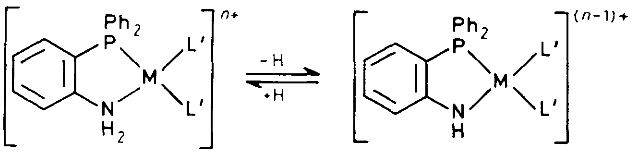
Synthesis and Oxidation Reactions of Mono- and Di-nuclear Rhodium Carbonyl Complexes of (*o*-Diphenylphosphinophenyl)amine, H_2L; *X*-Ray Structure Analysis of a Rhodium(II) Amido-bridged Dimer, $[\{Rh(\mu\text{-}HL)(CO)Cl\}_2]\cdot EtOH$ ‡

Mervyn K. Cooper and Gregory J. Organ *†
School of Chemistry, University of Sydney, Sydney 2006, Australia
Paul A. Duckworth, Kim Henrick, and Mary McPartlin *
School of Chemistry, The Polytechnic of North London, London N7 8DB

Reaction of *cis*-$[NBu^n_4][Rh(CO)_2Cl_2]$ or $[\{Rh(CO)_2Cl\}_2]$ with one or two molar equivalents of (*o*-diphenylphosphinophenyl)amine (H_2L) respectively gives the mononuclear halogenocarbonylrhodium(I) complexes $[Rh(H_2L)(CO)X]$ [X = Cl (**2a**), Br (**2b**), or I (**2c**)]. These new compounds were found to react with air to give the novel amido-bridged rhodium(II) metal–metal bonded dimers $[\{Rh(\mu\text{-}HL)(CO)X\}_2]$ [X = Cl (**5a**), Br (**5b**), or I(**5c**)]. The chloro species (**2a**) was also shown to react with base in an inert atmosphere to generate the rhodium(I) amido-bridged dimer $[\{Rh(\mu\text{-}HL)(CO)\}_2]$ (**4**), which reacts with one molar equivalent of halogen to produce (**5**) or with excess halogen to give the monomeric rhodium(III) *mer*-trihalogeno complexes $[Rh(H_2L)(CO)X_3]$ [X = Cl (**7a**), Br (**7b**), or I (**7c**)]. The chloro rhodium(II) dimer (**5a**) has been characterised by *X*-ray structure analysis. Crystals of (**5a**)·EtOH are monoclinic, space group $P2_1/c$, with a = 14.669(3), b = 14.754(3), c = 18.233(4) Å, β = 92.46(4)°, and Z = 4. Full-matrix refinement of 3 498 unique data with $I \geqslant 3\sigma(I)$ $(3 < \theta < 25°)$ gave R = 0.045 and R' = 0.042.

The reactions of oxygen with transition-metal atoms are ubiquitous, ranging from the indispensable biological transport of oxygen to the undesirable corrosion of metals. Accordingly such reactions have been studied for many years.[1–3] In this paper we report the unusual reaction of oxygen with rhodium(I) carbonyl complexes of (*o*-diphenylphosphinophenyl)amine, H_2L, to form only the second reported[4] examples of rhodium(II) amido-bridged dimers. These species were also prepared by oxidative addition of halogen to a rhodium(I) amido-bridged dimer, which is the more usual route used in the synthesis of rhodium(II) dimers.[4–8]

Possible mechanisms for the various reactions discussed in this paper are presented. A common feature lies in the facile and reversible loss of an acidic nitrogen-bonded hydrogen atom which is characteristic of complexes containing H_2L as a bidentate chelate and provides a route to both amino and amido complexes.[9]



Results and Discussion

The yellow monomeric complex $[Rh(H_2L)(CO)Cl]$ (**2a**) was prepared by reaction of *cis*-$[NBu^n_4][Rh(CO)_2Cl_2]$ or $[\{Rh(CO)_2Cl\}_2]$ with one or two molar equivalents of H_2L respectively (Scheme). The bromo and iodo analogues, (**2b**) and (**2c**), were obtained by metathesis *in situ* by performing the reaction in the presence of excess LiX (X = Br or I). The species (**2**) contain phosphorus *trans* to the halide since ^{31}P n.m.r. spectra of (**2**) exhibit J(RhP) *ca.* 165 Hz (Table 1) which is characteristic of this stereochemistry [J(RhP) 155—205 Hz[10]]. The alternative P *trans* to CO geometry leads to smaller J(RhP), *e.g.* 113 and 124 Hz.[11] Additional support for the assigned geometry of (**2**) is that *X*-ray analysis of similar rhodium[12] and iridium[13b] complexes has shown the same donor atom arrangement.

When the addition of H_2L to either *cis*-$[NBu^n_4][Rh(CO)_2Cl_2]$ or $[\{Rh(CO)_2Cl\}_2]$ was performed below −50 °C in dichloromethane a low-temperature intermediate, (**1**), could be observed by ^{31}P n.m.r. spectroscopy with δ 28.8 p.p.m. [J(RhP) 92 Hz]. On warming the solution to above −30 °C a pronounced effervescence occurred with the appearance of ^{31}P n.m.r. signals characteristic of (**2**). A control experiment showed that warming dichloromethane saturated with carbon monoxide at −50 °C to room temperature results in a barely perceptible evolution of gas thus indicating that the intermediate contains two carbonyl ligands. Formation of the same intermediate from either the mono- or di-nuclear starting materials suggests that it is mononuclear while the position of the ^{31}P n.m.r. signal some 20—30 p.p.m. upfield of the resonances for (**2a**) and $[Rh(H_2L)(CO)_2]^+$,§ indicates that H_2L is co-ordinated through the phosphorus donor only. The 'Δ*R*' effect[14] produces a downfield shift of the ^{31}P n.m.r. resonance of this magnitude when a co-ordinated phosphorus is part of a five-membered chelate ring. Thus the probable structure of the low-temperature intermediate (**1**) is *cis*-$[Rh(H_2L)(CO)_2Cl]$, a *cis* stereochemistry being chosen on the basis of the small value of J(RhP).

The rhodium(I) amido-bridged species $[\{Rh(\mu\text{-}HL)(CO)\}_2]$ (**4**) was isolated after the reaction, in the absence of oxygen, of an acetone solution of (**2a**) with base (aqueous lithium hydroxide). Other dinuclear amido-bridged compounds have been reported.[15] Complex (**4**) is likely to have the hinged

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† *Present address:* Bond Brewing (N.S.W.) Ltd., P.O. Box 58, Lidcome, 2141 Sydney, Australia.

‡ Di-μ-[(*o*-diphenylphosphinophenyl)amido-*NP*]-bis[carbonylchlororhodium(II)]–ethanol (1/1) (*Rh–Rh*).

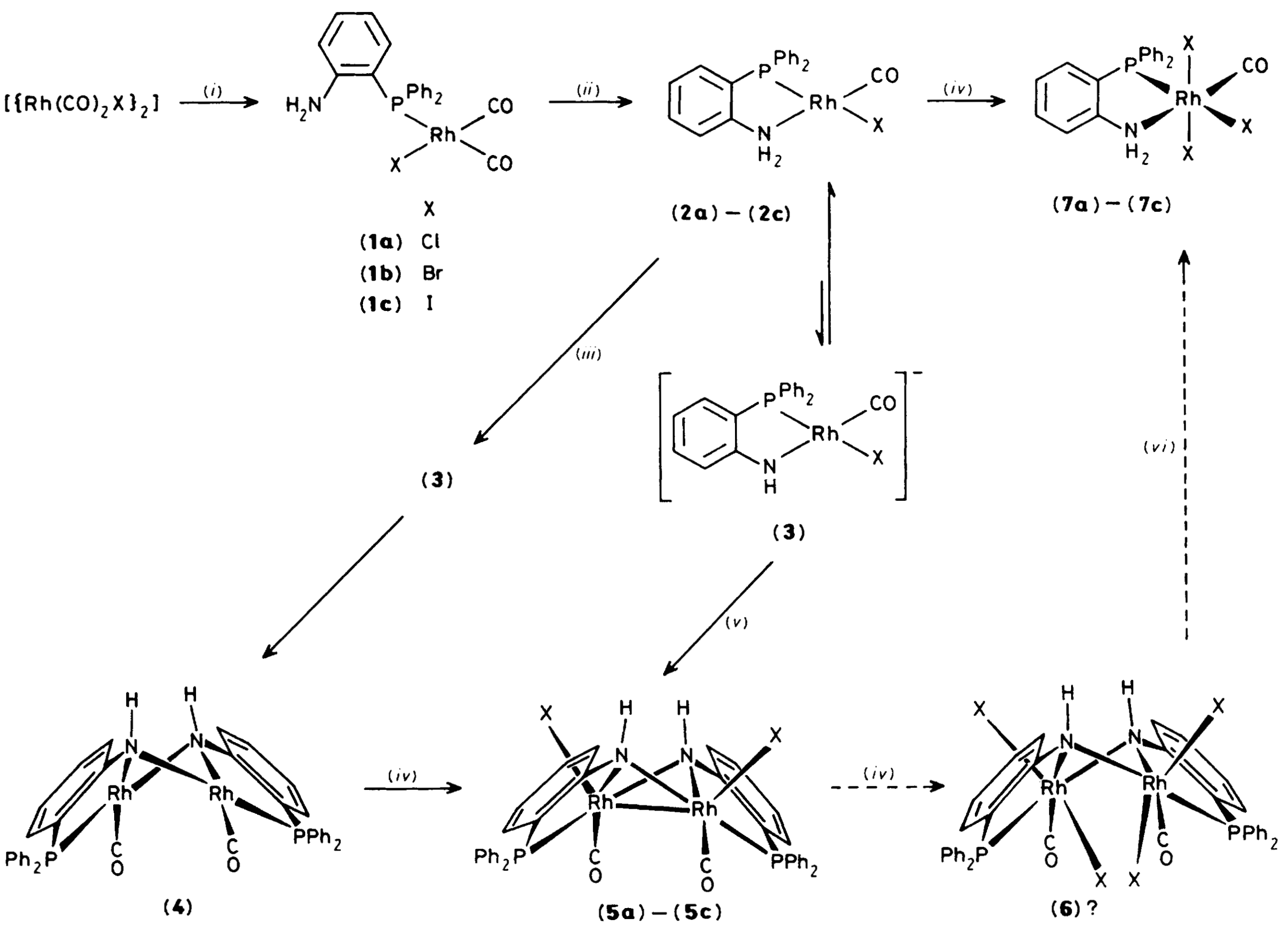
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

§ Prepared *in situ* from (**2a**), $AgClO_4$, and CO in acetone; ^{31}P n.m.r.: δ, 48.0 p.p.m. [J(RhP) 129 Hz].

Table 1. Spectroscopic data for the complexes[a,b]

Complex	I.r. ν(CO)/cm^{-1}	^{31}P N.m.r. δ/p.p.m.	^{31}P N.m.r. J(RhP)/Hz	U.v.–visible $\lambda_{max.}$/nm	U.v.–visible ε/dm^3 mol^{-1} cm^{-1}
(2a)	2 000[c]	57.5[d]	165	300[c]	6 170
(2c)	2 000[c]	57.0[d]	166	*e*	
(4)	1 970w[d] 1 960vs	54.4[d]	155	315[c]	10 065
(5a)	2 020s[c] 2 030 (sh)	57.2[c]	126	320[c] 395 500 (sh)	17 680 11 380 2 450
(5b)	2 020s[c] 2 030 (sh)	58.2[c]	126	*e*	
(5c)	2 020s[c] 2 030 (sh)	60.0[c]	126	305[c] 430 505	19 120 13 140 9 290
(7a)	2 110[d]	55.1[d]	95	335[d] 405 (sh)	15 400 4 100
(7b)	*e*	55.4[d]	94	*e*	
(7c)	2 090[c]	54.0[c]	93	290[c] 375	22 100 8 640

[a] ν(RhCl)/cm^{-1} (Nujol): **(2a)**, 296; **(7a)**, 350s, 305w, and 280s. [b] ^{13}C N.m.r.: δ(CO)/p.p.m., J(RhC)/Hz, ^2J(PC)/Hz: **(2a)** (in dmf), 190.5, 71, and 18; **(7a)** (in dmf), 191.6, 63, and 13. The remaining compounds were insufficiently soluble. [c] In dichloromethane. [d] In *N,N*-dimethylformamide (dmf). [e] Not recorded.



Scheme. (*i*) H_2L, $T < -50$ °C; (*ii*) $T > -30$ °C; (*iii*) LiOH; (*iv*) X_2; (*v*) O_2; (*vi*) HX

geometry shown (Scheme) since this is the configuration adopted by other halogeno-,[16] thiolato-,[17] and phosphido-bridged[18] dinuclear rhodium(I) species and is consistent with the steric requirements of the sp^3-hybridised bridging nitrogen donors. The magnitudes of ν(CO)[3,4,19] and J(RhP)[10,20] were each consistent with a rhodium(I) species. Furthermore, the

Table 2. Selected bond lengths (Å) and angles (°) for (**5a**)·EtOH

Rh(1)–Rh(2)	2.549(1)			C(11)–O(11)	1.131(13)	C(21)–O(21)	1.143(11)
Rh(1)–N(1)	2.053(6)	Rh(2)–N(2)	2.042(6)	P(1)–C(116)	1.807(8)	P(2)–C(216)	1.815(8)
Rh(1)–N(2)	2.113(6)	Rh(2)–N(1)	2.121(6)	P(1)–C(121)	1.827(9)	P(2)–C(221)	1.806(9)
Rh(1)–Cl(1)	2.472(3)	Rh(2)–Cl(2)	2.408(2)	P(1)–C(131)	1.802(9)	P(2)–C(231)	1.801(9)
Rh(1)–C(11)	1.866(10)	Rh(2)–C(21)	1.862(9)	N(1)–C(111)	1.434(10)	N(2)–C(211)	1.428(10)
Rh(1)–P(1)	2.277(2)	Rh(2)–P(2)	2.264(2)	N(1)–H[N(1)]	1.10	N(2)–H[N(2)]	1.09
Cl(1)–Rh(1)–C(11)	94.2(3)	Cl(2)–Rh(2)–C(21)	92.1(3)	N(2)–Rh(1)–Rh(2)	50.9(2)	N(1)–Rh(2)–Rh(1)	51.1(2)
Cl(1)–Rh(1)–P(1)	106.3(1)	Cl(2)–Rh(2)–P(2)	98.1(1)	Rh(1)–C(11)–O(11)	177.3(9)	Rh(2)–C(21)–O(21)	176.0(8)
Cl(1)–Rh(1)–N(1)	99.3(2)	Cl(2)–Rh(2)–N(2)	98.5(2)	Rh(1)–P(1)–C(116)	100.9(3)	Rh(2)–P(2)–C(216)	101.3(3)
Cl(1)–Rh(1)–Rh(2)	134.6(1)	Cl(2)–Rh(2)–Rh(1)	136.3(1)	Rh(1)–P(1)–C(121)	123.9(3)	Rh(2)–P(2)–C(221)	114.3(3)
Cl(1)–Rh(1)–N(2)	91.8(2)	Cl(2)–Rh(2)–N(1)	94.6(2)	Rh(1)–P(1)–C(131)	115.1(3)	Rh(2)–P(2)–C(231)	123.0(3)
P(1)–Rh(1)–C(11)	95.6(3)	P(2)–Rh(2)–C(21)	94.7(3)	C(116)–P(1)–C(121)	106.3(4)	C(216)–P(2)–C(221)	106.9(4)
P(1)–Rh(1)–N(1)	84.1(2)	P(2)–Rh(2)–N(2)	84.1(2)	C(116)–P(1)–C(131)	105.7(4)	C(216)–P(2)–C(231)	105.5(4)
P(1)–Rh(1)–Rh(2)	105.9(1)	P(2)–Rh(2)–Rh(1)	109.5(1)	C(121)–P(1)–C(131)	103.3(4)	C(221)–P(2)–C(231)	104.5(4)
P(1)–Rh(1)–N(2)	156.5(2)	P(2)–Rh(2)–N(1)	159.5(2)	Rh(1)–N(1)–C(111)	119.4(5)	Rh(2)–N(2)–C(211)	119.9(5)
C(11)–Rh(1)–N(1)	166.0(3)	C(21)–Rh(2)–N(2)	169.4(3)	Rh(1)–N(1)–Rh(2)	75.3(2)	Rh(2)–N(2)–Rh(1)	75.7(2)
C(11)–Rh(1)–Rh(2)	113.6(3)	C(21)–Rh(2)–Rh(1)	117.8(3)	Rh(2)–N(1)–C(111)	118.6(5)	Rh(1)–N(2)–C(211)	118.4(5)
C(11)–Rh(1)–N(2)	98.0(3)	C(21)–Rh(2)–N(1)	100.9(3)	Rh(1)–N(1)–H[N(1)]	129	Rh(2)–N(2)–H[N(2)]	117
N(1)–Rh(1)–Rh(2)	53.6(2)	N(2)–Rh(2)–Rh(1)	53.4(2)	Rh(2)–N(1)–H[N(1)]	116	Rh(1)–N(2)–H[N(2)]	110
N(1)–Rh(1)–N(2)	78.1(2)	N(2)–Rh(2)–N(1)	78.1(2)	C(111)–N(1)–H[N(1)]	99	C(211)–N(2)–H[N(2)]	112

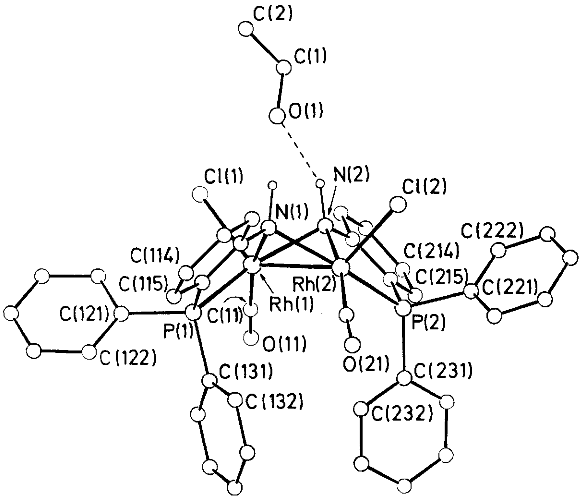


Figure 1. Molecular structure of (**5a**)·EtOH

solid-state i.r. spectrum showed a strong band at 3 120 cm^{-1}, assigned to the nitrogen–hydrogen stretch of the bridging-amido group.[4,15b] The mechanism of formation of the amido-bridged species (**4**) from the monomeric amino complex (**2**) presumably involves initial deprotonation of the co-ordinated amino ligand[9] by hydroxide with production of the terminal amido species $[Rh(HL)(CO)Cl]^-$ (**3**). Subsequent elimination of chloride ion and dimerisation must be extremely favourable since the monitoring of *in situ* reactions, by ^{31}P n.m.r. spectroscopy, did not reveal any intermediate.

A yellow chloroform solution of the rhodium(I) species (**2a**) on exposure to air rapidly turned red and dark red crystals of the rhodium(II) amido-bridged dimer $[\{Rh(\mu\text{-}HL)(CO)Cl\}_2]$ (**5a**) were isolated in low yield (17%). The corresponding bromo and iodo species were prepared in an analogous manner. The structure of (**5a**) was determined by *X*-ray structure analysis and is shown in Figures 1 and 2. Selected bond lengths and angles are given in Table 2. The overall geometry of (**5a**) may be described as two edge-sharing square pyramids with each rhodium atom surrounded by five donor atoms (excluding the second rhodium). This arrangement is similar to that reported for a number of rhodium(II) and iridium(II) dimers.[4a,6,7,21] The central Rh_2N_2 core consists of two rhodium atoms at a distance of 2.549(1) Å, which is consistent with the presence of a Rh–Rh single bond.[4a,7,8,22] The two amido nitrogen donors bridge the metal atoms with the mean of Rh(1)–N(1) and Rh(2)–N(2), 2.048(4) Å, significantly shorter than the corresponding distance for Rh(1)–N(2) and Rh(2)–N(1) of 2.117(4) Å. The shorter Rh–N bonds are part of five-membered chelate rings which probably accounts for the asymmetry in the central core. The four donor atoms defining the base of each pyramid, N(1), N(2), C(1), and P(1) for Rh(1), and N(1), N(2), C(2), and P(2) for Rh(2) are planar with maximum displacement from the respective least-squares planes of 0.04 and 0.02 Å. The rhodium atoms lie above these planes by an average of 0.27 Å towards the chlorine atoms which form the apexes of the two pyramids. The dihedral angle between the two planes is 87.0°. The two nitrogen-bonded hydrogen atoms are cisoidal with respect to each other across the shared edge, N(1)···N(2) 2.62 Å. The corresponding metal–donor atom bond lengths do not differ significantly from each other in either half of the molecule except for Rh(1)–Cl(1) 2.472(3) and Rh(2)–Cl(2) 2.408(2) Å which may be due to the presence of a hydrogen bond between Cl(1) and the hydroxy group of the ethanol of solvation, Cl(1)···O(1) 3.12 Å. This oxygen atom is also strongly hydrogen bonded to the hydrogen atom attached to N(2), H[N(2)]···O(1) 2.13 Å, Figure 1.

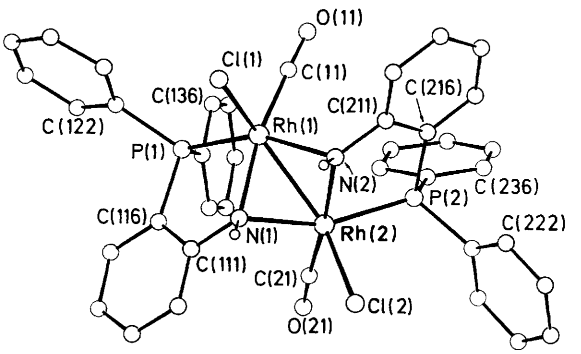


Figure 2. The structure of (**5a**) viewed down the molecular C_2 axis

The spectroscopic properties of (**5**) were consistent with each rhodium atom having an oxidation state of II. For example, the magnitudes (Table 1) of ν(CO)[3–8] and *J*(RhP)[9d,10,20] were intermediate between the values expected for rhodium(I) and rhodium(III) species. In addition, the u.v.–visible spectra of (**5a**) and (**5c**) showed bands at *ca.* 500 nm. Absorptions of similar energy in other dimeric rhodium(II) complexes have been assigned to a metal-to-ligand charge-transfer transition which is lowered in energy by the metal–metal bond.[5]

The likely mechanism for the oxidation of (**2**) to (**5**) involves initial deprotonation to form the terminal amido anionic complex [Rh(HL)(CO)X]$^-$ (**3**), which may then be oxidised[23] to the neutral rhodium(II) species [Rh(HL)(CO)X] which, as formed, would rapidly dimerise to the stable dinuclear amido-bridged compound (**5**), Scheme. The anionic amido complex (**3**) would be more vulnerable to attack by oxygen than the neutral amino species (**2**) because of the greater electron density made available at the metal by the formally negatively charged *sp*^{2}-hybridised amido nitrogen donor.[2,3] Evidence for the important initial proton-transfer step comes from the observation that solutions of (**2**) treated with trifluoroacetic acid are quite air stable. Indeed, the most effective preparation of (**5**) was performed in chloroform that had been freshly shaken with anhydrous sodium carbonate to free it from all acidic impurities. This suggests that the rate of reaction is determined by the equilibrium concentration of (**3**). It has been observed that neutral solutions of the platinum and nickel complexes of H_2L often show faint colouration due to partial deprotonation of the co-ordinated amino group.[9] In contrast, other compounds related to (**2**) but which have *sp*^{3} nitrogen donors that cannot deprotonate, *viz.* [Rh(L′)(CO)Cl][13a] [L′ = $NMe_2C_6H_4PPh_2$-*o* or $(NMe_2CH_2)C_6H_4PPh_2$-*o*], and the rhodium(I) dimer (**4**), are all relatively air stable in solution. The iridium(I) complex [Ir(L′)(CO)Cl] is oxidised by air but follows a different pathway to produce an iridium(IV) hydroxy-bridged compound.[24]

The dirhodium(II) species (**5**) may also be prepared in high yield (80%) by the addition of a stoicheiometric quantity of halogen to dichloromethane solutions of the dirhodium(I) complex (**4**). Similar preparations[4–8] of other rhodium(II) dimers have been reported.

Addition of excess halogen to suspensions of the rhodium-(I) and -(II) dimers, (**4**) and (**5**), gave the monomeric rhodium(III) complexes *mer*-X, X-*trans*-P-[Rh(H_2L)(CO)X_3] [X = Cl (**7a**), Br (**7b**), or I (**7c**)]. These compounds could be prepared in slightly higher yield by oxidative addition of the appropriate halogen to the rhodium(I) monomeric compound (**2**). The i.r. spectrum of (**7a**) showed three low-energy bands assignable to ν(RhCl). The bands at 305 and 350 cm^{-1} are characteristic, in frequency and relative intensity, of the asymmetric and symmetric stretching modes respectively of a *trans*-Cl–Rh–Cl system.[25–28] The remaining band at 280 cm^{-1} is in the region of Rh–Cl stretching where chlorine lies *trans* to phosphorus.[25,27] The ^{31}P n.m.r. spectra of (**7**) comprised in each case of a single doublet, *J*(RhP) *ca.* 95 Hz. A similar *J*(RhP) value has been reported for [Rh($Ph_2PCH_2CH_2PPh_2$)(CO)I_2Cl] which also has phosphorus *trans* to halogen geometry.[29] Attempted deprotonation of (**7**) led to extensive decomposition.

Formation of the rhodium(III) monomeric species (**7**) from (**4**) or (**5**) could involve a rhodium(III) amido-bridged dimer such as [{Rh(μ-HL)(CO)X_2}$_2$] (**6**). The addition of halogen to halogeno- and thiolato-bridged monovalent metal dimers has been reported to yield the corresponding rhodium(III)[30] and iridium(III)[6] dinuclear complexes. Furthermore, some iridium(III) amido-bridged species have recently been prepared starting from the reaction of [Ir(PEt_3)$_2$(C_2H_4)$_2$Cl] and liquid ammonia.[31] However, no evidence for a rhodium(III) dimer, similar to (**6**), was obtained when the progressive addition of halogen solution to a solution of (**4**) was monitored by i.r. and ^{31}P n.m.r. spectroscopy. Molecular models suggest that the overall structure of (**6**) would be hinged due to the inclusion of the bridging amido groups in the five-membered chelate rings. Octahedral geometry around the metal centres would not be favoured because of the limited amount of space between the two rhodium(III) atoms. [Dimeric rhodium(III) or iridium(III) compounds with halogeno-,[32] thiolato-,[33] or amido-[31] bridges have less steric crowding as they can adopt a planar M_2X_2 core.] The Rh_2N_2 core of (**6**) should therefore be unstable thus leading to facile cleavage of the amido bridges. Protonation of the resulting terminal amido groups, by HX arising from reaction of excess halogen with extraneous water, would then lead to formation of the observed monomeric complexes (**7**).[15c,34]

Experimental

Materials and techniques used were as described in previous papers from our laboratories.[9]

P-*trans*-Cl-[Rh(H_2L)(CO)Cl] (**2a**).—*Method 1.* [$NBu^n{}_4$]-[Rh(CO)$_2$Cl$_2$] (1 g, 2.12 mmol) and H_2L (585 mg, 2.11 mmol) were stirred in methanol (10 cm^3) for 15 min. Water (5 cm^3) was added to complete precipitation of the yellow solid which was collected by filtration and washed with MeOH and water and dried to give (**2a**) in *ca.* 95% yield.

Method 2. [{Rh(CO)$_2$Cl}$_2$] (500 mg, 1.29 mmol) and H_2L (715 mg, 2.58 mmol) were stirred in benzene (20 cm^3) for 15 min. The product was filtered off, washed with benzene, and dried (1.08 g, 95%).

The complex can be recrystallised from CH_2Cl_2–MeOH–trace CF_3CO_2H, m.p. 258—261 °C (decomp.) (Found: C, 51.3; H, 3.75; Cl, 7.85; N, 3.1; P, 7.15. $C_{19}H_{16}ClNOPRh$ requires C, 51.4; H, 3.65; Cl, 8.0; N, 3.15; P, 7.0%).

The bromo and iodo species, (**2b**) and (**2c**), were prepared by carrying out the reaction of [$NBu^n{}_4$][Rh(CO)$_2$Cl$_2$] and H_2L in the presence of a large excess of LiX and were isolated in *ca.* 80% yield.

[{Rh(μ-HL)(CO)}$_2$] (**4**).—Lithium hydroxide (40 mg, 1.67 mmol) in water (5 cm^3) was added to a solution of complex (**2a**) (500 mg, 1.13 mmol) in acetone (100 cm^3) under an atmosphere of nitrogen. The mixture was stirred for 2 h and water (100 cm^3) was then slowly added with stirring. The fine yellow precipitate was filtered off, washed with water, and dried (410 mg, 90%), m.p. 288—289 °C (decomp.) (Found: C, 55.4; H, 3.7; N, 3.35. $C_{38}H_{30}N_2O_2P_2Rh_2$ requires C, 56.0; H, 3.7; N, 3.45%).

[{Rh(μ-HL)(CO)X}$_2$] (**5**).—*Method 1.* Chloroform (50 cm^3), freshly shaken with anhydrous Na_2CO_3 and filtered, was used to dissolve (**2a**) (500 mg, 1.13 mmol) and the solution was stirred for 2 h in air. The solution was concentrated and passed down a short Florisil column (2.5 × 10 cm) using $CHCl_3$, Na_2CO_3 treated, as eluant. The red fraction was collected and evaporated to near dryness on a rotary evaporator set at 25 °C. The residue was dissolved in hot EtOH (25 cm^3, 50—70 °C) and allowed to stand at room temperature for 2 d. The dark red crystals of (**5a**) were collected, washed with a little ice-cold EtOH, and dried (80 mg, 17%).

Method 2. Complex (**4**) (500 mg, 0.61 mmol) was suspended in CH_2Cl_2 (500 cm^3). Two molar equivalents of chlorine, as a low molarity (*ca.* 0.05 mol dm^{-3}) CCl_4 solution,[35] were slowly added. The resulting dark red solution was evaporated to near dryness on a rotary evaporator set at 25 °C. The residue was dissolved in CH_2Cl_2 (1 cm^3) and passed down a silica column (2.5 × 10 cm) using CH_2Cl_2–diethyl ether (1 : 1) as eluant. After evaporation to near dryness the residue was crystallised from EtOH (25 cm^3) as in Method 1 (135 mg, 25%).

The dark red bromo and iodo analogues (**5b**) and (**5c**) can be prepared by either method in an analogous manner except that when recrystallising (**5c**) the solution must be stored at −5 °C

Table 3. Atomic co-ordinates for (**5a**)·EtOH

Atom	*x*	*y*	*z*
Rh(1)	−0.320 70(4)	0.098 62(4)	0.299 21(4)
Cl(1)	−0.360 3(2)	0.032 5(2)	0.418 3(1)
C(11)	−0.300 2(6)	0.214 5(7)	0.337 6(5)
O(11)	−0.286 5(5)	0.285 7(5)	0.358 2(5)
P(1)	−0.455 4(1)	0.133 2(2)	0.239 0(1)
N(1)	−0.326 8(4)	−0.016 4(4)	0.235 8(3)
C(111)	−0.403 0(5)	−0.029 6(5)	0.185 0(5)
C(112)	−0.407 1(6)	−0.106 7(6)	0.140 4(5)
C(113)	−0.481 3(7)	−0.117 5(6)	0.092 8(5)
C(114)	−0.550 2(6)	−0.056 2(7)	0.088 0(5)
C(115)	−0.546 9(6)	0.018 9(6)	0.132 9(5)
C(116)	−0.471 6(5)	0.034 4(5)	0.181 3(5)
C(121)	−0.562 7(6)	0.150 1(6)	0.284 5(5)
C(122)	−0.637 2(6)	0.190 3(7)	0.246 7(5)
C(123)	−0.720 0(6)	0.198 8(8)	0.281 6(7)
C(124)	−0.729 7(7)	0.168 4(8)	0.350 0(8)
C(125)	−0.655 9(7)	0.131 0(7)	0.388 5(6)
C(126)	−0.570 6(6)	0.123 1(6)	0.357 2(5)
C(131)	−0.451 3(5)	0.228 3(6)	0.177 2(5)
C(132)	−0.441 9(5)	0.218 5(6)	0.102 0(5)
C(133)	−0.437 5(6)	0.295 0(8)	0.059 1(6)
C(134)	−0.442 4(7)	0.381 1(8)	0.087 3(6)
C(135)	−0.450 7(7)	0.389 0(6)	0.163 0(6)
C(136)	−0.454 7(6)	0.314 0(6)	0.206 6(5)
Rh(2)	−0.211 34(4)	0.055 08(5)	0.200 12(4)
Cl(2)	−0.129 9(2)	−0.079 3(2)	0.166 3(1)
C(21)	−0.247 3(5)	0.079 1(6)	0.102 9(5)
O(21)	−0.264 5(4)	0.096 0(5)	0.042 7(4)
P(2)	−0.092 6(1)	0.153 2(2)	0.202 2(1)
N(2)	−0.185 5(4)	0.049 8(4)	0.311 0(3)
C(211)	−0.117 5(5)	0.107 4(6)	0.344 5(4)
C(212)	−0.101 2(6)	0.109 0(7)	0.420 8(5)
C(213)	−0.038 7(7)	0.168 0(7)	0.451 9(5)
C(214)	0.008 9(7)	0.226 5(7)	0.406 5(5)
C(215)	−0.005 0(6)	0.225 6(7)	0.331 0(5)
C(216)	−0.067 9(5)	0.164 3(6)	0.300 2(5)
C(221)	0.009 2(5)	0.109 1(6)	0.162 8(5)
C(222)	0.076 6(6)	0.066 2(7)	0.204 3(6)
C(223)	0.147 9(7)	0.024 1(9)	0.172 4(7)
C(224)	0.153 0(7)	0.021 6(8)	0.096 9(7)
C(225)	0.087 6(7)	0.065 5(7)	0.053 6(6)
C(226)	0.014 3(6)	0.108 9(7)	0.086 9(5)
C(231)	−0.102 0(5)	0.267 3(6)	0.167 8(4)
C(232)	−0.188 0(6)	0.303 9(7)	0.149 3(5)
C(233)	−0.194 9(7)	0.394 6(8)	0.125 2(6)
C(234)	−0.118 0(8)	0.445 5(7)	0.119 4(6)
C(235)	−0.035 3(7)	0.409 5(8)	0.137 9(6)
C(236)	−0.025 9(6)	0.321 5(7)	0.161 2(5)
O(1)	0.251 7(6)	0.362 5(6)	0.129 4(5)
C(1)	0.214 0(9)	0.310 7(11)	0.071 7(9)
C(2)	0.273 5(11)	0.241 6(10)	0.047 1(9)
H[N(1)]	−0.315 0	−0.087 0	0.252 3
H[N(2)]	−0.185 4	−0.016 9	0.336 5

for 3 d before isolation of the product. The yields are *ca.* 15% (X = Br or I), and 25% (X = Br) and 80% (X = I) for Methods 1 and 2 respectively.

(**5a**)·EtOH, m.p. >350 °C (Found: C, 51.4; H, 3.9; Cl, 7.7; N, 2.95; P, 6.9. $C_{40}H_{36}Cl_2N_2O_3P_2Rh_2$ requires C, 51.6; H, 3.9; Cl, 7.6; N, 3.0; P, 6.65%). (**5c**), m.p. >350 °C (Found: C, 42.65; H, 2.95; I, 23.9; N, 2.55; P, 5.7. $C_{38}H_{30}I_2N_2O_2P_2Rh_2$ requires C, 42.7; H, 2.85; I, 23.75; N, 2.6; P, 5.8%).

mer-X, X-*trans*-P-[Rh(H_2L)(CO)X_3] (**7**).—*Method 1.* The species (**4**) (500 mg, 0.61 mmol) was suspended in acetone (25 cm^3) [CH_2Cl_2 (25 cm^3) for (**7c**)] and excess X_2–CCl_4 solution (>four molar equivalents) was slowly added. The mixture was stirred for 15 min and then evaporated to dryness. For the chloro and bromo species the residue was redissolved in CH_2Cl_2 (250 cm^3) and toluene (50 cm^3) was added. The CH_2Cl_2 was then removed on a rotary evaporator. The yellow (**7a**) and orange (**7b**) were filtered off, washed with toluene and diethyl ether and dried (*ca.* 60% yield). For the iodo species (**7c**) n-hexane (25 cm^3) was added and the CH_2Cl_2 allowed to evaporate overnight. The brown product was filtered off, washed with n-hexane, and dried (80% yield).

Method 2. Complex (**2**) (500 mg, 1.13 mmol) was dissolved in CH_2Cl_2 (50 cm^3) and excess X_2–CCl_4 solution added. The mixture was stirred for 15 min. The products were isolated by adding diethyl ether (50 cm^3) and storage at −5 °C for 4 h for (**7a**), by adding toluene (50 cm^3) as in Method 1 for (**7b**), or by adding n-hexane (50 cm^3) as in Method 1 for (**7c**); yields 95, 90, and 80% respectively.

(**7a**), m.p. >350 °C (decomp.) (Found: C, 44.2; H, 3.0; Cl, 20.4; N, 2.7. $C_{19}H_{16}Cl_3NOPRh$ requires C, 44.35; H, 3.15; Cl, 20.65; N, 2.7%).

Crystal Data and Data Collection.—(**5a**)·EtOH. $C_{40}H_{36}Cl_2N_2O_3P_2Rh_2$, *M* = 662.5, monoclinic, *a* = 14.669(3), *b* = 14.754(3), *c* = 18.233(4) Å, β = 92.46(4)°, *U* = 3 942.5 Å^3 (by least-squares refinement of diffractometer angles for 25 automatically-centred reflections, λ = 0.710 69 Å), space group $P2_1/c$, *Z* = 4, D_c = 1.11 g cm^{-3}, *F*(000) = 1 872. A dark red crystal with μ(Mo-K_α) = 9.86 cm^{-1} was used in the data collection which was carried out using a Phillips PW 1100 four-circle single-crystal diffractometer in the θ range 3.0—25.0° with a scan width of 0.9° using the technique previously described.[36] No absorption corrections were applied.

Structure Analysis and Refinement.[37]—The rhodium atoms were located from a Patterson synthesis. The positions of the remaining non-hydrogen atoms and the N-bonded hydrogen atoms were found from subsequent difference-Fourier syntheses. The remaining hydrogen atoms were placed in geometrically idealised positions (C–H 1.08 Å) and constrained to ride on the relevant carbon atoms with independent isotropic thermal parameters tied to a single free variable which was refined. The N-bonded H-atoms were included at the positions in which they were found with fixed isotropic thermal parameters of 0.05 Å^2. In the final cycles of blocked full-matrix refinement, using 3 498 unique data with $I \geqslant 3\sigma(I)$, all the non-hydrogen atoms were assigned anisotropic thermal parameters giving a final *R* = 0.045 and *R'* = 0.042 {using a weighting scheme of $w = 1/[\sigma^2(F_o)]$}. A final difference-Fourier map showed no significant regions of electron density. The final atomic co-ordinates are given in Table 3.

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

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