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Activation of a Carbon–Oxygen Bond of Benzofuran by Precoordination of Manganese to the Carbocyclic Ring: A Model for Hydrodeoxygenation[**]

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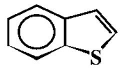
The use of hydrogen in the presence of a catalyst to remove the heteroatoms S, N, and O from petroleum is practiced on a massive scale and is known as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO).[1] Generally, the most difficult molecules to treat by hydroprocessing contain highly stable unsaturated heterocyclic ring systems, for example, those based on thiophene, pyrrole, pyridine, and furan. In the case of sulfur and nitrogen, this results in significant contamination of fossil fuels. Problems associated with the presence of oxygen compounds are less severe but nevertheless significant.[2] For these reasons, there has been substantial interest in developing homogeneous model systems for C–X bond cleavage (X = S, N, O) and subsequent removal of the X atom in unsaturated heterocycles.[3, 4]

We have shown[5] that precoordination of a metal center to the carbocyclic ring of benzothiophene (BT, **1**) and dibenzothiophene activates a C–S bond towards cleavage by reducing agents and by metal nucleophiles. For example, the weak nucleophiles $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_2(C_2H_4)]$ do not react with free BT, but react rapidly with $[(\eta^6\text{-BT})ML_n]$ (**2**, $ML_n = Mn(CO)_3^+$, $FeCp^+$, $RuCp^+$, etc.) to afford the metallathiacycles **3**. Similar activation of a C–O bond in benzofuran (BF, **4**) is expected to be more difficult due to the much greater strength of C–O bonds compared to C–S bonds and because most late transition metal centers prefer S to O ligands. Nevertheless, we report here that insertion of a metal center into the C(2)–O bond of $[(\eta^6\text{-BF})Mn(CO)_3]^+$ (**5**) is readily achieved. Addition of free **4** to $[Pt(PPh_3)_2(C_2H_4)]$ produces no reaction, but **5** ($\tilde{\nu}_{CO} = 2079, 2020\ cm^{-1}$) reacts rapidly at room temperature to produce initially two products, both of which rapidly revert to **5** upon addition of CO or PPh_3. Scheme 1 summarizes the chemistry proposed to be occurring. Although the minor initial product could not be isolated, IR ($\tilde{\nu}_{CO} = 1775$, ca. $1980\ cm^{-1}$), ^1H NMR, and ^{31}P NMR spectroscopic data strongly suggest that it has structure **6**. Similar species are formed with a wide variety of $[(arene)Mn(CO)_3]^+$ complexes on treatment with $[Pt(PPh_3)_2(C_2H_4)]$.[6] Furthermore, analogous bonding to that proposed for **6** is found in the related complexes $[(CO)_4Re(\mu\text{-H})(\mu\text{-CO})Pt(PPh_3)_2]$ and $[(CO)_4Mn(\mu\text{-H})(\mu\text{-CO})Pt(PEt_3)_2]$.[7]



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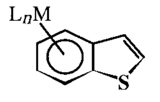

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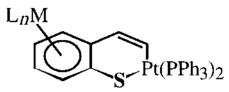

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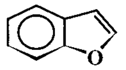

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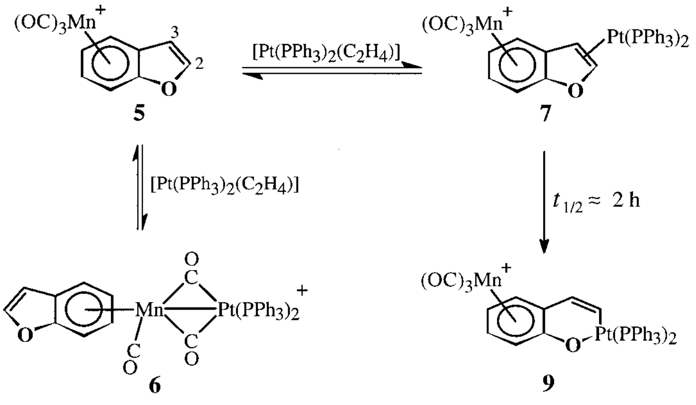

Scheme 1. Insertion of $Pt(PPh_3)_2$ into activated benzofuran.

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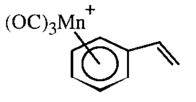
The major initial product ($\tilde{\nu}_{CO} = 2062$, 1998 cm^{-1}) in the reaction of **5** also could not be isolated, but ^{1}H and ^{31}P NMR data strongly suggest that it is the simple η^2-olefin complex **7**, which results from ethylene displacement by the C–C double bond of benzofuran. In particular, the $J_{P,Pt}$ coupling constants are quite similar to those of a range of [Pt(PR$_3$)$_2$(olefin)] complexes.[8] From this result we conclude that the electron-withdrawing ability of the Mn(CO)$_3^+$ moiety in **5** renders coordination of the Pt center to the furan double bond thermodynamically favorable because of increased metal-to-ligand π bonding. As might be expected, the styrene complex **8** reacts similarly with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] to afford an η^2-olefin adduct ($\tilde{\nu}_{CO} = 2062$, 2002 cm^{-1}) and the styrene analogue of **6**.[6]



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In CH$_2$Cl$_2$ at room temperature, the initial products of the reaction of **5** with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)], which consist of **7** and smaller amount of **6**, were transformed cleanly into a new species **9** ($\tilde{\nu}_{CO} = 2054$, 1991 cm^{-1}). The ^{1}H NMR spectra and $J_{P,Pt}$ coupling constants obtained from the ^{31}P NMR spectrum suggested that insertion into the C(2)–O bond had occurred. The X-ray structure of **9**-BF$_4$ (Figure 1) verified that insertion had indeed taken place.[9] The metallacyclic ring of **9** is almost planar (rms deviation 0.015 Å) and is coplanar with the carbocyclic ring. The platinum atom adopts the usual square-planar geometry, although the P(1)-Pt-P(2) angle is larger (98.4°) and the C(2)-Pt-P(1) and O(1)-Pt-P(2) angles are smaller (87.9, 84.0°) than the ideal 90°, most likely due to steric constraints imposed by the phosphane ligands.

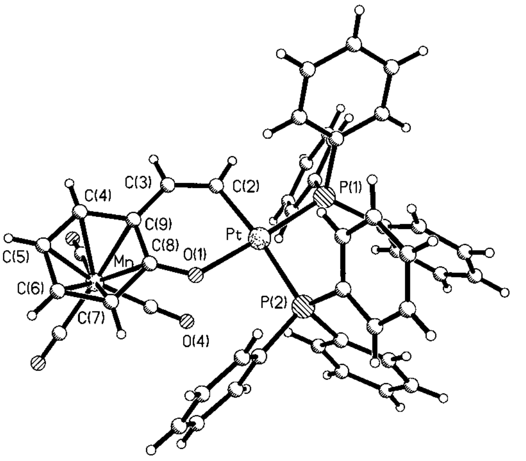
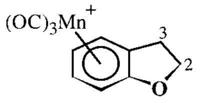


Figure 1. Crystal structure of the cation in **9**-BF$_4$. Selected bond lengths [Å] and angles [°]: C(8)–O(1) 1.279(8), O(1)–Pt 2.067(4), Pt–C(2) 2.044(7), C(2)–C(3) 1.328(10), C(3)–C(9) 1.451(10), C(9)–C(8) 1.432(10), Pt–P(1) 2.243(2), Pt–P(2) 2.363(2); C(8)-O(1)-Pt 128.6(4), O(1)-Pt-C(2) 89.8(2), Pt-C(2)-C(3) 125.2(5), C(2)-C(3)-C(9) 127.8(7), C(3)-C(9)-C(8) 122.7(6), C(9)-C(8)-O(1) 125.7(6), C(2)-Pt-P(1) 87.9(2), O(1)-Pt-P(2) 84.00(13), P(1)-Pt-P(2) 98.37(6).

The mechanism of C–O bond cleavage was probed by using ^{31}P NMR spectroscopy to monitor the reaction between **5** and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]. At room temperature, a mixture of **7** [$\delta = 29.3$ ($J_{P,Pt} = 4190$, $J_{P,P} = 31$ Hz), 26.9 ($J_{P,Pt} = 3260$, $J_{P,P} = 31$ Hz)] and **6** [$\delta = 32.5$ ($J_{P,Pt} = 3980$)] was rapidly formed. Signals due to **9** [$\delta = 31.9$ ($J_{P,Pt} = 1910$, $J_{P,P} = 17$ Hz), 17.1 ($J_{P,Pt} = 4440$, $J_{P,P} = 17$ Hz)] grew continuously over 6 h, while those of **7** and **6** disappeared. Scheme 1 illustrates a likely reaction mechanism for the transformation **5** → **9**, which involves reversible adduct formation (**5** ↔ **7**) followed by irreversible insertion. The equilibrium **5** ↔ **6** is assumed to be a dead end. In this concept, insertion into the C–O bond is preceded by coordination of Pt to the C=C bond of furan. In accordance with this, it was found that the 2,3-dihydrobenzofuran complex **10**, which lacks the requisite double bond, reacts with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] to give only the bimetallic complex [(η^6-2,3-dihydrobenzofuran)Mn(CO)(μ-CO)$_2$Pt(PPh$_3$)$_2$]$^+$ (analogous to **6**; $\tilde{\nu}_{CO} = 1773$, 1979 cm^{-1}). It is noteworthy that insertion into **10** does not occur although its C(2)–O bond is weaker than that of **5**.



10

The use of transition metal complexes to cleave strained or weak C–O bonds is well known.[10] Similarly, metal-promoted reactions involving C–O bond scission in esters, ketones, and allylic substrates were reported.[11] In comparison, the activation of unstrained and unfunctionalized C–O single bonds by metal complexes is quite uncommon, but has been achieved in several cases by using highly reactive metal nucleophiles to promote oxidative addition.[12] Insertions into the C–O bonds of anisole, 2,5-dihydrofuran, and 2,3-dihydrofuran were accomplished in this way. Alternatively, C–O bonds were cleaved intramolecularly by attachment of a pendant phosphorus donor group that coordinates to the metal center and forces it into a position near to the C–O bond.[11e, 13] In the reaction **5** → **9**, remote activation of the C–O bond of benzofuran is induced by coordination of the Mn(CO)$_3^+$ moiety to the carbocyclic ring. This precoordination leads to stronger binding of Pt(PPh$_3$)$_2$ to the C–C double bond and subsequent insertion into the adjacent C–O bond. No evidence was found for intermediates or products arising from C–H activation.

In conclusion, we have shown that insertion of a metal center into the strong C(2)–O bond of benzofuran is possible when the electrophilic fragment Mn(CO)$_3^+$ is coordinated to the carbocyclic ring. This general idea of remote activation was previously shown[5] to be highly successful for benzothiophene and analogues. The success with benzofuran suggests that a similar strategy may be applicable to indole derivatives for modeling HDN reactions, and studies to probe this are underway. In HDO chemistry, it is thought[2, 3b] that removal of oxygen can precede or follow hydrogenation. For complex **5** we have demonstrated that insertion of a metal center into the C–O bond is facilitated by the adjacent C=C bond and that hydrogenation (to give complex **10**) hinders this process by eliminating the possibility of initial coordination to the C=C bond.

Experimental Section

Complexes **5**-BF$_4$ and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] were synthesized by published procedures.[14, 15] The ^{1}H and ^{31}P NMR spectra were recorded on Bruker 300- and 400-MHz spectrometers. The ^{31}P NMR chemical shifts are relative to that of 85 % phosphoric acid as external reference.

9-BF$_4$: [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (85 mg, 0.114 mmol) was added to a suspension of **5**-BF$_4$ (35 mg, 0.102 mmol) in CH$_2$Cl$_2$ (10 mL) under N$_2$ at room temperature. An immediate color change from yellow to orange occurred, and IR analysis indicated complete conversion into a mixture of **7** (major) and **6** (minor). The solution was stirred in the dark for an additional 5 h, during which IR analysis indicated complete conversion into **9**. The volume was reduced to 2 mL, and diethyl ether added to precipitate the product as a yellow powder. Reprecipitation from acetone with diethyl ether afforded pure **9**-BF_4. Yield 83 % (90 mg); IR (CH_2Cl_2): $\tilde{\nu}_{CO} = 2054(s), 1991\ cm^{-1}(s)$; ^1H NMR (CD_2Cl_2): $\delta = 7.0-7.6$ (m, 30 H, Ph), 6.92 (m, 1 H), 6.36 (d, $J_{H,H} = 6$ Hz, 1 H), 6.30 (m, 1 H), 6.04 (t, $J_{H,H} = 6$ Hz, 1 H), 5.52 (t, $J_{H,H} = 6$ Hz, 1 H), 4.49 (d, $J_{H,H} = 7$ Hz, 1 H); ^{31}P NMR (CD_2Cl_2): $\delta = 31.9$ ($J_{P,Pt} = 1910$, $J_{P,P} = 17$ Hz), 17.1 ($J_{P,Pt} = 4440$, $J_{P,P} = 17$ Hz); elemental analysis: calcd: C 53.08, H 3.41; found: C 53.50, H 3.46. Crystals of **9**-$BF_4 \cdot Et_2O \cdot \frac{1}{4}CH_2Cl_2$ suitable for X-ray diffraction analysis were grown by room-temperature vapor diffusion of Et_2O into a solution containing an equimolar mixture of **5**-BF_4 and $[Pt(PPh_3)_2(C_2H_4)]$ in CH_2Cl_2. The crystals lose the diethyl ether molecules of crystallization rapidly at room temperature when exposed to air. Hence, the crystal selected for diffraction studies was cut and stored under Et_2O until used. Coating with fluoro-lube and maintaining a temperature of −30 °C prevented loss of Et_2O of crystallization during X-ray data collection.

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[9] Crystal structure of **9**-BF_4: Data were collected on a Siemens P4 diffractometer at −30 °C with $Mo_{K\alpha}$ radiation, and refinements based on F^2 were carried out with the SHELXTL package. The compound crystallized as a solvate with the formula **9**-$BF_4 \cdot Et_2O \cdot \frac{1}{4}CH_2Cl_2$. Crystal data: crystal dimensions 0.40 × 0.45 × 0.28 mm, triclinic, space group $P\bar{1}$, $a = 10.8468(1)$, $b = 14.9083(1)$, $c = 17.3062(1)$ Å, $\alpha = 67.790(1)$, $\beta = 74.334(1)$, $\gamma = 78.408(1)^\circ$, $V = 2479.23(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.538\ g\,cm^{-3}$, $\mu = 3.211\ mm^{-1}$, θ range 1.3–26.39°, 594 variables and 40 restraints were refined for 8623 independent reflections with $I > 2\sigma(I)$ to $R = 0.0518$, $wR2 = 0.1280$, and GOF = 1.115. Crystallographic 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-114337. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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An Effective Fluorescent Sensor for Choline-Containing Phospholipids[**]

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The design and synthesis of abiotic receptors based on uncommon binding units are of particular interest in molecular recognition research since they allow for the manifestation of nonconventional binding forces such as those originating from the CH⋯O hydrogen bond.[1] While this interaction dictates the hydrogen bonding pattern and crystal

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