

Carbon–Carbon Bond Activation in Biphenylene. Effect of η^6 -Coordination to Manganese Tricarbonyl

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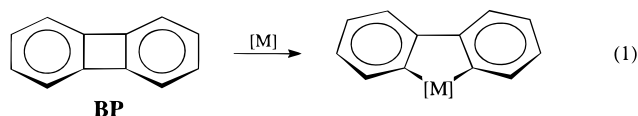
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Summary: Cleavage of a strained C–C bond in the four-membered ring in biphenylene (BP) is enormously facilitated by coordination of the electrophilic fragment $\text{Mn}(\text{CO})_3^+$ to one of the aromatic rings. Thus, the weak nucleophile $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ is inert toward free BP, but reacts within seconds with $[\eta^6\text{-BP}]\text{Mn}(\text{CO})_3^+$ to insert $\text{Pt}(\text{PPh}_3)_2$ into a C–C bond.

Introduction

For both kinetic and thermodynamic reasons, the activation of C–C bonds with transition metal complexes is generally more difficult than is the activation of C–H bonds. For these reasons, oxidative addition or metal insertion into C–C bonds has most often been demonstrated with systems that are predisposed to react because the C–C bond cleavage results in relief of strain or results in a product with increased aromatic character. The activation of *unstrained* C–C bonds has been achieved intramolecularly by precoordination of the metal in such a way that the C–C bond in question is forced into close proximity.¹

Metal insertion into the strained C–C bond of biphenylene (BP) according to eq 1 has been reported with a



number of nucleophilic metal reagents.^{2–7} These include systems based on Ni(0), Pd(0), Pt(0), Co(I), Rh(I), and Ir(I). The results suggest that the reaction is facilitated by increasing the electron density on the metal nucleophile. We became interested in examining how the ease of metal insertion into BP would be influenced by precoordination of one of the aromatic rings to an electrophilic metal fragment. Herein it is shown that C–C bond fission in $(\eta^6\text{-BP})\text{Mn}(\text{CO})_3^+$ (**1**) is enormously accelerated in comparison to that found with free BP.

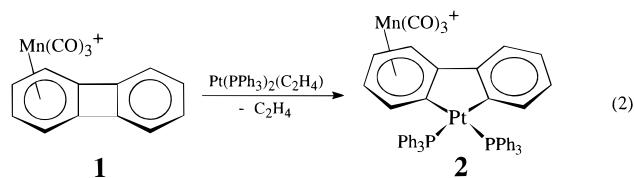
Results and Discussion

To compare the reactivity of free and coordinated BP, we choose the mild nucleophiles $\text{Pt}(\text{PPh}_3)_3$ and Pt

- (1) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 870.
- (2) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Krüger, C.; Tsay, Y. H. *Organometallics* **1985**, *4*, 224.
- (3) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647.
- (4) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Sigalas, M. P.; Eisenstein, O.; Crabtree, R. H. *Organometallics* **1995**, *14*, 1168.
- (5) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016.
- (6) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843.
- (7) Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784.

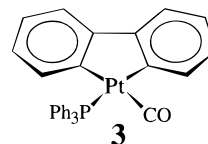
$(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$. Both were found to show no detectable reaction with free BP at room temperature after 24 h in a CH_2Cl_2 solution. This result was anticipated in light of a recent report⁶ that the much stronger nucleophile $\text{Pt}(\text{PEt}_3)_3$ requires 10 days at 80 °C to react according to eq 1 to afford (biphenyl)Pt(PEt₃)₂.

The reactivity of BP was found to change dramatically upon coordination. Thus, **1** reacted with either $\text{Pt}(\text{PPh}_3)_3$ or $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ to give the insertion product **2** according to eq 2. Both nucleophiles reacted so rapidly



at room temperature that the reaction was complete before an IR spectrum could be recorded. This means that the reaction half-life must be less than 30 s. Hence, it may be concluded that the $\text{Mn}(\text{CO})_3^+$ moiety in eq 2 decreases the reaction half-life by many orders of magnitude. In an analogous manner, coordination of $\text{Mn}(\text{CO})_3^+$ to the carbocyclic ring in the stable heterocycles benzothiophene and benzofuran has been shown to greatly accelerate metal insertion into the C–S and C–O bonds, respectively.^{8–10}

Spectroscopic and elemental analysis data (see Experimental Section) provide convincing evidence for the structural formulation of **2** shown in eq 2. In particular, IR and ³¹P NMR data are precisely what would be expected for structure **2**. Attempts to crystallize **2** by diffusing diethyl ether into a dichloromethane solution produced only microcrystals unsuitable for X-ray diffraction studies. After a period of weeks, however, small clear yellow crystals formed that gave a single ν_{CO} band in the IR (2068 cm^{-1} in CH_2Cl_2). X-ray diffraction showed this product to have structure **3**, indicating that



complex **2** had slowly lost a PPh_3 ligand and scavenged a CO from the manganese. It is tempting to suggest that

- (8) (a) Dullaghan, C. A.; Sun, S.; Carpenter, G. B.; Weldon, B.; Sweigart, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 212. (b) Zhang, X.; Dullaghan, C. A.; Watson, E. J.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **1998**, *17*, 2067.

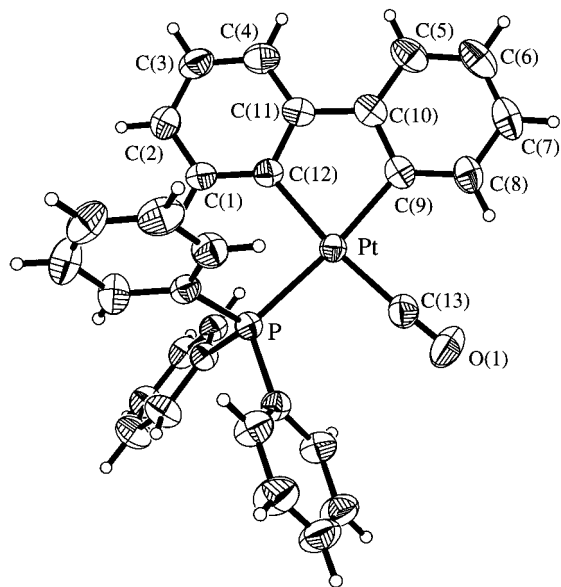


Figure 1. ORTEP drawing of (biphenyl)Pt(CO)(PPh₃) (**3**) with the ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Pt(1)–C(13) 1.917(4), Pt(1)–P(1) 2.3514(9), Pt(1)–C(9) 2.068(4), Pt(1)–C(12) 2.076(4), C(13)–O(1) 1.128(5), C(9)–C(10) 1.416(6), C(10)–C(11) 1.475(5), C(11)–C(12) 1.407(5), Pt(1)–C(13)–O(1) 176.5(4), P(1)–Pt(1)–C(13) 93.13(13), P(1)–Pt(1)–C(12) 94.85(10), C(9)–Pt(1)–C(13) 91.72(17), C(9)–Pt(1)–C(12) 80.58(16), Pt(1)–C(9)–C(10) 114.4(3), Pt(1)–C(12)–C(11) 114.2(3), C(10)–C(11)–C(12) 115.5(3), C(9)–C(10)–C(11) 115.0(3).

this transformation is driven by the relief of steric congestion around the platinum in **2**.

The structure of the air-stable **3** is shown in Figure 1. The biphenyl carbons C(1)–C(12) are nearly planar (mean deviation = 0.039 Å), with a C(9)–C(10)–C(11)–C(12) torsion angle of 1.8(4)°. The platinum is in an approximately planar environment consisting of C(9), C(12), Pt, P, and C(13) (mean deviation 0.072 Å).

The conclusion from the results described above is that metal coordination to an adjacent π -network can be a viable way to electrophilically activate C–C bonds, which can then be cleaved by metal nucleophiles.

Experimental Section

Materials. Standard reagents were purchased from commercial sources and used without further purification. Literature procedures were used to synthesize [(η^6 -biphenylene)Mn(CO)₃]BF₄¹¹ (**1**) and Pt(PPh₃)₂(C₂H₄)¹². ³¹P NMR chemical shifts are relative to 85% phosphoric acid external reference.

Crystal Structure of (Biphenyl)Pt(CO)(PPh₃) (3**).** A single crystal of **3** 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

Table 1. Crystallographic Data for (Biphenyl)Pt(CO)(PPh₃) (3**)**

formula	C ₃₁ H ₂₃ OPPt
fw	637.55
temperature, K	298
wavelength, Å	0.71073
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	9.5309(4)
<i>b</i> , Å	13.2397(5)
<i>c</i> , Å	20.0843(7)
β , deg	102.878(1)
<i>V</i> , Å ³	2470.61(16)
<i>Z</i>	4
<i>d</i> _{calcd} , g cm ⁻³	1.714
μ , mm ⁻¹	5.766
<i>F</i> (000)	1240
crystal dims, mm	0.34 × 0.28 × 0.21
θ range, deg	1.86–28.34
no. of reflns collected	38583
no. of indept reflections	6038 (<i>R</i> _{int} = 0.0834)
no. of data/restraints/params	6038/0/307
GOF on <i>F</i> ²	1.081
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0287, 0.0672
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0370, 0.0733
largest diff peak, hole	0.944 and –1.259 e Å ⁻³

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 of **3** was determined by direct methods and refined on *F*² using the SHELXTL PC version 5 package. Twenty-one of the 23 hydrogen atoms appeared in a difference map. 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% greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters. Crystallographic data are provided in Table 1.

[(Biphenyl)Pt(PPh₃)₂Mn(CO)₃]BF₄ (2**).** Pt(PPh₃)₂(C₂H₄) (82 mg, 0.11 mmol) was added to a suspension of [(η^6 -BP)Mn(CO)₃]BF₄ (40 mg, 0.11 mmol) in CH₂Cl₂ (20 mL) at room temperature under nitrogen. An immediate color change from yellow to orange occurred, and an IR spectrum indicated that the conversion of **1** to **2** was complete in less than 1 min. The solution was then concentrated, and [2]BF₄ precipitated as a yellow powder by the addition of diethyl ether. Yield: 98% (114 mg). IR (CH₂Cl₂): ν_{CO} 2058 (s), 2002 (s, br) cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.7–7.0 (34H, Ph), 6.66 (br, 1H), 6.58 (br, 1H), 6.25 (br, 1H), 5.76 (br, 1H). ³¹P NMR (CD₂Cl₂): δ 26.6 (dd, *J*_{P–P} = 15 Hz, *J*_{P–Pt} = 2487 Hz), 18.9 (dd, *J*_{P–P} = 15 Hz, *J*_{P–Pt} = 1940 Hz). Anal. Calcd for C₅₁H₃₈O₃P₂MnPtBF₄: C, 55.78; H, 3.49. Found: C, 56.00; H, 3.56.

As described above, attempts to grow crystals of [2]BF₄ from CH₂Cl₂/Et₂O led to the isolation of small crystals of **3**. Spectroscopic data for **3** are as follows. IR (CH₂Cl₂): ν_{CO} 2068 (s) cm⁻¹. ¹H NMR (CD₂Cl₂): δ 7.73–7.68 (m, 5H, Ph), 7.65 (d, *J* = 7 Hz, H4), 7.53–7.45 (m, 9H, Ph), 7.40 (d, *J* = 7 Hz, H1), 7.35 (d, *J* = 8 Hz, H5), 7.09 (t, *J* = 7 Hz, H3), 6.93 (t, *J* = 7 Hz, H2), 6.87 (t, *J* = 7 Hz, H6), 6.85 (d, *J* = 7 Hz, H8), 6.37 (t, *J* = 7 Hz, H7). ³¹P NMR (CD₂Cl₂): δ 25.9 (*J*_{P–Pt} = 1811 Hz).

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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

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

(11) Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A. *Chem. Eur. J.* **1997**, *3*, 75.

(12) Nagel, U. *Chem. Ber.* **1982**, *115*, 1998.