Photoreactions of decacarbonyl-dirhenium with branched derivatives of Allene ☆

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Abstract

Decacarbonyl-dirhenium (1) reacts upon UV irradiation with 3-methyl-1,2-butadiene (2) and 2-methyl-2,3-pentadiene (3) by CO substitution to the corresponding octacarbonyl(μ-$\eta^{2:2}$-cumulene)dirhenium complexes 5 and 11. In addition, by isomerization of the cumulenes to the conjugated dienes, octacarbonyl(μ-$\eta^{2:2}$-1,3-diene)dirhenium (7, 13) and (followed by C—H bond splitting) octacarbonyl-μ-hydrido-(μ-$\eta^{1:2}$-1,3-dien-1-yl)dirhenium (6, 12) are formed. With 3, a fourth isomer, i.e. octacarbonyl(μ-$\eta^{1:2}$-4-methyl-3-penten-2-ylidene)dirhenium (14), was obtained. By hydrogen addition to the cumulenes, tetracarbonyl-η^3-enyl-rhenium (8, 9, 15) result. Minor byproducts, octacarbonyl[1″-2″-η-1,3-bis(isopropenyl)-1-cyclopenten-2-ol-κ-O]dirhenium (10) and heptacarbonyl(μ-$\eta^{1:2:2:1}$-2,4,5,7-tetramethyl-2,6-octadien-3,6-diyl)dirhenium (16), from the reaction of 1 with 2 and of 1 with 3, respectively, were isolated with ligands formed from two cumulene molecules. In contrast, 1 yields only octacarbonyl(μ-$\eta^{1:2}$-2,4-dimethyl-1,3-pentadien-1-yl)-μ-hydrido-dirhenium (17) and preferentially octacarbonyl(μ-$\eta^{2:2}$-2,4-dimethyl-1,3-pentadiene)dirhenium (18) with 2,4-dimethyl-2,3-pentadiene (4). Tricarbonyl(η^5-2,4-dimethyl-2,4-pentadien-1-yl)rhenium (19) is also afforded by this reaction. At elevated temperatures, the dienyl hydrido complexes 6, 12, 17 rearrange to the diene complexes 7, 13, 18. The 4-methyl-3-penten-2-ylidene complex 14 also forms upon heating 13. The structures of the reaction products have been derived from the IR and ^{1}H NMR spectra. The molecular structure of 10 has been determined by X-ray diffraction analysis.

Keywords: Decacarbonyldirhenium; Photoreactions; Branched allene derivatives; Isomerizations; Complexes

1. Introduction

Cumulene complexes of the Group 7 elements are accessible by photochemical reactions of decacarbonyl-dimanganese [1–3] and -dirhenium [4,5] with the corresponding cumulenes. In the case of decacarbonyl-dirhenium allene and unbranched allene derivatives such as 1,2-butadiene or 2,3-pentadiene, μ-$\eta^{3:1}$-2-en-1,2-diyl-bridged enneacarbonyl-dirhenium and μ-$\eta^{2:2}$-cumulene-bridged octacarbonyl-dirhenium complexes are formed preferentially. In solution, the μ-$\eta^{3:1}$-2-en-1,2-diyl complexes lose carbon monoxide and are transformed into octacarbonyl-μ-$\eta^{2:2}$-cumulene-dirhenium [5]. As part of our studies on the photoreactivity of dinuclear complexes towards unsaturated hydrocarbons,

we have extended our investigations to the decacarbonyl-dirhenium and branched cumulene system, which show a quite different reactivity in comparison to allene and unbranched cumulenes.
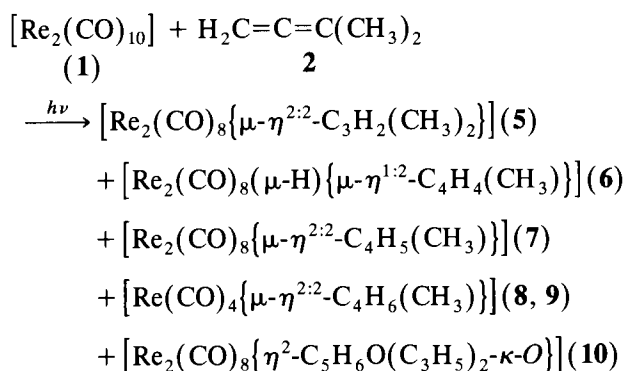
2. Results

The photoreactions of decacarbonyl-dirhenium (1) with the branched cumulenes 3-methyl-1,2-butadiene (2), 2-methyl-2,3-pentadiene (3) and 2,4-dimethyl-2,3-pentadiene (4) were conducted in n-hexane solutions at 243 K. The progress of the reactions was monitored IR spectroscopically using the ν(CO) bands of 1 and of the products. In all cases, mixtures of reaction products were formed which were separated by HPL chromatography and purified by crystallization.

The photoreaction of 1 with 2 leads to six different compounds. The main product is a mixture of tetracarbonyl-η^3-enyl-rhenium isomers with 3-methyl-2-buten-
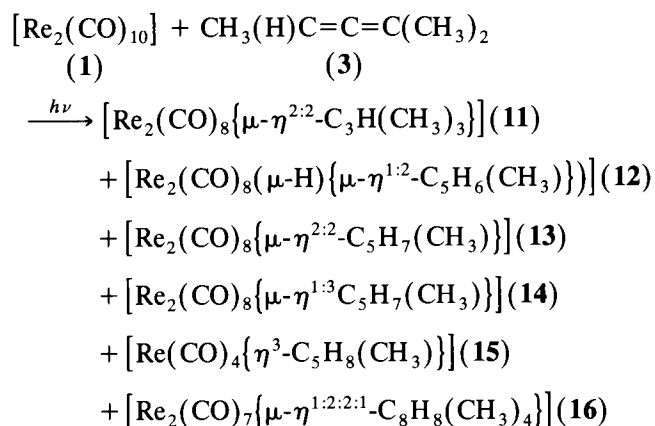

☆ Dedicated to Professor Dr. Henri Brunner on the occasion of his 60th birthday.

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1-yl (**8**) and *Z*-2-methyl-2-buten-1-yl ligands (**9**). Separation of **8** and **9** was not possible by chromatographic means. Three isomeric octacarbonyl-dirhenium complexes were formed in comparable amounts. The μ-$\eta^{2:2}$-3-methyl-1,2-butadiene complex **5** contains the cumulene unchanged, whereas in octacarbonyl(μ-$\eta^{2:2}$-2-methyl-1,3-butadiene)dirhenium (**7**) the cumulene is isomerized to a conjugated diene and in octacarbonyl-μ-hydrido(μ-$\eta^{1:2}$-3-methyl-1,3-butadien-1-yl)dirhenium (**6**) a C—H bond splitting of the conjugated diene has occurred. The red crystalline byproduct **10** was isolated in only small amounts; this which contains an unexpected 1,3-bis(isopropenyl)-1-cyclopenten-2-ol ligand, coordinated via one isopropenyl group and the hydroxo oxygen to one rhenium.
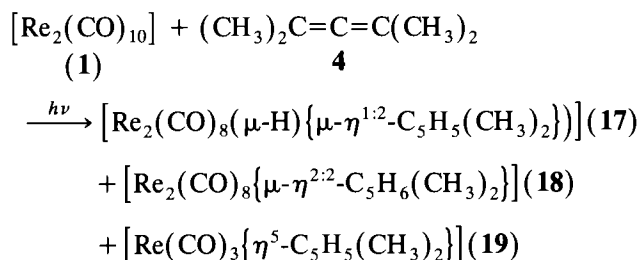
$$[Re_2(CO)_{10}] + H_2C=C=C(CH_3)_2$$
$$(1) \qquad\qquad 2$$

$$\xrightarrow{h\nu} \left[Re_2(CO)_8\{\mu\text{-}\eta^{2:2}\text{-}C_3H_2(CH_3)_2\}\right](5)$$

$$+ \left[Re_2(CO)_8(\mu\text{-H})\{\mu\text{-}\eta^{1:2}\text{-}C_4H_4(CH_3)\}\right](6)$$

$$+ \left[Re_2(CO)_8\{\mu\text{-}\eta^{2:2}\text{-}C_4H_5(CH_3)\}\right](7)$$

$$+ \left[Re(CO)_4\{\mu\text{-}\eta^{2:2}\text{-}C_4H_6(CH_3)\}\right](8, 9)$$

$$+ \left[Re_2(CO)_8\{\eta^2\text{-}C_5H_6O(C_3H_5)_2\text{-}\kappa\text{-}O\}\right](10)$$

Similar products were formed with **3**. Again the mononuclear tetracarbonyl(η^3-*E*-2-methyl-3-penten-2-yl)rhenium (**15**) was the main product and three isomeric octacarbonyl complexes (**11–13**) of the same type as **5–7** were also obtained. In addition, a further octacarbonyl complex with a 4-methyl-3-penten-2-ylidene bridging ligand (**14**) was isolated. Red crystals of heptacarbonyl(μ-$\eta^{1:2:2:1}$-2,4,5,7-tetramethyl-2,6-octadiene-3,6-diyl)dirhenium (**16**) were formed as a minor byproduct.

$$[Re_2(CO)_{10}] + CH_3(H)C=C=C(CH_3)_2$$
$$(1) \qquad\qquad\qquad (3)$$

$$\xrightarrow{h\nu} \left[Re_2(CO)_8\{\mu\text{-}\eta^{2:2}\text{-}C_3H(CH_3)_3\}\right](11)$$

$$+ \left[Re_2(CO)_8(\mu\text{-H})\{\mu\text{-}\eta^{1:2}\text{-}C_5H_6(CH_3)\}\right](12)$$

$$+ \left[Re_2(CO)_8\{\mu\text{-}\eta^{2:2}\text{-}C_5H_7(CH_3)\}\right](13)$$

$$+ \left[Re_2(CO)_8\{\mu\text{-}\eta^{1:3}C_5H_7(CH_3)\}\right](14)$$

$$+ \left[Re(CO)_4\{\eta^3\text{-}C_5H_8(CH_3)\}\right](15)$$

$$+ \left[Re_2(CO)_7\{\mu\text{-}\eta^{1:2:2:1}\text{-}C_8H_8(CH_3)_4\}\right](16)$$

The reaction of **1** and **4** yields octacarbonyl(μ-$\eta^{2:2}$-2,4-dimethyl-1,3-pentadiene)dirhenium (**18**) as the main product. Reasonable amounts of octacarbonyl(μ-$\eta^{1:2}$-2,4-dimethyl-1,3-pentadien-1-yl)-μ-hydrido-dirhenium

(**17**) and mononuclear tricarbonyl(η^5-2,4-dimethyl-2,4-pentadien-1-yl)rhenium (**19**) were formed in addition.

$$[Re_2(CO)_{10}] + (CH_3)_2C=C=C(CH_3)_2$$
$$(1) \qquad\qquad\qquad 4$$

$$\xrightarrow{h\nu} \left[Re_2(CO)_8(\mu\text{-H})\{\mu\text{-}\eta^{1:2}\text{-}C_5H_5(CH_3)_2\}\right](17)$$

$$+ \left[Re_2(CO)_8\{\mu\text{-}\eta^{2:2}\text{-}C_5H_6(CH_3)_2\}\right](18)$$

$$+ \left[Re(CO)_3\{\eta^5\text{-}C_5H_5(CH_3)_2\}\right](19)$$

Upon heating the octacarbonyl(μ-$\eta^{1:2}$-dien-1-yl)-μ-hydrido-dirhenium complexes **6**, **12** and **17**, they rearranged easily into the corresponding μ-$\eta^{2:2}$-diene complexes **7**, **13** and **18**. The 4-methyl-3-penten-2-ylidene bridged complex **14** also formed on heating **13**.

3. ¹H NMR spectra

The ¹H NMR data for complexes **5–19** are listed under Experimental details. The chemical shifts, assignments, relative intensities, shape and coupling constants are given for all signals.

The ¹H NMR spectrum of the octacarbonyl(μ-$\eta^{2:2}$-cumulene)dirhenium complex **5** showed four signals of relative intensity 1 : 1 : 3 : 3. They are in agreement with a μ-$\eta^{2:2}$-coordinated 3-methyl-1,2-butadiene ligand. Two doublets for the methylene protons with a geminal coupling constant of 4.4 Hz were observed at lower fields. The signal corresponding to 1*Z*-H showed further splittings due to small couplings with the two methyl groups. In contrast, the methyl signals were not resolved into the expected doublets since small couplings to 1*E*-H and between the methyl groups caused the appearance of somewhat broadened singlets.

Complex **11** exhibited four signals of relative intensity 1 : 3 : 3 : 3 for μ-$\eta^{2:2}$-coordinated 2-methyl-2,3-pentadiene. This indicates that only one of two possible isomers was present, probably for steric reasons. The methine proton was observed as a quartet at 4.07 ppm, each line being split further by long-range couplings with the 5- and 2*E*-methyl groups. These couplings are more likely for 4-H in the *Z* rather than the *E* position. Hence, the 2-methyl group most likely occupies the *E* position. For this stereochemistry, less interaction between the methyl group and adjacent carbonyl ligands is to be expected.

For the octacarbonyl(μ-$\eta^{1:2}$-1,3-diene-1-yl)-μ-hydrido-dirhenium complex **6**, two AB spin systems one with large (16.5 Hz) *trans* and the other with small (3.2 Hz) *gem* couplings are found in the olefinic region. A singlet of threefold intensity at 1.78 ppm and one of single intensity strongly shifted upfield are assigned to a 3-methyl-1,3-butadien-1*E*-yl and a hydrido ligand,

which are formed from **2** after isomerization into 2-methyl-1,3-butadiene and by oxidative addition of the 4*E*-C—H unit to rhenium.

Similarly for **12** an AMX system is found in the olefinic region, two singlets of threefold intensity at 1.92 and 1.89 ppm and one hydrido signal at −14.18 ppm indicating isomerization of **3** into 4-methyl-1,3-pentadiene and oxidative addition of the 1*E*-C—H bond to rhenium by which the 4-methyl-1,3-pentadien-1*E*-yl ligand is formed.

The spectrum of **17** contains six signals with the relative intensities 1:1:3:3:3:1. Two singlets in the olefinic region, one of which is slightly broadened without resolvable fine structure, three methyl signals, two with small doublet splittings and a singlet at −13.56 ppm, are in accord with a 2,4-dimethyl-1,3-pentadien-1*E*-yl and a hydrido ligand, formed from **4** after isomerization into 2,4-dimethyl-1,3-pentadiene as in **12**. The assignment of the signals is as according to **12**.

The octacarbonyl(μ-$\eta^{2:2}$-*s*-*trans*-diene)dirhenium complex **7** shows five signals with single intensities, belonging to AMX and AX spin systems with typical coupling constants for coordinated vinyl and sp^2-methylene groups. The geminal couplings are quite small with values of 1.0 and 1.5 Hz. In addition, a singlet of threefold intensity is observed. The signals demonstrate the existence of a 2-methyl-1,3-butadiene ligand in **7**. The IR data are practically identical with those of μ-$\eta^{2:2}$-*s*-*trans*-1,3-butadiene-octacarbonyl-dirhenium [6,7], and hence an analogous structure can be taken as granted.

This assumption is further supported by the spectrum of the corresponding complex **13**, one of the products of **1** and **3**. Two methyl singlets and a four-spin system show the presence of coordinated *s*-*trans*-4-methyl-1,3-pentadiene. The *s*-*trans* conformation of the ligand causes the large vicinal coupling of 11.0 Hz between 2-H and 3-H. The geminal coupling of the 1-methylene protons with 0.5 Hz is even smaller than in **7**.

The spectrum of **18** only contains singlets with the relative intensities 1:3:1:3:1:3. From the IR spectrum, **18** is of the same type as complexes **7** and **13**. The assignment of the signals is based on the similarities of the chemical shifts in comparison with **13**.

The octacarbonyl-dirhenium complex **14**, obtained from the reaction of **1** with **3**, shows four signals (1:3:3:3). One of the methyl signals is split by 0.6 Hz into a doublet, the other two being slightly broadened. The signal of single intensity is distinctly broadened without a resolvable pattern. From the small couplings of the single proton, it must be concluded that a 1,2-H shift occurs in **3** generating the 4-methyl-3-penten-2-ylidene ligand. The IR data also support this assumption, being very similar to those of octacarbonyl-μ-$\eta^{1:3}$-3-methyl-2-buten-1-ylidene-dirhenium which is formed from octacarbonyl-μ-$\eta^{1:2}$-1-butene-1-yl-μ-hydrido-di-

rhenium and 2,2-dimethyl-1-cyclopropene and has been well characterized by X-ray diffraction studies [8,9].

The dinuclear heptacarbonyl complex **16**, a minor byproduct of the reaction of **1** with **3**, shows four NMR signals (2:6:6:6). The colour and IR spectrum are similar to those of heptacarbonyl(μ-$\eta^{1:2:1:2}$-4,5-dimethyl-2,6-octadien-3,6-diyl)dirhenium, which has been obtained from **1** and 2,3-pentadiene and characterized by X-ray diffraction [5]. The presence of a 2,4,5,7-tetramethyl-2,6-octadien-3,6-diyl ligand is supported by the AA'X$_3$X'$_3$ spin system at 3.16 and 1.08 ppm ($J_{AA'}$ = 4.5 Hz, J_{AX} = $J_{A'X'}$ = 6.6 Hz, J'_{XX} < 0.1 Hz) and are assigned to 4-, 5-H and 4-,5-CH$_3$. The remaining methyl singlets arise from 1-, 8-H and 2*Z*-,7*Z*-CH$_3$.

A mixture of the mononuclear tetracarbonyl η^3-enyl complexes **8** and **9** was obtained from the reaction of **1** with **2**. The different populations (0.73/0.27) allow a full assignment of all the NMR signals to the complexes **8** and **9**. Five signals see associated with **8** (1:1:3:1:3), so the ligand contains one hydrogen more than **2**. The signals clearly demonstrate a vinyl group and two methyl groups with no vicinal hydrogen. They correspond well for a 3-methyl-2-buten-1-yl ligand formed from **2** by hydrogenation at 2-C.

Five signals (1:1:1:3:3) are also observed for the minor component. On the basis of coupling constants and chemical shifts they belong to a *Z*-2-methyl-2-buten-1-yl ligand.

The reaction of **1** with **3** also yields a tetracarbonyl η^3-enyl complex. The NMR spectrum of **15** shows five signals (1:1:3:3:3), three of which show mutual couplings. The methyl doublet at 1.62 ppm demonstrates the existence of an ethylidene group. The coupling between the methine protons is typically that for a *trans* position in an enyl ligand. Taking into account the remaining methyl singlets, an *E*-2-methyl-3-penten-2-yl ligand properly explains the spectrum. As in **8**, this ligand is formed by hydrogenation of the sp carbon atom of the allene derivative **3**.

In contrast to **2** and **3**, cumulene **4** forms no tetracarbonyl η^3-enyl complex. Instead the tricarbonyl **19** is obtained in reasonable yield. The spectrum contains four signals with the relative intensities 1:2:6:2. Two double doublets with a mutual coupling of 2.7 Hz are further coupled with a single proton and form an AA'MM'X spin system. No noticeable interaction was observed between this system and the two equivalent methyl groups. The spectrum clearly demonstrates a 2,4-dimethyl-2,4-pentadien-1-yl ligand, formed from **4** by hydrogen abstraction from 1-C and a 1,3-H shift from 5-C.

4. Crystal and molecular structure of 10

Complex **10** crystallizes with the orthorhombic space group $P2_12_12_1$ with $a = 1247.7(2)$ pm, $b = 1453.7(1)$

Table 1

Atomic coordinates and equivalent isotropic deviation parameters ($pm^2 \times 10^{-1}$) for the non-hydrogen atoms of 10

Atom	x	y	z	U_{eq}
Re(1)	0.2925(1)	0.2479(1)	0.6213(1)	30(1)
Re(2)	0.3409(1)	0.0406(1)	0.6301(1)	35(1)
O(1)	0.1301(14)	0.2149(12)	0.6720(14)	25(5)
O(11)	0.2722(16)	0.1918(13)	0.3737(17)	48(5)
O(12)	0.5264(20)	0.2837(17)	0.5868(21)	73(8)
O(13)	0.2541(21)	0.4360(16)	0.5326(21)	70(8)
O(21)	0.1692(17)	0.0445(15)	0.8178(17)	48(6)
O(22)	0.5203(22)	0.1011(19)	0.7932(22)	73(8)
O(23)	0.4970(20)	0.0765(16)	0.4297(19)	61(7)
O(24)	0.1403(18)	0.0116(15)	0.4758(19)	55(6)
O(25)	0.3909(21)	−0.1654(17)	0.6392(27)	81(8)
C(1)	−0.0101(23)	0.2483(22)	0.8048(22)	33(7)
C(2)	0.0842(22)	0.2592(20)	0.7462(22)	30(7)
C(3)	0.1445(22)	0.3435(16)	0.7964(20)	18(6)
C(4)	0.0960(26)	0.3524(21)	0.9156(25)	42(8)
C(5)	−0.0189(24)	0.3207(20)	0.8978(26)	42(8)
C(1')	−0.0859(24)	0.1740(18)	0.7826(22)	35(7)
C(2')	−0.0703(26)	0.1109(19)	0.6974(23)	43(8)
C(3')	−0.1836(28)	0.1639(22)	0.8534(29)	54(9)
C(1'')	0.2675(26)	0.3336(19)	0.7907(27)	49(9)
C(2'')	0.3125(24)	0.2459(23)	0.8149(24)	40(8)
C(3'')	0.3330(24)	0.4177(17)	0.8041(23)	38(8)
C(11)	0.2816(22)	0.2147(17)	0.4649(17)	20(6)
C(12)	0.4361(21)	0.2733(20)	0.6005(26)	43(9)
C(13)	0.2645(26)	0.3639(17)	0.5685(23)	35(8)
C(21)	0.2331(23)	0.0425(25)	0.7491(24)	50(9)
C(22)	0.4535(27)	0.0850(26)	0.7305(29)	55(11)
C(23)	0.4365(24)	0.0656(23)	0.4999(23)	44(9)
C(24)	0.2148(22)	0.0233(23)	0.5290(25)	44(8)
C(25)	0.3737(26)	−0.0880(19)	0.6355(34)	58(10)

Table 2

Selected bond lengths (pm) and bond angles (°) of 10

Bond lengths (pm)

Re(1)–Re(2)	307.5(1)	C(1)–C(2)	137.7(32)
Re(1)–O(1)	216.8(14)	C(1)–C(5)	153.1(32)
Re(1)–C(1'')	239.0(25)	C(1)–C(1')	146.0(31)
Re(1)–C(2'')	231.7(24)	C(2)–C(3)	155.7(28)
Re(1)–C(11)	192.7(17)	C(2)–O(1)	123.4(25)
Re(1)–C(12)	184.6(21)	C(3)–C(4)	154.7(32)
Re(1)–C(13)	183.3(18)	C(3)–C(1'')	154.3(34)
Re(2)–C(21)	195.3(24)	C(4)–C(5)	152.1(35)
Re(2)–C(22)	195.4(28)	C(1')–C(2')	138.1(30)
Re(2)–C(23)	198.9(23)	C(1')–C(3')	148.9(37)
Re(2)–C(24)	199.6(23)	C(1'')–C(2'')	142.3(31)
Re(2)–C(25)	191.5(19)	C(1'')–C(3'')	147.9(29)

Bond angles (°)

Re(2)–Re(1)–O(1)	87.5(6)	C(1)–C(2)–O(1)	134.3(36)
Re(2)–Re(1)–C(1'')	120.5(10)	O(1)–C(2)–C(3)	117.5(31)
Re(2)–Re(1)–C(2'')	86.1(10)	C(2)–C(3)–C(4)	103.2(28)
Re(2)–Re(1)–C(11)	78.5(10)	C(2)–C(3)–C(1'')	113.0(29)
Re(2)–Re(1)–C(12)	90.6(12)	C(1'')–C(3)–C(4)	115.9(31)
Re(2)–Re(1)–C(13)	161.9(12)	C(3)–C(4)–C(5)	102.5(31)
Re(1)–Re(2)–C(21)	82.9(12)	C(4)–C(5)–C(1)	104.0(32)
Re(1)–Re(2)–C(22)	80.7(14)	C(2'')–C(1'')–C(3'')	120.1(36)
Re(1)–Re(2)–C(23)	85.0(12)	C(2'')–C(1'')–C(3)	117.9(35)
Re(1)–Re(2)–C(24)	87.0(12)	C(3'')–C(1'')–C(3)	117.9(33)
Re(1)–Re(2)–C(25)	179.0(14)	Re(1)–O(1)–C(2)	121.2(23)
C(1)–C(2)–C(3)	108.0(31)	Re(1)–C(1'')–C(3)	102.4(24)

pm and $c = 1189.9(1)$ pm. The fractional atomic coordinates are listed in Table 1, the selected bond lengths and angles are listed in Table 2 and the crystallographic details are given in Table 3. The molecular structure of the complex is depicted in Fig. 1. The dinuclear complex is a derivative of $[Re_2(CO)_{10}]$ with two coordination sites cisoid to the Re—Re bond occupied by the chelating 1,3-bis(isopropenyl)-1-cyclopenten-2-ol lig-

and, which is coordinated by O(1) of the hydroxo function and by the olefin bond C(1''), C(2'') of the 2-isopropenyl group to Re(1). The $Re(CO)_5$ and the $Re(CO)_3\{\eta^2$-1,3-bis(isopropenyl)-1-cyclopenten-2-ol-κ-$O\}$ moieties are staggered with respect to each other. The Re—Re bond, with 307.5(1) pm, is somewhat elongated in comparison to $[Re_2(CO)_{10}]$ in the gas phase (304 pm) [10] and in the solid state (302 pm) [11]. The geometry of the $Re(CO)_5$ group is square pyramidal with C(25), O(25) colinear to the Re—Re bond. In comparison to $[Mn_2(CO)_{10}]$ [12] or $[Tc_2(CO)_{10}]$ [10], CO ligands 21 to 24 are tilted towards Re(1). This is

Table 3

Crystallographic data for 10

| Formula	$C_{19}H_{16}O_9Re_2$	Radiation	Mo Kα
Mw($C_{19}H_{16}O_9Re_2$) (g mol^{-1})	760.73	Wavelength (pm)	71.073
Crystal system	orthorhombic	Absorption coefficient	114.072
Space group	$P2_12_12_1$	Scan mode	ω-scan
a (pm)	1247.7(2)	2θ range (°)	3.0–45.0
b (pm)	1453.7(1)	Scan rate	0.91–5.03
c (pm)	1189.9(1)	Width of reflexes	$0.75 + 0.35 \tan \theta$
α (°)	90.00	No. of indep. reflections	2057
β (°)	90.00	No. of obs. reflections	1665
γ (°)	90.00	Rejection criterion	$I_{obs} < 3.00\sigma^2(I_{obs})$
V (mm^3)	2.1581(8)	No. of parameters	132
Z	4	R	5.3
ρ(calc.) (g cm^{-3})	2.33	R_w	5.1
Crystal dimension (mm)	0.36 × 0.32 × 0.40	Instability factor	0.014
Temperature (K)	293	Residual electron density	1.60
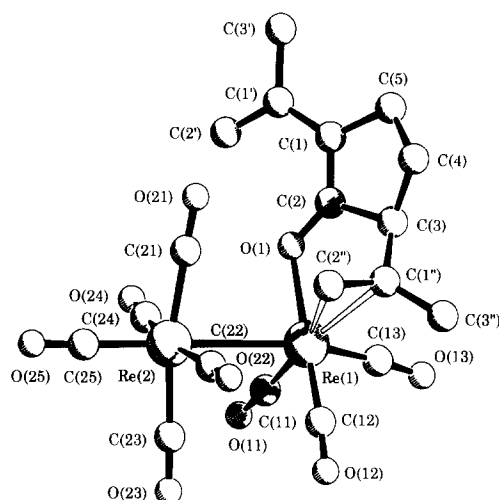
Fig. 1. SCHAKAL projection of the molecular structure of octacarbonyl[1″–2″-η-1,3-bis(isopropenyl)-1-cyclopenten-2-ol-κ-O]dirhenium (10).

also reflected by a distance of Re(2) from the plane of C(21)–C(24) of 21 pm (rmsd = 0.1 pm). In contrast, C(13), O(13) at Re(1) form an angle of 161.9(12)° at Re(1) with Re(2). Therefore the coordination sphere at Re(1) can be described as being distorted pentagonal bipyramidal or distorted octahedral. The atoms Re(1), Re(2), C(1″), C(2″), C(11) and C(13) form a plane (rmsd = 9.0 pm), the axis perpendicular to this plane being occupied by O(1) and C(12). The average C—O bond lengths of the carbonyl ligands are 114.2 pm. As in other octahedral olefin complexes, the coordinated C—C double bond is parallel or respectively perpendicular to the main axis of the coordination octahedron [13–16]. The C—C bond lengths and angles of the 1,3-bis(isopropenyl)-1-cyclopenten-2-ol ligand are within the normal range. The C—C double bonds between C(1)–C(2), C(1′)–C(2′) and C(1″)–C(2″) are clearly distinguished by their reduced bond lengths. As a consequence of the C–C double bond between C(1) and C(2), the carbon atoms C(1), C(2), C(3), C(5) and C(1′) and O(1) form a plane (rmsd = 2.5 pm) from which C(4) is displaced by 56.6 pm. The five-membered ring has an envelope form with a dihedral angle of 146.2°.

5. Discussion

The products of the photoreaction of 1 with the branched cumulenes 2–4 can be divided into two groups. Complexes of one group contain unchanged cumulenes as ligands (5, 11), ligands derived from the cumulenes by the addition of one hydrogen (8, 15) or ligands formed by dimerization of the cumulenes (16). The ligands of the other group are conjugated 1,3-dienes (7, 13, 18) or conjugated 1,3-dien-1-yls (6, 12, 17) which are derived from the cumulenes by H-shifts.

All of these products can be explained by reactions of the primary photoproducts of 1 [17] with 2–4. UV light cleaves the Re—Re bond with the formation of pentacarbonylrhenium radicals (20). Reaction of 20 with the unsymmetrically substituted cumulenes 2 and 3 yields four different radical intermediates, e.g. 21–24 in the case of 2 (Scheme 1) by attack at 2-C (21, 22), at 3-C (23) or at 1-C (24). Radicals 21 and 22 are mesomeric while 23 and 24 represent diastereomers. The existence of intermediates of this kind is substantiated by the isolation of decacarbonyl(μ-η^{1:1}-3,4-diphenyl-1,5-hexadien-2,5-diyl)dirhenium from 1 and phenylallene [4] and octacarbonyl(μ-η^{3:3}-2,3-methylene-buta-1,4-diyl)dirhenium from 1 and allene [5]. These two complexes are dimers of the pentacarbonyl(2-η-1-phenyl-2-propen-1,2-diyl)rhenium or pentacarbonyl(1-η-2-propen-1,2-diyl)rhenium radicals, respectively. The latter dimer is further stabilzed by the loss of two carbonyl ligands and η^1–η^3 rearrangements.

The formation of the tetracarbonyl-η^3-enyl-rhenium complex 8 provides additional evidence for the intermediates 23 and 24. Radicals 23, 24 can be expected to react with the solvent by hydrogen abstraction, yielding the pentacarbonyl(η^1-enyl)rhenium complexes 25, 26. By a well-known reaction, 25, 26 lose carbon monoxide and rearrange to 8. Similarly 15 is formed from 3 and 20 via the corresponding intermediates. Complex 8 is
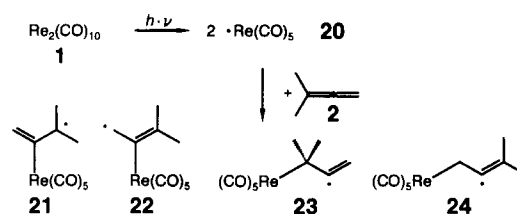

Scheme 1.
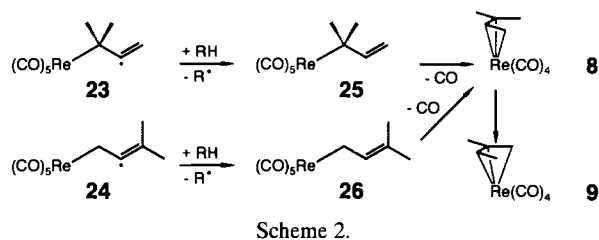
Scheme 2.

always obtained together with its isomer **9** in a ratio of 73:27, the latter presumably being formed from **8** by an 1,4-H shift (Scheme 2).

In addition to CO loss and η^1–η^3 rearrangement, **25** obviously reacts in another direction in contrast to **26**. The enyl ligand of **25** contains C—H bonds in the β-position to Re and is therefore susceptible to a β-elimination of 2-methyl-1,3-butadiene (**27**) and the formation of pentacarbonyl-hydrido-rhenium. By means of comparable steps, **3** is isomerized into 4-methyl-1,3-pentadiene (**28**) or 2-methyl-1,3-pentadiene (**29**) and **4** into 2,4-dimethyl-1,3-pentadiene (**30**) (Scheme 3). Interestingly, no complexes of **29** have been detected so far.

A second important primary photoproduct of **1** is the electronically and coordinatively unsaturated 32-electron complex enneacarbonyl-dirhenium (**31**) [17]. Complexes of this type readily coordinate unsaturated hydrocarbons such as the cumulenes **2**, **3** or the dienes **27**, **28** and **30**, preferrably at the least substituted C—C double bond. The cumulene **2** will therefore react with **31** to yield **32** via 1-C, 2-C addition, while diene **27** reacts with **31** to yield **33** via 3-C, 4-C addition (see Scheme 4). Substitution of one CO in **32** by a free C—C bond leads to the cumulene-bridged complex **5**. By comparable steps, **3** and **31** will produce **11**. The limit for this reaction seems to be reached with the highly substituted cumulene **4**, for which no complex such as **5** or **11** has been detected so far.

The molecular structure of (μ-$\eta^{2:2}$-allene)octacarbonyl-dimanganese has been determined by an X-ray diffraction analysis [2]. Complexation of allene to two metal centres causes a 141° bending of the linear allene and orientates the methylene protons into two chemically different surroundings which are *E* and *Z*

Scheme 3.

Scheme 4.
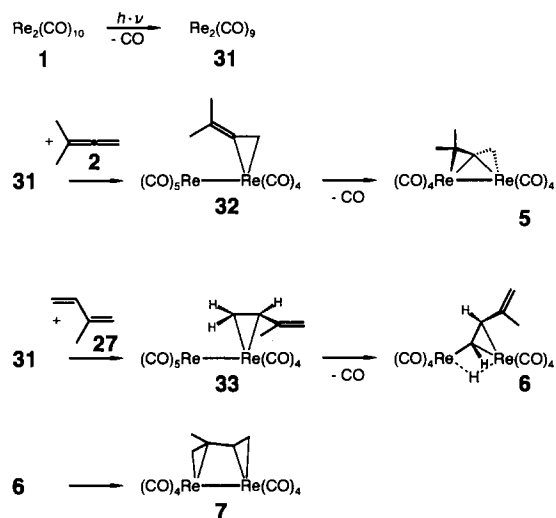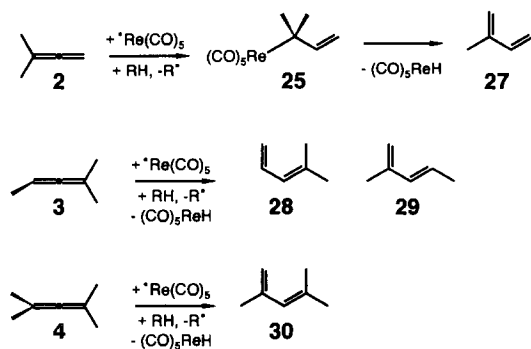
oriented with respect to the metal centres. Hence, mono-, 1,3-di- and tri-substituted allenes may form isomeric complexes. The plane defined by the three carbon atoms is intersected by the Mn—Mn bond at approximately 45°. Comparable stereochemistries are quite reasonable for **5** and **11**. In addition to manganese and rhenium, a number of other transition metals form homo- [18–26] and hetero-dinuclear complexes [27] with μ-$\eta^{2:2}$-cumulene ligands. Complexes with metal–metal bonds show a similar stereochemistry as (μ-$\eta^{2:2}$-allene)octacarbonyl-dimanganese. Complexes without metal–metal bonds have also been described [21,26]. The structure of [$W_2(O$-t-butyl)$_6(\eta^{2:2}$-allene)] with a unique planar W_2C_3 unit [28] differs from all the other cumulene complexes.

All branched cumulenes react with **1** upon UV irradiation to give octacarbonyl(μ-$\eta^{1:2}$-1,3-diene-1-yl)-μ-hydrido-dirhenium (**6, 12, 17**). Obviously, these complexes originate from coordination of the dienes **27, 28, 30** or **31** via intermediates like **33** (see Scheme 4). By photochemically-induced loss of CO from the Re(CO)$_5$ group, two reactions are possible. First an oxidative addition of a C—H bond to the unsaturated rhenium atom, by which complexes **6, 12, 17** result. The oxidative C—H attack must occur selectively from the 1E position of the dienes **27, 28**. For **17**, ^{1}H NMR data have established the existence of only one isomer but have not allowed its stereochemistry to be determined unambiguously. We suppose for **17** also attack of the 1E C—H bond at rhenium due to its reduced steric hindrance in comparison with the 1Z C—H bond. Upon heating complexes **6, 12, 17**, they rearrange rapidly and quantitatively by reductive elimination of 1E C—H and are converted into octacarbonyl(μ-$\eta^{2:2}$-s-trans-1,3-diene)dirhenium (**7, 13, 18**).

One has also to consider alternative generation of **7, 13, 18** by CO substitution of the free double bond in

intermediates such as **33**. However, photoreaction of **1** with 1,3-butadiene, when conducted at low temperatures, yields no octacarbonyl(μ-$\eta^{2:2}$-s-trans-1,3-butadiene)dirhenium at all. Hence it is quite likely that **7, 13, 18** originate from **6, 12, 17**.

Only from the reaction of **1** with **4** was a tricarbonyl(η^5-2,4-pentadien-1-yl)rhenium complex (**19**) obtained. Comparable products were also formed from decacarbonyl-dimanganese and conjugated dienes with chains of five or more carbon atoms [3]. Dinuclear complexes with methyl-substituted 2-buten-1,4-diyl bridges are reasonable intermediates and yield η^5-2,4-pentadien-1-yl complexes by the loss of CO and β-elimination of HRe(CO)$_5$.

Only in the reaction mixture of **1** with **3** was an octacarbonyl(μ-$\eta^{1:3}$-3-propen-2-ylidene)dirhenium (**14**) observed; such a complex exhibits triple methyl substitution. Formally, the 4-methyl-3-penten-2-ylidene ligand is formed from **3** by a 1,2-H shift. Such shifts have been reported for free allenes [29] and are also resonable for coordinated cumulenes.

The generation of the minor by-product **16** can be explained by dimerization of two pentacarbonyl(3-η-4-methyl-3-penten-2,3-diyl)rhenium radicals (**34**) (see Scheme 5). This dimerization must proceed stereospecifically, because the final product exhibits C_2 symmetry with two asymmetric C atoms of the same chirality. A similar stereochemistry was observed for the analogous product from **1** and 2,3-pentadiene which was characterized by an X-ray diffraction analysis [5].

An unexpected byproduct (**10**) was isolated in very small yields from the photoreaction of **1** with **2**. The molecular structure of **10** was determined by X-ray diffraction analysis and shows the unusual chelating ligand 1,3-bis(isopropenyl)-1-cyclopenten-2-ol, coordinated by 1″-C, 2″-C and the oxygen of the hydroxy group to a Re$_2$(CO)$_8$ complex fragment. A reasonable explanation for the generation of this ligand is cyclotrimerization of two molecules of cumulene **2** and carbon monoxide to give 1,3-bis(isopropylidene)cyclopentan-2-one (**36**), which rearranges by two 1,3-H shifts to 1,3-bis(isopropenyl)cyclopentan-2-one (**37**) which fi-
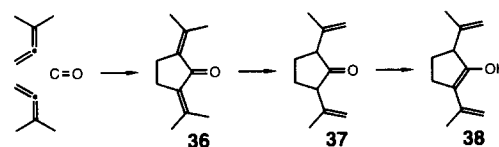
Scheme 6.

nally tautomerizes to the enol 1,3-bis(isopropenyl)-1-cyclopenten-2-ol (Scheme 6). Possibly all of these reactions occur in the coordination sphere of rhenium, but only to a very small extent.
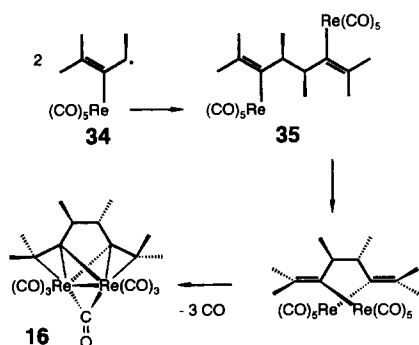
The photoreactivity of the branched cumulenes **2–4** differs markedly from that of allene and the unbranched cumulenes 1,2-butadiene and 2,3-pentadiene [5]. For branched cumulenes, no enneacarbonyl-μ-$\eta^{1:3}$-endiyl-dirhenium complexes were detected. In contrast, unbranched cumulenes yield no photoproducts with **1** containing conjugated dienes as ligands having been generated by isomerization from the cumulenes. Parallels between branched and unbranched cumulenes only occur in the case of the octacarbonyl(μ-$\eta^{2:2}$-cumulene)dirhenium and the mononuclear tetracarbonyl(η^3-enyl)rhenium complexes.

There is also a different reactivity pattern, when decacarbonyl-dimanganese is photolyzed in the presence of **2**. In addition to the manganese homologues of **5, 8** and **9**, the electron-deficient complexes tricarbonyl[$\eta^{3:CH}$-2-methyl-E-3-(3(8),6-m-menthadien-6-yl)2-buten-1-yl]manganese and hexacarbonyl[$\eta^{3:CH:3:CH}$-2,3,4,5-tetramethyl-2,5-hexadien-1,4-diyl)dimanganese with ligands composed from three and two molecules of **2** and with C—H—Mn two-electron–three-centre bonds are isolated [3].

Our results show that the reactivity of carbonyl metal complexes towards unsaturated hydrocarbons differs markedly when the components are varied, either due to a different substitution pattern or the effect of different central metal atoms.

6. Experimental details

Scheme 5.

For high-pressure liquid chromatography, a modular system was used containing three pumps model 303, a dynamic mixer model 811, a manometric module model 803C, a UV detector model 116 (254 nm) (Abimed/Gilson, Langenfeld) and a differential refractometer (R 403, Waters, Königstein). The system was connected by a contact modem with an IBM PC AT and was operated with the Gilson 714 HPLC system controller software. For separation of the reaction mixtures, a HPLC column ($l = 250$ mm, $d = 50$ mm) filled with LiChrosorb Si 60 (Merck, Darmstadt), paticle size 10 μ (Merck/Darmstadt) was used with flow rates of 30 ml min^{-1} for the mobile phase.

Elemental analyses for carbon and hydrogen were obtained with a microanalyzer 240 (Perkin-Elmer). IR spectra in the 2200–1500 cm^{-1} spectral region were run on a grating spectrometer (Perkin-Elmer, model 297) using n-hexane solutions in CaF$_2$ cells with a path length of 0.2 mm. The ^{1}H NMR spectra were recorded at 200.13 MHz on a Bruker WP-200 spectrometer (Bruker, Karlsruhe).

The starting materials, 2-methyl-2,3-pentadiene (**3**) and 2,4-dimethyl-2,3-pentadiene (**4**) [30–32] were prepared according to literature methods. Other reagents were commercial products.

6.1. Photoreaction of decacarbonyl-dirhenium (1) with 3-methyl-1,2-butadiene (2)

Re$_2$(CO)$_{10}$ (**1**) (1.20 g, 1.84 mmol) was disolved in 800 ml of n-hexane in a photoreactor. After cooling to 243 K, 2.0 ml of 3-methyl-1,2-butadiene (**2**) were added to the solution. During UV irradiation, nitrogen was bubbled slowly through the reaction mixture. The progress of the reaction was monitored by IR spectroscopy. The irradiation was stopped when the IR bands of **1** had disappeared (after 60 min). The colour of the solution had changed from colourless to orange–red over this period.

The cold reaction mixture was filtered through a short column of filter flakes, the solvent removed at room temperature with a rotation evaporator, the residue dissolved in 10 ml of dichloromethane and prepurified on a column ($l = 15$ cm, $d = 2$ cm) of alumina, first with pure n-hexane and than with pure dichloromethane. The solvent was removed from the eluate under high vacuum and then 20 ml of n-hexane were added to the residue followed by dichloromethane until a clear solution was obtained. This solution was separated into 5 ml portions and subjected to isocratic preparative HPLC with n-hexane/dichloromethane as eluents to allow its components to be isolated.

Six fractions were collected in Schlenk tubes and dried under high vacuum. If not of an oily consistency, the residues were recrystallized from n-pentane at 240

K, the crystals being collected on sintered glass frits and dried under high vacuum.

Fraction 1: Mixture of isomers, 63% tetracarbonyl-(η^3-3-methyl-2-buten-1-yl)rhenium (**8**) and 27% tetracarbonyl(η^3-Z-2-methyl-2-buten-1-yl)rhenium (**9**), pale yellow oil. Yield, 101 mg (13% based on **1**). C$_9$H$_9$O$_4$Re (367.37). IR (cm^{-1}): 2091 (m); 1991 (s); 1981 (vs); 1963 (vs). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: Compound **8** (0.73): 4.68 (2-H, 1, dd, $J = 12.5$, 7.3 Hz); 2.81 (1E-H, 1, dd, $J = 7.3$, 3.0 Hz); 2.12 (4-H, 3, s); 1.94 (1Z-H, 1, dd, $J = 12.5$, 3.0 Hz); 1.86 (3Z-CH$_3$, 3, s) ppm. Compound **9** (0.27): 3.89 (3E-H, 1, qdd, $J = 6.8$, 2.0, 0.7 Hz); 3.13 (1E-H, 1, dd, $J = 2.5$, 2.0 Hz); 2.49 (1Z-H, 1, dd, $J = 2.5$, 0.7 Hz); 2.47 (2-CH$_3$, 3, s); 1.78 (4-H, 3, d, $J = 6.8$ Hz) ppm.

Fraction 2: Re$_2$(CO)$_{10}$ (**1**).

Fraction 3: Octacarbonyl(μ-$\eta^{2:2}$-3-methyl-1,2-butadiene)dirhenium (**5**), lemon yellow crystals. Yield, 49 mg (4% based on **1**). Anal. Found: C, 23.60; H, 1.20%. C$_{13}$H$_8$O$_8$Re$_2$ (664.60) Calc.: C, 23.49; H, 1.21%. IR (cm^{-1}): 2106 (m); 2059 (s); 2000 (m); 1989 (vs); 1984 (vs); 1967 (s). ^{1}H NMR, (CD$_2$Cl$_2$, 293 K) δ: 3.65 (1E-H, 1, d, $J = 4.4$ Hz); 3.35 (1Z-H, 1, dqq, $J = 4.4$, ≈ 1.0, ≈ 0.8 Hz); 2.70 (3E-CH$_3$, 3, bs); 2.25 (4-H, 3, bs) ppm.

Fraction 4: Octacarbonyl-μ-hydrido(μ-$\eta^{1:2}$-3-methyl-1,3-butadien-1-yl)dirhenium (**6**), yellow needles. Yield, 86 mg (7% based on **1**). Anal. Found: C, 23.55; H, 1.23% C$_{13}$H$_8$O$_8$Re$_2$ (664.60) Calc.: C, 23.49; H, 1.21%. IR (cm^{-1}): 2124 (w); 2089 (m); 2013 (vs); 1992 (s); 1984 (s); 1976 (m); 1970 (s). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 6.74 (1Z-H, 1, d, $J = 16.5$ Hz); 6.13 (4E-H, 1, d, $J = 3.2$ Hz); 6.06 (2-H, 1, d, $J = 16.5$ Hz); 5.35 (4Z-H, 1, d, $J = 3.2$ Hz); 1.78 (3-CH$_3$, 3, s); -14.20 (Re—H, 1, s) ppm.

Fraction 5: Octacarbonyl(μ-$\eta^{2:2}$-2-methyl-1,3-butadiene)dirhenium (**7**), grey–yellow crystals. Yield, 49 mg (4% based on **1**). Anal. Found: C, 22.80; H, 1.12%. C$_{13}$H$_8$O$_8$Re$_2$ (664.60) Calc.: C, 23.49; H, 1.21%. IR (cm^{-1}): 2102 (w); 2054 (m); 1994 (vs); 1978 (s); 1962 (m). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 3.46 (1E-H, 1, d, $J = 1.0$ Hz); 2.81 (4E-H, 1, dd, $J = 8.3$, 1.5 Hz); 2.52 (1Z-H, 1, d, $J = 1.0$ Hz); 2.42 (3-H, 1, dd, $J = 13.3$, 8.3 Hz); 2.02 (4Z-H, 1, dd, $J = 13.3$, 1.5 Hz); 1.79 (2-CH$_3$, 3, s) ppm.

Fraction 6: Octacarbonyl[η^2-1,3-bis(isopropenyl)-1-cyclopenten-2-ol-κ-O]dirhenium (**10**), red rhomboids. Yield, 7 mg (0.5% based on **1**). Anal. Found: C, 29.71; H, 1.82%. C$_{19}$H$_{16}$O$_9$Re$_2$ (760.73) Calc.: C, 30.00; H, 2.12%. IR (cm^{-1}): 2092 (w); 2005 (m); 1998 (s); 1983 (vs); 1971 (m); 1962 (s); 1929 (m); 1911 (s); 1598 (w).

6.2. Photochemical reaction of Re$_2$(CO)$_{10}$ (1) with 2-methyl-2,3-pentadiene (3)

Re$_2$(CO)$_{10}$ (**1**) (1.00 g, 1.53 mmol) and 2.0 ml of 2-methyl-2,3-pentadiene (**3**) were irradiated with UV

light for 45 min in 800 ml of n-hexane at 248 K. The reaction mixture was worked-up as described above. Eight fractions were obtained by HPL chromatography.

Fraction 1: Tetracarbonyl(η^3-E-2-methyl-3-penten-2-yl)rhenium (15), pale yellow oil. Yield, 111 mg (19% based on 1). The compound was contaminated with another tetracarbonyl rhenium complex of unknown structure. IR (cm^{-1}): 2091 (m); 1991 (s); 1980 (vs); 1961 (vs). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 4.06 (3-H, 1, d, J = 11.7 Hz); 2.50 (4Z-H, 1, dq, J = 11.7, 5.9); 1.71 (1-H, 3, s); 1.62 (5-H, 3, d, J = 5.9 Hz); 1.39 (2-CH$_3$, 3, s) ppm.

Fraction 2: Octacarbonyl(μ-$\eta^{1:3}$-4-methyl-3-penten-2-ylidene)dirhenium (14), brown–orange crystals. Yield, 42 mg (4% based on 1). Anal. Found: C, 24.50; H, 1.41%. C$_{14}$H$_{10}$O$_8$Re$_2$ (678.63) Calc.: C, 24.78; H, 1.49%. IR (cm^{-1}): 2103 (w); 2063 (m); 1998 (vs); 1990 (s); 1980 (w); 1966 (m); 1950 (s). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 4.23 (3-H, 1, bs); 2.98 (1-H, 3, d, J = 0.6 Hz); 2.26 (5-H, 3, s); 2.14 (4Z-CH$_3$, 3, s) ppm.

Fraction 3: Re$_2$(CO)$_{10}$ (1).

Fraction 4: Octacarbonyl(μ-$\eta^{2:2}$-2-methyl-2,3-pentadiene)dirhenium (11), pale yellow crystals. Yield, 156 mg (15% based on 1). Anal. Found: C, 24.80; H, 1.51%. C$_{14}$H$_{10}$O$_8$Re$_2$ (678.63) Calc.: C, 24.78; H, 1.49% IR (cm^{-1}): 2109 (m); 2058 (s); 2000 (s); 1983 (vs); 1966 (s). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 4.07 (4Z-H, 1, qqq, J = 6.2, 1.0, 0.7 Hz); 2.67 (2E-CH$_3$, 3, d, J = 1.0 Hz); 2.18 (1-H, 3, d, J = 0.7 Hz); 1.78 (5-H, 3, d, J = 6.2 Hz) ppm.

Fraction 5: Octacarbonyl-μ-hydrido(μ-$\eta^{1:2}$-4-methyl-1,3-pentadien-1-yl)dirhenium (12), yellow needles. Yield, 52 mg (5% based on 1). Anal. Found: C, 24.91; H, 1.58%. C$_{14}$H$_{10}$O$_8$Re$_2$ (678.63) Calc.: C, 24.78; H, 1.49%. IR (cm^{-1}): 2125 (w); 2086 (m); 2013 (vs); 1993 (s); 1982 (s); 1975 (m); 1968 (s). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 6.58 (1Z-H, 1, d, J = 16.0 Hz); 6.18 (2-H, 1, dd, J = 16.0, 9.7 Hz); 5.60 (3-H, 1, d, J = 9.7 Hz); 1.92 (5-H, 3, s); 1.89 (4Z-CH$_3$, 3, s); −14.18 (Re—H, 1, s) ppm.

Fraction 6: Heptacarbonyl(μ-$\eta^{1:2:1:2}$-2,4,5,7-tetramethyl-2,6-octadiene-3,6-diyl)dirhenium (16), red rhomboids. Yield, 12 mg (1% based on 1). Anal. Found: C, 29.80; H, 2.74%. Re$_2$C$_{19}$H$_{20}$O$_7$ (732.77) Calc.: C, 31.14; H, 2.75%. IR (cm^{-1}): 2023 (s); 1969 (vs). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 3.16 (4-, 5-H, 2, m, J = 6.6, 4.5 Hz); 2.36 (2Z-, 7Z-CH$_3$, 6, s); 2.34 (1-, 8-H, 6, s); 1.08 (4-, 5-CH$_3$, 6, m, J = 6.6 Hz) ppm.

Fraction 7: Octacarbonyl(μ-$\eta^{2:2}$-4-methyl-1,3-pentadiene)dirhenium (13), yellow crystals. Yield, 62 mg (6% based on 1). Anal. Found: C, 24.80; H, 1.56%. C$_{14}$H$_{10}$O$_8$Re$_2$ (678.63) Calc.: C, 24.78; H, 1.49%. IR (cm^{-1}): 2099 (w); 2048 (m); 1996 (vs); 1980 (s); 1976 (m); 1962 (m). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 2.91 (2-H, 1, ddd, J = 12.7, 11.0, 8.0 Hz); 2.68 (1E-H, 1, dd, J = 8.0, 0.5 Hz); 2.38 (5-H, 3, s); 2.35 (4Z-CH$_3$, 3, s); 2.40 (3-H, 1, d, J = 11.0 Hz); 2.08 (1Z-H, 1, dd, J = 12.7, 0.5 Hz) ppm.

Fraction 8: HRe$_3$(CO)$_{14}$.

6.3. Photochemical reaction of Re$_2$(CO)$_{10}$ (1) with 2,4-dimethyl-2,3-pentadiene (4)

Re$_2$(CO)$_{10}$ (1) (1.00 g, 1.53 mmol) and 3.0 ml of 2,4-dimethyl-2,3-pentadiene (4) were irradiated with UV light in 800 ml of n-hexane for 75 min at 248 K. The reaction mixture was worked-up as described above. HPL chromatography showed that four fractions were obtained.

Fraction 1: Re$_2$(CO)$_{10}$ (1).

Fraction 2: Octacarbonyl(μ-$\eta^{1:2}$-2,4-dimethyl-1,3-pentadiene-1-yl)-μ-hydrido-dirhenium (17), yellow crystals. Yield, 138 mg (13% based on 1). Anal. Found: C, 26.00; H, 1.73%. C$_{15}$H$_{12}$O$_8$Re$_2$ (692.66) Calc.: C, 26.01; H, 1.75%. IR (cm^{-1}): 2118 (w); 2083 (m); 2009 (vs); 1991 (s); 1982 (s); 1978 (m); 1966 (s). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 6.52 (1-H, 1, s); 6.11 (3-H, 1, bs); 2.44 (2-CH$_3$, 3, s); 1.94 (5-H, 3, d, J = 0.7 Hz); 1.75 (4Z-CH$_3$, 3, d, J = 0.6 Hz); −13.56 (Re—H, 1, s) ppm.

Fraction 3: Octacarbonyl(μ-$\eta^{2:2}$-2,4-dimethyl-1,3-pentadiene)dirhenium (18), yellow–green crystals. Yield, 286 mg (27% based on 1). Anal. Found: C, 26.00; H, 1.73%. Re$_2$C$_{15}$H$_{12}$O$_8$ (692.66) Calc.: C, 26.01; H, 1.75%. IR (cm^{-1}): 2090 (w); 2040 (m); 1998 (vs); 1989 (s); 1976 (m); 1959 (m). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 3.15 (1E-H, 1, s); 2.55 (5-H, 3, s); 2.42 (3-H, 1, s); 2.31 (4Z-CH$_3$, 3, s); 2.28 (1Z-H, 1, s); 2.07 (2-CH$_3$, 3, s) ppm.

Fraction 4: Tricarbonyl(η^5-2,4-dimethyl-2,4-pentadien-1-yl)rhenium (19), pale yellow crystals. Yield, 34 mg (3% based on 1). Anal. Found: C, 33.30; H, 3.19%. ReC$_{10}$H$_{11}$O$_3$ (365.40) Calc.: C, 32.87; H, 3.04%. IR (cm^{-1}): 2024 (s); 1961 (vs); 1941 (vs). ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ: 5.68 (3-H, 1, bs); 3.00 (1E-, 5E-H, 2, dd, J = 2.7, 1.5 Hz); 2.48 (2-, 4-H, 6, s); 1.15 (1Z-, 5Z-H, 2, dd, J = 2.7, 0.5 Hz) ppm.

6.4. Thermolysis of the octacarbonyl-μ-hydrido(μ-$\eta^{1:2}$-1,3-dien-1-yl)dirhenium-complexes 6, 12 and 17

In a 100 ml round-bottomed flask fitted with a reflux condenser and a bubble counter, solutions consisting of 100 mg of the hydrido complexes 6, 12 or 17 in 50 ml of i-octane were heated to 353 K for 60 min. Without noticeable decomposition, compounds 7, 13 or 18 were formed in quantitative yield. After removal of the solvent, the complexes were dried under high vacuum and characterized by IR and ^{1}H NMR spectroscopy.

6.5. Thermolysis of octacarbonyl(μ-η$^{1:2}$-4-methyl-3-penten-2-ylidene)dirhenium (14)

Compound **14** (30 mg) was dissolved in 1.6 ml of benzene-d_6 in an NMR tube and heated in the NMR spectrometer to 363 K. ^{1}H NMR spectra were run at intervals of 5 min and showed the transformation of **14** into **13** within 75 min without any decomposition.

6.6. X-Ray structural analysis of 10

The crystallographic data for [Re$_2$(CO)$_8$(η^2-C$_{11}$H$_{16}$O-κ-O)] (**10**) are listed in Table 3. The X-ray reflections were collected on a CAD4 diffractometer (Enraf-Nonius) in the ω-scan mode using graphite monochromated Mo Kα radiation with reflection angles in the range $3° \leq 2\theta \leq 45°$. After reduction of the 2057 independent reflections, 1665 observed reflections resulted. The structure was solved by direct methods and refined to $R = 0.053$, $R_w = 0.051$. The programs Xanadu and SCHAKAL were employed.

Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, D 76344 Eggenstein-Leopoldshafen 2, by making reference to deposition number CSD 58674 and citing this paper and the authors.

Acknowledgement

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