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STRUCTURAL ASPECTS OF THIOPHENE COORDINATION IN TRANSITION METAL COMPLEXES†

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CONTENTS

A. INTRODUCTION

Although Fred Basolo has not studied the chemistry of transition metal thiophene complexes, at least to my knowledge, he did write [1] a review, with David L. Kershner, on "η^5-Heterocyclic Metal Carbonyls" in 1987. The section on thiophene was very short simply because so little was known about thiophene coordination even though it was only a few years ago. The situation has changed dramatically in the past three years and is now at a stage where it is useful to review the various modes of thiophene coordination in transition metal complexes. This summary focuses on the structural aspects of this coordination and is intended to be comprehensive in its coverage of structural reports of these compounds.

The structure of thiophene itself has been determined by microwave spectroscopy [2a] and electron diffraction [2b,c], but since the microwave results are more precise, they are given in Fig. 1 and in Table 1. The C(2)-C(3) and C(4)-C(5) distances (1.370(2)Å) are clearly shorter

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† With my very best wishes to Professor Fred Basolo on the occasion of his 70th birthday.

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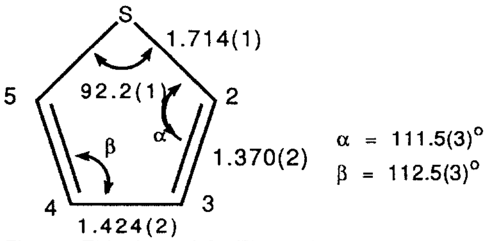
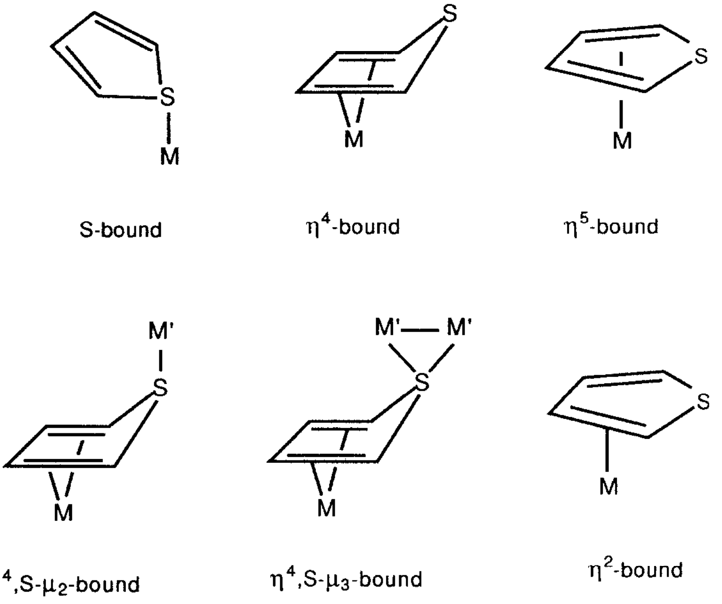


Fig. 1. Thiophene [2]. The carbon numbering scheme in this figure is used throughout the discussion in this paper.

than the C(3)-C(4) bond (1.424(2)Å); however, all three C-C bond lengths differ from normal $C(sp^2)=C(sp^2)$ double (1.34Å) and $C(sp^2)$-$C(sp^2)$ single (1.48Å) bond distances [3]. The C-S bonds (1.714(1)Å) are somewhat shorter than normal $C(sp^2)$-S single bond lengths (1.76Å) [4] but are not nearly as short as $C(sp^2)=S$ double bonds (1.61Å) [5]. Thus, the thiophene structure indicates some delocalization of the π-electrons but not nearly as much as suggested by other studies [6] which have been interpreted to indicate that the aromatic character of thiophene is not much less than that of benzene.

It is evident from the structure (Fig. 1) that the most likely coordination sites in thiophene are the C(2)=C(3) and C(4)=C(5) bonds where π-electron density is presumably concentrated and at the sulfur. Coordination at all of these sites is known, as summarized by the known structural types in Fig. 2.



S-bound

η^4-bound

η^5-bound

η^4,S-μ_2-bound

η^4,S-μ_3-bound

η^2-bound

Fig. 2. Known types of thiophene binding in transition metal complexes, where M and M' are transition metal complex fragments.

Examples of all of these types have been characterized by X-ray diffraction studies except that of the η^2-bound thiophene. This latter mode of bonding was proposed [7] to occur in $(NH_3)_5Os(2,3\text{-}\eta^2\text{-}T)^{2+}$, where T=thiophene, based on ^1H NMR data. Each structural type in Fig. 2 will be discussed in a separate section. In all of the complexes, the metals achieve a formal 18-electron count.

B. S-BOUND THIOPHENE COMPLEXES

In contrast to dialkyl or aryl-alkyl sulfides (R_2S) or tetrahydrothiophene ($(CH_2)_4S$), thiophene is a very weak sulfur-donor ligand and few S-bound thiophene complexes are known [8]. The first structurally characterized compound of this type was $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^+$ (Fig. 3) [9] in which the S-bound thiophene is linked to the cyclopentadienyl ligand through a $-CH_2-$ group. This structure was important because it established that the Ru lies out of the thiophene plane such that the sulfur has trigonal pyramidal coordination (i.e., is roughly sp^3 hybridized); the angle between the Ru-S vector and the vector from S to the C(3)-C(4) bisector is 126° (Table 1). Prior to this it was widely assumed that thiophene would bind to metals like pyridine with the metal in the plane of the thiophene or pyridine ring.

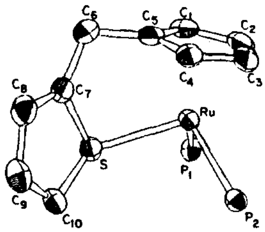


Fig. 3. $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^+$ [9].

The complex $Cp^*(CO)_2Re(T)$, where $Cp^*=\eta^5\text{-}C_5Me_5$, (Fig. 4) [10] contains a simple S-bound thiophene, again with the metal out of the thiophene plane; in this case, the angle between the Re-S vector and the vector from S to the midpoint of the C(3)-C(4) bond is 140.4°, which is somewhat larger than that (126°) in the Ru complex above. The thiophene ring is essentially planar with a possible folding along the C(2)-C(5) vector which produces a marginally significant angle of 6.1(4.5)° between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes.

TABLE 1.

S- and η^5-Bound Thiophenes in Transition Metal Complexes

Compound	C(2)-S	C(5)-S	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(2)-S-C(5)	M-S-ring[a]	M-S	Ref
Free T	1.714(1)	1.714(1)	1.370(2)	1.424(2)	1.370(2)	92.2(1)			2
				S-Bound					
Cp*(CO)$_2$Re(T)	1.72(1)	1.73(1)	1.40(2)	1.37(2)	1.36(2)	92.8(7)	140.4(2)	2.360(3)	10
(PPh$_3$)$_2$Ru(C$_5$H$_4$CH$_2$C$_4$H$_3$S)$^+$	1.754(6)	1.734(6)	1.344(8)	1.409(8)	1.339(8)	91.1(3)	126°	2.408(1)	9
				η^5-Bound					
(PPh$_3$)$_2$Rh(T)$^+$	1.73(1)	1.73(1)	1.40(2)	1.38(2)	1.43(2)	90.0(6)		2.567(3)	17
Ru(Me$_4$T)$_2$$^{2+}$	1.77(1)	1.78(1)	1.39(1)	1.43(1)	1.39(1)	91.6(4)		2.359(2)	18
	1.77(1)	1.70(1)	1.40(1)	1.39(1)	1.47(1)	92.0(4)		2.351(2)	18
[(Me$_4$T)RuCl]$_3$S$^+$	1.77(1)	1.81(1)	1.39(2)	1.46(2)	1.41(2)	89.3(6)		2.387(3)	18
(Me$_4$T)Ru(OH$_2$)$_3$$^{2+}$	1.77(2)	1.77(2)	1.42(2)	1.41(2)	1.42(2)	89.5(8)		2.307(6)	19

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[a] Angle between the M-S vector and the vector from S to the midpoint of the C(3)-C(4) bond.

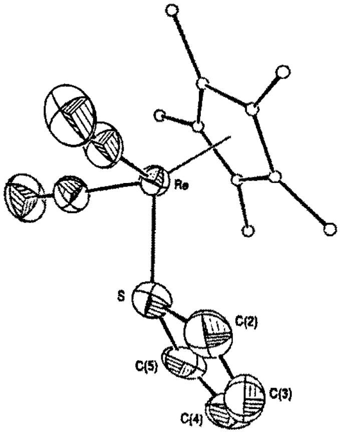
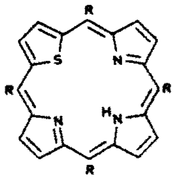


Fig. 4. Cp*$(CO)_2$Re(T) [10].

Bond distances and angles within the coordinated thiophene of $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^+$ and Cp*$(CO)_2$Re(T) are compared with those in free thiophene (T) in Table 1. The C(2)-S-C(5) angle is the same within experimental error in the complexes and in free T. In the Ru complex, which has somewhat smaller standard deviations, the C(2)-C(3) and C(4)-C(5) bonds are shorter than the C(3)-C(4) bond, as found in free T. The C(2)-S and C(5)-S bonds appear to be slightly longer (0.03Å) than in free T. All of the thiophene bond distances in the Re complex are the same as in free T; however, the standard deviations are higher for this complex, and bond distance comparisons are not meaningful. In fact, errors in the C-C distances of the thiophene ligands in many of the complexes discussed throughout this paper are sufficiently large to make comparisons questionable.

The strong tendency of the thiophene sulfur to be pyramidal when S-bound is evident in the coordination of thiophene when it is incorporated into a porphyrin by replacing a pyrrole unit:



STPPH for R = Ph
STTPH for R = p-tolyl

Latos-Grazynski, Lisowski, Olmstead, and Balch [11-13] reported the structures of a series of metal complexes (Fe(II), Ni(I), Ni(II), Cu(II), and Rh(III)) with these ligands. The structure of $Rh^{III}(STPP)Cl_2$ (Fig. 5) is typical of these compounds and shows the trigonal pyramidal coordination of the sulfur S(1). However, it also shows a bending of the thiophene ring along the C(2)-C(5) vector such that the angle between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes is 26.4°. This bending is attributed [13] to the crowded six-coordinate nature of the Rh(III) since this angle is much smaller in the less crowded five-coordinate complexes, $Cu^{II}(STPP)Cl$(15.2°), $Ni^{II}(STPP)Cl$(13.4°), and $Fe^{II}(STPP)Cl$(11.8°).

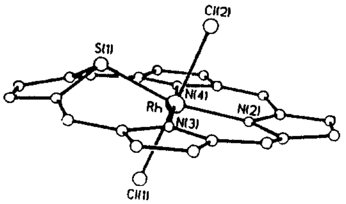
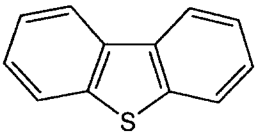


Fig. 5. $Rh^{III}(STPP)Cl_2$ [13].

Related to the above thiophene structures are two complexes containing an S-bound dibenzothiophene (DBT) ligand:



DBT

In both $Cp(CO)_2Fe(DBT)^+$ [14] and $RuCl_2[4\text{-}(p\text{-tolyl})_2P(DBT)]_2$ [15], in which the DBT contains a coordinating $(p\text{-tolyl})_2P$ group in the 4-position, the sulfur has a trigonal pyramidal geometry. The angle between the metal-S vector and the vector from S to the midpoint of the C(3)-C(4) bond is 119.4° in the Fe complex and 132.0° and 130.1° in the Ru complex. The C-S bond lengths in the DBT ligands of these complexes are within experimental error the same as those in free DBT.

C. η^5-BOUND THIOPHENE COMPLEXES

The first reported structure of an η^5-thiophene complex was that of $(CO)_3Cr(\eta^5\text{-T})$ [16] in 1965; because of disorder, it was not possible to obtain accurate bond distances. More recently (1986), the structure of $(PPh_3)_2Rh(\eta^5\text{-T})^+$ (Fig. 6) was reported [17]; it shows the bond distances and angles in the thiophene ring to be similar, within experimental error, to those in free T. However, the ring is not exactly planar since the sulfur is slightly out of the plane of the four carbons. The Rh-C distances are all the same (2.246(12)Å) within experimental error. These together with the Rh-S distance (2.567(3)Å) clearly indicate that all five atoms in the thiophene ligand are bonded to the metal. Still more recently, Rauchfuss and his coworkers published three structures (Table 1) containing the η^5-tetramethyl thiophene (Me_4T) ligand: $Ru(Me_4T)_2{}^{2+}$ (Fig. 7) [18], $[(Me_4T)RuCl]_3S^+$ (Fig. 8) [18], and $(Me_4T)Ru(OH_2)_3{}^{2+}$ [19].

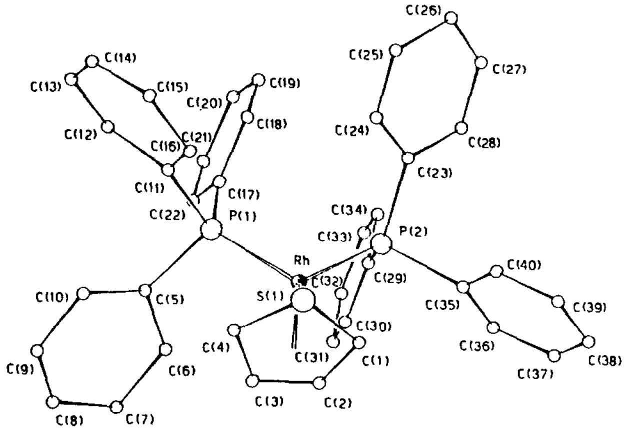


Fig. 6. $(PPh_3)_2Rh(\eta^5\text{-T})^+$ [17].

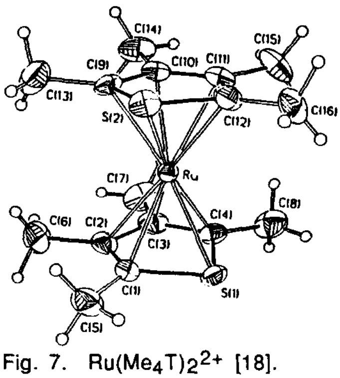


Fig. 7. $Ru(Me_4T)_2{}^{2+}$ [18].

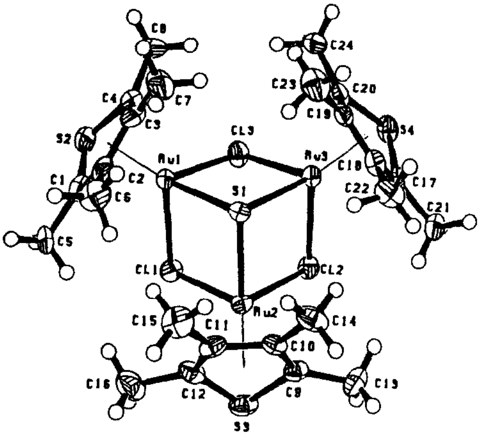


Fig. 8. $[(Me_4T)RuCl]_3S^+$ [18].

In these structures, the thiophene C-S distances are approximately 1.77(1)Å which is 0.06Å longer than in free T, perhaps indicating a weakening of this bond; on the other hand, it is possible that this lengthening is due to the presence of the methyl groups. The C(2)-S-C(5) angles (90.0-92.0°) in these complexes are essentially the same as in free T (92.2(1)°). As for $(PPh_3)_2Rh(\eta^5\text{-}T)^+$, the Me_4T rings are not entirely planar, the sulfur being bent out of the four-carbon plane away from the metal. In $Ru(Me_4T)_2{}^{2+}$, the angle between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes is 5.0(5)° and 3.7(1.5)° for the two rings. In $[(Me_4T)RuCl]_3S^+$, these angles are 11.8(1.9)°, 13.4(1.9)°, and 13.7(1.9)° for the three rings. A likely reason for this bending is the larger size of the sulfur as compared with the carbons in the ring. Since the four carbons seem to prefer to have essentially equal M-C distances, this forces the larger sulfur to adopt a short M-S distance and/or bend away from the metal. For these three $\eta^5\text{-}Me_4T$ ruthenium complexes, the Ru-S distance ranges from 2.307(6) to 2.387(3)Å (Table 1). These are shorter than or comparable to Ru-S distances in the S-bound thiophene complex $(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)^+$ (2.408(1)Å) (Table 1) and in the S-bound thioether complex $Cp(PPh_3)_2Ru(\overline{SCH_2CH_2})^+$ (2.367(3)Å) [20]. In contrast, the Ru-C distances (2.19-2.25Å) in, e.g. $Ru(Me_4T)_2{}^{2+}$ [18], are significantly longer than Ru-C(sp^2) distances (2.08-2.09Å) in Ru-vinyl or Ru-aryl complexes [21]; this difference is normally observed in comparisons of M-C distances in π-complexes with M-C η^1-bound analogs. Thus, it is unusual for the M-S distance in η^5-thiophene complexes to be so short, almost suggesting that the sulfur behaves more as if it were in a thioether ligand than as part of a π-complex. The M-C bond distances to the four carbons of the thiophene suggest that the four-carbon fragment coordinates as a normal π-hydrocarbon system. Clearly, more studies of the bonding in η^5-thiophene complexes would be useful.

D. η^4-BOUND THIOPHENE COMPLEXES

Only two structures of complexes with η^4-thiophene ligands have been reported. The first was Cp*Ir(η^4-2,5-Me_2T) [Fig. 9] [22] which was published by my group in 1989. This was followed a few months later by Cp*Rh(η^4-Me_4T) [23] from the Rauchfuss group. Because the Rh complex structure did not refine well (R_W=0.15), this discussion will focus primarily on Cp*Ir(η^4-2,5-Me_2T). However, it appears that both complexes have basically the same structure (Table 2).

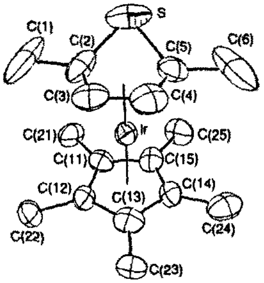
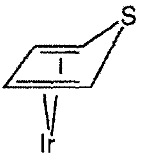
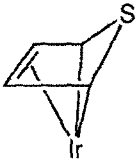


Fig. 9. Cp*Ir(η^4-2,5-Me_2T) [22].

In Cp*Ir(η^4-2,5-Me_2T), the η^4-thiophene ligand is no longer planar; the sulfur atom is bent out of the plane of the four carbons away from the Ir which leaves the Ir with a formal 18-electron count. The Ir-S distance (2.969(4)Å) is much longer than typical Ir-S bonding distances (2.35Å) [21]. The dihedral angle between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes, another measure of the folded thiophene ring, is 138° (Table 2). The 2,5-methyl groups are slightly (0.047Å average) below the C(2)-C(3)-C(4)-C(5) plane toward the Ir. Again, standard deviations associated with the ring C-C bond distances are sufficiently large that no bonding conclusions can be drawn from them; however, the four-carbon fragment may be viewed as a typical conjugated diene ligand with C-C distances varying between single and double bonds as represented by the two resonance forms,





The C(2)-S and C(5)-S bond distances (1.76(2) and 1.79(2)Å) are longer than the 1.714(1)Å distances in thiophene and are approximately single bonds if compared with normal

TABLE 2.

η^4-, η^4,S-μ_2-, and, η^4,S-μ_3-Bound Thiophenes in Transition Metal Complexes

Compound	C(2)-S	C(5)-S	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(2)-S-C(5)	Dihedral[a] Angle	Ref
Free T	1.714(1)	1.714(1)	1.370(2)	1.424(2)	1.370(2)	92.2(1)	180.0	2
			η^4-Bound					
Cp*Ir(2,5-Me_2T)	1.76(2)	1.79(2)	1.43(2)	1.39(2)	1.46(2)	80.8(6)	138°	22
Cp*Rh(Me_4T)	1.84(5)	1.81(5)	1.33(7)	1.54(8)	1.36(7)	77(2)	152(5)[b]	23
			η^4,S-μ_2-Bound					
Cp*Ir(2,5-Me_2T)BH_3	1.81(1)	1.80(1)	1.47(2)	1.42(1)	1.43(1)	82.6(5)	140.2(6)	25
Cp*Ir(2-MeT)BH_3	1.79(1)	1.79(1)	1.46(2)	1.41(2)	1.47(2)	82.8(5)	140.4(8)	26
Cp*Ir(2,5-Me_2T)Fe$(CO)_4$	1.811(6)	1.808(5)	1.464(8)	1.421(8)	1.452(7)	82.8(2)	142.1(4)	27
$(CO)_3$Fe(T)Re$(CO)_2$Cp*	1.807(6)	1.802(5)	1.458(8)	1.379(9)	1.427(8)	82.3(3)	143.1(4)	28
			η^4,S-μ_3-Bound					
Cp*Ir(2,5-Me_2T)[$Mo_2(CO)_4Cp_2$]	1.81(2)	1.83(1)	1.44(2)	1.48(2)	1.40(2)	81.7(6)	136.4(8)	29
Cp*Ir(2,5-Me_2T)[$Fe_2(CO)_7$]	1.813(7)	1.811(7)	1.45(1)	1.41(1)	1.45(1)	85.1(3)	141.2(3)	27

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[a] The dihedral angle between the planes defined by C(2)-S-C(5) and C(2)-C(3)-C(4)-C(5).

[b] There are 3 independent molecules in the unit cell. Dihedral angles for the other 2 molecules are 144(4)° and 142(4)°.

C(sp^2)-S (1.75Å) and C(sp^3)-S (1.81Å) single bond lengths [24]. The acute C(2)-S-C(5) angle (80.8(6)°), as compared with that (92.2(1)°) in free T, results from the already noted lengthening of the C-S bonds and from small decreases in the C(2)-C(3)-C(4) (107(1)°) and C(3)-C(4)-C(5) (110(1)°) bond angles from those (112.5(3)°) in free thiophene (Fig. 1).

As contrasted with the weak S-donor ability of free thiophene, the sulfur in η^4-thiophene complexes is an excellent donor and therefore coordinates to various Lewis acids including transition metals. The resulting η^4,S-μ_2- and η^4,S-μ_3-thiophene complexes are described in the next two sections.

E. η^4,S-μ_2-BOUND THIOPHENE COMPLEXES

The four compounds which exhibit this mode of bonding contain a bridging thiophene ligand which is η^4-bound to one metal and S-bound to a second metal (or Lewis acid). The simplest examples are the BH_3 adducts which are formed by the reaction of a Cp*Ir(η^4-thiophene) complex with THF•BH_3 or Me_2S•BH_3. Structures of both Cp*Ir(η^4,S-μ_2-2,5-Me_2T)BH_3 [25] (Fig. 10) and Cp*Ir(η^4,S-μ_2-2-MeT)BH_3 [26] have been reported and are very similar to each other. The geometry of the thiophene is nearly the same as it is in Cp*Ir(η^4-2,5-Me_2T) (Fig. 9) (Table 2). The sulfur folds up out of the four-carbon plane at a distance of 2.937(3) - 2.944(3)Å from the Ir, which compares with 2.969(4)Å in Cp*Ir(η^4-2,5-Me_2T). The dihedral angle between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes is 140°, which is essentially the same as that (138°) in Cp*Ir(η^4-2,5-Me_2T), and the C(2)-S-C(5) angles are the same within experimental error. There does appear to be a slight lengthening of the C-S bonds (1.80(1)Å) from those (1.76(2), 1.79(2)Å) in Cp*Ir(η^4-2,5-Me_2T), as might be expected when a Lewis acid is added to the sulfur.

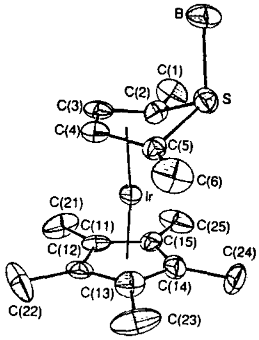

Fig. 10. Cp*Ir(η^4,S-μ_2-2,5-Me_2T)BH_3 [25].

Reactions of iron carbonyls with Cp*Ir(η^4-2,5-Me_2T) give the sulfur-coordinated Fe$(CO)_4$ adduct Cp*Ir(η^4,S-μ_2-2,5-Me_2T)Fe$(CO)_4$ (Fig. 11) [27]. Its structure is very similar (Table

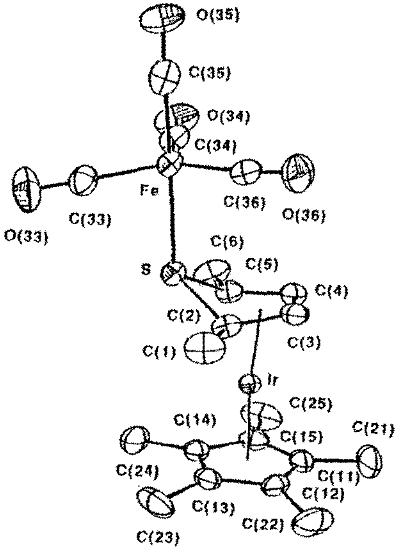

Fig. 11. Cp*Ir(η^4,S-μ_2-2,5-Me$_2$T)Fe(CO)$_4$ [27].

2) to that of Cp*Ir(η^4-2,5-Me$_2$T) and its BH$_3$ adduct. The angle between the C(2)-C(3)-C(4)-C(5) and C(2)-S-C(5) planes is 142.1(4)°, and the Ir-S distance is 2.924(1)Å.

The synthesis of (CO)$_3$Fe(η^4,S-μ_2-T)Re(CO)$_2$Cp* (Fig. 12) [28] begins with the S-bound

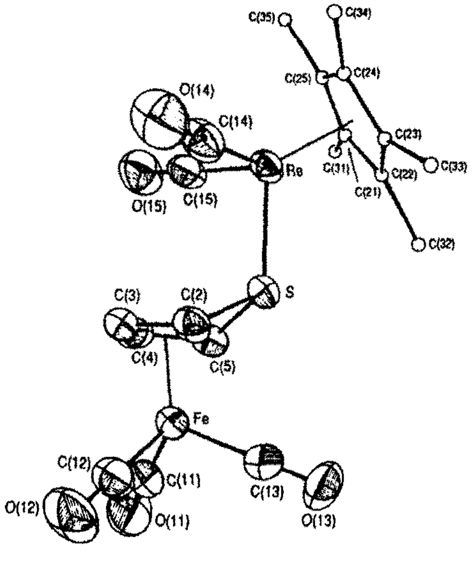

Fig. 12. (CO)$_3$Fe(η^4,S-μ_2-T)Re(CO)$_2$Cp* [28].

thiophene complex $Cp^*(CO)_2Re(T)$. The diene part of the T reacts with $Fe_2(CO)_9$ to give the product in which the bridging thiophene coordinates to the $Fe(CO)_3$ through the diene and to the $Re(CO)_2Cp^*$ via the sulfur. Despite the fact that $(CO)_3Fe(\eta^4,S\text{-}\mu_2\text{-}T)Re(CO)_2Cp^*$ has different metals with different ligands than does $Cp^*Ir(\eta^4,S\text{-}\mu_2\text{-}2,5\text{-}Me_2T)Fe(CO)_4$, the geometry of the bridging thiophene (bond distances, angles, and fold angle) is the same (Table 2) in both complexes. Thus, the η^4-thiophene ligand has a well-defined geometry not only in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ but also in its BH_3, $Fe(CO)_4$, and $Cp^*Re(CO)_2$ S-bound adducts.

F. η^4,S-μ_3-BOUND THIOPHENE COMPLEXES

In these complexes, the bridging thiophene is η^4-coordinated through the diene to one metal and S-coordinated to two other metals. Both of the complexes in Table 2 were prepared from $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ by reaction with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ or iron carbonyls. As for most of the syntheses of the η^4,S-μ_2- adducts, these preparations depend upon the unusually strong donor ability of the sulfur in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$. The structures of $Cp^*Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)[Mo_2(CO)_4Cp_2]$ (Fig. 13) [29] and

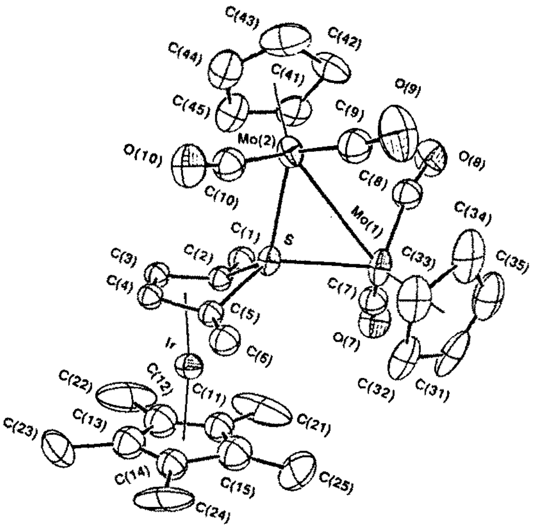

Fig. 13. $Cp^*Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)[Mo_2(CO)_4Cp_2]$ [29].

$Cp^{*}Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)[Fe_2(CO)_7]$ (Fig. 14) [27] both contain metal-metal (Mo-Mo or Fe-Fe) units which are bridged by the sulfur of the η^4-2,5-Me_2T. The geometry around the four-coordinate sulfur is approximately tetrahedral, and the M-M-S (where M=Mo or Fe) plane is essentially perpendicular to the C(2)-C(3)-C(4)-C(5) plane. In the molybdenum complex, the Ir-S distance is 2.993(5)Å, while the same distance in the iron complex is 2.918(17)Å Coordination of the sulfur by two metals results in very little change in the thiophene geometry (Table 2) from what it was in the η^4- or η^4,S-μ_2-thiophene complexes. These structures again reinforce the observation that the η^4-thiophene structure remains unperturbed by the nature and number of metal fragments coordinated to the sulfur.

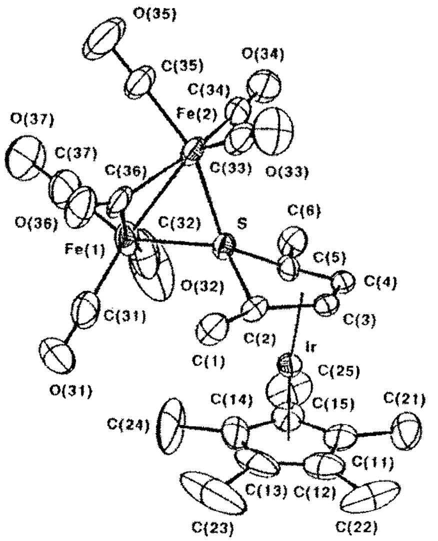

Fig. 14. $Cp^{*}Ir(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)[Fe_2(CO)_7]$ [27].

G. CONCLUDING COMMENTS

It was our interest in understanding mechanism(s) of the catalytic hydrodesulfurization (HDS) of petroleum feedstocks [8] that led us to explore the various possible modes of thiophene coordination in transition metal complexes. Presumably these modes represent possible types of thiophene adsorption at metal sites on heterogeneous HDS catalysts. The availability of these various thiophene complexes offers opportunities to compare their spectroscopic properties with those of thiophene adsorbed on HDS catalysts, thereby inferring the nature of thiophene binding to the catalyst surfaces. Prior to 1989, only the η^5- and S-coordination modes were known, but the addition of the η^2-, η^4-, η^4,S-μ_2-, and η^4,S-μ_3- binding types to the list substantially enlarges our view of thiophene coordination. In fact, there are few conceivable new ways of binding metals to thiophene that have not already been discovered.

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