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Annelation of Phenylacetylide Groups by Thermolysis of $(OC)_5ReC{\equiv}CPh$. X-Ray Crystal Structure of $Re_2(CO)_7(C_2Ph)_4$

Avtandil A. Koridze,* Valeriya I. Zdanovich, Andrei S. Batsanov and Yurii T. Struchkov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the USSR, 117813 Moscow, USSR. Fax: 095 135 5085

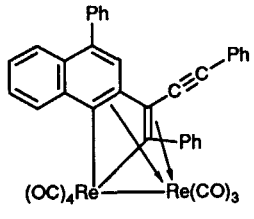
Thermolysis of $(OC)_5ReC{\equiv}CPh$ in refluxing toluene yields the binuclear complex $Re_2(CO)_7(C_2Ph)_4$ **2**, characterized by an X-ray diffraction study; **2** contains a rheniacyclopentadiene moiety, formed by coupling of four $PhC{\equiv}C$ groups, two of which undergo additional annelation producing the 1-phenylnaphthalene system.

Alkynes react with transition metal carbonyls to form a number of organometallic complexes, including clusters of different nuclearity. Unlike alkyne-substituted carbonyl clusters of the iron, cobalt and nickel triads,[1] the corresponding rhenium derivatives[2] have been much less investigated. Since thermolysis of carbonyl complexes is one of the well-recognized methods of cluster preparation it seemed of interest to study the thermolysis products of $(OC)_5ReC{\equiv}CPh$ **1**, which contains both metal carbonyl and alkyne moieties.

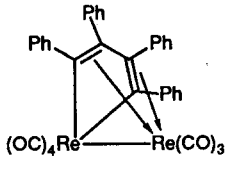
$$(OC)_5ReC{\equiv}CPh$$

1

Heating **1** in refluxing toluene yields a mixture of rhenium complexes. One of the major products, isolated by chromatography on silica gel, is a light yellow crystalline complex **2**. The mass spectrum of **2** indicates the molecular formula $Re_2(CO)_7(C_2Ph)_4$: in addition to the parent ion (m/z 972) it shows



2



3

ions corresponding to the successive loss of seven CO groups.† The molecular structure of **2** was established by an X-ray single crystal diffraction study‡ and is presented in Fig. 1.

The molecule **2** represents an unexpected dirhenium complex, wherein the metal atoms are linked by a single Re–Re bond, bridged by an organic ligand formed by unusual condensation of four $PhC{\equiv}C$ groups. The Re–Re bond length (2.895 Å) is significantly shorter than in $Re_2(CO)_{10}$ (3.041 Å),[4] probably due to the tightening effect of the bridging organic ligand.

Complex **2** belongs to the class of metallacyclopentadiene complexes, which are common products of the reactions between alkynes and iron carbonyls.[5] Formation of the related dirhenium complex **3** in the reaction of $Re_2(CO)_{10}$ with PhCCPh was postulated previously.[2] However, as far as we know, **2** is the first representative of the tetracarbonylrheniacyclopentadiene-$Re(CO)_3$ complexes.

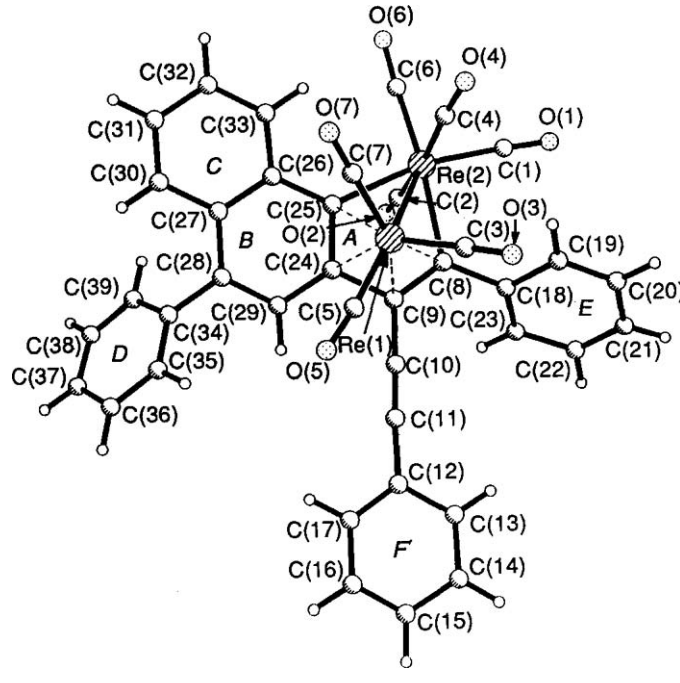


Fig. 1 Molecular structure of **2**. Selected bond distances (Å): Re(1)–Re(2) 2.895(1), Re(1)–C(3) 1.88(2), Re(1)–C(5) 1.85(2), Re(1)–C(7) 1.93(2), Re(1)–C(8) 2.24(2), Re(1)–C(9) 2.29(1), Re(1)–C(24) 2.37(1), Re(1)–C(25) 2.31(1), Re(2)–C(1) 1.98(1), Re(2)–C(2) 2.00(2), Re(2)–C(4) 1.96(1), Re(2)–C(6) 1.92(2), Re(2)–C(8) 2.23(2), Re(2)–C(25) 2.21(1), C(8)–C(9) 1.34(2), C(9)–C(24) 1.50(2), C(24)–C(25) 1.40(2), C(9)–C(10) 1.45(2), C(10)–C(11) 1.19(2), C(11)–C(12) 1.44(2). Torsion angles C(9)C(8)C(18)C(23) 39°, C(27)C(28)C(34)C(39) 56°.

A remarkable feature of complex **2** is the structure of its organic moiety. This is formally a product of a linear 'head-to-head' coupling of two pairs of $PhC{\equiv}C$ groups, cyclization of the two thus emerging $PhC{\equiv}CC{\equiv}CPh$ ligands with the rhenium carbonyl group with formation of the five-membered metallacycle and, finally, additional aromatic annelation of one of the $PhC{\equiv}C$ pairs generating the 1-phenylnaphthalene system.

The Re(2)C(8)C(9)C(24)C(25) metallacycle adopts an envelope conformation, folded by 18° along the C(8)···C(25) line with the Re(2) atom tilted by 0.54 Å out of the C_4 plane of ring *A* away from the Re(1) atom. The C(9)–C(24) bond length of 1.50 Å is, in fact, ordinary and the C(8)–C(9) and C(24)–C(25) bond lengths of 1.34 and 1.40 Å show the absence of electronic delocalization over four carbon atoms of the five-membered cycle. However, such delocalization is typical of η^4-diene systems and is observed in the related complexes[6] $Os_2(CO)_6(C_8H_6)$, $Os_2(CO)_6(C_4H_2Me_2)$ and $Ru_2(CO)_6[C_4(CO_2Me)_4]$. It is noteworthy that a quite different (as compared with **2**) distribution of C–C bond distances has been found recently[7] in the platinacyclopentadiene ring of $(cod)Pt(C_4H_2Ph_2)Fe(CO)_3$ (cod = cycloocta-1,5-diene), wherein the central C–C bond of 1.39 Å is the shortest one, while the two outer C–C bond lengths are 1.44 Å.

† *Selected spectroscopic data* for **2**: IR (hexane) ν(CO)/cm^{-1} 2091 m, 2036vs, 2017s, 1974vs, 1970sh, 1961m, 1945w and 1937w; ^{1}H NMR ([$^2H_6$]acetone) δ 7.25–8.29.

‡ *Crystal data* for **2**: $C_{39}H_{20}O_7Re_2$, M = 973.0, triclinic, space group $P\bar{1}$, a = 8.753(2), b = 11.676(2), c = 17.142(4) Å, α = 74.73(1), β = 80.50(2), γ = 81.81(1)°, V = 1657.8(5) Å^3, Z = 2, D_c = 1.89 g cm^{-3}. Intensities of 5779 independent reflections with $2\theta \leq 60°$ were measured with a Siemens P3/PC automatic diffractometer at 293 K (graphite-monochromated Mo-Kα radiation, λ = 0.71069 Å). The structure was solved by the heavy-atom method and refined by least-squares in anisotropic approximation (including H atoms as fixed contributions in calculated positions). The refinement of 433 independent parameters on 4409 reflections with $F > 4\sigma$, corrected for absorption [μ(Mo-Kα = 74.4 cm^{-1}] by the DIFABS technique,[3] converged to R = 0.53 (R_w = 0.051). Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, Issue No. 1, 1991.

The Re(2)–C(8) and Re(2)–C(25) σ-bond lengths [av. 2.22(1) Å] are essentially the same as the Re–C(sp^2) bond distances in rhenium-carbonyl complexes of the non-chelate type.[8]

The naphthalene moiety, the C(10)≡C(11) triple bond and the phenyl ring *E* are tilted out of the plane *A* by 5°, 10° and 20° respectively towards the Re(1) atom. In ring *B* of the naphthalene system the C(26)–C(27) [1.42(2) Å], C(28)–C(29) [1.38(2) Å] and coordinated C(24)–C(25) [1.40(2) Å] bonds are more double in character than the others [av. 1.45(2) Å].

The C(4)–O(4) carbonyl ligand is significantly non-linear [with a Re(2)–C(4)–O(4) angle of 171(1)°] and directed towards the Re(1) atom, and thus may be considered as semi-bridging.

Further investigations into the thermolysis of $(OC)_5$-ReC≡CPh and related complexes as a possible route for the construction of unusual condensed aromatics are in progress.

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