

*Acta Cryst.* (1975). B31, 897**Dinitrosylbis(triphenylphosphine)ruthenium**

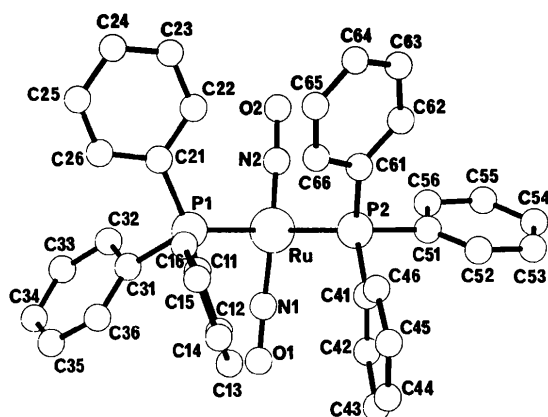
BY S. BHADURI AND G. M. SHELDRIK

*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England*

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**Abstract.**  $\text{Ru}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , monoclinic,  $P2_1/n$ ,  $a = 9.96$  (1),  $b = 37.01$  (2),  $c = 9.31$  (1) Å,  $\beta = 111.44$  (3)°,  $Z = 4$ ,  $D_x = 1.425$ ,  $V = 3194$  Å<sup>3</sup>,  $F(000) = 662$ ,  $\mu(\text{Mo } K\alpha) = 5.28$  cm<sup>-1</sup>. The structure has been refined by full-matrix least-squares calculations to  $R_w = 0.0485$  for 927 unique observed reflexions. There is a distorted tetrahedral coordination about ruthenium, with mean bond lengths and angles: Ru-P, 2.339 (7); Ru-N, 1.72 (3); N-O, 1.22 (2) Å; P-Ru-P, 105.5 (3); N-Ru-N, 139.9 (8)°. Ru-N-O angles are 168.0 (1.6) and 174.7 (1.7)°. Apart from the conformation of the triphenylphosphine groups the molecular structure is similar to that found in crystals of  $\text{Ru}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ .

**Introduction.** The N-M-N and M-N-O angles in four-coordinate transition metal nitrosyls provide some evidence as to whether these can be regarded as  $\text{NO}^+$ , NO or  $\text{NO}^-$  complexes. Shortly after we had completed the determination of the structure of dinitrosylbis(triphenylphosphine)ruthenium, Gaughan, Corden, Eisenberg & Ibers (1974) reported a crystal structure in which four molecules of the same compound crystallize with two molecules of benzene in the monoclinic unit cell, with different packing and cell dimensions from the modification reported here. We thought that it would be of interest to compare the two independent determinations, especially since some parameters - e.g. the Ru-N-O angles - may be the result of a fine energy balance and hence influenced by the packing of the bulky triphenylphosphine ligands.

Fig. 1. The molecule of  $\text{Ru}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ .

The sample was prepared by the method reported by Grundy, Laing & Roper (1970) and recrystallized from a benzene-ethanol mixture. Data were collected on a Stoe two-circle diffractometer in an approximately constant count mode, for two crystals (layers  $h0-21l$  and  $0-4kl$  respectively), with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) and a graphite crystal monochromator. Where a prescan indicated that the count could not be achieved within a specified time, the reflexion was ignored. 2680 reflexions were measured, of which 103 were rejected because of background imbalance or because the net count was less than  $3\sigma$  based on counting statistics. Averaging equivalent reflexions led to 928 unique observed reflexions. Cell dimensions were obtained by a least-squares fit to the median  $\omega$  values for all the zero-layer reflexions (Clegg & Sheldrick, 1974). Absorption corrections did not result in any improvement in the internal consistency  $R$  index for common reflexions, and so were not applied in the final data reduction; the crystals were very small diamond-shaped platelets, with prominent (010) faces.

The systematic absences ( $k$  odd for  $0k0$ ,  $h+l$  odd for  $h0l$ ) indicate the space group  $P2_1/n$ . The structure was solved by interpretation of Patterson and difference electron density maps, and refined by full-matrix least-squares calculations with an anisotropic temperature factor for ruthenium and isotropic temperature factors for the remaining atoms, and the weighting scheme  $w = [\sigma^2(N) + 0.001N^2]^{-1} / [28.85 + |F_o| + 0.0491 F_o^2]$ , where  $N$  is the net peak count, and the summation is over equivalent reflexions. Complex neutral-atom scattering factors were employed for all atoms (Cromer, 1965; Cromer & Waber, 1965). With rigid phenyl groups (C-C, 1.395; C-H, 1.08 Å; all angles 120°) the refinement converged to  $R_w = \sum w^{1/2} |F_o - F_c| / \sum w^{1/2} |F_o| = 0.0517$ ; allowing the carbon atoms to refine freely, but with the hydrogen atoms still constrained to lie on the external angle bisectors with C-H = 1.08 Å, reduced  $R_w$  to 0.0485, with a corresponding unweighted  $R$  index of 0.0495. Atom coordinates and temperature factors are given in Table 1 and bond lengths and angles in Tables 2 and 3. An overall isotropic temperature factor was employed for the hydrogen atoms.\*

\* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30656 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i>
Ru(1)	2619 (2)	3804 (1)	3068 (2)	
P(1)	1731 (6)	4284 (2)	4083 (6)	
P(2)	1262 (6)	3299 (2)	3237 (6)	
N(1)	1842 (17)	3952 (4)	1158 (21)	50 (5)
O(1)	1066 (16)	4048 (4)	-126 (18)	87 (5)
N(2)	4252 (20)	3699 (4)	4392 (20)	67 (6)
O(2)	5397 (18)	3631 (4)	5448 (19)	104 (6)
C(11)	-198 (18)	4270 (5)	3761 (19)	31 (5)
C(12)	-1125 (21)	4215 (5)	2204 (21)	43 (6)
C(13)	-2606 (24)	4183 (5)	1920 (26)	52 (6)
C(14)	-3155 (22)	4203 (5)	3098 (23)	54 (7)
C(15)	-2223 (22)	4262 (5)	4589 (23)	61 (7)
C(16)	-719 (21)	4308 (5)	4933 (20)	42 (6)
C(21)	2565 (20)	4373 (5)	6113 (20)	40 (6)
C(22)	3270 (18)	4103 (5)	7135 (20)	38 (6)
C(23)	3827 (20)	4170 (6)	8738 (23)	62 (7)
C(24)	3705 (19)	4501 (5)	9352 (21)	43 (6)
C(25)	3015 (18)	4773 (5)	8326 (19)	44 (7)
C(26)	2458 (20)	4713 (5)	6768 (21)	43 (6)
C(31)	1990 (21)	4702 (5)	3206 (19)	38 (6)
C(32)	3439 (23)	4798 (6)	3372 (20)	52 (7)
C(33)	3653 (22)	5115 (6)	2696 (22)	55 (7)
C(34)	2544 (24)	5335 (6)	1915 (24)	57 (6)
C(35)	1210 (24)	5254 (6)	1738 (22)	58 (7)
C(36)	888 (22)	4941 (6)	2390 (20)	50 (6)
C(41)	-655 (22)	3298 (6)	2131 (24)	60 (7)
C(42)	-1088 (24)	3371 (6)	599 (24)	69 (8)
C(43)	-2576 (24)	3376 (6)	-413 (26)	76 (8)
C(44)	-3501 (27)	3286 (7)	301 (31)	97 (9)
C(45)	-3166 (27)	3207 (7)	1804 (30)	105 (10)
C(46)	-1657 (24)	3222 (6)	2795 (26)	74 (7)
C(51)	1757 (21)	2877 (5)	2518 (20)	36 (6)
C(52)	852 (25)	2598 (7)	2018 (23)	74 (8)
C(53)	1342 (26)	2284 (7)	1454 (23)	76 (8)
C(54)	2723 (27)	2255 (6)	1539 (22)	71 (8)
C(55)	3631 (29)	2534 (8)	2104 (26)	96 (9)
C(56)	3199 (23)	2858 (6)	2600 (22)	56 (7)
C(61)	1415 (19)	3187 (6)	5148 (21)	46 (6)
C(62)	2166 (21)	2887 (6)	5950 (24)	61 (7)
C(63)	2462 (22)	2828 (7)	7522 (24)	85 (9)
C(64)	1900 (23)	3068 (7)	8273 (25)	74 (8)
C(65)	1079 (24)	3356 (7)	7536 (26)	80 (8)
C(66)	872 (23)	3421 (7)	6009 (26)	77 (8)

Anisotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ). The anisotropic temperature factor takes the form:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}khl^*c^* + 2U_{31}lhc^*a^* + 2U_{13}hka^*b^*)]$ .

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ru(1)	45 (1)	31 (1)	60 (1)	-3 (2)	25 (1)	-3 (2)
P(1)	35 (4)	34 (5)	47 (4)	0 (4)	16 (3)	0 (3)
P(2)	43 (4)	36 (5)	55 (4)	-4 (4)	20 (3)	4 (3)

**Discussion.** In the structure reported here, both the triphenylphosphine groups adopt the usual approximate propeller conformation when viewed along the local threefold axes (Fig. 1), but unlike  $\text{Ir}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2^+$  (Mingos & Ibers, 1970) and  $\text{Fe}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  (Albano, Araneo, Bellon, Ciani & Manassero, 1974), there is no molecular twofold axis bisecting the N-M-N and P-M-P angles. A different conformation of one of the triphenylphosphine groups is found in  $\text{Ru}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ , and this probably accounts for the significant differences in P-Ru-P angles [ $103.85(6)^\circ$ ,  $105.5(2)^\circ$ ] and Ru-N-O angles [ $177.7(6)^\circ$ ,

Table 2. Selected interatomic distances ( $\text{\AA}$ )

Ru(1)-P(1)	2.332 (9)	N(1)-O(1)	1.215 (18)
Ru(1)-P(2)	2.346 (9)	N(2)-O(2)	1.229 (18)
Ru(1)-N(1)	1.748 (20)	N(1)-N(2)	3.228
Ru(1)-N(2)	1.688 (20)	P(1)-C(21)	1.796 (20)
P(1)-C(11)	1.834 (19)		
C(11)-C(12)	1.419 (22)	C(21)-C(22)	1.383 (23)
C(12)-C(13)	1.405 (26)	C(22)-C(23)	1.410 (23)
C(13)-C(14)	1.395 (27)	C(23)-C(24)	1.376 (25)
C(14)-C(15)	1.376 (23)	C(24)-C(25)	1.387 (24)
C(15)-C(16)	1.423 (25)	C(25)-C(26)	1.369 (25)
C(11)-C(16)	1.377 (23)	C(21)-C(26)	1.419 (24)
P(2)-C(41)	1.808 (22)	P(2)-C(51)	1.835 (22)
C(41)-C(42)	1.357 (24)	C(51)-C(52)	1.339 (25)
C(42)-C(43)	1.437 (25)	C(52)-C(53)	1.433 (29)
C(43)-C(44)	1.361 (29)	C(53)-C(54)	1.353 (27)
C(44)-C(45)	1.346 (27)	C(54)-C(55)	1.346 (28)
C(45)-C(46)	1.449 (30)	C(55)-C(56)	1.409 (29)
C(41)-C(46)	1.381 (28)	C(51)-C(56)	1.411 (26)
P(1)-N(1)	3.025		
P(1)-N(2)	3.247		
P(1)-P(2)	3.723		
P(1)-C(31)	1.810 (22)	P(2)-C(61)	1.778 (21)
C(31)-C(32)	1.439 (25)	C(61)-C(62)	1.394 (25)
C(32)-C(33)	1.385 (26)	C(62)-C(63)	1.400 (25)
C(33)-C(34)	1.352 (24)	C(63)-C(64)	1.370 (28)
C(34)-C(35)	1.312 (26)	C(64)-C(65)	1.366 (28)
C(35)-C(36)	1.401 (26)	C(65)-C(66)	1.382 (27)
C(31)-C(36)	1.398 (25)	C(61)-C(66)	1.414 (28)

$170.6(5)^\circ$  (Gaughan *et al.*);  $174.7(1.7)^\circ$ ,  $168.0(1.6)^\circ$  (this work)]. The susceptibility of the Ru-N-O angles to molecular conformation suggests that little energy is required to bend the Ru-N-O linkage, *i.e.* the potential energy is a fairly flat function of the valence angle. Thus it would be unwise to use the precise values of the M-N-O angles in related compounds as a criterion of bond type. Other bond lengths and angles do not differ very significantly in the two ruthenium structures; *e.g.* the N-Ru-N angles are  $139.2(3)$  and  $139.9(8)^\circ$ .

The NMN and MNO angles in the isoelectronic series  $\text{M}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Ir}^+$ ) (Table 4) are consistent with a trend from a  $d^{10}$  approximately tetrahedral  $\text{NO}^+$  complex towards a  $d^8$  square planar NO complex. Steric factors must also be invoked to account for the variations in PMP angles. It is difficult to explain the 'low' N-O stretching frequencies in the ruthenium derivative, but the separation of the two  $\nu(\text{NO})$  frequencies increases with increasing N-M-N angle, consistent with better mechanical coupling in the more linear conformation.

Although the *R* indices do not differ much, the molecular parameters reported by Gaughan *et al.* are both more precise than those reported here (by a factor of about three), and also more accurate (as evidenced by the smaller spread of P-C bond lengths). We attribute this primarily to the fact that they measured about three times as many unique observed reflexions, because we used Mo  $K\alpha$  rather than Cu  $K\alpha$  radiation and very small crystals (even with two-axis data, there were also some reflexions inaccessible to our two-circle diffractometer). The use of rigid phenyl groups - fully

Table 3. Selected bond angles ( $^{\circ}$ )

O(1)—N(1)—Ru(1)	168.0 (15)	O(2)—N(2)—Ru(1)	174.7 (16)
N(2)—Ru(1)—N(1)	139.9 (7)	P(2)—Ru(1)—P(1)	105.5 (3)
N(1)—Ru(1)—P(1)	94.6 (6)	N(2)—Ru(1)—P(1)	106.6 (7)
N(1)—Ru(1)—P(2)	105.5 (6)	N(2)—Ru(1)—P(2)	101.1 (7)
C(11)—P(1)—Ru(1)	116.2 (7)	C(41)—P(2)—Ru(1)	118.5 (8)
C(21)—P(1)—Ru(1)	118.0 (8)	C(51)—P(2)—Ru(1)	114.5 (8)
C(31)—P(1)—Ru(1)	109.3 (7)	C(61)—P(2)—Ru(1)	114.3 (8)
C(21)—P(1)—C(11)	103.4 (9)	C(51)—P(2)—C(41)	99.2 (10)
C(31)—P(1)—C(11)	105.3 (10)	C(61)—P(2)—C(41)	104.8 (11)
C(31)—P(1)—C(21)	103.3 (9)	C(61)—P(2)—C(51)	103.4 (10)
C(12)—C(11)—P(1)	115.0 (15)	C(42)—C(41)—P(2)	117.5 (19)
C(16)—C(11)—P(1)	122.9 (14)	C(46)—C(41)—P(2)	122.0 (19)
C(16)—C(11)—C(12)	122.1 (19)	C(46)—C(41)—C(42)	120.5 (22)
C(13)—C(12)—C(11)	116.8 (21)	C(43)—C(42)—C(41)	123.2 (23)
C(14)—C(13)—C(12)	122.3 (22)	C(44)—C(43)—C(42)	113.4 (23)
C(15)—C(14)—C(13)	119.1 (23)	C(45)—C(44)—C(43)	127.3 (27)
C(16)—C(15)—C(14)	120.9 (20)	C(46)—C(45)—C(44)	117.3 (27)
C(15)—C(16)—C(11)	118.7 (18)	C(45)—C(46)—C(41)	118.3 (24)
C(22)—C(21)—P(1)	120.9 (16)	C(52)—C(51)—P(2)	123.1 (19)
C(26)—C(21)—P(1)	122.5 (16)	C(56)—C(51)—P(2)	115.2 (18)
C(26)—C(21)—C(22)	116.4 (18)	C(56)—C(51)—C(52)	121.6 (23)
C(23)—C(22)—C(21)	120.4 (20)	C(53)—C(52)—C(51)	118.5 (24)
C(24)—C(23)—C(22)	122.4 (21)	C(54)—C(53)—C(52)	121.2 (26)
C(25)—C(24)—C(23)	117.3 (19)	C(55)—C(54)—C(53)	119.1 (27)
C(26)—C(25)—C(24)	121.2 (20)	C(56)—C(55)—C(54)	122.6 (27)
C(25)—C(26)—C(21)	122.3 (20)	C(55)—C(56)—C(51)	116.8 (23)
C(32)—C(31)—P(1)	117.7 (16)	C(62)—C(61)—P(2)	123.6 (19)
C(36)—C(31)—P(1)	124.9 (18)	C(66)—C(61)—P(2)	120.9 (18)
C(36)—C(31)—C(32)	117.4 (21)	C(66)—C(61)—C(62)	115.2 (21)
C(33)—C(32)—C(31)	118.4 (21)	C(63)—C(62)—C(61)	123.4 (24)
C(34)—C(33)—C(32)	121.6 (23)	C(64)—C(63)—C(62)	117.6 (24)
C(35)—C(34)—C(33)	121.4 (24)	C(65)—C(64)—C(63)	122.0 (24)
C(36)—C(35)—C(34)	121.1 (23)	C(66)—C(65)—C(64)	119.4 (25)
C(35)—C(36)—C(31)	120.1 (22)	C(65)—C(66)—C(61)	122.1 (24)

Table 4. Comparison of  $M(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  structures

	M—N—O	N—M—N	P—M—P	$\nu(\text{NO})$
M=Fe	178.2 (7) $^{\circ}$	123.8 (4) $^{\circ}$	111.9 (1) $^{\circ}$	1723, 1679 $\text{cm}^{-1}$ (in $\text{CCl}_4$ )
M=Ru	174.7 (17)	139.9 (8)	105.5 (2)	1665, 1615 (in Nujol)
(B & S)				
M=Ru	168.0 (16)	139.2 (3)	103.85 (6)	1760, 1715 (in Nujol)
(G, C, E & I)				
M=Ir $^{+}$	177.7 (6)			
	170.6 (5)			
	163.5 (10)	154.2 (7)	116.3 (2)	

justified by the small decrease in  $R$  indices when we allowed the carbon atoms to refine freely – probably also improves the accuracy, as well as halving the computer time required for the complete structure determination.

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