Journal of Organometallic Chemistry, 411 (1991) 193–205
Elsevier Sequoia S.A., Lausanne
JOM 21631

Antiferromagnetic complexes with metal–metal bonds

XXIV *. Bi- and trinuclear cyclopentadienyl clusters of chromium with nitrene bridges

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(Received December 5th, 1990)

Abstract

An antiferromagnetic trinuclear cluster $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})$ (I) has been obtained by refluxing of chromocene with azobenzene in toluene. Chromatography of the cluster on Al_2O_3 (with MeOH as an eluent) leads to its oxidation into the diamagnetic ionic cluster $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+\ OH^-\cdot MeOH$ (II) (Cr–Cr 2.530(3)–2.561(3) Å). The same cation (Cr–Cr 2.544–2.575 Å) may be isolated with $Co(CO)_4^-$ (III) as the outer anion if I is oxidized by cobalt carbonyl. III has been studied by means of X-ray structural analysis (space group $C2/c$, $a = 31.860(6)$, $b = 16.246(3)$, $c = 24.178(5)$ Å, $\beta = 138.21(1)°$, $V = 8338.94$ Å^3, $Z = 8$). Bond lengths (Cr–Cr) in II are 2.544–2.575 Å.

The dimeric complex $Cp_2Cr_2(OCMe_3)_2(\mu\text{-NPh})_2$ (V), with a chromium–chromium bond length of 2.627 Å and the Cp ligands located in *trans* position relative to the Cr–Cr bond, has been obtained by reaction of the binuclear complex $Cp_2Cr_2(OCMe_3)_2$ with azobenzene. It is antiferromagnetic ($-2J = 146$ cm^{-1}) and does not interact with $Co_2(CO)_8$; however, it may readily be oxidized by oxygen to form $Cp_2Cr_2(O)_2(\mu\text{-NPh})_2$ (VI) (space group $P2_1/c$, $a = 6.723(1)$, $b = 16.303(4)$, $c = 9.220(3)$ Å, $\beta = 96.43(2)°$, $V = 1004.2$ Å^3, $Z = 2$).

Calculations of electronic structures of V and VI have been performed by the extended Hückel method. It has been shown that in VI there is, along with the existence of a Cr–Cr bond (2.532 Å), an antiferromagnetic interaction ($-2J = 600$ cm^{-1}) between Cr^V ions (electronic configuration d^1). This has been explained by there being only a small gap between the Cr–Cr σ- and the non-bonding vacant δ-orbitals.

Introduction

The nitrene ligands NR are isoelectronic analogues of O, S, Se and Te atoms and are frequently used for synthesis of clusters of Group VIII elements [1,2]. These

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* For Part XXIII see ref. 21.

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compounds are usually electronically saturated and are diamagnetic. A 50-electron cluster with mixed ligands, $Cp_3Co_3(\mu_3\text{-NR})(\mu_3\text{-S})$ has recently been synthesized, whose magnetic properties depend on the nature of the bridging groups [3].

So far as the early transition metals are concerned, the diamagnetic complexes of Ti^{IV}, $Cp_2Ti_2(X)_2(\mu\text{-NR})_2$ (X = Cl, Me) [4] and $Cp_2Ti_2(Cl)_2(\mu\text{-NR})(\mu\text{-}N_2R_2)$ [5] are known, while the only one to have been structurally characterized is the dimeric diamagnetic complex of Cr^V, $Cp_2Cr_2(NSiMe_3)_2(\mu\text{-NSiMe}_3)_2$ where there is *cis*-location of the Cp-rings and proof of the existence of the Cr–Cr bond (2.569 Å) [6].

The present paper concerns synthesis and structure of antiferromagnetic chromium clusters with μ-bridged nitrene ligands. Preliminary results have been reported [7,8].

Results and discussion

Chromocene, Cp_2Cr, which readily loses one ring, and the binuclear $Cp_2Cr_2(\mu\text{-OCMe}_3)_2$ complex (capable of oxidative addition of halogen atoms, two OR groups, an S_4 fragment or Se and Te atoms to Cr^{II} atoms [9–11]) have been used as starting materials for synthesis of chromium clusters with nitrene ligands.

Trinuclear clusters $Cp_3Cr_3(\mu_3\text{-NPh})(\mu\text{-NPh})_3^{n+}$ (n = 0, 1)

Chromocene reacts with azobenzene in refluxing toluene to form a neutral triangular cluster $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})$ (I) which has been isolated in the form of needle-like crystals and characterized by means of mass- and IR-spectroscopy [8] (Scheme 1). I is formally an electron-deficient complex (it contains 43 electrons) and demonstrates antiferromagnetic properties. The value of μ_{eff} decreases from 2.05 to 1.79 μ_B in the temperature range of 290–77 K, which can be described in terms of the Heisenberg–Dirac–Van Vleck model for a trimer [12] for chromium atoms with spins of $S_1 = 3/2$; $S_2 = S_3 = 1$ and exchange parameters $-2J = 160$ cm^{-1}. I is oxidized in the course of chromatography on Al_2O_3 with methanol as an eluent. With the solvating MeOH molecule the cationic diamagnetic cluster Cr^{IV}, $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+OH^-$ (II) is thus formed. According to X-ray structural analysis * the cation contains an almost equilateral triangle Cr_3 ($Cr\text{–}Cr_{mean}$ 2.547 Å) with three μ-bridging NPh groups ($Cr\text{–}N_{mean}$ 1.84 Å) located above its plane while three Cp-rings and μ_3-NPh bridge ($Cr\text{–}N_{mean}$ 1.88 Å) are located below the plane (Table 1). In general the geometry of cation II resembles that well-known for the sulphide clusters $Cp_3Mo_3(\mu\text{-S})_3(\mu_3\text{-S})^n$ ($n = 0$ [13]; $n = +1$ [14]). However the presence of the phenyl substituents at nitrogen atoms in II hinders the attachment of the fourth CpCr fragment, thus preventing the formation of the Cr-containing analogue of $Cp_4Mo_4S_4$ with NPh-bridges.

The Co(CO) fragment is linear and thus preferable in sterically strained systems. However, even the linear Co(CO) fragment, which is readily attached to $Cp_3Cr_3S_4$, cannot be attached to I and reaction of I with $Co_2(CO)_8$ (at 5 °C in benzene) results only in formation of a cationic diamagnetic cluster $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+Co(CO)_4^-$ (III) (Scheme 1), without further transformation even by irradiation with UV.

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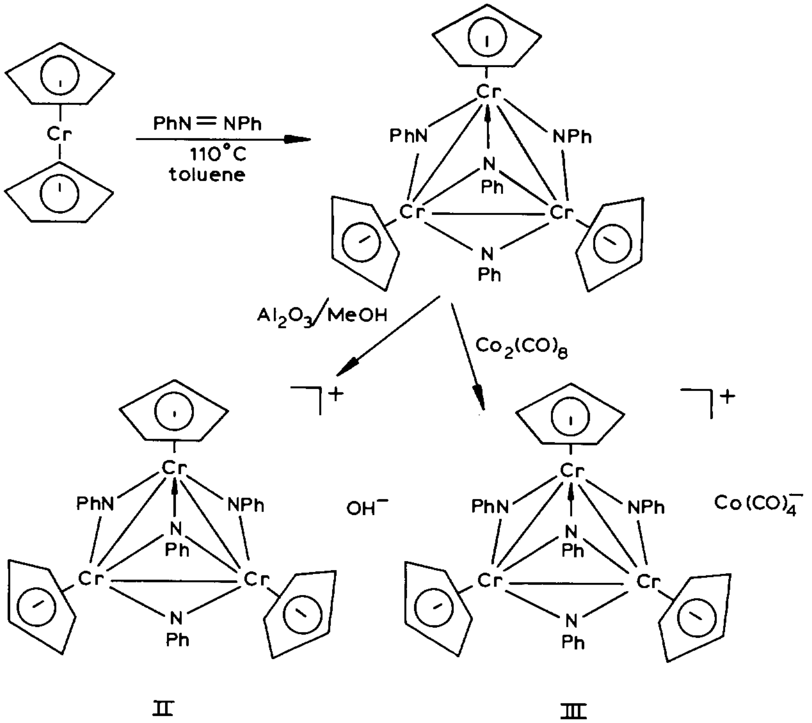
* The full data on the geometry of II are presented in ref. 8, atomic coordinates are deposited in the Cambridge Crystallographic Data Centre.



Scheme 1. Synthesis of triangular clusters with Cr_3N_4-core.

X-ray structural analysis of III (Tables 1, 5) implies the geometry of the cluster cation III hardly differs from that observed in II (Cr–Cr 2.544 (1)–2.565(1) Å), although the Cr–N bond lengths are closely similar (Cr-μ-NPh 1.827(4)–1.855(4) Å; Cr-μ_3-NPh 1.954(4)–1.963(4) Å) unlike their analogues in II, presumably because of the high symmetry of the outer anion $Co(CO)_4^-$ in which the cobalt atom has a tetrahedral surrounding (Co–C 1.739(8)–1.766(9) Å; C–Co–C 106.9(3)–111.7(3)°) (Fig. 1).

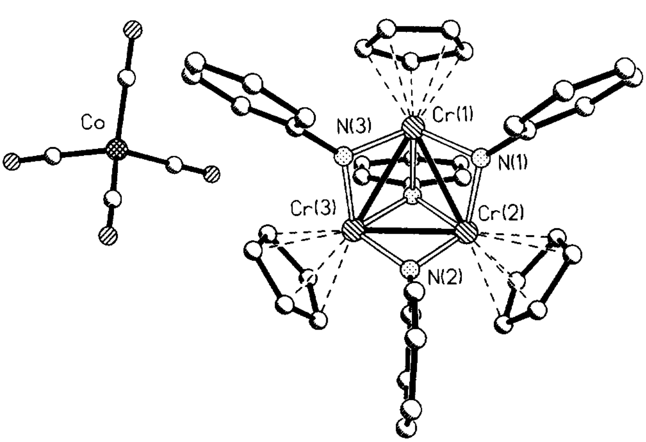


Fig. 1. The molecular structure of $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+ Co(CO)_4^-$.

Table 1

The main structural data of $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+X^-$ ($X = OH$, $Co(CO)_4$) clusters [a]

Compound	Bond length (Å) bond angles (°)					
	Cr–Cr	Cr–μ-NPh	Cr–μ_3-NPh	Cr–Cr–Cr	Cr–μ-NPh–Cr	Cr–μ_3-NPh–Cr
$Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+OH^-$ (II) [8]	2.530(3) 2.550(3) 2.561(3)	1.78(1)– 1.90(1)	1.81(1)– 1.96(1)	59.35(9) 60.10(9)	86.2(5)– 90.1(6)	79.9(5)– 85.3(6)
$Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})^+Co(CO)_4{}^-$ (III)	2.544(1) 2.565(1) 2.575(1)	1.827(4)– 1.855(4)	1.954(5)– 1.963(5)	59.32(3) 60.14(3) 60.54(3)	87.5(2)– 88.2(2)	81.1(2)– 82.4(2)

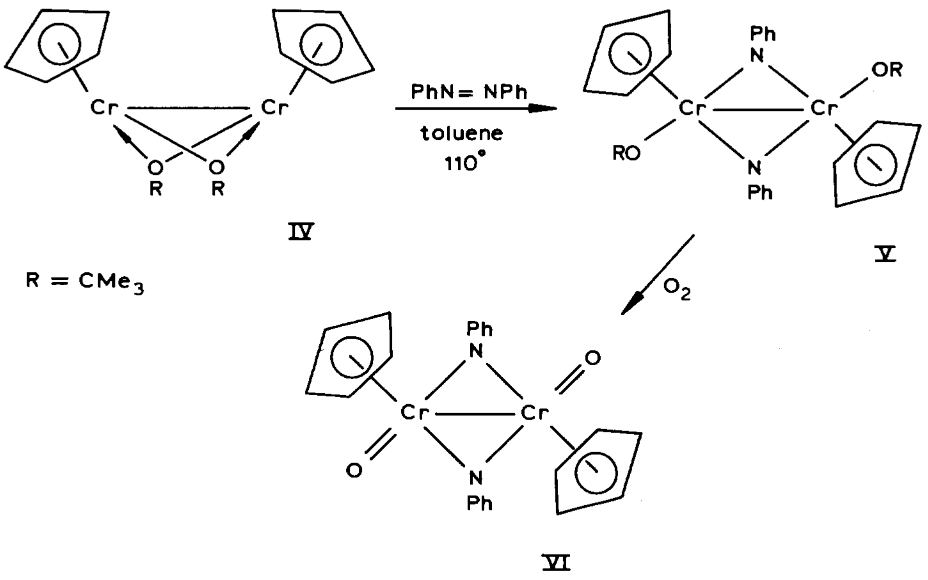
[a] Single crystal of II contains one MeOH molecule and one half of a C_5H_6 molecule per cluster molecule. Single crystal of III contains one half of a THF molecule per cluster molecule.

In the IR spectrum there is a band at 1870 cm^{-1} characteristic of the $Co(CO)_4^-$ anion. Shortening of the Cr-μ-NPh bond points presumably to supplementary π-bonding attributable to the interaction of lone electron pairs of nitrogen and vacant orbitals to make the formally electron-deficient 42-electron cluster a 48-electron cluster. It is noteworthy that reaction of chromocene with azobenzene (with formation of cluster I) differs greatly from the reaction of nickelocene under the same conditions where orthometallation of the phenyl ring results, along with preservation of the N=N bond and formation of the monomer $CpNi(C_6H_4N{=}NPh)$ [15] with 18-electron surrounding.

Binuclear chromium complexes with nitrene bridges

We have shown that in the reaction of PhN=NPh with the binuclear $Cp_2Cr_2(\mu\text{-}OCMe_3)_2$ (IV), which has a short Cr^{II}–Cr^{II} bond (2.635 Å) [16] and three half-occupied orbitals [10], the N=N bond in azobenzene is ruptured to form nitrene groups. However, in this case the binuclear structure of the complex is preserved, although $OCMe_3$ bridges are replaced by nitrene bridges [8]. $Cp_2Cr_2(OCMe_3)_2(\mu\text{-}NPh)_2$ (V) (which has been isolated in the form of dark-brown crystals) contains in its mass spectra peaks of the molecular ion (m/z 562) and demonstrates antiferromagnetic properties. The value of μ_{eff} decreases from 2.27 to 0.96 M.B. in the temperature range of 293–77 K. Such behaviour may be described in terms of the Heisenberg–Dirac–Van Vleck model for a dimer [12] with the exchange parameter $-2J = 140$ cm^{-1} for the spin values of $S_1 = S_2 = 1$ [7].

X-ray structural analysis of V shows Cr^{IV} atoms with electronic configuration of d^2 to have a Cr–Cr bond length of 2.627 Å, the same as in the initial IV with electronic configuration d^4 for Cr^{II} ions. Besides, the C_5H_5 rings in V are located in the *trans* position relative to the Cr–Cr bond while in IV they are located in the *cis*



position. The Cr_2N_2 cycle in V is practically planar in contrast to the "butterfly" geometry of the Cr_2O_2 fragment in IV. Each chromium atom in V has ligands surrounding it in "piano stool" configuration with non-equivalent Cr–N distances (the mean values are 1.80 and 1.93 Å). The Cr–N and Cr–OR distances (1.832(6) Å) are shortened considerably in comparison with the sum of the covalent radii of the Cr and N or O atoms [17] presumably as a result of the supplementary π-interaction of the lone electron pairs of oxygen and nitrogen atoms with the free orbitals of Cr^{IV}.

V cannot be oxidized by weak oxidizing agents such as $Co_2(CO)_8$ or $Cp_2Mo_2(CO)_6$ but reacts with atmospheric oxygen to form an oxo-derivative $Cp_2Cr_2(O)_2(\mu\text{-}NPh)_2$ (VI). Mass-spectra of the dark-violet crystals of VI reveals a peak corresponding to the molecular ions (m/z 448), while in the IR-spectrum there are vibration bands corresponding to C_5H_5 (810, 1010, 3040 cm^{-1}), C_6H_5 (695 cm^{-1}) and Cr=O (890 cm^{-1}).

According to X-ray structural analysis the general geometry of VI resembles that of the alkoxide complex V: the Cp-rings are located in the *trans* position relative to the Cr–Cr line, besides which there exists a planar cycle Cr_2N_2 (Table 2) (Fig. 2). When OR groups are replaced by oxygen atoms short Cr=O bonds (1.609(2) Å) are found. The Cr–Cr–O value in VI, 112.59(8)°, being greater than the mean value of 104.2° for Cr–Cr–O in V, affects the position of the Cp rings, with the angle (Cp-centre)–Cr–Cr being reduced to 129.75° in VI compared with 134.6° in V. As a result the distance between the Cr^V ions in VI, 2.5322(5) Å, is shorter than in V (2.627(1) Å) and in IV (2.635 Å). In this situation the antiferromagnetic properties in V seem quite unexpected: μ_{eff} decreases from 1.16 to 0.88 M.B. in the temperature range of 296–77 K in accordance with the Heisenberg–Dirac–Van Vleck model for a dimer [12] with the exchange parameter $-2J = 586$ cm^{-1} (the admixture of the monomer is 5%; the root-mean-square error 4%). It is noteworthy that the *cis*-structure formation of the known isoelectronic binuclear complex $Cp_2Cr_2(=NSiMe_3)_2(\mu\text{-}NSiMe_3)_2$ (Cr=N 1.65 Å), with the only slight elongation of the Cr–Cr bond (2.569 Å), makes the complex diamagnetic [6].

In these complexes V and VI the combination of a short distance between the metal atoms and an antiferromagnetic pattern of behaviour is quite unusual because the number of unpaired electrons at the chromium atom is low (2 in V and only 1 in VI). In order to elucidate the character of Cr–Cr bonding in these compounds the electronic structure of the molecules V and VI has been calculated by the extended Hückel method, following the technique we described earlier [10,18].

In V, d-orbitals proved to form a compact group with an energy gap between them (0.5 eV) comparable with the Hund energy (Fig. 3). Effective spin Hamiltonian calculation reveals that the most advantageous solution is the decoupling of two of the four electrons located on δ and $\delta^\star$ orbital. Thus appears the σ^2 δ^1 $\delta^{\star 1}$ electronic configuration (Table 3). The local spin of each centre thus becomes equal to 1/2 and in accordance with the symmetry of overlapping magnetic orbitals, antiferromagnetic interaction may be anticipated.

Calculation shows that there is no difference if the radicals in the alkoxide and nitrene groups of the complex V are replaced by methyl groups (Fig. 3, Table 3). If the terminal OR groups in VI are replaced by the strongly polarized Cr=O groups, the energy of d-orbitals becomes overrated unless the dependence of atomic potentials on the efficient charges on atoms is taken into consideration. This causes

Table 2

The main structural and magnetic data of $Cp_2Cr_2(OCMe_3)_2(\mu\text{-}NPh)_2$ (V) and $Cp_2Cr_2(O)_2(\mu\text{-}NPh)_2$ (VI) complexes

Compound	Cr–Cr	Cr–μ-NPh	Cr=O	Cr–N–Cr	Cr–Cr–O	Cp–Cr–Cr [a]	$-2J$ (cm^{-1})
$Cp_2Cr_2(OCMe_3)_2(\mu\text{-}NPh)_2$ (V) [8]	2.627(1)	1.796(5) 1.934(6) 1.807(6) 1.926(6)	1.832(6)	89.1(2)–89.2(2)	103.3(2)–105.0(2)	134.6	140
$Cp_2Cr_2(O)_2(\mu\text{-}NPh)_2$ (VI)	2.5322(5)	1.844(2) 1.845(2)	1.609(2)	86.70(9)	112.59(8)	129.8	586

[a] Cp = centre of C_5H_5-ring.

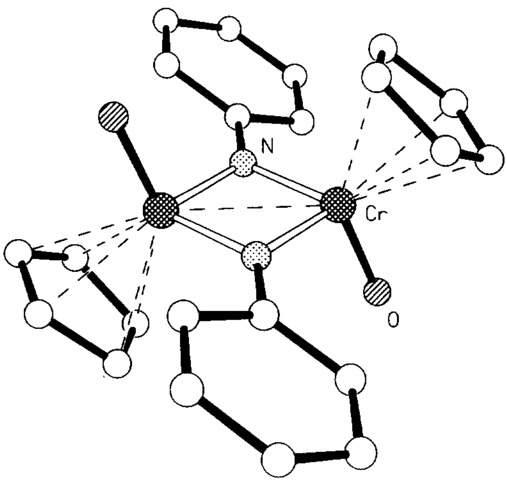


Fig. 2. The molecular structure of $Cp_2Cr_2(O)_2(\mu\text{-}NPh)_2$.

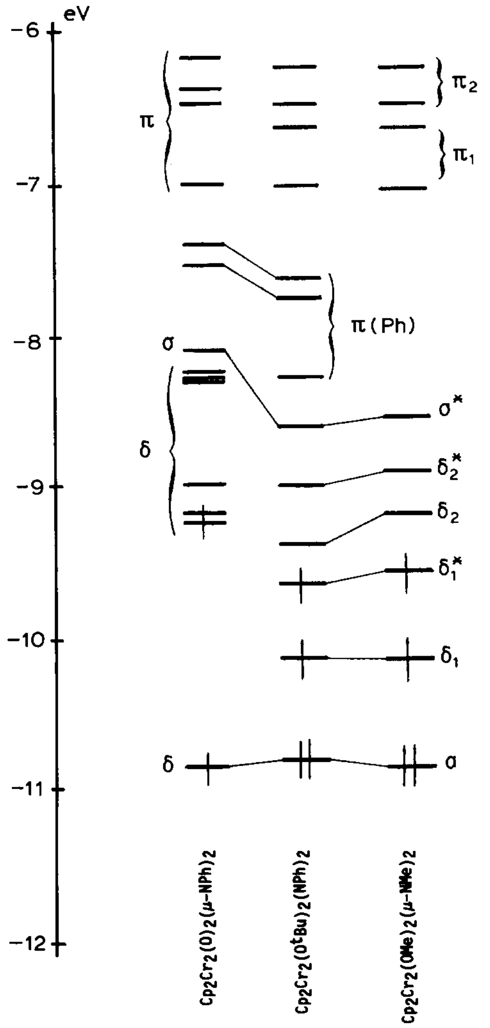


Fig. 3. Energy level diagram.

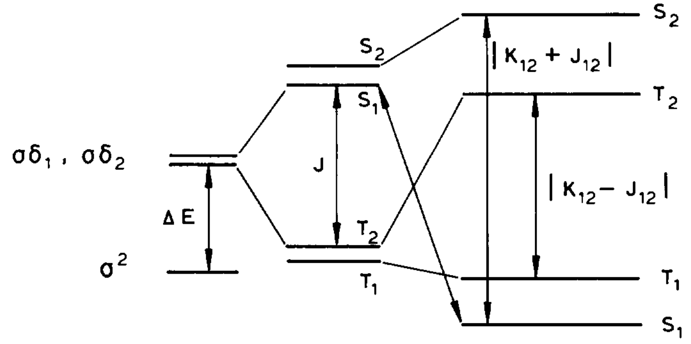
Table 3

Relative energies of states with different local spins in $Cp_2Cr_2(OR^1)_2(NR^2)_2$ [a]

	$(R^1 = R^2 = Me)$		$(R^1 = {}^tBu;\ R^2 = Ph)$	
	Cr(1)	Cr(2)	Cr(1)	Cr(2)
Local spin	1/2	1/2	1/2	1/2
n	0.738	0.733	0.701	0.695
Electronic configuration $(d/s+p)$	3.980/0.724	3.976/0.714	3.950/0.686	3.953/0.752
$\bar{J}$ (eV)	0.730		0.732	
$\Delta E + \Delta\epsilon$ (eV)	$-0.734+0.584=-0.150$		$-0.689+0.489=-0.200$	
Local spin	1	1	1	1
n	1.543	1.361	1.409	1.364
Electronic configuration $(d/s+p)$	3.954/0.712	3.718/0.703	3.986/0.686	3.798/0.758
$\bar{J}$ (eV)	0.741		0.745	
$\Delta E + \Delta\epsilon$ (eV)	$-1.860+2.260=+0.400$		$-1.749+1.932=+0.183$	

[a] n = number of unpaired d-electrons at Cr centres. $\bar{J}$ = mean parameter of local spin Hamiltonian. $\Delta E + \Delta\epsilon$ = contribution to the energy changes occurring on unpairing of electrons; one centre (ΔE) and excitation energy ($\Delta\epsilon$).

the obvious splitting between the σ-orbital and the block of δ-orbitals. However as the basic scheme of occupation of the energy levels in IV and V is quite similar, the value of the σ–δ splitting in VI may be of the same order as in IV and V, i.e. comparable with the Hund energy. In this case there occurs degeneracy of the electronic states $\sigma^1\delta_1^1$ and $\sigma^1\delta_2^1$ rather than the δ–δ* decoupling which takes place in IV, V and Cp_2Cr_2-(μ-$SCMe_3)_2$(μ-S) [18]. σ- and δ-orbitals in VI have different symmetry and thus cannot form localized states. That is why for these states with open electron shells the singlet state is located higher than the triplet by double the value of the exchange integral. However, beyond the scope of the one-electron approximation the degenerate S_1, S_2, and T_1, T_2 states interact strongly with each other through correlation effects. It should be taken into account that the matrix element of interelectronic interaction between the singlet and triplet states differs with the signs of K_{12} and J_{12} being the same while the singlet states are lowered more than the triplet ones.



This is one possible model of the electronic structure of complex VI. It should however be mentioned that this is the first reported example of antiferromagnetic properties of this kind when there exists a metal–metal bond between metal atoms in the low spin state ($S_1 = S_2 = 1/2$).

According to the suggested model antiferromagnetism is caused by random factors because a certain hierarchy of interaction should be observed. On the one hand the J_1 value in the figure should be rather high for the T_1 and T_2 states to be lower than the σ^2 state in the one-electron figure. On the other hand, $|J_1|$ must not be too high, as the difference between $|K_{12} + J_{12}|$ and $|K_{12} - J_{12}|$ is not enough for the inversion of the singlet and triplet levels.

Experimental

Synthesis and isolation of Cp_2Cr and the complexes I–V were carried out in an atmosphere of pure argon in absolute solvents. IR spectra were measured with a Specord 75 IR instrument, in KBr pellets. Magnetic susceptibility was measured by the Faraday method using the set designed in the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR [19]. X-ray structural data for III and VI were obtained with a CAD-4 automatic diffractometer (λ(Mo-K_α), θ–2θ scan, $T = 23°$C). Crystal data are summarized in Table 4. The structure was solved by a direct method and refined in full-matrix approximation for all non-hydrogen atoms with application of the SDP program package [20] on a PDP 11/23-plus computer (Tables 5, 6). Hydrogen atoms in VI were located in the Fourier difference synthesis without refinement of atomic coordinates. Crystal data for II and V as well as bond lengths and bond angles are given in ref. 8; atomic coordinates are deposited in the Cambridge Crystallographic Data Base.

Experimental techniques for synthesis of clusters $Cp_3Cr_3(\mu\text{-}NPh)_3(\mu_3\text{-}NPh)$ (I), $Cp_3Cr_3(\mu\text{-}NPh)_3(\mu_3\text{-}NPh)^+$ $OH^- \cdot MeOH$ (II) as well as of the complex $Cp_2Cr_2(OCMe_3)_2(\mu\text{-}NPh)_2$ (V) have been discussed in detail in ref. 8.

Table 4

Crystal data for $[Cp_3Cr_3(\mu\text{-}NPh)_3(\mu_3\text{-}NPh)]^+[Co(CO)_4]^-$ (III) and $Cp_2Cr_2(O)_2(\mu\text{-}NPh)_2$ (VI)

	III	VI
Space group	$C2/c$	$P2_1/c$
a (Å)	31.860(6)	6.723(1)
b (Å)	16.246(3)	16.303(4)
c (Å)	24.178(5)	9.220(3)
β (°)	138.21(1)	96.43(2)
V (Å^3)	8338.9	1004.2
Z	8	2
Number of reflections measured	6694	2499
Number of reflections with $I > 5\sigma$	3134	1743
R_1	0.045	0.045
R_w	0.062	0.062

Table 5

Atomic coordinates (for Co and Cr $\times 10^5$, for O, N and C $\times 10^4$) for the cluster $Cp_3Cr_3(\mu\text{-}NPh)_3(\mu_3\text{-}NPh)^+ Co(CO)_4^- \cdot \frac{1}{2}THF$ (III)

Atom	x	y	z
Co	15169(4)	58310(7)	−24121(5)
Cr(1)	27681(4)	42083(7)	13646(5)
Cr(2)	32059(4)	53046(8)	24545(5)
Cr(3)	30377(4)	56614(7)	12756(5)
O(1)	2794(2)	6498(6)	−1117(3)
O(2)	957(2)	6563(4)	−3939(3)
O(3)	1554(3)	4049(5)	−2437(4)
O(4)	809(2)	6254(5)	−2117(3)
N(1)	3384(2)	4206(4)	2511(2)
N(2)	3714(2)	5739(3)	2405(2)
N(3)	3183(2)	4612(4)	1153(2)
N(4)	2439(2)	5290(4)	1248(2)
C(1)	2285(3)	6211(6)	−1628(4)
C(2)	1163(3)	6268(5)	−3352(4)
C(3)	1534(3)	4750(6)	−2432(4)
C(4)	1092(3)	6092(6)	−2240(4)
C(5)	3753(3)	3587(5)	3119(3)
C(6)	4316(3)	3363(6)	3425(5)
C(7)	4668(4)	2702(7)	4005(6)
C(8)	4475(4)	2348(6)	4303(5)
C(9)	3920(3)	2596(6)	4003(4)
C(10)	3554(3)	3207(6)	3413(4)
C(11)	4342(2)	6029(5)	3004(3)
C(12)	4490(3)	6848(5)	3235(4)
C(13)	5115(3)	7101(6)	3819(4)
C(14)	5586(3)	6549(6)	4170(4)
C(15)	5430(3)	5730(7)	3936(5)
C(16)	4814(3)	5466(6)	3351(5)
C(17)	3388(2)	4261(5)	855(3)
C(18)	3002(3)	4274(5)	5(3)
C(19)	3216(3)	3907(6)	−274(4)
C(20)	3796(3)	3533(6)	273(4)
C(21)	4194(3)	3514(6)	1132(4)
C(22)	3988(3)	3885(6)	1437(4)
C(23)	1785(2)	5422(4)	699(3)
C(24)	1378(3)	5607(5)	−137(4)
C(25)	727(3)	5697(6)	−700(4)
C(26)	471(3)	5563(6)	−416(4)
C(27)	864(3)	5342(6)	401(4)
C(28)	1522(2)	5274(5)	965(4)
Cp(11)	2661(3)	2838(5)	1392(4)
Cp(12)	2160(3)	3239(6)	1165(4)
Cp(13)	1800(3)	3640(5)	407(5)
Cp(14)	2089(3)	3495(6)	186(4)
Cp(15)	2603(3)	3013(5)	777(4)
Cp(21)	2887(3)	5313(6)	3028(3)
Cp(22)	2748(3)	6106(5)	2666(4)
Cp(23)	3310(3)	6493(6)	3065(3)
Cp(24)	3828(3)	5932(6)	3704(3)
Cp(25)	3563(3)	5200(6)	3685(3)
Cp(31)	3101(3)	6180(5)	474(3)
Cp(32)	2460(3)	6224(5)	15(4)

Table 5 (continued)

Atom	x	y	z
Cp(33)	2448(3)	6767(5)	475(4)
Cp(34)	3065(3)	7041(5)	1182(4)
Cp(35)	3476(3)	6673(5)	1190(3)
O_t [a]	0	685(3)	1/4
$C_t(1)$ [a]	50(1)	658(2)	276(1)
$C_t(2)$ [a]	28(1)	584(2)	259(1)

[a] Atomic coordinates of atoms for THF molecule multiplied by 10^3.

$Cp_3Cr_3(\mu\text{-}NPh)_3(\mu_3\text{-}NPh)^+Co(CO)_4^-$ *(III)*

A solution containing 0.14 g (0.41 mmol) of $Co_2(CO)_8$ in 20 ml of benzene was added dropwise to 20 ml of benzene solution containing 0.59 g (0.83 mmol) of $Cp_3Cr_3(\mu\text{-NPh})_3(\mu_3\text{-NPh})$ (I) at +5 °C. The resulting fine crystalline red precipitate was washed in cold benzene and then dissolved in 30 ml of THF. The red-brown solution was then concentrated to 10–15 ml at 50 °C/20 torr and chromatographed on the Al_2O_3 column (3 × 20 cm). The dark-red zone was eluted by 60 ml of THF. 7 ml of benzene was added to this solution and concentrated at 50 °C/20 torr to 7–10 ml. This concentrated solution was stored for 2 days at +5 °C. The black-red needle-like crystals precipitated were isolated from the mother liquor by decantation, washed in cold benzene and dried under vacuum. Yield 0.55 g (76%).

Table 6

Atomic coordinates (for Cr $\times 10^5$, for O, N and C $\times 10^4$) for the complex $Cp_2Cr_2(O)_2(\mu\text{-NPh})_2$ (VI)

Atom [a]	x	y	z
Cr	1410(6)	6100(2)	41678(4)
O	2180(3)	603(1)	3405(3)
N	−921(3)	−428(1)	3877(2)
C(1)	−3002(5)	1066(2)	3436(8)
C(2)	−1721(7)	1396(3)	2522(5)
C(3)	−496(7)	1890(3)	3297(3)
C(4)	−814(9)	1889(3)	4611(6)
C(5)	−2395(7)	1415(3)	4819(5)
$C_n(1)$	−1938(4)	−852(2)	2739(3)
$C_n(2)$	−1666(6)	−677(2)	1291(3)
$C_n(3)$	−2784(6)	−1086(3)	156(3)
$C_n(4)$	−4117(6)	−1682(2)	436(4)
$C_n(5)$	−4390(5)	−1873(2)	1852(4)
$C_n(6)$	−3295(5)	−1467(2)	3011(3)
Hc(1)	−416	82	334
Hc(2)	−125	125	141
Hc(3)	82	209	277
Hc(4)	41	230	500
Hc(5)	−291	125	584
$Hc_n(2)$	−43	−42	109
$Hc_n(3)$	−250	−84	−82
$Hc_n(4)$	−500	−188	−29
$Hc_n(5)$	−541	−229	226
$Hc_n(6)$	−375	−168	391

[a] C_n indicates carbon atoms in NPh groups; Hc_n indicates hydrogen atoms in NPh groups.

Large black-red prisms suitable for the X-ray structural study were obtained by recrystallization from the THF/benzene mixture (3 : 1).

IR-spectrum (ν, cm^{-1}): 545m, 695m, 755m, 820m, 1015w, 1060m, 1250m, 1435m, 1465m, 1865vs.

$Cp_2Cr_2(O)_2(\mu\text{-}NPh)_2$ (VI)

Al_2O_3 (4–5 g) was added to a solution of 0.5 g (1 mmol) of $Cp_2Cr_2(OCMe_3)_2(\mu\text{-}NPh)_2$ (V) in 20 ml of toluene. The solvent was then evacuated at 40 ° C/0.1 torr. The dry residue was transferred on the Al_2O_3 column (3 × 40 cm) and the violet zone was eluted by a THF/benzene mixture (1 : 1). The violet solution thus obtained (50–70 ml) was concentrated at 60 ° C/20 torr to 5–7 ml and stored for 5 days at 20 ° C. Large violet prisms precipitated were isolated from the mother liquor by decantation, washed in cold benzene and dried under vacuum. Yield 0.08 g (17%).

IR-spectrum: (ν, cm^{-1}): 695m, 705w, 810s, 890m, 1010w, 1090w, 1290s, 1435m, 1460m, 1490m.

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