Mild Thermal Activation of Benzene C–H Bonds by Alkene Displacement from a Rhodium Complex

Chanchal K. Ghosh, Damian P. S. Rodgers, and William A. G. Graham*

Department of Chemistry, University of Alberta Edmonton, Alberta, Canada T6G 2G2

Complexes [Rh(HBPz*$_3$)(CO)(η^2-alkene)] (Pz* = 3,5-dimethylpyrazol-1-yl) lose alkene at 70—100 °C in benzene solution forming [Rh(HBPz*$_3$)(H)(Ph)(CO)] in high yield; the equilibrium constant for the reaction with alkene = cyclo-octene is 0.016 at 100 °C.

We reported recently[1] the highly efficient photochemical activation of carbon–hydrogen bonds by dicarbonyltris(3,5-dimethylpyrazol-1-yl)boratorhodium(I), [Rh(HBPz*$_3$)(CO)$_2$], (**1**) (Pz* = 3,5-$Me_2HC_3N_2$). Photochemistry has often been used to eject ligands from appropriate metal complexes, thereby generating high energy unsaturated intermediates such as [W(η-C_5H_5)$_2$],[2] [Ir(η-C_5Me_5)(PMe_3)],[3] [Ir(η-C_5R_5)(CO)] (R = Me, H),[4] or [Fe(dmpe)$_2$] (dmpe = 1,2-bisdimethylphosphinoethane),[5] which will activate C–H bonds. However, these interesting and important reactions shed little light on the overall energetics of the activation. Moreover, from the standpoint of very large scale industrial processes, photochemical reactions are not appealing.

We therefore examined thermal reactions of the trispyrazolylborate complex (**1**). In a closed, foil-wrapped tube, (**1**) activates benzene solvent forming [Rh(HBPz*$_3$)(H)(Ph)(CO)] (**2**).[1] A reasonable rate is achieved only at 140 °C, at which temperature the reaction is complicated by formation of other products, including two binuclear hydrides whose structures have not yet been defined. We accordingly sought a more labile ligand to permit reaction at lower temperatures.

Derivatives of (**1**) in which one carbonyl group has been replaced by an alkene met this requirement, and the new complexes [Rh(HBPz*$_3$)(CO)(η^2-alkene)] (**3a**, alkene = C_2H_4; **3b**, alkene = CH_2CHMe; **3c**, alkene = cyclo-octene) activated benzene cleanly in yields of *ca.* 90% or more in the 70—100 °C range as shown in Scheme 1.†

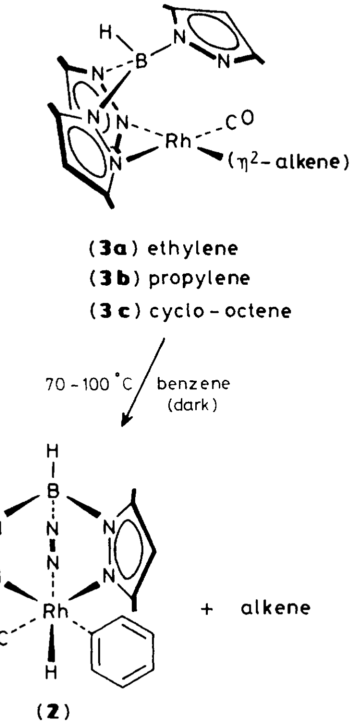
Mixed alkene-carbonyl complexes (**3**) have not been reported. We have prepared them by reaction of KHBPz*$_3$[6] with [Rh(μ-Cl)(CO)(η^2-alkene)]$_2$[7] in the case of (**3a**) or (**3c**), or for (**3b**) by photolysis of a propene-purged cyclohexane solution of (**1**). They are stable, pale yellow crystalline solids which have been fully characterized by analysis (C, H, N) and spectroscopy.‡ Comparison with the corresponding bisdimethylpyrazolylborate complexes shows that they are four-co-ordinate in solution; thus, [Rh($H_2BPz^*_2$)(CO)(η^2-C_2H_4)] has ν_{CO} (n-hexane) 2012 cm^{-1}, only 1 cm^{-1} different from that of (**3a**).

Some years ago, [Rh(η-C_5H_5)(η^2-C_2H_4)$_2$] was observed to catalyse deuterium exchange between ethylene and C_6D_6 solvent at 130 °C;[8] a mechanism involving ethylene loss and solvent activation was proposed. However, activation of an aromatic C–H bond by thermal loss of an electron-pair donor ligand is not a common process, and it usually does not proceed to a measurable extent unless driven by some other energetically favourable step.[9,10] A recent exception is the activation of benzene by [Ir(η-C_5Me_5)(CO)(η^2-NCC$_6H_4$-*p*-Cl)] {5 weeks, 50 °C, 90% yield of [Ir(η-C_5Me_5)(CO)(H)(Ph)]}.[11]

The uniqueness of the latter reaction and of those reported here is that benzene oxidative addition *alone* is enough to drive them to a measurable extent. There is no intervention of other reagents or formation of other products. The energies of M–H and M–Ph bonds formed must to a first approximation compensate for the M–L′ and Ph–H bonds lost in equation (1).

$$[ML_nL'] + Ph\text{–}H \xrightarrow{\text{dark}} [ML_n(H)(Ph)] + L' \qquad (1)$$

For first row transition metals, M–H and M–C bond strengths have been estimated at 250 and 125 kJ, respectively.[12] In [Ir(η-C_5Me_5)(CO)(H)(Ph)], *D*(Ir–H) and *D*(Ir–Ph) have been reported as 310 and 337 kJ respectively.[13] Given *D*(H–Ph) = 460 kJ, we were initially surprised that Scheme 1 proceeded with such high yields and thought it important to verify that an equilibrium was actually involved. The system involving (**3c**), cyclo-octene (COE), and benzene was well suited for this. We have measured the equilibrium constant as 0.016 at 100 °C, approaching it from both directions.§ Although not large, it corresponds to a calculated



Scheme 1

---

† Reactions were carried out in sealed, foil-wrapped n.m.r. tubes or in closed, foil-wrapped Schlenk vessels of total volume *ca.* 45 ml. For (**3a**) (13.2 mM in benzene, 105 °C, 5 days) the yield of (**2**) by n.m.r. was 89%; (**3b**) (29.8 mM, 75 °C, 45 h) 94%; (**3c**) (20 mM, 102 °C, 15 h) 95%.

‡ *Selected spectroscopic data:* i.r. (n-hexane): (**3a**), 2013 cm^{-1}; (**3b**), 2007 cm^{-1}; (**3c**), 2001 cm^{-1}.

§ Starting with (**3c**) (6.9 mM), benzene (11.0 M) and COE (0.195 M) the ratio [**2**]/[**3c**] was 0.91 after 3 h, from which K_{eq} = 0.016. Starting with (**2**) (6.4 mM), benzene (11.0 M) and COE (0.195 M), the ratio was 0.86, from which K_{eq} = 0.015. Ratios were determined from i.r. intensities using extinction coefficients. Beyond 3 h at 100 °C there was a slow irreversible drop in the intensities of ν_{CO} for both (**2**) and (**3c**).

91% conversion of (**3c**) at an initial concentration of 20 mM in pure benzene (11.25 M).

We have also measured the activation enthalpy for reaction of (**3c**) in Scheme 1 as 148 kJ, which sets an upper limit for D(Rh–COE). Assuming that $\Delta S^\circ \cong 0$, we have $\Delta H^\circ \cong \Delta G^\circ_{373} = 13$ kJ, enabling a crude upper limit of 595 kJ to be placed on [D(Rh–H) + D(Rh–C_6H_5)]. This limit may be substantially too high, since Scheme 1 provides a clear example of extensive molecular reorganization complicating an analysis of energetics. In particular, a third pyrazole–rhodium linkage is formed in the reaction, and the larger its contribution, the further D(Rh–H) + D(Rh–Ph) will fall below the stated upper limit.

After 8 days at 75 °C, (**3b**) in pure cyclohexane is converted to one of the binuclear hydrides mentioned above and cyclohexene is formed. This suggests solvent activation, although the primary product [Rh(HBPz*$_3$)(H)(C_6H_{11})(CO)] would not survive this temperature.[1] We are attempting, by the use of more labile ligands, to lower reaction temperatures to the point where the primary products of alkane activation can be identified.

We thank the Natural Sciences and Engineering Research Council (Canada) for financial support through Operating and Strategic Grants.

Received, 3rd June 1988; Com. 8/02217H

References

1 C. K. Ghosh and W. A. G. Graham, *J. Am. Chem. Soc.*, 1987, **109**, 4726.
2 C. Giannotti and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1972, 1114; M. Berry, K. Elmitt, and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1979, 1950.
3 A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; 1983, **105**, 3939.
4 J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3723; J. K. Hoyano, A. D. McMaster, and W. A. G. Graham, *J. Am. Chem. Soc.*, 1983, **105**, 7190.
5 M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1986, **108**, 7433, 7436; 1987, **109**, 2825.
6 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 6288.
7 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1968, 211; Y. S. Varshavskii, T. G. Cherkasova, N. A. Buzina, and V. A. Kormer, *J. Organomet. Chem.*, 1974, **77**, 107.
8 L. P. Seiwell, *J. Am. Chem. Soc.*, 1974, **96**, 7134.
9 K. I. Gell and J. Schwartz, *J. Am. Chem. Soc.*, 1981, **103**, 2687.
10 P. J. Desrosiers, R. S. Shinomoto, and T. C. Flood, *J. Am. Chem. Soc.*, 1986, **108**, 1346, 7964.
11 P. A. Chetcuti and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1987, **109**, 942.
12 J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 238.
13 S. P. Nolan, C. D. Hoff, P. O. Stoutland, L. J. Newman, J. M. Buchanan, R. G. Bergman, G. K. Yang, and K. S. Peters, *J. Am. Chem. Soc.*, 1987, **109**, 3143.

Typeset and printed by Black Bear Press Limited, Cambridge, England