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The activation and transformations of vinyl acetate at a dirhenium carbonyl center

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ABSTRACT

The reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** with vinyl acetate in methylene chloride by heating at 40 °C yielded three new products: $Re_3(CO)_{13}(\mu\text{-}\eta^2\text{-}C_2H_3)$, **3**, (24% yield), $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}H)$, **4**, (9% yield) and $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}CHCHO_2CCH_3)(\mu\text{-}H)$, **5**, (13% yield). Compound **3** was also obtained in a similar yield from the reaction of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$, **2** with vinyl acetate, but compounds **4** and **5** were not obtained. All of the products were characterized structurally by single-crystal X-ray diffraction analysis. Compound **3** consists of an open trirhenium cluster containing two rhenium – rhenium bonds. One of the rhenium – rhenium bonds contains a $\mu\text{-}\eta^2\text{-}(\sigma+\pi)$-coordinated C_2H_3 (vinyl) ligand. Compound **4** contains two rhenium atoms with a bridging η^2-acetate ligand and a bridging hydrido ligand. Compound **5** contains two mutually bonded Re–Re atoms with a bridging $(\sigma+\pi)$-coordinated acetate-substituted vinyl group and a bridging hydrido ligand by the cleavage of one of the CH bonds on the β–carbon atom of the vinyl group of the vinyl acetate. The reaction of compound **3** with I_2 resulted in cleavage of the $Re(CO)_5$ group to yield the known complex $Re(CO)_5I$ and the new dirhenium complex $Re_2(CO)_8I(\mu\text{-}\eta^2\text{-}C_2H_3)$, **6** containing a $\mu\text{-}\eta^2\text{-}(\sigma+\pi)$-coordinated vinyl group.

1. Introduction

There is great interest in synthesis and applications of polymers derived from polar vinyl monomers such as acrylates, acrylamides, acrylonitrile and vinyl acetate [1]. Copolymers of ethylene and vinyl acetate, known as ethylene vinyl acetate (EVA), have a variety of applications [2]. There is considerable interest in the activation and coupling of vinyl acetate to ethylene by using metal complexes [3–5].

We have recently investigated the activation of vinyl acetate by the pentaruthenium complex $Ru_5(\mu_5\text{-}C)(CO)_{15}$ including its stoichiometric coupling to ethylene, see Scheme 1 [6,7]. CH activation at the α–carbon of the vinyl group was followed by C–C coupling to ethylene with subsequent CH shifts to yield two isomeric Ru_5 products containing methylallylacetate ligands.

In the present work, we have investigated the reaction of vinyl acetate with the dirhenium complexes $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** [8] and $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$, **2** [9]. CH activation at the vinyl group and cleavage of the acetate group from the vinyl acetate molecule were observed. These results are reported herein.

2. Experimental details

2.1. General data

All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet IS10 Midinfrared FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe by using electron impact ionization (EI) were made on a VG 70S instrument. $Re_2(CO)_{10}$ and vinyl acetate were obtained from Pressure Chemical and Sigma Aldrich, respectively, and were used without further purification. $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, **1** [8] and $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H)=C(H)Bu^n]$, **2** [9] were prepared according to previously reported procedures. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

2.2. Reaction of $Re_2(CO)_8(\mu\text{-}C_6H_5)(\mu\text{-}H)$, 1 with vinyl acetate

A 24.0 mg amount (0.036 mmol) of **1** and 7.0 μL (0.077 mmol)

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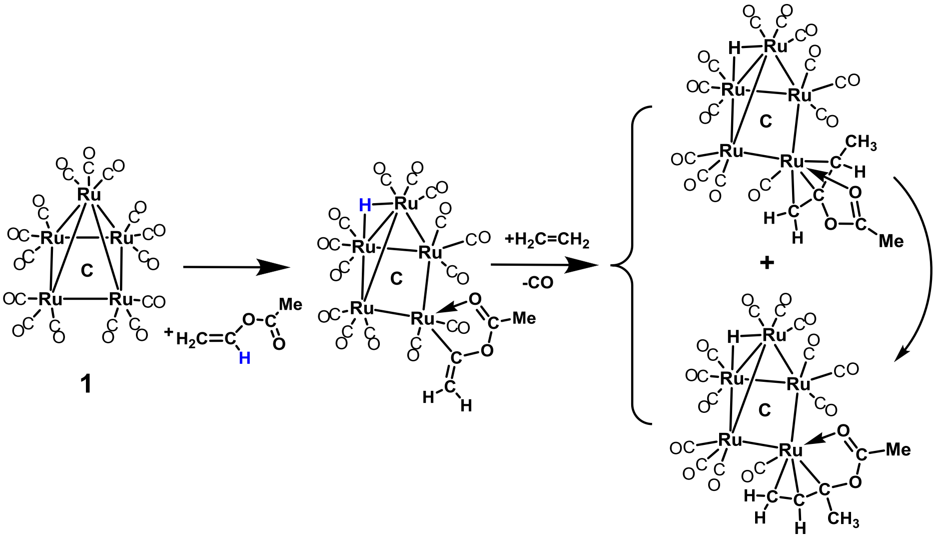


Scheme 1. A schematic of the activation of vinyl acetate and its coupling to ethylene by a Ru_5 cluster complex [6,7].

of vinyl acetate were dissolved in 1.5 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated at 40 °C and allowed to stand at that temperature for 24 h. A ^1H NMR spectrum obtained after this period showed new resonances at $\delta = -12.65$ and -14.54. The solution was then cooled and the solvent was removed *in vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using hexane to give in order of elution: a yellow band of $Re_3(CO)_{13}(\mu\text{-}\eta^2\text{-}C_2H_3)$, **3**, 6.0 mg (24% yield) and two colorless bands of $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}H)$, **4**, 2.0 mg (9% yield) and $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}CHCHO_2CCH_3)(\mu\text{-}H)$, **5**, 3.0 mg (13% yield). Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2119 (w), 2092 (m), 2043 (w), 2017 (s), 1972 (b). ^1H NMR (CD_2Cl_2, δ in ppm): δ 4.02 (dd, 1H, $^3J_{H\text{-}H} = 15.6$ Hz, $^3J_{H\text{-}H} = 0.9$ Hz); 5.65 (dd, 1H, $^3J_{H\text{-}H} = 9.3$ Hz, $^3J_{H\text{-}H} = 0.9$ Hz); 8.54 (dd, 1H, $^3J_{H\text{-}H} = 15.6$ Hz, $^3J_{H\text{-}H} = 9.3$ Hz). Mass Spec. EI/MS *m/z*: 950, M^+, 922, $M^+ - CO$, 894, M^+-2CO. This isotope distribution pattern is consistent with the presence of three rhenium atoms. Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2121 (w), 2101 (m), 2085 (w), 2022 (s), 2005 (sh), 1958 (m). ^1H NMR (CD_2Cl_2, δ in ppm) 1.93 (s, 3H), -12.65 (s, 1H, hydrido ligand). Mass Spec. EI/MS *m/z*: 656, M^+, 628, M^+-CO. This isotope distribution pattern is consistent with the presence of two rhenium atoms. Spectral data for **5**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2116 (w), 2085 (s), 2021 (vs), 1991 (sh), 1975 (s), 1956 (sh), 1759 (w). ^1H NMR (CD_2Cl_2, δ in ppm): 7.19 (d, 1H, $^2J = 13.2$ Hz), 6.13 (d, 1H, $^2J = 13.0$ Hz), -14.54 (s, 1H, hydride). Mass Spec. EI/MS *m/z*: 682, M^+, 654, M^+-CO. This isotope distribution pattern is consistent with the presence of two rhenium atoms.

2.3. Reaction of $Re_2(CO)_8(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}C(H){=}C(H)Bu^n]$, 2 with vinyl acetate

A 50.0 mg amount (0.147 mmol) of **2** and 13.0 μL (0.147 mmol) of vinyl acetate were dissolved in 1.5 mL of deuterated benzene in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated at 60 °C and allowed to stand at that temperature for 48 h. A ^1H NMR spectrum obtained after this period showed new resonances at $\delta = 8.49\text{–}8.58$. The contents were then transferred to a flask and solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using hexane to give a yellow band of **3**, 12.0 mg (26% yield).

2.4. Reaction of 3 with I_2

A 20.0 mg amount (0.021 mmol) of **3** and 6.0 mg (0.024 mmol) of iodine were dissolved in 1.5 mL CD_2Cl_2 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then allowed to stand for 2 h at room temperature. The color of iodine disappeared. A ^1H NMR spectrum obtained after this period showed new resonances at $\delta = 8.96\text{–}9.04$. The contents were then transferred to a flask and the solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and then separated by TLC by using hexane to give a yellow band of $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}C_2H_3)(I)$, **6**, 4.0 mg (25% yield) and a colorless band of $Re(CO)_5I$, 7 mg (73% yield). Spectral data for **6**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2119 (w), 2091 (m), 2057 (vw), 2018 (s), 1995 (m), 1973 (m). ^1H NMR (CD_2Cl_2, δ in ppm): δ 4.23 (d, 1H, $^3J_{H\text{-}H} = 14.7$ Hz); 5.54 (d, 1H, $^3J_{H\text{-}H} = 9$ Hz); 9.00 (dd, 1H, $^3J_{H\text{-}H} = 14.7$ Hz, $^3J_{H\text{-}H} = 9$ Hz). Mass Spec. EI/MS *m/z*: 750, M^+, 722, $M^+ - CO$, 694, M^+-2CO. This isotope distribution pattern is consistent with the presence of two rhenium atoms.

Crystallographic Analyses: Yellow single crystals of **3** and colorless single crystals of **4**, **5** and **6** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a solution in pure hexane at 15 °C. All the crystal data were collected at 100 (2) K by using a Bruker D8 QUEST diffractometer equipped with a PHOTON-100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å) [10]. The raw area detector data frames were reduced, scaled and corrected for absorption effects using the SAINT [10] and SADABS [11] programs. All structures were solved by using SHELXT [12]. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018[5] using OLEX2 [13]. Crystal data and results of the structural refinements are given in Table 1. For additional information, see Supplementary Materials.

3. Results and discussion

Three products $Re_3(CO)_{13}(\mu\text{-}\eta^2\text{-}C_2H_3)$, **3**, (24% yield), $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}O_2CCH_3)(\mu\text{-}H)$, **4**, (9% yield) and $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}CHCHO_2CCH_3)(\mu\text{-}H)$, **5**, (13% yield) were obtained from the reaction of **1** with vinyl acetate in methylene chloride by heating at 40 °C for 24 h. All three products were characterized by IR, H NMR, mass spectrum and single crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of compound **3** is

Table 1
Crystal data, and results of the structural analyses for compounds **3-6**.

Compound	3	4	5	6
Empirical formula	$Re_3C_{15}H_3O_{13}$	$Re_2C_{10}H_4O_{10}$	$Re_2C_{12}H_6O_{10}$	$Re_2C_{10}H_3O_8I$
Formula weight	957.75	656.53	682.57	750.44
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Lattice parameters				
a (Å)	9.6455 (4)	6.8391 (5)	9.1003 (3)	7.5814 (4)
b (Å)	12.5742 (4)	9.8742 (7)	10.9036 (3)	12.8324 (6)
c (Å)	16.8946 (6)	11.4795 (8)	16.3144 (4)	15.5972 (8)
α (deg)	90.00	87.318 (2)	90.00	90
β (deg)	101.975 (2)	82.358 (2)	101.129 (1)	100.516 (2)
γ (deg)	90.00	73.215 (2)	90.00	90
V ($Å^3$)	2004.46 (13)	735.57 (9)	1588.37 (8)	1491.93 (13)
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/n$
Z value	4	2	4	4
ρ_{calc} (g/cm^3)	3.174	2.964	2.854	3.341
μ (Mo Kα) (mm^{-1})	18.147	16.489	15.278	18.314
Temperature (K)	100 (2)	100 (2)	100 (2)	100 (2)
$2\theta_{max}$ (°)	60.201	56.74	61.36	65.36
No. Obs. ($I > 2\sigma(I)$)	9757	7239	9809	5470
No. Parameters	280	205	230	190
Goodness of fit (GOF)[a]	1.071	1.046	1.322	1.079
Max. shift/error on final cycle	0.003	0.001	0.039	0.002
Residuals[a]: R1; wR2	0.0233; 0.0356	0.0294; 0.0430	0.0184; 0.0362	0.0193; 0.0338
Absorption Correction, Max/min	0.3807/0.2429	0.4311/0.2544	0.1852/0.0949	0.5655/0.3637
Largest peak in Final Diff. Map ($e^-/Å^3$)	1.481	1.684	1.073	1.409

[a] $R1 = \Sigma hkl\,(||Fobs|-|Fcalc||)/\Sigma hkl|Fobs|$; $wR2 = [\Sigma hklw\,(|Fobs|-|Fcalc|)^2/\Sigma hklwF^2obs]^{1/2}$; $w = 1/\sigma 2(Fobs)$; $GOF = [\Sigma hklw\,(|Fobs|-|Fcalc|)^2/(ndata - nvari)]^{1/2}$.

shown in Fig. 1. This complex contains three rhenium atoms in an open cluster. There are only two metal – metal bonds. The Re(1)–Re (2) bond contains a bridging vinyl group and it is slightly shorter, 3.0231 (2) Å, than the Re(2)–Re (3) bond, 3.0684 (2) Å, which contains no bridging ligands. The Re(1)-Re(2)-Re (3) bond angle is 130.925 (6)°. Both Re–Re bonds are similar in length to the Re–Re bond distance, 3.041 (1) Å, observed in $Re_2(CO)_{10}$, [14]. The σ+π coordinated vinyl group is σ–bonded to Re2, Re(2)–C(2) = 2.165 (4) Å and π–bonded to Re1, Re(1)–C(1) = 2.372 (4) Å and Re(1)–C(2) = 2.259 (4) Å. The C–C bond in the vinyl group, C(1) – C(2) = 1.347 (6) Å is short and contains a significant amount of double bond character. Compound **3** contains a total of 50 valence electrons which is consistent with the observed open cluster structure of three metal atoms. The formation of **3** is a result of both fragmentation of the dirhenium precursor **1** and a fragmentation of the vinyl acetate reagent with a loss of the acetate group. Compound **3** was obtained in a similar yield (26%) from the reaction of **2** with vinyl acetate under slightly more forcing conditions, 48 h at 60 °C.

An ORTEP diagram of the molecular structure of compound **4** is shown in Fig. 2. Compound **4** contains a $Re_2(CO)_8$ group with a bridging acetate ligand and a bridging hydrido ligand across a Re–Re single bond, Re(1)–Re(2) = 3.3139 (4) Å. The Re–Re bond is significantly longer than the Re–Re bonds in **3** and $Re_2(CO)_{10}$ [14] due to the presence of the bridging hydrido ligand [15]. The chemical shifts for the acetate methyl group and hydrido ligand are δ = 1.93, −12.65, respectively. The acetate ligand has a μ-η^2-coordination to the rhenium atoms, Re(1)–O(1) = 2.145 (4) Å and Re(2)–O(2) = 2.161 (4) Å. There are a number of examples of similarly coordinated bridging acetato ligands in dirhenium

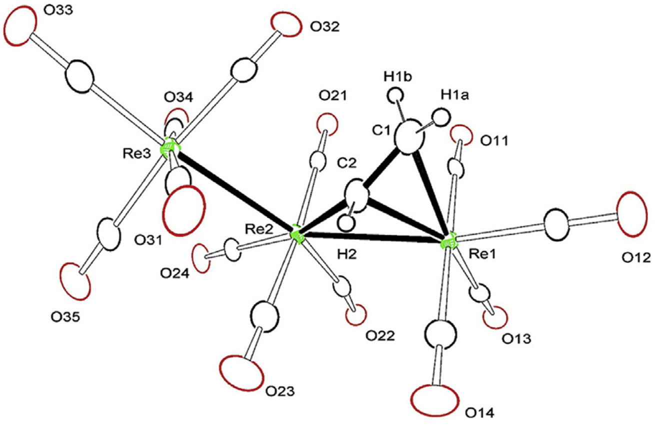


Fig. 1. An ORTEP diagram of the molecular structure of $Re_3(CO)_{13}(\mu\text{-}\eta^2\text{-}C_2H_3)$, **3**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (deg) are as follows: Re(1)–Re(2) = 3.0231 (2), Re(2)–Re(3) = 3.0684 (2), Re(1)–C(2) = 2.259 (4), Re(1)–C(1) = 2.372 (4) and Re(2)–C(2) = 2.165 (4), C(1) – C(2) = 1.347 (6), Re(1)-Re(2)-Re(3) = 130.925 (6).

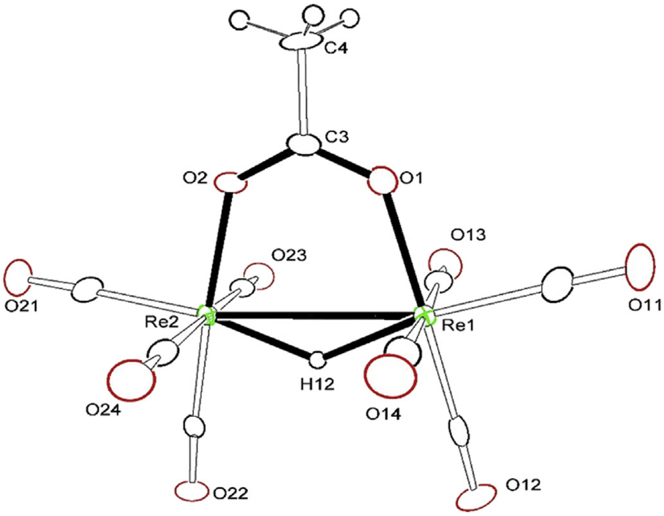


Fig. 2. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu\text{-}\eta^2\text{-}O_2CCH_3)(H)$, **4**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Re(1)–Re(2) = 3.3139 (4), Re(1)–H(12) = 1.81 (8), Re(2)–H(12) = 1.83 (7) Re(1)–O(1) = 2.145 (4) and Re(2)–O(2) = 2.161 (4).

complexes in the literature; two that are closely related to that observed in **4** were found in the complexes $Re_2(AuPPh_3)_2(\eta$-$PCy_2)(CO)_6[\mu$-$OC(Me)O]$ [16] and $Re_2Cl_4(PPh_3)_2(\mu$-$O_2CMe)$ [17]. Compound **4** contains a total of 34 valence electrons as required for a dinuclear metal complex in which both metal atoms formally have 18 electron configurations. The formation of **4** is this reaction accounts for the acetate group that was lost in the formation of compound **3**.

An ORTEP diagram of the molecular structure of **5** is shown in Fig. 3. Compound **5** contains a $Re_2(CO)_8$ group with an Re—Re bond, Re(1)—Re(2) = 3.0430 (16) Å, that is bridged by a μ-η^2-coordinated acetate-substituted vinyl group and a bridging hydrido ligand. The substituted-vinyl group is σ−coordinated to the Re2 by atom C1, Re(2)—C(1) = 2.172 (3) Å and π-coordinated to Re1, Re(1)—C(1) = 2.369 (3) Å, Re(1)—C(2) = 2.504 (3) Å and C(1)—C(2) = 1.370 (4) Å. The acetate-substituent is not coordinated to a metal atom. Compound **5** contains a total of 34 valence electrons and is electronically saturated. Compound **5** was formed by the loss of C_6H_6 from **1** and the addition of one equivalent of vinyl acetate to the $Re_2(CO)_8$ intermediate which is accompanied by a CH activation at the β−carbon atom of the vinyl group. Compound **5** decomposes when heated, but we have not been able to characterize the decomposition products due to the small amounts involved. However, we have not been able to find any evidence for the formation of compounds **3** or **4** among the decomposition products. Accordingly, it is concluded that the CH and CO cleavage reactions leading to the formation of **5** and **3** or **4** are occurring by different reaction pathways.

When compound **3** was allowed to react with I_2, the pendant $Re(CO)_5$ group was cleaved from the molecule to yield the known complex $Re(CO)_5I$ [18] and the new dirhenium complex $Re_2(CO)_8I(\mu$-η^2-$C_2H_3)$, **6** in 25% yield. Compound **6** was also characterized by IR, ^1H NMR and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **6** is shown in Fig. 4. Compound **6** contains a $Re_2(CO)_8$ group with an Re—Re single bond, Re (1)—Re (2) = 3.0120 (2) Å that is supported by a σ+π coordinated vinyl group that bridges the metal − metal bond. Atom C2 is σ-bonded to Re2, Re(2)—C(2) = 2.135 (3) Å and C1 and C2 are π-bonded to Re1, Re(1)—C(2) = 2.234 (3) Å, Re(1)—C(1) = 2.386 (3) Å. The C—C bond, C(1)—C(2) is 1.371 (4) Å is only slightly longer than the vinyl C—C bond in **3**, 1.347 (6) Å. There is an iodo ligand, I1, coordinated to Re2, Re(2)-I1 = 2.8075 (2) Å, trans to the vinyl carbon atom C2. Both rhenium atoms formally have 18 electron configurations.

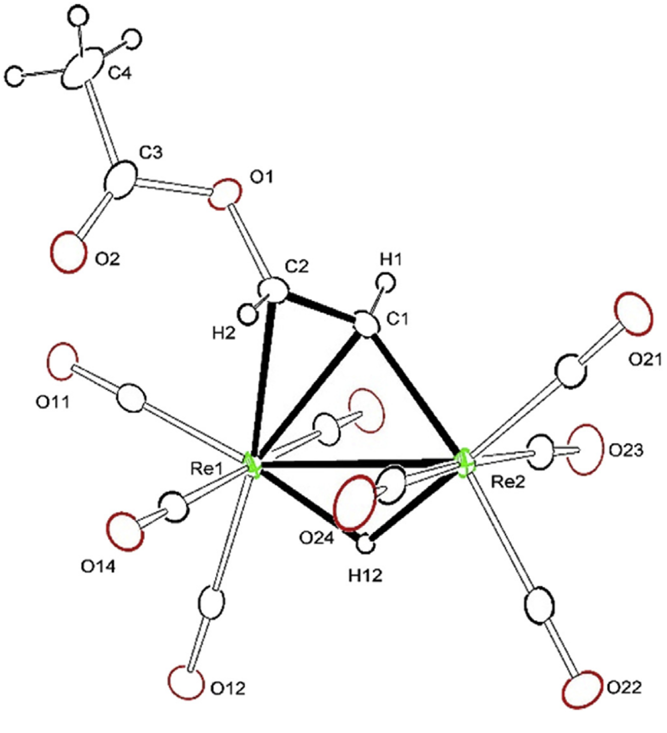


Fig. 3. An ORTEP diagram of the molecular structure of $Re_2(CO)_8(\mu$-η^2-$CHCHO_2CCH_3)(\mu$-$H)$, **5**, showing 50% thermal ellipsoid probability. Selected interatomic bond distances (Å) are as follows: Re(1)—Re(2) = 3.0430 (16), Re(1)—H(12) = 1.82 (5), Re(2)—H(12) = 1.82 (5), Re(1)—C(1) = 2.369 (3), Re(2)—C(1) = 2.172 (3), Re(1)—C(2) = 2.504 (3) and C(1)—C(2) = 1.370 (4).

4. Summary and conclusions

Compound **1** readily undergoes reductive elimination of its bridging hydrido and phenyl ligands with formation of benzene under mild conditions [19]. It is believed that this is the first step in its reaction of **1** with vinyl acetate. A transient "$Re_2(CO)_8$" intermediate then reacts with vinyl acetate by an addition at the vinyl group with oxidative addition of a CH bond at the β-carbon atom to yield the complex **5** containing a bridging acetatovinyl ligand, see Scheme 2. Concurrently, the products **3** and **4** are formed from the reaction of **1** with vinyl acetate by cleavage of the C—O bond in the vinyl acetate. Compound **5** decomposes upon mild heating but neither of the compounds **3** and **4** were observed among those products. Accordingly, it is concluded that the CH and CO cleavage reactions leading to the formation of **5** and **3** and **4** respectively are occurring by different reaction pathways. Compound **2** reacts with vinyl acetate at higher temperatures by loss of hexene to yield the compound **3**, but the compounds **4** and **5** were not obtained from this reaction. The $Re(CO)_5$ group was cleaved from the complex **3** by reaction with I_2 to yield the iodo-dirhenium complex **6** containing a bridging vinyl group and $Re(CO)_5I$.

Accession codes

Files CCDC 1950670-1950673 with the Cambridge Crystallographic Data Centre contain the supplementary crystallographic data for the compounds **3** - **6** in this report. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The

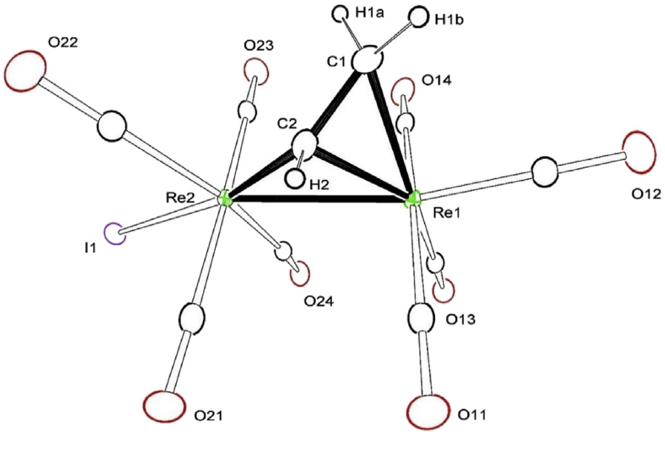
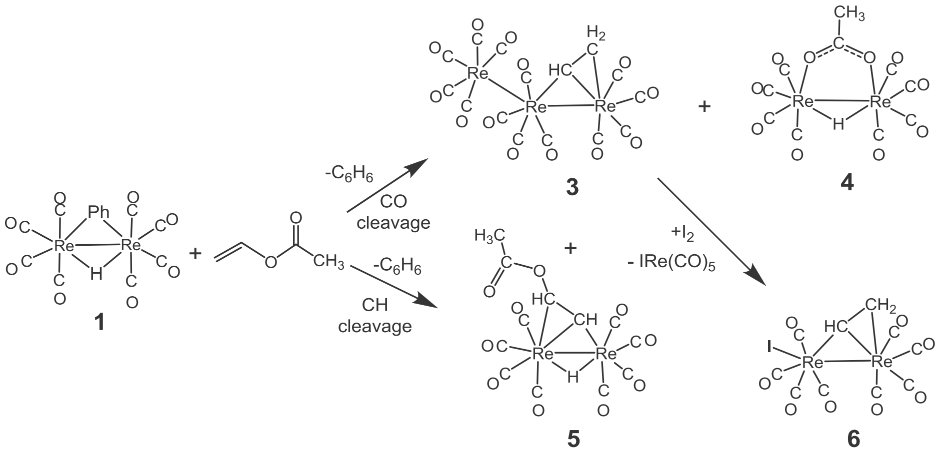


Fig. 4. An ORTEP diagram of the molecular structure of $Re_2(CO)_8I(\mu$-η^2-$C_2H_3)$, **6**, showing 40% thermal ellipsoid probability. Selected interatomic bond distances (Å) and angles (°) are as follows: Re(1)—Re(2) = 3.0120 (2), Re(2)-I1 = 2.8075 (2), Re(1)—C(2) = 2.234 (3), Re(2)—C(2) = 2.135 (3), Re(1)—C (1) = 2.386 (3), C(1)—C(2) = 1.371 (4), C2-Re2-I1 = 160.14 (8).



Scheme 2. A summary of the reactions of **1** with vinylacetate described in this report.

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Declaration of competing interest

The authors declare no competing financial interest. We are interested in publishing our manuscript in the Journal of Organometallic Chemistry. This is an original report and has not been published in whole or in part anywhere else previously.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.120969.

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