Dornberger–Schiff, can lead to stacking faults. These stacking faults would have to be very occasional in this case since there is no evidence for them in the Fourier maps. However, we do not intend to carry out further work on this compound, and a more complete set of data would be needed to pursue this point.

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## References

Britton, D., Hardgrove, G. L., Hegstrom, R. & Nelson, G. V. (1972). *Acta Cryst.* **B28**, 1121.
Britton, D., Konnert, J., Hammer, J. & Trefonas, L. M. (1972). *Acta Cryst*, **B28**, 1123.
Britton, D. & Noland, W. E. (1962). *J. Org. Chem.* **27**, 3218.
Britton, D. & Noland, W. E. (1972). *Acta Cryst.* **B28**, 1116.
Corfield, P. W. R., Doedens, R. J., & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 197.
Dornberger-Schiff, K. (1956). *Acta Cryst.* **9**, 593.
Dornberger-Schiff, K. & Grell-Niemann, H. (1961). *Acta Cryst.* **14**, 167.
Webster, M. S. (1956). *J. Chem. Soc.* p. 2841.

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*Acta Cryst.* (1972). B**28**, 1130

# The Molecular Structure of Nitrosyltris(trifluorophosphine)rhodium in the Gas Phase, Determined by Electron Diffraction

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The structure of nitrosyltris(trifluorophosphine)rhodium, $Rh(NO)(PF_3)_3$, has been determined by gas phase electron diffraction. The molecular intensity functions derived from photographically recorded sectored diffraction patterns were fitted by full-matrix least-squares refinements of a molecular model. Assuming that the molecule has a threefold axis of symmetry, the principal parameters have been found to be: N–O 1·149 ± 0·019, P–F 1·558 ± 0·003, Rh–P 2·245 ± 0·005, Rh–N 1·858 ± 0·018 Å, ∠ PRhP 110·4 ± 0·5, ∠ FPF 100·1 ± 0·7°. The trifluorophosphine groups are twisted by about 10° from the configuration in which each $PF_3$ group is eclipsed with respect to the $RhP_2N$ group.

## Introduction

Although well over a hundred transition metal complexes of trifluorophosphine have been characterized (Nixon, 1970), very little structural work on them has been reported. The complexes generally are low melting, and are therefore unsuitable for crystallographic study except at low temperatures. However, fairly high volatilities make many of the compounds, particularly those possessing some symmetry, suitable for structure determination by electron diffraction. Results have been published for tetrakis(trifluorophosphine)nickel (Marriott, Salthouse & Ware, 1970; Almenningen, Andersen & Astrup, 1970) and for tetrakis(trifluorophosphine)platinum (Marriott *et al.*, 1970), tetrahedrally coordinated derivatives of first and third series transition metals, and for hydridotetrakis(trifluorophosphine)cobalt (Frenz & Ibers, 1970). The only structure of a trifluorophosphine complex of a second transition series metal reported to date is that of the octahedral complex pentacarbonyl(trifluorophosphine)molybdenum (Bridges, Holywell, Rankin & Freeman, 1971).

The most striking feature of these results concerns the metal—phosphorus bond lengths. In the nickel and cobalt complexes, these bonds are about 0·12 Å shorter than in most phosphine complexes of these metals. The molybdenum complex shows a similar shortening of about 0·10 Å, but the platinum compound has metal—phosphorus bonds which are very little, if at all, shorter than usual.

In this present investigation of a tetrahedrally coordinated derivative of a second transition series metal, nitrosyltris(trifluorophosphine)rhodium, $Rh(NO)(PF_3)_3$, the rhodium–phosphorus bond lengths have been found to be about 0·10 Å shorter than the average reported length, but they are not the shortest of all.

## Experimental

Nitrosyltris(trifluorophosphine)rhodium is an orange volatile liquid, first obtained in 50–60% yield (Kruck & Lang, 1967) by passing carbon dioxide into an aqueous solution of potassium tetrakis(trifluorophosphine)rhodate containing nitrite. The compound can also be obtained (Clement & Nixon, 1971) in 26–39 % yield by shaking tetrakis(trifluorophosphine)dichlorodirhodium, $[(PF_3)_2RhCl]_2$ (Clement, Nixon & Sexton, 1969) with copper, trifluorophosphine and nitric oxide at room temperature or more efficiently by displacement of the $\pi$-allyl group in $\pi$-allyltris(trifluorophosphine)rhodium (Clement, Nixon & Wilkins, 1971) with nitric oxide.

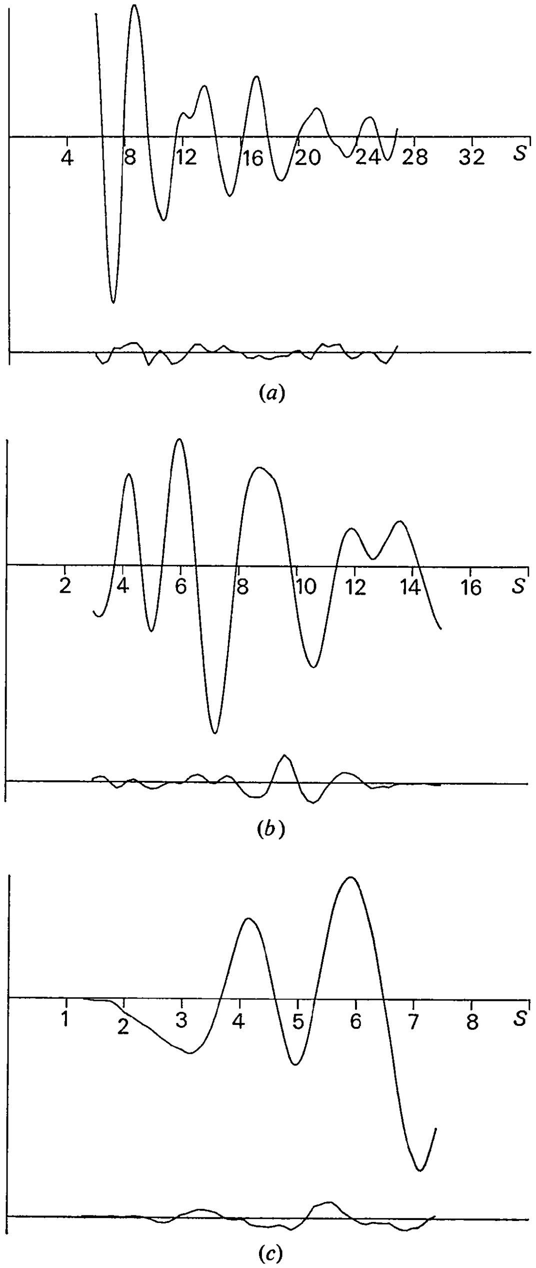

Fig. 1. Observed and final weighted difference molecular intensities for data sets obtained with nozzle-to-plate distances of (*a*) 250 mm, (*b*) 500 mm and (*c*) 1000 mm.

The gas phase infrared spectrum of the nitrosyl complex above 650 $cm^{-1}$ shows bands at 1820 $cm^{-1}$ (*vs*) (NO stretch), and 925(*vs*), 898(*vs*), 885(*m,sh*), 865(*s*) and 858 $cm^{-1}$ (*s*) (PF stretching modes). The $^{19}F$ nuclear magnetic resonance spectrum is complex but has been analysed recently (Nixon, 1971) as an $[X_3A]_3$ nuclear spin system, suggesting that the molecule has $3m$ ($C_{3v}$) symmetry, or $C_3$ symmetry with rapid rotation of the $PF_3$ groups.

Electron diffraction patterns were recorded photographically on Ilford N60 plates using a Balzers' KD.G2 gas diffraction instrument (Beagley, Clark and Hewitt, 1968). The electron wavelength, $\lambda$, obtained both by direct measurement of the accelerating voltage and from the diffraction pattern of powdered thallous chloride, was 0·05665 ± 0·00003 Å. The sample and inlet nozzle were maintained at 295 °K and 328 °K respectively during the exposures. Data from three plates, exposed with nozzle-to-plate distances of 250, 500 and 1000 mm, were used, giving a range of 1·3 to 26·8 $Å^{-1}$ in the scattering variable $s$, where $s = 4\pi \sin \theta/\lambda$. The data were transferred to punched tape using an automated Joyce–Loebl microdensitometer.

All calculations were carried out using an IBM 360/50 computer at the Edinburgh Regional Computing Centre, and data reduction and least-squares refinement programs that have been described elsewhere (Bridges, Holywell, Rankin & Freeman, 1971; Holywell, Rankin, Beagley & Freeman, 1971). The complex scattering factors of Cox & Bonham (1967) were used, with the phase shift factors modified as described later. In the full-matrix least-squares refinement program, the expression used to calculate the theoretical molecular scattering is

$$I_{\text{calc}}(s) - k_m \sum_{ij} G_{ij} \sin [s(r_{ij} - \kappa_{ij} s^2)] \exp(-u_{ij}{}^2 s^2/2) s r_{ij}$$

where $k_m$ is the refinable scale factor for the data set $m$, $G_{ij}$ is the term calculated from the scattering amplitudes and phase shift parameters for the $i$–$j$ atom pair, and $r_{ij}$, $u_{ij}$ and $\kappa_{ij}$ are the interatomic distance [$r_a$, (Bartell, 1955)], amplitude of vibration and anharmonicity for the atom pair.

The latter values were calculated using the relation $\kappa_{ij} = (a_{ij} u_{ij}^4)/6$ where $a_{ij}$ is an asymmetry parameter, set at 2 $Å^{-1}$ for all bonded distances and zero for nonbonded distances.

Table 1. *Weighting functions, correlation parameters and scale factors*

| Camera height | $\Delta s$ | $s_{\min}$ | $s_1$ | $s_2$ | $s_{\max}$ | $p/h$ | Scale factor |
|---|---|---|---|---|---|---|---|
| 250 mm | 0·4 | 6·0 | 9·0 | 22·0 | 26·8 | 0·4410 | 1·196 ± 0·031 |
| 500 | 0·2 | 3·0 | 5·0 | 12·5 | 15·0 | 0·4922 | 0·978 ± 0·024 |
| 1000 | 0·1 | 1·3 | 2·5 | 5·6 | 7·4 | 0·4993 | 0·753 ± 0·043 |

The refinement program uses an off-diagonal weight matrix to allow for the correlation between adjacent data points (MacGregor and Bohn, 1971). For a data set $m$, extending from $s_{\min}$ to $s_{\max}$, two weighting points, $s_1$ and $s_2$, are chosen by inspection. The weight matrix elements are then

$$\begin{array}{ll} w_{ii}=(s_i-s_{\min})/(s_1-s_{\min}) & s_{\min}\leqslant s_i\leqslant s_1 \\ w_{ii}=1 & s_1\leqslant s_i\leqslant s_2 \\ w_{ii}=(s_{\max}-s_i)/(s_{\max}-s_2) & s_2\leqslant s_i\leqslant s_{\max} \\ w_{ij}=0 & i\neq j\pm 1 \\ w_{ij}=-0{\cdot}5(w_{ii}+w_{jj})\,(p/h)_{\mathrm{m}} & i=j\pm 1. \end{array}$$

The values of the weighting points used, together with the correlation parameters, $p/h$, and the scale factors, are given in Table 1.

If this weight matrix is $\mathsf{W}$, and $\mathsf{I}$ and $\mathsf{U}$ represent the sectors of observed intensities ($I_{\mathrm{obs}}$) and differences ($I_{\mathrm{obs}}-I_{\mathrm{calc}}$) respectively, then the quantity minimized in the refinements is $\mathsf{U'WU/I'WI}$. The square root of this quantity is the 'generalized' $R$ value, $R_G$. A 'diagonal' $R$ value, $R_D$, is defined by

$$R_D=\sum_i w_{ii}U_i^2/\sum_i w_{ii}I_i^2\,.$$

## Molecular model

In almost all refinements the molecule was assumed to have a threefold rotation symmetry axis, with a linear Rh–N–O group, and local threefold symmetry for each Rh–PF$_3$ group. With these restrictions the molecular geometry may be defined by the four different bonded interatomic distances and three angles, chosen as PRhP, FPF and a twist angle. If the fluorine atoms attached to one phosphorus atom are labelled F(1), F(2) and F(3), and zero twist is defined for F(1) eclipsing the nitrosyl group, then a positive twist $\theta$ involves rotation of the PF$_3$ group about the Rh–P bond, atom F(1) moving towards the site of F(2) *etc.* The other fluorine atoms, F(1′), F(2′), F(3′), F(1″), F(2″) and F(3″), are similarly rotated about their respective Rh–P′ and Rh–P″ bonds by $\theta$, in the same

Table 2. *Molecular parameters*

($t-u$17) after an amplitude means that the amplitude is tied to amplitude number 17 *etc.*

| | Refinement *A* | | Refinement *B* | | |
|---|---|---|---|---|---|
| Independent distances | Distance (Å) | Amplitude (Å) | Distance (Å) | Amplitude (Å) | Shrinkage correction (Å) |
| *r*1 P–F | 1·558±0·003 | 0·053±0·004 | 1·558±0·003 | 0·053±0·004 | – |
| *r*2 Rh–P | 2·246±0·005 | 0·065±0·007 | 2·245±0·005 | 0·065±0·007 | – |
| *r*3 Rh–N | 1·848±0·021 | 0·060 (fixed) | 1·858±0·018 | 0·060 (fixed) | – |
| *r*4 N–O | 1·147±0·020 | 0·037 (fixed) | 1·149±0·019 | 0·037 (fixed) | – |
| Dependent distances | | | | | |
| *d*5 Rh–F | 3·274±0·009 | 0·158±0·010 | 3·273±0·011 | 0·157±0·009 | 0·0055 |
| *d*6 Rh–O | 2·995±0·024 | 0·065 (fixed) | 2·978±0·024 | 0·065 (fixed) | 0·0285 |
| *d*7 P–N | 3·346±0·019 | 0·091 (fixed) | 3·331±0·017 | 0·091 (fixed) | 0·0100 |
| *d*8 P–O | 4·296±0·023 | 0·120±0·027 | 4·269±0·021 | 0·129±0·031 | 0·0190 |
| *d*9 P–P | 3·683±0·012 | 0·225±0·053 | 3·681±0·017 | 0·179±0·031 | 0·0130 |
| *d*10 F(1)–F(2) | 2·396±0·009 | 0·075 (fixed) | 2·389±0·011 | 0·075 (fixed) | 0·0007 |
| *d*11 P–F(1′) | 4·901±0·016 | 0·203±0·030 | 4·887±0·013 | 0·206±0·022 | 0·0220 |
| *d*12 P–F(2′) | 4·731±0·020 | 0·203 (*t*–*u*11) | 4·730±0·025 | 0·206 (*t*–*u*11) | 0·0220 |
| *d*13 P–F(3′) | 3·811±0·014 | 0·229±0·070 | 3·812±0·025 | 0·263±0·080 | 0·0220 |
| *d*14 P′–F(1) | 4·722±0·016 | 0·203 (*t*–*u*11) | 4·707±0·022 | 0·206 (*t*–*u*11) | 0·0220 |
| *d*15 P′–F(2) | 3·814±0·015 | 0·229 (*t*–*u*13) | 3·819±0·024 | 0·263 (*t*–*u*13) | 0·0220 |
| *d*16 P′–F(3) | 4·908±0·013 | 0·203 (*t*–*u*11) | 4·905±0·022 | 0·206 (*t*–*u*11) | 0·0220 |
| *d*17 F(1)–F(1′) | 5·624±0·019 | 0·169±0·031 | 5·619±0·017 | 0·152±0·027 | 0·0280 |
| *d*18 F(1)–F(2′) | 5·998±0·023 | 0·169 (*t*–*u*17) | 5·985±0·027 | 0·152 (*t*–*u*17) | 0·0280 |
| *d*19 F(1)–F(3′) | 4·719±0·022 | 0·213 (fixed) | 4·711±0·026 | 0·213 (fixed) | 0·0280 |
| *d*20 F(2)–F(1′) | 5·099±0·015 | 0·213 (fixed) | 5·097±0·025 | 0·213 (fixed) | 0·0280 |
| *d*21 F(2)–F(2′) | 4·728±0·029 | 0·213 (fixed) | 4·736±0·026 | 0·213 (fixed) | 0·0280 |
| *d*22 F(2)–F(3′) | 3·320±0·017 | 0·213 (fixed) | 3·335±0·030 | 0·213 (fixed) | 0·0280 |
| *d*23 F(3)–F(1′) | 6·244±0·017 | 0·169 (*t*–*u*17) | 6·232±0·018 | 0·152 (*t*–*u*17) | 0·0280 |
| *d*24 F(3)–F(2′) | 5·663±0·025 | 0·169 (*t*–*u*17) | 5·672±0·029 | 0·152 (*t*–*u*17) | 0·0280 |
| *d*25 F(3)–F(3′) | 5·103±0·023 | 0·213 (fixed) | 5·107±0·021 | 0·213 (fixed) | 0·0280 |
| *d*26 N–F(1) | 3·590±0·013 | 0·123±0·040 | 3·565±0·017 | 0·157±0·054 | 0·0190 |
| *d*27 N–F(2) | 4·562±0·020 | 0·110±0·033 | 4·543±0·022 | 0·104±0·032 | 0·0190 |
| *d*28 N–F(3) | 4·404±0·021 | 0·110 (*t*–*u*27) | 4·383±0·021 | 0·104 (*t*–*u*27) | 0·0190 |
| *d*29 O–F(1) | 4·217±0·017 | 0·154 (*t*–*u*26) | 4·183±0·021 | 0·197 (*t*–*u*26) | 0·0250 |
| *d*30 O–F(2) | 5·523±0·023 | 0·138 (*t*–*u*27) | 5·496±0·026 | 0·130 (*t*–*u*27) | 0·0250 |
| *d*31 O–F(3) | 5·313±0·026 | 0·138 (*t*–*u*27) | 5·283±0·029 | 0·130 (*t*–*u*27) | 0·0250 |
| Angles | | | | | |
| ∠1 PRhP | 109·8±0·6° | | 110·4±0·5° | | |
| ∠2 FPF | 100·5±0·5 | | 110·1±0·7 | | |
| ∠3 Twist | 9·7±0·5 | | 9·8±0·6 | | |

Table 3. *Least squares correlation matrix multiplied by* $10^3$

| $R1$ | $R2$ | $R3$ | $R4$ | $<1$ | $<2$ | $<3$ | $U1$ | $U2$ | $U5$ | $U8$ | $U9$ | $U17$ | $U26$ | $U27$ | $K1$ | $K2$ | $K3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1000 | −37 | 396 | −63 | 221 | −314 | −83 | 87 | 85 | 9 | −60 | −30 | 45 | 34 | −134 | 54 | 22 | −12 |
| −37 | 1000 | −16 | −85 | −459 | 320 | −73 | −317 | −228 | −231 | −28 | 18 | −60 | −151 | 96 | −385 | −224 | −38 |
| 396 | −16 | 1000 | −390 | 250 | −143 | −284 | 208 | 54 | −262 | −184 | −128 | 125 | −97 | −140 | 124 | −74 | −167 |
| −63 | −85 | −390 | 1000 | 341 | −240 | 9 | −48 | 141 | 305 | 298 | 163 | 268 | 34 | 214 | 2 | −59 | −35 |
| 221 | −459 | 250 | 341 | 1000 | −628 | −246 | 193 | 438 | 190 | 145 | −174 | 127 | 202 | −331 | 179 | 110 | −6 |
| −314 | 320 | −143 | −240 | −628 | 1000 | −504 | −100 | −572 | −68 | −64 | 75 | −60 | −108 | 107 | −62 | −22 | 15 |
| −83 | −73 | −284 | 9 | −246 | −504 | 1000 | −37 | 128 | −48 | −68 | 60 | −45 | 15 | 272 | −9 | −24 | 1 |
| 87 | −317 | 208 | −48 | 193 | −100 | −37 | 1000 | 252 | 122 | −9 | −44 | 88 | 36 | −47 | 674 | 235 | 3 |
| 85 | −228 | 54 | 141 | 438 | −572 | 128 | 252 | 1000 | 158 | 98 | −36 | 17 | 59 | −150 | 285 | 187 | 61 |
| 9 | −231 | −262 | 305 | 190 | −68 | −48 | 122 | 158 | 1000 | −158 | 456 | 66 | 572 | 35 | 175 | 347 | 239 |
| −60 | −28 | −184 | 298 | 145 | −64 | −68 | −9 | 98 | −158 | 1000 | −270 | 90 | −354 | 203 | 22 | −28 | −53 |
| −30 | 18 | −128 | 163 | −174 | 75 | 60 | −44 | −36 | 456 | −270 | 1000 | 4 | 26 | −1 | −49 | 7 | 86 |
| 45 | −60 | 125 | 268 | 127 | −60 | −45 | 88 | 17 | 66 | 90 | 4 | 1000 | 20 | 289 | 113 | 15 | −53 |
| 34 | −151 | −97 | 34 | 202 | −108 | 15 | 36 | 59 | 572 | −354 | 26 | 20 | 1000 | 77 | 37 | 221 | 180 |
| −134 | 96 | −140 | 214 | −331 | 107 | 272 | −47 | −150 | 35 | 203 | −1 | 289 | 77 | 1000 | −19 | −43 | −23 |
| 54 | −385 | 124 | 2 | 179 | −62 | −9 | 674 | 285 | 175 | 22 | −49 | 113 | 37 | −19 | 1000 | 246 | 14 |
| 22 | −224 | −74 | −59 | 110 | −22 | −24 | 235 | 187 | 347 | −28 | 7 | 15 | 221 | −43 | 246 | 1000 | 114 |
| −12 | −38 | −167 | −35 | −6 | 15 | 1 | 3 | 61 | 239 | −53 | 86 | −53 | 180 | −23 | 14 | 114 | 1000 |

sense, thus preserving the threefold axis. The molecular point group is therefore $3(C_3)$, and for twist angles of 0 or 60° it is $3m$ $(C_{3v})$.

## Results

The molecular intensity curves for the three data sets are presented in Fig. 1. The corresponding uphill curves are available from the authors on request.

Fig. 2 shows the radial distribution curve, and the difference between the experimental and calculated curves. Most of the principal features of the curve may be assigned to the four types of atom pairs involving rhodium, and to the strong phosphorus–fluorine peak at 1·56 Å. These five distances define all the geometrical parameters except for the PRhP and twist angles. These depend on the complex series of overlapping peaks extending from 3·3 to 6·2 Å. After several trial refinements with the twist angle fixed at various values between 0 and 60°, both these additional angles refined satisfactorily. It is possible that the $PF_3$ groups are rotating rapidly, but the considerably longer $R$ values found for twist angles away from 10° suggest that one conformation is more populated than others.

Owing to the complexity of the series of overlapping peaks, it was impossible to refine all the amplitudes of vibration, and so a number of constraints were applied. Thus, for example, the amplitudes for the N–F(2) and N–F(3) distances were assumed to be equal, and moreover, to be 0·8 times as great as the O–F(2) and O–F(3) amplitudes. All such constraints that were applied are noted in the table of parameters, Table 2. The quoted error for the first named amplitude of each such group applies in fact to the whole group. Even with these restrictions, attempts to refine all four groups involving phosphorus and fluorine atoms in different $PF_3$ units led to instability, and so these values were refined independently in sequence until a mutually consistent solution was obtained.

For molecules that include atom pairs with widely differing atomic numbers, it is usually found that tabulated phase angles ($\eta$) are inadequate. Normally, cubic functions derived from tabulated values given by Cox & Bonham (1967) are used, the phase shift term for the $i$–$j$ atom pair being

$$\eta_i-\eta_j=a_i-a_j+(b_i-b_j).s+(c_i-c_j).s^2+(d_i-d_j).s^3.$$

This may be rewritten as

$$\Delta\eta=\pi/2+\Delta b'.(s-s_c)+\Delta c'.(s-s_c)^2+\Delta d.(s-s_c)^3,$$

where $s_c$ is the point at which $\cos(\Delta\eta)$ becomes zero. The initial values of $s_c$, calculated from the tabulated phases, for Rh–P, Rh–F, Rh–O and Rh–N were 39·5, 26·6, 26·1 and 24·6 $Å^{-1}$. The values for Rh–P and Rh–F were allowed to refine, optimum values of 37·2 and 24·8 $Å^{-1}$ being obtained. The Rh–O and Rh–N cut-off points were then reduced to 24·3 and 22·8 $Å^{-1}$ respectively, and all four values were subsequently fixed.

The parameters at this stage, before application of shrinkage corrections, are listed in Table 2 as refinement *A*. In the absence of any vibrational analysis of nitrosyltris(trifluorophosphine)rhodium, the shrinkage corrections had to be estimated on the basis of published values for various carbonyl complexes (Brunvoll, 1965; Cyvin, Brunvoll & Rajalakshmi, 1966; Brunvoll, 1967) and for trifluorophosphine (Morino, Kuchitsu & Moritani, 1969).

It has been noted that $\pi$-cyclopentadienyl(nitrosyl)-nickel appears to be a symmetric top when studied by microwave spectroscopy (Cox & Brittain, 1970*a*), whereas a NiNO angle of 160° is found by electron diffraction (Berndt, 1957). This large shrinkage effect is due to the large amplitude bending motion of the Ni–N–O group, the frequency of vibration being 153 $\text{cm}^{-1}$ (Cox & Brittain, 1970*b*). The possibility of a similar effect in the present case was therefore studied, and an apparent RhNO angle of 163° was found. This result implies that a shrinkage correction for the Rh–O distance of 0·0285 Å is necessary, assuming that in the average structure the Rh–N–O group is linear.

The results of the best refinement including these shrinkage corrections are listed as refinement *B* in Table 2, together with values of all the corrections. It should be noted that in estimating the corrections no account was taken of the effects of torsional oscillations about the rhodium–phosphorus bonds. It is quite possible, therefore, that the observed twist angle of 9·8° does not represent the mean position of the trifluorophosphine groups, which may be oscillating about the fully eclipsed position, with the molecular point group being $3m$ as is suggested by n.m.r. spectroscopy.

The errors quoted in Table 2 are estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. The use of an off-diagonal weight matrix ensures that the least-squares derived errors are realistic (MacGregor & Bohn, 1971).

Final *R* values were $R_G=0{\cdot}15$, $R_D=0{\cdot}12$. The final least-squares correlation matrix is given in Table 3. The structure of nitrosyltris(trifluorophosphine)rhodium is illustrated in Fig. 3.

Table 4. *Some rhodium–phosphorus bond lengths*

| Complex | Rhodium coordination polyhedron | Bond lengths (e.s.d. in brackets) | Reference |
|---|---|---|---|
| $RhCl_3(PBu^n{}_3)_2P(OMe)_3$ | octahedral | 2·400 (5) Å<br>2·379 (5)<br>2·199 (5) | Allen, Chang, Cheung, Lai & Lee (1970). |
| $RhH(CO)(PPh_3)_3$ | trigonal bipyramidal | 2·315 (8)<br>2·316 (9)<br>2·336 (8) | La Placa & Ibers (1965). |
| $Rh[P(OMe)_3]_2BPh_4$ | (one phenyl group $\pi$-bonded) | 2·18 (1)<br>2·18 (1) | Nolte, Gafner & Haines (1969). |
| $RhI_2Me(PPh_3)_2 . C_6H_6$ | square pyramidal | 2·35 | Skapski & Troughton (1968). |
| $[Rh(O_2)(Ph_2PCH_2CH_2PPh_2)_2](PF_6)$ | trigonal bipyramidal | 2·326 (4)<br>2·362 (4)<br>2·354 (4)<br>2·350 (4) | McGinnety, Payne & Ibers (1969). |
| $RhCl(CO)(SO_2)(PPh_3)_2$ | distorted square pyramidal | 2·371 (2)<br>2·367 (2) | Muir & Ibers (1969). |
| $RhHCl(SiCl_3)(PPh_3)_2 . xSiHCl_3$ | distorted trigonal bipyramidal | 2·344 (4)<br>2·332 (4) | Muir & Ibers (1970). |
| $RhCl(CS)(PPh_3)_2$ | square planar | 2·335 (2)<br>2·337 (2) | DeBoer, Rogers, Skapski & Troughton (1966). |
| $RhCl(PPh_3)_3$ | distorted tetrahedral | 2·218 (8)<br>2·315 (8)<br>2·327 (8) | Hitchcock, McPartlin & Mason (1969). |
| $RhCl(C_2F_4)(PPh_3)_2$ | distorted square planar | 2·374 (8)<br>2·370 (8) | Hitchcock, McPartlin & Mason (1969). |
| $RhH(PPh_3)_4 . \frac{1}{2}C_6H_6$ | tetrahedral | 2·34 (5)<br>2·39 (3) | Baker & Pauling (1969). |
| $Rh(NO)(PF_3)_3$ | tetrahedral | 2·245 (5) | This work. |
| $RhCl(PPh_3)(Et_2NPF_2)_2$ | square planar | 2·352 (3)<br>2·215 (3)<br>2.136 (3) | Bennett, Robertson, Turney & Whimp (1971). |

## Discussion

The geometrical parameters for the trifluorophosphine ligands found in this present study fit in well with the trends that have been noted (Bridges, Holywell, Rankin & Freeman, 1971), with shorter phosphorus–fluorine bonds and wider FPF angles than in the free ligand (Morino, Kuchitsu & Moritani, 1969). These changes are small, and have little significance in any one structural determination, but the overall picture is clear, and further studies should confirm the trends.

The significance of the rhodium–phosphorus bond length in nitrosyltris(trifluorophosphine)rhodium may be seen when the value is compared with other reported lengths. Table 4 lists some values (all crystallographic) that have been reported for tetrahedral, square planar, square pyramidal, trigonal bipyramidal and octahedral rhodium phosphine complexes. From the table it is apparent that the oxidation state and coordination pattern of the rhodium atom have little bearing on the lengths of the rhodium–phosphorus bonds. The major part of the variations observed may be ascribed to the nature of the phosphorus substituents. Thus all the trimethyl phosphite complexes have rhodium–phosphorus bond lengths of about 2·19 Å (although this shortness may be due to the other ligands present in the particular complexes that have been studied), whereas in the trifluorophosphine complex the length is about 2·24 Å, and in aryl- or alkylphosphine derivatives lengths of 2·31 to 2·40 Å are reported. Presumably the electron-withdrawing properties of fluorine atoms or methoxy groups attached to phosphorus enhance the $\pi$-acceptor properties of the phosphine group as a ligand.

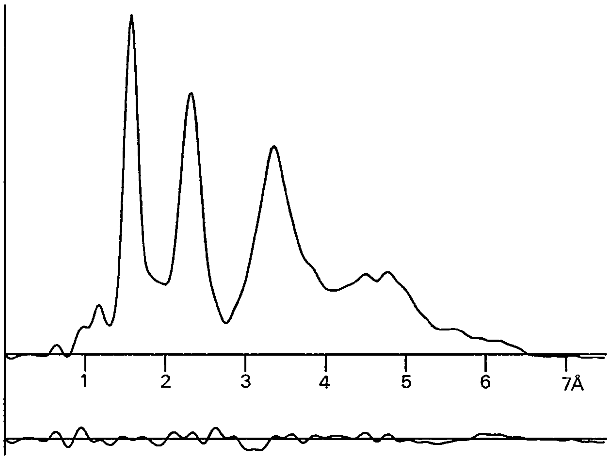

Fig. 2. Radial distribution curve, $P(r)/r$, and final deviations between experimental and calculated curves. Before Fourier inversion the data were multiplied by $s.\exp(-0{\cdot}0015s^2)/(z_{\rm Rh}-f_{\rm Rh})\,(z_{\rm F}-f_{\rm F})$.

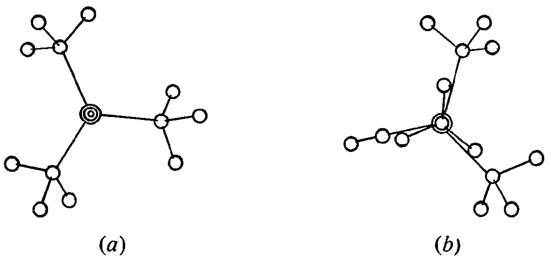

Fig. 3. Views of nitrosyl-tris(trifluorophosphine)rhodium (*a*) along the threefold axis and (*b*) along one phosphorus—rhodium bond.

The linear metal–N–O grouping is consistent with the idea of the complexing ligand being $NO^+$, rather than a neutral group. A similar situation has been reported for tetracarbonyl(nitrosyl)manganese, which has a nitrogen–oxygen bond length of 1·152 ± 0,015 Å (Frenz, Enemark & Ibers, 1969).

In other nitrosyl complexes angles at nitrogen close to 120° have been reported (Hodgson & Ibers, 1968; Hodgson & Ibers, 1969; Mingos & Ibers, 1971), and in these cases the complexing ligand is thought to be $NO^-$. Intermediate cases are of course possible. Mingos & Ibers (1971) have discussed the nature of nitrosyl ligands, but reliable information, particularly concerning nitrogen–oxygen bond lengths, is sparse.

It is of interest that the difference between the experimental rhodium–phosphorus and rhodium–nitrogen distances is 0·398 Å, compared with a difference of 0·386 Å between the carbon–phosphorus and carbon–nitrogen lengths in trimethylphosphine (Lide & Mann, 1958) and trimethylamine (Beagley & Hewitt, 1968). This suggests that the bond orders of the two types of rhodium bonds are similar. This type of relationship has also been noted for metal–phosphorus and metal–carbon bonds in a molybdenum carbonyl complex (Bridges, Holywell, Rankin, & Freeman 1971).

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## References

Allen, F. H., Chang, G., Cheung, K. K., Lai, T. F. & Lee, L. M. (1970). *Chem. Commun.* p. 1297.

Almenningen, A., Andersen, B. & Astrup, E. E. (1970). *Acta Chem. Scand.* **24**, 1579.

Baker, R. W. & Pauling, P. (1969). *Chem. Commun.* p. 1495.

Bartell, L. S. (1955). *J. Chem. Phys.* **23**, 1219.

Beagley, B., Clark, A. H. & Hewitt, T. G. (1968). *J. Chem. Soc.* (*A*), p. 658.

Beagley, B. & Hewitt, T. G. (1968). *Trans. Faraday Soc.* **64**, 2561.

Bennett, M. A., Robertson, G. B., Turney, T. W. & Whimp, P. O. (1971). *Chem. Commun.* p. 762.

Berndt, A. F. (1957). Thesis, California Institute of Technology.

Boer, J. L. de, Rogers, D., Skapski, A. C. & Troughton, P. G. H. (1966). *Chem. Commun.* p. 756.

BRIDGES, D. M., HOLYWELL, G. C., RANKIN, D. W. H. & FREEMAN, J. M. (1971). *J. Organomet. Chem.* **32**, 87.
BRUNVOLL, J. (1965). *J. Mol. Spectrosc.* **15**, 386.
BRUNVOLL, J. (1967). *Acta Chem. Scand.* **21**, 1390.
CLEMENT, D. A. & NIXON, J. F. (1972). Paper in preparation.
CLEMENT, D. A., NIXON, J. F. & SEXTON, M. D. (1969). *Chem. Commun.* p. 1509.
CLEMENT, D. A., NIXON, J. F. & WILKINS, B. (1971). Unpublished results.
COX, A. P. & BRITTAIN, A. H. (1970*a*). *Trans. Faraday Soc.* **66**, 557.
COX, A. P. & BRITTAIN, A. H. (1970*b*). *J. Mol. Spectrosc.* **35**, 49.
COX, H. L. & BONHAM, R. A. (1967). *J. Chem. Phys.* **47**, 2599.
CYVIN, S. J., BRUNVOLL, J. & RAJALAKSHMI, K. V. (1966). *Acta Chem. Scand.* **20**, 1991.
FRENZ, B. A., ENEMARK, J. H. & IBERS, J. A. (1969). *Inorg. Chem.* **8**, 1288.
FRENZ, B. A. & IBERS, J. A. (1970). *Inorg. Chem.* **9**, 2403.
HITCHCOCK, P. B., MCPARTLIN, M. & MASON, R. (1969). *Chem. Commun.* p. 1367.
HODGSON, D. J. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 2345.
HODGSON, D. J. & IBERS, J. A. (1969). *Inorg. Chem.* **8**, 1282.
HOLYWELL, G. C., RANKIN, D. W. H., BEAGLEY, B. & FREEMAN, J. M. (1971). *J. Chem. Soc.* (*A*), p. 785.
KRUCK, T. & LANG, W. (1967). Unpublished results, quoted by KRUCK, T., *Angew. Chem. Int. Ed. Engl.* **6**, 53.
LA PLACA, S. J. & IBERS, J. A. (1965). *Acta Cryst.* **18**, 511.
LIDE, D. R. & MANN, D. E. (1958). *J. Chem. Phys.* **29**, 914.
MCGINNETY, J. A., PAYNE, N. C. & IBERS, J. A. (1969). *J. Amer. Chem. Soc.* **91**, 6301.
MACGREGOR, M. A. & BOHN, R. K. (1971). *Chem. Phys. Lett.* **11**, 29.
MARRIOTT, J. C., SALTHOUSE, J. A. & WARE, M. J. (1970). *Chem. Commun.* p. 595.
MINGOS, D. M. P. & IBERS, J. A. (1971). *Inorg. Chem.* **10**, 1035.
MORINO, Y., KUCHITSU, K. & MORITANI, T. (1969). *Inorg. Chem.* **8**, 867.
MUIR, K. W. & IBERS, J. A. (1969). *Inorg. Chem.* **8**, 1921.
MUIR, K. W. & IBERS, J. A. (1970). *Inorg. Chem.* **9**, 440.
NIXON, J. F. (1970). *Advanc. Inorg. Chem. Radiochem.* **13**, 363.
NIXON, J. F. (1971). Unpublished results.
NOLTE, M. J., GAFNER, G. & HAINES, L. M. (1969). *Chem. Commun.* p. 1406.
SKAPSKI, A. C. & TROUGHTON, P. G. H. (1968). *Chem. Commun.* p. 575.

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# The Crystal and Molecular Structures of Some Condensation Products of Succinaldehyde and *p*-Bromophenylhydrazine

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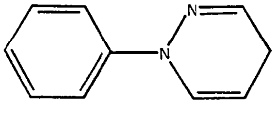
The crystal structures of two isomeric condensation products ($C_{20}H_{18}Br_2N_4$) of succinaldehyde and *p*-bromophenylhydrazine have been determined using three-dimensional diffractometer-collected X-ray data. Both compounds crystallize in the space group $P2_1/c$, with 4 molecules in the unit cell. The cell dimensions are $a=12{\cdot}20$ (3), $b=10{\cdot}12$ (1), $c=16{\cdot}37$ (2) Å, $\beta=110{\cdot}4$ (1)°, and $a=7{\cdot}429$ (3), $b=15{\cdot}444$ (8), $c=15{\cdot}991$ (9) Å, $\beta=93{\cdot}47$ (6)°. The compounds were found to be the diastereomeric racemates (4a*RS*, 4b*SR*,13b*RS*)-12-bromo-1-(*p*-bromophenyl)-1,4a,4b,5,6,13b-hexahydro-4*H*-dipyridazino[1,6-*a*:4,3-*c*]-quinoline and (4a*RS*,4b*RS*,13b*RS*)-12-bromo-1-(*p*-bromophenyl)-1,4a,4b,5,6,13b-hexahydro-4*H*-dipyridazino-[1,6-*a*:4,3-*c*]quinoline. The crystal structure of one of the enantiomers of the former, which spontaneously resolved from the solution of the racemate, was also determined. The enantiomer crystallizes in the space group $P2_12_12_1$ with $Z=4$ and cell parameters $a=13{\cdot}11$ (3), $b=14{\cdot}96$ (5), $c=9{\cdot}41$ (1) Å. Only small differences in the conformations of the molecules were found, but the packing of the molecules are quite different.

## Introduction

Ciamician & Zanetti (1890) determined a condensation product of succinaldehyde and phenylhydrazine to have the molecular formula $C_{20}H_{20}N_4$, and the constitutional formula was proposed to be 'a double molecule of a pyridazine derivative'. Desaty, Hadžija & Keglević (1965) proposed the structure of the condensation product on the basis of spectral and chemical evidence to be the dihydropyridazine derivate $C_{10}H_{10}N_2$.



However, recent investigations (Hjeds & Larsen, 1971) showed that the condensation product consisted