Structure and Reactivity of a Dimetallic Rhenium Hydride Complex with a Rhenium–Rhenium Double Bond: *X*-Ray Crystal Structures of $[Re_2(CO)_6(Ph_2PCH_2PPh_2)H_2]$ and $[Re_2(CO)_6(Ph_2PCH_2PPh_2)(NCHMe)H]$

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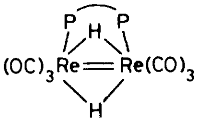
Summary The complex $[Re_2(CO)_6(Ph_2PCH_2PPh_2)H_2]$ with an Re–Re double bond has been prepared and its crystal structure determined, it reacts with $(MeO)_3P$, RNC, and MeCN under mild conditions giving 1:1 adducts in which the dimetallic unit is preserved and with MeCN two separable isomers are obtained one of which has been shown by *X*-ray analysis to be the insertion product $[Re_2(CO)_6(Ph_2PCH_2PPh_2)(NCHMe)H]$

THE reaction of polynuclear metal carbonyl complexes with small molecules such as R_3P, RCN, RNC, alkenes, and alkynes normally requires the dissociation of one or more CO ligands and/or metal–metal bond fission This limits the range of reactions which can be studied since either the products or the reactants may not be sufficiently stable to withstand the vigorous conditions which are required for the reaction to take place

A small number of polynuclear metal carbonyl derivatives are known which are 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, $[Os_3(CO)_{10}H_2]$, 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] Other unsaturated polynuclear carbonyl derivatives include $[W_2(CO)_8H_2]^{2-}$,[1] $[Re_2(CO)_8H_2]$,[4] $[Re_3(CO)_{10}H_3]^{2-}$,[5] $[Re_3(CO)_{10}H_4]^{-}$,[6] and $[Re_4(CO)_{12}H_4]$,[7] but their chemistry remains virtually unexplored because of instability or practical problems

Both $[Re_2(CO)_8H_2]^8$ and $[Re_4(CO)_{12}H_4]^9$ decompose to give mononuclear products when treated with Ph_3P at room temperature



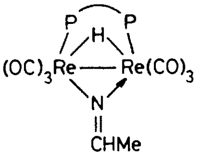
(1)

$[Re_2(CO)_6(dpm)\{P(OMe)_3\}H_2]$

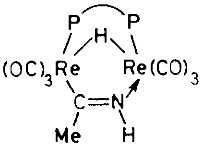
(2)

$[Re_2(CO)_6(dpm)(RN{=}CH)H]$

(3) R = Bu^t Bu^n, p-$MeOC_6H_4$



(4)



(5)

= dpm

We report an unsaturated rhenium complex $[Re_2(CO)_6(dpm)H_2]$ (**1**) (dpm = $Ph_2PCH_2PPh_2$) in which the dimetallic unit is stable towards reaction with many small molecules It was prepared in *ca* 30% yield by refluxing $[Re_3(CO)_{12}H_3]^{10}$ with dpm in octane for 40 min A mixture of products was obtained from which (**1**) was separated (t l c) The i r spectrum of (**1**) showed ν(CO) absorptions at 2041(s) 1947(m) and 1918(brs) cm^{-1} (CH_2Cl_2 soln) and the ^1H n m r spectrum showed a triplet at $\delta - 7$ 51 (J_{PH} 10 Hz) (CD_2Cl_2) due to the bridging H ligands Orange-yellow block-shaped crystals for the *X*-ray analysis were obtained by slow evaporation from hexane-dichloro methane †

The molecular structure of (**1**) is shown in Figure 1 together with some important bond parameters The Re–Re bond length is considerably shorter than that found in systems containing Re–Re single bonds {3 02 Å in $[Re_2(CO)_{10}]^{11}$} or those with hydride bridged Re–Re single bonds {3 177 Å in $[H_2Re_3(CO)_{12}]^{-\ 12}$} It is in close agreement with the Re–Re bond length of 2 896 Å in $[Re_2H_2(CO)_8]^8$ where a double bond has been proposed An Re–Re double bond is required if the E A N rule is to be satisfied for (**1**) From the arrangement of the carbonyl ligands the two hydrides are thought to bridge the metal–metal bond symmetrically

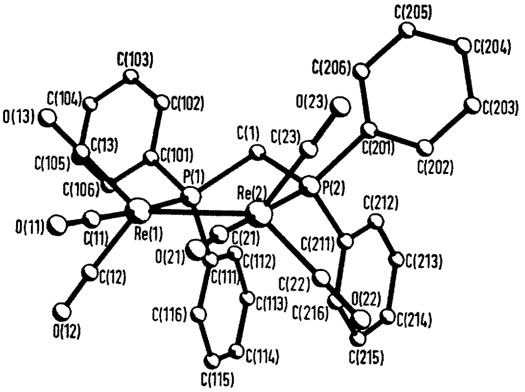


FIGURE 1 The molecular structure of $[Re_2(CO)_6(dpm)H_2]$ (**1**) including the atom numbering scheme Hydrogen atoms have been omitted for clarity Bond lengths Re(1)–Re(2) 2 893(2) Re(1)–P(1) 2 449(4) Re(2)–P(2) 2 457(4) Å bond angles P(1)–Re(1)–Re(2) 90 0(1) P(2)–Re(2)–Re(1) 92 5(1)°

The reactions of (**1**) with small molecules are in many respects similar to those of $[Os_3(CO)_{10}H_2]$ With $(MeO)_3P$, at room temperature (**1**) reacts to give $[Re_2(CO)_6(dpm)\{P(OMe)_3\}H_2]$ (**2**) With RNC (R = Bu^t Bu^n, p-$MeOC_6H_4$) in CH_2Cl_2 solutions at room temperature a single product (**3**) was obtained in near quantitative yield, and was shown by a mass spectroscopy to be a 1 1 adduct The ^1H n m r spectrum of (**2**) at −70 °C (CD_3COCD_3) revealed the presence of two isomers Thus two equal intensity resonances at $\delta - 5$ 96(s) and −14 36(s) can be assigned respectively to a terminal and a bridging H ligand of one isomer A further pair of resonances at $\delta - 6$ 62(s) and −15 86(s) of slightly greater intensity are correspondingly assigned to the second isomer The structures of these isomers are presumably analogous to those of the complexes $[H_2Os_3(CO)_{10}L]^3$ with the terminal hydrogen on one rhenium atom and the $(MeO)_3P$ group on the other The two isomers must differ in the relative orientation of these two substituents

On warming the solution of (**2**) to −30 °C the 4 hydride resonances collapse and at +50 °C a single resonance centred at the chemical shift average of the four initial signals is observed indicating that isomer exchange is rapid on the n m r time-scale at this temperature The presence of a C*H* resonance in the ^1H n m r spectrum of (**3**) at δ 10 85 is typical of a formimidoyl ligand[13] and shows that the complex should be formulated as $[Re_2(CO)_6(dpm)(RNCH)H]$ It is formally derived from (**1**) by insertion of

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† *Crystal data* (**1**) $C_{31}H_{24}O_6P_2Re_2$ *M* 926 84 orthorhombic $a = 19$ 220(5) $b = 29$ 820(9) $c = 10$ 655(4) Å $U = 6106$ 8 Å^3 $Z = 8$, $D_c = 2$ 02 g cm^{-3} μ(Mo K_α) = 81 40 cm ^{1} space group *Pbca* 2769 intensities (layers *hk*0 *hk*12) were recorded on a Stoe STADI 2 two circle diffractometer and merged to give 2264 unique observed reflections $[F > 3\sigma(F)]$ The residuals are $R = 0$ 033 and $R_w[= \Sigma\omega^{1/2}\Delta/\Sigma\omega^{1/2}|F_0|] = 0$ 036 The structure was solved by a combination of Patterson and Fourier difference techniques and refined by full matrix least squares (Re P anisotropic) (**4**) $C_{33}H_{27}NO_6P_2Re_2$ *M* 967 97 monoclinic $a = 9$ 765(3) $b = 29$ 940(8) $c = 11$ 813(4) Å $\beta = 104$ 69(2)° $U = 3340$ 80 Å^3 $Z = 4$ $D_c = 1$ 92 g cm ^{3} μ(Mo K_α) = 74 36 cm^{-1} space group $P2_1/n$ 4809 intensities ($2\theta_{max} = 55$ 0°) were recorded on an A E D four circle diffractometer and averaged to give 2614 unique observed reflections $[F > 2\sigma(F)]$ The structure was solved by a combination of multisolution Σ_2 sign expansion and Fourier difference techniques and refined by full matrix least squares (O and P anisotropic) to current residuals $R = 0$ 071 and $R_w = [\Sigma\omega^{1/2}\Delta/\Sigma\omega^{1/2}|F_0|] = 0$ 078 The atomic co ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory Lensfield Road Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

an RNC ligand into an Re–H bond. The Re–*H* resonance for (**3**) is observed at δ −12·92. $[Os_3(CO)_{10}H_2]$ reacts similarly with RNC but under more vigorous conditions.[13]

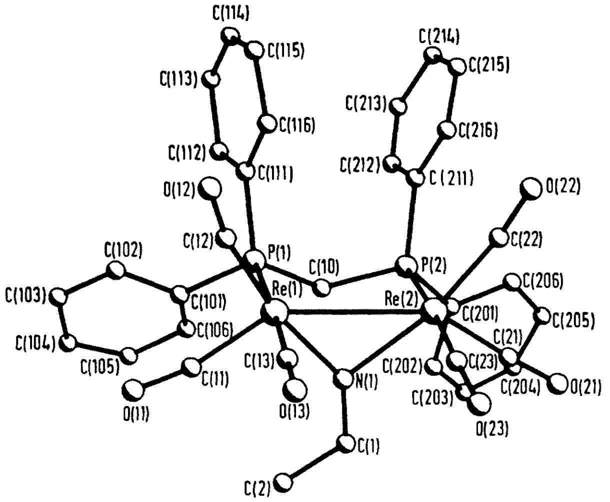

FIGURE 2. The molecular structure of $[Re_2(CO)_6(dpm)(NCHMe)H]$ (**4**) including the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Bond lengths: Re(1)–Re(2), 3·035(3); Re(1)–P(1), 2·471(7); Re(2)–P(2), 2·485(7); Re(1)–N(1), 2·08(2); Re(2)–N(1), 2·18(3); C(1)–N(1), 1·39(6) Å; bond angles: N(1)–Re(1)–Re(2), 46·0(7); N(1)–Re(2)–Re(1), 43·3(6); P(1)–Re(1)–Re(2), 89·9(3); P(2)–Re(2)–Re(1), 91·2(2); P(1)–Re(1)–N(1), 85·3(5); P(2)–Re(2)–N(1), 84·3(5); Re(2)–N(1)–Re(1), 90·7(10)°.

Complex (**1**) also reacts with MeCN under reflux to give two products (**4**) and (**5**) which both have the stoicheiometry $[Re_2(CO)_6(dpm)(MeCN)H_2]$ but could be separated by t.l.c. on silica. Under the same conditions $[Os_3(CO)_{10}H_2]$ does not give an insertion product with MeCN. Compound (**4**) is the major product of the reaction and has been shown by spectroscopic and *X*-ray crystallographic data to be $[Re_2(CO)_6(dpm)(NCHMe)H]$. Colourless, plate-like crystals for the *X*-ray analysis were grown by slow evaporation from hexane–dichloromethane.†

Figure 2 shows a molecule of (**4**), together with some important bond parameters. The complex is electron precise and this is reflected in the Re–Re bond length as compared to (**1**) which indicates that it should be considered as a single bond. The NCHMe ligand symmetrically bridges the metal–metal bond, as does the hydride from analysis of the carbonyl distribution.

Spectroscopic data show that (**5**) is best formulated as $[Re_2(CO)_6(dpm)(HNCMe)H]$, and is formally derived from (**1**) by insertion of MeCN into an Re–H bond in the opposite sense of that required for the formation of (**4**).

Somewhat surprisingly (**1**) does not react with acetylene to give a vinyl complex analogous to that obtained with $[Os_3(CO)_{10}H_2]$.[1] This may be because (**1**) is more sterically hindered than $[Os_3(CO)_{10}H_2]$, and the reactions of less sterically hindered analogues of (**1**) are under study.

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