Catalytic Hydrogenolysis of an Aryl-Aryl Carbon-Carbon Bond with a Rhodium Complex

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Received December 27, 1993

Recent publications have brought renewed interest to the quest for homogeneous catalytic activation of carbon-carbon bonds.¹ Researchers in the field have often relied on the reactivity of strained cycles² or the increased aromaticity of the product³ to perform C-C bond activation. Unstrained carbon-carbon bonds have been successfully cleaved by directing the metal to the target C-C bond via precoordination of substituted cyclopentadienes.⁴ 8-substituted guinolines,⁵ and bisphosphines.^{1a} However, except for a few reports of biphenylene cleavage,⁶ the mechanism and scope of aryl-aryl C-C bond activation remains relatively uninvestigated. In the hope of overcoming the obstacle of weak $M-C^{\gamma}$ bonds, we used a rhodium system that should provide a thermodynamically favored C-C cleaved complex by making strong metal-aryl bonds.

Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)(H)(1)^8$ with 1.5 equiv of biphenylene in cyclohexane- d_{12} at 65 °C resulted in the quantitative formation of (C₅Me₅)Rh(PMe₃)(biphenylenyl)(H) (2),9 along with a small amount of a red complex (3, vide infra). Unexpectedly, no downfield singlet for an isolated aromatic proton could be found in the 1H NMR spectrum, as would be expected if C-H activation was taking place at the less hindered β position (cf. $(C_5Me_5)Rh(PMe_3)(\beta$ -naphthyl)(H), which displays a singlet at δ 7.69¹⁰), suggesting the formulation of complex **2** as the α C-H activated product. A ¹H-¹H TOCSY of complex 2 revealed two groups of three (δ 6.089, 6.192, 6.606) and four (δ 6.293, 6.416, 6.456, 6.666) mutually coupled resonances, which is consistent with C–H activation in the α position. Electrophilic

(1) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. Nature 1993, 364, 699-701. (b) Evans, W. J.; Keyer, R. A.; Rabe, G. W.; Drummond, D. K.; Ziller, J. W. Organometallics 1993, 12, 4664-4667. (c) Jones, W. D. Nature 1993, 364, 676-677. (d) Chiang, H.-J.; Liu, C.-S. J. Organomet. Chem. 1993, 458, 167-171.

(2) Periana, R. A.; Bergman, R. G. J. Am. Chem. Soc. 1986, 108, 7346-7355 and references therein.

(3) (a) Crabtree, R. H.; Dion, R. P. J. Chem. Soc., Chem. Commun. 1984, 1260–1261. (b) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. J. Am. Chem. Soc. **1986**, 108, 7222–7227 and references therein

(4) (a) Eilbracht, P.; Dalher, P. J. Organomet. Chem. 1977, 127, C48-C50. (b) Eilbracht, P. Chem. Ber. 1976, 109, 3136-3141. (c) Green, M.; Wong, L. J. Chem. Soc., Chem. Commun. 1984, 1442-1443. (d) Baretta, A.; Chong, K. S.; Cloke, F. G.; Feigenbaum, A.; Green, M. J. Chem. Soc, Dalton Trans. 1983, 861-864. (e) Baretta, A.; Cloke, F. G.; Feigenbaum, A.; Green, M. J. Chem. Soc, Chem. Commun. 1981, 156-158. (f) Benfield, F. W.; Green, M. J. Chem. Soc., Dalton Trans. 1974, 1324-1331.

(5) (a) Suggs, J. W.; Jun, C.-H. J. Am. Chem. Soc. 1986, 108, 4679-4681. (b) Suggs, J. W.; Jun, C.-H. J. Chem. Soc., Chem. Commun. 1985, 92–93.
(c) Suggs, J. W.; Wovkulich, M. J.; Lee, K. S. J. Am. Chem. Soc. 1985, 107, 5546-5548. (d) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. Organometallics 1985, 4, 1101–1107. (e) Suggs, J. W.; Jun, C.-H. J. Am. Chem. Soc. 1984, 106, 3054–3056. (f) Suggs, J. W.; Cox, S. D. J. Organomet. Chem. 1981, 221, 199-201.

(6) (a) Becker, S.; Fort, Y.; Vanderesse, R.; Caubere, P. J. Org. Chem. 1989, 54, 4848-4853. (b) Eisch, J. J.; Piotrowski, A. M.; Han, K. I.; Kruger, C.; Tsay, Y. H. Organometallics 1985, 4, 224-231. (c) Lu, Z.; Jun, C.; De Gala, S. R.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. J. Chem. Soc., Chem. Commun. 1993, 1877-1880. (d) Atkinson, E. R.; Levins, P. L.; Dickelman, T. E. Chem. Ind. (London) 1964, 934.

(7) Halpern, J. Acc. Chem. Res. **1982**, *15*, 238–244. (8) Jones, W. D.; Feher, F. J. J. Am. Chem. Soc. **1984**, *106*, 1650–1663. (9) NMR data for **2**: ¹H (C₆D₁₂) δ –13.550 (dd, J_{Rh-H} = 31.6, J_{P-H} = 49.1 Hz, 1 H), 1.195 (d, J = 9.7 Hz, 9 H), 1.850 (d, J = 1.6 Hz, 15 H), 6.089 (d, J = 6.4 Hz, 1 H), 6.192 (d, J = 8.1, 6.6 Hz, 1 H), 6.293 (d, J = 6.4 Hz, 1 H), 6.606 (d, J = 8.1, 6.6 Hz, 1 H), 6.293 (d, J = 6.4 Hz, 1 H), 6.606 (d, J = 8.1, 6.5 Hz, 1 H), 6.606 $(d, J = 8.1 \text{ Hz}, 1 \text{ H}), 6.666 (d, J = 6.6 \text{ Hz}, 1 \text{ H}); {}^{31}P{}^{1}H} (C_6D_{12}) \delta 8.26 (d, J = 6.6 \text{ Hz}, 1 \text{ H});$ J = 152.6 Hz

(10) Jones, W. D.; Dong, L. J. Am. Chem. Soc. 1989, 111, 8722-8723.



Figure 1. ORTEP drawing of (C₅Me₅)Rh(PMe₃)(2,2'-biphenyl) (3), with atoms at 30% probability ellipsoids. Selected distances (Å) and angles (deg) for 3: Rh(1)-C(1) = 2.029(9), C(1)-C(6) = 1.418(12), C(6)-C(6) = 1.396(20), P(1)-Rh(1)-C(1) = 86.4(2), C(1)-Rh(1)-C(1)= 79.4(6), Rh(1)-C(1)-C(6) = 114.7(8), Rh(1)-C(1)-C(2) = 126.2-(8).

substitution of biphenylene reportedly occurs only at the β position,¹¹ while metalation takes place at the α carbon.¹² In this system, C-H activation seems most consistent with the buildup of negative charge on the biphenylene rather than electrophilic attack by the metal. Reaction of biphenylene with an excess of (C₅Me₅)Rh(PMe₃)(Ph)(H) at 65 °C for 12 h resulted in the selective formation of 2, along with unreacted 1.

Complex 2 reacts slowly upon further heating at 65 °C and is completely converted to the dark red complex 3 in 19 days. Only a very small amount of decomposition in the form of $(C_5$ -Me₅)Rh(PMe₃)₂¹³ could be seen by NMR spectroscopy. Complex 3 was purified by fractional crystallization from hexane solution at -20 °C and was characterized by 1H, 31P{1H}, and 13C NMR spectroscopies as the C–C inserted complex $(C_5Me_5)Rh(PMe_3)$ -(2,2'-biphenyl).¹⁴ Further substantiation of this structural assignment came from X-ray crystallography (Figure 1).¹⁵ One of the C-C bonds has been cleaved to form a five-membered metallacycle, giving a symmetrical molecule with a crystallographic mirror plane running through the Rh and the P and bisecting both the C_5Me_5 ring and the coordinated biphenyl. The aromaticity of the latter does not appear to be disturbed except for a slight bend of the ligand toward the PMe₃ group, as evidenced by a dihedral angle of 9.5° between the two aromatic rings. The reaction of 1 with biphenylene carried out at 85 °C was essentially complete in 5 days, with no detectable decomposition.

(11) Cava, M. P.; Mitchell, M. J. Cyclobutadiene and Related Compounds; Academic Press Inc.: New York, 1967; Chapter 10. (12) (a) Blatchy, J. M.; Taylor, R. J. Chem. Soc. **1964**, 4641–4642. (b)

Baker, W.; Boulton, A. J.; Harrison, C. R.; McOmie, J. F. W. Proc. Chem. Soc. 1964, 414.

Soc. 1904, 414. (13) Klingert, B.; Werner, H. Chem. Ber. 1983, 116, 1450–1462. (14) NMR data for 3: ¹H (C₆D₁₂) δ 0.800 (d, J = 9.9 Hz, 9 H), 1.693 (d, J = 2.1 Hz, 15 H), 6.759 (td, J = 7.3, 1.2 Hz, 2 H), 6.868 (t, J = 7.3 Hz, 2 H), 7.302 (d, J = 7.4 Hz, 2 H), 7.354 (dd, J = 7.5, 1.1 Hz, 2 H); ³¹P{¹H} (C₆D₁₂) δ 9.91 (d, J = 160.2 Hz); ¹³C (C₆D₁₂) δ 10.1 (s), 15.1 (d, J = 32.6Hz), 98.6 (s), 120.9 (s), 123.0 (s), 125.5 (s), 136.6 (s), 154.8 (s), 171.1 (dd, $J_{B,C} = 33.1$ Hz, $J_{B,C} = 18.8$ Hz) $J_{P-C} = 33.1 \text{ Hz}, J_{Rh-C} = 18.8 \text{ Hz}).$

(15) Crystals were grown from a solution of 3 in hexane at -20 °C. Crystal (15) Crystais were grown from a solution of 5 in location $a^2 - 2c^2$ (15) crystais were grown from a solution of 5 in location $a^2 - 2c^2$ (14) data for 3: monoclinic space group $P2_1/m$, a = 8.514(2) Å, b = 14.849(4) Å, c = 9.267(3) Å, $\beta = 106.40$ (2)°, V = 1123.9(10) Å³, Z = 2, $d_{calcd} = 1.38$ g/cm^3 . Data were collected at -20 °C utilizing Mo K α radiation ($\lambda = 0.71073$ Å) and 2 θ limits of 4-50°. Hydrogens in the mirror plane were found and used to generate the methyl hydrogens; hydrogens on the biphenyl ring were placed in idealized positions. Final residuals were R = 0.0552 and $R_w = 0.0570$ for 1284 reflections with $F_{o} > 3\sigma(F_{o})$.

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Scheme 1



We believe that this reaction proceeds through a series of C-H activation and η^2 coordination prior to attack of the C-C bond (Scheme 1), as has been suggested in the work of Milstein.^{1a} It is unclear at the present time if C-H activation in the β position takes place prior to the formation of the α C-H activated product 2. During the synthesis of 2, however, ¹H NMR spectroscopy revealed the presence of a minor product (15%) that was found in the $^{1}H-^{1}H$ TOCSY to have two resonances at δ 2.57 and 2.93 coupling to each other and to another peak in the aromatic region, suggesting the involvement of an η^2 coordinated species in the formation of 2.16

The thermal conversion of 2 into 3 in the presence of an excess (7 equiv) of deuterated biphenylene is consistent with an intramolecular rearrangement. Only 50% of the free deuterated biphenylene is incorporated into compound 3, indicating that reductive elimination is competitive with intramolecular C-C cleavage in 2.17 We interpret this result in terms of partitioning of the η^2 complex(es) formed from 2 between dissociation and C-C cleavage (see Scheme 1).

 $(C_5Me_5)Rh(PMe_3)(2,2'-biphenyl)$ was found to be stable toward hydrogenation. Reaction of 3 with 500 Torr of H_2 in C_6D_{12} at 130 °C for several days did not result in the formation of biphenvl and demonstrated the thermal stability of 3, since only very small amounts of decomposition in the form of $(C_5$ -Me₅)Rh(PMe₃)₂ could be seen by ¹H NMR spectroscopy.

However, reaction of 1 with 3 equiv of biphenylene and 500 Torr of H_2 in cyclohexane- d_{12} at 85 °C resulted in the formation of 2, 3, $(C_5Me_5)Rh(PMe_3)(H)_2$ (4),¹⁸ 1 equiv of benzene, and free biphenyl.¹⁹ After 3.5 h, 1 had disappeared and the reaction mixture was mostly composed of free biphenylene and 2 with small amounts (2% each) of 3, 4, and biphenyl. After 70 h. catalytic conversion of biphenylene to biphenyl was obtained and only 3, 4 and biphenyl remained, in a 20:10:70 ratio (eq 1). The

concentration of 4 remained low and constant throughout the reaction until all of the biphenylene was consumed, suggesting that it might be involved in the catalytic cycle. In light of its resistance to hydrogenation, 3 cannot be involved in the formation of free biphenyl and other intermediates must be invoked in this catalytic hydrogenolysis of biphenylene. The mechanism of this reaction is still under investigation, but preliminary results indicate that the catalytic species is indeed the rhodium dihydride complex 4. Biphenylene is catalytically hydrogenolyzed to biphenyl (7 turnovers/7 days) in the presence of a catalytic amount of 4 and H₂ (500 Torr) in cyclohexane- d_{12} at 85 °C (eq 2). Use of D₂

$$\bigcirc \bigcirc \bigcirc \bigcirc + H_2 \xrightarrow{85 \circ C} \bigcirc \bigcirc \bigcirc (2)$$

(620 psi) in place of H_2 resulted in 50% selective deuteration at the α position of biphenyl, consistent with a metal-based hydrogenolysis (the high pressure of D_2 was used to eliminate deuterium exchange in biphenylene prior to hydrogenolysis). Complex 4 has been shown to undergo stepwise hydride exchange with D_2^{20} by initial migration of an hydride ligand to the C₅Me₅ ring. An $\eta^5 \rightarrow \eta^3$ ring slippage has also been proposed to occur, and one of these reactions could be part of the catalytic cycle involving 4.

The cleavage of the well-hidden carbon-carbon bond of biphenylene described here relies both on a strained fourmembered ring²¹ and on the formation of a stable pentametallacycle. The above results already show that C-H activation and η^2 coordination are probably involved in the process leading to C-C bond cleavage, and valuable information can be obtained from studies of this system. Successful understanding of the parameters controlling the mechanism of this reaction may lead to the fall of other, stronger, aryl-aryl carbon-carbon bonds.

Acknowledgment. This work was supported by DOE Grant FG02-86ER13569.

Supplementary Material Available: Table of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters (7 pages); calculated and observed structure factors for 3 (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

^{(16) (}a) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. J. Am. Chem. Soc. 1993, 115, 7685-7695. (b) Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. Organometallics 1992, 11, 871-876.

⁽¹⁷⁾ Reaction of (C₅Me₅)Rh(PMe₃)(biphenylenyl)(H) with 7 equiv of deuterated biphenylene (90% deuteration in the α position) in C₆H₁₂ resulted in quantitative conversion to 3, where the α position was found to be 45% deuterated, indicating that 50% of the C-H activated product had been exchanged through reductive elimination followed by readdition of deuterated biphenvlene.

⁽¹⁸⁾ Reported previously, see: Isobe, K.; Bailey, P. M.; Maitlis, P. M. J. Chem. Soc., Dalton Trans. **1981**, 2003–2008. NMR data in C₆D₁₂: ¹H δ -14.100 (dd, $J_{Rh-H} = 29.7$ Hz, $J_{P-H} = 43.2$ Hz, 2 H), 1.223 (dd, J = 9.7, 1.1 Hz, 9 H), 1.990 (s, 15 H); ³¹P[¹H] δ 7.89 (d, J = 153.8 Hz).

⁽¹⁹⁾ NMR data for free biphenyl: ¹H (C₆D₁₂) δ 7.190 (tt, $J \approx 8.1$, 1.3 Hz, H), 7.289 (t, J = 7.6 Hz, 2 H), 7.464 (d, J = 7.0 Hz, 2 H).
(20) Jones, W. D.; Kuykendall, V. L.; Seimeczy, A. D. Organometallics

^{1991, 10, 1577-1586.}

⁽²¹⁾ The strengh of a C-C bond in this ring was estimated to be 55-60 kcal/mol, which compares to 115 kcal/mol for the aryl-aryl bond of biphenyl.