Rhodium Carbonyl Clusters with Interstitial Nitrogen Atoms. Part 1. Crystal and Molecular Structure † of the Bis(triphenylphosphine)iminium Salt of the Anion Ennea-μ-carbonyl-hexacarbonyl-μ_6-nitrido-*polyhedro*-hexarhodate(1−)

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The title compound, $[N(PPh_3)_2][Rh_6N(CO)_{15}]$, crystallizes in the triclinic space group $P\bar{1}$, with cell constants a = 19.841(5), b = 9.156(3), c = 16.066(5) Å, α = 95.88(3), β = 70.12(3), γ = 87.99(3)°, and Z = 2. The structure solution and refinements have been based on 6 401 significant single-crystal *X*-ray counter data, the final conventional *R* value being 0.034. The anion contains a trigonal prism of rhodium atoms with a central nitrogen atom. The Rh–Rh bond lengths belong to two classes: those within the two basal triangles (mean 2.763 Å) and the interbasal ones (mean 2.828 Å). The Rh–N interactions have a mean value of 2.130 Å. Six carbonyl ligands are bound terminally, one per rhodium atom (mean Rh–C and C–O 1.863 and 1.134 Å), and nine bridge all the polyhedral edges (mean Rh–C and C–O 2.095 and 1.153 Å). The structure is discussed in comparison with those of related carbido-carbonyl cluster species.

Nitrido-carbonyl cluster compounds are a new class of clusters of which only few members are presently known. We recently reported the first examples of this family, namely the anions $[M_6N(CO)_{15}]^-$ (M = Co or Rh), with the nitrogen atom at the centre of a trigonal-prismatic cluster.[1] Other nitrides were subsequently characterized by Muetterties and co-workers,[2] with the nitrogen atoms in exposed rather than interstitial positions, *i.e.* the square-pyramidal species $[Fe_5H(N)(CO)_{14}]$, $[Fe_5N(CO)_{14}]^-$, and $[Fe_5H(N)(CO)_{13}]^{2-}$, and the 'butterfly' species $[Fe_4H(N)(CO)_{12}]$ and $[Fe_4N(CO)_{12}]^-$.

The anion $[Rh_6N(CO)_{15}]^-$ gives rise, by condensation with $[PtRh_4(CO)_{14}]^{2-}$, to a novel nitrido-carbonyl mixed-metal species, $[PtRh_{10}N(CO)_{21}]^{3-}$, containing an interstitial five-co-ordinate nitrogen,[3] and, by pyrolysis reactions, it yields large nitrido-carbonyl cluster compounds, which are presently under investigation.[4]

While a brief account of the crystal structure of $[N(PPh_3)_2][Co_6N(CO)_{15}]$ has been reported,[1] we describe here the complete results of an *X*-ray structural analysis of the isomorphous species $[N(PPh_3)_2][Rh_6N(CO)_{15}]$, which are discussed in comparison with the closely related carbido-carbonyl cluster compounds such as $[Rh_6C(CO)_{15}]^{2-}$ (ref. 5) and $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$.[6]

Experimental

Crystal Data.—$C_{51}H_{30}N_2O_{15}P_2Rh_6$, M = 1 590.2, yellow triclinic crystals, space group $P\bar{1}$ (no. 2), a = 19.841(5), b = 9.156(3), c = 16.066(5) Å, α = 95.88(3), β = 70.12(3), γ = 87.99(3)°, U = 2 722.6 Å^3, D_m = 1.91(3) g cm^{-3}, Z = 2, D_c = 1.94 g cm^{-3}, $F(000)$ = 1 540, Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) = 18.5 cm^{-1}.

Intensity Measurements.—The crystal sample was a multifaceted polyhedron of maximum dimensions 0.28 × 0.33 × 0.40 mm. The intensity data were recorded on a BASIC diffractometer,[7] with Mo-K_α graphite-monochromated radiation, by the ω-scan method, within the range $3 \leqslant \theta \leqslant 25°$. The scan range was 1.2° and the scan speed 3° min^{-1}; the background was measured at each side of the scan interval for half of the peak scanning time. No crystal decay was observed during the data collection. The total number of collected reflections was 9 586. The integrated intensities were corrected for Lorentz, polarization, and absorption effects. Transmission factors were computed using the method of Busing and Levy,[8] and were found in the range 0.64—0.75. After rejection of all data having $\sigma(I)/I > 0.30$, a final set of 6 401 reflections was used in the crystal-structure solution and refinements.

Structure Solution and Refinements.—The structure was solved using for the six metals the positional parameters previously determined for the cobalt atoms in isomorphous $[N(PPh_3)_2][Co_6N(CO)_{15}]$.[1] After a preliminary refinement, a successive difference-Fourier map showed the location of all the non-hydrogen atoms.

The refinements were carried out by the least-squares method in the block-diagonal approximation. The phenyl rings of the $[N(PPh_3)_2]^+$ cation were treated as rigid bodies (D_{6h} symmetry, C–C 1.392 Å). All the non-phenyl atoms were refined anisotropically. The phenyl hydrogen atoms were not refined but their contribution to the structure factors was taken into account by locating them in their ideal positions (C–H 1.08 Å) at the end of each cycle of refinement and with an isotropic thermal factor equal to that of the corresponding carbon atom. The final values of the reliability indices *R* and *R′* were both equal to 0.034.

The observations were weighted according to the formula $w = 1/(A + BF_o + CF_o^2)$, where in the final cycles A, B, and C had values of 9.916, −0.086, and 0.001 25, respectively, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 9 for the non-hydrogen atoms and from ref. 10 for hydrogen. Anomalous scattering effects were taken into account.[11] The final difference-Fourier map was flat, showing no residual peaks exceeding *ca.* 0.8 e Å^{-3}.

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† *Supplementary data available* (No. SUP 23447, 27 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Final positional parameters ($\times$ 10^4) for the salt $[N(PPh_3)_2][Rh_6N(CO)_{15}]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	3 357(1)	4 407(1)	810(1)	C(7)	3 816(4)	3 658(9)	−564(5)
Rh(2)	2 721(1)	3 321(1)	−387(1)	O(7)	4 362(3)	3 581(8)	−1 138(4)
Rh(3)	1 870(1)	4 513(1)	1 320(1)	C(8)	1 609(3)	3 863(8)	163(4)
Rh(4)	3 354(1)	1 607(1)	1 407(1)	O(8)	1 120(3)	3 953(7)	−66(4)
Rh(5)	2 744(1)	526(1)	195(1)	C(9)	2 553(4)	5 532(9)	1 940(5)
Rh(6)	1 890(1)	1 689(1)	1 899(1)	O(9)	2 501(3)	6 423(7)	2 526(4)
N	2 651(2)	2 693(5)	878(3)	C(10)	4 008(3)	3 297(7)	1 335(4)
C(1)	3 899(4)	6 069(8)	660(5)	O(10)	4 516(2)	3 550(6)	1 512(4)
O(1)	4 227(3)	7 053(7)	571(4)	C(11)	2 678(3)	1 223(7)	−950(4)
C(2)	2 803(4)	4 111(8)	−1 432(5)	O(11)	2 608(3)	702(6)	−1 596(3)
O(2)	2 875(4)	4 603(7)	−2 078(4)	C(12)	1 180(3)	3 506(8)	2 319(4)
C(3)	1 261(4)	6 219(9)	1 595(6)	O(12)	633(3)	3 836(6)	2 890(4)
O(3)	881(4)	7 239(8)	1 776(6)	C(13)	3 849(3)	488(7)	97(4)
C(4)	3 838(4)	349(8)	1 886(4)	O(13)	4 403(2)	32(7)	−382(3)
O(4)	4 115(3)	−439(6)	2 200(3)	C(14)	1 622(3)	517(8)	868(5)
C(5)	2 838(4)	−1 459(7)	−243(5)	O(14)	1 144(3)	−9(7)	738(4)
O(5)	2 906(3)	−2 673(6)	−520(4)	C(15)	2 554(4)	2 196(9)	2 655(5)
C(6)	1 358(4)	533(9)	2 741(5)	O(15)	2 490(3)	2 509(9)	3 394(4)
O(6)	1 053(4)	−175(7)	3 262(4)				
P(1)	−1 698(1)	1 088(2)	3 650(1)	C(135)	−272(2)	2 473(7)	1 446(4)
P(2)	−3 314(1)	917(2)	4 353(1)	C(136)	−581(2)	1 960(6)	2 268(3)
N(1)	−2 535(2)	1 461(6)	4 032(4)	C(211)	−3 744(2)	1 071(5)	3 543(3)
C(111)	−1 288(2)	1 973(6)	4 397(3)	C(212)	−4 122(2)	−52(4)	3 304(3)
C(112)	−619(2)	1 424(4)	4 379(3)	C(213)	−4 458(2)	132(4)	2 686(3)
C(113)	−291(2)	2 141(5)	4 928(3)	C(214)	−4 415(2)	1 441(5)	2 306(3)
C(114)	−631(2)	3 405(6)	5 495(3)	C(215)	−4 037(2)	2 564(4)	2 544(3)
C(115)	−1 299(2)	3 953(4)	5 513(3)	C(216)	−3 701(2)	2 379(4)	3 163(3)
C(116)	−1 628(2)	3 237(5)	4 964(3)	C(221)	−3 858(2)	2 123(5)	5 333(2)
C(121)	−1 414(4)	−831(5)	3 488(3)	C(222)	−3 575(2)	2 506(5)	6 001(3)
C(122)	−1 185(3)	−1 636(5)	2 645(3)	C(223)	−3 978(2)	3 445(5)	6 759(2)
C(123)	−996(3)	−3 139(5)	2 545(3)	C(224)	−4 665(2)	4 002(5)	6 849(2)
C(124)	−1 035(4)	−3 836(5)	3 289(3)	C(225)	−4 948(2)	3 619(5)	6 181(3)
C(125)	−1 264(3)	−3 031(5)	4 132(3)	C(226)	−4 544(2)	2 679(5)	5 423(2)
C(126)	−1 453(3)	−1 528(5)	4 231(3)	C(231)	−3 383(3)	−945(3)	4 624(2)
C(131)	−1 316(3)	1 802(6)	2 597(3)	C(232)	−3 036(2)	−2 101(4)	3 964(2)
C(132)	−1 743(2)	2 157(7)	2 105(4)	C(233)	−3 077(2)	−3 545(4)	4 166(2)
C(133)	−1 434(2)	2 670(6)	1 283(3)	C(234)	−3 464(3)	−3 834(3)	5 026(2)
C(134)	−698(3)	2 828(6)	953(3)	C(235)	−3 810(2)	−2 679(4)	5 685(2)
				C(236)	−3 769(2)	−1 234(4)	5 484(2)

The results of the refinements are reported in Table 1. All computations were performed on a UNIVAC 1100/80 computer using local programs.

Results and Discussion

The structure consists of discrete $[Rh_6N(CO)_{15}]^-$ anions and bis(triphenylphosphine)iminium cations in the ratio 1 : 1, separated by normal van der Waals contacts.

The anion is illustrated in the Figure. It contains a trigonal prism of rhodium atoms with an interstitial nitrogen atom. Of the 15 carbonyl ligands six are terminally bound, one to each rhodium atom, and nine are bridging all the edges of the metallic polyhedron. The overall idealized symmetry of the anion is D_{3h}. Bond distances and angles are reported in Table 2.

The metallic skeleton and the carbonyl stereochemistry of the anion is of the same type present in $[Co_6N(CO)_{15}]^-$ and in the carbido-species $[M_6C(CO)_{15}]^{2-}$ (M = Co [12] or Rh [5]). Other related compounds are $[Co_6C(\mu_3\text{-}S)_2(CO)_{12}]$ [13] and $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$,[6] both containing a carbide atom at the centre of a trigonal-prismatic hole.

The Rh–Rh bond lengths can be assigned to two classes: (*i*) those within the two basal triangles, with a mean value of 2.763 Å, and (*ii*) the axial or interbasal ones, which are longer, with a mean value of 2.828 Å. The same type of elongation in the direction of the three-fold axis is also observed in the other known trigonal-prismatic species, and it is particularly evident in $[Co_6C(\mu_3\text{-}S)_2(CO)_{12}]$ (2.67 *vs.* 2.44 Å),[13] where the interbasal edges are not bridged by ligands. The trigonal-prismatic anion $[Pt_6(CO)_{12}]^{2-}$, without interstitial atoms, also shows the same marked elongation of the unbridged axial edges (3.04 *vs.* 2.77 Å).[14]

The six terminal carbonyl ligands are nearly in *trans* positions with respect to the interstitial nitride, with N–Rh–C angles in the range 169—173°. The mean values of the Rh–C and C–O interactions within these ligands are 1.863 and 1.134 Å, respectively. The nine edge-bridging CO groups are all almost symmetric and belong to two sets: those bridging the edges of the basal triangles and those on the interbasal edges, with mean Rh–C bond lengths of 2.117 and 2.050 Å, respectively. The mean value of the C–O interactions for the bridging groups is 1.153 Å.

The interstitial nitrogen atom shows almost identical bonds with the six metal atoms, in the range 2.123(5)—2.138(5) Å, mean 2.130 Å. Assigning to the rhodium atoms a radius of 1.39 Å (one half of the overall mean Rh–Rh bond length, of 2.785 Å) we obtain an apparent radius for the interstitial nitride of 0.74 Å, somewhat larger than the corresponding radius in $[Co_6N(CO)_{15}]^-$ (0.67 Å).[1]

It is particularly interesting to compare in detail the structural parameters of this nitride species with the corresponding

Table 2. Bond distances (Å) and angles (°) within the salt $[N(PPh_3)_2][Rh_6N(CO)_{15}]$

Rh(1)–Rh(2)	2.761(1)	Rh(1)–C(1)	1.883(8)	Rh(1)–C(10)	2.060(8)	C(10)–O(10)	1.161(10)
Rh(1)–Rh(3)	2.775(1)	Rh(2)–C(2)	1.856(9)	Rh(4)–C(10)	2.040(7)	C(11)–O(11)	1.150(9)
Rh(2)–Rh(3)	2.770(1)	Rh(3)–C(3)	1.861(8)	Rh(2)–C(11)	2.056(7)	C(12)–O(12)	1.164(8)
Rh(4)–Rh(5)	2.744(1)	Rh(4)–C(4)	1.858(9)	Rh(5)–C(11)	2.053(8)		
Rh(4)–Rh(6)	2.736(1)	Rh(5)–C(5)	1.860(7)	Rh(3)–C(12)	2.049(7)		
Rh(5)–Rh(6)	2.761(1)	Rh(6)–C(6)	1.861(9)	Rh(6)–C(12)	2.040(7)		
Rh(1)–Rh(4)	2.827(1)	Rh(1)–C(7)	2.111(7)	C(1)–O(1)	1.122(11)	P(1)–N(1)	1.575(5)
Rh(2)–Rh(5)	2.818(1)	Rh(2)–C(7)	2.131(8)	C(2)–O(2)	1.140(11)	P(2)–N(1)	1.570(6)
Rh(3)–Rh(6)	2.839(1)	Rh(2)–C(8)	2.099(7)	C(3)–O(3)	1.126(11)		
		Rh(3)–C(8)	2.128(9)	C(4)–O(4)	1.145(11)	P(1)–C(111)	1.807(6)
Rh(1)–N	2.126(5)	Rh(3)–C(9)	2.125(10)	C(5)–O(5)	1.140(9)	P(1)–C(121)	1.792(5)
Rh(2)–N	2.130(6)	Rh(1)–C(9)	2.105(7)	C(6)–O(6)	1.133(11)	P(1)–C(131)	1.803(5)
Rh(3)–N	2.123(5)	Rh(4)–C(13)	2.127(6)			P(2)–C(211)	1.796(6)
Rh(4)–N	2.131(6)	Rh(5)–C(13)	2.143(7)	C(7)–O(7)	1.153(8)	P(2)–C(221)	1.808(4)
Rh(5)–N	2.138(5)	Rh(5)–C(14)	2.120(7)	C(8)–O(8)	1.158(11)	P(2)–C(231)	1.802(4)
Rh(6)–N	2.130(5)	Rh(6)–C(14)	2.110(9)	C(9)–O(9)	1.155(11)		
		Rh(6)–C(15)	2.109(10)	C(13)–O(13)	1.141(7)		
		Rh(4)–C(15)	2.094(7)	C(14)–O(14)	1.149(11)		
				C(15)–O(15)	1.154(10)		
Rh(1)–C(1)–O(1)	179.4(8)	Rh(5)–C(14)–O(14)	137.3(6)	Rh(4)–C(13)–Rh(5)	80.0(2)	Rh(3)–Rh(1)–C(1)	124.5(2)
Rh(2)–C(2)–O(2)	177.9(9)	Rh(6)–C(14)–O(14)	140.8(6)	Rh(5)–C(14)–Rh(6)	81.5(3)	Rh(1)–Rh(2)–C(2)	123.9(3)
Rh(3)–C(3)–O(3)	178.5(8)	Rh(6)–C(15)–O(15)	137.9(6)	Rh(6)–C(15)–Rh(4)	81.2(3)	Rh(2)–Rh(3)–C(3)	124.9(3)
Rh(4)–C(4)–O(4)	177.7(6)	Rh(4)–C(15)–O(15)	140.6(7)			Rh(6)–Rh(4)–C(4)	120.3(2)
Rh(5)–C(5)–O(5)	179.0(6)			Rh(1)–C(10)–Rh(4)	87.2(3)	Rh(4)–Rh(5)–C(5)	122.6(3)
Rh(6)–C(6)–O(6)	177.9(10)	Rh(1)–C(10)–O(10)	135.5(6)	Rh(2)–C(11)–Rh(5)	86.6(3)	Rh(5)–Rh(6)–C(6)	122.7(3)
		Rh(4)–C(10)–O(10)	137.3(6)	Rh(3)–C(12)–Rh(6)	87.9(2)		
Rh(1)–C(7)–O(7)	140.0(7)	Rh(2)–C(11)–O(11)	136.0(6)			P(1)–N(1)–P(2)	149.2(4)
Rh(2)–C(7)–O(7)	138.5(7)	Rh(5)–C(11)–O(11)	137.2(6)	N–Rh(1)–C(1)	171.2(3)		
Rh(2)–C(8)–O(8)	139.1(6)	Rh(3)–C(12)–O(12)	136.1(6)	N–Rh(2)–C(2)	172.5(3)	N(1)–P(1)–C(111)	110.1(3)
Rh(3)–C(8)–O(8)	138.3(5)	Rh(6)–C(12)–O(12)	135.9(6)	N–Rh(3)–C(3)	173.0(3)	N(1)–P(1)–C(121)	115.2(3)
Rh(3)–C(9)–O(9)	137.9(7)			N–Rh(4)–C(4)	168.0(3)	N(1)–P(1)–C(131)	110.0(3)
Rh(1)–C(9)–O(9)	139.1(7)	Rh(1)–C(7)–Rh(2)	81.2(2)	N–Rh(5)–C(5)	171.2(3)	N(1)–P(2)–C(211)	111.7(3)
Rh(4)–C(13)–O(13)	140.1(7)	Rh(2)–C(8)–Rh(3)	81.9(3)	N–Rh(6)–C(6)	169.4(3)	N(1)–P(2)–C(221)	108.4(3)
Rh(5)–C(13)–O(13)	139.8(6)	Rh(3)–C(9)–Rh(1)	82.0(3)			N(1)–P(2)–C(231)	116.0(3)

Table 3. Selected mean bond distances (Å) within rhodium trigonal-prismatic clusters

Distance	$[Rh_6N(CO)_{15}]^-$	$[Rh_6C(CO)_{15}]^{2-}$	$[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$
Rh-Rh (basal)	2.763	2.776	2.765
Rh-Rh (interbasal)	2.828	2.817	2.810
Rh-Rh (overall)	2.785	2.790	2.780
Rh-C,N (interstitial)	2.130	2.134	2.127
Rh-C (terminal)	1.863	1.89	1.88
C-O (terminal)	1.134	1.13	1.18
Rh-C (basal bridging)	2.117	2.12	2.13
C-O (basal bridging)	1.151	1.14	1.17
Rh-C (interbasal bridging)	2.050	2.04	2.05
C-O (interbasal bridging)	1.158	1.17	1.18

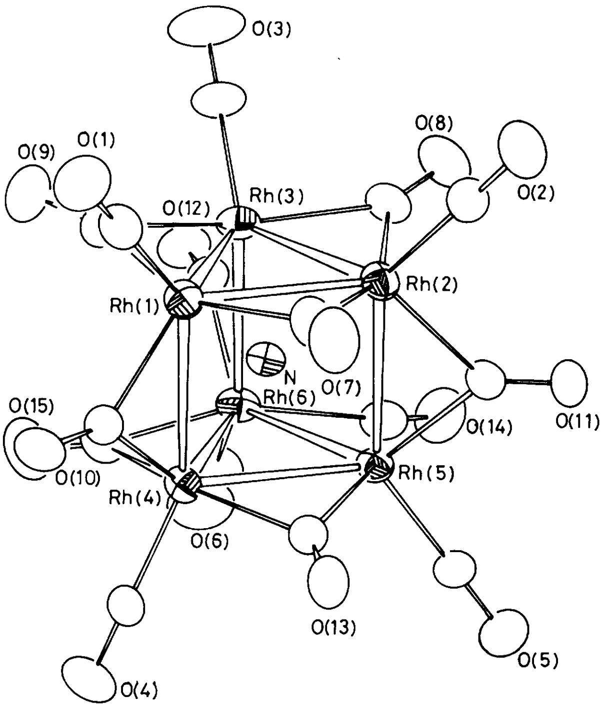

Figure. A view of the anion $[Rh_6N(CO)_{15}]^-$. The carbonyl groups are indicated by the numbers of their oxygen atoms

interactions in the strictly related carbide anion $[Rh_6C(CO)_{15}]^{2-}$ and in the analogous $Rh_6C(CO)_{15}$ moiety of the neutral compound $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$, in which two Cu(NCMe) groups cap the triangular faces of the prism. A comparison of the mean bond parameters within these species is given in Table 3. As can be seen, the corresponding interactions are very similar in the three compounds. The nitride species exhibits the largest difference between basal and interbasal metal-metal bonds. The average Rh-Rh bond length slightly decreases in the order $[Rh_6C(CO)_{15}]^{2-} > [Rh_6N(CO)_{15}]^- > [Cu_2Rh_6C(CO)_{15}(NCMe)_2]$ with decreasing net charge (Rh-Rh overall mean values 2.790, 2.785, and 2.780 Å, respectively).

The values of the metal-carbonyl interactions in the three species are difficult to interpret, since they do not show the expected trend, *i.e.* lengthening of the Rh-C and shortening of the C-O bonds on passing from the dianion to the neutral species, as suggested also by the increasing values of the CO stretching frequencies in their i.r. spectra.

The apparent radius of the interstitial atoms is the same in the three species (0.74 Å), and it seems determined by the cage dimensions. A comparison with the relevant covalent radii (0.77 Å for C and 0.70 Å for N) indicates that the interstitial atom can moderately contract or expand in order to meet the steric requirements of the cavity. This effect is more relevant in octahedral species, which exhibit a smaller interstitial hole, less suitable than a trigonal-prismatic one for a second period element. In the octahedral $[Rh_6C(CO)_{13}]^{2-}$ anion, for instance, the apparent radius of carbon is 0.60 Å [15] and this causes a lengthening of the polyhedral edges, observed also in the octahedral moieties of $[Os_{10}C(CO)_{24}]^{2-}$,[16] $[Re_7C(CO)_{21}]^{3-}$,[17] and $[Re_8C(CO)_{24}]^{2-}$.[18]

Finally, the bonding parameters within the $[N(PPh_3)_2]^+$ cation are normal: mean P-N 1.572, mean P-C 1.801 Å; P-N-P 149.2(4)°.

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