Dirhenium Complexes containing Two, Three, and Four Linked Acetylene Molecules derived from the Reaction of $[Re_2(CO)_{10}]$ with RC_2R (R = Ph or Me); the *X*-Ray Crystal Structure of $[Re_2(CO)_4\{(PhCCPh)_3\}(CNCH_2SO_2C_6H_4Me\text{-}p)_2]\cdot CH_2Cl_2$†

By **Martin J. Mays,* David W. Prest,** and **Paul R. Raithby,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The reaction of $[Re_2(CO)_{10}]$ with PhCCPh at 190 °C gives $[Re_2(CO)_7(PhCCPh)_2]$ (1), $[Re_2(CO)_6(PhCCPh)_3]$ (2), and $[Re_2(CO)_4(PhCCPh)_4]$ (3). Complex (3) reacts instantaneously at room-temperature with excess of RNC (R = Bu^t, Bu^n, *p*-$MeOC_6H_4$, or *p*-$MeC_6H_4SO_2CH_2$) to give $[Re_2(CO)_4(PhCCPh)_3(CNR)_2]$ (4). A single-crystal *X*-ray analysis of (4d) (R = $CH_2SO_2C_6H_4Me$-*p*) reveals that the acetylene molecules are linked in a chain. The end carbon atoms of the chain are each bonded to one metal atom and, with the two neighbouring carbon atoms, form an η^3-allyl linkage to the other metal atom. The two RNC ligands are terminally bonded to only one rhenium atom. The complex crystallises with a molecule of CH_2Cl_2 solvent in the triclinic space group $P\bar{1}$ with a = 13.190(3), b = 14.066(3), c = 17.554(5) Å, α = 83.06(2), β = 75.75(2), γ = 70.40(2)°, and Z = 2. The structure was solved by a combination of Patterson and Fourier-difference techniques, and refined by blocked-cascade least squares to R = 0.032 for 6 315 unique observed intensities [$F > 3\sigma(F)$]. The reaction of $[Re_2(CO)_{10}]$ with MeCCMe at 190 °C leads to extensive decomposition, but a yellow product, isolated in low yield, was identified spectroscopically as $[Re_2(CO)_5(MeCCMe)_4]$ (5). On the basis of the known structure of (4d) and on chemical and spectroscopic evidence, structures are proposed for all the complexes which have been isolated. Complex (3) probably contains a Re–Re multiple bond.

THE reactions of alkynes with polynuclear transition-metal complexes have been well studied, and an extensive range of polynuclear acetylene complexes have been obtained for many different transition metals. Surprisingly, however, the reactivity of $[Re_2(CO)_{10}]$ towards alkynes has not been investigated; in fact the only well characterised example of a rhenium–acetylene complex is $[ReCl(PhCCH)_2]$.[1] In this paper we report the results we have obtained by treating $[Re_2(CO)_{10}]$ with RCCR (R = Ph or Me) at high temperatures. A number of new dirhenium complexes containing linked acetylene ligands have been prepared and characterised, and the course of the reaction appears similar to that which has recently been reported to take place between the unsaturated complexes $[\{M(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (M = Cr or Mo) and alkynes.[2] Apart from the complexes described in this paper only two other dinuclear rhenium acetylene complexes, $[Re_2H_2(CO)_7(PhCCPh)_2]$ and $[Re_2H_2(CO)_5(PhCCPh)_3]$, are known. These were prepared by the photolysis of $[Re_3H_3(CO)_{12}]$ in the presence of an excess of PhCCPh but have not been fully characterised.[3]

RESULTS AND DISCUSSION

Three products are obtained on heating $[Re_2(CO)_{10}]$ in hexane with an excess of PhCCPh in an autoclave at 190 °C for 16 h. These were identified mass spectroscopically (Table 1) as $[Re_2(CO)_7(PhCCPh)_2]$ (1), $[Re_2(CO)_6(PhCCPh)_3]$ (2), and $[Re_2(CO)_4(PhCCPh)_4]$ (3). Complexes (1), (2), and (3) are most probably formed sequentially, since heating (1) with excess of PhCCPh gives (2) and (3) and similar treatment of (2) gives (3). In addition, more (2) and (3) are obtained in the reaction

TABLE 1

Mass spectroscopic and microanalytical data for dirhenium acetylene derivatives

Compound	Mass spectra		Analyses (%) [a]		
	M^+	Fragmentation	C	H	N
(1) $[Re_2(CO)_7(PhCCPh)_2]$	924	$M - n$CO (n = 0—7), $M - n$CO – PhCCPh (n = 1—7)			
(2) $[Re_2(CO)_6(PhCCPh)_3]$	1 076	$M - n$CO (n = 0—6), $M - n$CO – PhCCPh (n = 0—6)			
(3) $[Re_2(CO)_4(PhCCPh)_4]$ [b]	1 196	$M - n$CO (n = 0—4)	54.0 (54.5)	3.5 (3.2)	
(4a) $[Re_2(CO)_4(PhCCPh)_3(CNBu^t)_2]$	1 184	$M - n$CO (n = 0—4), $M - n$CO – RNC (n = 0—4)	56.7 (56.8)	4.3 (4.1)	2.2 (2.4)
(4b) $[Re_2(CO)_4(PhCCPh)_3(CNBu^n)_2]$	1 184	$M - n$CO (n = 0—4), $M - n$CO – RNC (n = 0—4)	56.9 (56.8)	4.5 (4.1)	2.3 (2.4)
(4c) $[Re_2(CO)_4(PhCCPh)_3(CNC_6H_4OMe\text{-}p)_2]$	1 284	$M - n$CO (n = 0—4), $M - n$CO – RNC (n = 1—4)			
(4d) $[Re_2(CO)_4(PhCCPh)_3(CNCH_2SO_2C_6H_4Me\text{-}p)_2]$	1 408	$M - n$CO – PhCCPh – RNC (n = 0—4)			
(5) $[Re_2(CO)_5(MeCCMe)_4]$	728	$M - n$CO (n = 0—5)			

[a] Calculated values are given in parentheses. [b] Analytical data for $[Re_2(CO)_4(PhCCPh)_4]\cdot 2CH_2Cl_2$.

† μ-(1—3-η:4—6-η-1,2,3,4,5,6-Hexaphenylhexa-1,5-diene-1,3,4,6-tetrayl-C^1C^{4-6}:$C^{1-3}C^6$)-[tricarbonylrhenium][carbonylbis(*p*-tolylsulphonylmethyl isocyanide)rhenium](*Re–Re*)-dichloromethane (1/1).

of $[Re_2(CO)_{10}]$ with PhCCPh if longer reaction times are used. Thus it appears that the reaction sequence is as shown.

$$[Re_2(CO)_{10}] \xrightarrow[-3CO]{2PhCCPh} [Re_2(CO)_7(PhCCPh)_2] \quad (1)$$

$$\downarrow \text{PhCCPh}, -CO$$

$$[Re_2(CO)_4(PhCCPh)_4] \quad (3) \xleftarrow[-2CO]{PhCCPh} [Re_2(CO)_6(PhCCPh)_3] \quad (2)$$

In an attempt to reverse this reaction sequence (3) was stirred in hexane under 5 atm * pressure of CO at 190 °C for 16 h. Under these conditions (3) was converted essentially quantitatively to (2) and free PhCCPh. No (1) was formed. This experiment suggests that (3) contains one molecule of PhCCPh co-ordinated to one or both metal atoms as an acetylene ligand but that the other three PhCCPh ligands may be co-ordinated in a modified form. This conclusion is reinforced by the reaction of (3) with an excess of RNC. At room temperature (3) reacts instantaneously with this ligand to give $[Re_2(CO)_4(PhCCPh)_3(CNR)_2]$ (4a; R = Bu^t, 4b; Bu^n, 4c; C_6H_4OMe-*p*, 4d; $CH_2SO_2C_6H_4Me$-*p*) and free PhCCPh. The ^1H n.m.r. spectra of these derivatives (Table 2) clearly show that the CNR ligands occupy non-equivalent positions, while the i.r. spectra (Table 2), which are very similar for all the CNR derivatives, contain two resonances in the region expected for terminally bonded CNR ligands. In order to determine the structure of (4) a single-crystal *X*-ray analysis was undertaken for the complex with R = *p*-$MeC_6H_4SO_2CH_2$, (4d). Suitable crystals containing one molecule of CH_2Cl_2 crystallisation of (4d) were obtained by recrystallisation of (4d) from dichloromethane–hexane.

The structure of (4d) is shown in Figure 1 and a line diagram of the structure is given in Figure 2. Tables 3 and 4 list the final bond lengths and interbond angles respectively. The three acetylene molecules are linked in a chain comprising carbon atoms C(23), C(30), C(37), C(44), C(51), and C(58). The two end carbon atoms of the chain bridge the two rhenium atoms asymmetrically with both carbon atoms being significantly closer to

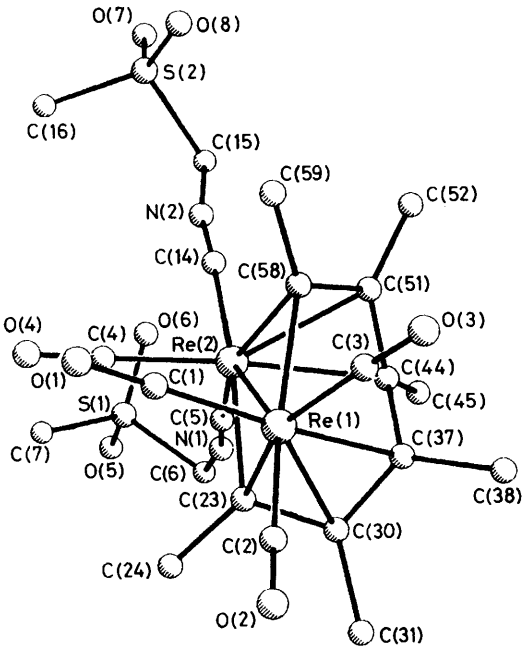

FIGURE 1 The molecular structure of $[Re_2(CO)_4(PhCCPh)_3(CNCH_2SO_2C_6H_4Me\text{-}p)_2]$, (4d), including the atom-numbering scheme. The phenyl rings have been omitted for clarity

Re(2) (2.15 Å) than to Re(1) (2.22 Å). Such asymmetry is hardly surprising in view of the differing ligands attached to the two metal atoms. The remaining four carbon atoms in the chain are further away from the rhenium with C(30) and C(37) being bonded to Re(1) and C(44) and C(51) to Re(2) at an average distance of 2.32 Å. A simple description of the bonding which is compatible with the ligand geometry is that the carbon atom at each

TABLE 2

Infrared and ^1H n.m.r. data for dirhenium acetylene derivatives

Compound	Solvent	I.r. (cm^{-1}) ν(CNR) and ν(CO)	^1H n.m.r. (δ/p.p.m.) *
(1)	Hexane	2 086m, 2 034s, 2 016m, 1 978s, 1 966m, 1 935m	7.2 (m)
(2)	Hexane	2 051m, 2 029s, 1 986s, 1 981s, 1 960m, 1 944m, 1 932w	7.2 (m)
(3)	CH_2Cl_2	2 025s, 1 988m, 1 948m, 1 927m	5.86—7.28 (m)
(4a)	CH_2Cl_2	ν(CNR), 2 156m (br), 2 124w (br); ν(CO), 2 014s, 1 947m, 1 920m, 1 881w	7.21 (m, 30 H, Ph), 1.36 (s, 9 H, Bu^t), 1.01 (s, 9 H, Bu^t)
(4b)	CH_2Cl_2	ν(CNR), 2 169m (br), 2 141w (br); ν(CO), 2 015s, 1 947m, 1 921m, 1 880w	7.06 (m, 30 H, Ph), 3.75 (m, 2 H, CH_2), 3.21 (m, 2 H, CH_2), 0.85—1.5 [m, 14 H, Me $(CH_2)_2$]
(4c)	CH_2Cl_2	ν(CNR), 2 133w (br), 2 097w (br); ν(CO), 2 017s, 1 951m, 1 925m, 1 888w (sh)	7.02 (m, 38 H, Ph), 3.77 (s, 3 H, Me), 3.74 (s, 3 H, Me)
(4d)	CH_2Cl_2	ν(CNR), 2 144m (br), 2 114w (sh); ν(CO), 2 020s, 1 957m, 1 930m, 1 910w (sh)	7.18 (m, 38 H, Ph), 4.59 (s, 2 H, CH_2), 4.28 (s, 2 H, CH_2), 2.48 (s, 3 H, Me), 2.39 (s, 3 H, Me)
(5)	Hexane	2 030m, 1 973s, 1 959m, 1 947m, 1 894m	3.31 (s, 6 H, Me), 2.35 (s, 6 H, Me), 2.28 (s, 6 H, Me), 1.70 (s, 6 H, Me)

* Recorded in CD_2Cl_2 solution at 100 MHz and 35 °C; s = singlet, m = multiplet.

* Throughout this paper: 1 atm = 101 325 Pa.

end of the chain is σ-bonded to one metal atom and, with its two neighbouring carbon atoms, forms an η^3-allyl linkage to the other metal atom. The C–C bonds within the allyl linkages are considerably shorter at 1.43—1.45 Å than the remaining essentially single C–C bond (1.55 Å) which joins them together. This type of linkage of a six-atom carbon chain to two metal atoms has been

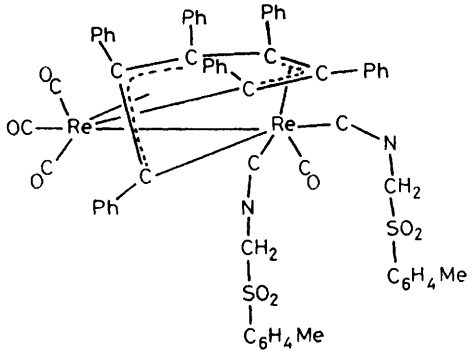

FIGURE 2 Line diagram of the molecular structure of (4d)

identified previously in the cobalt complexes $[Co_2(CO)_4(RC_2R)_3]$ [4,5] and some closely related molybdenum derivatives of the type $[Mo_2(\eta\text{-}C_5H_5)_2(R^1CCR^2)_3]$ have also been reported.[2] The rhenium–rhenium distance in (4) at 2.83 Å is considerably shorter than in $[Re_2(CO)_{10}]$ (3.02 Å) [6] and would be compatible with some multiple bond character, as has been postulated for the related molybdenum complexes.[2] Assuming, however, that the $(PhCCPh)_3$ ligand donates eight electrons to the metal atoms and that the CO and RNC ligands each donate

TABLE 3

Bond lengths (Å)

Re(1)–Re(2)	2.786(1)	Re(2)–C(4)	1.931(7)
Re(1)–C(1)	1.919(7)	Re(2)–C(5)	2.019(9)
Re(1)–C(2)	1.958(7)	Re(2)–C(14)	2.017(7)
Re(1)–C(3)	1.946(10)	Re(2)–C(23)	2.142(6)
Re(1)–C(23)	2.213(8)	Re(2)–C(44)	2.295(6)
Re(1)–C(30)	2.314(7)	Re(2)–C(51)	2.342(7)
Re(1)–C(37)	2.316(6)	Re(2)–C(58)	2.153(9)
Re(1)–C(58)	2.234(7)	C(5)–N(1)	1.153(11)
C(1)–O(1)	1.148(9)	N(1)–C(6)	1.422(12)
C(2)–O(2)	1.138(9)	C(6)–S(1)	1.803(7)
C(3)–O(3)	1.137(13)	S(1)–O(5)	1.433(8)
C(4)–O(4)	1.132(9)	S(1)–O(6)	1.445(7)
C(23)–C(24)	1.509(10)	S(1)–C(7)	1.724(5)
C(23)–C(30)	1.442(8)	C(10)–C(13)	1.517(10)
C(30)–C(31)	1.526(8)	C(14)–N(2)	1.143(9)
C(30)–C(37)	1.427(11)	N(2)–C(15)	1.429(10)
C(37)–C(38)	1.535(7)	C(15)–S(2)	1.801(8)
C(37)–C(44)	1.547(8)	S(2)–O(7)	1.426(6)
C(44)–C(45)	1.530(8)	S(2)–O(8)	1.434(8)
C(44)–C(51)	1.449(10)	S(2)–C(16)	1.737(5)
C(51)–C(52)	1.500(8)	C(19)–C(22)	1.505(12)
C(51)–C(58)	1.444(9)	C(58)–C(59)	1.495(10)
C(100)–Cl(1)	1.759(10)	C(100)–Cl(2)	1.763(10)

two, then only a single Re–Re bond is required to satisfy the effective atomic number (E.A.N.) rule.

The CNR ligands in (4) are both terminally bonded to one metal atom and their non-equivalent positions are compatible with the ^1H n.m.r. and i.r. spectra already referred to. The bond parameters in the two $CNCH_2SO_2C_6H_4Me$-*p* ligands do not vary significantly from the expected values. The four carbonyl groups are terminal and essentially linear. None of the atoms of the CH_2Cl_2 molecule is within bonding distance of the rhenium complex.

In the light of the structure of (4) the displacement of

TABLE 4

Bond angles (°)

Re(2)–Re(1)–C(1)	93.9(2)	Re(1)–Re(2)–C(4)	93.8(2)
Re(2)–Re(1)–C(2)	147.0(3)	Re(1)–Re(2)–C(5)	133.4(2)
Re(2)–Re(1)–C(3)	129.7(2)	Re(1)–Re(2)–C(14)	148.6(3)
Re(2)–Re(1)–C(23)	49.1(2)	Re(1)–Re(2)–C(23)	51.4(2)
Re(2)–Re(1)–C(30)	72.7(2)	Re(1)–Re(2)–C(44)	72.3(2)
Re(2)–Re(1)–C(37)	71.8(2)	Re(1)–Re(2)–C(51)	73.3(2)
Re(2)–Re(1)–C(58)	49.3(2)	Re(1)–Re(2)–C(58)	51.9(2)
C(1)–Re(1)–C(3)	85.0(3)	C(4)–Re(2)–C(5)	95.6(3)
C(1)–Re(1)–C(3)	95.1(4)	C(4)–Re(2)–C(14)	87.2(3)
C(2)–Re(1)–C(3)	83.1(4)	C(5)–Re(2)–C(14)	77.5(3)
C(1)–Re(1)–C(23)	106.8(3)	C(4)–Re(2)–C(23)	92.2(3)
C(2)–Re(1)–C(23)	99.7(3)	C(5)–Re(2)–C(23)	82.7(3)
C(3)–Re(1)–C(23)	158.1(3)	C(14)–Re(2)–C(23)	160.0(3)
C(1)–Re(1)–C(30)	140.7(4)	C(4)–Re(2)–C(44)	166.1(3)
C(2)–Re(1)–C(30)	87.4(3)	C(5)–Re(2)–C(44)	94.2(3)
C(3)–Re(1)–C(30)	122.2(3)	C(14)–Re(2)–C(44)	104.6(2)
C(23)–Re(1)–C(30)	37.1(2)	C(23)–Re(2)–C(44)	79.2(2)
C(1)–Re(1)–C(37)	165.7(3)	C(4)–Re(2)–C(51)	140.4(3)
C(2)–Re(1)–C(37)	106.9(3)	C(5)–Re(2)–C(51)	120.8(3)
C(3)–Re(1)–C(37)	94.2(3)	C(14)–Re(2)–C(51)	86.0(3)
C(23)–Re(1)–C(37)	64.1(2)	C(23)–Re(2)–C(51)	106.6(2)
C(30)–Re(1)–C(37)	35.9(3)	C(44)–Re(2)–C(51)	36.4(3)
C(1)–Re(1)–C(58)	91.1(3)	C(4)–Re(2)–C(58)	105.8(3)
C(2)–Re(1)–C(58)	163.3(4)	C(5)–Re(2)–C(58)	157.9(3)
C(3)–Re(1)–C(58)	81.1(3)	C(14)–Re(2)–C(58)	97.7(3)
C(23)–Re(1)–C(58)	97.0(3)	C(23)–Re(2)–C(58)	101.7(3)
C(30)–Re(1)–C(58)	105.6(2)	C(44)–Re(2)–C(58)	65.8(3)
C(37)–Re(1)–C(58)	79.7(2)	C(51)–Re(2)–C(58)	37.2(2)
Re(1)–C(1)–O(1)	178.3(9)	Re(2)–C(5)–N(1)	175.7(6)
Re(1)–C(2)–O(2)	173.5(9)	C(5)–N(1)–C(6)	167.4(6)
Re(1)–C(3)–O(3)	177.5(7)	N(1)–C(6)–S(1)	109.7(5)
Re(2)–C(4)–O(4)	176.7(9)	C(6)–S(1)–O(5)	105.1(4)
Re(2)–C(14)–N(2)	173.5(8)	C(6)–S(1)–O(6)	107.0(4)
C(14)–N(2)–C(15)	167.7(7)	O(5)–S(1)–O(6)	119.5(4)
N(2)–C(15)–S(2)	109.8(6)	C(6)–S(1)–C(7)	104.5(3)
C(15)–S(2)–O(7)	104.1(4)	O(5)–S(1)–C(7)	110.3(3)
C(15)–S(2)–O(8)	108.4(4)	O(6)–S(1)–C(7)	109.2(3)
O(7)–S(2)–O(8)	119.3(4)	C(9)–C(10)–C(13)	121.1(5)
C(15)–S(2)–C(16)	104.7(4)	C(11)–C(10)–C(13)	118.6(5)
O(7)–S(2)–C(16)	109.5(3)	S(1)–C(7)–C(8)	119.9(2)
O(8)–S(2)–C(16)	109.7(3)	S(1)–C(7)–C(12)	120.0(2)
C(18)–C(19)–C(22)	119.8(5)	C(24)–C(23)–C(30)	120.6(6)
C(20)–C(19)–C(22)	120.1(5)	C(23)–C(24)–C(25)	118.8(3)
S(2)–C(16)–C(17)	121.2(2)	C(23)–C(24)–C(29)	121.2(3)
S(2)–C(16)–C(21)	118.2(2)	C(23)–C(30)–C(31)	122.1(6)
Re(1)–C(23)–Re(2)	79.5(3)	C(23)–C(30)–C(37)	113.8(6)
Re(1)–C(58)–Re(2)	78.8(3)	C(31)–C(30)–C(37)	124.0(5)
Re(1)–C(23)–C(24)	133.1(4)	C(30)–C(31)–C(32)	120.6(3)
Re(2)–C(23)–C(24)	120.4(4)	C(30)–C(31)–C(36)	118.8(3)
Re(1)–C(23)–C(30)	75.2(5)	C(30)–C(37)–C(38)	122.4(5)
Re(2)–C(23)–C(30)	115.0(5)	C(30)–C(37)–C(44)	115.7(6)
Re(1)–C(30)–C(23)	67.7(4)	C(38)–C(37)–C(44)	116.8(5)
Re(1)–C(30)–C(31)	126.5(4)	C(37)–C(38)–C(39)	120.2(3)
Re(1)–C(30)–C(37)	72.1(4)	C(37)–C(38)–C(43)	119.8(3)
Re(1)–C(37)–C(30)	72.0(4)	C(37)–C(44)–C(45)	118.6(5)
Re(1)–C(37)–C(38)	117.9(4)	C(37)–C(44)–C(51)	116.2(6)
Re(1)–C(37)–C(44)	101.1(3)	C(45)–C(44)–C(51)	122.4(5)
Re(2)–C(44)–C(37)	101.6(4)	C(44)–C(45)–C(46)	121.5(3)
Re(2)–C(44)–C(45)	110.3(4)	C(44)–C(45)–C(50)	118.3(3)
Re(2)–C(44)–C(51)	73.6(3)	C(44)–C(51)–C(52)	125.0(5)
Re(2)–C(51)–C(44)	70.0(4)	C(44)–C(51)–C(58)	113.6(6)
Re(2)–C(51)–C(52)	132.0(4)	C(52)–C(51)–C(58)	121.3(6)
Re(2)–C(51)–C(58)	64.3(4)	C(51)–C(52)–C(53)	117.1(2)
Re(1)–C(58)–C(51)	112.1(4)	C(51)–C(52)–C(57)	122.9(2)
Re(2)–C(58)–C(51)	78.5(5)	C(51)–C(58)–C(59)	121.9(6)
Re(1)–C(58)–C(59)	120.3(4)	C(58)–C(59)–C(60)	119.3(3)
Re(2)–C(58)–C(59)	132.9(4)	C(58)–C(59)–C(64)	120.7(3)
Cl(1)–C(100)–Cl(2)	111.1(6)		

only one acetylene molecule from (4) in its reactions with CNR or CO is understandable, if it is assumed that three of the acetylene molecules in (3) are bonded in the same way as in (4). In order to determine the mode of bonding of the fourth acetylene molecule in (3) a single-crystal *X*-ray analysis was undertaken.[7] Unfortunately disorder problems did not allow refinement of the structure, but the chain of three acetylene molecules bonded in a similar fashion to those in (4) was clearly revealed. The fourth acetylene ligand is separately bonded to one of the metal atoms and takes the place of the two CNR ligands in (4). Complex (3) thus has the structure shown in Figure 3(*a*). The Re–Re distance is *ca.* 2.78 Å and is

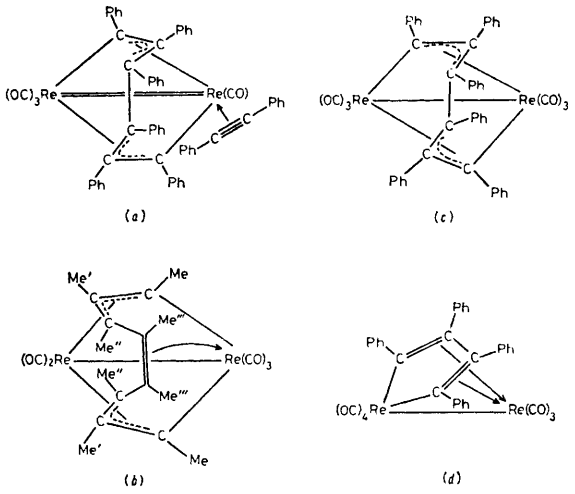

FIGURE 3 Proposed structures for some dirhenium acetylene complexes: (*a*) $[Re_2(CO)_4(PhCCPh)_4]$, (3); (*b*) $[Re_2(CO)_5(MeCCMe)_4]$, (5); (*c*) $[Re_2(CO)_6(PhCCPh)_3]$, (2); (*d*) $[Re_2(CO)_7(PhCCPh)_2]$, (1)

again compatible with the presence of a multiple bond. In this instance such a multiple bond may be present, since it is difficult to see how the lone PhCCPh ligand can act as more than a two-electron donor when co-ordinated to only one metal atom. If the PhCCPh ligand does donate two electrons then the complex is overall two electrons short of the number required to satisfy the E.A.N. rule, unless a Re–Re double bond is postulated. It should, however, be noted that co-ordinatively unsaturated complexes containing acetylene ligands are not uncommon.[8] An alternative possibility is that one of the carbonyl ligands in (3) acts as a four-electron donor, bonding to one metal atom through carbon and to the other through oxygen. The solution i.r. spectrum of (3), however, showed four ν(CO) bands in the terminal region and none at *ca.* 1 650 cm^{-1} in the region expected for a bridging CO group bonded through both carbon and oxygen.[9]

In the reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with R^1CCR^2 the products obtained depended on the reaction condition and the nature of the R groups. Complexes containing two, three, and four acetylene molecules linked in a chain were characterised.[2] Complex (3), which we have isolated, presumably represents an intermediate stage between complexes containing three and four linked acetylenes and is the first intermediate of this type to have been reported. The failure of (3) to undergo further reaction to give a dirhenium complex containing four linked acetylenes is probably due to steric factors. That this is the case is strongly suggested by the reaction of $[Re_2(CO)_{10}]$ with MeCCMe. At 190 °C this reaction resulted in extensive decomposition but a single light yellow product was isolated in low yield and identified by mass spectroscopy as $[Re_2(CO)_5(MeCCMe)_4]$ (5). This complex does not react with CNR and therefore seems unlikely to contain a simple π-bonded acetylene. Its ^1H n.m.r. spectrum (Table 2) contains four equally intense peaks in the methyl region, which is compatible with a linked chain of four acetylene molecules bonded to the two rhenium atoms as shown in Figure 3(*b*). This structural proposal for (5) is supported by the results of a single-crystal *X*-ray analysis on the related molybdenum complex $[Mo_2(\eta\text{-}C_5H_5)_2\{MeO_2CC_2CO_2Me(HC_2H)(MeO_2CC_2CO_2Me)_2\}]$ which shows that the four acetylene molecules are disposed about the two Mo atoms in a similar way.[2]

The stoicheiometry of complex (2) differs from that of (4) only in that two CO groups take the place of two CNR groups. It seems unlikely that this difference markedly affects the arrangement of the three linked PhCCPh groups about the metal atoms, and the proposed structure for (2) on this basis is as shown in Figure 3(*c*). The solution i.r. spectrum of (2) is in agreement with this structure, showing that all the carbonyl groups are terminally bonded and that none is incorporated into the organic part of the molecule.

The solution i.r. spectrum of (1) again shows that all of the carbonyl ligands are terminally bonded and does not contain any resonance in the region typical of a cyclic dienone stretch (*ca.* 1 650 cm^{-1}). In addition the mass spectrum of (1) shows prominent ions due to the loss of seven carbonyl ligands from the parent ion. Several structures can be postulated on the basis of this limited evidence but the similarity of the overall reaction sequence to that previously reported for the reaction of $[\{M(\eta\text{-}C_5H_5)(CO)\}_2]$ with acetylenes (M = Cr or Mo) suggests that the most probable structure for (1) is as shown in Figure 3(*d*). It might have been expected that two separate phenyl resonances would be observed in the ^1H n.m.r. spectrum; however, in the related complex $[Fe_2(CO)_6(PhCCPh)_2]$ the phenyl resonances also occur as one broad signal.[10]

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.

(*i*) *Reaction of* $[Re_2(CO)_{10}]$ *with* PhCCPh.—The reaction was carried out in a 100-cm³ laboratory autoclave. The complex $[Re_2(CO)_{10}]$ (0.10 g, 0.15 mmol) and PhCCPh (0.136 g, 0.75 mmol) were stirred together in the autoclave, which was then evacuated and filled with nitrogen three times. Dry nitrogen-saturated hexane (20 cm³) was introduced into the autoclave against a counter current of nitrogen and the solution was then heated, with stirring, at 190 °C for 16 h. After allowing the autoclave to cool, the hexane solution was decanted and the autoclave rinsed with acetone, these washings being combined with the hexane solution. The solvent was removed on a rotary evaporator and the residue taken up in a minimum of dichloromethane. The products were then separated by thin-layer chromotography (t.l.c.) on silica using 40% CH_2Cl_2–60% hexane as eluant. The order of elution (decreasing R_F values) was $[Re_2(CO)_7(PhCCPh)_2]$, $[Re_2(CO)_6(PhCCPh)_3]$, and $[Re_2(CO)_4(PhCCPh)_4]$. Yields of these individual complexes varied from run to run but the total product yield was usually *ca.* 80%. The compounds $[Re_2(CO)_6(PhCCPh)_3]$ and $[Re_2(CO)_7(PhCCPh)_2]$ suffered extensive decomposition during attempts at recrystallisation and could not be obtained in a degree of purity adequate for microanalysis. The complex $[Re_2(CO)_4(PhCCPh)_4]$ (3) was obtained as the orange crystalline $[Re_2(CO)_4(PhCCPh)_4]\cdot 2CH_2Cl_2$ on recrystallisation from this solvent.

(*ii*) *Reaction of* $[Re_2(CO)_{10}]$ *with* MeCCMe.—This reaction was carried out under the same conditions as the reaction of $[Re_2(CO)_{10}]$ with PhCCPh but using 1 cm³ of MeCCMe. Considerable decomposition to rhenium metal occurred but t.l.c. on silica using 40% CH_2Cl_2–60% hexane as eluant gave the single product, $[Re_2(CO)_5(MeCCMe)_4]$ (5), as a yellow powder, in *ca.* 10% yield.

(*iii*) *Reaction of* $[Re_2(CO)_4(PhCCPh)_4]$ *with* CO.—Dry nitrogen-saturated hexane (10 cm³) was added to $[Re_2(CO)_4(PhCCPh)_4]$ (0.02 g, 0.017 mmol) in a nitrogen filled autoclave. The autoclave was then pressurised to 5 atm with commercial grade CO and heated with stirring at 190 °C for 6 h. The products of the reaction were separated by t.l.c. on silica using 30% CH_2Cl_2–70% hexane and identified as $[Re_2(CO)_6(PhCCPh)_3]$ (2) (i.r. spectroscopy) and PhCCPh [high-resolution mass spectroscopy: *m/e* observed = 178.077 4(17); calculated, 178.079]. No starting material or other products were present.

(*iv*) *Preparation of* $[Re_2(CO)_4(PhCCPh)_3(CNR)_2]$, (4).—In a typical reaction $[Re_2(CO)_4(PhCCPh)_4]$ (0.01 g, 0.008 4 mmol) was dissolved in CH_2Cl_2 (5 cm³). Excess of CNR was added (neat for R = Bu^t, Bu^n; in CH_2Cl_2 solution for R = *p*-$MeOC_6H_4$, *p*-$MeC_6H_4SO_2CH_2$) and an immediate reaction occurred as indicated by the colour change of the solution from orange-red to deep red. After solvent removal with a stream of nitrogen the products were dissolved in a minimum of CH_2Cl_2 and separated by t.l.c. using 30% CH_2Cl_2–70% hexane as eluant. The complex $[Re(CO)_4(PhCCPh)_3(CNR)_2]$ was obtained as a red crystalline product in essentially quantitative yield. The other reaction product was identified by mass spectroscopy as the displaced PhCCPh.

(*v*) *Molecular Structure Determination of* $[Re_2(CO)_4(PhCCPh)_3(CNCH_2SO_2C_6H_4Me\text{-}p)_2]\cdot CH_2Cl_2$, (4d).—A black crystal of dimensions *ca.* 0.42 × 0.42 × 0.12 mm was mounted on a glass fibre with epoxy resin adhesive. This crystal was transferred to a Stoe A.E.D. four-circle diffractometer, and accurate cell parameters obtained by centring 20 strong reflections ($2\theta < 20 < 30°$). 7 718 Intensities were recorded in the range $3.0 < 2\theta < 50.0°$, using graphite-monochromated Mo-K_α radiation and a 140-step ω—θ scan procedure; the step scan angle was fixed at 0.01° with a counting time of 0.5 s per step, stationary backgrounds being recorded for 17.5 s at each end of the scan range; reflections with intensities of <10 counts s^{-1} from a 1-s prescan were not measured. Two check reflections were

TABLE 5

Atom co-ordinates (× 10^4)

Atom	*x/a*	*y/b*	*z/c*
Re(1)	7 766(1)	1 519(1)	8 751(1)
Re(2)	6 597(1)	2 710(1)	7 664(1)
C(1)	6 693(7)	2 172(6)	9 643(5)
O(1)	6 032(5)	2 561(5)	10 169(4)
C(2)	7 997(6)	306(6)	9 448(5)
O(2)	8 186(5)	−360(4)	9 886(4)
C(3)	9 025(7)	1 632(6)	9 080(5)
O(3)	9 784(6)	1 684(5)	9 247(5)
C(4)	5 221(6)	3 122(6)	8 433(5)
O(4)	4 441(5)	3 370(5)	8 907(3)
C(5)	5 951(6)	2 394(5)	6 833(4)
N(1)	5 636(5)	2 223(5)	6 324(4)
C(6)	5 035(7)	2 188(6)	5 763(5)
S(1)	3 813(2)	3 278(2)	5 841(1)
O(5)	3 227(5)	3 124(5)	5 304(3)
O(6)	4 171(5)	4 159(4)	5 733(3)
C(7)	3 093(5)	3 202(4)	6 797(3)
C(8)	2 648(5)	2 416(4)	7 042(3)
C(9)	2 128(5)	2 313(4)	7 828(3)
C(10)	2 053(5)	2 997(4)	8 369(3)
C(11)	2 497(5)	3 782(4)	8 124(3)
C(12)	3 018(5)	3 885(4)	7 339(3)
C(13)	1 603(8)	2 839(7)	9 240(6)
C(14)	6 077(6)	4 067(5)	7 108(4)
N(2)	5 724(6)	4 798(5)	6 763(4)
C(15)	5 494(7)	5 626(6)	6 205(5)
S(2)	4 912(2)	6 797(2)	6 706(1)
O(7)	4 563(5)	7 537(4)	6 112(4)
O(8)	5 701(5)	6 890(5)	7 104(4)
C(16)	3 764(4)	6 664(4)	7 393(3)
C(17)	3 754(4)	6 538(4)	8 195(3)
C(18)	2 804(4)	6 478(4)	8 736(3)
C(19)	1 864(4)	6 544(4)	8 476(3)
C(20)	1 874(4)	6 671(4)	7 674(3)
C(21)	2 824(4)	6 731(4)	7 132(3)
C(22)	818(9)	6 550(8)	9 065(6)
C(23)	6 848(5)	1 144(5)	7 994(4)
C(24)	5 896(4)	728(4)	8 166(2)
C(25)	5 757(4)	228(4)	7 578(2)
C(26)	4 883(4)	−164(4)	7 722(2)
C(27)	4 148(4)	−56(4)	8 453(2)
C(28)	4 287(4)	444(4)	9 040(2)
C(29)	5 161(4)	836(4)	8 897(2)
C(30)	7 968(5)	489(5)	7 755(4)
C(31)	8 265(4)	−660(3)	7 811(2)
C(32)	7 680(4)	−1 135(3)	8 418(2)
C(33)	7 854(4)	−2 168(3)	8 404(2)
C(34)	8 613(4)	−2 725(3)	7 784(2)
C(35)	9 197(4)	−2 250(3)	7 177(2)
C(36)	9 023(4)	−1 217(3)	7 191(2)
C(37)	8 758(5)	1 015(5)	7 502(4)
C(38)	10 004(3)	475(3)	7 390(2)
C(39)	10 420(3)	−225(3)	7 961(2)
C(40)	11 554(3)	−707(3)	7 859(2)
C(41)	12 272(3)	−488(3)	7 186(2)
C(42)	11 857(3)	213(3)	6 614(2)
C(43)	10 723(3)	694(3)	6 716(2)
C(44)	8 391(5)	2 006(5)	7 008(4)
C(45)	8 448(4)	1 941(3)	6 134(3)
C(46)	8 208(4)	2 806(3)	5 643(3)
C(47)	8 182(4)	2 724(3)	4 864(3)
C(48)	8 396(4)	1 778(3)	4 577(3)
C(49)	8 63(54)	913(3)	5 068(3)
C(50)	8 661(4)	995(3)	5 847(3)

TABLE 5 (*continued*)

	Atom co-ordinates ($\times 10^4$)		
C(51)	8 343(5)	2 920(5)	7 338(4)
C(52)	8 752(3)	3 743(3)	6 885(3)
C(53)	9 831(3)	3 457(3)	6 436(3)
C(54)	10 280(3)	4 189(3)	6 030(3)
C(55)	9 650(3)	5 208(3)	6 071(3)
C(56)	8 572(3)	5 495(3)	6 520(3)
C(57)	8 123(3)	4 762(3)	6 926(3)
C(58)	7 794(6)	3 011(5)	8 159(4)
C(59)	7 739(3)	3 855(4)	8 625(3)
C(60)	6 715(3)	4 456(4)	9 027(3)
C(61)	6 648(3)	5 257(4)	9 455(3)
C(62)	7 606(3)	5 456(4)	9 482(3)
C(63)	8 630(3)	4 855(4)	9 080(3)
C(64)	8 697(3)	4 054(4)	8 652(3)
C(100)	12 887(9)	1 650(7)	4 151(6)
Cl(1)	11 529(3)	1 882(2)	4 707(2)
Cl(2)	13 806(3)	595(2)	4 547(2)

monitored every 50 measurements throughout data collection and showed no significant variation.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 372 azimuthal scan data from 39 independent reflections was applied. Transmission factors ranged from 0.579 to 0.999 for the full data set. Lorentz polarization corrections were also applied and equivalent reflections averaged to give 6 316 unique observed intensities [$F > 3\sigma(F)$].

Crystal data. $C_{65}H_{50}Cl_2N_2O_8Re_2S_2$, $M = 1\,494.49$, Triclinic, $a = 13.190(3)$, $b = 14.066(3)$, $c = 17.554(5)$ Å, $\alpha = 83.06(2)$, $\beta = 75.75(2)$, $\gamma = 70.40(2)°$, $U = 2\,971.1$ Å^3, $Z = 2$, $D_c = 1.670$ g cm^{-3}, D_m not measured, $F(000) = 467.8$, μ(Mo-K_α) radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 43.03 cm^{-1}, space group $P\bar{1}$ from successful refinement.

The positions of the two rhenium atoms were derived from a Patterson synthesis. These atoms were assigned isotropic thermal parameters, and subjected to three cycles of least-squares refinement. The refined parameters of these atoms were used for calculating a difference electron-density synthesis from which all the non-hydrogen atoms were located. At this stage the hydrogens of the primary CH_3, the secondary CH_2, and the phenyl groups were placed in idealised positions, and constrained to ride 1.08 Å from the relevant carbon atom; the methyl and phenyl groups were refined as rigid bodies. Each type of hydrogen atom was assigned a common isotropic temperature factor. All these parameters were included in further cycles of refinement. The Re, S, O, N, and Cl atoms were assigned anisotropic thermal parameters as were the C and O atoms of the carbonyl atoms. Blocked-cascade least-squares refinement continued until the average shift-to-error ratio for the parameters was <0.04. In the final cycles of refinement the (100) reflection, which was considered to be suffering from extinction, was zero weighted, and a weighting scheme of the form $w = [\sigma^2(F)]^{-1}$ introduced; this minimised the dependence of $w\Delta^2$ on $|F_o|$ and sin θ. The final residuals for the 6 315 unique observed reflections were $R = 0.032$ and $R' = (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|) = 0.032$, and a difference map calculated at this stage showed no regions of significant electron density.

Complex neutral-atom scattering factors were employed, and were modified for anomalous dispersion.[11] All the computations were performed on the University of Cambridge IBM 370/165 computer using programs written by Prof. G. M. Sheldrick. The molecular plots were drawn using 'PLUTO' written by Dr. W. D. S. Motherwell. The atomic fractional co-ordinates for the non-hydrogen atoms are given in Table 5, while lists of thermal parameters, hydrogen-atom co-ordinates and bond angles involving these atoms, observed and calculated structure factors, and details of least-squares planes have been deposited as Supplementary Publication No. SUP 22968 (46 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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