alanine must also involve a step whereby the amino function is converted to a hydroxyl group, the overall transcarboxylation is very similar to the conversion of methylmalonyl coenzyme A to succinyl coenzyme A.[10] This reaction also involves a simultaneous 1,2-migration of a carboxyl group (as a coenzyme A ester) and hydrogen.

Acknowledgment. This work was supported by a research grant (GM 13246) from the National Institutes of Health.

Registry No. 1, 101-31-5; **2**, 51-34-3; **3**, 63-91-2; **4**, 16202-15-6.

(10) Cf. for leading ref: Grate, J. H.; Grate, J. W.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 1588. Retey, J. In "New Comprehensive Biochemistry. Volume 3. Stereochemistry"; Tamm, Ch., Ed.; Elsevier Biochem. Press, 1982; p 261-265.

Rapid Intramolecular Rearrangement of a Hydridocyclopropylrhodium Complex to a Rhodacyclobutane. Independent Synthesis of the Metallacycle by Addition of Hydride to the Central Carbon Atom of a Cationic Rhodium π-Allyl Complex

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Received July 16, 1984

Hydridoalkylmetal complexes (general structure R-M-H) are very sensitive; most undergo decomposition at temperatures substantially below ambient. This ease of decomposition is generally due to rapid reductive elimination of hydrocarbon R-H.[1] We wish to report that hydridocyclopropylrhodium complex **2** (the product of rhodium-based C-H activation of cyclopropane[2]) is unique: like its congeners it decomposes rapidly at temperatures above 0 °C, but it does *not* only regenerate hydrocarbon. Rather, it undergoes a competitive, unprecedented rearrangement to the corresponding C-C insertion product, rhodacyclobutane **3**. In addition, we report (a) that **3** may be prepared independently by treatment of the corresponding π-allyl complex **5** with hydride reagents, to our knowledge only the second system in which nucleophiles add to the center, rather than the end carbon, of a coordinated allyl ligand,[3] (b) the results of an X-ray diffraction study of metallacycle **3**, and (c) preliminary mechanistic results which indicate that the rearrangement of hydride **2** to metallacycle **3** is intramolecular.

Our synthetic results are summarized in Scheme I. As reported earlier,[2] ultraviolet irradiation of $Cp^*(L)RhH_2$ (**1a**) in liquid cyclopropane at −60 °C results in selective formation of hydrido cyclopropyl complex **2**. This material can also be prepared thermally by warming the hydrido *n*-propyl complex[2,4] **1b** to −10 °C in liquid cyclopropane (sealed tube). Upon further warming of **2** in cyclopropane, apparent rearrangement occurs, leading to C-C insertion product **3** in quantitative yield as estimated by ^1H NMR. This material can be obtained in 70% isolated yield as yellow crystals by slow crystallization from pentane at −40 °C. The complex has been fully characterized by spectral and analytical techniques and by X-ray diffraction.[5,6] An ORTEP diagram of the structure is illustrated in Figure 1; it shows clearly that the metallacyclobutane ring is essentially planar and symmetrical about the $Rh-C_{12}$ axis.

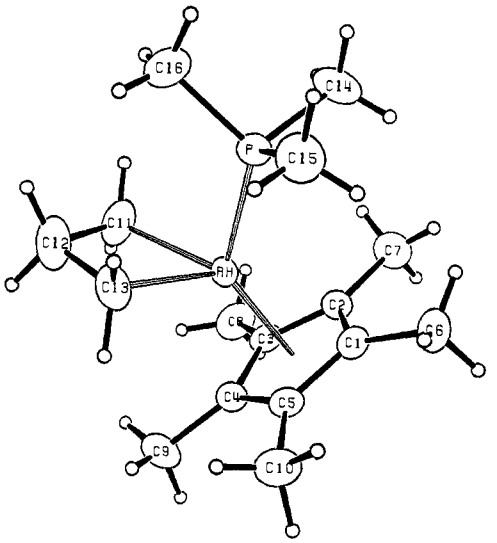
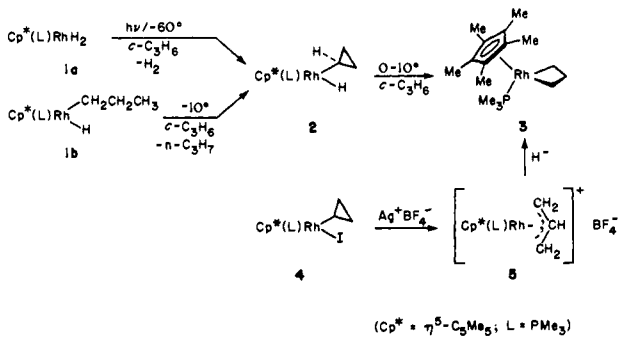
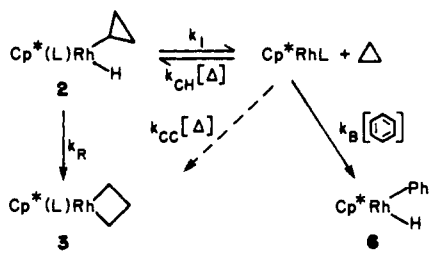


Figure 1. ORTEP diagram illustrating the structure of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(CH_2)_3$ (**3**). Selected bond distances (Å): $Rh-C_{11} = Rh-C_{13} = 2.085$, $C_{11}-C_{12} = 1.512$, $C_{12}-C_{13} = 1.527$. Selected bond angles: $C_{11}C_{12}C_{13} = 99.55°$, $C_{12}C_{13}Rh = 96.24°$, $RhC_{11}C_{12} = 96.59°$, $C_{11}RhC_{13} = 67.61°$.

Scheme I



Scheme II



(1) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396. Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332.

(2) (a) Periana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508. See also: (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(3) The previously reported example of C-2 attack is: (a) Ephretikine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. For an excellent recent discussion of the factors controlling these reactions, see: (b) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887. A recent cyclopropanation reaction that utilizes π-allyl complexes has been postulated to involve a similar type of addition; cf.: (c) Hegedus, L. S.; Darlington, W. H.; Russell, C. E. *J. Org. Chem.* **1980**, *45*, 5193. We thank Dr. J. Stryker for calling this reference to our attention.

(4) (a) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562; (b) *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(5) Selected data for X-ray structure of **3**: space group $P2_1/n$; $a = 10.2713$ (14) Å, $b = 12.9644$ (15) Å, $c = 12.8022$ (21) Å; $\beta = 94.249$ (12)°; $V = 1700.1$ (7) Å^3; $D_c = 1.392$ g cm^{-3}; μ_{calcd} (Mo Kα) = 10.66 cm^{-1}. A total of 2330 reflections were collected; 2206 unique reflections were used to solve the structure by standard least-squares and Fourier techniques. Peaks for all hydrogen atoms were found by using difference Fourier techniques following refinement of the Rh and P atoms with anisotropic thermal parameters. Final residuals for which $F^2 > 3\sigma(F^2)$ were $R = 1.67\%$, $R_w = 2.77\%$, and GOF = 2.001. Full details of the structure determination are provided as supplementary information.

(6) Supplementary information provided with this paper also includes (a) low-temperature (−40 °C) ^1H, ^{13}C, and ^{31}P NMR data for **2** and (b) spectral, analytical, and melting point data for complexes **3**, **4**, and **5**.

0002-7863/84/1506-7272$01.50/0

Halide complexes corresponding to hydride **2** may be prepared by treatment of **2** with haloform at low temperature or by reaction of $Cp^*(L)RhI_2$ with 1 equiv of cyclopropyllithium. Conversion of the iodide **4** to the corresponding π-allyl complex **5** may be achieved[7] by treatment with silver fluoroborate in THF. This salt was isolated in 92% yield as yellow crystals by recrystallization from THF at −40 °C; both ^1H and ^{13}C NMR data[5] are consistent with its formulation as an η^3-allyl structure. Treatment of this material with $NaBH_4$ or $LiEt_3BH$ converted it quantitatively (NMR) to metallacycle **3**. This product was isolated from the latter reaction in 90% yield as yellow crystals by slow recrystallization from pentane; it was completely identical in all spectral characteristics with the sample of **3** obtained from the rearrangement of hydrido cyclopropyl complex **2**. Interestingly, treatment with $LiEt_3BD$ led to metallacycle in which the deuterium atom was selectively syn to the cyclopentadienyl ring.[8] Thus the reaction is both regiospecific and completely stereoselective. This result confirms the recent suggestion of Curtis and Eisenstein that $[(C_5H_5)(L)M(allyl)]^+$ systems might provide a second example of this type of reactivity.[3b,9]

Our observations on the generation and chemistry of hydrido cyclopropyl complex **2** require that the kinetic product of reaction of "Cp*RhL" with cyclopropane is formed by insertion into the strong C–H bonds of the organic molecule, whereas the thermodynamic product is formed by insertion into the relatively much weaker C–C bonds. The simplest mechanism that can account for the conversion of **2** to **3** in cyclopropane solvent (cf. Scheme II) suggests that reversible cyclopropane reductive elimination (k_1)/C–H activation (k_{CH}) takes place above 0 °C. Occasionally, however, C–C insertion (k_{CC}) occurs, leading irreversibly to the much more stable metallacycle **3**. This mechanism predicts that replacing the cyclopropane solvent with benzene, known to react with Cp*RhL with a rate constant k_B twice as large as that of k_{CH} for cyclopropane,[2] should divert the rearrangement entirely to hydrido phenyl complex **6**. Accordingly, we generated hydride **2** in cyclopropane, replaced this solvent at low temperature with benzene,[10] and allowed the system to warm to 0 °C. To our surprise, fully 50% of the hydride had still been converted to metallacycle, the remainder giving cyclopropane and hydrido phenyl complex **6** by reductive elimination.

These results require that at least 50% of the metallacycle formed from **2** cannot arise from free Cp*RhL, because it would have been scavenged quite effectively by benzene in the above reaction. We must conclude that the C_3 fragment and rhodium atom remain associated with one another during the conversion of **2** to **3**; i.e., we are observing a true intramolecular rearrangement (k_R in Scheme II). Several possible mechanisms may account for this. Among the most interesting are the formation of η^2-σ complexes having finite lifetimes and expansion of the three-membered ring in **2** to a hydridorhodacyclobutene intermediate. Labeling studies are under way aimed at distinguishing these possibilities and at seeking C–H to C–C activation rearrangements in other (hopefully less highly strained) systems.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U. S. Department of Energy under Contract DE-AC03-76SF00098. The X-ray structure analysis was performed by Dr. F. J. Hollander of the UC Berkeley X-ray diffraction facility (CHEXRAY). Funds for the analysis were provided by the above DOE contract; partial funding for the equipment in the facility was obtained from NSF Grant CHE79-007027. We thank William D. McGhee for helpful discussions. R.G.B. acknowledges a Sherman Fairchild Scholarship from the California Institute of Technology (Jan–June, 1984).

Supplementary Material Available: NMR spectral data for **2–5**, mass spectral, analytical, and melting point data for **3–5**, and X-ray diffraction data as discussed in the text and a crystal packing diagram (27 pages). Ordering information is given on any current masthead page.

(7) This rearrangement is analogous to that observed with some cyclopropylhaloplatinum complexes. Philips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1970**, 1733.

(8) The orientation of the ^2H atom at position C-2 was determined by a combination of difference NOE and spin-decoupling techniques. We are grateful to Prof. R. H. Grubbs for suggesting these experiments.

(9) A referee has raised the possibility that this reaction may occur by addition of hydride to the metal, leading to a hydridoallylrhodium complex, followed by rearrangement to the metallacycle. We cannot rule this out in the rhodium system. However, in the corresponding $(C_5Me_5)(PMe_3)Ir$ series, we have been able to prepare and isolate the π-allyl cation, as well as the π- and σ-allyl hydrido complexes. The cation mimics its rhodium analogue in generating metallacyclobutane on treatment with H^-; the hydrido allyl complexes do not rearrange to the metallacycle under the H^- reaction conditions and so cannot be intermediates (McGhee, W. D.; Bergman, R. G., unpublished results).

(10) A small amount of toluene was also added to keep the solution from freezing; the toluene concentration was kept low enough that the amount of hydridotolylrhodium complex formed was negligible.

Observation of Two Oxygen Isotope Sensitive Bands in the Low-Frequency Resonance Raman Spectrum of Oxy(phthalocyanato)iron(II)

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Received July 2, 1984

Resonance Raman (RR) spectroscopy has been employed extensively to study the nature of bound dioxygen in oxyhemoglobin (HbO_2), oxymyoglobin (MbO_2), and their model compounds.[1] In 1974, Brunner[2] made the first observation of the $\nu(Fe-O_2)$ (ν, stretch) of HbO_2 at 567 cm^{-1} with 488-nm excitation. Since then, his assignment has been tacitly assumed to explain the cooperativity of oxygen binding[3,4] and the splitting of the $\nu(O_2)$ in IR spectra[5] as well as to confirm the end-on coordination of dioxygen in HbO_2.[6] Similarly, the 537-cm^{-1} band of $CoHbO_2$ was assigned to the $\nu(Co-O_2)$.[7] Recently, this assignment was questioned by Benko and Yu[8] on the basis of the "zigzag" isotope shift pattern which was similar to those observed for the $\delta(FeCO)$ (578 cm^{-1}) (δ, bending) of HbCO and the $\delta(FeNO)$ (551 cm^{-1}) of HbNO.[8] They propose to assign the 567-cm^{-1} band to the $\delta(FeOO)$ rather than the $\nu(Fe-O_2)$. However, they were not able to observe the second oxygen isotope sensitive band which should correspond to the $\nu(Fe-O_2)$. In fact, no workers have thus far observed two oxygen isotope sensitive bands in the low-frequency spectra of oxyhemoproteins. In this communication, we report such an observation in the RR spectra of oxy(phthalocyanato)iron(II), $Fe(Pc)O_2$, and present evidence that provides support for the original assignment by Brunner.

The experimental techniques used for the measurements of RR spectra of $Fe(Pc)O_2$ in O_2 matrices at ~15 K have already been reported.[9] The 676.4-nm line of Kr ion laser was used for excitation. The accuracy of frequency reading was ±1 cm^{-1}. In contrast with the recent report on $Fe(TPP)O_2$,[9] laser irradiation of $Fe(Pc)O_2$ did not produce the ferryl species. Although the $\nu(O_2)$ of $Fe(Pc)O_2$ was observed in IR spectra,[10] it was not observed in

(1) For example, see: Spiro, T. G. In "Iron Porphyrins"; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; Part II, p 91.

(2) Brunner, H. *Naturwissenschaften* **1974**, *61*, 129.

(3) Walters, M. A.; Spiro, T. G.; Suslick, K. S.; Collman, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 6857.

(4) Hori, H.; Kitagawa, T. *J. Am. Chem. Soc.* **1980**, *102*, 3608.

(5) Alben, J. O.; Bare, G. H.; Moh, P. P. "Biochemical and Clinical Aspects of Hemoglobin Abnormalities"; Caughey, W. S., Ed.; Academic Press: New York, 1978; p 607.

(6) Duff, L. L.; Appelman, E. H.; Shriver, D. F.; Klotz, I. M. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 1098.

(7) Tsubaki, M.; Yu, N.-T. *Proc. Natl. Acad. Sci. U.S.A.*, **1981**, *78*, 3581.

(8) Benko, B.; Yu, N.-T. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7042.

(9) Bajdor, K.; Nakamoto, K. *J. Am. Chem. Soc.* **1984**, *106*, 3045.

0002-7863/84/1506-7273$01.50/0