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Oxidative dehydrodimerization of rhenium vinylidene complex $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$: two competitive routes of coupling of σ-phenylethynyl intermediate $[(\eta^5\text{-}C_5H_5)(CO)_2Re{-}C{\equiv}CPh]^{\cdot}$. X-ray structures of rhenium mononuclear $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$ and binuclear $[(\eta^5\text{-}C_5H_5)(CO)_2Re]_2(\mu_2\text{-}C{=}C(Ph)C{\equiv}CPh)$ vinylidene compounds

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Abstract

The oxidation of the rhenium vinylidene complex $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$ (**2**) with one equivalent of $AgBF_4$ or $(C_5H_5)_2FeBF_4$ leads to the radical cation $[(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph]^{+\cdot}$ ($\mathbf{2}^{+\cdot}$) which undergoes dehydrodimerization only in the presence of triethylamine affording a mixture of the binuclear compounds $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(Ph)C(Ph){=}C{=}Re(CO)_2(\eta^5\text{-}C_5H_5)$ (**6**, 55%) and $[(\eta^5\text{-}C_5H_5)(CO)_2Re]_2(\mu_2\text{-}C{=}C(Ph)C{\equiv}CPh)$ (**9**, 22%). Both **6** and **9** are believed to arise via competitive C_β–C_β and C_β–Re couplings of the intermediate σ-phenylethynyl radicals $[(\eta^5\text{-}C_5H_5)(CO)_2Re{-}C{\equiv}CPh]^{\cdot}$ ($\mathbf{5}^{\cdot}$). The former process directly yields **6** and the latter one produces **9** after reductive elimination and a 1,2-shift of the metal containing moiety. The enthalpies of C_β–C_β (−30.3 kcal/mol) and C_β–Re (+0.3 kcal/mol) coupling processes estimated by DFT calculations are in accordance with the **6**:**9** ratio observed. The electrochemical behavior of **2**, **6**, **9** was studied by cyclic voltammetry. The X-ray structures of **2** and **9** are reported.

Keywords: Oxidative dehydrodimerization; Rhenium vinylidene complex; Cyclic voltammetry; DFT calculations; X-ray analysis

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1. Introduction

Binuclear complexes with the transition metal atoms linked by a conjugated chain of sp- and/or sp^2-carbon atoms has attracted the attention of researchers primarily as models for electron conductivity phenomena at a molecular level [1], as well as generating compounds with uses in nonlinear optics [2] and liquid crystal materials [3]. Such compounds are also promising as reagents for organic syntheses [4]. The main attention was paid to μ-1,3-butadiyne-1,4-diyl [M]—C≡C—C≡C—[M] and in the considerably lesser extent to μ-1,3-butadiene-1,4-diyl [M]—CH=CH—CH=CH—[M] and other compounds.

One of the most effective and frequently used methods for the synthesis of such binuclear compounds is a redox activated process of dimerization or dehydrodimerization of σ- and σ,π-complexes of transition metals [4a–4d,5]. In particular, it was shown that oxidative dehydrodimerization of mononuclear vinylidene

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complexes $[M]{=}C{=}C(H)R$ (**I**) to μ_2-η^1:η^1-2,3-R_2-1,3-butadiene-1,4-diylidene (μ-divinylidene) compounds $[M]{=}C{=}C(R){-}C(R){=}C{=}[M]$ (**II**) can proceed by three possible routes (Scheme 1) differing by the type of transformation of the primary oxidation product – 17-e radical cation $\mathbf{I}^{+\cdot}$.

(**1**) $\mathbf{I}^{+\cdot}$ undergoes homolytic rupture of the C_β–H bond leading to the 16-e σ-ethynyl cation $[M]^+{-}C{\equiv}CR$ ($\mathbf{III}^+$) (step (b)). The following dimerization of $\mathbf{III}^+$ to 2-butene-1,4-diylidyne dication $[M]^+{\equiv}C{-}C(R){=}C(R){-}C{\equiv}[M]^+$ ($\mathbf{IV}^{2+}$) and two-electron reduction (steps (c) and (d), respectively) result in the product **II**. Isolated instances of processes (b), (c) and (d) [5d–5f] are known. According to the route (a) + (b) + (c) + (d) the electrochemical or chemical dehydrodimerization of manganese vinylidene complex ($[M]$–$Mn(CO)_2(\eta^5\text{-}C_5H_5)$, R = Ph) can be performed without base [5f].

(**2**) $\mathbf{I}^{+\cdot}$ undergoes direct C_β–C_β coupling to the 18-e μ-η^1:η^1-2,3–R_2–butane–1,4–diylidyne intermediate $[M]^+{\equiv}C{-}CH(R){-}CH(R){-}C{\equiv}[M]^+$ ($\mathbf{V}^{2+}$); two-electron reduction of $\mathbf{V}^{2+}$ leads to the corresponding 19-e, 19-e diradicals $[M]^{\cdot}{\equiv}C{-}CH(R){-}CH(R){-}C{\equiv}[M]^{\cdot}$ ($\mathbf{V}^{\cdot\cdot}$) and finally to the formation of **II** via homolytic scission of C_β–H bond ((a) + (e) + (f) + (g)). According to this route the oxidative dehydrodimerization of the manganese complexes ($[M] = Mn(CO)_2(\eta^5\text{-}C_5Me_5)$ and $Mn(CO)(PPh_3)(\eta^5\text{-}C_5H_5)$, R = Ph), occurs [5g].

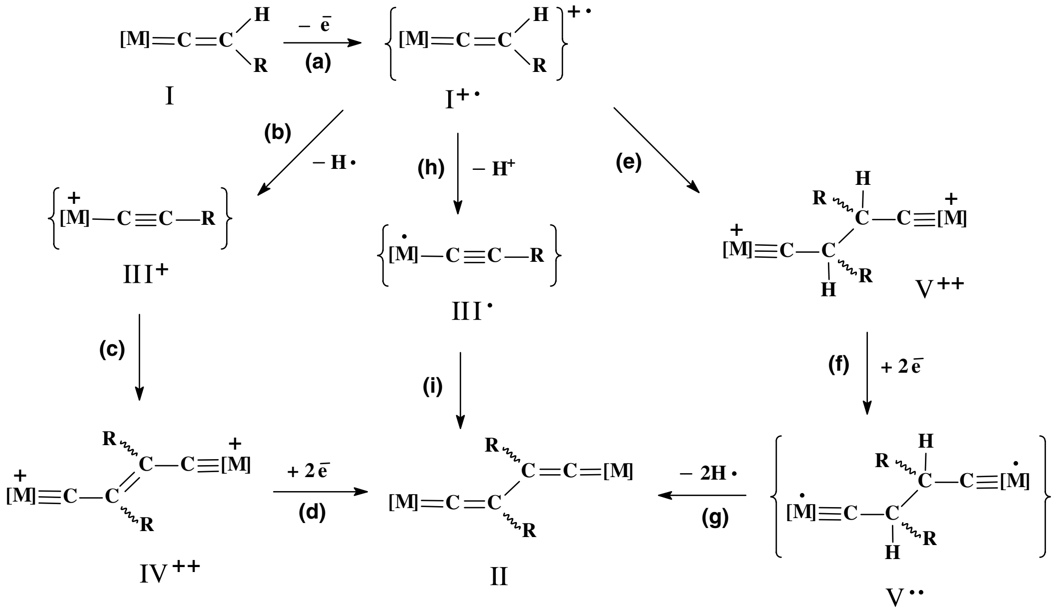
(**3**) The presence of base makes possible the dehydrodimerization through deprotonation of $\mathbf{I}^{+\cdot}$ to the radical $\{[M]{-}C{\equiv}CR\}^{\cdot}$ ($\mathbf{III}^{\cdot}$) followed by C_β–C_β dimerization of the latter (steps (h) and (i), respectively). It is this route according to which the oxidative dehydrodimerization of $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(H)Ph$ occurs in the presence of triethylamine [5f].

Earlier we have studied the oxidative dehydrodimerization of the manganese phenylvinylidene complexes $(\eta^5\text{-}C_5R_5)(CO)(L)Mn{=}C{=}C(H)Ph$ (R = H, Me; L = CO, PPh_3) [5f,5g]. In this work we developed the new method for the synthesis of the π-phenylacetylene $(\eta^5\text{-}C_5H_5)(CO)_2Re(\eta^2\text{-}PhC{\equiv}CH)$ (**1**) and phenylvinylidene $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(H)Ph$ (**2**) complexes of rhenium and studied the oxidative dehydrodimerization of **2**.

2. Results and discussion

2.1. The synthesis of the vinylidene complex 2 and the study of its oxidative dehydrodimerization

The chemistry of **2** is much less explored in comparison to its manganese analogue $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(H)Ph$ probably because of its low accessibility. The complex **2** was synthesized earlier by photochemical reaction of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ with phenylacetylene in THF at 5 °C with the overall yield 12%. The binuclear complexes **3** ((μ-η^1:η^2-2,3-diphenyl-1, 3-butadien-1-ylidene)-bis-(cyclopentadienyldicarbonylrhenium), 4.3%) and **4** ((μ_2-phenylvinylidene)-bis-(cyclopentadienyldicarbonylrhenium), 3%) were also isolated [6a]. The small yield of **2** and a laborious chromatographic separation encouraged us to develop a new more effective procedure. UV-irradiation of a cyclopentadienyltricarbonylrhenium solution in THF with the immersed lamp at −50 ÷ −15 °C resulted in the forma-



Scheme 1.

tion of (η^5-C_5H_5)$(CO)_2$Re(THF), the conversion of the initial compound being 80–90% as estimated by IR-spectroscopy (Scheme 2). The reaction of this product with phenylacetylene at room temperature led to the formation of the π-phenylacetylene complex (η^5-C_5H_5)$(CO)_2$Re(η^2-PhC≡CH) (**1**) as the main product. Compounds **2**–**4** were also formed. Usually the reaction sequence was carried out without isolation of pure **1**; it was fully characterized by spectral methods and its structure is certain.

The acetylene–vinylidene rearrangement of **1** proceeds in refluxing THF and in contrast to the relative manganese compounds [5g,6b] requires no basic catalysis. The yield of **2** in this procedure is 30% based on the initial (η^5-C_5H_5)Re$(CO)_3$. The molecular structure of **2** was determined by X-ray analysis (see Fig. 2 and the text below).

The oxidative dehydrodimerization of **2** was studied under conditions used previously for the manganese analogue (η^5-C_5H_5)$(CO)_2$Mn=C=C(H)Ph [5f]. The oxidation of **2** with one equivalent of $AgBF_4 \cdot$3dioxane in dichloromethane led to the radical cation $\mathbf{2}^{+\cdot}$. The course of the process can be conveniently IR monitored by the decrease of the intensity of 1992 (s), 1916 (s) (ν_{CO}), 1620 (w), 1588 (w) ($\nu_{C=C}$) bands of **2** and the increase of the intensity of new 2088 (s), 2032 (s) (ν_{CO}) bands of $\mathbf{2}^{+\cdot}$. According to the IR-spectroscopy data the formation of $\mathbf{2}^{+\cdot}$ proceeds quantitatively within several minutes at −20 °C. The intermediate $\mathbf{2}^{+\cdot}$ persists in solution at −5–0 °C and during 1 h no new compounds were detected; the reduction of this solution by the excess of cobaltocene regenerates the initial **2** with 79% yield. The radical cation $\mathbf{2}^{+\cdot}$ gradually decomposes at higher temperature. Under CV conditions **2** undergoes an irreversible one electron oxidation at +0.36 V (vs. F_c) (Fig. 1(a), peak A_1), no reduction peaks of dimerization products being detected by the reverse scanning of potential. The compound **2** also has an irreversible one electron reduction peak at −2.38 V (Fig. 1(a), peak A_2). Thus, in contrast to the relative manganese com-

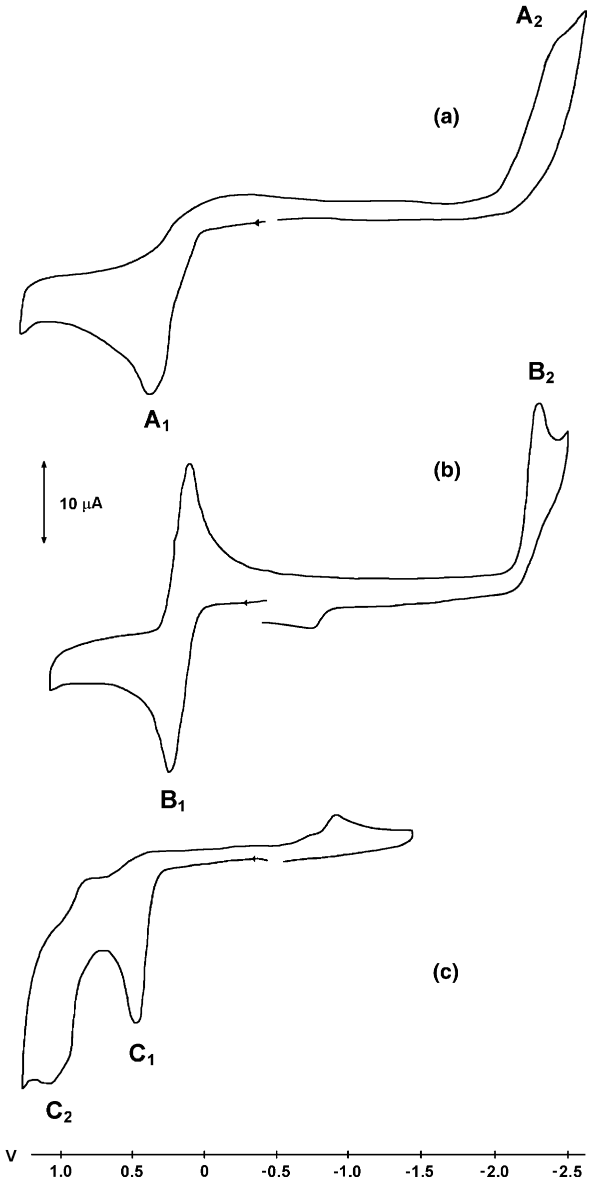
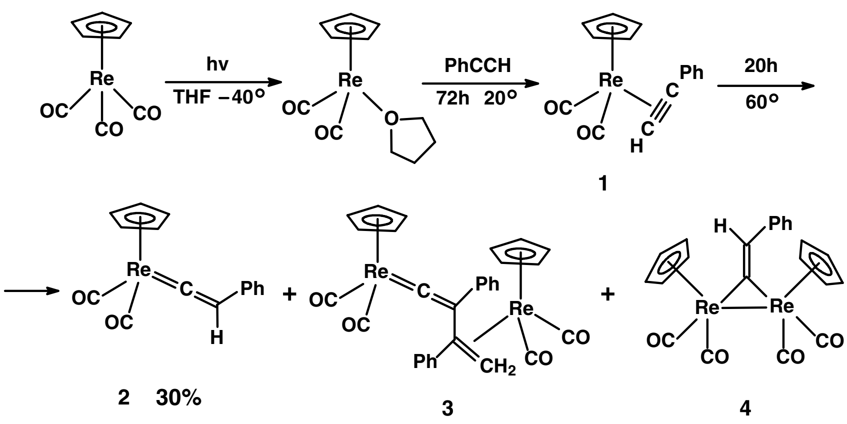


Fig. 1. Cyclic voltammograms of complexes **2** (a), **6** (b), **9** (c) (CH_2Cl_2, GC-electrode, 0.1 M Bu_4NPF_6, v = 200 mV, 2×10^{-3} M, relative to the $Cp_2Fe/Cp_2Fe^{+\cdot}$ couple (+0.46 V, ΔE = 60 mV).



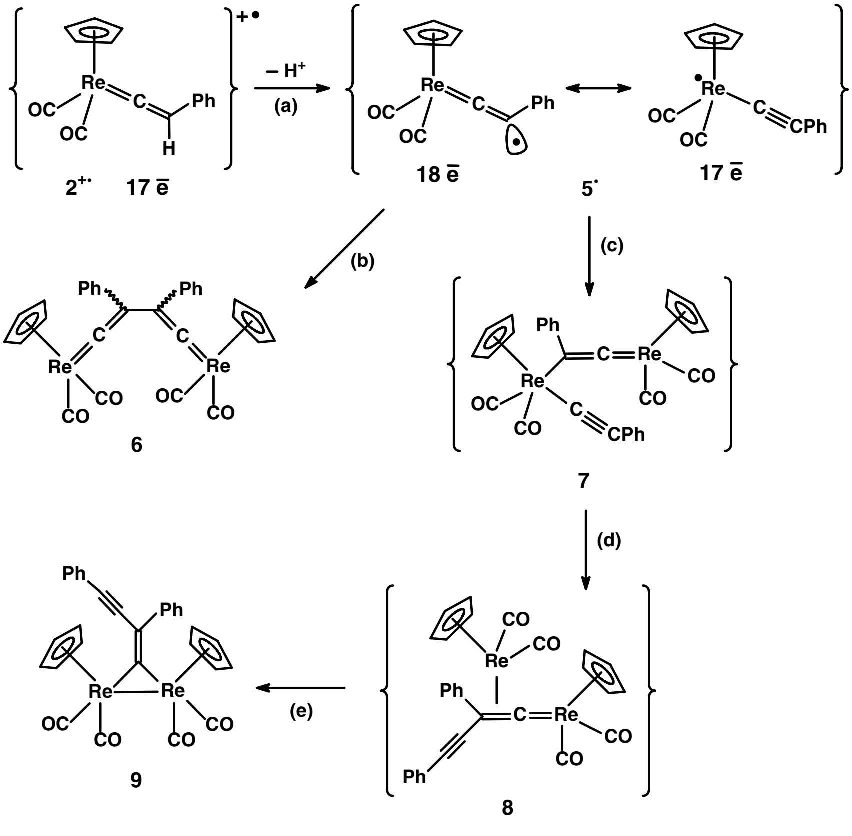
Scheme 2.

pounds the intermediate radical cation $\mathbf{2}^{+\cdot}$ does not react through the routes (1) and (2) of Scheme 1 and does not afford any dimerization products.

We obtained the dehydrodimerization products only by oxidation of **2** in the presence of base. The treatment of **2** with $[(\eta^5\text{-}C_5H_5)_2Fe]BF_4$/triethylamine couple in dichloromethane at room temperature resulted in a mixture of two isomeric binuclear complexes **6** (55%) and **9** (22%) (Scheme 3). Complexes **6** and **9** were separated by column chromatography on silica and fully characterized. The structure of **9** was established by X-ray analysis (see Fig. 3 and the text below).

Electrochemical properties of the binuclear complexes were studied by CV. The μ-divinylidene complex **6** undergoes an irreversible one electron oxidation at +0.23 V (Fig. 1(b), peak B_1) with no other oxidation peaks being observed up to +1.5 V (vs. F_c). This fact is in some discrepancy with the literature data for the structurally similar manganese μ-divinylidene complexes $(\eta^5\text{-}C_5R_5)(CO)LMn{=}C{=}C(Ph){-}C(Ph){=}C{=}MnL(CO)(\eta^5\text{-}C_5R_5)$ (R = H, L = CO, PPh_3; R = CH_3, L = CO) [4e,5f–5g] as well as with the data for silver tetrafluoroborate oxidation of **6** (**6** in dichloromethane was oxidized stepwise to the cation radical $\mathbf{6}^{+\cdot}$ and to the dication $\mathbf{6}^{2+}$). The absence of the second oxidation peak under CV conditions can be explained by the specific behavior of the cation radical $\mathbf{6}^{+\cdot}$ on the electrode surface. The voltammogram of the isomeric complex **9** shows two one electron irreversible peaks C_1 and C_2 (Fig. 1(c)) at +0.47 and +1.03 V, respectively.

The oxidative dehydrodimerization of **2** involves a deprotonation of the radical cation $\mathbf{2}^{+\cdot}$ by triethylamine (Scheme 3, step (a)) to the σ-phenylethynyl radical $\mathbf{5}^{\cdot}$ – the direct precursor of the dimeric products **6** and **9**. The structure of $\mathbf{5}^{\cdot}$ can be presented as a resonance hybrid of the metal- and carbon-centered radicals. The C_β–C_β type dimerization (step (b)) results in the expected μ-divinylidene product **6**, whereas the C–Re type one (step (c)) results in **9** after reductive elimination in **7** and a 1,2-shift of the metal moiety in **8** (steps (d) and (e), respectively). The carbon-metal couplings for the 17-e transition metal σ-alkynyl complexes were not yet described. The enthalpies of C_β–C_β ($\mathbf{5}^{\cdot} \rightarrow \mathbf{6}$, −30.3 kcal/mol) and C–Re ($\mathbf{5}^{\cdot} \rightarrow \mathbf{7}$, +0.3 kcal/mol) dimerizations were calculated by DFT method (RB3LYP/LanL2DZ) with full optimization of the geometry. Thus the predominant formation of **6** is caused by the thermodynamic preference of carbon–carbon coupling over C–Re coupling. At the same time according to the calculated data the final product of C–Re dimerization **9** is more stable than the C_β–C_β dimerization product **6** by 5.2 kcal/mol. Detailed DFT investigation of some even-



Scheme 3.

and odd-electron rhenium complexes relevant to this study is in progress and the results will be published separately.

We ascertained by a special experiment that **6** cannot be converted into **9** by the treatment with Cp_2FeBF_4/NEt_3 couple (dichloromethane, room temperature). Ferrocenium was partially converted (up to 40–45%) into ferrocene but no products of the μ-divinylidene **6** transformation were found and it was recovered almost quantitatively. We believe that the primary oxidation products $\mathbf{6}^{+\bullet}$ and $\mathbf{6}^{2+}$ were reduced to **6** by triethylamine as was found earlier for the manganese analogues of $\mathbf{6}^{+\bullet}$ and $\mathbf{6}^{2+}$, i.e. $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(Ph){-}C(Ph){=}C{=}Mn(CO)_2(\eta^5\text{-}C_5H_5)]^{n+}$ ($n = 1, 2$) [5f].

Attention should be paid to the difference in the course of the oxidative dehydrodimerizations of **2** and its manganese analogue $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(H)Ph$ in the presence of triethylamine. In the case of the manganese complex the C_β–C_β dimerization product $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(Ph){-}C(Ph){=}C{=}Mn(CO)_2(\eta^5\text{-}C_5H_5)$ is exclusively formed under these conditions [5f]. It is obvious that the C–Mn dimerization product $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(Ph){-}Mn(C{\equiv}CPh)(CO)_2(\eta^5\text{-}C_5H_5)$ is thermodynamically unfavourable, because the formation of cyclopentadienyl complexes of manganese with a four leg piano stool geometry is sterically prohibited. This assumption was confirmed by DFT calculations data, according to which the formation enthalpy of the C–Mn dimer from $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{-}C{\equiv}CPh]^\bullet$ is +70.7 kcal/mol.

2.2. X-ray study of the complexes 2 and 9

The molecular structure of **2** is presented in Fig. 2. The geometry of **2** is very close to that of the corresponding manganese compound $(\eta^5\text{-}C_5H_5)(CO)_2Mn{=}C{=}C(H)Ph$ [6b]. All bond distance and angle values (Table 1) are in a good agreement with those of analogous rhenium compounds.

Table 1
Selected bond distances (Å) and angles (°) for complex **2**

Re(1)–C(1)	1.892(14)	Re(1)–Cp	1.963(15)
Re(1)–C(2)	1.926(15)	C(8)–C(9)	1.296(18)
Re(1)–C(8)	1.912(14)	C(9)–C(10)	1.471(19)
C(1)–Re(1)–C(2)	83.6(5)	C(2)–Re(1)–Cp	125.3(6)
C(1)–Re(1)–C(8)	92.5(5)	C(8)–Re(1)–Cp	126.0(6)
C(2)–Re(1)–C(8)	91.8(6)	C(9)–C(8)–Re(1)	171.1(12)
C(1)–Re(1)–Cp	125.7(6)	C(8)–C(9)–C(10)	127.1(13)

The molecular structure of **9** is presented in Fig. 3, and selected bond distances and angles are given in Table 2. The crystal unit cell of **9** contains two independent molecules which are stereoisomers differing by mutual disposition of the cyclopentadienyl and carbonyl ligands in relation to the organometallic core. Phenyl rings in the bridging ligand are perpendicular to each other (angles between the planes are 94.2° and 93.7°

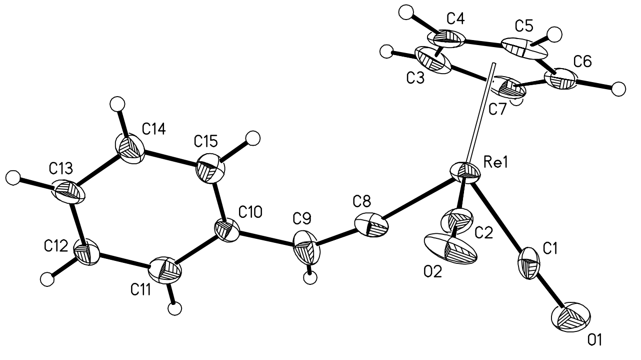


Fig. 2. Molecular structure of **2** (50% probability ellipsoids).

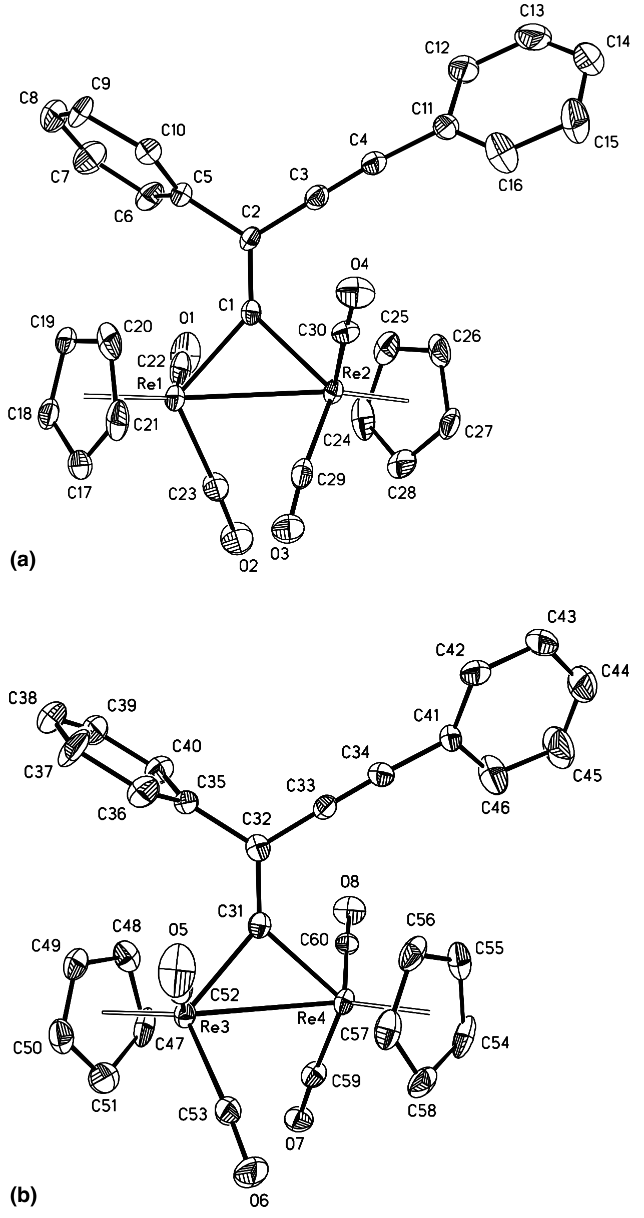


Fig. 3. Molecular structure of **9** (50% probability ellipsoids).

Table 2
Selected bond distances (Å) and angles (°) for complex **9**

Re(1)–C(1)	2.079(7)	Re(4)–C(60)	1.870(9)
Re(1)–C(22)	1.861(9)	Re(4)–C(59)	1.904(9)
Re(1)–C(23)	1.909(9)	Re(4)–Cp	1.957(8)
Re(1)–Cp	1.945(8)	Re(3)–Re(4)	2.8999(4)
Re(2)–C(1)	2.082(7)	C(1)–C(2)	1.342(9)
Re(2)–C(29)	1.892(9)	C(2)–C(3)	1.437(11)
Re(2)–C(30)	1.900(8)	C(2)–C(5)	1.495(9)
Re(2)–Cp	1.946(8)	C(3)–C(4)	1.185(10)
Re(1)–Re(2)	2.9031(5)	C(4)–C(11)	1.446(12)
Re(3)–C(31)	2.053(7)	C(31)–C(32)	1.373(10)
Re(3)–C(52)	1.856(9)	C(32)–C(33)	1.434(11)
Re(3)–C(53)	1.917(9)	C(32)–C(35)	1.498(10)
Re(3)–Cp	1.952(8)	C(33)–C(34)	1.196(10)
Re(4)–C(31)	2.072(7)	C(34)–C(41)	1.447(11)
C(1)–Re(1)–C(22)	83.0(3)	Cp–Re(2)–C(29)	124.3(3)
C(1)–Re(1)–C(23)	114.7(3)	Cp–Re(2)–C(30)	124.1(3)
C(2)–Re(1)–C(22)	99.7(2)	Cp–Re(2)–Re(1)	125.4(2)
C(2)–Re(1)–C(23)	74.8(2)	C(31)–Re(3)–C(52)	83.1(3)
C(22)–Re(1)–C(23)	83.4(4)	C(31)–Re(3)–C(53)	114.7(3)
C(1)–Re(1)–Re(2)	45.8(2)	C(52)–Re(3)–C(53)	85.9(4)
Cp–Re(1)–C(1)	116.0(3)	C(31)–Re(3)–Re(4)	45.6(2)
Cp–Re(1)–C(22)	127.4(3)	C(52)–Re(3)–Re(4)	100.9(2)
Cp–Re(1)–C(23)	122.6(3)	C(53)–Re(3)–Re(4)	74.5(2)
Cp–Re(1)–Re(2)	129.3(2)	Cp–Re(3)–C(31)	116.2(3)
C(1)–Re(2)–C(29)	113.8(3)	Cp–Re(3)–C(52)	125.3(3)
C(1)–Re(2)–C(30)	81.2(3)	Cp–Re(3)–C(53)	122.1(3)
C(29)–Re(2)–C(30)	84.0(3)	Cp–Re(3)–Re(4)	130.2(2)
C(1)–Re(2)–Re(1)	45.7(2)	C(31)–Re(4)–C(59)	113.4(3)
C(29)–Re(2)–Re(1)	78.4(2)	C(31)–Re(4)–C(60)	81.2(3)
C(30)–Re(2)–Re(1)	105.5(2)	C(59)–Re(4)–C(60)	83.7(3)
Cp–Re(2)–C(1)	117.1(3)	C(31)–Re(4)–Re(3)	45.1(2)
C(59)–Re(4)–Re(3)	79.2(2)	C(1)–C(2)–C(5)	124.1(7)
C(60)–Re(4)–Re(3)	105.9(2)	C(3)–C(2)–C(5)	116.4(7)
Cp–Re(4)–C(31)	117.1(3)	C(2)–C(3)–C(4)	178.4(9)
Cp–Re(4)–C(59)	124.8(3)	C(3)–C(4)–C(11)	175.6(9)
Cp–Re(4)–C(60)	124.2(3)	C(32)–C(31)–Re(3)	137.8(5)
Cp–Re(4)–Re(3)	124.4(3)	C(32)–C(31)–Re(4)	132.9(5)
C(2)–C(1)–Re(1)	136.7(5)	Re(3)–C(31)–Re(4)	89.3(3)
C(2)–C(1)–Re(2)	134.7(5)	C(31)–C(32)–C(33)	120.1(7)
Re(1)–C(1)–Re(2)	88.5(3)	C(31)–C(32)–C(35)	123.7(7)
C(1)–C(2)–C(3)	119.3(6)	C(33)–C(32)–C(35)	116.1(7)

for isomers **a** and **b**, respectively). The rhenium moieties in molecules of **9** are in a transoid conformation (pseudo-torsional angles Cp(1)···Re(1)–Re(2)···Cp(2) and Cp(3)···Re(3)–Re(4)···Cp(4) are 175.3° and −175.3°, respectively). The cyclopentadienyl ligand planes are almost parallel (angles between planes are 4.7° and 6.6°); cyclopentadienyl rings in the isomer **a** are in an eclipsed conformation, and in the isomer **b** are rotated of each other for 7.1°.

3. Experimental

3.1. General considerations

All operations were carried out under a purified argon atmosphere using Schlenk techniques. Reagent grade benzene and THF were dried and distilled from sodium benzophenone-ketyl prior to use. Saturated hydrocarbons, triethylamine, and dichloromethane were freshly distilled from CaH_2. Phenylacetylene was distilled in vacuo and stored under an argon atmosphere. Silica gel (70–230 mesh, 60 Å) was obtained from Aldrich Chemical. The starting $(\eta^5\text{-}C_5H_5)Re(CO)_3$ was prepared according to the described method [7]. The reagents used were either prepared by described methods ($(\eta^5\text{-}C_5H_5)_2FeBF_4$, $AgBF_4 \cdot 3(\text{dioxane})$) [8] or purchased from Aldrich Chemical ($(\eta^5\text{-}C_5H_5)_2Co$).

All photochemical procedures were performed with an immersed ultraviolet mercury lamp (125 W) under low temperature conditions ($-50 \div -15$ °C interval) using ethanol/dry ice bath.

Cyclic voltammograms were measured on a “ПИ-50-1” instrument (Gomel’, Belarus) in the dichloromethane solution with a glassy carbon working electrode ($S = 2$ mm^2), a platinum plate as an auxiliary electrode, and a SCE as a reference. 0.1 M Bu_4NPF_6 was used as the supporting electrolyte. All peak potentials are given relative to the ferrocene/ferrocenium couple ($E = +0.46$ V vs. SCE, $\Delta E = 60$ mV). The number of electrons consumed was estimated by comparison of the currents of the peaks observed with those of the one-electron decamethylferrocene/decamethylferrocenium couple of the same concentrations.

Melting points were determined in sealed capillaries under argon atmosphere. Solution IR spectra were measured on Specord M80 (Carl Zeiss Jena) instrument and given in cm^{-1} with relative intensity in parenthesis. NMR ^1H (400 MHz) and ^{13}C (100 MHz) spectra were obtained using a Bruker AMX 400 spectrometer and referenced to residual solvent protons. Elemental analyses were performed in the Laboratory of Microanalysis of A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences. EI mass-spectra (70 eV, 150 °C) were obtained using a Kratos MS 890 spectrometer. All mass-spectral data are given for ^{187}Re (correct isotope pattern was observed in all cases).

3.2. Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}CHPh$ (**2**)

A vigorously stirred solution of 800 mg (2.4 mmol) of $(\eta^5\text{-}C_5H_5)Re(CO)_3$($\nu_{CO}$ 2016 (s), 1920 (vs) cm^{-1}) in 400–500 ml of THF was irradiated at $-50 \div -15$ °C for 50 min, affording $(\eta^5\text{-}C_5H_5)Re(CO)_2(THF)$($\nu_{CO}$ 1904 (s), 1832 (s) cm^{-1}). Then 0.6 ml (0.5 mmol) of phenylacetylene was added and the reaction mixture was transferred via cannula into a 0.5 L Schlenk flask. The mixture was then refluxed until disappearance of bands of the alkyne intermediate $(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}PhC{\equiv}CH)$ (**1**) (ν_{CO} 1964 (s), 1880 (s) cm^{-1}) (18–22 h). The solvent was removed in vacuo and the resulting red–brown oil was chromatographed on silica (15 × 3 cm) under argon atmosphere. Three main fractions were consequently eluted with petroleum ether: colorless phenylacetylene (discarded), colorless $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (105 mg), and rose $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}CHPh$ (**2**) (480 mg). **2** was obtained (440 mg, 30%) as red crystals after recrystallization from hexane at −70 °C.

2: M.p. (from hexane) 82–83 °C. Anal. Found: C, 44.46; H, 3.05. Calc. for $C_{15}H_{11}O_2Re$: C, 44.01; H, 2.69%. IR (hexane, cm^{-1}): 2000 (s), 1932 (s) (ν_{CO}), 1648 (w), 1628 (br. w), 1596 (w) ($\nu_{C=C}$). ^1H NMR (C_6D_6): δ 4.47 (s, 1H, =C—H), 4.86 (s, 5H, C_5H_5), 6.99 (t, $J = 7.5$ Hz, 1H, *para*-Ph), 7.28–7.18 (t overlapping with residual benzene protons, $J = 7.8$ Hz, ~2H, *meta*-Ph), 7.32 (d, $J = 7.5$ Hz, 2H *ortho*-Ph). $\{^1H\}$ ^{13}C NMR (C_6D_6): δ 85.6 (C_5H_5), 116.0 (C_β), 121.1, 121.6, 124.6 (Ph), 125.6 (*ipso*-Ph), 194.5 (Re–CO), 326.2 (C_α). MS (EI) *m/z*: 410 (M^+), 382 ($M^+ - CO$), 354 ($M^+ - 2CO$).

3.3. Reaction of $(\eta^5\text{-}C_5H_5)(CO)_2Re(THF)$ with $PhC{\equiv}CH$ at room temperature

To a solution of $(\eta^5\text{-}C_5H_5)(CO)_2Re(THF)$ generated from 800 mg (2.4 mmol) of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ as described above 0.6 ml (0.5 mmol) of phenylacetylene was added. The reaction mixture was concentrated to 50 ml and maintained at room temperature until the bands of $(\eta^5\text{-}C_5H_5)(CO)_2Re(THF)$ (ν_{CO} 1904 (s), 1832 (s) cm^{-1}) disappeared (30–36 h). During the reaction course the bands of $(\eta^5\text{-}C_5H_5)(CO)_2Re(\eta^2\text{-}PhC{\equiv}CH)$ (**1**) (ν_{CO} 1964 (s), 1880 (s) cm^{-1}) were observed in IR spectrum together with the bands of the side products [6a]. The conditions used are optimal for preparation of **1** because at lower temperature the reaction is very slow and at higher temperature the rearrangement of the product to the vinylidene **2** proceeds faster. After the end of reaction the solvent was evaporated and the residue was dried in vacuo to remove the excess of phenylacetylene. The brown solid was extracted with hexane (5 × 10 ml), the extract was filtered through Celite, concentrated to one-fifth of the initial volume, and cooled to −20 °C. The orange solid obtained consisted of the complex **1** as the major component (~45% based on integral intensity of C_5H_5 protons) together with the unreacted $(\eta^5\text{-}C_5H_5)Re(CO)_3$ (~5%), the vinylidene complex **2** (~11%), the binuclear vinylidene-alkene compound $\{(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C{=}C(Ph){-}C(Ph){=}CH_2\}[Re(CO)_2(\eta^5\text{-}C_5H_5)]$ (**3**) (~25%), and the binuclear complex with a bridging phenylvinylidene ligand $[(\eta^5\text{-}C_5H_5)(CO)_2Re]_2(\mu\text{-}C{=}CHPh)$ (**4**) (~14%). The ratio of total integral intensities of C_5H_5 protons and Ph protons of listed compounds is close to 1:1. The isolation of pure **1** was not achieved neither by crystallization nor by column chromatography (fast decomposition of the target complex **1** was observed during chromatography on silica and alumina).

1: ^1H NMR (C_6D_6): δ 2.93 (s, 1H, C≡CH), 4.70 (s, 5H, C_5H_5), 7.13 (t, $J = 7.5$ Hz, 1H, *para*-Ph), 7.76 (d, $J = 7.5$ Hz, 2H *ortho*-Ph), signal of *meta*-Ph was overlapped with residual benzene protons. $\{^1H\}$ ^{13}C NMR (C_6D_6): δ 47.2 (PhC≡*C*H), 61.5 (Ph*C*≡CH), 83.7 (C_5H_5), 124.4, 126.5, 128.4 (Ph), 200.2 (Re–CO). MS (EI) *m/z*: 410 (M^+), 382 ($M^+ - CO$), 354 ($M^+ - 2CO$).

$(\eta^5\text{-}C_5H_5)Re(CO)_3$: ^1H NMR (C_6D_6): δ 5.72 (s, 5H, C_5H_5). $\{^1H\}$ ^{13}C NMR (C_6D_6): δ 94.9 (C_5H_5), 207.7 (Re–CO).

3: ^1H NMR (C_6D_6): δ 4.71 (s, 1H, C=CH_2), 4.94 (s, 5H, C_5H_5), 4.98 (s, 5H, C_5H_5), 5.14 (s, 1H, C=CH_2), signals of phenyl protons were not separated. $\{^1H\}$ ^{13}C NMR (C_6D_6): δ 84.0 (C=*C*H_2), 85.7 (C_5H_5), 86.1 (C_5H_5), 121.2 (C_β), 122.5, 123.2, 124.6, (Ph), 140.2 (*C*=CH_2), 192.5, 192.9 (Re–CO), 199.6, 201.0 (Re–CO).

4: ^1H NMR (C_6D_6): δ 4.40 (s, 5H, C_5H_5), 4.58 (s, 1H, C=CHPh), 4.74 (s, 5H, C_5H_5), signals of phenyl protons were not separated. $\{^1H\}$ ^{13}C NMR (C_6D_6): δ 82.4 (C_5H_5), 83.3 (C_5H_5).

3.4. Oxidative dehydrodimerization of the complex **2**

A solution of 204 mg (0.5 mmol) of **2** and 0.15 ml (1 mmol) of triethylamine in 10 ml of dichloromethane was treated with 136 mg (0.5 mmol) of $(\eta^5\text{-}C_5H_5)_2FeBF_4$ at room temperature. After 10 min the color of the solution changed from orange–red to red–brown and new bands of the μ-divinylidene complex **6** (1984 (s), 1916 (s) (ν_{CO}), 1612 (w), 1584 (w) ($\nu_{C=C}$)) and the another dimeric compound **9** (1944 (vs) (ν_{CO})) appeared in the IR spectrum instead of bands of the initial complex **2** (1992 (s), 1916 (s) (ν_{CO}), 1620 (w), 1588 (w) ($\nu_{C=C}$)). The solution was evaporated to dryness and the residue was extracted with petroleum ether until the extracts were colorless (6 × 10 ml). The combined extracts were concentrated and placed on a silica column (8 × 3 cm). Ferrocene was eluted with petroleum ether. Then the yellow fraction of complex **9** was eluted with the 1:1 benzene/petroleum ether mixture. Evaporation of the solvent and recrystallization of the crude product from hexane gave 45 mg (22%) of **9** as yellow crystals. The main dimeric product **6** was thoroughly extracted with benzene from the above residue and chromatographed (benzene). The complex **6** was obtained (110 mg, 54%) as red microcrystalline solid after solvent evaporation and reprecipitation of the residue from THF with heptane at −20 °C.

6: M.p. (THF/heptane) 238 °C (dec.) Anal. Found: C, 44.45; H, 2.62. Calc. for $C_{30}H_{20}O_4Re_2$: C, 44.12; H, 2.45%. IR (CH_2Cl_2, cm^{-1}): 1984 (s), 1916 (s) (ν_{CO}), 1612 (w), 1584 (w) ($\nu_{C=C}$). ^1H NMR (THF-d_8): δ 6.58 (s, 10H, C_5H_5) 7.71 (t, $J = 7.5$ Hz, 2H, *para*-Ph), 7.96 (t, $J = 7.8$ Hz, 4H, *meta*-Ph), 8.15 (d, $J = 7.8$ Hz, 4H *ortho*-Ph). $\{^1H\}$ ^{13}C NMR (THF-d_8): δ 91.5 (C_5H_5), 122.2, 126.2, 129.3 (Ph), 134.2 (C_β), 200.2 (Re–CO), 328.6 (C_α). MS (EI) *m/z*: 818 (M^+), 706 ($M^+ - 4CO$).

9: M.p. (hexane) 164–165 °C. Anal. Found: C, 44.65; H, 2.86%. Calc. for $C_{30}H_{20}O_4Re_2$: C, 44.12; H, 2.45%. IR (C_6H_6, cm^{-1}): 2176 (w) ($\nu_{C=C}$), 1976 (m), 1940 (vs), 1904 (s), 1884 (m) (ν_{CO}), 1588 (w) ($\nu_{C\equiv C}$). ^{1}H NMR (C_6D_6) (the label A corresponds to the signals of phenylethynyl moiety): δ 4.58 (s, 5H, C_5H_5-A), 5.03 (s, 5H, C_5H_5-B) 6.99 (t, $J = 7.45$ Hz, 1H, *para*-Ph-A), 7.08 (t overlapped with another t signal, $J = 7.45$ Hz, 2H + 1H, *meta*-Ph-A + *para*-Ph-B), 7.24 (t, $J = 7.4$ Hz, 2H, *meta*-Ph-B), 7.59 (d, $J = 6.95$ Hz, 2H, *ortho*-Ph-A), 7.76 (d, $J = 7.8$ Hz, 2H, *ortho*-Ph-B). {^{1}H} ^{13}C NMR (C_6D_6): 88.3 ($C\equiv$CPh), 89.0 (C_5H_5-A), 89.9 (C_5H_5-B), 96.1 (C$\equiv C$Ph), 125.5, 126.4, 127.4, 128.7, 129.3, 131.6, 140.5 (Ph), 144.9 (C_β), 200.1, 201.1, 201.4, 202.7 (Re–CO), 228.8 (C_α). MS (EI) *m*/*z*: 818 (M^+), 706 (M^+ – 4CO).

*3.5. Oxidation of the complex **2** with $AgBF_4\cdot 3$(dioxane) followed by the reverse reduction of $\mathbf{2}^+$ with cobaltocene*

102 mg (0.25 mmol) of **2** in 10 ml of dichloromethane was oxidized with 115 mg (0.25 mmol) of $AgBF_4\cdot 3$(dioxane) at −20 °C. The immediate change of the reaction mixture color from orange-red to deep red–violet was observed and new IR bands (2088 (s), 2032 (s) (ν_{CO})) assigned to the radical cation $\mathbf{2}^{+\cdot}$ appeared. Warming of the solution to $-5 \div -0$ °C and stirring at this temperature for 1 h caused no changes in IR spectrum. An excess (80–100 mg) of a solid cobaltocene was added and the solution was allowed to reach a room temperature. The IR spectrum of the resulting solution contained only the bands of the initial compound. The vinylidene complex **2** (82 mg, 79%) was isolated after chromatography as described above.

3.6. Deprotonation of the radical cation $\mathbf{2}^+$ with triethylamine

The radical cation $\mathbf{2}^{+\cdot}$ was generated as described above from 204 mg (0.5 mmol) of **2** and 230 mg (0.5 mmol) of $AgBF_4\cdot 3$(dioxane) in 20 ml of dichloromethane and 0.15 ml (1 mmol) of triethylamine was added in one portion to the resulted red–violet solution at −20 °C. The color of the solution became light yellow in several seconds and after 5–10 min turned red–brown. The IR spectral pattern was identical to that obtained using ferrocenium salt as an oxidant (see above). After usual chromatographic work up 43 mg (21%) of **9** and 125 mg (61%) of **6** were isolated.

*3.7. Stepwise oxidation of the μ-divinylidene complex **6***

To the red solution of **6** (20 mg, 0.025 mmol) in 4 ml of dichloromethane 12 mg (0.025 mmol) of $AgBF_4\cdot 3$(dioxane) was added at −20 °C. After 5 min the deep brown solution of the radical cation $\mathbf{6}^{+\cdot}$ (2044 (s), 2024 (vs), 1980 (s) (ν_{CO})) was obtained. The addition of the second equivalent of the oxidant to the reaction mixture led to the disappearance of the brown color and a partial precipitation of the dicationic complex $\mathbf{6}^{2+}$ from the solution. After warming up to 0 °C IR spectrum of the solution contained the bands of the 2-ene-1,4-diylidyne complex $\mathbf{6}^{2+}$ only (2100 (s), 2084 (s), 2048 (s), 2036 (s) (ν_{CO})). Addition of cobaltocene (30–40 mg) led to regeneration of the initial bis-vinylidene complex **6** with nearly quantitative yield (estimated by IR spectroscopy).

4. DFT calculations

The calculations of the rhenium compounds $\mathbf{5}^\cdot$, **6**, **7**, **9** and manganese compounds (η^5-C_5H_5)(CO)$_2$Mn=C=C

Table 3
Crystallographic Data for **2** and **9**

Compound	2	9
Empirical formula	$C_{15}H_{11}O_2Re$	$C_{30}H_{20}O_4Re_2$
Formula weight	409.44	816.86
Temperature (K)	173(2)	293(2)
Crystal size (mm)	0.50 × 0.50 × 0.08	0.40 × 0.24 × 0.18
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	7.4866(15)	9.6157(9)
b (Å)	33.142(7)	41.217(4)
c (Å)	10.370(2)	13.2417(13)
α (°)	90	90
β (°)	90	90.487(3)
γ (°)	90	90
V (Å^3)	2573.0(9)	5247.9(9)
Z	8	8
d_{calc} (g cm^{-3})	2.114	2.068
F(000)	1536	3056
μ (mm^{-1})	9.435	9.251
θ range (°)	2.32–28.05	1.83–28.22
Index range	$0 \Leftarrow h \Leftarrow 9$ $0 \Leftarrow k \Leftarrow 43$ $-13 \Leftarrow l \Leftarrow 0$	$-12 \Leftarrow h \Leftarrow 12$ $-54 \Leftarrow k \Leftarrow 54$ $-17 \Leftarrow l \Leftarrow 17$
Number of reflections collected	3004	49602
Number of unique reflections	3004	12836
Number of reflections with $I > 2\sigma(I)$	2482	7771
R_1, wR_2 [$I > 2\sigma(I)$]	0.0853, 0.2375	0.0405, 0.0724
R_1, wR_2 (all data)	0.0965, 0.2460	0.0800, 0.0778
Data/restraints/parameters	3004/0/163	2193/0/103
GOF on F^2	1.044	1.027
Maximum shift/error	0.001	0.001
Largest difference peak/hole (e Å^{-3})	2.111/−2.808	1.818/−1.249
Absorption corrected, T_{max}, T_{min}	None	0.287, 0.119

(Ph)—Mn(C≡CPh)$(CO)_2(\eta^5\text{-}C_5H_5)$ and $[(\eta^5\text{-}C_5H_5)(CO)_2$Mn—C≡CPh$]^{\cdot}$ were performed at the density functional B3LYP level of theory [9,10]. Optimized geometry parameters and frequencies of normal vibrational modes for the molecular systems studied were computed employing the LanL2DZ atomic basis sets [11,12]. The calculations were performed with the use of the GAUSSIAN-98 program [13] on a CRAY J-90 supercomputer (National Energy Research Supercomputer Center, Oakland, CA, USA) and mini supercomputer SC760-D (Institute of Organoelement Compounds Russian Academy of Science, Moscow, Russia).

4.1. X-ray structure determination

Data were collected on a Bruker SMART 1000 CCD diffractometer and corrected for Lorentz and polarization effects and for absorption [14]. For details see Table 3. The structures were determined by direct methods and by full-matrix least squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined in riding model with fixed thermal parameters. All calculations were carried out by use of the SHELXTL PLUS (PC Version 5.0) program [15]. Crystallographic data for **2** and **9** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 234739 and 234740, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +441223336033; e-mail deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

5. Conclusions

In this work it has been shown that the oxidative dehydrodimerization of the rhenium vinylidene complex **2** to the μ-divinylidene complex **6** can be performed only by the route (h) + (i) of Scheme 1, involving deprotonation of the cation radical $\mathbf{2}^{+\cdot}$ and C_β–C_β coupling of the intermediate radicals $\mathbf{5}^{\cdot}$. The formation of the isomeric binuclear complex **9** with a bridging phenyl(phenylethynyl)vinylidene ligand indicates that a competitive process of C–Re coupling became possible because of the spin density distribution in the intermediate $\mathbf{5}^{\cdot}$ between the C_β (0.234) and Re (0.438) atoms and due to relatively large size of the rhenium atom allowing the formation of the intermediate **7** with a four leg piano stool geometry. It is noteworthy that the carbon–metal coupling in the 17-e σ-alkynyl transition metal complex is found for the first time.

6. Supporting information

Tables of atom coordinates, bond lengths and angles, anisotropic displacement parameters for **2** and **9**. Ordering information is given on any current masthead page.

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