Oxidative Addition of Diphenylphosphinoacetic Acid to Rhodium: Crystal Structures of the Intermediate, $[RhCl(H)(Ph_2PCH_2CO_2\text{-}OP)(Ph_2PCH_2CO_2H\text{-}P)_2]$ and of the Final Product, $[Rh(Ph_2PCH_2CO_2\text{-}OP)_3]$†

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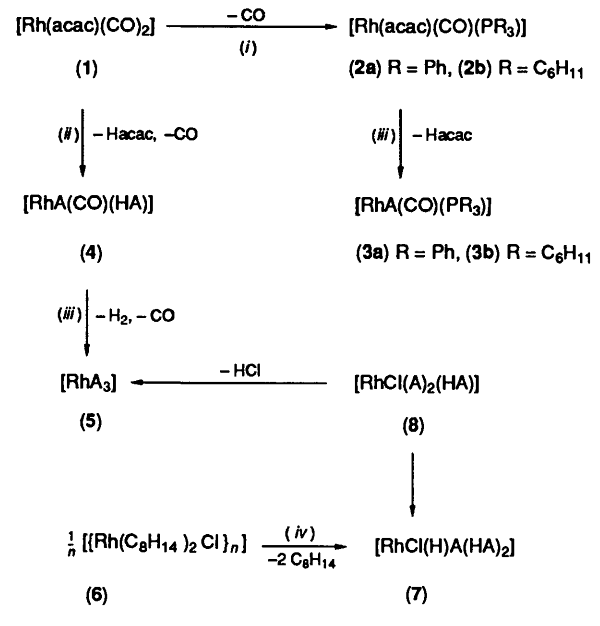
The difference in reactivity towards Rh^I between simple tertiary phosphines and diphenylphosphinoacetic acid can be explained by the assumption that the latter ligand, besides monodentate P bonding, tends also to react by oxidative addition of its carboxyl group, yielding P,O-chelated rhodium(III) complexes. Crystal structures of the final product, *fac*-$[Rh(Ph_2PCH_2CO_2)_3]\cdot PhNO_2\cdot H_2O$, and of the key intermediate, *mer*-$[RhCl(H)(Ph_2PCH_2CO_2)(Ph_2PCH_2CO_2H)_2]\cdot C_4H_8O$, were determined. The latter structure is unique in that it contains both hydride and a carboxylic proton in one molecule.

Tertiary phosphines are known[1,2] to substitute one molecule of carbon monoxide in $[Rh(acac)(CO)_2]$ complexes (Hacac = acetylacetone). In contrast, diphenylphosphinoacetic acid, HA, a hybrid phosphine, is capable of substituting acetylacetonate as well, yielding directly [RhA(CO)(HA)].[3] The specific behaviour of HA, which is similar to that of related phosphinoacetic acids of the general formulae $Ph_{3-n}P(CH_2CO_2H)_n$ and $[(HO_2CCH_2)_mPPh_{2-m}CH_2]_2$ ($n = 2$ or 3, $m = 1$ or 2),[4] suggests that oxidative addition of the carboxyl group yielding a rhodium(III) hydride intermediate, followed by reductive elimination of acetylacetone, should be the important step of the reaction mechanism.

Platinum metal carboxylates are involved extensively in homogeneous catalytic systems,[5] where oxidative addition and reductive elimination of carboxyl groups are supposed to play the key role. In general the tendency towards oxidative addition increases with increasing electron density on the metal in the order Au^{III}, $Ni^{II} < Pd^{II}$, $Co^{II} < Rh^I < Ir^I$, $Fe^0 < Ru^0 < Os^0$, and the stability of the adducts of the third-row transition metals is usually higher than of those of the second-row metals.[6,7] A number of oxidative additions of HX molecules to rhodium(I) complexes have been described, including strong (HCl, HBr)[8] and weak acids (H_2S, HCN, H_2O).[9,10] The stability of the adducts is substantially affected by the coordination ability of the conjugate base.[11] Due to the very low nephelauxetic effect of RCO_2^- anions and their 'hard' character, the formation of stable hydride complexes as intermediates of the oxidative addition of RCO_2H cannot be expected. In accordance with these trends, several iridium(III) hydride complexes were isolated *via* oxidative addition of various carboxylic acids[5,11] but only the $[RhCl(H)(CF_3CO_2)(PPh_3)_2]$ complex has been characterized by n.m.r. spectroscopy in solution so far.[5,12]



Scheme. (*i*) PR_3; (*ii*) 2HA; (*iii*) HA; (*iv*) 3HA

The present paper deals with the Rh^I–HA system in more detail in order to confirm the suspected oxidative addition of the CO_2H group, as well as to contribute to the understanding of the role of phosphinoacetic acids in catalytic systems.

Results and Discussion

The reactions and products studied are summarized in the Scheme.

The reaction of $[Rh(acac)(CO)_2]$ (**1**) with HA gave the bis(phosphine) complex (**4**) directly,[3] and attempts to isolate any intermediate failed. Complexes (**2a**) and (**2b**) were therefore

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† Chloro(diphenylphosphinoacetato-κ*O*,*P*)bis(diphenylphosphinoacetic acid-κ*P*)hydridorhodium(III)–2-butanone (1/1) and tris(diphenylphosphinoacetato-κ*O*,*P*)rhodium(III) hydrate–nitrobenzene (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

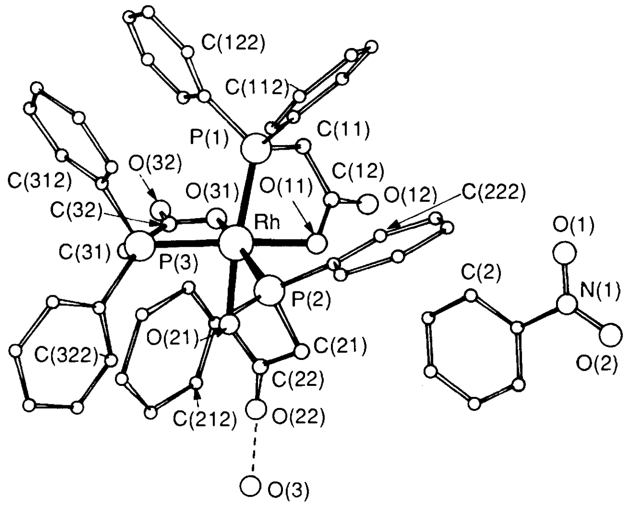

Figure 1. Molecular Structure of *fac*-[$Rh(Ph_2PCH_2CO_2)_3$]·$PhNO_2$·H_2O (**5**) giving the crystallographic numbering scheme.

chosen as substrates permitting the replacement of $acac^-$ by A^- in a separate step, (**2**) $\longrightarrow$ (**3**). This reaction gave the mixed-ligand complexes, (**3a**) and (**3b**), in almost quantitative yield. The course of the reaction (**2**) $\longrightarrow$ (**3**) depends on the particular acidobasic form of the ligand. With the acid HA qualitative observations, such as colour changes in the course of the reaction, indicate that oxidative addition of HA coupled with reductive elimination of Hacac might be involved, but direct evidence for it was not obtained. If this mechanism is operative oxidative addition should lead to an octahedral complex either with *O*-monodentate $Ph_2PCH_2CO_2$- or with monodentate[13] $acac^-$, based on the number of co-ordination sites available. As monodentate co-ordination of $acac^-$ as well as of A^- to Rh^I through its hard donor atom only will be unstable towards chelation, isolation of a stable intermediate could hardly be expected in this case. In contrast to the free acid, the reaction (**2**) $\longrightarrow$ (**3**) with A^- as a nucleophile, *e.g.* with sodium diphenylphosphinoacetate, proceeds through a dissociative pathway; in general, it gives higher yields of (**3**) because of favourable solubility relations in polar solvents.

According to $J(RhP) \approx 120$ Hz and $J(PP) \approx 300$ Hz, (**3a**) and (**3b**) possess *trans*-square planar geometry.[14] Depending on the temperature and polarity of the solvent, both (**3a**) and (**3b**) can be obtained in several crystalline forms, easily distinguishable by their ν(CO) i.r. frequencies.[3] This feature was described also for the [$RhCl(CO)(PPh_3)_2$] complex,[15] the forms of which differ in mutual (eclipsed or staggered) orientation of the phenyl groups.[16] Crystal-structure determination of α-[RhA(CO)(HA)] (**4**) suggested[3] further reasons for the isomerism, *i.e.* (*i*) mutual-orientation of substituents at the phosphorus atoms, (*ii*) interaction of *o*-phenyl hydrogens with rhodium [for (**3a**) and (**4**) only], and (*iii*) formation of hydrogen bonds [with (**4**) only].

Oxidative addition of the CO_2H group undoubtedly takes place in the reaction of (**4**) with an excess of HA, yielding complex (**5**). In the absence of a free ligand, the [RhA(CO)(HA)] complex is fairly stable over a very broad range of experimental conditions. This suggests that during the oxidative addition of HA yielding (**5**) a free rather than the co-ordinated ligand takes part and [$RhH(Ph_2PCH_2CO_2$-*OP*) ($Ph_2PCH_2CO_2$-*O*) (CO)-($Ph_2PCH_2CO_2H$-*P*)] rather than [$RhH(Ph_2PCH_2CO_2$-$OP)_2$-(CO)] is involved as the intermediate. The consecutive displacement of CO by the phosphine ligand, and formation of (**5**) as a sole product are undoubtedly supported by the strong *trans* effect of the hydride anion[17] in the presumed rhodium(III) intermediate and/or by the decrease in the bond energy of CO in rhodium(III) complexes in general, as well as by stabilization of the complex by chelation. The single value of $J(RhP) \approx 115$ Hz found for the [RhA_3] complex indicates[18,19] that the phosphorus atoms possess facial arrangement in an octahedral co-operation sphere created by three chelating A^- ligands. The determination of the crystal structure confirmed this geometry (Figure 1, Tables 1 and 2).

As a consequence of the difference of 0.211 Å between the mean Rh–P and Rh–O distances the octahedron around Rh is remarkably distorted. The four equatorial donor atoms are almost coplanar for all three sets but the Rh atom is displaced by 0.163–0.208 Å from these planes towards the apical phosphorus atoms. Surprisingly, the mode of chelate-ring puckering differs considerably from one ring to another but can be formally described as intermediate between half-chair and envelope for all three rings. The corresponding puckering parameters φ_m and Δ^{20} (in °) are 30.4 and 15.0, 41.3 and 22.9, and 30.6 and 4.3 with approximate C_2 axes passing through C(12), C(22), and O(31) in the rings involving P(1), P(2), and P(3) respectively and approximate mirror planes containing P(2) and P(3). These differences can be explained in terms of crystal packing as follows. The water molecule forms hydrogen bonds with the carbonyl oxygens, O(22) and O(32′), resulting in zigzag chains of the complex molecules arranged along the *c*-axis; disordered nitrobenzene molecules are located between the chains and the intermolecular distances of their oxygens to the methylene carbon atoms display a distinct correlation with the mode of chelate-ring puckering which is reflected most markedly on the fact that the 'envelope' atoms are disposed away from the nitrobenzene oxygens.

The intermediates of the reaction (**2**) $\longrightarrow$ (**3**) and (**4**) $\longrightarrow$ (**5**) were obviously not observed because of rapid conversion into more stable products (*e.g.* those with the chelated ligand). The non-conjugated olefins are readily displaced by phosphines such as PPh_3 affording [$RhCl(PR_3)_3$] complexes;[21] we used (**6**) as a starting material, since just two sites are available here for the target oxidative addition of HA to Rh^I. Careful tuning of experimental conditions made it possible to isolate the key intermediate of the anticipated oxidative addition, (**7**). The most unusual feature of (**7**), *i.e.* the presence of both the hydride and the carboxylic hydrogen in one molecule, is clearly demonstrated by ^1H n.m.r. and i.r. spectra, and the final proof of the structure (**7**) was obtained from *X*-ray crystallography. According to the crystal-structure determination, complex (**7**) has meridional arrangement of phosphorus atoms in the P_3Rh core. In solution, subsequent acidobasic reaction of the hydride with the CO_2H group[5] yields (**8**) which, on prolonged heating in aqueous solvents, loses HCl and affords the final product, (**5**). Practically the same values of *J*(RhP) from complexes (**5**) and (**8**), *i.e.* about 115 Hz, and the crystal-structure determination of complex (**5**) suggest that the reaction (**7**) $\longrightarrow$ (**8**) is accompanied by rearrangement of the octahedral sphere.

Since the reactivity of compound (**7**) prevents the use of conventional crystallization methods, the crystal-structure determination suffers from the poor quality of the crystals. Although the hydrogen atoms could not be directly located, the structure can be unambiguously established (Figure 2, Tables 3 and 4). The co-ordination polyhedron around Rh consists of an approximately coplanar (within ±0.06 Å) P_3O core constituted of one *P,O*-chelating A^- and two monodentate HA ligands. Despite the fact that the Rh atom is displaced 0.14 Å above this plane towards the apical chloride, the Rh–Cl distance remains abnormally long.[22–25] This geometry strongly indicates that the sixth octahedral site is occupied by the markedly *trans*-influencing hydride anion.[8,26] Steric protection at the presumed hydride position by the C(221)—C(226) phenyl and by the C(111), C(116), and C(121) atoms is likely to explain the solid-state stability of the complex. The conformation of the chelate ring is similar to that of the ring containing P(2) in (**5**).

Table 1. Atomic co-ordinates (× 10^4) for non-H atoms of $[RhA_3]\cdot PhNO_2\cdot H_2O$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Rh	3 221.3(4)	1 498.7(2)	2 051.8(4)
P(1)	3 255(1)	733(1)	1 738(2)
P(2)	4 104(1)	1 627(1)	3 022(2)
P(3)	3 703(1)	1 827(1)	895(2)
O(11)	2 557(3)	1 251(2)	3 002(4)
O(12)	1 616(4)	821(2)	3 258(5)
O(21)	2 930(3)	2 155(2)	2 412(4)
O(22)	2 921(4)	2 700(2)	3 359(5)
O(31)	2 289(3)	1 476(2)	1 334(4)
O(32)	1 674(4)	1 684(3)	237(5)
C(11)	2 352(5)	590(3)	2 137(6)
C(12)	2 160(5)	896(3)	2 839(6)
C(21)	3 560(5)	2 000(3)	3 650(6)
C(22)	3 115(5)	2 319(3)	3 133(6)
C(31)	2 856(5)	2 015(4)	426(7)
C(32)	2 219(6)	1 699(4)	643(6)
C(111)	3 916(4)	357(2)	2 223(4)
C(112)	4 652(4)	474(2)	2 217(4)
C(113)	5 168(4)	172(2)	2 534(4)
C(114)	4 948(4)	−249(2)	2 858(4)
C(115)	4 214(4)	−366(2)	2 864(4)
C(116)	3 696(4)	−63(2)	2 547(4)
C(121)	3 217(3)	523(2)	685(4)
C(122)	3 784(3)	258(2)	371(4)
C(123)	3 759(3)	105(2)	−439(4)
C(124)	3 166(3)	216(2)	−935(4)
C(125)	2 599(3)	481(2)	−621(4)
C(126)	2 624(3)	634(2)	189(4)
C(211)	4 900(3)	1 952(2)	2 726(4)
C(212)	4 915(3)	2 425(2)	2 846(4)
C(213)	5 525(3)	2 677(2)	2 611(4)
C(214)	6 121(3)	2 456(2)	2 257(4)
C(215)	6 106(3)	1 983(2)	2 138(4)
C(216)	5 495(3)	1 731(2)	2 372(4)
C(221)	4 432(3)	1 194(3)	3 740(4)
C(222)	3 930(3)	885(3)	4 066(4)
C(223)	4 149(3)	570(3)	4 662(4)
C(224)	4 869(3)	564(3)	4 930(4)
C(225)	5 371(3)	873(3)	4 604(4)
C(226)	5 153(3)	1 188(3)	4 009(4)
C(311)	4 194(4)	1 478(3)	173(5)
C(312)	3 991(4)	1 433(3)	−648(5)
C(313)	4 425(4)	1 182(3)	−1 187(5)
C(314)	5 063(4)	976(3)	−906(5)
C(315)	5 267(4)	1 021(3)	−85(5)
C(316)	4 832(4)	1 271(3)	454(5)
C(321)	4 211(4)	2 360(3)	897(4)
C(322)	3 912(4)	2 743(3)	1 283(4)
C(323)	4 269(4)	3 164(3)	1 241(4)
C(324)	4 924(4)	3 202(3)	815(4)
C(325)	5 223(4)	2 819(3)	430(4)
C(326)	4 867(4)	2 398(3)	471(4)
O(3)	1 807(9)	3 520(4)	3 553(8)
C(1A)	2 463	1 123	6 102
C(2A)	2 266	1 115	5 276
C(3A)	1 940	1 498	4 920
C(4A)	1 810	1 889	5 390
C(5A)	2 007	1 897	6 217
C(6A)	2 334	1 514	6 573
C(1B)	2 462	1 195	6 284
C(2B)	2 340	1 072	5 469
C(3B)	2 015	1 383	4 931
C(4B)	1 812	1 816	5 209
C(5B)	1 934	1 939	6 024
C(6B)	2 259	1 629	6 562
N(1A)	2 806	718	6 478
N(1B)	2 804	867	6 852
O(1A)	2 906	387	6 040
O(2A)	2 971	733	7 195
O(1B)	2 970	494	6 578
O(2B)	2 903	982	7 555

Table 2. Selected distances (Å) and angles (°) for $[RhA_3]\cdot PhNO_2\cdot H_2O$. Primed atoms at $x, \frac{1}{2} - y, \frac{1}{2} + z$

Rh–P(1)	2.294(3)	Rh–O(21)	2.074(6)
Rh–P(2)	2.296(3)	Rh–O(31)	2.076(6)
Rh–P(3)	2.293(3)	O(22) ··· O(3)	3.17(1)
Rh–O(11)	2.100(6)	O(3) ··· O(32′)	2.82(1)
P(1)–Rh–P(2)	107.1(1)	P(2)–Rh–O(31)	167.6(2)
P(1)–Rh–P(3)	102.3(1)	P(3)–Rh–O(11)	167.1(2)
P(2)–Rh–P(3)	103.0(1)	P(3)–Rh–O(21)	86.9(2)
P(1)–Rh–O(11)	81.1(2)	P(3)–Rh–O(31)	82.5(2)
P(1)–Rh–O(21)	166.0(2)	O(11)–Rh–O(21)	87.7(2)
P(1)–Rh–O(31)	82.3(2)	O(11)–Rh–O(31)	85.7(2)
P(2)–Rh–O(11)	87.7(2)	O(21)–Rh–O(31)	88.6(2)
P(2)–Rh–O(21)	80.6(2)	O(22) ··· O(3) ··· O(32′)	122.2(4)

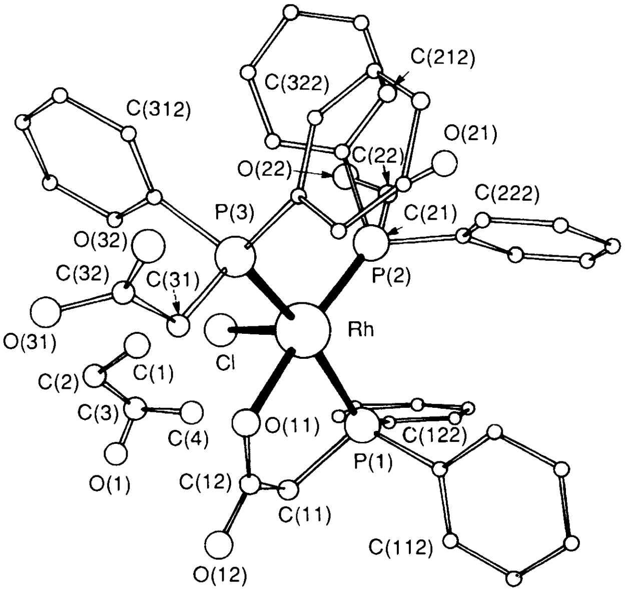

Figure 2. Molecular Structure of *mer*-$[RhCl(H)(Ph_2PCH_2CO_2H)_2]\cdot C_4H_8O$ (**7**) giving the crystallographic numbering scheme.

Experimental

Instrumentation.—Infrared spectra (4 000—200 cm^{-1}) were obtained for Nujol mulls on a Perkin-Elmer 684 spectrometer with a PE 3600 Data Station, ^1H, $^{13}C-\{^1H\}$, and $^{31}P-\{^1H\}$ n.m.r. spectra on a Varian XL-200 instrument with internal $SiMe_4$ (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P) as standards.

Preparations.—The following compounds were prepared by the literature methods: HA and NaA,[27] $[Rh(acac)(CO)_2]$ (**1**),[28] $[RhA(CO)(HA)]$ (**4**),[3] and $[\{Rh(C_8H_{14})_2Cl\}_n]$ (**6**).[29] The preparations with the HA ligand were carried out under nitrogen.

Acetylacetonato(carbonyl)(triphenylphosphine)rhodium(I) (**2a**). Triphenylphosphine (289 mg, 1.1 mmol) in Et_2O (5 cm^3) was added slowly to complex (**1**) (258 mg, 1 mmol) dissolved in Et_2O (12 cm^3). After standing for 10 min the yellow crystals of the product were washed with Et_2O and then hot MeOH and

Table 3. Atomic co-ordinates (× 10^4) for non-H atoms of $[RhCl(H)A(HA)_2]{\cdot}C_4H_8O$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	8 158(2)	1 609(1)	5 640(1)
Cl	6 539(6)	2 273(3)	6 085(3)
P(1)	8 419(6)	2 270(3)	4 705(3)
P(2)	9 701(6)	1 954(3)	6 407(3)
P(3)	7 689(6)	737(3)	6 251(3)
O(11)	6 823(15)	1 275(8)	4 843(8)
O(12)	5 670(17)	1 392(8)	3 797(10)
O(21)	11 388(22)	2 906(10)	7 348(10)
O(22)	9 488(18)	3 207(11)	7 662(11)
O(31)	6 967(24)	−669(10)	6 045(16)
O(32)	4 967(21)	−281(10)	5 910(12)
C(11)	6 809(19)	2 202(11)	4 255(11)
C(12)	6 423(21)	1 608(12)	4 321(16)
C(21)	9 577(23)	2 727(12)	6 552(14)
C(22)	10 182(30)	3 001(13)	7 253(16)
C(31)	6 629(23)	322(12)	5 649(13)
C(32)	6 213(43)	−284(14)	5 874(17)
C(111)	9 501(13)	2 094(7)	4 019(10)
C(112)	9 219(13)	2 309(7)	3 329(10)
C(113)	10 080(13)	2 237(7)	2 801(10)
C(114)	11 223(13)	1 950(7)	2 961(10)
C(115)	11 506(13)	1 735(7)	3 651(10)
C(116)	10 645(13)	1 806(7)	4 179(10)
C(121)	8 763(17)	3 017(9)	4 822(9)
C(122)	9 941(17)	3 257(9)	4 704(9)
C(123)	10 177(17)	3 834(9)	4 866(9)
C(124)	9 234(17)	4 170(9)	5 147(9)
C(125)	8 055(17)	3 929(9)	5 265(9)
C(126)	7 820(17)	3 353(9)	5 103(9)
C(211)	9 783(14)	1 713(8)	7 325(10)
C(212)	10 901(14)	1 531(8)	7 696(10)
C(213)	10 896(14)	1 383(8)	8 420(10)
C(214)	9 773(14)	1 417(8)	8 772(10)
C(215)	8 655(14)	1 599(8)	8 401(10)
C(216)	8 660(14)	1 747(8)	7 677(10)
C(221)	11 285(16)	1 796(7)	6 151(8)
C(222)	11 687(16)	1 231(7)	6 061(8)
C(223)	12 843(16)	1 122(7)	5 765(8)
C(224)	13 597(16)	1 578(7)	5 560(8)
C(225)	13 196(16)	2 142(7)	5 650(8)
C(226)	12 039(16)	2 251(7)	5 946(8)
C(311)	6 723(15)	709(8)	7 034(12)
C(312)	6 819(15)	234(8)	7 489(12)
C(313)	5 965(15)	166(8)	8 022(12)
C(314)	5 015(15)	574(8)	8 100(12)
C(315)	4 919(15)	1 049(8)	7 645(12)
C(316)	5 773(15)	1 117(8)	7 112(12)
C(321)	9 093(19)	260(7)	6 451(9)
C(322)	9 747(19)	297(7)	7 124(9)
C(323)	10 901(19)	11(7)	7 252(9)
C(324)	11 401(19)	−312(7)	6 708(9)
C(325)	10 747(19)	−349(7)	6 036(9)
C(326)	9 592(19)	−63(7)	5 907(9)
O(1)	2 700	4 550	5 700
C(1A)	4 400	3 400	6 600
C(1B)	4 000	3 500	6 500
C(2A)	3 200	3 800	6 500
C(2B)	2 800	3 900	6 500
C(3)	3 500	4 350	6 100
C(4A)	4 700	4 200	5 800
C(4B)	4 800	4 000	5 900

Table 4. Selected bond distances (Å) and angles (°) for $[RhCl(H)A(HA)_2]{\cdot}C_4H_8O$

Rh–Cl	2.488(7)	Rh–P(3)	2.396(7)
Rh–P(1)	2.359(7)	Rh–O(11)	2.13(2)
Rh–P(2)	2.244(7)		
Cl–Rh–P(1)	87.5(2)	P(1)–Rh–P(3)	160.7(2)
Cl–Rh–P(2)	92.8(2)	P(1)–Rh–O(11)	79.9(5)
Cl–Rh–P(3)	101.5(2)	P(2)–Rh–P(3)	99.5(2)
Cl–Rh–O(11)	91.3(5)	P(2)–Rh–O(11)	174.7(5)
P(1)–Rh–P(2)	97.1(2)	P(3)–Rh–O(11)	82.8(5)

air-dried (443 mg, 90%), m.p. 175 °C (lit.[1], 175 °C)(Found: P, 6.25; Rh 20.9. $C_{24}H_{22}O_3PRh$ requires P, 6.30; Rh, 20.90%); $\nu_{max.}$ 1 983vs cm^{-1} (CO); $\delta_P(C_6D_6)$, 50.0 p.p.m. [d, *J*(RhP) 177 Hz].

Acetylacetonato(*carbonyl*)(*tricyclohexylphosphine*)*rhodium*(I) (**2b**). Tricyclohexylphosphine (280 mg, 1 mmol) in Et_2O (5 cm^3) was added slowly to complex (**1**) (258 mg, 1 mmol) in Et_2O (12 cm^3). After adding MeOH (15 cm^3) and evaporating *in vacuo* to 10 cm^3, the product separated as yellow crystals which were washed with MeOH and air-dried (383 mg, 75%), m.p. 201 °C (Found: P, 6.00; Rh, 19.8. $C_{24}H_{40}O_3PRh$ requires P, 6.05; Rh, 20.15%); $\nu_{max.}$ 1 946vs cm^{-1} (CO); $\delta_P(C_6D_6)$, 58.9 p.p.m. [d, *J*(RhP) 168 Hz].

Carbonyl(*diphenylphosphinoacetato*)(*triphenylphosphine*)*rhodium*(I) (**3a**). Sodium diphenylphosphineacetate (346 mg, 1.3 mmol) in water (6 cm^3) was added slowly to (**2a**) (492 mg, 1 mmol) in boiling acetone (35 cm^3). The product which separated as yellow crystals on adding slowly water (20 cm^3) was washed with MeOH and air-dried (509 mg, 80%), m.p. 194 °C (Found: P, 9.70; Rh, 16.1. $C_{33}H_{27}O_3P_2Rh$ requires P, 9.75; Rh, 16.15%); $\nu_{max.}$ 1 966vs (CO) (α) [1 983vs (β), 1 963vs (γ)], and 1 656vs cm^{-1} (OCO); $\delta_H(C_6D_6)$ 3.32 (2 H, s, CH_2), 7.0, 7.8 (15 H, m, PPh_3), 6.95, 7.55 (10 H, m, PPh_2); $\delta_P(C_6D_6)$ 20.2 [AA′X, *J*(RhP) 119, *J*(PP) 310 Hz, A^-] and 26.2 p.p.m. [d, *J*(RhP) 133 Hz, PPh_3].

Carbonyl(*diphenylphosphinoacetato*)(*tricyclohexylphosphine*)*rhodium*(I) (**3b**). Sodium diphenylphosphinoacetate (346 mg, 1.3 mmol) in water (6 cm^3) and then water (6 cm^3) were added slowly to complex (**2b**) (510 mg, 1 mmol) in boiling acetone (24 cm^3). The product which crystallized as pale yellow needles on standing at 0 °C overnight was washed with MeOH and air-dried (458 mg, 70%), m.p. 201 °C (Found: P, 9.40; Rh, 15.7. $C_{33}H_{45}O_3P_2Rh$ requires P, 9.45; Rh, 15.70%); $\nu_{max.}$ 1 956vs (CO) (α), [1 950vs (β), and 1 661vs cm^{-1} (OCO); $\delta_H(C_6D_6)$ 1.0—2.4 (33 H, m, C_6H_{11}), 3.31 [2H, dd, $|^2J(PH) + {}^4J(PH)|$ 10.5, ^3J(RhH) 1.0, CH_2], 7.0, 7.6 (10 H, m, PPh_2); $\delta_P(C_6D_6)$ 17.9 [ABX, *J*(RhP) 114, *J*(PP) 293, A^-], and 43.9 p.p.m. [dd, *J*(RhP) 132 Hz, $P(C_6H_{11})_3$].

Tris(*diphenylphosphinoacetato*)*rhodium*(III) (**5**). (*i*) 2-*Butanone solvate.* Complex (**4**) (618 mg, 1 mmol) and HA (488 mg, 2 mmol) were refluxed in 2-butanone (30 cm^3) for 30 min to give a deep yellow solution from which well developed pale yellow crystals separated on standing for 1 week at 0 °C. The product was washed with cold 2-butanone and air-dried (270—450 mg, 30—50%), decomp. >200 °C (Found: P, 10.4; Rh, 11.6. $[RhA_3]{\cdot}C_4H_8O$ requires P, 10.25; Rh, 11.35%; $\nu_{max.}$ 1 704m (2-butanone), and 1 630vs cm^{-1} (OCO); $\delta_H[DCON(CD_3)_2]$ 1.05 (t), 2.13 (s), 2.45 (q) [6H, *J*(HH) 7.4 Hz, 2-butanone], 2.6—4.5 (6 H, m, PCH_2), and 6.6—7.8 (30 H, m, PPh_2); $\delta_P[DCON(CD_3)_2]$ 11.5 p.p.m. [d, *J*(RhP) 115 Hz]. An identical product was obtained by prolonged heating of complex (**8**) in aqueous 2-butanone.

(*ii*) *Monohydrate nitrobenzene solvate.* Single crystals suitable for crystal-structure determination were obtained by dissolving

15 mg of $[RhA_3]\cdot C_4H_8O$ in $PhNO_2$ (5 cm^3) at 120 °C in a sealed vessel and cooling to room temperature at 0.5—1 °C h^{-1}.

Chloro(diphenylphosphinoacetato)bis(diphenylphosphinoacetic acid)hydrido rhodium(III)*-2-butanone* (1/1) (**7**). To a solution of HA (244 mg, 1 mmol) in 2-butanone (5 cm^3) kept at 75 °C and stirred by a very slow stream of nitrogen were added six 15-mg batches of complex (**6**) (total 0.25 mmol Rh). Care was taken to allow each portion completely to dissolve before the next addition. During the last additions the product began to form as lemon-yellow crystals adhering to the walls of the flask. To obtain single crystals it appeared advantageous to use an unscratched flask (10 cm^3), reduce the nitrogen flow just to ensure mixing, and add (**6**) during *ca.* 15 min as a large number of small portions. The crystals were decanted with cold 2-butanone and air-dried (140—190 mg, 60—80%), decomp. >100 °C (Found: C, 58.05; H, 4.55; Cl, 3.85; P, 9.90; Rh, 10.9. $C_{46}H_{47}ClO_7P_3Rh$ requires C, 58.60; H, 4.90; Cl, 3.75, P, 9.85; Rh, 10.90%); $\nu_{max.}$ 2 098m (RhH), 1 730m (2-butanone), 1 715vs (CO_2H), and 1 563vs cm^{-1} (OCO); δ_H[solution prepared *in situ* in $(CD_3)_2CO$] −14.1 (symmetrical multiplet,[8] RhH).

Chloro-bis(diphenylphosphinoacetato)(diphenylphosphinoacetic acid)rhodium(III) (**8**). A solution of complex (**7**) (189 mg, 0.2 mmol) in chloroform (10 cm^3) was left to stand for 10 min and then evaporated *in vacuo* to 1 cm^3. The yellow crystals were washed with pentane and air-dried (185 mg, 93%), m.p. 176 °C (Found: Cl, 3.90; P, 10.5; Rh, 11.8. $C_{42}H_{37}ClO_6P_3Rh$ requires Cl, 4.10; P, 10.70; Rh, 11.85%); $\nu_{max.}$ 1 719vs (CO_2H), 1 658, 1 610vs cm^{-1} (OCO); $\delta_H(CDCl_3)$ 3.35 (m), 4.05 (m, 2 H, PCH_2), 7.10 (m), 7.38 (m), 7.60 (m, 10 H, PPh_2); $\delta_P(CDCl_3)$ 11.6 [d, *J*(RhP) 115, A^-], and 28.0 p.p.m. [d, *J*(RhP) 114 Hz, HA].

Crystallographic Studies.—Crystal data for $[RhA_3]\cdot PhNO_2\cdot H_2O$. $C_{48}H_{43}NO_9P_3Rh$, M = 973.7, orthorhombic, space group *Pbca* (No. 61), a = 18.377(3), b = 29.195(6), c = 16.296(2) Å, U = 8 743(2) $Å^3$ (by least-squares refinement on diffractometer angles for 19 automatically centred reflections, λ = 0.710 69 Å), D_m = 1.46(1), Z = 8, D_c = 1.479 g cm^{-3}, $F(000)$ = 4 000, light yellow needles, Crystal dimensions 0.3 × 0.3 × 0.1 mm, $\mu(Mo\text{-}K_\alpha)$ = 5.50 cm^{-1}.

CAD-4 diffractometer, ω—2θ mode, graphite-monochromated Mo-K_α radiation; 4 706 reflections measured (*h* 0—20, *k* 0—32, *l* 0—17, $\theta_{max.}$ = 23°), 3 157 of them 'observed' with $I > 1.96\sigma(I)$; no absorption correction. Heavy-atom method (Rh) followed by standard Fourier series and blocked full-matrix least squares with phenyl rings as rigid bodies because of computer time limitations, hydrogen atoms in calculated positions, and water hydrogen atoms constrained in positions found from a ΔF map; disordered nitrobenzene molecule approximated as two positions (A, B) of equal occupancy differing in rotation by 15° around the axis perpendicular to the phenyl group and passing through its centre (for an analogy, see ref. 30). The refinement converged at R = 0.063, R' = 0.065 with the largest residual peak of 0.88 e $Å^{-3}$. The weighting scheme was $1/(\sigma^2F_o + 0.0009F_o^2)$. The programs and computer used and the scattering factors data are given in ref. 3. Co-ordinates of non-H atoms are presented in Table 1 and selected bond lengths and angles in Table 2.

Crystal data for $[RhCl(H)A(HA)_2]\cdot C_4H_8O$. $C_{46}H_{47}ClO_7P_3Rh$, M = 943.2, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), a = 10.553(4), b = 23.296(9), c = 18.671(7) Å, β = 93.78(3), U = 4 580(3) $Å^3$, (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), D_m = 1.35(1), Z = 4, D_c = 1.367 g cm^{-3}, $F(000)$ = 1 944, yellow irregular crystals. Crystal dimensions 0.2 × 0.2 × 0.1 mm, $\mu(Mo\text{-}K_\alpha)$ = 5.78 cm^{-1}.

Syntex P2$_1$ diffractometer, ω—2θ mode, graphite-monochromated Mo-K_α radiation; 5 991 reflections measured (*h* −14 to 14, *k* 0—29, *l* 0—24, $\theta_{max.}$ = 23°), 2 075 of them 'observed' with $I > 1.96\sigma(I)$; no absorption correction. Heavy-atom method (Rh) followed by standard Fourier series and full-matrix least squares with phenyl rings as rigid bodies, hydrogen atoms in calculated positions; as indicated by a ΔF map, the disordered solvent molecule was fixed in two conformations[31] (70% *cis*, abbreviated as A, and 30% *gauche*, B). The refinement failed to proceed below R = 0.093, R' = 0.087, obviously because of poor diffraction by the crystals available. The largest residual electron density was 0.66 e $Å^{-3}$, weighting scheme $0.8385/[\sigma^2(F) + 0.0009F^2]$. Co-ordinates of non-H atoms are presented in Table 3 and selected bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

References

1 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.
2 A. M. Trzeciak and J. J. Ziólkowski, *Inorg. Chim. Acta*, 1985, **96**, 15.
3 A. Jegorov, B. Kratochvíl, V. Langer, and J. Podlahová, *Inorg. Chem.*, 1984, **23**, 4288.
4 J. Podlahová, B. Kratochvíl, J. Podlaha, and J. Hašek, *J. Chem. Soc., Dalton Trans.*, 1985, 2393 and refs. therein.
5 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 1912.
6 J. Halpern, *Acc. Chem. Res.*, 1970, **3**, 386.
7 L. Vaska, L. S. Chen, and W. V. Miller, *J. Am. Chem. Soc.*, 1971, **93**, 6671.
8 G. L. Geoffroy and J. R. Lehman, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 190.
9 H. Singer and G. Wilkinson, *J. Chem. Soc. A*, 1968, 2516.
10 T. Yoshida, T. Okano, Y. Ueda, and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 3411.
11 S. A. Smith, D. M. Blake, and M. Kubota, *Inorg. Chem.*, 1972, **11**, 660.
12 D. Commereuc, I. Douek, and G. Wilkinson, *J. Chem. Soc. A*, 1970, 1771.
13 S. Yoshida, Y. Ohgomori, Y. Watanabe, K. Honda, M. Goto, and M. Kurahashi, *J. Chem. Soc., Dalton Trans.*, 1988, 895.
14 B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc. A*, 1971, 1104.
15 J. Blum, E. Oppenheimer, and E. D. Bergman, *J. Am. Chem. Soc.*, 1967, **89**, 2338.
16 A. Ceriotti, G. Ciani, and A. Sironi, *J. Organomet. Chem.*, 1983, **247**, 345.
17 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1968, 617.
18 B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1972, 704.
19 S. O. Grim and L. C. Satek, *J. Coord. Chem.*, 1974, **3**, 307.
20 C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 1968, **24**, 13.
21 L. Porri and A. Lionetti, *J. Organomet. Chem.*, 1966, **6**, 422.
22 A. G. Orpen, L. Brammler, F. H. Allen, O. Kennard, and D. G. Watson, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
23 K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 440.
24 T. Yoshida, S. Otsuka, M. Matsumoto, and K. Nakatsu, *Inorg. Chim. Acta*, 1978, **29**, L257.
25 S. Remek, C. Jensen, R. Binamira-Soriaga, and W. C. Kaska, *Organometallics*, 1983, **2**, 1442.
26 C. Masters and B. L. Shaw, *J. Chem. Soc. A*, 1971, 3679.
27 T. Jarolím and J. Podlahová, *J. Inorg. Nucl. Chem.*, 1976, **38**, 125.
28 Yu. S. Varshavsky and T. G. Cherkasova, *Zh. Neorg. Khim.*, 1967, **12**, 1709.
29 A. van der Ent and A. L. Onderlindenen, *Inorg. Synth.*, 1973, **14**, 92.
30 T. Fujivara, E. Iwamoto, and Y. Yamamoto, *Inorg. Chem.*, 1984, **23**, 115.
31 M. Abe, K. Kuchitsu, and T. Shimanouchi, *J. Mol. Struct.*, 1969, **4**, 245.

Received 20*th December* 1989; *Paper* 9/05413H