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SYNTHESIS AND MOLECULAR STRUCTURE OF THE BINUCLEAR COMPLEX OF CHROMIUM WITH A BRIDGING BIS-CARBYNE LIGAND

N.A. USTYNYUK*, V.N. VINOGRADOVA, V.G. ANDRIANOV and Yu.T. STRUCHKOV

A.N. Nesmeyanov Institute of Organo-Element Compounds, U.S.S.R. Academy of Sciences, 117813 Moscow, 28 Vavilov St. (U.S.S.R.)

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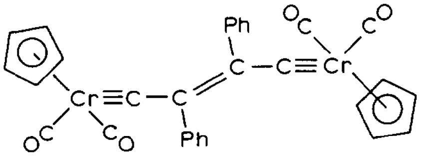
Summary

The binuclear bis-carbyne-chromium complex $(\eta\text{-}C_5H_5)(CO)_2Cr{\equiv}CC(Ph){=}C(Ph)C{\equiv}Cr(CO)_2(\eta\text{-}C_5H_5)$ has been obtained from $(\eta\text{-}C_5H_5)(CO)_3CrC{\equiv}CC_6H_5$ via a multi-stage redox cycle. The structure of this complex has been determined by an X-ray study.

We have found that after mixing the complex $(\eta\text{-}C_5H_5)(CO)_3CrC{\equiv}CC_6H_5$ (I) with a K/Na alloy in tetrahydrofuran (THF) at 25°C separation from the reducing agent by filtration and subsequent chromatography on silica gel gives complex II. Elemental analysis and mass spectrometry have shown the complex to have the composition $[C_5H_5(CO)_2Cr]_2(C{\equiv}CC_6H_5)_2$. Since the structure of II could not be reliably established from spectral data (^1H and ^{13}C NMR, IR and mass spectra), it was studied by an X-ray method. As a result of this study, complex II was shown to have a bis-carbyne structure:



(II)

The conversion of I to II is a fairly complicated process. It can be assumed that this process represents a redox cycle in which the initial stage of reduction of the triple bond with K/Na and the final stage of oxidation of the reduction products, involving rearrangement into the carbyne structure, are divided by cleavage of the CO group and β,β-dimerization. An additional study is now under way to elucidate the conversion scheme I → II; the results will be described in a separate paper.

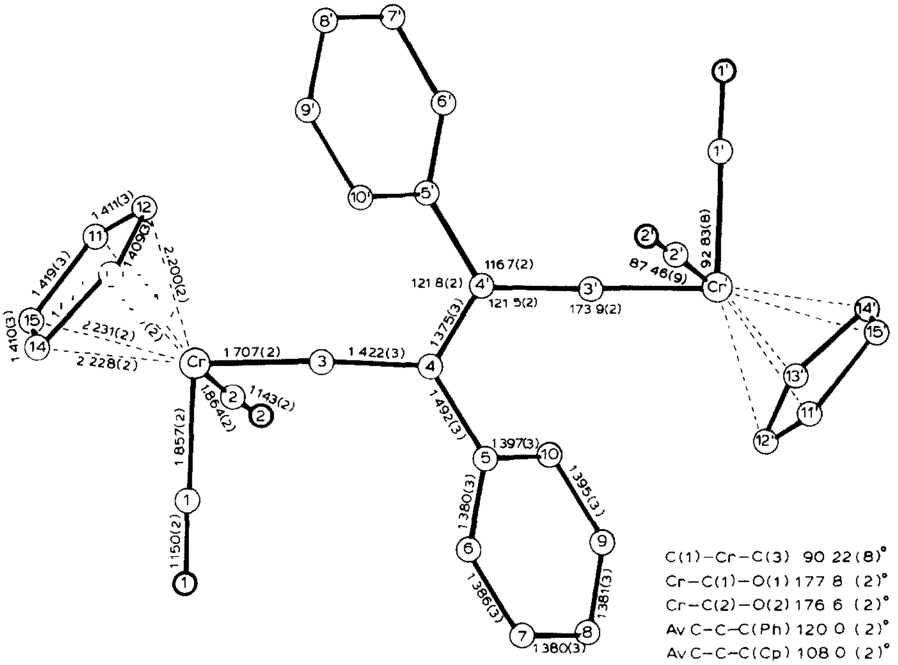


Fig. 1. Molecular structure of complex II.

In molecule II (Fig. 1), two "carbyne" moieties joined by a 1,2-diphenylethylene group can be distinguished. Note that due to crystallographic symmetry C_i, the complex has a transoid configuration *.

Although the structures and chemistry of a fairly large number of carbyne complexes of chromium and other transition metals have been studied up to now, compound II represents, to our knowledge, the first example of a binuclear complex incorporating a bridging bis-carbyne ligand. Moreover, it is the first carbyne chromium complex to contain a cyclopentadienyl ligand.

The chromium atom in II has a "piano stool" coordination, the coordination polyhedron being slightly distorted as a result of unequal bond angles between the "legs" of the stool and their deviation from an ideal value of 90°. The geometry of II can be compared with that of $[(\eta\text{-}C_5H_5)Cr(CO)_2]_2$ (III) [1] and $[(\eta\text{-}C_5Me_5)Cr(CO)_2]_2$ (IV) [2], where the $Cp(CO)_2Cr\equiv$ moieties may also be distinguished as these compounds contain a triple metal–metal bond. However, all the carbonyl ligands in the dimeric molecules III and IV turn out to be semi-bridging, which is responsible for the marked difference between the bond angles C–Cr–C (84.7 in III, 88.9° in IV) and C–Cr–Cr (73.6 in III, 76.0° in IV). Furthermore, the distortion observed is accompanied with an opening of the Q–Cr–Cr angle (Q being the Cp ring centroid) to 161.8 in III and 158.7° in IV, compared with 125.3° ** typical of octahedral

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* As follows from the ^1H NMR, ^{13}C NMR and IR spectra, complex II is formed as a mixture of a *cis* and a *trans*-isomer, with the latter predominating in the mixture (1/4.7).

** Note that in the structure $[(\eta\text{-}C_5H_5)Mo(CO)_2]_2$ [3], similar to those of III and IV, the Q–Mo–Mo–Q group is linear, i.e. the Q–Mo–Mo angle is opened to 180°

TABLE 1

PLANAR MOLECULAR MOIETIES (atoms with a prime are related to the reference ones by the centre of symmetry)

(a) Deviations of atoms, Δ (Å), from mean-root-square planes

Plane 1	C(3)	C(4)	C(5)	C(3′)	C(4′)	C(5′)	Cr [a]
Δ	0.000	−0.002	0.000	−0.000	0.002	−0.000	0.099
Δ/σ	0.19	0.83	0.18	0.19	0.83	0.18	390.84
Plane 2	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(4) [a]
Δ	−0.009	0.011	−0.005	−0.004	0.004	0.005	−0.037
Δ/σ	4.76	5.10	2.03	1.63	1.47	2.18	17.75
Plane 3	C(11)	C(12)	C(13)	C(14)	C(15)	Cr [a]	
Δ	−0.004	0.004	−0.002	−0.001	0.003	−1.860	
Δ/σ	2.54	2.36	1.28	0.28	1.82	7386.2	

(b) Equations of planes, $Ax + By + Cz - D = 0$

Plane	A	B	C	D
1	0.0475	0.7947	−0.6051	0.7207
2	0.8437	0.0023	−0.5369	1.2461
3	−0.1394	−0.6156	−0.7756	−2.0947

(c) Dihedral angles τ (deg.)

Planes	1,2	1,3	2,3
τ	68.5	88.5	107.3

[a] Atoms not included in the calculation of the equations of planes.

coordination. At the same time, in II the Q–Cr≡C angle is 132.5°. Nevertheless, this distortion of the octahedral coordination of the metal atom in III and IV, as well as in the genetically related complex $[(\eta\text{-}C_5H_5)_2Cr_2(CO)(\mu\text{-}C_4Ph_4)]$ (V) [4], only slightly affects the characteristics of the other structurally equivalent bond lengths and angles. Therefore comparison of the geometry of II with those of III, IV and V is quite justified.

The tridentate cyclopentadienyl ligand in molecule II is planar (Table 1) with a usual mean value of the C–C bond lengths of 1.412 Å (1.388, 1.413 and 1.403 Å in III, IV and V, respectively). However, the C atoms of the cycle are bonded to the Cr atom somewhat differently as two of the Cr–C distances are slightly greater than the remaining three. A similar situation is observed in all cyclopentadienyl chromium derivatives, including III, IV and V, although the mean Cr–C(Cp) distance remains virtually the same: 2.214 in II, 2.190 in III, 2.213 in IV and 2.223 Å in V. The reason for the different Cr–C(Cp) distances appears to be due to steric factors, viz. substantially shortened intramolecular contacts of the C atoms of the carbonyl groups with those of the cyclopentadienyl ligand: C(1) ··· C(14) 2.833(3), C(2) ··· C(11) 2.951(3), C(2) ··· C(15) 3.109(3), C(3) ··· C(12) 3.041(2) and C(3) ··· C(13) 3.170 Å, the doubled Van der Waals radius of carbon being 3.60 Å [5].

TABLE 2

GEOMETRIES OF SOME CARBYNE CHROMIUM COMPLEXES

Complex	$Cr{\equiv}C$ (Å)	$Cr{\equiv}C-R$ (deg.)	Ref.
$I(CO)_4Cr(CMe)$	1.69	180	7
$Br(CO)_3(PMe_3)Cr(CMe)$	1.68	177	7
$[(CO)_4(PMe_3)Cr(CMe)]BCl_4$	1.67	–	8
$Cl(CO)_4Cr(CPh)$	1.68	180	9
$Br(CO)_4Cr(CPh)$	1.68	180	9
$Br(CO)_2[P(OPh_3)]_2Cr(CPh)$	1.68	178.5	10
$Br(CO)_2(t\text{-}C_4H_9NC)_2Cr(CPh)$	1.76	171	10
$Br(CO)_4Cr(CC_6H_4CF_3\text{-}p)$	1.68	171	11
$Ph_3Sn(CO)_4Cr(CNEt_2)$	1.74	177	12
$Br(CO)_3(PPh_3)Cr(CNEt_2)$	1.75	173	13
$[(CO)_4(PPh_3)Cr(CNEt_2)]BF_4$	1.76	175	13
$Br(CO)_4Cr(CNEt_2)$	1.72	172	14
$[(CO)_5Cr(CNEt_2)]BF_4$	1.78	175	15
$[(CO)_2(C_5H_5)Cr(CCPh)]_2$	1.707	173.9	This work

The metal carbonyl groups of II are linear, the Cr–C–O bond angles being 177.8(2) and 176.6(2)°, and the mean Cr–C and C–O bond lengths 1.860 and 1.146 Å, respectively.

The bridging ethylene moiety C(3)C(4)C(5)C(4′)C(5′)C(3′), including the C(5) and C(5′) *ipso* atoms of the Ph substituents, is completely planar (Table 1). The Cr atoms deviate upwards and downwards from the plane of this moiety by 0.099 Å, the Cr–C(3)–C(4)–C(4′) torsion angle being 148(1)°, and the Ph rings are turned by 68.5° with respect to the ethylene group and brought out of conjugation with the ethylene bond, which is, among other features, confirmed by a normal C(4)–C(5) bond length. Concerning the distribution of the C–C bond lengths in this part of molecule II, it is interesting to note an unusual elongation of the C(4)=C(4′) double bond to 1.375(3) Å, compared with the standard value of 1.333 Å [5]. On the other hand, the C(3)–C(4) and C(4)–C(5) distances, 1.422(3) and 1.492(3) Å, are typical of bonds of the type $C(sp)-C(sp^2)$ and $C(sp^2)-C(sp^2)$, respectively [5].

The bridging ligand in II should act as a six-electron donor for the effective atomic number rule to be fulfilled for both Cr atoms. In fact, the Cr–C(3) distance of 1.707(2) Å is considerably shorter than the Cr–CO distances. The latter bonds are of a multiple type and the Cr–C(3) distance seems to correspond to the triple metal–carbon bond *. Table 2 gives some examples of the structurally studied chromium carbyne complexes which are characterized by the following two features: the shortest (of all known) Cr–C distances and linearity of the metal–carbyne $Cr{\equiv}C-R$ moiety in full agreement with the carbon atom *sp*-hybridization. Slight bending of the carbyne group is most likely due to the effect of the crystal field. It is interesting that the Cr–C bond length is, in fact, unaffected by either the type of substituent R at the C atom or the individual features of the other ligands in the chromium coordination sphere. Nevertheless, a trend towards a certain lengthening

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* A qualitative treatment of the metal–carbon interaction in carbyne complexes is given in ref. 6.

of the Cr–C bonds has been noted in a few complexes containing $CNEt_2$ ligands. This trend is probably due to the delocalization of electron density in the Cr–C–N unit with a probable (for example, in the case of II) contribution of the resonance structures:

The crystal structure of II consists of discrete molecules joined by usual Van der Waals interactions with no anomalous intermolecular contacts.

Experimental

All experimental operations, except preparative TLC, were carried out in argon atmosphere. ^1H NMR and ^{13}C NMR spectra were measured with a Bruker WP 200 SY spectrometer, IR spectra with a UR-20 instrument, and mass spectra with an AEI MS-30 spectrometer.

Preparation of II

To a yellow solution of 0.5 g (15 mmol) of I in 30 ml of absolute THF was added 0.2 ml of a K/Na alloy. The reaction mixture, which immediately turned red, was stirred for 1 h at 25°C until the complete disappearance of I (TLC and IR spectrum monitoring). The solution was filtered from the alloy and evaporated in vacuo. The residue was chromatographed on silica gel plates in a petroleum ether/benzene mixture (1/1). Reprecipitation from a CH_2Cl_2/heptane mixture gave shiny dark brown crystals of II. Yield 0.11 g, m.p. 163–165°C.

Analysis: Found: C, 65.50; H, 3.78; Cr, 18.98. $C_{30}H_{20}Cr_2O_4$ calcd.: C, 65.69; H, 3.68; Cr, 18.98%. IR: $\nu(CO)$ ($CHCl_3$) 1934, 1990 cm^{-1} (*trans*); 1934, 2007 cm^{-1} (*cis*); $\nu(CO)$ (cyclohexane) 1945, 1995 cm^{-1} (*trans*); 1945, 2012 cm^{-1} (*cis*). ^1H NMR (δ, $CDCl_3$): *trans*-isomer 4.72 (C_5H_5), 7.25–7.70 (C_6H_5); *cis*-isomer 4.53 (C_5H_5), 7.25–7.70 (C_6H_5). ^{13}C NMR (δ, CH_2Cl_2): *trans*-isomer 90.8 (C_5H_5), 128.4 and 130.4 (*o*-, *m*- and *p*-C_6H_5), 136.1 (*ipso*), 138.1 or 153.6 ($>C=$), 240 (CO), 321.3 ($Cr{\equiv}C$); *cis*-isomer 89.0 (C_5H_5), 248.0 (CO), 337.4 ($Cr{\equiv}C$). The signals of the aromatic and olefinic C atoms of the *cis*-isomer were overlapped by the signals of the predominating *trans*-isomer. Mass spectrum, m/z (intensity), ion: 548 (3.9), M^+; 492 (4.3), $M^+ - 2CO$; 464 (2.5), $M^+ - 3CO$; 436 (64.4), $M^+ - 4CO$; 182 (78.7), $C_{10}H_{10}Cr^+$; 173 (1.2), $C_5H_5(CO)_2Cr^+$; 145 (2.5), $C_5H_5(CO)Cr^+$; 117 (44.2), $C_5H_5Cr^+$; 52 (100), Cr^+.

An X-ray study was carried out with a four-circle Syntex $P2_1$ automatic diffractometer (λMo-K_α, graphite monochromator) at −120°C.

Crystals of II are monoclinic; a 19.474(4), b 15.282(3), c 8.710(2) Å, β 110.06(1)°, V 2434.9(8) $Å^3$, d_{calc} 1.50 g cm^3 for $Z = 4$, space group $C2/c$ (the molecule occupies a special position at the centre of symmetry). The above diffractometer was used to measure ($\theta/2\theta$ scan) the intensities of 2180 reflections with $I \geqslant 3\sigma$ in the range $2° \leqslant 2\theta \leqslant 60°$ with no correction for absorption (μ(Mo-K_α) 9.69 cm^{-1}). The structure was solved by the direct method using the MULTAN program and was refined by a least-squares technique in a full-matrix anisotropic approximation (an isotropic approximation for the H atoms whose positions were calculated geometrically). The final values were $R = 0.027$ and $R_w = 0.040$. The coordinates and

TABLE 3

ATOMIC COORDINATES ($\times 10^5$) AND TEMPERATURE FACTORS ($Å^2$) IN THE FORM $B_{iso}^{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (a_i a_j)$

Atom	x	y	z	B_{iso}^{eq}
Cr	34765(2)	15249(2)	26583(3)	1.13(1)
O(1)	47744(8)	9695(9)	55343(16)	2.04(4)
O(2)	41144(9)	32862(9)	23963(19)	2.65(4)
C(1)	42871(10)	11889(11)	44205(21)	1.37(4)
C(2)	38854(11)	26050(11)	24724(22)	1.71(5)
C(3)	31098(10)	20173(12)	29588(21)	1.57(5)
C(4)	28621(11)	24985(13)	50652(23)	1.80(5)
C(5)	34251(10)	30025(11)	63655(20)	1.36(4)
C(6)	39558(12)	25634(12)	75947(23)	1.90(5)
C(7)	44694(13)	30196(14)	88410(24)	2.48(6)
C(8)	44697(12)	39229(14)	88448(27)	2.44(6)
C(9)	39522(14)	43725(13)	76058(29)	2.72(6)
C(10)	34286(12)	39163(12)	63576(25)	2.20(5)
C(11)	29689(12)	13842(12)	−154(21)	1.82(5)
C(12)	24895(12)	10409(12)	7339(21)	1.78(5)
C(13)	28368(11)	3273(12)	17185(23)	1.97(5)
C(14)	35312(12)	2193(12)	15686(22)	2.06(5)
C(15)	36135(12)	8682(13)	4947(22)	1.95(5)

temperature factors of non-hydrogen atoms are listed in Table 3. Table 1 gives the geometric parameters of some of the planar moieties of molecule II.

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