Transformation of $[PPh_4][Fe_5RhC(CO)_{16}]$ under Hydroformylation Conditions: Synthesis and Crystal Structure of $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ †

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The cluster $[PPh_4][Fe_5RhC(CO)_{16}]$ (**1**), used as the catalyst precursor for the hydroformylation of 1-pentene (60 atm of a 1 : 1 mixture of CO + H_2, 100 °C), evolves to a mixture of $[Fe_4Rh_2C(CO)_{16}]$ (**2**) and $[PPh_4][Fe_4RhC(CO)_{14}]$ (**3**). When hydroformylation is performed with (**3**) as the catalyst precursor, the new cluster $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ (**4**) is formed. The structure of (**4**) has been determined by a single-crystal *X*-ray diffraction study and was found to consist of an octahedral cluster anion with the three rhodium and the three iron atoms in *fac* positions. The encapsulated carbido-carbon atom is octahedrally co-ordinated to the six metal atoms. The transformations (**1**) $\longrightarrow$ (**2**) + (**3**) and (**3**) $\longrightarrow$ (**4**) are nearly quantitative with regard to the rhodium metal and are also observed under CO pressure at 100 °C without adding 1-pentene or hydrogen. Complexes (**2**) and (**4**) are catalyst precursors for the hydroformylation of 1-pentene and are the only spectroscopically detectable compounds after catalysis, (**4**) being recovered in 70—80% yield after catalysis.

Homogeneous catalysis by cluster complexes has attracted considerable interest in the last few years,[1] but in most cases the cluster framework was broken under catalytic conditions[2] and the question of true catalysis by clusters remains open. Many efforts to avoid fragmentation of the cluster using capping ligands such as carbyne[3] or phosphinidene ligands,[3a,4] or heteroatoms such as oxygen or sulphur[5] have been exerted with more or less success.

We considered that a similar approach could be attempted using a ligand inside the cluster metal core, such as the carbide ligand. Indeed, this ligand allows polyhedron expansion and contraction,[6] generally with good yields. To check the validity of our hypothesis, we have selected as the starting material the carbido cluster $[PPh_4][Fe_5RhC(CO)_{16}]$ (**1**), which is easily prepared.[6a]

The catalytic reaction chosen was the hydroformylation reaction. Since only one of the two metals (Rh) in (**1**) is known to have a good activity in this reaction if the active species results from the fragmentation of (**1**) its transformation should be more easily observed.

Results and Discussion

Hydroformylation of 1-*Pentene with* (**1**) *as Catalytic Precursor*.—The catalytic runs were carried out with a 1 : 1 mixture of CO and H_2 under 60 atm pressure, at 100 °C. Complex (**1**) showed only a moderate activity since 70% of 2 cm^3 of 1-pentene were converted after 24 h into a 2.7 : 1 mixture of hexanal and 2-methylpentanal. The remaining 30% of 1-pentene was converted into 2-pentene. Examination of the i.r. spectrum of the solution after the catalytic run gave evidence that (**1**) had disappeared and that new complexes were formed. Two products have been isolated: the new neutral cluster $[Fe_4Rh_2C(CO)_{16}]$ (**2**), identified by mass spectroscopy {the isoelectronic $[Fe_4RhCoC(CO)_{16}]$ cluster has recently been described[7]} and the known $[PPh_4][Fe_4RhC(CO)_{14}]$,[8] (**3**). These complexes were isolated in 18 and 74% yield, respectively (calculated from Rh) and were the only components of the solution after catalysis. This result showed that (**1**) was not preserved and that a redistribution of the metals had occurred. Moreover, in this redistribution most (if not all) of the rhodium metal was recovered in (**2**) and (**3**).

The recovery of clusters (**2**) and (**3**) after the catalytic run suggests that these clusters could be more stable than (**1**) under hydroformylation conditions. Thus we studied their catalytic activity under the same conditions as for (**1**).

Hydroformylation of 1-*Pentene with* (**2**) *as Catalytic Precursor*.—Complex (**2**) showed a better activity than (**1**). In the presence of (**2**) (30 mg, 0.03 mmol), 1-pentene (2 cm^3) was converted into a 1 : 1 mixture of hexanal and 2-methylpentanal in 6 h, with only traces of pentane. At the end of the reaction, an i.r. spectroscopic study of the solution only gave evidence of the starting cluster. The presence of aldehydes prevented a good recovery of (**2**) and it was difficult to ascertain whether (**2**) was not partially decomposed in the reaction, but the solution remained clear and no trace of metal was detected.

Hydroformylation of 1-*Pentene with* (**3**) *as Catalytic Precursor*.—Complex (**3**) showed a similar activity to (**1**) and 65% of 1-pentene (2 cm^3) was converted into a 2.7 : 1 mixture of hexanal and 2-methylpentanal after 24 h, the remaining 35% being converted into a mixture of 2-pentene isomers. At the end of the reaction there was no evidence by i.r. spectroscopy for the presence of (**3**), but new absorptions were observed in the ν(CO) stretching region.

It was possible to isolate a new complex, (**4**), with the same ν(CO) stretching frequencies as observed in the solution after catalysis [this complex was observed in trace quantities in the experiment starting with (**1**)]. Chemical analysis of this product indicated that it contained three iron, three rhodium, and one phosphorus atoms, but its exact formulation was difficult to ascertain on this basis alone. For this reason, an *X*-ray crystal-structure determination of (**4**) was undertaken.

Structure of $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ (**4**).—An ORTEP plot of the anionic part of the cluster is shown in the Figure and

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† Tetraphenylphosphonium μ_6-carbido-1,2;1,3;2,3-tri-μ-carbonyl-1,2,-3,4,4,4,5,5,5,6,6,6-dodecacarbonyl-*octahedro*-trirhodiumtriferrate(1 −).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, atm = 101 325 N m^{-2}.

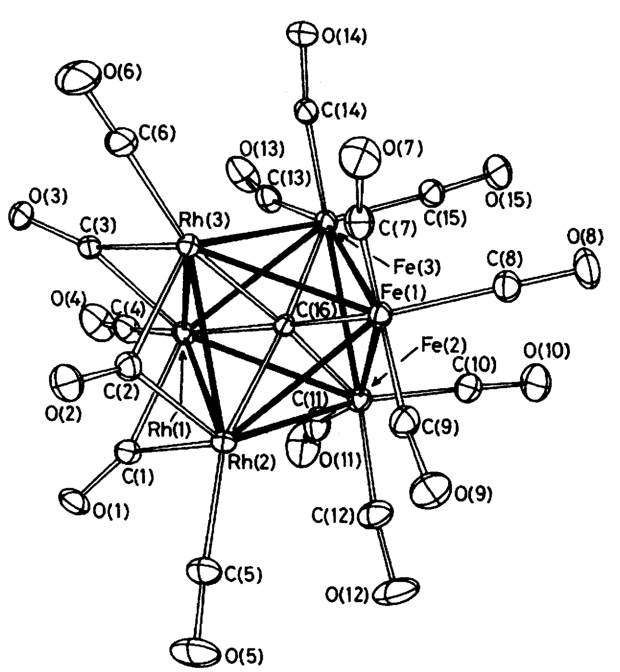

Figure. ORTEP view of [PPh_4][$Fe_3Rh_3C(CO)_{15}$] (**4**) showing the atomic numbering scheme

bond distances and angles of interest are given in Table 1. The anion contains an octahedron of metal atoms with the three rhodium atoms and the three iron atoms in *fac* positions. The carbide atom occupies the cavity of the octahedron. The three rhodium atoms are connected by bridging carbonyl groups in a nearly symmetrical fashion and are bonded to one terminal carbonyl ligand.

Each iron atom is surrounded by three carbonyl groups, which are clearly of two types. On each iron atom, two carbonyl groups are interacting with rhodium atoms as evidenced by the Fe-C-O bond angles ranging from 168.8(8) to 172.9(8)°, and contact distances of the carbon with rhodium ranging from 2.674(8) to 2.872(7) Å. These carbonyl groups can be classified as pertaining to the semi-bridging type. The third carbonyl on each iron atom is linear and no interaction with a rhodium atom is allowed for geometrical reasons.

The rhodium–rhodium distances are of the same order of magnitude as found in the isoelectronic carbido cluster [$Rh_6C(CO)_{13}$]$^{2-}$ for metal–metal bonds bridged symmetrically by one carbonyl group.[9] The iron–iron distances are also of the same order of magnitude as found in [$Fe_6C(CO)_{16}$]$^{2-}$ for non-bridged metal–metal bonds.[10] The Rh–Fe distances fall in two sets: Rh(1)–Fe(2), Rh(2)–Fe(1) and Rh(3)–Fe(3) with a mean length of 2.810 Å, and Rh(1)–Fe(3), Rh(2)–Fe(2), and Rh(3)–Fe(1) with a mean length of 2.776 Å. However, both sets of distances are shorter than Rh–Fe [2.823(1) Å] found in the disordered octahedral cluster anion [$Fe_5RhC(CO)_{16}$]$^-$.[11] The carbide atom is nearly equidistant from the three iron atoms and the distances are very similar to those found for [$Fe_6C(CO)_{16}$]$^{2-}$.[10] It is also nearly equidistant from the three rhodium atoms and the distances are comparable with those found for [$Rh_6C(CO)_{13}$]$^{2-}$.[9] From the nearly linear Rh–C(16)–Fe bonds the apparent atomic radius, calculated as half the difference between the average of the Rh–C(16)–Fe bonds and of the Rh–Fe bonds, is 0.56 Å. It is nearly equal to the value found for [$Co_6C(CO)_{13}$]$^{2-}$,[12] but shorter than that found in [$Rh_6C(CO)_{13}$]$^{2-}$.[9]

Since (**4**) is now well identified, two problems may be examined: (*i*) is (**4**) an active catalyst for hydroformylation and is it stable under catalysis conditions; (*ii*) is the presence of 1-pentene necessary to observe the transformation (**1**) ⟶ (**4**).

Hydroformylation of 1-*Pentene with* (**4**) *as Catalyst Precursor*.—Complex (**4**) showed a similar activity to (**2**). In the presence of (**4**) (50 mg, 0.04 mmol), 1-pentene (2 cm^3) was converted into a 1:1 mixture of hexanal and 2-methylpentanal in 5 h, only traces of pentane being detected. Examination of the reaction after 1 h showed that the ratio of linear-to-branched aldehyde was 2.5:1. It slowly decreased to unity as the conversion of pentene increased. These results suggest that a parallel reaction to the hydroformylation was the isomerization of the olefin. Indeed, examination of the hydroformylation of 1-hexene (chosen for easiest chromatographic analysis) gave evidence that around the half-reaction time, the olefin fraction was a nearly 1:1 mixture of 1-hexene and 2-hexene.

At the end of the reaction, the i.r. spectrum in the ν(CO) stretching region only gave evidence for the presence of (**4**). It could be recovered in 70—80% yield after crystallization.

Complex (**4**) thus seems to fulfil our initial hypothesis: the carbide ligand can stabilize the cluster framework but the transformations (**1**) ⟶ (**2**) + (**3**) and (**3**) ⟶ (**4**) show that redistribution of the metals around the ligand cannot be avoided.

Transformation of (**1**) ⟶ (**4**) *without added* 1-*Pentene*.—To check whether the olefin was necessary to observe such metal redistribution, we performed an experiment under the same conditions as used for hydroformylation, but without the presence of the olefin. Starting with (**1**), we indeed observed the formation of (**2**) and (**4**), while (**3**) was spectroscopically detected as an intermediate. Moreover, the presence of hydrogen was not necessary: under 30 atm of carbon monoxide and at 100 °C, (**1**) (250 mg, 0.21 mmol) was converted in 3 d into (**2**) (30 mg, 0.033 mmol) and (**4**) (50 mg, 0.040 mmol). Examination of these results shows that *ca*. 90% of the rhodium was recovered in (**2**) and (**4**). Further, from our observations in catalytic runs, the transformation from (**1**) to (**4**) passes through the formation of (**3**), while (**2**) is formed only during this first stage, as summarized below.

$$\underset{(\mathbf{1})}{[Fe_5RhC(CO)_{16}]^-} \xrightarrow[100\ ^\circ C]{CO} \underset{(\mathbf{2})}{[Fe_4Rh_2C(CO)_{16}]} + \underset{(\mathbf{3})}{[Fe_4RhC(CO)_{14}]^-}$$

$$\underset{(\mathbf{3})}{[Fe_4RhC(CO)_{14}]^-} \xrightarrow[100\ ^\circ C]{CO} \underset{(\mathbf{4})}{[Fe_3Rh_3C(CO)_{15}]^-}$$

The mechanism of this metal redistribution seems quite complex. While the formation of (**3**) starting with (**1**) is closely related to the observation of Gubin and co-workers[7] on the similar [$Fe_5CoC(CO)_{16}$]$^-$ system, the formation of (**2**) and (**4**) remains obscure. Indeed, we have the unexpected observation that the formation of (**2**) and (**4**) requires rhodium fragmentation from (**1**) or (**3**), but at the end of the reaction all the rhodium is recovered in both clusters. Formation of [$Rh_4(CO)_{12}$] or [$Rh_6(CO)_{16}$] is not detected as is usually the case in hydroformylation reactions by rhodium compounds in the absence of added ligands.[13] Moreover, we have recently observed[14] that a mixed iron–rhodium cluster, not stabilized by a carbide ligand, gave [$Rh_4(CO)_{12}$] under hydroformylation conditions after destruction of the starting cluster.

The fate of the excess Fe has not been clearly established. The presence of [$Fe(CO)_5$] has been established by i.r. spectroscopy but some of the iron is certainly implicated in anionic complexes [*e.g*. the (**3**) ⟶ (**4**) transformation involves two negative

Table 1. Selected interatomic distances (Å) and angles (°) for $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ (**4**) with estimated standard deviations in parentheses

(*i*) Metal–metal							
Rh(1)–Rh(2)	2.770 8(5)	Rh(2)–Fe(2)	2.782(1)	Rh(1)–Fe(2)	2.820(1)	Fe(1)–Fe(2)	2.694(1)
Rh(1)–Rh(3)	2.772 8(7)	Rh(3)–Fe(1)	2.774(1)	Rh(1)–Fe(3)	2.773(1)	Fe(1)–Fe(3)	2.683 8(9)
Rh(2)–Rh(3)	2.763 4(9)	Rh(3)–Fe(3)	2.793(1)	Rh(2)–Fe(1)	2.817(1)	Fe(2)–Fe(3)	2.709(2)
(*ii*) Carbide–metal							
C(16)–Rh(1)	2.040(5)	C(16)–Rh(3)	2.033(7)	C(16)–Fe(1)	1.872(5)	C(16)–Fe(3)	1.878(6)
C(16)–Rh(2)	2.027(6)			C(16)–Fe(2)	1.881(7)		
(*iii*) Carbonyl ligands							
Rh(1)–C(1)	2.060(8)			Fe(1)–C(8)	1.785(9)	C(8)–O(8)	1.136(11)
Rh(2)–C(1)	2.075(6)	C(1)–O(1)	1.147(10)	Fe(1)–C(9)	1.779(7)	C(9)–O(9)	1.149(8)
Rh(2)–C(2)	2.051(8)			Fe(2)–C(10)	1.759(10)	C(10)–O(10)	1.145(14)
Rh(3)–C(2)	2.060(7)	C(2)–O(2)	1.147(9)	Fe(2)–C(11)	1.775(7)	C(11)–O(11)	1.156(10)
Rh(1)–C(3)	2.090(8)			Fe(2)–C(12)	1.790(10)	C(12)–O(12)	1.150(13)
Rh(3)–C(3)	2.058(6)	C(3)–O(3)	1.137(9)	Fe(3)–C(13)	1.785(5)	C(13)–O(13)	1.147(7)
Rh(1)–C(4)	1.897(6)	C(4)–O(4)	1.127(8)	Fe(3)–C(14)	1.788(9)	C(14)–O(14)	1.141(11)
Rh(2)–C(5)	1.892(8)	C(5)–O(5)	1.131(9)	Fe(3)–C(15)	1.764(9)	C(15)–O(15)	1.150(11)
Rh(3)–C(6)	1.908(11)	C(6)–O(6)	1.114(15)	Rh(1) ··· C(11)	2.792(10)	Rh(2) ··· C(12)	2.719(11)
Fe(1)–C(7)	1.787(9)	C(7)–O(7)	1.151(10)	Rh(1) ··· C(13)	2.674(8)	Rh(3) ··· C(7)	2.731(7)
				Rh(2) ··· C(9)	2.872(7)	Rh(3) ··· C(14)	2.788(8)
(*iv*) Metal–carbon–oxygen							
Rh(1)–C(1)–O(1)	137.9(4)	Fe(1)–C(7)–O(7)	170.1(7)	Rh(1)–C(3)–O(3)	136.7(5)	Fe(2)–C(11)–O(11)	169.3(9)
Rh(2)–C(1)–O(1)	137.9(5)	Fe(1)–C(8)–O(8)	179.2(5)	Rh(3)–C(3)–O(3)	139.4(6)	Fe(2)–C(12)–O(12)	171.0(9)
Rh(2)–C(2)–O(2)	138.2(7)	Fe(1)–C(9)–O(9)	172.9(8)	Rh(1)–C(4)–O(4)	176.4(9)	Fe(3)–C(13)–O(13)	168.8(8)
Rh(3)–C(2)–O(2)	137.2(7)	Fe(2)–C(10)–O(10)	177.5(9)	Rh(2)–C(5)–O(5)	177.0(7)	Fe(3)–C(14)–O(14)	171.0(7)
				Rh(3)–C(6)–O(6)	179.0(9)	Fe(3)–C(15)–O(15)	177.5(9)
(*v*) Metal–carbide–metal							
Rh(1)–C(16)–Rh(2)	85.9(3)	Rh(2)–C(16)–Fe(3)	175.0(3)	Rh(1)–C(16)–Fe(3)	90.0(2)	Fe(1)–C(16)–Fe(2)	91.8(3)
Rh(1)–C(16)–Rh(3)	85.8(2)	Rh(3)–C(16)–Fe(1)	90.4(2)	Rh(2)–C(16)–Rh(3)	85.8(2)	Fe(1)–C(16)–Fe(3)	91.4(3)
Rh(1)–C(16)–Fe(1)	176.0(4)	Rh(3)–C(16)–Fe(2)	176.0(4)	Rh(2)–C(16)–Fe(1)	92.5(2)	Fe(2)–C(16)–Fe(3)	92.2(3)
Rh(1)–C(16)–Fe(2)	91.9(2)	Rh(3)–C(16)–Fe(3)	91.1(3)	Rh(2)–C(16)–Fe(2)	90.7(3)		

charges in excess] which have not been isolated or identified by i.r. spectroscopy.

These observations illustrate further the great versatility of building mixed transition-metal clusters with an interstitial carbide atom by successive degradation of the *closo* octahedral structure and addition of metal carbonyl units to the resultant *nido* tetragonal-pyramidal cluster.

Furthermore, the close similarity of the results obtained in hydroformylation reactions with (**4**), or with rhodium complexes without added ligands as catalysts, would suggest that the equilibrium (1) could be the source of a mononuclear active catalytic species.

$$[Fe_3Rh_3C(CO)_{15}]^- \longrightarrow [Fe_3Rh_2C(CO)_{14}]^- + \text{`Rh(CO)'} \quad (1)$$

Experimental

All reactions were performed under a nitrogen atmosphere. I.r. spectra were recorded on a Perkin-Elmer 225 spectrometer in dichloromethane or hexane solutions. Microanalyses were carried out by the Service Central d'Analyse du C.N.R.S. Mass spectra were run on a Varian MAT 311A instrument using 70-eV electron-impact ionization.

$[PPh_4][Fe_5RhC(CO)_{16}]$ (**1**) was prepared with slight modifications of the published procedure.[6]

Catalytic experiments were carried out in a 100-cm^3 stainless-steel autoclave fitted with a glass vessel inside. Chromatographic analyses of catalysis reactions were performed on an Intersmat IGC 120F apparatus using a 4-m Carbowax column operating at 50 °C for olefin analyses and 110 °C for aldehydes.

In a typical experiment, the cluster (*ca.* 50 mg) was dissolved in dichloromethane (15 cm^3), olefin (2 cm^3), and benzene (1 cm^3), the last added as an internal standard. The solution was pressurized under 60 atm of a 1:1 mixture of hydrogen and carbon monoxide, and stirred at 100 °C. Evolution of the reaction was monitored by periodic sampling and chromatographic analyses of the samples.

In the experiments involving isolation of the complexes subsequent to catalysis, the amount of catalyst required was more important, but the olefin-catalyst ratio was kept constant.

Isolation of $[Fe_4Rh_2C(CO)_{16}]$ (**2**) *and* $[PPh_4][Fe_4RhC(CO)_{14}]$ (**3**).—The hydroformylation experiment was performed starting with (**1**) (450 mg, 0.38 mmol) during 21 h. The autoclave was then depressurized and the solution evaporated to dryness *in vacuo*.

The residue was first extracted with two 20-cm^3 portions of pentane, yielding a black solution. Reducing the volume to 5 cm^3 and cooling to −20 °C yielded (**2**) (30 mg, 0.034 mmol) as black crystals. Mass spectrum: m/z = 890 and successive loss of 16 CO. I.r.: ν(CO) (hexane solution) at 2 076vw, 2 055s, 2 045vs, 2 021m, 1 995w, and 1 983w cm^{-1}. Extraction of the residue with diethyl ether (2 × 20 cm^3) afforded a black solution which was then evaporated to dryness. Crystallization at −20 °C in methanol (5 cm^3) gave (**3**) (300 mg, 0.28 mmol) (Found: Fe, 21.30, P, 2.80; Rh, 9.00. Calc. for $C_{39}H_{20}Fe_4O_{14}PRh$: Fe, 21.00; P, 2.90; Rh, 9.60%). I.r.: ν(CO) (CH_2Cl_2 solution) at 2 068 vw, 2 028s, 2 002vs, and 1 980m cm^{-1}.

Table 2. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ (**4**)[a]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	0.717 15(4)	0.479 94(4)	0.296 97(4)
Rh(2)	0.592 81(4)	0.324 23(4)	0.062 54(4)
Rh(3)	0.498 82(4)	0.402 56(4)	0.211 65(4)
Fe(1)	0.493 79(7)	0.202 04(6)	0.171 84(8)
Fe(2)	0.705 36(7)	0.273 26(7)	0.248 58(8)
Fe(3)	0.617 11(7)	0.354 02(6)	0.397 47(7)
C(1)	0.716 3(5)	0.467 7(5)	0.125 0(6)
O(1)	0.762 9(4)	0.515 9(4)	0.083 9(5)
C(2)	0.476 0(5)	0.380 9(5)	0.030 7(6)
O(2)	0.420 6(4)	0.391 1(4)	−0.050 1(5)
C(3)	0.610 5(5)	0.553 4(5)	0.288 1(5)
O(3)	0.615 1(4)	0.637 0(3)	0.315 1(5)
C(4)	0.839 6(6)	0.605 2(6)	0.394 9(7)
O(4)	0.910 9(5)	0.680 0(5)	0.458 2(6)
C(5)	0.578 6(6)	0.274 2(6)	−0.103 8(6)
O(5)	0.567 1(6)	0.240 0(6)	−0.204 1(5)
C(6)	0.381 7(7)	0.441 3(7)	0.205 9(7)
O(6)	0.313 2(6)	0.463 9(7)	0.200 9(7)
C(7)	0.366 9(6)	0.203 2(5)	0.156 7(7)
O(7)	0.281 1(4)	0.189 0(4)	0.144 3(6)
C(8)	0.484 7(6)	0.102 2(5)	0.232 8(7)
O(8)	0.477 9(5)	0.037 7(4)	0.270 3(6)
C(9)	0.452 8(6)	0.118 1(5)	0.014 9(7)
O(9)	0.419 3(5)	0.056 2(4)	−0.084 1(5)
C(10)	0.728 5(7)	0.184 4(6)	0.316 4(8)
O(10)	0.747 1(6)	0.127 7(5)	0.360 6(7)
C(11)	0.839 9(6)	0.361 2(6)	0.318 5(8)
O(11)	0.930 7(5)	0.404 4(6)	0.360 4(8)
C(12)	0.702 5(7)	0.202 2(7)	0.102 0(8)
O(12)	0.707 4(6)	0.149 9(6)	0.015 9(6)
C(13)	0.719 2(6)	0.474 1(6)	0.514 2(6)
O(13)	0.778 7(5)	0.545 9(5)	0.602 2(5)
C(14)	0.510 2(6)	0.374 6(5)	0.431 1(6)
O(14)	0.446 1(4)	0.383 4(4)	0.465 0(5)
C(15)	0.634 4(6)	0.277 3(5)	0.486 3(6)
O(15)	0.643 3(5)	0.228 4(5)	0.546 0(5)
C(16)	0.604 3(4)	0.333 3(4)	0.234 5(5)
P	0.073 2(1)	0.854 7(1)	0.197 4(2)
C(17)	0.189 1(3)	0.964 5(3)	0.3119 (4)
C(18)	0.272 4(3)	0.950 5(3)	0.389 4(4)
C(19)	0.360 3(3)	1.037 3(3)	0.482 0(4)
C(20)	0.364 8(3)	1.138 2(3)	0.497 2(4)
C(21)	0.281 5(3)	1.152 2(3)	0.419 7(4)
C(22)	0.193 7(3)	1.065 3(3)	0.327 0(4)
C(23)	0.051 9(3)	0.855 1(3)	0.046 0(4)
C(24)	0.121 7(3)	0.933 0(3)	0.028 4(4)
C(25)	0.108 1(3)	0.926 9(3)	−0.091 4(4)
C(26)	0.024 7(3)	0.842 9(3)	−0.193 6(4)
C(27)	−0.045 1(3)	0.765 0(3)	−0.176 1(4)
C(28)	−0.031 5(3)	0.771 1(3)	−0.056 3(4)
C(29)	0.086 4(4)	0.735 5(4)	0.196 8(4)
C(30)	0.136 5(4)	0.693 1(4)	0.127 2(4)
C(31)	0.148 6(4)	0.600 5(4)	0.127 5(4)
C(32)	0.110 8(4)	0.550 3(4)	0.197 5(4)
C(33)	0.060 7(4)	0.592 7(4)	0.267 0(4)
C(34)	0.048 6(4)	0.685 3(4)	0.266 7(4)
C(35)*	−0.034 7(8)	0.870 7(9)	0.248 8(11)
C(36)*	−0.023 4(8)	0.966 6(9)	0.329 4(11)
C(37)*	−0.108 3(8)	0.976 6(9)	0.356 7(11)
C(38)*	−0.204 6(8)	0.890 7(9)	0.303 4(11)
C(39)*	−0.215 9(8)	0.794 8(9)	0.222 7(11)
C(40)*	−0.130 9(8)	0.784 8(9)	0.195 4(11)
C(35′)*	−0.037 7(6)	0.854 5(8)	0.224 3(9)
C(36′)*	−0.027 9(6)	0.875 6(8)	0.346 4(9)
C(37′)*	−0.113 5(6)	0.878 1(8)	0.376 3(9)
C(38′)*	−0.209 1(6)	0.859 5(8)	0.284 2(9)
C(39′)*	−0.218 9(6)	0.838 3(8)	0.162 2(9)
C(40′)*	−0.133 3(6)	0.835 8(8)	0.132 2(9)

[a] Atoms marked by asterisks have an occupancy factor of 0.5.

Isolation of $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ (**4**).—The hydroformylation experiment was performed starting with (**3**) (70 mg, 0.065 mmol) during 30 h. The solution was then evaporated to dryness. The residue was not soluble in pentane. Extraction of the residue with diethyl ether (2 × 20 cm^3) and evaporation to dryness of the extracted solution left a dark residue. Dissolution in methanol (5 cm^3) and cooling to −20 °C yielded (**4**) (25 mg, 0.020 mmol) as black crystals (Found: Fe, 11.85; P, 2.45; Rh, 23.55. Calc. for $C_{40}H_{20}Fe_3O_{15}PRh_3$: Fe, 13.5; P, 2.50; Rh, 24.75%). I.r.: ν(CO) (CH_2Cl_2 solution) at 2 072w, 2 015vs, 1 980m, 1 940wbr, 1 880w, 1 847w, and 1 817vw cm^{-1}.

Synthesis of (**2**) *and* (**4**) *by Reaction of Carbon Monoxide with* (**1**).—Complex (**1**) (250 mg, 0.21 mmol) dissolved in CH_2Cl_2 (15 cm^3) was pressurized under 30 atm of carbon monoxide in an autoclave and the solution stirred for 3 d at 100 °C. It was then evaporated to dryness. The residue was treated as for the synthesis of (**2**) and (**3**), affording (**2**) (30 mg, 0.03 mmol) and (**4**) (50 mg, 0.04 mmol).

X-*Ray Crystal-structure Determination of* $[PPh_4][Fe_3Rh_3C(CO)_{15}]$ (**4**).—*Crystal data.* $C_{40}H_{20}Fe_3O_{15}PRh_3$, M = 1 247.8, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 14.409(2), b = 14.415(2), c = 12.238(1) Å, α = 105.80(1), β = 107.24(1), γ = 106.23(1)°, U = 2 149.1(9) $Å^3$, Z = 2, D_c = 1.93 g cm^{-3}, $F(000)$ = 1 216, Mo-K_α radiation, λ = 0.710 73 Å, μ = 22.0 cm^{-1}, T = 293 K.

Data collection. A black, parallelepiped crystal of dimensions 0.35 × 0.20 × 0.20 mm was centred on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell dimensions were determined from the setting angles of 25 reflections in the range $9.6 < \theta < 16.3°$. A data set of 8 414 reflections ($1.5 < \theta < 26°$, $\pm h$, $\pm k$, l) was recorded as described previously[15] by the θ–2θ scan technique (scan width 0.80° + 0.35° tanθ, scan speed 1.1—10.1° min^{-1}). The intensities of three standard reflections monitored every 2 h showed no significant variation during data collection. Data reflections were corrected for Lorentz and polarization effects,[16] 6 507 with $I > 3\sigma(I)$ being considered 'observed' and corrected for absorption[17] (maximum, minimum transmission factors 1.00, 0.79) were used for the structure solution and least-squares refinement.

Structure determination. The structure was solved by the heavy-atom method. After locating two Rh atoms by a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps using SHELX[18] enabled all the non-hydrogen atoms in the structure to be located, with a disordered phenyl ring of the PPh_4 anion. All atoms, except phenyl ones, were refined anisotropically. Phenyl rings were refined as isotropic rigid groups (C–C = 1.395 Å, C–H = 0.97 Å). Hydrogens were not calculated for the disordered phenyl ring. Neutral-atom scattering factors were used, those for non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[19] Unit weights were applied and gave satisfactory weight analysis. In the last full-matrix least-squares refinement cycle, no shift was greater than 0.08 times the estimated standard deviation for non-disordered atoms parameters and the final R value was 0.037 (R' = 0.039). A final Fourier difference map showed a residual electron density of 1 e Å^{-3} near the disordered phenyl ring. All calculations were performed on a VAX-11/730 DEC computer. Atomic coordinates are listed in Table 2.

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