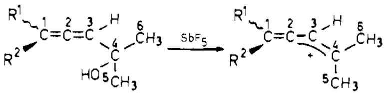
Table I. ^{13}C NMR Chemical Shifts of Vinyl Cations 3a-c and Their Precursors 2a-c[a]



2 3

compd	R^1	R^2	C-1	C-2	C-3	C-4	C-5	C-6	C_1-CH_3
3a	H	H	79.01	241.88	113.68	261.58	32.81	36.91	
3b	CH_3	H	90.34	243.97	114.43	259.16	32.64	36.63	9.46
3c	CH_3	CH_3	101.55	245.39	113.97	257.64	32.43	36.44	16.29
2a	H	H	77.28	205.24	99.90	68.89	29.33		
2b	CH_3	H	88.55	201.28	100.39	69.36	29.52[b]	29.59[b]	13.99
2c	CH_3	CH_3	97.86	197.92	99.01	69.54	29.51		20.10

[a] Specific assignments of C-5 and C-6 in the ions 3a-c tentatively analogous to allyl cations. [b] Assignment tentative.

Table II. Calculated Bond Lengths (Å) and π Densities ρ of Vinyl Cations 3[a]

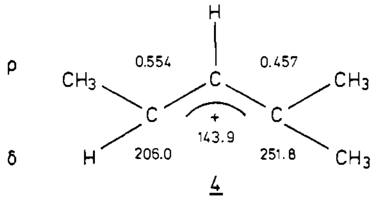
compd	C^1-C^2	C^2-C^3	C^3-C^4	ρ_2	ρ_3	ρ_4
3a	1.285	1.352	1.410	0.543	1.162	0.458
3b	1.287	1.358	1.403	0.518	1.167	0.481
3c	1.289	1.363	1.398	0.496	1.171	0.500

[a] All calculations were carried out with the Gaussian 76 series of programs[14] at the STO-3G basis set level.[15] C-C bond lengths were optimized; standard values were selected for angles and C-H bond lengths.

the electron-deficient orbital at C_2.[12] If corrections for the precursors are considered, 10.8-ppm deshielding of C_2 and 4.6-ppm shielding of C_4 can be attributed to the hyperconjugative electron donation of two methyl groups at C_1. As in ordinary allyl cations, electron donation at one end increases the positive charge at this terminus (C_2) and decreases the charge at the opposite end (C_4).[13]

This interpretation of spectroscopic data is supported by ab initio MO calculations[17] (Table II). The optimized bond lengths show that C_1-C_2 is identical with that in allene (1.288 Å),[16] whereas C_2-C_3 and C_3-C_4 are similar as in allyl cations,[13] in accord with the delocalized structure 3. The positive charge is located at C_2 and C_4, the termini of the allylic cation.

Hyperconjugative electron donation by C_1 methyl groups is also confirmed by the calculations. As derived from the ^{13}C NMR spectra, electron density increases at C_4 and decreases at C_2 when methyl groups are added at C_1. Simultaneously elongation of C_2-C_3 and shortening of the C_3-C_4 bond takes place. In valence bond terminology the contribution of resonance structure 3′ increases from 3a to 3c. Calculated π densities indicate similar charge distributions in cation 3a and allyl cation 4.[13] This is verified by the similarity of the ^{13}C chemical shifts of the tertiary carbons in both species. The other carbons cannot directly be compared, since they are differently hybridized.



4

As part of an allene unit, C_3 and C_2 absorb at higher or lower field, respectively, than the corresponding allyl carbons of 4. C_2 in 3a-c is, to our knowledge, the most deshielded sp hybridized carbon reported so far for carbocations. Experiment and theory are thus in good agreement concerning the delocalized structure of vinyl cations 3a-c.

Acknowledgment. Support of the Deutsche Forschungsgemeinschaft to H.U.S. and the Fonds der Chemischen Industrie to H.M. is gratefully acknowledged.

Registry No. 2a, 34761-53-0; **2b**, 56037-78-6; **2c**, 2424-45-5; **3a**, 80375-40-2; **3b**, 80375-41-3; **3c**, 80375-42-4.

---

[12] Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901.

[13] Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032; **1980**, *102*, 3663.

[14] Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J.; Hehre, W. J.; Newton, M. P. QCPE, Program No. 368, Indiana University.

[15] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

[16] Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5339.

[17] For MO calculations of the unsubstituted and monomethyl-substituted cations, see: Mirejovsky, D.; Drenth, W.; Duijneveldt, F. B. v. *Recl. Trav. Chim. Pays-Bas.* **1979**, *98*, 388.

Preparation, Structural Characterization, and Reactivity of $(PEt_3)_2(CO)Rh$-$Co(CO)_4$. A Quantitative Study of the Reversible Heterolytic Cleavage of the Polar Rh-Co Bond

David A. Roberts,[1a] William C. Mercer,[1a]
Susan M. Zahurak,[1a] Gregory L. Geoffroy,*[1a]
C. W. DeBrosse,[1a] Marion E. Cass,[1b] and
Cortlandt G. Pierpont*[1b]

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802
and the University of Colorado
Boulder, Colorado 80309

Received June 15, 1981

A large number of heteronuclear metal-metal bonded compounds have been prepared and characterized, but relatively few have had their chemistry explored and even less have been shown to express catalytic activity.[2-4] This is surprising in view of the unique reactivity features which should accrue as a result of adjacent metals with differing sets of chemical properties. The lack of catalytic activity appears to be due in part to the absence of open coordination sites or easily dissociable ligands in the complexes examined and the fact that relatively few contain one of the more active second-row metals such as rhodium. Another problem inherent with low-valent metal-metal bonded complexes is their susceptibility to cleavage of the metal-metal bond during reaction.[2,5,6] A number of examples of such cleavage reactions have been reported but little quantitative data are available.[5-10] We describe herein the preparation and characterization of $(PEt_3)_2(CO)Rh$-$Co(CO)_4$ (1), a coordinatively unsaturated polar

---

(1) (a) Pennsylvania State University. (b) University of Colorado.

(2) Roberts, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, in press; Chapter 40.

(3) Gladfelter, W. L.; Geoffroy, G. L., *Adv. Organomet. Chem.* **1980**, *18*, 207.

(4) Vyazankin, N. S.; Razuvaev, G. A.; Kruglaya, O. A. *Organomet. Chem. Rev.* **1968**, *3A*, 323.

(5) Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1.

(6) Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379.

(7) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

(8) Pearson, R. G.; Dehand, J. *J. Organomet. Chem.* **1969**, *16*, 485.

(9) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* **1972**, *36*, 113.

(10) (a) Burlitch, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 4562. (b) *Ibid.* **1969**, *91*, 4563.

0002-7863/82/1504-0910$01.25/0

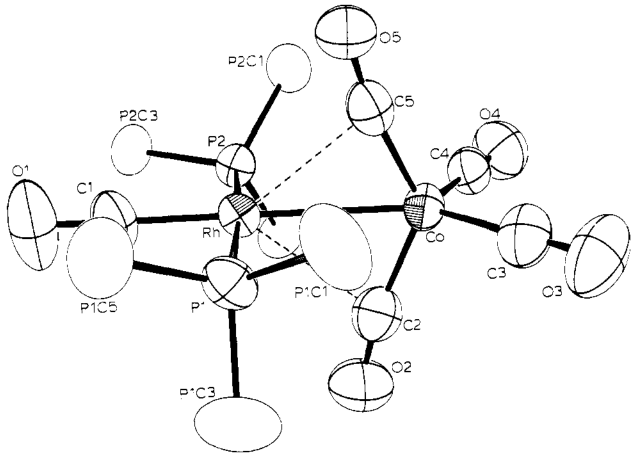


Figure 1. Perspective view of the $(PEt_3)_2(CO)Rh-Co(CO)_4$ molecule. For clarity only the carbons directly attached to the phosphorus atoms are shown. Selected bond lengths (Å): Rh–Co, 2.676 (1); Rh–C(1), 1.811 (7); Rh–P(1), 2.346 (2); Rh–P(2), 2.344 (2); Co–C(2), 1.774 (7); Co–C(3), 1.770 (7); Co–C(4), 1.758 (7); Co–C(5), 1.769 (7). Selected bond angles (deg): Co–Rh–C(1), 178.4 (2); Co–Rh–P(1), 87.1 (2); Co–Rh–P(2), 88.5 (2); P(1)–Rh–P(2), 175.18 (5); C(2)–Co–C(5), 129.1 (3); C(3)–Co–C(4), 107.0 (3).

heterobimetallic complex *which undergoes reversible heterolytic cleavage* of its metal-metal bond in weakly coordinating solvents. The reversibility of the reaction has allowed a quantitative assessment of the kinetic lability of the Co–Rh bond through detailed variable-temperature ^{31}P NMR studies.

The complex $(PEt_3)_2(CO)Rh-Co(CO)_4$ was prepared by the dropwise addition of a tetrahydrofuran (THF) solution of K[$Co(CO)_4$], prepared by the reaction of $Co_2(CO)_8$ (1.00 g; 2.92 mmol) with excess Na/K alloy,[11] to a THF solution of *trans*-$RhCl(CO)(PEt_3)_2$ (1.72 g; 4.28 mmol)[12] (reaction 1), all manipulations being conducted in Schlenk glassware under an N_2 atmosphere. After stirring at 50 °C for 24 h, THF was removed from the resultant red solution, and the residue was extracted with petroleum ether. Cooling this extract to −65 °C gave slightly air-sensitive orange-red crystals of $(PEt_3)_2(CO)Rh-Co(CO)_4$ (1.78 g; 3.30 mmol) in 77% yield.[13]

$$trans\text{-}RhCl(CO)(PEt_3)_2 + K[Co(CO)_4] \rightarrow KCl\downarrow + (PEt_3)_2(CO)Rh-Co(CO)_4 \quad (1)$$

The solid-state molecular structure of **1** is shown in Figure 1.[14] Relevant bond distances and angles are given in the figure caption. The structure is best described as indicated by its synthesis: a $[Co(CO)_4]^-$ substituted derivative of *trans*-$RhCl(CO)(PEt_3)_2$. The geometry about the Rh center is clearly square planar with *trans*-phosphines, typical of d^8-Rh(I) complexes. The geometry of the $Co(CO)_4$ fragment is that of a distorted tetrahedron, consistent with a d^{10}-Co(−I) formulation. Carbonyl bond angles about the Co atom show only small deviations from tetrahedral values with the exception of the C_2–Co–C_5 angle of 129.1 (3)° at the edge of the tetrahedron containing the Rh–Co bond. Carbonyl ligands CO(2) and CO(5) are directed toward the axial coordination sites of the Rh atom with Rh–C_2 and Rh–C_5 distances of 2.555 (8) and 2.466 (6) Å, respectively. The corresponding Co–C_2–O_2 and Co–C_5–O_5 angles are slightly bent, with respective values of 169.4 (2) and 170.0 (5)°. Although these values might suggest a weak interaction of CO(2) and CO(5) with the Rh(I) center,[15] they may be simply a consequence of the tetrahedral structure about Co. The most significant conclusion to be drawn from the structural data for **1** is that the compound is coordinatively unsaturated and is best formulated as possessing a polar metal-metal bond between Rh(I) and Co(−I) centers. This dipolar character is also manifested in the reactivity of the complex.

In every reaction thus far examined for **1** the Co–Rh bond is cleaved to give one product with a Rh(I) center. Treatment of **1** with $[(Ph_3P)_2N]Cl$ leads to an immediate and stoichiometric reaction to give *trans*-$RhCl(CO)(PEt_3)_2$ and $[(Ph_3P)_2N][Co(CO)_4]$, the reversal of reaction 10. The synthesis of **1** was successful because precipitation of KCl from THF solution served to drive the reaction toward products. Compound **1** also reacts rapidly with HCl to give *trans*-$RhCl(CO)(PEt_3)_2$ and $HCo(CO)_4$, (reaction 2).[16] Reaction with MeI in hexane solution slowly leads to *trans*-$RhI(CO)(PEt_3)_2$ and $CH_3Co(CO)_4$, (reaction 3).[16]

$$\mathbf{1} + HCl \xrightarrow[CH_2Cl_2]{25\ ^\circ C} trans\text{-}RhCl(CO)(PEt_3)_2 + HCo(CO)_4 \quad (2)$$

$$\mathbf{1} + CH_3I \xrightarrow[\text{hexane}]{25\ ^\circ C} trans\text{-}RhI(CO)(PEt_3)_2 + CH_3Co(CO)_4 \quad (3)$$

Surprisingly, no net reaction of **1** with H_2 was observed upon heating in isooctane at 90 °C for 6 h under 102 atm of H_2 pressure.

Even weakly nucleophilic solvents readily displace $[Co(CO)_4]^-$ from **1**. In the presence of acetonitrile, the equilibrium shown in reaction 4 is rapidly established.[17] Conductivity measurements

$$(PEt_3)_2(CO)Rh-Co(CO)_4 + CH_3CN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Rh(CO)(CH_3CN)(PEt_3)_2]^+ + [Co(CO)_4]^- \quad (4)$$

in neat acetonitrile gave an average value of $\Lambda = 128\ M^{-1}\ ohm^{-1}\ cm^{-1}$, indicating that **1** is largely dissociated in this solvent.[18] Evaporation of CH_3CN causes reversal of reaction 4 to quantitatively regenerate hexane-soluble **1**.

^{31}P NMR spectral studies also demonstrate the equilibrium shown in reaction 4 but further show that the rates of the reactions involved are surprisingly rapid. The $^{31}P\{^1H\}$ NMR spectrum of **1** in THF-d_8 shows only a temperature-invariant doublet at δ 17.7 ($J_{^{31}P-^{103}Rh} = 107$ Hz) due to intact complex **1**. Addition of CH_3CN to these solutions causes a decrease in intensity in this doublet in the −93 °C $^{31}P\{^1H\}$ spectrum and a new doublet appears at δ

---

[11] Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263. Modified as described in: Steinhardt, P. C.; Gladfelter, W. L.; Harley, A. D.; Fox, J. R.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 332.

[12] Prepared by substituting PEt_3 for PPh_3 in the reported procedure for *trans*-$RhCl(CO)(PPh_3)_2$ (Evans, D.; Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1971**, *11*, 99).

[13] Anal. Calcd for $C_{17}H_{30}O_5P_2CoRh$: C, 37.92; H, 5.58. Found: C, 37.84; H, 5.80. Mass spectrum, *m/e* 538 (parent ion), 510, 482, 454, 426, and 398; IR (hexane solution) 2928 s, 1990 w, 1963 vs, 1953 vs, 1920 m, 1888 s; ^{13}C NMR (CO region) (toluene-d_8 solution, 360-MHz spectrometer) δ 210.3 (br s, $Co(CO)_4$), 180.9 (d of t, $J_{^{13}C-^{103}Rh} = 80$ Hz, $J_{^{13}C-^{31}P} = 16$ Hz, Rh(CO), integrated 4:1 intensity ratio with $Cr(acac)_3$ added as a shiftless relaxation agent; $^{31}P\{^1H\}$ NMR (C_6D_6 solution) δ 17.7 (d, $J_{^{31}P-^{103}Rh} = 107$ Hz). Hz).

[14] Crystals of **1** form in the monoclinic space group $P2_1/c$. Cell constants of $a = 9.294$ (1) Å, $c = 16.575$ (3) Å, $\beta = 104.37$ (1)°, and $V = 2363.2$ (8) Å^3 were obtained from the refined settings of 15 reflections with 2θ settings greater than 20° (Mo Kα radiation). The intensities of 4323 independent reflections were measured by using an automated diffractometer. Of these, 3209 had $F_o^2 > 3\sigma(F_o^2)$ and were included in the refinement of the structure. The locations of the Rh and Co atoms were obtained from a Patterson map. The remaining atoms of the structure were located with phases from these atoms. Least-squares refinement of the complete structure converged with $R = 0.042$ and $R_w = 0.058$. Computer programs and calculational procedures have been described previously: Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636.

[15] Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

[16] The products of these reactions were identified by IR spectroscopy: (a) $HCo(CO)_4$, ν_{CO} (CH_2Cl_2) 2115 w, 2053 m, 2024 s cm^{-1}; this spectrum is identical with that obtained upon HCl acidification of a CH_2Cl_2 solution of $[PPN][Co(CO)_4]$ which gives $HCo(CO)_4$ (see, for example, Steinberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 2717). (b) *trans*-$RhCl(CO)(PEt_3)_2$, ν_{CO} (hexane) 1954 cm^{-1} (lit., ν_{CO} (Nujol) 1953 cm^{-1}: Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1437). (c) CH_3-$Co(CO)_4$, ν_{CO} (hexane) 2108, 2037 cm^{-1} (lit., ν_{CO} (gas phase) 2111, 2036, 1996 cm^{-1}; Hieber, V. W.; Vohler, O.; Brown, G. *Z. Naturforsch. B* **1958**, *13B*, 192. (d) *trans*-$RhI(CO)(PEt_3)_2$ was independently prepared by metathesis of *trans*-$RhCl(CO)(PEt_3)_2$ with NaI in acetone (see, for example: Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1966**, *1437*. Also see ref. 12): ν_{CO} (hexane) 1960 cm^{-1}; $^{31}P\{^1H\}$ NMR δ 20.8 ($J_{^{31}P-^{103}Rh} = 114$ Hz).

[17] $[Rh(CO)(CH_3CN)(PEt_3)_2]^+$ was identified by comparison of its ^{31}P NMR spectrum [(CD_2Cl_2) δ 22.6 (d, $J_{^{31}P-^{103}Rh} = 112$ Hz)] to an authentic sample of $[Rh(CO)(CH_3CN)(PEt_3)_2]PF_6$ prepared by treating RhCl(CO)-$(PEt_3)_2$ with $AgPF_6$ in CH_3CN solution (see, for example: Heras, J. V.; Pinilla, E.; Oro, L. A. *Trans. Met. Chem.* **1981**, *6*, 45).

[18] Under the same experimental conditions an acetonitrile solution of $[(C_4H_9)_4N]Br$ gave an average value of $\Lambda = 127\ M^{-1}\ ohm^{-1}\ cm^{-1}$. The concentrations of **1** and $[(C_4H_9)_4N]Br$ in these experiments were both 1.9×10^{-3} M.

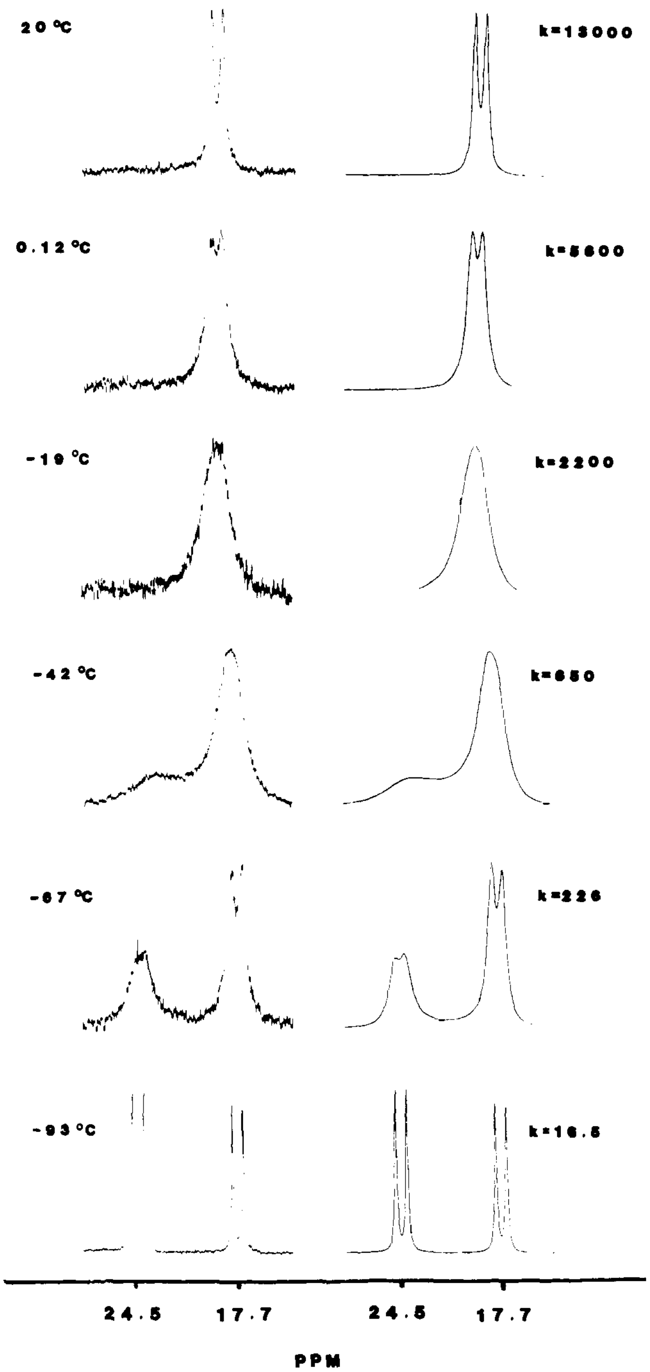
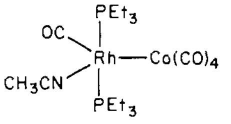


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $(PEt_3)_2(CO)$-Rh–$Co(CO)_4$ in THF-d_8 solution that is also 0.77 M in CH_3CN. Experimental spectra are shown on the left and the computer-simulated spectra are on the right. The rates given are the k_{obsd} values for the **1** $\rightleftharpoons$ $[Rh(CO)(CH_3CN)(PEt_3)_2]^+$ interconversion.

24.5 ($J_{^{31}P-^{103}Rh}$ = 110 Hz) which is attributed to $[Rh(CO)(CH_3CN)(PEt_3)_2]^+$. The relative intensity of the latter is directly proportional to CH_3CN concentration, as expected from reaction 4. Variable-temperature $^{31}P\{^1H\}$ NMR spectra obtained for a 0.039 M solution of **1** in THF-d_8 which is also 0.77 M in CH_3CN are shown in Figure 2. As the temperature is raised, the resonances due to **1** and $[Rh(CO)(CH_3CN)(PEt_3)_2]^+$ broaden, coalesce, and by 20 °C have sharpened into a single doublet at δ 19.4 ($J_{^{31}P-^{103}Rh}$ = 109 Hz), implying an average rhodium-phosphorus environment and rapid interconversion between these two species. Similar $^{31}P\{^1H\}$ NMR changes occur in CH_3CN (0.77 M)/CD_2Cl_2 solution.

Computer simulation of the spectra shown in Figure 2 has allowed a determination of the rate constants k_1 and k_{-1} and the equilibrium constant, K_{eq}, at each temperature for reaction 4, and from these data thermodynamic and activation parameters have been derived.[19] For the forward reaction of reaction 4 in the CH_3CN/THF-d_8 solvent system, $\Delta H°_{298} = -9.1 \pm 0.3$ kJ mol^{-1} and $\Delta S°_{298} = -81 \pm 3$ J mol^{-1} K^{-1} with $K_{eq} = 3.35 \times 10^{-3}$ at 20 °C. The large negative $\Delta S°$ value must be due to the increased organization of solvent molecules necessary to solvate the $[Rh(CO)(CH_3CN)(PEt_3)_2]^+$ and $[Co(CO)_4]^-$ ions which form as reaction 4 proceeds to the right. Similar large negative $\Delta S°$ values have been observed in replacement of halides by neutral ligands in planar Pt(II) complexes.[20] The more negative $\Delta S°$ value in CH_3CN/THF (−81 J mol^{-1} K^{-1}) compared to a similar concentration CH_3CN/CD_2Cl_2 solution (−50 ± 2 J mol^{-1} K^{-1}) probably reflects the greater solvating ability of THF compared to CD_2Cl_2. This increased solvation is also reflected in the slightly more negative $\Delta H°$ value obtained in CH_3CN/THF (−9.1 kJ mol^{-1}) compared to CH_3CN/CD_2Cl_2 (−2.7 ± 0.4 kJ mol^{-1}).

Preliminary kinetic data show an approximate first-order dependence of the rate of the forward reaction on both CH_3CN and **1** concentrations, implying an associative mechanism directly involving CH_3CN.[21] A short-lived intermediate such as **2** presumably obtains in both the forward and reverse reactions of reaction 4 and decays to products via loss of CH_3CN or $[Co(CO)_4]^-$. The rate constants obtained from analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra show that the rates of the reactions involved in equilibrium 4 are remarkably fast. At 20 °C in the CH_3CN/THF-d_8 solvent system, for example, $k_1 = 1.7 \times 10^4$ M^{-1} s^{-1} and $k_{-1} = 5.1 \times 10^6$ M^{-1} s^{-1}. It would be interesting to compare the rate of $[Co(CO)_4]^-$ displacement from **1** with displacement of Cl^- from *trans*-$RhCl(CO)(PEt_3)_2$ by CH_3CN, but such data do not appear to be available. A brief qualitative report does suggest that the latter reaction is fast.[22]



2

In summary, this study has shown that (i) $(PEt_3)_2(CO)Rh$-$Co(CO)_4$ possesses a polar metal–metal bond which structurally and chemically is best described as a Rh(I)–Co(−I) complex in which the $[Co(CO)_4]^-$ group behaves as a pseudohalide, (ii) the Rh–Co interaction is relatively weak, with $[Co(CO)_4]^-$ being easily displaced by weakly nucleophilic solvents, and (iii) the rate of metal–metal bond cleavage in **1** is remarkably fast. The latter observation has important implications in the potential use of metal–metal bonded compounds similar to **1** as catalysts, since reversible metal–metal bond cleavage could easily be competitive with individual reaction steps in an overall catalytic transformation. The further chemistry of **1** and other coordinatively unsaturated

---

[19] Representative data from the NMR analysis of spectra obtained in CH_3CN/CD_2Cl_2 and CH_3CN/THF-d_8 solutions and the thermodynamic and activation parameters which have been derived from these data are, respectively, given in Tables A and B of the supplementary material. The log K_{eq} vs. T^{-1} van't Hoff plot for the data obtained in CH_3CN/THF-d_8 solutions is linear over the −93–20 °C temperature range but deviates from linearity at higher temperatures. Accordingly, only the −93–20 °C data were used in the analysis reported herein; studies are continuing to determine the reason for the nonlinear van't Hoff plot in the high-temperature regime.

[20] (a) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967. (b) Mureinik, R. J. *Coord. Chem. Rev.* **1978**, *25*, 1. (c) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965.

[21] The rate equation generally applicable to substitution reactions of square-planar complexes is rate = $\{k_s + k_y[Y]\}$[complex].[20] Preliminary kinetic data indicate that k_s for the solvent-assisted path is small. For example, k_{obsd} = 36 s^{-1} for $[CH_3CN]$ = 0.508 M and 57 s^{-1} for $[CH_3CN]$ = 0.755 M. The ratio of k_{obsd} for these two experiments is 0.63 and compares well with the 0.67 $[CH_3CN]$ ratio. The second-order rate constants k_1 and k_{-1} given in Table A (supplementary material) were derived by assuming k_s = 0 and dividing the k_{obsd} values by the concentrations of CH_3CN and $[Co(CO)_4]^-$, respectively. These were determined from the unknown quantities of CH_3CN and **1** added to the solution, the relative concentrations of **1** and $[Rh(CO)(PEt_3)_2(CH_3CN)]^+$ from the NMR population analysis, and by assuming $[Co(CO)_4^-]$ = $[Rh(CO)(PEt_3)_2(CH_3CN]^+$ (reaction 4).

[22] Gray, H. B.; Wojcicki, A. *Proc. Chem. Soc. London* **160**, 358.

dinuclear complexes of Rh(I) is currently being explored in our laboratory and will be reported in detail in future publications.

Acknowledgment. This research was supported in part by the Office of Naval Research and a grant from the Standard Oil Company (Ohio). G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar award (1978-1983). Research at the University of Colorado was supported by the Department of Energy through the Solar Energy Research Institute. High-field ^{31}P NMR spectra were obtained using a Bruker Instruments WM-360, which was purchased through a grant from the National Institutes of Health (GM-27525).

Supplementary Material Available: Tables of kinetic and equilibrium data and thermodynamic and activation parameters for reaction 4 and a listing of atomic positional and thermal parameters for $(PEt_3)_2(CO)Rh-Co(CO)_4$ (3 pages). Ordering information is available on any current masthead page.

Biosynthetic Source of Oxygens in Griseofulvin. Spin-Echo Resolution of ^{18}O Isotope Shifts in ^{13}C NMR Spectroscopy[†]

Martin P. Lane, Thomas T. Nakashima, and
John C. Vederas*

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

Received October 13, 1981

Griseofulvin (**1**) is a commercially important antifungal antibiotic from *Penicillium* species[1] which has antimitotic[2] and porphyrogenic[3] activity. These biological effects and its unusual spiro structure have inspired a number of elegant syntheses[4] and biosynthetic studies.[5] However, despite the emergence of a coherent biogenetic picture displayed in Scheme I which is supported by incorporation of advanced precursors into griseofulvin (**1**),[5d,e] the possibility persisted that some of the proposed intermediates represent shunt metabolites[6] because of lack of knowledge about intermediate oxidation states. Although the development of ^{13}C NMR spectroscopy has greatly advanced our understanding of Nature's assembly of complex carbon skeletons from simple precursors,[7] the exact sequence and mechanism of oxidative and reductive transformations have frequently remained obscure, primarily due to inability to easily detect functional group changes during biosynthesis. Fortunately, partial conquest of this problem now seems imminent with the arrival of two new methodologies: ^{2}H NMR spectroscopy[5b,8] and detection of ^{18}O labels by upfield

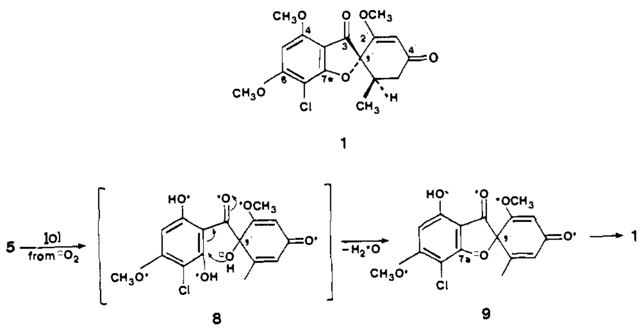
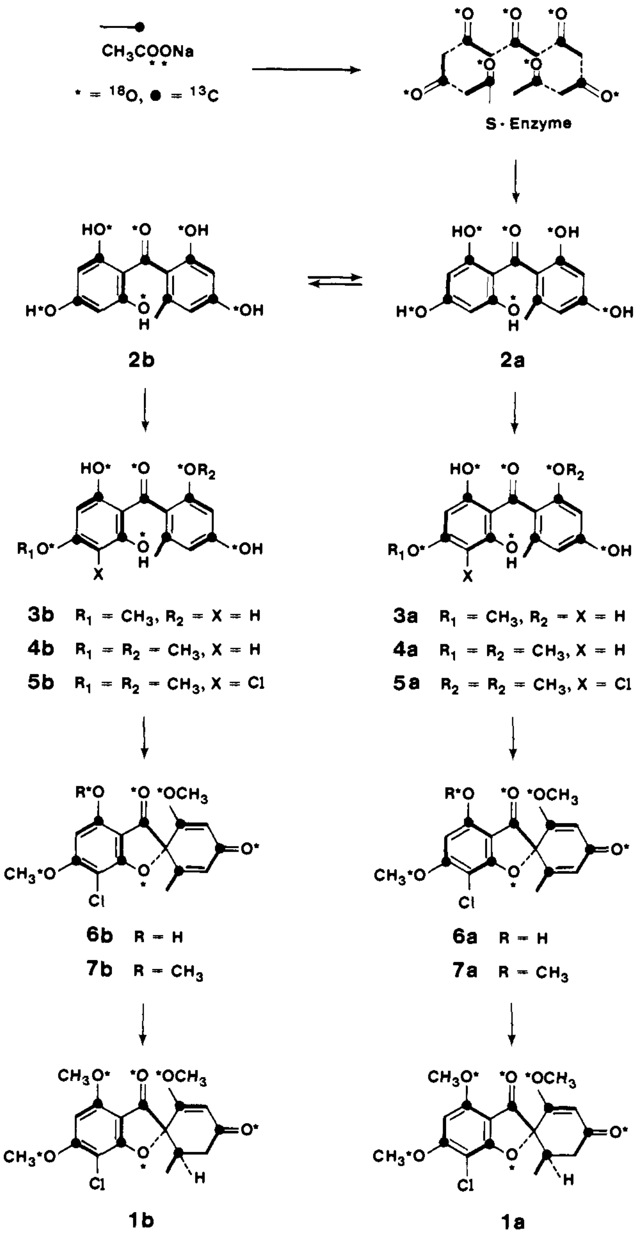


Figure 1.

Scheme I



[†] Dedicated to Professor George H. Büchi, Massachusetts Institute of Technology.

(1) For reviews, see: (a) Grove, J. F. *Fortschr. Chem. Org. Naturst.* **1964**, *22*, 203-264. (b) Huber, F. M. "Antibiotics", Corcoran, J. W., Hahn, F. E., Eds.; Springer Verlag: New York, 1975; Vol. 3, pp 606-613. (c) Wade, A., Ed. "Martindale: The Extra Pharmacopoeia, 27th Ed."; Pharmaceutical Press: London, 1977; pp 634-637.

(2) David-Pfeuty, T.; Simon, C.; Pantaloni, D. *J. Biol. Chem.* **1979**, *254*, 11696-11702 and references therein.

(3) (a) Denk, H.; Kalt, R.; Abdelfattah-Gad, M.; Meyer, U. A. *Cancer Res.* **1981**, *41*, 1535-1538. (b) De Matteis, F.; Gibbs, A. H. *Biochem. J.* **1980**, *187*, 285-288.

(4) (a) Danishefsky, S.; Walker, F. J. *J. Am. Chem. Soc.* **1979**, *101*, 7018-7020. (b) Stork, G.; Tomasz, M. *Ibid.* **1964**, *86*, 471-478. (c) Taub, D.; Kuo, C. H.; Slates, H. L.; Wendler, N. L. *Tetrahedron* **1963**, *19*, 1-17. (d) Day, A. C.; Nabney, J.; Scott, A. I. *J. Chem. Soc.* **1961**, 4067-4074. (e) Brossi, A.; Baumann, M.; Gerecke, M.; Kyburz, E. *Helv. Chim. Acta* **1960**, *43*, 2071-2082.

(5) For leading references, see: (a) Birch, A. J.; Massy-Westropp, R. A.; Rickards, R. W.; Smith, H. *J. Chem. Soc.* **1958**, 360-365. (b) Sato, Y.; Oda, T.; Miyata, E.; Saito, H. *FEBS Lett.* **1979**, *98*, 271-275. (c) Simpson, T. J.; Holker, J. S. E. *Phytochemistry* **1977**, *16*, 229-233. (d) Harris, C. M.; Roberson, J. S.; Harris, T. M. *J. Am. Chem. Soc.* **1976**, *98*, 5380-5386. (e) Rhodes, A.; Somerfield, G. A.; McGonagle, M. P. *Biochem. J.* **1963**, *88*, 349-357.

(6) Brown, S. A. *Biosynthesis* **1972**, *1*, 1-40.

(7) Wehrli, F. W.; Nishida, T. *Prog. Chem. Org. Nat. Prod.* **1979**, *36*, 1-229.

(8) For some recent examples, see: (a) Garson, M. J.; Staunton, J. *Chem. Soc. Rev.* **1979**, 539-561. (b) Bardshiri, E.; Simpson, T. J. *J. Chem. Soc., Chem. Commun.* **1981**, 195-196. (c) Hutchinson, C. R.; Sherman, M. M.; McInnes, A. G.; Walter, J. A.; Vederas, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5956-5959.

0002-7863/82/1504-0913$01.25/0