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η^2-Binding of Styrenes to Pt(PPh_3)$_2$. The Effect of Precoordination of Manganese Tricarbonyl Cation to the Aromatic Ring

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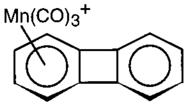
Summary: The ability of the olefinic C═C double bond in styrenes to bind to Pt(PPh_3)$_2$ is greatly increased by η^6-precoordination of Mn(CO)$_3^+$ to the arene ring.

Introduction

Transition metal fragments are commonly used to alter the chemical reactivity of π-hydrocarbons. For example, η^6-coordination of aromatic molecules to the Mn(CO)$_3^+$ moiety activates the arene ring to the addition of nucleophiles, affording cyclohexadienyl complexes which can be demetalated and rearomatized to yield functionalized products.[1] The electrophilic activation afforded by the Mn(CO)$_3^+$ group also results in increased acidity of alkyl side chains.[2]

A third type of electrophilic activation, which has only recently been demonstrated, involves the cleavage of bonds in side chains adjacent to the complexed arene.[3,4] Thus, addition of the mildly nucleophilic Pt(0) complex Pt(PPh_3)$_2$(C_2H_4) to coordinated biphenylene (**1**), benzothiophene (**2**), and benzofuran (**3**) results in clean insertion of Pt(PPh_3)$_2$ into a C−C, C−S, and C−O bond, respectively. In the case of insertion into **3**, it was shown that the reaction follows the sequence given in Scheme 1.[4] A key step in this mechanism is the precoordination of the Pt(0) to the free C═C double bond (**4**) prior to insertion into the C−O bond. Available evidence indicates[5] that a similar mechanism occurs with the benzothiophene analogue (**2**). In each case the Mn(CO)$_3^+$ moiety greatly facilitates Pt(0) coordination to the C═C bond, without which cleavage of the C−O or C−S bond does not occur.



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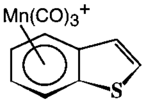

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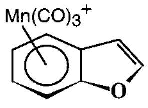

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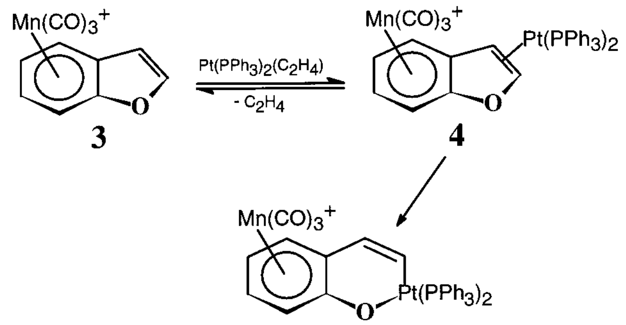
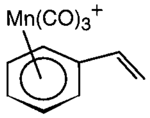
Scheme 1



Because the reactions of **2** and **3** with the platinum nucleophile serve to model industrially important hydroprocessing chemistry (HDS and HDO, respectively), we felt it worthwhile to examine in more detail the effect of Mn(CO)$_3^+$ coordination to an arene ring on the ligand-binding ability of olefinic side chains. Accordingly, in this report we describe the reaction of Pt(PPh_3)$_2$(C_2H_4) with the styrene complex **5**, as well as with the methylated derivatives **6**−**8**. The reason for studying complexes **6**−**8** is due to the known[7] large negative impact that methylation has on the hydroprocessing of molecules containing heterocyclic rings based on thiophene or furan.



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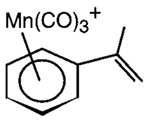

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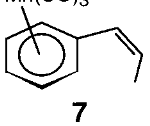

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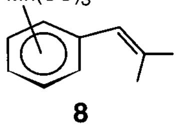

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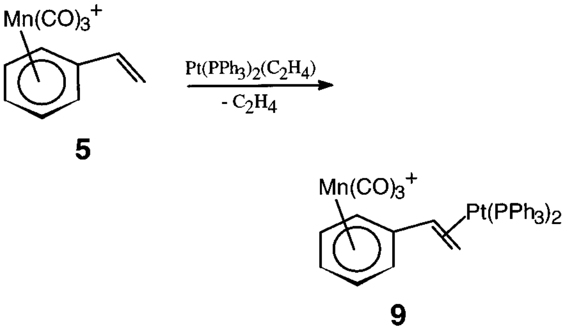
Results and Discussion

Before investigating the interaction of $Pt(PPh_3)_2(C_2H_4)$ with the styrene complexes **5**−**8**, the reaction with the free styrene ligands was studied. In a sealed NMR tube in CD_2Cl_2, ^{31}P NMR spectra indicated that the olefin exchange shown in eq 1 proceeds about 50%

$$Pt(PPh_3)_2(C_2H_4) + PhCHCH_2 \rightleftharpoons Pt(PPh_3)_2(PhCHCH_2) + C_2H_4 \quad (1)$$

to completion when the (styrene)/$Pt(PPh_3)_2(C_2H_4)$ ratio is 1:1. With a 10:1 ratio, the reaction was nearly complete. In contrast, α-methylstyrene, *cis*-β-methylstyrene, and β-dimethylstyrene did not react to a detectable extent even when present in a 10-fold excess over $Pt(PPh_3)_2(C_2H_4)$. This lack of reaction is probably partly steric in origin and partly due to the inductive effect of the methyl substituents, which would be expected to inhibit π-back-bonding from the platinum to the olefin when compared to free unsubstituted styrene.

The situation changes dramatically when the styrene has $Mn(CO)_3^+$ coordinated to the arene ring. Thus, when complexes **5**−**7** were mixed with $Pt(PPh_3)_2(C_2H_4)$ in a ratio close to 1:1, there was rapid and complete coordination of the styrene C=C bond to the platinum. Equation 2 illustrates the reaction with complex **5** to afford the bimetallic species **9**. A completely analogous reaction occurred with **6** and **7**, showing that the inhibiting effect of a methyl substituent is more than compensated for by the presence of a $Mn(CO)_3^+$ group. Most likely, the primary effect of the electron-withdrawing $Mn(CO)_3^+$ moiety is to increase the Pt → olefin π-back-bonding interaction, thus accounting for the increased stability. In accordance with this view, Rudd and Angelici[8] reported that binding of $CpRe(CO)_2$ to the double bond in benzothiophene is facilitated by coordination of $Cr(CO)_3$ to the carbocyclic ring.



(2)

The identity of complex **9** was verified by single-crystal X-ray diffraction. Table 1 gives relevant crystal data, and Figure 1 gives an ORTEP drawing. As would be expected, $Pt(PPh_3)_2$ is situated anti with respect to the $Mn(CO)_3^+$ group. The π-back-bonding from the platinum to the C=C double bond results in a fairly long C(7)−C(8) bond length of 1.444(8) Å.

Table 1. Crystallographic Data for [{styrene·Pt(PPh₃)₂}Mn(CO)₃]BF₄ (9)

formula	$C_{47}H_{38}BF_4MnO_3P_2Pt$
fw	1049.55
temperature, K	298
wavelength, Å	0.71073
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.9800(3)
b, Å	16.9000(5)
c, Å	26.10190(10)
β, deg	94.565(2)
V, Å^3	4388.43(19)
Z	4
d_{calcd}, g cm^{-3}	1.589
μ, mm^{-1}	3.602
$F(000)$	2072
cryst dimens, mm	0.24 × 0.20 × 0.18
θ range, deg	1.98−26.37
no. of reflns collected	63 135
no. of indept reflns	8974 (R_{int} = 0.0653)
no. of data/restraints/params	8974/0/532
GOF on F^2	1.156
R1, wR2 [$I > 2\sigma(I)$]	0.0337, 0.0724
R1, wR2 (all data)	0.0602, 0.0890
largest diff peak, hole, e Å^{-3}	1.117 and −0.744

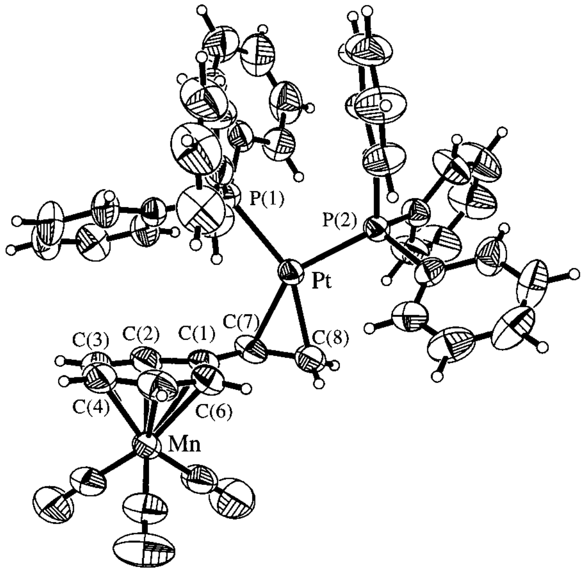


Figure 1. ORTEP drawing of the cation in [{styrene·Pt(PPh$_3$)$_2$}Mn(CO)$_3$]BF$_4$ (**9**) with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt(1)−P(1) 2.3006(13), Pt(1)−P(2) 2.2732(13), Pt(1)−C(7) 2.140(5), Pt(1)−C(8) 2.104(5), C(7)−C(8) 1.444(8), C(1)−C(7) 1.442(7), Mn(1)−C(1) 2.360(5), Mn(1)−C(2) 2.207(5), Mn(1)−C(3) 2.172(6), Mn(1)−C(4) 2.168(6), Mn(1)−C(5) 2.163(6), Mn(1)−C(6) 2.203(5), P(1)−Pt(1)−P(2) 101.44(5), P(1)−Pt(1)−C(7) 113.26(17), P(2)−Pt(1)−C(8) 105.66(16), C(7)−Pt(1)−C(8) 39.8(2), C(1)−C(7)−C(8) 124.1(5).

When $Pt(PPh_3)_2(C_2H_4)$ was added to the β-dimethylstyrene complex **8**, no coordination to the C=C double bond could be detected. Rather, the platinum nucleophile rapidly attacked a carbonyl ligand to afford the bimetallic complex **10**, which was characterized in situ, but could not be isolated due to its ready reversion to starting materials upon attempted precipitation. Species analogous to **10** are, in fact, the normal product formed

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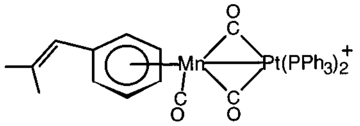
when $Pt(PPh_3)_2(C_2H_4)$ reacts with $(arene)Mn(CO)_3^+$ complexes.[9] It is only when there is a good alternative binding site for the platinum that an analogue of **10** is not formed. For complexes **5**−**7** this alternative site is the olefinic double bond, and the platinum prefers to bind there rather than at a carbonyl carbon. With **8**, however, the two methyl groups sufficiently inhibit binding of the platinum to the olefinic site that **10** is the only product formed.



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In conclusion, it has been demonstrated that η^6-coordination of $Mn(CO)_3^+$ to the arene ring in styrenes greatly facilitates η^2-binding of the olefinic double bond to $Pt(PPh_3)_2$. These results may be of relevance to the hydroprocessing of unsaturated heterocycles such as benzothiophenes and benzofurans, for which it is thought that η^2-bonding may precede hydrogenation and/or insertion reactions.

Experimental Section

Materials. All synthetic procedures were done under nitrogen. Styrenes were purchased from commercial sources and used without further purification. Solvents were HPLC grade and were opened only under nitrogen. $Pt(PPh_3)_2(C_2H_4)$ was prepared by a literature method.[10] ^1H and ^{31}P NMR spectra were recorded on a Bruker 400 MHz instrument; ^{31}P chemical shifts are relative to 85% phosphoric acid external reference.

Styrene Complexes [5−8]BF$_4$. The styrene and α-methylstyrene complexes **5** and **6** have been previously reported and characterized.[11] We synthesized **5**−**8** by two general methods, the first of which is a slightly modified version of that reported by Chung et al.[11]

Method 1. $Mn(CO)_5Br$ (1.0 g) and $AgBF_4$ (1.1 equiv) were dissolved in CH_2Cl_2 (40 mL) and refluxed for 30 min with the exclusion of light. The desired styrene (3 equiv) in CH_2Cl_2 (10 mL) was then added and the reaction mixture refluxed overnight. After cooling to room temperature, the solution was filtered through Celite and concentrated to ca. 10 mL. Diethyl ether was then added to precipitate [**5**−**8**]BF_4 as a yellow powder in yields in the range 70−85%.

Method 2. $[(Acenaphthene)Mn(CO)_3]BF_4$ (0.20 g), prepared by method 1 as previously reported,[12] was combined with the desired styrene (4 equiv in 15 mL of CH_2Cl_2) in a pressure tube and heated to 70 °C for 3 h. After cooling to room temperature, the solution was concentrated and the product precipitated with diethyl ether. The yields ranged from 75 to 94%.

For [**7**]BF_4: IR (CH_2Cl_2): ν_{CO} 2081 (s), 2023 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.75 (t, J = 6 Hz, 2H), 6.41 (m 4H), 6.20 (d, J = 11 Hz, 1H), 2.07 (d, J = 7 Hz, Me). For [**8**]BF_4: IR (CH_2Cl_2): ν_{CO} 2079 (s), 2022 (s, br) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 6.99 (t, J = 6 Hz, 2H), 6.71 (d, J = 6 Hz, 2H0, 6.61 (t, J = 6 Hz, 1H), 6.26 (s, 1H), 1.99 (s, 2Me). Complexes **7** and **8** were not submitted for elemental analysis because they are a straightforward extension of the previously reported complexes **5** and **6**.

[{Styrene·Pt(PPh$_3$)$_2$}Mn(CO)$_3$]BF$_4$ (9) and Related Complexes. $Pt(PPh_3)_2(C_2H_4)$ (142 mg, 0.19 mmol) was added to a suspension of $[(styrene)Mn(CO)_3]BF_4$ (**5**, 57 mg, 0.17 mmol) in CH_2Cl_2 (20 mL) at room temperature under nitrogen. An immediate color change from yellow to orange-red occurred, and an IR spectrum indicated that the conversion to **9** was complete within a few minutes. The solution was stirred for 1 h and then concentrated. Upon addition of diethyl ether, [**9**]BF_4 precipitated as a yellow powder. Yield: 85% (154 mg). IR (CH_2Cl_2): ν_{CO} 2062 (s), 2003 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.6−6.9 (m, 30H), 6.36 (m, 1H), 5.57 (m, 2H), 5.12 (d, J = 7 Hz, 1H), 4.27 (m, 1H), 3.33 (d, J = 9 Hz, 1H), 2.58 (m, 1H), 2.03 (m, 1H). ^{31}P NMR (CD_2Cl_2): δ 28.17 (dd, J_{P-P} = 23 Hz, J_{P-Pt} = 3510 Hz), 27.17 (dd, J_{P-P} = 23 Hz, J_{P-Pt} = 4250 Hz). Anal. Calcd for $C_{47}H_{38}O_3P_2MnPtBF_4$: C, 53.78; H, 3.65. Found: C, 53.60; H, 3.44.

Coordination of $Pt(PPh_3)_2$ to complexes **6** and **7** was accomplished by the same procedure. For [{α-methylstyrene·Pt(PPh$_3$)$_2$}Mn(CO)$_3$]BF$_4$: yield 92%. IR (CH_2Cl_2): ν_{CO} 2056 (s), 1993 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.5−6.9 (m, 30H), 6.25 (t, J = 6 Hz, 1H), 5.56 (t, J = 6 Hz, 1H), 5.47 (t, J = 6 Hz, 1H), 4.91 (d, J = 7 Hz, 1H), 4.25 (d, J = 6 Hz, 1H), 2.52 (m, 1H), 2.02 (m, 1H), 1.75 (Me). ^{31}P NMR (CD_2Cl_2): δ 28.29 (dd, J_{P-P} = 19 Hz, J_{P-Pt} = 3650 Hz), 25.45 (dd, J_{P-P} = 19 Hz, J_{P-Pt} = 4110 Hz). For [{*cis*-α-methylstyrene·Pt(PPh$_3$)$_2$}Mn(CO)$_3$]BF$_4$: yield 84%. IR (CH_2Cl_2): ν_{CO} 2061 (s), 1999 (s, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.5−7.0 (m, 30H), 6.40 (m, 1H), 6.25 (m, 1H), 5.61 (d, J = 5 Hz, 1H), 5.49 (m, 1H), 5.41 (m, 1H), 4.46 (m, 1H), 1.89 (d, J = 6 Hz, 1H), 1.17 (Me). ^{31}P NMR (CD_2Cl_2): δ 29.28 (dd, J_{P-P} = 28 Hz, J_{P-Pt} = 3950 Hz), 28.69 (dd, J_{P-P} = 27 Hz, J_{P-Pt} = 3770 Hz). Anal. Calcd for $C_{48}H_{40}O_3P_2MnPtBF_4$: C, 54.20; H, 3.79. Found: C, 54.17; H, 3.42.

Coordination of $Pt(PPh_3)_2$ to free styrene was followed by ^{31}P NMR. Upon addition of a 10-fold excess of styrene to $Pt(PPh_3)_2(C_2H_4)$ (30 mg) in CD_2Cl_2 (3 mL, 5 mm NMR tube, N_2), the ^{31}P resonance shifted from δ 36.14 (d, J_{P-Pt} = 3720 Hz) to new resonances at δ 34.30 (dd, J_{P-P} = 55 Hz, J_{P-Pt} = 3790 Hz), 32.22 (dd, J_{P-P} = 55 Hz, J_{P-Pt} = 3730 Hz), which are assigned to $Pt(PPh_3)_2$(styrene). With 1 equiv of styrene, the reaction proceeded about 50% to completion within several minutes, with no change occurring for 1 h thereafter. Similar experiments with α-methylstyrene and *cis*-β-methylstyrene showed no reaction over a period of several hours.

Addition of Pt(PPh$_3$)$_2$(C$_2$H$_4$) to [8]BF$_4$ To Generate 10. To [**8**]BF_4 (40 mg) in CH_2Cl_2 (10 mL) was added $Pt(PPh_3)_2(C_2H_4)$ (1.1 equiv) at room temperature. An immediate color change from yellow to red occurred, and IR analysis indicated complete and clean conversion to [**10**]BF_4. All attempts to isolate [**10**]BF_4 led to its reversion to starting cation, [**8**]BF_4. In situ characterization of [**10**]BF_4: IR (CH_2Cl_2): ν_{CO} 1983 (s), 1783 (s) cm^{-1}. ^{31}P NMR (CD_2Cl_2): δ 33.64 (d, J_{P-Pt} = 4000 Hz), 28.69 (dd, J_{P-P} = 27 Hz, J_{P-Pt} = 3770 Hz).

Crystal Structure of [{Styrene·Pt(PPh$_3$)$_2$}Mn(CO)$_3$]BF$_4$ (9). A single crystal of [**9**]BF_4, grown by vapor diffusion of diethyl ether into a CH_2Cl_2 solution at room temperature, was mounted on a glass fiber. X-ray data collection was carried out using a Siemens P4 diffractometer equipped with a CCD area detector and controlled by SMART version 5 software. Data reduction was carried out by SAINT version 5 software and by SADABS and included profile analysis and an empirical absorption correction. The structure was determined by direct methods and refined on F^2 using the SHELXTL PC version 5 package. Only half of the expected 38 hydrogen atoms appeared in a difference map because the scattering was dominated by the heavier atoms. Each hydrogen was introduced in an ideal position, riding on the atom to which it is bonded; each was refined with an isotropic temperature factor 20%

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greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters. Crystallographic data are provided in Table 1.

Acknowledgment. This work was supported by 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 [**9**]BF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Additions and Corrections

1999, Volume 18

Richard R. Schrock,* Scott W. Seidel, Yann Schrodi, and William M. Davis: Synthesis of Zirconium Complexes That Contain the Diamidophosphine Ligands $[(Me_3SiNCH_2CH_2)_2PPh]^{2-}$ or $[(RNSiMe_2CH_2)_2PPh]^{2-}$ (R = t-Bu or 2,6-$Me_2C_6H_3$).

Page 430. In Table 1 the space group for $[Ar_2NPN]Zr(CH_3)Cl$ should read *Pbca*, *not P*2/*c*.

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