Mono-, Bi-, and Tri-nuclear η-Cyclopentadienyl–Rhodium Complexes obtained from $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(CO)_2]$. Crystal Structure of $[\{Rh(\eta-C_5H_5)(\mu-CO)\}_3]\cdot 0.24Me_2CO$ †

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The reactivity of $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(CO)_2]$ (1) towards $SnCl_2$, tetracyanoethylene, I_2, $HgCl_2$, $PdCl_2$, $PtCl_2$, and NMe_2CN has been examined. From the reaction of (1) with $SnCl_2$ the trimer $[\{Rh(\eta-C_5H_5)(CO)(SnCl_2)\}_3]$ was obtained; for this compound is proposed a structure containing a six-membered ring with alternating rhodium and tin atoms. Tetracyanoethylene (tcne) reacts with (1) to give the mononuclear complex $[Rh(\eta-C_5H_5)(CO)(tcne)]$. $HgCl_2$ leaves unchanged the metallacyclic system $\overline{Rh-CO-Rh}$ and affords the adduct $[\{Rh(\eta-C_5H_5)(CO)(HgCl_2)\}_2(\mu-CO)]$; in this reaction the complex (1) acts as a Lewis base. The known complex $[Rh(\eta-C_5H_5)(CO)(I)_2]$ is the product of the reaction with iodine. Treatment of the compound (1) with $PdCl_2$ or $PtCl_2$, in acetone, leads in quantitative yields to $[\{Rh(\eta-C_5H_5)(\mu-CO)\}_3]\cdot 0.24Me_2CO$, which is a new modification of the known trimer $[\{Rh(\eta-C_5H_5)(\mu-CO)\}_3]$; the nature of the reaction intermediate is discussed. The crystal and molecular structure of the new crystalline form of the trimer has been determined by *X*-ray analysis. The complex crystallizes in the space group $P\bar{3}m1$ in a cell of dimensions $a = 12.815(2)$, $c = 6.916(1)$ Å, and $Z = 2$. Using 549 unique reflections, the structure was refined to $R = 0.022$ and $R' = 0.025$. The molecular structure consists of trimeric units, $[\{Rh(\eta-C_5H_5)(\mu-CO)\}_3]$, with crystallographic $3m$ symmetry. The trimer $[\{Rh(\eta-C_5H_5)(\mu-CO)\}_3]$ was also obtained, as the only product, from the reaction of (1) with NMe_2CN.

Recent literature reports have dealt with the syntheses, *X*-ray characterization, and dynamic behaviour in solution of bi- and poly-nuclear carbonylcyclopentadienyl-rhodium complexes.[1–9]

In the case of $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(CO)_2]$ (1), attention has mainly been focused on its reactions with molecules potentially able to bridge metal atoms, such as *N*-alkyl-*N*-nitrosourea [10] (which facilitates methylene transfer), SO_2,[11] and $F_3CC_2CF_3$.[12]

In connection with our current [13] interest concerning η-cyclopentadienyl-rhodium complexes and as part of a larger study dealing with the synthesis, structure, and chemical reactivity of bi- and poly-nuclear compounds containing rhodium atoms, we have investigated some reactions of (1) with the aim of gaining further information on the reactivity of this compound.

The results, here reported, show that mono-, bi-, and tri-nuclear cyclopentadienyl-rhodium complexes can be obtained using (1) as starting material.

Results and Discussion

Until now, $[Rh_2(\eta-C_5H_5)_2(\mu-CO)(CO)_2]$ has been obtained either by thermal reaction [3–5] or u.v. photolysis [1,2] of $[Rh(\eta-C_5H_5)(CO)_2]$. The first method,[3] in refluxing benzene, requires a long time (*ca.* 80 h); by adding hydrated Me_3NO the reaction time can be remarkably reduced to 1—2 h,[4,5] but in this case, complex (1) is obtained in low yields and its separation from the other by-products, namely $[Rh_3(\eta-C_5H_5)_3(\mu-CO)_3]$, $[Rh_3(\eta-C_5H_5)_3(\mu-CO)_2(CO)]$, and $[Rh_4(\eta-C_5H_5)_4(CO)_2]$, is quite difficult. Johnson and co-workers [2] reported a 5% yield of (1) by u.v. photolysis of $[Rh(\eta-C_5H_5)(CO)_2]$ in aliphatic solvents for 15 h. We found that by lowering the irradiation time the yields of the compound (1) can be increased to *ca.* 65% and that it is possible to obtain it in pure form by chromatographic separation (see Experimental section).

The few literature reports indicate that the formation of products requiring ring opening of the metallacyclic system formed by $\overline{Rh-CO-Rh}$ is one of the peculiar aspects of the reactivity of (1).[10–12] Such a process occurs, for instance, during the formation of $[Rh_2(\eta-C_5H_5)_2(\mu-CHR)(CO)_2]$ (R = H or Me),[10] $[Rh_2(\eta-C_5H_5)_2(\mu-SO_2)(CO)_2]$,[11] and $[Rh_2(\eta-C_5H_5)_2(\mu-F_3CC_2CF_3)(CO)_2]$.[12] The available data seem to indicate that, when the metallacyclic system is involved in the reaction, the product is still a binuclear rhodium compound; unfortunately kinetic and mechanistic aspects of these reactions are still unknown. The molecules SO_2 and $SnCl_2$ bear lone pairs and unoccupied orbitals; both can act as bridge ligands between two metallic atoms. The behaviour of these species in the reactions with (1) is quite different. The synthesis and structural determination of $[Rh_2(\eta-C_5H_5)_2(\mu-SO_2)(CO)_2]$ have been recently reported.[11] From the reaction of (1) with $SnCl_2$ in acetone we obtained a red compound which, according to elemental analysis, molecular weight measurements, i.r., and ^1H n.m.r. data, is formulated as $[\{Rh(\eta-C_5H_5)(CO)(SnCl_2)\}_3]$. The complex is a non-electrolyte, is stable over a long period of time in solution and indefinitively as solid; it is soluble in acetone and in chlorinated solvents but sparingly soluble in diethyl ether. The i.r. spectrum shows ν(CO) terminal bands at 2 062 and 2 041 cm^{-1} and a band at 830 cm^{-1} attributable to the out-of-plane bending of the C–H of the η-cyclopentadienyl moiety; the ν(Sn–Cl) vibrations are observed at 310 and 330 cm^{-1}. In the ^1H n.m.r. spectrum the resonance of the cyclopentadienyl protons is detected at τ 4.02 ([$^2H_6$]acetone) as a complex multiplet arising from the coupling of the hydrogens with the rhodium and tin atoms.

We suggest for the compound $[\{Rh(\eta-C_5H_5)(CO)(SnCl_2)\}_3]$

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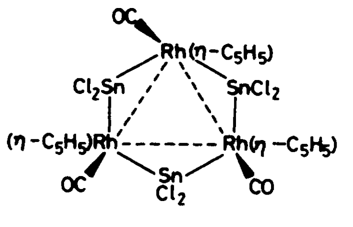
† Tri-μ-carbonyl-tris(η-cyclopentadienyl)-*triangulo*-trirhodium–acetone (1/0.24).

Supplementary data available (No. SUP 23636, 6 pp.): thermal parameters, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

a structure containing a six-membered ring with alternating rhodium and tin atoms (below). Unfortunately all attempts to obtain crystals for *X*-ray structure analysis failed. If the reaction between compound (1) and $SnCl_2$ is carried out in dichloromethane the complex $[\{Rh(\eta\text{-}C_5H_5)(CO)(SnCl_2)\}_3]$ is obtained with some solvent of crystallization.



A different initial step may be the reason of the different nuclearity and formal oxidation state of the metal of the products of the reactions with SO_2 and $SnCl_2$.

During the reaction with tin(II) chloride, the first step could be the insertion of $SnCl_2$ in the metal–metal bond of (1); the insertion of $SnCl_2$ in the metal–metal bond of organometallic complexes is a well known reaction.[14]

We also investigated the reactions of (1) with cyano-olefins aiming at ascertaining whether, in these reactions, ring opening of the metallacycle $\overline{Rh\text{-}CO\text{-}Rh}$ with concomitant formation of complexes containing the olefin bridge-bonded between two rhodium atoms occurs. Thus, when a benzene solution of (1) is treated with tetracyanoethylene (tcne), the compound $[Rh(\eta\text{-}C_5H_5)(CO)(tcne)]$ rapidly precipitates as a yellow solid, while the solution contains $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ as indicated by the i.r. spectrum. Analytical data and osmometric molecular weight measurements indicate that the tcne complex is a monomer. The i.r. spectrum shows, as noticeable features, bands at 2 225, 2 075, and 845 cm^{-1} attributable to ν(CN), ν(CO), and to the out-of-plane bending of η-cyclopentadienyl C–H, respectively. The ^1H n.m.r. spectrum of $[Rh(\eta\text{-}C_5H_5)(CO)(tcne)]$ shows a doublet at τ 4.44 [$J(HRh) = 0.6$ Hz] arising from the cyclopentadienyl protons.

The metal–olefin bond is dependent on the π interaction and can vary from a moderately perturbed olefin to the metal forming two σ bonds to the terminal carbon atoms (as in metallacyclopropanes). Although these two extremes are simply limiting cases of a continual change rather than distinct bonding forms,[15] because of the high value of ν(CO) indicative of a rhodium(III) derivative, we think the metal–olefin bond in the complex $[Rh(\eta\text{-}C_5H_5)(CO)(tcne)]$ is close to that of the metallacyclopropane. However, a strong π-bonding interaction in this metal–olefin bond is favoured by cyano-groups.

Other cyano-olefins such as fumaronitrile and acrylonitrile failed to react with the compound (1).

Mercury(II) dichloride reacts with (1) leaving unchanged the metallacyclic system; thus from this reaction the adduct $[\{Rh(\eta\text{-}C_5H_5)(CO)(HgCl_2)\}_2(\mu\text{-}CO)]$ was isolated. The compound is a yellow-brown solid, very little soluble in chlorinated solvents; this precluded a satisfactory ^1H n.m.r. spectrum. In agreement with the assigned formulation, the i.r. spectrum shows ν(CO) bands at 2 070, 2 055, and 1 858 cm^{-1}. In this reaction compound (1) acts as a Lewis base, as reported for other cyclopentadienyl–rhodium(I) and –iridium(I) compounds.[13,16,17] This result is in accordance with the high electron density of the two rhodium atoms in (1) shown by u.v. photoelectron spectroscopy.[18]

Recently it was reported [19] that polynuclear metal carbonyl complexes containing bridged CO, CNR, or CS ligands react with an electrophile E, such as $HgCl_2$, to give adducts containing μ–CA–E moieties (A = O, NMe, or S). We did not detect the formation of any adduct in which $HgCl_2$ is bonded to the bridge carbonyl. However, the nature of the product obtained rules out the possibility of the above mechanism operating.[19] Clearly, if the metallic centre is basic enough electrophilic attack on the metal is favoured.

To ascertain the behaviour of (1) towards small molecules we studied its reaction with I_2, which is known [20] to bridge two metallic centres and cause scission of the metal–metal bond before co-ordinating to the metal. From this reaction we obtained the previously reported [21] $[Rh(\eta\text{-}C_5H_5)(CO)(I)_2]$.

With the aim of obtaining heteronuclear metal complexes containing rhodium atoms, we studied the reaction of (1) with $PdCl_2$ and $PtCl_2$. By adding $PdCl_2$ or $PtCl_2$ to an acetone solution containing (1) the colour of the solution turns from red to yellow-brown. By slow evaporation of the solvent brown crystals were obtained. Elemental analysis, molecular weight determination in benzene solution, and i.r. and ^1H n.m.r. spectra suggested for the product the formulation $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]\cdot 0.2Me_2CO$; however, as its properties were different from those reported [4,5,7] for $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ and for $[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CO)_2(CO)]$ [8] we undertook an *X*-ray analysis. The results show that the compound obtained is a new form of the known complex $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$. The synthesis of the previous complex by the reaction of (1) with $PdCl_2$ or $PtCl_2$ is remarkable since, by this route, the trimer $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ is easily obtained quantitatively as the only product. With the synthetic methods reported in the literature [4,5] $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ is obtained mixed with the isomers $[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CO)_2(CO)]$ and $[Rh_4(\eta\text{-}C_5H_5)_4(CO)_2]$ whose separation is quite difficult.

The formation of $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ requires ring opening of the metallacyclic system by $PdCl_2$ or $PtCl_2$; we could not get mechanistic details of these reactions since, either following the reactions by i.r. or ^1H n.m.r. spectroscopy or carrying out the reactions at lower temperature, we did not detect formation of intermediates or carbonyl complexes of palladium(II) or platinum(II) as by-products. Bearing in mind that ring opening of the metallacyclic system and formation, in some cases, of a new metallacyclic system occurs in the reactions of (1) with molecules bearing lone pairs and unoccupied orbitals, we suggest that in the previous reactions the labile intermediates $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}PdCl_2)]$ or $[Rh_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}PtCl_2)]$ are formed; after releasing the weakly bonded $PdCl_2$ or $PtCl_2$ the intermediates generate the fragment $[Rh(\eta\text{-}C_5H_5)(CO)]$ which afterwards trimerizes.

Recently, Herrmann *et al.*[22] reported the synthesis of $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ by protonation of (1) with HBF_4. At low temperature the hydrido-complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2]BF_4$ was isolated as an intermediate, whereas at room temperature deprotonation occurs with concomitant formation of $[Rh(\eta\text{-}C_5H_5)(CO)_2]$ and $[Rh_3(\eta\text{-}C_5H_5)_3(\mu\text{-}CO)_3]$.

Also, the reaction of (1) with NMe_2CN gives as the only product the trimer $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$. No reaction intermediates were detected spectroscopically. Since the cyanamides can act as four-electron donor ligands to a bimetallic complex,[23] we suggest that in the above reaction the labile intermediate $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}NMe_2CN)(CO)_2]$ should be formed. This, after releasing NMe_2CN, generates $[Rh(\eta\text{-}C_5H_5)(CO)]$ which easily trimerizes.

In a subsequent paper [24] we will report on the reactions of (1) with isocyanides, tertiary phosphines, and diphosphines.

Structure of $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]\cdot 0.24Me_2CO$.—The molecular structure of the complex is shown in Figure 1; it consists of a trimeric unit with crystallographic symmetry 3*m*. The structure is essentially equal, within the experimental

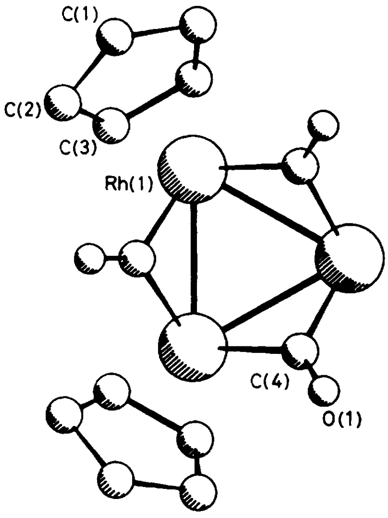


Figure 1. View of the trimeric unit down *c*

Table 1. Some relevant interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Rh–Rh^1	2.6195	C(2)–C(3)	1.416(4)
Rh–C(1)	2.239(4)	C(3)–C(3^1)	1.389(6)
Rh–C(2)	2.220(2)	C(4)–O	1.165(4)
Rh–C(3)	2.295(2)	C(1)–H(1)	0.79(4)
Rh–C(4)	1.999(2)	C(2)–H(2)	0.79(3)
C(1)–C(2)	1.387(3)	C(3)–H(3)	0.84(3)

(*b*) Angles

C(1)–C(2)–C(3)	108.3(2)
C(2)–C(3)–C(3^1)	107.7(3)
C(2)–C(1)–C(2^1)	108.0(3)
Rh–C(4)–O	139.0(2)
Rh–C(4)–Rh^1	81.9(2)

Superscript I indicates $-y$, $1 - x$, $1 + z$.

error, to that assigned to the monoclinic form of [{Rh(η-C_5H_5)(μ-CO)}$_3$][7] obtained by photolysis of [Rh(η-C_5H_5)-$(CO)_2$]. Bond distances and angles are listed in Table 1; Table 2 gives a comparison between significant bond distances and angles in the two forms, revealing a complete agreement between the two determinations. The molecular volumes of the two modifications are significantly different (861 Å^3 for the monoclinic form and 984 Å^3 in the trigonal modification). This is due (see structure determination) to the presence of disordered acetone, which could also be responsible for the formation of the more symmetric trigonal modification. (The presence of the acetone was also evidenced by a band at 1 720 cm^{-1} in the i.r. spectrum of the compound.) Then, in view of the absence of any significant change in the co-ordination sphere of the rhodium in the two modifications, the two complexes can be regarded as two dimorphic forms, one monoclinic and one trigonal. The unit-cell contents viewed down *a* are shown in Figure 2.

Experimental

[Rh(η-C_5H_5)$(CO)_2$] was prepared by the literature method.[25] Other reagents were used as obtained from commercial sources. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using polystyrene film for calibration. A Perkin-Elmer R 24B spectrometer was used to obtain ^{1}H n.m.r. spectra. Molecular weights were determined with a Knauer vapour pressure osmometer. Conductivity measurements were made with a WTW LBR conductivity meter. Elemental analyses were performed by Bernhardt Mikroanalytishes Laboratorium, Elbach, Germany and by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan.

All the reactions were carried out under an atmosphere of oxygen-free nitrogen.

Hydrogen-1 n.m.r. data could not be obtained for some new reported compounds because of their poor solubility.

Table 2. Selected interatomic distances (Å) and angles (°) in the two modifications

	Monoclinic	Trigonal
Rh–Rh^1	2.620	2.6195
Rh–C(1)	2.24(4)	2.239(4)
Rh–C(2)	2.20(4)	2.220(2)
Rh–C(3)	2.29(3)	2.295(2)
Rh–C(carbonyl)	2.00(2)	1.999(2)
Rh–Rh–Rh^1	60.0(1)	60
Rh–C–O	139(2)	138.9(7)
Angles (°) between the planes		
C_5H_5 plane/Rh_3 plane	58.8	60.3
C(carbonyl) plane/Rh_3 plane	0	0

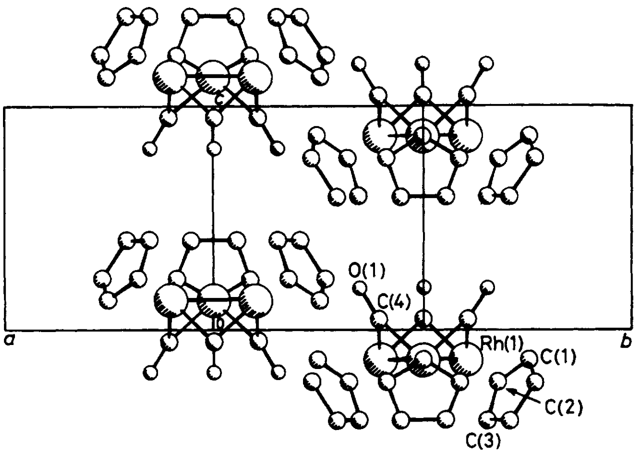


Figure 2. Crystal packing down *a*

μ-Carbonyl-bis[carbonyl(η-cyclopentadienyl)rhodium(I)], [Rh_2(η-C_5H_5)$_2$(μ-CO)$(CO)_2$] (1).—This compound was obtained by slight modification of the method of Lewis and co-workers.[2] A concentrated pentane solution of [Rh(η-C_5H_5)$(CO)_2$] (obtained in pentane (60 cm^3) from [{Rh$(CO)_2$-Cl}$_2$] (0.52 g)) was irradiated by a Hanavia immersion lamp for 3 h. The thickness of the irradiated solution was 7 mm. The solution was chromatographed on a basic alumina column saturated with pentane. A yellow fraction containing unchanged [Rh(η-C_5H_5)$(CO)_2$] was eluted with pentane; using pentane–diethyl ether (2 : 1) as eluant gave a red fraction containing compound (1), and a deep green fraction containing a small amount of [{Rh(η-C_5H_5)(μ-CO)}$_3$] and of its isomer [Rh_3(η-C_5H_5)$_3$(μ-CO)$_2$(CO)]. Evaporation of the solvent from the red solution gave the dinuclear compound as red crystals. Yield 65%, relative to reacted [Rh(η-C_5H_5)$(CO)_2$] (Found: C, 37.2; H, 2.45. $C_{13}H_{10}O_3Rh_2$ requires C, 37.15; H, 2.4%).

Tris[carbonyl(η-cyclopentadienyl)(dichlorostannio)rhodium], $[\{Rh(\eta\text{-}C_5H_5)(CO)(SnCl_2)\}_3]$.—To an acetone solution of (1) (0.20 g, 0.476 mmol), $SnCl_2$ (0.316 g, 1.571 mmol) was added and the mixture was left at room temperature, with stirring, until the i.r. spectrum showed the disappearance of the ν(CO) bands of the starting material (*ca.* 25 h). The solution was filtered and the solvent evaporated off at reduced pressure. The resultant solid was extracted with diethyl ether to give a red solution. The product was obtained as a red solid, yield 68% [Found: C, 18.4; H, 1.4; Cl, 19.1%; *M* (osmometry, acetone), 1 240. $C_6H_5Cl_2ORhSn$ requires C, 18.7; H, 1.3; Cl, 18.4%; *M* (as trimer), 1 180]. I.r. (Nujol mull, CsI): 2 062vs (sh), 2 041vs [ν(CO)]; 310m, 330m cm^{-1} [ν(Sn–Cl)]. ^1H n.m.r. ($[^2H_6]$-acetone): τ 4.02 (m, C_5H_5).

Carbonyl(η-cyclopentadienyl)(tetracyanoethylene)rhodium, $[Rh(\eta\text{-}C_5H_5)(CO)(tcne)]$.—To a benzene solution (20 cm^3) of (1) (0.150 g, 0.357 mmol), tetracyanoethylene (0.101 g, 0.786 mmol) in the same solvent (5 cm^3) was added. The solution was stirred for 2 h. During this time, the product precipitated as a yellow solid and the solution became yellow. The solid was filtered off, washed with small portions of benzene and dried. Further product was obtained by adding hexane to the mother-liquor, yield 98% [Found: C, 44.55; H, 1.55; N, 17.4%; *M* (osmometry, CH_2Cl_2), 330. $C_{12}H_5N_4ORh$ requires C, 44.45; H, 1.55; N, 17.3%; *M*, 324]. I.r. (Nujol mull, KBr): 2 225s [ν(CN)], 2 075vs cm^{-1} [ν(CO)]. ^1H n.m.r. ($CDCl_3$): τ 4.44 [d, C_5H_5, *J*(HRh) 0.6 Hz].

μ-Carbonyl-bis[carbonyl(η-cyclopentadienyl)(dichloromercurio)rhodium], $[\{Rh(\eta\text{-}C_5H_5)(CO)(HgCl_2)\}_2(\mu\text{-}CO)]$.—Compound (1) (0.170 g, 0.405 mmol) was dissolved in acetone (20 cm^3) and to the stirred solution was added dropwise $HgCl_2$ in the same solvent. A brown precipitate was formed and the solution turned orange. The solid was separated by filtration, washed with small portions of acetone, and then pentane, and dried; yield 97% (Found: C, 16.35; H, 1.1; Cl, 14.5. $C_{13}H_{10}Cl_4Hg_2O_3Rh_2$ requires C, 16.2; H, 1.05; Cl, 14.7%). I.r. (Nujol mull, CsI): 2 070vs, 2 055vs, 1 858s cm^{-1} [ν(CO)].

Reaction of (1) *with Iodine*.—To a pentane solution of (1) was added dropwise a solution of iodine in the same solvent. Formation of a black precipitate occurred immediately. After stirring for 2 h the precipitate, $[Rh(\eta\text{-}C_5H_5)(CO)(I)_2]$, was separated by filtration, washed with pentane and dried; yield 98% (Found: C, 16.2; H, 1.1; I, 56.5. $C_6H_5I_2ORh$ requires C, 16.0; H, 1.1; I, 56.4%). I.r. (Nujol mull, KBr): 2 065vs cm^{-1} [ν(CO)]. ^1H n.m.r. ($CDCl_3$): τ 4.09 [d, C_5H_5, *J*(HRh) 0.6 Hz].

Reaction of (1) *with* $PdCl_2$ *or* $PtCl_2$.—Solid $PdCl_2$ was added to a stirred solution of (1) in dry acetone. The colour of the solution changed from red to yellow-brown. After 5 h the solution was filtered. By slow evaporation of the solvent, brown-yellow crystals of $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]\cdot 0.2Me_2CO$ were obtained; yield 98%.

The reaction of (1) with $PtCl_2$, in acetone, takes place similarly, giving $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]\cdot 0.2Me_2CO$; yield 96% (Found: C, 37.3; H, 2.75; O, 8.6. $C_{18.6}H_{16.2}O_{3.2}Rh_3$ requires C, 37.25; H, 2.7; O, 8.55%). I.r. (Nujol mull, KBr): 1 825s, 1 770s [ν(CO)]; 1 720w cm^{-1} $[\nu(CO)_{acetone}]$. ^1H n.m.r. (CD_2Cl_2): τ 4.48 (s, C_5H_5).

Reaction of (1) *with* NMe_2CN.—To a pentane solution of (1) a slight excess of dimethylcyanamide was added. The colour changed from red to brown-yellow. After stirring for 3 h the volume of the solvent was reduced and the solution transferred to a pentane-packed column of silica gel. Elution with pentane–diethyl ether (3 : 1) gave a brown fraction. After evaporation of the solvent at reduced pressure, $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ was obtained; yield 94% (Found: C, 36.8; H, 2.6; O, 8.2. $C_{18}H_{15}O_3Rh_3$ requires C, 36.75; H, 2.55; O, 8.15%). I.r. (Nujol mull, KBr): 1 825s, 1 770s cm^{-1} [ν(CO)]. ^1H n.m.r. (CD_2Cl_2) τ 4.48 (s, C_5H_5).

Table 3. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses and occupancy factor, *K*

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*K*
Rh	2 652(0)	−2 652(0)	−1 335(1)	0.5
O(1)	4 347(2)	−4 347(2)	1 871(6)	0.5
C(4)	4 042(2)	−4 042(2)	501(8)	0.5
C(1)	1 643(3)	−1 643(3)	−1 325(3)	0.5
H(1)	1 512(35)	−1 512(35)	−269(118)	0.5
C(3)	1 592(5)	−2 676(4)	−4 027(6)	1
H(3)	1 568(50)	−3 146(47)	−4 905(85)	1
C(2)	969(4)	−2 720(4)	−2 311(8)	1
H(2)	325(53)	−3 284(54)	−2 106(77)	1
C(5)	0	0	780(279)	0.03
O(2)	0	0	8 236(218)	0.03

X-Ray Analysis.—Crystals of $[\{Rh(\eta\text{-}C_5H_5)(\mu\text{-}CO)\}_3]$ suitable for *X*-ray analysis were obtained as reported above.

Crystal data. $C_{18}H_{15}O_3Rh_3$, $M = 588$, Trigonal, $a = 12.815(2)$, $c = 6.916(1)$ Å, $U = 984$ Å^3, $D_c = 1.98$ g cm^{-3} (for two trimeric units in the cell), space group $P\bar{3}m1$ (no. 164) by intensity statistics and refinement of the structure, $F(000) = 636$, Mo-K_α radiation (λ = 0.710 69 Å), $\mu = 27.9$ cm^{-1}. All diffraction measurements were performed on a Siemens Stoe four-circle diffractometer using graphite-monochromatized Mo-K_α radiation. 20 Reflections in the range $10 < \theta < 15°$ were located by a random search procedure and subsequently centred.

These reflections were used as a basis for the indexing. The cell constants and the orientation matrix were refined by a least-squares fit. Intensities were collected at room temperature in the range $3 \leqslant \theta \leqslant 25°$. A θ/ω scan was used with a 0.5 s count at each of 120 steps of 0.01° for each reflection and a 10 s background count at each end of the scan. The stability of the crystal and electronics were confirmed by the constancy of three reflections whose intensities were monitored every 100 reflections. The 1 563 measured reflections, with $k,l \geqslant 0$, were averaged and reduced to a unique set of independent reflections and the 549 having a net intensity $I > 2.5\sigma(I)$ were used in the structure determination and refinement. The data were corrected for Lorentz and polarization effects.

Structure determination and refinement. The systematic absences did not determine unequivocally the space group, as all order reflections are present. Between the space groups possible, on the basis of the Patterson interpretation we chose the more symmetrical one, $P\bar{3}m1$, with the trimeric molecule lying on a three-fold axis. In this situation the asymmetric unit is given by a rhodium atom occupying a special position (i) on a mirror plane, a CO group lying in a second mirror at 60° from the former, and finally by half a cyclopentadienyl ring that is also seated on the rhodium mirror plane. The interpretation of the structure according to this space group and the subsequent refinement confirmed this choice.

The structure was refined by full-matrix least-squares techniques using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom contributions were used as fixed atoms in calculated positions [d(C–H) = 0.95 Å; $B_{iso.} = 5.0$ Å^2]. The discrepancy index was taken as $R = \Sigma w(|F_o| - |F_c|)/\Sigma F_o$ where $w = 1/(\sigma^2 F_o + 0.00119\, F_o{}^2)$.

The refinements converged to give $R = 0.022$ and $R' = 0.025$. An electron-density difference-Fourier map calculated at this stage showed residual peaks of about 1 e Å^{-3} in the direction of the z axis and close to it. They were interpreted as a disordered acetone molecule with the CO group lying on the z axis. The methyl groups are in this model disordered around the c axis between the six positions given by the $3m$ point symmetry. They were not introduced in the calculation. The best refinement of the CO group was reached considering a ratio of 0.24 acetone molecule per trimeric unit. The inclusion of the CO group of the solvent molecule in the refinement gave final R and R' values of 0.022 and 0.025 respectively. Final atomic co-ordinates are given in Table 3.

Atomic scattering factors were taken from ref. 26 as were the corrections for the real and imaginary parts of the anomalous dispersion for Rh. The calculations were carried out with the SHELX 76 system of programs.[27]

Acknowledgements

We thank the C.N.R. (Italy) for financial support.

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Received 24*th May* 1982; *Paper* 2/855