

**Structure of the Mixed-Valence Complex**  
 **$[\text{Rh}_2(\mu\text{-}\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2\})_2(\mu\text{-N}_2\text{C}_5\text{H}_7)(\text{tert-C}_4\text{H}_9\text{NC})_2](\text{PF}_6)_2$**

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(Received 19 August 1991; accepted 2 December 1991)

**Abstract.** 1,2-Di-(*tert*-butyl isocyanide)-1,2-di- $\mu$ -bis(diphenylphosphino)methane- $\mu$ -(3,5-dimethylpyrazolato)dirhodium(1.5+) dihexafluorophosphate, (1),  $M_r = 1525.9$ , tetragonal,  $I\bar{4}2d$ ,  $a = 21.817(3)$ ,  $c = 30.658(5)$  Å,  $V = 14592(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.389$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 6.4$  cm<sup>-1</sup>,  $F(000) = 6200$ ,  $T = 295(2)$  K,  $R = 0.0397$  for 2187 observed reflections. The molecule possesses crystallographic twofold symmetry. The dimetal framework is that of an *A*-frame structure and consists of two interpenetrating square pyramids with each metal atom located in a basal plane and serving as the apex of the pyramidal environment of the other metal atom. The Rh...Rh distance is 2.828(1) Å and is consistent with a bond order of  $\frac{1}{2}$  for the Rh<sub>2</sub><sup>3+</sup> core.

**Experimental.** The title complex was synthesized by electrochemical oxidation as previously described (Woods, Tortorelli, Rillema, Burn & DePriest, 1989). Dark purple prisms *ca* 0.25 × 0.35 × 0.40 mm were obtained from CH<sub>2</sub>Cl<sub>2</sub>/ether and mounted on a glass fibre. Siemens *R3mV* diffractometer,  $\omega/2\theta$  scans of 2–15° min<sup>-1</sup>; cell parameters obtained by least-squares fit of 21 setting angles ( $15 < 2\theta < 30^\circ$ );  $2\theta_{\text{max}} = 45^\circ$ ,  $h = 0$  to 23,  $k = 0$  to 23,  $l = 0$  to 32, 2 standard reflections measured every 48 reflections with no significant variation, 5202 data collected, 2602 unique ( $R_{\text{int}} = 0.0642$ ), 2187 observed [ $F > 3\sigma(F)$ ]; corrected for Lorentz and polarization, empirical absorption correction, min., max. transmission factors: 0.676, 0.816; solved by Patterson methods, full-matrix least-squares refinement on  $F$ ,  $R = 0.0397$ ,  $wR = 0.0395$ ;  $S = 1.01$ ; anisotropic thermal parameters for non-H atoms; H atoms included at calculated positions [ $d(\text{C}-\text{H}) = 0.96$  Å]. Function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/[\sigma^2(F_o) + 0.0004|F_o|^2]$ , max.  $\Delta/\sigma = 0.005$ ;  $\Delta\rho_{\text{max}} = 0.45$ ,  $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol.

IV); calculations carried out on a MicroVAX II computer using the *SHELXTL PLUS* (Sheldrick, 1990) library of programs. Final positional parameters are given in Table 1,† and selected bond distances and angles in Table 2; atomic labeling scheme and structure of the cation are shown in Fig. 1.

**Related literature.** The gross structural features of the title complex are very similar to those of the Rh<sup>I</sup>—Rh<sup>I</sup> dicarbonyl analogue (Oro, Carmona, Pérez, Esteban, Tiripicchio & Tiripicchio-Camellini, 1985), the major difference being in the Rh...Rh distances. The Rh...Rh distance in the Rh<sup>I</sup>—Rh<sup>I</sup>

† Lists of structure factors, anisotropic thermal parameters and calculated hydrogen positional parameters, and a complete listing of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54916 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0383]

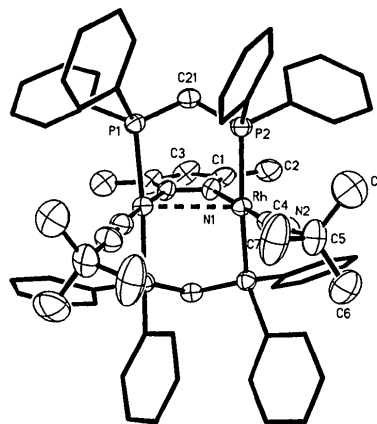


Fig. 1. Molecular structure of the cation of (1). For clarity the thermal ellipsoids of the phenyl C atoms are not shown while all other thermal parameters for anisotropic atoms are drawn at the 50% probability level. All unlabeled non-phenyl atoms are generated by symmetry.

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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	$U_{\text{eq}}^*$
Rh	2500 (1)	1877 (1)	1122 (1)	30 (1)
N(1)	1610 (3)	2206 (3)	1182 (2)	32 (2)
C(1)	1028 (4)	2021 (4)	1126 (3)	44 (4)
C(2)	864 (5)	1406 (5)	953 (3)	56 (4)
C(3)	655 (6)	2500	1250	53 (5)
C(4)	3336 (5)	1617 (4)	1060 (3)	39 (3)
N(2)	3843 (4)	1480 (4)	996 (3)	47 (3)
C(5)	4456 (4)	1255 (5)	891 (4)	54 (4)
C(6)	4623 (4)	750 (5)	1198 (4)	72 (5)
C(7)	4901 (5)	1776 (5)	923 (5)	97 (6)
C(8)	4427 (6)	1027 (6)	422 (4)	82 (5)
P(1)	2331 (1)	3515 (1)	670 (1)	34 (1)
C(9)	1745 (4)	4107 (4)	703 (3)	30 (3)
C(10)	1212 (5)	4102 (5)	457 (3)	48 (4)
C(11)	791 (5)	4568 (6)	507 (4)	65 (5)
C(12)	894 (6)	5048 (6)	790 (4)	66 (5)
C(13)	1432 (5)	5060 (6)	1028 (3)	63 (4)
C(14)	1857 (5)	4593 (4)	989 (3)	45 (4)
C(15)	2910 (5)	3891 (4)	333 (3)	45 (4)
C(16)	3343 (5)	4268 (5)	535 (4)	53 (4)
C(17)	3779 (6)	4553 (6)	289 (6)	84 (6)
C(18)	3793 (7)	4514 (6)	-151 (6)	92 (7)
C(19)	3362 (7)	4141 (6)	-364 (5)	82 (6)
C(20)	2924 (5)	3852 (5)	-119 (4)	58 (4)
C(21)	1998 (4)	2901 (4)	342 (3)	37 (3)
P(2)	2439 (1)	2189 (1)	408 (1)	35 (1)
C(22)	3122 (5)	2320 (4)	88 (3)	50 (4)
C(23)	3627 (5)	2599 (5)	277 (4)	53 (4)
C(24)	4129 (6)	2749 (5)	17 (5)	75 (5)
C(25)	4140 (7)	2647 (6)	-419 (5)	91 (7)
C(26)	3637 (8)	2375 (7)	-604 (4)	101 (7)
C(27)	3123 (6)	2201 (5)	-361 (3)	69 (5)
C(28)	2010 (5)	1608 (4)	112 (3)	45 (4)
C(29)	1495 (6)	1728 (5)	-138 (3)	65 (4)
C(30)	1168 (7)	1261 (6)	-319 (4)	93 (6)
C(31)	1367 (8)	670 (7)	-266 (5)	116 (8)
C(32)	1892 (7)	528 (5)	-35 (5)	106 (7)
C(33)	2199 (6)	1002 (5)	152 (4)	72 (5)
P(3)	633 (2)	1719 (1)	3233 (1)	59 (1)
F(1)	738 (4)	2392 (3)	3412 (2)	104 (3)
F(2)	526 (3)	1054 (3)	3060 (3)	94 (3)
F(3)	712 (4)	1447 (4)	3698 (3)	125 (4)
F(4)	558 (4)	1983 (3)	2759 (2)	101 (3)
F(5)	-79 (3)	1788 (4)	3317 (3)	109 (4)
F(6)	1338 (3)	1655 (5)	3140 (3)	122 (4)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Rh—N(1)	2.078 (6)	Rh—C(4)	1.920 (10)
Rh—P(2)	2.298 (2)	C(4)—N(2)	1.161 (13)
N(2)—C(5)	1.462 (13)	P(1)—C(21)	1.825 (9)
C(21)—P(2)	1.838 (9)		
N(1)—Rh—C(4)	177.0 (3)	N(1)—Rh—P(2)	85.9 (2)
C(4)—Rh—P(2)	92.7 (3)	Rh—N(1)—C(1)	140.2 (6)
N(1)—C(1)—C(2)	122.9 (8)	Rh—C(4)—N(2)	175.5 (8)
C(4)—N(2)—C(5)	174.1 (10)	P(1)—C(21)—P(2)	110.5 (5)
Rh—P(2)—C(21)	112.7 (3)		

dicarbonyl complex is 3.060  $\text{\AA}$  compared to 2.828 (1)  $\text{\AA}$  for the title complex. The shorter distance for the title complex is consistent with an Rh—Rh bond order of  $\frac{1}{2}$  for the Rh<sub>2</sub><sup>3+</sup> core. The increase in bond order was predicted from the electronic model developed by Hoffman and co-workers (Hoffmann & Hoffman, 1981) for *A*-frame complexes since oxidation of the parent Rh<sup>I</sup>—Rh<sup>I</sup> complex results in removal of an electron from an Rh—Rh antibonding orbital. The small bite size of the pyrazolate ligands results in a dihedral angle of 38.4° between the two least-squares planes formed by the square-plane core atoms of the two Rh atoms.

We are grateful to Johnson Matthey, Inc. for a loan of rhodium trichloride and Research Corporation for support of this work.

#### References

- HOFFMANN, D. J. & HOFFMAN, R. (1981). *Inorg. Chem.* **20**, 3543–3555.  
 ORO, L. A., CARMONA, D., PERÉZ, P. L., ESTEBAN, M., TIRIPICCHIO, A. & TIRIPICCHIO-CAMELLINI, M. (1985). *J. Chem. Soc. Dalton Trans.* pp. 973–979.  
 SHELDRICK, G. M. (1990). *SHELXTL PLUS User's Manual*, release 4.0. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.  
 WOODS, C., TORTORELLI, L. J., RILLEMA, D. P., BURN, J. L. E. & DEPRIEST, J. C. (1989). *Inorg. Chem.* **28**, 1673–1679.

*Acta Cryst.* (1992). **C48**, 1312–1314

## $\mu$ -[Bis(diphenylphosphino)methane]-bis[pentafluorophenylgold(I)] at 178 K

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(Received 10 October 1991; accepted 4 December 1991)

**Abstract.** [Au<sub>2</sub>(C<sub>25</sub>H<sub>22</sub>P<sub>2</sub>)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>],  $M_r = 1112.4$ , monoclinic,  $P2_1/c$ ,  $a = 14.141$  (4),  $b = 20.209$  (5),  $c = 14.207$  (4)  $\text{\AA}$ ,  $\beta = 95.85$  (3)°,  $V = 4039$  (2)  $\text{\AA}^3$ ,  $Z = 4$ ,

$D_x = 1.829$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$   $\text{\AA}$ ,  $\mu = 7.4$  mm<sup>-1</sup>,  $F(000) = 2088$ ,  $T = 178$  K,  $R = 0.046$  for 5181 reflections. The molecule crystallizes in a *cis*