represents an unlikely substance for such terrestrial photosynthetic processes, there are a number of other inorganic semiconductor systems, such as Fe_2O_3 and WO_3,[2] which may be capable of similar reactions. Such processes are currently under investigation in this laboratory.[18]

References and Notes

(1) (a) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978,** *100*, 2239; (b) *ibid.*, 5985.

(2) (a) Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1977,** *99*, 303; (b) *J. Phys. Chem.* **1977,** *81*, 1484.

(3) Kraeutler, B.; Jaeger, C. D.; Bard, A. J. *J. Am. Chem. Soc.* **1978,** *100*, 4903.

(4) Jaeger, D. C.; Bard, A. J., manuscript in preparation.

(5) (a) Miller, S. L. *Science* **1953,** *117*, 528; (b) *J. Am. Chem. Soc.* **1955,** *77*, 2351.

(6) Miller, S. L.; Urey, H. C. *Science* **1959,** *130*, 245.

(7) Produced by irradiation of a suspension of reduced anatase powder in a solution containing $PtCl_6^{2-}$ in a 1:1 mixture of water and acetic acid at pH ~5: Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978,** *100*, 4317.

(8) The standard contained 33 nmol each of the protein amino acids. The relative amounts of amino acids produced in the irradiation experiments follow: NH_3 solution, Gly (1):Glu (0.4):Ser (0.3):Ala (0.2):Asp (0.2); NH_4Cl solution, Gly (1):Glu (1):Ser (0.5):Ala (0.6):Asp (0.7). This identification assumes that amino acids produced by irradiation are those in the protein amino acid standard. Attempts at mass spectral identification of the reaction products are in progress.

(9) Gray, R. C.; Bard, A. J. *Anal. Chem.* **1978,** *50*, 1262.

(10) Anbar, M.; Meyerstein, D.; Neta, P. *J. Chem. Soc. B* **1966,** 742 and references therein.

(11) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 56th Ed.; CRC Press: Cleveland, 1975.

(12) Dickerson, R. E. *Sci. Am.* **1978,** *239*, 70.

(13) Fox, S. W.; Dose, K. "Molecular Evolution and the Origin of Life", Marcel Dekker: New York, 1977.

(14) Recent experiments[15] have shown that amino acid production with irradiation by sunlight is also possible. Thus irradiation of 2 L of a 2 M NH_4Cl solution contained in a Pyrex flask with TiO_2/Pt for 13 days yielded micromole amounts of glycine and alanine, with trace amounts of aspartic acid.

(15) Dunn W.; Bard, A. J., unpublished work.

(16) Krasnovsky, A. A. *Origins Life* **1976,** *7*, 133.

(17) Towe, K. M. *Nature (London)* **1978,** *274*, 657.

(18) The support of this research by the National Science Foundation and Robert A. Welch Foundation and by a grant to H.R. by Heinrich Hertz-Stiftung, Düsseldorf, is gratefully acknowledged.

Harald Reiche, Allen J. Bard*
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received January 8, 1979

Three-Center Oxidative Addition. Formation, Structure, and Dissociation of $(PhCH_2NC)_{12}Rh_3I_2^{3+}$ and Related Cations

Sir:

Although a wide variety of oxidative addition reactions involving low-valent metal complexes have been reported, only a few metal complexes are known to undergo simultaneous two-center oxidative addition. Most of these involve additions to complexes in which the two metal centers are held in fixed, close proximity by bridging ligands. An exception exists in the case of iodine and bromine addition to $(RNC)_4Rh^+$ where, in addition to normal oxidative addition to form $(RNC)_4RhX_2^+$,[2] two-center addition also occurs to form $X(RNC)_4RhRh(CNR)_4X^{2+}$.[3,4] We now report the first case of three-center oxidative addition; this also involves the rhodium isocyanide family of compounds.

Addition of 1 mol of iodine to 3 mol of $[C_6H_5CH_2NC)_4Rh]X$ (X = I or Br) in dichloromethane produces a violet solution from which $[(C_6H_5CH_2NC)_{12}Rh_3I_2]X_3$ is readily crystallized in 85% yield by the addition of cyclohexane. The infrared spectra (ν_{CN} 2236 (sh), 2213 cm^{-1} (X = Br); ν_{CN} 2235, 2209 (X = I) as Nujol mulls) of these salts indicate that only terminal isocyanide ligands are present. Similar compounds, e.g., $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]I_3$ (ν_{CN} 2227, 2205 cm^{-1}), have been obtained by air oxidation of methanol solutions of $[(RNC)_4Rh]I$ in the presence of excess iodide followed by recrystallization from dichloromethane-cyclohexane.

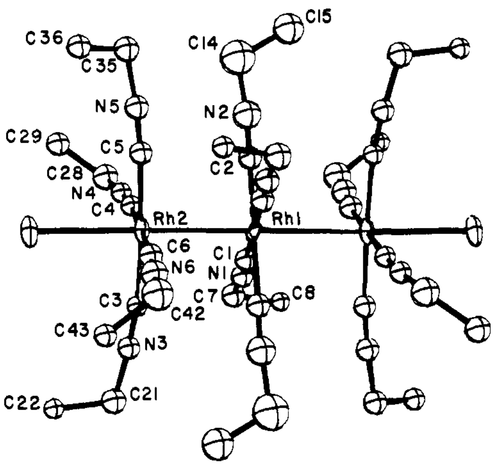


Figure 1. An ORTEP drawing of $[(C_6H_5CH_2NC)_{12}Rh_3I_2]^{3+}$ showing 50% thermal ellipsoids. Bond lengths follow: Rh-Rh, 2.796 (1), Rh-I, 2.761 (1) Å. The Rh-Rh-I angle is 175.5 (1)°. To avoid cluttering of the drawing, only the first carbon atom of each phenyl group has been shown.

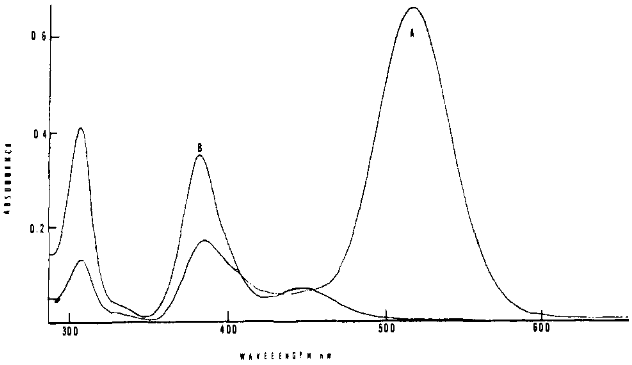


Figure 2. The electronic spectrum of a solution initially containing 7.6 × 10^{-5} M $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]I_3$ in acetonitrile with a 1-mm path length cell: curve A, sample within 5 min of preparation; curve B, after 2 h. The absorption at 525 nm is uniquely associated with $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]^{3+}$. Absorption bands of of pure $(n\text{-}C_4H_9NC)_4Rh^+$ occur at 381 nm (ϵ 11 000) and 309 (36 600), while $(n\text{-}C_4H_9NC)_8Rh_2I_2^+$ has absorption maxima at 448 and 380 nm and $(n\text{-}C_4H_9NC)_4RhI_2^+$ has a maximum at 387 nm (ϵ 11 200).

The structure of one typical salt, $[(C_6H_5CH_2NC)_{12}Rh_3I_2]Br_3$ (**1**) has been determined by X-ray crystallography. Compound **1** crystallizes as violet plates from dichloromethane-cyclohexane in space group $P\bar{1}$ with cell dimensions a = 11.788 (7), b = 12.750 (6), c = 16.095 (6) Å; α = 81.74 (3), β = 81.19 (4), γ = 85.85 (4)°; V = 2364 $Å^3$; ρ_{exptl} (298 K) = 1.54 g cm^{-3}; Z = 1; μ_{Mo} = 25.4 cm^{-1}. A crystal of dimensions 0.050 × 0.35 × 0.425 mm was selected for data collection. A total of 6169 unique reflections were collected at 140 K using a Syntex $P2_1$ automatic diffractometer graphite-monochromatized Mo Kα radiation and a variable-speed ω scan technique. The solution and refinement of data were carried out using Patterson, Fourier, and full-matrix least-squares methods. Refinement using intensity data having $F_o^2 > 3\sigma(F_o^2)$ (4586 reflections) and anisotropic thermal parameters for I, Rh, and Br lead to a conventional R index of 0.073.

The crystal contains the complex cation, which possesses a center of symmetry and is shown in Figure 1, and individual bromide ions. The coordination about each rhodium is pseudooctahedral with four isocyanide ligands at the corners of a square; these squares are staggered 38° from one rhodium to the next. The I-Rh-Rh-Rh-I unit is nearly linear. The Rh-Rh and Rh-I bond lengths are similar those of the related cation,

0002-7863/79/1501-3128$01.00/0

(p-$CH_3C_6H_4NC)_8Rh_2I_2{}^{2+}$ (Rh-Rh, 2.785 (2); Rh-I, 2.735 (1) Å).[4] Despite the fractional oxidation state of rhodium (average value $^5\!/_3$) an electron counting scheme which assigns a simple electron pair bond between each pair of rhodium atoms results in an 18-electron count for each of the metal centers.

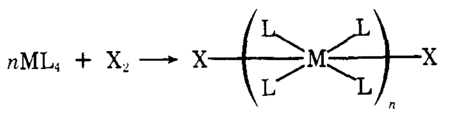
The solution behavior of these cations is complex. It is dominated by dissociation into smaller fragments by the following equations:[5]

$$(\mathrm{RNC})_{12}\mathrm{Rh_3X_2}^{3+} \rightleftharpoons (\mathrm{RNC})_8\mathrm{Rh_2X_2}^{2+} + (\mathrm{RNC})_4\mathrm{Rh}^+ \quad (1)$$

$$(\mathrm{RNC})_8\mathrm{Rh_2X_2}^{2+} \rightleftharpoons (\mathrm{RNC})_4\mathrm{RhX_2}^{+} + (\mathrm{RNC})_4\mathrm{Rh}^+ \quad (2)$$

Dissociation has been monitored by both electronic and infrared spectral changes. The behavior of $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]I_2$ (**2**) is typical. Its electronic spectral changes are shown in Figure 2. The violet color due to the characteristic absorption at 525 nm fades in 2-4 h to give yellow (dichloromethane)[6] or yellow-brown (acetonitrile)[6] solutions containing an equilibrium mixture of $(n\text{-}C_4H_9NC)_8Rh_2I_2{}^{2+}$, $(n\text{-}C_4H_9NC)_4RhI_2{}^+$, and $(n\text{-}C_4H_9NC)_4Rh^+$. The spectra of the equilibrated solutions may be quantitatively reproduced by preparing solutions containing a 2:1 ratio of $[(n\text{-}C_4H_9NC)_4Rh][BPh_4]$ and $[(n\text{-}C_4H_9NC)_4RhI_2][BPh_4]$ at the appropriate concentrations. The dissociation reaction 1 is photoaccelerated; exposure of a 5×10^{-5} M solution of **2** to room light causes the violet color to bleach within 3 min. The infrared spectra of dichloromethane solutions of **2** initially show an isocyanide stretching frequency at 2218 cm^{-1}. As dissociation proceeds, bands at 2229 and 2182 cm^{-1} grow owing to the formation of $(n\text{-}C_4H_9NC)_8Rh_2I_2{}^{2+}$ and $(n\text{-}C_4H_9NC)_4Rh^+$, respectively. Subsequently a fourth band at 2248 cm^{-1} grows owing to the formation of $(n\text{-}C_4H_9NC)_4RhI_2{}^+$. These changes due to dissociation are reversible. Evaporation of dissociated solutions prepared from $[(RNC)_{12}Rh_3I_2]I_3$ yields violet crystals of the starting complex.

The dissociation of $(RNC)_{12}Rh_3I_2{}^{2+}$ may provide a model for the breakup of longer linear chain species such as the partially oxidized platinum cyanides and oxalates.[7,8] In this context it is also interesting to note that electron precise complexes may be generated by addition of a two-electron oxidant such as iodine or bromine across any number of planar d[8] complexes (ML_4) as represented by eq 3. For the rhodium isocyanide system the products have n = 1, 2, or 3 with the composition controlled largely by the stoichiometry of the reactants. For this system the length of the chains which may be prepared is probably limited to n = 3 because of the increase in total charge that accompanies the incorporation of each $(RNC)_4Rh^+$ unit into the chain. For uncharged d[8] complexes with sterically undemanding ligands, however, it should be possible to obtain even longer chains.



(3)

Acknowledgment. This work has been supported by the National Science Foundation. Acquisition of the X-ray diffractometer used in this study was made possible through an National Science Foundation instrument grant.

Supplementary Material Available: A table of atomic positions and thermal parameters (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Examples of ligand bridged complexes which undergo two-center, oxidative addition follow: $(RNC)_4Rh_2(Ph_2PCH_2PPh_2)_2{}^{2+}$, A. L. Balch, *J. Am. Chem. Soc.*, **98**, 8049 (1976); $[R_2P(CH_2)_2]_2Au_2$, H. Schmidbaur, J. R. Mandl, A. Frank, and G. Huttner, *Chem. Ber.*, **109**, 466 (1976); $[CN(CH_2)_3NC]_4Rh_2{}^{2+}$, N. S. Lewis, K. R. Mann, J. G. Gordon II, and H. B. Gray, *J. Am. Chem. Soc.*, **98**, 7461 (1976); $(Ph_2PCH_2PPh_2)_2Rh_2(CO)_2Cl_2$, A. L. Balch and B. Tuylathan, *Inorg. Chem.*, **16**, 2840 (1977).

(2) A. L. Balch and J. Miller, *J. Organomet. Chem.*, **32**, 263 (1971); R. V. Parish and P. G. Simms, *J. Chem. Soc., Dalton Trans.*, 809 (1972); P. R. Branson and M. Green, *ibid.*, 1303 (1972); J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McClevery, *ibid.*, 2039 (1973).

(3) A. L. Balch and M. M. Olmstead, *J. Am. Chem. Soc.*, **98**, 2354 (1976).

(4) M. M. Olmstead and A. L. Balch, *J. Organomet. Chem.*, **148**, C15 (1978).

(5) The independent occurrence of reaction 2 and its solvent dependence has been previously demonstrated in ref 3.

(6) In dichloromethane solution under these dilute conditions little $[(n\text{-}C_4H_9NC)_8Rh_2I_2]^{2+}$ (λ_{max} 448 nm) is present and the solution is yellow, whereas in acetonitrile an appreciable amount of $[(n\text{-}C_4H_9NC)_8Rh_2I_2]^{2+}$ is present and is responsible for the brown color.

(7) H. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).

(8) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976).

Alan L. Balch,* Marilyn M. Olmstead
Department of Chemistry, University of California
Davis, California 95616

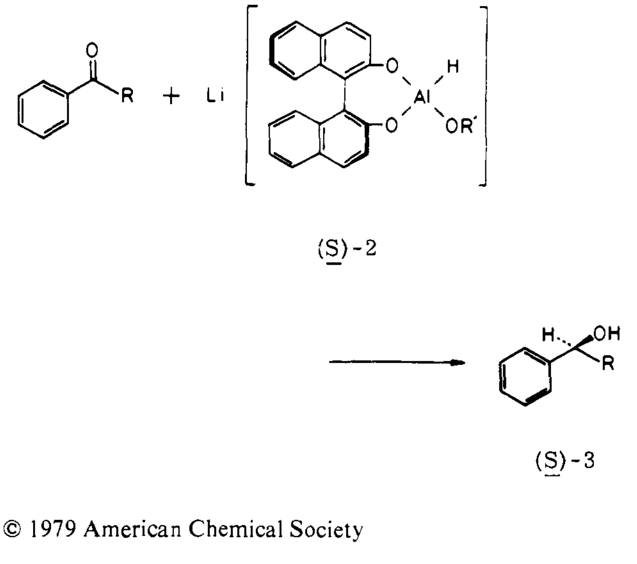
Received January 31, 1979

Virtually Complete Enantioface Differentiation in Carbonyl Group Reduction by a Complex Aluminum Hydride Reagent[1]

Sir:

Based on the pioneering efforts of Cram and co-workers, molecules containing an axially dissymmetric 1,1′-binaphthyl moiety were shown to have extremely high ability of chiral recognition.[2] Here we describe an effective asymmetric reduction of prochiral carbonyl compounds with a hydride reagent containing such chiral auxiliary ligand. In certain cases, the enantioselectivity is virtually complete.

We used complex aluminum hydride reagents of type **2** (empirical formula) prepared in situ from $LiAlH_4$, optically pure 2,2′-dihydroxy-1,1′-binaphthyl (**1**),[3] and a hydroxylic compound (R′OH). A typical experimental procedure is exemplified by the reduction of butyrophenone. To a 1.63 M THF solution of $LiAlH_4$ (8.31 mmol) placed under argon atmosphere was added ethanol in THF (2.00 M, 8.40 mmol) at 0 °C. Then (S)-(−)-**1** ($[\alpha]^{20}{}_D$ −38.0° (c 1.00, THF)) in THF (0.65 M, 8.43 mmol) was added at 0 °C[4] and the resulting white, cloudy mixture was stirred at room temperature for 1 h.[5] The chiral reagent thus formed was cooled to −100 °C and to this was added a 1.00 M THF solution of butyrophenone (2.50 mmol). The mixture was stirred at this temperature for 3 h and then at −78 °C for 16 h and quenched by adding 2 N HCl at −78 °C. Extractive workup with ether followed by evaporative distillation afforded optically pure (S)-(−)-phenylpropylcarbinol ((S)-**3** (R = n-C_3H_7), 291 mg, 78%



0002-7863/79/1501-3129$01.00/0