Reactions of the Nitridocarbonyl Cluster Anion $[Rh_6N(CO)_{15}]^-$ with Strong Bases: Synthesis and Crystal Structure of the Hydridic Dianion $[Rh_6(\mu\text{-}H)N(CO)_{14}]^{2-}$ †

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The reaction of the nitridocarbonyl anion $[Rh_6N(CO)_{15}]^-$, as its K^+ salt, in water or alcoholic solution with alkali metal hydroxides afforded the novel hydridic species $[Rh_6(\mu\text{-}H)N(CO)_{14}]^{2-}$, isolated as the caesium (**2a**) and the bis(triphenylphosphine)iminium (**2b**) salts. Both species have been investigated by X-ray structural analysis. Compound **2a** crystallizes in the hexagonal system, space group *P*6_3/*mmc* (no. 194), with $a = b = 11.089(2)$, $c = 12.308(4)$ Å, $Z = 2$. Compound **2b** gives monoclinic crystals, space group *C*2/*c* (no. 15), with $a = 26.896(3)$, $b = 17.143(6)$, $c = 20.250(2)$ Å, $\beta = 118.80(1)°$, $Z = 4$. The structures were refined on the basis of 355 (**2a**) and 2170 (**2b**) significant independent reflections to final *R* values of 0.0427 and 0.0491 for **2a** and **2b**, respectively. The anion contains a trigonal prismatic cluster centred by the nitrido ligand. The hydrido ligand bridges an interbasal Rh–Rh edge replacing a bridging CO group of the parent anion $[Rh_6N(CO)_{15}]^-$. This substitution causes some stereochemical effects which are discussed for **2b**; in **2a** the anion has essentially the same stereochemistry but the interbasal ligands (two CO and one H) are disordered, due to the presence of a three-fold crystallographic axis.

After the report, in 1979, of the synthesis and structural characterization of the first carbonyl-cluster compounds containing a fully encapsulated nitrogen atom, namely the trigonal prismatic anions $[M_6N(CO)_{15}]^-$ (M = Co or Rh),[1,2] found to be isostructural with the corresponding carbidocarbonyl dianions $[M_6C(CO)_{15}]^{2-}$,[3,4] one could have been erroneously induced to foresee a strict parallelism between the nitridocarbonyl cluster chemistry and that, more extensively studied, of carbidocarbonyl species, the only difference being one extra electron to be assigned in the 'bookkeeping' to the interstitial atom. Instead, since then, a limited but significant number of novel nitrido species have been characterized, showing many interesting and distinctive structural features which indicate a quite different chemistry. The unprecedented skeletal geometries and the peculiar environments for the nitrogen atoms, especially in the large polynitrido species (with two,[5,6] three[7] and four[8] interstitial nitrogen atoms), provide novel information for a clearer insight into the cluster bonding and electron-counting schemes.

Our efforts in this field, which were previously mainly devoted to the synthesis of high-nuclearity clusters, are now concerned also with the basic reactivity of the parent anions, $[Rh_6N(CO)_{15}]^-$ and $[Co_6N(CO)_{15}]^-$, toward various classes of reagents. Thus, we have already reported the reactions of $[Rh_6N(CO)_{15}]^-$ with nucleophiles like $[M(CO)_4]^-$ (M = Co, Rh or Ir),[9] which lead to cluster growth with the formation of species containing a trigonal prism capped on a square face by the seventh metal atom. In the present paper we report the preliminary results of a study on the nucleophilic attack of OH^- ions on $[Rh_6N(CO)_{15}]^-$ in water or alcohol, which leads to the formation of the novel hydridic species $[Rh_6HN(CO)_{14}]^{2-}$, isolated as the caesium and the bis(triphenylphosphine)iminium salts. Both salts have been investigated by X-ray single-crystal analysis.

Results and Discussion

The compound $K[Rh_6N(CO)_{15}]$ **1** slowly dissolves in 10% aqueous NaOH under CO to give a solution from which, by controlled addition of CsCl and standing, orange crystals were obtained. X-Ray structural analysis showed this compound to be the salt $Cs_2[Rh_6HN(CO)_{14}]$ **2a**. The formation of the novel anion implies the nucleophilic attack of OH^- ions on a carbonyl group according to reaction (1). This same reaction, carried out

$$[Rh_6N(CO)_{15}]^- + 3OH^- \longrightarrow [Rh_6HN(CO)_{14}]^{2-} + CO_3^{2-} + H_2O \quad (1)$$

with more concentrated hydroxide solutions, affords more reduced species, presently under investigation.

The yields of the above reaction are rather low, because the caesium salt separates out as crystals only under particularly critical conditions, and therefore we searched for a cleaner and reproducible synthesis. This was done also with the aim of obtaining, with other cations, crystals suitable for a more precise X-ray structural investigation, since that on $Cs_2[Rh_6HN(CO)_{14}]$ was affected by some disorder problems (see below).

Thus compound **1** was treated at room temperature under CO with a 0.5 mol dm^{-3} methanolic NaOH solution. The progress of the reaction, which was slower with respect to the previous one, was monitored by IR spectroscopy, showing the progressive transformation of the parent compound into the novel hydridic dianion, without evidence of intermediate steps. When the reaction was complete, the addition of $N(PPh_3)_2Cl$ caused the precipitation of the yellow salt

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

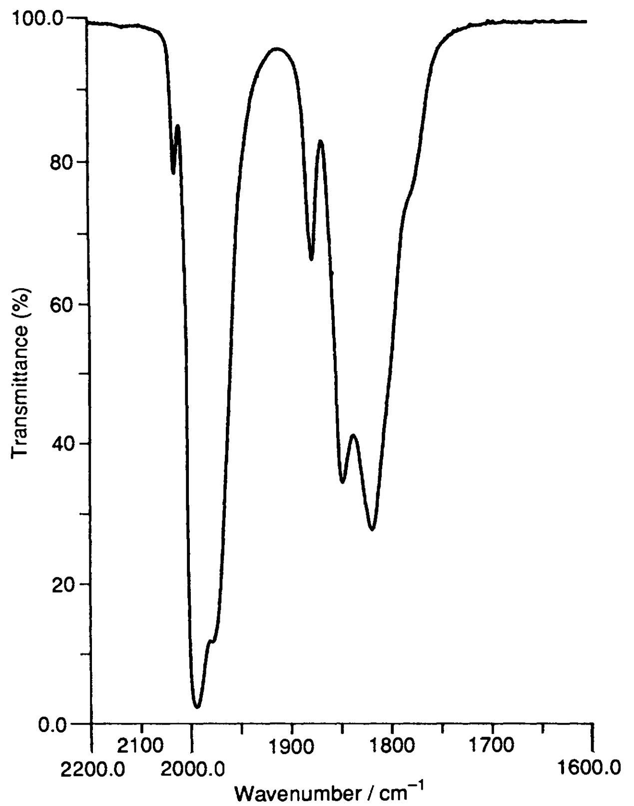

Fig. 1 The IR spectrum of $Cs_2[Rh_6HN(CO)_{14}]$ in thf

Table 1 IR data for $[Rh_6HN(CO)_{14}]^{2-}$

Cation	Solvent	ν(CO)/cm^{-1}
Cs^+ (**2a**)	thf	2028w, 1995s, 1977(sh), 1878mw, 1848m, 1819ms
	MeCN	2030w, 1997s, 1982(sh), 1875w, 1842m, 1825ms
$[N(PPh_3)_2]^+$ (**2b**)	thf	2021w, 1987s, 1968ms, 1872w, 1842m, 1825ms
	MeCN	1997s, 1982(sh), 1842m, 1826ms
	Acetone	2021w, 1991s, 1976(sh), 1872w, 1842m, 1827ms
	CH_2Cl_2	1994s, 1872w, 1840(sh), 1822ms

$[N(PPh_3)_2]_2[Rh_6HN(CO)_{14}]$ **2b** and recrystallization from acetone–propan-2-ol afforded, in very good yields (*ca.* 80%), crystals suitable for the X-ray analysis (see below).

The caesium salt is soluble in tetrahydrofuran (thf), acetone, CH_2Cl_2 and MeCN, where the bis(triphenylphosphine)iminium derivative shows a reduced solubility. The solutions are stable under CO, but slowly decompose under nitrogen to give unknown products under investigation.

When **2a** in thf is treated with CF_3CO_2H under a CO atmosphere, monitoring by IR spectroscopy shows a quantitative transformation of the hydridic dianion into the parent $[Rh_6N(CO)_{15}]^-$.

Spectroscopic Measurements.—The IR spectrum of $Cs_2[Rh_6HN(CO)_{14}]$ **2a** in thf under a CO atmosphere is shown in Fig. 1. Table 1 reports CO stretchings of both **2a** and **2b** in several solvents.

The variable temperature (298–193 K), 80 MHz ^1H NMR spectrum of salt **2b** in $[^2H_6]$acetone shows in the range δ +25 to −60 just one sharp triplet [$\delta(^1H)$ −10.66, $^1J(^{103}Rh-^1H)$ 34.6 Hz, $W_{\frac{1}{2}}$ *ca.* 4 Hz]. This is in agreement with the presence of an hydrido ligand bridging a Rh–Rh cluster edge.

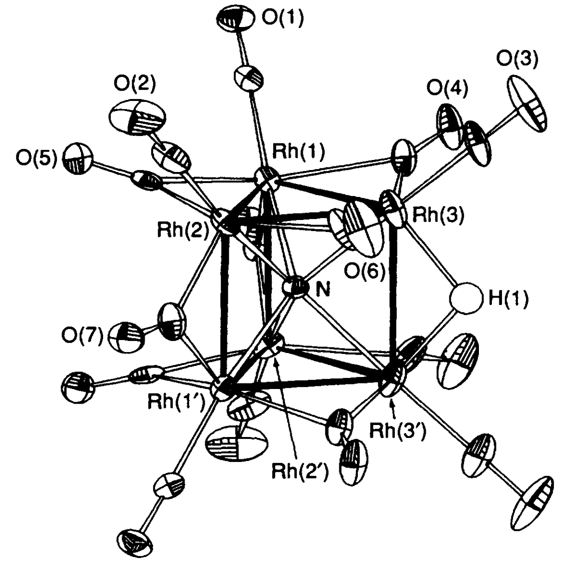

Fig. 2 ORTEP[10] drawing of the anion $[Rh_6(\mu-H)N(CO)_{14}]^{2-}$ as determined in the salt **2b**. For clarity the numbering of the carbonyl groups is indicated only by the labels of their oxygen atoms

Description of the Structures of the Salts **2a** *and* **2b**.—We first describe the structure of the salt **2b** since the anion $[Rh_6(\mu-H)N(CO)_{14}]^{2-}$ was elucidated in greater detail in this species. The crystal structure consists of the packing of discrete anions and bis(triphenylphosphine)iminium cations in the ratio 1:2, separated by normal van der Waals contacts. The anion, containing a trigonal prismatic cluster centred by the interstitial nitrogen atom, is shown in Fig. 2 and bond distances and angles are given in Table 2. It exhibits an idealized overall C_{2v} symmetry, the two-fold axis passing through the nitrogen atom and the midpoint of the Rh(3)–Rh(3′) edge, and presents six terminal and eight edge-bridging carbonyl ligands. The hydrido ligand was indirectly located in a bridging position on the interbasal Rh(3)–Rh(3′) edge using pair potential-energy minimization (HYDEX).[11] This location is in agreement with the ^1H NMR spectrum of the compound in solution.

The bond parameters are strictly comparable with those of the parent anion $[Rh_6N(CO)_{15}]^-$, as well as with those of the corresponding carbido species $[Rh_6C(CO)_{15}]^{2-}$. The Rh–Rh bond lengths within the basal triangles are shorter than the interbasal bond lengths (mean 2.763 *vs.* 2.837 Å). The mean Rh–N bond distance, 2.135 Å, is almost the same as that found in $[Rh_6N(CO)_{15}]^-$ (2.130 Å).[2] However, the presence of a hydrido ligand in place of a bridging CO is accompanied by small but significant changes with respect to the parent anion (of D_{3h} idealized symmetry) both in the metallic cluster and in the carbonyl geometry, due to the peculiar electronic and steric requirements of this ligand. In fact, the hydrogen bridged Rh–Rh edge is somewhat stretched with respect to the other interbasal edges [2.866(3) *vs.* 2.823(2) Å], as usually observed for these three-centre two-electron bonds. Moreover, the carbonyl ligands show shorter bonds with Rh(3) and Rh(3′) than with the other metal atoms, especially the bridging ones on the basal triangles, which are significantly asymmetric [mean Rh(3)–C 2.08, Rh(1,2)–C 2.20 Å]. The other bridging CO groups are almost symmetrical. A decrease of the Rh–Rh–C(terminal) angles within the interbasal metal–metal hydrogen-bridged edge with respect to the other CO-bridged interbasal ones is also observed (132.1 *vs.* 137.1°). In the

Table 2 Bond distances (Å) and angles (°) for the anion $[Rh_6(\mu\text{-}H)N(CO)_{14}]^{2-}$ in the salt **2b**

Rh(1)–Rh(2)	2.769(2)	Rh(1)–C(5)	2.12(2)
Rh(1)–Rh(3)	2.765(2)	Rh(2)–C(5)	2.15(2)
Rh(2)–Rh(3)	2.756(2)	Rh(2)–C(6)	2.21(2)
Rh(1)–Rh(2′)	2.823(2)	Rh(3)–C(6)	2.08(2)
Rh(3)–Rh(3′)	2.866(3)	Rh(1)–C(7)	2.00(2)
Rh(1)–N(1)	2.134(6)	Rh(2′)–C(7)	1.96(2)
Rh(2)–N(1)	2.131(5)	C(1)–O(1)	1.12(2)
Rh(3)–N(1)	2.14(1)	C(2)–O(2)	1.14(2)
Rh(1)–C(1)	1.87(2)	C(3)–O(3)	1.15(2)
Rh(2)–C(2)	1.86(2)	C(4)–O(4)	1.14(2)
Rh(3)–C(3)	1.83(2)	C(5)–O(5)	1.16(2)
Rh(1)–C(4)	2.19(2)	C(6)–O(6)	1.14(2)
Rh(3)–C(4)	2.09(2)	C(7)–O(7)	1.24(2)
Rh(2)–Rh(1)–C(1)	127.1(4)	Rh(3′)–Rh(3)–C(3)	132.1(7)
Rh(2′)–Rh(1)–C(1)	137.4(5)	N(1)–Rh(3)–C(3)	177.2(5)
Rh(3)–Rh(1)–C(1)	124.2(5)	Rh(3′)–Rh(3)–C(4)	99.2(6)
N(1)–Rh(1)–C(1)	173.6(5)	C(3)–Rh(3)–C(4)	93.7(7)
Rh(2′)–Rh(1)–C(4)	90.3(5)	Rh(3′)–Rh(3)–C(6)	94.5(7)
C(1)–Rh(1)–C(4)	89.8(7)	C(3)–Rh(3)–C(6)	89.9(7)
Rh(2′)–Rh(1)–C(5)	97.2(5)	C(4)–Rh(3)–C(6)	158.3(8)
C(1)–Rh(1)–C(5)	94.2(6)	C(3)–Rh(3)–H(1)	92.9
C(4)–Rh(1)–C(5)	152.5(6)	C(4)–Rh(3)–H(1)	103.2
C(1)–Rh(1)–C(7)	93.6(7)	C(6)–Rh(3)–H(1)	98.1
C(4)–Rh(1)–C(7)	98.5(6)	Rh(3)–H(1)–Rh(3′)	101.4
C(5)–Rh(1)–C(7)	108.4(6)	Rh(1)–C(1)–O(1)	178(1)
Rh(1)–Rh(2)–C(2)	126.9(6)	Rh(2)–C(2)–O(2)	179(2)
Rh(1′)–Rh(2)–C(2)	136.8(7)	Rh(3)–C(3)–O(3)	177(2)
Rh(3)–Rh(2)–C(2)	125.2(5)	Rh(1)–C(4)–Rh(3)	80.5(6)
N(1)–Rh(2)–C(2)	174.5(6)	Rh(1)–C(4)–O(4)	135(1)
Rh(1′)–Rh(2)–C(5)	95.9(5)	Rh(3)–C(4)–O(4)	144(1)
C(2)–Rh(2)–C(5)	93.7(7)	Rh(1)–C(5)–Rh(2)	80.8(6)
Rh(1′)–Rh(2)–C(6)	95.8(7)	Rh(1)–C(5)–O(5)	140(2)
C(2)–Rh(2)–C(6)	93.6(8)	Rh(2)–C(5)–O(5)	138(1)
C(5)–Rh(2)–C(6)	154.1(6)	Rh(2)–C(6)–Rh(3)	79.9(7)
C(2)–Rh(2)–C(7′)	91.8(8)	Rh(2)–C(6)–O(6)	137(2)
C(5)–Rh(2)–C(7′)	107.3(7)	Rh(3)–C(6)–O(6)	142(2)
C(6)–Rh(2)–C(7′)	97.1(7)	Rh(1)–C(7)–Rh(2′)	90.8(8)
Rh(1)–Rh(3)–C(3)	132.1(6)	Rh(1)–C(7)–O(7)	134(1)
Rh(2)–Rh(3)–C(3)	128.3(6)	Rh(2′)–C(7)–O(7)	135(2)

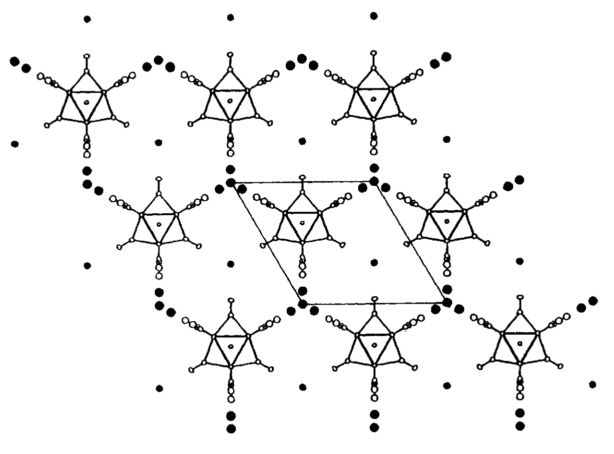

Fig. 3 A view of one layer of the packing down the *c* axis in the salt **2a** (for a discussion of the disorder see text). Filled circles indicated the Cs^+ cations

crystalline species $Cs_2[Rh_6(\mu\text{-}H)N(CO)_{14}]$ **2a** the anion lies on a crystallographic special position of D_{3h} symmetry (*c* in Wyckoff notation). It has a stereochemistry essentially identical to that of **2b** but, due to its crystallographic site symmetry, the two interbasal CO groups and the bridging hydride are disordered. A view of a layer of the crystal packing down the crystallographic *c* axis is illustrated in Fig. 3.

Table 3 Comparison of selected mean bond parameters (Å) within the salts **2a** and **2b** and the parent anion $[Rh_6N(CO)_{15}]^-$

	2a	**2b**	$[Rh_6N(CO)_{15}]^-$ (ref. 2)
Rh–Rh (basal)	2.731	2.763	2.763
Rh–Rh (interbasal)	2.851	2.837	2.828
Rh–Rh (overall)	2.771	2.788	2.785
Rh–N	2.126	2.135	2.130
Rh–C (terminal)	1.85	1.85	1.863
C–O (terminal)	1.16	1.14	1.134
Rh–C (basal bridging)	2.13	2.14	2.117
C–O (basal bridging)	1.14	1.15	1.151
Rh–C (interbasal bridging)	1.99	1.98	2.050
C–O (interbasal bridging)	1.12	1.24	1.158

One independent Rh–Rh bond length within the basal triangles and one independent Rh–Rh interbasal bond length have been determined, showing values of 2.731(2) and 2.851(2) Å, respectively. The main bond parameters are given in Table 3, in comparison with the corresponding mean values in **2b** and in the parent anion. One of the two independent caesium cations lies at the centre of a trigonal prismatic environment of six carbonyl oxygen atoms (in special positions of D_{3h} symmetry, *d* in Wyckoff notation). The carbonyl groups involved are those bridging the basal triangular cluster edges (see Fig. 3) and the Cs···O distance is 3.25(1) Å. The other Cs^+ cation is disordered in the large cavity formed by the CO groups around another special position of D_{3h} symmetry (*b* in Wyckoff notation). The centre of the cavity cannot be occupied by the cation because of the two short contacts with the oxygen atoms of the interbasal carbonyl ligands. The model of disorder implies the population of five sites (only two independent) at the vertices of a trigonal bipyramid, with a nearly equal occupancy for all of *ca.* 0.2. This disorder is strictly related to that involving the interbasal ligands (two CO and one H) in the sense that the cationic position depends upon the type of ligands directed toward the centre of the cavity: when one H ligand is present the cation occupies the equatorial site which lies by the same side of the hydride and not by that of a CO group, while, when three CO groups are present, the two axial sites are those populated. With this model the cation displays Cs··· O contacts down to *ca.* 3 Å and a Cs··· H contact of 2.62 Å. A certain preference of the caesium ions for interactions with the bridging CO groups is in agreement with the slightly larger negative polarization of the oxygen atoms of these ligands with respect to the terminally bonded ones.

Experimental

All operations were carried out under carbon monoxide with a standard Schlenk-tube apparatus. Tetrahydrofuran was distilled from sodium diphenylketyl and propan-2-ol from aluminium–isopropoxide. All the other analytical grade solvents were degassed under vacuum and stored under nitrogen. The salt $K[Rh_6N(CO)_{15}]$ was prepared by the published method.[1] Infrared spectra were recorded on the Perkin Elmer 16PC FTIR or the conventional grating 781 spectrophotometer equipped with Data Station for spectra elaboration, using 0.1 mm CaF_2 cells previously purged with nitrogen. The ^1H NMR spectrum was recorded at 80 MHz on a Varian instrument, with a resolution of ± 1.72 Hz.

Analyses were done by the Analytical Laboratory of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Universitá di Milano and by Mikroanalytisches Labor Pascher, Remagen, Germany.

Synthesis of $Cs_2[Rh_6HN(CO)_{14}]$ **2a**.—The salt $K[Rh_6N(CO)_{15}]$·*ca.* 1 thf (360.6 mg, *ca.* 0.31 mmol) was placed in a Schlenk tube under CO (*ca.* 100 kPa) and treated with a solution of NaOH in water (10%, 10 cm^3). The suspension was stirred until complete dissolution of the starting material occurred (*ca.* 1 h), yielding a brown-yellow solution. The stirring bar was removed and CsCl (2% in water, 5 cm^3) was quickly added and the solution, after mixing, was left standing under CO. Within minutes (*ca.* 15) a precipitation of yellow-orange crystals began and these crystals were left to grow overnight. The solution was filtered and the crystals were washed twice with 2 cm^3 of the mixture of NaCl (15%, 2.5 cm^3)–CsCl (2%, 1.5 cm^3), then briefly dried *in vacuo* and stored under CO. The crystals obtained in this way proved suitable for X-ray diffraction, but the whole product possessed NaCl and CsCl impurities. Purification was performed by extraction with thf (5 cm^3) under CO; the clear yellow solution was syringed and dropped into *n*-hexane (40 cm^3) with stirring to give a yellow precipitate; after decantation the colourless mother liquor was syringed off and the precipitate washed twice by decantation with *n*-hexane (10 cm^3) and vacuum dried. Yield 71.3 mg (17%). Elemental analysis revealed the presence of clathrated thf [Found: C, 16.15; H, 0.75; Cs, 20.00; K < 0.1; N, 1.10; Na < 0.2; O (by difference), 17.90; Rh, 44.10. Calc. for $Cs_2[Rh_6HN(CO)_{14}]\cdot C_4H_8O$: C, 15.85; H, 0.65; Cs, 19.50; N, 1.05; O, 17.60; Rh, 45.30%].

Synthesis of $[N(PPh_3)_2]_2[Rh_6HN(CO)_{14}]$ **2b**.—A solution of $K[Rh_6N(CO)_{15}]\cdot$*ca.* 1 thf (378.9 mg, *ca.* 0.33 mmol) in methanol (15 cm^3) under CO was treated with NaOH in methanol (2.08 mol dm^{-3}, 5 cm^3) and stirred until the bands of the starting anion at 2030s, 1879s and 1852w cm^{-1} were replaced by new bands at 1998s, *ca.* 1990(sh), 1879w, 1849m and 1832ms cm^{-1} (*ca.* 24 h). The resulting solution was treated dropwise, while stirring, with $N(PPh_3)_2Cl$ (0.5 g in 5 cm^3 MeOH) to give a yellow precipitate which was filtered off, washed with propan-2-ol (2 × 10 cm^3) and vacuum dried. The product was extracted with acetone (15 cm^3) and layered with propan-2-ol (40 cm^3) previously saturated with CO. When the diffusion of the solvents was complete, the mother liquor was syringed off and the orange crystals were washed twice with propan-2-ol (10 cm^3), then briefly dried *in vacuo* and stored under CO. Yield 550 mg (79%) (Found: C, 49.30; H, 2.85; N, 2.00. Calc. for $[N(PPh_3)_2]_2[Rh_6HN(CO)_{14}]$: C, 49.15; H, 2.95, N, 2.00%).

X-Ray Analysis of the Salts **2a** *and* **2b**.—*Crystal data.* Salt **2a**. $C_{14}HCs_2NO_{14}Rh_6$, $M = 1290.4$, hexagonal system, space group $P6_3/mmc$ (no. 194), with $a = b = 11.089(2)$, $c = 12.308(4)$ Å, $U = 1310.4$ Å^3, $Z = 2$, $D_c = 3.270$ g cm^{-3}, $F(000) = 1168$, μ(Mo-Kα) = 64.19 cm^{-1}, Mo-Kα radiation ($\lambda = 0.71073$ Å). Salt **2b**. $C_{86}H_{61}N_3O_{14}P_4Rh_6$, $M = 2101.8$, monoclinic, space group $C2/c$ (no. 15), with $a = 26.896(3)$, $b = 17.143(6)$, $c = 20.250(2)$ Å, $\beta = 118.80(1)°$, $U = 8181.9$ Å^3, $Z = 4$, $D_c = 1.706$ g cm^{-3}, $F(000) = 4160$, μ(Mo-Kα) = 13.05 cm^{-1}, Mo-Kα radiation ($\lambda = 0.71073$ Å).

Intensity measurements. The crystal samples, of dimensions 0.08 × 0.09 × 0.19 mm (**2a**) and 0.15 × 0.20 × 0.43 mm (**2b**), were mounted on glass fibres in air. The intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer using graphite monochromatized Mo-Kα radiation. The setting angles of 25 random intense reflections ($16 < 2\theta < 25°$) were used in both cases to determine by least-squares fit accurate cell constants and the orientation matrix. The collections were performed by the ω-scan method, within the limit $6 < 2\theta < 50°$. A variable scan speed (2–20° min^{-1}) and a variable scan range of $(\alpha + 0.35 \tan \theta)°$, with $\alpha = 2.5$ (**2a**) and 0.85° (**2b**), were used, with a 25% extension at each end of the scan range for background determination. Three standard intense reflections, monitored every 2 h, showed a moderate crystal decay upon X-ray exposure for **2b**, of *ca.* 10% at the end of the collection, while for **2a** a strong decay up to *ca.* 50% was observed. The intensities were corrected for Lorentz, polarization and decay effects. An empirical absorption correction was applied to the data, based on ψ scans (ψ 0–360° every 10°) of three suitable reflections with χ values close to 90°; the relative transmission factors had values in the range 1.00–0.85 (**2a**) and 1.00–0.93 (**2b**). The number of collected data was 1382 and 7495, for **2a** and **2b**, respectively. Two sets of 355 (**2a**) and 2170 (**2b**) significant $[I > 3\sigma(I)]$ independent reflections were used in the structure solutions and refinements.

Structure solution and refinement. The data reductions were performed on a PDP 11/73 computer, using the Enraf-Nonius Structure Determination Package (SDP PLUS)[12] and the physical constants tabulated therein. All the other crystallographic computations were carried out by using the SHELX programmes.[13]

The structures were solved by Patterson and Fourier methods, which revealed the locations of all the non-hydrogen atoms.

In the case of **2a** the anion lies in a special position (D_{3h} symmetry, *c* in Wyckoff notation) and the local three-fold axis causes a disorder involving the interbasal ligands (two bridging CO groups and the hydride). The unique independent ligand was treated as $\frac{2}{3}$ CO (with isotropic thermal parameters) and $\frac{1}{3}$ H (located in a calculated position with a Rh–H bond length of 1.85 Å and a thermal parameter of 3.9 Å^2, but not refined). A related disorder was observed for one of the two caesium cations, in the proximity of another special position of D_{3h} symmetry (*b* in Wyckoff notation). Two independent sites were occupied, one in position *e* and the second one in position *h* in Wyckoff notation. This gives rise to five positions disposed at the vertices of a trigonal bipyramidal polyhedron with the centre in position *b*. The two independent fractional cations were treated isotropically and their occupancies refined, with the constraint that the sum of the populations in the cell should result in two cations. The refined occupancy values were 0.0292 for the former site and 0.0541 for the second one.

The refinements were carried out by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. In **2a** all non-disordered atoms were treated anisotropically. In **2b** anisotropic thermal parameters were assigned to all atoms of the anion and to the cationic P atoms. The phenyl groups of the cations were treated as rigid bodies of idealized D_{6h} symmetry with individual isotropic thermal parameters for all the carbon atoms. The hydrogen atoms of the phenyl groups were located in ideal positions (C–H 0.95 Å, with $B = 6.32$ Å^2) after each cycle of refinement and their contribution to the structure factors was taken into account. Since no direct evidence was obtained from the Fourier-difference maps, the hydrido ligand in **2b** was located using Orpen's HYDEX program,[11] with a Rh–H interaction of 1.85 Å. It was also included in the final structure-factor calculation ($B = 6.32$ Å^2) but not refined.

The final Fourier-difference maps were rather flat, showing only some residual peaks not exceeding *ca.* 2.0 e Å^{-3} (**2a**) and 1.0 e Å^{-3} (**2b**).

Weights were assigned according to the formula $w = k/[\sigma^2(F_o) + gF_o^2]$, with $k = 5.5549$ and $g = 3.50 \times 10^{-5}$ for **2a** and $k = 1.8852$ and $g = 1.33 \times 10^{-4}$ for **2b**. The final values of the conventional agreement indices R and R' are 0.0427 and 0.0430 (**2a**) and 0.0491 and 0.0433 (**2b**), respectively. The final positional parameters for **2b** are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises a complete list of atomic coordinates for **2a**, H-atom coordinates for **2b**, and thermal parameters and remaining bond lengths and angles for both **2a** and **2b**.

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Table 4 Final positional parameters for the salt **2b**

Atom	*x*	*y*	*z*
Rh(1)	0.026 74(5)	0.100 42(8)	0.174 76(6)
Rh(2)	0.080 16(5)	0.098 74(9)	0.330 75(7)
Rh(3)	0.053 95(7)	−0.039 72(7)	0.251 89(8)
N(1)	0.000 00	0.053 0(9)	0.250 00
O(1)	0.074 3(5)	0.156 8(7)	0.076 9(6)
O(2)	0.197 8(5)	0.156(1)	0.435 7(8)
O(3)	0.133 2(7)	−0.168 0(9)	0.266 4(7)
O(4)	0.018 9(6)	−0.047 8(7)	0.082 8(6)
O(5)	0.074 4(5)	0.258 6(7)	0.254 9(7)
O(6)	0.130 0(7)	−0.055 8(9)	0.421 7(7)
O(7)	−0.074 8(5)	0.155 8(7)	0.034 2(7)
C(1)	0.057 1(6)	0.134 5(9)	0.113 8(8)
C(2)	0.153 1(8)	0.133(1)	0.396(1)
C(3)	0.101 9(9)	−0.119(1)	0.258 6(9)
C(4)	0.026 6(7)	−0.019 5(9)	0.137 7(9)
C(5)	0.062 5(6)	0.193(1)	0.253 0(9)
C(6)	0.100 0(9)	−0.024(1)	0.368(1)
C(7)	−0.052 7(8)	0.130(1)	0.099(1)
P(1)	0.873 5(2)	0.572 9(2)	0.291 3(2)
P(2)	0.831 4(2)	0.518 2(2)	0.133 6(2)
N(2)	0.872 3(4)	0.547 9(6)	0.215 6(6)
C(111)	0.896 8(4)	0.493 6(5)	0.356 3(6)
C(112)	0.912 2(4)	0.507 6(5)	0.431 6(6)
C(113)	0.926 0(4)	0.445 4(5)	0.481 9(6)
C(114)	0.924 4(4)	0.369 2(5)	0.456 8(6)
C(115)	0.909 1(4)	0.355 2(5)	0.381 5(6)
C(116)	0.895 3(4)	0.417 4(5)	0.331 3(6)
C(121)	0.923 1(3)	0.650 8(6)	0.332 5(5)
C(122)	0.920 1(3)	0.704 5(6)	0.382 2(5)
C(123)	0.959 8(3)	0.764 5(6)	0.412 1(5)
C(124)	1.002 7(3)	0.770 9(6)	0.392 3(5)
C(125)	1.005 7(3)	0.717 2(6)	0.342 6(5)
C(126)	0.966 0(3)	0.657 2(6)	0.312 7(5)
C(131)	0.806 6(4)	0.605 3(5)	0.278 8(5)
C(132)	0.785 3(4)	0.677 5(5)	0.245 2(5)
C(133)	0.731 7(4)	0.701 6(5)	0.232 0(5)
C(134)	0.699 4(4)	0.653 5(5)	0.252 3(5)
C(135)	0.720 7(4)	0.581 3(5)	0.285 8(5)
C(136)	0.774 3(4)	0.557 2(5)	0.299 1(5)
C(211)	0.815 8(4)	0.596 0(7)	0.067 1(4)
C(212)	0.841 3(4)	0.668 7(7)	0.092 1(4)
C(213)	0.832 3(4)	0.727 9(7)	0.040 2(4)
C(214)	0.797 7(4)	0.714 3(7)	−0.036 7(4)
C(215)	0.772 2(4)	0.641 6(7)	−0.061 7(4)
C(216)	0.781 3(4)	0.582 4(7)	−0.009 8(4)
C(221)	0.765 5(5)	0.478 3(5)	0.120 5(5)
C(222)	0.717 5(5)	0.525 7(5)	0.094 0(5)
C(223)	0.667 8(5)	0.496 8(5)	0.090 5(5)
C(224)	0.666 1(5)	0.420 7(5)	0.113 5(5)
C(225)	0.714 0(5)	0.373 3(5)	0.140 0(5)
C(226)	0.763 8(5)	0.402 1(5)	0.143 5(5)
C(231)	0.868 2(3)	0.444 7(6)	0.112 1(5)
C(232)	0.840 2(3)	0.390 8(6)	0.054 2(5)
C(233)	0.871 2(3)	0.336 0(6)	0.038 1(5)
C(234)	0.930 3(3)	0.335 2(6)	0.079 9(5)
C(235)	0.958 3(3)	0.389 1(6)	0.137 8(5)
C(236)	0.927 3(3)	0.443 9(6)	0.153 9(5)
H(1)	0.000 0	−0.108 1	0.250 0

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