FeCp$^+$ (**62**).



(42)

When a CH$_2$Cl$_2$ solution of the chlorobenzene complex [(η^6-ClC$_6$H$_5$)FeCp]PF$_6$ and **5** was photolyzed with a 450 W mercury ultraviolet lamp, the dark purple **62** was obtained in 80% yield [59]. The higher field chemical shift of the cyclopentadienyl protons in **62** (4.46 ppm) as compared with that in [(η^6-ClC$_6$H$_5$)FeCp]PF$_6$ (5.19 ppm) suggests that the iridathiabenzene ligand is more strongly electron-donating than chlorobenzene.

X-ray diffraction studies of **60** and **62** (Figs. 23 and 24) show that the iridathiabenzene ring in **5** is η^6-coordinated to the Mo and Fe. All of the atoms in the

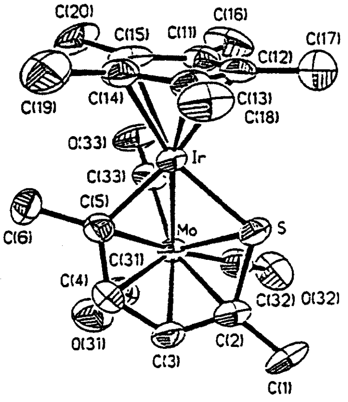


Fig. 23. Molecular structure of **60**.

six-membered rings in both structures lie in the same plane, and bond distances (Å) within the rings are the same within experimental error as those in uncoordinated **5**. Thus, as in η^6-arene complexes [60], the iridathiabenzene is not significantly distorted by its η^6 coordination to the metal in **60** and **62**. Recently, another example of an η^6-iridathiabenzene complex, $[\eta^6\text{-}(Et_3P)_3Ir(C,S\text{-}3,4\text{-}Me_2T)]Mo(CO)_3^+$, was reported [61].

The reaction (Eq. (43)) of $(\eta^6\text{-}C_6H_3Me_3)Co_4(CO)_9$ with **5** gives the η^6-iridathiabenzene cluster $[\eta^6\text{-}Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)]Co_4(CO)_9$ (**63**) [50] in yields up to 20%. The structure of **63** (Eq. (43)) is based on its ^{1}H-NMR and IR spectra. The low yield of the η^6-iridathiabenzene complex appears to be due to competing reactions. However, in general, the iridathiabenzene ring in **5** is a strongly coordinating η^6-ligand. A variety of reactions of the η^6-iridathiabenzene ligand in its complexes will be published [62].

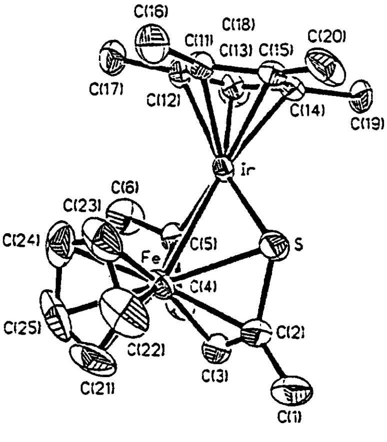
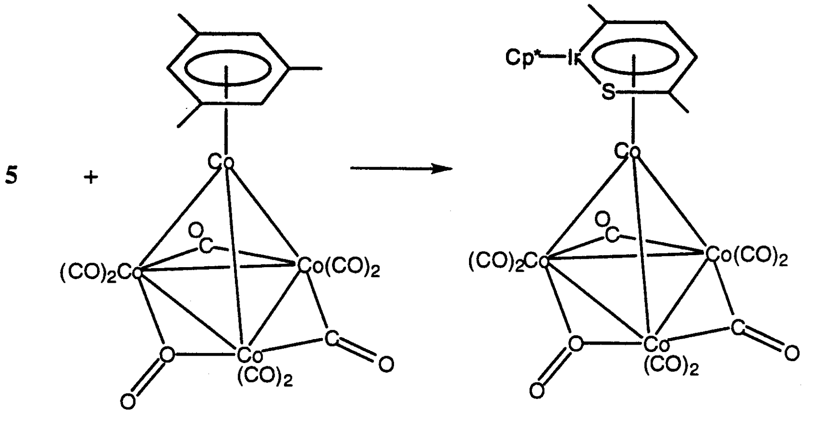


Fig. 24. Molecular structure of **62**.



69

(43)

9. Concluding comments

The Cp*Ir(2,5-Me$_2$T)$^{m+}$ system exhibits a remarkable range of reactivity. Fortunately, the products of these reactions often formed crystals that could be characterized by X-ray diffraction studies. The dication, Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**), undergoes attack by a variety of non-metal- and metal-containing nucleophiles. Reduction of the dication **1** gave two isomers of Cp*Ir(2,5-Me$_2$T). In one isomer Cp*Ir(η^4-2,5-Me$_2$T) (**4**), the thiophene is coordinated only through the four carbons while the uncoordinated sulfur is a strong Lewis base, coordinating to a variety of non-metal Lewis acids and to the metal in many mono-, di- and trinuclear metal complexes. In the isomer Cp*Ir(C,S-2,5-Me$_2$T) (**5**), Ir is inserted into a C–S bond to give a six-membered ring that is planar and gives every evidence of being a delocalized 6π-electron system, even forming η^6-complexes with transition metals. This isomer **5** also readily adds two-electron donor ligands. However, both **4** and **5** usually form the same products in their reactions with both Lewis acids and bases.

Of particular interest for the hydrodesulfurization of thiophenes are reactions that lead to cleavage of one or both C–S bonds in thiophene. This is observed in the reduction of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**) to Cp*Ir(C,S-2,5-Me$_2$T) (**5**) as well as the isomerization of Cp*Ir(η^4-2,5-Me$_2$T) (**4**) to **5**. In addition, reactions of both **4** and **5** with several metal complexes, especially the iron carbonyls, lead to the cleavage of both C–S bonds. Such reactions form the basis for a proposed mechanism for thiophene HDS [37] on commercial hydro-treating catalysts.

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