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Directly Observed Oxidative Addition of a Strong Carbon−Carbon Bond to a Soluble Metal Complex

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Whereas oxidative addition reactions are known for many bonds, examples of metal complex insertion into C−C bonds in solution are rare. Since such a reaction can lead to new, selective approaches to structural modification and functionalization of hydrocarbons and other organic compounds, this area is of much current interest.[1−7] When a metal approaches a hydrocarbon, it first "sees" the more accessible C−H bonds, rendering C−H insertion kinetically more favorable than insertion into the "deep-seated" C−C bond. In order to render the process of C−C insertion thermodynamically favorable, an extra driving force is normally required, such as strain relief,[1,2] the drive to aromaticity in prearomatic systems,[1,3] or the presence of an activating functionality, such as a carbonyl group.[4,5] Carbon−carbon bond cleavage of cyclopentadiene on a ruthenium hydride cluster[6] and of agostic cations formed by protonation of cobalt diene complexes[7] was recently observed.

We have shown that cleavage of a regular, strong C−C bond by transition metal insertion under mild conditions can be rendered thermodynamically favorable by utilization of hydrogen gas, resulting in methane liberation.[8a] Hydrogen was also very recently utilized for effecting catalytic cleavage of the activated C−C bond α to the carbonyl group in ketones[5] and in the strained biphenylene.[2c] Use of reagents other than hydrogen has recently resulted in selective methylene transfer reactions.[8b] A central question is whether oxidative addition of a strong C−C bond to a soluble metal complex (eq 1) can be thermodynamically favorable in the absence of added reagents and, if so, whether it can be thermodynamically more favorable than the competing C−H oxidative addition.

$$M^n + C{-}C \rightarrow C{-}M^{n+2}{-}C \qquad (1)$$

We report here a system that allows, for the first time, the *direct* observation of *oxidative addition of a strong unactivated C−C bond to a metal complex in solution*, including isolation and crystallographic characterization of the insertion product. This insertion takes place into an aryl−methyl bond of a phosphine-functionalized arene. This oxidative addition process is highly dependent on the electron density of the metal center and can be *thermodynamically more favorable than the competing C−H activation process.*

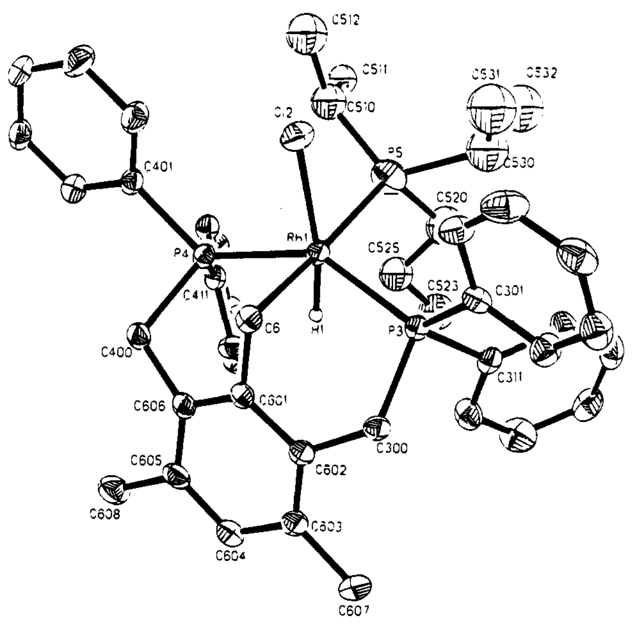
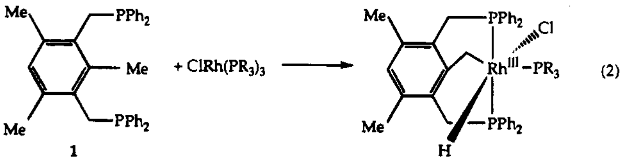


Figure 1. Perspective view (ORTEP) of complex **2b**, showing that the rhodium atom has inserted into a C−H bond. Bond distances (Å) and angles (deg, errors in last digits in parentheses): Rh(1)−C(6) = 2.142(4); C(6)−C(601) = 1.462(6); Rh(1)−P(3) = 2.326(2); Rh(1)−P(4) = 2.344(1); Rh(1)−P(5) = 2.371(2); C(602)−C(300) = 1.498(6); C(602)−C(601) = 1.407(6); C(605)−C(608) = 1.501(6); Rh(1)−C(6)−(C601) = 103.6(3); P(3)−Rh(1)−P(4) = 145.5(4); P(5)−Rh(1)−C(6) = 175.8(1).

Reaction of the aromatic compound **1** with $HRh(PPh_3)_4$ under H_2 leads to a sequence of reactions, resulting in selective cleavage of one of the C−C bonds with methane liberation.[8a] However, the fundamentally important metal insertion into the C−C bond (prior to methane elimination) could not be observed. Aiming at its observation, we have studied the reaction of **1** with $ClRh(PPh_3)_3$. At 25 °C, C−H oxidative addition takes place, quantitatively yielding the Rh(III) hydride **2a**, which was fully characterized spectroscopically[9] (eq 2). An analogous reaction with $ClRh[P(i\text{-}Pr)_2(n\text{-}Pr)]_3$ yields complex **2b**, which was characterized spectroscopically[9] and by X-ray crystallography (Figure 1).[9,10]



(2)

1

2a: $PR_3 = PPh_3$
2b: $PR_3 = P(i\text{-}Pr)_2n\text{-}Pr$

The aromaticity is not distorted in this complex and no interaction between the metal and the aromatic ring is indicated. The P−Rh−P angle of 145.5(4)° is significantly distorted from linearity, while the Rh−C−C angle of 103.6(4)° is fairly normal. Complexes **2a,b** are thermally stable, even at 150 °C.

Remarkably, the analogous reaction of $ClRh(PEt_3)_3$ with the more basic aromatic phosphine **3** at 150 °C results after 6 h in quantitative oxidative addition of one of the C−C bonds to the rhodium center to yield complex **4**[11] (Scheme 1), which was unequivocally characterized spectroscopically.[9] The Rh−Me group appears as a doublet of quartets at −0.30 ppm in ^1H NMR

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[1] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

[2] (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (b) Hemond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239. (c) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647.

[3] (a) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (b) Kang, J. W.; Moseley, R.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970. (c) Benfield, F. W. C.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (d) Eilbracht, P. *Chem. Ber.* **1980**, *113*, 542. (e) Hemond, R. C.; Hughes, R. P.; Locker, M. B. *Organometallics* **1986**, *5*, 2392.

[4] (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054; (b) **1986**, *108*, 4679. (c) Hartwig, J. F.; Anderson, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717.

[5] Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540.

[6] Suzuki, H.; Takaya, Y.; Takemoir, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779.

[7] (a) Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781. (b) Bennett, M. A.; Nicholls, J. C.; Rahman, A. K. F.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328.

[8] (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (b) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42.

[9] See supporting information.

[10] Crystal data for **2b**: $C_{44}H_{55}P_3ClRh + 2.5(C_6H_6)$, fw = 1010.42, yellow, triclinic, P-1 (No. 2), $a = 13.425(5)$ Å, $b = 19.800(7)$ Å, $c = 10.412(5)$ Å, $T = 110(2)$ K, $v = 2553(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.314$ g/cm^3, Mo Kα, 11 846 independent reflections ($R_{int} = 0.0488$), final $R_1 = 0.0682$.

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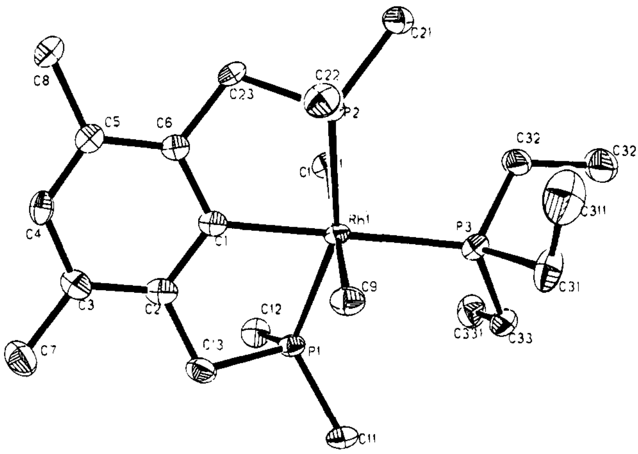
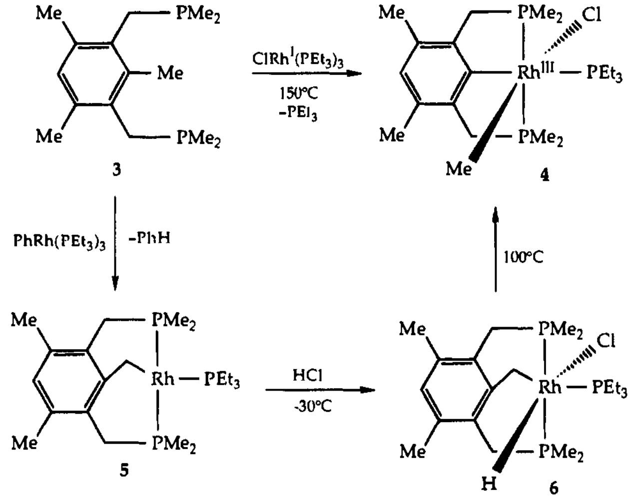


Figure 2. Perspective view (ORTEP) of complex **4**, clearly showing that the rhodium atom has selectively inserted into one of the aryl–carbon bonds. Bond distances (Å) and angles (deg, errors in last digits in parentheses) are Rh(1)–C(1) = 2.094(3); Rh(1)–C(9) = 2.114(3); Rh(1)–P(1) = 2.287(1); Rh(1)–P(3) = 2.372(1); C(1)–C(2) = 1.409(5); C(3)–C(7) = 1.511(5); C(1)–Rh(1)–C(9) = 88.4 (1); C(1)–Rh(1)–P(3) = 178.2(1); P(1)–Rh(1)–P(2) = 157.64(3).

Scheme 1. Direct Insertion of a Rhodium Complex into a C–C Bond and a Reaction Sequence Proving That This Process Is Thermodynamically More Favorable Than Insertion into a C–H Bond



and at −12.9 ppm in ^{13}C NMR. Its *cis* orientation with regard to the aromatic ring is confirmed by an NOE experiment, showing interaction between the Rh–*Me* and P–C*H*$_2$–Ar protons. Finally, the molecular structure of **4** in the solid state was elucidated by an X-ray crystallographic study (Figure 2).[9,12]

This structure clearly shows that the rhodium atom has selectively inserted into one of the Ar–CH$_3$ bonds. The configuration around the rhodium is distorted octahedral. The ligand arrangement is the one expected to be most stable on both steric and electronic grounds. The strongest *trans* director, the methyl ligand, is situated *trans* to the weakest one, the chloride ligand. The strong *trans* influence of the aryl ligand is manifested in the Rh–P$_3$ bond distance being significantly longer than Rh–P$_1$ (or Rh–P$_2$). The Rh–CH$_3$ bond length of 2.114(3) Å is quite normal. This is the first direct observation of metal insertion into a strong unactivated C–C bond in solution.

An important question is whether this complex is thermodynamically more stable than the product of Rh insertion into the C–H (rather than C–C) bond of **3**. Although the thermal stability of **4** suggests that it is so, it does not constitute proof. Since the C–H activation complex could not be obtained directly from **3** and ClRh(PEt$_3$)$_3$,[13] we prepared it by the route presented in Scheme 1. Reaction of **3** with PhRh(PEt$_3$)$_3$ at 80 °C leads to C–H activation with benzene liberation to yield the Rh(I) compound **5**, which was fully characterized.[9] This indicates that C–H activation is *kinetically* favorable in this system. Oxidative addition of HCl to complex **5** generates the fully characterized Rh(III) complex **6**,[9] analogous to complex **2**. Significantly, upon heating at 100 °C, **6** is quantitatively converted into the C–C activation product **4**, unambiguously proving that Rh insertion into the C–C bond in this system is thermodynamically more favorable than its insertion into C–H. This conclusion stems from direct observation of the single mechanistic insertion step. It should be noted that the Ar–C bond in **1** is much stronger than the ArCH$_2$–H bond [compare BDE(C$_6$H$_5$–CH$_3$) = 101.8 ± 2 kcal mol^{-1} vs BDE(C$_6$H$_5$CH$_2$–H) = 88 ± 1 kcal mol^{-1} [14]], indicating that this process is product controlled and that here it is likely that BDE(Rh–Ar + Rh–CH$_3$) > BDE(Rh–CH$_2$Ar + Rh–H).[15] The order of reactivity of various C–H bonds is also dominated by the strength of the M–C bond generated rather than the reactant C–H bond strength.[16]

The fine balance between the observed metal insertion into C–H and C–C bonds is remarkable, with compound **3** resulting in a more stable C–C insertion product, but compound **1**, involving the less basic phenylphosphines, thermodynamically favoring C–H insertion. We believe that, in comparing the relative stability of the C–H and C–C insertion products, it is important to consider the electron density on the metal center. When higher electron density is involved, metal insertion into Ar–CH$_3$ becomes thermodynamically more favorable as compared with insertion into ArCH$_2$–H, perhaps because of the possibility of increased back-bonding from the metal in Ar–M into the aromatic π^* system, which stabilizes the Ar–M relative to ArCH$_2$–M.

In conclusion, we demonstrate here that oxidative addition of a very strong, unstrained C–C bond to a metal complex in solution can be thermodynamically favorable. Moreover, it can be thermodynamically more favorable than the competing C–H bond oxidative addition. There is a fine balance between the C–H and C–C activation processes, which depends strongly on the ligands attached to the metal center. Although demonstrated here for a special case of an Ar–CH$_3$ bond in a phosphino–arene, this work indicates that design of metal complexes that can be directed at will either at C–C or at C–H insertion may be possible.

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Supporting Information Available: Spectroscopic characterization of complexes **2a,b** and **4–6** and text of X-ray crystal structure analysis and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **2b** and **4** (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) No reaction is observed at room temperature or at 90 °C, probably because of the need to displace a PEt$_3$ ligand from ClRh(PEt$_3$)$_3$. Reaction of **1** with [(C$_8$H$_{14}$)$_2$RhCl]$_2$ in the presence of 1 equiv of PEt$_3$ leads to a polymeric mixture.

(12) Crystal data for **4**: C$_{21}$H$_{41}$P$_3$ClRh, fw = 524.81, colorless, rhombic, R$\bar{3}$ (No. 148), a = 26.968(4) Å, b = 26.968(4) Å, c = 18.331(4) Å, T = 110 K, v = 11546(4) Å^3, Z = 18, D_{calcd} = 1.359 g/cm^3, Mo Kα, 5602 independent reflections (R_{int} = 0.0561), final R_1 = 0.0610.

(13) At the temperature required for a reaction between **3** and ClRh(PEt$_3$)$_3$, only C–C insertion is observed.

(14) McMillen, D. F.; Golden, D. M. *Rev. Phys. Chem.* **1982**, *33*, 492.

(15) It should be noted that the different coordination geometries of complexes **4** and **6** (e.g., five- vs six-membered chelate rings) also contribute to the thermodynamic balance. Complex **4** has a less distorted coordination geometry than **6**, as evidenced from a comparison of the X-ray structure of **2b** (analogous to **6**) with that of **4** [e.g., the P–Rh–P angle of 145.4(4)° in **2b** is more distorted from linearity than the P–Rh–P angle in **4** (157.64(3))]. Note, however, that the Rh–C–C angle in **2b** is 103.6(3), almost tetrahedral.

(16) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.