Bonding and Reactivity in Transition Metal Complexes Containing Thiophenic Ligands

Suzanne Harris

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

Received April 1, 1994[⊗]

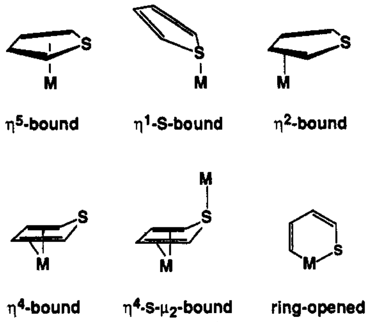
The results of Fenske–Hall molecular orbital calculations are reported for transition metal complexes containing thiophenic ligands. These ligands interact with the metals in several different binding modes, and complexes of Cr, Mn, Fe, Ru, Rh, and Ir which incorporate η^5, η^1, η^4, and ring-opened thiophenic ligands have been studied. Although metal–ligand interactions in η^5-thiophene complexes are very similar to the interactions in metal cyclopentadienyl (Cp^-) complexes, thiophene is a poorer electron donor but more effective electron acceptor than Cp^-. In the η^5 complexes, metal–thiophene binding is strongest when the acceptor ability of thiophene becomes important. The pyramidal bonding which is always observed around the ring sulfur atom in η^1(S)-bound thiophene and dibenzothiophene (DBT) complexes is related to the need for the ligand to act as a two- (and not four-) electron donor. The slightly better donor ability of DBT, when compared with thiophene, appears to be responsible for the greater stability of the Fe–(η^1-DBT) complex. The unusual η^4 and ring-opened complexes Cp*Ir(η^4-2,5-Me_2T) and Cp*Ir(*C*,*S*-2,5-Me_2T) are related by a formal oxidative addition. The electronic structures of these complexes suggest that a very electron rich metal center is a necessary precursor for insertion of the metal center into the C–S bond of the thiophene ring.

Introduction

Hydrodesulfurization (HDS) of heavy crude oils and coal-derived liquids is one of the most important catalytic processes in the petroleum refining industry. Sulfur is contained in these feedstocks in thiophene or thiophene derivatives such as benzothiophene or dibenzothiophene, and during HDS sulfur is removed when the feedstock is passed at high temperature and hydrogen puressure over a transition metal sulfide based catalyst. Since the actual industrial catalyst systems are quite complex (e.g. sulfided Co/Mo or Ni/Mo supported on Al_2O_3), much of our basic understanding of the HDS process has resulted from fundamental experimental and theoretical studies.[1-6]

In spite of an extensive research effort our knowledge of the mechanism of the HDS reactions remains limited. For example, while it is generally accepted that active sites on the transition metal sulfide surfaces involve a coordinatively unsaturated transition metal center, we do not know how a thiophenic molecule binds to this active site or how, once the sulfur-containing molecule is bound to this site, the HDS reactions proceed. Understanding the HDS process will thus require a better understanding of how thiophenic molecules interact with and are activated by transition metal centers. With this motivation, a number of metal thiophene complexes have been synthesized and characterized in recent years, and several different bonding modes of thiophenic ligands have been identified.[7,8] These modes (Chart 1) include η^5 bound, where thiophene binds much like the cyclopentadienyl (Cp^-) ligand, η^1(S) bound, η^4 bound, where the ring sulfur bends well out of the plane of the ring carbon atoms so that binding to the metal involves only the four ring C atoms, and a ring-opened form where a transition metal has inserted into a C–S bond of the thiophene ring.

Chart 1



The first structurally characterized η^5-T (T = thiophene) transition metal complex was $Cr(CO)_3T$, synthesized in 1958 by Fischer[9] and later characterized by the Dahl group.[10] The structure of this complex resembles that of the more familiar isoelectronic η^5-Cp complex $[Cr(CO)_3Cp]^-$.[11] As more η^5-T complexes were characterized, it became apparent that nearly all of these complexes have η^5-Cp analogues. With d^6 metals, the η^5-T complexes range from the early transition metal $M(CO)_3T$ complexes (analogous to $M(CO)_3Cp$) to the later transition metal MCpT and MT_2 complexes (comparable to the metallocenes MCp_2). With d^8 metals the five-coordinate d^8 complex $[Rh(PPh_3)_2T]^+$ [12] can be compared to similar ML_2Cp complexes.

Until recently, few η^1(S)-bound complexes of thiophenic ligands were known. The first structurally characterized

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

(1) Zdrazil, M. *Catal. Today* **1988**, *3*, 269.

(2) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361.

(3) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 1.

(4) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

(5) Harris, S.; Chianelli, R. R. In *Theoretical Aspects of Heterogeneous Catalysis*; Moffat, J. B., Ed.: Van Nostrand: New York, 1990.

(6) Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491.

(7) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.

(8) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 251.

(9) Fischer, E. O.; Öfele, K. *Chem. Ber.* **1958**, *91*, 2395.

(10) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1306.

(11) Feld, V. R.; Hellner, E.; Klopsch, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1978**, *442*, 173.

(12) Sánchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35.

0276-7333/94/2313-2628$04.50/0

complexes of this type, synthesized by the Rauchfuss group, were $[(C_5H_4CH_2\text{-}2\text{-}C_4H_3S)Ru(PPh_3)_2]^+$ [13] and $RuCl_2\{(p\text{-tol})_2P\text{-DBT}\}_2$(*p*-tol = *p*-tolyl).[14] Although neither of these complexes contained a simple S-bound thiophenic ligand (in both complexes T or DBT *is* bound to the metal through the ring sulfur, but in the first complex T is linked through a CH_2 group to an η^5-Cp ring and in the second complex the phosphine and DBT ligands chelate to the Ru center through both the S and P atoms), the structures of these complexes were important in that they showed that the bonding around the ring sulfur is not planar, as had been assumed, but pyramidal. That is, the metal does not lie in the same plane as the thiophenic ligand. The structural characterization of $[Cp(CO)_2Fe(DBT)]^+$ [15] confirmed that the pyramidal binding of the ring sulfur atom did not result from the tethering or chelating of the thiophenic ring, since the simple S-bound DBT ligand found in this compound also exhibited pyramidal binding at the ring sulfur atom. Similar complexes incorporating Re,[16] Ru,[17] and Ir[18] have since been shown to exhibit this same pyramidal binding at the ring sulfur atom.

The mononuclear η^4-T complexes have all been prepared by reduction of the corresponding η^5-T complexes. For example, the Rauchfuss and Angelici groups showed that reductions of the d^6 metallocene analogs $[Cp^*Rh(TMT)]^{2+}$ (TMT = tetramethylthiophene) and $[Cp^*Ir(2,5\text{-}Me_2T)]^{2+}$ lead to η^4-T complexes.[19,20] In the (η^4-T)–Ir complex, which has been structurally characterized, the ring sulfur atom is bent out of the plane of the four ring carbons by 42°.[20]

Under particular circumstances, the η^5, η^1, and η^4 binding modes all activate the bound thiophene ring toward further reaction. In cationic η^5 complexes the thiophene ring is susceptible to nucleophilic attack,[21,22] and in η^4 complexes the ring sulfur atom itself becomes strongly nucleophilic.[20,23] In addition, both the η^4 and η^1 binding modes can serve as precursors to insertion of a transition metal into the C–S bond of the thiophene ring.[24,25] For example, the η^4 Ir complex described in the previous paragraph readily rearranges to an "iridathiabenzene", in which Ir has inserted into the S–C bond of the thiophene ring.[24]

Although the interaction between thiophene and the $Mo(CO)_3$ fragment has been studied theoretically,[26] there has been no systematic theoretical study of the electronic structure of metal thiophene complexes. We report here the results of Fenske–Hall molecular orbital calculations[27] on a group of transition metal complexes incorporating thiophenic ligands. These include η^5 complexes of Cr, Mn, Ru, and Rh, an η^1 complex of Fe, and η^4 and ring-opened complexes of Ir. These results provide a basis for understanding the binding (and in some cases activation) of thiophenic ligands in many complexes.

The first section of this report provides a brief description of the calculational details. This is followed by a detailed discussion of the electronic structures of the thiophene complexes. The η^5-T complexes, which are most numerous, are described first. Molecular orbital calculations were carried out for several η^5-T complexes and their η^5-Cp counterparts. These include the following: $Cr(CO)_3T$ and $[Mn(CO)_3T]^+$ [21,28] and the isoelectronic η^5-Cp complexes $[Cr(CO)_3Cp]^-$ and $Mn(CO)_3Cp$;[21] $[RuCpT]^+$,[29] $[RuT_2]^{2+}$, and $[Ru(TMT)_2]^{2+}$ [30] and the isoelectronic ruthenocene, $RuCp_2$;[31] the five-coordinate complex $[Rh(PPh_3)_2T]^+$. The general features of the bonding in these complexes are described, and a comparison is made between the binding abilities of thiophene and the cyclopentadienyl anions (in particular the relative σ-donor and π-acceptor abilities of the ligands) in the different types of complexes. In addition, the electronic structures of the bound thiophene ligands are examined for perturbations which may be related to the increased susceptibility of these ligands to nucleophilic attack.

The next section discusses the electronic structure of the S-bound complex $[Cp(CO)_2Fe(DBT)]^+$. We have studied the bonding in $[Cp(CO)_2Fe(DBT)]^+$ in both the actual pyramidal (or "bent") structure and another "planar" structure where the metal and the DBT ligand lie in the same plane, and a comparison of the bonding in these two geometries provides an explanation for the preference for pyramidal binding around the S atom. Calculations were also carried out for a similar complex in which DBT was replaced by T, and comparisons of the T and DBT complexes enable us to evaluate the relative binding abilities of the two heterocyclic ligands.

Finally, the last section of the paper discusses the bonding in both $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ and the ring-opened complex $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$. The calculated electronic structures for these complexes provide an explanation for the very nucleophilic character of the ring S atom in the η^4 complex, the driving force for the rearrangement of the η^4 complex to the ring-opened complex, and the planar structure of the metallacylic ring observed in $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$.

Calculational Details

All of the results described here were obtained from Fenske–Hall molecular orbital calculations.[27] Mulliken population analyses were used to determine orbital populations, overlap populations, and atomic charges.[32]

When possible, the molecular structures used in the molecular orbital calculations were taken from X-ray structure determinations. Structures have been determined for the η^5-Cp and η^5-T complexes $Cr(CO)_3T$,[10] $[Cr(CO)_3Cp]^-$,[11] $Mn(CO)_3Cp$,[33] $RuCp_2$,[31] $[Ru(TMT)_2]^{2+}$,[30] and $[Rh(PPh_3)_2T]^+$,[12] and calculations for these complexes utilized the known structures. The crystal structures of $[Mn(CO)_3T]^+$, $[RuCpT]^+$, and $[RuT_2]^{2+}$ have not been determined. Since the bond distances and angles in $[Cr(CO)_3Cp]^-$

---

(13) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

(14) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5379.

(15) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.

(16) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.

(17) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922.

(18) Rao, K. M.; Day, C. L.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 5046.

(19) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739.

(20) Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.

(21) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901.

(22) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

(23) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002.

(24) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

(25) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559.

(26) Ruette, F.; Valencia, N.; Sánchez-Delgado, R. *J. Am. Chem. Soc.* **1989**, *111*, 40.

(27) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(28) Singer, H. *J. Organomet. Chem.* **1967**, *9*, 135.

(29) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

(30) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828.

(31) Hardgrove, G. L.; Templeton, D. H. *Acta Crystallogr.* **1959**, *12*, 28.

(32) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

(33) Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1963**, *16*, 118.

and $Mn(CO)_3Cp$ are so similar, calculations for $[Mn(CO)_3T]^+$ utilized the known structure of $Cr(CO)_3T$, with Mn substituted for Cr. Calculations for $[RuT_2]^{2+}$ assumed the same structure as that of $[Ru(TMT)_2]^{2+}$ after removal of the ring methyl groups. $[RuCpT]^+$ was constructed using distances and angles from both $RuCp_2$ and $[Ru(TMT)_2]^{2+}$. The structure of the η^1(S)-bound complex $[Cp(CO)_2Fe(DBT)]^+$ has been determined,[15] and this structure was utilized for the calculations on both $[Cp(CO)_2Fe(DBT)]^+$ and $[Cp(CO)_2Fe(T)]^+$. In the thiophene complex, the DBT ring was replaced by a similarly oriented thiophene ring. The known structures of both Cp*Ir(η^4-2,5-Me_2T)[20] and Cp*Ir(*C*,*S*-2,5-Me_2T)[24] were used in the calculations for these complexes.

The 1s through *n*d functions for Cr, Mn, Fe, Ru, and Rh were taken from Richardson et al.[34,35] while the $(n + 1)$s and $(n + 1)$p functions were chosen to have exponents of 2.0 for Cr, Mn, and Fe and 2.2 for Ru and Rh. The Ir 1s through 5d functions were generated by a best fit to Herman–Skillman atomic calculations[36] using the method of Bursten, Jensen, and Fenske.[37] The 6s and 6p functions were chosen to have exponents of 2.4. The carbon, oxygen, and sulfur functions were taken from the double-ζ functions of Clementi.[38] The valence p functions were retained as the double-ζ functions, while all other functions were reduced to single-ζ functions. An exponent of 1.2 was used for hydrogen.

Results and Discussion

η^5 Complexes of Thiophene. In the η^5 binding mode, thiophene can be viewed as a formal six-electron donor, and metal–ligand binding in η^5-T complexes can be compared to metal–ligand binding in η^5-Cp complexes. As noted above, nearly all of the characterized η^5-T complexes have η^5-Cp analogues. Because the characters of the frontier orbitals in thiophene and Cp^- are very similar, η^5 binding of thiophene to a transition metal can readily be compared to η^5 binding of Cp^-. The molecular orbitals of both Cp^- and thiophene which play a role in binding to a transition metal are illustrated in Figure 1. Although introduction of the sulfur atom into the five-membered ring lowers the symmetry from D_{5h} in Cp^- to C_{2v} in thiophene, it is straightforward to relate the π orbitals of the two ligands.

In Cp^-, the degenerate e_1'' pair of orbitals is the highest occupied molecular orbital (HOMO), and these two orbitals serve as the principal donor orbitals in metal–ligand bonding. Although the lower energy a_2'' orbital also has the potential to serve as a donor orbital, it generally interacts less effectively with the metal orbitals, and most of the ligand to metal electron donation involves the e_1'' HOMO. The lowest energy unoccupied orbital (LUMO) is also a degenerate pair, e_2'', of π orbitals. Since these orbitals lie relatively high in energy and often do not overlap effectively with occupied metal orbitals, Cp^- does not generally serve as a good acceptor ligand.

In thiophene the two highest energy occupied orbitals, $1a_2$ and $2b_1$, are similar in character to the degenerate e_1'' HOMO in Cp^-. The Fenske–Hall calculations used in this study find the $2b_1$ and $1a_2$ orbitals in thiophene to have nearly the same energy, with the actual HOMO being the $2b_1$ orbital. Ab initio calculations also find the two orbitals to be close in energy but find the $1a_2$ orbital to be the HOMO.[39] The lower energy $1b_1$ π orbital is similar to the a_2'' orbital of Cp^-. Just as in Cp^-, these three π orbitals serve as potential donor orbitals in metal–ligand bonding. The presence of the S atom in thiophene results in a high-energy occupied orbital which has no counterpart in Cp^-. This $1a_1$ orbital, localized principally on the S atom, can be described as a σ lone pair orbital. It is less important in metal–ligand bonding when thiophene binds in the η^5 mode, but it becomes an important donor orbital when thiophene binds to a metal through the S atom. The two lowest energy unoccupied orbitals, $3b_1$ and $2a_2$, resemble the two orbitals of the degenerate e_2'' set in Cp^-, but the $3b_1$ and $2a_2$ orbitals are now well separated in energy. The $3b_1$ LUMO lies about 5 eV lower in energy than the $2a_2$ orbital and has the potential to act as an acceptor orbital.

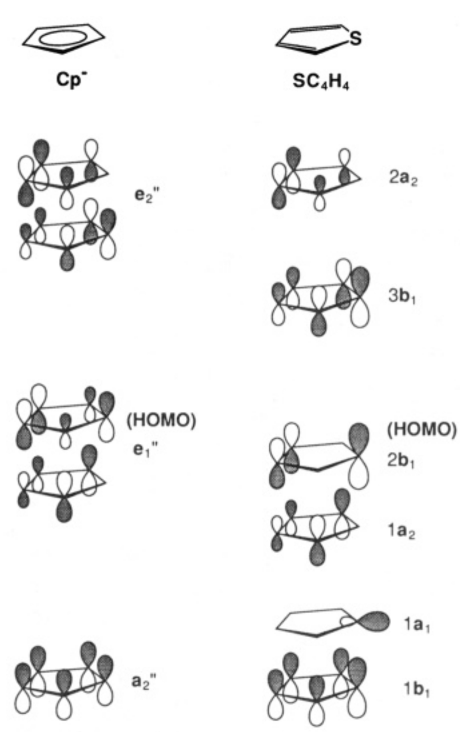


Figure 1. Comparison of the character, symmetry, and ordering of the high-energy occupied and low-energy unoccupied molecular orbitals of cyclopentadienyl anion and thiophene.

(a) $Cr(CO)_3T$, $[Cr(CO)_3Cp]^-$, $[Mn(CO)_3T]^+$, and $Mn(CO)_3Cp$. Since both $Cr(CO)_3T$ and $[Cr(CO)_3Cp]^-$ have been structurally characterized, it is useful to begin a discussion of bonding in the η^5 complexes by comparing the electronic structures of these two Cr complexes. Energy level diagrams for both $Cr(CO)_3T$ and $[Cr(CO)_3Cp]^-$ are shown in Figure 2. Bonding in the complexes can be described in terms of interactions between the $Cr(CO)_3$ fragment and the Cp^- or T ligand, and the important levels of $Cr(CO)_3$ and the two ligands are shown in Figure 2. (The labels on the orbitals in the three separated fragments reflect the symmetry of the individual fragments and not the overall lower symmetry of the complexes.) Considering first the more familiar $[Cr(CO)_3Cp]^-$, the three Cp^- donor orbitals, e_1'' and a_2'', interact with the vacant 2e and $2a_1$ orbitals on $Cr(CO)_3$. The Cp^- a_2'' orbital also interacts weakly, in an antibonding manner, with the filled $1a_1$ orbitals on $Cr(CO)_3$, but this

---

(34) Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. F. *J. Chem. Phys.* **1962**, *36*, 1057.

(35) Richardson, J. W.; Blackman, M. J.; Ranochak, J. E. *J. Chem. Phys.* **1973**, *58*, 3010.

(36) Herman, F.; Skillman, S. *Atomic Structure Calculations*; Prentice-Hall: Englewood Cliffs, NJ, 1963.

(37) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320.

(38) Clementi, E. *J. Chem. Phys.* **1964**, *40*, 1944.

(39) Von Niessen, W.; Kraemer, W. P.; Cederbaum, L. S. *J. Electron Spectrosc.* **1976**, *8*, 179.

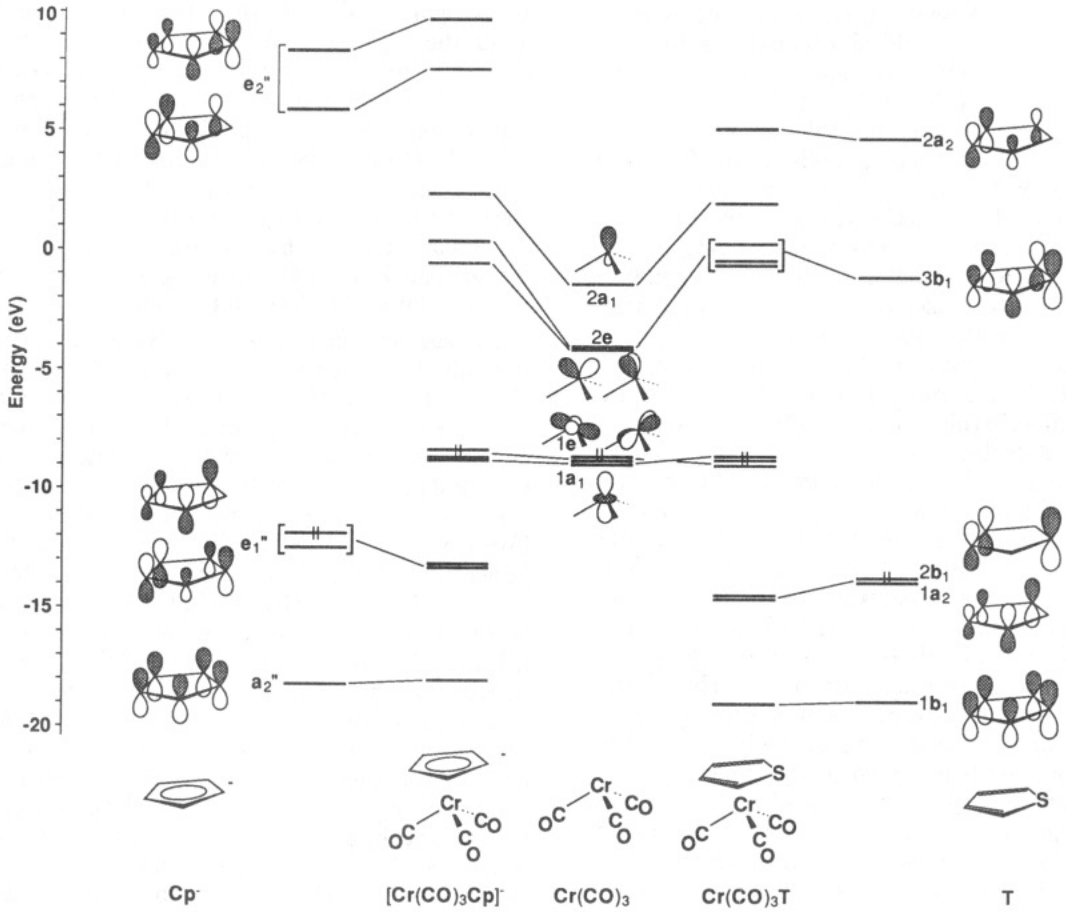


Figure 2. Calculated energy level diagrams for $[Cr(CO)_3Cp]^-$ and $Cr(CO)_3T$ and for the fragments Cp^-, $Cr(CO)_3$, and T. The energy scale refers to the calculated energies in $Cr(CO)_3T$. The energies of the levels in $[Cr(CO)_3Cp]^-$ and its component fragments have been scaled so that the energies of the $Cr(CO)_3$ fragment levels are the same in both complexes.

Table 1. Comparison of Cyclopentadienyl and Thiophene Orbital Occupations

	$[Cr(CO)_3Cp]^-$	$Cr(CO)_3T$	$Mn(CO)_3Cp$	$[Mn(CO)_3T]^+$	$RuCp_2$	$[RuCpT]^+$	$[RuT_2]^{2+}$	$[Ru(TMT)_2]^{2+}$
				Cyclopentadienyl				
e_2''	0.04		0.04		0.09	0.08		
	0.05		0.05		0.09	0.08		
e_1''	1.69		1.59		1.58	1.48		
	1.77		1.60		1.58	1.49		
				Thiophene				
$2a_2$		0.06		0.04		0.09	0.06	0.05
$3b_1$		0.20		0.12		0.23	0.18	0.17
$2b_1$		1.75		1.65		1.63	1.60	1.53
$1a_2$		1.80		1.71		1.67	1.59	1.61

weak interaction is mitigated by the bonding interaction between a_2'' and $2a_1$, and the $Cr(CO)_3$ $1a_1$ orbital is not destabilized in the complex. The unoccupied Cp e_2'' orbital interacts with the filled $Cr(CO)_3$ 1e orbitals, but this interaction is also weak. This bonding picture is similar to the one developed by Lichtenberger and co-workers[40,41] for the bonding in the isoelectronic $Mn(CO)_3Cp$ and $Mn(CO)_3Cp^*$.

In $Cr(CO)_3T$ the occupied $2b_1$, $1a_2$, and $1b_1$ thiophene orbitals can act as donors, while the empty $3b_1$ and $2a_2$ orbitals can act as acceptors. Most noticeable in Figure 2 are the differences in the relative energies, with respect to the metal-based $Cr(CO)_3$ orbitals, of the thiophene and Cp^- orbitals. For example, the Cp^- donor orbitals, e_1'', lie approximately 1.5 eV closer in energy to the metal-based orbitals than the corresponding thiophene donor ortibals, $1a_2$ and $2b_1$. On the other hand, the thiophene acceptor orbitals, $3b_1$ and $2a_2$, lie much lower in energy (as much as 7 eV for the $3b_1$ orbital) and therefore closer to the occupied metal-based orbitals than the corresponding Cp^- acceptor orbitals, e_2''. These differences suggest that thiophene should be a poorer donor but better acceptor than Cp^-.

The relative donor and acceptor strengths of Cp^- and T are reflected in the Mulliken populations of the ligand donor and acceptor orbitals in the complexes. The populations of these orbitals are listed in Table 1. In the isolated Cp^- and T ligands each of the donor orbitals (e_1'' in Cp^- and $1a_2$ and $2b_1$ in T) is occupied by two electrons while each of the acceptor orbitals (e_2'' in Cp^- and $3b_1$ and $2a_2$ in T) is empty. The occupations of the lower energy a_2'' orbital in Cp^- and $1b_1$ orbital in T are not included in the table since variations in these orbital occupations are

---

(40) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H. II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.

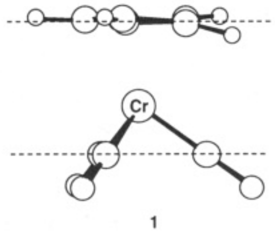
(41) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

small in the complexes considered here. The sizes of the donor and acceptor orbital occupations in both $[Cr(CO)_3Cp]^-$ and $Cr(CO)_3T$ are a measure of the relative donor and acceptor abilities of Cp^- and T. As expected from the relative orbital energies, thiophene is a poorer donor but somewhat better acceptor than Cp^-. The very small increases in the Cp^- acceptor occupations are indicative of the weak interactions between these orbitals and filled metal orbitals and the corresponding poor π back-donation from the metal to the Cp^- ligand in $[Cr(CO)_3Cp]^-$. The increased acceptor ability of T results almost entirely from the much lower energy thiophene $3b_1$ orbital. This increase is not large, however, and even though thiophene is a better π acceptor than Cp^-, it still cannot be described in this complex as a "good" π acceptor.

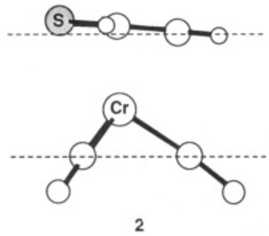
The calculated electronic structures of the isoelectronic $[Mn(CO)_3T]^+$ and $Mn(CO)_3Cp$ complexes display features very similar to those observed in the isoelectronic Cr complexes. (Because the orbital diagrams for the Mn complexes are so similar to those for the Cr complexes, the Mn diagrams are not illustrated.) The only significant differences arise because the Mn 3d orbitals lie lower in energy than the corresponding Cr 3d orbitals. This places them closer in energy to the ligand donor orbitals and more removed from the ligand acceptor orbitals. As a result, more ligand to metal donation and less metal to ligand back-donation is observed in the Mn complexes. Comparisons of the appropriate orbital occupations in Table 1 confirm these observations. Just as in the Cr complexes, however, thiophene remains a poorer donor but better acceptor than Cp^-, and we expect this to be the case in most transition metal complexes.

Although the natures of the bonding interactions between the T or Cp^- ring and the metal center are similar in these isoelectronic complexes, the relative strengths of the donor and acceptor interactions differ for the two ligands. Since it is well-known that the η^5-T ligand generally binds less strongly than the η^5-Cp ligand to a metal center and that η^5-T is readily displaced by other six-electron-donor ligands,[8] we would like to know whether the weaker binding by T is simply the result of the different donor and acceptor abilities of the two ligands, or whether other factors are involved. While the discussion so far has stressed similarities in the binding of Cp^- and T, it is important to recognize that replacing a C atom by the much larger S atom affects both the size of the ring and the individual character of the ring MO's. Can either of these factors be related to the weaker metal–ligand interactions in the thiophene complexes?

The large size of the S atom in the T ring and its effect on the preferred η^5 binding geometry of the T ring can be seen clearly in a comparison of the structures of $[Cr(CO)_3Cp]^-$ and $Cr(CO)_3T$, illustrated in **1** and **2**, respectively. In $[Cr(CO)_3Cp]^-$ the Cp ring lies approximately parallel to the plane formed by the C atoms of the three CO ligands. This is indicated in the diagrams by two parallel dotted lines. In $Cr(CO)_3T$, on the other hand, the large size of the S atom results in the tilting of the entire ring relative to a plane parallel to the three C atoms of the CO ligands. Tilting of the thiophene ring is also accompanied by a small slip of the ring. The combined tilt and slip accommodates the larger S atom and leaves the average Cr–C(ring) distance in $Cr(CO)_3T$ (2.20 Å) very close to the comparable distance in $[Cr(CO)_3Cp]^-$ (2.19 Å). This reorientation of the ring thus serves to optimize, rather than weaken, the bonding between the metal and both the large S and small C atoms.



1



2

The second factor to be considered, differences in the individual orbital characters of the ring MO's in Cp^- and T, could have an effect on the metal–ligand interactions. In particular, the large size of the S 3p orbitals, in comparison to the smaller C 2p orbitals, suggests the possibility of stronger repulsive interactions between filled metal and filled ligand orbitals in the thiophene complex. For example, in $[Cr(CO)_3Cp]^-$ a weak repulsion exists between the filled Cp^- a_2'' orbital and the filled $Cr(CO)_3$ $1a_1$ orbital. In $Cr(CO)_3T$ a similar repulsive interaction occurs between the filled thiophene $1b_1$ orbital and the filled $Cr(CO)_3$ $1a_1$ orbital. Because of the larger size of the S 3p orbital this interaction might be more repulsive and thus destabilizing. In addition, a repulsive interaction could occur between the filled thiophene $1a_1$ (σ lone pair) orbital and the $Cr(CO)_3$ $1a_1$ orbital. Even though this thiophene orbital lies in the plane of the thiophene ring, the sulfur orbital is so large that this type of interaction cannot immediately be discounted. In fact, however, metal–ligand overlap populations suggest that both of these repulsive interactions are sufficiently weak that they do not have any real destabilizing effect on the thiophene complex.

These comparisons of the bonding in the Cr and Mn complexes, along with comparisons described below of the donor and acceptor abilities of Cp^-, T, and TMT when bound to Ru^{2+}, suggest that even though the differences in donor abilities of the ligands are not large, it is usually the difference in donor ability which accounts for the differences in binding ability of the two ligands. We shall find, however, that the π acceptor ability of thiophene *does*, in some complexes, also have an effect on the binding ability of the thiophene ligand.

(b) $RuCp_2$, $[RuCp(T)]^+$, $[Ru(T)_2]^{2+}$, and $[Ru(TMT)_2]^{2+}$. In η^5-T and η^5-Cp complexes containing metals further to the right in the periodic table, the stabilization of the metal orbitals should contribute to an increase in the donor capacity and a corresponding decrease in the acceptor capacity of both ligands. At the same time, however, in complexes containing the larger 4d or 5d transition metals, stronger metal–ligand overlaps should contribute to stronger metal–ligand interactions. Both of these effects are observed in the electronic structure of a group of metallocene complexes containing Ru and Cp^-, T, and TMT ligands. Calculations were carried out for $RuCp_2$, $[RuCp(T)]^+$, $[Ru(T)_2]^{2+}$, and $[Ru(TMT)_2]^{2+}$, and the orbital structures of these complexes confirm that, as expected, the Cp^- donor orbitals lie closer in energy than the thiophene donor orbitals to the metal-based orbitals. At the same time, the Cp^- acceptor orbitals lie higher in energy than the thiophene acceptor orbitals and are further removed from the metal-based orbitals.

The most interesting observations regarding the electronic structures of these ruthenocene analogs come from

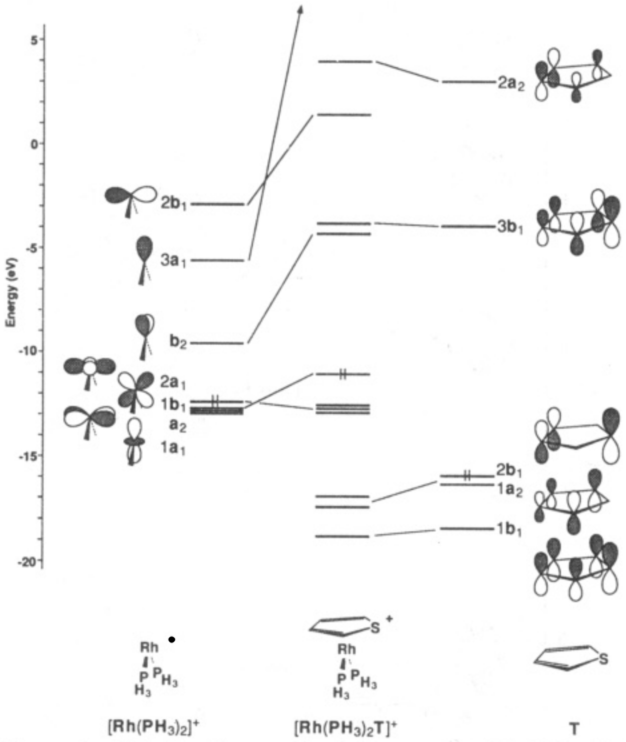


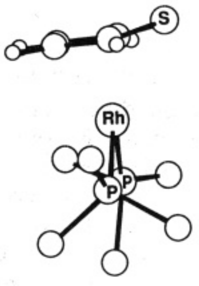
Figure 3. Calculated energy level diagrams for $[Rh(PH_3)_2T]^+$ and for the $[Rh(PH_3)_2]^+$ and T fragments.

the ligand orbital occupations listed in Table 1. For example, comparing the donor and acceptor orbital occupations in $[Ru(T)_2]^{2+}$, $[Ru(TMT)_2]^{2+}$, and $RuCp_2$ shows that while thiophene remains a slightly poorer donor (although the donor ability of TMT appears comparable to that of Cp^-) and somewhat better acceptor than Cp^-, the total ligand to metal donation and metal to ligand back-donation is quite similar in all three of these complexes. A factor which levels the donor abilities of the two ligands in these complexes, as opposed to their differing donor abilities in the 3d $M(CO)_3Cp$ and $M(CO)_3T$ complexes, is the large size of the Ru 4d orbitals. The relative strengths of the metal–ligand orbital interactions depend both on the energy separation between the metal and ligand orbitals and on the size of the overlap between these orbitals. In these Ru complexes the strong overlaps between the metal 4d orbitals and the very large S orbitals in T compensate for the larger energy separations between the T donor and metal acceptor orbitals and thus strengthen the metal–ligand interactions.

The occupations in Table 1 also illustrate, however, that when Cp^- and T are simultaneously coordinated to the metal, the different donor and acceptor capabilities of the two ligands are amplified rather than leveled. For example, comparing the ligand orbital occupations in $RuCp_2$, $[RuCp(T)]^+$, and $[Ru(T)_2]^{2+}$ shows that in $[RuCp(T)]^+$ the simultaneous coordination of Cp^- and T enhances both the donor ability of Cp^- and the acceptor ability of T. That is, the superior acceptor ability of T facilitates the transfer of charge from the Cp^- ligand to the metal and ultimately to the $3b_1$ thiophene acceptor orbital. The $3b_1$ occupation indicates that this orbital acts as a particularly effective acceptor orbital in $[RuCp(T)]^+$.

Comparisons between the binding abilities of T and Cp^- (or other arenes) are usually made in complexes where these ligands function primarily as *donors* (e.g. the 3d Cr and Mn complexes described above). In these cases Cp^- is usually a more effective donor, although the similar charge distributions in $RuCp_2$ $[Ru(T)_2]^+$, and $[Ru(TMT)_2]^{2+}$ indicate that thiophene's donor ability increases when it is bound to larger 4d or 5d metals. The bonding in $[RuCp(T)]^+$, on the other hand, indicates that when both thiophene and a ligand (or ligands) having superior donor ability are simultaneously bound to a metal, the acceptor ability of thiophene becomes important. Taken all together, the charge distributions in these complexes suggest that η^5-T binding may be at its strongest in a complex incorporating T and a 4d or 5d metal which is also coordinated to donor ligands.

(c) $[Rh(PPh_3)_2T]^+$. The large size of the sulfur atom and the electronic structure of the thiophene ring play an important role in determining both the electronic and molecular structures of another η^5-T complex, $[Rh(PPh_3)_2T]^+$. Although nearly all of the well-characterized η^5 complexes of thiophene contain a d^6 six-coordinate metal, $[Rh(PPh_3)_2T]^+$ incorporates a five-coordinate d^8 Rh(III). The structure of the complex (where the PPh_3 groups have been replaced by PH_3 groups) is illustrated in **3**,[12] and a particularly interesting feature of the complex is the nonplanarity of the thiophene ring. Although, as discussed above, a *tilt* of the thiophene ring is observed in a number of the η^5-thiophene complexes, this Rh complex provided the first example of a noticeable *bend* in the thiophene ring. In order to understand the molecular structure of this thiophene complex, it is helpful to again recognize that analogous Cp complexes are known. For example, $Co(CO)_2Cp^*$ is structurally (and electronically) similar to $[Rh(PPh_3)_2T]^+$. In the Co complex, however, a distinct puckering,[42] rather than bend, in the Cp^* ring is observed. This puckering has been attributed to an antibonding interaction between filled Cp^* and Co orbitals,[43,44] and we find, not surprisingly, that the bend of the thiophene ring in the Rh complex arises from a similar electronic interaction.



3

Calculations were carried out for $[Rh(PH_3)T]^+$, and the orbital diagrams for this complex and the component fragments $[Rh(PH_3)_2]^+$ and T are shown in Figure 3. (While replacing PPh_3 groups by PH_3 groups has some effect on both the energies and compositions of the molecular orbitals in the complex, the general features of the orbital structure are not changed by this simplification.) The labels on the two fragments correspond to the near-C_{2v} symmetries of both fragments (although the orientation of the H's in the PH_3 groups and the small bend in the thiophene ring mean that the symmetry of neither fragment is strictly C_{2v}, the characters of the individual fragment orbitals show little change from their

---

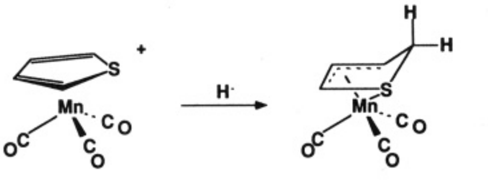
[42] Byers, L. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *19*, 278.

[43] Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

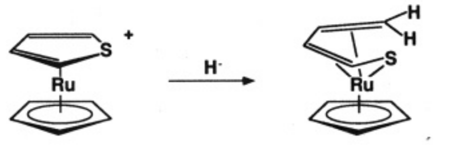
[44] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

character in real C_{2v} symmetry). The diagram shows that once again the filled $1b_1$, $1a_2$, and $2b_1$ orbitals of thiophene serve as donor orbitals, while the empty $1b_2$, $3a_1$, and $2b_1$ orbitals of the $[Rh(PH_3)_2]^+$ fragment act as acceptors. The thiophene $1b_1$, $1a_2$, and $2b_1$ orbitals match up with the Rh fragment $3a_1$, $1b_2$, and $2b_1$ orbitals, respectively. The empty thiophene $3b_1$ orbital is also oriented correctly to accept charge from the filled metal $2a_1$ fragment orbital. Although a small donation into this orbital is observed, the major bonding component involves donation from the thiophene to the metal. In addition to these donor–acceptor type interactions, however, there is a substantial interaction between the *filled* thiophene $2b_1$ orbital and the *filled* Rh $1b_1$ orbital. The energetic proximity of these orbitals and the large size of the sulfur 3p orbital mean that this interaction is strongly antibonding. Mixing in of the corresponding Rh–thiophene bonding b_1 interaction mitigates this repulsive interaction to some degree, and the bending of the sulfur atom up out of the plane of the thiophene ring further reduces the repulsion. Still, the net result is a destabilized HOMO which, although primarily metal in character, is antibonding between the metal and the thiophene ring sulfur. If the sulfur atom were not bent away from the Rh atom, however, this destabilization would be considerably larger.

This same type of antibonding interaction has previously been related to the nonplanarity (puckering) of the Cp ring in $Co(CO)_2Cp^*$. In $[Rh(PH_3)_2T]^+$, the metal–ring antibonding interaction involves a thiophene orbital with a substantial sulfur component. Given the large size of the sulfur 3p orbitals (in comparison to the much more compact carbon 2p orbitals), both the metal–sulfur orbital overlap and the resulting metal–sulfur antibonding interaction are sizable. The necessity of maintaining good bonding interactions with the ring while at the same time alleviating to at least some degree the antibonding interaction involving the sulfur atom requires that the large sulfur atom actually bend up out of the ring.



(1)



(2)

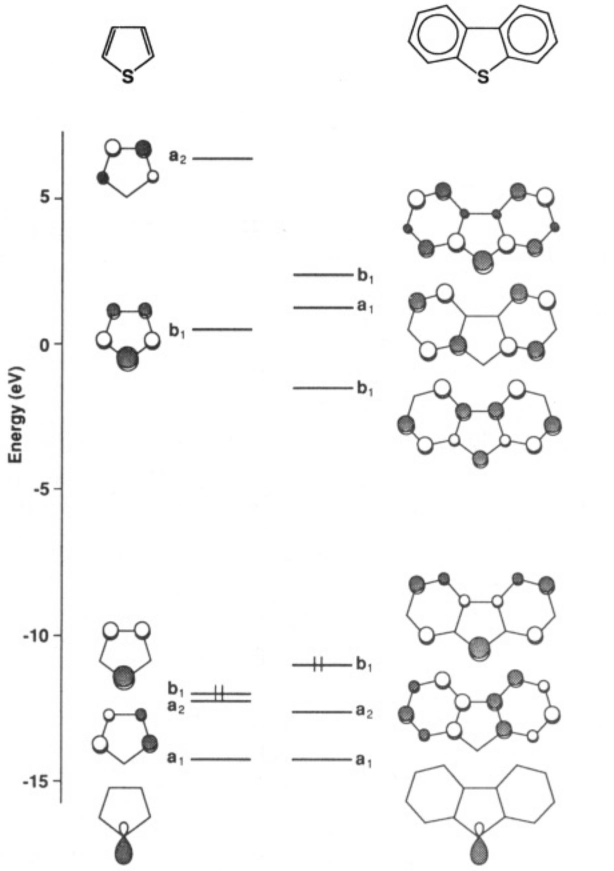


Figure 4. Calculated energy level diagrams for the high-energy occupied and low-energy unoccupied orbitals of thiophene and dibenzothiophene.

Ring Activation in η^5-Thiophene Complexes. An intriguing feature of several of the η^5-T complexes is the activation of the thiophene ring toward nucleophilic attack. For example, a hydride ion adds to the α-C of the coordinated thiophene ring in $[Mn(CO)_3T]^+$ (eq 1)[21] and $[RuCpT]^+$ (eq 2).[22] In the reaction involving the Ru complex, hydride addition actually leads to cleavage of a C–S bond. Since isolated thiophene is not subject to nucleophilic attack, activation of the thiophene ring in the Mn and Ru complexes suggests that changes in the electronic structure of the coordinated thiophene ring may be responsible for this activation. Changes in the electronic structure might include (1) increased positive charge on the α-C in the ring, (2) significant α-C orbital character in the LUMO of the complex, and/or (3) weakening of the α-C–S bond in the ring. Examination of the calculated electronic structure of these complexes indicates, however, that the charge distribution in the thiophene ring is not significantly altered in the complex. No significant positive charge develops on the α-C, the LUMO is principally a metal-based orbital and, on the basis of Mulliken overlap populations, the C–S bond in the coordinated thiophene ring is not noticeably weaker than the C–S bond in the free thiophene ligand. Why, then, is the ring activated in these complexes? Previous theoretical investigators also found little correlation between the ring electronic structure and aromatic ring activation in organometallic complexes.[45] They suggested that since ring activation is observed only in positively charged complexes, it is the charge on the complex, rather than significant alteration of the electronic structure of the coordinated aromatic ligand, which accounts for the ring activation in a complex. The overall positive charge of the complex is expected to stabilize the unoccupied ligand ring orbitals, thus making them energetically more accessible to a nucleophile. When combined with the experimental observation that ring activation occurs only in the positively charged thiophene complexes, the absence of significant electronic perturbation in the calculated electronic structure of the bound thiophene ligands suggests that it is also the charge on these complexes, rather than significant changes in the electronic structure of the bound thiophene ligands, which leads to activation of the thiophene ring.

---

[45] Kane-Maquire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

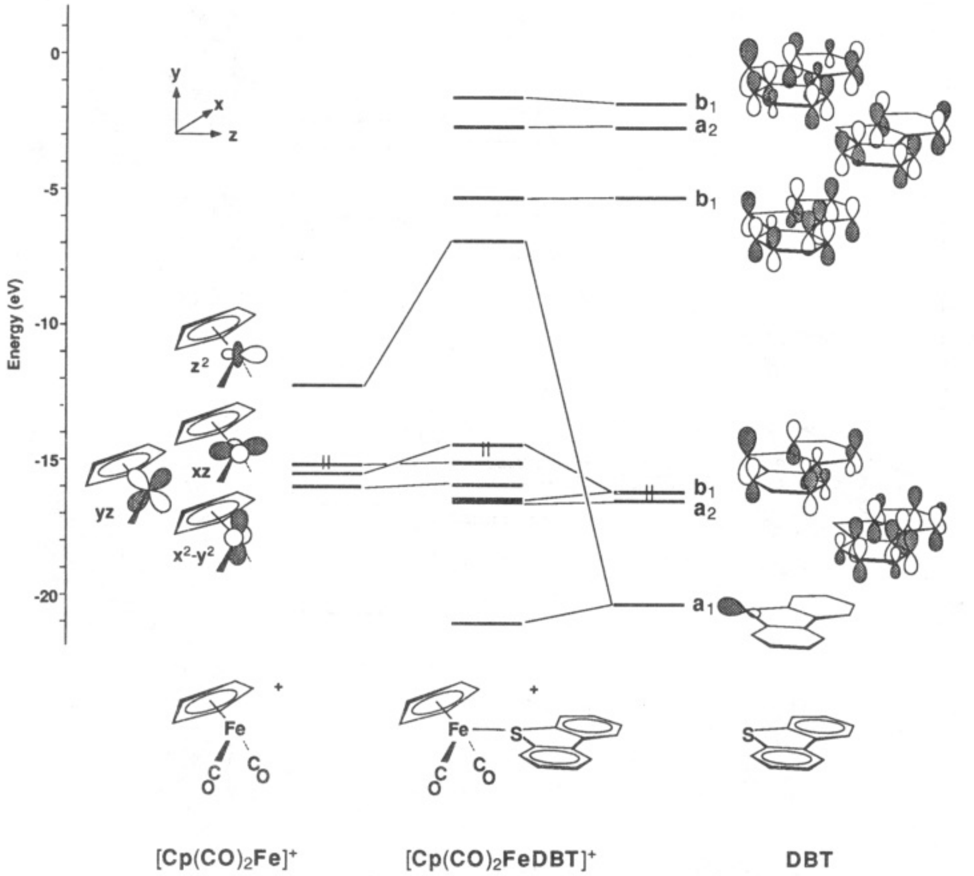


Figure 5. Calculated energy level diagrams for $[Cp(CO)_2FeDBT]^+$ and for the $[Cp(CO)_2Fe]^+$ and DBT fragments when the DBT ligand lies in a "perpendicular" configuration, i.e. a configuration in which the Fe atom and the DBT ligand lie in the same plane.

η^1(S) Complexes of Thiophene and Dibenzothiophene. In the η^1(S) mode, thiophene has the potential to donate electrons from both the $2b_1$ and $1a_1$ orbitals and can therefore act as a π (b_1) and/or σ (a_1) donor (Figure 1). (While the $1b_1$ orbital could also serve as a π donor orbital, it is quite low in energy and is found not to participate in metal–ligand interactions to any significant degree.) When bound through the sulfur, thiophene also has the potential to accept electrons into the unoccupied LUMO, $3b_1$. Although the orbitals of DBT are more complex than those of thiophene, the orbital structures of both compounds refect their overall C_{2v} symmetry. Comparisons of the HOMO and LUMO of thiophene and dibenzothiophene (Figure 4) show that similar sulfur contributions to these orbitals result in a_1 and b_1 donor orbitals and b_1 acceptor orbitals in both DBT and thiophene. In DBT, however, sulfur contributes to two rather than one low-energy unoccupied π b_1 acceptor orbital, and the larger sulfur orbital contribution is actually found in the higher energy b_1 orbital. As a result, even though DBT has a π acceptor orbital at lower energy than the π acceptor orbital in thiophene, this DBT orbital has less sulfur character than the thiophene b_1 acceptor orbital.

Calculations were carried out for $[Cp(CO)_2Fe(DBT)]^+$ both in the pyramidal or "bent" configuration observed in the actual complex and in a configuration where the plane of the DBT ring is perpendicular to the plane formed by the Fe and two CO ligands. This allowed us to compare the bonding in the two ligand configurations and to understand the preference for the bent configuration. Calculations were also carried out for a similar complex $[Cp(CO)_2FeT]^+$, where the DBT was replaced by thiophene. This enabled us to compare DBT and thiophene η^1(S) binding and to look for any differences in the effects of η^5 and η^1 binding on the electronic structure of the thiophene ring.

(a) $[Cp(CO)_2Fe(DBT)]^+$. The calculated energy level diagram for $[Cp(CO)_2Fe(DBT)]^+$ (with DBT in the perpendicular configuration) is shown in Figure 5, and an examination of this diagram quickly reveals why this configuration is undesirable. While the filled DBT a_1 orbital (σ lone pair) is properly oriented to donate into the unoccupied metal-based d_{z^2} type orbital, and the unoccupied DBT b_1 orbitals are oriented properly to accept electron density from the filled metal-based d_{yz} orbital, the filled DBT b_1 π lone pair type orbital is also properly oriented to interact with the *filled* d_{yz} orbital. In addition, the filled DBT b_1 and metal d_{yz} orbitals lie very close together in energy. As a result, the predominant $d\pi$–$S\pi$ interaction is the antibonding one resulting from the filled–filled interaction of these orbitals. In this "perpendicular" configuration, DBT thus acts as both a σ and π donor, i.e. a 4-electron donor, even though the 16-electron $[Cp(CO)_2Fe]^+$ fragment only requires two additional electrons.

As shown in Figure 6, tipping of the DBT ring away from this perpendicular configuration alleviates the filled DBT b_1–metal d_{yz} antibonding interaction. Equally important, this filled DBT b_1 orbital can now overlap with and donate into the empty metal d_{z^2} type orbital. This donor interaction is important because tipping of the ring weakens the DBT a_1–metal d_{z^2} bonding interaction, and the a_1 orbital now donates less effectively than in the perpendicular configuration. On the basis of Mulliken populations of the DBT orbitals in the two complexes,

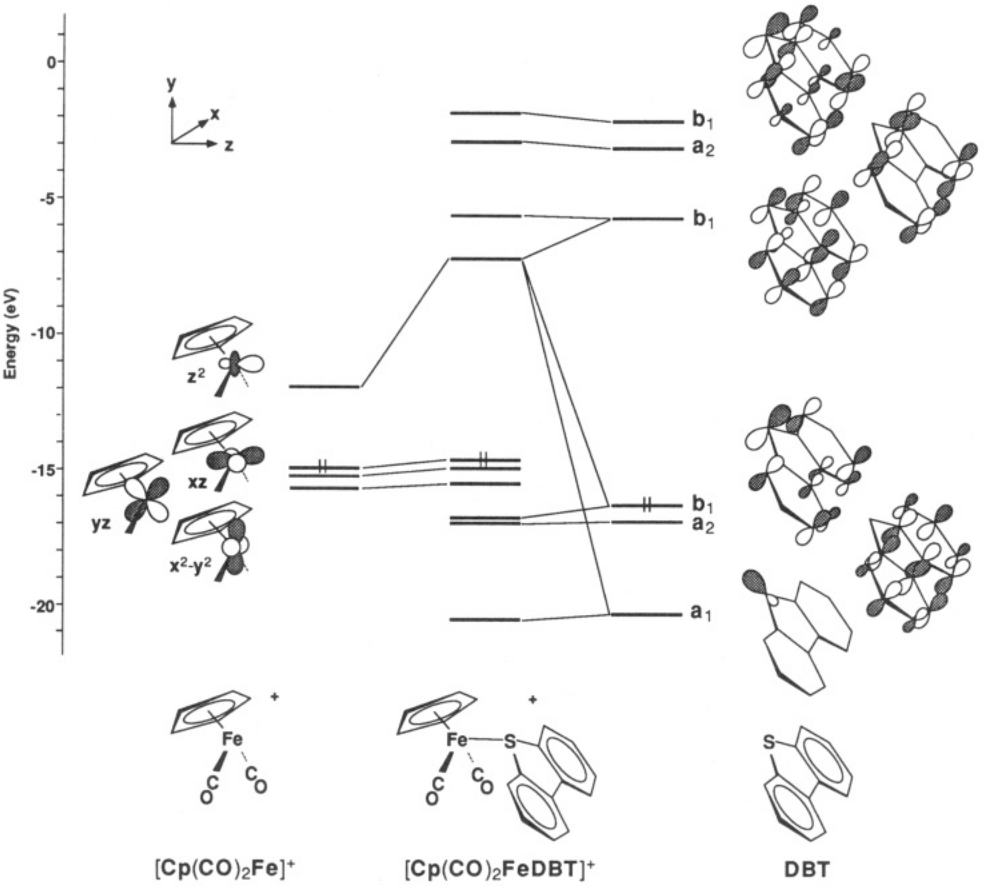


Figure 6. Calculated energy level diagrams for $[Cp(CO)_2FeDBT]^+$ and for the $[Cp(CO)_2Fe]^+$ and DBT fragments when the DBT ligand lies in a "tipped" configuration, i.e. a configuration in which the Fe atom and the DBT ligand do not lie in the same plane. This is the configuration actually observed in the molecule.

however, the combined donation from the DBT a_1 and b_1 orbitals in the actual tipped-ring configuration (0.48 electron) is nearly the same as the donation from the a_1 orbital alone (0.42 electron) in the perpendicular configuration. The tipped configuration can be thus be associated with the ring acting as a two-electron, rather than four-electron, donor. A preference for this same type of tipped bonding has also been calculated for several model transition metal complexes containing cyclic nonaromatic sulfides.[46] Comparisons between the frontier orbitals in DBT or thiophene and those in these nonaromatic cyclic sulfides show that in all of these molecules the natures of the donor orbitals are similar; that is, both σ and π donor orbitals are available. In all of these systems tipping of the sulfur-containing ring both relieves an antibonding interaction between a filled π ring orbital and a filled metal orbital and allows the filled π ring orbital to begin to donate into an empty metal orbital.

Although the sulfur atom in free DBT or thiophene is probably best described as sp^2 hybridized, pyramidal sulfur bonding such as that observed in the DBT and T complexes is often associated with sp^3 hybridization at the sulfur. Tipping of DBT does not appear to indicate rehybridization of the sulfur orbitals in the bound DBT, however, since binding has little effect on bond lengths or bond strengths (as measured by overlap populations in free and bound DBT) in DBT. Instead, the tipping is a consequence of the orbital structures of the metal fragment and the DBT ring and the need for DBT to act only as a two-electron donor.

(b) $[Cp(CO)_2FeT]^+$. Calculations were also carried out for a similar complex, $[Cp(CO)_2FeT]^+$, where DBT was replaced by thiophene. Both the thiophene and DBT ligands are quite labile in these complexes, although the DBT ligand appears to bind somewhat more strongly to the Fe center.[15] One of the problems we wished to address was the reason for the increased lability of thiophene. As can be seen from Figure 7, the features of the energy level diagrams for the thiophene and DBT complexes are very similar. When the diagrams in Figures 6 and 7 are compared, however, it is apparent that the energies of the ligand orbitals, relative to the metal-based orbitals, are different. In DBT, the occupied orbitals are higher in energy, relative to the metal fragment orbitals, than the corresponding thiophene orbitals. This is particularly true for the HOMO of DBT (the π lone pair orbital), where the separation between the metal d_{z^2} acceptor orbital and the ligand HOMO is some 2.5 eV smaller in the DBT complex than in the thiophene complex. This results in a small increase in ligand to metal donation in the DBT complex. The unoccupied DBT orbitals are lower in energy, relative to the metal fragment orbitals, than the corresponding thiophene orbitals. Since the metal to ligand back-donation is negligible in these complexes, however, the relative energies of the acceptor orbitals have little effect on the metal–sulfur interactions. The differences in lability of the two ligands, at least in these Fe complexes, appear to be related to the slightly better donor ability of the DBT ligand.

There is no remarkable perturbation of the thiophene and DBT rings in these complexes. This is not surprising, since not only is the metal–sulfur interaction a weak one

---

[46] Calhorda, M. J.; Hoffmann, R.; Friend, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 50.

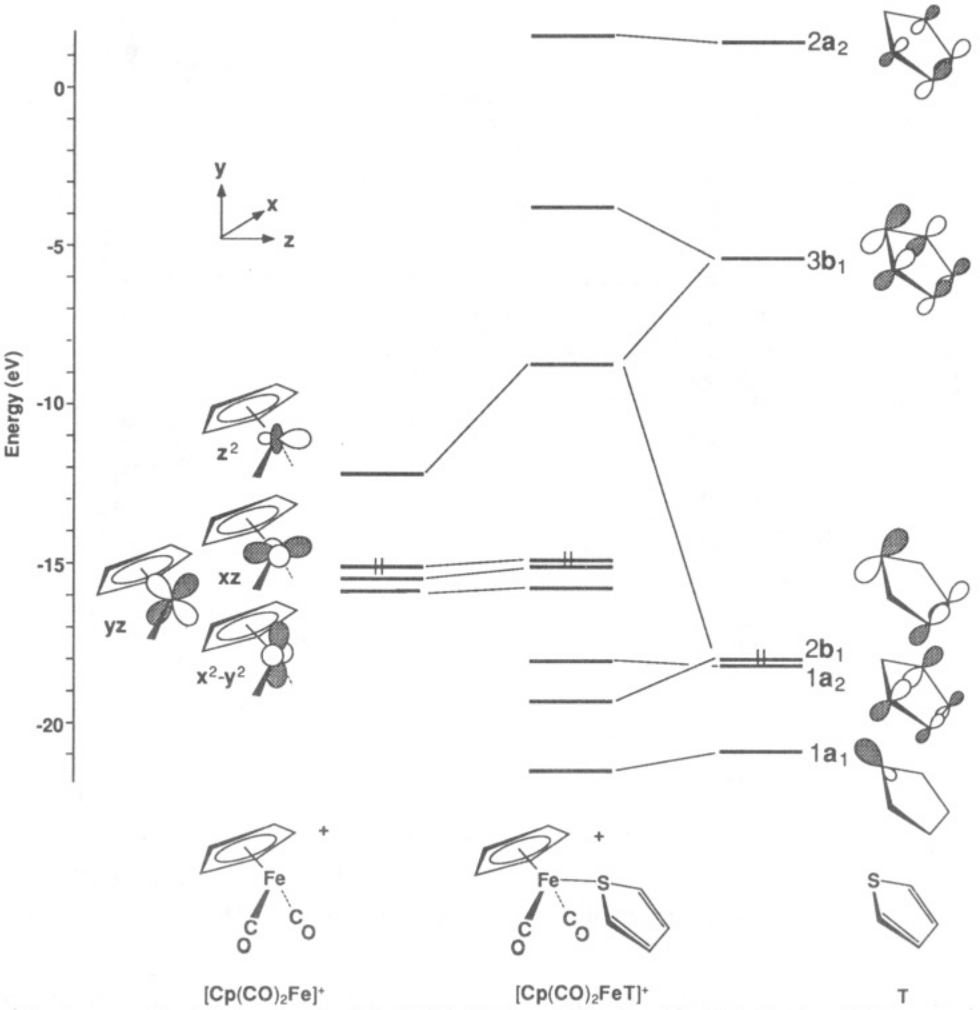
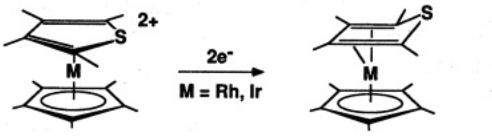


Figure 7. Calculated energy level diagrams for $[Cp(CO)_2FeT]^+$ and for the $[Cp(CO)_2Fe]^+$ and T fragments. The structure of this molecule is assumed to be the same as that of $[Cp(CO)_2FeDBT]^+$, where the DBT ring has merely been replaced by the simpler thiophene ring.

but also the ligand to metal donation depopulates ligand orbitals which are primarily sulfur lone pair orbitals. Binding through the ring sulfur atom, at least in these iron complexes, thus has little effect on either the S–C bond or the ligand as a whole.

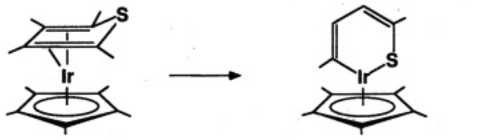
A number of similar six-coordinate S-bound thiophene and DBT complexes containing second- and third-row transition metal complexes have also been synthesized and characterized,[16,17,31] and even though M–S binding is expected to be somewhat stronger in these complexes, no activation of the C–S bond has been observed. All of these stable complexes also contain a six-coordinate d^6 transition metal, and the M–S binding should be quite similar to that observed in the iron complexes. Recently, the Jones group has shown that in some cases an S-bound thiophene serves as a precursor to insertion of the metal into the C–S bond of the thiophene ring, but in these cases the S-bound precursor is a five-coordinate d^8 complex.[25,47] The electronic structure of these five-coordinate intermediates is quite different from that of the stable six-coordinate complexes. We have made detailed comparisons of the electronic structures of these complexes, and this work will be reported in a separate communication.[48]

η^4 Coordination of Thiophene and C–S Bond Insertion. The Rauchfuss and Angelici groups have shown that reduction of the d^6 metallocene analogs $[Cp^*Rh(TMT)]^{2+}$ and $[Cp^*Ir(2,5\text{-}Me_2T)]^{2+}$ leads to η^4 complexes (eq 3).[19,20]



(3)

Unlike the sulfur atom in free thiophene or in the η^5 complexes, the sulfur in the thiophene ring of the η^4 complexes is extremely nucleophilic.[23,49] In the reduced Ir complex, which has been structurally characterized, the ring sulfur atom is bent out of the plane of the four ring carbons by 42°.[20] This Ir complex readily rearranges to an "iridathiabenzene" (eq 4), in which Ir has inserted into



(4)

the S–C bond of the thiophene ring.[24] While the bend in the thiophene ring in the reduced complexes can be associated with the need for thiophene to serve as a formal four-electron donor, the ultimate insertion of the Ir metal

---

(47) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698.
(48) Harris, S.; Carter, K. L. Manuscript in preparation.
(49) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 849.

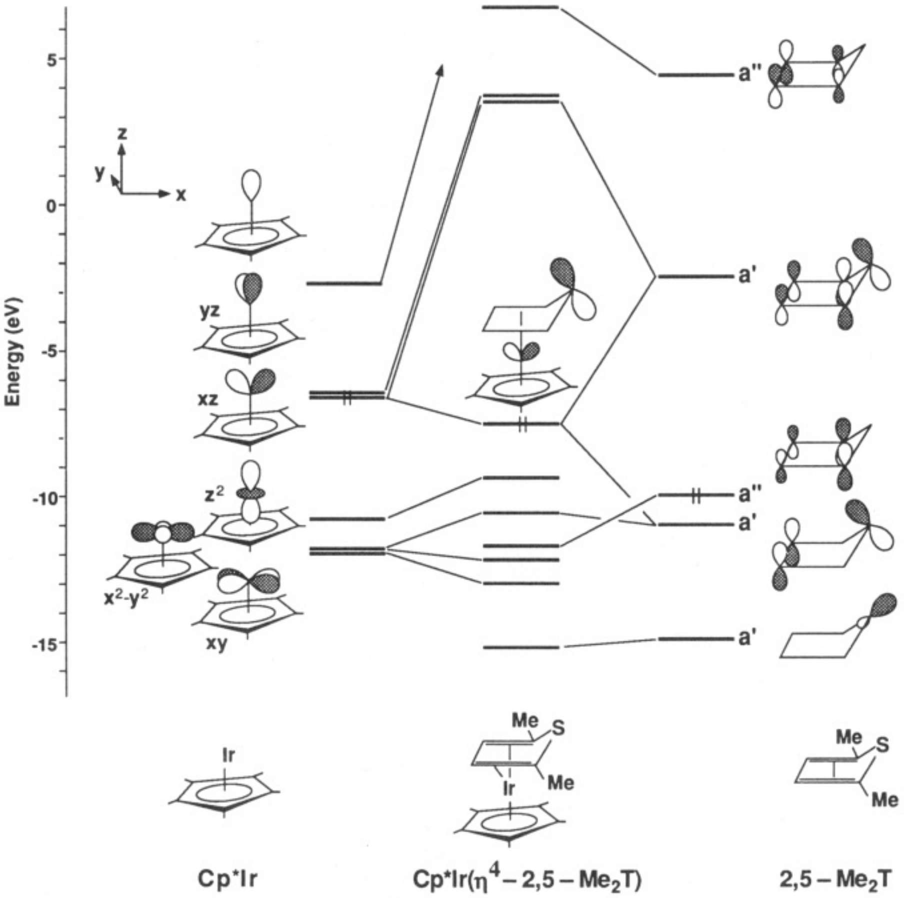


Figure 8. Calculated energy level diagrams for the η^4-thiophene complex Cp*Ir(η^4-2,5-Me$_2$T) and for the Cp*Ir and 2,5-Me$_2$T fragments.

center into the thiophene ring is not so readily explained. In order to understand the electronic structure of these complexes, the increased nucleophilicity of the ring sulfur in the η^4 complex, and the driving force for the rearrangement of the Ir complex, calculations were carried out for both Cp*Ir(η^4-2,5-Me$_2$T) and the ring-opened complex Cp*Ir(*C*,*S*-2,5-Me$_2$T).

(a) Cp*Ir(η^4-2,5-Me$_2$T). The calculated energy level diagram for Cp*Ir(η^4-2,5-Me$_2$T) is shown in Figure 8. The frontier orbitals of the d^8 Cp*Ir fragment and the bent thiophene ligand are illustrated on the left and right of the diagram, respectively. Although the bent thiophene ligand has at most C_s symmetry, comparisons of the frontier orbitals of the bent (Figure 8) and planar (Figure 1) thiophene ligands show that the forms of these orbitals are very similar in the two ligands. Because of the near-C_s symmetry of the η^4 complex, interactions between the metal fragment and thiophene orbitals are determined to a large degree by whether these orbitals are symmetric or antisymmetric with respect to reflection through the *xz* plane. The dominant bonding interaction involves the "antisymmetric" a″ thiophene HOMO and the metal fragment (d$_{yz}$) LUMO. Interactions between the "symmetric" metal fragment and thiophene orbitals are somewhat more complex, but the major contributors are the occupied and unoccupied thiophene a′ orbitals having sulfur "π" character and the occupied metal fragment d$_{xz}$ orbital. The interactions among these three ligand and metal orbitals result in three molecular orbitals, two occupied and one unoccupied. As expected, the lowest energy (occupied) orbital is bonding between the ligand and metal while the highest energy (unoccupied) orbital is antibonding. The molecular orbital of primary interest is the middle orbital of this set, the HOMO of the molecule. This MO is illustrated on the diagram in Figure 8. The mixing of both the occupied and unoccupied a′ ligand orbitals with the metal d$_{xz}$ orbital results in a HOMO which, were it not for the very large size of the sulfur 3p orbital, would be nearly nonbonding between the ligand and metal. The HOMO is approximately 50% sulfur p orbital in character, however, and the large size of this orbital means that even with the sharp bend of the sulfur away from the metal atom, there is still considerable overlap between the sulfur and metal orbitals. Not only does the HOMO have significant sulfur character, this orbital is actually *antibonding* between the metal and sulfur atoms. Thus, in spite of the fact that bending of the sulfur atom out of the plane of the ring carbon atoms is associated with the formal conversion of the thiophene ring from a six-electron to four-electron donor, the large size of the sulfur p orbital means that even in this bent η^4 configuration the thiophene ring cannot truly act as a strict four-electron donor.

The character of the HOMO provides an explanation for the greatly increased nucleophilicity of the thiophene sulfur atom in the η^4 complex. Since η^4 coordination of the thiophene ring leads to both the loss of aromaticity in the thiophene ring and an occupied high-energy molecular orbital which is 50% sulfur in character, this coordination mode results in a very accessible sulfur p orbital. This contrasts sharply with the relatively inaccessible sulfur orbitals in the aromatic planar thiophene ring.

The nature of the HOMO also provides us with some insight into why the rearrangement shown in eq 4 is favored. Even though the η^4 complex is formally a stable

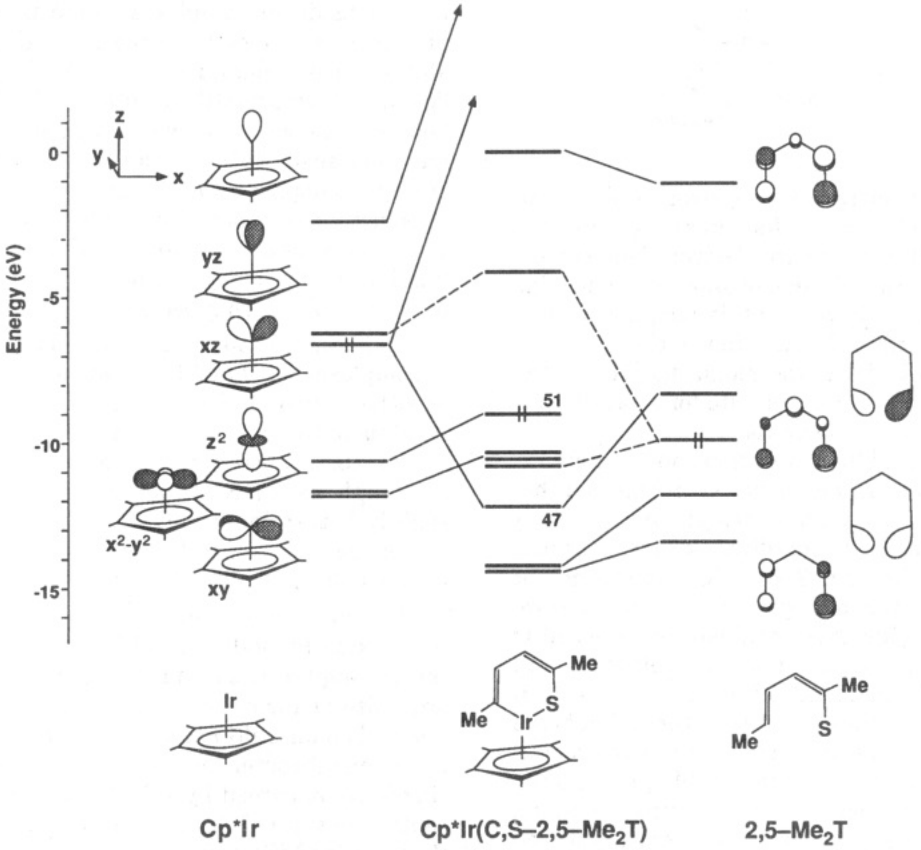


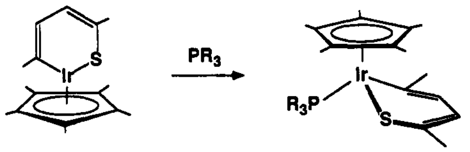
Figure 9. Calculated energy level diagrams for the ring-opened thiophene complex Cp*Ir(*C*,*S*-2,5-Me$_2$T) and for the Cp*Ir and opened 2,5-Me$_2$T fragments.

18-electron complex, there is clearly a substantial metal–sulfur antibonding interaction which persists even after the sulfur bends sharply up out of the plane of the ring carbon atoms. This suggests that a rearrangement which removes electron density from the metal and/or relieves this destabilizing interaction should be favorable. The calculated electronic structure for Cp*Ir(*C*,*S*-2,5-Me$_2$T) indicates that the conversion from an η^4 to a ring-opened complex removes electron density from the metal through a formal oxidative addition.

(b) Cp*Ir(*C*,*S*-2,5-Me$_2$T). The calculated energy level diagram for Cp*Ir(*C*,*S*-2,5-Me$_2$T) is shown in Figure 9. The bonding can be viewed in terms of a d^8 Cp*Ir fragment and a planar opened thiophene ring, and the orbitals for both of these fragments are illustrated in Figure 9. The two highest energy occupied orbitals on the opened thiophene ring are π and σ orbitals which are oriented properly to donate into the two lowest energy unoccupied orbitals on the metal fragment. Equally important with this donation from the ligand to the metal, however, is the donation in the other direction, from the metal to the ligand. Opening of the thiophene ring leads to a very low energy ligand LUMO. This ligand LUMO lies very close in energy to the metal fragment d_{xz} HOMO and can interact quite strongly with the metal HOMO. The net effect of this interaction is a transfer of electrons from a metal to a ligand orbital, i.e. a formal oxidative addition. A simple interpretation of the bonding suggests that insertion of the metal into the thiophene ring is accompanied by a straightforward oxidation of the metal from Ir(I) to Ir(III). Careful examination of the occupied MO's shows, however, that although we can identify this formal oxidative transfer of a pair of electrons from the metal to ligand orbitals, the strong mixing of several metal and ligand orbitals delocalizes a considerable amount of electron density between the ligand and metal and stabilizes the resulting charge on the metal. For example, although approximately 75% of the charge density in MO's 50 and 51, the two highest energy occupied orbitals in the complex, is localized in the metal $d_{x^2-y^2}$ and d_{z^2} orbitals, respectively, the charge density in both MO's 48 and 49 is distributed much more evenly between the metal (primarily d_{xy} with a small contribution from d_{yz}) and ligand π orbitals. Although we formally describe the metal in this complex as Ir(III), the participation of the metal orbitals in the π system of the "metallathiabenzene" ring greatly reduces the actual charge on the metal. In fact, the calculated Ir charge in Cp*Ir(*C*,*S*-2,5-Me$_2$T) (+0.51) is actually *less* positive than the calculated Ir charge (+0.64) in Cp*Ir(η^4-2,5-Me$_2$T), where the metal is formally Ir(I).

In summary, the driving force for the rearrangement from the η^4 complex to the iridathiabenzene complex appears to be a sizable antibonding, and thus destabilizing, interaction between the ring sulfur atom and a filled Ir 4d orbital in the η^4 Ir(I) complex. Although insertion of the metal into the thiophene ring can be viewed as a formal oxidative addition, it is clear from the character of the molecular orbitals in this complex that incorporation of the metal into the planar ring results in considerable delocalization of electronic charge from the ring atoms back onto the metal.

In further studies of these Ir complexes, Angelici and co-workers found that a phosphine ligand readily adds to Cp*Ir(*C*,*S*-2,5-Me$_2$T) (eq 5). They have suggested that



(5)

this reactivity may be related to an electron deficiency in Cp*Ir(*C*,*S*-2,5-Me$_2$T).[50] Our results, while suggesting that Cp*Ir(*C*,*S*-2,5-Me$_2$T) is not really electron deficient, do suggest a pathway for the addition of another ligand. The MO diagram in Figure 9 shows that this complex exhibits a relatively low energy LUMO. Since the principal component of this LUMO is the metal d_{yz} orbital, the LUMO provides a readily available site for attack by the phosphine ligand σ donor electrons.

The product of the addition reaction shown in eq 5 is very similar to a group of ring-opened complexes synthesized and characterized by the Jones group.[25,47] All of these complexes contain six-coordinate d^6 metals and a nonplanar metallacycle ring. A complete description of the bonding in these systems is given elsewhere,[48] but we note here that unlike the five-coordinate ring-opened Ir complex shown in eq 4, all of the complexes which incorporate a nonplanar metallacycle ring are electron precise. No delocalization of charge throughout the metallacycle ring is necessary. The bend in the metallacycle ring in these complexes presumably prevents the metal orbitals from participating in the ring π system, thus decreasing the amount of ring electron density shared with the metal.

Conclusions

The results presented here provide an overview of several different modes of thiophene binding. Because the structure and ordering of the π orbitals in thiophene and Cp$^-$ are quite similar, the metal–ligand interactions in η^5-T and η^5-Cp complexes are also very similar. Thiophene, however, is generally a poorer π donor but better acceptor ligand than Cp$^-$. Since comparisons between the binding ability of thiophene and Cp$^-$ or other arene ligands are usually made in complexes where these ligands serve primarily as donors, it is usually the difference in donor ability which accounts for weaker binding by the thiophene ligands. The electron distributions in [RuCpT]$^+$ illustrate, however, that when thiophene and a superior donor ligand are simultaneously bound to a metal center, the π acceptor ability of thiophene plays an important role in the metal–thiophene interactions. Our results indicate that thiophene can function as a π acceptor and that η^5 metal–thiophene binding will be strongest when the π acceptor capability of the thiophene ring becomes important.

The pyramidal bonding around the ring sulfur atom in η^1 complexes is related to the ability of thiophene to act as either a two- or four-electron donor. The pyramidal bonding in the iron complexes studied here, as well as in other stable six-coordinate η^1 complexes, reflects the need for thiophene or DBT to act as a two-electron donor. The slightly better donor ability of DBT, in comparison to thiophene, appears to be responsible for the increased stability of the Fe–DBT bond.

The unusual η^4 and ring-opened Ir complexes are related by an oxidative addition. Although the thiophene ring in the η^4 complex acts as a formal four-electron donor, the large size of the sulfur π orbital results in a significant residual metal–sulfur antibonding interaction. Insertion of the metal center into the C–S bond of the thiophene ring is accompanied by a formal oxidation of the metal center. In spite of this formal oxidation the character of the resulting MO's suggests that delocalization of electron density throughout the planar metallacycle ring compensates for the formal loss of electronic charge at the metal.

The electronic structure of the Ir complexes suggests that a very electron rich metal center may be a necessary precursor for insertion of a metal center into the C–S bond of the thiophene ring, and we are continuing to try to understand how metal binding may activate a thiophenic ring. Results of calculations which describe the electronic structure of additional S-bound thiophene and DBT complexes and several ring-opened thiophene complexes will be described in another paper.[48]

OM940251E

---

(50) Chen, J.; Daniels, L. M.; Angelici, R. J. *Polyhedron* **1990**, *9*, 1883.