Models for Deep Hydrodesulfurization (HDS). Remote Activation of C−S Bonds in Alkylated Benzothiophenes and Dibenzothiophenes by Metal Coordination to a Carbocyclic Ring

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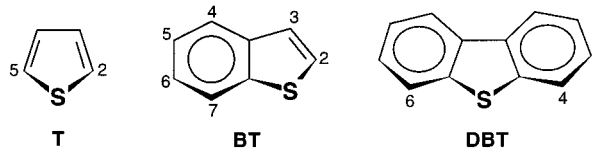
Received March 26, 2001

A series of alkylated benzothiophene and dibenzothiophene complexes containing a manganese tricarbonyl moiety coordinated to a carbocyclic ring have been synthesized. Reaction of these with the mild nucleophile $Pt(PPh_3)_2(C_2H_4)$ leads to rapid room-temperature insertion of $Pt(PPh_3)_2$ into a C−S bond to afford metallathiacyclic complexes. With benzothiophene complexes bearing no substitutent at the 2- or at the 3-position, it is shown that initial rapid coordination of the platinum to the C═C bond in the heterocyclic ring takes place prior to insertion into the C(vinyl)−S bond. When a substituent is present at the benzothiophene 2- and/or 3-position, formation of the η^2-(C═C) intermediate is blocked, the reaction rate slows, and insertion into the C(aryl)−S bond becomes possible or even dominant. An η^1-S intermediate is suggested in these cases. Insertion into the C−S bond nearer the coordinated ring in dibenzothiophene complexes, even ones alkylated at the 4- and/or 6-positions, occurs rapidly at rates similar to those found for alkylated benzothiphene complexes. Even the normally intractable 4,6-Me_2DBT is "remotely activated" to rapid C−S bond cleavage by $Pt(PPh_3)_2$ when precoordinated to the $Mn(CO)_3^+$ moiety. On the basis of observed regioselectivities, low-temperature infrared studies, and room-temperature stopped-flow kinetics, a mechanism is proposed for the insertion of platinum into precoordinated benzothiophenes and dibenzothiophenes. The palladium complex $Pd(PPh_3)_2(C_2H_4)$ is capable of inserting into C−C, C−S, and C−Se bonds in coordinated biphenylene, thiophenes, and selenophenes. The X-ray structure of the biphenylene insertion product is reported. It is concluded that the metallacycles formed from $Pd(PPh_3)_2(C_2H_4)$ are in general not as rapidly formed or as stable as those obtained with $Pt(PPh_3)_2(C_2H_4)$. X-ray structures are reported for (η^5-selenophene)$Mn(CO)_3^+$ and its $Pt(PPh_3)_2$ insertion product.

Introduction

The hydrodesulfurization (HDS) of petroleum feedstocks is a heterogeneous reaction of major industrial importance that is practiced on a massive scale.[1] Removal of sulfur from organosulfur molecules occurring in petroleum is essential for both industrial and environmental reasons, and recent federal regulations aim to severely limit sulfur oxide emissions from gasoline and diesel fuels. The sulfur-containing molecules benzothiophene (BT) and dibenzothiophene (DBT) are of special interest because their alkylated derivatives are difficult to desulfurize.[1,2] This is particularly true of DBTs, and consequently, much of the sulfur contamination in fossil fuels can be traced to these species. For this reason, the successful processing of such thiophenic materials is termed "deep hydrodesulfurization".



T BT DBT

A variety of organometallic systems have been studied as models for the homogeneous HDS of thiophenes.[3] The key steps include cleavage of a C−S bond by metal insertion, hydrogenolysis of the M−C bonds, and elimination of RSH or H_2S. Thiophenes are relatively unreactive because the sulfur atom is a very weak donor, and they become even less reactive when there are substitutents near the sulfur that offer steric interference. A few studies of C−S bond cleavage and/or desulfurization of alkylated DBTs with nucleophilic metal species have appeared.[4−6] With the most intractable substrate, 4,6-Me_2DBT, some success has been noted with reactive nickel and platinum reagents.[5,6]

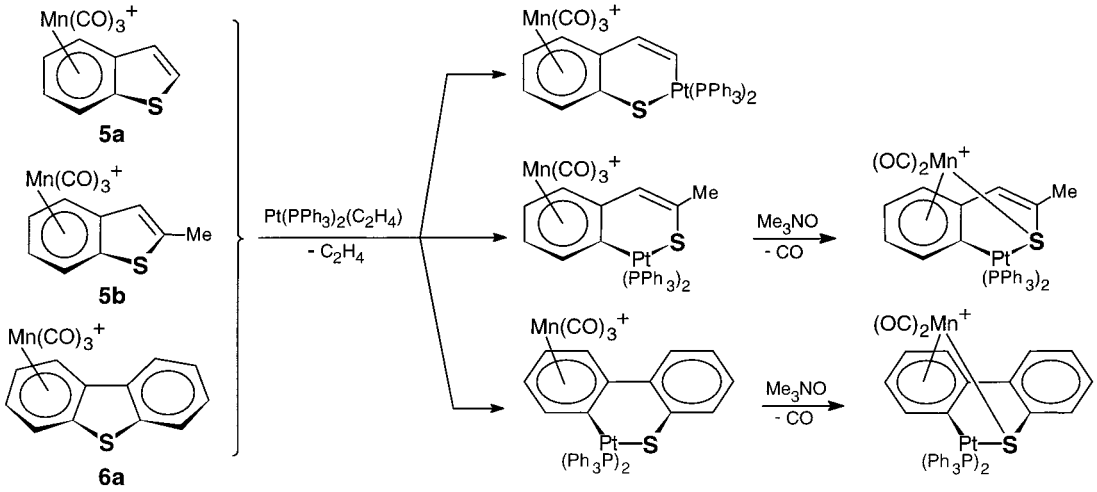
(1) (a) Topsøe, H.; Clausen, B. A.; Massoth, F. E. *Hydrotreating Catalysis*; Springer: Berlin, 1996. (b) *Petroleum Chemistry and Refining*; Speight, J. G., Ed.; Taylor & Francis: Washington, DC, 1998.

(2) (a) Shih, S. S.; Mizahi, S.; Green, L. A.; Sarli, M. S. *Ind. Eng. Chem. Res.* **1992**, *31*, 1232. (b) Topsøe, H.; Gates, B. C. *Polyhedron* **1997**, *16*, 3212.

(3) (a) Sanchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (b) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073. (c) Angelici, R. J. *Organometallics* **2001**, *20*, 1259. (d) Bianchini, C.; Meli. *J. Chem. Soc., Dalton Trans.* **1996**, 801. (e) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109. (f) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

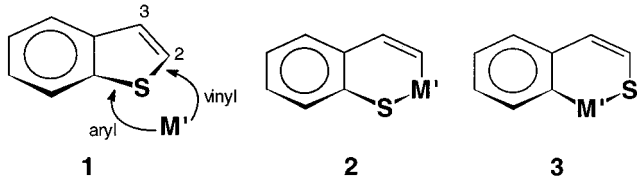
10.1021/om0102448 CCC: $20.00
Publication on Web 07/07/2001

Scheme 1



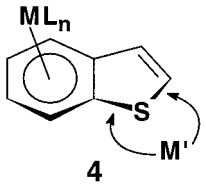
However, other reagents that normally cleave C−S bonds do not do so with 4,6-Me_2DBT and lead instead to C−H activation or simple η^1-S binding.[4a,b]

A considerable amount of research has been directed at C−S bond cleavage reactions of benzothiophenes. Most studies have utilized highly reactive coordinatively unsaturated nucleophilic metal fragments, which generally insert into the C(vinyl)−S bond in **1** to afford the metallathiacycle **2**. Insertion into the stronger C(aryl)−S bond in *free* benzothiophene to afford **3** has not been observed. However, there are several reported cases of



C(aryl)−S bond insertions in 2-MeBT. Thus, Cp*Rh(PMe_3) reacts to give **2** as the kinetic product, which then undergoes an intramolecular isomerization to a mixture of **2** and **3**.[7] Similarly, $Pt(PEt_3)_2$ is reported[6] to give **2** as an initial product, which subsequently rearranges to **3** and then dimerizes with loss of a PEt_3 ligand to give a complex whose X-ray structure proves that the C(aryl)−S bond was broken. In the latter case, however, the complex formulated as **2** was not proven to have this structure and in our view could quite possibly have been, in fact, the isomer **3**. Whether the reasons are thermodynamically or kinetically based, the conclusion from these two studies is that the 2-methyl substituent provides the steric environment responsible for the eventual formation of a C(aryl)−M−S linkage.

An alternative to the use of highly reactive transition metal fragments to cleave C−S bonds in BT and DBT systems is to activate the heterocyclic ring by precoordination of a metal to a carbocyclic ring. For example, this "remote activation" of the thiophene ring in **4** can be achieved with a number of electrophilic ML_n moieties: $Mn(CO)_3^+$, $FeCp^+$, $RuCp^+$, $Ru(C_6Me_6)^{2+}$, and $Cr(CO)_3$.[8] As a result, the C−S bonds in **4** become far more



susceptible to nucleophilic cleavage than in the corresponding free BTs. For example, even the mild nucleophile $Pt(PPh_3)_2$, generated from $Pt(PPh_3)_3$ or $Pt(PPh_3)_2(C_2H_4)$, reacts rapidly at room temperature with **4** ($ML_n = Mn(CO)_3^+$) to give the corresponding metallathiacycle, as depicted in Scheme 1. In comparison, $Pt(PPh_3)_2(C_2H_4)$ does not react with free BT, and the far more nucleophilic $Pt(PEt_3)_3$, which does react with free BT and DBT, reaches *equilibrium* only after several hours at 80 °C.[9]

As can be seen in Scheme 1, (η^6-BT)$Mn(CO)_3^+$ reacts with $Pt(PPh_3)_2$ to give the C(vinyl)−S insertion product, while both the 2-MeBT and DBT analogues lead initially to fission of the C−S bond *nearer* the coordinated carbocyclic ring. In solution, these initial products undergo a subsequent very slow spontaneous decarbonylation as the sulfur in the metallathiacyclic ring attacks the manganese center.[10] This CO substitution reaction can be made "instantaneous" by using the decarbonylating agent Me_3NO.

In the present study, we examine more closely the effect of alkylation on the insertion of $Pt(PPh_3)_2$ into C−S bonds in coordinated BT and DBT complexes. It is shown, for example, that even 4,6-Me_2DBT reacts rapidly in this manner. The regiochemistry that is obtained in these reactions is discussed with reference to possible mechanisms of C−S bond cleavage. A key mechanistic question concerns the presence of platinum-

(4) (a) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (b) Bianchini, C.; Casares, J. A.; Masi, D.; Meli, A.; Pohl, W.; Vizza, F. *J. Organomet. Chem.* **1997**, *541*, 143. (c) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606.

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(6) Arévalo, A.; Bernès, S.; García, J. J.; Maitlis, P. M. *Organometallics* **1999**, *18*, 1680.

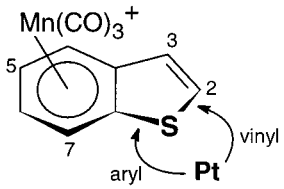
(7) Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11704.

(8) Dullaghan, C. A.; Zhang, X.; Greene, D. L.; Carpenter, G. B.; Sweigart, D. A.; Camiletti, C.; Rajaseelan, E. *Organometallics* **1998**, *17*, 3316.

(9) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179.

(10) Li, H.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2000**, *19*, 1823.

Chart 1



label	substituent	C-S cleavage
5a	none	vinyl
5b	2-Me	aryl
5c	3-Me	vinyl & aryl
5d	5-Me	vinyl
5e	7-Me	vinyl
5f	2,3-Me_2	aryl
5g	3,7-Me_2	vinyl
5h	2,7-Me_2	aryl

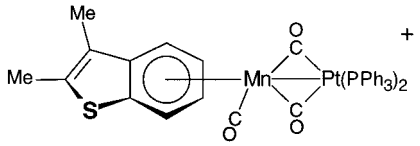
bonded η^1-S and/or η^2-(C=C) intermediates. These generic types of species are thought to occur prior to insertion and prior to hydrogenation, respectively, under HDS conditions. Low-temperature IR and room-temperature stopped-flow kinetics were used to investigate the probable role of such intermediates in the insertion reaction. We also report results concerning the use of a palladium(0) nucleophile to effect C−S fission and the use of both Pt(0) and Pd(0) in related C−Se cleavage reactions.

Results and Discussion

Platinum Insertion into Coordinated Benzothiophenes. The BT complexes **5c**,**d**,**f**−**h**, which have not been previously reported, were easily synthesized by a standard procedure (see Chart 1 and Experimental Section). The addition of $Pt(PPh_3)_2(C_2H_4)$ to **5a**−**h** at room temperature in dichloromethane results in rapid insertion of $Pt(PPh_3)_2$ into the C(vinyl)−S bond or the C(aryl)−S bond, or both. The regiochemistry of platinum insertion into **5a**, **5b**, and **5e** was shown previously to occur at C(vinyl)−S, C(aryl)−S, and C(vinyl)−S, respectively, to afford metallathiacycles that were isolated and characterized by single-crystal X-ray diffraction.[8,10] Chart 1 lists the results obtained with these, along with the previously unreported methylated BT complexes **5c**,**d**,**f**−**h**. The assignment of the C−S cleavage as vinyl or aryl was based on (1) a distinctive difference between the ^{31}P NMR chemical shifts and the J_{P-Pt} coupling constants for vinyl versus aryl insertions with **5a**,**b**,**e** and (2) the observation, shown in Scheme 1, that the C(aryl) metallathiacycle from **5b** undergoes rapid decarbonylation with Me_3NO to give a stable isolable product, whereas the C(vinyl) analogue from **5a** decomposes upon treatment with Me_3NO.[10]

Complex **5d** was included in the study because of a favorable low-temperature solubility compared to **5a** (vide infra). As expected, the reaction of **5d** with $Pt(PPh_3)_2(C_2H_4)$ resulted in exclusive formation of the "vinyl" product. It was anticipated that the 3-MeBT complex **5c** would lead to vinyl insertion, but ^{31}P NMR spectra of the reaction mixture showed a 1:1 mixture of vinyl and aryl products. This conclusion was confirmed by subsequent treatment with Me_3NO, which converted the aryl species into a dicarbonyl product, in analogy with that shown in Scheme 1 for **5b**, while the vinyl species decomposed. The formation of a 1:1 aryl:vinyl mixture from **5c** suggests that steric congestion in the vicinity of the sulfur atom, as in 2-MeBT, is not necessarily required to access C(aryl)−S insertion. This matter is discussed further below. Interestingly, reaction of $Pt(PPh_3)_2(C_2H_4)$ with (η^6-3-MeBT)$Mn(CO)_2[P(OEt)_3]^+$ gave only vinyl insertion, possibly because the phosphite ligand sterically limits access to the C(aryl)−S bond.

Reaction of the 2,3-Me_2BT complex **5f** gave conversion to the anticipated aryl product only, along with a trace amount of the bimetallic **7f** (ν_{CO} = 1985, 1775 cm^{-1}). The bimetallic, which cannot be isolated because it readily reverts to reactants upon attempted precipitation, arises from nucleophilic attack of the platinum on a carbonyl ligand. This type of reaction is, in fact, the



7f

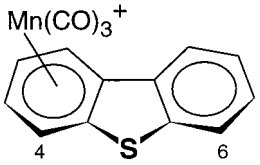
normal one seen when $Pt(PPh_3)_2(C_2H_4)$ reacts with $(arene)Mn(CO)_3^+$ complexes.[11] It is only when an alternative binding site or reaction pathway is available for the platinum that the bimetallic is not formed. Platinum insertion into the 3,7-Me_2BT complex **5g** was found to cleanly form the vinyl product only, thus demonstrating that a 7-Me group can influence the regioselectivity. A trace amount of bimetallic **7g** was also formed from the reaction of **5g**. Since a substituent at the 7-position favors the vinyl product while a substituent at the 2-position favors the aryl product, it was not clear what to expect from the 2,7-Me_2BT complex **5h**. In situ IR spectra showed that $Pt(PPh_3)_2(C_2H_4)$ does indeed insert into **5h**. ^{31}P NMR spectra indicated that the primary product is the aryl metallathiacycle, along with much smaller amounts of the vinyl isomer and the bimetallic **7h**. As expected, treatment of the reaction mixture with Me_3NO converted the aryl product to a dicarbonyl species (see Scheme 1). Attempted precipitation of the aryl product by addition of diethyl ether to the reaction mixture gave only starting complex **5h**, which demonstrates that the insertion/deinsertion is reversible and rapid in both directions in this case.

Platinum Insertion into Coordinated Dibenzothiophenes. Chart 2 lists the DBT complexes studied, all of which are new except **6a**. During the synthesis of **6b** and **6c**, the $Mn(CO)_3^+$ moiety was found to coordinate to both arene rings, but separation of the two isomers was possible by fractionalization crystallization. The structure of complex [**6c**]BF_4 was examined by X-ray crystallography and the atom connectivity was unequivocally established, although the small size of the crystal, resulting in very low intensities, and disorder in the BF_4^- anion combined to limit the refinement to R1 = 0.115 and wR2 = 0.169.

It was shown previously that the parent complex **6a** reacts with $Pt(PPh_3)_2(C_2H_4)$ to insert platinum into the

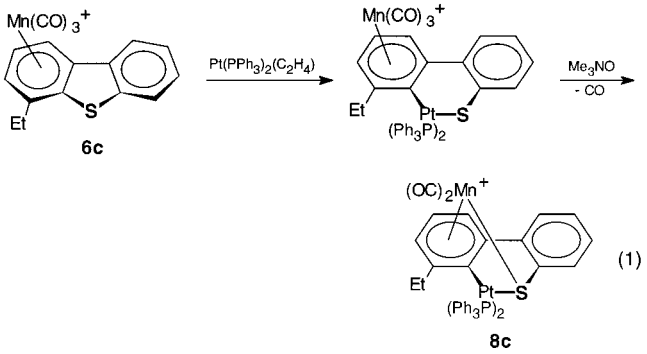
(11) Zhang, X.; Watson, E. J.; Dullaghan, C. A.; Gorun, S. M.; Sweigart, D. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2206.

Chart 2



label	substituent
6a	none
6b	4-Me
6c	4-Et
6d	4,6-Me_2
6e	4,6-Et_2

C−S bond *nearer* the coordinated ring and that the resulting metallathiacycle can be converted with Me_3NO to the dicarbonyl, as outlined in Scheme 1.[10] With the alkylated complexes in Chart 2, we were interested in seeing if they would insert platinum at all and, if so, at what rate and with what regiochemistry. With **6b** and **6c** the insertion reaction occurred rapidly at room temperature and in good yield. The regiochemistry was established by reacting the product from **6c** with Me_3NO according to eq 1. The dicarbonyl thus formed (**8c**) was fully characterized spectroscopically and by MS and EA. For steric reasons, formation of a dicarbonyl product is consistent only with the platinum having inserted into the C−S bond indicated.[10]



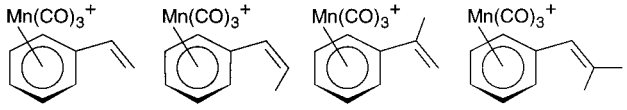
(1)

In view of the results with **6b**,**c**, one would expect that the 4,6-dialkylated DBT complexes **6d**−**e** would undergo cleavage of the C−S bond nearer the coordinated ring. In the case of **6d**, solution IR spectra taken after the addition of $Pt(PPh_3)_2(C_2H_4)$ indicated that rapid insertion had taken place. However, attempted precipitation with diethyl ether yielded only starting cation, **6d**. As with the 2,7-Me_2BT analogue discussed above, it is concluded that the insertion/deinsertion steps are reversible and relatively rapid. Proof that insertion into **6d** had taken place was obtained by treatment of the reaction mixture with Me_3NO, which produced a good yield of dicarbonyl complex **8d**, which was fully characterized. The 4,6-Et_2DBT complex **6e** reacted with $Pt(PPh_3)_2(C_2H_4)$ to give a mixture of insertion and bimetallic products in a ratio of ca. 2:1, the latter (**7e**) arising from attack on a CO ligand by the platinum.

Intermediates and the Reaction Mechanism. To probe the mechanism of platinum insertion into the BT and DBT complexes, a series of low-temperature infrared and room-temperature stopped-flow experiments were performed. In the infrared, the relevant species that may be detected, other than the starting material and the insertion product, are (1) a platinum-bonded η^2-(C═C) intermediate with the BT systems and (2) the bimetallic **7**. A possible η^1-S intermediate may be important mechanistically, but would likely not be detected spectroscopically because the sulfur is too weak a donor. This assumption is supported by the observation that free benzothiophene does not react with $Pt(PPh_3)_2(C_2H_4)$. Complexation to $Mn(CO)_3^+$ would make the sulfur an even weaker donor.[12] Complexes containing a thiophenic η^1-S bond are known, but generally only with highly reactive unsaturated systems such as $Cp^*Re(CO)_2$, $Cr(CO)_5$, $CpMn(CO)_2$, etc.[12,13]

The background information available with which to compare data obtained with the thiophenic complexes includes platinum insertion into coordinated benzofuran and platinum binding to the C═C bond in coordinated styrenes. Scheme 2 gives the mechanism observed for insertion into the C−O bond in the benzofuran complex **9**.[11] In this case there is very rapid coordination of the platinum to the C═C double bond to give the observable η^2-intermediate **10** prior to slow insertion ($t_{1/2} \approx 2$ h). The probable role of an η^2-intermediate was further probed in the benzofuran system by studying the reactions of the 2-methylbenzofuran and 2,3-dihydrobenzofuran complexes. The former presents steric hindrance to η^2-coordination at the C═C bond, while the latter does not possess a C═C bond in the heterocyclic ring. Neither complex reacted with $Pt(PPh_3)_2(C_2H_4)$ to give C−O bond fission, but rather gave bimetallics analogous to **7**, e.g., $[(\eta^6\text{-2-methylbenzofuran})Mn(CO)(\mu\text{-}CO)_2Pt(PPh_3)_2]^+$. Furthermore, in neither case were any reaction intermediates detectable by IR.[11] These observations support the mechanism indicated in Scheme 2, in which an η^2-intermediate is on the lowest energy reaction pathway to C−O fission. If access to this intermediate is blocked, the kinetically favored product becomes the bimetallic (**7**).

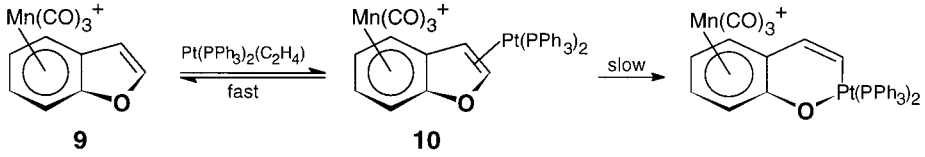
Binding of $Pt(PPh_3)_2$ to the exocyclic C═C bond in the styrene complexes **11a**−**d** was recently reported.[14] As



expected, it was found that precoordination of the $Mn(CO)_3^+$ moiety greatly facilitates the platinum η^2-(C═C) binding. In the insertion reaction with $(\eta^6\text{-BT})Mn(CO)_3^+$ (**5a**), the environment in the vicinity of the C═C bond that is available to the platinum for possible initial coordination is most closely approximated by the *cis*-β-methylstyrene complex **11b**. It is relevant to note, therefore, that free *cis*-β-methylstyrene does not react with $Pt(PPh_3)_2(C_2H_4)$, but **11b** reacts rapidly and completely under ordinary experimental conditions. Complex **11c** behaves likewise. The most sterically encumbered system, **11d**, fails to give a detectable η^2-(C═C)

(12) Rudd, J. A.; Angelici, R. J. *Inorg. Chim. Acta* **1995**, *240*, 393.
(13) (a) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328. (b) Reynolds, M. A.; Guzei, I. A.; Logsdon, B. C.; Thomas, L. M.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1999**, *18*, 4075.
(14) Zhang, X.; Yu, K.; Carpenter, G. B.; Sweigart, D. A.; Czech, P. T.; D'Acchioli, J. S. *Organometallics* **2000**, *19*, 1201.

Scheme 2



9 **10**

Table 1. Approximate Half-Lives in Minutes at −20 °C for Insertion of Platinum into a C−S Bond in (η^6-Thiophene)$Mn(CO)_3^+$ Complexes[a]

thiophene	half-life	thiophene	half-life
5-MeBT	fast[b]	2,7-Me_2BT	10
7-MeBT	fast[b]	3,7-Me_2BT	$5^1/_2$
2-MeBT	$4^1/_2$	DBT	$1^1/_2$
3-MeBT	6	4,6-Me_2DBT	$3^1/_2$
2,3-Me_2BT	6	4,6-Et_2DBT	7
2,3-Et_2BT	6		

[a] Measured by IR in dichloromethane solvent with 2 equiv of $Pt(PPh_3)_2(C_2H_4)$ per equivalent of manganese complex (as the BF_4^- salt). [b] Half-life ≪ 30 s.

species, reacting instead via attack at a CO to afford the bimetallic [(η^6-β-dimethylstyrene)$Mn(CO)(\mu$-$CO)_2$Pt-$(PPh_3)_2]^+$.

In view of the results noted above for the benzofuran and styrene reactions, and in view of the demonstrated existence of η^2-(C=C) complexes with benzothiophene,[3,12] it is reasonable to speculate that the mechanism in Scheme 2 may be applicable to the platinum C−S insertion reaction with (η^6-BT)$Mn(CO)_3^+$ (**5a**). In other words, oxidative addition into the C−S bond is preceded by η^2-coordination to the C=C bond. It must be noted, however, that the benzofuran and benzothiophene systems differ sharply in that methyl substituents at the benzothiophene 2- and/or 3-positions do not prevent the insertion reaction. This could be interpreted to mean that η^2-(C=C) coordination is not required for C−S insertion in BT complexes. Obviously, the fact that the reaction occurs with DBT analogues also argues for an accessible pathway not incorporating η^2-binding.

The platinum insertion reactions were followed in the infrared at −20 °C using a fiber optic probe. The results are presented in Table 1. At higher temperatures, the reactions were too rapid to be conveniently tracked, and at lower temperatures the reactions were either too slow or solubility problems arose. The "half-life" values listed in Table 1 refer to the time for half of the reactant (**5** or **6**) to be converted to product. The conditions were not strictly pseudo-first-order, so that the half-lives are only semiquantitative absolutely, but in a relative sense they are highly meaningful. It may be seen that the BT complexes unhindered to η^2-(C=C) coordination (5-MeBT, 7-MeBT) react very rapidly, with only final product being observed as fast as the first IR spectrum collection could be completed (ca. 30 s). For *all* of the other reactions listed in Table 1, it was possible to follow the time evolution of the products, and in no case were any intermediate species observed. The lack of any detectable η^2-(C=C) intermediate in any of the systems slow enough to be followed is entirely consistent with the benzofuran and styrene results given above.

From a first glance at the data one would not conclude very much mechanistically about the unhindered systems, 5-MeBT and 7-MeBT (but see below). However, the results for the other thiophenes suggest strongly that η^2-(C=C) coordination is *not* on the insertion reaction pathway for *these* hindered complexes. Looking at the hindered BTs, it is striking that mono- and dialkylation cause about the same rate reduction, with barely a factor of 2 separating the six hindered BTs listed! To us, the only conclusion is that any alkylation at the 2- and/or 3-position shuts down the possibility of η^2-(C=C) bonding. If there is any intermediate in the insertion reactions of these hindered systems, it is probably of the η^1-S type. The similarity in rate of 2-MeBT and 3-MeBT complexes could be taken as evidence for the absence of an η^1-S intermediate due to anticipated differential steric hindrance. However, X-ray structures of simple η^1-S−M thiophenic complexes generally show the metal "M" moiety to be well out of the thiophene plane, so that the effects of methyl substituents at the 2- and 3-positions need not be either large or much different. The same reasoning applies to any η^1-S intermediate occurring with the dibenzothiophenes. As Table 1 shows, there is, incredibly, only a factor of about 2 separating the rates of insertion into the DBT and 4,6-Me_2DBT complexes.

We suggest that the most likely mechanism for all DBT and hindered BT complexes involves an η^1-S intermediate. The unhindered complexes (BT, 5-MeBT, 7-MeBT) *must* have available a different lower energy pathway. This follows because the mechanism obeyed by the former must also be available to the latter. That the latter react so much more rapidly means that they follow a pathway unavailable to the hindered complexes.[15] Results with benzofuran and styrene complexes mentioned above lead one to predict confidently[16] that an η^2-(C=C) intermediate should be *rapidly* formed when the unhindered complexes and $Pt(PPh_3)_2(C_2H_4)$ are mixed. In turn, it follows that the η^2-(C=C) complex must be a true intermediate and not represent a dead-end; otherwise the unhindered complexes would be the slowest to react, not the fastest. The vinyl insertion obtained with unhindered systems (BT, 5-MeBT, 7-MeBT) has the regiochemistry expected from an η^2-intermediate that converts directly to insertion product. If the intermediate is of the η^1-S type, however, it appears that either vinyl or aryl insertion is kinetically viable.

The regiochemical and infrared data presented above suggest, very simply, that BT complexes **5** that are unsubstituted at the C=C bond react with $Pt(PPh_3)_2$-(C_2H_4) via initial rapid formation of an η^2-(C=C) intermediate that subsequently converts directly to product. This intermediate cannot form with DBT or appropri-

(15) Inherent is the assumption that the hindered and unhindered complexes would not differ greatly in the rate of formation of any η^1-S intermediate or in its conversion to insertion product. This assumption is supported by the observed small effect that multiple alkylation has on the insertion rate of the hindered BT systems.

(16) IR spectra obtained at −20 °C under conditions identical to that in Table 1 showed that $Pt(PPh_3)_2(C_2H_4)$ coordinates to (η^6-benzofuran)-$Mn(CO)_3^+$ in an η^2-(C=C) fashion at a rate too large to measure by IR ($t_{1/2}$ ≪ 30 s). Subsequent stopped-flow experiments were performed at room temperature (vide supra).

ately substituted (hindered) BT complexes, and accordingly, these are forced to follow a different reaction pathway, possibly one containing an η^1-S intermediate. To further test these conclusions, we performed room-temperature stopped-flow experiments with a variety of (arene)$Mn(CO)_3^+$ complexes reacting with $Pt(PPh_3)_2$-(C_2H_4). These were conducted in dichloromethane under nitrogen, with the manganese complex at about 1.0 mM and with a slightly higher concentration (ca. 1.1 mM) of $Pt(PPh_3)_2(C_2H_4)$. The purpose of these experiments was to search for intermediates and obtain a semiquantitative relative reactivity order and not to determine accurate rate constants, which would have been difficult in any case due to the sensitivity of the solutions.

Complexes **11a**,**b**,**d** gave a clean single-step optical density change when mixed with $Pt(PPh_3)_2(C_2H_4)$. The times required for half of the reactant to be consumed ($t_{1/2}$) were as follows: **11a** (5 ms), **11b** (40 ms), **11d** (1.2 s). The first two reactions involve only coordination to the C=C bond, and the stopped-flow results prove that this is very rapid, as previously thought. The somewhat slower reaction of **11b** compared to **11a** is due to the β-methyl substituent. The much slower reaction of **11d** reflects the fact that this complex is sterically prevented from forming a η^2-(C=C) product and forms instead the bimetallic $[(\eta^6\text{-}\beta\text{-dimethylstyrene})Mn(CO)(\mu\text{-}CO)_2Pt$-$(PPh_3)_2]^+$. The same type of bimetallic complex formation occurs in the reaction with (mesitylene)$Mn(CO)_3^+$, which gave a $t_{1/2}$ of 3 s. The benzofuran complex **9** is known[11] to initially form a mixture of η^2-(C=C) and bimetallic species that ultimately convert to insertion product. In accordance with this, the kinetics showed two hard-to-separate steps, with the slower one having a $t_{1/2}$ of 1.3 s and the faster one roughly estimated as ca. a factor of 10 shorter. With (η^6-dihydrobenzofuran)-$Mn(CO)_3^+$, which has no C=C bond, only bimetallic (**7**) formation was observed with $t_{1/2} = 1.5$ s.

The results with the styrene and benzofuran complexes establish the kind of rate to expect for η^2-(C=C) formation and for formation of the bimetallic **7**. The eight thiophene complexes, **5b**,**c**,**f**−**h** and **6a**,**d**,**e**, all of which can be classified as "hindered" with respect to η^2-(C=C) formation, gave a single optical density change with $t_{1/2}$ values in the 1.5−4 s range. IR spectra of product solutions verified that insertion had occurred in each case. With the two "unhindered" complexes studied by the stopped-flow method, namely, (η^6-5-MeBT)$Mn(CO)_3^+$ (**5d**) and (η^6-7-MeBT)$Mn(CO)_3^+$ (**5e**), the kinetic behavior was quite different. Instead of a single "slow" step, the reaction of **5d** and of **5e** produced a two-step optical density change in each case. For both complexes the $t_{1/2}$ was estimated as ca. 70 ms for the first step and 280 ms for the second step. On the basis of the results given above for the styrene complex **11b**, the 70 ms time is nicely in the range of what would be expected for the postulated η^2-(C=C) coordination to platinum. We suggest that the second (280 ms) step is due to the insertion into the C(vinyl)−S bond, which is accelerated by about a factor of 10 over that found for the hindered complexes under our experimental conditions.

The low-temperature infrared studies provided strong evidence for the existence of an η^2-intermediate in some cases and for its absence in others. The stopped-flow results corroborated the IR results with direct spectral evidence for this intermediate when predicted to be present, as well as for its absence when so predicted. It is concluded that C−S bond cleavage occurs substantially more rapidly when initial η^2-coordination to the platinum is possible, but such coordination is not *required* for insertion.

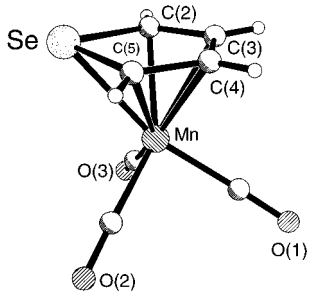
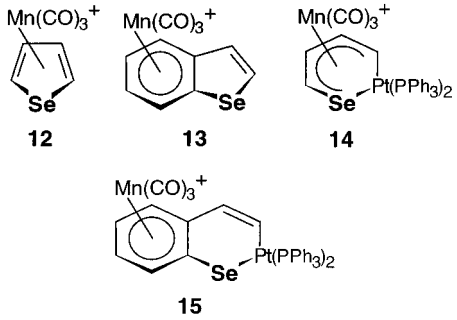


Figure 1. Crystal structure of the cation in [**12**]BF_4. Selected bond lengths (Å) and angles (deg): Se−C(2) 1.877-(4), Se−C(5) 1.883(4), Mn−Se 2.4298(6), Mn−C(2) 2.160-(3), Mn−C(3) 2.161(3), Mn−C(4) 2.157(3), Mn−C(5) 2.159-(3), O(1)−C(6)−Mn 178.3(3), O(2)−C(7)−Mn 177.8(3), O3−C(8)−Mn 176.6(4).

Platinum Insertion into C−Se Bonds. Angelici has shown[17] that selenophene and thiophene act similarly with respect to metal coordination to the π-system. Likewise, the insertion of a metal into a C−Se bond in selenophene occurs similarly to C−S bond insertion in thiophene.[17,18] We thought it worthwhile to examine the effect of metal coordination to the π-system on the ease of C−Se fission in selenophene and benzoselenophene. It was found that the nucleophile $Pt(PPh_3)_2(C_2H_4)$ inserts rapidly and cleanly into **12** and **13** to afford the metallaselenacycles **14** and **15**, respectively. Complex



12 was reported previously.[17] Herein a higher yield synthesis is presented, along with the X-ray structure of [**12**]BF_4, shown in Figure 1 and tabulated in Table 2. The structure of **12** is analogous to that reported[17] for (η^5-2,5-dimethylselenophene)$Cr(CO)_3$, with the selenium atom slightly (0.13 Å) out of the plane of the ring carbon atoms. The C−Se bond lengths are longer by about 0.025 Å than that found in free selenophene. The X-ray structure of [**14**]BF_4, the product of platinum insertion into a C−Se bond in **12**, is shown in Figure 2. In **14**, the C(2)−C(3)−C(4)−C(5)−Se atoms are nearly planar (mean deviation 0.039 Å), with the platinum atom displaced 0.88 Å from this plane. This contrasts with

(17) White, C. J.; Angelici, R. J.; Choi, M.-G. *Organometallics* **1995**, *14*, 332.
(18) Vicic, D. A.; Myers, A. W.; Jones, W. D. *Organometallics* **1997**, *16*, 2751.

Table 2. Crystallographic Data for [12]BF_4, [14]$BF_4 \cdot CH_2Cl_2$, and [16]$BF_4 \cdot CH_2Cl_2$

	[**12**]BF_4	[**14**]$BF_4 \cdot CH_2Cl_2$	[**16**]$BF_4 \cdot CH_2Cl_2$
formula	$C_7H_4BF_4MnO_3Se$	$C_{44}H_{36}Cl_2BF_4MnO_3P_2PtSe$	$C_{52}H_{40}Cl_2BF_4MnO_3P_2Pd$
fw	356.81	1161.37	1093.83
temp	298	298	298
wavelength	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P1$	$P2_1/n$
a, Å	12.0723(13)	10.9840(9)	15.2761(18)
b, Å	7.3028(8)	13.7558(12)	10.7032(12)
c, Å	12.7774(14)	16.0753(14)	30.097(4)
α, deg	90	74.4470(10)	90
β, deg	103.618(2)	75.1980(10)	100.903(2)
γ, deg	90	79.6590(10)	90
V, Å^3	1094.8(2)	2246.2(3)	4832.2(10)
Z	4	2	4
d_{calcd}, g cm^{-3}	2.165	1.717	1.504
μ, mm^{-1}	4.575	4.447	0.868
F(000)	680	1132	2208
cryst dimens, mm	0.36 × 0.34 × 0.26	0.25 × 0.24 × 0.21	0.26 × 0.20 × 0.15
θ range, deg	2.09−28.28	1.80−28.36	2.02−26.55
no. of reflns collected	16 039	35 923	64 982
no. of indept reflns	2629 (R_{int} = 0.0521)	10 768 (R_{int} = 0.0515)	10 014 (R_{int} = 0.0654)
no. of data/restraints/params	2629/0/154	10 768/4/522	10 014/0/595
GOF on F^2	1.071	1.087	1.191
R1, wR2 [$I > 2\sigma(I)$]	0.0384, 0.1031	0.0535, 0.1434	0.0571, 0.1206
R1, wR2 (all data)	0.0436, 0.1085	0.0708, 0.1612	0.0806, 0.1324

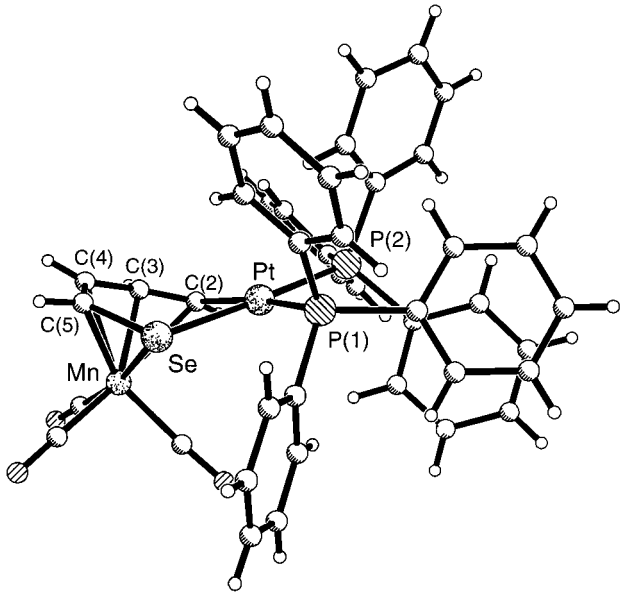
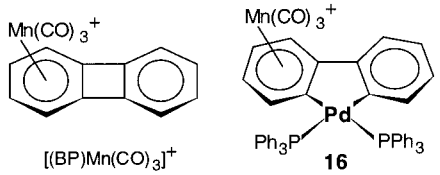


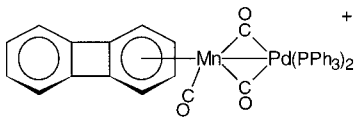
Figure 2. Crystal structure of the cation in [**14**]BF_4. Selected bond lengths (Å) and angles (deg): Se−C(5) 1.869(11), Pt−Se 2.4219(10), Pt−C(2) 2.256(5), Pt−P(1) 2.3477(19), Pt−P(2) 2.2927(18), Mn−Se 2.4840(17), Mn−C(2) 2.430(6), Mn−C(3) 2.214(13), Mn−C(4) 2.167(10), Mn−C(5) 2.108(11), C(2)−Pt−Se 85.55(14), Se−Pt−P(1) 86.82(5), P(1)−Pt−P(2) 96.79(7), C(2)−Pt−P(2) 90.92(15), C(2)−Pt−P(1) 171.61(15), Se−Pt−P(2) 176.14(5).

the structure of the product of Cp*Rh(PMe_3) insertion into selenophene, in which the six-membered metallaselenacyclic ring is planar.[18] The coordination geometry about the platinum in **14** is planar (mean deviation 0.042 Å). The chemical shifts for the ^{77}Se NMR spectra of **12** and **14** occur at 276 and −246 ppm relative to selenophene, which is assigned at 605 ppm.[17] This upfield shift of 522 ppm upon platinum insertion is consistent with the loss of conjugation in the nonplanar heterocyclic ring present in **14**.

Just as with benzothiophene, precoordination of Mn$(CO)_3^+$ to the carbocyclic ring in benzoselenophene to afford **13** was easily achieved. Also in analogy with the BT analogue, and as would be expected, complex **13** rapidly inserted Pt(PPh_3)$_2$ into a C−Se bond to give a high yield of the metallaselenacycle **15**.

Palladium Insertion into C−C, C−S, and C−Se Bonds. The palladium analogue[19] of the platinum nucleophile utilized in the reactions described above, Pd(PPh_3)$_2$(C_2H_4), was briefly investigated in order to compare the chemical behavior and relative usefulness of these two systems. The strained C−C bond in biphenylene becomes especially susceptible to cleavage when precoodinated by the manganese tricarbonyl fragment.[20] It was found that Pd(PPh_3)$_2$(C_2H_4) inserts into (η^6-BP)Mn$(CO)_3^+$ to afford a good yield of the insertion product **16**. Interestingly, monitoring the reaction in dichloromethane by IR spectroscopy showed that the dimetallic **17** formed initially (ν_{CO} = 1996, 1818 cm^{-1}) and then converted over an hour at room temperature to **16**. The formation of **17** is reversible, and the reaction





system eventually transforms to the thermodynamically favored product, **16**. The bimetallic **17** is analogous to **7** in the case of platinum and arises from nucleophilic attack at a carbonyl. The palladium nucleophile seems to be considerably more prone generally than is the

(19) Visser, A.; van der Linde, R.; de Jongh, R. O. *Inorg. Synth.* **1976**, *16*, 127.
(20) Zhang, X.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **1999**, *18*, 4887.

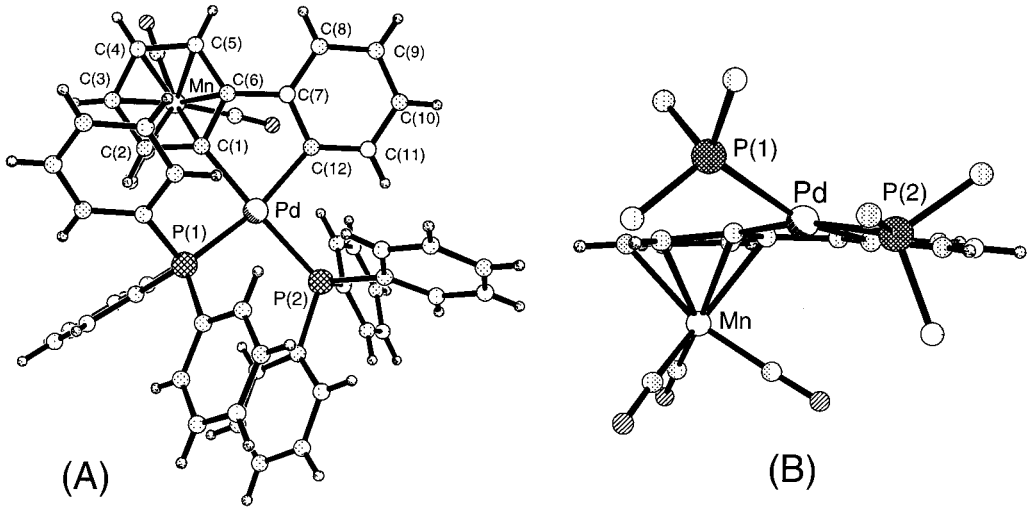
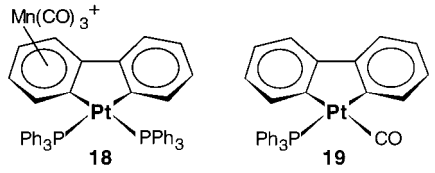


Figure 3. Crystal structure of the cation in [**16**]BF_4. The phenyl groups are omitted in (B) for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(1) 2.078(4), Pd−C(12) 2.089(4), Pd−P(1) 2.3892(12), Pd−P(2) 2.3601(11), C(6)−C(7) 1.463(6), C(1)−C(6) 1.425(6), C(12)−C(7) 1.412(6), Mn−C(1) 2.308(4), Mn−C(2) 2.186(5), Mn−C(3) 2.179(5), Mn−C(4) 2.182-(5), Mn−C(5) 2.190(5), Mn−C(6) 2.242(5), C(1)−Pd−C(12) 80.15(17), C(1)−Pd−P(1) 90.48(13), P(1)−Pd−P(2) 97.10(4), C(12)−Pd−P(2) 95.41(12), P(1)−Pd−C(12) 158.59(12), P(2)−Pd−C(1) 168.45(12).

platinum to form the bimetallic species with (arene)-$Mn(CO)_3^+$ complexes. For example, $Pt(PPh_3)_2(C_2H_4)$ reacts completely with (η^6-BP)$Mn(CO)_3^+$ to give **18** as the sole product within 1 min at room temperature, without any evidence of bimetallic formation.[20]

Platinum and palladium also differ in that a solution of the insertion product **18** slowly (weeks) eliminates PPh_3 to give **19**. It was postulated that formation of **19**,



which was characterized by X-ray diffraction, may be sterically driven. With palladium, it was possible to obtain good crystals of the bis-phosphine insertion product, and the X-ray structure of **16** is shown in Figure 3. The five-membered metallacyclic ring C1−C6−C7−C12−Pd is fairly planar (mean deviation 0.058 Å). The most interesting feature of the structure of **16** is the large deviation from planar coordination around the palladium. This is especially apparent in Figure 3B, which shows a P(1) phosphorus that is 1.0 Å out of the plane of the metallacyclic ring. It is presumed that this large deviation from the expected planarity is attributable to steric congestion in **16**.

$Pd(PPh_3)_2(C_2H_4)$ reacted with the styrene complexes **11b**,**c** by coordinating to the C=C bond, but upon attempted isolation, the products reverted back to reactants **11b**,**c**. With (η^5-thiophene)$Mn(CO)_3^+$ and (η^6-benzothiophene)$Mn(CO)_3^+$, $Pd(PPh_3)_2(C_2H_4)$ did react to give C−S insertion, but again attempted precipitation of products with diethyl ether merely reversed the insertion. With 2-MeBT, 3-MeBT, and DBT systems (**5b**, **5c**, **6a**), the only observable product was the bimetallic analogue of **17**. $Pd(PPh_3)_2(C_2H_4)$ was found to insert cleanly into a C−Se bond in (η^5-selenophene)$Mn(CO)_3^+$ to give the palladium analogue of **14**, which was isolated and characterized (see Experimental Section).

Conclusions

On the basis of substituent effects on regioselectivity and on rate studies, it is concluded that C−S bond cleavage in (η^6-BT)$Mn(CO)_3^+$ proceeds via initial rapid coordination of the $Pt(PPh_3)_2$ nucleophile to the C=C bond in the heterocyclic ring, followed by rapid insertion into the C(vinyl)−S bond. When a substituent is present at the benzothiophene 2- and/or 3-position, formation of the η^2-(C=C) intermediate is blocked, the reaction rate slows, and insertion into the C(aryl)−S bond becomes possible or even dominant. An η^1-S intermediate is suggested in these cases. Insertion into the C−S bond nearer the coordinated ring in dibenzothiophene complexes, even ones alkylated at the 4- and/or 6-positions, occurs rapidly at rates similar to those found for alkylated benzothiphene complexes. Thus, even the normally intractable 4,6-Me_2DBT is "remotely activated" to rapid C−S bond cleavage by $Pt(PPh_3)_2$ when precoordinated to the $Mn(CO)_3^+$ moiety. These results suggest that η^6-coordination of BTs and DBTs on a Mo/Co sulfide heterogeneous HDS catalyst constitutes a viable mechanism for C−S activation prior to insertion and subsequent hydrogenolysis.

The palladium complex $Pd(PPh_3)_2(C_2H_4)$ is capable of inserting into C−C, C−S, and C−Se bonds in coordinated biphenylene, thiophenes, and selenophenes. However, it is concluded that the resulting matallacyclic products are in general not as rapidly formed or as stable as those obtained with $Pt(PPh_3)_2(C_2H_4)$.

Experimental Section

General Procedures. Standard materials were purchased from commercial sources and used without further purification. Solvents were HPLC grade and opened under nitrogen. Literature methods were used to synthesize $Pt(PPh_3)_2(C_2H_4)$,[21] $Pd(PPh_3)_2(C_2H_4)$,[19] [η^6-biphenylene)$Mn(CO)_3$]BF_4,[22] complexes **5a**−**c**,**e** and **6a**,[23] 7-MeBT,[24] 3,7-Me_2BT,[25] 2,3-Me_2BT,[26] 2,7-Me_2-BT,[27] and dibenzothiophenes 4-MeDBT, 4-EtDBT, and 4,6-Et_2-DBT.[28] ^{31}P NMR chemical shifts are relative to a 85% phosphoric acid external reference. ^{77}Se chemical shifts are relative to selenophene external reference, assigned a value

of 605 ppm.[17] Low-temperature IR experiments were performed using a Remspec IR fiber optic immersion probe.

Synthesis of Benzothiophene Complexes 5d,f−h. These complexes were easily made by a procedure essentially identical to that used for **5a**−**c**.[23] For [**5d**]BF_4: Yield 90%. IR (CH_2Cl_2): ν_{CO} 2074 (s), 2016 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.29 (d, J = 5.5, 1H), 7.67−7.58 (m, 2H), 7.22 (s, H4), 6.36 (d, J = 6.9, 1H), 2.57 (s, Me). Anal. Calcd for $C_{12}H_8SMnO_3BF_4$: C, 38.54; H, 2.16. Found: C, 38.95; H, 2.17. For [**5f**]BF_4: Yield 85%. IR (CH_2Cl_2): ν_{CO} 2074 (s), 2016 (s, br) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.47 (d, J = 7.4, H7), 7.12 (d, J = 7.6, H4), 6.50 (m, H5,6), 2.62 (s, Me), 2.43 (s, Me). Anal. Calcd for $C_{13}H_{10}SMnO_3BF_4$: C, 40.24; H, 2.60. Found: C, 40.08; H, 2.27. For [**5g**]BF_4: Yield 85%. IR (CH_2Cl_2): ν_{CO} 2070 (s), 2012 (s, br) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 8.33 (s, H2), 7.52 (dd, J = 6.9, 0.8, H6), 6.90 (dd, J = 6.2, 0.8, H5), 6.81 (d, J = 6.2, H4), 3.06 (s, Me), 2.68 (s, Me). Anal. Calcd for $C_{13}H_{10}SMnO_3BF_4$: C, 40.24; H, 2.60. Found: C, 40.15; H, 2.54. For [**5h**]BF_4: Yield 85%. IR (CH_2Cl_2): ν_{CO} 2069 (s), 2010 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.28 (s, H3), 7.1 (d, J = 7.3, H4), 6.52 (t, J = 7.3, H5), 6.22 (d, J = 6.7, H4), 2.86 (s, Me), 2.75 (s, Me). Anal. Calcd for $C_{13}H_{10}SMnO_3BF_4$: C, 40.24; H, 2.60. Found: C, 39.74; H, 2.69.

Synthesis of Dibenzothiophene Complexes 6b−e. These complexes were easily made by a procedure essentially identical to that used for **6a**.[23] For [**6b**]BF_4: The overall yield was 60%, which consisted of a 3:1 mixture of complexes containing the metal coordinated to the methylated ring (isomer A) and the unmethylated ring (isomer B). Isomer A was separated from the mixture by fractional crystallization from acetone/diethyl ether. IR (CH_2Cl_2): ν_{CO} 2074 (s), 2016 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.46 (d, J = 7.5, H9), 8.08 (d, J = 8.0, H6), 7.86 (m, H7,8), 7.55 (d, J = 6.4, H1), 6.69 (t, J = 6.6, H2), 6.50 (d, J = 6.3, H3), 2.92 (s, Me). Anal. Calcd for $C_{16}H_{10}SMnO_3BF_4$: C, 45.32; H, 2.38. Found: C, 45.23; H, 2.87. For [**6c**]BF_4: The overall yield was 67%, which also consisted of a 3:1 mixture of isomers A and B. Isomer A was separated from the mixture by fractional crystallization from acetone/diethyl ether. IR (CH_2Cl_2): ν_{CO} 2074 (s), 2016 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.48 (d, J = 7.4, H9), 8.07 (d, J = 7.6, H6), 7.85 (m, H7,8), 7.64 (d, J = 7.6, H1), 6.72 (t, J = 6.6, H2), 6.51 (d, J = 6.4, H3), 3.20 (q, J = 8.3, CH_2), 1.59 (t, J = 7.5, Me). Anal. Calcd for $C_{17}H_{12}SMnO_3BF_4$: C, 46.61; H, 2.76. Found: C, 46.59; H, 2.97. For [**6d**]BF_4: Yield 65%. IR (CH_2Cl_2): ν_{CO} 2073 (s), 2017 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.29 (d, J = 7.2, H9), 7.70 (m, H7,8), 7.52 (d, J = 6.9, H1), 6.71 (t, J = 6.5, H2), 6.50 (d, J = 6.0, H3), 2.93 (s, Me), 2.66 (s, Me). Anal. Calcd for $C_{17}H_{12}SMnO_3BF_4$: C, 46.61; H, 2.76. Found: C, 46.55; H, 2.80. For [**6e**]BF_4: Yield 50%. IR (CH_2Cl_2): ν_{CO} 2072 (s), 2012 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.31 (d, J = 7.5, H9), 7.74 (m, H7,8), 7.60 (d, J = 6.5, H1), 6.73 (t, J = 6.1, H2), 6.53 (d, J = 5.5, H3), 3.23 (m, CH_2), 2.99 (q, J = 7.3, CH_2)1.60 (t, J = 7.2, Me), 1.43 (t, J = 7.2, Me). Anal. Calcd for $C_{19}H_{16}SMnO_3BF_4$: C, 48.96; H, 3.46. Found: C, 49.09; H, 3.36.

Platinum Insertion into Benzothiophene and Dibenzothiophene Complexes. In general, the insertion reactions were performed as described previously.[8,10] All reactions were done at room temperature under nitrogen, typically with about 50 mg of thiophene complex and a slight molar excess of $Pt(PPh_3)_2(C_2H_4)$. **Insertion into 5c**: In situ ^{31}P NMR showed a 1:1 mixture of vinyl and aryl insertion products IR (CH_2Cl_2): ν_{CO} 2058 (s), 2004 (s, br) cm^{-1}. ^{31}P NMR (CD_2Cl_2) for vinyl product: δ 27.35 (dd J_{P-P} = 22, J_{Pt-P} = 3485), 20.27 (dd, J_{P-P} = 22, J_{Pt-P} = 1890). ^{31}P NMR (CD_2Cl_2) for aryl product: δ 25.55 (dd J_{P-P} = 20, J_{Pt-P} = 3160), 15.28 (dd, J_{P-P} = 20, J_{Pt-P} = 2130). The addition of Me_3NO to a mixture of the isomers was found to convert the aryl product only to a dicarbonyl species [IR (CH_2Cl_2): ν_{CO} 1989 (s), 1943 (m) cm^{-1}] in analogy to the chemistry shown in Scheme 1. **Insertion into 5d**: Yield 75%. IR (CH_2Cl_2): ν_{CO} 2057 (s), 1999 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.32−7.16 (m, 32H), 6.54 (d, J = 6.7, 1H), 6.23 (s, H4), 5.94 (d, J = 5.5, 1H), 2.31 (s, Me). ^{31}P NMR (CD_2Cl_2): δ 25.49 (dd J_{P-P} = 23, J_{Pt-P} = 3410), 21.14 (dd, J_{P-P} = 23, J_{Pt-P} = 1900). HR MS: M+ (m/z) calcd 1006.1046, obsd 1006.1015. Anal. Calcd for $C_{48}H_{38}SMnO_3PtP_2BF_4$: C, 52.72; H, 3.50. Found: C, 52.80; H, 3.65. **Insertion into 5f**: Yield 70%. IR (CH_2Cl_2): ν_{CO} 2055 (s), 2003 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.65−7.03 (m, 30H), 6.58 (d, J = 7.0, H7), 6.36 (d, J = 7.0, H4), 5.78 (t, J = 5.9, H6), 5.68 (t, J = 5.9, H5), 2.53 (s, Me), 2.32 (s, Me). ^{31}P NMR (CD_2Cl_2): δ 25.29 (dd J_{P-P} = 20, J_{Pt-P} = 3140), 16.57 (dd, J_{P-P} = 20, J_{Pt-P} = 2130). **Insertion into 5g**: Yield 60%. IR (CH_2Cl_2): ν_{CO} 2055 (s), 1996 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.36−7.05 (m, 32H), 6.41 (br, 1H), 6.20 (br, 1H), 2.54 (s, Me), 2.49 (s, Me). ^{31}P NMR (CD_2Cl_2): δ 25.97 (dd J_{P-P} = 22, J_{Pt-P} = 3475), 21.02 (dd, J_{P-P} = 22, J_{Pt-P} = 1880). **Insertion into 5h**. The reaction mixture was probed in situ, as attempted precipitation with diethyl ether led to formation of starting material. IR (CH_2Cl_2): ν_{CO} 2054 (s), 1987 (s, br) cm^{-1}. ^{31}P NMR (CD_2Cl_2): δ 18.46 (dd J_{P-P} = 20, J_{Pt-P} = 3220), 15.00 (dd, J_{P-P} = 20, J_{Pt-P} = 2120). Treatment with Me_3NO converted the product to the dicarbonyl **7**, thus proving that the insertion was into C(aryl)−S. **Insertion into 6b**: Yield 75%. IR (CH_2Cl_2): ν_{CO} 2058 (s), 2007 (s), 1993 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.53−7.06 (m, 34H), 6.02 (d, J = 6.8, 1H), 5.74 (t, J = 6.4, 1H), 5.48 (t, J = 5.8, 1H), 2.29 (s, Me). ^{31}P NMR (CD_2Cl_2): δ 16.41 (dd J_{P-P} = 19, J_{Pt-P} = 3170), 13.70 (dd, J_{P-P} = 19, J_{Pt-P} = 2150).). MS FAB: 1056 (M^+). Anal. Calcd for $C_{52}H_{40}SMnO_3PtP_2BF_4$: C, 54.61; H, 3.53. Found: C, 54.75; H, 3.64. **Insertion into 6c**: Yield 70%. IR (CH_2Cl_2): ν_{CO} 2058 (s), 2004 (s), 1993 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.7−6.8 (m, 34H), 6.11 (d, J = 6.3, 1H), 5.80 (t, J = 6.5, 1H), 5.49 (t, J = 6.3, 1H), 3.3−3.0 (m, CH_2), 1.40 (m, Me). ^{31}P NMR (CD_2Cl_2): δ 16.28 (dd J_{P-P} = 20, J_{Pt-P} = 3730), 13.97 (dd, J_{P-P} = 20, J_{Pt-P} = 1730). MS FAB: 1070 (M^+). Anal. Calcd for $C_{53}H_{42}SMnO_3PtP_2BF_4$: C, 54.98; H, 3.66. Found: C, 55.28; H, 3.72. The reaction of the insertion product of **6c** with 1.1 equiv of Me_3NO in CH_2Cl_2 gave the dicarbonyl complex **8c**: Yield 60%. IR (CH_2Cl_2): ν_{CO} 1986 (s), 1940 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.5−7.1 (m, 34H), 6.64 (d, J = 5.8, 1H), 6.04 (d, J = 7.6, 1H), 4.78 (t, J = 6.2, 1H), 3.43 (q, J = 7.0, CH_2), 1.71 (t, J = 7.0, Me). ^{31}P NMR (CD_2Cl_2): δ 13.04 (dd J_{P-P} = 14, J_{Pt-P} = 2280), 12.15 (dd, J_{P-P} = 14, J_{Pt-P} = 3500). MS FAB: 1042 (M^+). Anal. Calcd for $C_{52}H_{42}SMnO_2PtP_2BF_4$: C, 55.28; H, 3.75. Found: C, 55.39; H, 3.64. **Insertion into 6d**: In situ IR spectra indicated clean insertion: [ν_{CO} 2057 (s), 1992 (s), 1993 (s) cm^{-1}], but attempted precipitation with diethyl ether afforded starting material **6d**. To prove that insertion had occurred at the C−S bond nearer the coordinated carbocyclic ring, 1.1 equiv of Me_3NO was added to the reaction mixture to afford dicarbonyl **8d**: Yield 75%. IR (CH_2Cl_2): ν_{CO} 1986 (s), 1941 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.5−7.0 (m, 33H), 6.44 (d, J = 5.9, 1H), 5.02 (d, J = 6.2, 1H), 4.70 (t, J = 6.2, 1H), 2.67 (s, Me), 1.71 (s, Me). ^{31}P NMR (CD_2Cl_2): δ 17.30 (dd J_{P-P} = 14, J_{Pt-P} = 2290), 11.92 (dd, J_{P-P} = 14, J_{Pt-P} = 3425). MS FAB: 1042 (M^+). Anal. Calcd for $C_{52}H_{42}SMnO_2PtP_2BF_4$: C, 55.28; H, 3.75. Found: C, 55.09; H, 3.72. **Insertion into 6e**: In situ IR spectra indicated formation of a 2:1 mixture of insertion product and bimetallic **7e**, but attempted precipita-

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tion with diethyl ether afforded only starting material **6e**. For the insertion product formed in situ: IR (CH_2Cl_2): ν_{CO} 2056 (s), 1989 (br, s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.99−2.92 (m, 2H), 2.62−2.55 (m, 2H), 1.13 (t, $J = 6.8$, Me), 0.87 (t, $J = 7.7$, Me). ^{31}P NMR (CD_2Cl_2): δ 15.45 (dd $J_{P-P} = 18$, $J_{Pt-P} = 3150$), 14.57 (dd, $J_{P-P} = 18$, $J_{Pt-P} = 2160$).

Stopped-Flow Kinetics. All stopped-flow measurements were made at room temperature in HPLC grade CH_2Cl_2 under nitrogen, using a Dionex apparatus. Manganese complex concentrations were about 1.0×10^{-3} M, and the platinum nucleophile was typically in slight excess. Due to the sensitivity of solutions of $Pt(PPh_3)_2(C_2H_4)$ to oxygen, it was not deemed worthwhile to attempt pseudo-first-order conditions. Rather, semiquantitative reactivity comparisons and the detection of intermediates were the goal. To this end, a wavelength between 405 and 475 nm was used to follow optical density changes after mixing. It was possible to record output within 5 ms of mixing of the solutions. Data were stored on a digital oscilloscope for subsequent plotting.

Insertion into Selenophene and Benzoselenophene Complexes. The selenophene complex **12** has been reported previously.[17] We found that the manganese tricarbonyl transfer method[23a] using (η^6-acenaphthene)$Mn(CO)_3^+$ gives an improved yield. For [**12**]BF_4: Yield 92%. IR (CH_2Cl_2): ν_{CO} 2071 (s), 2008 (s, br) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.62 (s, H2,5), 7.28 (s, H3,4). ^{77}Se NMR (CD_3COCD_3): δ 276. MS FAB: 271 (M^+). Anal. Calcd for $C_7H_4SeMnO_3BF_4$: C, 23.56; H, 1.13. Found: C, 23.91; H, 1.25. A golden yellow crystal of [**12**]BF_4 suitable for X-ray diffraction was grown by vapor diffusion of diethyl ether into an acetone solution at −15 °C over several days. **Insertion of Pt into 12**: It was found that $Pt(PPh_3)_2(C_2H_4)$ rapidly inserts into a C−Se bond in **12** to afford **14**. The procedure used was the same as that for insertions into **5** and **6**. For [**14**]BF_4: Yield 88%. IR (CH_2Cl_2): ν_{CO} 2045 (s), 1987 (s), 1971 (s) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.58−7.47 (m, 12H, Ph), 7.45−7.21 (m, 19H), 7.26 (m, 1H), 5.74 (m, 1H), 4.82 (m, 1H). ^{31}P NMR (CD_2Cl_2): δ 20.30 (dd $J_{P-P} = 20$, $J_{Pt-P} = 3560$), 18.23 (dd, $J_{P-P} = 20$, $J_{Pt-P} = 2120$). ^{77}Se NMR (CD_2Cl_2): δ −246 (dd, $J_{Se-P} = 73$, 40). Anal. Calcd for $C_{43}H_{34}SeMnO_3PtP_2BF_4$: C, 47.98; H, 3.18. Found: C, 47.56; H, 3.03. A yellow crystal of [**14**]BF_4 suitable for X-ray diffraction was grown by vapor diffusion of diethyl ether into a CH_2Cl_2 solution at −15 °C over several days. **Insertion of Pd into 12**: The use of $Pd(PPh_3)_2(C_2H_4)$ leads to the palladium analogue of **14**: Yield 78%. IR (CH_2Cl_2): ν_{CO} 2045 (s), 1988 (s), 1970 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.45−7.21 (m, 30H, Ph), 7.70 (d, $J = 6.2$, 1H), 6.62 (t, $J = 7.5$, 1H), 5.54 (m, 1H), 4.11 (t, $J = 7.5$, 1H). ^{31}P NMR (CD_2Cl_2): δ 34.21 (d $J_{P-P} = 39.5$), 22.95 (d, $J_{P-P} = 39.4$). ^{77}Se NMR (CD_2Cl_2): δ −267 (dd, $J_{Se-P} = 33$, 39). Anal. Calcd for $C_{43}H_{34}SeMnO_3PdP_2BF_4$: C, 52.28; H, 3.47. Found: C, 52.21; H, 3.62. **Synthesis of [13]BF_4.** This benzoselenophene complex was prepared as described for the benzothiophene analogue.[23] For **[13]BF_4**: Yield 75%. IR (CH_2Cl_2): ν_{CO} 2072 (s), 2014 (s, br) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 9.19 (d, $J = 5.9$, H2), 8.14 (d, $J = 6.0$, H7), 8.03 (d, $J = 5.9$, H3), 7.75, (d, $J = 5.0$, H4), 6.84 (m, H5,6). ^{77}Se NMR (CD_3COCD_3): δ 617. MS FAB: 321 (M^+). **Insertion of Pt into 13**: It was found that $Pt(PPh_3)_2(C_2H_4)$ rapidly inserts into a C−Se bond in **13** to afford **15**. The procedure used was the same as that for insertions into **5** and **6**. For [**15**]BF_4: Yield 93%. IR (CH_2Cl_2): ν_{CO} 2061 (s), 2004 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.43−7.19 (m, 32H, Ph, H2,3), 6.83 (br, 1H), 6.38 (br, 1H), 6.12 (br, 1H), 6.04 (br, 1H). ^{31}P NMR (CD_3COCD_3): δ 24.98 (dd $J_{P-P} = 20$, $J_{Pt-P} = 3440$), 20.43 (dd, $J_{P-P} = 20$, $J_{Pt-P} = 1920$). ^{77}Se NMR (CD_3COCD_3): δ 361 (dd, $J_{Se-P} = 74$, 70). MS FAB: 1040 (M^+). Anal. Calcd for $C_{47}H_{36}SeMnO_3PtP_2BF_4$: C, 50.11; H, 3.22. Found: C, 50.70; H, 3.44.

Palladium Insertion into [(η^6-Biphenylene)$Mn(CO)_3$]BF_4. $Pd(PPh_3)_2(C_2H_4)$ (140 mg, 0.21 mmol) was added to a suspension of [(η^6-biphenylene)$Mn(CO)_3$]BF_4 (76 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) at room tempertaure under nitrogen. An IR spectrum within a few minutes indicated that the reactant had been converted to bimetallic **17**. After stirring the solution for 1 h in the dark, IR indicated complete conversion to insertion product **16**. The volume was reduced to a few milliliters, and the product precipitated with diethyl ether as a yellow powder. Reprecipitation from acetone afforded a pure material. For [**16**]BF_4: Yield 81%. IR (CH_2Cl_2): ν_{CO} 2059 (s), 2002 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.44−7.19 (m, 30H, Ph), 7.17 (1H), 7.03 (t, $J = 7.5$, 1H), 6.92 (d, $J = 4.9$, 1H), 6.56 (m, 2H), 6.18 (t, $J = 6.4$, 1H), 5.62 (d, $J = 5.5$, 1H), 5.28 (d, $J = 6.4$, 1H). ^{31}P NMR (CD_2Cl_2): δ 33.95 (d $J_{P-P} = 31.5$), 25.60 (d, $J_{P-P} = 31.5$). MS FAB: 922 (M^+). Anal. Calcd for $C_{51}H_{38}MnO_3PdP_2BF_4 \cdot CH_2Cl_2$: C, 57.10; H, 3.69. Found: C, 57.12; H, 3.76. A crystal of [**16**]$BF_4 \cdot CH_2Cl_2$ suitable for X-ray diffraction was grown by vapor diffusion of diethyl ether into a CH_2Cl_2 solution at −20 °C over several days.

Acknowledgment. This work was supported by grant CHE-9705121 from the National Science Foundation.

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for [**12**]BF_4, [**14**]BF_4, and [**16**]BF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0102448