Transition-Metal Methylene Complexes. 14.[1] Reactions of an Electron-Rich Dimetallacyclopropane with Protic Acids: Synthesis and X-ray Crystal Structures of Novel Rhodium–Methyl and –Methylidyne Complexes

Wolfgang A. Herrmann,[*2a,3] **Johann Plank,**[2a] **Doris Riedel,**[2a] **Manfred L. Ziegler,**[2b] **Klaus Weidenhammer,**[2b] **Ernst Guggolz,**[2b] **and Barbara Balbach**[2b]

Contribution from the Institut für Chemie, Universität Regensburg, D-8400 Regensburg 1, West Germany, and the Anorganisch-chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, West Germany. Received May 27, 1980

Abstract: The dimetallacyclopropane-type μ-methylene complex $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(CO)}]_2$ (**2**) reacts with fluoroboric acid in water/tetrahydrofuran to unexpectedly yield the novel μ_3-methylidyne cluster $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})_2(\mu_3\text{-CH})][\text{BF}_4]$ (**5a**) in near quantitative yield. The analogous product $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})_2(\mu_3\text{-CH})][\text{CF}_3\text{CO}_2]$ (**5b**) is correspondingly formed from **2** and trifluoroacetic acid and has been structurally characterized by means of X-ray diffraction techniques (space group C_{2h}^6—$C2/c$, $a = 1772.5$ (6) pm, $b = 1060.7$ (3) pm, $c = 2270.9$ (7) pm, $\beta = 103.90$ (3)°, $Z = 8$, $R_F = 0.031$). The cluster cation of **5b** consists of an almost equilateral triangle of rhodium atoms each of which bears a π-bonded cyclopentadienyl ligand; the carbonyl groups display unsymmetrically edge-bridging functions, whereas the carbyne unit represents an essentially symmetrical face bridge, with the mean C(methylidyne)–Rh distance amounting to 196.3 pm. While the formation of the air-stable and also thermally exceedingly stable cluster **5a** occurs with concomitant evolution of methane and hydrogen, direct protonation of the electron-rich metal-to-metal bond of **2** has been established from the reaction with fluoroboric acid in diethyl ether, which immediately leads to the novel dinuclear 1:1 electrolyte of composition $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CH}_2)\text{H}]^+\text{BF}_4^-$ (**3a**). This thermally sensitive compound as well as the corresponding fluorosulfonate **3c** and the trifluoromethane sulfonate **3d** can be reversibly deprotonated to the precursor **2** by the action of even weak bases such as dimethylformamide instantaneously—by sodium methoxide. In nitromethane solution, **3** adopts μ-methylene/μ-hydrido structures with terminal CO ligands. Labeling experiments and the nature of the gaseous byproducts (CH_4 and H_2) prove mechanistically important methyl tautomers **4** to participate in the formation of the μ_3-methylidyne clusters **5**. Further support for a metal-centered hydrido methylene/methyl tautomerism comes from the irreversible formation of stable methyl halogeno complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})_2(\text{CH}_3)(X)$ (X = Cl, **6a**; X = Br, **6b**) upon interaction of HCl and HBr, respectively, with **2** via the isolable ionic type **3** intermediates [e.g., **3e** (X = Br)]. The structure of the bromo complex **6b** has been proved unequivocally by an X-ray diffraction study (space group D_{2h}^{16}—$Pmcn$, $a = 890.7$ (2) pm, $b = 1016.8$ (2) pm, $c = 1567.1$ (3) pm, $\alpha = 89.87$ (2)°, $\beta = 90.07$ (2)°, $\gamma = 90.00$ (2)°, $Z = 4$, $R_F = 0.068$) which revealed cis configuration of the C_5H_5–Rh–Rh–C_5H_5 frame held together by two symmetrically bridging carbonyl ligands. The ring-opening reaction is shown to occur via a nonsynchronous two-step mechanism initiated by protonation of the metal-to-metal bond of **2** as well. In a comparative study, the protonation reaction of $(\mu\text{-CO})[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(CO)}]_2$ (**7**) was discovered to yield $\{(\mu\text{-CO})(\mu\text{-H})[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(CO)}]_2\}^+\text{BF}_4^-$ (**8**) in quantitative yields.

Introduction

Our discovery of the first stable μ-methylene transition-metal compounds[4–6] containing bridging –CH_2– (carbene[7]) groups has so far focused considerable attention on both the structural features and the theory of bonding of this class of organometals[8] which is thought to play a major role in the catalytic hydrogenation of carbon monoxide.[9,56] Spectroscopic results,[10] X-ray diffrac-

tion,[5,6,10a–15] and neutron diffraction[16,17] work as well as an experimental electron density determination[18] have provided ample evidence that the roughly sp³-hybridized bridgehead carbon atom represents the inherent structural characteristics of type **1** com-
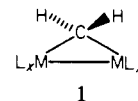
1

pounds which, thus, are expected to display a basically different chemistry as compared with Fischer-type metal carbenes, $\text{L}_x\text{M}=\text{CRR}'$, containing sp²-hybridized, pronounced electron-deficient carbene units attached to only one metal center.[19] Moreover, Hückel MO calculations for $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})]_2$ have revealed a significantly increased electron density for the bridging methylene carbon atom in comparison with

(1) Presented in part at the Chemiedozententagung 1980, Universität Erlangen-Nürnberg, and at the Gordon Research Conference on Organometallic Chemistry, August 11–15, 1980, Andover, N.H. (USA). Preceding communication in this series: W. A. Herrmann, J. Plank, M. L. Ziegler, and B. Balbach, *J. Am. Chem. Soc.*, **102**, 5906 (1980).

(2) (a) Universität Regensburg. (b) Universität Heidelberg.

(3) Karl Winnacker Scholarship recipient, 1979–1984.

(4) W. A. Herrmann, B. Reiter, and H. Biersack, *J. Organomet. Chem.*, **97**, 245 (1975).

(5) W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *Angew. Chem., Int. Ed. Engl.*, **16**, 334 (1977).

(6) W. A. Herrmann, C. Krüger, R. Goddard, and I. Bernal, *J. Organomet. Chem.*, **140**, 73 (1977).

(7) As regards the nomenclature of this class of compounds, the reader is referred to the general remarks by W. A. Herrmann, J. Plank, I. Bernal, and M. Creswick, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **35B**, 680 (1980). See also: W. A. Herrmann, Habilitationsschrift, pp 45–48, Universität Regensburg, 1977; a copy is available upon request from the author.

(8) Reviews: (a) W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, **17**, 800 (1978); (b) W. A. Herrmann, *Adv. Organomet. Chem.*, in preparation.

(9) Review: E. L. Muetterties and J. Stein, *Chem. Rev.*, **79**, 479 (1979).

(10) (a) M. Creswick, I. Bernal, and W. A. Herrmann, *J. Organomet. Chem.*, **172**, C39 (1979); (b) K. K. Mayer and W. A. Herrmann, *ibid.*, **182**, 361 (1979).

(11) M. Creswick, I. Bernal, W. A. Herrmann, and I. Steffl, *Chem. Ber.*, **112**, 1377 (1980).

(12) Reference 7 and literature quoted therein.

(13) W. A. Herrmann, I. Schweizer, M. Creswick, and I. Bernal, *J. Organomet. Chem.*, **165**, C17 (1979).

(14) W. A. Herrmann, J. Plank, M. L. Ziegler, and E. Guggolz, *Angew. Chem., Int. Ed. Engl.*, **19**, 651 (1980).

(15) R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. L. Suib, and G. D. Stucky, *J. Am. Chem. Soc.*, **100**, 6240 (1978).

(16) A. J. Schultz, J. M. Williams, R. B. Calvert, J. R. Shapley, and G. D. Stucky, *Inorg. Chem.*, **18**, 319 (1979).

(17) T. F. Koetzle, F. Takusagawa, A. Fumagalli, and W. A. Herrmann, *Inorg. Chem.*, in preparation (neutron diffraction study of $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(CO)}]_2$).

(18) D. A. Clemente (C.N.R., Padova, Italy), unpublished work on $(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_2]_2$,[4] 1978–1980.

(19) For reviews, see: (a) E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976); (b) R. R. Schrock, *Acc. Chem. Res.*, **12**, 98 (1979).

terminally coordinated carbenes[20] and classify compounds containing both a methylene bridge and a metal-to-metal bond as dimetallacyclopropanes,[21-24] in regards their structural and electronic appearance.[20] In this paper, we describe the largely unexpected reactions of μ-methylene-bis[carbonyl(η^5-cyclopentadienyl)rhodium](Rh–Rh) with strong protic acids and report the molecular structures of two key products arising from proton-induced activation of the electron-rich metal-to-metal bond of their μ-methylene precursor. Preliminary accounts for this and related work have appeared.[1,14,25]

Experimental Section

Reagents and Solvents. All operations were performed under rigorous exclusion of air and moisture (oxygen-free nitrogen; Schlenk technique). Solvents (reagent grade) were carefully dried over sodium–potassium alloy (pentane, diethyl ether, benzene, tetrahydrofuran), phosphorus pentoxide (Granusic, Baker Chemicals; methylene chloride), or molecular sieves (DMF, Me$_2$SO, acetone, methanol, ethanol); reagent grade acetonitrile and nitromethane were stirred over potassium carbonate for ca. 1 day and then distilled under reduced pressure (ca. 10^{-3} torr). All solvents were distilled in a nitrogen stream before use (storage of the purified solvents no longer than approximately 2 weeks). Oven-dried glassware was repeatedly evacuated on a high-speed pumping system (ca. 10^{-3} torr) and subsequently filled with inert gas.

μ-Methylene-bis[carbonyl(η^5-cyclopentadienyl)rhodium](Rh–Rh) (2) was synthesized from (μ-CO)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (7)[26] and *N*-methyl-*N*-nitrosourea on a 3-g scale according to the published procedure[5,6,26] and was crystallized from pentane–diethyl ether (10:1; -35/-78 °C). Tetrafluoroboric acid was used without further purification as a 48% aqueous solution (Aldrich) and as a 54% solution in diethyl ether (Merck), respectively. Trifluoromethanesulfonic acid (ca. 99%, bp 162 °C), trifluoroacetic acid (99%, bp 72 °C), trifluoroacetic acid-d_1 (99% [D], bp 75 °C), and fluorosulfonic acid-d_1 (98% [D], bp 163 °C) were obtained from Aldrich and handled under exclusion of air and moisture. HCl and HBr were used as anhydrous gases from lecture bottles (Merck-Schuchardt; 99.0 and 99.8%, respectively). [13]CO-Labeled μ-methylene complex 2-[13]CO was synthesized from 7-[13]CO which, in turn, was obtained from (η^5-C$_5$H$_5$)$_2$Rh$_2$(CO)$_3$[26] by direct carbon monoxide exchange as described by Lewis et al.[27] ([13]CO enrichment 65 ± 2%; mass spectra). [13]CO (90.6% isotopic purity) was obtained from BOC Limited, London (Amersham-Buchler, Braunschweig, Germany), and was handled by use of a Töpler-pump system.

Analyses and Physical Measurements. Microanalyses were performed in the Mikrolaboratorium of the Universität Regensburg (C, H, Cl, Br, N) and in the Mikroanalytische Laboratorien at Elbach-Engelskirchen, Germany (B, F, O, Rh, S). Melting and decomposition points are uncorrected and were taken in sealed capillaries on a Büchi apparatus SMP-20 (heating speed 1-2 °C/min). ^{1}H NMR and ^{13}C NMR spectra

(20) P. Hofmann, *Angew. Chem., Int. Ed. Engl.*, **18**, 554 (1979). See also: A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, **63**, 29 (1980).

(21) Note that μ-methylene transition-metal complexes are to be divided into two fairly different subclasses, as we have pointed out earlier:[10a] (i) compounds containing metal–metal bonds ("dimetallacyclopropanes"[20]), M–CH$_2$–M (class A), and (ii) μ-methylene complexes in which the methylene bridge is not assisted by an extra metal-to-metal bond, M–CH$_2$–M (class B), no matter whether the metal centers are spanned by additional bridging ligands[22] or not.[23,24] Rare examples of compounds belonging to class B are nowadays known and can be distinguished from their class A counterparts by ^{1}H and ^{13}C NMR spectroscopy.[8b,10a] This paper is dealing only with a μ-methylene complex which typically represents the characteristics of class A compounds.

(22) (a) M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 749 (1978); (b) M. P. Brown, J. R. Fisher, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, **18**, 2808 (1979); (c) F. N. Tebbe, *J. Am. Chem. Soc.*, **100**, 3611 (1978).

(23) However, class B compounds with only *one* CH$_2$ bridge and no metal–metal bond are not known to date. By way of contrast ω,ω'-ethanediyl derivatives, L$_x$M–CH$_2$CH$_2$–M'L$_y$, have been reported: (a) W. Kaminsky, J. Kopf, H. Sinn, and H.-J. Vollmer, *Angew. Chem., Int. Ed. Engl.*, **15**, 629 (1976); (b) W. Beck and B. Olgemüller, *J. Organomet. Chem.*, **127**, C45 (1977).

(24) M. B. Hursthouse, R. A. Jones, K. M. Abdul Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, **101**, 4128 (1979).

(25) W. A. Herrmann, J. Plank, and D. Riedel. *J. Organomet. Chem.*, **190**, C47 (1980).

(26) W. P. Fehlhammer, W. A. Herrmann, and K. Öfele, in "Handbuch der Präparativen Anorganischen Chemie", Vol. III, G. Brauer, Ed., 3rd ed., Ferdinand Enke Verlag, Stuttgart, West Germany, 1980, pp 1800ff.

(27) J. Evans, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 79 (1973).

were recorded with a Bruker WH-90 spectrometer, and IR spectra were taken with a Beckman infrared grating spectrophotometer 4240 connected with a data interface system 4060-A; IR data are reproducible within ±1 cm^{-1}. Mass spectra were recorded either on a Varian MAT CH-5 spectrometer (low resolution) or on a Varian MAT 311-A spectrometer (high resolution; field desorption). Conductivity data were obtained on a WTW conductivity bridge Type LBR 40 (Wissenschaftlich-technische Werkstätten, Weilheim, Bavaria) with a matching conductivity cell (f = 1.00 cm^{-1}; 40 Hz) using a thermostatable Schlenk-type cylinder.

Di-μ-carbonyl-μ_3-methylidyne-*cyclo*-tris[(η^5-cyclopentadienyl)rhodium]($3Rh$–Rh) Tetrafluoroborate (5a). A solution of 812 mg (2.0 mmol) of (μ-CH$_2$)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (2) in 30 mL of tetrahydrofuran is combined with fluoroboric acid (0.8 mL of a 48% aqueous solution; excess). The mixture is stirred for a few minutes and then allowed to stand without further movement for a period of 3-4 days at 10-20 °C. After ca. 15 min, the first crystals begin to separate from the solution; at the same time, the color of the reaction mixture starts to change from red to dark brown. The black, lustrous, completely air-stable needles are finally washed with THF (4 × 5 mL) and diethyl ether (3 × 10 mL) and dried in a high vacuum before analysis: yield 1.26 g (96%); no melting point below 280 °C; soluble in acetonitrile, acetone, dimethylformamide, and methanol and insoluble in diethyl ether and methylene chloride. Anal. Calcd for C$_{18}$H$_{16}$BF$_4$O$_2$Rh$_3$ (659.8): C, 32.77; H, 2.44; B, 1.64; F, 11.52; Rh, 46.79. Found: C, 32.84; H, 2.69; B, 1.67; F, 11.11; Rh, 48.33.

The easiest way to prepare ^{13}CO-labeled samples of the μ_3-methylidyne cluster 5a is to stir a solution of 660 mg (1 mmol) of unlabeled 5a in acetonitrile (30 mL) under an atmosphere of excess ^{13}CO (250-mL flask, 3 days, room temperature). The solution is then evaporated to dryness (10^{-2} mm), washed with 3 × 5 mL of tetrahydrofuran, and subsequently crystallized from acetone/acetonitrile at -30 °C. Isotopic enrichment: 80 ± 5% (IR). Anal. Found: C, 32.90; H, 2.48; N, 0.05.

Di-μ-carbonyl-μ_3-methylidyne-*cyclo*-tris[(η^5-cyclopentadienyl)rhodium]($3Rh$–Rh) Trifluoroacetate (5b). A 406-mg (1.0-mmol) sample of 2 is dissolved in a mixture of 10 mL of diethyl ether and 0.5 mL of tetrahydrofuran. After the addition of 0.2 mL (ca. 2.5 mmol) of trifluoroacetic acid, the reaction mixture is stirred thoroughly for a period of 5 min. Afterwards it should stand without any vibration for 5 days at 10-20 °C. After the reaction time is over, the originally red solution has adopted a dark brown color; at the same time, black, lustrous needles (sometime 1.5 cm in length) have separated at the bottom of the Schlenk tube. After decantation of the supernatant solution, the crystalline carbyne complex 5b is washed with diethyl ether (4 × 5 mL), vacuum-dried, and afterwards crystallized from acetonitrile at temperatures ranging between -15 and -20 °C. Yield: 310 mg (87%). A further batch of crystalline 5b can be obtained from the vacuum-concentrated mother liquor. Total yield: 331 mg (93%). The compound, like 5a, is indefinitely air stable in the crystalline state. The solubility of the trifluoroacetate 5b in acetonitrile, acetone, nitromethane, dimethylformamide, methanol, and tetrahydrofuran is very good and even better than that of the analogous tetrafluoroborate 5a. Solutions of 5a as well as 5b are neither significantly sensitive to air nor to moisture. Anal. Calcd for C$_{20}$H$_{16}$F$_3$O$_4$Rh$_3$ (686.1): C, 35.02; H, 2.35; F, 8.31; Rh, 45.00. Found: C, 35.22; H, 2.54; F, 8.35; Rh, 44.80.

The same reaction was carried out with CF$_3$CO$_2$D [500 mg (1.23 mmol) of 2, 0.7 mL (excess) of CF$_3$CO$_2$D, 10 mL of diethyl ether, and 0.5 mL of THF, +15 °C, 14 days]. The black needles of 5b-*d* are washed with diethyl ether and pentane and recrystallized from acetone/THF (-35 °C). Yield: 270 mg (96%). Anal. Calcd for C$_{20}$H$_{15}$DF$_3$O$_4$Rh (687.1): C, 35.01; H + D, 2.36; Found: C, 35.40; H + D, 2.47. Deuterium enrichment: 80 ± 5% (^{1}H NMR); mol wt 686 (D$_0$), 687 (D$_1$); field-desorption mass spectrometry, acetone).

Di-μ-carbonyl-μ_3-methylidyne-*cyclo*-tris[(η^5-cyclopentadienyl)rhodium]($3Rh$–Rh) Trifluoromethanesulfonate (5d). A vigorously stirred solution of 203 mg (0.5 mmol) of 2 in 10 mL of THF is slowly treated with 5 drops (ca. 0.2 mL) of trifluoromethanesulfonic acid at room temperature. (One has to avoid a large excess of this acid since it otherwise polymerizes the solvent THF and, thus, precludes isolation of the desired μ_3-methylidyne complex 5d.) The solution is now allowed to stand without further agitation. Black, lustrous needles of 5d begin to separate from the mother liquor after a few minutes. At the same time, the color of the solution gradually changes from red to dark brown. After a reaction period of 2 h is over, the crystalline, air-stable product 5d is filtered (D3 frit), is washed with THF (2 × 5 mL) and diethyl ether (3 × 5 mL), and is finally recrystallized from acetonitrile at -15 °C (black rhombohedron). Yield: 345 mg (96%). Correct elemental analyses are obtained after the compound has been dried under a high vacuum for approximately 5 h. Anal. Calcd for C$_{19}$H$_{16}$F$_3$O$_5$Rh$_3$S (722.1): C, 31.60;

Transition-Metal Methylene Complexes

J. Am. Chem. Soc., Vol. 103, No. 1, 1981 65

H, 2.23; Rh, 42.75. Found: C, 31.66; H, 2.52; Rh, 42.79. **5d** does not show any sign of decomposition, neither in the solid state nor in solution, even under prolonged exposure to air. No melting point is observed up to 280 °C (sealed capillary). It is soluble in nitromethane, acetonitrile, dimethylformamide, methanol, and acetone (brown solutions) and is insoluble in diethyl ether, methylene chloride, benzene, and hydrocarbons.

GC Analysis. The gaseous byproducts of the formation of [(η^5-C_5H_5)$_3$Rh$_3$(μ-CO)$_2$(μ_3-CH)]BF$_4$ (**5a**) were collected by Töpler pumping and analyzed by gas chromatography (Varian 1860-42; Porapak Q; l = 5 m, ϕ = $^1/_8$ in.; N$_2$ flow 35 mL/min, 17.5 psi; program -43 °C, isothermic) and were found to consist of a 63:37 mixture (vol %) of hydrogen and methane, containing only traces (!) of carbon monoxide; no ethylene and ethane were detected. The solvent was examined by the same method after vacuum distillation in a closed system. In accordance with an IR analysis, (η^5-C$_5$H$_5$)Rh(CO)$_2$ is the only CO-containing byproduct of the reaction; formaldehyde, methanol, acetaldehyde, acetic acid, and ethanol are formed in negligible amounts (<0.2% each).

Dicarbonyl-μ-hydrido-μ-methylene-bis[(η^5-cyclopentadienyl)rhodium](*Rh–Rh*) Tetrafluoroborate (3a). A vigorously stirred solution of 203 mg (0.5 mmol) of **2** in 10 mL of diethyl ether is treated at 0 °C with 10 drops (ca. 0.4 mL) of fluoroboric acid (54% HBF$_4$ in diethyl ether). A powdery, yellow precipitate immediately occurs, if the HBF$_4$ solution was added slowly and drop by drop; otherwise, an oily product is obtained which can be transformed into a fluffy powder by scratching with a spatula. After all of the acid has been added, the resulting precipitate is quickly filtered (D3 frit) and washed with precooled diethyl ether (4 × 5 mL; 0 °C). The product is analytically pure after it has been dried in a high vacuum for a period of 15 h at -10 °C. Yield: 235 mg (100%). Anal. Calcd for C$_{13}$H$_{13}$BF$_4$O$_2$Rh$_2$ (493.9): C, 31.62; H, 2.65; B, 2.19; F, 15.39; Rh, 41.67. Found: C, 31.71; H, 2.79; B, 2.57; F, 15.37; Rh, 41.90. **3a** is quite sensitive to air (slow decomposition in the solid state at room temperature) and exceedingly sensitive to even weakly basic solvents such as THF, Me$_2$SO, DMF, or acetonitrile which effect slow deprotonation, yielding the neutral precursor **2**. Rapid deprotonation **3a** → **2** can be achieved by addition of small amounts of a saturated solution of sodium methoxide in methanol. (Identification of recovered **2** by means of mass spectroscopy[10b] and IR spectroscopy.[6])

Dicarbonyl-μ-deuterio-μ-methylene-bis[(η^5-cyclopentadienyl)rhodium](*Rh–Rh*) Fluorosulfonate (3c). A solution of 203 mg (0.5 mmol) of **2** in 10 mL of diethyl ether is slowly treated, under magnetic stirring, with 10 drops (ca. 0.4 mL) of a precooled 50% solution of fluorosulfuric acid-*d* in absolutely dry diethyl ether at -25 °C. After a few seconds, a light yellow precipitate occurs which is quickly separated by filtration over a D3 frit (-25 °C) and subsequently washed with diethyl ether (2 × 5 mL; -25 °C) and pentane (3 × 5 mL; -25 °C). The final product is dried at -10 °C under high vacuum for a few hours. Yield: 235 mg (93%). Light yellow powder which rapidly decomposes upon exposure to air (color change to brown). Solutions in nitromethane are stable for a few hours at temperatures around -20 °C. The compound exhibits a very high tendency of deprotonation: even with cold diethyl ether, a small amount of soluble **3c** is converted into the μ-methylene precursor **2**. Due to its pronounced thermolability, reliable elemental analyses could not be obtained of compound **3c**.

Dicarbonyl-μ-hydrido-μ-methylene-bis[(η^5-cyclopentadienyl)rhodium](*Rh–Rh*) Trifluoromethanesulfonate (3d). The same procedure as given above for the preparation of **3c** is used for the synthesis of the trifluoromethanesulfonate complex **3d** (CF$_3$SO$_3$H instead of FSO$_3$D): yield 270 mg (97%); a light yellow, very air-sensitive powder. If a sample of **3d** shows a brownish color, it has already decomposed, at least partially: slow decomposition (under N$_2$) above ca. 45 °C, mp 64-68 °C under effervescence (rapid decomposition). The solubilities of **3d** are identical with those of **3a**. Solutions of **3d** in nitromethane are reasonably stable under rigorous exclusion of air and moisture at ca. -20 °C. Anal. Calcd for C$_{14}$H$_{13}$F$_3$O$_5$Rh$_2$S (556.1): C, 30.24; H, 2.36; Rh, 37.01. Found: C, 29.78; H, 2.49; Rh, 37.12. The same procedure is also used (-80 °C instead of -25 °C) for the synthesis of **3e** from **2**/HBr; yield 100%.

Deprotonation Reactions of 3c and 3d. A 278-mg (0.5-mmol) sample of **3d** or 253 mg (0.5 mmol) of **3c** are treated, at -20 °C, with a precooled solution of 30 mg (0.55 mmol, slight excess) of NaOCH$_3$ (Aldrich) in 10 mL of methanol. The reaction mixture, which instantaneously adopts a red color, is allowed to warm up to room temperature. The solvent is stripped off on a water aspirator, and the μ-methylene complex **2** is quickly extracted from the dark brown residue with pentane (20 mL). After filtration, the extract is evaporated (vacuum) to dryness; the remaining brick red powder is further purified by crystallization from a nearly saturated solution in pentane (ca. 4 mL; -25/-78 °C). Yield: 190-195 mg (94-96%). The μ-methylene complex **2** formed by deprotonation of either **3c** or **3d** has been characterized by means of IR and mass spectroscopy as well as by elemental analyses (C, H) and its melting

point; all data agreed with the reported values.[6,10b] As discussed in section B, the following deuterium distribution was found by mass spectrometry for the deprotonation product obtained from deuterated **3c** and NaOCH$_3$: 36 ± 1% D$_0$, 38 ± 1% D$_1$, 26 ± 1% D$_2$ (total [^{2}H] enrichment = 45%). The same enrichment data were obtained when CD$_3$OD was used instead of CH$_3$OH.

Deprotonation of the bromo derivative **3e** occurs similarly at -80 °C. At temperatures above ca. -25 °C, **3e** is converted to the neutral compound **6b** both in the solid state (yields lower than ca. 20%) and in nitromethane (near quantitative yields; characterization of **6b**: IR spectrum, C and H analysis).

***cis*-Chloro(methyl)bis[μ-carbonyl-(η^5-cyclopentadienyl)rhodium](*Rh–Rh*) (6a).** At room temperature, a vigorously stirred solution of 406 mg (1.0 mmol) of **2** in 10 mL of diethyl ether is dropwise treated with 2 mL (excess) of a saturated solution of dry HCl gas in the same solvent. The powdery precipitate, which immediately occurs, originally has a light yellow color which changes to dark brown upon further addition of HCl. After all HCl has been added, the precipitate is quickly filtered (D3 frit), washed four times with 5-mL portions of diethyl ether, and finally crystallized from a nearly saturated solution in methylene chloride (-35/-78 °C): yield 420 mg (95%); black, slightly air-sensitive, rhombic crystals; slow decomposition above ca. 145 °C, mp 152-154 °C under rapid and complete decomposition; soluble in methylene chloride (approximately 5 mg/mL; yellow-brown, very air-sensitive solutions) with partial decomposition at temperatures above ambient, with the decomposition products displaying terminal CO's. Solutions in Me$_2$SO (solubility ca. 40 mg/mL) show slow decomposition with concomitant increase of the conductivity ($\sim$5 cm^2 Ω^{-1} mol^{-1} after 2 h at 25 °C). **6a** dissolves only sparingly in chloroform, nitromethane, acetone, acetonitrile, and tetrahydrofuran (decreasing solubility in the order given) and is insoluble in tetrachloromethane, methanol, and ethanol. Anal. Calcd for C$_{13}$H$_{13}$ClO$_2$Rh$_2$ (442.5): C, 35.29; H, 2.96; Cl, 8.01; Rh, 46.51. Found: C, 35.04; H, 3.12; Cl, 7.78; Rh, 46.61; mol wt 442 (^{35}Cl; mass spectrometry, field desorption).

***cis*-Bromo(methyl)bis[μ-carbonyl-(η^5-cyclopentadienyl)rhodium](*Rh–Rh*) (6b).** Preparation and workup are the same as described above for the chloro analogue, but employing HBr instead of HCl: yield 445 mg (91%); black rhombohedra (from methylene chloride) which are completely air stable for at least a few hours; slow decomposition above ca. 138 °C with concomitant sintering; no melting point observed up to 280 °C. As regards solubility, compound **6b** very much resembles the chloro derivative **6a**; however, **6b** dissolves significantly better in methylene chloride (ca. 15 mg/mL) than the latter. A suspension of **6b** in diethyl ether does not show any sign of reaction with excess KOH/ethanol or triethylamine; in both cases, **6b** was recovered quantitatively after 2 days at room temperature. Anal. Calcd for C$_{13}$H$_{13}$BrO$_2$Rh$_2$ (487.0): C, 32.07; H, 2.69; Br, 16.41; Rh, 42.26. Found: C, 32.18; H, 2.84; Br, 16.49; Rh, 42.63; mol wt 486 (^{79}Br; mass spectrometry, field desorption).

μ-Carbonyl-μ-hydrido-bis[carbonyl(η^5-cyclopentadienyl)rhodium](*Rh–Rh*) Tetrafluoroborate (8). Under rigorous exclusion of oxygen and water, a stirred solution of 300 mg (0.71 mmol) of **7** in 10 mL of diethyl ether is slowly treated with 10 drops (ca. 0.4 mL) of $\sim$54% HBF$_4$ in the same solvent at ca. -30 °C. The light red, fluffy precipitate which occurs after a few seconds is immediately separated from the nearly colorless solution by filtration over a precooled (-20 °C) D3 frit equipped with a cooling mantle, repeatedly washed with 5-mL portions of cold diethyl ether and pentane (-20 °C), and finally dried in a high vacuum (-20 °C, 15 h). Yield: 355 mg (98%). Anal. Calcd for C$_{13}$H$_{11}$BF$_4$O$_3$Rh$_2$ (507.8): C, 30.75; H, 2.18; B, 2.13; F, 14.96; Rh, 40.53. Found: C, 30.77; H, 2.44; B, 2.48; F, 15.27; Rh, 40.75. The cationic hydrido complex **8** is very sensitive to air and moisture but can be stored for a few days at temperatures around -20 °C without noticeable decomposition: dark yellow to light red powder; decomposes slowly at room temperature, even under an atmosphere of dry nitrogen; rapid decomposition above ca. 40 °C. In nitromethane solution, **8** is converted at room temperature (24 h) into the C_{3v} isomer of (η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_3$ (**9**) (65% yield, Scheme II) and (η^5-C$_5$H$_5$)Rh(CO)$_2$.

Deprotonation of **8** occurs within a period of a few hours in basic solvents such as DMF, Me$_2$SO, acetonitrile, or THF at +25 °C. This reaction proceeds instantaneously, under complete dissolution of **8**, if a suspension of **8** in methanol [20 mg (0.04 mmol)/3 mL] is treated with sodium methoxide [Aldrich; 30 mg (0.06 mmol)]. The resulting neutral parent complex **7** which is isolated in quantitative yield after quick extraction of the vacuum-dried solution with pentane and subsequent low-temperature crystallization from this solvent has been characterized by IR and mass spectroscopy: red needles; mp 139 °C (lit. 139 °C).[6,26]

The only solvent in which the cationic μ-hydrido complex can be handled is cold nitromethane (-20 °C). All other solvents which we have checked cause decomposition (chlorinated hydrocarbons), deprotonation to **7** (see above), or production of **9** and CpRh(CO)$_2$ (nitromethane).

Reaction of $(\mu\text{-CO})[(\eta^5\text{-C}_5\text{H}_5),\text{rh}(\text{CO})]_2$ (7) with HBF$_4$/H$_2$O/Tetrahydrofuran. A solution of 396 mg (0.94 mmol) of 7 in 10 mL of THF is combined with 1.0 mL (excess) of 48% HBF$_4$ in H$_2$O and allowed to stand without stirring under exclusion of light. Gradually, green fibrous needles of the trinuclear carbonyl complex 9 crystallize from the solutions the color of which turns from red to brownish green during the reaction. 9 is filtered off after 3–4 days (D3 frit), washed with THF (2 × 4 mL), and dried under vacuum (10^{-4} torr). Anal. Calcd for C$_{18}$H$_{15}$O$_3$Rh$_3$ (588.0): C, 36.77; H, 2.57. Found: C, 36.79; H, 2.60; mol wt 588 (mass spectra). Yield: 170 mg (92%, Scheme II). The mononuclear fragmentation product $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ is isolated by evaporation of the filtrate (water aspirator) and subsequent microdistillation (trap-to-trap condensation at 45 °C (10^{-3} torr)). Yield: 196 mg (93%, Scheme II). The identity of both $(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})_3$ (9) and $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ has been proved independently by comparison of their IR and ^{1}H NMR spectra with the data of authentic samples.[26,52]

Tri-μ-carbonyl-μ_3-hydrido-*cyclo*-tris[(η^5-cyclopentadienyl)rhodium]-(*3Rh–Rh*) Trifluoromethanesulfonate (10). A stirred suspension of 294 mg (0.5 mmol) of $(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})_3$ (9) in 20 mL of nitromethane is treated dropwise and slowly with a total of 0.1 mL (excess) of CF$_3$-SO$_3$H at 0 °C. During the protonation reaction, the starting material 9 is completely dissolved while the solution develops an intense grass green color. (The initial suspension is olive green.) After all the acid has been added, the solution is stirred for another 10 min at room temperature and is then concentrated down to ca. 5 mL in a vacuum (oil pump). The cationic μ_3-hydrido complex 10 is isolated from this solution by precipitation with 100 μL of diethyl ether at 0 °C. (Vigorous stirring during the addition of diethyl ether is required in order to achieve a microcrystalline precipitate!) The dark brown precipitate, which occasionally appears as a maroon–green powder, depending on how fast the precipitate was formed, is separated from the greenish mother liquor by filtration over a D3 frit. After washing with diethyl ether (3 × 5 mL) and *n*-pentane (3 × 10 mL), the compound is dried under vacuum (10^{-4} torr, 25 °C, 5 h). Yield: 360 mg (98%). Anal. Calcd for C$_{19}$H$_{16}$F$_3$-O$_6$Rh$_3$S (738.1): C, 30.92; H, 2.19; F, 7.72; Rh, 41.83; S, 4.34. Found: C, 30.78; H, 2.45; F, 7.61; Rh, 42.05; S, 4.35. Dark brown, greenish shiny powder or microcrystals; air-stable for at least a few days; indefinitely stable at room temperature under an atmosphere of dry nitrogen. Slow decomposition above ca. 135 °C, sintering at 167–170 °C, mp 177–179 °C with effervescence (complete decomposition; sealed capillary). 10 readily dissolves in nitromethane with partial isomerization but without deprotonation. Deprotonation occurs with solvents which are basic in character, such as acetonitrile, DMF, THF, acetone. Attempts to crystallize 10 from THF/acetone mixtures failed due to formation of the parent carbonyl 9. Insoluble in diethyl ether and aliphatic hydrocarbons. IR (ν(CO)): 1889 (vst), 1835 (vst), 1795 (m), 1767 (w) [KBr].

Exactly the same product is formed in almost quantitative yield as well, by protonation of the partially carbonyl-bridged C_s isomer (η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_2$(CO) by employing the procedure given above for the protonation of the C_{3v} isomer (η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_3$ (9) (identification: IR spectrum,[52] C, H analyses).

X-Ray Crystallography

A. Data Collection. For both compounds 5b and 6b suitable crystals were glued on Lindemann capillaries, which were fastened to a goniometer head. The crystal system, space groups, and preliminary unit cell parameters were determined by oscillation and Weissenberg photographs. In the case of 6b the centrosymmetric space group *Pmcn* was proven to be correct due to successful refinement. Accurate cell parameters and orientation matrices for data collection were determined by least-squares refinement of setting angles for series of reflections (5b, 5° < 2θ < 19°; 6b, 4° < 2θ < 22°) automatically centered on a Syntex (P3/DATA GENERAL NOVA 3 system) diffractometer.

The same instrument was used for intensity data collection, graphite-monochromatized Mo Kα radiation was used with a θ-scan technique. Two standard reflections were measured after every 100th reflection; no decay was observed. Reflections with $I < 2.5\sigma(I)$ were not considered, and 2045 (5b) and 1050 (6b) independent intensities remained for calculation. These were corrected for Lorentz and polarization factors. Absorption corrections were applied, although the size of the crystals used for intensity measurements being smaller than the optimum thickness (t_{opt}(5b) = 0.08 cm^{-1}; t_{opt}(6b) = 0.04 cm^{-1}). The crystallographic data for both compounds are listed in Table V.

B. Structure Analyses and Refinement. Compounds 5b and 6b. The structures of 5b and 6b were solved by Patterson and Fourier syntheses. In the case of 5b, a difference map allowed the location of the μ_3-methylidyne hydrogen. Since the cyclopentadienyl hydrogens could be taken from this map could only in part, their positions were obtained by searching with the SHELXTL program[57] at a distance of 98 pm from the corresponding ring carbon atoms leaving the thermal parameter U of

Table I. Conductivity Data of the Novel Rhodium Complexes 3, 5, 6, and 8[a]

compd	Λ_M, cm^2 mol^{-1} Ω^{-1}	10^4 concn, mol/L	temp, °C
3a	95	5.5	−2.0
3c	65	4.4	−11.0
3d	64	2.3	−6.0
5a	96	2.0	+21.6
5b	81	1.2	+21.1
5d	87	2.3	+20.8
6a	1.4	4.0	+21.6
6b	1.5	4.1	+21.6
8	85	2.7	−9.0

[a] The conductivity data were obtained from freshly prepared nitromethane solutions under scrupulous exclusion of air and moisture. With the exception of the neutral complexes 6a and 6b, all compounds are 1/1 electrolytes. For the deuteration product [D]-3c, the same conductivity data as measured for the protonated species 3c was obtained within experimental error.

hydrogen free. Refinement of 5b continued first with isotropic and then anisotropic thermal parameters for nonhydrogen atoms, the hydrogen atoms were refined only isotropically, and U of the methylidyne hydrogen was held constant. The refinement converged at $R = 0.031$. A final difference map revealed no peaks or troughs of any significance. Fractional coordinates and anisotropic parameters for nonhydrogen atoms and coordinates and isotropic parameters for hydrogen atoms and bond lengths and angles are given in Tables VII and VI, respectively.
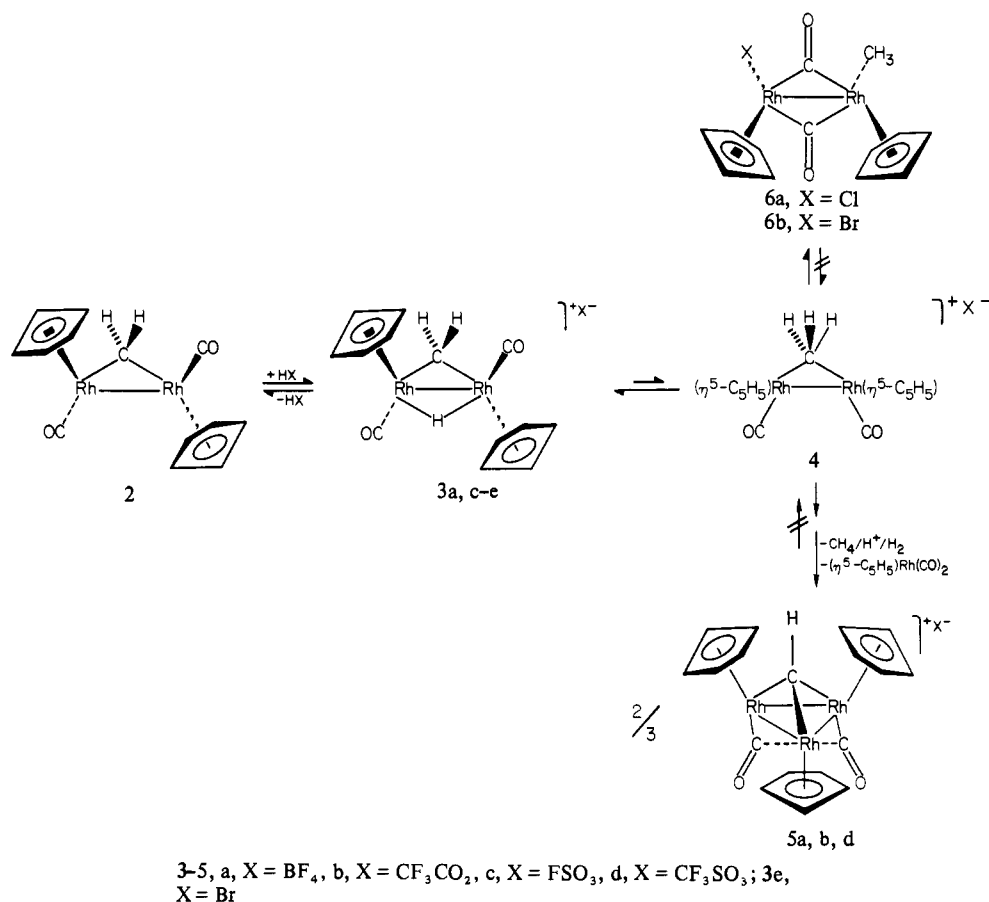
With $Z = 4$, the dinuclear molecule 6b is required to possess a crystallographic mirror plane bisecting the cyclopentadienyl rings and the angle between the carbonyl groups. The two Rh and the Br atoms and the methyl carbon atoms, respectively, are located on this plane. We did not succeed in locating the hydrogen atoms in 6b, either by means of difference maps or by the help of a model. This is certainly due to the statistical distribution of the bromine atom and the methyl group, which was recognized by the relatively large temperature factors and was confirmed during the process of refinement. It was found necessary to use two positions each of which having fractional occupancies (0.5, bromine and the methyl carbon atom). The structure of 6b was refined first with isotropic and then with anisotropic thermal parameters, and the refinement converged at $R = 0.068$. A final difference map revealed no peaks or troughs of any significance. Fractional coordinates and anisotropic parameters are given in Table X and bond lengths and angles in Table IX.

All calculations were performed on computers IBM 370/168 (Rechenzentrum der Universität Heidelberg) with local versions of the X-Ray 70 system[58] and DATA GENERAL NOVA 3 with the SHELXTL program.[57] Scattering factors were those of Hanson, Herman, Lea, and Skillman;[59] the atom numbering corresponds to that in the figures.
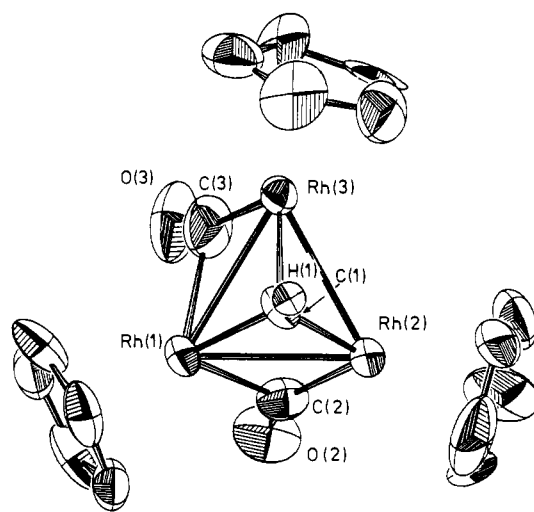
Synthetic and Crystallographic Results

A. Proton-Induced Synthesis of Novel μ_3-Methylidyne Rhodium Clusters from an Organometallic μ-Methylene Precursor. According to Scheme I, the dimetallacyclopropane-type μ-methylene rhodium complex 2 reacts with a slight excess of strong protic acid such as tetrafluoroboric acid, trifluoroacetic acid, or trifluoromethanesulfonic acid in tetrahydrofuran solution to unexpectedly give the novel trinuclear complexes 5a, 5b, and 5d, respectively, in near quantitative yields. The black, lustrous products, which crystallize directly from solutions kept at temperatures around ambient for a several days period, are exceedingly thermally stable and also resistant to air both in the solid state and in solution. Interestingly, the transformation 2 → 5 proceeds with different speed and stoichiometry depending on the particular acid used: with HBF$_4$, for instance, the conversion is roughly five times faster than with CF$_3$COOH (in THF). The exact stoichiometry for the last named reaction was found to obey the equation: $2(2) + \text{CF}_3\text{COOH} \rightarrow 5\text{b} + (\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2 + \text{CH}_4$;[61] note that no hydrogen is formed in this particular case. The initial evidence of μ_3-methylidyne (CH) functions as the dominant structural elements of the diamagnetic cationic compounds characterized by elemental analyses, field desorption (FD) mass spectra, and conductivity measurements (Table I) came from their NMR spectra (Tables II and III): the extremely deshielded *CH* proton shows up as a symmetric quartet, with τ values ranging between −6 and −7 in the proton NMR spectra and Rh,H coupling

Scheme I

6a, X = Cl
6b, X = Br

2

3a, c-e

4

$-CH_4/H^+/H_2$
$-(\eta^5-C_5H_5)Rh(CO)_2$

5a, b, d

3-5, a, X = BF_4, b, X = CF_3CO_2, c, X = FSO_3, d, X = CF_3SO_3; 3e, X = Br

constants on the order of 2.6 Hz. The chemical shifts of the methylidyne protons are even further downfield than those of the related neutral cobalt complex (μ_3-CH)[$Co_3(CO)_9$] and the osmium cluster (μ_3-CH)[$H_3Os_3(CO)_{10}$] found at τ -2.08 ($CDCl_3$)[28] and τ 0.64 (CD_2Cl_2),[29] respectively, while the observed magnitude of $^2J_{Rh,H}$ is characteristic of CH_x groups (x = 2, 3) so far directly bound to either one or two rhodium centers (e.g., 2.7 Hz for (η^5-C_5H_5)Rh(CH_3)$_2$[S(CH_3)$_2$][30a] and 2.2 Hz for [(η^5-C_5H_5)Rh-(PMe$_3$)$_2$(CH_3)]PF$_6$[30b]).

In the {^{1}H}^{13}C NMR spectra of highly ^{13}CO-enriched samples of [(η^5-C_5H_5)$_3$Rh$_3$(μ-CO)$_2$(μ_3-CH)]$^+$BF$_4^-$ (5a), the bridgehead carbon nucleus gives rise to a low-field quartet centered around δ 303.6 ($^1J_{Rh,C}$ = 38 Hz, Table III) which once again demonstrates the triply bridging coordination mode of the methylidyne moiety; these data are quite close to the corresponding values of the doubly bridged μ_3-(diethylamino)methylidyne complex (η^5-C_5H_5)$_3$Rh$_3$-{μ_3-C[N(C_2H_5)$_2$]}$_2$ [δ(μ_3-C) 280.8 ($^1J_{Rh,C}$ = 40 Hz) ($CDCl_3$)][31] which constitutes the only other rhodium–methylidyne complex known to date. While the infrared spectra convincingly demonstrate the carbonyl ligands to coordinate in the edge-bridging fashion both in solution and in the crystalline state (Table IV), the ^{13}C resonances of these carbonyl groups represent a single symmetric quartet at temperatures down to -25 °C (nitromethane; Table III). This observation proves rapid CO scrambling around the trimetallic system. Since the face-bridging carbyne ligand does not share the dynamic behavior of the carbon monoxide groups, the only mechanism for CO scrambling which we think can be envisaged in this case is best described as a merry-go-round-type movement of both carbonyls along the metal–metal bonds. Unfortunately, the low solubility of our cluster salts 5 in

(28) D. Seyferth, J. E. Hallgreen, and P. L. K. Hung, *J. Organomet. Chem.*, **50**, 265 (1973).

(29) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99**, 5225 (1977).

(30) (a) H. P. Fritz and K.-E. Schwarzhans, *J. Organomet. Chem.*, **5**, 283 (1966); (b) H. Werner, R. Feser, and W. Buchner, *Chem. Ber.*, **112**, 834 (1979), and literature cited therein.

(31) R. B. King and C. A. Harmon, *Inorg. Chem.*, **15**, 879 (1976).

Figure 1. ORTEP representation of the cation di-μ-carbonyl-μ_3-methylidyne-*cyclo*-tris[(η^5-cyclopentadienyl)rhodium]($3Rh$–Rh) of 5b. The thermal ellipsoids correspond to 50% probability.

solvents other than high freezing ones (acetonitrile, nitromethane, DMF, Me_2SO) precluded a complete characterization of this interesting fluxional process by ^{13}C NMR spectroscopy at lower temperatures. In this context, it is fitting to note that the μ_3-methylidyne clusters also show rapid intermolecular carbonyl exchange as has been proven by labeling experiments: if, for instance, a solution of 5a in acetonitrile is stirred, under exclusion of light, in an atmosphere of a roughly fivefold excess of ^{13}CO gas (90.6% ^{13}C) for several days, the starting complex incorporates the labeled carbon monoxide to a fairly high extent; typically, ^{13}CO enrichment data in the order of 80% have been estimated from IR analyses. While the mechanism of intermolecular CO exchange is still far from clear, we suggest that the rhodium–rhodium bond which is not spanned by an extra ligand (see solid-state

Table II. ^{1}H NMR Data of the Rhodium Compounds 2, 3, 5, 6–9[a]

compd	τ(CH), τ(CH$_2$), τ(CH$_3$)	τ(C$_5$H$_5$)	τ(RhH)	solv; temp, °C
2	^{m}2.93 (2)	^{1}4.52 (10)[b]		acetone-d_6; +29
2	^{4}2.90 (2)	^{3}4.50 (10)[c]		CD$_3$NO$_2$; +29
3a	^{3}0.81 (0.72), ^{3}1.41 (0.56), ^{1}2.05 (0.72) (total intens 2)	^{m}4.01 (10, $^2J_{Rh,H}$ = ca. 0.3 Hz)	^{3}22.90 (0.28, $^1J_{Rh,H}$ = 23.0 Hz), ^{3}22.99 (0.72, $^1J_{Rh,H}$ = 22.8 Hz) (total intens 1)	CD$_3$NO$_2$; −20
3a	^{3}0.81 (0.52), ^{3}1.41 (0.96), ^{1}2.05 (0.52) (total intens 2)	^{m}4.01 (10, $^2J_{Rh,H}$ = ca. 0.3 Hz)	^{3}22.90 (0.55, $^1J_{Rh,H}$ = 23.0 Hz), ^{3}22.99 (0.45, $^1J_{Rh,H}$ = 22.9 Hz)	CD$_3$NO$_2$; +20
3d	^{3}0.84 (0.25), ^{3}1.43 (0.50), ^{1}2.08 (0.25) (total intens 2)	^{m}4.03 (10)	^{3}22.92 and ^{3}23.01 (total intens 1, $^1J_{Rh,H}$ = 22.8 Hz)	CD$_3$NO$_2$; −20
3d	^{3}0.84 (0.31), ^{3}1.43 (0.38), ^{1}2.08 (0.31) (total intens 2)	^{m}4.03 (10)	^{3}22.92 and ^{3}23.01 (total intens 1, $^1J_{Rh,H}$ = 22.8 Hz)	CD$_3$NO$_2$; +20
5a	^{4}−6.28 ($^2J_{Rh,H}$ = 2.60 Hz) (intens 1)	^{1}4.06 (15)		acetone-d_6; +29
5a	^{4}−6.28 ($^2J_{Rh,H}$ = 2.60 Hz) (intens 1)	^{1}4.00 (15)		DMF-d_7; +30
5b	^{4}−6.71 ($^2J_{Rh,H}$ = 2.60 Hz) (intens 1)	^{1}4.12 (15)		DMF-d_7; +30
6a	^{2}9.55 ($^2J_{Rh,H}$ = 2.50 Hz) (intens 3)	^{m}4.37 (10) (10, $^2J_{Rh,H}$ = ca. 0.6 Hz)		CD$_2$Cl$_2$; +27
6b	^{2}9.51 ($^2J_{Rh,H}$ = 2.50 Hz) (intens 3)	^{2}4.33 (5, $^2J_{Rh,H}$ = 0.60 Hz), ^{2}4.37 (5, $^2J_{Rh,H}$ = 0.75 Hz)		CD$_2$Cl$_2$; +27
7		^{3}4.41 (10, $^2J_{Rh,H}$ = 0.75 Hz)		CD$_3$NO$_2$; +29
8		^{1}3.93 (10, $^2J_{Rh,H}$ < 0.3 Hz)	^{3}20.67 (1, $^1J_{Rh,H}$ = 18.3 Hz)	CD$_3$NO$_2$; −20
9		^{m}4.44		CD$_2$Cl$_2$; +29

[a] Spectra were recorded on a Bruker 90-MHz spectrometer and referenced to internal Me$_4$Si. Multiplicities are given as superscripts in front of the τ values; relative intensities in parentheses. If the cyclopentadienyl proton signals are assigned multiplicity 1, no splitting due to C$_5$H$_5$, Rh coupling was observed in the 90-MHz spectra. [b] 60-MHz spectra (Varian T60-A). [c] Virtual triplet resulting from superposition of two doublets. See also data reported in ref 47.

structure of **5b**, Figures 1 and 2) provides a vacant coordination site open for external attack by carbon monoxide. We believe that CO equilibration in molecules like **5** originates from their tendency to counterbalance the electronic requirements of all metal atoms sharing this process and to consequently meet the EAN rule.

Before we started out to investigate the mechanism of the curious proton-induced μ-methylene → μ_3-methylidyne transformation described above, a single-crystal X-ray diffraction study was performed in order to unequivocally establish the geometry of the cluster cations in full detail. The trifluoroacetate salt **5b** crystallizes from acetonitrile at −18 °C in the monoclinic space group C_{2h}^6—$C2/c$. Further crystallographic data are given in Table V. The interatomic distances and angles are listed in Table VI, and the positional and thermal parameters in Table VII. There is no intermolecular contact distance which could be considered to imply a bonding interaction. The cation centers around a nearly equilateral triangular array of rhodium atoms each of which bears a π-bonded cyclopentadienyl ring (Figure 1). As can be seen from a comparison with the structural data of related rhodium compounds presented in Table VIII, all rhodium–rhodium distances, which are thought to involve single bonds, are very much the same (255–271 pm).[32–39] However, carbonyl-bridged Rh–Rh
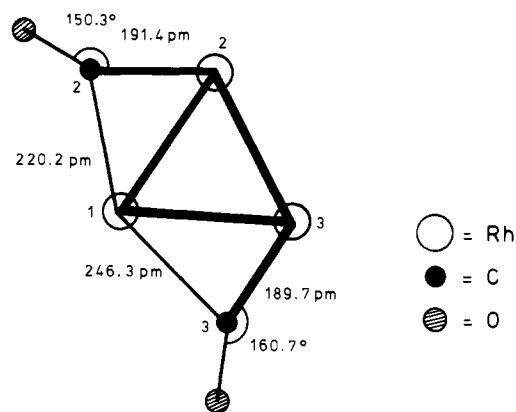

Figure 2. Drawing showing the unsymmetric arrangement of both carbonyl ligands around the metal triangle of **5b**.

bonds are generally significantly shorter than those not being supported by a bridging single-faced π-acceptor ligand such as

(32) O. S. Mills and J. P. Nice, *J. Organomet. Chem.*, **10**, 337 (1967).

(33) O. S. Mills and E. F. Paulus, *Chem. Commun.*, 815 (1966).

(34) E. F. Paulus, *Acta Crystallogr., Sect. B*, **25B**, 2206 (1969); E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *J. Organomet. Chem.*, **10**, 3 (1967).

(35) E. O. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Commun.*, 643 (1967).

(36) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

(37) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

(38) H. Ueda, Y. Kai, N. Yasuoka, and N. Kasai, *Bull. Chem. Soc. Jpn.*, **50**, 2250 (1977).

Table III. [^{1}H]^{13}C NMR Data of the Rhodium Complexes 2, 3a, 5a, 7-9^a

compd	δ(CO, bridging)	δ(CO, terminal)	δ(CH)	δ(CH$_2$)	δ(C$_5$H$_5$)	solv; temp, °C
2		193.6 (d, $^1J_{Rh,CO}$ = 88 Hz)			89.7 ("s", $^1J_{Rh,C}$ = ca. 2 Hz)	toluene-d_8
3a$^{-13}CO^c$		185.8 (d, $^1J_{Rh,CO}$ = 78 Hz)		102.3 (t, $^1J_{Rh,C}$ = 28 Hz)^e	94.7 (m), 94.1 (m)	CD$_3$NO$_2$; -25
5a$^{-13}CO^c$	210.5 (q, $^1J_{Rh,CO}$ = 27 Hz)				98.4 ("q", $^1J_{Rh,C}$ = ca. 1.6 Hz)	DMF-d_7; -55/+27
7^{27}	203.8 (t, $^1J_{Rh,CO}$ = 43 Hz)		303.6 (q, $^1J_{Rh,C}$ = 38 Hz)		not given^b	CD$_2$Cl$_2$
8$^{-13}CO^d$		195.0 (t, $^1J_{Rh,CO}$ = 37 Hz)			95.85 ("s")	CD$_3$NO$_2$; +26
8$^{-13}CO^d$		195.6 (br, $\Delta\nu_{1/2}$ = 108 Hz)			95.7 ("s")	CD$_3$NO$_2$; -20
9^{52a}	232.5 (t, $^1J_{Rh,CO}$ = 49 Hz)				not given	CD$_2$Cl$_2$; -65
9^{52a}	232.5 (q, $^1J_{Rh,CO}$ = 32 Hz)				not given	CD$_2$Cl$_2$; +26

^{a} All spectra were taken of nearly saturated solutions at ordinary spectrometer temperature unless otherwise noted and are referenced against Me$_4$Si (downfield shifts). s = singlet, d = doublet, t = triplet, q = quartet, and br = broad. ^{b} Not observed due to insufficient solubility. ^{c} ^{13}CO enrichment ca. 80% (IR spectroscopy). ^{d} ^{13}CO enrichment 46% (mass spectrometry). ^{e} $^1J_{C,H}$ = 146 Hz; compare also data reported in ref 47.

CO or CH$_2$.[5,6,32] Moreover, nonbonding rhodium–rhodium separations are found to be drastically longer than bonding ones (e.g., 371.9 pm in (μ-Cl)$_2$[(η^5-C$_5$Me$_5$)RhCl]$_2$[40] vs. 266.5 pm in (μ-CH$_2$)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$,[5,6] Table VIII). In agreement with the NMR spectroscopic evidence, the methylidyne (CH) ligand occupies a face-bridging position, with the mean carbon–rhodium distance amounting to 196.3 pm. The bridgehead carbon atom is essentially sp^3-hybridized, although the "internal" angles Rh–C(1)–Rh are considerably smaller (average 86.6°) than the "external" angles H(1)–C(1)–Rh (average 127.5°). A similar geometry is also typical of the related methylidynecobalt complexes of the well-known (μ_3-CR)[Co$_3$(CO)$_9$] series[41] and their isoelectronic ruthenium analogue (μ_3-CCH$_3$)[Ru$_3$(CO)$_9$(μ-H)$_3$],[42] as well as the doubly bridged silylmethylidyne complex (μ_3-CSiMe$_3$)(μ_3-C—C≡C—SiMe$_3$)[(η^5-C$_5$H$_5$)Co]$_3$, recently reported by Vollhardt et al.[43,44] Remarkable, however, is the pronounced asymmetric arrangement of the edge-bridging carbonyl ligands: by comparison with the geometric data of well-behaved carbon monoxide bridges found in a variety of other di- and trinuclear rhodium compounds[32-34,38,39] (Table VIII), the structure of the (μ-CO)$_2$Rh$_3$ frame of 5b is best described as sort of a half-way situation between the bridging-type coordination modes being classified these days as "unsymmetrical" and "semibridging", respectively.[45] This view is justified from the following reasons: (i) the Rh–C(μ-CO)–O angles deviate considerably, in both directions, from the average value of ca. 137° (Table VIII) measured for representative fully symmetrical carbonyl bridges; (ii) at the same time, the internal Rh–C(μ-CO)–Rh angles drop below the mean value (ca. 83°) calculated for the compounds which are compiled in Table VIII; (iii) accordingly, the corresponding rhodium–carbon distances [e.g., Rh(1)–C(3) vs. Rh(3)–C(3)] are markedly different from each other. The on-scale drawing given in Figure 2 gives the impression that the bent carbonyl ligands attached to Rh(2) and Rh(3) are leaning toward the remaining metal center Rh(1), with the Rh(1)–C(2) and Rh(1)–C(3) distances very much resembling those of "semibridging" contacts. One can well understand these weaker Rh⋯CO interactions as a convenient type of electron balance in the solid state, an explanation which was first proposed by Cotton to rationalize the unusual "semibridging" coordination mode which he has first established for (η^5-C$_5$H$_5$)$_2$V$_2$(CO)$_5$ and structurally related molecules.[45,46] However, the Rh(1)–O(2) and Rh(1)–O(3) separations are definitely nonbonding in character (307 and 324 pm, respectively).[61]

B. Protonation of the Electron-Rich Rhodium–Rhodium Bond: Novel Cationic Hydrido Methylene Complexes from (μ-CH$_2$)-[(η^5-C$_5$H$_5$)Rh(CO)]$_2$.

The proton-induced synthesis of the first rhodium compounds 5 containing unsubstituted methylidyne (CH) as ligands, from the dinuclear methylene precursor 2, sharply contrasts the formation of stable cationic μ-methyl derivatives upon protonation of (μ-CH$_2$)$_3$Ru$_2$[P(CH$_3$)$_3$]$_6$ recently described by Wilkinson et al.[24] As a matter of fact, the above-mentioned

(39) Trinh-Toan, R. W. Broach, S. A. Gardner, M. D. Rausch, and L. F. Dahl, *Inorg. Chem.*, **16**, 279 (1977).

(40) M. R. Churchill, S. A. Julis, and F. Rotella, *Inorg. Chem.*, **16**, 1137 (1977).

(41) Reviews: (a) R. S. Dickson and P. J. Fraser, *Adv. Organomet. Chem.*, **12**, 812 (1974); (b) D. Seyferth, *ibid.* **14**, 97 (1976).

(42) G. M. Sheldrick and J. P. Yesinowski, *J. Chem. Soc., Dalton Trans.*, 873 (1975).

(43) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, *J. Am. Chem. Soc.*, **101**, 2768 (1979).

(44) Unsymmetrically face-bridged μ_3-ethylidyne cobalt complexes of type (η^5-C$_5$R$_5$)$_3$Co$_3$(CO)$_2$(μ-CO)(μ_3-CCH$_3$) (R = H, CH$_3$) have been reported as well: (a) R. S. McCallum and B. R. Penfold, *Acta Crystallogr., Sect. B*, **34B** (1978) 1688; (b) W. I. Bailey, Jr., F. A. Cotton, and J. D. Jamerson, *J. Organomet. Chem.* **173**, 317 (1979).

(45) For a comprehensive recent review on this subject, see: R. Colton and M. J. McCormick, *Coord. Chem. Rev.*, **31**, 1 (1980). The oxygen–metal distances reported for semibridging M$_x$CO groups vary between 230 and 250 pm (M = V, Mo, Rh, Pt); the shortest M⋯O separations yet reported (221–224 pm) were found for the unique η^2 (μ_3-C,μ_2-O) carbon monoxide ligand of (η^5-C$_5$H$_5$)$_3$Nb$_3$(CO)$_7$: W. A. Herrmann, M. L. Ziegler, K. Weidenhammer, and H. Biersack, *Angew. Chem., Int. Ed. Engl.*, **18**, 960 (1979).

(46) F. A. Cotton, *Prog. Inorg. Chem.*, **21**, 1 (1976).

Table IV.   Infrared Data (cm⁻¹) of the Rhodium Complexes 2, 3, 5, 6-9[a]

compd	ν(CO) freq	other significant bands	solv; temp, °C
2	1959 vs (br)	2963 w, 2903 w (ν(CH₂))	KBr
	2000 m (sh), 1967 vs (br)	2915 w (ν(CH₂))	CH₃NO₂
3a	1992 w, 1963 w,[b] 1881 m, 1843 vs	1124 s, 1085 vs, 1038 s (BF₄)	KBr
	2072 vs, 2049 s, 2009 w, 1859 w		CH₃NO₂; −18
	2072 s, 2048 s, 2011 s; 1862 s (br)		CH₃NO₂; +23
3c	2041 s, 1991 w, 1963 w; 1878 m, 1838 vs	2910 w (ν(CH₂)); 1305 s (sh), 1286 vs (ν(SO))	KBr
3d	1959 s;[c] 1880 w, 1839 vs	2908 w (ν(CH₂)); 1257 s (br) (νSO)	KBr
5a	1929 s, 1884 ms	2911 w (ν(CH)), 1127 s, 1087 vs, 1036 s (BF₄)	KBr
	1928 s, 1886 ms	2910 w (ν(CH)); 1054 s, 1041 m (sh) (BF₄)	CH₃NO₂
5a-¹³CO[d]	1888 s, 1852 ms	1127 s, 1087 vs, 1036 s (BF₄)	KBr
	1882 s, 1845 ms	1054 s, 1041 m (sh) (BF₄)	CH₃NO₂
5b	1918 s, 1870 ms	1710 s, 1695 vs (CO₂⁻)	KBr
	1925 s, 1868 ms	1702 vs (CO₂⁻)	CH₃NO₂
5d	1932 s, 1895 ms	2915 w (ν(CH)); 1276 s, 1264 s (ν(SO))	KBr
	1926 s, 1883 ms	2916 w (ν(CH)); 1268 s, 1074 vs (ν(SO))	CH₃NO₂
6a	1878 w, 1843 s	2915 w (ν(CH₃))	KBr
	1890 w, 1847 s[e]		CH₂Cl₂
6b	1879 w, 1844 s	2911 w (ν(CH₃))	KBr
	1892 w, 1849 s[e]		CH₂Cl₂
7	1967 vs, 1818 s		KBr
	1988 vs, 1811 s		CH₃NO₂
8	1970 s–vs, 1818 vs[f]		KBr
	2082 vs, 2058 s; 1978 w; 1869 s		CH₃NO₂; −25
	2082 s, 2058 s; 1977 s; 1869 w		CH₃NO₂; +20
9	1827 s; 1783 m, 1766 s[52a]		KBr
	1843 vs; 1786 s, 1775 ms (sh)		CH₃NO₂

[a] All spectra were recorded at room temperature (NaCl windows) unless otherwise noted. Low-temperature spectra were obtained with a temperature-controlled Beckman infrared cell (AgBr windows). [b] These absorptions which are weak in intensity were present even in samples prepared at −70 °C and dried in vacuo at −30 °C. [c] Samples slowly decomposed upon preparing the KBr pellet to partially yield the parent compound 2. [d] ¹³CO enrichment >80% (IR). Only the ¹³CO bands are given. ¹²CO absorptions: see entry above. [e] Data obtained from freshly prepared solutions; upon standing for 15 min, weak absorptions for terminal CO ligands [e.g. 6a: 1980, 2036 (sh), 2300 cm⁻¹ (CH₂Cl₂)] begin to appear; temperature-dependent IR spectroscopy clearly demonstrates this effect not to be due to an isomerization phenomenon of the double CO-bridged complexes 6a and 6b but rather to be originating from partial decomposition. [f] Converted to the neutral parent compound 7 during the preparation of the KBr disk.

Table V.   Crystallographic Data and Intensity Measurement Parameters

parameter or exptl detail	5b	6b
cryst size, mm	0.25 × 0.15 × 0.10[a]	0.35 × 0.35 × 0.40[b]
a, pm	1772.5 (6)	890.7 (2)
b, pm	1060.7 (3)	1016.8 (2)
c, pm	2270.9 (7)	1567.1 (3)
α, deg	90.00 (3)	89.87 (2)
β, deg	103.90 (3)	90.07 (2)
γ, deg	90.00 (3)	90.00 (2)
V, pm³	4144.53 × 10⁶	1419.29 × 10⁶
mol wt or fw	686.1	486.8
d_{measd}, g cm⁻³		2.28
Z	8	4
d_{calcd}, g cm⁻³	2.288	2.292
F_{000}	2752	928
space group	C_{2h}^5–C2/c	D_{2h}^{16}–Pmcn
μ(Mo Kα), cm⁻¹	23.83	50.71
λ(Mo Kα), A	0.710 69	0.710 69
scan parameters A and B, deg	0.8, 0.8	0.8, 0.5
reflctns measd	h,k,±l	h,k,±l
θ, deg	65 ⩾ 2θ ⩾ 4	60 ⩾ 2θ ⩾ 0
total no. recorded	2347	2347
significance test	I > 2.5σ(I)	I > 2.5σ(I)
reflctns remaining	2045	1050
decay during collectn	none	none
R(isotropically)	0.082	0.081
R(anisotropically)	0.031	0.068

[a] Crystallized from acetonitrile at 0 to −18 °C. [b] Crystallized from methylene chloride/acetone at −25 to −35 °C.

ruthenium complex resisted hydride abstraction which was hoped would afford a μ-CH group; instead, even with trityl tetrafluoroborate a very high yield of the protonated product {(μ-CH₃)(μ-CH₂)₂Ru₂[P(CH₃)₃]₆}⁺BF₄⁻ was obtained in tetrahydrofuran. This curious reaction is most likely initiated by a carbocation-assisted proton transfer from the solvent.[24] Our

observation that both methane and hydrogen are produced in large amounts during the acid-induced transformation of 2 → 5 conducted in tetrahydrofuran, whereas not even traces of other plausible byproducts except (η⁵-C₅H₅)Rh(CO)₂ could be detected by gas chromatography, initiated the following experiments which led to some key intermediates responsible for the final methylidyne products.

(1) If Brønsted acids such as HBF₄, FSO₃H, or CF₃SO₃H are added to solutions of (μ-CH₂)[(η⁵-C₅H₅)Rh(CO)]₂ (2) in diethyl ether rather than tetrahydrofuran at temperatures around −20 °C, yellow precipitates 3a, 3c, and 3d, respectively, are formed immediately and quantitatively according to Scheme I (see Experimental Section). Conductivity measurements (Table I) and elemental analyses as well as the infrared and ¹H NMR spectra (Tables II and IV) convincingly prove these compounds to constitute the expected 1/1 protonation products of composition [(C₅H₅)₂Rh₂(CO)₂(CH₂)H]⁺X⁻ (X = BF₄, 3a; X = CF₃SO₃, 3d; X = FSO₃, 3c). Despite the fact that we could not obtain good quality single crystals of the protonation products 3 for X-ray diffraction studies, the relevant structural features became quite clear from the following spectroscopic results.

(i) The IR spectra exhibit only CO bands arising from terminal groups at −25 °C in nitromethane. Due to the cationic character of the complexes, these ν(CO) absorptions are well shifted to higher wavenumbers as compared to the neutral precursor 2. At higher temperatures, new bands in the CO-bridging area slowly begin to appear, which are not in a reversible equilibrium with the terminal CO's.

(ii) The carbonyl groups resonate as doublets in the ¹³C NMR spectra of highly ¹³CO-enriched samples (nitromethane, −20 °C; Table III). In accordance with the IR spectra, this result not only proves the CO ligands of 3 to constitute terminal ones but furthermore rules out intramolecular CO exchange. As regards the IR and ¹³C NMR data, the protonation products 3 very much resemble those of the neutral precursor 2,[6,26,47] thus indicating

(47) R. J. Lawson and J. R. Shapley, *Inorg. Chem.*, 17, 2963 (1978).

Transition-Metal Methylene Complexes

J. Am. Chem. Soc., Vol. 103, No. 1, 1981 71

Table VI. Interatomic Distances and Angles for the Cationic
μ_3-Methylidyne Rhodium Complex 5b[a]

A. Bond Lengths (pm)[b]			
Rh(1)-Rh(2)	267.7 (1)	Rh(2)-C(15)	221.4 (13)
Rh(1)-Rh(3)	271.3 (1)	Rh(2)-C(16)	219.6 (11)
Rh(2)-Rh(3)	268.3 (1)	Rh(2)-C(17)	223.8 (17)
Rh(1)-C(1)	193.5 (6)	Rh(2)-C(18)	220.9 (13)
Rh(1)-C(2)	220.2 (11)	Rh(2)-C(19)	220.3 (18)
Rh(1)-C(3)	246.3 (13)	Rh(3)-C(10)	225.3 (13)
Rh(2)-C(1)	195.6 (9)	Rh(3)-C(11)	220.6 (11)
Rh(2)-C(2)	191.4 (9)	Rh(3)-C(12)	221.2 (14)
Rh(3)-C(1)	199.5 (10)	Rh(3)-C(13)	221.3 (13)
Rh(3)-C(3)	189.7 (10)	Rh(3)-C(14)	224.8 (13)
Rh(1)-C(5)	219.5 (11)	C(1)-H(1)	97.9 (86)
Rh(1)-C(6)	221.7 (11)	C(2)-O(2)	116.8 (12)
Rh(1)-C(7)	218.3 (12)	C(3)-O(3)	114.0 (14)
Rh(1)-C(8)	223.7 (10)		
Rh(1)-C(9)	223.3 (19)		

B. Nonbonding Intramolecular Contacts (pm)					
Rh(1)-O(2)	307	Rh(3)-O(3)	300	F(1)-C(18)	349
Rh(1)-O(3)	324	Rh(2)-C(3)	326	F(2)-O(2)	340
Rh(3)-C(2)	332	Rh(2)-O(2)	299		

C. Bond Angles (Deg)[c]			
Rh(3)-Rh(1)-Rh(2)	59.7 (0)	C(1)-Rh(1)-C(2)	92.1 (5)
Rh(1)-Rh(2)-Rh(3)	60.8 (0)	C(1)-Rh(1)-C(3)	88.3 (5)
Rh(1)-Rh(3)-Rh(2)	59.5 (0)	C(1)-Rh(2)-C(2)	100.3 (5)
C(1)-Rh(1)-Rh(2)	46.9 (3)	C(1)-Rh(3)-C(3)	105.8 (6)
C(1)-Rh(1)-Rh(3)	47.3 (8)	Rh(3)-C(1)-Rh(2)	86.9 (3)
C(1)-Rh(2)-Rh(3)	47.9 (3)	Rh(3)-C(1)-Rh(1)	87.3 (3)
C(1)-Rh(2)-Rh(1)	46.2 (2)	Rh(3)-C(1)-Rh(2)	85.5 (3)
C(1)-Rh(2)-Rh(1)	46.2 (2)	Rh(1)-C(2)-Rh(2)	80.4 (4)
C(2)-Rh(2)-Rh(1)	54.3 (3)	C(2)-Rh(1)-Rh(2)	44.9 (2)
C(3)-Rh(3)-Rh(1)	61.6 (4)	C(3)-Rh(1)-Rh(2)	78.8 (3)
C(1)-Rh(3)-Rh(1)	45.4 (2)	C(3)-Rh(1)-Rh(3)	42.7 (2)
C(1)-Rh(3)-Rh(2)	46.6 (3)	Rh(1)-C(3)-Rh(3)	75.7 (4)
Rh(1)-C(2)-O(2)	127.3 (8)	H(1)-C(1)-Rh(1)	126.6 (5.6)
Rh(2)-C(2)-O(2)	150.3 (9)	H(1)-C(1)-Rh(2)	133.7 (5.7)
Rh(1)-C(3)-O(3)	123.5 (9)	H(1)-C(1)-Rh(3)	122.2 (5.7)
Rh(3)-C(3)-O(3)	160.7 (11)		

D. Selected Interplanar Angles (Deg)	
Rh(1),Rh(2),Rh(3) vs. Rh(1),Rh(2),C(2)	114.8
Rh(1),Rh(2),Rh(3) vs. Rh(1),Rh(3),C(3)	72.4
Rh(1),Rh(2),Rh(3) vs. Rh(2),Rh(3),C(3)	55.7
Rh(1),Rh(2),Rh(3) vs. Rh(3),Rh(1),C(1)	57.5
Rh(1),Rh(2),Rh(3) vs. C(5-9)	96.4
Rh(1),Rh(2),Rh(3) vs. C(10-14)	73.1
Rh(1),Rh(2),Rh(3) vs. C(15-19)	79.2
Rh(1),Rh(2),C(1) vs. Rh(1),C(2),Rh(2)	7.1
Rh(1),Rh(3),C(1) vs. Rh(1),C(3),Rh(3)	14.9

[a] Estimates of standard deviations corresponding to the last digit(s) are given in parentheses in this and other tables throughout this paper. The anion $CF_3CO_2^-$ is characterized by the following parameters: C(20)-C(21) = 152.5 (15) pm, C(20)-O(5) = 117.6 (13) pm, C(20)-O(6) = 113.3 (16) pm, C(21)-F(1) = 128.9 (15) pm, C(21)-F(2) = 132.2 (18) pm, C(21)-F(3) = 129.5 (17) pm, C(21)-C(20)-O(5) = 114.2 (1.0)°, C(21)-C(20)-O(6) = 118.1 (0.9)°. [b] The C-C distances of the cyclopentadienyl rings range between 132.8 and 140.8 pm, with a maximum standard deviation of 2.9 pm. [c] The C-C-C angles of the cyclopentadienyl ligands amount to 106-110° (standard deviation ≤1.7°. [d] The O(2) and O(3) atoms deviate by −6 and −3 pm, respectively, from the corresponding Rh,C,Rh planes.

analogous structures. Solubility problems unfortunately precluded the observation of the CH_2 group in the ^{13}C NMR spectra of 3.

(iii) The ^1H NMR spectra are quite informative as well. Notably, no resonances originating from methyl groups could be detected in the range τ 7-17 in which both terminal and bridging CH_3 ligands are expected to show up. On the other hand, the spectra are characterized by two symmetric triplets centered around ca. τ 23; the chemical shifts, multiplicity, and coupling constants as well as the relative intensities of these signals (Table II) provide diagnostic proof for Rh-H-Rh functions to be present in the primary products 3. At the same time, absorptions in the downfield area (τ 0-5) can only be attributed to methylene protons
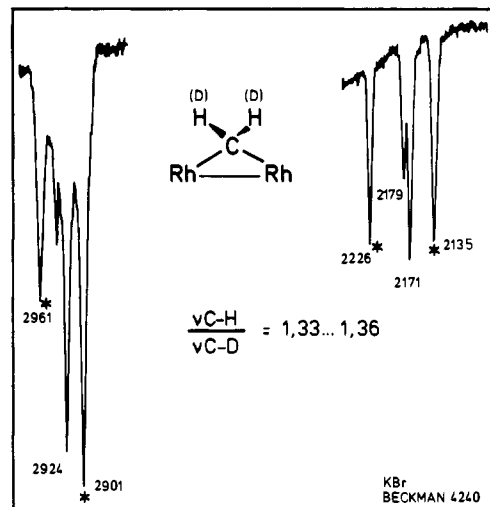

Figure 3. IR spectrum in the ν(CH) and ν(CD) region of labelled (μ-CH_2)[(η^5-C_5H_5)Rh(CO)]$_2$ formed by deprotonation of [(η^5-C_5H_5)$_2$Rh$_2$(CO)$_2$(CH$_2$)(D)]$^+$FSO$_3^-$ ([D]-3c).

which have previously been found in the same range for the related neutral complexes (μ-CH_2)[(η^5-C_5H_5)M(CO)$_x$]$_2$ (M = Mn, x = 2; M = Rh, x = 1),[4-6] (μ-CH_2)[Os$_3$(CO)$_{10}$H$_2$],[29] [μ-C(H)CH= CMe$_2$][W$_2$(CO)$_8$],[48] and especially the cationic μ-methylene μ-methyl system [Ru$_2$(μ-CH$_3$)(μ-CH$_2$)$_2$(PMe$_3$)$_6$](BF$_4$).[24] As a matter of fact, dimetallacyclopropane-type μ-methylene complexes belonging to class A[21] are easily distinguished from class B compounds[21] not displaying metal–metal bonds, as well as from the closely related alkyl complexes, by means of their low-field ^1H NMR absorptions[8,10a] for a rather wide variety of metal–ligand combinations reported to date.[8b]

The occurrence of two sets of signals for both the Rh-H-Rh and the Rh-CH_2-Rh functions is another striking feature of the ^1H NMR spectra of 3. The corresponding groups are found to form a temperature-dependent equilibrium with each other, the molecular origin of which is still open to further debate. As the most reasonable explanation, we offer the interconversion of the diastereoisomers arising from cis and trans-oriented cyclopentadienyl and carbonyl groups, respectively. The equilibrium ratio K amounts to 45:55 at +20 °C.

(2) While the spectroscopic data clearly establish the geometry of the cationic primary protonation products in solution to be defined by a four-membered dimetallic μ-methylene μ-hydrido frame with a cyclopentadienyl and a terminal carbonyl group attached to each metal center, the solid-state structure is still missing conclusive evidence. Unlike the solution IR spectra, CO absorptions are found solely in the bridging metal–carbonyl area (Table IV)! Taking into account that the ν(CH) pattern of 3a is very similar to that of the precursor 2, quadruply bridged structures of type [(η^5-C_5H_5)$_2$Rh$_2$(μ-CO)$_2$(μ-CH$_2$)(μ-H)]$^+$X$^-$ must be considered as viable in the solid state, unless there is definite evidence to the contrary. It should be noted, however, that the solid-state structure of the compound 3 is not of crucial importance for their clean chemical transformations proceeding only in solution anyway.

Deprotonation of 3 is effected by even weakly basic solvents such as THF, Me$_2$SO, HMPT, or methanol, yielding the authentic neutral precursor 2 after a few hours at room temperature. A rapid CH_2/RhHRh proton exchange is proven to occur by labeling experiments. Thus, the ionic complex {(μ-D)(μ-CH$_2$)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$}$^+$FSO$_3^-$ ([D]-3c) obtained by deuteration of (μ-CH$_2$)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (2) with FSO$_3$D instantaneously and quantitatively gives its *labeled* precursor 2 upon treatment with CD$_3$OD/NaOCH$_3$ or CH$_3$OH/NaOCH$_3$. The μ-CH$_x$D$_{2-x}$ complex formed in this way displays a roughly statistical deuterium distribution over the methylene proton sites, despite the fact that

(48) J. Levisalles, H. Rudler, F. Dahan, and Y. Jeannin, *J. Organomet. Chem.*, **188**, 193 (1980).

Table VII.   Positional Parameters ($\times 10^5$ for Rh, $\times 10^4$ for C and O, $\times 10^3$ for H) and Thermal Parameters ($\times 10^5$ for Rh, $\times 10^4$ for Others)[a] for the Methylidynerhodium Complex 5b

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	13597 (3)	17558 (9)	13400 (3)	231 (3)	411 (4)	351 (4)	1 (5)	48 (2)	−26 (4)
Rh(2)	26618 (4)	04984 (7)	13174 (4)	292 (3)	356 (5)	449 (5)	22 (4)	99 (3)	23 (3)
Rh(3)	26915 (4)	30261 (7)	13610 (4)	302 (3)	345 (5)	401 (5)	−4 (4)	83 (3)	−64 (3)
C(1)	2384 (4)	1704 (10)	1882 (4)	27 (3)	49 (6)	33 (4)	−8 (5)	8 (3)	−10 (5)
C(2)	1735 (6)	539 (10)	678 (5)	51 (6)	59 (7)	36 (6)	−7 (6)	6 (5)	−6 (5)
C(3)	1889 (6)	3069 (12)	640 (5)	53 (6)	61 (9)	76 (8)	15 (7)	−9 (6)	−7 (6)
C(5)	390 (5)	735 (11)	1567 (5)	39 (5)	64 (8)	67 (8)	−11 (6)	19 (5)	−25 (5)
C(6)	571 (5)	1772 (13)	1964 (5)	42 (5)	96 (9)	53 (6)	19 (8)	25 (5)	10 (7)
C(7)	467 (5)	2861 (13)	1621 (5)	43 (5)	91 (11)	62 (7)	−18 (7)	16 (5)	9 (5)
C(8)	172 (6)	2570 (13)	995 (6)	38 (5)	73 (9)	73 (10)	12 (8)	14 (6)	19 (6)
C(9)	113 (5)	1266 (13)	960 (5)	24 (4)	101 (4)	53 (8)	−10 (7)	−4 (4)	−6 (5)
C(10)	3387 (8)	4181 (15)	2138 (6)	96 (10)	89 (11)	58 (9)	−12 (8)	3 (7)	−55 (9)
C(11)	3885 (6)	3401 (14)	1899 (6)	45 (6)	74 (10)	122 (11)	5 (10)	−25 (7)	−29 (7)
C(12)	3831 (7)	3796 (13)	1296 (8)	59 (7)	69 (10)	122 (13)	−39 (10)	46 (8)	−43 (7)
C(13)	3281 (7)	4777 (11)	1183 (6)	93 (9)	42 (9)	77 (9)	14 (7)	6 (8)	−46 (7)
C(14)	3011 (7)	4988 (13)	1707 (6)	73 (8)	70 (9)	84 (9)	−32 (8)	25 (7)	−21 (7)
C(15)	3857 (6)	−49 (14)	1287 (7)	47 (6)	89 (10)	162 (14)	36 (10)	60 (8)	27 (7)
C(16)	3775 (6)	−182 (13)	1877 (7)	38 (5)	67 (9)	122 (12)	−2 (9)	−2 (7)	14 (6)
C(17)	3260 (10)	−1077 (17)	1902 (8)	105 (13)	94 (13)	110 (13)	59 (11)	31 (11)	50 (11)
C(18)	2959 (8)	−1523 (12)	1310 (11)	53 (7)	26 (8)	255 (24)	17 (12)	28 (11)	12 (5)
C(19)	3355 (9)	−875 (16)	944 (8)	116 (12)	112 (15)	109 (14)	−14 (11)	10 (10)	86 (11)
C(20)	963 (5)	−3295 (14)	1501 (5)	43 (5)	111 (10)	48 (6)	−27 (8)	1 (4)	−7 (7)
C(21)	756 (6)	−3251 (14)	810 (5)	50 (6)	88 (9)	64 (8)	−7 (9)	2 (5)	−8 (7)
O(2)	1376 (4)	191 (9)	206 (3)	72 (7)	92 (7)	44 (5)	−24 (5)	−4 (4)	−1 (5)
O(3)	1548 (5)	3323 (10)	162 (4)	76 (5)	119 (8)	67 (6)	49 (7)	−16 (4)	−27 (6)
O(5)	1614 (6)	3044 (15)	1727 (4)	90 (7)	263 (15)	70 (6)	−19 (9)	−7 (5)	−20 (9)
O(6)	0475 (6)	−3431 (22)	1738 (5)	76 (7)	542 (29)	78 (7)	−42 (14)	28 (6)	−58 (13)
F(1)	1321 (5)	−3258 (13)	0543 (3)	106 (6)	278 (13)	66 (5)	−37 (8)	45 (5)	−25 (9)
F(2)	335 (8)	−2258 (12)	0584 (5)	218 (12)	199 (4)	112 (8)	60 (8)	19 (8)	95 (10)
F(3)	300 (7)	−4152 (12)	0555 (4)	213 (11)	206 (13)	87 (7)	−44 (7)	14 (7)	−130 (10)

	x/a	y/b	z/c	U_{11}, $Å^2$		x/a	y/b	z/c	U_{11}, $Å^2$
H(1)	251 (5)	177 (9)	232 (4)	7 (0)	H(9)	−7 (1)	79 (1)	59 (1)	5 (3)
H(5)	43 (1)	−14 (1)	167 (1)	27 (8)	H(10)	332 (1)	413 (1)	254 (1)	12 (5)
H(6)	74 (1)	172 (1)	240 (1)	13 (5)	H(11)	421 (1)	274 (1)	211 (1)	19 (7)
H(7)	58 (1)	370 (1)	178 (1)	4 (3)	H(12)	411 (1)	346 (1)	102 (1)	8 (4)
H(8)	3 (1)	316 (1)	066 (1)	5 (3)	H(13)	312 (1)	523 (1)	081 (1)	3 (2)

[a] Anisotropic thermal parameters given for the nonhydrogen atoms; hydrogen atoms: isotropic thermal parameters ($\times 10^2$).

Table VIII.   Comparative Geometrical Data of the Metal Carbonyl Backbones of Structurally Significant Di- and Trinuclear Rhodium Complexes[a]
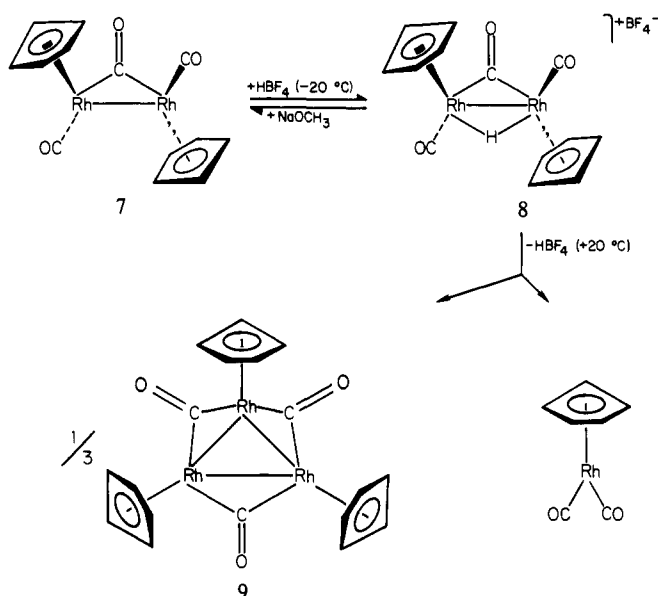
compd	d(Rh–Rh)	d(Rh–μ-CO)	$\angle$(Rh–μ-CO–Rh)	$\angle$(Rh–C–O)	ref
(μ-CH$_2$)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (2)	266.49 (4)				5, 6
(μ-CO)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (7)	268.1 (2)	201.7 (17), 199.0 (17)	84.0 (6)	136.5 (17), 139.2 (16)	32
[(η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_2$(μ_3-CH)]$^+$CF$_3$CO$_2^-$ (5b)	267.7 (1)	191.4 (9), 220.2 (11)	80.4 (4)	128.7 (8), 150.3 (9)	this work
	271.3 (1)	189.7 (10), 246.3 (13)	75.7 (4)	123.5 (9), 160.7 (11)	
	268.3 (1)	(no bridging CO)			
(η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_3$	262	200, 201		d	33
(η^5-C$_5$H$_5$)$_3$Rh$_3$(CO)(μ-CO)$_2$[b]	262.0 (2)	200.3 (14), 189.0 (14)	84.5 (5)	d	34
	266.3 (2)	194.7 (14), 197.2 (14)	83.9 (5)		
	270.5 (2)	(no bridging CO)			
(η^5-C$_5$H$_5$)$_3$(η^5-μ_3-C$_5$H$_5$)Rh$_3$(μ_3-H)[c]	271.5 (3)				35
	273.0 (2)				
(η^5-C$_5$H$_5$)$_2$Rh$_2$(μ-CO)$_2$(Br)(CH$_3$) (6b)	266.0 (3)	199.3 (20), 199.5 (20)	83.7 (9)	137.7 (15), 138.6 (15)	this work
Rh$_2$(CO)$_2$(μ-Cl)$_2$	331				36
Rh$_6$(CO)$_{12}$(μ_3-CO)$_4$	277.6 (1)				37
(μ-CO)[μ-C(C$_6$H$_5$)$_2$]$_2$[(η^5-C$_5$H$_5$)Rh]$_2$	254.8 (1)	199.5 (9)	79.4 (3)	140.3 (7)	38
(η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)(η^2,μ_3-C$_6$F$_5$C≡CC$_6$F$_5$)	259.2 (2)	196 (1)	82.9 (3)	132.9 (6)	39
	258.8 (1)			136.3 (7)	
	267.2 (1)				
(μ-Cl)$_2$[(η^5-C$_5$Me$_5$)RhCl]$_2$	371.9 (1)				40

[a] Distances in pm and angles in deg.   [b] Only one of the three rhodium–rhodium bonds is bridged by two carbonyl ligands.   [c] This compound contains a face-bridging Cp ligand.   [d] Not given; cannot be calculated either.

compound [D]-3c is a *monodeuterated* species. A rough estimate obtained from an IR analysis of the ν(CH) and ν(CD) absorptions (Figure 3) reflects the quantitative enrichment data determined by mass spectrometry (36% D$_0$, 38% D$_1$, 26% D$_2$). Deuterated 3c gives the same label distribution in deprotonated product 2 upon treatment with either labeled or unlabeled methoxide/methanol. Accordingly, highly [^{2}H]-labeled samples of the methylidyne cluster [(η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_2$(μ_3-CH)]$^+$CF$_3$CO$_2^-$ (5b) with 80

± 5% deuterium enrichment (^{1}H NMR) are formed if an excess of CF$_3$CO$_2$D reacts with 2 in tetrahydrofuran. We consider these results which are fully consistent with the observed production of methane and hydrogen to clearly demonstrate—mechanistically of salient importance—that organometallic intermediates containing methyl groups participate in the synthesis of the final μ_3-methylidyne compounds. Though we were not able to directly observe methyl groups by ^{1}H NMR spectroscopy at any stage of

Scheme II

7   8   9

Table IX. Interatomic Distances and Angles for the Dinuclear Bromo(methyl)rhodium Compound 6b

bond lengths, pm		bond angles, deg	
Rh(1)–Rh(2)	266.0 (3)		
Rh(1)–Br(1)^a	250.4 (13)	C(2)–Rh(1)–Rh(2)	102.3 (13)
Rh(2)–Br(2)^a	254.1 (6)	C(1)–Rh(1)–Rh(2)	48.1 (6)
Rh(1)–C(1)	199.5 (20)	C(1)–Rh(1)–C(1')	91.1 (11)
Rh(2)–C(1)	199.3 (20)	Rh(1)–C(1)–Rh(2)	83.7 (9)
Rh(2)–C(3)^a	234.1 (48)	Rh(1)–C(1)–O(1)	137.7 (15)
Rh(1)–C(2)^a	248.6 (54)	Rh(2)–C(1)–O(1)	138.6 (15)
Rh(1)–C(4)	228.8 (32)	C(5)–C(4)–C(5')	104.6 (26)
Rh(1)–C(5)	229.5 (21)	C(4)–C(5)–C(6)	111.2 (20)
Rh(1)–C(6)	222.3 (16)	C(5)–C(6)–C(6')	106.1 (12)
Rh(2)–C(7)	208.4 (38)	Br–Rh(2)–Rh(1)	100.3 (1)
Rh(2)–C(8)	217.8 (38)	C(1)–Rh(2)–Rh(1)	48.2 (6)
Rh(2)–C(9)	222.4 (25)	C(1)–Rh(2)–C(1')	91.3 (12)
C(4)–C(5)	142.4 (29)	C(8)–C(7)–C(8')	108.1 (47)
C(5)–C(6)	144.5 (31)	C(7)–C(8)–C(9)	108.1 (36)
C(6)–C(6')	145.0 (41)	C(8)–C(9)–C(9')	107.7 (23)
C(7)–C(8)	123.2 (45)		
C(8)–C(9)	130.2 (48)		
C(9)–C(9')	120.4 (69)		
C(1)–O(1)	118.6 (26)		

^{a} See footnote *a*, Table X.

the reaction sequence starting from **2** and leading to **5**, the methylene/methyl tautomerism proposed here is the only mechanism which fully accounts for the entire set of reactions reported in this paper. This pathway of metal-centered hydrogen mobility, a fascinating and important one as well, was first established in a beautiful and convincing series of experiments performed by Shapley et al. for the neutral osmium cluster Os$_3$(CO)$_{10}$(CH$_2$)H$_2$ which reversibly equilibrates with its tautomer of composition Os$_3$(CO)$_{10}$(CH$_3$)H.[15,16,29,49] Since the rhodium–methyl tautomers escaped from any *direct* characterization due to their intermediate character, formula **4** should not be misunderstood in terms of representing the precise structure. The observed proton exchange of the μ-hydrido μ-methylene species **3** very likely occurs via unsymmetrical μ-CH$_3$ complexes (e.g., Rh–CH$_2$···H···Rh), a type of coordination which has been detected for the above-mentioned stable methyleneosmium cluster by neutron diffraction techniques.[15,16]

(3) NMR kinetics of the transformation [D]-**3c** → [D]-**5c** show the synthesis of the μ$_3$-methylidyne derivatives **5** also to proceed with *partial* deprotonation of the μ-hydrido μ-methylene compounds **3**. In addition, the transitory appearance of new cyclopentadienyl signals during the *irreversible* reaction sequence **3** ⟶ **5** indicates the intermediate formation of mono-, di-, and/or trinuclear species to be responsible for the μ$_3$-methylidyne synthesis. It proved impossible to more closely characterize these species which entirely disappear—with the exception of (η^5-C$_5$H$_5$)Rh(CO)$_2$—as the formation of the cationic clusters goes to completion. We note parenthetically that the observed hydrogen production could directly originate from a cationic metal-bound μ-CH$_3$ group comparable to the well-documented loss of hydrogen from the related CH$_5^+$ cation. In our opinion, methane elimination arises from methyl hydrido species, either intra- or (much more likely in this case) intermolecularly.

(4) The primary attack of the electron-rich rhodium–rhodium bond of **2** by a proton receives independent support from analogous experiments dealing with the μ-carbonyl complex (μ-CO)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (**7**) which structurally differs from the μ-methylene system solely by replacement of the CH$_2$ group for a CO ligand. Both compounds are geometrically and electronically virtually equivalent. Therefore, it was no longer surprising that action of HBF$_4$ upon solutions of **7** in diethyl ether at –30 °C results in immediate and quantitative formation of a light red precipitate **8** which can be kept under dry nitrogen at –20 °C for several days without decomposition. The 1/1 electrolyte **8** is

exceedingly sensitive to solvents displaying basic properties such as THF, Me$_2$SO, HMPT, or methanol which effect slow reversible deprotonation with formation of the starting compound **7**. Rapid deprotonation occurs with sodium methoxide (Scheme II). The composition and the structure of this simple protonation product **8** have been established unequivocally by means of elemental analyses, conductivity measurements (Table I), ^{1}H NMR (Table II), ^{13}C NMR (Table III), and IR spectroscopy (Table IV) already discussed in a preliminary communication.[25] Strikingly, the chemistry of [(μ-CO)(μ-H)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$]$^+$BF$_4^-$ (**8**) very much parallels the fate of our primary protonation products **3** derived from (μ-CH$_2$)[(η^5-C$_5$H$_5$)Rh(CO)]$_2$ (**2**). The initially dark red solutions of **8** in nitromethane, which are completely stable for many hours at –20 °C, gradually change to grass green at room temperature. As observed for [(η^5-C$_5$H$_5$)$_2$Rh$_2$(CO)$_2$(CH$_2$)H]$^+$X$^-$ (**3**), partial deprotonation proceeds with concomitant formation of (η^5-C$_5$H$_5$)Rh(CO)$_2$ and the C_{3v} isomer of the trinuclear carbonyl cluster (η^5-C$_5$H$_5$)Rh$_3$(μ-CO)$_3$ (**9**), the latter not only being isoelectronic with the μ$_3$-methylidyne cluster cations **5** but also sharing their fundamental structural features. This neutral cluster compound previously synthesized by Fischer[50] and Shapley[52] and structurally characterized by Mills[32,53] is also formed in 92% yield under exactly the same conditions which convert the dinuclear μ-CH$_2$ complex **2** into the trinuclear μ$_3$-CH$^+$ derivatives (HBF$_4$/H$_2$O in THF; compare section A and Experimental Section); in this case, the intermediate occurrence of a Rh–H–Rh bridge is evident from the ^{1}H NMR spectra. Once again, activation of the rhodium–rhodium bond by direct protonation constitutes the product-determining prerequisite for the spontaneous acid-induced fragmentation of dinuclear compounds discussed here. This method offers a straightforward preparative alternative for the well-known photoactivation of these and related metal carbonyls.[60]

It is of interest to note that protonation reactions presented here are not restricted to single rhodium–rhodium bonds. The triangular rhodium frames of both isomers of the neutral compound (η^5-C$_5$H$_5$)$_3$Rh$_3$(CO)$_3$ are open to proton attack as well: if suspensions or solutions of these clusters are treated with excess CF$_3$SO$_3$H in nitromethane, the exceedingly stable ionic protonation product of composition [(η^5-C$_5$H$_5$)$_3$Rh$_3$(μ-CO)$_3$(μ$_3$-H)]$^+$SO$_3$CF$_3^-$ (**10**) is formed in clean and prompt reactions (Experimental

(49) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **100**, 7726 (1978).

(50) E. O. Fischer and K. Bittler, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **16B**, 225 (1961).
(51) W. A. Herrmann, J. Plank, and D. Riedel, in preparation.
(52) (a) R. J. Lawson and J. R. Shapley, *J. Am. Chem. Soc.*, **98**, 7433 (1976); (b) R. J. Lawson and J. R. Shapley, *Inorg. Chem.*, **17**, 772 (1978); (c) R. J. Lawson and J. R. Shapley, *Inorg. Chem.*, **17**, 2963 (1978).
(53) O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, **10**, 331 (1967).

Table X. Fractional Coordinates ($\times 10^4$ for Rh and Br, $\times 10^3$ for Others),[a,b] Occupation Factors ($PP*$), and Anisotropic Thermal Parameters ($\times 10^4$)[c] for the Dinuclear Bromo(methyl)rhodium Complex 6b

|	x/a	y/b	z/c	$PP*$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh(1)	2500 (0)	391 (2)	2938 (1)	0.5	336 (10)	300 (9)	330 (9)	−8 (7)	0 (0)	0 (0)
Rh(2)	2500 (0)	9815 (2)	1283 (1)	0.5	296 (10)	396 (10)	331 (9)	−7 (8)	0 (0)	0 (0)
Br(1)	2500 (0)	2852 (13)	2894 (9)	0.25	602 (82)	715 (71)	933 (78)	32 (61)	0 (0)	0 (0)
Br(2)	2500 (0)	2116 (6)	650 (3)	0.25	453 (30)	576 (31)	466 (28)	152 (24)	0 (0)	0 (0)
C(1)	410 (3)	51 (2)	205 (1)	1.0	773 (144)	553 (105)	355 (85)	165 (79)	−118 (109)	−43 (113)
O(1)	538 (1)	82 (2)	201 (1)	1.0	325 (68)	976 (108)	711 (92)	−64 (83)	80 (75)	−192 (73)
C(2)	250 (0)	284 (5)	293 (3)	0.25	591 (605)	1 (211)	1 (183)	−245 (182)	0 (0)	0 (0)
C(3)	250 (0)	180 (5)	53 (3)	0.25	1024 (426)	569 (279)	104 (182)	65 (181)	0 (0)	0 (0)
C(4)	250 (0)	835 (3)	355 (2)	0.5	1346 (321)	712 (195)	297 (138)	91 (137)	0 (0)	0 (0)
C(5)	376 (2)	905 (2)	387 (1)	1.0	642 (141)	823 (140)	547 (118)	310 (109)	−444 (111)	−65 (119)
C(6)	331 (2)	26 (2)	428 (1)	1.0	653 (127)	1077 (165)	254 (78)	110 (99)	−110 (87)	−271 (135)
C(7)	250 (0)	887 (4)	10 (2)	0.5	3098 (872)	447 (205)	374 (175)	−102 (150)	0 (0)	0 (0)
C(8)	362 (4)	−160 (3)	45 (3)	1.0	1269 (315)	856 (245)	1794 (408)	−579 (249)	370 (314)	−328 (244)
C(9)	318 (4)	−227 (2)	111 (2)	1.0	2027 (477)	606 (142)	1208 (213)	−106 (140)	−996 (266)	236 (182)

[a] The positions of Br(1), C(3) and of Br(2), C(2) are statistically distributed (see occupation factors). [b] Note that the molecule has a plane of symmetry along the Rh–Rh vector, including C(2)/C(3) and Br(1)/Br(2) and also bisecting the C_5H_5 groups. Therefore, only three atomic parameters of each ring ligand are given. [c] The anisotropic temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)$.

Section) which will be described in detail in a forthcoming paper.[51]

C. Proton-Induced Ring Opening of the μ-Methylene Rhodium Complex. A Straightforward Novel Route to Halo Methyl Complexes. Our mechanistic proposal called for a competition experiment which was able to chemically characterize the methyl tautomers **4**. Protic acids derived from anions capable of metal coordination were expected to produce neutral complexes either from the cationic primary products (e.g., **3a**) or their immediate precursor **2**.

If the dimetallacyclopropane-type μ-methylene rhodium complex **2** is allowed to react with excess dry hydrogen halides such as HCl or HBr in diethyl ether at room temperature, brown, slightly air-sensitive compounds **6a** and **6b**, respectively, are quickly precipitated according to Scheme I in essentially quantitative yields. Unlike the products **3** and **5** presented above (sections A and B), these halogen-containing dinuclear compounds of composition $(C_5H_5)_2Rh_2(CO)_2(CH_3)X$ (X = Cl, **6a**; X = Br, **6b**) are in fact nonelectrolytes (Table I). Although the ^{1}H NMR and IR data (Tables II and IV) strongly indicated dinuclear structures containing two cyclopentadienylrhodium fragments linked together by two well-behaved carbonyl bridges both in solution and in the crystalline state, we decided to undertake a single-crystal X-ray diffraction study of the bromo derivative **6b** in order to unequivocally determine its stereochemistry. This compound crystallizes from methylene chloride/acetone in the centric space group D_{2h}^{16}—*Pmcn*, with the cell parameters and other crystallographic data listed in Table V. An ORTEP representation is given in Figure 4. Bond distances and angles are compiled in Table IX, while a list of positional parameters, occupation factors, and thermal parameters is found in Table X.

The geometry of the C_s symmetric molecule is characterized by a short metal-to-metal bond which is comparable in length with other rhodium–rhodium bonds symmetrically bridged by two carbonyl groups (Table VIII). Strikingly, the four-membered frame defined by the two metal atoms and the carbonyl carbons is not planar but rather tilted toward the terminal ligand sites (CH$_3$ and Br, respectively), the interplanar angle [Rh(1),C(1),Rh(2) vs. Rh(1),C(1'),Rh(2)] amounting to 147.0 (10)°. The most interesting feature of this molecule is its stereochemistry regarding the metal centers: although the methylene starting compound **2** (C_{2v} symmetry) displays kinetically stable S,S (or R,R) configurations as regards the chiral rhodium centers, arising from trans-oriented sets of terminal ligands (C$_5$H$_5$, CO),[5,6,17,54] its ring-opening product **6b** exhibits both the cyclopentadienyl groups and the remaining terminal functions CH$_3$ and Br, respectively, in cis positions to each other, this observation suggesting rotation
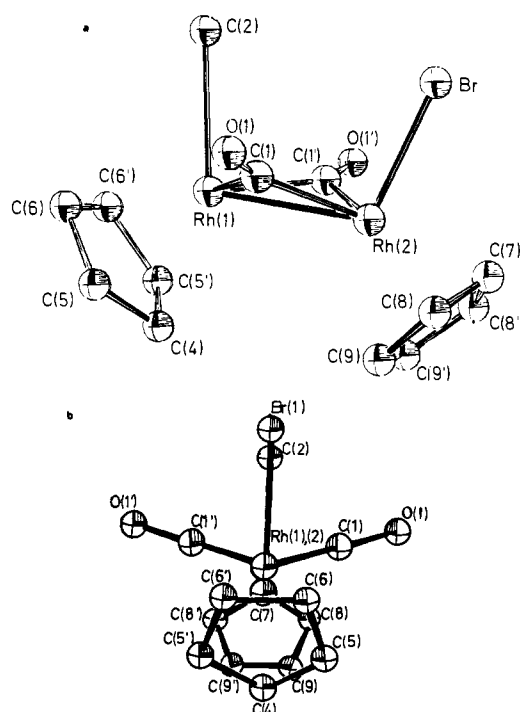
Figure 4. (a) ORTEP drawing of bromo(methyl)bis[μ-carbonyl-(η^5-cyclopentadienyl)rhodium] (Rh–Rh) (**6b**). The thermal ellipsoids correspond to 50% probability. Since bromine and the methyl carbon atoms are statistically disordered (see Tables IX and X), only one position of each is shown for clarity. (b) ORTEP representation of **6b** along the rhodium rhodium vector.

of the CpRh fragments around a nonbridged metal–metal bond in the course of the reaction sequence **2** → **6b**. In this context, we obtained clear-cut results as regards the question as to when ring opening occurs: if the protonation reaction of **2**, employing HBr as described above, is conducted at low temperatures (−80 °C), a light yellow precipitate is formed which has been characterized as the cationic hydrido methylene species **3e** by conductivity measurements (1/1 electrolyte) and chemical transformations. For example, the initial product **3e** instantaneously is deprotonated by the action of sodium methoxide in methanol at −80 °C, yielding exclusively authentic μ-methylene precursor **2**. This reaction is completely consistent with our observations on the behavior of $\{(\mu\text{-H})(\mu\text{-CH}_2)[(\eta^5\text{-C}_5\text{H}_5\text{Rh(CO)}]_2\}^+X^-$ (X = BF$_4$, CF$_3$SO$_3$, FSO$_3$) and $\{(\mu\text{-H})(\mu\text{-CO})[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(CO)}]_2\}^+$-BF$_4^-$ (section B). Upon being warmed up to room temperature, the cationic hydrido methylene complex **3e** rapidly undergoes effective irreversible ring opening either in the solid state or else

(54) The only reasonable mechanism for epimerization of **2** involves carbonyl exchange which, however, is not observed by NMR spectroscopy even at temperatures as high as +90 °C (F. A. Cotton, personal communication, 1979; see also ref 47, footnote 17).

in nitromethane solution, finally yielding the thermally stable bromo methyl derivative **6b**, initiated by coordination of the halide counterion (Scheme I). Combination of the hydrido and the methylene bridges originally oriented trans to each other was shown to proceed via hydrido methylene/methyl tautomerism, a process which has already been established for $Os_3(CO)_{10}(C-H_2)H_2$.[29,49]

The reaction sequence **2** → **3e** → **6b** demonstrates that a nonsynchronous, two-step mechanism which requires the prerequisite of proton-induced metal-to-metal bond activation is responsible for this kind of reaction. The salient product-determining importance of the nucleophilic halide counterions is evident from comparison with the chemistry of hydrido methylene complexes containing anions which lack coordination capabilities: thus, the compound **3a**, isolated in pure form as well, spontaneously forms $[(\eta^5\text{-}C_5H_5)_3Rh_3(\mu\text{-}CO)_2(\mu_3\text{-}CH)]^+BF_4^-$ in 96% yield with concomitant elimination of hydrogen and methane (cf. sections A and B). In conclusion, ring opening of dimetallacyclopropanes points to a promising new synthetic entry into the hitherto only little investigated class of dinuclear organometals having alkyl and halide groups attached to adjacent metal centers. In this context, the reader's attention is drawn to the somewhat related homodinuclear dimethyl complexes of type $[(\mu\text{-}CO)(CH_3)(\eta^5\text{-}C_5H_5)Co]_2$ reported by Bergman et al., which exhibit some fascinating decomposition pathways as regards carbon–carbon bond formation.[55]

Closing Remarks

What is the salient message arising from our results outlined in the foregoing discussion? Apart from straightforward synthetic routes for μ_3-methylidyne rhodium clusters and dinuclear halo methyl complexes, this study has brought about ample evidence that direct protonation of the electron-rich metal–metal bond of the prototype μ-methylene rhodium complex $(\mu\text{-}CH_2)[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$ (**2**) is greatly preferred over proton attack at the bridging methylene function, this important process inducing a spectacular sequence of reactions proceeding via both intra- and intermolecular pathways which finally yield the above-mentioned stable derivatives. Despite a fair amount of caution which has to be exercised in predicting the general applicability of these reactions for μ-methylene complexes with metals other than rhodium, the few results hitherto reported on the nucleophilic activity of this class of compounds seem to indicate that protonation of the bridgehead carbon atom comes to the fore if an electron-rich metal-to-metal bond either is not present or is sterically not available. This view at least accounts for the basically different results obtained by Wilkinson et al. for the protonation of $(\mu\text{-}CH_2)_3[Ru_2(PMe_3)_6]$.[24] To settle this and related questions on the widely unexplored chemistry of μ-methylene organometals is one of the main goals presently being persued with the utmost activity in our laboratories.[60]

Supplementary Material Available: Structure factor tables of **5b** and **6b** (20 pages). Ordering information is given on any current masthead page.

(55) (a) I. E. Schore, C. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **98**, 7436 (1976); (b) H. E. Bryndza and R. G. Bergman, *ibid.*, **101**, 4766 (1979); (c) M. A. White and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, 1056 (1979).

(56) Just before this manuscript was submitted for publication, another significant μ-methylene complex belonging to Class A[21] was reported: $(\mu\text{-}CH_2)[Fe_2(CO)_8]$ results from the reaction of the $Fe_2(CO)_8$ dianion with CH_2I_2 (Ch. E. Summer, Jr., P. E. Riley, R. E. Davis, and R. Pettit, *J. Am. Chem. Soc.*, **102**, 1752 (1980)).

(57) G. M. Sheldrick, SHELXTL Version 1979, Anorganisch-chemisches Laboratorium der Universität Göttingen, Germany.

(58) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, X-Ray 70 System, Computer Science Center, University of Maryland, College Park, Md., U.S.A.

(59) H. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040–1044 (1964).

(60) We were also able to synthesize the novel dinuclear rhodium compound $(\eta^5\text{-}C_5Me_5)_2Rh_2(CO)_2(\mu\text{-}CO)$ from the monomeric precursor $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ by this method in near quantitative yield. $(\eta^5\text{-}C_5Me_5)_2Rh_2(CO)_2(\mu\text{-}CO)$ is converted into Maitlis' $(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)_2$ upon photolysis or else thermolysis (J. Plank, D. Riedel, and W. A. Herrmann, *Angew. Chem.*, in press; see also: W. A. Herrmann, Ch. Bauer, J. Plank, W. Kalcher, D. Speth, and M. L. Ziegler, *Angew. Chem.*, in press; W. A. Herrmann and Ch. Bauer, *J. Organomet. Chem.*, in press).

(61) After this paper was submitted for publication, we learned from Professor Shapley (Urbana-Champaign, Ill., U.S.A.) that he and his co-workers have also observed the transformation **2** → **5b** (J. R. Shapley, personal communication; J. R. Shapley et al., *J. Am. Chem. Soc.*, submitted for publication).