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SYNTHESIS AND STRUCTURE OF DIMERIC METALLOCENE DERIVATIVES OF TRANSITION METALS OF GROUPS IV AND V. CRYSTAL AND MOLECULAR STRUCTURES OF $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}OEt)$ AND $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}H)(\mu\text{-}Cl)$

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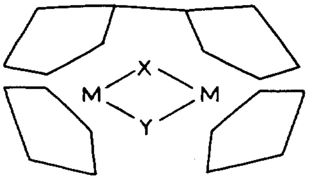
Summary

Reduction of Cp_2MCl_2 (M = Nb and Ti) with potassium in toluene yields binuclear fulvalene complexes $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}Cl)$ (IIa) and $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}H)(\mu\text{-}Cl)$ (III). Treatment of IIa with KOR gives $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}OR)$ (IIb, $R = CH_3$; IIc, $R = C_2H_5$) X-ray structural investigations of complexes IIc (4593 reflections, $R = 0.041$) and III (2951 reflections, $R = 0.042$) show similar geometric structures, Nb–Nb 3.136(1) Å (IIc), Ti–Ti 3.126(1) Å (III), M–Cp 2.04 Å (IIc) and 2.04 Å (III), bond angles Nb–O–Nb 94.6°, Ti–Cl–Ti 77.6°, dihedral angles Cp/Cp in the metal sandwiches 135.2° (IIc) and 137.3° (III) and the bending angle of the fulvalene ligand 15.6° in both IIc and III.

Introduction

Complexes of the general formula I are the most typical of the binuclear dicyclopentadienyl compounds of early transition metals, Ti and Nb in particular. These compounds involve a bridging fulvalene ligand and two bridging hetero ligands X and Y.

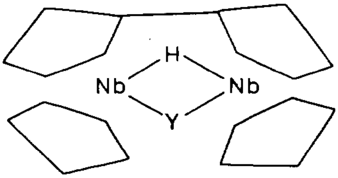


(I)

The majority of the complexes of type I are highly sensitive to moisture and oxygen, so there is not much spectral and chemical evidence concerning their behaviour.

Complexes of type I with one or two bridging hydride ligands are extremely rare even in this scarcely studied field of chemistry. In particular, this fact was emphasized in the literature in connection with Ti compounds (see for example the review in ref. 1). There are very few convenient synthesis techniques for such compounds and not enough reliable data on their structures.

In the present paper we propose useful preparative synthesis techniques of the dicyclopentadienylniobium derivatives II; Y = Cl (IIa), OMe (IIb), OEt (IIc) and of the dicyclopentadienyltitanium derivative III and we present the results of X-ray structural investigations of IIc and III.



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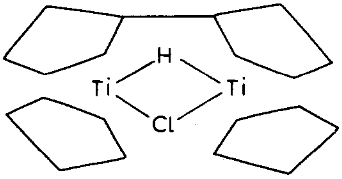
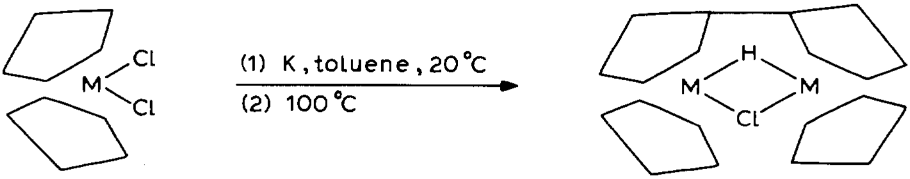
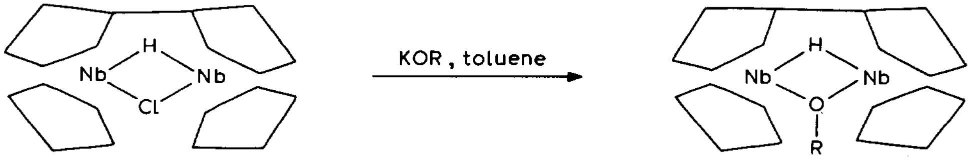


(III)

The compounds IIa and III are obtained from the corresponding dicyclopentadienylmetal dichlorides, using potassium in toluene as a reducing agent. The reaction was carried out first at room temperature and the reaction mixture was then heated to 100°C for several hours.



The alkoxydicyclopentadienylniobium complexes IIb and IIc were obtained in quantitative yields from IIa by treatment with KOR in toluene.



Although the metal atoms in II and III have different electron configuration the geometry of the complexes is very similar. Comparison of the structures IIc and III with the structures of other compounds of type I is based on X-ray investigation.

Experimental

Synthesis of IIa, IIb, IIc and III

All operations were carried out in standard Schlenk-type apparatus. All solvents were purified from moisture and oxygen using conventional techniques.

Synthesis of IIa and III. The Ti and Nb complexes were obtained by the same technique. In a standard run 1.0 g of the corresponding Cp_2MCl_2 was vigorously stirred in toluene (the reaction can be carried out in any other aromatic solvent) with potassium powder for 20 h at room temperature. The molar ratio of the reagents Cp_2MCl_2/K was kept from 1/1.5 to 1/1.7. Then the reaction mixture was heated to 100°C for at least 10 h. After cooling to room temperature and separation of the insoluble residue, the transparent solution was evaporated to dryness in vacuo. The residue was recrystallized from toluene. Yields 50–70%. For IIa and III good elemental analyses were obtained.

Synthesis of IIb and IIc. Equimolecular quantities of IIa (1.0 g per run) and KOR (R = Me or Et) were heated in toluene at 100°C for 5 h. The solvent was removed in vacuo and the solid residue extracted with hot hexane. The complexes were crystallized from hexane. Yields 100%. For both complexes good elemental analyses were obtained.

X-ray study of IIc and III

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}H)(\mu\text{-}OEt)$ (IIc). Crystals of IIc are triclinic, at 20°C *a* 7.956(1), *b* 15.317(2), *c* 15.502(2) Å, α 95.44(2), β 97.30(2), γ 93.52(2)°, $Z = 4$, space group $P\bar{1}$ (two independent molecules A and B). The unit cell parameters and intensities of 6380 reflections were measured at room temperature with a Hilger–Watts Y/290 diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan technique, $2\theta < 50°$, no absorption correction). 4593 reflections with $I > 2\sigma(I)$ were used in the calculations. The structure was solved by direct method using the MULTAN program and refined by full matrix least-squares technique in anisotropic approximation. The difference electron density map revealed all hydrogen atoms, including bridging ones, and the second orientation of the terminal C(22) atom in the disordered OEt substituent of molecule A. Hydrogen atoms were included in the refinement in isotropic approximation; the C(22) and C(22′) atoms were given the populations 0.7 and 0.3, respectively. Finally $R = 0.041$, $R_w = 0.047$ for 4018 reflections with $I > 4\sigma(I)$. Atomic coordinates and thermal parameters are listed in Table 1.

$(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}H)(\mu\text{-}Cl)$ (III). Crystals of III are monoclinic, *a* 13.864(5), *b* 15.481(5), *c* 16.331(5) Å, β 110.02(3)°, space group $P2_1/c$, $Z = 8$ (two independent molecules). The unit cell parameters and intensities of 2999 reflections were measured at −120°C with a Syntex $P2_1$ diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$ scan, $2\theta < 48°$, no absorption correction). 2951 reflections with $I > 2\sigma(I)$ were used in the calculations. The structure of III was solved by direct method using the MULTAN program and refined by block-diagonal least-squares technique in anisotropic approximation using 2875 reflections with $I > 5\sigma(I)$. The difference electron density map revealed all hydrogen atoms including the hydride bridging ligand. The H atoms were refined in isotropic approximation, finally $R = 0.042$, $R_w = 0.056$. Atomic coordinates are listed in Table 2. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [2].

TABLE 1

ATOMIC COORDINATES IN IIc ($\times 10^4$) (FOR Nb $\times 10^5$; FOR H $\times 10^3$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb(1)	38147(9)	34826(4)	35872(5)	C(22)	5257(25)	2190(13)	1675(13)
Nb(2)	40508(9)	49048(5)	22644(5)	C(22′)	5294(82)	3139(43)	993(43)
Nb(3)	14294(8)	86561(5)	12056(4)				
Nb(4)	12888(7)	89403(4)	32202(4)				
O(1)	4322(7)	3527(3)	2270(4)	C(23)	−856(11)	7491(6)	890(5)
O(2)	303(6)	9523(3)	2079(3)	C(24)	−1567(10)	8278(6)	699(5)
C(1)	5024(12)	2794(6)	4769(6)	C(25)	−764(11)	8601(6)	40(5)
C(2)	5603(12)	3689(7)	4953(6)	C(26)	402(11)	7998(6)	−190(5)
C(3)	6695(11)	3855(6)	4343(7)	C(27)	381(13)	7326(6)	346(6)
C(4)	6743(11)	3111(7)	3808(7)	C(28)	4008(8)	9264(6)	1957(5)
C(5)	5682(12)	2447(6)	4045(6)	C(29)	4282(9)	8441(7)	1510(5)
C(6)	1151(9)	3891(5)	3064(5)	C(30)	4017(12)	8556(9)	628(6)
C(7)	1417(10)	4057(6)	3999(6)	C(31)	3567(11)	9366(8)	475(6)
C(8)	1427(12)	3233(7)	4327(7)	C(32)	3569(9)	9837(6)	1297(6)
C(9)	1213(11)	2574(6)	3635(7)	C(33)	3937(8)	9451(5)	2887(5)
C(10)	1022(10)	2964(5)	2858(6)	C(34)	4137(9)	8841(5)	3540(5)
C(11)	1280(9)	4541(5)	2443(5)	C(35)	3644(10)	9253(6)	4298(5)
C(12)	1630(11)	5475(5)	2662(6)	C(36)	3076(10)	10095(5)	4136(5)
C(13)	1868(12)	5829(6)	1887(6)	C(37)	3319(10)	10204(5)	3275(5)
C(14)	1678(13)	5156(7)	1210(6)	C(38)	−499(10)	7607(5)	3282(5)
C(15)	1261(11)	4371(6)	1543(5)	C(39)	519(10)	7774(6)	4072(5)
C(16)	7064(14)	4972(10)	2274(13)	C(40)	125(11)	8565(6)	4456(5)
C(17)	6257(18)	5260(9)	1466(11)	C(41)	−1152(11)	8911(6)	3915(6)
C(18)	5573(16)	5997(9)	1694(9)	C(42)	−1501(9)	8304(6)	3179(5)
C(19)	5878(14)	6220(8)	2582(9)	C(43)	−382(11)	10325(6)	1925(6)
C(20)	6809(15)	5564(10)	2883(10)	C(44)	−1648(13)	10584(7)	2497(8)
C(21)	4248(15)	2889(7)	1578(8)	H(1)	432(11)	500(6)	335(6)
				H(2)	140(7)	816(4)	237(4)

The binuclear dicyclopentadienylfulvalene complexes IIc (Fig. 1) and III (Fig. 2) form molecular crystals with two molecules in the asymmetric unit. Intermolecular contacts in crystals correspond to usual Van der Waals interactions. The bond distances in IIc and III are listed in Tables 3 and 4, respectively.

The transition metal atoms in the molecules of IIc and III are in a bent sandwich ligand environment with geometrical parameters usual for Nb and Ti derivatives. The metallocene moiety conformation is nearly staggered, the average rotation angle values in the sandwiches of IIc and III are 26.8, 39.0° (molecule A), 37.8, 40.5° (molecule B) and 11.8, 32.2° (molecule A), 28.9, 27.5° (molecule B), respectively. Both complexes seem to exhibit a rotational disorder of η^5-C_5H_5 ligands, which gives rise to very high values of temperature parameters of their C atoms and to variation of C–C bond distances in a rather wide range (Tables 3 and 4). However, the difference electron density map did not reveal atomic positions corresponding to any ring orientation other than the most favourable. In rigidly fixed $\eta^5:\eta^5$-fulvalene ligands the temperature parameters of C atoms are significantly smaller and the C–C bond distances vary in a more narrow range. Nevertheless their bond distances do not reveal a regular alternation reported earlier in the accurate structure of $(\eta^5:\eta^5$-$C_{10}H_8)(C_5H_5)_2Ti_2(\mu$-$Cl)_2$ [3].

TABLE 2

ATOMIC COORDINATES IN III ($\times 10^4$) (for Ti and Cl $\times 10^5$; for H $\times 10^3$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ti(1)	52047(9)	11243(8)	21085(7)	C(19)	2087(7)	830(6)	2517(7)
Ti(2)	38561(9)	8945(8)	32835(8)	C(20)	2382(8)	357(8)	3498(9)
Ti(3)	9444(9)	14252(8)	62679(8)	C(21)	217(6)	677(8)	7205(5)
Ti(4)	−7267(9)	28057(7)	53589(8)	C(22)	710(7)	1439(7)	7647(5)
Cl(1)	52741(14)	−395(11)	31825(11)	C(23)	1731(6)	1319(6)	7796(5)
Cl(2)	−8718(14)	12078(11)	52752(11)	C(24)	1871(8)	526(7)	7416(6)
C(1)	4352(8)	87(7)	1076(5)	C(25)	951(9)	170(7)	7045(6)
C(2)	5365(7)	−22(5)	1210(6)	C(26)	1216(6)	2043(5)	5076(5)
C(3)	5688(9)	621(8)	959(6)	C(27)	1188(5)	1146(5)	4949(5)
C(4)	5037(9)	1204(6)	631(5)	C(28)	2039(6)	793(5)	5581(6)
C(5)	4057(8)	929(8)	684(5)	C(29)	2593(6)	1446(6)	6118(6)
C(6)	5736(5)	2053(4)	3293(4)	C(30)	2118(5)	2230(5)	5816(6)
C(7)	6625(5)	1579(5)	3315(5)	C(31)	438(6)	2660(5)	4639(4)
C(8)	6871(5)	1772(5)	2587(5)	C(32)	423(6)	3545(5)	4858(5)
C(9)	6169(6)	2390(5)	2097(5)	C(33)	−536(7)	3890(5)	4400(5)
C(10)	5466(5)	2564(4)	2517(5)	C(34)	−1115(7)	3236(5)	3871(5)
C(11)	5104(5)	1947(4)	3840(4)	C(35)	−536(6)	2492(5)	4006(4)
C(12)	5237(6)	1346(5)	4517(4)	C(36)	−2302(6)	2778(7)	5559(6)
C(13)	4392(7)	1348(5)	4774(5)	C(37)	−2146(8)	3621(8)	5313(6)
C(14)	3699(7)	1968(5)	4264(6)	C(38)	−1309(7)	3946(5)	6040(6)
C(15)	4138(6)	2329(4)	3697(5)	C(39)	−1018(6)	3307(6)	6637(5)
C(16)	2896(7)	−340(6)	3314(5)	C(40)	−1614(6)	2586(6)	6355(6)
C(17)	2912(6)	−316(5)	2496(7)	H(1)	379(4)	153(3)	223(3)
C(18)	2423(7)	339(6)	2081(8)	H(2)	69(1)	218(1)	161(1)

The bridging atoms, H and O in IIc and H and Cl in III, are situated near bisectorial planes of the bent sandwich moieties. In A and B molecules the average for dihedral angles between the M(μ-H)(μ-L) plane and mean squares planes of the

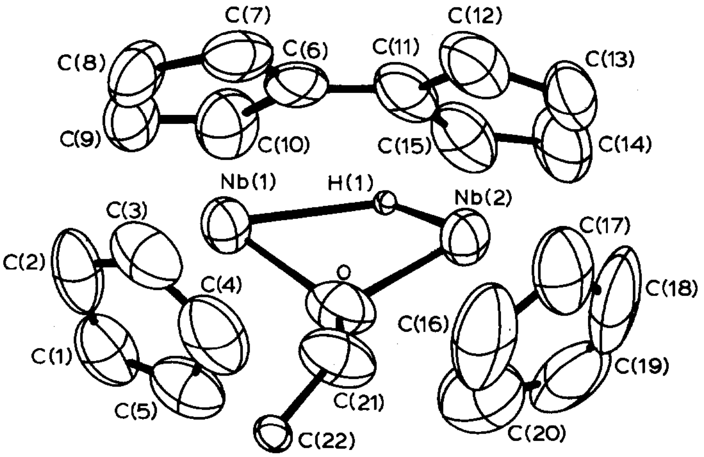


Fig. 1. Molecule IIc(A). Non-hydride hydrogen atoms omitted for clarity. Only one position of the disordered Me substituent (C(22)) is shown.

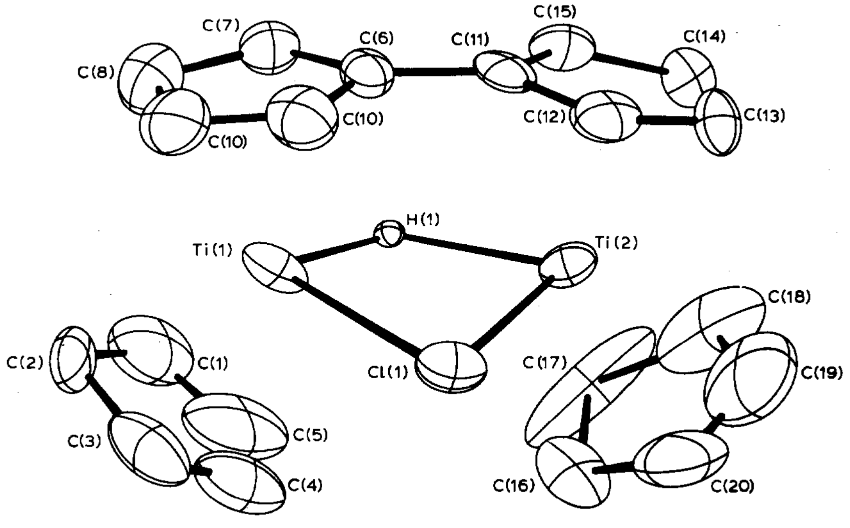


Fig. 2. Molecule III(A). Non-hydride hydrogen atoms omitted for clarity.

five-membered rings of the Cp and fulvalene ligands in the sandwiches are 23.4 and 19.7° in IIc and 25.0 and 20.5° in III. The values of Nb–O distances in IIc (2.125(5) to 2.139(5), average 2.134 Å) are somewhat greater than the values of Ti–O distances in the binuclear molecule $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}OH)_2$ (2.05 to 2.10 Å [4]) and the values of the Ti–Cl distances in III (2.482(2) to 2.507(2), average 2.493 Å) are in satisfactory agreement with the value of 2.519 Å in the molecule $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}Cl)_2$ [3]. The M–H distances are determined with less accuracy and vary widely, but the average Nb–H distance of 1.95 Å is in fact equal to the value of 1.93 Å obtained by Teller and Bau [5] on the basis of neutron diffraction data. The Ti–H distance 2.17 Å in III is significantly greater than the standard value of 1.81 Å obtained by the same authors, due to a low accuracy of localization of H atoms in structure III.

Discussion

Previous to the present work structural data for seven binuclear fulvalene complexes of type I were reported. The main geometrical parameters of these complexes compared with corresponding data on IIc and III are presented in Table 5. A relatively slow development of X-ray investigations of compounds of this type is due to their very high reactivity and thence arising difficulties in obtaining suitable monocrystals.

The compounds listed in Table 5 may be divided into two groups. The first group comprises complexes II–VI with two different bridging ligands in the binuclear fragment M(μ-H)(μ-L)M (in the structural study of VI the μ-H ligand was not located and on the basis of magnetic susceptibility measurements the presence of only one bridging Cl ligand was proposed [8]). Geometrical parameters of the molecules of these compounds are similar. The second group comprises complexes VII–X, and each of them exhibits its own structural characteristics.

(Contined on p. 328)

TABLE 3

BOND LENGTHS d(Å) IN IIc

Molecule A		Molecule B	
Bond	d(Å)	Bond	d(Å)
Nb(1)–Nb(2)	3.143(1)	Nb(3)–Nb(4)	3.129(1)
Nb(1)–O(1)	2.137(5)	Nb(3)–O(2)	2.125(5)
Nb(2)–O(1)	2.135(5)	Nb(4)–O(2)	2.139(5)
Nb(1)–H(1)	2.40(9)	Nb(3)–H(2)	2.02(6)
Nb(2)–H(1)	1.66(9)	Nb(4)–H(2)	1.71(6)
Nb(1)–C(1)	2.332(9)	Nb(3)–C(23)	2.437(9)
Nb(1)–C(2)	2.379(9)	Nb(3)–C(24)	2.430(8)
Nb(1)–C(3)	2.445(9)	Nb(3)–C(25)	2.339(8)
Nb(1)–C(4)	2.422(9)	Nb(3)–C(26)	2.324(8)
Nb(1)–C(5)	2.338(9)	Nb(3)–C(27)	2.370(9)
Nb(1)–C(6)	2.316(7)	Nb(3)–C(28)	2.320(7)
Nb(1)–C(7)	2.287(8)	Nb(3)–C(29)	2.309(8)
Nb(1)–C(8)	2.370(9)	Nb(3)–C(30)	2.355(9)
Nb(1)–C(9)	2.436(9)	Nb(3)–C(31)	2.420(9)
Nb(1)–C(10)	2.413(9)	Nb(3)–C(32)	2.388(9)
Nb(2)–C(11)	2.298(8)	Nb(4)–C(33)	2.338(7)
Nb(2)–C(12)	2.293(9)	Nb(4)–C(34)	2.275(7)
Nb(2)–C(13)	2.359(9)	Nb(4)–C(35)	2.340(8)
Nb(2)–C(14)	2.410(9)	Nb(4)–C(36)	2.422(8)
Nb(2)–C(15)	2.412(9)	Nb(4)–C(37)	2.432(8)
Nb(2)–C(16)	2.39(1)	Nb(4)–C(38)	2.433(8)
Nb(2)–C(17)	2.34(2)	Nb(4)–C(39)	2.415(3)
Nb(2)–C(18)	2.31(1)	Nb(4)–C(40)	2.335(8)
Nb(2)–C(19)	2.38(1)	Nb(4)–C(41)	2.337(9)
Nb(2)–C(20)	2.40(1)	Nb(4)–C(42)	2.359(8)
C(1)–C(2)	1.41(1)	C(23)–C(24)	1.40(1)
C(1)–C(5)	1.37(1)	C(23)–C(27)	1.39(1)
C(2)–C(3)	1.39(1)	C(24)–C(25)	1.39(1)
C(3)–C(4)	1.35(1)	C(25)–C(26)	1.40(1)
C(4)–C(5)	1.39(1)	C(26)–C(27)	1.38(1)
C(6)–C(7)	1.43(1)	C(28)–C(29)	1.42(1)
C(6)–C(10)	1.42(1)	C(28)–C(32)	1.44(1)
C(6)–C(11)	1.46(1)	C(28)–C(33)	1.45(1)
C(7)–C(8)	1.41(1)	C(29)–C(30)	1.39(1)
C(8)–C(9)	1.39(1)	C(30)–C(31)	1.35(2)
C(9)–C(10)	1.39(1)	C(31)–C(32)	1.40(1)
C(11)–C(12)	1.44(1)	C(33)–C(34)	1.44(1)
C(11)–C(15)	1.39(1)	C(33)–C(37)	1.40(1)
C(12)–C(13)	1.39(1)	C(34)–C(35)	1.39(1)
C(13)–C(14)	1.39(1)	C(35)–C(36)	1.43(1)
C(14)–C(15)	1.39(1)	C(36)–C(37)	1.40(1)
C(16)–C(17)	1.45(2)	C(38)–C(39)	1.37(1)
C(16)–C(20)	1.29(2)	C(38)–C(42)	1.38(1)
C(17)–C(18)	1.32(2)	C(39)–C(40)	1.37(1)
C(18)–C(19)	1.37(2)	C(40)–C(41)	1.40(1)
C(19)–C(20)	1.37(2)	C(41)–C(42)	1.39(1)
O(1)–C(21)	1.37(1)	O(2)–C(43)	1.40(1)
C(21)–C(22)	1.39(2)	C(43)–C(44)	1.47(1)
C(21)–C(22′)	1.37(7)		

TABLE 4

BOND LENGTHS *d*(Å) IN III

Molecule A		Molecule B	
Bond	*d*(Å)	Bond	*d*(Å)
Ti(1)–Ti(2)	3.124(2)	Ti(3)–Ti(4)	3.128(2)
Ti(1)–Cl(1)	2.493(2)	Ti(3)–Cl(2)	2.507(2)
Ti(2)–Cl(1)	2.491(2)	Ti(4)–Cl(2)	2.482(2)
Ti(1)–H(1)	2.14(6)	Ti(3)–H(2)	2.29(2)
Ti(2)–H(1)	1.96(5)	Ti(4)–H(2)	2.29(2)
Ti(1)–C(1)	2.336(9)	Ti(3)–C(21)	2.399(9)
Ti(1)–C(2)	2.362(9)	Ti(3)–C(22)	2.383(9)
Ti(1)–C(3)	2.33(1)	Ti(3)–C(23)	2.363(8)
Ti(1)–C(4)	2.347(8)	Ti(3)–C(24)	2.336(9)
Ti(1)–C(5)	2.345(9)	Ti(3)–C(25)	2.32(1)
Ti(1)–C(6)	2.318(6)	Ti(3)–C(26)	2.313(8)
Ti(1)–C(7)	2.366(7)	Ti(3)–C(27)	2.333(8)
Ti(1)–C(8)	2.391(8)	Ti(3)–C(28)	2.384(9)
Ti(1)–C(9)	2.375(8)	Ti(3)–C(29)	2.380(9)
Ti(1)–C(10)	2.320(7)	Ti(3)–C(30)	2.359(8)
Ti(2)–C(11)	2.323(7)	Ti(4)–C(31)	2.311(8)
Ti(2)–C(12)	2.361(7)	Ti(4)–C(32)	2.327(9)
Ti(2)–C(13)	2.394(8)	Ti(4)–C(33)	2.371(8)
Ti(2)–C(14)	2.369(9)	Ti(4)–C(34)	2.396(8)
Ti(2)–C(15)	2.315(7)	Ti(4)–C(35)	2.364(7)
Ti(2)–C(16)	2.399(9)	Ti(4)–C(36)	2.316(9)
Ti(2)–C(17)	2.393(9)	Ti(4)–C(37)	2.32(1)
Ti(2)–C(18)	2.42(1)	Ti(4)–C(38)	2.372(9)
Ti(2)–C(19)	2.34(1)	Ti(4)–C(39)	2.387(9)
Ti(2)–C(20)	2.34(1)	Ti(4)–C(40)	2.376(9)
C(1)–C(2)	1.36(2)	C(21)–C(22)	1.43(2)
C(1)–C(5)	1.45(2)	C(21)–C(25)	1.38(2)
C(2)–C(3)	1.22(1)	C(22)–C(23)	1.36(1)
C(3)–C(4)	1.26(2)	C(23)–C(24)	1.42(1)
C(4)–C(5)	1.45(2)	C(24)–C(25)	1.33(2)
C(6)–C(7)	1.42(1)	C(26)–C(27)	1.40(1)
C(6)–C(10)	1.43(1)	C(26)–C(30)	1.44(1)
C(6)–C(11)	1.46(1)	C(26)–C(31)	1.43(1)
C(7)–C(8)	1.38(1)	C(27)–C(28)	1.39(1)
C(8)–C(9)	1.40(1)	C(28)–C(29)	1.39(1)
C(9)–C(10)	1.40(1)	C(29)–C(30)	1.39(1)
C(11)–C(12)	1.41(1)	C(31)–C(32)	1.42(1)
C(12)–C(13)	1.37(1)	C(32)–C(33)	1.39(1)
C(13)–C(14)	1.41(1)	C(33)–C(34)	1.39(1)
C(14)–C(15)	1.39(1)	C(34)–C(35)	1.38(1)
C(11)–C(15)	1.41(1)	C(31)–C(35)	1.42(1)
C(16)–C(17)	1.35(1)	C(36)–C(37)	1.40(2)
C(16)–C(20)	1.38(2)	C(36)–C(40)	1.36(1)
C(17)–C(18)	1.28(1)	C(37)–C(38)	1.44(1)
C(18)–C(19)	1.24(1)	C(38)–C(39)	1.35(1)
C(19)–C(20)	1.68(2)	C(39)–C(40)	1.37(1)

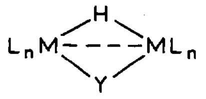
TABLE 5

MOST IMPORTANT GEOMETRICAL PARAMETERS IN THE $Cp_2M_2(C_{10}H_8)(\mu\text{-}L)(\mu\text{-}L')$ DINUCLEAR MOLECULES

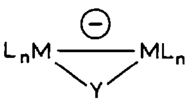
Compound	M–M (Å)	M–C (Å)	M–Cp, (Å)	M–L (Å) (M–L′)	$\varphi_{MLM'}$ (°) ($\varphi_{ML'M}$)	$\varphi_{LML'}$ (°)	θ [a] (°)	ω [b] (°)	C–C fulv. (Å)	[d^n]	References
$Cp_2Nb_2(C_{10}H_8)(H)(OEt)$ (IIc)	3.136	2.37	2.04	2.13 (1.95)	94.6 (107)	77	135.2	15.6	1.46	d^2	[c]
$Cp_2Ti_2(C_{10}H_8)(H)(Cl)$ (III)	3.125	2.35	2.04	2.49 (2.17)	77.6 (93)	92	137.3	15.6	1.45	d^1	[c]
$Cp_2Ti_2(C_{10}H_8)(H)(H_2AlEt_2)$ (IV)	3.374	2.35	–	(1.80)	(138)	–	134.1	12.5	1.45	d^1	[6]
$[Cp_2Mo_2(C_{10}H_8)(H)(OH)]^{2+}$ (V)	3.053	2.32	1.97	2.08	94.3	–	136.7	18.1	1.42	d^2	[7]
$Cp_2Nb_2(C_{10}H_8)(Cl)$ (VI)	3.270	2.37	2.04	2.57	79.2	–	135.6	15.1	1.46	$d^{2.5}$(??)	[8]
$Cp_2Ti_2(C_{10}H_8)(Cl)_2$ (VII)	3.638	2.38	2.06	2.52	92.5	81.3	134.4	5.3	1.46	d^1	[3]
$Cp_2Ti_2(C_{10}H_8)(OH)_2$ (VIII)	3.195	2.40	2.08	2.08	100.7	75.4	133.5	15.1	1.42	d^1	[4]
$Cp_2Nb_2(C_{10}H_8)(NC_6H_4OMe)_2$ (IX)	2.834	2.48	2.17	2.04	92.0	88.0	129.0	32.0	1.53	d^1	[9]
$[Cp_2Nb_2(C_{10}H_8)(NC_6H_4OMe)_2]^+$ (X)	2.921	2.45	2.14	2.04	91.3	87.6	131.7	24.5	1.46	$d^{0.5}$	[9]

[a] Dihedral angle between Cp and C_5H_4 planes in bent sandwiches. [b] Dihedral angle between C_5H_4 planes in fulvalene ligand. [c] This work.

Let us begin with the first group. On the basis of the approach proposed in ref. 5 and 10 complexes II–V, belonging to the structural type XI, can be considered as products of proton addition to a hypothetical or an existing conjugated base XII.



(XI)



(XII)

Many structural data demonstrate that such an addition, i.e. insertion of a proton into a M–M bond does not destroy it. The insertion results only in lengthening of this bond by 0.1 to 0.2 Å and does not affect general steric overcrowding of the complex [10]. In the hydride complexes formed in this way (XI) the geometry of the central fragment is determined mainly by the relation between covalent radii of the metal atom and of the bridging ligands, and in the case of similarity of these parameters molecules II–V have similar structural features. The difference in steric requirements of the bridging ligands Y, viz. Cl, OR, OH and H_2AlR_2, on the one hand, and of the bridging H atom, on the other hand, leads to small but noticeable bending of the five-membered rings towards the less bulky hydride ligand. Therefore in molecules IIc and III the CpMCp′ planes of the mononuclear sandwich fragments (Cp and Cp′ denote centroids of η^5-C_5H_5 and η^5-C_5H_4 ligands, respectively) become non-parallel and form dihedral angles of 144.6° (IIc, molecule A), 144.1° (IIc, molecule B) and 152.5° (III, A), 155.8° (III, B). The corresponding angle in the dication V is 148.8° [7]. It is noteworthy that geometrical parameters of our earlier studied complex VI are similar to those of II–V and are very close to those found in the chloride hydride III. Taking into account the nearness of covalent radii of Nb and Ti the presence of a bridging hydride H atom in structure VI can be suggested. This possibility was not excluded in the discussion of the results of X-ray structural investigations in ref. 8.

Parameters of the central $M_2(H)L$ fragment of the complexes in Table 5 do not vary significantly in different extents of filling of non-bonding MO of the bent sandwich moiety (electron configuration of the metal atoms d^0–d^2). Further increase of the number of electrons causes, however, reconstruction of a binuclear complex molecule. Thus, in contrast to the dication V, the central fragment in neutral complexes of molybdenum of the type $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Mo_2(X)(Y)$ becomes non-cyclic and turns into the linear form X–M–M–Y [11].

The second group of binuclear complexes comprises compounds VII–X with identical bridging ligands in a symmetrical binuclear $M(\mu\text{-}X)_2M$ moiety. Here the non-metal atoms (X = Cl, OH, NR) are involved in bonding with M atoms employing at least two AO. In contrast to compounds of the first group, wherein σ-bonding in the central moiety is provided by three pairs of valence electrons (see XI and XII), in the central fragment of the complexes of the second group four pairs of valence electrons are employed. The central $M(\mu\text{-}X)_2M$ moiety is much more flexible than the system XI. Thus we find in the second group complex VII with the $Ti(\mu\text{-}Cl)_2Ti$ fragment of butterfly configuration with Ti...Ti distance of 3.638 Å and complex IX with a planar Nb_2N_2 bicyclic form with direct Nb–Nb bond of 2.834 Å. It is noteworthy that both complexes are diamagnetic but unlike IX there is no satisfactory explanation of diamagnetism of VII. Evidently increased stability of IX is favoured by a strong $n\pi$-donating ability of sp^2-planar triangular coordinated nitrogen atoms resulting in the electron transfer $\pi(N) \rightarrow \pi(Nb)$. With regard to Nb–Cp bonding such transfer is a destabilizing factor, leading to substantial increase of Nb–C(Cp) distances (see Table 5). Disturbance of the closed electron configuration in the Nb_2N_2 bicyclic fragment (upon transition to the cation X) causes this bicyclic moiety to have a butterfly configuration [9]. Intermediate between VII and IX (by its M–M distance and bending angle in the fulvalene ligand) complex VIII has an even electron number, but it is paramagnetic [4]. The reasons for different geometrical and magnetic characteristics of VII–X are as yet unclear.

Each of the complexes VII–X has 34 valence electrons per two transition metal atoms (throughout the electronic configuration of the M atom is d^1). Thus in all these complexes metal atoms retain the ability to form M–M bonds. Addition of two extra electrons in any molecule of this group should lead to achievement of the inert gas electronic configuration by each M atom without formation of the M–M bond and thus a close proximity of two M atoms becomes energetically unfavourable [12]. In accordance with this conclusion the 34-electron complex VII is easily formed by action of HCl on the chloride hydride III or 32-electron bis-titanocene $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Ti_2(\mu\text{-}H)_2$ [1,3], whereas our attempts to obtain the 36-electron $(\eta^5:\eta^5\text{-}C_{10}H_8)(C_5H_5)_2Nb_2(\mu\text{-}Cl)_2$ by the same reaction from IIa were fruitless. The above-mentioned rearrangement of the central M(X)(Y)M cycle into the linear binuclear X–M–M–Y moiety may provide an alternative possibility to formation of 36-electron binuclear complexes without bridging ligands.

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