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Coupling and annelation of two acetylide groups and alkyne molecules in the reaction of $(OC)_5ReC\equiv CPh$ with ferrocenylacetylene. Crystal and molecular structure of $Re_2(CO)_7\{C_8H_2Ph_2(C_5H_4FeC_5H_5)_2\} \cdot \text{acetone}$

A.A. Koridze, V.I. Zdanovich, O.A. Kizas, A.I. Yanovsky and Yu.T. Struchkov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov ul. 28, 117813 Moscow (Russian Federation)

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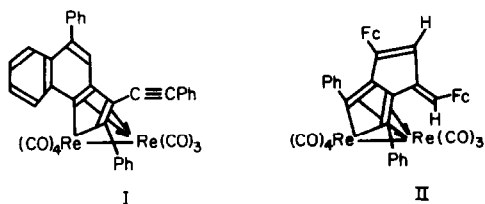
Abstract

X-Ray diffraction study was carried out of the binuclear complex $Re_2(CO)_7(C_8H_2Ph_2Fc_2)$ (II), obtained in the reaction of $(OC)_5ReC\equiv CPh$ with ferrocenylacetylene $FcC\equiv CH$ in refluxing toluene. Complex II crystallizes in the monoclinic space group $P2_1/n$ with a 20.363(5), b 10.121(2), c 22.952(7) Å, β 112.49(2)°, V 4302(2) Å³, and $Z=4$. Compound II possesses a rhenacyclopentadiene ring, fused with the methylenecyclopentene moiety along the central C–C bond, and π -bonded by the $Re(CO)_3$ group. The hydrocarbon ligand of compound II is formed by condensation of two $PhC\equiv C$ groups and two $FcC\equiv CH$ molecules. Preparative methods of synthesis of $(OC)_5ReC\equiv CPh$, $(OC)_5ReC\equiv CCO_2Me$ and $(OC)_5ReC\equiv CSiMe_3$ are reported.

Key words: Rhenium; Ferrocene; Alkyne; Carbonyl; Crystal structure

1. Introduction

Recently we reported the formation of the dirhenium compound $Re_2(CO)_7(C_2Ph)_4$ (I) as a result of the unusual oligomerization/annelation of four $PhC\equiv C$ groups in the thermolysis of $(OC)_5ReC\equiv CPh$ [1]. Formation of complex I may be envisaged as a result of head-to-head coupling of two pairs of $PhC\equiv C$ groups, cyclization of two thus emerging $PhC\equiv CC\equiv C$ diynes with rhenium carbonyl group with formation of rhenacyclopentadiene ring and, finally, additional annelation of one of the $PhC\equiv C$ pairs generating the 1-phenylnaphthalene system.



It was interesting to modify this reaction and to carry out the thermolysis of $(OC)_5ReC\equiv CPh$ in the

presence of terminal alkyne. In this case one may expect to obtain dirhenium complexes with organic ligands, derived from acetylide-alkyne and acetylide-acetylide coupling. With this purpose we studied the thermal reaction of $(OC)_5ReC\equiv CPh$ with ferrocenylacetylene $FcC\equiv CH$. One of the products of this reaction, complex $Re_2(CO)_7(C_8H_2Ph_2Fc_2)$ (II), was isolated from the reaction mixture and fully characterized by X-ray diffraction study. A preliminary communication of this work has been published [2].

2. Experimental section

All reactions were carried out under an atmosphere of argon. All column and thin layer chromatographic separations were performed in air. IR spectra were recorded on a Bruker IFS-113v spectrometer in *n*-hexane solutions. ¹H NMR spectra were taken on a Bruker WP 200SY instrument in acetone-*d*₆ solution at 25°C. Reagent grade toluene and THF were distilled from sodium and sodium benzophenone ketyl respectively, before use. Ferrocenylacetylene was obtained according to the published procedure [3].

Correspondence to: Prof. A.A. Koridze.

2.1. Synthesis of $(OC)_5ReC\equiv CPh$

4.11 ml of hexane solution of n-butyllithium (1.65 N) was added to a solution of 0.76 ml (6.75 mmol) of phenylacetylene in 15 ml of THF at $-10^\circ C$. The resulting solution was transferred into a cooled ($-40^\circ C$) dropping funnel and added dropwise to the cooled ($-40^\circ C$) solution of 1.0 g (2.7 mmol) of $(OC)_5ReCl$ under stirring. The solution gradually changed from colourless to yellow. The solution was allowed to reach room temperature and it then became light brown. Some drops of water were then added to the reaction mixture, the solvent was removed on a rotary evaporator, the residue taken up in chloroform, washed with water and then the chloroform solution was dried over anhydrous Na_2SO_4 . Solvent was removed and the residue was chromatographed on a silica column, using 3:1 mixture hexane:benzene as eluent. The first brown band gave, after crystallization from hexane, 0.68 g (55%) of product. Complex $(OC)_5ReC\equiv CPh$ identified by IR spectroscopy [4,5]: $\nu(C=O)$ 2150, 2045, 2000; $\nu(C\equiv C)$ 2120 cm^{-1} .

2.2. Synthesis of $(OC)_5ReC\equiv CSiMe_3$

5.3 ml (1.3 N, 6.8 mmol) of hexane solution of n-butyllithium was added to a solution of 0.94 ml (6.8 mmol) of $Me_3SiC\equiv CH$ in 15 ml of THF at $-20^\circ C$ under stirring. The resulting solution of $LiC\equiv CSiMe_3$ was transferred into a dropping funnel cooled with dry ice and added for 0.5 h to a cooled ($-40^\circ C$) stirred solution of 1.0 g (2.7 mmol) of $(OC)_5ReCl$ in 80 ml of THF. After the reaction mixture was stirred for 1 h, it was allowed to reach room temperature, then 5 ml of water was added and solvent was removed on a rotary evaporator. The residue was dissolved in benzene and the benzene solution was washed with water and dried over anhydrous $MgSO_4$. Solvent was evaporated, and the residue was chromatographed on a silica column. Elution with 3:1 hexane-benzene gave a yellow band, which contained 0.42 g (37%) of product. Complex $(OC)_5ReC\equiv CSiMe_3$ may be further purified by vacuum sublimation. Found: C, 28.41; H, 2.03; Si, 6.52. $C_{10}H_9O_5ReSi$ calc.: C, 28.37; H, 2.10; Si, 6.60%. IR spectrum (CH_2Cl_2): $\nu(C=O)$ 2040, 2000; $\nu(C\equiv C)$ 2150 cm^{-1} .

2.3. Synthesis of $(OC)_5ReC\equiv CCO_2Me$

1.2 ml (1.48 N, 1.64 mmol) of hexane solution of n-butyllithium was added to a solution of 0.123 ml (1.64 mmol) of diisopropylamine in 300 ml of diethyl ether at $-10^\circ C$ under stirring. The mixture was stirred for 20 min at $-10^\circ C$, then cooled to $-78^\circ C$; 0.138 ml (1.64 mmol) of $HC\equiv CCO_2Me$ was added to the solution of $LiN(iPr)_2$. The mixture was stirred for 1 h and then to the solution of $LiC\equiv CCO_2Me$ was added drop-

wise cooled ($-78^\circ C$) THF solution (70 ml) of 0.3 g (0.82 mmol) of $(OC)_5ReCl$. Reaction mixture was stirred for 1 h, then several drops of water were added and the solution allowed to reach room temperature. At this moment the solution acquired the deep brown colour. Solvent was removed on a rotary evaporator, the residue was dissolved in chloroform, washed with water and dried over anhydrous Na_2SO_4 . After evaporation of solvent the residue was chromatographed on a silica column. Elution with methylene chloride gave a cream-coloured, almost colourless compound in 0.03 g (10%) yield, identified as $(OC)_5ReC\equiv CCO_2Me$. Mass spectrum: 410 (M^+ , ^{187}Re), 382 ($M^+ - CO$), 352 ($M^+ - CO - CH_2O$), 351 ($M^+ - CO - OMe$), 326 ($M^+ - C_2COOMe$). IR spectrum: $\nu(C\equiv O)$ 2040, 2010; $\nu(C\equiv C)$ 2110; $\nu(C=O)$ 1692 cm^{-1} .

2.4. Reaction of $(OC)_5ReC\equiv CPh$ with ferrocenylacetylene

A mixture of 0.39 g (0.87 mmol) of $(OC)_5ReC\equiv CPh$ and 0.30 g (1.5 mmol) of ferrocenylacetylene in 45 ml of toluene was refluxed for 3 h. After cooling, solvent was removed on a rotary evaporator, and the residue chromatographed on silica column. Elution with petroleum ether gave a small yellow band which contained $Re_2(CO)_{10}$ and $Re_2(CO)_7(PhC_2)_4$. Elution with 1/1 petroleum ether-benzene gave a broad red-brown band, from which the fraction, containing the mixture of ferrole type dirhenium complexes in the amount of 0.13 g was isolated. Further careful separation of this fraction by TLC on silica and subsequent crystallization from pentane gave deep-red, almost black crystals of $Re_2(CO)_7[C_8H_2Ph_2(C_5H_4FeC_5H_5)_2]$ (II). Found: C, 46.69; H, 2.37. $C_{47}H_{30}Fe_2O_7Re_2$ calc.: C, 47.35; H, 2.60%. IR spectrum: $\nu(C=O)$ 2091m, 2036vs, 2017s, 1984vs, 1970sh, 1961m, 1945w, 1937w cm^{-1} . 1H NMR spectrum: δ 3.00 (m, 1H), 3.87(m, 1H), 4.09(s, 5H), 4.10(m, 1H), 4.14(s, 5H), 4.31(m, 1H), 4.52(m, 3H), 4.65(m, 1H), 6.12(s, 1H), 6.9–7.7(m, 10H), 7.90(s, 1H).

2.5. X-ray diffraction study of $Re_2(CO)_7(C_8H_2Ph_2Fc_2) \cdot acetone, II \cdot Me_2CO$

Crystals of $II \cdot Me_2CO$ are monoclinic at 296 K: a 20.363(5), b 10.121(2), c 22.592(7) Å, $\beta = 112.49(2)^\circ$, $V = 4302(2)$ Å³, $Z = 4$, $d_{calc.} = 1.928$ g cm^{-3} , space group $P2_1/n$. The unit cell dimensions as well as the intensities of 6586 reflections with $F^2 \geq 35(F^2)$ were measured with an automated 4-circle Siemens P3/PC diffractometer (296 K, $\lambda(Mo, K\alpha)$, graphite monochromator, $\theta/2\theta$ -scan, $\theta \leq 26.5^\circ$, absorption correction by means of the DIFABS technique [6] was applied).

The structure was solved by the direct method. Four metal atoms were located in the E-map, all other nonhydrogen atoms were found in the subsequent

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}^a
Re(1)	6051(1)	2051(1)	2226(1)	31(1)
Re(2)	5990(1)	4895(1)	2221(1)	30(1)
Fe(1)	4658(1)	7260(1)	3668(1)	33(1)
Fe(2)	2670(1)	7344(1)	513(1)	42(1)
O(1)	6240(4)	498(8)	1120(4)	84(4)
O(2)	6713(3)	-52(7)	3280(4)	69(3)
O(3)	4611(3)	608(7)	1991(3)	71(3)
O(4)	7610(3)	3052(6)	2587(3)	61(3)
O(5)	6783(3)	5661(7)	1349(3)	66(3)
O(6)	5393(3)	7699(6)	2038(3)	62(3)
O(7)	7193(4)	6017(8)	3396(3)	80(3)
C(1)	6181(4)	1047(9)	1536(5)	50(4)
C(2)	6509(4)	739(8)	2896(4)	44(3)
C(3)	5132(4)	1109(8)	2069(4)	41(3)
C(4)	7030(4)	2788(7)	2443(4)	42(3)
C(5)	6487(4)	5371(8)	1671(4)	44(3)
C(6)	5632(4)	6642(8)	2108(4)	44(3)
C(7)	6760(4)	5587(8)	2953(4)	45(3)
C(8)	5726(3)	3365(6)	2856(3)	29(2)
C(9)	5100(3)	4077(6)	2519(3)	28(2)
C(10)	4826(3)	4059(7)	1818(3)	28(2)
C(11)	5248(4)	3395(7)	1537(3)	32(3)
C(12)	4619(3)	4945(6)	2700(3)	29(2)
C(13)	4053(3)	5251(7)	2154(3)	30(2)
C(14)	4137(3)	4766(7)	1582(3)	31(2)
C(15)	3707(4)	4905(7)	960(3)	35(3)
C(16)	6003(4)	3091(6)	3545(3)	31(3)
C(17)	6735(4)	3070(8)	3920(4)	42(3)
C(18)	6987(5)	2716(8)	4556(4)	52(3)
C(19)	6539(5)	2323(9)	4841(4)	55(4)
C(20)	5825(5)	2287(8)	4476(4)	51(4)
C(21)	5545(4)	2674(7)	3832(4)	39(3)
C(22)	5001(4)	3088(7)	844(4)	35(3)
C(23)	5350(5)	3511(9)	451(4)	59(4)
C(24)	5133(6)	3080(10)	-173(5)	69(5)
C(25)	4561(6)	2269(10)	-433(4)	67(4)
C(26)	4198(5)	1847(9)	-59(4)	57(4)
C(27)	4413(4)	2256(8)	572(4)	47(3)
C(28)	4737(4)	5378(7)	3350(3)	33(3)
C(29)	4210(4)	5446(7)	3629(4)	38(3)
C(30)	4549(5)	5848(7)	4270(4)	45(3)
C(31)	5278(5)	6085(8)	4397(4)	50(3)
C(32)	5403(4)	5793(7)	3830(3)	36(3)
C(33)	4434(5)	8522(8)	2919(4)	50(4)
C(34)	3879(5)	8517(8)	3140(5)	54(4)
C(35)	4167(6)	8933(9)	3788(6)	70(5)
C(36)	4891(6)	9158(9)	3952(5)	71(5)
C(37)	5050(5)	8929(9)	3416(5)	63(4)
C(38)	2984(4)	5408(7)	668(4)	38(3)
C(39)	2626(4)	5654(8)	-6(4)	48(3)
C(40)	1938(4)	6108(9)	-116(4)	54(3)
C(41)	1844(4)	6159(9)	465(4)	52(3)
C(42)	2490(4)	5726(8)	971(4)	47(3)
C(43)	3521(6)	8531(10)	898(7)	73(5)
C(44)	3209(9)	8735(10)	246(8)	93(8)
C(45)	2509(8)	9140(11)	99(7)	102(7)
C(46)	2401(6)	9213(10)	659(6)	75(5)
C(47)	3043(6)	8795(9)	1167(6)	69(5)
O(1S)	2513(4)	700(8)	2400(4)	89(4)

TABLE 1 (continued)

	x	y	z	U_{eq}^a
C(1S)	2878(5)	1563(9)	2349(5)	58(4)
C(2S)	2797(7)	2130(13)	1707(7)	96(7)
C(3S)	3464(8)	2084(15)	2930(7)	119(8)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fourier synthesis. The structure was refined by the full-matrix least-squares technique at first in the isotropic and then in the anisotropic approximation. The four highest peaks found in the difference Fourier synthesis were identified as the atoms of solvate acetone molecule and were included in the subsequent refinement. All H-atoms were placed geometrically and included in the final cycles of refinement in the riding model approximation with the common isotropic temperature factors which refined to $0.061(5) \text{\AA}^2$ for H atoms of the complex and $0.17(3)$ for H atoms of the acetone molecule. The refinement converged to $R = 0.0375$, $R_w = 0.0453$. All calculations were carried out with an IBM PC computer using the SHELXTL PLUS program package [7]. The coordinates of atoms are listed in Table 1.

3. Results and discussion

The complex $(OC)_5ReC\equiv CPh$ used in the present study, as well as in our earlier publications on interaction of $(OC)_5ReC\equiv CPh$ with osmium clusters $H_2Os_3(CO)_{10}$ [8], $HOs_3(CO)_{10}(C\equiv CPh)$ [9], and also on thermolysis of $(OC)_5ReC\equiv CPh$, was obtained by reaction of $(OC)_5ReCl$ with lithium phenylacetylide. Our synthesis of this rhenium acetylide complex, which allows yields of up to 55%, is to our view the most convenient. Therefore, in the Experimental section we describe the details of synthesis of $(OC)_5ReC\equiv CPh$, as well as of two other rhenium acetylides, $(OC)_5ReC\equiv CSiMe_3$ and $(OC)_5ReC\equiv CCO_2Me$ [10].

Complex $(OC)_5ReC\equiv CPh$ reacts with ferrocenylacetylene in refluxing toluene yielding a mixture of products, from which fractions containing dirhenium compounds may be isolated by chromatography on silica. According to the IR spectral data, almost all of them are dirhenium complexes of the ferrole type. 1H NMR spectral data of separate fractions indicate the presence of two ferrocenyl moieties in each compound. Careful chromatographic work-up and subsequent crystallization gave one of these compounds, complex $Re_2(CO)_7(C_8H_2Ph_2Fc_2)$ (II), in the individual form.

The IR spectrum of compound II in the carbonyl region reveals a similarity to that of the known ferrole type dirhenium complexes [1,11]. 1H NMR spectrum of

compound II contains two singlet resonances at δ 4.09(5H) and 4.14(5H), and also multiplets at 3.00(1H), 3.87(1H), 4.10(1H), 4.31(1H), 4.52(3H) and 4.52(1H) ppm of two ferrocenyl groups; complex multiplet of two phenyl groups at 6.9–7.6 ppm, and two single resonances at 6.12(1H) and 7.90(1H) ppm.

The structure of compound II was established by a single crystal X-ray diffraction study of its acetone solvate, $II \cdot Me_2CO$. Molecular structure of II is shown in Fig. 1 and bond lengths in Table 2. Fig. 1 clearly shows that molecule II belongs to the class of metallacyclopentadiene complexes. A few rhenium complexes of this type have been reported, *viz.*, complex $Re_2(CO)_7(PhC_2Ph)_2$ (III), formation of which was postulated in thermal reaction of $Re_2(CO)_{10}$ with diphenylacetylene [11], and three fully characterized and structurally studied $Re_2(CO)_7(C_2Ph)_4$ (I) [1], $Re_2(CO)_7(MeC_2NMe_2)$ (IV) [12] and $Re_2(CO)_5(PhC_2Ph)_2$ (PhC₂Ph) (V) [13]. For compound IV two isomers have been isolated—one of them corresponding to head-to-tail and another representing the product of a tail-to-tail ynamine coupling [12].

The Re–Re bond length in molecule II (2.881(1) Å) is significantly shorter than that in $Re_2(CO)_{10}$ (3.041 Å) [14] and quite close to that found in complexes I (2.895 Å [1]), IV (2.8868 Å [12]) and V (2.878 Å [13]).

The overall geometry of rhenacyclopentadiene ring in molecule II is similar to that observed in complexes I, IV and V. Thus, the C–C bond lengths of the η^4 -diene fragment are essentially unequal, the central C(9)–C(10) bond length (1.463(10) Å) being longer in comparison with C(8)–C(9) (1.408(8) Å) and C(10)–

TABLE 2. Bond lengths (Å)

Re(1)–Re(2)	2.881(1)	Re(1)–C(1)	1.962(11)
Re(1)–C(2)	1.960(8)	Re(1)–C(3)	2.008(8)
Re(1)–C(4)	2.005(8)	Re(1)–C(8)	2.226(8)
Re(1)–C(11)	2.236(6)	Re(2)–C(5)	1.939(10)
Re(2)–C(6)	1.893(8)	Re(2)–C(7)	1.923(7)
Re(2)–C(8)	2.310(8)	Re(2)–C(9)	2.314(8)
Re(2)–C(10)	2.348(6)	Re(2)–C(11)	2.278(6)
Fe(1)–C(28)	2.065(7)	Fe(1)–C(29)	2.036(8)
Fe(1)–C(30)	2.042(9)	Fe(1)–C(31)	2.033(8)
Fe(1)–C(32)	2.054(7)	Fe(1)–C(33)	2.028(9)
Fe(1)–C(34)	2.027(8)	Fe(1)–C(35)	2.036(11)
Fe(1)–C(36)	2.023(10)	Fe(1)–C(37)	2.042(11)
Fe(2)–C(38)	2.049(7)	Fe(2)–C(39)	2.056(9)
Fe(2)–C(40)	2.047(8)	Fe(2)–C(41)	2.036(9)
Fe(2)–C(42)	2.044(9)	Fe(2)–C(43)	2.011(10)
Fe(2)–C(44)	2.014(16)	Fe(2)–C(45)	2.012(12)
Fe(2)–C(46)	2.031(11)	Fe(2)–C(47)	2.015(10)
O(1)–C(1)	1.136(14)	O(2)–C(2)	1.136(11)
O(3)–C(3)	1.126(11)	O(4)–C(4)	1.130(10)
O(5)–C(5)	1.146(13)	O(6)–C(6)	1.160(10)
O(7)–C(7)	1.137(10)	C(8)–C(9)	1.408(8)
C(8)–C(16)	1.464(10)	C(9)–C(10)	1.463(10)
C(9)–C(12)	1.485(11)	C(10)–C(11)	1.419(11)
C(10)–C(14)	1.481(9)	C(11)–C(22)	1.482(10)
C(12)–C(13)	1.364(8)	C(12)–C(28)	1.460(11)
C(13)–C(14)	1.452(11)	C(14)–C(15)	1.349(9)
C(15)–C(38)	1.456(10)	C(16)–C(17)	1.406(9)
C(16)–C(21)	1.390(13)	C(17)–C(18)	1.376(12)
C(18)–C(19)	1.361(16)	C(19)–C(20)	1.371(12)
C(20)–C(21)	1.400(12)	C(22)–C(23)	1.400(15)
C(22)–C(27)	1.399(10)	C(23)–C(24)	1.376(14)
C(24)–C(25)	1.360(15)	C(25)–C(26)	1.386(17)
C(26)–C(27)	1.384(13)	C(28)–C(29)	1.439(13)
C(28)–C(32)	1.439(9)	C(29)–C(30)	1.405(11)
C(30)–C(31)	1.421(13)	C(31)–C(32)	1.429(13)
C(33)–C(34)	1.398(16)	C(33)–C(37)	1.388(12)
C(34)–C(35)	1.416(15)	C(35)–C(36)	1.394(18)
C(36)–C(37)	1.388(19)	C(38)–C(39)	1.437(11)
C(38)–C(42)	1.451(14)	C(39)–C(40)	1.403(13)
C(40)–C(41)	1.399(15)	C(41)–C(42)	1.441(10)
C(43)–C(44)	1.379(20)	C(43)–C(47)	1.357(21)
C(44)–C(45)	1.396(23)	C(45)–C(46)	1.364(24)
C(46)–C(47)	1.435(14)	O(1S)–C(1S)	1.180(13)
C(1S)–C(2S)	1.510(19)	C(1S)–C(3S)	1.492(16)

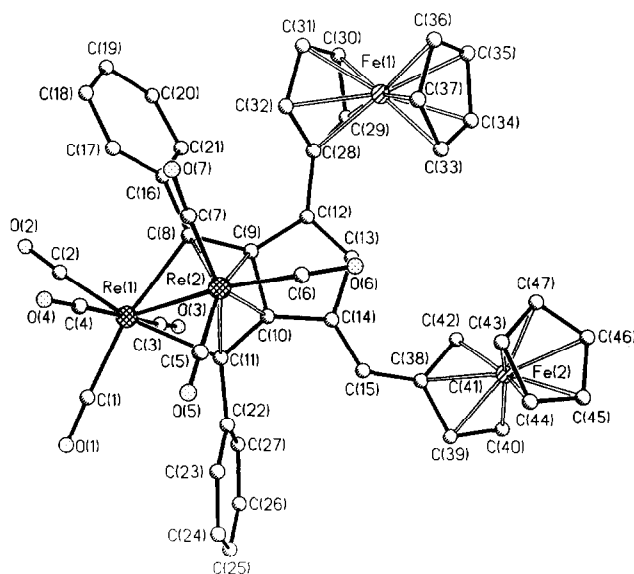
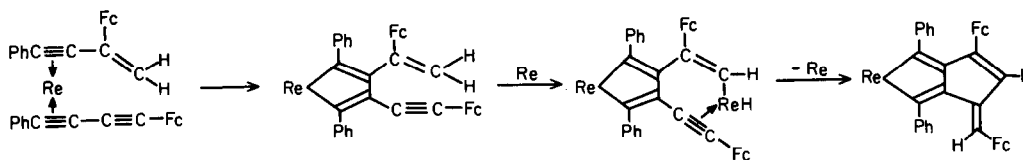


Fig. 1.

C(11) (1.419(11) Å). However, this difference is less pronounced than in complexes I and IV, which is probably due to the peculiar position of the C(9)–C(10) bond, simultaneously involved both in the rhenacyclopentadiene and methylenecyclopentene rings. The C–C bond lengths, as well as bond angles in the methylenecyclopentene moiety exhibit no exceptional features.

The rhenacyclopentadiene ring has an envelope conformation with the folding angle of 16.4° along the C(8)···C(11) line. The Re(1) atom is tilted by 0.496 Å out of the C(8)C(9)C(10)C(11) plane (plane A) away from the Re(2) atom; the Re(2)–plane A distance is 1.833 Å.



Scheme 1.

It should be noted that these geometrical parameters of metallacycle are quite similar to those observed in molecule I, where the rhenacyclopentadiene cycle is characterized by the folding angle of 18° and 0.54 \AA displacement of the Re(1) atom from the C_4 plane.

The five-membered C(9)C(10)C(14)C(13)C(12) ring is planar within 0.04 \AA . However, its mean plane (B) is not actually identical with the plane A and forms a small dihedral angle (4.7°) with the latter. It is also noteworthy that although the C(15) atom lies almost exactly in the plane B (its deviation being only 0.018 \AA), the C(28) and C(38) atoms exhibit quite significant displacements (0.166 and -0.239 \AA , respectively) out of this plane. The planes of the cyclopentadienyl rings C(28)–C(32) and C(38)–C(42) form the dihedral angles of 41.3° and 18.6° with the plane B.

Similarly to structures I and IV, in complex II one of the carbonyl ligands, *viz.*, C(4)O(4), is noticeably non-linear (the Re(1)C(4)O(4) bond angle being $171.7(7)^\circ$). Its orientation relative to the Re(2) atom allows us to consider it as slightly semi-bridging (the Re(2) \cdots C(4) distance is $2.910(2) \text{ \AA}$).

The most remarkable feature of complex II is the structure of its organic ligand. Earlier, discussing the possible way of formation of complex I prepared by thermolysis of $(OC)_5ReC\equiv CPh$, we suggested the intermediate formation of the diyne $PhC\equiv CC\equiv CPh$, and subsequent coupling of two such molecules on the rhenium centre, thus yielding compound I. The structure of compound II provides the basis for the assumption that this compound may be formed as a result of

cyclization of diyne $PhC\equiv CC\equiv CPh$ and enyne $PhC\equiv CC(Fc)=CH_2$ as illustrated in Scheme 1.

Formation of the diyne $PhC\equiv CC\equiv CPh$ and the enyne $PhC\equiv CC(Fc)=CH_2$ in the reaction of $(OC)_5ReC\equiv CPh$ with ferrocenylacetylene, evidently, should involve oxidative addition of rhenium acetylide and ferrocenylacetylene respectively to the rhenium atom, and subsequent reductive elimination.

Transient formation of $PhC\equiv CC(Fc)=CH_2$ in the reaction of $(OC)_5ReC\equiv CPh$ with ferrocenylacetylene agrees with previous results on $RhCl(PPh_3)_3$ catalysed dimerization of phenylacetylene which yields the isomeric enynes $PhC\equiv CC(Ph)=CH_2$ and $PhC\equiv CC(H)=C(H)Ph$ [15].

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