ORGANOMETALLICS

Volume 20, Number 7, April 2, 2001

Reviews

Thiophenes in Organotransition Metal Chemistry: Patterns of Reactivity

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Received January 22, 2001

Thiophenes, including benzothiophenes and dibenzothiophenes, undergo a variety of reactions with transition metal complexes that lead to products in which the thiophene is partially reduced or cleaved at a C−S bond. The specific types of reactivity depend on the modes of thiophene coordination to the metal, which in turn depend on the particular metal and its associated ligands. It is the intent of this review to organize these numerous reactions of thiophenes into categories that illustrate distinct patterns of reactivity. It is hoped that an understanding of such patterns will stimulate the use of thiophene−organotransition metal chemistry in synthetic organic chemistry.

I. Introduction

Most studies of thiophene coordination and reactivity in transition metal complexes have been directed toward understanding the role of the metal(s) in heterogeneous catalysts that promote the hydrodesulfurization (HDS) of organosulfur compounds in hydrocarbon feedstocks. Several reviews of various aspects of these model HDS studies have been published.[1] In the course of these investigations, numerous other reactions of thiophenes in organotransition metal complexes have been discovered. It is the purpose of this present review to organize these reactions in a way that emphasizes patterns of reactivity of thiophenes in their complexes. The parent thiophenes that are discussed are those (Scheme 1) of thiophene (T), benzothiophene (BT), and dibenzothiophene (DBT). When referring to a general type of thiophene that includes ring-substituted derivatives, such as 2-methylthiophene, an asterisk is also used, e.g., T*, BT*, and DBT*.

The thiophenes (T*) are known[1b,c,2] to coordinate to single metal centers through the sulfur (η^1(S)), through two carbon atoms (η^2), through four carbons (η^4), or through all five atoms in the thiophene ring (η^5). Benzothiophenes (BT*) coordinate through the sulfur (η^1(S)), through the 2,3-carbon atoms (η^2), through four carbons (C4−C7) of the benzo ring (η^4),[3] or through all six carbons (η^6) of the benzo ring.[1c] Dibenzothiophenes (DBT*) coordinate through the sulfur (η^1(S)), through four carbons (η^4) of a benzo ring,[3] or through all six carbon atoms (η^6) of a benzo ring.[1c] The η^1(S) coordination mode is common to all of these thiophenes, and the metal does not lie in the plane of the thiophene, suggesting sp^3 hybridization of the sulfur atom. Their

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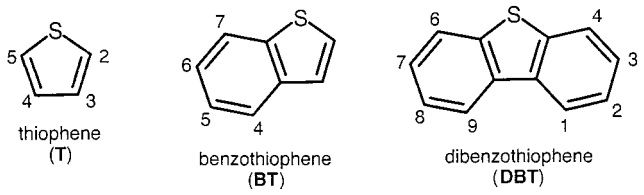
10.1021/om010040r CCC: $20.00
Publication on Web 03/08/2001

Scheme 1



tendencies to coordinate to metal ions generally increase in the order T* < BT* < DBT*.[4-7] The binding ability of T* usually increases with the number of electron-donating methyl substituents on the thiophene ring. Yet all of them are weakly coordinating as compared with dialkyl sulfide ligands such as tetrahydrothiophene (THT). In equilibrium studies of the displacement of T from $Cp(CO)(Ph_3P)Ru(T)^+$ by a variety of sulfur ligands, it was found that THT binds at least 7.1×10^6 times more strongly than T.[4a] In fact, methyl iodide (MeI) binds slightly more strongly than T in this system. The weak η^1(S) coordinating ability of thiophene means that isolable complexes of T can be obtained in only selected types of metal complexes. Our strategy for choosing metal complex systems that might coordinate T was to try those[8] that were capable of binding the weakly binding alkyl halides such as MeI. This strategy was successful for the synthesis of $CpRe(NO)(PPh_3)(T)^+$,[9] $CpRe(CO)_2(T)$,[10] $CpRu(CO)(PPh_3)(T)^+$,[4] and $IrH_2(PPh_3)_2(T)_2^+$.[6] Another useful observation is that metals with d^6 electron configurations tend to form the most stable η^1(S) thiophene complexes.

Attempts to promote η^1(S) T coordination by incorporating the thiophene unit into a multidentate ligand have been partially successful. The ligand 2,5-bis(2-diphenylphosphinoethyl)thiophene (Q)[11] forms $Mo(CO)_3$(Q), in which the thiophene sulfur is coordinated along with the two phosphine donor groups; this appears to be the only isolable η^1(S)-thiophene complex[5] of molybdenum, a key metal in the commercial HDS catalyst. Thioporphyrins, porphyrins in which a thiophene unit replaces one of the pyrrole rings,[12] bind to a variety of metals through the sulfur as well as the three nitrogen atoms. The potentially tridentate 6-(2-thienyl)-2,2′-bipyridine ligand (L) binds through the pyridine nitrogen atoms (N_2) or through all three donors (N_2S). In the Ru(II) complex, $Ru(L)_2(Cl)^+$, one L ligand is N_2S-coordinated while the other is only N_2-coordinated.[13] In the Ru(III) complex, Ru(L)pyCl_3, L is only N_2-coordinated. In reactions of L with $PdCl_4^{2-}$, $PtCl_4^{2-}$, and $AuCl_4^-$,[14] only cyclometalated products, in which L is coordinated through both N atoms and a carbon of the thienyl unit that had undergone C−H cleavage, are isolated. Other potential bi- and tridentate thienylpyridines also react with Pt and Ir to give cyclometalated complexes.[15-17] Thiophene units in several macrocyclic thioether ligands coordinate weakly or not at all in Pd(II) and Cu(II) complexes.[18,19] Even the thienyl analogue of tetrakis(2-pyrazolyl)borate(1−),[20] tetrakis(2-thienyl)borate(1−), yields no isolable complexes with Fe, Co, Ni, Mo, or Cu.[21] Thus, thiophenes coordinate only weakly or not at all in most transition metal complexes. As a result, known η^1(S)-thiophene complexes often react in ways that lead to the loss of the η^1(S)-thiophene ligand from the metal. Complexes such as $Cp'Re(CO)_2(T^*)$, where $Cp' = \eta^5$-C_5H_5 or -C_5Me_5, in which the η^1(S)-thiophene ligand is kinetically slow to be displaced,[22] offer greater possibilities for reactions that occur at the thiophene ligand.

Thiophenes (T*) form a variety of η^5 complexes, often of metals with d^6 electron configurations.[1b,c,2] Equilibrium studies[23] of the displacement of thiophene from $CpRu(\eta^5\text{-}T)^+$ by a series of methyl-substituted η^5-thiophenes (T*) show that the equilibrium constant (K) for η^5-coordination of the thiophene increases by a factor of approximately 6 for each methyl group in the thiophene ring. The benzothiophenes BT and DBT bind more strongly than any of the thiophenes (T*) and completely displace them to form the η^6-BT and -DBT complexes $CpRu(\eta^6\text{-}BT)^+$ and $CpRu(\eta^6\text{-}DBT)^+$, indicating the preference for benzene over thiophene coordination. These trends are reinforced by calorimetric studies[24] of the displacement of T and 2,5-Me_2T from $Cr(CO)_3(\eta^5\text{-}T^*)$, which show the displacement of T to be 2.6 kcal/mol more favorable than the displacement of 2,5-Me_2T and 4.2 kcal/mol more favorable than the displacement of benzene. Kinetic studies[24] of the displacement of these π ligands from $Cr(CO)_3(\pi\text{-arene})$ by phosphines show that the rate of displacement increases in the same order: benzene ≪ 2,5-Me_2T < T. The higher affinity of metals for benzene over thiophene means that BT and DBT in all of their six-electron π complexes are η^6-coordinated through the benzene rather than through the thiophene ring.

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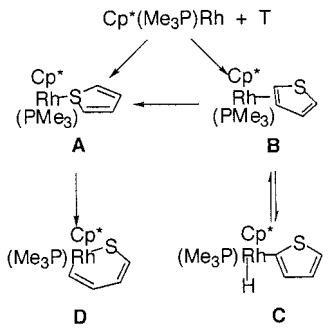
Scheme 2



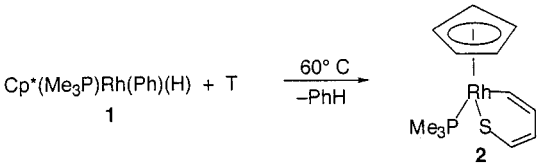
The availability of η^1(S) and η^5 thiophene complexes makes them logical starting compounds for exploring the reactivity of thiophenes in transition metal complexes. Such reactions are illustrated in the following sections. In addition, transformations of thiophenes that do not involve well-characterized η^1 or η^5 precursors are also described. Since reactions of thiophene complexes with hydrogen (H_2) have been discussed in reviews[1e,g] of organometallic models of HDS, these reactions will not be featured herein. Although thiophenes react with di- and polynuclear metal complexes,[1h,25] the goal here is to focus on patterns of thiophene reactivity in mononuclear organotransition metal complexes.

II. Metal Insertion into Thiophene C−S Bonds

Thiophenes react with coordinatively unsaturated, electron-rich metal complexes (ML_x) to give products in which the metal inserts into a C−S bond (eq 1). While

(1)

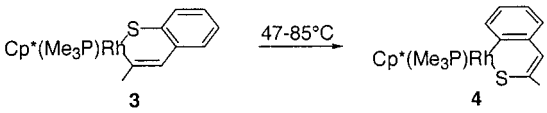
this remarkable reaction occurs with several complexes, the most thorough mechanistic study involves that of the 16-electron moiety Cp*(Me_3P)Rh, where Cp* = η^5-C_5Me_5.[26] This reactive intermediate is generated thermally by reductive-elimination of PhH from Cp*(Me_3P)Rh(Ph)(H) at 60 °C; in the presence of thiophene it gives the C−S insertion product Cp*(Me_3P)Rh(η^2(C,S)-C_4H_4S) (eq 2). Although no intermediates were detected in this



(2)

reaction, Jones and co-workers[26,27] showed in mechanistic studies of Cp*(Me_3P)Rh(H_2), Cp*(Me_3P)Rh(H)(2-thienyl), and selectively deuterated reactants that the most reasonable mechanism for reaction 2 is that shown in Scheme 2. It involves initial coordination of the Rh to the thiophene predominantly through the sulfur to give **A**, which then undergoes insertion into the C−S bond to give the observed product **D**. Thus, the precursor to **D** is the η^1(S)-coordinated thiophene complex **A** and not the η^2-complex **B**. Density functional theory calculations[28] of the transition state suggest that the actual insertion (**A** → **D**) occurs by formation of a Rh−C bond to an α-carbon while the C−S bond cleaves. Isomer **B**, which is the minor initial product, primarily undergoes C−H oxidative-addition to give **C**. Product **C** is, however, unstable with respect to **D** and isomerizes to **D** via **B**. (Parenthetically, one should note that the analogous photolytic or thermal reactions of Tp*(R_3P)Rh(C_2H_4) (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate, R = Me or Et) with thiophene give C−S inserted and hydride-thienyl products analogous to **D** and **C**, respectively.[29] However, in this system the hydride-thienyl complex is the more stable isomer.) Key features of this mechanism (Scheme 2) are the different precursors to **D** and **C** and the irreversible isomerization of **B** to **A**. This irreversibility is not characteristic of all η^1(S) ⇌ η^2 conversions (see section VI), and DFT calculations[28] suggest that **C** may convert directly to **A** without the intermediacy of **B**.

Cp*(Me_3P)Rh(Ph)(H) also reacts with benzothiophenes,[30] dibenzothiophenes,[31] and selenophene[32] to give C−S or C−Se inserted products. An interesting feature of the 2-MeBT reaction is the initial insertion into the S−C(vinyl) bond, which is followed by isomerization (eq 3) to the thermodynamically more stable product with Rh inserted into the S−C(aryl) bond. Since the reaction of BT gives only the S−C(vinyl) inserted product,[33] it is the 2-Me group that drives the isomerization to the S−C(aryl) inserted product in reaction 3.



(3)

Structures of many of the C−S inserted Cp*(Me_3P)Rh complexes of T*, BT*, and DBT* have been established by X-ray diffraction.[26,30,31] In some cases, the six-membered rings are planar, but in others, they are distorted from planarity. Molecular orbital calculations on these complexes indicate that electronic factors are not responsible for their planar or nonplanar geometries.[34] In fact, molecular mechanics calculations show that methyl groups on α-carbons of the six-membered ring sterically hinder the formation of a planar ring, which accounts for the bent ring in Cp*(Me_3P)Rh(η^2-(C,S)-2,5-Me_2T) but planar ring in Cp*(Me_3P)Rh(η^2(C,S)-T). The Rh center in all of these complexes has a formal 18-electron count and is therefore not expected to participate in π-bonding with electrons on the sulfur, which would lead to delocalization in the six-membered

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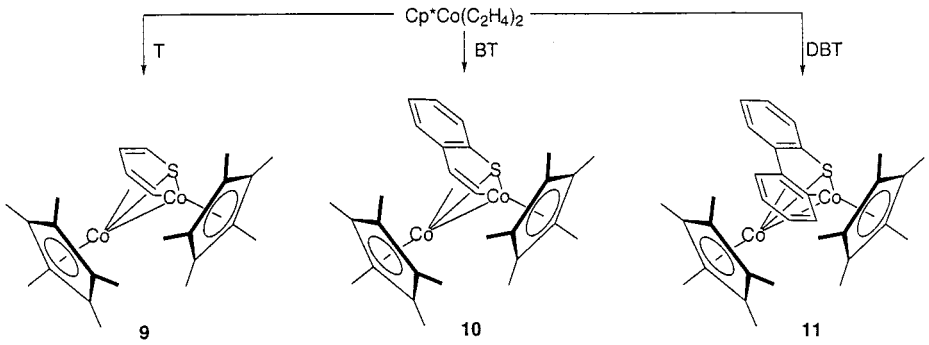
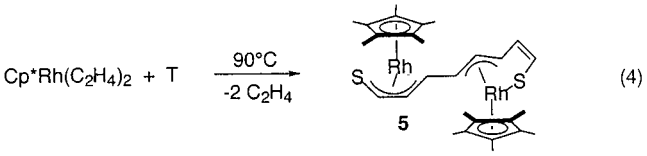
Scheme 3



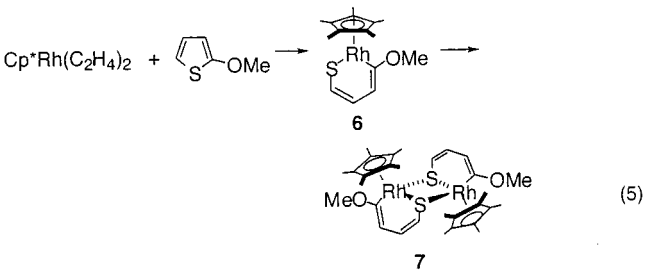
ring. Consistent with a localized bonding formalism in the Cp*(Me_3P)Rh(η^2(C,S)-T*) complexes are short−long−short carbon−carbon distances in the four-carbon unit of the ring, which is characteristic of 1,3-dienes.

While the 16-electron fragment Cp*(Me_3P)Rh gives Rh-inserted products, Cp*Rh(C_2H_4)$_2$, which could be the source of a 14-electron fragment upon loss of both ethylene ligands, would be expected to give different products. Indeed, Cp*Rh(C_2H_4)$_2$ reacts with thiophene at 90 °C with loss of ethylene to give complex **5** (eq 4),



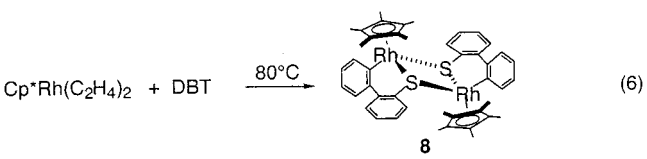
(4)

in which two Cp*Rh(C_4H_4S) units are coupled through a C−C bond. NMR evidence suggests Cp*Rh(η^2(C,S)-T) as an intermediate in this reaction. The analogous reaction with 2-methoxythiophene also gave evidence for a C−S inserted complex (**6**), which could not be isolated. When its solutions were concentrated, **6** dimerized in a different fashion (eq 5) than that of thiophene



(5)

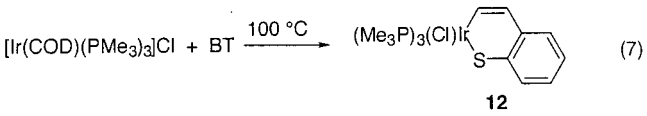
(eq 4) to give two isomers (only one **7** is shown) with two sulfur atoms bridging the Rh atoms. Although no C−S inserted intermediate is observed in the reaction (eq 6) of Cp*Rh(C_2H_4)$_2$ with DBT, sulfur-bridged isomers (only one **8** shown) analogous to **7** are formed.



(6)

The corresponding cobalt complex Cp*Co(C_2H_4)$_2$ reacts (Scheme 3) with T to also give a dimer **9**, but it contains only one thiophene unit per two Cp*Co units.[36] A likely intermediate in this reaction is the C−S inserted species Cp*Co(η^2(C,S)-T), which then forms a π complex with a second Cp*Co unit. An interesting dynamic feature of **9** is the rapid "flip-flop" of the bridging C_4H_4S unit, which makes the Cp* ligands on the two Co atoms equivalent in the ^{1}H NMR spectrum above room temperature. The reactions of BT and DBT with Cp*Co(C_2H_4)$_2$ give analogous complexes, **10** and **11**, with bridging thiophene ligands.[26,37]

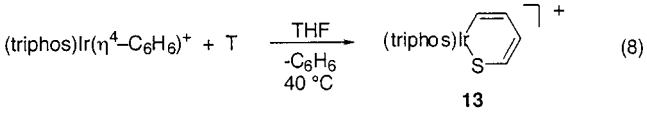
Inserted C−S thiophene complexes of Rh and Ir have also been prepared with supporting phosphine rather than Cp* ligands. Such complexes were obtained from the reactions (eq 7) of [Ir(1,5-cyclooctadiene)(PMe_3)$_3$]Cl



(7)

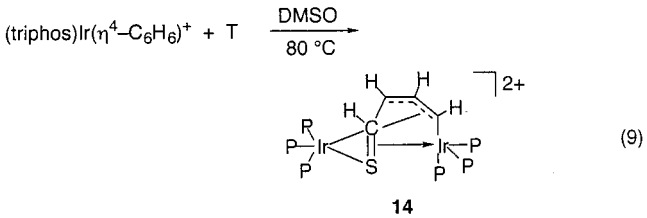
with T and BT.[38] The planarity of the metallacycle in the BT product **12** was attributed to steric interactions with the proximal PMe_3 ligands; this steric argument is supported by molecular mechanics calculations.[39] Inserted C−S thiophene complexes (R_3P)$_3$(H)Ir(η^2(C,S)-T) similar to that obtained from the reaction of [Ir(COD)(PMe_3)$_3$]Cl with T[38] have also been prepared from potassium thiopentadienide rather than thiophene.[40,41]

In a related reaction, (triphos)Ir(η^4-C_6H_6)$^+$ (triphos = MeC(CH_2PPh_2)$_3$) forms a C−S inserted product (**13**) upon reaction (eq 8) with thiophene.[42] When the reaction



(8)

was run in Me_2SO (80 °C) instead of THF,[43] a dinuclear



(9)

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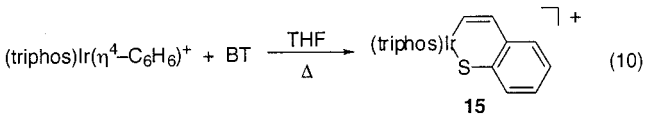
complex (**14**) was formed (eq 9). Although **14** has a structure in which one C−S cleaved thiophene unit bridges two 18-electron metal centers, it has a distinctly different structure than other bridging thiophenes, as for example in **9**. Complex **14** appears to form by a different mechanism than that for **9**, as the mononuclear C−S inserted **13** does not react with (triphos)Ir(η^4-C_6H_6)$^+$ under the conditions of reaction 9.

Like T, BT reacts (eq 10) with (triphos)Ir(η^4-C_6H_6)$^+$ to give the C−S inserted product (**15**).[44,45] When the

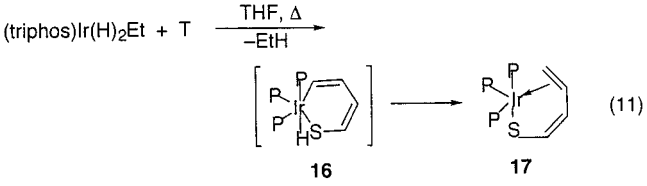


15 (10)

reaction was performed at only 25 °C, an intermediate could be isolated. This compound, (triphos)Ir(η^3-BT)$^+$, was assigned on the basis of spectroscopic studies a structure in which the BT is coordinated through the sulfur and the 2,3 double bond, the only example of this type of BT coordination to a metal center.

Unlike the other C−S inserted complexes discussed up to this point, complexes **13** and **15** are 16-electron centers when written as shown in eqs 8 and 10. A vacant orbital on the Ir opens the possibility for π delocalization of the six-membered iridathiabenzene ring. Consistent with this is the planar nature of the ring in **15**.[44,45] Iridathiabenzene complexes will be discussed in greater detail in section V.

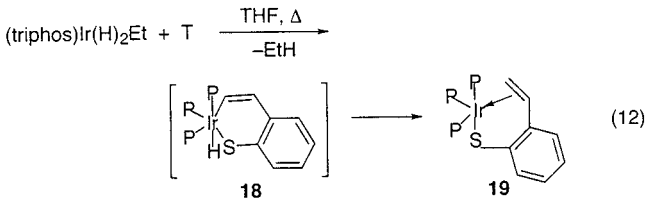
In addition to the (triphos)Ir(η^4-C_6H_6)$^+$ system, the Bianchini group also studied C−S thiophene insertion reactions of 16-electron metal complex fragments that also contained a hydride ligand. The (triphos)Ir(H) fragment is generated thermally by reductive elimination of ethane from (triphos)Ir(H)$_2$Et; it reacts with thiophene as in eq 11.[42] The final product **17** in this



16 **17** (11)

reaction results from the transfer of a hydride ligand to the terminal carbon of a putative iridathiacycle hydride intermediate **16** to give **17** with a butadienethiolate ligand. In fact, **16**, prepared independently by the reaction of **13** with Li[HBEt$_3$], does indeed form **17** upon warming to 50 °C. A byproduct of reaction 11 is the C−H oxidative-addition complex (triphos)Ir(H)$_2$(2-thienyl), which converts to the more stable isomer **17** upon heating to 130 °C.[46] A complex, (Me$_3$P)$_3$Ir(η^3-C_4H_5S), analogous to **17** has been prepared by a nonthiophene route involving the reaction of (Me$_3$P)$_3$IrCl with potassium thiapentadienide.[40,41]

The (triphos)Ir(H)$_2$Et complex reacts similarly with BT to give **19** (eq 12). The likely intermediate, **18**, which



18 **19** (12)

is prepared separately by reaction of **15** with Li[HBEt$_3$], rearranges to **19** upon heating.[45] As in reaction 11, a byproduct of reaction 12 is (triphos)Ir(H)$_2$(2-benzothienyl), which rearranges to the more thermodynamically stable **19** upon heating at 130 °C.[46,47] The reaction of (triphos)Ir(H)$_2$Et with DBT at 100 °C in THF gives several isomeric dibenzothienyl (DBTyl) products, (triphos)Ir(H)$_2$(DBTyl), resulting from C−H oxidative-addition.[48] Upon heating this mixture to higher temperatures, the DBTyl complexes convert to the C−S inserted product (triphos)Ir(H)(η^2(C,S)-DBT) analogous to **16** and **18**; however, unlike **16** and **18**, there is no rearrangement to another product at higher temperatures.

The (triphos)Rh(H) fragment, analogous to that of (triphos)Ir(H), is formed by loss of H_2 from (triphos)-Rh(H)$_3$ in refluxing THF. When this conversion is performed in the presence of T or BT, the Rh analogues of complexes **17** and **19** are formed.[49] When 2-substituted thiophenes are used in these reactions, the Rh inserts into the C−S bond that is away from the 2-substituent.[50] In none of these reactions of (triphos)-Rh(H)$_3$ with thiophenes is an intermediate of the type **16** or **18** observed, but they are presumed to be precursors to the (triphos)Rh(butadienethiolate) products. The kinetic inertness of iridium, as contrasted with that of rhodium, allows identification of **16** and **18** before hydride transfer gives the final products.

Electron-rich, 16-electron fragments of iron-group metals also react by insertion into the C−S bonds of thiophenes. The Fe(dmpe)$_2$ fragment (dmpe = Me$_2$PCH$_2$-CH$_2$PMe$_2$) generated by photolysis of *cis*-Fe(dmpe)$_2$(H)$_2$ reacts[51] with thiophenes to give both C−H and C−S inserted products (eq 13), which do not interconvert under the photolytic reaction conditions. An X-ray-determined structure of **20**, where R = Me, shows that Fe insertion occurs into the C−S bond away from the methyl group, as is normally observed. While the ferrathiacycle is almost planar, the localized single and double carbon−carbon bonds indicate that the ring is

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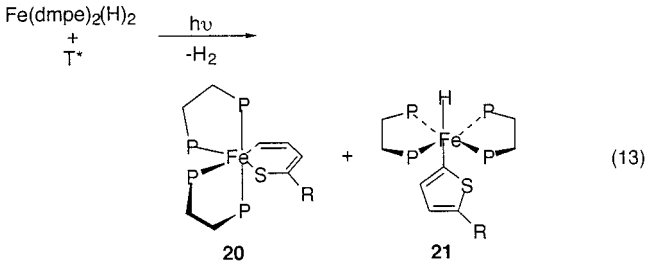
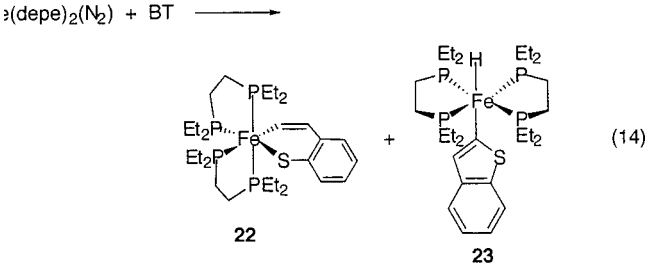


(13)

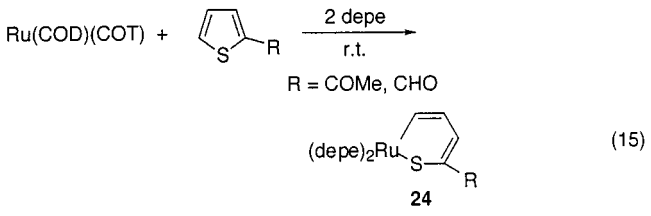
not a delocalized ferrathiabenzene. The thermal reaction (room temperature) of $Fe(depe)_2(N_2)$, where depe = $Et_2PCH_2CH_2PEt_2$, with T* likewise gives a mixture of C−H and C−S inserted products similar to those in eq 13.[52] For T* with a methyl or acyl group in the 2-position, the iron insertion occurs into the C−S bond away from the substituent, as in eq 13. The $Fe(depe)_2(N_2)$ complex does not react with 2,5-Me_2T, in which methyl groups are present at both carbons adjacent to the sulfur. Benzothiophene also reacts with $Fe(depe)_2(N_2)$ at room temperature to give both C−H and C−S inserted products (eq 14). The observation that the relative



(14)

amount of **22** increases at high concentrations of BT suggests that the two products are formed by separate pathways, and they do not interconvert even at 70 °C for 48 h. The more hindered 2-MeBT and DBT do not react with $Fe(depe)_2(N_2)$.

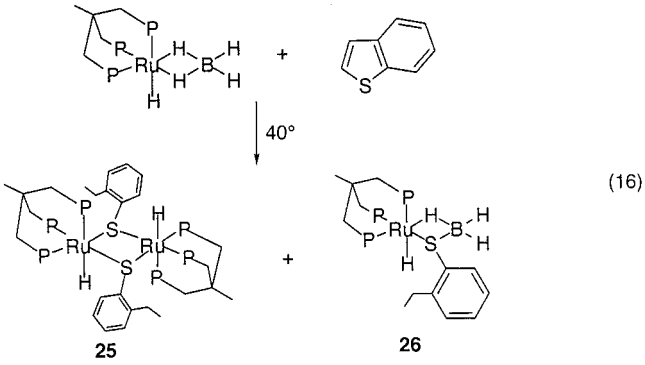
Unlike reactions of the $Fe(dmpe)_2$ and $Fe(depe)_2$ fragments, the (PP_3)Ru moiety (PP_3 = $P(CH_2CH_2PPh_2)_3$) generated by ultraviolet photolysis of $(PP_3)Ru(H)_2$ reacts with T and 2-ethoxycarbonylthiophene to give only C−H inserted products (PP_3)Ru(H)(2-thienyl).[53] On the other hand, Ru(COD)(COT) [COD = cycloocta-1,5-diene; COT = cycloocta-1,3,5-triene] reacts (eq 15) with 2-acyl and



(15)

2-formyl thiophenes in the presence of depe by inserting into the C−S bond away from the 2-substituent.[54] Alkyl thiophenes do not react under the same conditions. The 3-acyl and 3-formyl thiophenes react with Ru(COD)(COT) and depe to give C−S inserted products of type **24**, except the metal inserts into the C−S bond on the same side as the 2-substituent.

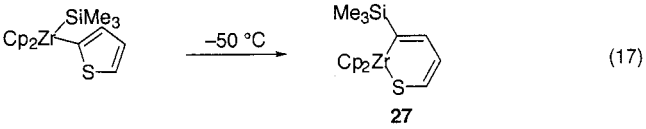
Only one reaction of a Ru complex with a hydride ligand has been reported.[55] The complex contains Ru, hydride, and BH_4 reactive centers, and its reaction with BT yields (eq 16) several products; the two (**25** and **26**)



(16)

containing ligands derived from BT show that C−S cleavage has occurred and the BT has been hydrogenated to 2-ethylthiophenolate. A complex, (triphos)Ru(BT·2H), with a partially hydrogenated BT ligand has been identified as a precursor to **25**.

Relatively few C−S inserted compounds have been reported for metals on the left side of the periodic table. Although not an insertion of the type described for other reactions in this section, the Zr thienyl complex in eq 17 undergoes C−S insertion together with Me_3Si migra-



(17)

tion to carbon to give a zirconathiacycle.[56] The structure of **27** shows the six-membered ring to be distinctly nonplanar, and the short−long−short carbon−carbon distances establish localized π bonding despite the formal 16-electron count of the Zr atom.

Of the group 6 metal complexes, only certain biscyclopentadienylmolybdenum and -tungsten complexes have been reported to insert into a C−S bond of thiophenes. Under ultraviolet photolysis, $Cp_2Mo(H)_2$[57] generates the reactive, 16-electron Cp_2Mo moiety which reacts with T to give only the C−H inserted product Cp_2Mo(H)(2-thienyl). The same product was observed when $Cp_2Mo(H)_2$ was reacted thermally with T in the presence of isoprene as a hydrogen acceptor. The pentamethylcyclopentadienyl analogue $Cp^*_2Mo(H)_2$ does not react with T under UV photolysis but instead generates a product resulting from intramolecular C−H cleavage of a methyl group in the Cp* ligand.[58] On the other hand, the *ansa*-$[Me_2Si(C_5H_4)_2]Mo(H)_2$ complex under photolysis with T gives the C−S inserted product **28** (eq 18). This product is also obtained thermally in the reaction of $[Me_2Si(C_5H_4)_2]$Mo(Ph)(H) with thiophene at 80 °C. In

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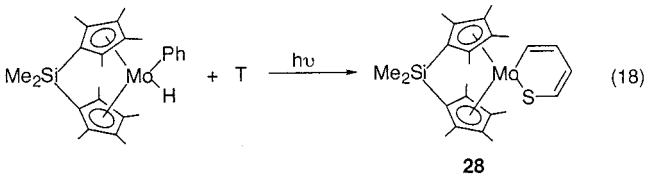


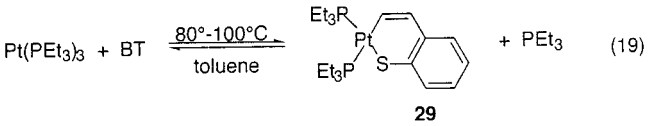
(18)

28

a competitive reaction, involving T and BT, insertion into the S−C(vinyl) bond of BT is favored over C−S insertion into T. Neither the photolytic nor thermal route gives a C−S inserted product with DBT; only the η^1(S) product $[Me_2Si(C_5H_4)_2]Mo[\eta^1(S)$-DBT] is obtained. The lability of the DBT ligand in this complex is illustrated by its room-temperature reaction with T to give **28**. Although it is not entirely clear why the *ansa*-bridged ligand induces the molybdocene system to favor C−S over C−H insertion, Parkin and co-workers[58] proposed that the short Me_2Si linker forces the cyclopentadienyl ligands to shift toward η^3,η^3-coordination, which reduces the electron density on the Mo. A lower electron population in the Mo orbitals opens the possibility of π donation from the sulfur, which stabilizes the C−S inserted product (**28**); such stabilization is less feasible in the Cp_2Mo system. As C−H and C−S insertions are competing processes in many oxidative-addition reactions of thiophenes, relatively minor changes in ligands can cause one type of insertion to be favored over the other.

While $Cp_2Mo(H)_2$ gives a C−H inserted product, the analogous $Cp_2W(H)_2$ gives both C−H and C−S inserted products, Cp_2W(H)(2-thienyl) and $Cp_2W[\eta^2$(C,S)-T], under photolysis (λ > 300 nm).[57] Shorter reaction times give predominantly $Cp_2W[\eta^2$(C,S)-T], which undergoes a photopromoted, intramolecular rearrangement to Cp_2W(H)(2-thienyl). The thermal (80 °C) reaction of $Cp_2W(H)(CH_3)$ with T also gives predominantly Cp_2W-$[\eta^2$(C,S)-T]. The C−S inserted product is labile, as indicated by the reaction of $Cp_2W[\eta^2$(C,S)-T] with C_6D_6 at 135 °C to give $Cp_2W(D)(C_6D_5)$. As expected for an 18-electron complex, the tungstathiacycle in $Cp_2W[\eta^2$(C,S)-T] is not aromatic, as indicated by its nonplanarity and the short−long−short carbon−carbon distances in the ring.

Of the group 10 metal complexes that undergo C−S insertion into thiophenes, $Pt(PEt_3)_3$ is the most studied system. Maitlis and co-workers[59] have shown that it reacts with T, BT, and DBT to give the C−S inserted products, e.g., eq 19. These are equilibrium reactions

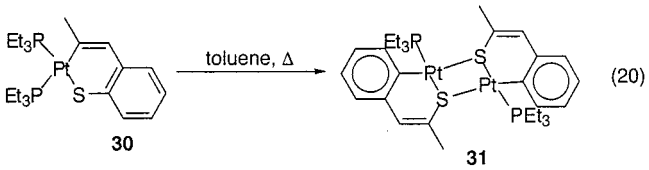


(19)

29

that have been studied at 100 °C in toluene-d_8. The results show that the C−S inserted product of BT (**29**) is more stable than those of T and DBT, which have similar stabilities. The X-ray structure of **29** shows the platinathiacycle to be nonplanar, and spectroscopic studies of $(Et_3P)_2Pt[\eta^2$(C,S)-T] suggest that the six-membered ring is not aromatic. The only other $Pt(PR_3)_x$ complex reported to react with thiophenes is $Pt(PMe_3)_4$, which gives the PMe_3 analogue of **29** with BT.[60] The corresponding dppe complex (dppe)$Pt[\eta^2$(C,S)-BT] was prepared by substitution of the PMe_3 ligands in $(Me_3P)_2$-$Pt[\eta^2$(C,S)-BT] with $Ph_2PCH_2CH_2PPh_2$.

Methyl substituents in BT and DBT influence their reactions with $Pt(PEt_3)_3$. While BT, 3-MeBT, and 2-MeBT yield the S−C(vinyl) insertion products, as shown for **29**, the 2-MeBT product (**30**) slowly rearranges and dimerizes as shown in eq 20.[61] This rearrangement

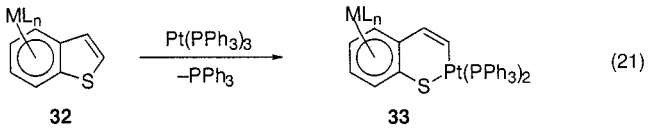


(20)

30 **31**

formally involves a deinsertion of Pt from the S−C(vinyl) bond and insertion into the S−C(aryl) bond. The driving force for this reaction (eq 20) is not clear, but the bulkiness of the 2-methyl substituent appears to be a factor. The methyl group in 4-MeDBT appears to have little effect, as $Pt(PEt_3)_3$ insertion occurs into both S−C(aryl) bonds, but the reaction of 4,6-Me_2DBT gives only a product in which Pt inserts into an aryl C−H bond. The C−S inserted product $(Et_3P)_2Pt[\eta^2$(C,S)-4,6-Me_2DBT] is obtained however when 4,6-Me_2DBT reacts with $PtCl_2(PEt_3)_2$ and metallic sodium under a H_2 atmosphere.

Although $Pt(PEt_3)_3$ reacts with thiophenes (eq 19) to give C−S inserted products, the corresponding $Pt(PPh_3)_3$ does not.[62] However, Sweigart and co-workers[62] have shown that electron-withdrawing metal fragments ML_n that are capable of η^6-coordination to the arene ring of BT greatly accelerate the rate of C−S insertion by Pt-$(PPh_3)_3$ (eq 21). Structural studies of the ML_n = Mn-



(21)

32 **33**

$(CO)_3^+$ or $FeCp^+$ complexes of **33** show that the Pt inserts into the S−C(vinyl) bond in all cases. The qualitative rates of these reactions decrease with the ML_n group in the order $Ru(C_6Me_6)^{2+}$, $Mn(CO)_3^+$ > $FeCp^+$, $RuCp^+ \gg Cr(CO)_3$. The fact that these reactions occur at room temperature for all of these complexes (except $Cr(CO)_3$) illustrates the substantial activating effect of the ML_n group. Moreover, the above trend establishes that the most electron-withdrawing ML_n groups give the fastest insertion rates, which is reasonable for a mechanism in which oxidative-addition into the C−S bond is rate-controlling.

Again illustrating the effect of a methyl substituent at the 2-position, (η^6-2-MeBT)$Mn(CO)_3^+$ reacts with Pt-$(PPh_3)_2(C_2H_4)$ to give the product **34**, in which the Pt

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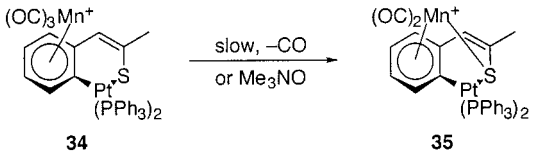
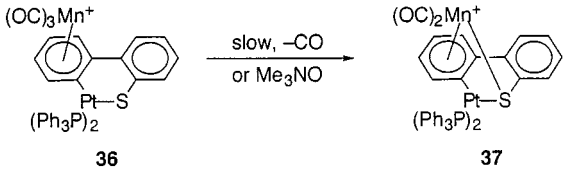
inserts into the S−C(aryl) bond.[63] Moreover, **34**, slowly at room temperature or quickly with the decarbonylating agent Me_3NO, loses a CO group and the sulfur atom coordinates to the Mn to give **35** (eq 22), whose structure was established by an X-ray study.



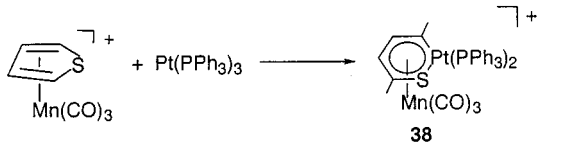
(22)

The analogous reaction of (η^6-DBT)$Mn(CO)_3^+$ with Pt(PPh_3)$_2$(C_2H_4) or Pt(PPh_3)$_3$ gives product **36**, in which Pt inserts into the S−C(aryl) bond.[63] Like **34**, **36** also loses CO to give **37** with a Mn−S bond (eq 23).



(23)

A somewhat different activating effect of $Mn(CO)_3^+$ is that on an η^5-thiophene ligand. Although neither Pt(PEt_3)$_3$ nor Pt(PPh_3)$_3$ reacts with 2,5-Me_2T, its η^5-complex (η^5-2,5-Me_2T)$Mn(CO)_3^+$ reacts rapidly at room temperature with Pt(PPh_3)$_3$ to give the C−S inserted product **38**, whose structure is based on analytical and

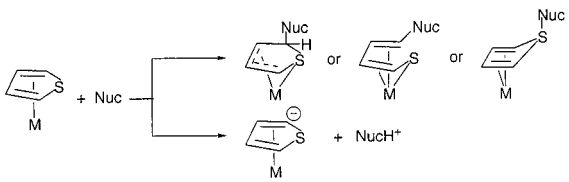


(24)

spectroscopic data. Thus, π-coordination of BT, DBT, and 2,5-Me_2T greatly activates the C−S bonds in these thiophenes to metal insertion reactions by Pt(PPh_3)$_3$/Pt(PPh_3)$_2$(C_2H_4).

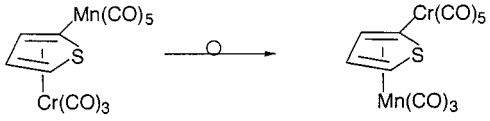
III. Reactions of η^5-Thiophene Complexes with Nucleophiles

The η^5-thiophene ligand generally reacts with nucleophiles in two ways. In cationic complexes, nucleophiles often add to the 2- or 5-position of the thiophene to give thioallyl or butadienethiolate products or to the sulfur (eq 25). On the other hand, neutral η^5-thiophene com-



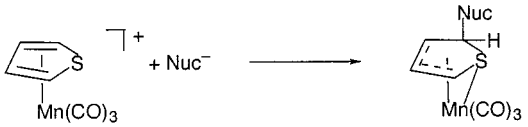
(25)
(26)

plexes typically resist attack but undergo deprotonation (eq 26) with strong nucleophiles/bases. This latter reactivity is found[64] in (η^5-T)$Cr(CO)_3$, which reacts with *n*-BuLi to give the lithiated product $(OC)_3Cr(\eta^5\text{-}C_4H_3SLi)$, which has been used to form a series of thienyl-bridged complexes[65,66] in which the thienyl ligand is η^5-coordinated to the $Cr(CO)_3$ unit and η^1-bonded to another metal. One such complex, **39**, undergoes the remarkable interchange of metals and CO ligands shown in eq 27.[67]



(27)

The isoelectronic but cationic analogue of (η^5-T)$Cr(CO)_3$, (η^5-T)$Mn(CO)_3^+$ (**41**), undergoes nucleophilic attack (eq 28) at the 2-position to give thioallyl products **42**.[68,69] The η^5-2-silatranylthiophene complex (η^5-2-R-



(28)

Nuc = CN^-, H^-, P(n-Bu)$_3$, $Re(CO)_5^-$

C_4H_3S)$Mn(CO)_3^+$ (R = $Si(OCH_2CH_2)_3N$) also undergoes attack at the 5-position when reacted with CN^-, BH_4^-, and $^-P(O)(OMe)_2$.[70] X-ray diffraction studies of $(OC)_3Mn(\eta^4\text{-T}\cdot CN)$,[68] $(OC)_3Mn[\eta^4\text{-R-}C_4H_3S\cdot P(O)(OMe)_2]$,[70] and $[(OC)_3Mn(\eta^4\text{-T})]_2Os(CO)_4$[71] show the thiophene coordinated through three carbons and the sulfur with the nucleophile in the *exo* position on the uncoordinated carbon. The deuterium derivative $(OC)_3Mn(\eta^4\text{-T}\cdot D)$ (**42**) exists as two isomers (*endo* and *exo* deuterium) and is formed by the reaction of **41** with the deuteride donors BD_4^- and $DFe(CO)_4^-$.[72] The *endo* isomer presumably results from initial D^- addition to a CO ligand, which is followed by D^- transfer from the formyl ligand to the *endo* side of the η^5-T ring. In contrast to this rather nonselective D^- addition, removal of D^- from $(OC)_3Mn(\eta^4\text{-T}\cdot D)$ with Ph_3C^+ to give **41** is exclusively from the *exo* side of the ring. Hydride (BH_4^-) addition to (η^5-2-MeT)$Mn(CO)_3^+$ occurs at the carbon position (C5) not bearing the methyl group, while (η^5-2,5-Me_2T)$Mn(CO)_3^+$ does not give a H^- addition product of type **42**.

As opposed to attack at the 2-position of **41**, carbanion nucleophiles add at the sulfur (eq 29).[70,73] In these reactions, attack at the sulfur is not blocked by methyl groups in the 2- and 5-positions in (η^5-2,5-Me_2T)$Mn(CO)_3^+$. The addition of the R^- groups to sulfur demonstrates that the sulfur is an electrophilic center. In fact, it may be argued that the sulfur is the initial site of

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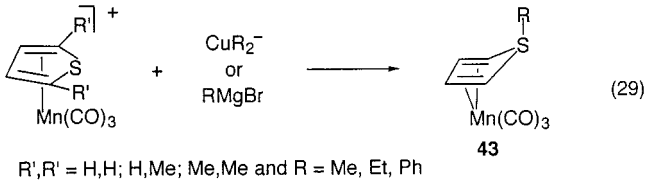


(29)

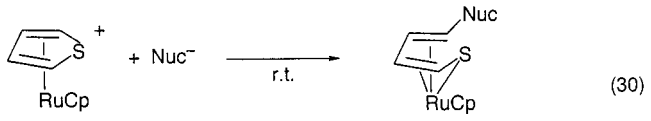
43

R',R' = H,H; H,Me; Me,Me and R = Me, Et, Ph

attack for other nucleophiles. With carbanionic nucleophiles the kinetically inert C−S bond prevents the nucleophile from migrating from the sulfur to an adjacent carbon; however, this migration could occur with other nucleophiles, e.g., CN^-, H^-, PR_3, that form weaker bonds with the sulfur. Evidence for initial attack at sulfur is also found in reactions of (arene)Ru(η^5-T*)$^{2+}$ with nucleophiles (see below).

As benzothiophene π-coordinates to $Mn(CO)_3^+$ through the benzo ring, rather than the thiophene, reactions of (η^6-BT)$Mn(CO)_3^+$ with nucleophiles (H^-, Me^-, Et^-, Ph^-, CH_2CN^-, $P(O)(OMe)_2^-$) occur by addition to either the 4- or 7-position of the benzo ring; there is no evidence for nucleophilic attack on the thiophene segment of the BT ligand.[74]

In contrast to the reactions (eq 28) of $(CO)_3Mn(\eta^5$-T*$)^+$, most nucleophiles that add to the 2- or 5-position of CpRu(η^5-T)$^+$ give ring-opened butadienethiolate complexes (eq 30).[75−77] In each product, the Nuc group is



(30)

44 **45**

Nuc^- = OMe^-, SR^-, $CH(CO_2Me)_2^-$, H^-

anti to the remainder of the diene ligand (as in **45**), except for D^- addition ($LiAlD_4$), which gives exclusively the product in which the deuterium is stereospecifically *syn* to the remainder of the dienethiolate ligand.[77] The mechanism of reaction 30 presumably involves nucleophilic attack at the 2- or 5-carbon to give a thioallyl intermediate analogous to **42** (eq 28), which undergoes C−S cleavage and formation of **45**. The observation of the *syn* isomer with $LiAlD_4$ suggests that this isomer is formed also with the other nucleophiles but subsequently rearranges to the *anti* isomer or that $LiAlD_4$ reacts by a mechanism different from that of the other nucleophiles and therefore gives a different isomer. In contrast to hydride removal from $(OC)_3Mn(\eta^4$-T·H) (**42**) by Ph_3C^+ to give $(CO)_3Mn(\eta^5$-T$)^+$, the dienethiolate complex CpRu[η^5-SC(Me)=CH−CH=CH(SEt)] does not react with Ph_3C^+ by SEt^- removal, which might be expected to give CpRu(η^5-2-MeT)$^+$.[75]

Reactions of the 2-MeT complex CpRu(η^5-2-MeT)$^+$ with OMe^-, SR^-, and $CH(CO_2Me)_2^-$ give the analogous ring-opened products in which the nucleophile adds to the carbon not bearing the methyl group. However, the reaction of CpRu(η^5-2-MeT)$^+$ with Na[$AlH_2(OCH_2CH_2OMe)_2$] gives the product CpRu(η^5-SCH=CH−CH=C(Me)H), in which the hydride adds to the carbon bearing the methyl group.[77] This contrasting behavior of the hydride donor suggests a radical reaction involving perhaps CpRu(η^5-2-MeT)$^\bullet$, analogous to CpFe(η^5-Me_4T)$^\bullet$, which is generated by $LiAlH_4$ reduction of CpFe(η^5-Me_4T)$^+$ at −50 °C.[78] The more electron-rich Cp*Ru(η^5-T*)$^+$, where T* = T and 2,5-Me_2T, also reacts with Na[$AlH_2(OCH_2CH_2OMe)_2$] to give the analogous ring-opened butadienethiolate products.[77] The analogous η^5-selenophene complex Cp*Ru(η^5-Sel)$^+$ also reacts with Na[$AlH_2(OCH_2CH_2OMe)_2$)] to give a ring-opened butadieneselenolate complex;[79a] reactions of the η^5-tellurophene derivative Cp*Ru(η^5-Tel)$^+$ with nucleophiles have not been reported.[79b]

A particularly puzzling aspect of the $(OC)_3Mn(\eta^5$-T·H) and CpRu(η^5-T·H) hydride addition products is that the Mn complex adopts the thioallyl structure **42** while the Ru derivative adopts the ring-opened butadienethiolate structure **45**. The greater electron density on the Ru is perhaps sufficient to promote the C−S cleavage. In section V is discussed a Ru complex with a thioallyl η^4-T·H ligand that is observed to open to a butadienethiolate η^5-T·H ligand.

Unlike the other nucleophiles (eq 30), OH^- does not form adducts with CpRu(η^5-T*)$^+$, where T* = T, 2-MeT, 3-MeT, and 2,5-Me_2T. Instead, it catalyzes deuterium exchange with CD_3OD of the thiophene hydrogens, the 2- and 5-hydrogen atoms exchanging much faster than those in the 3- and 4-positions.[80,81] In complexes containing η^5-methylthiophene ligands, exchange of the methyl hydrogens is much slower than that of any of the thiophene ring hydrogens. Kinetic studies of this reaction in CD_3OD at 23 °C show that the rate of reaction is first order in the OH^- concentration, which suggests a mechanism involving deprotonation of the η^5-T by OH^- followed by D^+ addition to the carbanionic site. Deuterium isotope effects determined using deuterothiophene ligands fall in the range of 5−7, which supports this mechanism.

Reaction of the η^6-benzothiophene complex CpRu(η^6-BT)$^+$ with Na[BEt_3H] at room temperature gives a mixture of four CpRu(η^5-BT·H) cyclohexadienyl isomers in which H^- adds to the arene ring, with addition at the 7-position predominating,[82] as was also observed for hydride addition to $(OC)_3Mn(\eta^6$-BT$)^+$.[74] The H^- adds in the *exo* position, and the isomers do not interconvert at 25 °C over a 24 h period. Hydride removal by Ph_3C^+ from the CpRu(η^5-BT·H) isomeric mixture occurs most slowly from the isomer with H^- at the 7-position, but all isomers are eventually converted back to CpRu(η^6-BT)$^+$.

The OH^- nucleophile does not add to the arene ring of CpRu(η^6-BT)$^+$ or CpRu(η^6-3-MeBT)$^+$ but instead catalyzes the exchange of hydrogens at the 2- and 7-positions with CD_3OD solvent.[83] Kinetic studies at 23.8 °C give a rate law that is first order in both the Ru

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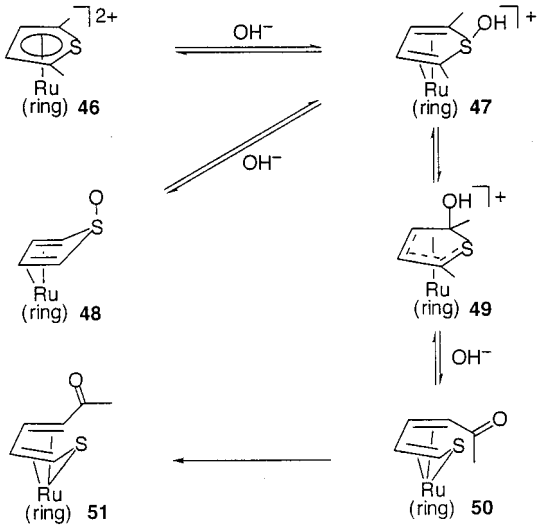
Scheme 4



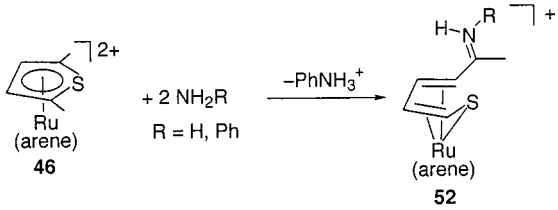
complex and OH^- concentrations, which suggests a mechanism involving OH^- deprotonation at the 2- or 7-position. Exchange of the 2-hydrogen is substantially faster than that at the 7-position.

The η^6-DBT complex $CpRu(\eta^6\text{-DBT})^+$ reacts with Na[BEt_3H] to give two cyclohexadienyl isomers $CpRu(\eta^5\text{-DBT}\cdot H)$ in which H^- adds to either the 4- or 1-position of the arene ring coordinated to the $CpRu^+$.[84] Reaction of the $CpRu(\eta^5\text{-DBT}\cdot H)$ isomeric mixture with electrophiles and oxidizing agents (Ph_3C^+, $HBF_4\cdot OEt_2$, Me_3O^+, and Cp_2Fe^+) give back $CpRu(\eta^6\text{-DBT})^+$. When the mixture of four isomers of $CpRu(\eta^5\text{-DBT}\cdot Me)$, obtained from the reaction of $CpRu(\eta^6\text{-DBT})^+$ with LiMe, reacts with Ph_3C^+, hydride (H^-) is removed, and all four isomers of $CpRu(\eta^6\text{-DBT}\cdot Me)^+$ are formed. Reactions of $CpRu(\eta^6\text{-DBT})^+$ with OMe^- and NMe_2^- also give isomeric mixtures of $CpRu(\eta^5\text{-DBT}\cdot Nuc)$ resulting from addition of a nucleophile (Nuc^-) to the coordinated arene ring. Reaction of $(CpRu)_2(\eta^6,\eta^6\text{-DBT})^{2+}$, in which a $CpRu^+$ unit coordinates to each benzo group on opposite sides of the DBT plane, with BEt_3H^- gives two products: $(CpRu)_2(\eta^5,\eta^5\text{-DBT}\cdot 2H)$, characterized only spectroscopically because of its low yield and air sensitivity, and $(CpRu)_2(\eta^6,\eta^6\text{-DBT})$, whose structure was established by X-ray diffraction studies. Both compounds react with Ph_3C^+ to give back $(CpRu)_2(\eta^6,\eta^6\text{-DBT})^{2+}$.

In contrast to the lack of reaction (except to catalyze deuterium exchange) between $CpRu(\eta^5\text{-T*})^+$ and OH^-, the 2+ complexes $(ring)Ru(\eta^5\text{-T*})^{2+}$, where ring = η^6-cymene, C_6Me_6, or η^5-Me_4T and T* = T, 2,5-Me_2T, and Me_4T, give products that incorporate the O^{2-} group. Most studies of this system (Scheme 4) were performed by Rauchfuss and co-workers[85] with (η^6-cymene)Ru(η^5-2,5-Me_2-T)$^{2+}$; however, some of the following conclusions are based on studies of other $(ring)Ru(\eta^5\text{-T*})^{2+}$ derivatives as well. The reaction of **46** with 1 equiv of aqueous KOH gives the *S*-hydroxythiophene complex **47**, which was characterized by NMR spectroscopy. Upon standing in solution, **47** rearranges to **49**, which reacts with another OH^- to give the ring-opened *syn* acylthiolate **50**, which rearranges to the *anti* isomer **51**. Isomer **50** reacts rapidly with CF_3SO_3H to give back **46** and H_2O. Thus, the acid reverses all steps (through **49** and **47**) to eliminate H_2O, a remarkable ring-closure reaction. The *anti* isomer **51** does not react with acid to give **46**.

When an excess of KOH is used initially, **46** is converted to **48** because deprotonation of the *S*-hydroxy group in **47** is faster than migration of the OH^- group from the sulfur to carbon-2. Although **48** is formed initially, it rearranges over a period of hours at room temperature in solution to give the acylthiolate isomers, **50** and **51**, presumably via protonated intermediate **47**. In fact, the *S*-oxide **48** reacts rapidly with CF_3SO_3H to give **46**. Depending on the ring and η^5-T* ligands in the $(ring)Ru(\eta^5\text{-T*})^{2+}$ complexes, equilibrium constants and rates of each step in Scheme 4 vary, but the pattern of reactivity is the same for all of these complexes.

The $(\eta^6\text{-arene})Ru(\eta^5\text{-T*})^{2+}$ complexes (where arene = C_6Me_6 and cymene, and T* = T, 2-MeT, and 2,5-Me_2T) also react with NH_3 and aniline to give iminium-thiolate complexes (eq 31) analogous to the acylthiolates ob-



(31)

tained in the reactions (Scheme 4) with OH^-.[86] As for the OH^- reactions, the formation of the final *anti* isomer **52** is preceded by a kinetic *syn* isomer. The reaction of $(\eta^6\text{-cymene})Ru(\eta^5\text{-}Me_4T)^{2+}$ with NH_3 does not give an iminium-thiolate product but instead stops at the thioallyl stage, $(\eta^6\text{-cymene})Ru(\eta^4\text{-}Me_4T\cdot NH_2)^+$, where NH_2 has added to carbon 2 to give a structure analogous to **49**; this complex reacts with acid to give back (η^6-cymene)Ru(η^5-Me_4T)$^{2+}$. There is no evidence in these amine reactions for a thioimine product analogous to **48**. The reaction of $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-2-MeT})^{2+}$ with the chiral primary amine (Ph)(Me)(H)CNH_2 gives two diastereomers of the *syn* isomer of the iminium-thiolate complex analogous to **50**.[87] Partial separation of these diastereomers and treatment with CF_3SO_3H converts them to partially resolved $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-2-MeT})^{2+}$. Other $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-2-RT})^{2+}$ complexes were resolved similarly.

Because of the reactivity of the $(ring)Ru(\eta^5\text{-T*})^{2+}$ complexes toward OH^- (Scheme 4), base-catalyzed exchange of the protons in the η^5-T* ligand is not possible, in contrast to the OH^--catalyzed exchange in $CpRu(\eta^5\text{-T*})^+$.[81] However, protons in the 2- and 5-methyl groups in $Ru(\eta^5\text{-}Me_4T)_2^{2+}$ do undergo exchange with D_2O at 150 °C.[88]

Similar to the reaction[86] of (η^6-cymene)Ru(η^5-Me_4T)$^{2+}$ with NH_3 to give (η^6-cymene)Ru(η^4-$Me_4T\cdot NH_2$)$^+$, (κ^3-[9]-$aneS_3$)Ru(η^5-Me_4T)$^{2+}$, where [9]$aneS_3$ is 1,4,7-trithiacyclononane, reacts with EtO^- to give the analogous thioallyl complex (κ^3-[9]$aneS_3$)Ru(η^4-$Me_4T\cdot OEt$)$^+$, whose

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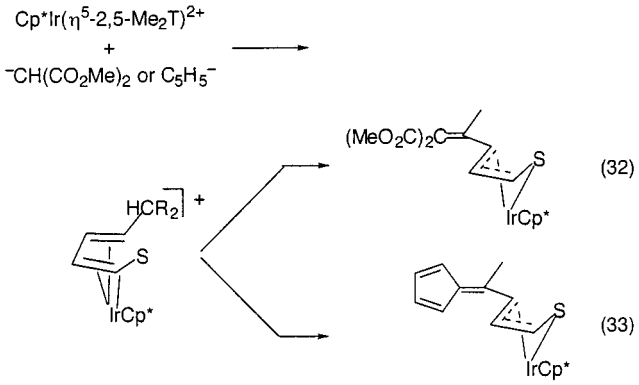
structure established by an X-ray diffraction study shows that the OEt^- has added to carbon-2 and the other three carbons and sulfur remain bonded to the metal as in the related $(OC)_3Mn(\eta^4\text{-T}\cdot\text{Nuc})$ complexes (eq 28).[89] Cleavage of the C−S bond does not occur, in contrast to reactions (eq 30) of the more electron-rich $CpRu(\eta^5\text{-T*})^+$ complexes with nucleophiles (including OEt^-), which give butadienethiolate complexes $CpRu(\eta^5\text{-T*}\cdot\text{Nuc})$.

Relatively few studies of analogous osmium complexes have been reported, but $(\eta^6\text{-cymene})Os(\eta^5\text{-Me}_4\text{T})^{2+}$ reacts[90] with aqueous KOH to give the acylthiolate $(\eta^6\text{-cymene})Os(\eta^4\text{-SC}_3\text{Me}_3\text{C(=O)Me})$ analogous to **50** or **51** in Scheme 4. More detailed studies[91] of the reaction of $(\eta^6\text{-cymene})Os(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ with KOH show that, as for the reaction of $(\eta^6\text{-cymene})Ru(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ with OH^-, a sulfoxide of structure type **48** in Scheme 4 forms first, but this rearranges to the acylthiolate, whose structure has not been definitively assigned to either **50** or **51**.

Reactions of $Cp'Rh(\eta^5\text{-Me}_4\text{T})^{2+}$, where $Cp' = C_5Me_5$, C_5Me_4H, or C_5Me_4Et,[85b,92,93] with OH^- follow essentially the same pattern (Scheme 4) as that observed for the $(ring)Ru(\eta^5\text{-T*})^{2+}$ complexes. High concentrations of KOH give the S-oxide complex $Cp'Rh(\eta^4\text{-T*}\cdot\text{O})$, analogous to **48**. Lower OH^- concentrations give the acylthiolate isomer, analogous to **50**, in which the acyl group is *syn* to the other part of the dienethiolate ligand, as established by an X-ray study.[92] As isomer **50** is converted back to **46** upon treatment with CF_3SO_3H acid, $Cp'Rh(\eta^4\text{-SC}_3\text{Me}_3\text{C(=O)Me})$ returns to $Cp'Rh(\eta^5\text{-Me}_4\text{T})^{2+}$ upon reaction with CF_3SO_3H. One equivalent of acid reacts rapidly with $Cp^*Rh(\eta^4\text{-SC}_3\text{Me}_3\text{C(=O)Me})$ to give the 2-hydroxy intermediate $Cp^*Rh(\eta^4\text{-Me}_4\text{T-2-OH})^+$ (analogous to **49**), which was characterized crystallographically. The C−S bond involving the C(OH)Me carbon is unusually long (1.906(5) Å), suggesting that this bond is already weakened prior to its conversion to the acylthiolate product $Cp^*Rh(\eta^4\text{-SC}_3\text{Me}_3\text{C(=O)Me})$.

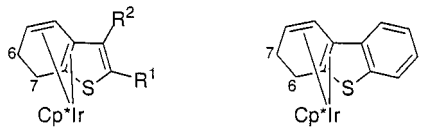
Although studied less extensively than the $Cp'Rh(\eta^5\text{-Me}_4\text{T})^{2+}$ system, $Cp^*Ir(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ also reacts rapidly with OH^- to give both the S-oxide $Cp^*Ir(\eta^5\text{-2,5-Me}_2\text{T}\cdot\text{O})$, analogous to **48**, and the acythiolate $Cp^*Ir(\eta^4\text{-SC}_3\text{H}_2\text{MeC(=O)Me})$, whose structure was shown by X-ray studies to have an *anti* acyl group,[94] as in structure **51**, rather than a *syn* acyl as found in $Cp^*Rh(\eta^4\text{-SC}_3\text{Me}_3\text{C(=O)Me})$.[92] The $Cp^*Ir(\eta^4\text{-SC}_3\text{H}_2\text{MeC(=O)Me})$ acythiolate is also obtained unexpectedly in the reaction of $Cp^*Ir(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ with PhLi in THF, along with $Cp^*Ir(2,5\text{-Me}_2\text{T}\cdot 2\text{Ph})$, which was not structurally characterized. The source of the oxygen atom in the acylthiolate product is presumably the THF solvent.

The $Cp^*Ir(\eta^5\text{-2,5-Me}_2\text{T})^{2+}$ dication has also been observed to undergo reactions with other nucleophiles with acidic protons. Thus, $^-CH(CO_2Me)_2$ and cyclopentadienide react to give the products shown in eqs 32[94] and 33.[95] The acidic protons in the proposed intermediates are removed by a second mole of nucleophile to give the products, whose structures were established crystallographically and are very similar to that of the related acylthiolate $Cp^*Ir(\eta^4\text{-SC}_3\text{H}_2\text{MeC(=O)Me})$.[94] In a quite different type of reaction with a nucleophile, $Cp^*Ir(\eta^5\text{-T})^{2+}$ reacts with PMe_3, PPh_2Me, and PPh_3 to give $Cp^*Ir(\eta^4\text{-T}\cdot\text{PR}_3)^{2+}$, in which PR_3 is proposed to have added to C-2, as in $(OC)_3Mn(\eta^4\text{-T}\cdot\text{Nuc})^+$ (**42**).[82]



The η^6-benzothiophene complex $Cp^*Ir(\eta^6\text{-BT})^{2+}$ reacts with BH_4^- to give a mixture of four $Cp^*Ir(\eta^5\text{-BT}\cdot\text{H})^+$ cyclohexadienyl isomers in which H^- adds to each of the four nonbridgehead carbons of the benzo ring;[82] in the predominant isomer, whose structure was established by an X-ray study, H^- addition occurs at C-7, as also occurred in $CpRu(\eta^6\text{-BT})^+$. With the nucleophiles OMe^-, $^-CH(CO_2Me)_2$, and SEt^-, again four isomers of the benzo addition products $Cp^*Ir(\eta^5\text{-BT*}\cdot\text{OMe})^+$, $Cp^*Ir(\eta^5\text{-BT*}\cdot\text{CH(CO}_2\text{Me)}_2)^+$, and $Cp^*Ir(\eta^5\text{-BT*}\cdot\text{SEt})^+$, where BT* = BT or 3-MeBT, are obtained, also with addition at C-7 predominating. The reaction of the isomeric mixture of $Cp^*Ir(\eta^5\text{-BT}\cdot\text{OMe})^+$ with Ph_3C^+ cleanly gives back $Cp^*Ir(\eta^6\text{-BT})^{2+}$. Somewhat surprisingly, $Cp^*Ir(\eta^5\text{-BT}\cdot\text{CH(CO}_2\text{Me)}_2)^+$ reacts with HBF_4 to also give $Cp^*Ir(\eta^6\text{-BT})^{2+}$, resulting from C−C cleavage. The phosphines, PMe_3 and PPh_2Me, also react with $Cp^*Ir(\eta^6\text{-BT})^{2+}$ to give a mixture of $Cp^*Ir(\eta^5\text{-BT}\cdot\text{PR}_3)^{2+}$ isomers that could not be isolated, but NMR studies suggest that addition at C-7 predominates.

With the more reactive hydride source $Na[H_2Al(OCH_2CH_2OMe)_2]$,[96] $Cp^*Ir(\eta^6\text{-BT*})^{2+}$ (where BT* = BT, 2-MeBT, 3-MeBT, and 2,3-Me_2BT) gives $Cp^*Ir(\eta^4\text{-BT*}\cdot 2\text{H})$ (**53**), in which carbons 6 and 7 are saturated and the other four carbons of the benzo ring are coordinated to the Ir, as established by an X-ray diffraction study of $Cp^*Ir(\eta^4\text{-3-MeBT}\cdot 2\text{H})$. When $Cp^*Ir(\eta^4\text{-3-MeBT}\cdot 2\text{H})$ reacts with 1 equiv of Ph_3C^+, only the H^- at C-6 is abstracted, giving the cyclohexadienyl complex Cp^*Ir-



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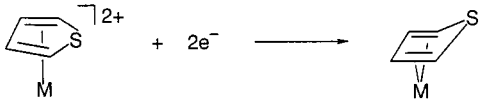
$(\eta^5$-3-MeBT·H$)^+$, in which the CH_2 group is at C-7. Similarly, the selective removal of H^- from the mixture of four isomers of CpRu(η^5-BT·H) with Ph_3C^+ left only the CpRu(η^5-BT·H) isomer with the CH_2 group at C-7.[82] The reaction of Cp*Ir(η^4-3-MeBT·2H) with 2 equiv of Ph_3C^+ results in the removal of two hydrides to give Cp*Ir(η^6-3-MeBT)$^{2+}$.

The reaction of Cp*Ir(η^6-DBT)$^{2+}$ with Na[H_2Al(OCH$_2$CH$_2$OMe)$_2$] gives the product Cp*Ir(η^4-DBT·2H) (**54**), in which H^- adds at carbons 6 and 7, as established by the X-ray-determined structure of **54**.[96] Paralleling the reactions of Cp*Ir(η^4-3-MeBT·2H), **54** reacts with 1 equiv of Ph_3C^+ to give Cp*Ir(η^5-DBT·H)$^+$, in which the CH_2 group is at C-6, and with 2 equiv of Ph_3C^+ to give the starting dication Cp*Ir(η^6-DBT)$^{2+}$.

IV. Reduction of η^5-Thiophene Complexes

The most common reaction of η^5-thiophene complexes with reducing agents is the formation of η^4-thiophene complexes (eq 34). In reactions of this type that have



(34)

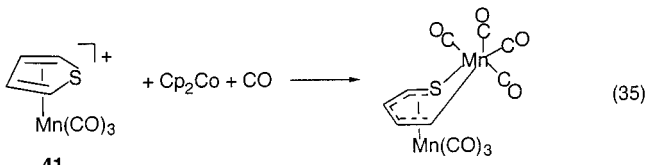
been reported so far, the dicationic η^5-complexes are 18-electron species. Thus, the two added electrons force the displacement of a two-electron segment of the thiophene ligand from the metal; this segment is the sulfur in all reported cases.

The reduction of Ru(η^5-Me$_4$T)$_2^{2+}$ with 2 equiv of Cp_2Co at −20 °C in THF gives (η^5-Me$_4$T)Ru(η^4-Me$_4$T), a compound that is marginally stable at room temperature.[97] Its ^{1}H and ^{13}C NMR spectra show, even at −90 °C, that both Me$_4$T ligands are equivalent on the NMR time scale. Thus, the η^5-Me$_4$T and η^4-Me$_4$T ligands, which differ only by a coordinated sulfur, are rapidly interconverting. A stable derivative of (η^5-Me$_4$T)Ru(η^4-Me$_4$T) was isolated from its reaction with Fe(CO)$_5$ and Me$_3$NO. The resulting adduct (η^5-Me$_4$T)Ru(η^4-Me$_4$T·Fe(CO)$_4$), whose structure was established crystallographically, retains η^4-Me$_4$T coordination to the Ru while coordinating to the Fe through the sulfur; many other adducts of η^4-T* complexes are given in the next section. The hexamethylbenzene complexes (η^6-C$_6$Me$_6$)Ru(η^5-T*)$^{2+}$, where T* = T, 2,5-Me$_2$T and Me$_4$T, are also reduced by Cp_2Co at low temperature (−78 °C) in THF to give (η^6-C$_6$Me$_6$)Ru(η^4-T*). While the η^4-T derivative is unstable at room temperature, (η^6-C$_6$Me$_6$)Ru(η^4-Me$_4$T) was characterized by elemental analysis.

The reduction of Cp*Rh(η^5-Me$_4$T)$^{2+}$ with Cp_2Co gives Cp*Rh(η^4-Me$_4$T), which is stable at room temperature, but low-quality crystals prevented the determination of a definitive structure for the compound.[98] Reduction of the analogous tellurophene complex Cp*Rh(η^5-C$_4$H$_4$Te)$^{2+}$ does not give the expected η^4-tellurophene complex but instead a dinuclear product, Cp*Rh(μ-C$_4$H$_4$)RhCp*, containing a bridging metallacyclopentadiene unit and no tellurium.[99]

Reduction of the related Ir complexes Cp*Ir(η^5-T*)$^{2+}$, where T* = T, 2-MeT, 3-MeT, 2,5-Me$_2$T, and Me$_4$T, with Cp_2Co (or Na[H_2Al(OCH$_2$CH$_2$OMe)$_2$]) at room temperature gives the corresponding Cp*Ir(η^4-T*) complexes.[100] An X-ray-determined structure of (Cp*Ir(η^4-2,5-Me$_2$T) shows the two CH_3 carbons to lie slightly (0.047 Å average) below the diene plane toward the Ir, while the S lies 0.905 Å out of this plane away from the Ir. The C−S bond distances (1.76(2), 1.79(2) Å) are longer than those (1.72 Å) in free thiophene and are comparable to C(sp^2)−S (1.76 Å) and C(sp^3)−S (1.81 Å) single-bond lengths. The cobaltocene reductions of Cp*Ir(η^6-BT)$^{2+}$ and Cp*Ir(η^6-DBT)$^{2+}$ give very air-sensitive compounds that have been assigned η^4-structures, Cp*Ir(η^4-BT) and Cp*Ir(η^4-DBT), in which the Ir is coordinated to four carbons of a benzo ring, on the basis of their ^{1}H NMR spectra.[96]

In contrast to reductions of the dicationic complexes, Sweigart and co-workers[101] observed that the monocationic (OC)$_3$Mn(η^5-T*)$^+$, where T* = T, 2-MeT, 3-MeT, and 2,5-Me$_2$T, react in a totally different fashion. Their reductions with 1 equiv of Cp_2Co under a CO atmosphere at room temperature yield products of the type shown in eq 35 in approximately 75% yield.[101,102] Structural studies of the type **55** complexes show that



41 **55**

(35)

the Mn of the Mn(CO)$_4$ fragment is about 1.2 Å above the C_4S plane that is η^5-coordinated to the Mn(CO)$_3$ unit. Although the mechanism of reaction 35 has not been investigated, it has been proposed[102] that (OC)$_3$Mn(η^5-T*)$^+$ initially undergoes a two-electron reduction to (OC)$_3$Mn(η^4-T*)$^-$, which contains a nucleophilic sulfur that displaces the η^5-T* ligand from a (OC)$_3$Mn(η^5-T*)$^+$ reactant to form an intermediate that transforms to the product.

The Cp_2Co reduction of the analogous (OC)$_3$Mn(η^6-BT*)$^+$ under a CO atmosphere at room temperature gives quite different products (Scheme 5) depending on alkyl (R) substitution at the 7-position.[101,103,104] This reaction of the parent BT complex (OC)$_3$Mn(η^6-BT)$^+$ gives a complex of type **57**, in which a Mn(CO)$_4$ unit has inserted into the S−C(aryl) bond, as established by a diffraction study.[101] It should be noted that other insertions into C−S bonds of benzothiophenes occur at the S−C(vinyl) bond (see section II). When the benzothiophene contains a methyl or ethyl substituent at

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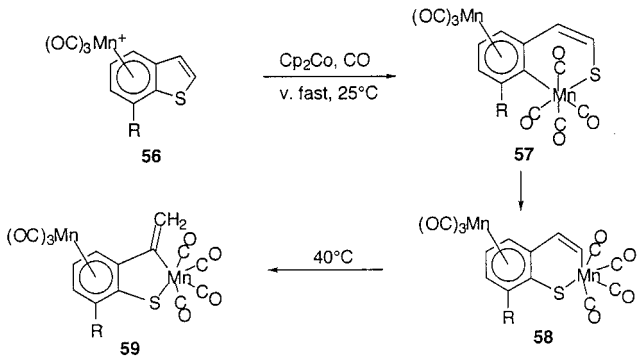
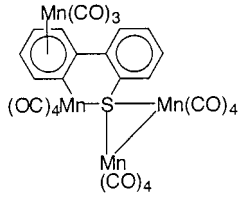
Scheme 5



the 7-position, the $(OC)_3Mn(\eta^6\text{-BT*})^+$ gives a complex of type **57** initially, which rearranges to the S−C(vinyl) inserted product **58**. This rearrangement is the reverse of that observed in eq 3,[30] where the S−C(vinyl) inserted product of the reaction of $Cp^*(Me_3P)Rh$ with 2-MeBT rearranges to the S−C(aryl) inserted compound. Finally, in Scheme 5, complex **58** rearranges to the thermodynamic isomer **59**. This remarkable series of rearrangements is documented by X-ray-determined structures of **57**, **58**, and **59** resulting from the reduction of $(OC)_3Mn(\eta^6\text{-7-MeBT})^+$. A mechanism proposed[104] for the conversion of **56** to **57** involves an $(OC)_3Mn(\eta^4\text{-BT})^-$ intermediate analogous to $Cp^*Ir(\eta^4\text{-BT})$[96] in which the benzo ring is η^4-coordinated to the metal. Support for an η^4-BT intermediate is found in the reaction of $(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-BT})^{2+}$ with Cp_2Co in the presence of CO and $(OC)_3Mn(\eta^6\text{-naphthalene})^+$, which contains a readily displaceable naphthalene, to give the analogue of compound **57** in which the $(OC)_3Mn$ is replaced by $(\eta^6\text{-}C_6Me_6)Ru$. This reaction presumably occurs by initial reduction of $(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-BT})^{2+}$ to $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-BT})$, which reacts with $(OC)_3Mn(\eta^6\text{-naphthalene})^+$ by displacement of naphthalene and Mn insertion into the S−C(aryl) bond.

Reduction of the DBT analogue $(OC)_3Mn(\eta^6\text{-DBT})^+$ with Cp_2Co or Na/Hg with or without CO gives a complex mixture of products.[105] The one that was isolated in 10−20% yield and characterized crystallographically is **60**. It consists of a $(OC)_3Mn(\eta^6\text{-DBT})^+$ unit

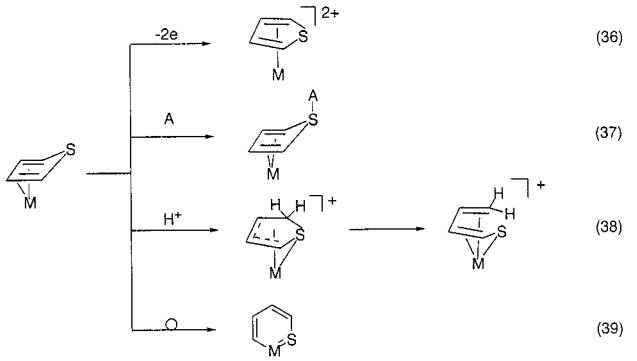


60

in which a $Mn(CO)_4$ group has been inserted into a S−C(aryl) bond somewhat similar to $Pt(PPh_3)_3$ insertion into the same bond in $(OC)_3Mn(\eta^6\text{-DBT})^+$ (eq 23).[63] In addition, the sulfur bridges a $(OC)_4Mn-Mn(CO)_4$ unit.

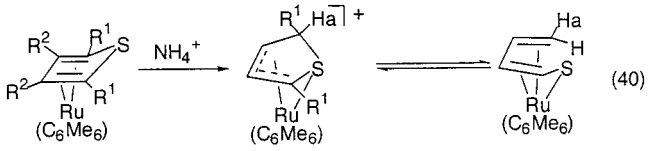
V. Reactions of η^4-Thiophene Complexes with Electrophiles and Nucleophiles

Known η^4-thiophene complexes, which are synthesized by two-electron reduction of η^5-thiophene dications (eq 34), are relatively electron-rich and tend to undergo reactions that result in oxidation back to their η^5-precursor (eq 36), formation of adducts at the sulfur with Lewis acids (eq 37), protonation at the 2-position (eq 38), or rearrangement to the metallathiabenzene (eq 39).



In the Ru series of η^4-thiophene complexes, both $(\eta^5\text{-}Me_4T)Ru(\eta^4\text{-}Me_4T)$ and $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}Me_4T)$ are oxidized to their parent dications, $(\eta^5\text{-}Me_4T)_2Ru^{2+}$ and $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-}Me_4T)^{2+}$.[97] They also react with $Fe(CO)_4$ and $Mo(CO)_5$ fragments to form Lewis acid adducts, $(\eta^5\text{-}Me_4T)Ru(\eta^4\text{-}Me_4T{\cdot}Fe(CO)_4)$ and $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}Me_4T{\cdot}Mo(CO)_5)$, of the type in eq 37. The $Fe(CO)_4$ adduct was characterized by X-ray diffraction studies.[97a]

The $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-T*})$ complexes, where T* = T, 2,5-Me_2T, and Me_4T, react[97b] with the weak acid $NH_4(PF_6)$ (eq 40) to give thioallyl complexes $(\eta^6\text{-}C_6Me_6)Ru$-



$(\eta^4\text{-T*}{\cdot}H)^+$ of the type prepared by nucleophilic attack of H^- on $(OC)_3Mn(\eta^5\text{-T*})^+$ (eq 28). Studies with ND_4^+ show that the protonation occurs stereospecifically on the *endo* side of the ring, suggesting that protonation occurs initially at the Ru. The *endo* stereochemistry is also established by the X-ray-determined structure of $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}H)^+$. An interesting feature of this structure is the long $C(sp^3)-S$ bond (1.91(1) Å). In fact, Rauchfuss and co-workers[106] subsequently showed that this bond in $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-T}{\cdot}H)^+$ cleaves (eq 40) in both the solid state and solution to give the butadienethiolate product $(\eta^6\text{-}C_6Me_6)Ru(\eta^5\text{-SCH=CH-CH=CH}_2)^+$; this ligand is also obtained from the reaction of $CpRu(\eta^5\text{-T})^+$ with H^- in eq 30. Deuterium-labeling studies show that the *endo* hydrogen (Ha) in $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-T}{\cdot}H)^+$ is found in only the *anti* position in the butadienethiolate product, establishing that the sp^3 carbon retains its configuration during the C−S cleavage. While the thioallyl and butadienethiolate forms of $(\eta^6\text{-}C_6Me_6)Ru(T{\cdot}H)^+$ are in equilibrium in solution and in the solid state, it is interesting that the analogous $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}H)^+$ and $(\eta^6\text{-}C_6Me_6)Ru(\eta^4\text{-}Me_4T{\cdot}H)^+$ show no evidence for C−S cleavage.

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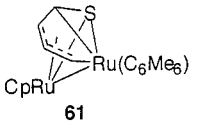
(106) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993**, *115*, 4943.

Reactions of (η^6-C_6Me_6)Ru(η^4-T*), where T* = 2,5-Me_2T and Me_4T, with the Lewis acids Cp′Ru$(NCMe)_3^+$, where Cp′ = Cp or Cp*, containing three potential coordination sites give (eq 41) a product, (η^6-C_6Me_6)Ru-

(η^6-C_6Me_6)Ru(η^4-Me_4T) + CpRu$(NCMe)_3^+$ —25°, -3 MeCN→ (41)

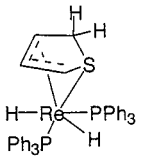


61

(μ-T*)Ru(Cp′)$^+$, in which a C−S cleaved thiophene bridges the Ru centers,[107] in a fashion similar to that in compound **14**.[43] A crystallographic study of **61** shows the bridging Me_4T ligand to be an overall eight-electron donor to the two Ru atoms. Presumably, this product results from initial displacement of a MeCN ligand by the strongly donating sulfur of (η^6-C_6Me_6)Ru(η^4-2,5-Me_2T).

A thioallyl complex (**62**) of the type in eqs 38 and 40 is also isolated from the reaction of $ReH_7(PPh_3)_2$ with T in the presence of the hydrogen acceptor 3,3-dimethylbutene (eq 42).[108]The reaction is proposed to occur

$ReH_7(PPh_3)_2$ +  + T —40°→ (42)



62

through the η^4-T intermediate $(Ph_3P)_2(H)_3Re(\eta^4$-T), which is converted to the product **62** by transfer of one of the hydride ligands to an *endo* position of the η^4-T ring. Such a transfer is supported by deuterium-labeling experiments, as well as evidence for such a stereospecific transfer in the protonation of (η^6-C_6Me_6)Ru(η^4-T*) (eq 40). The structure of **62** shows the C(sp^3)−S bond length to be 1.72(3) Å, which is shorter than comparable bonds in other thioallyl complexes, (η^6-C_6Me_6)Ru(η^4-2,5-Me_2T·H)$^+$ (1.91 (1) Å)[97b] and $(OC)_3$Mn(η^4-T·CN) (1.831 (6) Å).[68]

It should also be noted that uncoordinated Me_4T itself can be protonated[109] with the strong acid HCl/$TiCl_4$ to give Me_4T·H$^+$ with a structure very similar to those of the thioallyl groups in the Mn, Ru, and Re complexes. The C(sp^3)−S distance in Me_4T·H$^+$ is 1.804(5) Å. Attempts to protonate thiophene under the same conditions yield only thiophene polymers.

As for the other η^4-T* complexes, Cp*Rh(η^4-Me_4T) is oxidized electrochemically to the η^5-Me_4T complex Cp*Rh(η^5-Me_4T)$^{2+}$ and forms the adduct Cp*Rh(η^4-Me_4T·Fe$(CO)_4$), in which the Fe$(CO)_4$ group is coordinated to the sulfur, as established by an X-ray diffraction study.[98] A particularly interesting sulfur adduct is that of Cp*Rh(η^4-Me_4T·O) with an oxygen atom bonded to the sulfur of the η^4-Me_4T ligand. This compound is formed by the reaction of Cp*Rh(η^4-Me_4T) with O_2 at room temperature.[110] Clearly the η^4 thiophene is activated to undergo this reaction as free thiophenes give S-oxides only when reacted with peroxy acids. The same S-oxide compound is formed in reactions of Cp*Rh(η^5-Me_4T)$^{2+}$ with $^-OSiMe_3$[110] and OH^- [92,93] (see Scheme 4). There is a brief report[97b] of the reaction of Cp*Rh(η^4-Me_4T) with $NH_4(PF_6)$ analogous to that of (η^6-C_6Me_6)Ru(η^4-T*) in eq 40. The thioallyl product Cp*Rh(η^4-Me_4T·H)$^+$ was characterized by an X-ray diffraction study.

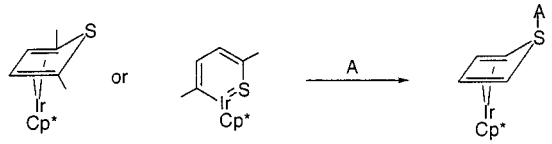
A remarkable reaction of Cp*Ir(η^4-T*) that does not occur with its Rh analogue Cp*Rh(η^4-T*) is its isomerization to the ring-opened structure Cp*Ir(η^2(C,S)-T*).[3,100] This reaction (eq 43) has been studied in

(43)

63 **64**

greatest detail for Cp*Ir(η^4-2,5-Me_2T) (**63**) and is catalyzed by basic Al_2O_3 or Et_3N[100] or by photolysis with UV light.[111] On the basis of its planar structure and ^{1}H NMR spectrum, the six-membered ring in **64** is best described as a π-delocalized system, an iridathiabenzene. This bonding description is supported by MO calculations.[33,34,112]

Like Cp*Rh(η^4-Me_4T),[98] Cp*Ir(η^4-2,5-Me_2T) (**63**) is oxidized to Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ by 2 equiv of Cp_2Fe^+.[100] Surprisingly, the ring-opened isomer **64** is also rapidly oxidized by Cp_2Fe^+ to give CpIr(η^5-2,5-Me_2T)$^{2+}$ in a reaction that reassembles the η^5-thiophene ring. Unlike Cp*Rh(η^4-Me_4T), which gives the thioallyl Cp*Rh(η^4-Me_4T·H)$^+$ upon protonation,[97b] Cp*Ir(η^4-2,5-Me_2T) reacts with CF_3SO_3H and HCl to give Cp*Ir(η^4-2,5-Me_2T)·HX products whose ^{1}H NMR spectra indicate that they do not have a thioallyl structure, but crystals for an X-ray study could not be obtained.[113] Also unlike Cp*Rh(η^4-Me_4T), which reacts with O_2 to give the S-oxide Cp*Rh(η^4-2,5-Me_2T·O), **63** and **64** react with O_2 to give the acylthiolate isomer Cp*Ir(η^4-SC_3H_2MeC(=O)Me).[114] However, Cp*Ir(η^4-2,5-Me_2T) does react (eq 44) with



(44)

63 **64** **65**

A = BH_3,[115†] CH_3^+,[112,116†] CS_2,[113] Ru(η^6-C_6H_6)Cl_2,[117] Fe$(CO)_4$,[118†] $Co_4(CO)_{11}$,[119†] $Ru_3(CO)_{11}$,[117†] $Re_2(CO)_9$[117†]

(† indicates characterization by X-ray diffraction).

numerous Lewis acids (including metal complexes) to give the sulfur adducts **65**.[3] Although the sulfur in free thiophenes is a very weak Lewis base, as noted earlier, it becomes in **63** a donor even stronger than Me_2S, as demonstrated by the reaction of **63** with Me_2S·BH_3 to form Cp*Ir(η^4-2,5-Me_2T·BH_3).[115] Another surprising reaction of the ring-opened isomer **64** is that with BH_3, which also gives[116] Cp*Ir(η^4-2,5-Me_2T·BH_3). This reaction, which results in a reassembly of the thiophene ring, presumably occurs by addition of the BH_3 at the

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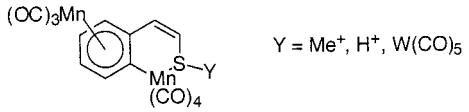
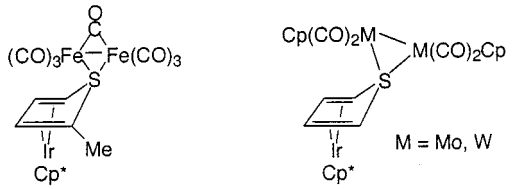
sulfur, which is calculated to be the most electron-rich center in **64**.[112] Moreover, the Mn-inserted complex **57** (Scheme 5) reacts with Lewis acids, MeOTf, HBF_4, and $W(CO)_5(THF)$, to give S-adducts of type **66**.[104]



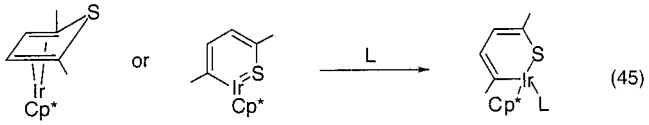
66

Besides the reactions with BH_3, **63** and **64** often react with Lewis acids to give the same adduct. In fact, all of the reactions shown in eq 44 occur for both **63** and **64**, which demonstrates that the iridathiabenzene ring in **64** is readily converted to the η^4-thiophene complex when the end product is a stable $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}A)$ adduct. This stability probably[112] is a result of the reduced repulsion between filled orbitals on the metal and the sulfur, which destabilize the η^4 isomer **63**. The sulfur in $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ is also capable of donating to two metal atoms, as in **67** and **68**,[111,120] whose structures were established by X-ray studies.



67 **68**

Besides reactions with Lewis acids/electrophiles (eq 44), **63** and **64** also react (eq 45) with bases/nucleophiles (L)[121] to give adducts **69** of the ring-opened **64**. This



(45)

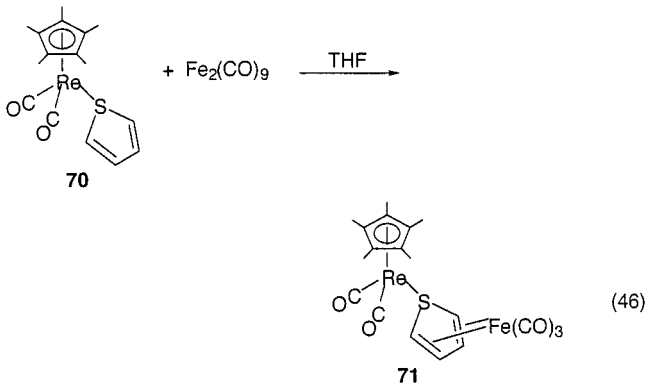
63 **64** **69**

L = CO, PR_3

reaction of **63** presumably occurs by a base-catalyzed rearrangement of **63** to **64**, as noted above (eq 43). Then, the base (L) coordinates to the Ir, thereby disrupting the aromatic character of the iridathiabenzene ring in **64**. The lack of any reported reactions of $(\eta^6\text{-arene})Ru(\eta^4\text{-T*})$ and $Cp^*Rh(\eta^4\text{-}Me_4T)$ with Lewis bases to give products of type **69** is presumably due to the inability of these η^4-thiophene complexes to rearrange to their ring-opened isomers. A variety of other reactions of **63** and **64** are known but do not fit discernible patterns of reactivity.[3,113]

VI. Reactions of η^1(S) and η^2 Thiophene Complexes with Electrophiles and Bases

The aromatic character of thiophenes appears to be disrupted by η^1(S) or η^2 coordination in metal complexes, which makes these ligands susceptible to reactions with electrophiles. Thus, the uncoordinated diene segment of the η^1(S)-T ligand in $Cp^*(CO)_2Re(\eta^1\text{-T})$ reacts (eq 46)[122] with $Fe_2(CO)_9$ to give an $Fe(CO)_3$(diene) complex,



70 **71**

(46)

70, whose structure is very similar to those of other sulfur adducts of η^4-thiophene complexes prepared by reacting η^4-T* complexes with Lewis acids (eqs 37 and 44). As free T does not react with $Fe_2(CO)_9$, its η^1(S) coordination in **70** clearly enhances its diene-coordinating ability. The observation that the ν(CO) values of the $Cp^*(CO)_2Re$ unit in **71** (1922, 1862 cm^{-1}) are lower than those in **70** (1934, 1874 cm^{-1}) shows that the sulfur in the thiophene ligand is a stronger donor when its diene is coordinated to $Fe(CO)_3$ in **71** than when its diene is uncoordinated as in **70**, a conclusion that is not surprising in view of the many other examples of the strong donor properties of the sulfur in η^4-thiophene complexes (eqs 37 and 44).

A series of selenophene analogues $Cp'(OC)_2Re(Seln)$ of **70** exist in solution as rapidly equilibrating mixtures of η^1(Se) and η^2 isomers.[123,124] Increasing the electron density on the Re by substituting Cp* for Cp favors the η^2 isomer as a result of increased π-back-bonding from the Re to the olefin. On the other hand, substituting methyl groups onto the selenophene ring favors the η^1-(Se) isomer because the electron-donating methyl groups make the Se atom a better donor toward the Re. While $Cp^*(OC)_2Re(\eta^2\text{-Sel})$ (**72**), where Sel = C_4H_4Se, exists almost exclusively in the η^2 form, its reactions with electrophiles give products that could originate from either the η^2 or η^1(Se) isomers. Thus, **72** reacts with Me_3O^+ to give the Se-methyl product $Cp^*(OC)_2Re(\eta^2\text{-Sel}{\cdot}Me)^+$. Likewise, $M(CO)_5$ (M = Cr, Mo, W) and $W(CO)_4(PPh_3)$ add to the Se of **72** (eq 47) to give the Se adducts **73**. On the other hand, **72** reacts with $Fe_2(CO)_9$ to give products that presumably originate not only from the η^2-isomer (**74**) but also from the η^1(Se) isomer (**75**). In **71**, selenophene is clearly much more reactive toward all of these electrophiles than is free selenophene.

As for the $Cp'(CO)_2Re(Seln)$ complexes, the $Cp'(OC)_2Re(BT)$ complexes, where Cp′ = Cp or Cp*, exist in solution as relatively slowly interconverting mixtures ($t_{1/2}$ = 1.7−13 min at 22 °C) of η^1(S) and η^2 isomers, the η^2 form being favored by the more electron-donating Cp*

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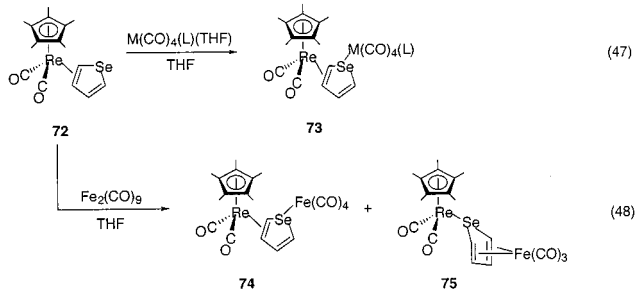
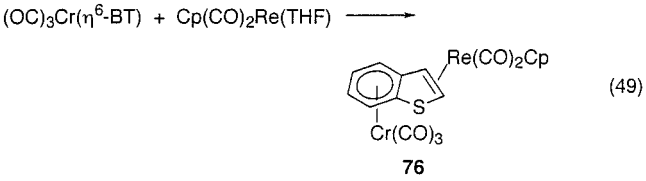


(47)

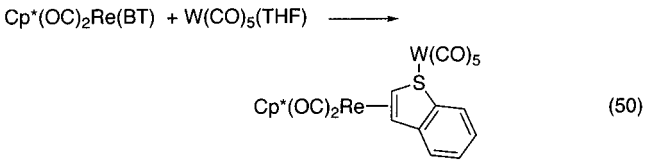
(48)

ligand.[125,126] The methylbenzothiophene ligands, 2-MeBT and 3-MeBT, give exclusively η^1(S) forms of their Cp*-$(OC)_2$Re(MeBT) complexes, which is consistent with their enhanced S-donor abilities and sterically hindered olefinic groups. When the BT is η^6-coordinated to the electron-withdrawing $Cr(CO)_3$ group, only the η^2 isomer **76** is isolated (eq 49) as a result of the greater π-acceptor ability of the olefin in $(OC)_3Cr(\eta^6$-BT).



(49)

Electrophiles react exclusively at the sulfur of the BT ligand in the mixture of η^1(S) and η^2 isomers of Cp′$(OC)_2$-Re(BT).[126] The BT ligand in these products is η^2-coordinated to the Cp′$(OC)_2$Re fragment. Methylation of Cp$(OC)_2$Re(BT) with Me_3O^+ gives the S-methyl product Cp$(OC)_2$Re(η^2-BT·Me)$^+$. Reaction of Cp*$(OC)_2$Re-(BT) with $W(CO)_5$(THF) gives the S-adduct (eq 50). Reactionsof Cp′$(OC)_2$Re(BT) with Cp′$(OC)_2$Re(THF) give

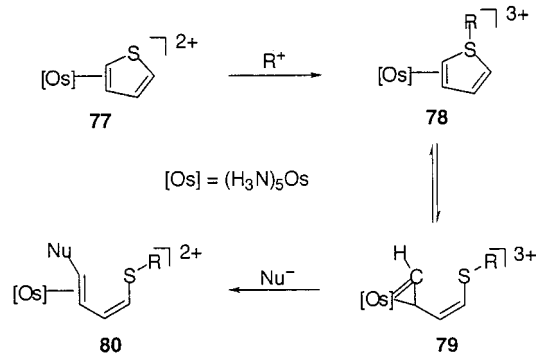


(50)

similar products in which the BT ligand is η^1(S)-coordinated to one Cp′$(OC)_2$Re group and η^2- to the other; the Cp′$(OC)_2$Re units are on opposite sides of the BT plane.[128] When Cp*$(OC)_2$Re(BT) reacts with Cp-$(OC)_2$Re(THF), the only product isolated is that in which the Cp*$(OC)_2$Re unit is coordinated to the olefin and Cp-$(OC)_2$Re is coordinated to the sulfur. These site preferences are entirely consistent with the more electron-rich Cp*$(OC)_2$Re fragment coordinating to the π-accepting olefin and the less electron-rich Cp$(OC)_2$Re accepting electron-density from the sulfur donor. Thus, bonding to both Re centers is mutually enhanced; π-back-bonding from Cp*$(OC)_2$Re to the olefin provides electron density to the sulfur, which strengthens its bond to the Cp$(OC)_2$Re.

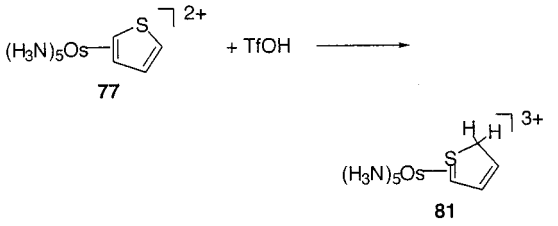
Reactions of the η^2-thiophene complexes of cationic, but electron-rich, $(H_3N)_5Os(\eta^2$-T*$)^{2+}$ (**77**), where T* includes a variety of substituted thiophenes, with electrophiles have been investigated by Harman and co-

Scheme 6



workers.[129,130] With alkylating agents such as MeOTf, Et_3O^+, and 3,5-dimethylbenzyl bromide, addition occurs at the sulfur (Scheme 6) to give complexes **78**,[131,132] which are stable and similar to Cp*$(OC)_2$Re(η^2-Sel·Me)$^+$ and Cp*$(OC)_2$Re(η^2-BT·Me)$^+$ described above. In solution **78** is proposed to be in equilibrium with a ring-opened η^2-vinyl cation, **79**. Although not observed, the intermediacy of **79** is based on related precedents and the conclusion that it logically explains the reactions of **78** with a variety of nucleophiles (H^-, CN^-, OAc^-, py, $PrNH_2$, N_3-, PPh_3, PhO^-, and PhS^-) to give η^2-4-(alkylthio)-1,3-butadiene complexes **80**.

In contrast to its reactions with alkylating agents, $(H_3N)_5Os(\eta^2$-T*$)^{2+}$ reacts (eq 51) with triflic acid by adding H^+ to the *exo* side of the ring to give an η^2-2*H*-thiophenium product, $(H_3N)_5Os(\eta^2$-T*·H$)^{3+}$ (**81**).[133] Ac-



(51)

etaldehyde diethyl acetal with (*t*-Bu)Me_2SiOTf reacts with **77** to add $(CH_3)(EtO)CH^+$ to the 2-position to give a product analogous to **81**.[132] Electrophilic additions to the analogous η^2-selenophene complex $(H_3N)_5Os(\eta^2$-Sel$)^{2+}$ follow trends very similar to those of **77**.[134] The 2,3-η^2-BT complex $(H_3N)_5Os(\eta^2$-BT$)^{2+}$ reacts with an excess of TfOH to give the S-protonated product $(H_3N)_5$-$Os(\eta^2$-BT·H$)^{3+}$, which was too unstable to be isolated.[132] The η^2-T ligand in **77** is hydrogenated over Pd/C at the noncoordinated C=C bond to give the η^2-2,3-dihydrothiophene (DHT) complex $(H_3N)_5Os(\eta^2$-DHT$)^{2+}$, while $(H_3N)_5Os(\eta^2$-BT$)^{2+}$ undergoes desulfurization with Raney Nickel to give the η^2-styrene complex $(H_3N)_5Os(\eta^2$-styrene$)^{2+}$.[129] On the basis of all of these reactions of η^2-thiophene ligands in $(H_3N)_5Os(\eta^2$-T*$)^{2+}$, it is clear that the $(H_3N)_5Os^{2+}$ unit activates thiophenes to react with electrophiles, but not nucleophiles.[132]

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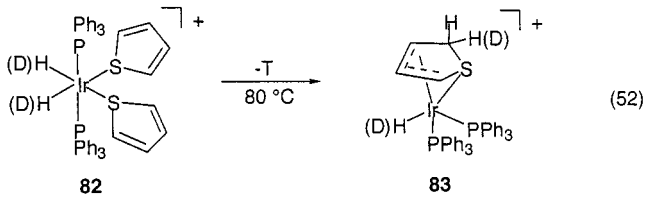
In one of the few reactions of η^1(S)-thiophene complexes, Bianchini and Sánchez-Delgado[135] showed that $(Ph_3P)_2Ir(H)_2(\eta^1(S)\text{-}T)_2^+$ (**82**) reacts by hydride migration from Ir to the C2 position of a thiophene ligand to give (eq 52) thioallyl complex **83**; other routes to thioallyl

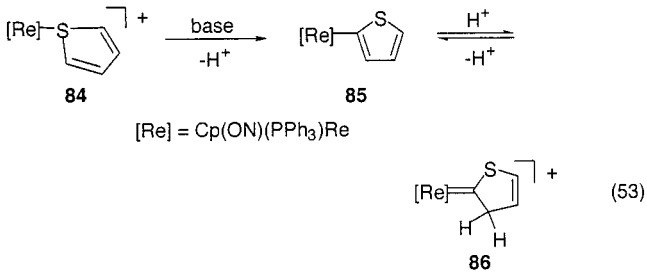


(52)

82 **83**

complexes are shown in eqs 28, 40, and 42. When the dideuteride form of **82** is converted to **83**, the deuterium is specifically in the *endo* position of the thioallyl ligand, as expected for such a migration. A possible intermediate in this reaction is an η^2-2H-thiophenium complex of type **81**; dissociation of the T ligand from this intermediate together with coordination of the other double bond of the η^2-2*H*-thiophenium ligand would give the observed product **83**.

A totally different type of reaction occurs when the η^1(S)-thiophene complex $Cp(ON)(Ph_3P)Re(\eta^1(S)\text{-}T)^+$ (**84**) reacts with a base such as DABCO ($N(CH_2CH_2)_3N$) or KOH/MeOH. This rapid reaction (eq 53) leads to simple deprotonation of the thiophene ligand together with migration of the Re from the sulfur to the deprotonated carbon.[136,137] Although the mechanism of this reaction



(53)

84 **85** **86**

is not known, precedents suggest an intermediate in which the η^1(S)-T ligand rearranges to the η^2-T coordination mode, and it is the η^2-T that actually undergoes deprotonation with concomitant formation of the Re−C(thienyl) bond.[136] The same reaction occurs for $Cp(ON)(Ph_3P)Re^+$ complexes of selenophene and benzothiophene and their monomethyl derivatives. On the other hand, the 2,5-Me_2T complex $Cp(ON)(Ph_3P)Re(\eta^1\text{-}(S)\text{-}2,5\text{-}Me_2T)^+$ is also deprotonated under the same conditions to give the thienyl complex in which the proton at carbon-3 is replaced by the Re. All of the 2-thienyl, 2-selenyl, and 2-benzothienyl complexes of type **85** were expected to be reprotonated to give the η^1(S)- and η^1(Se)-coordinated starting complexes of type **84**; however, instead they react with TfOH by protonating the carbon adjacent to the Re−C bond to give **86** as illustrated for thiophene in eq 53. This generates a thiocarbene or selenocarbene ligand. The structure of the benzothiophene carbene complex $Cp(ON)(Ph_3P)Re(2\text{-BTylcarbene})^+$ shows a typical Re=C thiocarbene distance. Bases such as DABCO deprotonate these carbene complexes (**86**) to give the thienyl precursors (**85**). Some of the carbene complexes rearrange spontaneously to the η^1(S) or η^1(Se) isomers (**84**). It should be noted that in contrast to the protonation of the 2-benzothienyl complex of $Cp(ON)(Ph_3P)Re(\eta^1(C)\text{-}2\text{-BTyl})$, which gives the carbene complex (eq 53), protonation of $Cp(OC)(Ph_3P)Ru(\eta^1(C)\text{-}2\text{-BTyl})$ and $Cp(Me_3P)_2Ru(\eta^1\text{-}(C)\text{-}2\text{-BTyl})$ gives only the η^1(S)-BT complexes $Cp(OC)(Ph_3P)Ru(\eta^1(S)\text{-BT})^+$ and $Cp(Me_3P)_2Ru(\eta^1(S)\text{-BT})^+$.[138]

VII. Conclusions

The results presented in this review suggest that there is a certain degree of predictability to the reactions of thiophenes in organometallic complexes. This predictability has led at least two groups[129,139] to utilize specific reactions of coordinated thiophenes for the synthesis of organosulfur compounds that are difficult to prepare by other methods. Building on our present understanding of reaction patterns of thiophenes in transition metal complexes, it seems likely that the use of thiophene complexes in organic synthesis will continue to grow.

Acknowledgment. I am grateful to the U.S. Department of Energy (Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-Eng-82 with Iowa State University) and to the many co-workers who contributed to studies in my group and whose names are cited in the references.

OM010040R

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