Molecular and Crystal Structure of Tris(acetonitrile)nitrosylbis(triphenylphosphine)rhodium(III) Dication as its Hexafluorophosphate Salt †

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Crystals of $[Rh(NCMe)_3(NO)(PPh_3)_2][PF_6]_2$ are monoclinic, space group $P2_1/n$, with $a = 14.053(8)$, $b = 27.512(15)$, $c = 11.914(8)$ Å, $\beta = 97.29(5)°$, and $Z = 4$. The structure has been elucidated by the analysis of 8 502 observed intensities recorded at *ca.* 215 K on a four-circle diffractometer, and refined by least squares to R 0.075. In the cation the metal is octahedrally bound to *trans*-phosphorus atoms (mean Rh–P 2.405 Å) and three acetonitrile ligands [Rh–N 2.030(7), 2.104(7), and 2.308(8) Å], the last lying *trans* to the nitrosyl function [Rh–NO 2.026(8) Å] which acts as the one-electron donor $[NO]^-$ [Rh–N–O 118.4(6)°]. The two hexafluorophosphate counter ions exhibit differing thermal activity which is correlated to their crystal environments.

RECENT synthetic work [1] by one of the groups of this department has yielded a model series of five-co-ordinate nitrosylrhodium dications $[Rh(NCMe)_4(NO)]^{2+}$ (1), $[Rh(NCMe)_2(NO)(PPh_3)_2]^{2+}$ (2), and $[Rh(NO)(dppe)_2]^{2+}$ (3; dppe = $Ph_2PCH_2CH_2PPh_2$). The $[RhL_4]^{2+}$ fragment is a 15-electron system, allowing either bent ($[NO]^-$, 1 e) or linear ($[NO]^+$, 3 e) nitrosyl co-ordination to be envisaged; indeed, measurement of $\bar{\nu}(^{14}NO)$ followed by empirical correction after the method of Haymore and Ibers [2] suggested the former bonding mode for (1) and (2), the latter for (3).

We therefore undertook to unequivocally assign the nature of the nitrosyl co-ordination in these complexes *via X*-ray diffraction. Suitable crystals, thought to be of (2), were obtained as the hexafluorophosphate salt. The diffraction study, however, has subsequently revealed the presence of an additional co-ordinated acetonitrile ligand.

EXPERIMENTAL

The sample was prepared in an analogous manner [1] to the $[BF_4]^-$ salt, and was recrystallised from acetonitrile–diethyl ether as bright green transparent plates. On standing in air the crystals soon revert to powder, and since this could be interpreted as a possible indication of solvent weakly held in the lattice a freshly recrystallised specimen (0.2 × 0.2 × 0.05 mm) was mounted in a 0.5-mm Lindemann capillary in an atmosphere of nitrogen–acetonitrile–diethyl ether. The external crystal faces were {001}, {1$\bar{1}$0}, and {110} and their inversion equivalents. Space group and initial cell dimensions were determined photographically.

The crystal was then transferred to a Syntex $P2_1$ four-circle autodiffractometer equipped with a ϕ-axis low-temperature device (N_2 stream) and slowly cooled to *ca.* 215 K. Setting and data collection followed an established procedure.[3] 15 Reflections, $14 < 2\theta < 26°$, taken from a 30-m rotation photograph, were centred in 2θ, ω, and χ and used to generate the real space vectors and intervector cosines by which the unit cell was chosen by inspection. The orientation matrix, cell dimensions, and associated errors were calculated by a least-squares fit. For data collection, $2.9 \leqslant 2\theta \leqslant 60.0$ using graphite-monochromated Mo-K_α *X*-radiation ($\lambda_{\alpha1}$ 0.709 26, $\lambda_{\alpha2}$ 0.713 54 Å) and a θ—2θ scan in 96 steps. Peaks were scanned from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$ at speeds between 0.042 5 and 0.488 3 ° s^{-1}, the precise rate being dependent on an initial 2-s peak count in which 200.0 and 2 000.0 were used as threshold counts. Three check reflections ($1\bar{8}\bar{3}$, $\bar{4}$ 11 2, and $50\bar{1}$) were re-monitored once every 28 reflections, but subsequent analysis [4] of their net counts as individual functions of time revealed no significant crystal decomposition or movement or source variance over the *ca.* 343-h *X*-ray exposure. Of 13 432 independent reflections measured ($+h,+k,\pm l$ with equivalent $0kl$ and $0kl$ intensities afterwards merged), 9 243 had $I \geqslant 1.0\sigma(I)$ and were retained. No absorption correction was applied.

Crystal Data.—$C_{42}H_{39}N_4OP_2Rh{\cdot}2PF_6$, $M = 1\,070.6$, Monoclinic, $a = 14.053(8)$, $b = 27.512(15)$, $c = 11.914(8)$ Å, $\beta = 97.29(5)°$, $U = 4\,569(5)$ Å^3, D_m not measured, $Z = 4$, $D_c = 1.556$ g cm^{-1}, $F(000) = 2\,160$, $\mu(\text{Mo-}K_{\bar{\alpha}}) = 6.0$ cm^{-1}, space group $P2_1/n$ (alternative setting of $P2_1/c$, C_{2h}^5, no. 14).

Intensities were corrected for Lorentz and polarisation effects and the structure was solved by conventional Patterson (Rh) and iterative refinement–electron-density difference syntheses. Weights were applied according to $w^{-1} = xy$ with $x = F_o/a$ if $F_o > a$, $x = 1$ if $F_o \leqslant a$, $y = b/\sin\theta$ if $\sin\theta < b$, or $y = 1$ if $\sin\theta \geqslant b$, in which a and b took values of 70.0 and 0.3 respectively. Phenyl hydrogen atoms were introduced into calculated positions with r(C–H) 1.0 Å and U_H 0.05 Å^2,§ and, although not themselves

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† No reprints available.

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§ The isotropic temperature factor is defined as $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

[1] N. G. Connelly, M. Green, and T. A. Kuc, *J.C.S. Chem. Comm.*, 1974, 542; N. G. Connelly, P. T. Draggett, M. Green, and T. A. Kuc, *J.C.S. Dalton*, 1977, 70.

[2] B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060.

[3] A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[4] A. G. Modinos, DRSYN, a Fortran program for data analysis.

TABLE 1

Final co-ordinates (fractional: × 10^5, Rh and P; × 10^4, C, N, O, and F) of the non-hydrogen atoms

Atom	*x*	*y*	*z*
Rh	22 184(4) *	11 439(2)	8 698(5)
N(1)	3 278(5)	788(3)	1 859(5)
C(1)	3 931(6)	662(3)	2 441(8)
C(11)	4 794(7)	505(5)	3 181(11)
N(2)	1 140(5)	1 516(3)	−19(6)
C(2)	467(6)	1 692(3)	−470(7)
C(21)	−416(7)	1 906(4)	−1 044(11)
N(3)	3 372(5)	1 633(3)	235(6)
C(3)	3 837(7)	1 859(4)	−268(9)
C(31)	4 417(11)	2 146(7)	−987(14)
N(4)	1 243(5)	683(3)	1 402(6)
O(4)	477(5)	675(3)	910(6)
P(1)	20 393(14)	16 818(7)	24 169(16)
C(101)	3 012(6)	1 682(3)	3 575(6)
C(102)	3 950(6)	1 746(4)	3 337(7)
C(103)	4 712(7)	1 792(4)	4 206(9)
C(104)	4 520(8)	1 807(5)	5 323(9)
C(105)	3 584(8)	1 756(5)	5 558(8)
C(106)	2 838(7)	1 698(4)	4 710(7)
C(111)	1 915(6)	2 331(3)	2 109(7)
C(112)	2 082(6)	2 529(3)	1 074(7)
C(113)	2 102(7)	3 031(3)	937(8)
C(114)	1 946(7)	3 333(3)	1 809(9)
C(115)	1 750(7)	3 139(3)	2 833(9)
C(116)	1 756(6)	2 642(3)	2 995(7)
C(121)	980(6)	1 487(3)	3 006(7)
C(122)	104(6)	1 728(4)	2 693(8)
C(123)	−723(7)	1 519(5)	3 011(10)
C(124)	−708(8)	1 086(5)	3 618(9)
C(125)	161(8)	850(4)	3 911(9)
C(126)	1 012(7)	1 059(4)	3 622(7)
P(2)	23 872(14)	6 094(7)	−6 919(15)
C(201)	1 390(5)	700(3)	−1 799(6)
C(202)	1 345(6)	1 127(4)	−2 447(7)
C(203)	531(7)	1 225(4)	−3 202(8)
C(204)	−251(8)	893(4)	−3 318(9)
C(205)	−202(6)	479(4)	−2 671(8)
C(206)	623(6)	381(4)	−1 913(7)
C(211)	3 504(6)	677(3)	−1 298(7)
C(212)	4 365(7)	656(4)	−551(7)
C(213)	5 253(7)	661(4)	−967(9)
C(214)	5 283(6)	703(4)	−2 112(8)
C(215)	4 442(7)	738(4)	−2 860(8)
C(216)	3 543(6)	724(3)	−2 468(7)
C(221)	2 374(6)	−42(3)	−422(7)
C(222)	2 201(6)	−244(3)	617(6)
C(223)	2 145(6)	−746(3)	737(8)
C(224)	2 266(7)	−1 052(3)	−166(8)
C(225)	2 467(7)	−847(3)	−1 184(8)
C(226)	2 512(7)	−349(3)	−1 321(7)
P(3)	15 607(21)	27 034(11)	68 585(27)
F(31)	1 805(8)	3 117(4)	7 779(8)
F(32)	1 306(8)	2 303(4)	5 906(10)
F(33)	521(9)	2 637(6)	7 120(14)
F(34)	2 555(11)	2 806(6)	6 462(17)
F(35)	1 929(20)	2 316(6)	7 696(18)
F(36)	1 228(15)	3 105(6)	5 918(14)
P(4)	72 007(17)	2 342(10)	52 707(19)
F(41)	8 272(5)	85(3)	5 123(7)
F(42)	6 129(4)	395(3)	5 421(5)
F(43)	7 436(5)	236(4)	6 616(5)
F(44)	6 927(5)	237(4)	3 934(5)
F(45)	7 507(6)	786(3)	5 249(7)
F(46)	6 890(6)	−323(3)	5 304(8)

* Estimated standard deviations are given in parentheses throughout this paper.

refined, were positionally updated every fourth cycle. No attempt was made to locate the nine methyl hydrogens.

In the final stages of refinement the criterion by which a reflection is deemed 'observed' was slightly modified such that all data with $I > 2.5\sigma(I)$ were used (7 120), together with those 1 382 reflections with $2.5\sigma \geqslant I \geqslant 1.0\sigma$ that satisfied the requirement $|F_o| > F_c$. This procedure has the effect of increasing the data : variable ratio (and hence decreasing the error in atomic parameters) but avoids the contribution from erroneously measured reflections. Refinement continued until no significant change occurred in any variable. (All the refined atoms were allowed anisotropic thermal motion.) Final residuals of R 0.075 and R' 0.095 were recorded at a data : variable ratio better than 14.6 : 1. The ultimate difference Fourier (0.29 Å resolution) revealed a maximum of *ca.* 1.14 eÅ^{-3} at *ca.* 0.069 6, 0.302 3, 0.661 7.

Atomic-scattering factors for neutral atoms were taken from refs. 5 (Rh and F), 6 (P, N, O, and C), and 7 (H), with all the non-H sets corrected for both components of anomalous dispersion.[8] Table 1 lists the final atomic co-ordinates for refined atoms. Appendices A, B, and C respectively contain the anisotropic thermal parameters, calculated hydrogen-atom positions, and a comparison of $|F_o|$ and F_c.* We are grateful to the University of London Computer Centre for use of the '*X*-RAY '72' crystallographic package [9] with which all the calculations were performed.

DISCUSSION

The asymmetric fraction of the unit cell contains one $[Rh(NCMe)_3(NO)(PPh_3)_2]^{2+}$ and two independent $[PF_6]^-$ ions, none of which has crystallographically imposed symmetry. Interatomic distances (uncorrected for thermal effects) and interbond angles are presented in Tables 2 and 3 respectively.

The $[Rh(NCMe)_3(NO)(PPh_3)_2]^{2+}$ *Dication.*—The central portion of this ion and atomic-numbering scheme adopted are shown in Figure 1. The crystallographic analysis demonstrates that the cation carries a third acetonitrile ligand and is not the five-co-ordinate species (2) described by Connelly *et al.*[1] The overall geometry is octahedral with two pairs of like ligands mutually *trans*. Two extra electrons are available to the metal atom by virtue of the additional cyanide ligand, thereby favouring nitrosyl co-ordination as the one-electron donor $[NO]^-$; the metal is thus in the formal oxidation state (III).

As far as we are aware there are no previously reported structural results on six-co-ordinate rhodium(III) nitrosyls. The Rh–N(4) distance [2.026(8) Å], is, however, a simple extension of the corresponding values of 1.818(4) Å in the four-co-ordinate species [10,] † $[Rh(NO)_2(PPh_3)_2]^+$ and 1.905(15) Å in the five-co-ordinate species [11] [Rh{PhP-

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* All the Appendices may be recovered from Supplementary Publication No. SUP 22135 (45 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

† We are aware of the difficulty in assigning a formal oxidation state to the metal in this structure [N–O 1.158(6) Å, Rh–N–O 158.9(4)°] and the associated implications for atomic radius.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[8] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[9] Technical Report TR-192, the Computer Science Centre, University of Maryland, June 1972.

[10] J. A. Kaduk and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3070.

[11] T. E. Nappier, jun., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 4194.

$(CH_2CH_2CH_2PPh_2)_2\}Cl(NO)]^+$ or 1.912(10) Å in $[RhCl_2(NO)(PPh_3)_2]$.[12] The N(4)–O(4) separation [1.159(10) Å] and Rh–N–O angle [118.4(6)°], are both entirely consistent with the formal description $[NO]^-$.[13] The plane defined by the atomic sequence RhN(4)O(4) bears no special relation to the metal co-ordination geometry, being twisted *ca.* 15.7° from N(4)RhN(2) towards N(4)RhP(2).

TABLE 2

Interatomic distances (Å)

Rh–N(1)	2.030(7)	C(101)–C(102)	1.394(12)
Rh–N(2)	2.014(7)	C(102)–C(103)	1.398(13)
Rh–N(3)	2.308(8)	C(103)–C(104)	1.392(16)
Rh–N(4)	2.026(8)	C(104)–C(105)	1.387(17)
Rh–P(1)	2.402(2)	C(105)–C(106)	1.370(13)
Rh–P(2)	2.407(2)	C(106)–C(101)	1.406(12)
		C(111)–C(112)	1.394(13)
N(1)–C(1)	1.132(11)	C(112)–C(113)	1.393(13)
C(1)–C(11)	1.470(14)	C(113)–C(114)	1.369(14)
N(2)–C(2)	1.136(11)	C(114)–C(115)	1.390(15)
C(2)–C(21)	1.463(13)	C(115)–C(116)	1.380(12)
N(3)–C(3)	1.127(13)	C(116)–C(111)	1.399(12)
C(3)–C(31)	1.483(20)	C(121)–C(122)	1.406(12)
N(4)–O(4)	1.159(10)	C(122)–C(123)	1.391(15)
		C(123)–C(124)	1.393(18)
P(1)–C(101)	1.814(8)	C(124)–C(125)	1.387(16)
P(1)–C(111)	1.827(9)	C(125)–C(126)	1.407(15)
P(1)–C(121)	1.807(9)	C(126)–C(121)	1.386(13)
P(2)–C(201)	1.816(7)	C(201)–C(202)	1.403(12)
P(2)–C(211)	1.819(9)	C(202)–C(203)	1.388(12)
P(2)–C(221)	1.820(9)	C(203)–C(204)	1.422(16)
		C(204)–C(205)	1.373(16)
P(3)–F(31)	1.588(10)	C(205)–C(206)	1.402(12)
P(3)–F(32)	1.589(11)	C(206)–C(201)	1.384(12)
P(3)–F(33)	1.543(14)	C(211)–C(212)	1.410(11)
P(3)–F(34)	1.556(17)	C(212)–C(213)	1.400(14)
P(3)–F(35)	1.506(19)	C(213)–C(214)	1.376(14)
P(3)–F(36)	1.600(17)	C(214)–C(215)	1.391(12)
		C(215)–C(216)	1.403(14)
P(4)–F(41)	1.592(7)	C(216)–C(211)	1.407(12)
P(4)–F(42)	1.601(7)	C(221)–C(222)	1.405(11)
P(4)–F(43)	1.596(7)	C(222)–C(223)	1.393(11)
P(4)–F(44)	1.590(7)	C(223)–C(224)	1.394(13)
P(4)–F(45)	1.578(8)	C(224)–C(225)	1.399(14)
P(4)–F(46)	1.597(8)	C(225)–C(226)	1.384(13)
		C(226)–C(221)	1.398(12)

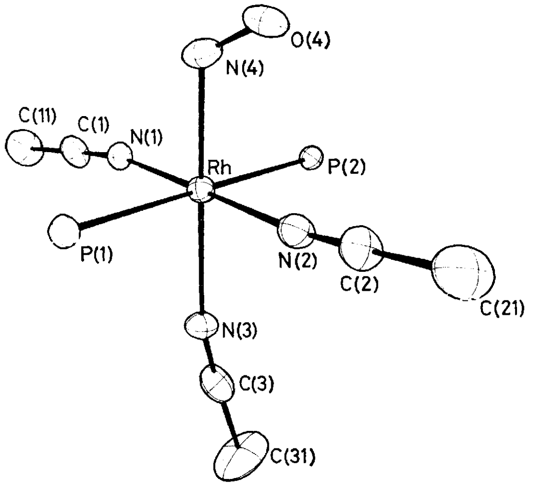

FIGURE 1 Perspective view of the $[Rh(NCMe)_3(NO)(PPh_3)_2]^{2+}$ cation. Phenyl rings are not shown for clarity. Boundary ellipses represent 50% electron probability

Only one previous example of a crystallographically studied acetonitrile complex of rhodium is known.[14] The $[Rh(C_2H_4)_3(NCMe)_2]^+$ cation has a trigonal-bipyramidal (precise D_{3h}) geometry with the cyanide ligands along the C_3 axis. Rh–N for this five-co-ordinate rhodium(I)

TABLE 3

Interbond angles (°)

N(1)–Rh–N(2)	176.3(3)	P(2)–C(201)–C(202)	119.5(6)
N(1)–Rh–N(3)	88.7(3)	P(2)–C(201)–C(206)	120.3(6)
N(1)–Rh–N(4)	89.5(3)	C(202)–C(201)–C(206)	119.8(7)
N(1)–Rh–P(1)	89.6(2)	C(201)–C(202)–C(203)	119.6(9)
N(1)–Rh–P(2)	91.0(2)	C(202)–C(203)–C(204)	120.2(10)
N(2)–Rh–N(3)	92.5(3)	C(203)–C(204)–C(205)	119.6(9)
N(2)–Rh–N(4)	89.3(3)	C(204)–C(205)–C(206)	120.0(9)
N(2)–Rh–P(1)	86.9(2)	C(205)–C(206)–C(201)	120.8(9)
N(2)–Rh–P(2)	92.6(2)		
N(3)–Rh–N(4)	177.0(3)	P(2)–C(211)–C(212)	117.4(6)
N(3)–Rh–P(1)	92.2(2)	P(2)–C(211)–C(216)	123.2(6)
N(3)–Rh–P(2)	87.7(2)	C(212)–C(211)–C(216)	119.4(8)
N(4)–Rh–P(1)	90.2(2)	C(211)–C(212)–C(213)	120.5(8)
N(4)–Rh–P(2)	89.8(2)	C(212)–C(213)–C(214)	119.6(8)
P(1)–Rh–P(2)	179.46(7)	C(213)–C(214)–C(215)	120.7(9)
		C(214)–C(215)–C(216)	120.9(9)
Rh–N(1)–C(1)	168.8(7)	C(215)–C(216)–C(211)	118.9(8)
N(1)–C(1)–C(11)	178.7(10)		
Rh–N(2)–C(2)	172.5(7)	P(2)–C(221)–C(222)	123.5(6)
N(2)–C(2)–C(21)	178.4(10)	P(2)–C(221)–C(226)	117.0(6)
Rh–N(3)–C(3)	167.0(7)	C(222)–C(221)–C(226)	119.5(8)
N(3)–C(3)–C(31)	176.8(11)	C(221)–C(222)–C(223)	120.1(8)
Rh–N(4)–O(4)	118.4(6)	C(222)–C(223)–C(224)	120.4(8)
		C(223)–C(224)–C(225)	118.9(8)
Rh–P(1)–C(101)	116.2(3)	C(224)–C(225)–C(226)	121.3(9)
Rh–P(1)–C(111)	117.7(3)	C(225)–C(226)–C(221)	119.7(8)
Rh–P(1)–C(121)	106.7(3)		
C(101)–P(1)–C(111)	101.4(4)	F(31)–P(3)–F(32)	178.1(6)
C(101)–P(1)–C(121)	106.4(4)	F(31)–P(3)–F(33)	94.1(7)
C(111)–P(1)–C(121)	107.8(4)	F(31)–P(3)–F(34)	87.5(8)
		F(31)–P(3)–F(35)	91.4(8)
Rh–P(2)–C(201)	109.6(3)	F(31)–P(3)–F(36)	90.4(7)
Rh–P(2)–C(211)	114.8(3)	F(32)–P(3)–F(33)	86.0(7)
Rh–P(2)–C(221)	117.4(3)	F(32)–P(3)–F(34)	92.2(8)
C(201)–P(2)–C(211)	108.8(4)	F(32)–P(3)–F(35)	90.5(8)
C(201)–P(2)–C(221)	103.9(4)	F(32)–P(3)–F(36)	87.7(7)
C(211)–P(2)–C(221)	101.6(4)	F(33)–P(3)–F(34)	172.8(9)
		F(33)–P(3)–F(35)	92.1(12)
P(1)–C(101)–C(102)	119.1(6)	F(33)–P(3)–F(36)	91.3(10)
P(1)–C(101)–C(106)	121.7(7)	F(34)–P(3)–F(35)	94.8(13)
C(102)–C(101)–C(106)	118.4(7)	F(34)–P(3)–F(36)	81.7(10)
C(101)–C(102)–C(103)	121.1(8)	F(35)–P(3)–F(36)	176.0(13)
C(102)–C(103)–C(104)	119.2(9)		
C(103)–C(104)–C(105)	119.6(9)	F(41)–P(4)–F(42)	178.8(4)
C(104)–C(105)–C(106)	121.3(10)	F(41)–P(4)–F(43)	91.9(4)
C(105)–C(106)–C(101)	120.3(9)	F(41)–P(4)–F(44)	90.1(4)
		F(41)–P(4)–F(45)	88.9(4)
P(1)–C(111)–C(112)	122.5(7)	F(41)–P(4)–F(46)	91.2(5)
P(1)–C(111)–C(116)	117.8(6)	F(42)–P(4)–F(43)	88.0(4)
C(112)–C(111)–C(116)	119.3(8)	F(42)–P(4)–F(44)	90.0(4)
C(111)–C(112)–C(113)	120.0(8)	F(42)–P(4)–F(45)	89.9(4)
C(112)–C(113)–C(114)	120.2(9)	F(42)–P(4)–F(46)	90.0(4)
C(113)–C(114)–C(115)	120.2(8)	F(43)–P(4)–F(44)	178.0(4)
C(114)–C(115)–C(116)	120.3(9)	F(43)–P(4)–F(45)	89.6(5)
C(115)–C(116)–C(111)	119.9(9)	F(43)–P(4)–F(46)	90.0(5)
		F(44)–P(4)–F(45)	90.7(5)
P(1)–C(121)–C(122)	119.6(7)	F(44)–P(4)–F(46)	89.8(5)
P(1)–C(121)–C(126)	119.0(7)	F(45)–P(4)–F(46)	179.5(5)
C(122)–C(121)–C(126)	120.7(8)		
C(121)–C(122)–C(123)	117.8(9)		
C(122)–C(123)–C(124)	122.4(10)		
C(123)–C(124)–C(125)	119.0(10)		
C(124)–C(125)–C(126)	119.8(10)		
C(125)–C(126)–C(121)	120.3(9)		

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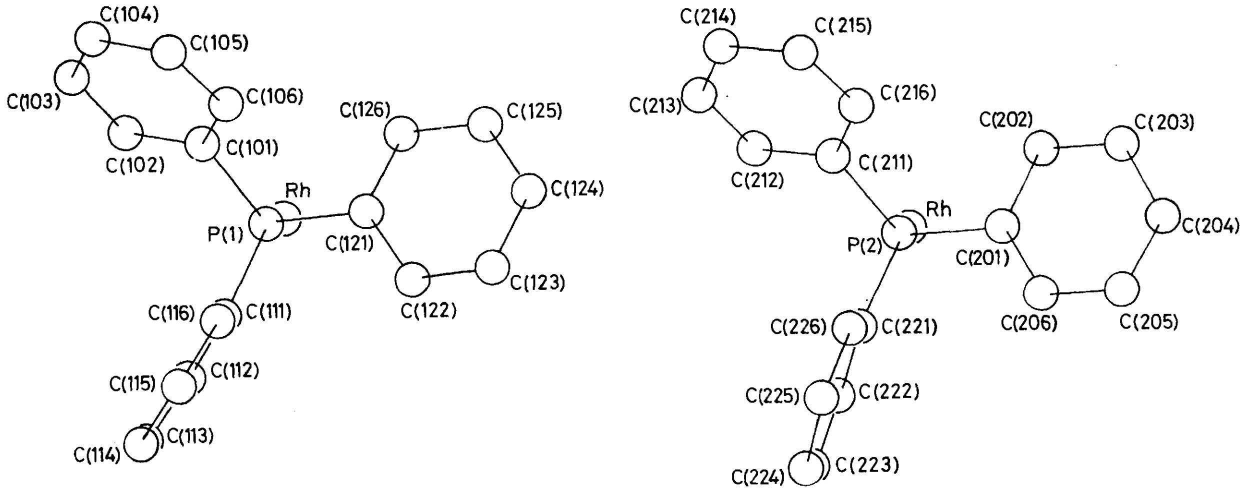
[12] S. Z. Goldberg, C. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, 1975, **14**, 1650.

[13] B. A. Frenz and J. A. Ibers, *M.T.P. Internat. Rev. Sci., Phys. Chem.*, 1972, **11**, 33.

[14] G. D. Piero, G. Perego, and M. Cesari, *Cryst. Struct. Comm.*, 1974, **3**, 15.

complex is 1.98(2) Å. Corresponding distances of 2.030(7) and 2.014(7) Å are determined for the mutually *trans* acetonitrile ligands in the present cation, whilst Rh–N(3), *trans* to the nitrosyl function, is 2.308(8) Å. Interestingly, the N–C separations follow the reverse sequence [*i.e.* N(3)–C(3) is shortest] although the differences here are clearly not significant. Nevertheless, the unique acetonitrile ligand is undoubtedly much more weakly bonded to rhodium,* and is easily removed [1] to generate the *trans*-square-pyramidal ion (2) in which the nitrosyl group occupies the apical position. The unambiguous determination of the nitrosyl bonding mode in (2) must await a further crystallographic analysis. It is noteworthy, however, that in the present cation, even though the *trans* acetonitrile is so loosely bound, no opening of the Rh–N–O angle occurs, suggesting consistent co-ordination (as $[NO]^-$) for (2), in agreement with the available spectroscopic data.



(*i*) (*ii*)

FIGURE 2 Conformations of the phenyl rings, as seen in projections along the respective P–Rh bonds

The Rh–P distances [2.402(2) and 2.407(2) Å] may again be viewed as a further extension of typical four-co-ordinate $Rh^{III}–P$ [10] [2.354(1) Å], and five-co-ordinate $Rh^{III}–P$ [11,12,16,17] (weighted mean 2.363 Å) separations, and bear direct comparison with other six-co-ordinate $Rh^{III}–P$ distances [18,19] (mean 2.394 Å).

P–C and C–C lengths and C–C–C angles are unexceptional, averaging 1.817(7) † and 1.394(12) Å and 120.0(9)° respectively. The planarities of the phenyl groups are demonstrated in Appendix D. Figure 2(*i*) and 2(*ii*) represents individual projections of the triphenylphosphine groups in roughly similar directions. In common with many structural determinations [20] of co-ordinated PPh_3 molecules, we find the plane of one aryl ring essentially contains the Rh–P vector, one is twisted *ca.* 90° about the P–C bond with respect to this, and the third is intermediate. In this way we may pair ring C(111)—C(116) with C(221)—C(226), C(121)—C(126) with C(201)—C(206), and C(101)—C(106) with C(211)—C(216). Corresponding twist angles ‡ are: 11.2, 4.8; 81.9, 72.0; and 51.7, 52.1°. Furthermore, the chirality of both $PhPPh_3$ moieties is the same for any one molecule, although equal numbers of both type occur in the (centrosymmetric) unit cell.

Having paired corresponding phenyl groups, the variation in Rh–P–C angles may be rationalised, since, for the rings with small twist angle, the relatively short contact to the *ortho*-hydrogen atom nearest rhodium [Rh · · · H(112) 3.25, Rh · · · H(222) 3.26 Å] causes Rh–P–C to widen. The effect is also shared by an increase in P–C–C(112,222) over P–C–C(116,226).

There is no evidence of the quasi-graphitic packing of pairs of phenyl rings (either generally or specifically

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[*] The molecular structure therefore provides another example of the significant *trans* influence of $[NO]^-$ in octahedral d^6 complexes.[15]

[†] The estimated standard deviation of the mean of N similar types is given by the expression $\sigma^2 = [\sum_{i=1}^{i=N} (\chi_i - \chi)^2]/(N - 1)$ where $\bar{\chi}_i$ is the ith and $\bar{\chi}$ the mean value.

[‡] The twist angle is defined here as the acute dihedral angle between the RhPC and PCC planes.

[15] D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2760 and refs. therein.

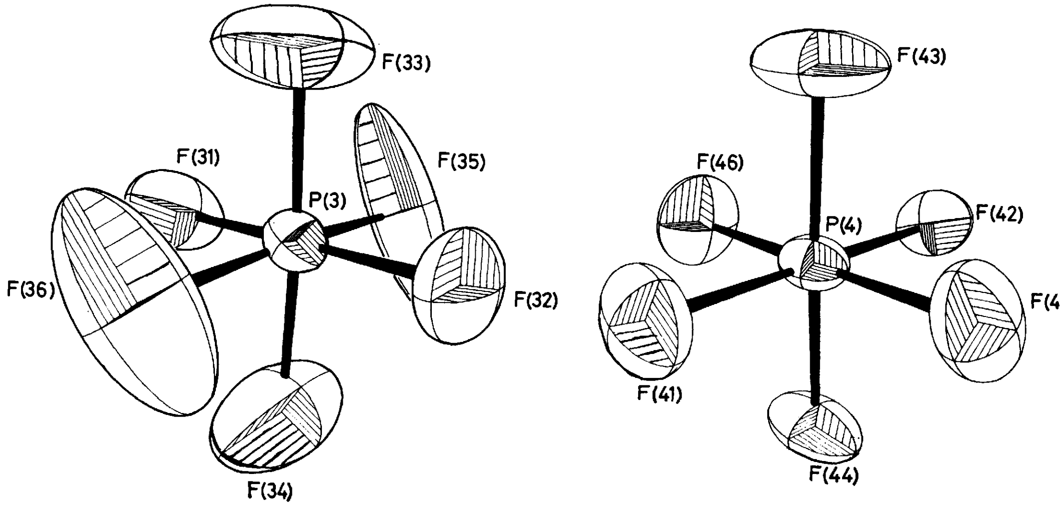
[16] P. G. H. Troughton and A. C. Skapski, *Chem. Comm.*, 1968, 575.

[17] A. P. Gaughan, jun., B. L. Haymore, J. A. Ibers, W. H. Meyers, T. E. Nappier, jun., and D. W. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 6859.

[18] F. H. Allen, G. Chang, K. K. Cheung, T. F. Lai, L. M. Lee, and A. Pidcock, *Chem. Comm.*, 1970, 1297.

[19] A. C. Skapski and F. A. Stephens, *J.C.S. Dalton*, 1973, 1789. Only the mutually *trans* phosphines are considered.

[20] V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2420.



(*i*) (*ii*)

FIGURE 3 The $[PF_6]^-$ anions. The thermal ellipsoids enclose 50% electron probability

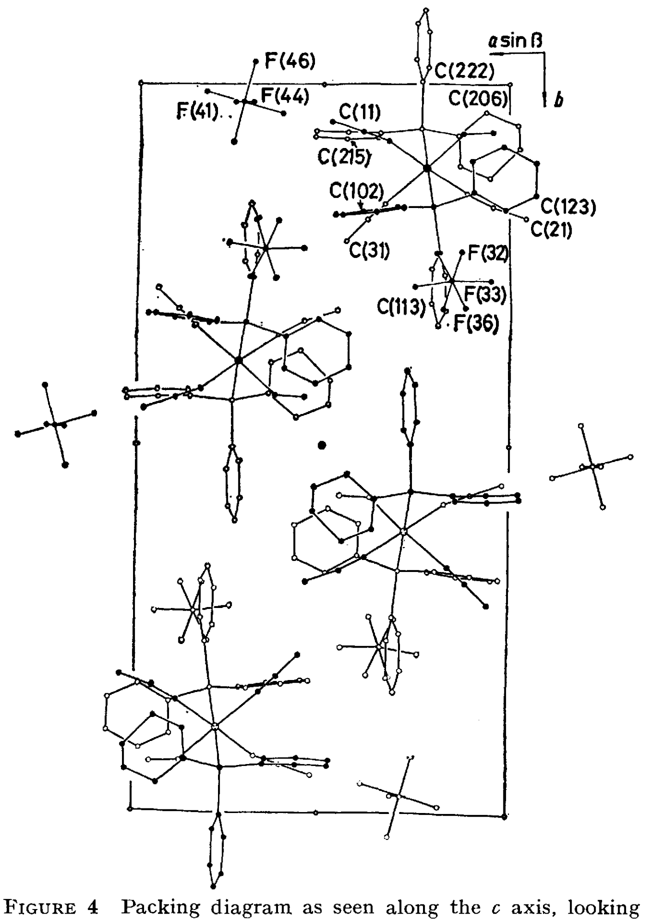


FIGURE 4 Packing diagram as seen along the *c* axis, looking towards the origin. Hydrogen atoms of the phenyl rings and a full complement of symmetry elements are omitted for the sake of clarity

across a symmetry centre) often observed in multi-ring structures.[21]

The $[PF_6]^-$ *Anions and Crystal Packing*.—Figure 3(*i*) and 3(*ii*) shows the two crystallographically independent hexafluorophosphate anions drawn to a common scale,

TABLE 4

Root-mean-square displacements (Å × 10^4) along the principle ellipsoidal axes for the hexafluorophosphate anions

	Axis		
Atom	1	2	3
P(3)	1 653	1 841	2 536
F(31)	2 036	2 294	4 026
F(32)	1 746	2 533	4 143
F(33)	1 978	2 557	5 689
F(34)	2 193	2 696	5 986
F(35)	1 886	3 225	7 334
F(36)	2 459	3 122	5 685
P(4)	1 458	1 698	1 987
F(41)	1 684	2 487	2 795
F(42)	1 737	2 025	2 564
F(43)	1 608	2 316	3 470
F(44)	1 656	2 312	3 176
F(45)	1 875	2 306	3 111
F(46)	1 733	2 730	3 035

TABLE 5

Non-bonded H · · · F contacts (Å)

Atom A [a]	Atom B	Position B	Distance
F(32) [b]	H(106) [c,d]	x, y, z	2.51
F(32)	H(203)	$x, y, 1 + z$	2.50
F(34)	H(123)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.49
F(43)	H(205)	$1 + x, y, 1 + z$	2.56
F(43)	H(222)	$1 - x, -y, 1 - z$	2.58
F(44)	H(226)	$1 - x, -y, -z$	2.39
F(45)	H(204)	$1 + x, y, 1 + z$	2.48
F(45)	H(124)	$1 + x, y, z$	2.54
F(45)	H(114)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.45
F(33)	C(21) [e]	$x, y, 1 + z$	3.360(21)
F(36)	C(31)	$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$	3.262(23)
F(42)	C(11)	x, y, z	3.077(13)
F(42)	C(11)	$1 - x, -y, 1 - z$	3.339(15)
F(44)	C(11)	x, y, z	3.107(13)
F(46)	C(11)	$1 - x, -y, 1 - z$	3.193(15)

[a] At x,y,z (Table 1). [b,c] van der Waals radii taken as 1.35 and 1.20 Å respectively. [d] Hydrogen atoms numbered according to their parent carbon. [e] van der Waals radius of methyl group estimated as 2.0 Å.

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[21] V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J.C.S. Dalton*, 1972, 171 and refs. therein.

and demonstrates the fluorine-numbering scheme. The positions of these ions relative to each other and to the cation may be seen in Figure 4, the contents of one unit cell as viewed along the shortest crystallographic axis, looking towards the origin.

The striking difference in thermal activity of the two anions, clearly visible in Figures 3 and quantified in Table 4 as root-mean-square amplitudes (Å) along the major ellipsoidal axes, may be traced to their differing degrees of cation–anion H · · · F interaction (Table 5). Overall there are twice as many H · · · FP(4) short contacts as H · · · FP(3) ones. Furthermore, only one H · · · FP(3) approach, between F(36) at x, y, z and C(31) at $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$, is of possible severity. The comparatively weak crystal forces experienced by the $P(3)F_6$ anion duly manifest themselves in a greater uncertainty in positional parameters and hence an increased spread and error in the bond lengths and angles determined, in spite of the fact that diffractometer data were recorded at low temperature.

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