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Transformation of phenylacetylene into *ortho*-metallated phenylvinylidene cluster having a Re_2Mo_2 core; molecular structure of $Cp_2Mo_2Re_2(\mu_4\text{-}C{=}C(H)C_6H_4)(\mu\text{-}H)(\mu\text{-}CO)(CO)_7$

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Abstract

The heterometallic cluster $Cp_2Re_2Mo_2(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}PhC{\equiv}CH)$ (I), obtained from the reaction of the binuclear complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ with $Cp_2Mo_2(CO)_6$ during the first 5 hours of refluxing in *o*-xylene; further refluxing transforms it into a heterometallic cluster $Cp_2Mo_2Re_2(\mu_4\text{-}C{=}C(H)C_6H_4)(\mu\text{-}H)(\mu\text{-}CO)(CO)_7$ (II) in which the coordinated phenylacetylene is converted into an *ortho*-metallated bridging phenylvinylidene ligand. The X-ray diffraction study indicates that crystals of II are monoclinic, space group $P2_1/c$, a 10.621(3), b 10.979(4), c 26.106(6) Å, β 96.91(1)°, V 3022.07 $Å^3$, $Z = 4$.

Cluster II possesses a heterometallic butterfly-like Re_2Mo_2 framework, consisting of the two triangles Mo_2Re and Re_2Mo, the planes of which form a dihedral angle of 119.5°. The phenylvinylidene ligand is coordinated by all four metal atoms. The *ortho*-metallated C_6H_4-fragment is σ bonded to the Mo^1 atom and is π-coordinated by the Re^1 atom.

Introduction

The transformations of alkynes at the transition metal centres that involve the formation of new C–M and C–C bonds are of considerable interest. Most of the

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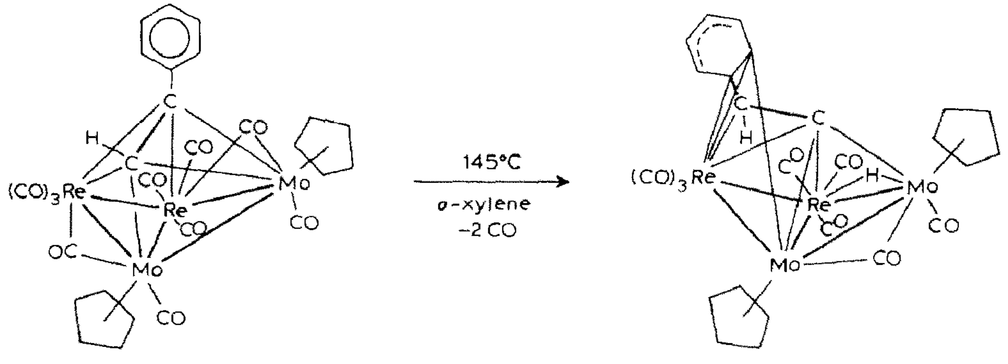
work published is on the irreversible rearrangement of the coordinated phenylacetylene group into the vinylidene ligand in the coordination sphere of mono-, bi-, and trinuclear complexes [1–3]. The unusual regeneration of phenylacetylene in the form of its complex with a heterometallic cluster was observed by us [4] in the reaction of a binuclear rhenium complex $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ with $Cp_2Mo_2(CO)_6$ in *o*-xylene under reflux [4]. The 60 $\bar{e}$ cluster that results $Cp_2Mo_2Re_2(CO)_8(\mu_4,\eta^2\text{-}PhC{\equiv}CH)$ (I) possesses a butterfly-like heterometallic core Re_2Mo_2 and a phenylacetylene ligand μ_4,η^2-coordinated by all four metal atoms. Here we report the transformation of the coordinated phenylacetylene into phenylvinylidene which is accompanied by the *ortho*-metallation of the phenyl radical.

Results and discussion

The prolonged refluxing of $Cp_2Mo_2Re_2(CO)_8(\mu\text{-}CO)_2(\mu_4, \eta^2\text{-}PhC{\equiv}CH)$ (I) in *o*-xylene (for 5 h) results in the elimination of the two CO molecules and formation of $Cp_2Mo_2Re_2(CO)_7(\mu\text{-}CO)(\mu\text{-}H)(\mu_4\text{-}C{=}C(H)C_6H_4)$ (II).



(I) (II)

Complex II was isolated as air-stable black-green crystals. The mass-spectrum of II shows the peaks of the fragmentation products, with the most intense peaks corresponding to $Cp_2Mo_2Re_2H(CO)_6C_6H_4C_2H)^+$ (*m/z* 964), $[Cp_2Mo_2Re_2C_6H_4C_2]^+$ (*m/z* 794), $[Cp_2Mo_2Re_2C_6H_4C_2 - C_2H_4]^+$ (*m/z* 766).

The bands characteristic of the stretching vibrations of the bridging and the terminal CO groups, 1805 and 1880–1995 cm^{-1}, respectively, are observed in the IR spectra of the cluster II.

The structure of II (Fig. 1) was determined by means of the X-ray diffraction study. Atomic coordinates, bond lengths and bond angles are listed in Tables 1, 2 and 3 respectively. Cluster II possesses a heterometallic butterfly-like Re_2Mo_2 framework which consists of the two triangles at a dihedral angle of 119.5° between the planes. The metal atoms in II are coordinated by the terminal CO groups (three at each rhenium atom and one CO at one of the molybdenum atoms) and one CO group bridges the Mo(1)–Mo(2) bond in the butterfly wing which has a length of 2.733 Å. The dihedral angle in II is increased to 119.5° compared with 110.7° in I, while the Mo(1)–Re(2) distance in the butterfly hinge in II is shortened to 2.979 Å (compared with 3.105(1) Å in I). The shortening of the Mo(1)–Mo(2) distance from

3.043 Å in I to 2.733 Å in II is due to the loss of the two CO groups and the formation of the CO bridge ligand. The phenylvinylidene ligand is coordinated via the terminal carbon atom by all four metal atoms. The double bond C(1)=C(2) is π-coordinated by the Re(1) atom, and its length is 1.481 Å. An unexpected *ortho*-metallation of the phenyl group is observed in complex II; the *ortho*-metallated C_6H_4 fragment is σ bonded to the Mo(1) atom and π-coordinated with the Re(1) atom. The hydride H(1) atom that was located during the structural study is a bridging atom between the Re(2) and Mo(2) atoms. The hydride atom is manifested in the ^{1}H NMR spectrum as a narrow singlet at high field (δ −13.31 ppm relative to TMS). The vinylidene proton H(2) gives a narrow singlet in low field (δ 7.84 ppm relative TMS). It is noteworthy that II is the first cluster having a butterfly metal framework and an μ_4-*ortho*-metallated phenylvinylidene ligand to have been structurally characterized. In spite of the deep rearrangement the cluster retains its 60 electrons, as the vinylidene bridge donates four electrons, as does PhC≡CH, and the elimination of two CO groups is compensated by σ,π-bonding of the C_6H_4 fragment and formation of a hydride bridge.

Experimental

The synthesis and isolation of the initial complexes and final products were carried out in a stream of argon. The hydrocarbon solvents were purified by distillation over dispersed sodium in a stream of argon. The initial complex I has been obtained previously [5]. The IR spectra were measured with a Specord 75 IR instrument in KBr pellets. The ^{1}H NMR spectra were recorded with a Bruker WP-200-SY (200, 13 MHz) in CD_2Cl_2 with TMS as internal standard. The X-ray diffraction data for cluster II were obtained with a four-circle automatic diffractometer CAD-4 (λ Mo-K_α, $\theta/2\theta$ scan). The crystal data are listed in Table 4). The structure was solved by direct method and refined in an anisotropic, full-matrix

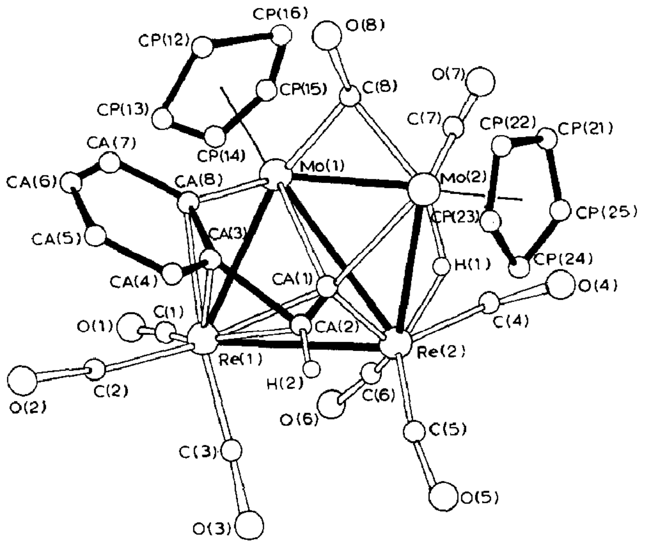


Fig. 1. The structure of $Cp_2Mo_2Re_2(\mu_4\text{-}C{=}C(H)\mu\text{-}CO(CO)_7(\mu\text{-}H)$.

Table 1

Atomic coordinates and their equivalent isotropic (for hydride H atom—isotropic) temperature factors for $Cp_2Mo_2Re_2(\mu_4\text{-}C{=}C(H)C_6H_4)(\mu\text{-}CO)(CO)_7(\mu\text{-}H)$

Atom	x	y	z	B (Å^2)
Re(1)	0.63845(8)	0.10263(7)	0.40139(3)	2.67(1)
Re(2)	0.87482(8)	0.13633(7)	0.34568(3)	2.82(1)
Mo(1)	0.7574(2)	−0.1042(1)	0.36278(5)	2.31(3)
Mo(2)	0.7639(2)	−0.0427(2)	0.26172(6)	2.69(3)
O(1)	0.831(2)	0.086(2)	0.4966(6)	6.4(4)
O(2)	0.435(2)	0.124(2)	0.4740(6)	6.3(5)
O(3)	0.641(2)	0.381(1)	0.3940(7)	5.8(4)
O(4)	1.089(2)	0.116(1)	0.2766(7)	5.0(4)
O(5)	0.823(2)	0.399(2)	0.3081(9)	8.0(5)
O(6)	1.072(2)	0.210(2)	0.4370(7)	9.1(5)
O(7)	1.023(1)	−0.177(1)	0.2835(6)	4.4(4)
O(8)	0.627(3)	−0.287(1)	0.2759(6)	4.5(4)
C(1)	0.758(2)	0.090(2)	0.4584(8)	3.7(4)
C(2)	0.511(2)	0.121(2)	0.4470(7)	3.5(4)
C(3)	0.643(2)	0.273(2)	0.3968(7)	2.6(4)
C(4)	1.008(2)	0.128(2)	0.3040(8)	4.0(5)
C(5)	0.844(2)	0.296(2)	0.3240(9)	3.8(5)
C(6)	0.999(3)	0.188(2)	0.399(1)	6.9(7)
C(7)	0.923(2)	−0.126(2)	0.2769(7)	3.8(5)
C(8)	0.681(2)	−0.192(2)	0.2795(7)	2.7(4)
CA(1)	0.703(2)	0.060(2)	0.3254(7)	2.6(4)
CA(2)	0.568(2)	0.092(2)	0.3158(8)	3.6(5)
CA(3)	0.488(2)	0.010(2)	0.3391(8)	3.8(5)
CA(4)	0.353(2)	0.018(2)	0.334(1)	4.7(6)
CA(5)	0.288(2)	−0.057(2)	0.363(1)	4.7(5)
CA(6)	0.352(2)	−0.147(2)	0.3922(9)	4.2(5)
CA(7)	0.477(2)	−0.160(2)	0.3997(8)	3.4(4)
CA(8)	0.564(2)	−0.087(2)	0.3705(7)	3.4(4)
CP(11)	0.840(2)	−0.304(2)	0.3601(9)	4.4(5)
CP(12)	0.735(2)	−0.304(2)	0.3931(8)	3.6(5)
CP(13)	0.768(2)	−0.226(2)	0.4385(9)	4.6(5)
CP(14)	0.889(2)	−0.180(2)	0.4360(9)	4.4(5)
CP(15)	0.934(2)	−0.231(2)	0.3921(8)	4.2(5)
CP(21)	0.788(3)	−0.078(2)	0.176(1)	6.1(7)
CP(22)	0.664(4)	−0.087(3)	0.1776(9)	8.6(9)
CP(23)	0.631(2)	0.038(4)	0.194(1)	8.8(9)
CP(24)	0.745(5)	0.101(3)	0.199(1)	8.1(1)
CP(25)	0.832(2)	0.034(4)	0.188(1)	8.1(8)
OW(1) [a]	0.400(5)	0.547(4)	0.477(3)	
OW(2) [a]	0.000	0.500	0.500	
H(1)	0.166	0.640	0.225	

[a] OW(1) and OW(2) were refined isotropically. Atoms refined anisotropically are in the form of the isotropic equivalent displacement parameter defined as $4/3\ [a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

approximation for all non-hydrogen atoms. The hydride atom is located in the difference Fourier synthesis but its parameters were not refined. All calculations were performed with a PDP 11/23 PLUS computer by use of the SDP program package.

Table 2

Bond lengths for $Cp_2Mo_2Re_2(\mu_4\text{-}C{=}C(H)C_6H_4)(\mu\text{-}H)\mu\text{-}CO)(CO)_7$

Bond	*d* (Å)	Bond	*d* (Å)
Re(1)–Re(2)	3.071(1)	CA(2)–CA(3)	1.42(4)
Re(1)–Mo(1)	2.841(2)	Re(1)–C(1)	1.84(2)
Re(2)–Mo(1)	2.977(2)	Re(1)–C(2)	1.92(3)
Mo(1)–Mo(2)	2.733(2)	Re(1)–C(3)	1.87(2)
Re(2)–Mo(2)	3.072(2)	C(1)–O(1)	1.19(3)
Re(1)–CA(1)	2.23(2)	C(2)–O(2)	1.14(3)
Re(1)–CA(2)	2.27(3)	C(3)–O(3)	1.19(2)
Re(1)–CA(3)	2.37(3)	Re(2)–C(4)	1.89(2)
Re(1)–CA(8)	2.33(3)	Re(2)–C(5)	1.86(2)
Re(2)–CA(1)	2.01(2)	Re(2)–C(6)	1.88(3)
Mo(1)–CA(1)	2.10(2)	C(4)–O(4)	1.20(3)
Mo(1)–CA(8)	2.11(2)	C(5)–O(5)	1.22(3)
Mo(1)–C(8)	2.43(2)	C(6)–O(6)	1.21(3)
Mo(2)–C(8)	1.96(2)	Mo(2)–C(7)	1.92(2)
Mo(2)–CA(1)	2.17(2)	C(7)–O(7)	1.19(3)
CA(1)–CA(2)	1.48(3)	C(8)–O(8)	1.18(2)

Table 3

Bond angles (°) for $Cp_2Mo_2Re_2(\mu_4\text{-}C{=}C(H)C_6H_4)(\mu\text{-}H)(\mu\text{-}CO)(CO)_7$

Re(1)Re(2)Mo(1)	56.01(4)
Re(1)Re(2)Mo(2)	89.75(4)
Re(1)Re(2)CA(1)	46.4(6)
Re(1)Mo(1)Re(2)	63.68(4)
Re(1)Mo(1)Mo(2)	102.08(6)
Re(1)Mo(1)CA(1)	50.9(5)
Re(1)Mo(1)CA(8)	53.8(6)
Re(2)Re(1)Mo(1)	60.31(4)
Re(2)Re(1)CA(2)	74.5(7)
Re(2)Re(1)CA(3)	104.5(6)
Re(2)Re(1)CA(8)	102.1(5)
Re(2)Mo(1)Mo(2)	64.94(6)
Re(2)Mo(1)CA(1)	42.5(5)
Re(2)Mo(1)CA(8)	111.4(6)
Mo(1)Re(1)CA(1)	47.0(5)
Mo(1)Re(1)CA(2)	73.6(5)
Mo(1)Re(1)CA(3)	72.9(5)
Mo(1)Re(1)CA(8)	46.6(5)
Mo(1)Re(2)Mo(2)	53.68(4)
Mo(1)Re(2)CA(1)	44.8(5)
Mo(1)Mo(2)CA(1)	49.1(5)
Mo(1)Mo(2)C(7)	78.9(6)
Mo(2)Re(2)CA(1)	44.9(4)
Mo(2)Mo(1)C(8)	43.9(4)
Mo(2)Mo(1)CA(1)	51.3(5)
CA(1)Re(1)CA(2)	38.3(7)
CA(1)Re(1)CA(3)	63.6(7)
CA(1)Re(1)CA(8)	68.6(7)
CA(2)Re(1)CA(3)	35.6(8)
CA(2)Re(1)CA(8)	63.6(6)
CA(3)Re(1)CA(80	37.5(7)

Table 4

Crystal data for II

Symmetry	monoclinic
Space group	$P2_1/c$
a (Å)	10.621(3)
b (Å)	10.979(4)
c (A)	26.106(6)
β (°)	96.91(1)
V (Å^3)	3022.07
Z	4
2θ (°)	54
Number of reflections measured	5656
Number of reflections with $I > 5\sigma(I)$ used in the refinement	2752
R_1	0.048
R_w	0.058

$Cp_2Mo_2Re_2(\mu_4$-$C{=}C(H)C_6H_4)(\mu$-$H)(\mu$-$CO)(CO)_7$ (II)

The dark-brown solution of $Cp_2Re_2Mo_2(CO)_8(\mu$-$CO)_2(\mu_4, \eta^2$-$PhC{\equiv}CH)$ (I) (0.6 g, 0.56 mmol) in *o*-xylene (30 ml) was refluxed in a stream of argon for 5 hours until the solution had attained a stable green colour. The solvent was evaporated and the residue chromatographed on a column with Al_2O_3 (5 × 20 cm), the dark green band was eluted by a mixture of hexane-benzene 1 : 4. The hexane-benzene solution was concentrated to 8–10 ml. After the addition of 4–5 ml of heptane the solution was kept at −5 °C for 24 h. The black-green crystals of II that separated were isolated by decantation, washed with pentane, and dried under vacuum. The yield was 0.25 g (41). IR spectrum (ν, cm^{-1}): 675 w, 750 s, 810 m, 830 m, 1010 w, 1805 s, 1910 v.s., 1925 sh., 1950 m, 1995 v.s., 2035 s.

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