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Efficient and Selective Carbon–Hydrogen Activation by a Tris(pyrazolyl)borate Rhodium Complex

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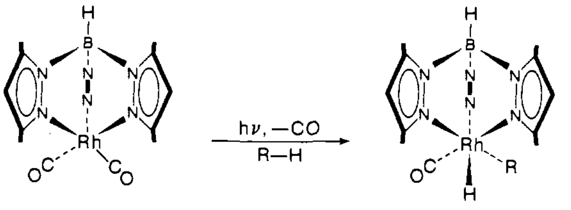
Pyrazolylborate-transition-metal chemistry has developed extensively over 20 years[1] but has not previously intersected the area of carbon–hydrogen activation. We now report that the tris(dimethylpyrazolyl)borato complex (HBPz*$_3$)Rh(CO)$_2$ (**1**, Pz* = 3,5-dimethylpyrazolyl)[2] photochemically activates aromatic and saturated hydrocarbons with great efficiency and high thermodynamic selectivity at room temperature. Unlike previously reported photochemical systems, activation proceeds under daylight or tungsten illumination as well as with use of a mercury arc.



(1)

1

2a : R = C_6H_5
2b : R = cyclohexyl
2c : R = CH_3

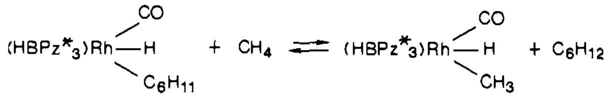
When a pale yellow solution of **1** (ca. 2 mM) in a closed, evacuated Pyrex Schlenk tube was irradiated under standard conditions[3] for 5 min by means of a 450-W Hanovia medium pressure mercury lamp, the solution became colorless, and conversion to the hydridophenyl rhodium(III) complex **2a** according to eq 1 was complete. Under the same conditions, conversion of (η^5-C_5Me_5)Ir(CO)$_2$ to the hydridophenyl complex was only ca. 60% after 6-h irradiation, and there was general degradation at longer times.[3] Activations using (η^5-C_5Me_5)Ir(PMe$_3$)H$_2$ also require long irradiation with a powerful UV source and do not proceed to completion.[4] After 2-h irradiation at a distance of 2–3 cm from an ordinary 75-W incandescent reflector flood light, a benzene solution of **1** (2.9 mM) was >95% converted to **2a**.

Complex **2a** is a moderately air stable colorless crystalline solid, although crystals of X-ray quality have not yet been obtained. The six methyl resonances in the ^{1}H NMR spectrum are consistent with the three nonequivalent pyrazole rings in the octahedral structure; phenyl protons are broad at ambient temperature but sharpen at −20 °C to show five sharp sets of multiplets as rotation about the rhodium–phenyl bond slows. Above room temperature solutions of **2a** in benzene-d_6 undergo exchange forming (HBPz*$_3$)Rh(CO)(D)(C_6D_5) ($t_{1/2}$ = 1.5 h at 60 °C) at a rate similar to that observed for (η^5-C_5Me_5)Rh(PMe$_3$)(H)(C_6H_5).[5]

Irradiation of **1** (ca. 1.8 mM) at room temperature in rigorously purified cyclohexane[6] in an evacuated vessel resulted in partial conversion to the cyclohexyl hydride **2b** (ν_{CO} 2028 cm^{-1} in cyclohexane). Infrared spectra showed complete conversion of **1** to **2b** within 5 min when a N$_2$ or Ar purge was used during photolysis to prevent the back reaction with released CO. In view of its lability and limited stability,[7] **2b** was not isolated but converted with minimum delay by reaction with CCl$_4$ to the chloro derivative (HBPz*$_3$)Rh(CO)(Cl)(C_6H_{11}) (**3**) for full characterization.[8]

Addition of a slight excess of benzene to a freshly prepared cyclohexane solution of **2b** at 25 °C results in its quantitative conversion to **2a** within 10 min. This transformation underlines the lability of **2b** and relative stabilities in the system;[9] **2b** is a remarkably efficient scavenger for aromatic hydrocarbons.

A fresh cyclohexane solution of **2b** (2.2 mM) was prepared with N$_2$ as purge. The lamp was extinguished, and the purge was changed to CH$_4$. After 17 min, the solution exhibited IR bands at 2035 cm^{-1} (assigned to (HBPz*$_3$)Rh(CO)(H)(CH$_3$), **2c**), 2028 cm^{-1} (**2b**), and weak bands of decomposition products.[7] The ratio of absorbances of the 2035- and 2028-cm^{-1} bands was ca. 0.6.[10] Another estimate of the molar ratio **2c**:**2b** was 0.63, obtained from the ^{1}H NMR of the mixture of stable chloride derivatives (HBPz*$_3$)Rh(CO)(Cl)(CH$_3$) (**4**) and **3** resulting from reaction with excess CCl$_4$. At 25 °C, the solubility of CH$_4$ is 0.0302 M,[11] [cyclohexane] is 9.20 M, and whence $K_{eq} \cong 190$ for eq 2. This indicates a reasonably high equilibrium selectivity favoring the primary rhodium–methyl bond and its minimal (though not negligible) steric requirement.[12]



$$(\mathrm{HBPz^*_3})\mathrm{Rh}\overset{\mathrm{CO}}{\underset{\mathrm{C_6H_{11}}}{—}}\mathrm{H} + \mathrm{CH_4} \rightleftharpoons (\mathrm{HBPz^*_3})\mathrm{Rh}\overset{\mathrm{CO}}{\underset{\mathrm{CH_3}}{—}}\mathrm{H} + \mathrm{C_6H_{12}}$$

2b **2c**

As judged from carbonyl-stretching frequencies, the electron richness of **1** (ν_{CO} 2054, 1981 cm^{-1} in hexane) is similar to that of (η^5-C_5H_5)Rh(CO)$_2$ (ν_{CO} 2049, 1986 cm^{-1} in hexane); the averages of the band pairs are identical. The ability of **1** to function with near UV light presumably results from the position of its lowest energy electronic absorption band at 353 nm.[15] High quantum efficiency is also necessary for response to the much less intense incandescent and daylight sources. Although the origin of this efficiency is not yet clear, we speculate that it may involve facile tridentate–bidentate interconversions of the tris(pyrazolyl)borate ligand. It is hoped that experiments in collaboration with Dr. A. J. Rest (University of Southampton) involving **1** in Nujol mulls at 12 K will clarify the primary photoprocess.

On the basis of the foregoing results, we are expanding our investigation of pyrazolylborate complexes and their interaction with hydrocarbons, with rhodium and iridium the current focus. It is now clear that there are the expected similarities[1] to C_5H_5 and C_5Me_5 systems, while preliminary results suggest some

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(7) Monitoring the cyclohexane solution by IR shows the disappearance of **2b** within 2–3 h in the dark at room temperature as new, weaker bands appear at 2048 and 2040 cm^{-1}. This process is under investigation.

(8) Reaction with CCl$_4$ was fast, and yields of isolated **3** after chromatographic purification were 70–75%.

(9) Displacement of alkane by arene in (η^5-C_5Me_5)M(PMe$_3$)(H)(R) complexes appears general. Rates are significant at −17 °C for M = Rh^5 but only above 100 °C for M = Ir.[4c]

(10) Absolute yields of **2c** and **2b** were not accurately determined but were estimated from IR band intensities to account for >90% of **1** used in the reaction.

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(12) With the assumption that $\Delta S° = 0$ in eq 2, $\Delta H° \cong -3$ kcal. By using established values of D(H–CH$_3$) and D(H–C$_6$H$_{11}$),[13] one estimates {D(Rh–CH$_3$) − D(Rh–C$_6$H$_{11}$)} = 13 kcal/mol at 25 °C, a further indication of the variability of D(M–R) with the organic group.[4c,5,14]

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(15) UV (solvent, λ_{max} nm, ϵ). (HBPz*$_3$)Rh(CO)$_2$ (**1**): *n*-hexane, 221 (17600), 353 (1820). (η^5-C_5Me_5)Ir(CO)$_2$: *n*-hexane, 220 (13000), 290 (5500). (η^5-C_5Me_5)Ir(PMe$_3$)H$_2$:[4b] cyclohexane, 259 (1600).

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processes which are unique to the pyrazolylborates.

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Supplementary Material Available: IR, NMR, and analytical data for **2a**, **3**, and **4** (1 page). Ordering information is given on any current masthead page.

Vibrational Circular Dichroism in the Carbon-Hydrogen and Carbon-Deuterium Stretching Modes of (*S*,*S*)-[2,3-$^2H_2$]Oxirane

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We report vibrational circular dichroism[1] (VCD) spectra of (*S*,*S*)-[2,3-$^2H_2$]oxirane (**1**) in the carbon-hydrogen and carbon-deuterium stretching regions. Three- and four-membered chiral ring molecules have been the focus of several previous VCD studies[2-7] owing to their conformational rigidity, low molecular weight, and the relative simplicity of their vibrational spectra. The chiral oxirane featured in this study is the smallest and simplest molecule for which VCD has been observed to date. The observed VCD spectra are correspondingly simple, consisting of a bisignate couplet in each spectral region corresponding to the in-phase and out-of-phase hydrogen, or deuterium, stretching modes. The general features of the couplets are readily interpreted in terms of the coupled oscillator[8] and ring current[9] intensity mechanisms as well as theoretical vibronic coupling calculations.[10] The significance of the reported VCD spectra is that they provide the experimental basis for comparison to the results of the most sophisticated theoretical calculations which can be performed for a molecule as large as oxirane.

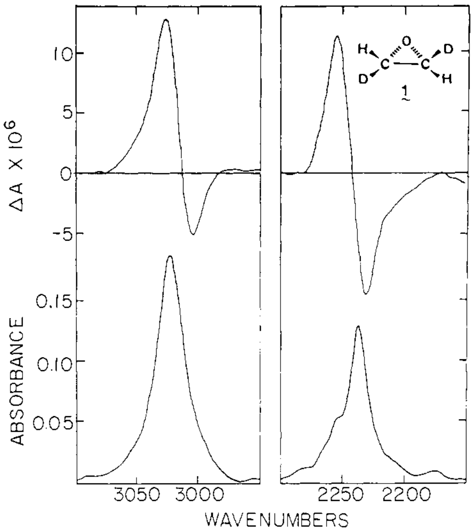

Figure 1. VCD (upper curves) and absorption (lower curves) spectra for (*S*,*S*)-[2,3-$^2H_2$]oxirane in CCl_4 in the CH- and CD-stretching regions, obtained at 8-cm^{-1} resolution with 10-s time constant and 100-μm sample path length.

(*R*,*R*)- and (*S*,*S*)-[2,3-$^2H_2$]oxirane were prepared as described previously,[11] except that 3-(triphenylsilyl)-2,3-epoxypropanol was oxidized to the corresponding aldehyde by using MnO_2[12] rather than Ag_2CO_3/Celite, and a modified version[13] of the Sharpless epoxidation[14] was employed. In the final reaction, 1.00 mmol of (triphenylsilyl)oxirane was treated with Et_4NF in Me_2SO, and the oxirane thus generated was trapped in 1.0 mL of CCl_4 at −18 °C. Enantiomeric excesses were greater than 90%.[15] ^1H NMR analysis of synthetic oxirane revealed the presence of a small amount of benzene (also detected by IR), presumably arising through attack of fluoride on silicon, with expulsion of the phenyl anion.[18]

The VCD spectra shown in Figure 1 represent an average of four scans for each enantiomer obtained on a dispersive VCD instrument.[20] Spectra recorded for samples from two earlier, less pure synthetic batches were similar to those in Figure 1. In order to eliminate base line artifacts, the VCD spectra in Figure 1 were obtained by subtraction of the raw VCD spectra of the (*R*,*R*)-enantiomer from that of the (*S*,*S*)-enantiomer and dividing by two.

Absorption features in the CH-stretching region due to benzene and an unidentified achiral impurity[21] in each synthetic batch were

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