The Reactivity of the Unsaturated Dimeric Rhenium Complexes $[Re_2H_2(CO)_6\{(EtO)_2POP(OEt)_2\}]$ and $[Re_2H_2(CO)_6(Ph_2PCH_2PPh_2)]$: *X*-Ray Crystal Structure of $[Re_2H(CO)_6(Ph_2PCH_2PPh_2)\{\mu\text{-}NC(H)Me\}]$ †

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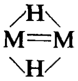
The complexes $[Re_2H_2(CO)_6(L\text{–}L)]$ [L–L = $(EtO)_2POP(OEt)_2$ (tedip)(1) or $Ph_2PCH_2PPh_2$ (dppm)(2)] react with $P(OMe)_3$ giving 1 : 1 adducts which exist in solution in two isomeric forms, both containing a terminal H and a (μ-H) ligand. Both (1) and (2) react with RNC (R = Bu^t, Bu^n, *p*-$MeOC_6H_4$, or *p*-$MeC_6H_4SO_2CH_2$) to give the complexes $[Re_2H(CO)_6(L\text{–}L)(\mu\text{-}HCNR)]$ (5) containing an *NC*-bonded formimidoyl ligand. With CH_3CN (1) and (2) react to give a major product formulated as $[Re_2H(CO)_6(L\text{–}L)\{\mu\text{-}NC(H)Me\}]$ [(6), L–L = tedip; (7a), L–L = dppm] and containing an *N*-bonded ethylideneimino group; for the product with L–L = dppm this formulation has been confirmed by an *X*-ray diffraction study. The complex crystallises in the monoclinic space group $P2_1/n$ with a = 9.765(3), b = 29.940(8), c = 11.813(4) Å, β = 104.69(2)°, and Z = 4. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least squares to R = 0.071 for 2 614 unique, observed diffractometer data. The minor product obtained in the reaction of (2) with CH_3CN is suggested on the basis of spectroscopic evidence to be $[Re_2H(CO)_6(dppm)(\mu\text{-}HNCMe)]$ (7b) containing an *NC*-bonded acetimidoyl ligand. Both (1) and (2) form an unstable adduct with CO but do not react with HC≡CH, $H_2C{=}CH_2$, or $MeO_2CC{\equiv}CCO_2Me$.

There are a number of polynuclear metal carbonyl complexes which may be regarded as formally unsaturated, in that multiple metal–metal bonds or electron deficient bonds are present.[1,2] Such molecules may react with electron-donor ligands without the need for CO dissociation or metal–metal bond fission. The best studied complex of this type, $[Os_3H_2(CO)_{10}]$, reacts with a wide variety of small molecules under mild conditions to give a range of complexes which are not accessible by other routes.[3] The reactivity of $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [4] and $[Rh_2(CO)_4(\eta^5\text{-}C_5H_5)_2]$ [5] have also received some attention, but the chemistry of other unsaturated polynuclear carbonyl hydride complexes such as $[W_2H_2(CO)_8]^{2-}$,[1] $[Re_2H_2(CO)_8]$,[6] $[Re_3H_3(CO)_{10}]^{2-}$,[7] $[Re_3H_4(CO)_{10}]^-$,[8] and $[Re_4H_4(CO)_{12}]$ [9] remains virtually unexplored due to synthetic difficulties or to their ready decomposition. Thus both $[Re_2H_2(CO)_8]$ and $[Re_4H_4(CO)_{12}]$ decompose to give mononuclear products when treated with PPh_3 at room temperature.[10]

The use of bridging and capping phosphorus donor ligands can stabilise polynuclear complexes with respect to break up into mononuclear fragments,[11] and in this paper we report on the reactivity of the stabilised unsaturated rhenium complexes $[Re_2H_2(CO)_6(L\text{–}L)]$ [L–L = $Ph_2PCH_2PPh_2$ (dppm) or $(EtO)_2POP(OEt)_2$ (tedip)], prepared from the reaction of $[Re_3H_3(CO)_{12}]$ with L–L in octane,[11] which may be regarded as derivatives of $[Re_2H_2(CO)_8]$. They are, in a sense, rhenium analogues of $[Os_3H_2(CO)_{10}]$ in that they can be regarded as containing the


$$M\overset{H}{\underset{H}{=}}M$$

unit and they show similar but not identical reactivity to the osmium complex.

Results and Discussion

(*a*) *Reaction with* PPh_3 *and* $P(OMe)_3$.—The reaction of $[Re_2H_2(CO)_8]$ with PPh_3 is the only reported reaction of this complex,[10] and it was repeated in an attempt to characterise the product more fully. On adding excess PPh_3 to a CH_2Cl_2 solution of $[Re_2H_2(CO)_8]$ at −50 °C, the yellow colour of the solution was discharged. The ^1H n.m.r. spectrum in the metal–hydride region at this temperature consisted of two equally intense signals, one in the region typical of a terminal hydride [δ − 5.85(s) p.p.m.] and one in the bridging region [δ − 15.02(d) p.p.m., J_{PH} 18 Hz]. On warming to −30 °C these signals broadened and collapsed (this change being reversible) suggesting bridge–terminal hydrogen atom exchange. Further warming, however, did not lead to a high temperature limiting spectrum since extensive sample decomposition to give $[ReH(CO)_4(PPh_3)]$ (δ − 5.23 p.p.m., Re*H*) occurred. The infrared spectrum of the adduct formed initially at −50 °C was in good agreement with that reported by Kaesz and co-workers.[10]

No reaction took place between $[Re_2H_2(CO)_6(L\text{–}L)]$ and PPh_3 at room temperature (r.t.). Addition of $P(OMe)_3$ to a yellow dichloromethane solution of $[Re_2H_2(CO)_6(tedip)]$ (1), however, resulted in immediate decolourisation and, on removal of solvent, a solid product (3) was isolated. The ^1H n.m.r. spectrum (CD_2Cl_2, −60 °C) of (3) shows a pair of equal intensity singlet ReH resonances at δ − 6.27 (terminal region) and −14.56 p.p.m. (bridging region) and a further pair of singlet resonances of greater, but again equal, intensity at δ − 6.96 and −16.02 p.p.m. (Table 1). This suggests that (3) is, as expected, the 1 : 1 adduct, $[Re_2H_2(CO)_6(tedip)\{P(OMe)_3\}]$, analogous to those formed between $[Os_3H_2(CO)_{10}]$ and organophosphines and, in the mass spectrum of (3), a molecular ion peak corresponding to this formulation was observed (Table 2). Presumably the two pairs of resonances observed at −60 °C in the ^1H n.m.r. spectrum correspond to the presence in solution of two of the three geometric isomers (3a)—(3c) shown in Figure 1 [each geometric isomer has an optical isomer, (3a′)—(3c′)]. The four resonances broaden and collapse on warming and, at +20 °C, a broad resonance at the chemical shift average of the four

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† μ-Bis(diphenylphosphino)methane-μ-ethylideneimino-μ-hydrido-bis(tricarbonylrhenium)(*Re–Re*).

Supplementary data available (No. SUP 23363; 19 pp.): observed and calculated structure factors, thermal parameters, least squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: 1 atm = 101 325 N m^{-2}.

Table 1. Infrared and ^{1}H n.m.r. data for bridged dirhenium complexes

	Compound	ν(CO)/cm^{-1}	δ */p.p.m.
(1)	$[Re_2H_2(CO)_6(tedip)]$	2 058s, 2 027s, 1 968m, 1 947s (sh), 1 933s, br	4.08 (m, $^{3}J_{HH}$ 6.9, 8 H, CH_2), 1.36 (t, $^{3}J_{HH}$ 6.9, 12 H, CH_3), −8.93 (t, J_{PH} 12.9, 2 H, ReH)
(2)	$[Re_2H_2(CO)_6(dppm)]$	2 041s, 2 012s, 1 947m, 1 918s, br	7.24 (m, 20 H, Ph), 3.13 (t, $^{2}J_{PH}$ 10.8, 2 H, CH_2), −7.51 (t, $^{2}J_{PH}$ 10.4, 2 H, ReH)
(3)	$[Re_2H_2(CO)_6(tedip)\{P(OMe)_3\}]$	2 054m, 2 029s, 2 011 (sh), 1 967s, 1 947s, 1 926 (sh), 1 907 (sh)	3.90 (m, 8 H, CH_2), 3.36 (s, br, 9 H, OMe), 1.22 (m, 12 H, CH_3): Isomer 1; −6.27 (s, 1 H, ReH), −14.56 (s, 1 H, ReH); Isomer 2; −6.96 (s, 1 H, ReH), −16.02 (s, 1 H, ReH)
(4)	$[Re_2H_2(CO)_6(dppm)\{P(OMe)_3\}]$	2 036s, 2 020m, 1 995s, 1 960s, 1 928s, 1 909s, 1 893 (sh)	
(5a)	$[Re_2H(CO)_6(tedip)(HCNBu^t)]$	2 043s, 2 013s, 1 954s, 1 934m, 1 907s	10.65 (d of d, $^{4}J_{HH}$ 1.8, 1 H, CH), 4.03 (m, br, 8 H, CH_2), 1.27 (m, 12 H, CH_3), 1.13 (s, 9 H, Bu^t), −14.16 (d of t, $^{2}J_{PH}$ 14.9, $^{4}J_{HH}$ 1.8, 1 H, ReH)
(5b)	$[Re_2H(CO)_6(tedip)(HCNC_6H_4OMe\text{-}p)]$	2 043s, 2 016s, 1 958s, 1 940m, 1 914s	10.63 (s, 1 H, CH), 6.8 (m, 4 H, C_6H_4), 4.04 (m, 8 H, CH_2), 3.77 (s, 3 H, Me), 1.34 (m, 12 H, CH_3), −14.21 (t, $^{2}J_{PH}$ 14.0, 1 H, ReH)
(5c)	$[Re_2H(CO)_6(dppm)(HCNBu^t)]$	2 038s, 2 012s, 1 952s, 1 933m, 1 912s	10.86 (s, 1, H, CH), 7.24 (m, 20 H, Ph), 3.21 (m, 2 H, CH_2) 2.54 (m, 9 H, Bu^t), −12.92 (d of d, $^{2}J_{PH}$ 15.4, $^{2}J_{PH}$ 9.5, 1 H, ReH)
(5d)	$[Re_2H(CO)_6(dppm)(HCNC_6H_4OMe\text{-}p)]$	2 041s, 2 015s, 1 957s, 1 938m, 1 905s, br	10.94 (s, 1 H, CH), 7.20 (m, 24 H, Ph), 3.75 (s, 3 H, Me), 3.40 (m, 8 H, CH_2), −12.86 (t, $^{2}J_{PH}$ 12.7, 1 H, ReH)
(5e)	$[Re_2H(CO)_6(dppm)(HCNBu^n)]$	2 030s, 2 004s, 1 946s, 1 929m, 1 905s	10.41 (s, 1 H, CH), 7.35 (m, 20 H, Ph), 3.20, 2.50 (m, 2 H, CH_2), 3.17, 1.50 (m, 9 H, Bu^n), −13.09 (t, $^{2}J_{PH}$ 12.5, 1 H, ReH)
(5f)	$[Re_2H(CO)_6(dppm)(HCNCH_2SO_2C_6H_4Me\text{-}p)]$	2 035s, 2 009s, 1 945s, 1 925 (sh), 1 907s, br	10.71 (s, 1 H, CH), 7.42 (m, 24 H, Ph), 4.23 (m, 2 H, CH_2N), 3.28 (m, 8 H, CH_2), 2.43 (s, 12 H, CH_3), −13.09 (t, $^{2}J_{PH}$ 11.7, 1 H, ReH)
(6)	$[Re_2H(CO)_6(tedip)\{NC(H)Me\}]$	2 042s, 2 013s, 1 951s, 1 929m, 1 910s	8.50 (s, br, 1 H, CH), 4.00 (m, br, 8 H, CH_2), 2.09 (d, $^{3}J_{HH}$ 4.1, 3 H, Me), 1.17 (m, 12 H, Me), −11.09 (t, $^{2}J_{PH}$ 12.7, 1 H, ReH)
(7a)	$[Re_2H(CO)_6(dppm)\{NC(H)Me\}]$	2 031s, 2 005s, 1 938s, 1 917m, 1 903s	8.61 (m, 1 H, CH), 7.15 (m, 20 H, Ph), 2.69, 2.22 (m, 2 H, CH_2), 2.08 (d, $^{3}J_{HH}$ 1.5, 3 H, Me), −10.76 (t, $^{2}J_{PH}$ 10.6, 1 H, ReH)
(7b)	$[Re_2H(CO)_6(dppm)(HNCMe)]$	2 046s, 2 022s, 1 952s, 1 932m, 1 914s	7.28 (m, 20 H, Ph), 3.59, 2.71 (m, 2 H, CH_2), 1.58 (s, 3 H, Me), −10.80 (t, $^{2}J_{PH}$ 10.3, 1 H, ReH)

* s = Singlet, d = doublet, t = triplet, m = multiplet, J values in Hz.

Table 2. Mass spectroscopic and microanalytical data for bridged dirhenium complexes

	Mass spectra		Analysis (%)[b]		
Compound	$M+$	Fragmentation[a]	C	H	N
(3)	924	$M - n$CO			
(5a)	883	$M - n$CO, M − RNC − nCO			
(5c)	1 009	M − H − nCO, M − RNC − nCO	42.5 (42.8)	3.5 (3.2)	1.4 (1.4)
(5d)	1 059	$M - n$CO, M − RNC − nCO	44.8 (44.2)	3.2 (2.9)	1.2 (1.3)
(5e)	1 009	M − H − nCO, M − RNC − nCO			
(5f)	1 121	$M - n$CO	43.6 (42.8)	3.8 (2.9)	2.1 (1.2)
(6)	841	$M - n$CO			
(7a)	967	$M - n$CO	41.0 (41.0)	2.9 (2.8)	1.5 (1.4)
(7b)	967	M − H − nCO			

[a] n = 0—6. [b] Calculated values are given in parentheses.

initial resonances is observed. On cooling, these changes are reversed. If isomers (3a) and (3b) are present then simple bridge-terminal hydrogen atom exchange converts these respectively into (3b′) and 3a′). It should be noted that

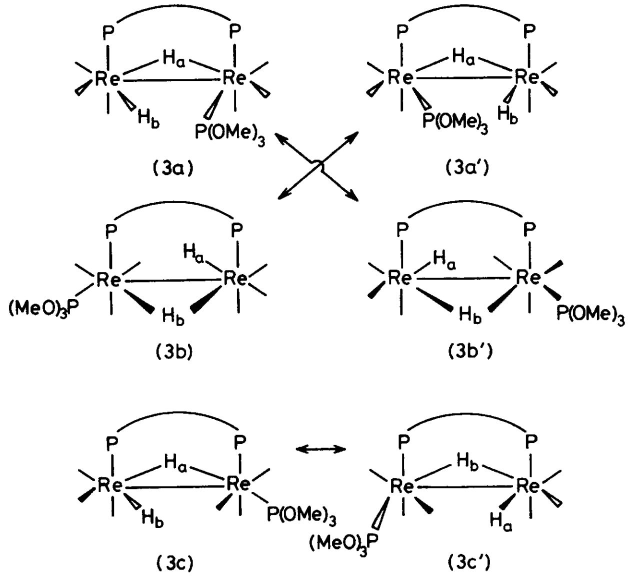


Figure 1. Some possible geometric (3a)—(3c) isomers of $[Re_2H_2(CO)_6(L\text{-}L)\{P(OMe)_3\}]$ together with their optical isomers (3a′)—(3c′) showing interconversions due to bridge-terminal H-atom exchange

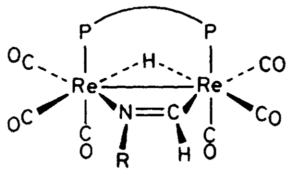


Figure 2. Proposed structure for the complexes $[Re_2H(CO)_6(L{-}L)(HCNR)]$ (5a)—(5f)

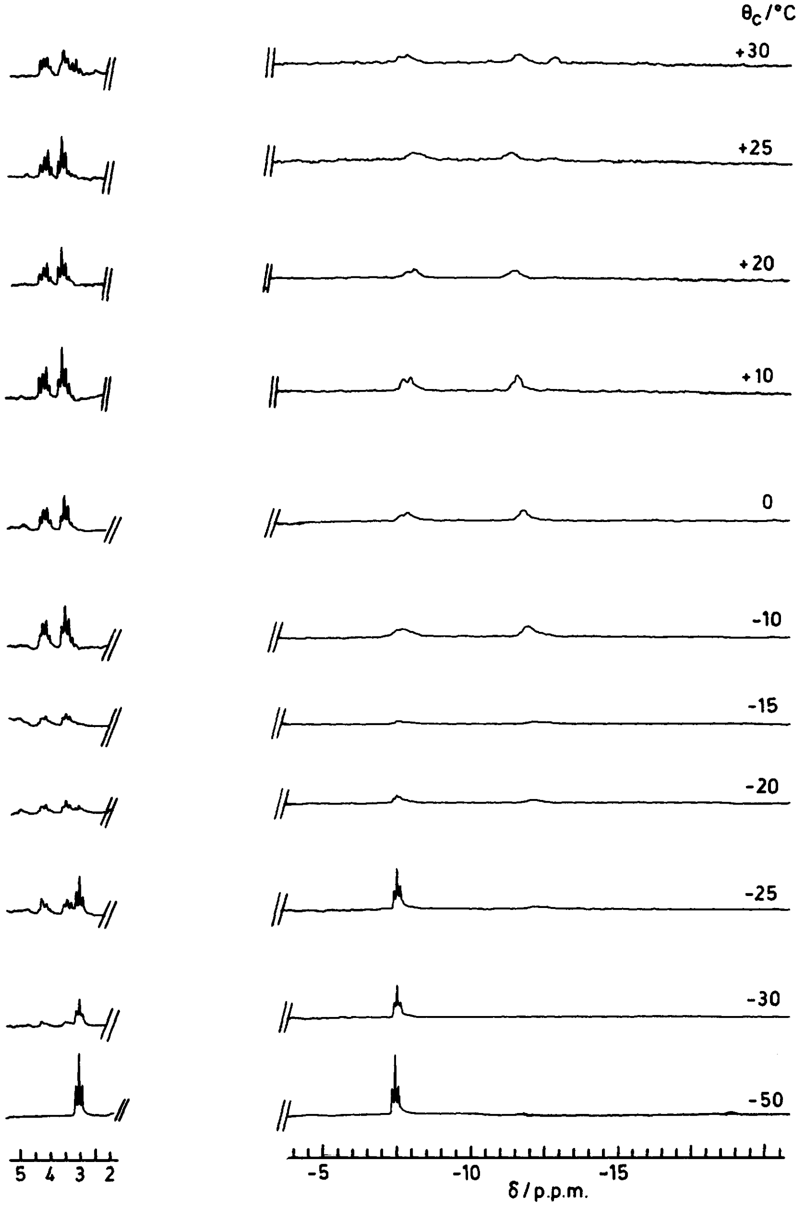


Figure 3. ^{1}H n.m.r. spectrum of $[Re_2H_2(CO)_6(dppm)]$ + Bu^tNC in the methylene and metal hydride regions

although this process interconverts the two geometric isomers, it does not lead to complete equivalence of the two hydrogen atoms, H_a and H_b. Instead, H(terminal) in one geometric isomer becomes averaged with H(bridging) in the other. If the process is rapid on the n.m.r. time-scale at +20 °C, then two equal intensity ^{1}H resonances should be observed but, since these would have similar δ values, the process is not incompatible with the observed spectrum. An alternative explanation is that two of the three geometric isomers (3a)—(3c) are present at −60 °C and that these interconvert rapidly on the n.m.r. time-scale by reversible $P(OMe)_3$ dissociation at higher temperatures. It is not possible to distinguish between these explanations on the basis of our data.

The reaction of $P(OMe)_3$ with (2) proceeds more slowly than that with (1) but is complete after 0.5 h to give $[Re_2H_2(CO)_6(dppm)\{P(OMe)_3\}]$ (4). Steric factors may account for this difference in reaction rates (also for the failure of PPh_3 to react at all), with the more bulky dppm ligand restricting access to the metal atom for the incoming donor ligand.[11]

(*b*) *Reaction with* RNC.—Addition of RNC (R = Bu^t, Bu^n, *p*-$MeOC_6H_4$, or *p*-$MeC_6H_4SO_2CH_2$) to a dichloromethane

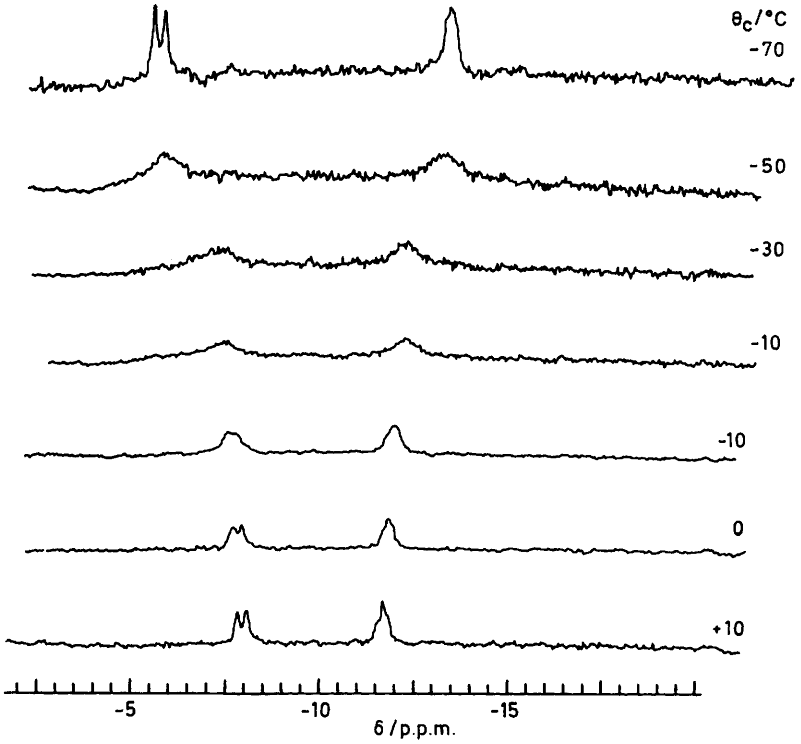
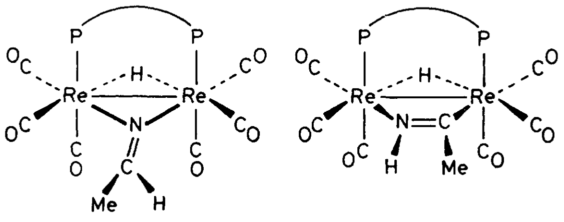


Figure 4. Reversible changes in ^1H n.m.r. spectra of $[Re_2H_2(CO)_6(dppm)]$ + Bu^{t}NC between +10 °C and −70 °C

solution of $[Re_2H_2(CO)_6(L\text{-}L)]$ at r.t. results in immediate reaction to give a single product in near quantitative yield, shown by mass spectroscopy and microanalysis to have the stoicheiometry $[Re_2H_2(CO)_6(L\text{-}L)(CNR)]$.

There is, however, no i.r. band which can be assigned to ν(NC) of a co-ordinated isocyanide ligand, and the ^1H n.m.r. spectra of the adducts (Table 1) all show a singlet resonance at δ 10—11 p.p.m. typical of the CH resonance of a formimidoyl ligand.[12] There is also a ^1H resonance due to a single (μ-H) ligand and it is thus apparent that the products should be formulated as $[Re_2H(CO)_6(L\text{-}L)(\mu\text{-}HCNR)]$ (5) and are derived from the insertion of RNC into an Re–H bond as shown in Figure 2. This insertion reaction proceeds much more readily than does the analogous reaction with $[Os_3H_2(CO)_{10}]$ which requires refluxing octane temperatures. At lower temperatures, only the simple adduct, $[Os_3H_2(CO)_{10}(CNR)]$, is formed, analogous to those obtained with CO and organophosphines.[12] An attempt to identify such an adduct as an intermediate in the reaction between (2) and p-MeOC$_6$H$_4$NC was made by monitoring the reaction at r.t. using i.r. spectroscopy. However, the new ν(CO) bands appearing as the peaks due to the starting material diminished in intensity were all due to the formimidoyl containing product (5). Following the same reaction by variable temperature ^1H n.m.r. spectroscopy gave an identical result; the only resonances observed as a dichloromethane solution was warmed from −70 °C to r.t. being due to (2) and (5d). Using Bu^{t}NC in place of p-MeOC$_6$H$_4$NC, however, did provide evidence that intermediate complexes are formed. Thus, if an excess of Bu^{t}NC is added to a CD_2Cl_2 solution of (2) in an n.m.r. tube at −78 °C the variable temperature ^1H n.m.r. spectra shown in Figure 3 may be obtained as the n.m.r. probe is allowed to warm from −70 to +30 °C. It will be seen that the resonances due to (2) gradually decrease in intensity and are replaced by a new AB methylene system and two hydride resonances which have maximum intensity at +10 °C. Above +20 °C these signals then begin to decrease in intensity and resonances due to the final insertion product appear. An interesting feature of these variable temperature spectra is seen in Figure 4 which shows the *reversible* changes which take place if the intermediate obtained at +10 °C is cooled to −70 °C. The metal hydride signals due to the intermediate first broaden and collapse and then become relatively sharp again at new chemical shift values. A possible explanation of these reversible changes is that there are two isomers of the intermediate present in solution corresponding, it may be assumed for illustrative purposes, to the isocyanide analogues of (3a) and (3b) shown in Figure 1. If one isomer is present in considerably greater concentration than the other, then the ^1H n.m.r. spectrum at −70 °C (Figure 4) may be assigned as being entirely due to the ‘ frozen out ’ spectrum of the major isomer. Alternatively, the resonances due to the minor isomer may coincide with those of the major isomer. If the equilibrium processes interconverting (3a) and (3b) are rapid on the n.m.r. time-scale at +10 °C then the signal due to the terminal hydride of the major isomer will become averaged with that due to the bridging hydride of the minor isomer and *vice versa*. This would give a spectrum such as is observed at +10 °C (Figure 4). Although this explanation cannot be regarded as proven, there is no other which seems to fit the data as well.

It is interesting to compare the formation of formimidoyl containing products in essentially quantitative yield on reaction of (1) and (2) with RNC at r.t., with the reaction between $[Os_3H_2(CO)_{10}]$ and Bu^{t}NC which, even in refluxing octane, does not give a formimidoyl containing product. Instead, the only complexes isolated were $[Os_3H_2(CO)_9(CNBu^t)]$ and $[Os_3(CO)_{11}(CNBu^t)]$. In strong donor solvents such as tetrahydrofuran (thf) the reaction did give an insertion product but this contained a bridging imino ligand, $>C=N(H)R$, rather than a formimidoyl group. Similar results in donor solvents were obtained with other RNC ligands.[12]



(I) (II)

Figure 5. Possible isomers for insertion products (6) and (7) obtained from reaction of $[Re_2H_2(CO)_6(L{-}L)]$ with CH_3CN

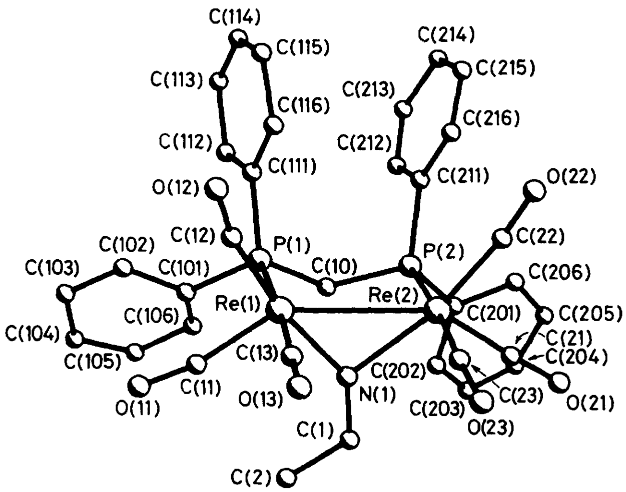


Figure 6. The molecular structure of $[Re_2H(CO)_6(dppm)\{NC(H)Me\}]$ (7a)

(*c*) *Reaction with Acetonitrile.*—The compound $[Re_2H_2(CO)_6(L{-}L)]$ can be dissolved in CH_3CN at r.t. without reaction. If the solutions are refluxed for 10 h, however, the light yellow colour of the initial solution is discharged. Using (1) a single product was obtained in essentially quantitative yield; with (2) two products were obtained, one in very low yield.

The single product (6) obtained from reaction with (1) and the major product (7a) from reaction with (2) have similar ^1H n.m.r. spectra, characterised by a triplet in the hydride region and a broad signal at *ca.* δ 8.5 p.p.m. in the organic region. Analytical and mass spectroscopic data indicate that the products have the stoicheiometry $[Re_2H_2(CO)_6(L{-}L)(NCMe)]$ [(6), L–L = tedip; (7a), L–L = dppm] but it is apparent from the ^1H n.m.r. spectra that the acetonitrile is not simply co-ordinated as a two-electron donor ligand and that an insertion reaction has again occurred. Under the same conditions $[Os_3H_2(CO)_{10}]$ does not undergo an insertion reaction with MeCN although cyanides do give simple adducts in solution at r.t. which dissociate in the absence of excess ligand.[2]

There are two possible isomers for the insertion products (6) and (7a), shown in Figure 5. It is expected that the N–H hydrogen atom of an acetimidoyl ligand would exchange readily with D_2O but shaking with D_2O had no effect on the ^1H n.m.r. spectra of (6) and (7a). This suggested that isomer (I), containing an *N*-bonded bridging ethylidenimino-ligand, had been formed and to confirm this suggestion an *X*-ray structure determination of (7a) was undertaken. Colourless plate-like crystals suitable for such a determination were grown by slow evaporation of a hexane–dichloromethane solution of the complex.

Table 3. Bond lengths (Å) in $[Re_2H(CO)_6(dppm)\{NC(H)Me\}]$ (7a)

Re(2)–Re(1)	3.035(3)	N(1)–Re(2)	2.184(27)
N(1)–Re(1)	2.081(24)	P(2)–Re(2)	2.485(7)
P(1)–Re(1)	2.471(7)	C(21)–Re(2)	1.867(33)
C(11)–Re(1)	1.869(37)	C(22)–Re(2)	1.904(31)
C(12)–Re(1)	1.870(31)	C(23)–Re(2)	1.936(24)
C(13)–Re(1)	1.890(22)	C(1)–N(1)	1.385(59)
C(10)–P(1)	1.843(34)	C(2)–C(1)	1.461(80)
C(10)–P(2)	1.812(38)	C(201)–P(2)	1.761(31)
C(101)–P(1)	1.829(39)	C(211)–P(2)	1.883(37)
C(111)–P(1)	1.788(38)	C(201)–C(202)	1.464(51)
C(101)–C(102)	1.457(62)	C(203)–C(202)	1.363(49)
C(103)–C(102)	1.442(75)	C(204)–C(203)	1.237(65)
C(104)–C(103)	1.523(61)	C(205)–C(204)	1.415(67)
C(105)–C(104)	1.384(61)	C(206)–C(205)	1.372(55)
C(106)–C(105)	1.517(69)	C(201)–C(206)	1.454(51)
C(101)–C(106)	1.306(51)	C(211)–C(212)	1.304(38)
C(111)–C(112)	1.424(40)	C(213)–C(212)	1.323(68)
C(113)–C(112)	1.534(58)	C(214)–C(213)	1.455(79)
C(114)–C(113)	1.371(61)	C(215)–C(214)	1.375(56)
C(115)–C(114)	1.429(45)	C(216)–C(215)	1.412(80)
C(116)–C(115)	1.465(55)	C(211)–C(216)	1.399(68)
C(111)–C(116)	1.358(54)	O(21)–C(21)	1.160(1)
O(11)–C(11)	1.160(1)	O(22)–C(22)	1.160(1)
O(12)–C(12)	1.160(1)	O(23)–C(23)	1.160(1)
O(13)–C(13)	1.160(1)		

The molecular structure of (7a) is shown in Figure 6. The final bond lengths and inter-bond angles are presented in Tables 3 and 4, respectively. The crystal structure consists of discrete $[Re_2H(CO)_6(dppm)\{\mu\text{-}NC(H)Me\}]$ molecules separated by normal van der Waals distances.

The two Re atoms and the two P atoms of the bridging dppm ligand are coplanar. The six carbonyl groups are linear and terminal. The NC(H)Me ligand symmetrically bridges the Re–Re bond which is also thought to be bridged by the hydride ligand. Although this atom was not located directly in the *X*-ray study its position can be ascertained from the distribution of the other ligands. The carbonyls C(12)O(12) and C(22)O(22) bend away from the Re(1)–Re(2) bond with an average *cis* Re–Re–C angle of 122.6° compared to an angle of 90.6° for the other pair of *cis* carbonyls. The steric effect of the hydride causes the carbonyls to bend away from it. Similar arguments have been used to locate hydrides in a large number of Re cluster compounds.[13] The geometry of the dppm ligand is as expected, and generally similar to that observed in the structure of $[Re_2H_2(CO)_6(dppm)]$,[11] only in the case of (7a) the Re–P distances are *ca.* 0.025 Å longer.

An electron count indicates that (7a) is 'electron precise' and this is reflected in the Re(1)–Re(2) bond length of 3.035(3) Å which is in close agreement with the single bond value of 3.041(1) Å in $[Re_2(CO)_{10}]$.[14] The Re(1)–Re(2) distance is slightly shorter than the average value of 3.177(8) Å reported for hydride bridged Re–Re single bonds in $[Re_3H_2(CO)_{12}]^-$.[15] Presumably the bond lengthening effect of a bridging hydride has been counter-balanced by a bond shortening effect of the NC(H)Me group in the case of (7a).

There are few examples of dinuclear Re compounds bridged by nitrogen-donor ligands. In (7a) the atoms N(1) and C(1) are best considered as sp^2 hybridised and the plane defined by Re(1)Re(2)N(1)C(1) makes an angle of 94.5° with the Re_2P_2 plane. The bond parameters within the NC(H)Me ligand do not deviate significantly from the expected values.

The minor product (7b) obtained on the reaction of CH_3CN with (2) was also shown by mass spectroscopy to be a 1 : 1 adduct of stoicheiometry $[Re_2H_2(CO)_6(dppm)(NCMe)]$ and its i.r. spectrum reveals a similar pattern of ν(CO) bands to

Table 4. Bond angles (°) in [$Re_2H(CO)_6$(dppm){NC(H)Me}] (7a)

N(1)-Re(1)-Re(2)	46.0(7)	C(116)-C(111)-C(112)	120.2(32)	C(22)-Re(2)-P(2)	99.5(9)
P(1)-Re(1)-Re(2)	89.9(3)	C(111)-C(112)-C(113)	118.9(33)	C(22)-Re(2)-C(21)	89.9(17)
C(11)-Re(1)-Re(2)	143.4(13)	C(114)-C(113)-C(112)	115.2(34)	C(23)-Re(2)-N(1)	91.1(13)
C(12)-Re(1)-Re(2)	123.3(13)	C(115)-C(114)-C(113)	127.2(40)	C(23)-Re(2)-P(2)	173.6(12)
C(13)-Re(1)-Re(2)	92.6(12)	C(116)-C(115)-C(114)	113.2(35)	C(23)-Re(2)-C(21)	90.2(14)
N(1)-Re(2)-Re(1)	43.3(6)	C(111)-C(116)-C(115)	124.1(32)	C(23)-Re(2)-C(22)	86.1(15)
P(2)-Re(2)-Re(1)	91.2(2)	C(212)-C(211)-P(2)	117.2(30)	C(102)-C(101)-P(1)	113.1(31)
C(21)-Re(2)-Re(1)	148.0(12)	C(216)-C(211)-P(2)	121.2(27)	C(106)-C(101)-P(1)	120.6(33)
C(22)-Re(2)-Re(1)	121.9(12)	C(211)-C(212)-C(213)	119.8(46)	C(106)-C(101)-C(102)	125.8(43)
C(23)-Re(2)-Re(1)	88.5(12)	C(215)-C(214)-C(213)	115.4(46)	C(101)-C(102)-C(103)	114.7(45)
Re(2)-N(1)-Re(1)	90.7(10)	C(211)-C(216)-C(215)	119.6(46)	C(104)-C(103)-C(102)	120.5(47)
C(1)-N(1)-Re(1)	141.9(31)	O(21)-C(21)-Re(2)	172.1(32)	C(105)-C(104)-C(103)	120.1(47)
C(1)-N(1)-Re(2)	126.2(30)	O(22)-C(22)-Re(2)	169.3(36)	C(106)-C(105)-C(104)	117.1(43)
C(2)-C(1)-N(1)	120.7(52)	O(23)-C(23)-Re(2)	165.0(31)	C(101)-C(106)-C(105)	121.0(44)
C(10)-P(1)-Re-(1)	108.8(9)	P(1)-Re(1)-N(1)	83.3(5)	C(202)-C(201)-P(2)	126.1(29)
C(101)-P(1)-Re(1)	112.1(10)	C(11)-Re(1)-N(1)	97.6(15)	C(206)-C(201)-P(2)	120.7(27)
C(101)-P(1)-C(10)	103.3(16)	C(11)-Re(1)-P(1)	90.4(10)	C(206)-C(201)-C(202)	112.9(31)
C(111)-P(1)-Re(1)	118.8(11)	C(12)-Re(1)-N(1)	169.3(15)	C(201)-C(202)-C(203)	125.8(40)
C(111)-P(1)-C(10)	108.3(16)	C(12)-Re(1)-P(1)	95.6(9)	C(204)-C(203)-C(202)	116.3(46)
C(111)-P(1)-C(101)	104.4(17)	C(12)-Re(1)-C(11)	93.0(18)	C(205)-C(204)-C(203)	125.7(49)
P(2)-C(10)-P(1)	115.2(17)	C(13)-Re(1)-N(1)	95.3(12)	C(206)-C(205)-C(204)	120.4(49)
C(10)-P(2)-Re(2)	108.9(9)	C(13)-Re(1)-P(1)	177.0(13)	C(201)-C(206)-C(205)	117.9(40)
C(201)-P(2)-Re(2)	112.6(9)	C(13)-Re(1)-C(11)	86.6(16)	C(216)-C(211)-C(212)	121.6(36)
C(201)-P(2)-C(10)	102.5(16)	C(13)-Re(1)-C(12)	84.3(14)	C(214)-C(213)-C(212)	123.8(45)
C(211)-P(2)-Re(2)	123.0(11)	P(2)-Re(2)-N(1)	84.3(5)	C(216)-C(215)-C(214)	119.5(63)
C(211)-P(2)-C(10)	105.5(16)	C(21)-Re(2)-N(1)	104.8(14)	O(11)-C(11)-Re(1)	167.1(42)
C(211)-P(2)-C(201)	102.2(15)	C(21)-Re(2)-P(2)	86.7(9)	O(12)-C(12)-Re(1)	164.1(38)
C(112)-C(111)-P(1)	116.3(26)	C(22)-Re(2)-N(1)	165.1(13)	O(13)-C(13)-Re(1)	179.3(37)
C(116)-C(111)-P(1)	123.4(25)				

that of (7a) together with a weak band at 3 275 cm^{-1}. Its ^1H n.m.r. spectrum shows a triplet due to a single (μ-H) ligand at δ — 10.8 p.p.m. (J_{PH} 10.3 Hz), a singlet methyl resonance at δ 1.58 p.p.m., and multiplets typical of the dppm ligand. It seems likely that this complex is the other isomer, (II), shown in Figure 5, containing a μ-HNCMe acetimidoyl ligand and that the failure to observe an *N*H resonance is perhaps due to rapid exchange of this proton or to broadening by the nitrogen nucleus. The reaction of [$Os_3H_2(CO)_{10}$] with the activated cyanide CF_3CN gives a major product analogous to (7a) and a minor product analogous to (7b) containing a 1,1,1-trifluoroacetimidoyl ligand in which a singlet N*H* resonance is observed (δ 9.75 p.p.m.) but the signal is extremely broad, lending some support to the above suggestion.[16] Unfortunately crystals of (7b) suitable for an *X*-ray determination could not be obtained. Andrews and Kaesz[17] previously reported the stepwise reduction of acetonitrile on a trinuclear iron cluster and obtained the neutral complexes [$Fe_3H(CO)_9${NC(H)Me}] and [$Fe_3H(CO)_9$(HNCMe)] which are closely related to (7a) and (7b). Here too the N*H* ^1H n.m.r. resonance in the complex containing the μ-HNCMe ligand was not observed.[17]

(*d*) *Reaction with* CO.—The compound [$Os_3H_2(CO)_{10}$] reacts with CO at r.t. to form the stable 1 : 1 adduct [$Os_3H_2(CO)_{11}$].[2] A yellow dichloromethane solution of [$Re_2H_2(CO)_6$(L-L)] was decolourised on being pressurised (5 atm) with CO but the colour was immediately restored when the pressure was released, and the starting complex was recovered. It seems likely that the adducts [$Re_2H_2(CO)_7$(L-L)] are formed under CO pressure in solution but they are clearly less stable with respect to reversible dissociation of CO than their osmium analogues.

(*e*) *Reaction with Acetylene*.—By analogy with [$Os_3H_2(CO)_{10}$] it might have been expected that acetylene would insert readily into the Re-H bond of (1) and (2) to give complexes containing the vinyl ligand.[1,3] Rather surprisingly, however, in view of the enhanced reactivity of (1) and (2) with RNC and RCN as compared to the osmium complex, no reaction takes place on bubbling acetylene through a dichloromethane solution of (1) or (2) at r.t. Similarly no reaction takes place with excess $MeO_2CC{\equiv}CCO_2Me$ or with ethylene at 1 atm after 24 h. It may be that the ligands, which are presumably more sterically demanding than RNC or RCN, are not able to undergo initial co-ordination to one of the rhenium atoms. This suggestion is supported by the results obtained on the reaction of PPh_3 and $P(OMe)_3$ with [$Re_2H_2(CO)_6$ (L-L)].

Experimental

All manipulations were carried out under dry oxygen-free nitrogen. Solvents were dried, deoxygenated, and distilled before use according to standard literature methods.

Infrared spectra were recorded in 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer using CO gas as calibrant. Mass spectra were obtained on an A.E.I. MS12 spectrometer, using tris(perfluoroheptyl)-*s*-triazine as reference. Hydrogen-1 n.m.r. spectra were recorded using a Varian Associates XL-100 spectrometer and calibrated relative to $SiMe_4$ using the solvent resonances as internal standard. Microanalyses were carried out at the University of Cambridge Chemical Laboratory. The compounds [$Re_2H_2(CO)_8$],[10] [$Re_2H_2(CO)_6$(tedip)],[11] and [$Re_2H_2(CO)_6$(dppm)][11] were prepared by literature methods.

(*i*) *Reaction of* [$Re_2H_2(CO)_8$] *with* PPh_3.—The compound [$Re_2H_2(CO)_8$] (0.008 g, 0.013 mmol) was dissolved in CD_2Cl_2 (0.5 cm^3) in an n.m.r. tube. Excess PPh_3 (0.01 g, 0.038 mmol) in CD_2Cl_2 (0.5 cm^3) was added and the tube was then immediately transferred to the n.m.r. spectrometer at a probe temperature of −50 °C.

(*ii*) *Reaction of* [$Re_2H_2(CO)_6$(L-L)] *with* $P(OMe)_3$.—In a typical experiment [$Re_2H_2(CO)_6$(tedip)] (0.015 g, 0.058 mmol) was dissolved in CH_2Cl_2 (5 cm^3). To the stirred yellow solution so obtained excess $P(OMe)_3$ was added whereupon the solution was immediately decolourised. Solvent and excess $P(OMe)_3$ were removed using a stream of nitrogen and the residue was then taken up in a minimum of CH_2Cl_2. Thin layer chromatography (t.l.c.) on silica using 30% CH_2Cl_2–70% hexane as eluant gave $[Re_2H_2(CO)_6(tedip)\{P(OMe)_3\}]$ (3) as a single product in *ca.* 80% yield. The reaction between $[Re_2H_2(CO)_6(dppm)]$ and $P(OMe)_3$ proceeded more slowly (0.5 h to completion) but was otherwise analogous.

(*iii*) *Reaction of* $[Re_2H_2(CO)_6(L{-}L)]$ *with* RNC.—In a typical experiment $[Re_2H_2(CO)_6(L{-}L)]$ (0.015 g, 0.06 mmol) was dissolved in CH_2Cl_2 (5 cm^3) and a slight excess of RNC was added (neat for R = Bu^t or Bu^n; in 5 cm^3 of CH_2Cl_2 for R = *p*-$MeOC_6H_4$ or *p*-$MeC_6H_4SO_2CH_2$). The light yellow colour of the solution rapidly faded and t.l.c. on silica (30% CH_2Cl_2–70% hexane) then gave $[Re_2H(CO)_6(L{-}L)(HCNR)]$ (5) as the product in essentially quantitative yield.

(*iv*) *Reaction of* $[Re_2H_2(CO)_6(L{-}L)]$ *with* MeCN.—In a typical experiment $[Re_2H_2(CO)_6(L{-}L)]$ (0.015 g, 0.06 mmol) was dissolved in MeCN (10 cm^3) and the solution refluxed overnight. The solvent was then removed *in vacuo* and the residue dissolved in CH_2Cl_2. T.l.c. (30% CH_2Cl_2–70% hexane) gave two colourless products for (L–L) = dppm, $[Re_2H(CO)_6(dppm)(HNCMe)]$ (7b) (0.002 g, 13% yield) and $[Re_2H(CO)_6(dppm)\{NC(H)Me\}]$ (7a) (0.01 g, 65% yield), with the former product having the higher R_f value. For (L–L) = tedip $[Re_2H(CO)_6(tedip)\{NC(H)Me\}]$ (6) (0.01 g, 65% yield) was the only product. All products were purified by recrystallisation from CH_2Cl_2–hexane.

X-*Ray Structural Analysis of* $[Re_2H(CO)_6(dppm)\{NC(H)Me\}]$ (7a).—Colourless plate-like crystals of (7a) were grown by the slow evaporation of a hexane–dichloromethane solution of the complex. The unit-cell dimensions and space group were determined by Weissenberg photography. A single crystal with dimensions *ca.* 0.35 × 0.21 × 0.10 mm, mounted on a glass fibre, was transferred to a Stoe STADI four-circle diffractometer and accurate cell dimensions were derived by a least-squares fit to the diffractometer setting angles for 20 reflections in the range $15 < 2\theta < 25°$. 4 809 Intensities were measured in the range $3.0 < 2\theta < 55.0°$ using a 140 step ω/θ scan technique and graphite monochromatised Mo-K_α radiation; the scan time for each step was 0.5 s and the step width was 0.01°, backgrounds were measured for 17.5 s at each end of the scan; reflections which registered <7 counts s^{-1} for a 1 s pre-scan were not measured. Two standard reflections were monitored periodically throughout data collection and showed no significant variation in intensity. The measured intensities were corrected for absorption using a five parameter fit to 290 azimuthal scan data; transmission coefficients for the full data set varied between 0.174 and 0.742. Lorentz and polarisation corrections were also applied and equivalent reflections merged to give 2 614 unique observed data $|F > 4\sigma(F)|$ which were used in structure determination and refinement.

Crystal data. $C_{33}H_{27}O_6P_2Re_2$, $M = 967.97$, Monoclinic, $a = 9.765(3)$, $b = 29.940(8)$, $c = 11.813(4)$ Å, $\beta = 104.69(2)°$, $U = 3\,340.8$ Å^3, $D_c = 1.92$ g cm^{-3}, $Z = 4$, D_m = not measured, $F(000) = 1\,735.6$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 74.36 cm^{-1}, space group $P2_1/n$ from systematic absences.

The positions of the two Re atoms were determined by Σ_2 sign expansion and all the remaining non-hydrogen atoms from subsequent Fourier-difference synthesis. The structure was refined by full-matrix least squares with the Re and P atoms assigned anisotropic thermal parameters and the N, C, and O atoms assigned individual isotropic thermal parameters. Additional constraints were placed on the carbonyl C–O distances with the average C–O bond length refined to 1.160(1) Å. The hydrogen atoms in the structure were not located. In the final cycles of refinement a weighting of the form $w = 0.2611/[\sigma^2(F) + 0.0025(F^2)]$ was introduced, and refinement converged to $R = 0.071$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}(F_o)] = 0.078$. A final difference electron-density synthesis showed no regions of significant electron density.

Table 5. Atomic co-ordinates (× 10^4) for $[Re_2H(CO)_6(dppm)\{NC(H)Me\}]$ (7a)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	3 239(1)	3 245(1)	1 835(2)
Re(2)	3 986(1)	4 074(1)	3 344(1)
N(1)	4 236(19)	3 352(9)	3 591(21)
C(1)	4 677(45)	3 132(21)	4 651(48)
C(2)	4 769(50)	2 645(25)	4 694(53)
P(1)	5 659(7)	3 231(4)	1 547(9)
P(2)	6 470(8)	4 047(4)	3 174(9)
C(10)	6 885(28)	3 480(13)	2 840(29)
C(101)	6 330(28)	2 661(13)	1 524(30)
C(102)	5 661(45)	2 419(22)	457(48)
C(103)	6 140(40)	1 965(19)	419(42)
C(104)	7 295(39)	1 777(17)	1 424(40)
C(105)	7 957(40)	2 049(19)	2 348(42)
C(106)	7 416(39)	2 524(18)	2 341(40)
C(111)	5 967(31)	3 487(14)	266(33)
C(112)	7 260(31)	3 374(14)	−12(32)
C(113)	7 592(41)	3 583(18)	−1 098(41)
C(114)	6 589(36)	3 874(17)	−1 710(38)
C(115)	5 245(35)	3 973(16)	−1 499(37)
C(116)	5 079(33)	3 792(16)	−390(34)
C(201)	7 710(26)	4 148(12)	4 516(27)
C(202)	8 248(33)	3 819(16)	5 439(34)
C(203)	9 258(31)	3 894(15)	6 452(33)
C(204)	9 652(43)	4 286(20)	6 649(45)
C(205)	9 103(40)	4 659(18)	5 942(41)
C(206)	8 195(32)	4 599(15)	4 858(33)
C(211)	7 147(30)	4 412(14)	2 136(32)
C(212)	8 402(31)	4 322(14)	2 000(32)
C(213)	8 946(54)	4 575(25)	1 306(55)
C(214)	8 247(38)	4 968(17)	698(37)
C(215)	6 905(58)	5 047(27)	822(54)
C(216)	6 321(49)	4 758(23)	1 519(49)
C(11)	3 214(35)	2 621(12)	1 881(37)
O(11)	3 112(26)	2 241(12)	1 683(28)
C(12)	2 312(29)	3 263(14)	243(28)
O(12)	1 600(30)	3 363(14)	−665(27)
C(13)	1 388(26)	3 222(14)	2 050(32)
O(13)	252(25)	3 203(13)	2 181(30)
C(21)	4 713(30)	4 315(13)	4 832(30)
O(21)	5 019(31)	4 494(14)	5 734(29)
C(22)	3 480(32)	4 657(12)	2 739(32)
O(22)	3 030(24)	4 977(11)	2 228(24)
C(23)	2 118(29)	4 019(14)	3 624(31)
O(23)	1 167(28)	4 039(13)	4 044(29)

Complex neutral-atom scattering factors were employed throughout.[18] Final atomic co-ordinates are given in Table 5. All computations were carried out on the University of Cambridge IBM 370/165 computer using the SHELX 76 program system.[19] The molecular diagram was drawn with the PLUTO program written by Dr. W. D. S. Motherwell.

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