The Remote Activation of Chemical Bonds *via* Metal Coordination

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Abstract: The activation of chemical bonds to cleavage by mild metal nucleophiles can be achieved by precoordination of a transition metal fragment to a site remote from the bond in question. The following bonds have been activated in this manner by η^6-coordination to an internal arene ring: C–C in biphenylene, C–S in benzothiophene and dibenzothiophene, C–Se in benzoselenophene, C–O in benzofuran, and N–H in indole.

Keywords: bond activation; heterocycles; homogeneous catalysis; hydrodesulfurization; manganese; metallocycles

1 Introduction

The selective activation of normally robust chemical bonds is a research field with major implications in both synthesis and catalysis. Selective cleavage of chemical bonds, particularly non-polar C–C and C–H ones, has been accomplished with varying degrees of success by employing (1) high temperature/pressure conditions and/or (2) highly nucleophilic or electrophilic metal species to attack the bond in question.[1,2] Obviously, being able to conduct the chemistry under mild conditions with fairly stable reagents and in a catalytic manner is a highly desirable goal, and one that has precedence in the biological world (cytochrome P450, methane monooxygenase, tyrosinase, etc.). Within the context of organometallic chemistry and with the goal of being able to break and form relatively unreactive chemical bonds in a controlled and catalytic manner, it is necessary to find a way to suitably activate the desired bond to cleavage by a metal reagent. In most scenarios, this involves oxidative addition of the bond to a metal center as the initial step, which can then be followed by insertion and elimination to generate useful products in a catalytic fashion.

The activation of C–H bonds in alkanes is sometimes categorized as one of the Holy Grails of chemistry. Major challenges in this field include (1) controlling the chemo- and regioselectivity in molecules containing multiple but similar C–H bonds and (2) overcoming the inherently low reactivity for C–H cleavage relative to other chemical pathways that may be available. The problem of low reactivity is usually addressed by using reactive unsaturated metal fragments to attack the C–H bond. The need for a reactive metal reagent (usually nucleophilic) is in itself a problem because the reagent may be difficult to prepare and the great reactivity may preclude high selectivity.

In this brief account we summarize a different approach to the activation of covalent bonds. The idea is to "preactivate" the bond in question by coordination of a transition metal fragment to a part of the molecule remote from the bond to be broken. This is termed "remote activation". The chief advantage of this approach is that it permits the use of mild and conveniently synthesized reagents to break the required bond, usually in a regioselective manner. Herein we describe the use of ML_n transition metal fragments π-bonded in an η^6-manner to carbocyclic rings adjacent or near to bonds to be activated. Figure 1 provides a sample of the molecular systems that have been examined by the remote activation approach. The arrows in Figure 1 indicate the particular bond to be cleaved by an appropriate metal nucleophile. In each case, the adjacent carbocyclic ring was coordinated to a metal fragment, most commonly $Mn(CO)_3^+$. It is shown below that this leads to remarkable and in some cases unprecedented levels of activation for C–C, C–O, C–S, C–Se and N–H bonds. The ultimate goal of such work is to make these activations catalytic.

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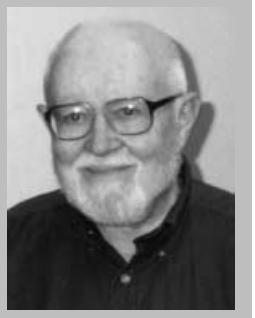

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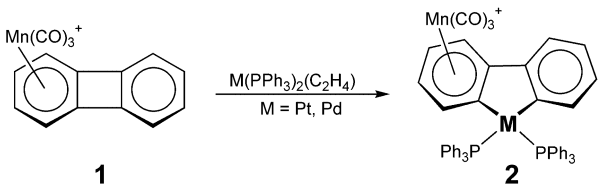
Dwight A. Sweigart received a B. A. from Franklin & Marshall College and a Ph. D. from Northwestern University. He was an AFOSR-NRC, NATO, and Ramsay Postdoctoral Fellow at Oxford University and the University of Wales. He joined the faculty of the Chemistry Department of Brown University in 1980, with research interests that currently are focused in organometallic chemistry and include kinetics, electrochemistry, bond activations, and supramolecular coordination networks. Prof. Sweigart has been an associate editor of *Organometallics* since 1997.

2 C–C Bond Activation

The controlled activation of C–C bonds with transition metals is an industrially important process, but one that is difficult to achieve under mild conditions. The difficulty in activating C–C bonds is both kinetic and thermodynamic in origin. Correspondingly, most reported oxidative addition or metal insertion reactions into C–C bonds have involved systems that are predisposed to react because the C–C bond is strained, or the products have increased aromaticity, or the attacking metal is forced into close proximity to the C–C bond *via* precoordination.[2]

Insertion of a metal into the strained C–C bond of biphenylene (Figure 1) to give a metallacyclic complex has been reported with nucleophilic reagents based on Pt(0), Pd(0), Ni(0), Co(I), Rh(I) and Ir(I).[3–5] The results of these studies demonstrate that oxidative addition to the C–C bond is facilitated by increasing electron density at the metal in the nucleophile. An alternative way to facilitate C–C bond cleavage is to attach an electrophilic metal fragment to the arene π-system before attempted insertion with the nucleophilic reagent. This was attempted with the reactions shown in Scheme 1.[6,7] It was first determined that free biphenylene undergoes no reaction whatsoever with the mild nucleophiles $M(PPh_3)_2(C_2H_4)$ (M = Pt, Pd). However, the reactivity changed dramatically when $Mn(CO)_3^+$ was coordinated to one of the arene rings to give complex **1**. It was found that $Pt(PPh_3)_2(C_2H_4)$, as well as $Pt(PPh_3)_3$, react completely in less than *one minute* at *room temperature* in dichloromethane solution to afford the metallacycle **2**. $Pd(PPh_3)_2(C_2H_4)$ is somewhat less reactive and requires *ca.* 30 min, but nevertheless also cleanly generates **2** at room temperature.[7] By way of comparison, the far more nucleophilic $Pt(PEt_3)_3$ requires *days* of reaction at 80 °C in benzene to insert into the C–C bond in *free* biphenylene.[5] Thus, it is apparent that the $Mn(CO)_3^+$ moiety in **1** increases the reactivity of the C–C bond by many orders of magnitude. This in turn nicely demonstrates that the "remote activation" concept has considerable merit.

Of course, there are some drawbacks to the remote activation methodology. First, the electrophilic activating fragment such as $Mn(CO)_3^+$ must be attached to the arene ring. This is generally not difficult, but nevertheless does constitute a required step.[8] Second, it is necessary to remove the activating group after the reaction, and to recover it if the overall process is to be made catalytic. Third, the presence of an activating group may render sites other than those desired to be accessible to nucleophilic attack. The arrows in Figure 2 indicate the variety of sites available for a nucleophile approaching an $(\eta^6\text{-arene})Mn(CO)_3^+$ complex. In the context of bond activation, it is necessary that the nucleophilic attack be directed to the "R" position in Figure 2. In spite of these "drawbacks", however, remote activation towards mild nucleophiles proved to be successful for all of the molecules shown in Figure 1.



Scheme 1. The remote electrophilic activation of a C–C bond in biphenylene to insertion by mild platinum and palladium nucleophiles.

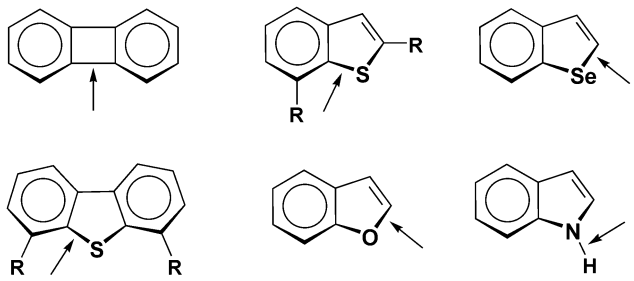


Figure 1. Molecules discussed in this study. The bonds indicated by arrows can be activated by the attachment of a transition metal fragment to the adjacent arene ring.

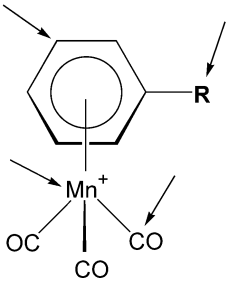
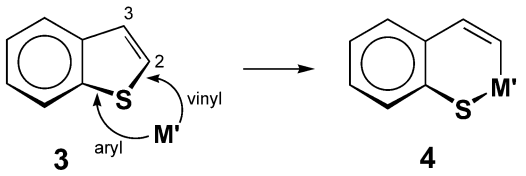


Figure 2. Possible sites of nucleophilic attack on the electrophilic complex $(\eta^6\text{-arene})Mn(CO)_3^+$.

3 C–S and C–O Bond Activation

The activation of C–S bonds in benzothiophenes (BTs) and dibenzothiophenes (DBTs) is especially important because these and other stable conjugated heterocyclic molecules constitute major pollutants in crude petroleum. The combustion of fuels containing these species contributes significantly to environmental pollution through the release of sulfur oxides. For this and other reasons, crude petroleum is treated with hydrogen to remove sulfur as H_2S (and nitrogen as NH_3), generally with a heterogeneous Mo/Co sulfide on alumina catalyst, in what constitutes the largest industrial chemical reaction in the world.[9,10] Thiophenic molecules such as benzothiophene (BT) and dibenzothiophene (DBT) are



Scheme 2. Insertion of a metal nucleophile into a C–S bond in benzothiophene.

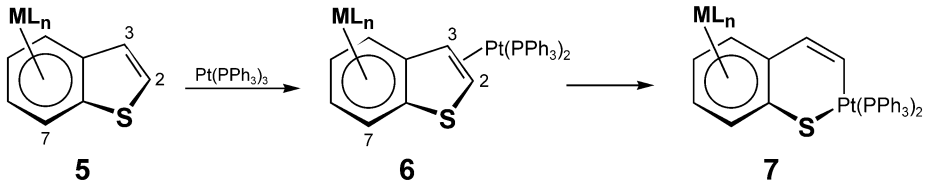
of special concern because their alkylated derivatives are difficult to desulfurize by present technology and, as a consequence, much of the fossil fuel sulfur contamination can be traced to these species. Proposed U. S. government regulations to take effect in the near future will require deep cuts in sulfur content in gasoline and diesel fuels and this, in turn, will require substantial improvements in "deep" hydrodesulfurization (HDS) technology. In effect, this means finding better ways to desulfurize alkylated thiophenes.

Homogeneous organometallic models for HDS have contributed substantially to our understanding of this chemistry.[11,12] Taking benzothiophene as an example, most model studies have utilized highly reactive and coordinatively unsaturated nucleophilic transition metal fragments (M'), which generally insert into the C(vinyl)–S bond in **3** to give the metallathiacycle **4** according to Scheme 2. Generally, insertion into the C(aryl)–S bond is not observed (*vide infra*). Several studies suggest that C–S insertion is preceded by η^1-S coordination to the entering metal, and in the case of thiophene itself this has been verified by comparing spectroscopic data for species adsorbed on the Mo/Co catalyst with data for model complexes.[13] We began work in this field by asking if precoordination of a metal to a carbocyclic ring in BT or DBT would promote the remote activation of the C–S bonds in the adjacent thiophenic ring.[14] To our delight, it was found that this type of precoordination can indeed result in hitherto unseen levels of activation regarding C–S bond cleavage by nucleophiles *or* by electrons.

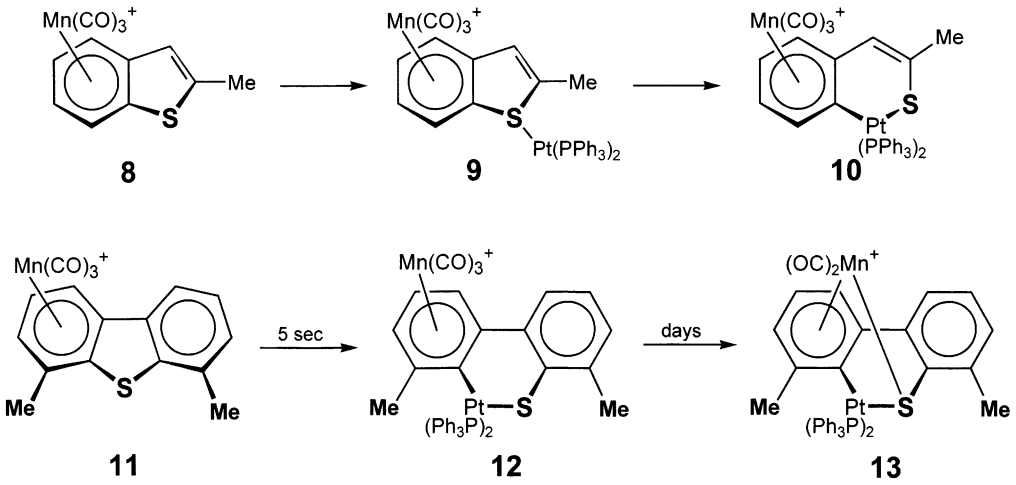
Scheme 3 illustrates the reaction of η^6-coordinated benzothiophene with the weak nucleophile $Pt(PPh_3)_3$.[15] In general the reactions were found to be clean and fairly rapid at room temperature, with *no reaction* in the absence of the ML_n moiety. The activation order was established as $ML_n = Ru(C_6Me_6)^{2+}$, $Mn(CO)_3^+ > FeCp^+$, $RuCp^+ > Cr(CO)_3$. With the weak nucleophile $Pt(PPh_3)_2(C_2H_4)$ and with $Mn(CO)_3^+$ as the activating group, detailed kinetic studies[7] established that the first step in Scheme 3 is the very rapid (50 msec) coordination to the thiophenic double bond to give **6** as an intermediate, which inserts into the C(vinyl)–S bond within a few seconds. The C–S bond cleavage in **5** can be made regioselective by placement of a methyl substituent at position 2. As indicated in Scheme 4, this blocks the formation of the η^2-complex **6**, so that the η^1-S intermediate **9** forms instead, which then undergoes insertion into the C(aryl)-S bond to afford metallacycle **10**.

Importantly, this η^1-S mechanism is followed by dibenzothiophenes, which always cleave the C–S bond nearer the coordinated ring, as shown in Scheme 4. It is really quite incredible that the most refractory sulfur contaminant in petroleum, 4,6-dimethyldibenzothiophene, undergoes C–S bond fission within seconds at room temperature when precoordinated in the form of complex **11**. The initial product in this reaction, complex **12**, contains a nucleophilic sulfur that slowly displaces a CO ligand to afford **13**.[16] The take-home message from this work is that η^6-coordination to a carbocyclic ring in BTs or DBTs is an effective way to activate the system and that simultaneous η^6, η^1-S coordination is an attractive mechanism for HDS of congested BTs and DBTs, with the η^6-coordination activating the C–S bond to insertion by a second, η^1-S bonded, metal. It is noteworthy that the C–S activation chemistry described above for benzothiophenes was found to apply just as well to the selenium analogue, benzoselenophene (Figure 1).[7]

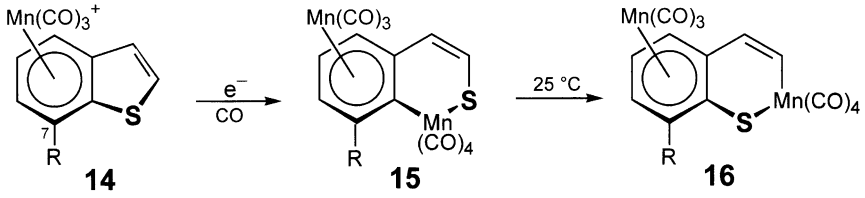
BT and DBT complexes are also activated to rapid *reductive* C–S bond cleavage, as illustrated in Scheme 5 for coordinated benzothiophenes. Interestingly, the initial product **15**, which is stable if R = H, derives from insertion into the C(aryl)–S bond in BT. Our studies are suggestive[14,17,18] of a radical mechanism, which may be relevant to electron transfer processes thought to occur in HDS. The isomerization **15** → **16** occurs over several hours for R = Me *via* reductive elimination to η^1-S bonded $Mn(CO)_4$ followed by oxidative addition. The fact that a substituent at C-7 in **14** induces isomerization of the C(aryl)–Mn–S to the C(vinyl)–Mn–S metallathiacycle (**15** → **16**) suggests that precoordination of a metal to the carbocyclic ring in BTs results in regioselective kinetic activation favoring C(aryl)–S over C(vinyl)–S scission, even when the



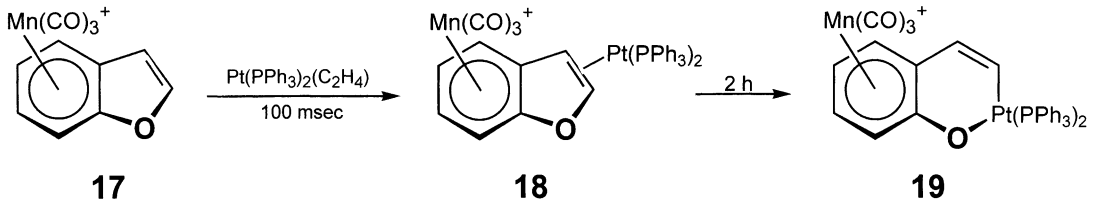
Scheme 3. Mechanism of insertion of platinum into a C–S bond in coordinated benzothiophene.



Scheme 4. Effect of steric congestion on the mechanism of platinum insertion into a C–S bond in coordinated benzothiophene and dibenzothiophene.



Scheme 5. Reductive activation of the C(aryl)–S bond in coordinated benzothiophenes.



Scheme 6. Mechanism of insertion into a C–O bond in coordinated benzofuran.

latter is the thermodynamic product. The sulfur atom in **15** is easily protonated and subsequent hydrogenation affords desulfurized product along with $[Mn(CO)_4SH]_2$ and H_2S. DFT calculations were performed to help understand the role of precoordination in C–S bond activation and insertion processes. The results nicely explained the observed regioselectivity in the C–S cleavage reactions and confirmed that an η^1-S species is a viable intermediate in HDS chemistry.[18]

In analogy with the activation of BTs and DBTs described above, the C–S bonds in thiophene itself (T) can be activated by the direct η^5-attachment of a metal fragment to the heterocyclic ring, as in $(\eta^5\text{-T})Mn(CO)_3^+$.[19] In this case the metal is directly bonded to the C–S linkage that is subsequently cleaved, so the activation can not be classified as "remote". However, remote activation of the C–S bonds to cleavage by a metal nucleophile was recently demonstrated with 2- and 3-phenylthiophenes having the electron-withdrawing $Cr(CO)_3$ fragment attached to the phenyl rings.[20]

In a significant achievement, the remote activation methodology that works so well for C–S activation was successfully applied to the much more difficult problem of C–O activation.[21] As indicated in Scheme 6, the coordinated benzofuran **17** reacts with a mechanism identical to that found with coordinated benzothiophene, with the significant difference that the rapidly formed η^2-(C=C) intermediate **18** *slowly* converts to insertion product **19**. The rate difference is no doubt due to the stronger C–O bond in benzofuran compared to the C–S bond in benzothiophene. The chemistry in Scheme 6 constitutes a model for hydrodeoxygenation (HDO). More importantly, the use of this methodology to cleave strong bonds may point the way to better hydrodenitrogenation (HDN) catalysts, an area of major technological importance (*vide infra*).

4 N–H Bond Activation

Hydrodenitrogenation of aromatic *N*-heterocycles is an enormously important industrial reaction. It constitutes a major technological challenge now and will only increase in importance in the future as higher nitrogen-containing crude petroleum is brought on line.[9,22] Nitrogen in petroleum occurs in a variety of forms, with the more intractable species containing, for example, a stable indole or quinoline nucleus. Such compounds poison catalysts used in cracking and reforming reactions, and contribute substantially to environmental pollution through the formation of nitrogen oxides upon fuel combustion. Because of the stronger C–N bond, HDN is more difficult to achieve than is HDS, and has been correspondingly less studied in model systems. On the industrial Mo/Co heterogeneous catalyst, it is thought that indole π-binds through the carbocyclic ring, while the more basic quinoline σ-binds through the nitrogen. The nature of this initial interaction of an *N*-heterocycle with a metal site must be important in directing subsequent elementary reactions leading to denitrogenation.

a) $Mn(CO)_3^+$ N PPh$_3$ Pt PPh$_3$ N $Mn(CO)_3^+$

20

b)

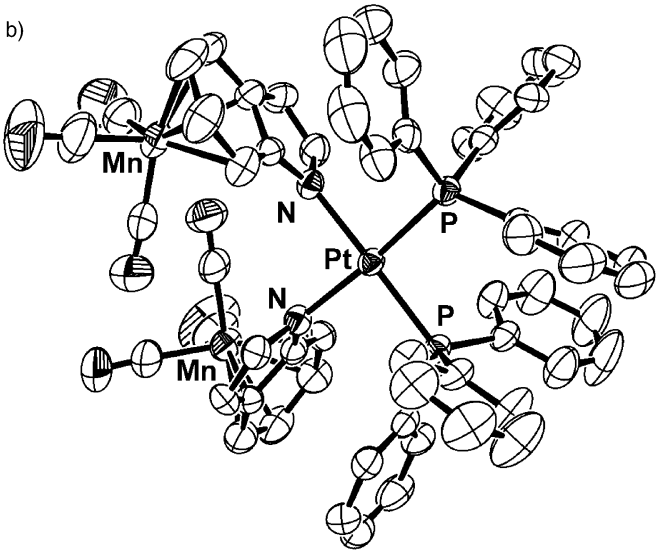


Figure 3. Crystal structure of the dicationic compound **20**. The perchlorate anions are not shown.

Ideally, the lessons learned from the remote activation of C–S and C–O bonds as described above could be usefully applied to C–N bond activation in HDN models. To this end (η^6-indole)$Mn(CO)_3^+$, which was found[23] to have the metal coordinated to the carbocyclic ring, was examined as a model for remote C–N bond activation. Reaction of this complex with the mild nucleophile $Pt(PPh_3)_2(C_2H_4)$ led to the rapid formation of a product that was isolated and structurally characterized. Instead of the hoped-for cleavage of the C–N bond, it was found that insertion into the N–H bond had occurred. A picture of the dicationic product (**20**) is given in Figure 3. The mechanism of formation of **20** was not investigated, although it is highly likely that platinum hydride species occur as intermediates. The nature of the reduced product that must form concomitantly with the Pt(II) in **20** was not established, although one could speculate that it is C_2H_6. Cleavage of the N–H bond in indole by precoordination to the arene ring is noteworthy and may be relevant to HDN catalysis. Even more relevant is the likelihood that initial hydrogenation of the heterocyclic double bond to afford, for example, (η^6-indoline)$Mn(CO)_3^+$ would render the C–N bond more susceptible to cleavage. Investigations in this direction are planned.

5 Experimental Details

Synthetic and structural details for many of the compounds described above may be found in refs.[7,14–19,21] Compound **20** was prepared as a perchlorate salt by combining equivalent amounts of [(η^6-indole)$Mn(CO)_3$]ClO_4 and $Pt(PPh_3)_2(C_2H_4)$ in CH_2Cl_2 at room temperature. The mixture was stirred for several minutes and then chromatographed on neutral alumina to give a yellow powder that was washed with diethyl ether and recrystallized from CH_2Cl_2/Et_2O. A crystal of [**20**][ClO_4]$_2 \cdot CH_2Cl_2$ was mounted with epoxy cement. X-ray data collection was carried out using a Siemens P4 single-crystal diffractometer equipped with a CCD area detector and controlled by SMART version 4 software. Data collection was carried out by SAINT version 4 software and included profile analysis; this was followed by absorption correction by use of the program SADABS. The structure was determined by direct methods with use of programs in the SHELXTL version 5 package. Refinement on F squared was done with SHELXL-97. Many hydrogen atoms appeared in the difference map (34 out of 44); they were introduced in ideal positions, riding on the carbon atom to which they are bonded, and were refined with isotropic temperature factors 20% greater than those of the ridden atoms. All other atoms were refined with anisotropic thermal parameters. Crystal data for [**20**][ClO_4]$_2 \cdot CH_2Cl_2$: formula $C_{59}H_{44}Cl_4Mn_2N_2O_{14}P_2Pt$, $fw = 1513.67$, triclinic, space group $P\text{-}1$, $T = 298$ K, $\lambda = 0.71073$ Å, $a = 12.9436(5)$, $b = 13.8455(6)$, $c = 18.5801(8)$ Å, $\alpha = 85.695(1)$, $\beta = 87.167(1)$, $\gamma = 64.200(1)$ deg, $V = 2988.9(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.682$ g cm^{-3}, $\mu = 3.049$ mm^{-1}, $F(000) = 1500$, θ range 1.10 – 24.73 deg, max and min trans 0.719 and 0.568, 757 variables refined with 9919 independent reflections to final R indices [$I > 2\sigma(I)$] of $R_1 = 0.0441$ and $wR_2 = 0.0983$, and $GOF = 1.105$. Crystallo-

graphic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-207908. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336 – 033; E-mail: deposit@ccdc.cam.ac.uk].

6 Conclusion

In summary, it has been shown that the activation of chemical bonds to regioselective cleavage by mild metal nucleophiles can be achieved in some cases by precoordination of a transition metal fragment to a site remote from the bond in question. The following bonds have been activated in this manner by η^6-coordination of $Mn(CO)_3^+$ to an internal arene ring: C–C in biphenylene, C–S in benzothiophene and dibenzothiophene, C–Se in benzoselenophene, C–O in benzofuran, and N–H in indole.

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