Reactions of Co-ordinated Ligands. Part 40.[1] Synthesis, Structure, and Reactivity of Dirhenium μ-Allylidene Complexes; Crystal Structures† of $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$ and $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_9]$

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Reaction of $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ with 3,3-dimethylcyclopropene at room temperature leads to the formation of the μ-allylidene complex $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$ (**1**), which has been structurally characterised by *X*-ray crystallography. The molecule contains two $Re(CO)_4$ fragments bridged by a μ-$CHCHCMe_2$ ligand where the Re–Re separation is 3.058(1) Å. The μ-allylidene fragment adopts a transoid geometry, and possible reasons for this preference are discussed. A plausible reaction pathway for the formation of (**1**) is described. Reaction of (**1**) with carbon monoxide leads to metal–metal bond cleavage and the formation of $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_9]$ (**2**), which has also been characterised by *X*-ray crystallography. The reaction has resulted in the transformation of (**1**) into a $Re(CO)_5$ substituted η^3-allyl moiety, which is η^3-bonded to a $Re(CO)_4$ unit. The Re–Re separation in (**2**) is 4.190(1) Å. Complex (**2**) is thermally stable, however u.v. photolysis leads to the formation of a μ-butadienyl complex.

We have previously[2,3] shown that reaction of the unsaturated dimolybdenum complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with 3,3-dimethylcyclopropene leads to 2,3 σ-bond cleavage of the three-membered ring, and formation of the μ-allylidene complex $[Mo_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_4(\eta\text{-}C_5H_5)_2]$. In considering possible mechanisms for the formation of this complex it was suggested that ring-opening occurs on co-ordination of the cyclopropene to one metal centre, this being followed by stabilisation of the resulting vinylcarbene complex on interaction of the vinyl π system with the second adjacent unsaturated metal centre. In seeking to obtain further understanding of this type of reaction we have examined the interaction of 3,3-dimethylcyclopropene with the dirhenium complex $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$. Some aspects of this work have been described in a preliminary publication.[4]

Results and Discussion

Room-temperature u.v. photolysis of a hexane solution of $[Re_2(CO)_{10}]$ in the presence of an excess of but-1-ene led as previously described by Nubel and Brown[5,6] to the formation of $[Re_2(\mu\text{-}H)\{\mu\text{-}(E)\text{-}CH{=}CHEt\}(CO)_8]$ in high yield. Addition of an excess of 3,3-dimethylcyclopropene to a hexane solution of the dirhenium complex led to a slow (2 d) reaction and the formation (78% yield) of the yellow crystalline complex $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$ (**1**). Elemental analysis and mass spectroscopy indicated that (**1**) was a 1:1 adduct of the cyclopropene and a $[Re_2(CO)_8]$ fragment, and examination of the ^1H n.m.r. spectrum suggested that the molecule was a μ-allylidene complex. Thus, the spectrum showed two methyl singlets at δ 1.94 and 2.09 p.p.m. as well as two, single proton doublets [$^3J(HH)$ 12.45 Hz] at δ 7.65 and 4.53 p.p.m. attributable respectively to the protons on the C_α and C_β carbons of a μ-$CHCHCMe_2$ ligand.[3] The coupling constant is larger than expected (8—10 Hz) for *cis* $^3J(HH)$ in η^3-allyls and

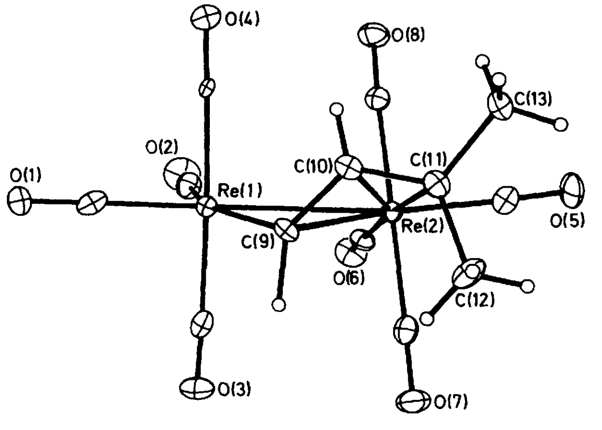

Figure 1. Molecular structure of $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$ (**1**) showing atom labelling. Ellipsoids are drawn to enclose 20% probability density

other μ-σ:η^3-allylidene species implying a relative *trans* orientation of the two formerly *cis*-olefinic hydrogen atoms of the 3,3-dimethylcyclopropene. There was no evidence for a high-field resonance characteristic of a bridging hydride. The ^{13}C n.m.r. data are likewise consistent with the μ-allylidene formulation. At room temperature there are eight sharp, equal intensity terminal carbonyl resonances demonstrating that (**1**) is non-fluxional at this temperature unlike the complexes $[Re_2(\mu\text{-}H)(\mu\text{-alkenyl})(CO)_8]$[6] and $[Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CH)(CO)_8]$.[5] Methine (CH) resonances were observed at δ 139.0 [$^1J(CH)$ 138, $^2J(CH)$ 9.2] and 105.3 p.p.m. [$^1J(CH)$ 156.3 Hz] and are characteristic of the C_α and C_β carbons of a μ-allylidene ligand, respectively, although as with the $C_\alpha H$ proton the C_α carbon is at higher field than in many other μ-alkylidene or μ-allylidene species. In order unequivocally to characterise (**1**), particularly with regard to the unusual implied *trans* geoemtry of the μ-allylidene ligand, a single-crystal *X*-ray diffraction study was undertaken. The molecular structure is illustrated in Figure 1 and selected bond lengths and angles are listed in Table 1.

In (**1**) two $Re(CO)_4$ fragments are bridged by a μ-allylidene ligand where the rhenium to rhenium separation is 3.058(1) Å. Such a distance is in the range normally assigned to a Re–Re

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† μ-[σ:1—3-η-3-Methylbutenediyl-C^1(Re),C^{1-3}(Re′)]-bis(tetracarbonylrhenium) (*Re–Re*) and 1,1,1,1,1,2,2,2,2-nonacarbonyl-μ-[σ:1—3-η-3-methylbutenediyl-C^1(Re^1),C^{1-3}(Re^2)]-dirhenium respectively.

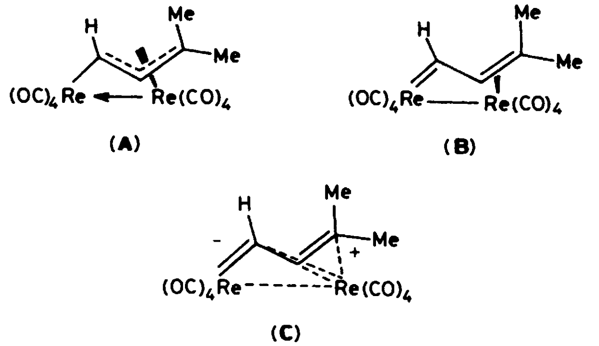
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 Pa.

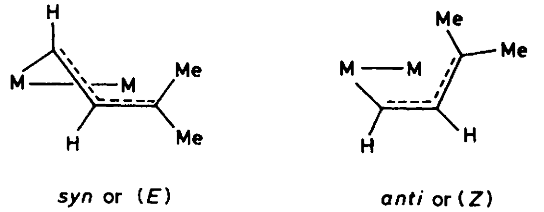
Table 1. Bond lengths (Å) and interbond angles (°) for (**1**)

Re(1)–Re(2)	3.058(1)	Re(1)–C(1)	1.889(15)
Re(1)–C(2)	1.948(13)	Re(1)–C(3)	2.003(13)
Re(1)–C(4)	1.983(11)	Re(1)–C(9)	2.109(11)
Re(2)–C(5)	1.947(14)	Re(2)–C(6)	1.963(13)
Re(2)–C(7)	1.982(12)	Re(2)–C(8)	1.979(11)
Re(2)–C(9)	2.353(11)	Re(2)–C(10)	2.281(11)
Re(2)–C(11)	2.494(13)	O(1)–C(1)	1.162(18)
O(2)–C(2)	1.141(17)	O(3)–C(3)	1.106(16)
O(4)–C(4)	1.138(14)	O(5)–C(5)	1.128(17)
O(6)–C(6)	1.097(17)	O(7)–C(7)	1.163(16)
O(8)–C(8)	1.136(14)	C(9)–H(9)	1.201(114)
C(9)–C(10)	1.441(16)	C(10)–H(10)	0.910(78)
C(10)–C(11)	1.385(18)	C(11)–C(12)	1.517(17)
C(11)–C(13)	1.519(18)		
Re(2)–Re(1)–C(1)	164.9(4)	Re(2)–Re(1)–C(2)	103.4(4)
C(1)–Re(1)–C(2)	91.3(6)	Re(2)–Re(1)–C(3)	91.4(4)
C(1)–Re(1)–C(3)	91.1(6)	C(2)–Re(1)–C(3)	91.9(6)
Re(2)–Re(1)–C(4)	90.2(3)	C(1)–Re(1)–C(4)	86.4(5)
C(2)–Re(1)–C(4)	91.1(5)	C(3)–Re(1)–C(4)	176.2(5)
Re(2)–Re(1)–C(9)	50.2(3)	C(1)–Re(1)–C(9)	115.1(5)
C(2)–Re(1)–C(9)	153.6(5)	C(3)–Re(1)–C(9)	88.5(5)
C(4)–Re(1)–C(9)	89.9(4)	Re(1)–Re(2)–C(5)	168.1(3)
Re(1)–Re(2)–C(6)	77.7(4)	C(5)–Re(2)–C(6)	95.0(5)
Re(1)–Re(2)–C(7)	97.6(4)	C(5)–Re(2)–C(7)	91.1(5)
C(6)–Re(2)–C(7)	86.0(5)	Re(1)–Re(2)–C(8)	82.4(4)
C(5)–Re(2)–C(8)	88.2(5)	C(6)–Re(2)–C(8)	89.5(5)
C(7)–Re(2)–C(8)	175.4(5)	Re(1)–Re(2)–C(9)	43.5(3)
C(5)–Re(2)–C(9)	146.9(5)	C(6)–Re(2)–C(9)	116.2(5)
C(7)–Re(2)–C(9)	81.0(4)	C(8)–Re(2)–C(9)	102.0(4)
Re(1)–Re(2)–C(10)	70.3(3)	C(5)–Re(2)–C(10)	116.2(5)
C(6)–Re(2)–C(10)	147.8(5)	C(7)–Re(2)–C(10)	100.2(4)
C(8)–Re(2)–C(10)	84.2(4)	C(9)–Re(2)–C(10)	36.2(4)
Re(1)–Re(2)–C(11)	102.7(3)	C(5)–Re(2)–C(11)	85.5(5)
C(6)–Re(2)–C(11)	174.7(4)	C(7)–Re(2)–C(11)	88.7(5)
C(8)–Re(2)–C(11)	95.8(4)	C(9)–Re(2)–C(11)	62.4(4)
C(10)–Re(2)–C(11)	33.3(4)	Re(1)–C(1)–O(1)	179.6(11)
Re(1)–C(2)–O(2)	177.2(13)	Re(1)–C(3)–O(3)	177.5(12)
Re(1)–C(4)–O(4)	178.2(10)	Re(2)–C(5)–O(5)	174.9(13)
Re(2)–C(6)–O(6)	176.3(11)	Re(2)–C(7)–O(7)	175.2(11)
Re(2)–C(8)–O(8)	176.6(11)	Re(1)–C(9)–Re(2)	86.3(4)
Re(1)–C(9)–H(9)	108.1(58)	Re(2)–C(9)–H(9)	111.5(59)
Re(1)–C(9)–C(10)	123.1(7)	Re(2)–C(9)–C(10)	69.2(6)
H(9)–C(9)–C(10)	128.5(61)	Re(2)–C(10)–C(9)	74.7(6)
Re(2)–C(10)–H(10)	109.7(55)	C(9)–C(10)–H(10)	121.5(59)
Re(2)–C(10)–C(11)	81.8(8)	C(9)–C(10)–C(11)	125.8(11)
H(10)–C(10)–C(11)	112.3(60)	Re(2)–C(11)–C(10)	64.8(7)
Re(2)–C(11)–C(12)	107.9(8)	C(10)–C(11)–C(12)	122.4(11)
Re(2)–C(11)–C(13)	115.5(8)	C(10)–C(11)–C(13)	118.5(11)

single bond, *e.g.* [Re_2(μ-CO)$(CO)_4$(η-$C_5H_5)_2$],[7] 2.957(1); [$Re_2(CO)_{10}$],[8] 3.041(1); [Re_2(μ-H)(μ-$SiPh_2)(CO)_8$],[9] 3.121(2); and [Re_2(μ-H)(μ-η^2-$NC_6H_4)(CO)_8$],[10] 3.202(1) Å, consistent with the 34-electron count around the Re_2 unit in (**1**). In contrast with [$Re_2(CO)_{10}$], which adopts[8] a staggered approximately D_{4d} geometry, (**1**) is constrained to a compromise between a staggered and eclipsed geometry around the Re–Re vector [C(3)–Re(1)–Re(2)–C(7) torsion angle 18.6°] presumably as a result of the geometric requirements imposed by the allylidene ligand. This is σ bound to Re(1) [Re(1)–C(9), 2.109(11) Å] and η^3 bound to Re(2) [Re(2)–C(9), 2.353(11); Re(2)–C(10), 2.281(11); and Re(2)–C(11), 2.494(13) Å]. The carbon atom C(9) clearly bridges in a highly asymmetric fashion, the bond to Re(1) being of comparable length to the Re–C bonds found in [Re(CHO)(NO)(PPh_3)(η-C_5H_5)][11] [Re—CHO, 2.055(10) Å] and [MnRe{C(Me)OMe}$(CO)_8$][12] [Re–C(Me)OMe, 2.094(7) Å], suggesting partial double bond character. The Re(2)–C(9) distance is, however, much longer and falls on the limit of normal Re–C σ-bond lengths. This may reflect the imbalance in the formal electron count at Re(1) and Re(2) which results if the binding of the allylidene fragment is as is shown in structure (**A**) (Scheme 1).



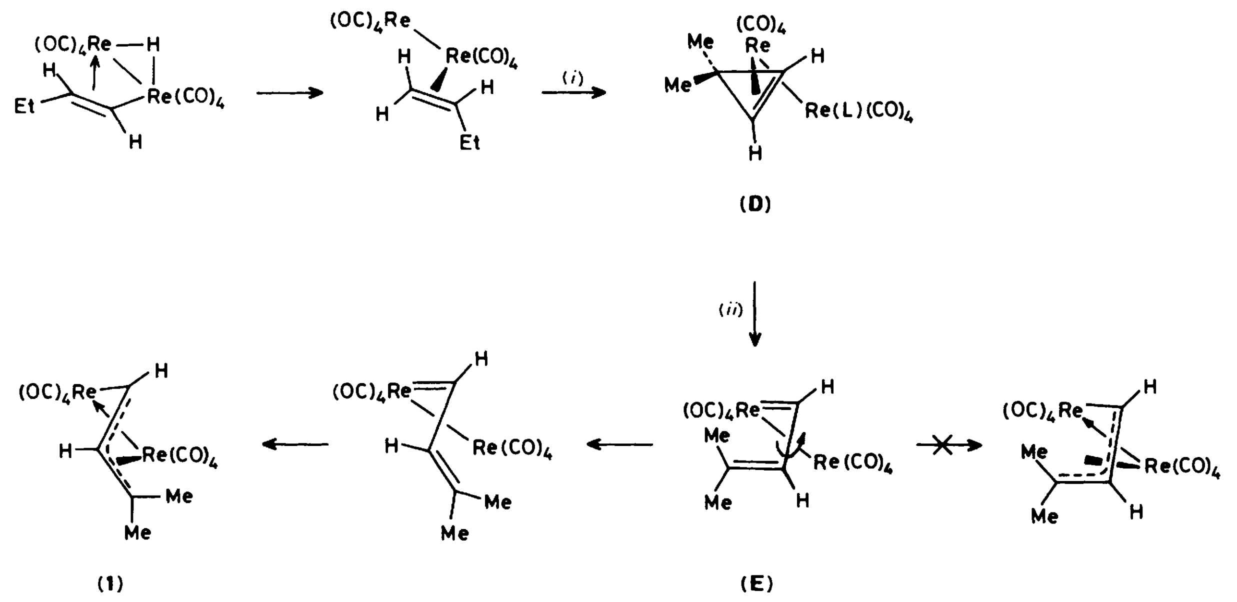
Scheme 1.



Scheme 2.

However, an alternative and perhaps more satisfactory description of the bonding is represented by either (**B**) or (**C**) where a transoid rhenabuta-1,3-diene is co-ordinated to the Re(2)$(CO)_4$ unit *via* a Re–Re single bond and a η^2-bonded vinyl moiety or *via* an η^4 interaction respectively. In support of such a representation the C–C bond lengths within the allylidene fragment are C(9)–C(10), 1.441(16); C(10)–C(11), 1.385(18) Å.

As noted above the conformation of the Re(1)–μ-allylidene moiety in (**1**) is transoid [torsion angle Re(1)–C(9)–C(10)–C(11), −138.5°], in contrast to all other μ-allylidene complexes except [W_2(μ-σ:η^3-$CHCHCMe_2)(CO)_9$].[13] As illustrated in Scheme 2 there exist two conformations in which μ-allylidene complexes may be viewed as containing *syn* and *anti* 1-metallated-allyl or (*E*)- or (*Z*)-metalladiene ligands co-ordinated to a second metal. In the dimolybdenum complex [Mo_2(μ-σ:η^3-$CHCHCMe_2)(CO)_4$(η-$C_5H_5)_2$],[2,3] the ditungsten complex [W_2(μ-σ:η^3-CMeCMeCHCH=$CMe_2)(CO)_9$],[14] and other μ-allylidenes the *anti* (*Z*) geometry is adopted. The reasons for the preference of one geometry over another are not obvious, even assuming that the observed geometries are the thermodynamically favoured isomers in each case. In (**1**) the requirements of the Re$(CO)_4$ fragments, which have local C_{2v} symmetry, in terms of electronic preferences, appear to be well satisfied by the *syn* (*E*) geometry. Thus, as discussed by Albright *et al.*,[15,16] the M$(CO)_4$ fragment preferentially binds η^2-olefins, η^3-allyls, or η^4-dienes approximately in the plane containing the *cis*-M$(CO)_2$ unit, as here for Re(2) [*viz.* torsion angles (°): C(5)–Re(2)–C(1) ··· C(9), 171.8; C(6)–Re(2)–C(9) ··· C(11), −174.2; C(8)–Re(2)–C(9) ··· C(11), −93.2; C(7)–Re(2)–C(9) ··· C(11), 90.4]. It is noticeable that for Re(1) the Re(2)–C(9) vector lies close to the *cis*-Re$(CO)_2$ plane [hence torsion angles (°): C(1)–Re(1)–C(9)–Re(2), 176.3; C(2)–Re(1)–C(9)–Re(2), −1.8; C(3)–Re(1)–C(9)–Re(2), −93.1; C(4)–Re(1)–C(9)–Re(2), 90.4]. Retaining these aspects of conformation about Re(1) and Re(2), as well as the observed bond lengths, is not possible in the *anti* (*Z*) isomer of (**1**) as computer modelled by, *e.g.*, rotation of the Re(1)$(CO)_4$CH unit about the C(9)–C(10) bond, since this *syn* to *anti* transformation leads to severe steric problems involving short C(12) ··· Re(1) and C(7) ··· Re(1)



Scheme 3. L = but-1-ene. (*i*) +3,3-dimethylcyclopropene; (*ii*) −L

contacts. However, it is clear that this is a very simplistic model for the *anti* (*Z*) isomer. As discussed above $[W_2(\mu\text{-allylidene})(CO)_9]$ [13,14] species, which contain $M(CO)_4$ units are known in both conformations.

It has been previously shown that ethylene reacts with $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ to form $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_8]$.[5,6] This was explained[6] by assuming that reductive elimination of $CH_2{=}CHEt$ occurs giving the unsaturated species $[Re_2(\eta^2\text{-}CH_2{=}CHEt)(CO)_8]$, which is captured by an ethylene molecule, oxidative insertion into a co-ordinated ethylene C–H bond accompanied by loss of $CH_2{=}CHEt$ affording $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_8]$. It is, therefore, reasonable to suggest that in the reaction of 3,3-dimethylcyclopropene with $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ a similar sequence of reactions occurs leading to the formation of $[Re_2(\eta^2\text{-}\overline{CH{=}CHC}Me_2)(\eta^2\text{-}CH_2{=}CHEt)(CO)_8]$ [intermediate (**D**) in Scheme 3]. It is interesting, however, that a similar oxidative insertion into one of the olefinic CH bonds of the co-ordinated cyclopropene does not now occur. This could be explained if in the reaction of $[Re_2(\eta^2\text{-}CH_2{=}CHEt)(CO)_8]$ with C_2H_4 to form $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_8]$ initial co-ordination of the ethylene is not actually required, but instead involves direct attack by $[Re_2(\eta^2\text{-}CH_2{=}CHEt)(CO)_8]$ on the CH bond of unco-ordinated ethylene in the same way as has recently[17] been demonstrated for the formation of $[IrH(\sigma\text{-}CH{=}CH_2)(PMe_3)(\eta\text{-}C_5Me_5)]$ from C_2H_4 and a $[Ir(PMe_3)(\eta\text{-}C_5Me_5)]$ fragment. Thus, in the reaction between 3,3-dimethylcyclopropene and $[Re_2(\eta^2\text{-}CH{=}CHEt)(CO)_8]$ the strained olefin, which would be expected[18] to have enhanced donor and π-acceptor properties, would react so rapidly with the unsaturated rhenium centre that attack on an olefinic CH does not compete. Once co-ordinated the 3,3-dimethylcyclopropene undergoes 2,3 carbon–carbon bond cleavage[3] to form the vinylcarbene complex (**E**), illustrated in Scheme 3, which initially adopts a cisoid geometry. However, if such a species was to begin to collapse by co-ordination of the vinylcarbene onto the second rhenium centre then significant non-bonding interactions would develop between the *gem*-methyl groups and terminal carbonyl ligands. This can be avoided by rotation of the vinycarbene moiety about the carbon–carbon single bond so adopting a transoid geometry. Then interaction with the adjacent metal centre leads directly to (**1**).

In previous studies[19,20] of the reactions of binuclear μ-allylidene complexes with donor ligands such as carbon monoxide and phosphines simple displacement of the vinyl group occurs leading to the formation of a μ-σ:σ-allylidene. In contrast, reaction of (**1**) with carbon monoxide (100 atm, 25 °C, 16 h) results in cleavage of the metal–metal bond and formation of $[Re_2(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCMe_2)(CO)_9]$ (**2**). Thus, the proton-coupled ^{13}C n.m.r. spectrum of (**2**) showed methine (CH) resonances at δ 111.7 [$^1J(CH)$ 147] and 21.7 p.p.m. [$^1J(CH)$ 138, $^2J(CH)$ 7.4 Hz] there being no low-field μ-alkylidene carbon resonance in the region 140—150 p.p.m. characteristic of a $\mu\text{-}\sigma{:}\sigma\text{-}CH(CH{=}CMe_2)$ group. A similar upfield shift of the C*H*CHCMe₂ proton from δ 7.65 in (**1**) to 2.52 p.p.m. in (**2**) was evident in the ^1H spectrum. In order to elucidate the precise structural changes involved in the transformation (**1**) to (**2**), a single-crystal *X*-ray diffraction study was undertaken. The structure is illustrated in Figure 2, and selected bond lengths and angles are listed in Table 2.

The μ-allylidene fragment has been transformed into a $Re(CO)_5$ substituted η^3-allyl moiety, which is η^3-bonded to a $Re(CO)_4$ unit. The Re ··· Re separation in (**2**) is now 4.190(1) Å, and the Re(μ-C)Re angle has increased from 86.3(4) in (**1**) to 128.5(4)° in (**2**). The bridging carbon C(9) is asymmetrically bound to the two rhenium atoms [Re(1)–C(9), 2.239(13); Re(2)–C(9), 2.413(13) Å]. These distances compare with typical Re–C σ-bond lengths of 2.25 Å in $[ReMe_2(\eta^4\text{-}C_5H_5Me)(\eta\text{-}C_5H_5)]$,[21] and 2.32 Å in $[ReMe(Br)(CO)_2(\eta\text{-}C_5H_5)]$.[22] The bridging carbon C(9) is no longer constrained to a distorted geometry by the presence of a rhenium–rhenium interaction, although the Re(1)–C(9)–Re(2) angle [128.5(4)°] is greater than that for idealised sp^3 hybridisation. This may be due to non-bonding interactions, although the Re(1)–C(9)–C(10) angle changes little [123.1(7) in (**1**) *versus* 127.6(8)° in (**2**)]. It is interesting that the structurally related diruthenium μ-methylene species $[Ru_2(\mu\text{-}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$,[23] which also does not possess a metal–metal bond, has a similar geometry at the bridging carbon [Ru(μ-CH₂)Ru, 123°], and an identical value of 138 Hz for $^1J(CH)$.

Thus, the formation of (**2**) can be seen as the result of capture by carbon monoxide of a co-ordinatively unsaturated species centred on Re(1), which is formed by dissociative loss of the donor bond from Re(2), followed by rotation of the $Re(CO)_5$

Table 2. Bond lengths (Å) and interbond angles (°) for (**2**)

Re(2)–C(5)	1.939(17)	Re(2)–C(7)	1.981(11)
Re(2)–C(6)	1.953(12)	Re(2)–C(8)	2.017(11)
Re(2)–C(9)	2.413(13)	Re(2)–C(10)	2.263(11)
Re(2)–C(11)	2.346(10)	Re(1)–C(4)	2.020(11)
Re(1)–C(1)	1.987(16)	Re(1)–C(2)	2.022(12)
Re(1)–C(3)	2.007(12)	Re(1)–C(0)	1.996(12)
Re(1)–C(9)	2.239(13)	C(5)–O(5)	1.133(22)
C(7)–O(7)	1.136(15)	C(6)–O(6)	1.122(16)
C(8)–O(8)	1.129(13)	C(4)–O(4)	1.115(14)
C(1)–O(1)	1.131(21)	C(2)–O(2)	1.100(16)
C(3)–O(3)	1.118(15)	C(0)–O(0)	1.137(15)
C(9)–C(10)	1.378(14)	C(9)–H(9)	0.961(107)
C(10)–C(11)	1.426(18)	C(11)–C(12)	1.514(14)
C(11)–C(13)	1.497(16)		
C(5)–Re(2)–C(7)	86.5(6)	C(5)–Re(2)–C(6)	98.7(6)
C(7)–Re(2)–C(6)	88.5(5)	C(5)–Re(2)–C(8)	89.1(5)
C(7)–Re(2)–C(8)	174.6(6)	C(6)–Re(2)–C(8)	89.0(5)
C(5)–Re(2)–C(9)	160.7(4)	C(7)–Re(2)–C(9)	99.5(6)
C(6)–Re(2)–C(9)	99.7(6)	C(8)–Re(2)–C(9)	85.7(5)
C(5)–Re(2)–C(10)	130.6(4)	C(7)–Re(2)–C(10)	82.8(5)
C(6)–Re(2)–C(10)	128.8(6)	C(8)–Re(2)–C(10)	102.5(4)
C(9)–Re(2)–C(10)	34.1(3)	C(5)–Re(2)–C(11)	98.0(5)
C(7)–Re(2)–C(11)	95.0(4)	C(6)–Re(2)–C(11)	163.0(6)
C(8)–Re(2)–C(11)	88.8(4)	C(9)–Re(2)–C(11)	63.3(4)
C(10)–Re(2)–C(11)	36.0(4)	C(4)–Re(1)–C(1)	90.7(5)
C(4)–Re(1)–C(2)	91.3(5)	C(1)–Re(1)–C(2)	92.9(6)
C(4)–Re(1)–C(3)	175.6(5)	C(1)–Re(1)–C(3)	93.2(6)
C(2)–Re(1)–C(3)	90.4(5)	C(4)–Re(1)–C(0)	90.5(5)
C(1)–Re(1)–C(0)	91.9(6)	C(2)–Re(1)–C(0)	174.9(6)
C(3)–Re(1)–C(0)	87.5(5)	C(4)–Re(1)–C(9)	90.2(5)
C(1)–Re(1)–C(9)	177.8(4)	C(2)–Re(1)–C(9)	85.1(5)
C(3)–Re(1)–C(9)	85.9(5)	C(0)–Re(1)–C(9)	90.0(5)
Re(2)–C(5)–O(5)	176.6(10)	Re(2)–C(7)–O(7)	176.3(17)
Re(2)–C(6)–O(6)	179.2(13)	Re(2)–C(8)–O(8)	176.2(10)
Re(1)–C(4)–O(4)	178.9(9)	Re(1)–C(1)–O(1)	177.3(9)
Re(1)–C(2)–O(2)	177.0(15)	Re(1)–C(3)–O(3)	177.7(15)
Re(1)–C(0)–O(0)	177.1(13)	Re(2)–C(9)–Re(1)	128.5(4)
Re(2)–C(9)–C(10)	67.0(7)	Re(1)–C(9)–C(10)	127.6(8)
Re(2)–C(9)–H(9)	78.1(78)	Re(1)–C(9)–H(9)	130.4(63)
C(10)–C(9)–H(9)	100.3(59)	Re(2)–C(10)–C(9)	79.0(7)
Re(2)–C(10)–C(11)	75.2(7)	C(9)–C(10)–C(11)	126.1(9)
Re(2)–C(11)–C(10)	68.8(6)	Re(2)–C(11)–C(12)	113.5(7)
C(10)–C(11)–C(12)	121.1(10)	Re(2)–C(11)–C(13)	117.9(8)
C(10)–C(11)–C(13)	117.1(10)	C(12)–C(11)–C(13)	112.0(10)

fragment around the Re(1)–C(9) bond, so retaining an octahedral co-ordination sphere with a corresponding increase in the Re ··· Re separation (Scheme 4). Clearly, it was important to examine whether this reaction could be reversed, because if successful, this would be of importance in relation to the synthesis of other μ-allylidene complexes. However, (**2**) proved to be thermally stable, and on u.v. irradiation underwent an unexpected reaction.

Photolysis (u.v.) of a hexane solution of (**2**) resulted in a rapid change in the i.r. spectrum of the reaction mixture. After 2 h the spectrum showed terminal carbonyl bands characteristic of a $[Re_2(\mu\text{-}H)(\mu\text{-alkenyl})(CO)_8]$ complex, and removal of the solvent and recrystallisation from pentane gave a low melting (< 0 °C) pale yellow μ-hydrido, μ-butadienyl complex* $[Re_2(\mu\text{-}H)(\mu\text{-}\sigma\text{:}\eta^2\text{-}CH{=}CHCMe{=}CH_2)(CO)_8]$ (**3**), which exists in solution as two rotameric species. This is implied from the ^1H n.m.r. spectrum which showed two resonances at δ −14.28 and −14.02 p.p.m. (2:1 ratio) characteristic of species containing the arrangement Re(μ-H)Re, the isomerisation arising due to restricted rotation about the C(2)–C(3) bond of the $\mu\text{-}CH{=}CHCMe{=}CH_2$ ligand. This suggests that photolysis leads not to loss of CO from the $Re(CO)_5$ unit, but from the $Re(CO)_4$ group creating a vacant co-ordination site for hydrogen abstraction from a methyl group. Irradiation of (**1**) does not lead to the formation of (**3**).

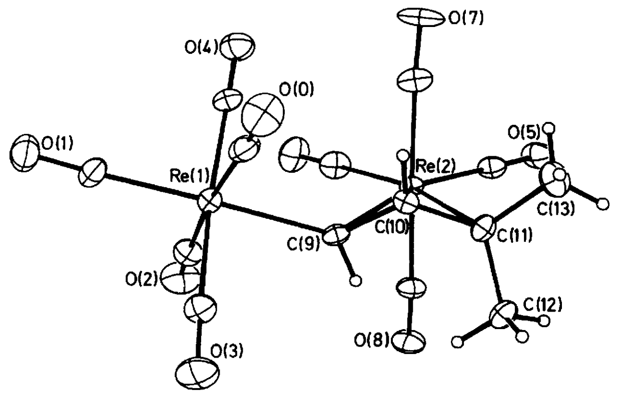
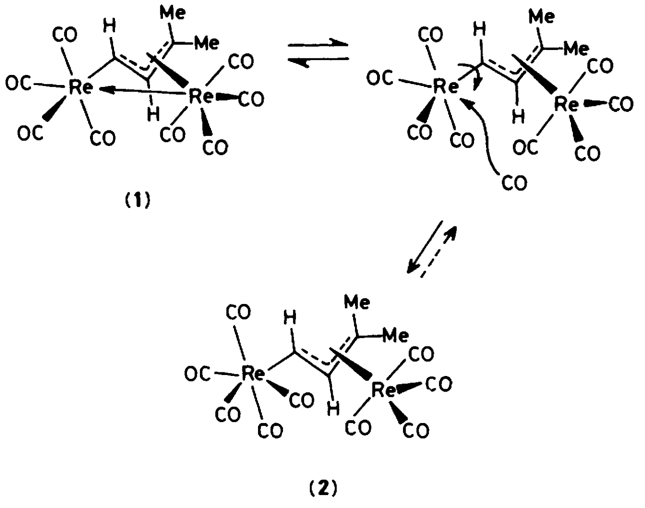


Figure 2. Molecular structure of $[Re_2(\mu\text{-}\sigma\text{:}\eta^3\text{-}CHCHCMe_2)(CO)_9]$ (**2**) showing atom labelling. Ellipsoids are drawn to enclose 20% probability density



Scheme 4.

Experimental

All experiments were performed in an atmosphere of dry, oxygen-free nitrogen using standard Schlenk-tube techniques. Solvents were freshly distilled in a nitrogen atmosphere. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, ^1H and ^{13}C n.m.r. spectra on JEOL FX 90Q and FX 200 spectrometers; chemical shifts were referenced to $SiMe_4$ (internal), and coupling constants are in Hz. 3,3-Dimethylcyclopropene[25] and $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$[5,6] were prepared as in the literature.

Preparation of $[Re_2(\mu\text{-}\sigma\text{:}\eta^3\text{-}CHCHCMe_2)(CO)_8]$ (**1**).—An excess of 3,3-dimethylcyclopropene (0.2 cm^3) was added to a solution of $[Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHEt)(CO)_8]$ (0.45, 0.61 mmol) in hexane (10 cm^3) contained in a Young's tube. On stirring at room temperature for 2 d a yellow powder began to precipitate. The supernatant liquid was removed and cooled (−20 °C) affording a further quantity of the yellow material. The com-

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* See ref. 24 for related species.

bined precipitates were recrystallised (−78 °C) from hexane–diethyl ether (1:1) to give yellow *crystals* of (**1**) (0.32 g, 78%) (Found: C, 23.8; H, 1.3%; *M*, 664. $C_{13}H_8O_8Re_2$ requires C, 23.5; H, 1.2%; *M*, 664): $\nu_{max.}$(CO) at 2 097w, 2 059m, 2 000vs, 1 985s, 1 973m, 1 961m, and 1 941s cm^{-1} (hexane). N.m.r.: ^{1}H (CDCl$_3$), δ 7.65 [d, 1 H, C$_\alpha$H, ^3J(HH) 12.45], 4.53 [d, 1 H, C$_\beta$H, ^3J(HH) 12.45], 2.09 (s, 3 H, Me), 1.94 (s, 3 H, Me); ^{13}C-{^{1}H} (CDCl$_3$), δ 195.1, 193.4, 191.9, 190.0, 188.9, 187.3, 186.9, 185.8 (8 × CO), 139.0 [C$_\alpha$H, ^{1}H-coupled spectrum, ^1J(CH) 138, ^2J(CH) 9.2], 105.3 [C$_\beta$H, ^{1}H-coupled spectrum, ^1J(CH) 156.3], 90.2 (*C*Me$_2$), 29.2 (Me), and 23.3 p.p.m. (Me).

Preparation of [$Re_2(\mu\text{-}\sigma\text{:}\eta^3\text{-}CHCHCMe_2)(CO)_9$] (**2**).—A solution of (**1**) (0.2 g, 0.3 mmol) in hexane (100 cm^3) contained in a glass autoclave liner was subjected to a pressure of 100 atm of carbon monoxide. After 16 h at room temperature the CO and hexane were removed, and the residue recrystallised (−78 °C) from hexane–diethyl ether (4:1) to give light yellow *crystals* of (**2**) (0.18 g, 90%) (Found: C, 24.6; H, 1.1%; *M*, 692. $C_{14}H_8O_9Re_2$ requires C, 24.3; H, 1.2%; *M*, 692); $\nu_{max.}$(CO) at 2 069w, 2 021s, 2 017 (sh), 1 985m, 1 977m, 1 963m, and 1 941m cm^{-1} (hexane). N.m.r.: ^{1}H (CDCl$_3$), δ 4.83 [d, 1 H, C$_\beta$H, ^3J(HH) 14.65], 2.52 [d, 1 H, C$_\alpha$H, ^3J(HH) 14.65], 2.08 (s, 3 H, Me), 1.74 (s, 3 H, Me); ^{13}C-{^{1}H} (CDCl$_3$), δ 195.1, 193.6, 192.8, 191.7 (4 × CO), 183.1 (4 × CO), 179.7 (CO), 111.7 [C$_\alpha$H, ^{1}H-coupled spectrum, ^1J(CH) 147], 67.8 (*C*Me$_2$), 32.3 (Me), 25.2 (Me), and 21.7 p.p.m. [C$_\beta$H, ^{1}H-coupled spectrum, ^1J(CH) 138, ^2J(CH) 7.4].

Photolysis of [$Re_2(\mu\text{-}\sigma\text{:}\eta^3\text{-}CHCHCMe_2)(CO)_9$] (**2**).—A solution of (**2**) (0.1 g, 0.14 mmol) in hexane (50 cm^3) contained in a Pyrex tube was irradiated (u.v., 250-W medium pressure lamp). After 2 h the solvent was removed and the residue recrystallised (−78 °C) from pentane affording pale yellow low melting (<0 °C) *crystals* of [$Re_2(\mu\text{-}H)(\mu\text{-}\sigma\text{:}\eta^2\text{-}CH{=}CHCMe{=}CH_2)(CO)_8$] (**3**) (90%); $\nu_{max.}$(CO) at 2 105w, 2 079w, 2 009s, 1 989m, 1 975s, and 1 961m cm^{-1} (hexane). N.m.r.: ^{1}H (CDCl$_3$), major isomer, δ 7.50 (m, 2 H, CH$_2$), 6.68 [d, 1 H, CH, ^3J(HH) 16.4], 6.00 [d, 1 H, CH, ^3J(HH) 16.4], 1.67 (s, 3 H, Me), −14.28 p.p.m. (s, 1 H, μ-H); minor isomer, 7.50 (m, 2 H, CH$_2$), 6.70 [d, 1 H, CH, ^3J(HH) 12.2], 5.28 [d, 1 H, CH, ^3J(HH) 12.2], 1.07 (s, 3 H, Me), −14.02 p.p.m. (s, 1 H, μ-H). From integration of the hydride resonances major:minor isomer ratio is 2:1.

X-*Ray Structure Determinations of* (**1**) *and* (**2**).—*Crystal data for* (**1**). $C_{13}H_8O_8Re_2$, $M = 664.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 8.576(3)$, $b = 9.682(7)$, $c = 19.623(10)$ Å, $\beta = 99.54(3)^\circ$, $U = 1\,607(2)$ Å^3, $Z = 4$, $D_c = 2.75$ g cm^{-3}, $F(000) = 1\,200$, $\mu(\text{Mo-}K_\alpha) = 153.0$ cm^{-1}, $T = 293$ K. Crystal dimensions (mm) *ca.* 0.5 × 0.4 × 0.2.

Crystal data for (**2**). $C_{14}H_8O_9Re_2$, $M = 692.6$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.754(5)$, $b = 9.034(3)$, $c = 11.168(5)$ Å, $\alpha = 90.30(3)$, $\beta = 112.95(4)$, $\gamma = 93.40(4)^\circ$, $U = 903.5(7)$ Å^3, $Z = 2$, $D_c = 2.55$ g cm^{-3}, $F(000) = 628$, $\mu(\text{Mo-}K_\alpha) = 136.3$ cm^{-1}, $T = 293$ K. Crystal faces [distance from origin, mm]: (110) [0.28], ($\bar{1}\bar{1}0$) [0.28], (101) [0.04], ($\bar{1}0\bar{1}$) [0.04], ($1\bar{1}1$) [0.33], and ($01\bar{1}$) [0.33].

For both (**1**) and (**2**) *X*-ray diffraction intensity data were collected at room temperature using a Nicolet *R*3*m* diffractometer, with single crystals mounted in thin-walled glass capillaries under N$_2$. Unique portions of reciprocal space in the range $4 < 2\theta < 50^\circ$ were scanned, integrated intensities being measured by Wyckoff ω scans of width 1.0° for (**1**) and by θ—2θ scans of width 2.4° + $\Delta\alpha_1$, α_2 for (**2**). Absorption corrections were applied. For (**1**) transmission coefficients varied between 0.318 and 0.735, and were derived by a six-parameter fit to 400 azimuthal scan data. For (**2**) transmission coefficients varied between 0.042 and 0.327, and were calculated by Gaussian quadrature from the indexed crystal faces. For (**1**), 2 792 reflection intensities were collected, of which 2 466 were unique, non-absences, of which 2 314 with $I > 2\sigma(I)$ were used in structure solution and refinement. For (**2**) corresponding data were 3 278, 2 879, and 2 534. Structure solution was by Patterson and difference-Fourier methods. Refinement was by blocked-cascade full-matrix least squares with weights $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o based on counting statistics and g[0.000 75 for (**1**), 0.0010 for (**2**)] was chosen to minimise the variation of $\Sigma w(|F_o| - |F_c|)^2$ with $|F_o|$.

Table 3. Atomic co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*
Re(1)	1 839(1)	531(1)	1 498(1)
Re(2)	2 908(1)	−2 429(1)	1 287(1)
O(1)	918(13)	3 569(11)	1 320(7)
O(2)	1 876(14)	643(14)	3 073(5)
O(3)	−1 707(11)	−310(12)	1 205(6)
O(4)	5 334(11)	1 560(11)	1 701(5)
O(5)	4 392(13)	−5 325(10)	1 352(6)
O(6)	1 463(12)	−2 738(11)	2 603(5)
O(7)	−356(11)	−3 573(12)	534(5)
O(8)	6 046(10)	−1 454(11)	2 189(5)
C(1)	1 274(16)	2 413(15)	1 387(7)
C(2)	1 851(16)	636(15)	2 490(7)
C(3)	−438(16)	−36(14)	1 319(7)
C(4)	4 065(12)	1 169(11)	1 619(5)
C(5)	3 804(16)	−4 282(14)	1 350(6)
C(6)	1 945(14)	−2 595(13)	2 124(6)
C(7)	870(16)	−3 138(14)	784(6)
C(8)	4 885(13)	−1 768(13)	1 859(6)
C(9)	2 139(12)	−500(12)	581(5)
C(10)	3 642(13)	−1 027(13)	461(5)
C(11)	3 888(15)	−2 285(13)	161(6)
C(12)	2 659(17)	−2 946(15)	−387(6)
C(13)	5 578(15)	−2 767(15)	172(7)

Table 4. Atomic co-ordinates (× 10^4) for (**2**)

Atom	*x*	*y*	*z*
Re(2)	3 680(1)	2 302(1)	1 341(1)
Re(1)	1 842(1)	2 508(1)	4 158(1)
C(5)	4 437(14)	1 932(12)	7(13)
C(7)	2 349(15)	470(12)	659(15)
C(6)	5 024(15)	1 139(13)	2 718(14)
C(8)	5 183(13)	4 071(12)	1 999(12)
C(4)	2 053(13)	430(11)	3 608(12)
C(1)	1 433(15)	1 733(12)	5 658(13)
C(2)	4 066(15)	2 816(13)	5 216(13)
C(3)	1 592(15)	4 616(12)	4 563(13)
C(0)	−327(15)	2 336(11)	3 004(13)
C(9)	2 383(11)	3 427(10)	2 521(10)
C(10)	1 535(11)	3 247(10)	1 205(10)
C(11)	1 872(12)	3 922(11)	190(11)
C(12)	2 479(14)	5 530(11)	317(12)
C(13)	852(16)	3 480(16)	−1 180(13)
O(5)	4 809(14)	1 717(10)	−818(11)
O(7)	1 590(13)	−566(10)	205(13)
O(6)	5 807(14)	468(12)	3 515(11)
O(8)	6 079(11)	5 010(10)	2 410(10)
O(4)	2 145(13)	−720(9)	3 294(11)
O(1)	1 169(14)	1 245(11)	6 482(10)
O(2)	5 284(12)	2 996(12)	5 743(11)
O(3)	1 468(13)	5 806(10)	4 757(12)
O(0)	−1 575(10)	2 212(12)	2 389(11)

In both (**1**) and (**2**) all non-hydrogen atoms were assigned anisotropic atomic displacement parameters, and methyl-group hydrogens were constrained to tetrahedral geometry (H–C–H

109.5°, C–H 0.96 Å) with fixed, isotropic displacement parameters. For (**1**) H(9) and H(10) were fixed at positions observed in difference electron-density syntheses, while in (**2**) these atoms were refined without positional constraints. Final difference electron-density maps showed features <1 Å from rhenium atoms of +2.6 and −2.0 e $Å^{-3}$ for (**1**) and of +3.5 and −1.1 e $Å^{-3}$ for (**2**), the remainder of the maps being essentially featureless. For (**1**) an isotropic extinction parameter x was refined to a value 0.0091(6) $[F_c(x) = F_c\ (1 + 0.002\ x\ F_c^2/\sin 2\theta)^{-\frac{1}{4}}]$. Final residual indices* for (**1**) were $R = 0.042$, $R' = 0.042$, $S = 1.46$; for (**2**) they were $R = 0.045$, $R' = 0.044$, $S = 1.46$. Tables 3 and 4 list the final atomic co-ordinates for the non-hydrogen atoms in (**1**) and (**2**) respectively. Complex neutral-atom scattering factors were taken from ref. 26. All calculations were carried out with the programs of the SHELXTL package[27] on a Nicolet *R*3*m*/E system.

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$; N_o = number of observations, N_v = number of variables.

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