Journal of Organometallic Chemistry 979 (2022) 122490

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

C – C coupling of alkynes to the CH_2 group in a 1-phosphonioethenyl ligand in a zwitterionic dirhenium carbonyl complex

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A R T I C L E I N F O

Article history:
Received 24 July 2022
Revised 17 August 2022
Accepted 18 August 2022
Available online 21 August 2022

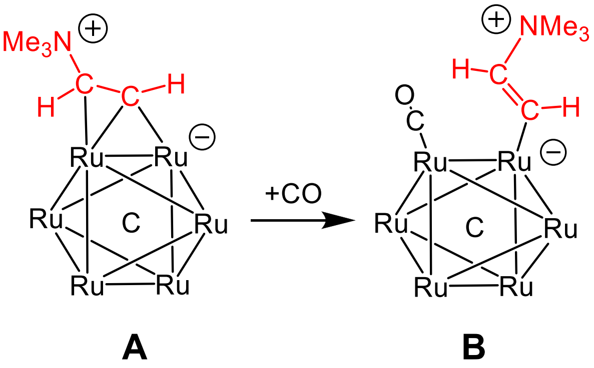
Keywords:
Zwitterion
Phosphonioethenyl
Dirhenium
Carbon-carbon coupling
P – C bond cleavage
Dynamical exchange
CH bond activation

A B S T R A C T

Reactions of the zwitterionic dirhenium complex $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}1\text{-}C(CH_2)(PMePh_2)]$, **3** with the terminal alkynes, $HC\equiv C(OEt)$ and $HC\equiv CPh$, have yielded two new isomeric ethoxy-substituted dirhenium complexes, $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)C(OCH_2CH_3)CH_2C(PMePh_2)]$, **5** and $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(OCH_2CH_3)C(H)CH_2C(PMePh_2)]$, **6** and one phenyl-substituted dirhenium complex $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)CPhCH_2C(PMePh_2)]$, **7**, respectively, with each containing a bridging, substituted 1-phosphonio-3,4-butenyl ligand formed by loss of CO and the addition and coupling of one alkyne to the CH_2 group of the 1-phosphonioethenyl ligand in **3**. The bridging 1-phosphonio-3,4-butenyl ligand in compound **6** exhibits a dynamical “flip-flop” exchange for the phosphonio-3,4-butenyl ligand between the two rhenium atoms that leads to an averaging of the inequivalent protons on its methylene group that is rapid on the NMR timescale. When heated to 70°C, compound **5** was converted to two new compounds: $Re_2(CO)_6(\mu\text{-}H)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHC(PMePh_2)]$, **8**, by loss of a CO ligand and a CH activation at the CH_2 group in its $C(H)C(OCH_2CH_3)CH_2C(^+PMePh_2)$ ligand and an isomer $Re_2(CO)_6(PMePh_2)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHCH]$, **9**. Compound **9** was also obtained from **8** by heating to 80 °C for 5 days by shifting the $PMePh_2$ group from its phosphonium carbon atom in **8** to one of the rhenium atoms to become a $PMePh_2$ ligand in **9** and then shifting the hydrido ligand back to the same carbon atom to form a bridging η^4-2-ethoxybutadiendiyl, $[C(H)C(OCH_2CH_3)CHCH]$, ligand. All new products were characterized structurally by single-crystal X-ray diffraction analyses.

1. Introduction

In recent studies, we have prepared a number of zwitterionic ammonioethenyl ligands in hexa- and pentaruthenium metal carbonyl complexes in both bridging **A** and terminal **B** coordination modes by the combination of NMe_3 with ethyne, C_2H_2, in the presence of suitable ruthenium carbonyl cluster complexes, see Eq. (1) [1,2]. The bridging and terminal forms of these ligands can be interconverted by the addition and elimination of CO ligands to the metal atoms.



(1)

We have also prepared the first examples of zwitterionic ammonioethenyl ligands in dirhenium carbonyl complexes and have shown that the NMe_3 group can be replaced by a tertiary-phosphine group to yield dirhenium complexes containing 2-phosphonioethenyl ligands, e. g. Eq. (2) [3].

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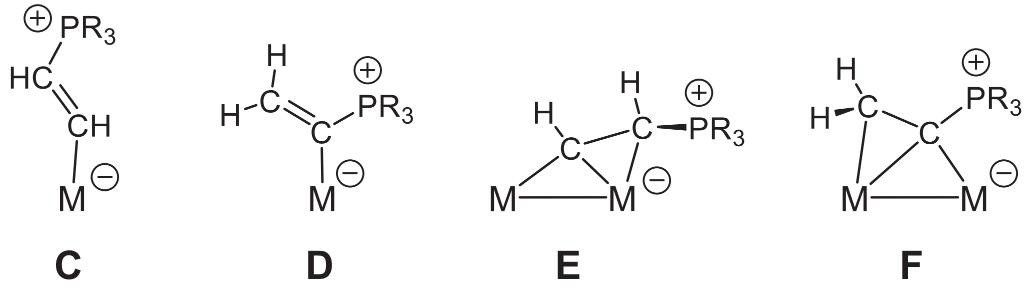
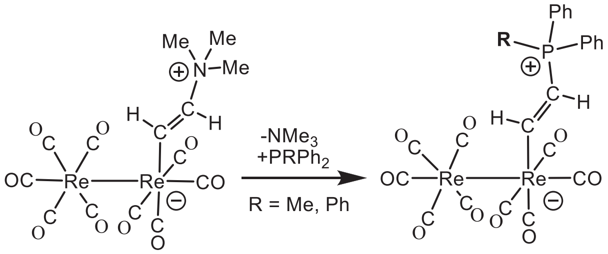
https://doi.org/10.1016/j.jorganchem.2022.122490



Structures of various phosphonioethenyl ligands.

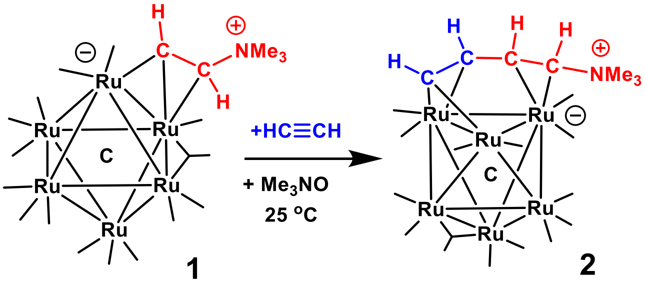


(2)

Zwitterionic phosphorus and sulfur ylides are valuable reagents in organic synthesis [4–6]. Ammonium ylides are less stable then their phosphonium- and sulfonium homologs, but recent studies have shown that they can be important intermediates in organic transformations [7]. Recently, metal containing zwitterions and ylides have been reported to exhibit useful reactivity for organic syntheses [8].

Phosphonioethenyl ligands are known exist in two isomeric forms: the 2-phosphonioethenyl ligand **C** [3,9] and the 1-phosphonioethenyl ligand **D** [3,10]. Both forms are known to exist in η^2-bridging forms, **E** [11] and **F** [3,12] formed by coordination of the π-bond of the olefinic group when two metal atoms M are present. These ligands may also have the ability to serve as intermediates in organic syntheses.

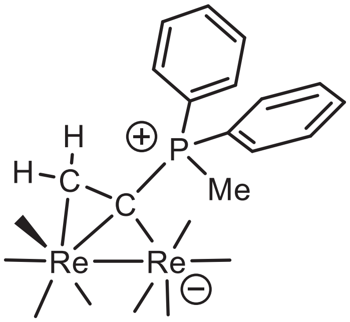
We have recently shown that ethyne (C_2H_2) can be coupled to the bridging ammonioethenyl ligand, η^2-CHCH($^+NMe_3$), in the complex $Ru_6(\mu_6\text{-}C)(CO)_{14}[\mu\text{-}\eta^2\text{-}CHCH(NMe_3)]$, **1** to form a triply-bridging η^4-trimethylammoniobutadienyl ligand, (μ_3-η^4-CHCHCHCH$^+NMe_3$), in the zwitterionic complex $Ru_6(\mu_6\text{-}C)(CO)_{14}[\mu_3\text{-}\eta^4\text{-}C_4H_4(NMe_3)]$, **2** by formation of a C – C bond, Eq. (3) [1].



(3)

Our current studies have been focused on reactions of the bridging 1-phosphonioethenyl ligand **F** in the dirhenium complex $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(CH_2)(PPh_2Me)]$, **3** [3] with two alkynes, HC≡C(OEt) and HC≡CPh, which yield new products by the coupling of the alkynes to the CH_2 group of the 1-phosphonioethenyl ligand.

The synthesis, structures and chemistry of these new dirhenium complexes are described in this report.



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2. Experimental section

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 Bruker AVANCE III-HD 300 spectrometer operating at 300.1 MHz. ^{31}P NMR spectra were recorded on a Bruker AVANCE III-HD 300 operating at 121.5 MHz. Variable temperature ^1H NMR spectra were run on a Bruker AVANCE III-HD 400 spectrometer operating at 400.02 MHz in toluene-d_8 solvent using the toluene-methyl resonance as the reference point. The $^1H\{^{13}C\}$ HSQC results were obtained on a Bruker AVANCE III-HD 500 spectrometer at 500.12 MHz and 125.78 MHz respectively using the vendor supplied pulse sequence (in Topspin 3.6.1). Mass spectral (MS) measurements performed by using a direct-exposure probe with electron impact ionization (EI) were made on a VG 70S instrument. $Re_2(CO)_{10}$, trimethylamine N-oxide, methyldiphenylphosphine, ethoxyacetylene, HC≡C(OEt), and phenylacetylene HC≡CPh were obtained from Pressure Chemicals, Tokyo Chemical Industry and Sigma-Aldrich Chemical Company, respectively. The compound $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(CH_2)(PPh_2Me)]$, **3** was prepared by the previously reported procedure [3]. All purchased reagents were used as received without further purification. Product separations were performed by TLC in air on Analtech 0.25 or 0.50 mm silica gel 60 Å F_{254} glass plates unless specified otherwise.

2.1. Reaction of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(CH_2)(PPh_2Me)]$, 3 with HC≡C(OEt)

A 19.0 mg (0.023 mmol) amount of **3** and 30 µL of HC≡C(OEt) (0.125 mmol) were dissolved in 1.5 mL of toluene-d_8 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 70 °C for 15 h. A ^1H NMR spectrum obtained after this period showed resonances at δ = 3.2–3.6, 1.6–2.0 and 0.9–1.2. The contents were then transferred to a flask and the solvent was removed in *vacuo*. The residue was extracted with CH_2Cl_2 and initially separated by TLC on silica gel by using a 3:1 hexane/CH_2Cl_2 (v/v) solvent mixture to give in order of elution: a colorless band of $Re_2(CO)_7(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}(CH_2C)P(Ph)Me(o\text{-}C_6H_4)]$, **4**, 2.0 mg (11% yield) [3]; and a mixture of two isomers, $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)C(OCH_2CH_3)CH_2C(PMePh_2)]$, **5** and $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(OCH_2CH_3)C(H)CH_2C(PMePh_2)]$, **6**, (combined total of 10.0 mg) and a yellow band of unreacted **3**, 2.0 mg.

Separation of Isomers, **5** and **6**.

The 10.0 mg mixture of the two isomers of **5** and **6** was dissolved in CH_2Cl_2 and separated by TLC on alumina (0.25 mm plates) by using hexane to yield two yellow bands which were obtained in order of elution: 4.0 mg of **5**, (20% yield) and 1.5 mg **6** (8% yield). Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane): 2067 (m), 2008 (s), 1988 (m), 1945(sh), 1941 (m), 1916 (m), 1896 (m). ^1H NMR (in toluene-d_8): δ = 7.41–7.00 (m, 2Ph), 5.36 (d, 2H, $^2J_{P\text{-}H}$ = 4.2 Hz, $CC\mathbf{H_2}C(OEt)CH$), 4.54 (s, 1H, $CCH_2C(OEt)C\mathbf{H}$), 3.32 (q, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, $COC\mathbf{H_2}CH_3$), 1.64 (d, 3H, $^2J_{P\text{-}H}$ = 12.3 Hz, $PC\mathbf{H_3}$), 1.00 (t, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz, $OCH_2C\mathbf{H_3}$). ^{31}P NMR (in CD_2Cl_2): δ = 31.61. Mass Spec. EI/MS *m*/*z*: 864, M^+, 836, M^+-CO, 808, M^+-2CO, 780, M^+-3CO. This isotope distribution pattern is consistent with the presence of two rhenium atoms. Spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane): 2070 (m), 2035 (w), 2009 (s), 1996 (m), 1950 (m), 1918 (m), 1900 (m). ^1H NMR (in CD_2Cl_2): δ = 7.7 – 7.5 (m, 10H, 2Ph), 5.22 (d, 1H, $^2J_{P\text{-}H}$ = 6 Hz, $CH_2C\mathbf{H}COEt$), 4.71 (d, 2H, $^2J_{P\text{-}H}$ = 3 Hz, $C\mathbf{H_2}CHCOEt$), 3.60 (q, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, $COC\mathbf{H_2}CH_3$), 1.98 (d, 3H, $^2J_{P\text{-}H}$ = 12 Hz, $PC\mathbf{H_3}$), 2.21 (t, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz, $COCH_2C\mathbf{H_3}$). ^{31}P NMR (in CD_2Cl_2): δ = 29.99. Mass Spec. EI/MS *m*/*z*: 864, M^+, 836, M^+-CO. This isotope distribution pattern is consistent with the presence of two rhenium atoms.

2.2. Reaction of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(=CH_2)(PPh_2Me)]$, 3 with HC≡CPh

A 10.0 mg (0.0122 mmol) amount of **3** and 3.0 µL of HC≡CPh (0.0273 mmol) was dissolved in 1.5 mL of toluene-d_8 in a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then allowed to stand for 9 h at 70 °C. A ^1H NMR spectrum obtained after this period showed resonances at δ = 2.0–2.04 and 5.50–5.52. The contents were then transferred to a flask and the solvent was removed in *vacuo*. The residue was extracted with CH_2Cl_2 and separated by TLC by using 2:1 hexane/CH_2Cl_2 (v/v) solvent mixture to give in order of elution: a bright yellow band of $Re_2(CO)_7(\mu\text{-}H)[\mu\text{-}\eta^3\text{-}C(H)CPhCH_2C(PMePh_2)]$, **7**, 4.0 mg (37% yield and a bright yellow band of unreacted starting material, **3**, 2.0 mg. Spectral data for **7**: IR ν_{CO} (cm^{-1} in hexane): 2072 (m), 2008 (s), 1990 (m), 1942 (m), 1910 (w). ^1H NMR (in CD_2Cl_2): δ = 7.67–7.52 (m, 10H, $P\mathbf{Ph_2}$), 7.33–7.25 (m, 5H, $C\mathbf{Ph}$), 7.29 (s, H4, 1H, $CCH_2C(Ph)C\mathbf{H}$), 5.51 (d, 2H, $^2J_{H\text{-}H}$ = 4.5 Hz, $CC\mathbf{H_2}C(Ph)CH$), 2.02 (d, 3H, $^2J_{P\text{-}H}$ = 12 Hz, $PC\mathbf{H_3}$). ^{31}P NMR (in CD_2Cl_2): δ = 31.32. Mass Spec. EI/MS *m*/*z*: 896, M^+, 868, M^+-CO, 840, M^+-2CO. This isotope distribution pattern is consistent with the presence of two rhenium atoms.

2.3. Thermal elimination of Co from 5

A 10.0 mg (0.0116 mmol) amount of **5** was dissolved in 1.5 mL of toluene-d_8 and then transferred to a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 70 °C for 48 h. A ^1H NMR spectrum obtained after this period showed resonances at δ = 3.2–3.6, 1.6–2.0 and 0.9–1.2. The contents were then transferred to a flask and the solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using 4:1 hexane/CH_2Cl_2 (v/v) solvent mixture to give in order of elution: a yellow band of $Re_2(CO)_6(PMePh_2)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHCH]$, **9** and 2.0 mg (21% yield) and a bright yellow band of $Re_2(CO)_6(\mu\text{-}H)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHC(PMePh_2)]$, **8**, 6.0 mg (62% yield). Spectral data for **8**: IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2038 (m), 1987 (s), 1958 (m), 1926 (w), 1892 (w), 1873 (sh). ^1H NMR (in CD_2Cl_2): δ = 7.53 (m, 10H, 2Ph), 6.60 (dd, 1H, $^4J_{H\text{-}H}$ = 2.7 Hz, $^3J_{P\text{-}H}$ = 21 Hz, $CC\mathbf{H}C(OEt)CH$, 5.45 (d, 1H, $^4J_{H\text{-}H}$ = 2.7 Hz, $CCHC(OEt)C\mathbf{H}$, 3.63 (m, 2H, $COC\mathbf{H_2}CH_3$), 2.34 (d, 3H, $^2J_{P\text{-}H}$ = 13.2 Hz, $PC\mathbf{H_3}$), 1.22 (t, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz, $COCH_2C\mathbf{H_3}$), −11.16 (s, 1H, hydride). ^{31}P NMR (in CD_2Cl_2): δ = 28.62. Mass Spec. EI/MS *m*/*z*: 836, M^+, 808, M^+-CO, 780, M^+-2CO, 752, M^+-3CO. The isotope distribution pattern is consistent with the presence of two rhenium atoms. Spectral data for **9**: IR ν_{CO} (cm^{-1} in hexane): 2037 (s), 1999(s), 1946 (m), 1928 (m), 1902 (sh). ^1H NMR (in CD_2Cl_2): δ = 7.45 (m, 10 H, 2Ph), 7.00 (d, 1H, $^3J_{H\text{-}H}$ = 7.8 Hz, $C\mathbf{H}CHC(OEt)CH$, 6.80 (d, 1H, $^3J_{H\text{-}H}$ = 7.8 Hz, $CHCHC(OEt)C\mathbf{H}$, 5.29 (m, 1H, $CHC\mathbf{H}C(OEt)CH$, 3.25 (q, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, ($COC\mathbf{H_2}CH_3$), 3.22 (q, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, $COC\mathbf{H_2}CH_3$), 2.17 (d, 3H, $^2J_{P\text{-}H}$ = 8.4 Hz, $PC\mathbf{H_3}$), 1.11 (t, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz, $COCH_2C\mathbf{H_3}$). ^{31}P NMR (in CD_2Cl_2): δ = −19.27. Mass Spec. EI/MS *m*/*z*: 836, M^+, 808, M^+-CO, 780, M^+-2CO, 752, M^+-3CO. The isotope distribution pattern is consistent with the presence of two rhenium atoms.

2.4. Conversion of 8 to 9

A 6.0 mg (0.0072 mmol) portion of **8** was dissolved in 1.5 mL of toluene-d_8 and then transferred to a 5 mm NMR tube. The NMR tube was evacuated and filled with nitrogen. The NMR tube was then heated to 80 °C for 5 days. The contents were then transferred to a flask and the solvent was removed in *vacuo*. The residue was extracted in CH_2Cl_2 and separated by TLC by using 2:1 hexane/CH_2Cl_2 (v/v) solvent mixture to give a yellow band of compound **9**, 2.0 mg (34% yield).

Crystallographic Analyses: Yellow single crystals of **5** and **6** were obtained by slow evaporation of solvent from solutions in hexane solvent at room temperature. Yellow single crystals of **7, 8** and **9** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions in mixtures of dichloromethane and hexane at room temperature. All the crystal data were collected at 100(2) K (except for compound **7**, 301(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) [13]. The raw area detector data frames were reduced, scaled and corrected for absorption effects by using the SAINT [13] and SADABS [14] programs. All structures were solved by using SHELXT [15]. Subsequent difference Fourier calculations and full-matrix least-squares refinements on F^2 were performed with SHELXL-2018 [15] by using OLEX2 [16].

3. Results and discussion

Three products were obtained from the reaction of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C(CH_2)(PPh_2Me)]$, **3** with ethoxyacetylene, HC≡COEt, toluene-d_8 at 70 °C for 15 h. These products have been identified as the previously reported compound $Re_2(CO)_7(\mu\text{-}H)[\mu\text{-}\eta^2\text{-}(CH_2C)P(Ph)Me(o\text{-}C_6H_4)]$, **4** [3] formed in 11% yield by the decarbonylation of **3** and a CH activation on one of the phenyl rings on the phosphonio group at an *ortho*-position and two new zwitterionic complexes, $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)C(OCH_2CH_3)CH_2C(PMePh_2)]$, **5** (20% yield) and $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(OCH_2CH_3)C(H)CH_2C(PMePh_2)]$, **6** (8% yield) which are isomers formed by loss of one CO ligand and the addition with head and tail couplings of one equivalent of ethoxyacetylene to the CH_2 group in **3**. Compound **4** has been reported previously and will not be further discussed in this report [3]. Compounds **5** and **6** are new and were characterized by a combination of IR, ^1H NMR, mass spectral and single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure compound **5** is shown in Fig. 1. Compound **5** contains two mutually-bonded rhenium atoms, Re1 - Re2 = 2.8480(3) Å that are bridged by two

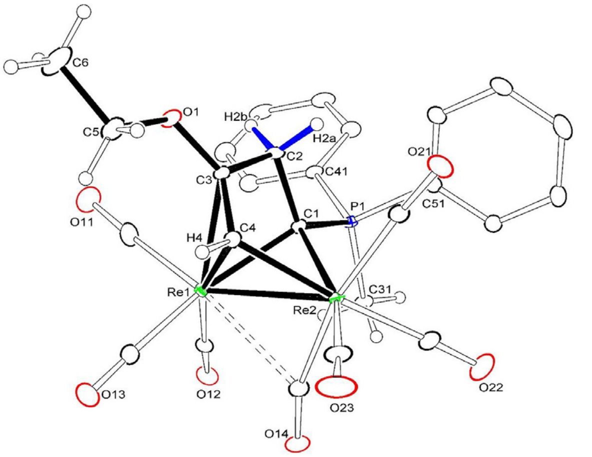


Fig. 1. An ORTEP diagram of the molecular structure of $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)C(OCH_2CH_3)CH_2C(PMePh_2)]$, **5** showing 30% thermal ellipsoid probability. Selected bond distances (Å) are as follows: Re1-Re2 = 2.8480(3), Re1-C1 = 2.194(4), Re1-C3 = 2.570(4), Re1-C4 = 2.298(4), Re2-C1 = 2.262(4), Re2-C4 = 2.207(4), C1-P1 = 1.736(4), C1-C2 = 1.541(5), C2-C3 = 1.517(6), C3-C4 = 1.368(6), C3-O1 = 1.345(5), O1-C5 = 1.442(5), C5-C6 = 1.518(7).

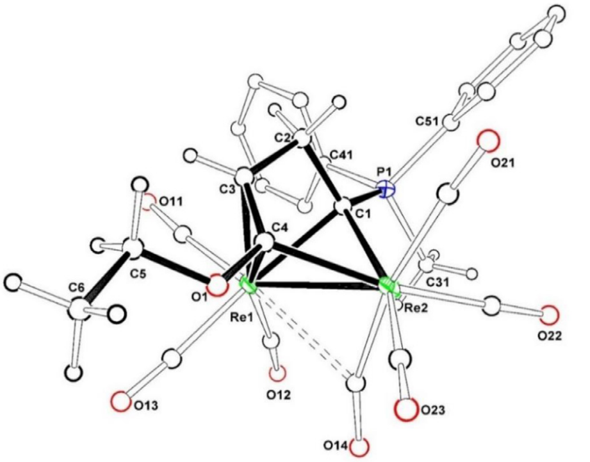


Fig. 2. ORTEP diagram of the molecular structure of $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(OCH_2CH_3)C(H)CH_2C(PMePh_2)]$, **6** showing 20% thermal ellipsoid probability. Selected bond distances (Å) are as follows: Re1-Re2 = 2.901(2), Re1-C1 = 2.167(12), Re1-C3 = 2.426(17), Re1-C4 = 2.325(18), Re2-C1 = 2.281(14), Re2-C4 = 2.213(17), C1-P1 = 1.730(15), C1-C2 = 1.53(2), C2-C3 = 1.50(2), C3-C4 = 1.26(2), C4-O1 = 1.402(18), O1-C5 = 1.410(19), C5-C6 = 1.49(2).

carbon atoms of a 3-ethoxy-1-phosphonio-3,4-butenyl ligand, $[\mu\text{-}\eta^3\text{-}C(H)C(OCH_2CH_3)CH_2C(PMePh_2)]^+$, that was formed by loss of a CO ligand and the formation of a C - C bond from the OEt substituted end of the alkyne, HC≡C(OEt), to the CH_2 group of the 1-phosphonioethenyl ligand, $(H_2CC)PMePh_2$, in **3**. Atoms C(1) and C(4) bridge both Re atoms, Re1-C1 = 2.194(4) Å, Re1-C4 = 2.298(4) Å, Re2-C1 = 2.262(4) Å, Re2-C4 = 2.207(4) Å. Atom C(3) is bonded only to Re(1) and the Re – C distance is much longer, Re1-C3 = 2.570(4) Å than the other Re – C bonds. Atom C(2) is the carbon of the CH_2 group in **3** and it has formed a bond to the OEt-substituted end of the ethoxyacetylene molecule that was added to it. Atom C(2) is tetravalent in **5** and thus, it has no bond to a rhenium atom, Re1···C2 = 2.906(4) Å. There is formally a double bond between the carbon atoms C(3) and C(4), C3-C4 = 1.368(6) Å which is π-coordinated to Re(1). The C – C bonds to atom C(2) are both single, C1-C2 = 1.541(5) Å and C2-C3 = 1.517(6) Å. There are seven carbonyl ligands in compound **5**. One of the CO ligands, C(14) – O(14), is a semibridging ligand to Re(1).

Although the protons of the methylene group at C(2) are diastereotopic, the ^1H NMR spectrum of **5** exhibits a single doublet at δ = 5.36 ($^2J_{P\text{-}H}$ = 4.2 Hz) for that group. This is believed to be the result of a dynamical exchange process that was studied in detail for its isomer compound **6**, see below. There is also a singlet at δ = 4.54 for the alkenyl hydrogen atom on atom C(4), a quartet at δ = 3.32 ($^3J_{H\text{-}H}$ = 6.9 Hz) for the methylene group of the OEt substituent, a doublet at δ = 1.64 ($^2J_{P\text{-}H}$ = 12.3 Hz) for the phosphonio methyl group PCH_3 and a triplet at δ = 1.00 ($^3J_{H\text{-}H}$ = 6.9 Hz) for the methyl group of the OEt substituent. The phosphonio phosphorus atom appears is a singlet at δ = 31.61 in the ^{31}P NMR spectrum. Compound **5** is a zwitterion. The tetravalent phosphorus atom P(1) contains a positive charge and a negative charge can formally be assigned to Re(2). Compound **5** contains a total of 34 valence electrons and each metal atom formally has an 18 electron configuration in the presence of a Re – Re single bond.

An ORTEP diagram of the molecular structure compound **6** is shown in Fig. 2. Compound **6** is an isomer of **5** formed by coupling of the unsubstituted end of a HC≡C(OEt) molecule to the CH_2 group of **3**, i.e. the OEt group is bonded to C(4) instead of C(3). Otherwise, the two isomers are virtually the same structurally. The Re – Re bond distance in **6**, 2.901(2) Å, is slightly longer by 0.062 Å than that in **5**. Except for the interchange of the OEt substituent and one H atom, the bridging 4-ethoxy-1-phosphonio-3,4-butenyl ligand, $\mu\text{-}\eta^3\text{-}C(OEt)C(H)CH_2C(PMePh_2)]^+$, is structurally and conformationally the same as that in **5**. The bond distance between the unsaturated atoms C(3) and C(4), 1.26(2) Å, in **6** is slightly shorter than that in **5**, but note the larger bond distance errors in **6** due to a minor disorder in the structural analysis of **6**.

The ^1H NMR spectrum of **6** in CD_2Cl_2 exhibits a multiplet at δ = 5.22 for the alkenyl hydrogen atom on atom C(3), a doublet at δ = 4.71 ($^2J_{P\text{-}}$= 4.7 Hz) for the CH_2 group at atom C(2) , a quartet at δ = 3.60 ($^3J_{H\text{-}H}$ = 6.9 Hz) for the methylene group of the OEt substituent, a doublet at δ = 1.98 ($^2J_{P\text{-}H}$ = 12 Hz) for the phosphonio methyl group PCH_3, and a triplet at δ = 2.21 ($^3J_{H\text{-}H}$ = 6.9 Hz) for the methyl group of the OEt substituent. The decoupled phosphonio phosphorus atom appears as a singlet at δ = 29.99 in the ^{31}P NMR spectrum. Interestingly, the protons of the CH_2 group on carbon C(2) are diastereotopic, but their resonances appear as a broadened (P-decoupled) singlet at 25 °C. Suspecting that this simple resonance could be the result of a dynamical exchange process that is rapid on the ^1H NMR timescale at room temperature, a variable temperature study was performed on **6** in a solution in toluene-d_8 solvent. A stacked plot of the ^1H NMR spectra of compound **6** at temperatures from −90 °C to + 65 °C in the range 2.7–5.5 ppm is shown in Fig. 3. This CH_2 resonance is observed at 4.66 ppm at 25 °C. As the temperature is lowered, this resonance broadens and collapses into the baseline at −35 °C and two new broad resonances emerge from the baseline at 4.15 and 5.19 ppm at −75 °C and resolve to two broad doublets at −90 °C. Interestingly, the quartet for the OCH_2 group of the OEt substituent at 3.4 ppm at 25 °C also broadens as the temperature is lowered and resolves into two broad resonances at 2.96 ppm and 3.18 ppm at −90 °C. Both observations can be explained by a slowing of an intramolecular exchange process involving the diastereotopic protons of the CH_2 groups at C(2) and in the OEt substituent.

A dynamical-exchange mechanism that can explain the simultaneous averaging of the protons on both methylene groups is shown in Scheme 1. By breaking the bond between the atoms Re(1) and C(3) shown in Fig. 2 and moving the semi-bridging CO ligand to a symmetrical bridging position across the Re – Re bond, an Intermediate **6′** is formed that has mirror-symmetry perpendicular to the Re – Re bond. Then, by reforming an equivalent Re – C bond between Re(2) and C(3) the enantiomer **6*** of **6** is formed and the environments of hydrogen atoms on the methylene car-

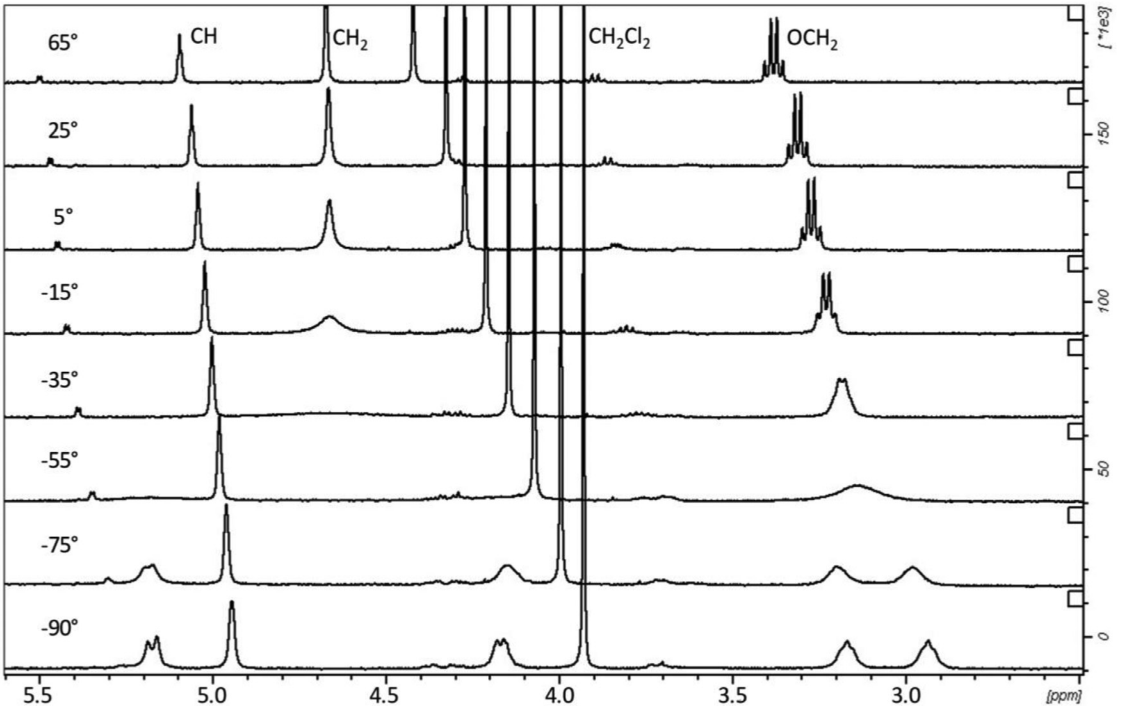


Fig. 3. A stacked plot of the ^{1}H NMR spectra of compound **6** in toluene-d$_8$ solvent at various temperatures in the range 2.7 – 5.5 ppm, ref. was the toluene-methyl resonance. The sample contains a trace of CH_2Cl_2 which exhibits a temperature dependent shift from 3.93 ppm at −90 °C to 4.40 ppm at 65 °C.

bon atoms C(2) and C(5) are exchanged. This back and forth “flip-flop” motion of the alkenyl carbon C(3) and the semi-bridging CO ligand can be repeated indefinitely. From the coalescence temperature (−35 °C) of the resonances of the hydrogen atoms on C(2) and the calculated rate of their exchange of 888 s^{-1} by using the equation $k = \pi\Delta/\sqrt{2}$, (Δ = chemical shift difference between the peaks in Hz at −90 °C, the free energy of activation $\Delta G^{\ddagger}_{238}$ for the exchange process was calculated to be 10.6 kcal/mol, by using the Eyring equation. A similar dynamical process can be used to explain the observation of a singlet and single quartet for the corresponding methylene resonances in compound **5**.

Compound **6** is a zwitterion like **5**. The phosphorus atom P(1) contains a positive charge and the negative charge can formally be assigned to Re(2). Compound **6** contains a total of 34 valence electrons and each metal atom formally has an 18 electron configuration. A schematic of the three products obtained from the reaction of **3** with HC≡C(OEt) is shown in Scheme 2.

The compound $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)CPhCH_2C(PMePh_2)]$, **7** was obtained from the reaction of **3** with HC≡CPh at 70 °C for 9 h. An ORTEP diagram of the molecular structure of **7** is shown in Fig. 4. Compound **7** is structurally analogous to compound **5** except that there is a phenyl group on the carbon C(3) instead of an OEt group. The Re – Re distance of 2.8548(2) Å and the Re – C distances to the bridging $\eta^3\text{-}C(H)CPhCH_2C(PMePh_2)$ ligand, Re1-C1 = 2.253(4), Re1-C4 = 2.188(4), Re2-C1 = 2.193(4), Re2-C3 = 2.470(4), Re2-C4 = 2.283(4), are similar to those in **5**. At 500 MHz the ^{1}H NMR spectrum of **7** exhibits second order multiplets between δ = 7.67–7.52 for the two phenyl rings on the phosphonio phosphorus atom P1, (PPh_2). The ortho and meta resonances are overlapped near 7.63 ppm, while the resonance of the para proton is centered at δ = 7.545. There is a second set of second order multiplets between δ = 7.33–7.25 (5H) for the phenyl ring on the carbon atom C(3). The ortho and meta protons are overlapped near δ = 7.31 and the para resonance is centered at δ = 7.250. There is a singlet at δ = 7.28 (1H) for the hydrogen atom on the bridging carbon C(4), a doublet at δ = 5.51 (2H, $^2J_{P\text{-}H}$ = 4.5 Hz) for the phosphorus-coupled methylene group at C(2) and a doublet at δ = 2.02 (3H, $^2J_{P\text{-}H}$ = 12 Hz) for the methyl group on the phosphonio phosphorus atom. The phosphorus resonance itself occurs at δ = 31.32 in the ^{31}P NMR spectrum. The identity of the hydrogen resonance on atom C(4) (δ = 7.28) was confirmed by a $^1H\{^{13}C\}$ HSQC (Heteronuclear Single Quantum Coherence) experiment which showed a correlation to a ^{13}C resonance at δ = 123.3 ppm that was well resolved from the three resonances of the phenyl group attached to bridging carbon C(3), see Fig. S11 in the Supplementary Data accompanying this report.

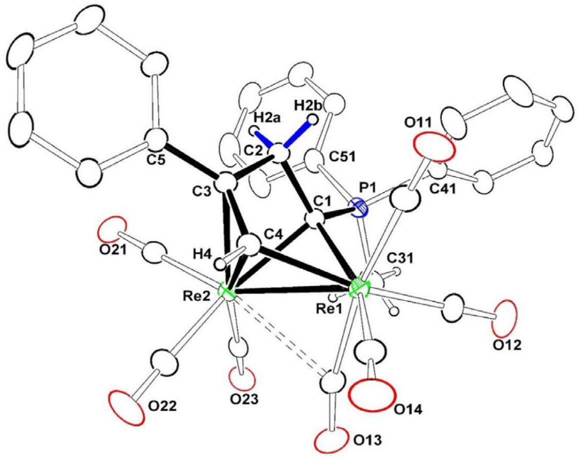


Fig. 4. An ORTEP diagram of the molecular structure of $Re_2(CO)_7[\mu\text{-}\eta^3\text{-}C(H)CPhCH_2C(PMePh_2)]$, **7** showing 15% thermal ellipsoid probability. Selected bond distances (Å) are as follows: Re1-Re2 = 2.8548(2), Re1-C1 = 2.253(4), Re1-C4 = 2.188(4), Re2-C1 = 2.193(4), Re2-C3 = 2.470(4), Re2-C4 = 2.283(4), C1-P1 = 1.730(4), C1-C2 = 1.536(5), C2-C3 = 1.525(6), C3-C4 = 1.365(5), C3-C5 = 1.484(5).

Upon heating to 70°C for 48 h in toluene-d$_8$ solvent, compound **5** was decarbonylated and converted to two new compounds:

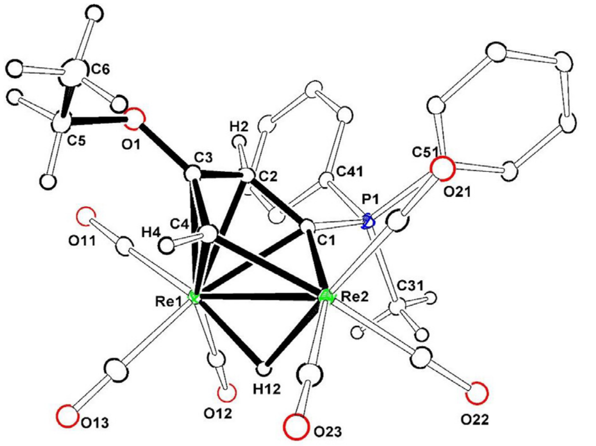


Fig. 5. An ORTEP diagram of the molecular structure of $Re_2(CO)_6(\mu\text{-}H)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHC(PMePh_2)]$, **8** showing 25% thermal ellipsoid probability. Selected bond distances (Å) are as follows: Re1-Re2 = 2.89183(14), Re1-H12 = 1.89(4), Re1-C1 = 2.299(2), Re1-C2 = 2.296(2), Re1-C3 = 2.386(2), Re1-C4 = 2.358(2), Re2-H12 = 1.89(4), Re2-C1 = 2.185(2), Re2-C4 = 2.182(2), C(1) – P(1) = 1.773(2), C1-C2 = 1.409(3), C2-C3 = 1.455(3), C3-C4 = 1.388(3), C3-O1 = 1.355(3), O1-C5 = 1.445(3), C5-C6 = 1.512(4).

$Re_2(CO)_6(\mu\text{-}H)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHC(PMePh_2)]$, **8**, (62% yield) and $Re_2(CO)_6(PMePh_2)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHCH]$, **9**, (21% yield). Both compounds were characterized by IR, NMR, mass spectral and single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of **8** is shown in Fig. 5. Compound **8** contains a bridging phosphonio-(3-ethoxy)butadiendiyl ligand $\eta^4\text{-}C(H)C(OCH_2CH_3)CHC(PMePh_2)]^+$ that was formed by the activation of one of the CH bonds on the CH_2 group of **5** with transfer of the hydrogen atom to the rhenium atoms to become a bridging hydrido ligand. The hydrido ligand was located and refined in the structural analysis, Re1-H12 = 1.89(4) Å, Re2-H12 = 1.89(4) Å, and was observed as a high-field resonance in the ^1H NMR spectrum at $\delta = -11.16$. The Re – Re bond distance in **8** is 2.89183(14) Å in length which is 0.0439(1) Å longer than that in **5** due to the presence of the bridging hydrido ligand [17]. All four carbon atoms in the phosphonio-(3-ethoxy)butadiendiyl ligand in **8** are π-bonded to rhenium atom Re(1), Re1-C1 = 2.299(2) Å, Re1-C2 = 2.296(2) Å, Re1-C3 = 2.386(2) Å and Re1-C4 = 2.358(2) Å. Atoms C(1) and C(4) are also σ-bonded to Re(2), Re2-C1 = 2.185(2) Å and Re2-C4 = 2.182(2) Å and there is a positively-charged phosphonio group, $^+PMePh_2$, bonded to atom C(1), C(1) – P(1) = 1.773(2) Å. The phosphorus resonance was observed at $\delta = 28.62$ in the ^{31}P NMR spectrum. The hydrogen atoms H(2) and H(4) on the butadienyl chain were observed at $\delta = 6.60$ ($^4J_{H\text{-}H} = 2.7$ Hz, $^3J_{P\text{-}H} = 21$ Hz) and 5.45 ($^4J_{H\text{-}H} = 2.7$ Hz), respectively in the ^1H NMR spectrum. Compound **8** is also a zwitterion with a positive charge on the phosphorus atom P(1) and a negative charge formally located on Re(2). Both rhenium atoms in **8** formally have 18 electron configurations.

When heated to 80°C for 5 days, compound **8** was converted to **9** in 34% yield. An ORTEP diagram of the molecular structure of **9** is shown in Fig. 6. Compound **9** contains two mutually-bonded rhenium atoms and a bridging 2-ethoxybutadiendiyl, $\eta^4\text{-}C(H)C(OCH_2CH_3)CHCH]$, ligand. The Re – Re bond distance, Re1-Re2 = 2.8388(2) Å, is significantly shorter, 0.053(1) Å, than that in **8**, because there is no hydrido ligand bridging the Re – Re bond [17]. The four carbon atoms in the (2-ethoxy)butadiendiyl ligand are π-bonded to rhenium atom Re(2): Re2-C1 = 2.2593(19) Å, Re2-C2 = 2.3804(18) Å, Re2-C3 = 2.3618(19) Å, Re2-C4 = 2.2805(18) Å, and atoms C(1) and C(4) are also σ-bonded to Re(1): Re1-C1 = 2.1680(18) Å and Re1-C4 = 2.1902(18) Å. The C – C bonds exhibit the short/long/short bonding pattern, C1-C2 = 1.395(3), C2-C3 = 1.457(3), C3-C4 = 1.387(2) that is characteristic of diendiyl ligands. There are six CO ligands in **9**; one of them, C(13) – O(13), is a semi-bridging ligand across the Re – Re bond. Interestingly, there is a $PMePh_2$ ligand coordinated to atom Re(1), Re1-P1 = 2.4624(5) Å. The phosphorus resonance was observed at $\delta = -19.27$ in its ^{31}P NMR spectrum. The resonances of the three diendiyl hydrogen atoms were observed as multiplets at $\delta = 7.00$ (C**H**CHCOEtCH), 6.80 (CHCHCOEtC**H**) and 5.29 (CHC**H**COEtCH) in the ^1H NMR spectrum. Other dirhenium complexes containing similar diendiyl ligands have been obtained by the coupling of alkynes in reactions with dirhenium carbonyl complexes [18].

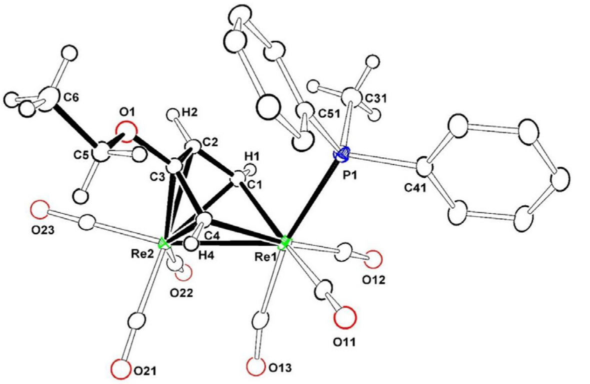
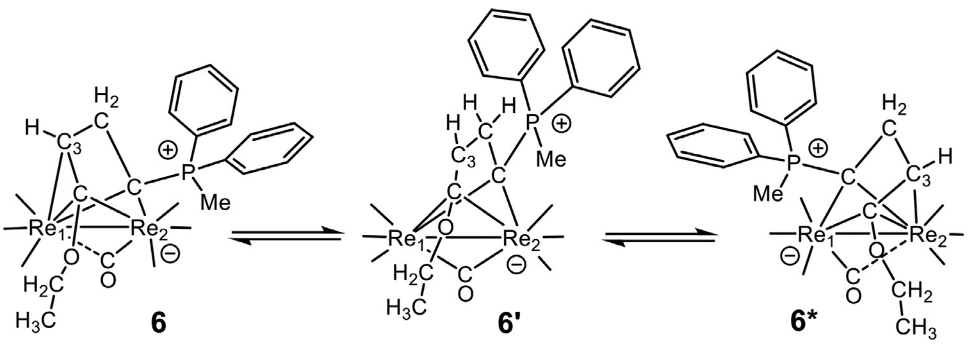


Fig. 6. An ORTEP diagram of the molecular structure of $Re_2(CO)_6(PMePh_2)[\mu\text{-}\eta^4\text{-}C(H)C(OCH_2CH_3)CHCH]$, **9** showing 40% thermal ellipsoid probability. Selected bond distances (Å) are as follows: Re1-Re2 = 2.8388(2), Re1-C1 = 2.1680(18), Re1-C4 = 2.1902(18), Re1-P1 = 2.4624(5), Re2-C1 = 2.2593(19), Re2-C2 = 2.3804(18), Re2-C3 = 2.3618(19), Re2-C4 = 2.2805(18), C1-C2 = 1.395(3), C2-C3 = 1.457(3), C3-C4 = 1.387(2), C3-O1 = 1.358(2), O1-C5 = 1.442(2), C5-C6 = 1.507(3).

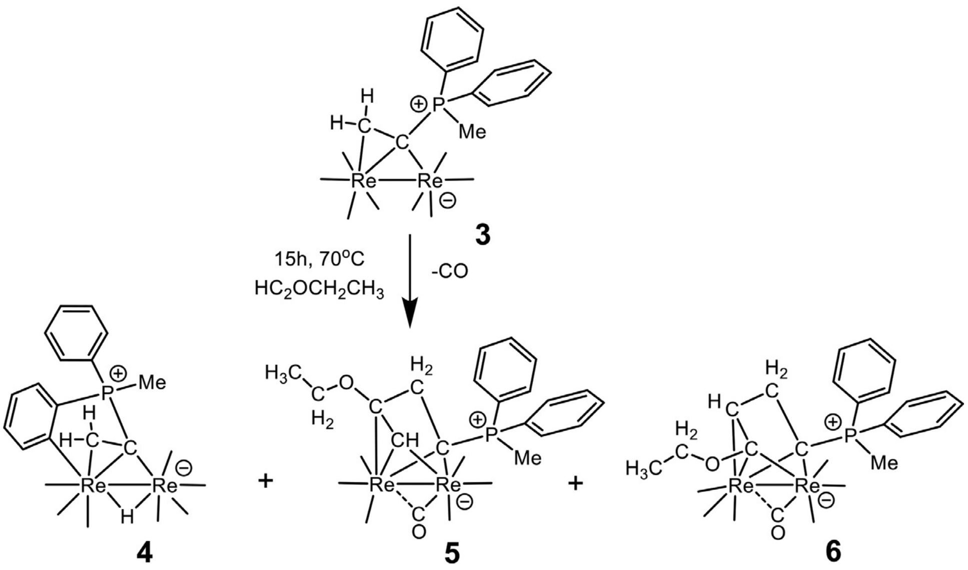
Compound **8** was formed by a loss of CO from **5** and the activation of one of the CH bonds of the CH_2 group of the $\eta^4\text{-}C(H)C(OCH_2CH_3)CH_2C(PMePh_2)$ ligand in **5**, see Scheme 3. The carbon atom C(2) then formed a bond to the rhenium atom Re(1), and the hydrogen atom was shifted to the rhenium atoms where it became a hydrido ligand bridging the Re – Re bond. Compound **9** is an isomer of **8** and was formed in two steps: 1) by shifting the $PMePh_2$ group from the carbon atom C(1) in **8** to the rhenium atom Re(1) in **9** shown in Fig. 5 to become a $PMePh_2$ ligand and 2) by shifting the bridging hydrido ligand H(12) in **8** to atom C(1) resulting in the formation of the bridging η^4-2-ethoxybutadiendiyl, $C(H)C(OCH_2CH_3)CHCH]$, ligand, see Scheme 3. Compound **9** is not a zwitterion, but both rhenium atoms in **9** still have 18 electron configurations.

4. Summary and conclusions

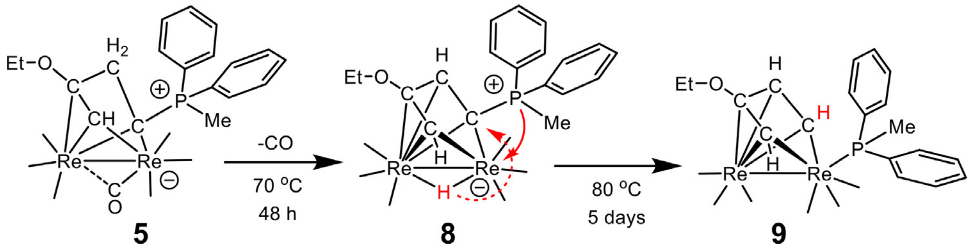
Previous studies have shown that alkynes strongly prefer to add to vinylidene ligands in mononuclear metal complexes at the unsubstituted *alpha*-carbon atom [19]. The present studies show that alkyne addition is redirected to the CH_2 *beta*-carbon atom when a tertiary-phosphine has been added to the vinylidene *alpha*-carbon atom and the ethenyl group has a bridging coordination for the resultant 1-phosphonioethenyl ligand, $H_2C{=}C(PMePh_2)$, as found in the zwitterionic dirhenium complex **3**. The CH_2 group in **3** reacts with alkynes by formation of a carbon – carbon bond to form substituted bridging 1-phosphonio-3,4-butenyl ligands across the two rhenium atoms as found in the compounds **5** – **7**. The bridging 1-phosphonio-3,4-butenyl ligand in compound **6** exhibits a dynamical "flip-flop" back and forth exchange process for the phosphonio-3,4-butenyl ligand between the two rhenium atoms that leads to



Scheme 1. A schematic of the "flip-flop" dynamical exchange of the two enantiomers **6** and **6*** via the symmetrical Intermediate **6′**.



Scheme 2. A schematic of the three products obtained from the reaction of **3** with HC≡C(OEt).



Scheme 3. A schematic of the transformation of compound **8** to compound **9** by loss of CO and rearrangements of the phosphonio-(3-ethoxy)butadiendiyl ligand. CO ligands are shown only as lines from the Re atoms.

an averaging of the inequivalent protons on its methylene group that is rapid on the NMR timescale at room temperature. A facile thermal loss of CO from **5** leads to the activation of one of the CH bonds on the CH_2 group with formation of a Re – C bond to yield a bridging η^4-C(H)C(OEt)CHC($PMePh_2$)] ligand and a hydrido ligand bridging the metal-metal bond in the compound **8**. When heated further, compound **8** was transformed into the isomer **9** by cleavage of the P – C bond to the $PMePh_2$ group and a shift of that group to a rhenium atom where it became a $PMePh_2$ ligand. In the course of the shift of the $PMePh_2$ group, the bridging hydrido ligand was shifted to the carbon atom from which the $PMePh_2$ group was removed to form a bridging η^4-2-ethoxybutadiendiyl ligand, μ-η^4-C(H)C(OEt)CHCH. Studies of the reactions of **3** with other unsaturated hydrocarbons are in progress.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

This research was supported by grant 1764192 from the National Science Foundation.

Supplementary materials

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Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2022.122490.

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