Synthesis and Crystal and Molecular Structure of [(η-C5H5)Rh(μ-CO)2Rh(PPh3)(η-C5H5)] † an Asymmetric Bimetallic Complex with a Polar Rhodium–Rhodium Bond

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Treatment of [{Rh(η-C5H5)(CO)}2(μ-CO)] with PPh3, in saturated hydrocarbons, affords [(η-C5H5)Rh(μ-CO)2Rh(PPh3)(η-C5H5)] which has been characterized by i.r., ^{1}H n.m.r., and X-ray diffraction methods. The complex crystallizes in the triclinic space group P$\bar{1}$, with a = 9.700(2), b = 11.076(2), c = 13.790(3) Å, α = 105.3(1), β = 109.6(1), γ = 99.1(1)°, and Z = 2. On the basis of 2 697 reflections with $I \geqslant 2.5\ \sigma(I)$, the structure has been refined to R 0.053 and R' 0.059. The molecule possesses a near mirror plane defined by the Rh–Rh bond [2.673(1) Å] and the phosphorus atom. The two carbonyl ligands form two different asymmetric bridges to the rhodium atoms [Rh(1)–C(19) 2.17(1), Rh(2)–C(19) 1.89(1), Rh(1)–C(20) 2.10(1), and Rh(2)–C(20) 1.90(1) Å]. The cyclopentadienyl ligands are in a *cis* position with an interplanar angle of 66.3° and both are perpendicular to the pseudo-mirror molecular plane. The co-ordination geometry about the two metal centres is different, being formally Rh(1) seven-co-ordinate and Rh(2) six-co-ordinate. The complex [(η-C5H5)Rh(μ-CO)2Rh(PPh3)(η-C5H5)] reacts with PPh3 to give the known [Rh(η-C5H5)(CO)(PPh3)] ; the same product can be obtained directly by reacting [{Rh(η-C5H5)(CO)}2(μ-CO)] with PPh3 in excess, in benzene solution.

Interest in the synthesis of bi- and poly-nuclear complexes of low-oxidation state transition metals has arisen due to their ability to give, in principle, new modes of activation of organic and inorganic molecules.[1] Such an ability is related to the possibility that a co-operative involvement of the metallic active sites occurs.[1]

So far there is no clear evidence that the binuclear complexes behave differently from the mononuclear ones as regards the activation processes.[2] In this respect the design of new types of binuclear complexes is interesting.

We report on the synthesis and the crystal and molecular structure of the unusual compound [(η-C5H5)Rh(μ-CO)2-Rh(PPh3)(η-C5H5)]; this substance is an asymmetric di-rhodium complex containing 34 valence electrons and represents a new model for the activation of molecules.[3] During the preparation of this paper some complexes of the same type as [(η-C5H5)Rh(μ-CO)2Rh(PPh3)(η-C5H5)] have been reported.[4,5] For their preparation a different route has been followed.

Results and Discussion

Addition of PPh3 to a solution of [{Rh(η-C5H5)(CO)}2(μ-CO)] in pentane afforded a green-brown crystalline complex, which according to molecular-weight measurements in benzene solution, analytical, i.r. and ^{1}H n.m.r. data, must be formulated as [(η-C5H5)Rh(μ-CO)2Rh(PPh3)(η-C5H5)]. The compound is stable indefinitely as a solid, but decomposes rapidly in chlorinated solvents; its solution in diethyl ether or benzene is stable over a long period of time. The i.r. spectrum (Nujol mull) showed bands at 1 815s and 1 760vs cm⁻¹ revealing the presence of bridging carbonyl ligands

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† Di-μ-carbonyl-1,2-bis(η-cyclopentadienyl)-1-triphenylphosphinedirhodium(*Rh–Rh*).

Supplementary data available (No. SUP 23619; 20 pp.): observed and calculated structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.
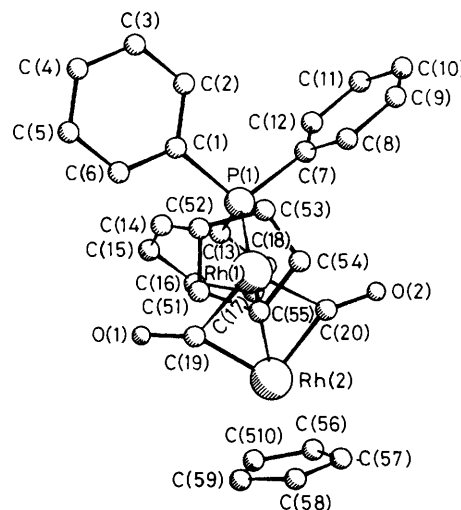

Figure. The molecular structure of [(η-C5H5)Rh(μ-CO)2Rh(PPh3)-(η-C5H5)], showing the atom-numbering scheme

only and bands at 830, 805, and 780 cm⁻¹ attributable to the out-of-plane bending of C–H modes of the C5H5 groups η⁵-co-ordinated to the rhodium atoms. Two signals in the ^{1}H n.m.r. spectrum (C6D6) appeared as an asymmetric doublet at δ 5.03 [J(HRh) = 0.70 Hz] and as an asymmetric triplet at δ 4.90 [J(HRh) = J(HP) = 0.68 Hz], indicating the non-equivalent environment of the C5H5 groups. The values of the coupling constants are in the range normally found for cyclopentadienyl–phosphine–rhodium(I) complexes.[6]

In order to define unambiguously the molecular structure of the prepared compound, [(η-C5H5)Rh(μ-CO)2Rh(PPh3)-(η-C5H5)], a single-crystal X-ray diffraction study was undertaken. The solid-state molecular structure of [(η-C5H5)-Rh(μ-CO)2Rh(PPh3)(η-C5H5)] is shown in the Figure together with the atom-numbering scheme. Atomic parameters from

Table 1. Final fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviation in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Rh(1)	−379(1)	2 257(1)	2 952(1)	C(1)	−1 666(8)	2 771(5)	522(5)
Rh(2)	2 401(1)	2 020(1)	3 944(1)	C(2)	−2 466(8)	3 574(5)	84(5)
P	−63(3)	3 410(2)	1 859(2)	C(3)	−3 681(8)	3 047(5)	−938(5)
O(1)	731(10)	325(8)	1 612(6)	C(4)	−4 096(8)	1 717(5)	−1 521(5)
O(2)	1 965(9)	4 604(7)	4 750(6)	C(5)	−3 296(8)	914(5)	−1 083(5)
C(19)	1 060(12)	1 128(11)	2 461(10)	C(6)	−2 081(8)	1 441(5)	−62(5)
C(20)	1 675(12)	3 526(11)	4 184(8)	C(7)	7(7)	5 129(6)	2 349(5)
C(51)	−2 147(14)	450(13)	2 693(13)	C(8)	−712(7)	5 545(6)	3 048(5)
C(52)	−2 872(13)	1 174(20)	2 110(13)	C(9)	−748(7)	6 840(6)	3 372(5)
C(53)	−2 655(15)	2 406(16)	2 929(18)	C(10)	−65(7)	7 719(6)	2 997(5)
C(54)	−1 870(16)	2 352(15)	3 940(14)	C(11)	654(7)	7 304(6)	2 298(5)
C(55)	−1 474(14)	1 177(13)	3 780(11)	C(12)	690(7)	6 009(6)	1 974(5)
C(56)	4 938(12)	2 552(16)	4 929(12)	C(13)	1 623(7)	3 445(7)	1 543(5)
C(57)	4 218(16)	2 410(16)	5 645(10)	C(14)	1 526(7)	2 797(7)	497(5)
C(58)	3 439(15)	1 139(21)	5 291(15)	C(15)	2 845(7)	2 829(7)	295(5)
C(59)	3 637(16)	513(14)	4 348(15)	C(16)	4 262(7)	3 509(7)	1 141(5)
C(510)	4 591(16)	1 444(16)	4 130(12)	C(17)	4 359(7)	4 157(7)	2 187(5)
				C(18)	3 039(7)	4 125(7)	2 388(5)

Table 2. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Distances

Rh(1)−P(1)	2.281(2)	Rh(1)−Rh(2)	2.673(1)
Rh(1)−C(19)	2.17(1)	Rh(1)−C(20)	2.10(1)
Rh(2)−C(19)	1.89(1)	Rh(2)−C(20)	1.90(1)
Rh(1)−C(51)	2.28(1)	Rh(2)−C(56)	2.26(1)
Rh(1)−C(52)	2.26(1)	Rh(2)−C(57)	2.29(1)
Rh(1)−C(53)	2.23(1)	Rh(2)−C(58)	2.33(1)
Rh(1)−C(54)	2.29(1)	Rh(2)−C(59)	2.28(1)
Rh(1)−C(55)	2.24(1)	Rh(2)−C(510)	2.27(1)
C(19)−O(1)	1.17(1)	C(20)−O(2)	1.17(1)
P−C(1)	1.831(7)	P−C(7)	1.826(6)
P−C(13)	1.826(8)	C(56)−C(57)	1.41(2)
C(51)−C(52)	1.39(2)	C(57)−C(58)	1.36(2)
C(51)−C(55)	1.36(2)	C(58)−C(59)	1.39(2)
C(52)−C(53)	1.45(2)	C(59)−C(510)	1.44(2)
C(53)−C(54)	1.37(2)	C(56)−C(510)	1.32(2)
C(54)−C(55)	1.40(2)		

(b) Angles

Rh(1)−C(19)−Rh(2)	82.0(2)	Rh(1)−C(20)−Rh(2)	83.6(4)
Rh(1)−C(19)−O(1)	126.8(8)	Rh(2)−C(19)−O(1)	150.9(9)
Rh(1)−C(20)−O(2)	131.2(8)	Rh(2)−C(20)−O(2)	144.7(9)
P−Rh(1)−C(19)	88.4(3)	P−Rh(1)−C(20)	87.7(3)
Rh(1)−P−C(1)	110.9(2)	Rh(1)−P−C(7)	115.9(2)
Rh(1)−P−C(13)	117.3(3)	C(1)−P−C(13)	104.7(3)
C(7)−P−C(13)	103.1(3)	C(1)−P−C(7)	103.4(3)
C(55)−C(51)−C(52)	109(1)	C(57)−C(56)−C(510)	111(1)
C(51)−C(52)−C(53)	105(1)	C(56)−C(57)−C(58)	107(1)
C(52)−C(53)−C(54)	108(1)	C(57)−C(58)−C(59)	107(1)
C(53)−C(54)−C(55)	108(1)	C(58)−C(59)−C(510)	109(1)
C(51)−C(55)−C(54)	109(1)	C(56)−C(510)−C(59)	105(1)

the last cycle of refinement are given in Table 1. Interatomic distances and bond angles are listed in Table 2 while selected least-squares planes and interplanar angles are given in Table 3.

The structure is characterized by the short Rh−Rh distance [2.673(1) Å], by the different co-ordination geometry of the two rhodium atoms (also implying a different co-ordination number), and by the presence of asymmetric CO bridging ligands. The metals Rh(1) and Rh(2) are, respectively, form-ally seven- and six-co-ordinate. A particular shape cannot be used to describe the co-ordination geometry of the molecule.

The $Rh_2(CO)_2$ frame is significantly non-planar as shown by

Table 3. Selected least-squares planes; distances of the atoms from the plane (Å) are given in square brackets

Plane 1: cyclopentadienyl ring (1)

$$8.6492X + 3.3079Y − 7.0522Z = 3.5852$$

[C(51) −0.022, C(52) 0.002, C(53) 0.019, C(54) −0.033, C(55) 0.034]

Plane 2: cyclopentadienyl ring (2)

$$6.9007X − 5.8904Y + 5.4292Z = 4.5678$$

[C(56) 0.013, C(57) −0.012, C(58) 0.007, C(59) 0.000, C(510) −0.008]

Plane 3: ring centroid Cp(1), Rh(1), P, Rh(2), ring centroid Cp(2)

$$−2.1535X + 7.2360Y + 7.3784Z = 3.8622$$

[Cp(1) −0.000, Cp(2) −0.014, Rh(1) 0.031, Rh(2) −0.008, P −0.010, C(19) −1.458, C(20) 1.4160, O(1) −2.595, O(2) 2.551]

Plane 4: Rh(1), Rh(2), C(19)(carbonyl)

$$3.9324X + 8.8819Y − 8.8981Z = −0.7711$$

[O(1) −0.0871]

Plane 5: Rh(1)−Rh(2); C(20)(carbonyl)

$$−5.0552X − 4.5223Y + 13.0862Z = 3.0339$$

[O(2) 0.0107]

Plane 6: Phenyl ring C(1)—C(6)

$$−8.0743X − 2.1896Y + 10.7334Z = 1.2985$$

Plane 7: Phenyl ring C(7)—C(12)

$$5.9208X − 1.5966Y + 7.0392Z = 0.8387$$

Plane 8: Phenyl ring C(13)—C(18)

$$−1.2591X + 10.7604Y − 6.5472Z = 2.4924$$

Plane 9: Rh(1), Rh(2), C(19), C(20)

$$−4.5008X − 7.1539Y + 11.5274Z = 1.7698$$

[Rh(1) 0.189, Rh(2) 0.251, C(19) −0.217, C(20) −0.223, O(1) −0.473, O(2) −0.472]

Angles (°) between planes

1—2	66.3	1—3	88.7	2—3	89.7
1—9	141.1	2—9	74.8	4—5	145.6
6—7	98.2	7—8	108.2	6—8	108.5

the best mean plane calculated through these atoms [the deviations: Rh(1) 0.189, Rh(2) 0.251, C(19) −0.217, and C(20) −0.223 Å] and by the dihedral angles of 142.7° between the two fused RhC_2 planes and 145.6° between the two fused CRh_2 planes.

The unsymmetrical arrangement of the two carbonyls is interesting. The Rh(2)$-$C(19) and Rh(2)$-$C(20) bond distances of 1.89(1) and 1.90(1) Å respectively are comparable and these carbonyls are closer to the six-co-ordinate Rh(2); their values are in agreement with those found in the trimer [{Rh(η-C$_5$H$_5$)-(CO)}$_3$].[7,8] The Rh(1)$-$C(19) bond distance is 2.17 Å while the Rh(1)$-$C(20) distance is 2.10 Å. These values are not comparable and are significantly larger than those of Rh(2)$-$C(19) and Rh(2)$-$C(20) above. This situation is very similar to that found in the Rh$_3$(μ-CO)$_2$ frame of the trinuclear rhodium compound [Rh$_3$(η-C$_5$H$_5$)$_3$(μ-CO)$_2$(μ_3-CH)][CF$_3$CO$_2$] where the 'unsymmetrical' bridge has Rh$-$C distances, Rh(2)$-$C(2) 1.914(9) Å and Rh(1)$-$C(2) 2.202(11) Å with a Rh(1)$-$Rh(2) separation of 2.677(1) Å [cf. Rh(2)$-$C(20) and Rh(1)$-$C(20)].

It is noteworthy that in both bridges of the present determination the asymmetrical bonding is not accompanied by a significant variation in the internal Rh$-$C(μ-CO)$-$Rh angles [Rh(1)$-$C(19)$-$Rh(2) 82.0(2) and Rh(1)$-$C(20)$-$Rh(2) 83.6(4)°], with respect to the values given for symmetrical bridges which are on average, 83°. The Rh$-$C(μ-CO)$-$O angle deviates considerably in both directions from the value of 137° obtained by an averaging of symmetrical bonding in a series of rhodium complexes,[9] being Rh(1)$-$C(20)$-$O(2) 131.2(8), Rh(2)$-$C(20)$-$O(2) 144.7(9), Rh(1)$-$C(19)$-$O(1) 126.8(8), and Rh(2)$-$C(19)$-$O(1) 150.9°.

With reference to these differences in bond distances and angles if we follow the Colton and McCormick [10] classification (for which when the difference in the M$-$C bond lengths is less than 0.3 Å and the difference in the M$-$C$-$O angles is less than 20°, the bridging carbonyl group is asymmetric and when the differences are larger the carbonyl group is semi-bridged) we should consider the bridging C(20)$-$O(2) carbonyl group as asymmetric, having a difference in the Rh$-$C(20) bond distances of 0.2 Å and a difference in the Rh$-$C$-$O angles of 13.5°. The second bridging carbonyl group, having a difference in the Rh$-$C(19) bond distances of 0.28 Å and a difference in the Rh$-$C$-$O angles of 24.1°, should be considered more as semi-bridging rather than asymmetric bridging. The second CO bridge is at the limit of the distinction between the two types of bridging and we have considered both bridges as asymmetric.

In this context the molecule provides an example of asymmetric carbonyl bridging ligands which can be explained, as suggested by Cotton [11] in the case of semibridging carbonyl ligands, as buffers to the polar electron distribution on the two rhodium atoms. In fact, if we consider the rhodium environment, we can count 18 electrons for Rh(1) and 16 electrons for Rh(2). A Rh(1)$-$Rh(2) single bond is present, as indicated by the value 2.673(1) Å, which is comparable to reported values in bridged dirhodium structures.[7,9,12-14] The metal$-$metal interaction in [(η-C$_5$H$_5$)Rh(μ-CO)$_2$Rh(PPh$_3$)-(η-C$_5$H$_5$)] can be regarded as arising from donation of an electron pair from Rh(1) to Rh(2). The highly polar Rh(1)$\rightarrow$ Rh(2) bond produced would lead to asymmetric CO bridging to mitigate the charge imbalance and to satisfy the Pauling electroneutrality principle, as in the complex [V$_2$(η-C$_5$H$_5$)$_2$-(μ-CO)$_2$(CO)$_3$].[15]

As shown in the Figure, which represents a view of the complex in the Rh(2)$-$O(1)$-$O(2) plane, apart from the PPh$_3$ ligand, the molecule exhibits an approximate mirror plane [Rh(1)$-$Rh(2)$-$P plane], about which there appears no particular ligand crowding around the two metal centres which could add some other justification for the asymmetric bridging carbonyls.

The cyclopentadienyl groups are in a *cis* position with an interplanar angle of 66°. This conformation is very close to that observed in [(η-C$_5$H$_5$)MeRh(μ-CO)$_2$RhBr(η-C$_5$H$_5$)] [9]

where the molecule possesses a crystallographic mirror plane. In this complex the rhodium atoms are symmetrically bridged by two carbonyl groups so that no difference in charge distribution on the rhodium atoms is present. The Rh$-$Rh bond distance [2.660(3) Å] together with the Rh$-$C(carbonyl) bond distance [1.994(20) Å] are in agreement with the present determination when we consider the average of the Rh$-$C(carbonyl) distances. The Rh$-$C(C$_5$H$_5$) distances range from 2.23(1) to 2.33(1) Å with averaged values for Rh(1)$-$C(C$_5$H$_5$) of 2.26 Å and for Rh(2)$-$C(C$_5$H$_5$) of 2.29 Å. These values are in agreement with the literature reports.[7,13,16] The corresponding Rh$-$C$_5$H$_5$ separations for Rh(1) and Rh(2), are respectively, 1.922 and 1.960 Å. The two C$_5$H$_5$ rings are planar in the limit of the errors with an averaged value for the C$-$C distance of 1.39 Å and for the C$-$C$-$C angles of 108°.

The packing diagram does not reveal particular intermolecular interactions less than the sum of the normal van der Waals radii.

The compound [(η-C$_5$H$_5$)Rh(μ-CO)$_2$Rh(PPh$_3$)(η-C$_5$H$_5$)] must be considered as an intermediate of the reaction of [{Rh(C$_5$H$_5$)$_2$(CO)}$_2$(μ-CO)] with PPh$_3$ to give, as a final product, the known complex [Rh(η-C$_5$H$_5$)(CO)(PPh$_3$)].[17] In fact [Rh(η-C$_5$H$_5$)(CO)(PPh$_3$)] can be obtained directly from [{Rh(η-C$_5$H$_5$)$_2$(CO)}$_2$(μ-CO)], by conducting the reaction in benzene or dichloromethane solution, or from [(η-C$_5$H$_5$)-Rh(μ-CO)$_2$Rh(PPh$_3$)(η-C$_5$H$_5$)] in diethyl ether or benzene solution. Differently from [(η-C$_5$H$_5$)Rh(μ-CO)$_2$Rh(PPh$_3$)-(η-C$_5$H$_5$)], the complexes [(η-C$_5$Me$_5$)Rh(μ-CO)$_2$RhL(η-C$_5$Me$_5$)] (L $=$ PMe$_2$H or PMe$_3$), recently obtained [5] by reacting [{Rh(η-C$_5$Me$_5$)(μ-CO)}$_2$] with L, are inert towards an excess of L and do not react to give the mononuclear compounds [Rh(η-C$_5$Me$_5$)(CO)L].

The reaction of [{Rh(η-C$_5$H$_5$)$_2$(CO)}$_2$(μ-CO)] with tertiary phosphines is strongly influenced by the electronic properties and steric requirements of the ligand. Recently it has been reported [18] that [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)] reacts with the phosphines PMe$_2$Ph and P(OPh)$_3$ to give the complexes [Rh$_2$(η-C$_5$H$_5$)$_2$(μ-CO)(CO)L] [L $=$ PMe$_2$Ph or P(OPh)$_3$] in which the CO groups are respectively bridging and terminally bonded; these complexes have been studied by variable-temperature ^{13}C n.m.r. spectroscopy to establish solution geometries and the CO-fluxional mechanism. We observed that P(C$_6$H$_4$Me-o)$_3$, which shows a large steric requirement, failed to react, even under forcing reaction conditions, with [{Rh(C$_5$H$_5$)(CO)}$_2$(μ-CO)].

Some recent literature reports indicate that the formation of products requiring ring opening of the metallacyclic system formed by Rh$-$CO$-$Rh is the most peculiar aspect of the [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)] reactivity.[8,19-21] However, depending on the nature of the reagents, the steps of reaction are rather different; as a matter of fact mono-, bi-, and trinuclear cyclopentadienyl–rhodium complexes have been isolated. Unfortunately the kinetic and mechanistic aspects of these reactions are still unknown and therefore the experimental data cannot be rationalized. The formation of [(η-C$_5$H$_5$)Rh(μ-CO)$_2$Rh(PPh$_3$)(η-C$_5$H$_5$)] in the reaction of [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)] with PPh$_3$ indicates the possibility of a different route, with respect to those reported, in the reactivity of [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)].

Experimental

The complex [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)] was prepared by a modification of a published procedure.[8,22] Other reagents were used as obtained from commercial sources. Infrared spectra were recorded with a Perkin–Elmer 457 spectrometer

using a polystyrene film for calibration. A WM 300 Bruker spectrometer was used to obtain ^1H 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 the microanalytical laboratory of the Organic Chemistry Institute of Milan.

Di-μ-carbonyl-bis(η-*cyclopentadienyl*)(*triphenylphosphine*)-*dirhodium*.—A solution of [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)] (0.15 g, 0.357 mmol) in pentane was treated dropwise with a slight excess of PPh$_3$ (0.088 g, 0.38 mmol) in the same solvent. After *ca.* 30 min the precipitated [(η-C$_5$H$_5$)Rh(μ-CO)$_2$(PPh$_3$)-(η-C$_5$H$_5$)] was formed almost quantitatively as green-brown crystals and isolated by washing with pentane and drying *in vacuo* (Found: C, 55.10; H, 3.90. C$_{30}$H$_{25}$O$_2$PRh$_2$ requires C, 55.05; H, 3.85%); ν(CO) 1 815s and 1 760vs, br cm^{-1}. ^1H N.m.r. (C$_6$D$_6$, 25 °C): δ, 7.55—6.71 (m, 15 H, Ph), 5.03 [d, 5 H, C$_5$H$_5$, *J*(HRh) 0.70 Hz], and 4.90 [t, 5 H, C$_5$H$_5$, *J*(HRh) = *J*(HP) = 0.68 Hz].

Carbonyl(η-*cyclopentadienyl*)*triphenylphosphinerhodium*(ɪ). —*Method A*. To a benzene solution of [{Rh(η-C$_5$H$_5$)(CO)}$_2$-(μ-CO)], triphenylphosphine in slight excess was added and the reaction mixture left at room temperature with stirring. Monitoring the course of the reaction by i.r. spectra, only the ν(CO) band of [Rh(η-C$_5$H$_5$)(CO)(PPh$_3$)], as reaction product, was observed. The product was identified by comparing i.r. and n.m.r. spectra with those of an authentic sample.[17]

Method B. Triphenylphosphine, in benzene solution, was added to a solution of [(η-C$_5$H$_5$)Rh(μ-CO)$_2$Rh(PPh$_3$)(η-C$_5$H$_5$)] in the same solvent. [Rh(η-C$_5$H$_5$)(CO)(PPh$_3$)] was formed almost immediately and identified by comparison with an authentic sample.[17]

Attempted Reaction of [{Rh(C$_5$H$_5$)(CO)}$_2$(μ-CO)] *with* P(C$_6$H$_4$Me-*o*)$_3$.—A heptane solution (100 cm^3) of [{Rh(η-C$_5$H$_5$)(CO)}$_2$(μ-CO)] (0.20 g, 0.476 mmol) and P(C$_6$H$_4$Me-*o*)$_3$ (0.319 g, 1.047 mmol) was refluxed for *ca.* 6 h. After this time the starting rhodium complex was recovered entirely, showing that the reaction did not occur.

X-Ray Crystal Structure.—Accurate unit-cell dimensions and crystal orientation matrices, together with their estimated standard errors, were obtained from least-squares refinement of the 2θ, ω, χ, and φ values of 25 carefully centred high-angle reflections. Intensity data were collected at room temperature from a crystal of approximate dimensions 0.09 × 0.12 × 0.13 mm on a Siemens-Stoe four circle diffractometer operating in the ω/θ scan mode (scan width = 1.2°, scan speed = 0.04° s^{-1}) and by using graphite-mono-chromatized Mo-$K_{\bar{\alpha}}$ radiation. 5 202 Independent reflections up to θ = 25° were measured, of which 2 697 had $I \geqslant 2.5\sigma(I)$, σ(*I*) being calculated from counting statistics. During the data collection two standard reflections were measured every 120 min to check the stability of the crystal and the electronics of the instrument. Intensities were corrected for Lorentz and polarization effects and put on an absolute scale by Wilson's method.

Crystal data. C$_{30}$H$_{25}$O$_2$PRh$_2$, *M* = 654.3, Triclinic, space group $P\bar{1}$, *a* = 9.700(2), *b* = 11.076(2), *c* = 13.790(3) Å, α = 105.3(1), β = 109.6(1), γ = 99.1(1)°, *U* = 1 295 Å^3, D_c = 1.677 g cm^{-3}, *Z* = 2, *F*(000) = 326, Mo-$K_{\bar{\alpha}}$ radiation, λ = 0.710 69 Å, μ(Mo-$K_{\bar{\alpha}}$) = 13.3 cm^{-1}.

Structure solution and refinement. The molecular structure of the complex was solved by conventional Patterson and Fourier syntheses. The refinement of the structural model, which was by the method of full-matrix least squares, was

carried out allowing the Rh, P, O, and C atoms of the cyclo-pentadienyl ring to vibrate anisotropically, while isotropic thermal parameters were applied to the phenyl carbon atoms which were refined as rigid groups (symmetry D_{6h}, C–C 1.395 Å). Hydrogen atoms could not be located from electron-density difference maps and therefore were included in the scattering model in calculated idealized positions (C–H = 0.95 Å) with a common thermal parameter (*B* = 7 Å^2) but not varied.

The function minimized was $\Sigma w\Delta^2$, in which $w = 3.3088/|\sigma^2(F_o) + 0.001 F_o^2|$ and $\Delta = |F_o| - |F_c|$; discrepancy indices used were $R = (\Sigma ||F_o| - |F_c||)/\Sigma|F_o|$ and $R' = |\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2|^{\frac{1}{2}}$. Weighting-scheme analyses showed no serious dependence of mean $w\Delta^2$ on either $|F_o|$ and $\lambda^{-1}\sin\theta$. The largest peaks on the final difference map were in proximity of the rhodium atoms (maximum value 0.8 e Å^{-3}). Atomic scattering factors were taken from ref. 23. Allowance was made for the anomalous scattering of the rhodium and phosphorus atoms, using values of $\Delta f'$ and $\Delta f''$ from ref. 23. The final conventional *R* value for the 2 697 observed reflections with $I \geqslant 2.5\sigma(I)$ was 0.053 ($R' = 0.059$). Final atomic parameters are presented in Table 1. All calculations were carried out on the IBM 4331 computer of the Centro di Calcolo Elettronico della Università di Messina with the SHELX 76 program for crystal structure determination.[24]

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