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TRANSITION METAL METHYLENE COMPLEXES

III *. METHYLENE (CH_2), A CARBONYL ANALOGOUS LIGAND; CRYSTAL STRUCTURE OF μ-METHYLENEBIS(CARBONYL-η^5-CYCLOPENTADIENYLRHODIUM)(*Rh—Rh*)

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Summary

μ-Carbonylbis(carbonyl-η^5-cyclopentadienylrhodium)(*Rh—Rh*) reacts with *N*-methyl- and *N*-ethyl-*N*-nitrosourea in boiling benzene to yield the dinuclear, diamagnetic, neutral rhodium complexes μ-methylene- (A) and μ-ethylidene-bis(carbonyl-η^5-cyclopentadienylrhodium)(*Rh—Rh*) (B), respectively. Deuterium labelled experiments prove the origin of the metal-stabilized methylene ligand to be the alkyl group of the organic precursor. This new method of preparation of transition metal—methylene complexes may be used as an alternative to the commonly used diazo method; the latter method was shown to work with diazodiethylmalonate and dicarbonyl-η^5-cyclopentadienylrhodium, the reaction yielding μ-bis(ethoxycarbonyl)methylenebis(carbonyl-η^5-cyclopentadienylrhodium)(*Rh—Rh*).

Compound A crystallizes in the triclinic system, $P\bar{1}$, and with cell constants of a 803.42(5), b 909.98(6), c 938.81(2) pm, α 74.402(3), β 81.923(3), and γ 83.685(6)°. The unit cell volume and the calculated density are 651.6 Å^3 and 2.069 g cm^{-3}, for one molecule in the asymmetric unit. The molecular geometry of μ-$CH_2[\eta^5$-$C_5H_5Rh(CO)]_2$ was established from 2718 unique reflections collected with a computer-controlled diffractometer and refined to a final $R(F)$ = 0.0379. The molecular parameters derived from the single-crystal X-ray

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* For part II see ref. 1.

study conform to a remarkable degree with those found for μ-CO[η^5-C_5H_5Rh(CO)]$_2$. Thus, the bridging ligands CH_2 and CO seem to be analogous in their effects on the structural characteristics of the molecular framework of the two molecules.

Introduction

After the discovery of the first transition metal carbene complex by Fischer and Maasböl in 1964 [2], hundreds of additional examples of this fascinating class of compounds have been prepared by various routes [*]. Suprisingly little is known, however, about carbenes bound to two metal centers. Moreover, there have been only two reports dealing with metal stabilized CH_2 groups: in 1975, Schrock reported the synthesis [4] and structure [5] of (η^5-C_5H_5)$_2$Ta(CH_3)(CH_2), the first mononuclear CH_2 complex characterized unambiguously. At the same time, one of us described the preparation of (η^5-C_5H_4R)$_2$Mn$_2$(CO)$_4$CH$_2$ (R = H, CH_3) [6], the first examples of bridged methylene complexes [**]. Later, we described the synthesis and structure of another methylene transition metal complex of this type in a preliminary note [1]. Determination of the crystal structure of (η^5-C_5H_5)$_2$Mn$_2$(CO)$_4$CH$_2$ is still in progress [***]. Below we present the details of the preparation and an X-ray crystallographic study of μ-methylene-bis(carbonyl-η^5-cyclopentadienylrhodium)(*Rh—Rh*), together with the preparative details and spectroscopic data for two other rhodium compounds analogous with it.

Experimental

The experiments were carried out under nitrogen using freshly distilled, dry solvents. Spectra were recorded using the following apparatus: IR: Perkin—Elmer Infrared Grating Spectrophotometer Model 325; ^{1}H NMR: Varian T-60 (TMS as internal standard); Mass spectra: Varian MAT CH 5 with direct inlet system.

Rhodium trichloride trihydrate (37.8% Rh) was a gift of Degussa Hanau (Germany). Microanalyses were performed by the Microanalytical Laboratory of the University of Regensburg (C, H, N) and by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach/Engelskirchen (Germany) (Rh, O). Melting points were taken in sealed capillaries and are uncorrected.

Dicarbonyl-η^5-cyclopentadienylrhodium (III) was prepared from bis-(μ-chlorodicarbonylrhodium) [9,10] and cyclopentadienylthallium [38] according to the procedure of Fischer [11] as modified by Mays et al. [12]. A reaction time of 15 h is required for complete consumption of the [Rh(CO)$_2$Cl]$_2$. The resulting (η^5-C_5H_5)Rh(CO)$_2$ was purified by repeated trap-to-trap distillation (ca. 40°C) under high vacuum.

The dinuclear rhodium carbonyl, (η^5-C_5H_5)$_2$Rh$_2$(CO)$_3$ (IV) initially prepared

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[*] For a recent review see the Nobel lecture by Prof. E.O. Fischer, Stockholm, Dec. 12, 1973 [3].

[**] In accord with IUPAC organic chemical nomenclature we describe CRR′ groups as "...-methylene"-ligands; the ligand is named "(alk)ylidene", if R is an alkyl group, while R′ represents H or another alkyl group (Rule A.4 in ref. 7).

[***] Preliminary data confirm the *trans* configuration of both cyclopentadienyl rings [8].

by Fischer and Bittler [13], was synthesized by thermal "dimerization" (see below) rather than by the previously reported photochemical procedure [16].

1. *μ-Carbonylbis(carbonyl-η^5-cyclopentadienylrhodium)(Rh—Rh) (IV)*

A solution of 4.0 g (17.9 mmol) dicarbonyl-η^5-cyclopentadienylrhodium in 80 ml benzene is gently refluxed for 80 h. Shortly after the solution begins to boil, the colour darkens from light orange to light red, and gas is evolved. The crude product is chromatographed on a silica gel column (Kieselgel 60, Merck, mesh 0.063—0.200 mm, Act. II—III; 30 × 2 cm; column temperature 10—15°C). A yellow-orange band containing unchanged $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ is eluted with n-pentane/benzene (5/1) and the compound (760 mg, 16.7%) is isolated by evaporation of the solvent mixture with a water aspirator. The dinuclear $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ (IV) is eluated with benzene as a rapidly moving, deep red band. The solvent is stripped off in a water aspirator to leave the product at the bottom of the Schlenck tube as microcrystals. Yield 2.52 g (67%), melting point of the material recystallized from n-pentane/diethyl ether 139°C (lit. [13] 123°C).

IR (cm^{-1}): ν(CO) 1963 vs, 1816 vs (KBr); Lit. [11] ν(CO) 1961, 1812 (KBr). Found: C, 37.05; H, 2.58; molecular weight (osmometry, benzene): 418. $C_{13}H_{10}O_3Rh_2$ (420.0) calcd.: C, 37.17; H, 2.40%.

If this reaction is performed in either higher boiling solvents (toluene or 1,4-dioxane) or under photolytic conditions, considerable amounts of the known trinuclear species $(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_3Rh_3$ and of its partially-bridged isomer $(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)_2Rh_3CO$ [14,15] are obtained. Johnson et al. [16] report a 5% yield of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ from UV-irradiation of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in an aliphatic solvent; this agrees well with our observations.

2. *μ-Methylenebis(carbonyl-η^5-cyclopentadienylrhodium)(Rh—Rh) (Va)*

A solution of 420 mg (1.0 mmol) $\mu\text{-}CO[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$ and 1.03 g (10 mmol) *N*-methyl-*N*-nitrosourea [17] in 50 ml benzene is refluxed for 25 h. The crude product is isolated by column chromatography (Kieselgel 60, as specified above); with n-pentane/benzene mixture (5/1). A small amount of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ is eluted first, the methylene complex Va is then eluted with n-pentane/benzene (2/1) as an orange-yellow band which is evaporated with a water aspirator. The residue is then crystallized from n-pentane at —78°C to give a yield of 349 mg (86%). The unchanged $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ (ca. 40 mg) can be recovered by elution from the column with pure benzene.

3. *μ-Ethylidenebis(carbonyl-η^5-cyclopentadienylrhodium)(Rh—Rh) (Vb)*

This substance can be prepared as described for the methylene derivative. 420 mg of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ and 1.17 g *N*-ethyl-*N*-nitrosourea * in 50 ml benzene yield 240 mg (57%) of the product Vb.

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* Product from Fluka-Feinchemikalien, Buchs (Switzerland). Acetic acid present as a stabilizer is removed by washing the compound with water. The dry material is stable at —35°C for months.

4. μ-Bis(ethoxycarbonyl)methylenebis(carbonyl-η^5-cyclopentadienylrhodium)-(Rh—Rh) (Vc)

A solution of 1.12 g (5 mmol) dicarbonyl-η^5-cyclopentadienylrhodium (III) and 930 mg (5 mmol) diethyl diazomalonate [18] in 80 ml tetrahydrofuran at 10—15°C is irradiated with a pyrex-filtered UV lamp * for 18 h, during which the yellow solution gradually acquires a reddish color. The crude product is purified by column chromatography (Kieselgel 60; as specified above). Unchanged $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ contaminated with $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ is removed with a n-pentane/benzene mixture (5/1) and pure benzene, respectively. The methylene derivative (Vc) is eluted with pure diethyl ether as a broad, orange-yellow band which is concentrated in a high vacuum until no more solvent can be removed. The remaining oil is crystallized from diethyl ether/methylene chloride (10/1) at −35°C to give Vc as light red, air-stable crystals. These darken at 150°C and melt at 197°C with complete decomposition. Yield 605 mg (41%).

Crystallographic studies

The orange-red crystal chosen for intensity measurements, 0.13 × 0.40 × 0.35 mm in size, was mounted on an Enraf—Nonius CAD-4 automatic-diffractometer and intensities were collected as described previously [19].

Since the unit cell parameters of this compound are similar to those for μ-carbonylbis(carbonyl-η^5-cyclopentadienylrhodium)(*Rh—Rh*), initial rhodium atom positions were taken from ref. 31. Subsequent electron-density-difference syntheses revealed the positions of the remaining 15 non-hydrogen atoms. Hydrogen atoms were incorporated at calculated positions (C—H 0.95 Å) and their positional and thermal parameters were kept invariant during refinement (U_H 0.05 Å^2). Rh, C, and O atoms were refined with anisotropic thermal parameters by full-matrix least-squares methods. Refinement converged at $R = 0.038$, with a mean shift to error ratio in the final cycle of 0.03. A final electron density difference synthesis showed no peaks >0.4 e Å^{-3} except in the vicinity of the Rh atoms where peaks of 1.5 e Å^{-3} were observed. In the case of Rh, corrections for the real and imaginary parts of anomalous dispersion were applied ($\Delta f = -1.29$, $\Delta f'' = 0.92$) [22].

(A) Crystal data. $C_{13}H_{12}O_2Rh_2$; mol. wt. 406.05; a 803.42(5), b 909.98(6), c 938.81(2) pm, α 74.402(3), β 81.923(3), γ 82.685(6)°, V 651.6 Å^3; space group $P\bar{1}$ [C_i^1; No. 2], $Z = 2$; $F(000)$ 392 e, D_c 2.069 g cm^{-3}; T 293 K; μ(Mo-K_α) 24.81 cm^{-1}.

(B) Measurement of intensity data; Radiation: Mo-K_α (λ 0.71069 cm^{-1}), graphite monochromated; reflections measured: $\pm h$, $\pm k$, l, maximum 2θ: 55°, scan type: coupled $\theta - 2\theta$. The intensities of 3 standard reflections measured every 100 reflections showed no significant variation during data collection.

(C) Treatment of intensity data; Conversion to $|F_o|$ and $\sigma|F_o|$: as in ref. 19; no absorption correction was applied. The (−2, 0, 2), (−1, 0, 1), (2, 0, 3) and (1, 0, 4) reflections were removed because of suspected secondary extinction effects.

(D) Details of refinement. Total independent reflections measured: 2960;

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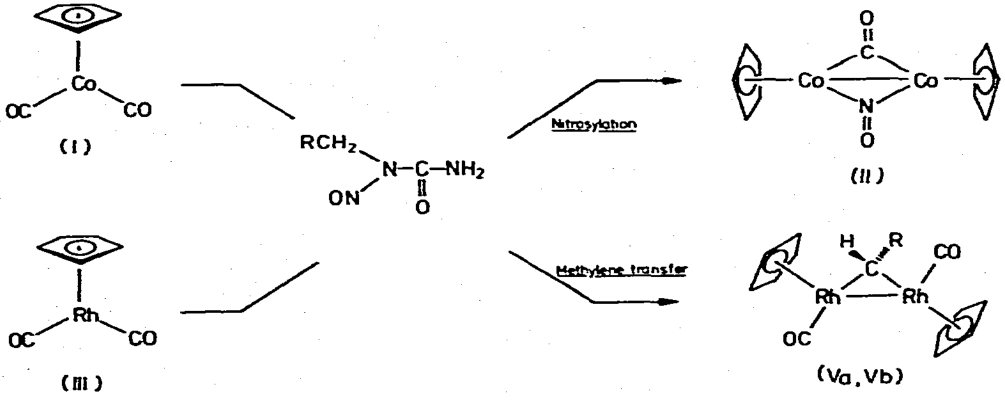
* Mercury high pressure lamp TQ 150; Quarzlampen-GmbH Hanau (Germany).

observed reflections: 2718 (according to the criterion $I \geqslant 2.0\ \sigma(I)$). Final number of variables: 154. Final error in an observation of unit weight: 2.14. Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.038$. Final $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.055$. Weighting scheme: $w = 1/\sigma(F_o)^2$. Neutral atom scattering factors for Rh, O, and C from ref. 20, spherical scattering factors for H from ref. 21.

Preparative results

It was recently demonstrated that some *N*-alkyl-*N*-nitrosourea derivatives possess very mild nitrosylating power towards organometallics [40]. In that study, the metal complex substrate was dicarbonyl(η-cyclopentadienyl)cobalt (I), which undergoes only partial nitrosylation upon reaction with *N*-methyl- or *N*-ethyl-*N*-nitrosourea in boiling benzene. The paramagnetic dinuclear compound II is formed exclusively, even when an excess of the nitroso reagents is employed (eq. 1).

Since dicarbonyl(η-cyclopentadienyl)rhodium (III) is the analogue of the cobalt compound, we decided to examine the behaviour of the complex towards these new reagents. Surprisingly, no nitrosylation occurred. The still unknown paramagnetic μ-carbonyl-μ-nitrosylbis(η-cyclopentadienylrhodium)(*Rh—Rh*) expected by analogy with the cobalt compound, was not formed. Instead, a red, crystalline diamagnetic compound was isolated by column chromatography in high yields. This air-stable material was identified as a novel organometallic (Va) containing a methylene group as a bridging ligand. The question as to whether the cyclopentadienyl rings were *cis* or *trans* to each other was decided by an X-ray crystallographic study, the detailed results of which are given below.



(1)

	a	b
R	H	CH_3

The new compound was characterized by means of total elemental analysis (Table 1), osmometric molecular weight determination (Table 1), mass spectrum (Fig. 1), infrared spectrum (Table 2), and ^{1}H NMR spectrum (Table 3).

The ^{1}H NMR spectrum (90 MHz; acetone-d_6) shows a triplet for the protons of both cyclopentadienyl ligands, which is due to identical splitting of either C_5H_5 spin system by both rhodium nuclei; the coupling constant amounts to

TABLE 1

ANALYTICAL DATA FOR THE NEW μ-METHYLENERHODIUM COMPLEXES μ-CRR'[η^5-$C_5H_5Rh(CO)]_2$ (Va, Vb AND Vc)

Compound	R	R'	Formula	Molecular weight	Elemental analysis (Found (calcd.) (%))				
					C	H	N	O	Rh
Va	H	H	$C_{13}H_{12}O_2Rh_2$	406 (MS) 418 [a] (406.0)	38.47 (38.45)	2.29 (2.98)	0.00 (0.00)	8.02 (7.88)	50.37 (50.69)
Vb	H	CH_3	$C_{14}H_{14}O_2Rh_2$	420 (MS) 435 [b] (420.1)	41.04 (40.03)	3.39 (3.36)	0.00 (0.00)	[c] (7.62)	49.17 (48.99)
Vc	$CO_2C_2H_5$	$CO_2C_2H_5$	$C_{19}H_{20}O_6Rh_2$	550 (MS) 553 [b] (550.2)	41.67 (41.48)	3.75 (3.66)	0.00 (0.00)	17.57 (17.45)	37.50 (37.41)

[a] Osmometrically in benzene. [b] Osmometrically in chloroform. [c] Not determined.

TABLE 2

INFRARED DATA (cm^{-1}) FOR THE NEW μ-METHYLENERHODIUM COMPOUNDS Va, Vb AND Vc

Compound	ν((M—)C≡O) frequencies	Other absorptions ^{d}
Va ^{a}	1984 vs	
Va ^{b}	1950 vs(br)	$\nu(CH_2)$ 2903w, 2963vw-w Further bands: 1434w, 1411w, 1347w, 1015w-m, 986w-m, 937w-m, 777m $\gamma(C_5H_5)$ 800m(sh), 787m
Vb ^{a}	1970vs	
Vb ^{b}	1948vs(br)	$\nu(CH, CH_3)$ 2965w, 2900w, 2837w $\gamma(C_5H_5)$ 800s(sh), 782s Further bands: 1437m, 1411w-m, 1357w-m, 1344w-m, 1286m, 1056m, 1015s, 987m
Vc ^{c}	1991vs	$\nu(CO_2R)$ 1676m(sh)
Vc ^{b}	1972vs 1980(sh)	$\nu(CO_2R)$ 1678s Further bands: 1178vs, 1093m, 1038m-s(sh), 1010m, 991m, 867m, 811m-s(sh), 737m

^{a} n-Pentane solution. ^{b} KBr pellet. ^{c} Methylene chloride. ^{d} Between 2000 and 600 cm^{-1} only bands with intensities greater than weak to medium (w-m) are given.

0.31 Hz, which compares well with those found in other C_5H_5Rh systems (e.g., $(\eta^5\text{-}C_5H_5)_2Rh_2(CH_3)_4\text{-}\mu\text{-}S(CH_3)_2$: 0.4 Hz [23]). The methylene protons give rise to a symmetrical four-line multiplet centered around τ 2.93 ppm. The appearance of this multiplet is consistent with the A-part of an A_2X_2 pattern (A: hydrogen; X: rhodium; $I = 1/2$). The $C\underline{H}_2$—Rh coupling is 0.55 Hz. The NMR spectrum of the methylene protons in Va show them to be strongly deshielded, as previously found for $(\eta^5\text{-}C_5H_4R)_2Mn_2(CO)_4\text{-}\mu\text{-}CH_2$ (R = H, CH_3) [6].

As expected on the basis of their structures, the mass spectra of Va and its methyl derivative Vb are very simple; in both the 70 and 12 eV spectra there are mostly peaks arising from fragments free of methylene, the base peak corresponding to the stable dicyclopentadienylrhodium ion. In agreement with earlier findings on $(\eta\text{-}C_5H_4R)_2Mn_2(CO)_4\text{-}\mu\text{-}CH_2$ [6], and comparable μ-CRR′ cobalt complexes [24], loss of free methylene could not be detected unambiguously (Fig. 1). A detailed study of the mass spectroscopic fragmentation patterns of μ-methylene complexes is in progress [39].

The unexpected formation of a CH_2—metal species initiated a search for the

TABLE 3

^{1}H NMR DATA (ppm) OF Va, Vb AND Vc ^{a}

Compound	$\tau(C_5H_5)$	$\tau(CH)/\tau(CH_2)$	$\tau(CH_3)$	$\tau(CO_2CH_2CH_3)$
Va ^{b,c}	^{3}4.52(5)	^{4}2.93(1)	—	—
Vb ^{c}	^{3}4.57(10)	^{m}1.32(1)	^{2}7.47(3)	—
Vc ^{d}	^{1}4.68(5)	—	—	^{4}5.97(2) and ^{3}8.78(3)

^{a} Multiplicity is shown as superscript before the τ-value; relative intensities in parentheses. ^{b} 90 MHz-PFT spectrum (Bruker WH-90). ^{c} Acetone-d_6. ^{d} Methylene-d_2 chloride.

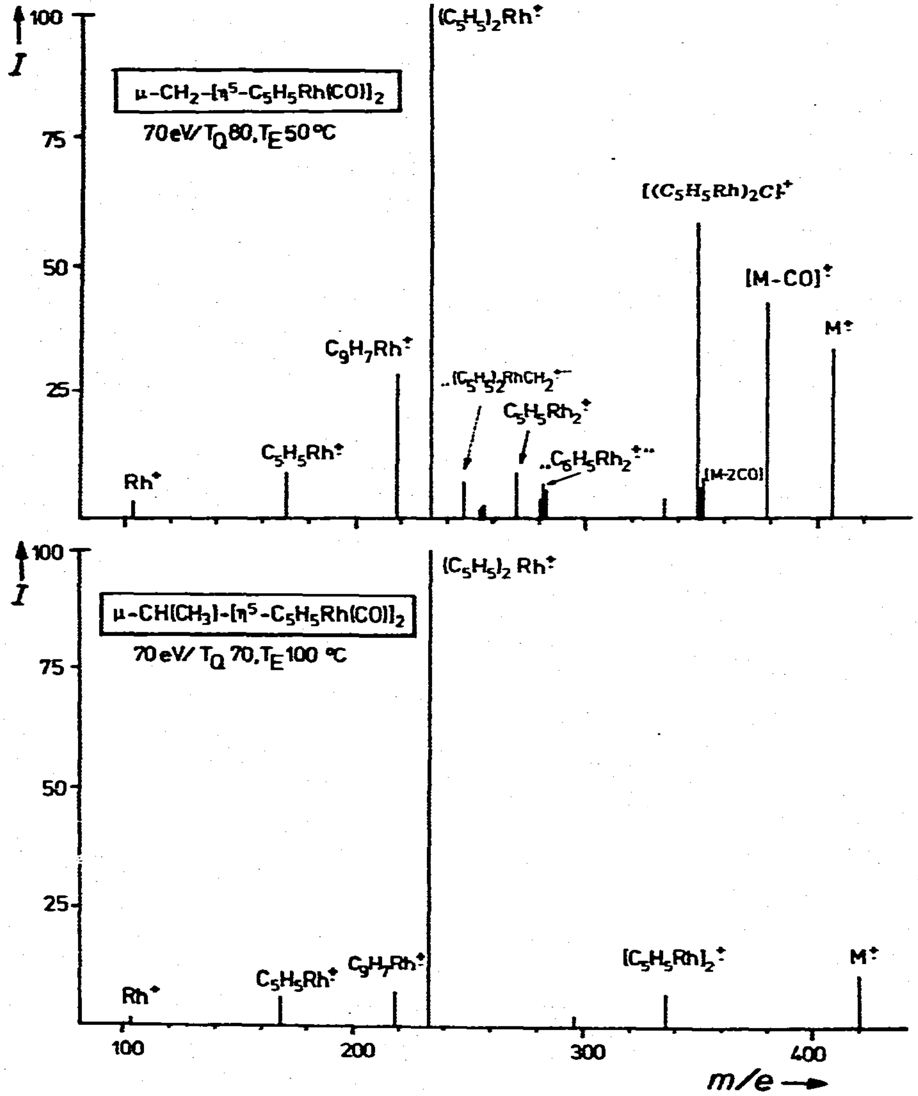


Fig. 1. Mass spectra of Va and Vb.

source of the hydrogens. It could arise a priori from reduction of the dinuclear $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ (IV) which could be formed in situ under the reaction conditions used; subsequent work has shown that this tricarbonyl is a better precursor for the CH_2 complex, as far as yields are concerned. Accordingly, we prepared Va from $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ (IV) which had been made by boiling $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ (III) in benzene for 80 h. This procedure yields 67% of IV, which is much higher than the yield reported for the photochemical conversion of III to IV.

Using IV as a substrate, we carried out the following experiments in an attempt to deuterate the CH_2 bridge, and thus, locate the origin of the methylene fragment:

(a) perdeuterobenzene was used instead of benzene as the solvent, but this did not lead to deuterium incorporation in the molecule Va. Therefore, the solvent is not the origin of hydrogens found in the product.

(b) The *N*-methyl-*N*-nitroso-urea[*N*-d_2] also did not give rise to deuterated products. This proves that NH_2 and ND_2 groups do not reduce the carbonyl bridge to a CH_2 bridge.

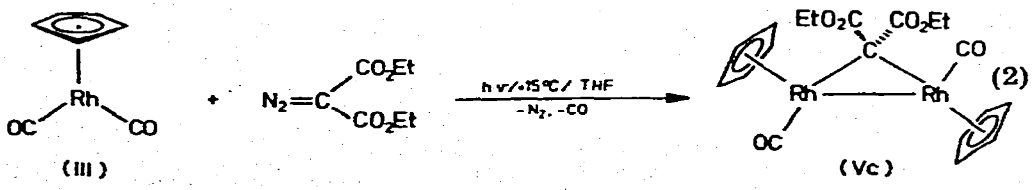
(c) Commonly-employed reducing agents such as hydrazine hydrate and sodium boranate did not produce any isolable products.

(d) Consideration of the above reactions (a—c) reduces the choice of hydrogen-containing fragments to the methyl group of *N*-methyl-*N*-nitrosourea. In order to demonstrate that this is the origin of the CH_2-bridging fragment, we used the homologous *N*-ethyl-*N*-nitrosourea for this synthesis and the corresponding ethylidene rhodium complex Vb was isolated.

From this finding, it appears that *N*-alkyl-*N*-nitrosoureas can release their alkyl groups under mild conditions, and that these groups are converted into bridging methylene groups. Since a vast number of such urea derivatives are known, and can be synthesized by simple procedures, our method provides a powerful new point of entry to the little investigated field of the chemistry of transition metal—methylene complexes.

In considering the mechanism of reaction 1, we assume that the reactive organometallic species is either η^5-$C_5H_5Rh(CO)_2$ or η^5-$C_5H_5Rh(CO)$, both of which are coordinatively unsaturated towards nucleophilic attack. Both species are expected to be formed upon dissociation of IV in boiling benzene. The dinuclear carbonyl IV seems to undergo easy ligand dissociation and/or metal—metal bond rupture in solution even at room temperature, since ^{13}CO is incorporated under such conditions in 80% yield in the course of two days. At the very least, the reactive fragment η^5-$C_5H_5Rh(CO)$ must be open to an alkyl transfer from the *N*-nitrosourea derivative. The next step leading to the alkylidene complex involves α-hydrogen abstraction which seems not to be as disfavoured a process as is commonly assumed [4,25—27]. Also there is mass-spectroscopic evidence for a reversible α-hydrogen abstraction from the methyl groups of $CH_3Co[P(C_6H_5)_3]_3$ and $CH_3Rh[P(C_6H_5)_3]_3$ involving intermediate carbene-hydride formation [28].

Among the few nitrosoureas not easily accessible is the possible precursor of the bis(ethoxycarbonyl)methylene ligand. Reaction 2 represents a case in which the older diazo method (that is, transfer of a carbene from an aliphatic diazo compound to a metal center [6,29,30]) can be used instead of the *N*-nitrosourea transalkylation/deprotonation method: diethyl diazomalonate reacts with dicarbonyl-η^5-cyclopentadienylrhodium (III) under UV irradiation to yield the dinuclear complex Vc containing a bis(ethoxycarbonyl)methylene ligand



bound to both metal atoms. The compound corresponds structurally to Va and Vb, as well as to some related compounds of the type μ-CRR'[η^5-$C_5H_5Co(CO)]_2$ (R, R' = H, CO_2CH_3, $CO_2C_2H_5$, CO_2-t-C_4H_9) [24].

Crystal structure determination of Va

A. Description of the structure

Figures 2 and 3 and the data of Tables 5 and 6 show the molecule containing a number of well-defined planes. The two C_5H_5 rings are planar with a maximum deviation of 2.0(9) pm of any atom from the best plane of its respective ring. The angle of the normals to the two cyclopentadienyl rings is 29.45° which is nearly the same as the value of 28° found by Mills and Nice [31] for (η^5-$C_5H_5)_2$-$Rh_2(CO)_3$. The planes defined by Rh(1), Rh(2), C(1) and by Rh(1), Rh(2), C(2) are almost coincident, the angle between them being 2.24°. The cyclopentadienyl rings make angles of about 75° with the planes defined by the two Rh atoms and either C(1) or C(2). Finally, the plane defined by Rh(1), Rh(2) and C(3) is almost normal to the planes defined by either Rh(1), Rh(2) and C(1) or by Rh(1), Rh(2) and C(2), the dihedral angles being 88.50 and 89.27°, respectively. The two carbonyl groups are almost exactly *trans*, as demonstrated by the value of the torsional angle C(1)—Rh(1)—Rh(2)—C(2) of 176.90°. Table 4 lists the positional and thermal parameters.

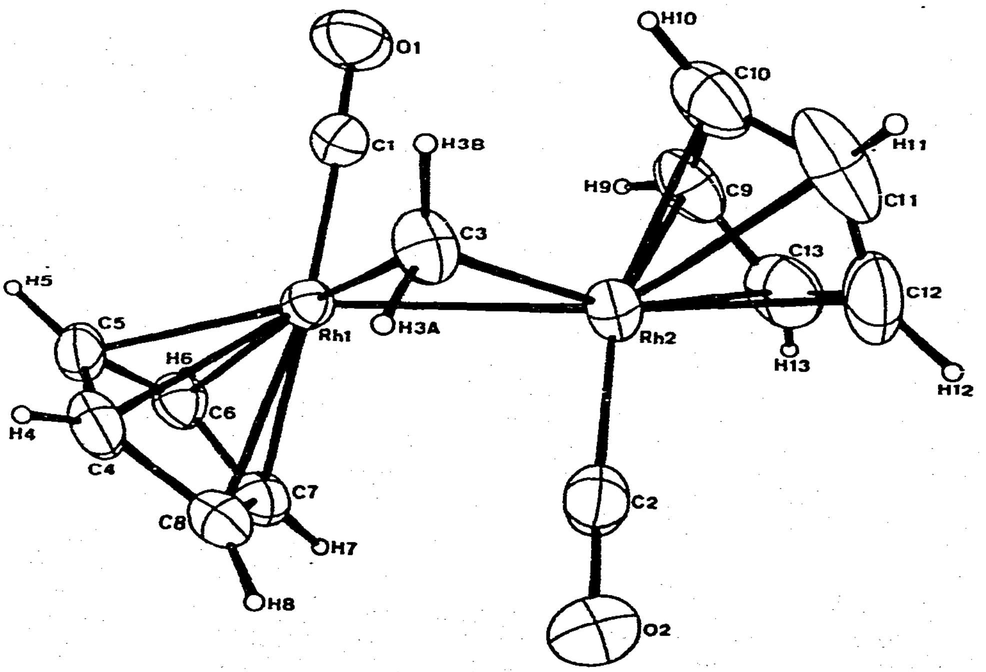


Fig. 2. The molecular structure of (η^5-$C_5H_5)_2Rh_2(CO)_2CH_2$.

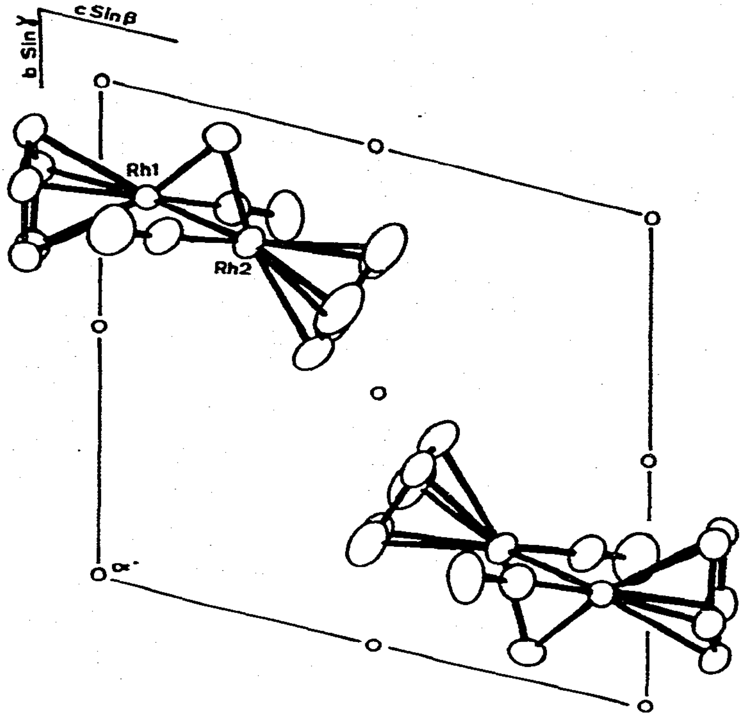


Fig. 3. Contents of the unit cell of Va, viewed down the a axis towards the origin.

B. Discussion

Since structural details are not available for any other compound containing a μ-methylene group, the obvious comparison to make is between $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2CH_2$ (Va) and $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ (IV) [31], in order to ascertain the changes which take place on transforming a CO into a CH_2 bridge. For this purpose, we have assembled Table 7, in which we compare the central portions of the two molecules. A more general comparison of the bonding parameters of Va with those of molecules containing similar fragments is presented in Table 8. Referring to Table 7, we note that the Rh—Rh distances in the two compounds differ by 1.6 pm or 0.6%. At the same time, the mean Rh—C distance for the bridging fragment is 200.4 pm for the carbonyl and 203.7 pm for the μ-methylene derivative.

As the Rh—Rh distance is shorter in Va than in IV and the bridging Rh—C distances are longer, it seems that the μ-methylene group does not interact with the Rh—Rh bond as effectively as CO.

Comparison of the C_5H_5—Rh parameters listed in Table 8 shows that there are two distinct metal—ring centroid ranges; one, associated with compounds of the class $(\eta^5\text{-Cp})RhL$ (L = unsaturated hydrocarbon), has the metal displaced by about 187 pm from the center of the cyclopentadienyl ring. The other have values close to 191 pm. The mean values of the metal—$C(C_5H_5)$ distances for the

TABLE 4

POSITIONAL (X 10^4) AND THERMAL (X 10^3) PARAMETERS

A. Positional parameters (fractional coordinates)

Atom	x	y	z
Rh(1)	1460(1)	2090(1)	834(1)
Rh(2)	3485(1)	2499(1)	2684(1)
C(1)	−226(5)	1901(4)	2382(4)
C(2)	5155(5)	2804(5)	1118(4)
C(3)	2991(5)	557(4)	2183(4)
C(4)	1911(5)	1352(4)	−1291(3)
C(5)	261(5)	2039(4)	−1157(4)
C(6)	345(5)	3625(4)	−1225(4)
C(7)	2044(5)	3889(4)	−1372(3)
C(8)	3043(5)	2440(5)	−1366(4)
C(9)	1713(6)	3722(5)	4213(4)
C(10)	2105(8)	2204(6)	4969(4)
C(11)	3803(8)	1945(7)	5125(5)
C(12)	4511(6)	3411(9)	4329(6)
C(13)	3169(8)	4409(6)	3866(5)
O(1)	−1307(4)	1774(5)	3326(3)
O(2)	6252(4)	2948(5)	204(3)
H(3A)	3886(1)	127(1)	1475(1)
H(3B)	2510(1)	−153(1)	2975(1)
H(4)	2225(1)	281(1)	−1358(1)
H(9)	708(1)	4320(1)	3797(1)
H(7)	2429(1)	4831(1)	−1559(1)
H(8)	4232(1)	2336(1)	−1629(1)
H(10)	1329(1)	1438(1)	5245(1)
H(5)	−738(1)	1536(1)	−1027(1)
H(6)	−604(1)	4364(1)	−1165(1)
H(11)	4466(1)	1048(1)	5569(1)
H(12)	5714(1)	3577(1)	4105(1)
H(13)	3307(1)	5468(1)	3376(1)

B. Thermal parameters

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
H(1)	42	33	37	−2	−8	−11
H(2)	46	53	44	4	−14	−21
C(1)	54	61	51	−9	−12	−12
C(2)	55	79	62	−8	−9	−32
C(3)	70	39	57	8	−23	−11
C(4)	84	51	42	−1	−13	−20
C(5)	71	59	45	−21	−16	−12
C(6)	67	55	46	5	−18	−11
C(7)	83	47	41	−23	−4	−4
C(8)	57	69	47	−3	1	−22
C(9)	84	82	52	18	−10	−34
C(10)	120	96	47	−19	−3	−29
C(11)	145	133	70	76	−69	−54
C(12)	69	190	98	−2	−21	−95
C(13)	140	87	72	−20	−7	−50
O(1)	64	134	61	−25	12	−18
O(2)	63	140	94	−33	12	−41
H(2A)	50					
H(3B)	50					
H(4)	50					
H(9)	50					
H(7)	50					

(to be continued)

TABLE 4 (continued)

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
H(8)	50					
H(10)	50					
H(5)	50					
H(6)	50					
H(11)	50					
H(12)	50					
H(13)	50					

two classes of compounds reveal the same trend. We note, at the same time, that while the Rh—C_5H_5 parameters for IV and Va are approximately the same, they differ in both Rh—Rh and in the Rh—C(CO) distances, both being a little longer for IV. Finally, given the stated standard deviations, the C=O bonds and the Rh—C=O angles for IV, Va and VI [15,31,32] are equal.

(continued on p. 88)

TABLE 5

DISTANCES (pm) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. Distances

Rh(1)—Rh(2)	266.49(4)	Rh(2)—C(2)	183.3(4)
Rh(1)—C(1)	183.1(4)	Rh(2)—C(3)	104.5(4)
Rh(1)—C(3)	202.9(4)	Rh(2)—C(9)	228.3(5)
Rh(1)—C(4)	224.1(4)	Rh(2)—C(10)	223.7(5)
Rh(1)—C(5)	223.4(4)	Rh(2)—C(11)	225.5(5)
Rh(1)—C(6)	228.2(4)	Rh(2)—C(12)	223.1(6)
Rh(1)—C(7)	230.0(4)	Rh(2)—C(13)	227.3(6)
Rh(1)—C(8)	223.6(4)	C(2)—O(2)	113.5(6)
C(1)—O(1)	114.4(5)	C(9)—C(10)	139.2(7)
C(4)—C(5)	139.6(6)	C(10)—C(11)	137.7(10)
C(5)—C(6)	143.7(6)	C(11)—C(12)	148.3(10)
C(6)—C(7)	139.8(6)	C(12)—C(13)	136.0(9)
C(7)—C(8)	145.3(6)	C(13)—C(9)	135.5(8)
C(8)—C(4)	141.0(6)	C(3)—H(3B)	92.0(4)
C(3)—H(3A)	102.3(4)	C(9)—H(9)	98.2(5)
C(4)—H(4)	99.2(4)	C(10)—H(10)	95.5(6)
C(5)—H(5)	95.2(4)	C(11)—H(11)	94.4(7)
C(6)—H(6)	95.7(4)	C(12)—H(12)	98.2(6)
C(7)—H(7)	91.3(4)	C(13)—H(13)	96.3(6)
C(8)—H(8)	95.2(4)		

B. Angles

C(3)—Rh(1)—Rh(2)	49.4(1)	C(3)—Rh(1)—Rh(2)	48.9(1)
Rh(1)—C(3)—Rh(2)	81.7(1)	H(3A)—C(3)—H(3B)	115.9(4)
C(1)—Rh(1)—C(3)	89.5(1)	C(2)—Rh(2)—C(3)	89.8(2)
Rh(1)—C(3)—H(3A)	104.8(3)	Rh(2)—C(3)—H(3A)	116.5(3)
Rh(1)—C(3)—H(3B)	118.8(3)	Rh(2)—C(3)—H(3B)	114.5(3)
Rh(1)—C(1)—O(1)	178.2(4)	Rh(2)—C(2)—O(2)	176.0(4)
C(1)—Rh(1)—Rh(2)	87.4(1)	C(2)—Rh(2)—Rh(1)	88.0(1)
C(8)—C(4)—C(5)	108.9(4)	C(13)—C(9)—C(10)	107.4(5)
C(4)—C(5)—C(6)	108.0(4)	C(9)—C(10)—C(11)	110.0(5)
C(5)—C(6)—C(7)	108.2(4)	C(10)—C(11)—C(12)	105.2(5)
C(6)—C(7)—C(8)	107.4(4)	C(11)—C(12)—C(13)	105.7(5)
C(7)—C(8)—C(4)	107.3(4)	C(12)—C(13)—C(9)	111.6(5)

TABLE 6

EQUATIONS OF LEAST SQUARES PLANES[a] AND DEVIATIONS (Å) OF ATOMS FROM THOSE PLANES

(a) Plane defined by C(4), C(5), C(6), C(7), and C(8)

$-0.08339x + 0.23459y - 0.96851z + 0.99116 = 0$

C(4)	0.02(1)	C(7)	0.01(1)
C(5)	−0.01(1)	C(8)	−0.02(1)
C(6)	0.00(1)	Rh(1)	−1.908(9)

(b) Plane defined by C(9), C(10), C(11), C(12), and C(13)

$0.00816x + 0.26808y + 0.96336z + 5.48999 = 0$

C(9)	0.000(9)	C(12)	−0.019(9)
C(10)	−0.013(9)	C(13)	0.013(9)
C(11)	0.019(9)	Rh(2)	−1.918(9)

(c) Plane defined by Rh(1), Rh(2), and C(1)

$-0.16418x + 0.98622y - 0.02023z + 1.52366 = 0$

Rh(1)	0.000(9)	O(1)	0.000(9)
Rh(2)	0.000(9)	C(3)	−1.540(9)
C(1)	0.001(9)		

(d) Plane defined by Rh(1), Rh(2) and C(2)

$-0.19228x + 0.98132y + 0.00647z + 1.50535 = 0$

Rh(1)	0.000(9)	O(2)	−0.012(9)
Rh(2)	−0.007(9)	C(3)	−1.544(9)
C(2)	0.019(9)		

(e) Plane defined by Rh(1), Rh(2) and C(3)

$-0.66955x - 0.12305y + 0.73250z - 0.32465 = 0$

Rh(1)	0.000(9)	C(1)	1.828(9)
Rh(2)	0.000(9)	C(2)	−1.831(9)
C(3)	0.000(9)		

(f) Angles between two planes

Plane 1	Plane 2	Angle
a	b	29.45°
a	c	74.65°
a	d	76.11°
b	c	75.90°
b	d	74.47°
c	d	2.24°
c	e	88.50°
d	e	89.27°

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[a] Equations are expressed as $px + qy + vz + s = 0$ in orthogonal Å space, where x, y and z define a right handed coordinate system with x parallel to a and y parallel to b^*.

TABLE 7

A COMPARISON OF THE GEOMETRIES OF $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2CH_2$ AND $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$

Compound		Rh—Rh (pm)	Rh—C[a] (pm)	Rh—C—Rh (°)	C—Rh—Rh (°)	Ref.
Va	$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2CH_2$	266.49(4)	202.9(4) 205.5(4)	81.7(1)	49.4(1) 48.9(1)	This study
IV	$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$	268.1(2)	201.7(17) 199.0(17)	84.0(6)	47.6(5) 48.4(5)	31

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[a] To bridging CH_2 or CO group, respectively.

TABLE 8

DISTANCES (pm) AND ANGLES (°) IN Rh MOLECULES AND FRAGMENTS CONTAINING Cp RINGS AND/OR CARBONYL LIGANDS

Compound		Rh—Rh	Rh—C[a]	Rh—Cp[b]	Rh—C(=O)[a]	C=O[c]	Rh—C=O	Reference
Va	$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2CH_2$	266,49(4)	225,9(30)	190,8	183,1(4)	114,4(5)	178,2(4)	This study
			225,6(22)	191,8	183,3(4)	113,5(6)	176,0(4)	
IV	$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2\text{-}\mu\text{-}CO$	268,1(2)	225,2(23)	190,0	189,4(20)	110,5(22)	177,0(17)	31
			227,2(61)	191,4	184,0(23)	115,1(25)	175,6(19)	
VI	$(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_3$[g]	262,0(2)	224,9(26)	191	—	—	—	15
		266,3(2)	223,5(32)	190				
		270,5(2)	224,1(48)	189				
	$(\eta^5\text{-}C_5H_5)_3Rh_3\text{-}\mu\text{-}(CO)_3$	262(—)	224	—[d]	—	—	—	32
	$[Rh(PPh_3)_2CO]_2 \cdot 2CH_2Cl_2$	263,0(1)	—	—	—	—	—	33
	$[(\eta^5\text{-}(CH_3)_5)Rh(dba)]$[e]	—	222,2(18)	186,7	—	—	—	34
	$(\eta^5\text{-}C_5H_5)Rh(\eta^4\text{-}C_4Ph_4)$	—	221,4(4)	186,8	—	—	—	35
	$(\eta^5\text{-}C_5H_5)Rh(cyphen)$[f]	—	222,9(7)	188,2	—	—	—	36
		—	222,6(7)	187,8				
	$Rh_2Cl_2(CO)(EtC_2Et)_2$	269,6(3)	—	—	183(1)	118(3)	176,2(19)	37
		270,2(3)	—	—	181(3)	119(3)	174,3(21)	

[a] Mean values and deviation from mean of Rh—C(Cp) distances; one value per independent cyclopentadienyl ring. [b] Distance to ring plane. [c] Terminal carbonyls. [d] Not given; cannot be calculated either. [e] (dba) = dibenzylideneacetone. [f] (cyphen) = 1,2-diphenyl-3,4-phenanthrenocyclobutadiene.

According to the EAN rule, the Rh—Rh distances in all of these compounds are those of single bonds and, as such, they are found to be approximately the same lengths; the differences, no doubt, are due to the variations in ligands around the rhodium coordination sphere. However, the largest difference is that between the Rh—Rh bonds of the asymmetric cluster VI [15,32] and this difference amounts to 8.5 pm, or 3%. The obvious conclusion is that in Va the introduction of a bridging methylene, while chemically interesting, causes only a very small perturbation of the system of bond lengths and angles, in so far as this can be documented with the existing data.

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