Registry No. 1, 56792-69-9; 2, 78955-19-8; 2-d_2, 87226-32-2; 3, 87226-33-3; 4, 13682-07-0; 5, 40747-34-0; 6, 13682-03-6; 7, 87226-34-4; 8, 87226-35-5; 9, 87207-14-5; 10, 917-92-0; 11, 75-83-2; 12, 926-36-3; $Co_2(CO)_8$, 10210-68-1; (η^5-C_5H_5)$Mo(CO)_3H$, 12176-06-6; $Co_2(CO)_6(HCCCH_2CH_2CCH)Co_2(CO)_6$, 78724-77-3; *t*-$BuCDCH_2$, 87207-16-7; $Co_2(CO)_6(HCCC(CH_3)_2CH_2CH_3)$, 87207-15-6; $Co_2(CO)_6(HCCPh)$, 12154-91-5; $Co_2(CO)_6(HCCC)$, 59954-60-8; 3,3-dimethyl-1-butyne, 917-92-0; 1,5-hexadiyne, 628-16-0.

(μ-Bicarbonato)bis(μ-methylene)bis(pentamethylcyclopentadienyl)dirhodium Tetrafluoroborate (Synthesis and X-ray Structure) and Related Complexes

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Summary: Reaction of *trans*-[$(C_5Me_5Rh$-μ-$CH_2)_2Cl_2$] with Na_2CO_3 gives the *cis*-μ-carbonato complex [$(C_5Me_5Rh$-μ-$CH_2)_2CO_3$]. This is protonated in acid to give the *cis*-μ-bicarbonato salt [$(C_5Me_5Rh$-μ-$CH_2)_2HCO_3$]BF_4, characterized by an X-ray structure determination; with more acid, CO_2 is lost to give the trans-diaqua dication [$(C_5Me_5Rh$-μ-$CH_2)_2(H_2O)_2$]$^{2+}$. The ^1H NMR spectra show the methylene bridges to be retained throughout these transformations.

We have noted on several occasions the ability of pentamethylcyclopentadienyl, when attached to rhodium, of stabilising bonds to formally hard ligands such as oxygen donors.[1-7] This may be related to the ability of C_5Me_5Rh to support ligands in complexes of unusually high oxidation states, e.g., Rh(IV)[8] or Rh(V).[9,10] Presumably this is because the C_5Me_5 ligand can act as a very effective electron reservoir and can thus respond to high electronic demand by the metal and the other ligands.

We here report that the dichlorobis(μ-methylene)dirhodium(IV) complex (1)[11] reacted readily with an excess of sodium carbonate in methanol (30 min, 20 °C) to give the yellow neutral *cis*-(μ-carbonato)bis(μ-methylene)dirhodium complex (2) in 79% yield, after crystallization from cold benzene. Complex 2 also dissolved in water; on addition of concentrated fluoroboric acid to an aqueous solution of 2 pale orange crystals of *cis*-(μ-bicarbonato)bis(μ-methylene)bis(pentamethylcyclopentadienyl)dirhodium tetrafluoroborate hydrate (3) precipitated in 44% yield. The complexes were identified by microanalysis[13] and spectroscopically.[14] The ^1H NMR spectrum in particular showed the characteristic pattern, of a higher field doublet and a lower field multiplet, for the diastereotopic μ-CH_2 resonances in a cis complex.[8]

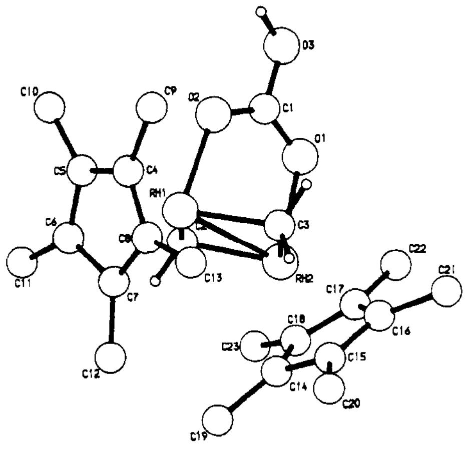
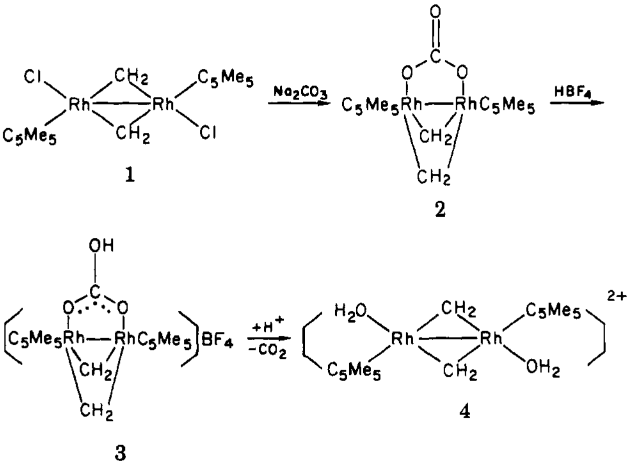


Figure 1.



A single-crystal X-ray determination was carried out on 3 to show the structure indicated in Figure 1.[15] The complex has two rhodiums, each η^5 bonded to a C_5Me_5 (mean Rh–C = 2.187 Å) and σ bonded to the two methylene carbons (mean Rh–C = 2.00 Å). They are also bridged by a somewhat asymmetrically bonded bicarbonato ligand

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[11] Readily obtained by reaction of *trans*-[$(C_5Me_5RhMe)_2(\mu$-$CH_2)_2$][8] with HCl in pentane.[12]

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[13] Anal. Calcd for $C_{23}H_{34}O_3Rh_2$ (2): C, 49.0; H, 6.1. Found C, 50.6; H, 6.3. Calcd for $C_{23}H_{37}BF_4O_4Rh$ (3): C, 41.2; H, 5.6. Found: C, 40.8; H, 5.7.

[14] IR: 1530 (s), 1544 (sh) (2) and 1572 (m), 1555 (sh) (3) cm^{-1} are associated with the coordinated CO_3. 2: ^1H NMR ($CDCl_3$) δ 1.69 (s, C_5Me_5), 9.06 [d, CH_2, H_{ax}, J(H–H) = 3 Hz] and 9.52 [m, CH_2, H_{eq}, J(H–H) = 3, J(Rh–H) = 2 Hz]. 3: ^1H NMR ($CDCl_3$) δ 1.69 (s, C_5Me_5), 3.79 (s, br, H_2O), 9.08 (d, CH_2, H_{ax} J(H–H) = 2.5 Hz) and 9.52 (m, CH_2, H_{eq}, J(H–H) = 2.5, J(Rh–H) = 2 Hz].

[15] Crystal data: [$C_{23}H_{35}O_3Rh_2$]$BF_4\cdot H_2O$, M_r = 670; monoclinic; a = 28.82 (3) Å, b = 8.803 (5) Å, c = 20.36 (2) Å, β = 93.86 (8)°; U = 5157 Å^3; Z = 8; D_{measd} = 1.73, D_{calcd} = 1.73 g cm^{-3}; $F(000)$ = 2703; space group $C2/c$; Mo Kα radiation (λ = 0.710 69 Å); μ = 13.14 cm^{-1}. X-ray data collected (3.5° $\leq 2\theta \leq$ 47°) on Nicolet R3M four-circle diffractometer to give 2030 independent reflections ($I \geq 4\sigma(I)$). Structure solved and refined by using SHELXTL programs to R = 0.061. The BF_4^- is disordered, and the water molecule (not shown) is hydrogen bonded to the bicarbonate and the BF_4^-.

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[Rh(1)–O(2) = 2.090 (7) Å and Rh(2)–O(1) = 2.140 (7) Å; C(1)–O(1) = 1.238 (14) Å, C(1)–O(2) = 1.268 (13) Å, and C(1)–O(3) = 1.314 (13) Å], with O(3) bearing the proton. Formally the Rh in **3** is in the +4 oxidation state, d^5, like the other complexes of this series.[8,12] Since it is diamagnetic, electron spin pairing must occur by a metal–metal bond; this is indicated by the short Rh–Rh distance of 2.591 (1) Å (significantly shorter than the 2.620 (1) Å in *cis*-$[(C_5Me_5RhMe)_2(\mu\text{-}CH_2)_2]$[8]).

Bicarbonato complexes remain rather rare; three mononuclear ones $[H_2(i\text{-}Pr_3P)_2RhO_2COH]$,[16] $[(Ph_3P)_2Rh(CO)(OCO_2H)]$,[17] and the hydrogen-bonded $[Me(PEt_3)_2PdOCO_2H]$[18] have had their structures determined. The bicarbonato ligand is bidentate only in the first rhodium complex and is much more loosely bonded there than in **3** (Rh–O = 2.306, 2.279 Å). This may well account for the surprising stability shown by complex **3**. The bicarbonato ligand is monodentate in the second rhodium complex and in the Pd complex, and these are not really comparable to **3**.

Addition of more acid to an aqueous solution of the carbonato complex **2** resulted in loss of CO_2 and the formation of a new complex. The ^1H NMR spectrum showed the CH_2 groups still to be present (*even at pH 1*) but indicated that the molecule now had the trans geometry[8] [δ (D_2O) 1.64 (C_5Me_5), 10.11 (t, J(Rh–H) = 1.5 Hz, μ-CH_2)]. On the basis of this and the analytical and IR spectroscopic data[19] on the crystals obtained by addition of BF_4^- to the solution, we formulate it as the *trans*-diaquabis(μ-methylene)dirhodium complex (**4**).

Other bidentate oxo ligands similar in shape and size to carbonate and bicarbonate will also bridge the two metal atoms in related structures. These include the μ-nitrato $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2(NO_3)]^+Y^-$ ($Y^- = NO_3$ or PF_6) and the μ-sulfato complex $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2SO_4]$.[20]

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Supplementary Material Available: Table I, atomic and temperature factors, Table II, bond lengths, Table III, bond angles, Table IV, anisotropic temperature factors, Table V, hydrogen coordinates and temperature factors, and tables of observed and calculated structure factors for $[(C_5Me_5Rh\text{-}\mu\text{-}CH_2)_2HCO_3]BF_4.H_2O$ complex (**3**) (18 pages). Ordering information is given in any current masthead.

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(19) Anal. Calcd for $C_{22}H_{38}B_2F_8O_2Rh_2$ (**4**): C, 37.0; H, 5.3. Found: C, 37.9; H, 5.5. **4**: IR $\nu(BF_4)$ 1050 cm^{-1}, $\nu(OH_2)$ 3400 cm^{-1}.

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Book Reviews

Silane Coupling Agents. By Edwin P. Plueddemann. Plenum Press, New York. 1981. 1X + 235 pages. $37.50.

It is fitting that the definitive book on silane coupling agents has been written by Ed Plueddemann. Known around the world as "Mr. Silanes", he is an expert in the technology of these specialty chemicals. His book addresses the preparation, chemistry, and applications of these organofunctional silanes from the viewpoint of a self-proclaimed "experimental laboratory chemist". Silane coupling agents (X–R–Si $(OR)_3$) have proven to be versatile, commercially valuable bifunctional reagents for bonding organic materials to mineral substrates.

The book starts by providing historical background on the value of coupling agents, then describes commercial and laboratory synthetic methods for silane coupling agents. The remaining chapters describe their use—first, the complex hydrolysis and condensation reactions in aqueous solutions and the difficult studies of reactions at surfaces and polymer/mineral interfaces. Proposed chemical mechanisms for the observed effects are discussed in the perspective of composite mechanical properties. Specific benefits in different polymer systems, with recommended coupling agents, as well as proven formulations for several adhesion promoting surface primers are given in detail. Finally, a chapter discusses miscellaneous uses for silane coupling agents: enzyme fixation, antimicrobial compositions, catalyst immobilization, chelation of metal ions, water proofing of minerals, etc.

All chapters contain extensive references to current literature through 1980; few references from 1981 or beyond were noted. The literature references are well discussed and provide good insight into the behavior of these materials and into some of the ingenious experiments—from simple lab tests to complicated spectroscopic techniques—that have been used. The user of silane coupling agents will get most benefit from reading through these examples. The attempt to synthesize a single coherent view of the chemical behavior of silanes at interfaces, while reasonably successful, highlights the number of different phenomena that may, but often do not, simultaneously occur at interfaces bridged by silane coupling agents.

The book suffers from a poor index; improvement would make the book a more valuable bibliographic source. For example, polyethylene is indexed at pages 241, 134, and 162–164, but important references are also discussed on p 178 and p 193. Essentially no reference is made to one of the most significant new commercial uses for silane coupling agents—polymer cross-linking. Extensive literature on silane cross-linking of (e.g.) thermoplastics and latexes is not discussed.

In spite of these shortcomings, any user of silane coupling agents will gain new insights from reading this book. Collecting these references in a single volume eases thoughtful comparison of different ideas. The chapters on applications are written so that a novice in the field can understand them yet contain sufficient depth and breadth to interest the expert.

F. D. Osterholtz, *Union Carbide Corporation*