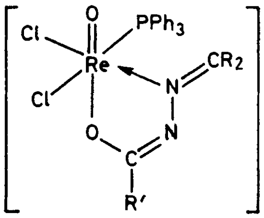
Crystal and Molecular Structure of [Acetone benzoylhydrazonido(1−)-*N′O*]dichloro-oxo(triphenylphosphine)rhenium(v)

By **Michael B. Hursthouse,*** Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS
S. Amarasiri A. Jayaweera and **Andrew Quick,** John Graymore Chemistry Laboratories, School of Environmental Sciences, Plymouth Polytechnic, Plymouth PL4 8AA

The crystal and molecular structures of the title compound have been determined from single-crystal *X*-ray diffractometer data. The crystals are monoclinic with a = 15.610, b = 18.510, c = 10.650 Å, β = 114.68°, space group $P2_1/a$, and Z = 4. The structure has been solved by Patterson and Fourier methods, and refined by least squares, using 2 678 independent reflections, to an R value of 0.052. The monomeric molecules have distorted octahedral co-ordination. The benzoylhydrazonide chelate adopts a predominantly enolic structure and there is no evidence for the incorporation of the metal into any delocalised system. The Re–O distance [2.013(7) Å] is shorter than the Re–N distance [2.127(10) Å] and does not appear to have been influenced by the multiply bonded oxo-function [Re$\overset{\leftarrow}{=}$O 1.685(8) Å] *trans* to it. The remaining metal–ligand distances are Re–Cl 2.388(3) (*trans* to P) and 2.344(4) Å (*trans* to N) and Re–P 2.472(2) Å.

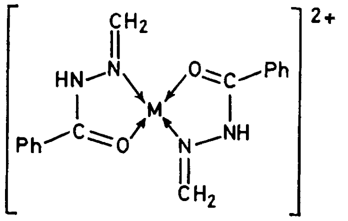
SUBSTITUTED hydrazines have been found to form a variety of metal complexes which, depending on the metal involved and the hydrazine substituents, can react further to give complexes containing other nitrogen ligands including dinitrogen itself. The relevance of such compounds and their reactions to the study of nitrogen fixation has been the stimulus for much research into this area. Recently we have concerned ourselves with the study of the structure and bonding in metal complexes of this type and report here the structure determination of one of a series of complexes derived from aroyl- or acyl-hydrazines, which contain an $\overline{\text{M–N–N–CPh–O}}$ chelate system.

Chatt *et al.*[1] have described a series of ketone hydrazonido-complexes of rhenium. Acyl- and aroyl-hydrazinium halides react with ketones and [$ReOCl_3(PPh_3)_2$] in refluxing benzene to give a derivative of the ketone hydrazone (1). These derivatives show two sharp i.r. bands at *ca.* 1 560 and 1 600 cm^{-1} assigned to ν(C=N). The absence of any bands assignable to ν(N–H) or ν(C=O) suggests that the hydrazine moiety is bonded in the enol form as shown in (1).



(1)

On the other hand, Issa *et al.*[2] reported the preparation of chelated benzoylhydrazone complexes (2) of some dipositive metal ions of the first-row transition series. An i.r. band at *ca.* 1 640 cm^{-1} was taken as confirmation that the aroylhydrazine group was co-ordinated in the keto-form and a band at *ca.* 1 620 cm^{-1} was assigned to ν(C=N). In order to ascertain unequivocally the mode of bonding of the hydrazine ligand in complexes of type (1), we have determined the structure of [acetone benzoylhydrazonido(1—)-*N′O*]dichloro-oxo(triphenylphosphine)rhenium(v), (1; R′ = Ph, R = Me).



(2)

M = Mn, Co, Ni, Zn, Cu or Cd

EXPERIMENTAL

Crystal Data.—$C_{28}H_{26}Cl_2N_2O_2PRe$, M = 710.6, Monoclinic, a = 15.610(1), b = 18.510(1), c = 10.650(1) Å, β = 114.68(5)°, U = 2 796.2 Å^3, D_m (by flotation) = 1.67, Z = 4, D_c = 1.69 g cm^{-3}, $F(000)$ = 1 392, space group $P2_1/a$, Cu-K_α radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 105.8 cm^{-1}.

The crystals are bright green prisms, stable in dry air. The crystal chosen for intensity-data collection had a maximum dimension of 0.2 mm, and was mounted with the b axis of the unit cell parallel to the ϕ axis of a General Electric XRD 6 manual diffractometer. The intensities of 3 408 independent reflections ($2\theta < 90°$) were recorded using Cu-K_α radiation with a Ni β filter, by the stationary-crystal–stationary-counter method. Throughout the data collection, the intensities of four reference reflections were measured every 100 reflections as a check on the electronic and crystal stability. No change in any of the standard reflections was noticed. Of the reflections measured, 2 678 had intensities significantly ($>3\sigma$) above background.[3] The structure was solved using standard Patterson and electron-density syntheses and refined by least-squares methods. With all the atoms assigned isotropic thermal parameters, R was reduced to 0.13. At this stage the data were corrected for absorption according to the method of Busing and Levy,[4] with the crystal pathlengths determined by the procedure of Coppens *et al.*[5] Refinement as before reduced R to 0.10. Further refinement, this time with anisotropic thermal parameters for the Re, P, and Cl atoms, reduced R to a final value of 0.052. In the final stages, the weighting scheme $w^{\frac{1}{2}} = 1$ for $F_o < F^*$ and F^*/F_o for

$F_o > F^*$ was used, with a best value for F^* of 58 on an absolute scale. Scattering factors for P, Cl, N, C, and O were taken from ref. 6, whilst those for Re were from ref. 7 with the real and the imaginary parts of the anomalous dispersion from ref. 8. A final difference electron-density synthesis showed no significant peaks.

Computations were made using programs written by Laing and Sale[9] on the Plymouth Polytechnic IBM 1130 and later with the '*X*-Ray '63' and '70' systems[10] on the University of London CDC 6600. Table 1 lists the final atomic fractional co-ordinates. The observed and calculated structure amplitudes and thermal parameters are listed in Supplementary Publication No. SUP 22374 (14 pp.).*

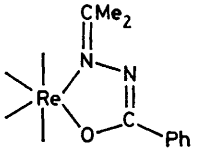
TABLE 1

Fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Re	2 323(1)	1 563(1)	508(1)
P	3 556(2)	1 919(2)	2 782(3)
Cl(1)	1 208(2)	1 120(2)	−1 668(3)
Cl(2)	3 039(2)	2 212(2)	−685(3)
O(1)	1 672(5)	2 187(4)	868(7)
O(2)	3 187(5)	731(4)	635(7)
N(1)	1 869(6)	684(5)	1 365(9)
N(2)	2 419(7)	48(5)	1 643(9)
C(1)	3 097(7)	125(6)	1 229(11)
C(2)	1 138(9)	602(7)	1 690(13)
C(3)	427(11)	1 222(9)	1 387(17)
C(4)	982(12)	−66(9)	2 345(17)
Ring (1) R(1)			
C(5)	3 746(8)	−465(6)	1 375(11)
C(6)	4 569(8)	−344(7)	1 213(13)
C(7)	5 196(10)	−926(8)	1 375(15)
C(8)	4 984(10)	−1 621(8)	1 681(15)
C(9)	4 155(9)	−1 750(7)	1 808(14)
C(10)	3 509(8)	−1 184(7)	1 633(13)
Ring (2) R(2)			
C(11)	3 750(7)	2 887(6)	3 038(11)
C(12)	4 424(9)	3 125(7)	4 294(14)
C(13)	4 544(10)	3 882(8)	4 587(16)
C(14)	4 019(9)	4 383(7)	3 601(14)
C(15)	3 358(8)	4 129(7)	2 298(12)
C(16)	3 212(8)	3 389(6)	2 008(12)
Ring (3) R(3)			
C(17)	4 725(7)	1 566(6)	3 228(11)
C(18)	5 280(9)	1 276(7)	4 538(13)
C(19)	6 229(11)	1 057(9)	4 842(16)
C(20)	6 570(9)	1 125(8)	3 817(14)
C(21)	6 007(9)	1 394(7)	2 530(13)
C(22)	5 083(8)	1 608(6)	2 234(12)
Ring (4) R(4)			
C(23)	3 181(8)	1 671(6)	4 116(12)
C(24)	2 693(9)	2 169(8)	4 552(14)
C(25)	2 309(10)	1 969(9)	5 491(15)
C(26)	2 378(10)	1 283(9)	5 948(16)
C(27)	2 863(11)	766(9)	5 526(16)
C(28)	3 248(9)	954(7)	4 560(14)

RESULTS AND DISCUSSION

The structure is found to contain discrete monomeric molecules in which the metal atom has distorted octahedral geometry, as seen in Figure 1,[11] with the two oxygen atoms *trans* to each other. Bond lengths and angles are given in Table 2, whilst values for the chelate ring are also shown in Figure 2. These indicate that the major contributor to the overall structure is the enol form (3) although the C–O bond length shows a small amount of multiple character. This may indicate that



(3)

other canonical forms make minor contributions to the overall structure, but the isopropylidene function effectively freezes out the form (3). The metallocycle is not exactly planar, but has a slight envelope conformation with the Re atom 0.13 Å out of the plane of the NNCO group. This, together with the fairly normal single-bond values for the Re–N and Re–O lengths in the chelate ring, suggests that there is no real involvement of the metal atom in any delocalisation which may be present in the ring.

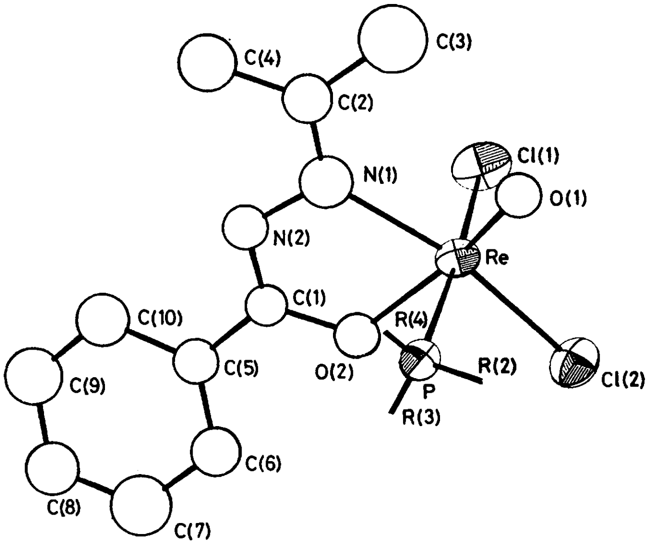


FIGURE 1 A single molecule of [ReOCl$_2${Ph(O)CNNCMe$_2$}(PPh$_3$)]. (The phenyl rings of the phosphine have been omitted for clarity)

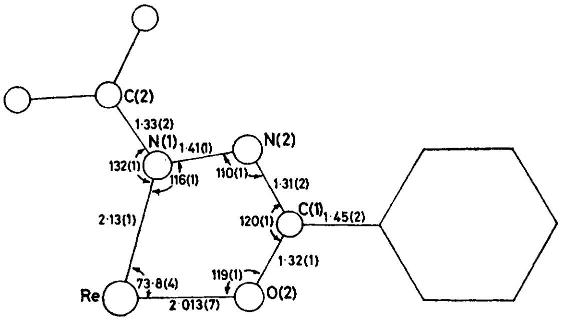


FIGURE 2 The geometry of the chelate ring

In Table 3 we present the results of various least-squares plane calculations. One interesting parameter

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

arising from these calculations is a dihedral angle of 15.6° between the planes of the chelate ring and the phenyl group. The approximate coplanarity of these rings is also seen in Figure 1. Although the difference between the C(1)–C(5) distance of 1.45(2) Å and the value normally accepted for a C(sp^2)–C(sp^2) bond (*ca.* 1.50 Å) is not strictly significant, the two effects together might indicate the possibility of some interaction between the π systems of the two rings. In most respects, however, the geometry of the ligand and the mode of bonding to the metal are similar to those of the related ligand in the complex [Pt{Ph(O)CNNC(O)Ph}(PPh_3)$_2$].[12]

TABLE 2

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses

(*a*) Distances

Re–P	2.472(2)		P–C–(11)	1.82(1)	
Re–Cl(1)	2.388(3)		C(11)–C(12)	1.38(2)	R(2)
Re–Cl(2)	2.344(4)		C(12)–C(13)	1.43(2)	
Re–N(1)	2.127(10)		C(13)–C(14)	1.38(2)	
Re–O(1)	1.685(8)		C(14)–C(15)	1.42(2)	
Re–O(2)	2.013(7)		C(15)–C(16)	1.40(2)	
O(2)–C(1)	1.32(1)		C(16)–C(11)	1.42(1)	
C(1)–N(2)	1.31(2)		P–C(17)	1.81(1)	
N(2)–N(1)	1.41(1)		C(17)–C(18)	1.41(2)	R(3)
N(1)–C(2)	1.33(2)		C(18)–C(19)	1.44(2)	
C(2)–C(3)	1.54(2)		C(19)–C(20)	1.41(3)	
C(2)–C(4)	1.49(2)		C(20)–C(21)	1.38(2)	
C(1)–C(5)	1.45(2)		C(21)–C(22)	1.40(2)	
C(5)–C(6)	1.38(2)	R(1)	C(22)–C(17)	1.39(2)	
C(6)–C(7)	1.42(2)		C(23)–C(24)	1.39(2)	R(4)
C(7)–C(8)	1.40(2)		C(24)–C(25)	1.41(3)	
C(8)–C(9)	1.38(2)		C(25)–C(26)	1.35(2)	
C(9)–C(10)	1.41(2)		C(26)–C(27)	1.41(3)	
C(10)–C(5)	1.44(2)		C(27)–C(28)	1.43(3)	
P–C(23)	1.81(2)		C(28)–C(23)	1.40(2)	

(*b*) Angles

P–Re–Cl(2)	92.4(1)		Re–P–C(11)	115(1)	
P–Re–N(1)	92.6(2)		P–C(11)–C(12)	118(1)	
N(1)–Re–Cl(1)	85.2(2)		P–C(11)–C(16)	122(1)	
Cl(1)–Re–Cl(2)	88.2(1)		C(11)–C(12)–C(13)	120(1)	R(2)
Cl(2)–Re–O(1)	103.9(3)		C(12)–C(13)–C(14)	121(1)	
Cl(1)–Re–O(1)	101.1(2)		C(13)–C(14)–C(15)	119(1)	
N(1)–Re–O(1)	94.9(4)		C(14)–C(15)–C(16)	122(1)	
P–Re–O(1)	83.7(2)		C(15)–C(16)–C(11)	119(1)	
Cl(2)–Re–O(2)	88.4(3)		C(16)–C(11)–C(12)	120(1)	
Cl(1)–Re–O(2)	90.0(2)		Re–P–C(17)	117(1)	
N(1)–Re–O(2)	73.8(4)		P–C(17)–C(18)	122(1)	
P–Re–O(2)	85.0(2)		P–C(17)–C(22)	118(1)	
O(1)–Re–O(2)	163.6(3)		C(17)–C(18)–C(19)	119(1)	R(3)
Re–N(1)–N(2)	116(1)		C(18)–C(19)–C(20)	119(1)	
N(1)–N(2)–C(1)	110(1)		C(19)–C(20)–C(21)	121(1)	
N(2)–C(1)–O(2)	121(1)		C(20)–C(21)–C(22)	121(1)	
C(1)–O(2)–Re	119(1)		C(21)–C(22)–C(17)	121(1)	
Re–N(1)–C(2)	132(1)		C(22)–C(17)–C(18)	120(1)	
N(2)–N(1)–C(2)	111(1)		C(17)–P–C(23)	109(1)	
N(1)–C(2)–C(3)	119(1)		C(17)–P–C(11)	103(1)	
N(1)–C(2)–C(4)	123(1)		C(23)–P–C(11)	103(1)	
C(3)–C(2)–C(4)	118(2)		Re–P–C(23)	109(1)	
O(2)–C(1)–C(5)	119(1)		P–C(23)–C(24)	120(1)	
N(2)–C(1)–C(5)	120(1)		P–C(23)–C(28)	120(1)	
C(1)–C(5)–C(6)	121(1)		C(23)–C(24)–C(25)	121(1)	R(4)
C(1)–C(5)–C(10)	120(1)		C(24)–C(25)–C(26)	121(2)	
C(5)–C(6)–C(7)	120(1)	R(1)	C(25)–C(26)–C(27)	120(2)	
C(6)–C(7)–C(8)	121(2)		C(26)–C(27)–C(28)	121(1)	
C(7)–C(8)–C(9)	120(1)		C(27)–C(28)–C(23)	119(1)	
C(8)–C(9)–C(10)	121(1)		C(28)–C(23)–C(24)	119(1)	
C(9)–C(10)–C(5)	119(1)				
C(10)–C(5)–C(6)	120(1)				

A direct consequence of representing the mode of bonding of the benzoylhydrazone ligand by structure (3) is that the metal is assigned a formal oxidation state of V. Bond lengths to the metal atom tend to confirm this. Thus the two Re–Cl distances [2.388(3) and 2.334(4) Å] are only slightly shorter than values found in the complexes [$ReCl_3$(NMe)($PEtPh_2$)$_2$][13] and [$ReCl_3$(NC_6H_4COMe)(PEt_2Ph)$_2$][14] which range from 2.399 to 2.433 Å. The Re–P distances in these two complexes (2.481 and 2.485 Å) also compare well with that found in the present study (2.472 Å). Both Re–Cl and Re–P distances also agree very well with the sum of covalent radii, using the value of 1.38 Å for Re^{V} derived from data for bromorhenates.[15] On this basis, the Re–O and Re–N distances to the chelating ligand are, respectively, slightly shorter (2.013 compared with 2.04 Å) and slightly longer (2.127 compared with 2.08 Å) than calculated values and this may represent some small asymmetry of the Re–O and Re–N strengths. The ' Re=O ' bond length (1.685 Å) is quite short, implying that the bond is best written as $\mathrm{R}\overset{\leftarrow}{=}\mathrm{O}$. In this way, the metal atom attains an 18-electron configuration.

TABLE 3

Results of least-squares-plane calculations

(*i*) Displacements (Å) of atoms from planes

A		B		C	
N(1)	0.001	N(1)	0.063	C(5)	0.021
N(2)	−0.002	N(2)	0.011	C(6)	−0.008
C(1)	0.002	C(1)	−0.022	C(7)	−0.007
O(2)	−0.001	O(2)	−0.018	C(8)	0.009
Re *	0.126	C(2)	0.007	C(9)	0.003
		C(3)	−0.026	C(10)	−0.018
		C(4)	−0.016		

(*ii*) Equations of planes in direct space

A $3.92x + 6.75y + 7.55z = 2.22$

B $3.39x + 7.12y + 7.71z = 2.11$

C $0.93x + 3.54y + 9.21z = 1.43$

* Not included in calculations of the plane.

The distortions from regular octahedral geometry in the co-ordination sphere do not correspond completely to the idea of equalisation of steric repulsions. A general feature in compounds containing an ' axial ' $\mathrm{M}\overset{\leftarrow}{=}\mathrm{O}$ system is a bending of the equatorial ligand atoms away from the high electron density in the multiple bond. This appears to be the case for the equatorial chlorine atoms [O(1)–Re–Cl 101, 104°] although this distortion is facilitated by the displacement of O(2) due to the restricted bite (74°) of the chelate [O(1)–Re–O(2) 164°]. It is also the case for the chelate nitrogen atom, with O(1)–Re–N(1) 95°. In contrast to these distortions however, is the O(1)–Re–P angle of 84° which corresponds to an O(1) · · · P contact of only 2.84 Å, much less than the sum of O and P van der Waals radii, and the P · · · O(2) contact of 3.05 Å. There does not seem to be a simple rationalisation of this feature. Certainly, the triphenylphosphine group is not involved in any significant steric repulsions, since there are no intermolecular contacts, involving atoms in this group, less than 3.6 Å. Although the phosphorus atom is renowned as an electron acceptor and the $\mathrm{Re}\overset{\leftarrow}{=}\mathrm{O}$ bond is electron rich, it is difficult to believe that there may be some form of interaction between the two.

Distance and angles in the remaining portions of the molecule are normal. All the phenyl groups are accurately planar, and in the triphenylphosphine group the P atom lies 0.13—0.17 Å out of the mean planes of the three phenyl groups bonded to it, a feature observed in a number of other structures.[16] Figure 3 shows the unit-cell contents as viewed down *b*. All the intermolecular contacts are normal, the shortest (3.26 Å) being $O(1) \cdots C(9'') = C(9) \times (\frac{1}{2} - x, \frac{1}{2} + x, -z)$.

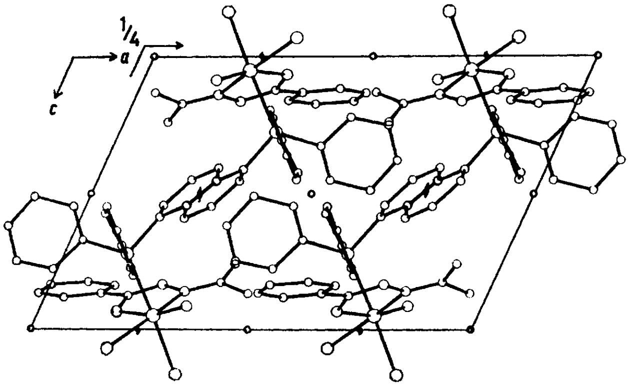

FIGURE 3 The unit-cell contents viewed down *b*

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