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THE IMPORTANCE OF STERIC FACTORS IN THE FORMATION AND STRUCTURES OF HETEROBINUCLEAR WEDGE-LIKE SANDWICH DERIVATIVES. THE CRYSTAL AND MOLECULAR STRUCTURE OF NIOBOCENEHYDRIDO-(σ,π-CYCLOPENTADIENYLIDENE)IRON-(DICARBONYL)(*Nb—Fe*) *

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Summary

$CpFe(CO)_2CH_3$ reacts with Cp_2NbH made from Cp_2NbBH_4 and Et_3N to give $Cp_2\overline{NbH(\mu\text{-}C_5H_4)Fe}$ (III). As shown by X-ray diffraction, III contains the Cp_2NbH sandwich fragment with a 46.8° angle between the rings linked with the dicarbonyliron moiety by the Nb—Fe bond (2.968 Å), observed for the first time, and a cyclopentadienyl bridge C_5H_4 involving the Nb—C.σ-bond (2.189 Å) and C_5H_4—Fe π-bond (2.085 Å). A probable reaction scheme leading to III and general patterns of formation of other heterobinuclear derivatives of sandwich complexes $Cp_2ML—M'(L')_n$ are discussed. The importance of steric effects due to nonbonded interligand interactions between the $M'(L')_n$ fragment and the sandwich system is emphasized. Increase of steric strain in the binuclear system facilitates its unusual transformations.

Introduction

The formation of complexes containing metal—metal bonds results in structural situations different in principle from those characteristic for mononuclear complexes. In fact, it involves spatial approach of ligands linked with different metal atoms. As a result, considerable steric strain may arise especially with bulky ligands. The strain may be relieved by various transformations of initially-formed complexes, first of all by elimination of some of the ligands, by conversion of terminal ligands to bridge ones, and by ligand shifts from one metal to another. These transformations should be particularly frequent with

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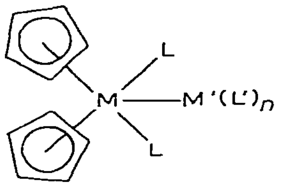
* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

binuclear systems derived from transition metal dicyclopentadienyl derivatives. The reaction sphere in those complexes is limited by two nonparallel rings forming a wedge-like cavity with all the other ligands (L) linked with the metal (M) by its valence orbitals lying in the bisector plane of the dihedral angle and directed towards the second metal (M′) participating in the formation of the $Cp_2M—M'$ bond:

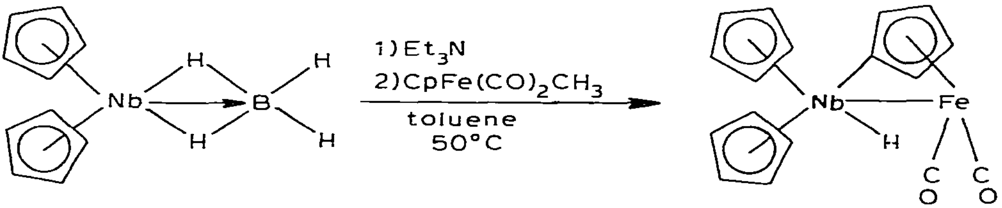


Under the circumstances, the nature of the ligands L′ and their geometrical arrangement about the M′ atom are of particular importance. In fact, with M—M′ bonds of usual lengths (below 3.0 Å), sterically unstrained structures containing M—M′ bonds may only be formed if the M′—L′ bonds are strongly bent from the metal M. Conversely, the presence of L′ in the plane perpendicular to the M—M′ bond would lead to short (below 3 Å) L—L′ contacts and considerable steric hindrances. The latter should be particularly great and readily cause radical transformations of the initially-formed binuclear complexes if the ligands L′ are bent towards the M metal.

To check these conclusion, we undertook a detailed study of reactions leading to sterically strained heterobinuclear compounds, in particular, reactions between niobocene hydride and metal methyl derivatives of the type $CH_3M'L'_n$. Recently, we reported the synthesis and structure of $Cp_2\overline{Nb(\mu\text{-}CO)(\sigma,\pi\text{-}CO)M'}$-(CO)Cp (M′ = Me, W) (I and II, respectively) made from Cp_2NbBH_4, Et_3N and $CpM'(CO)_3CH_3$ [1,2]. The present work describes the synthesis and structure of $Cp_2\overline{Nb(H)(\sigma,\pi\text{-}C_5H_4)Fe}(CO)_2$ (III).

Results

Compound III was isolated from the reaction of niobocene hydride generated in the Cp_2NbBH_4/Et_3N system with the methyl derivative of cyclopentadienyldicarbonyliron in toluene:



(III)

III is formed as red-brown prisms, m.p. 164—165°C (decomposes), stable in the air and insoluble in the usual organic solvents, which bars its study by the NMR technique. The IR spectrum of III contains bands due to vibrations of terminal carbonyl groups at Fe (ν(CO) 1880, 1951 cm^{-1}) and terminal Nb—H stretches

TABLE 1

NON-HYDROGEN ATOM COORDINATES AND TEMPERATURE FACTORS IN THE FORM $T = \exp - 1/40(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)$

Atoms	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nb	3135.4(3)	4010.9(6)	1184.0(2)	2.33(2)	2.50(2)	2.30(2)	−0.07(2)	0.16(1)	0.14(2)
Fe	1406.7(4)	2917.2(9)	1408.2(3)	2.26(3)	2.16(3)	2.54(3)	−0.03(3)	0.35(2)	0(2)
C(1)	3561(4)	1544(7)	1709(3)	2.8(3)	3.4(3)	4.5(3)	0.8(2)	0.4(2)	1.1(2)
C(2)	3906(4)	1491(8)	1156(3)	3.5(3)	3.9(3)	3.9(3)	1.7(2)	−0.6(2)	−0.2(2)
C(3)	4502(4)	2740(8)	1155(3)	2.5(2)	6.0(4)	4.5(3)	0.7(3)	0.6(2)	0.8(3)
C(4)	4517(4)	3576(8)	1702(3)	2.2(2)	5.8(4)	4.0(3)	0.2(2)	−0.3(2)	0.6(3)
C(5)	3945(3)	2808(8)	2047(3)	2.7(2)	4.8(3)	3.2(3)	0.5(2)	−0.7(2)	0.9(2)
C(6)	3742(4)	5531(7)	414(3)	5.0(3)	3.8(3)	4.6(3)	0.8(2)	2.6(3)	1.3(2)
C(7)	3741(4)	6548(8)	914(3)	4.3(3)	3.6(3)	4.6(3)	−1.4(2)	0.9(3)	0.8(2)
C(8)	2895(4)	6889(7)	1005(3)	5.4(4)	2.2(3)	4.7(3)	−0.2(2)	1.3(3)	0.4(2)
C(9)	2375(4)	6044(7)	569(3)	4.1(3)	3.3(3)	4.0(3)	0.0(3)	0.3(2)	2.1(2)
C(10)	2905(4)	5220(8)	208(3)	5.5(4)	4.1(3)	2.3(2)	−0.6(3)	−0.0(2)	1.0(2)
C(11)	2254(3)	4447(6)	1857(2)	2.6(2)	2.8(2)	2.3(2)	−0.2(2)	0.3(2)	−0.2(2)
C(12)	1456(3)	5291(7)	1710(2)	3.2(2)	2.5(2)	2.7(2)	0.4(2)	0.4(2)	−0.2(2)
C(13)	788(4)	4515(7)	1974(2)	2.9(2)	3.3(3)	3.0(2)	0.8(2)	0.7)2)	−0.2(2)
C(14)	1141(4)	3199(7)	2311(2)	3.4(2)	3.8(3)	3.1(3)	0.5(2)	1.0(2)	0.8(2)
C(15)	2031(3)	3187(7)	2257(2)	3.2(2)	2.9(2)	2.6(2)	−0.2(2)	0.4(2)	−0.2(2)
C(16)	1434(3)	816(7)	1334(3)	3.2(3)	3.3(3)	4.7(3)	−0.4(2)	1.3(2)	−0.2(2)
C(17)	836(4)	3172(7)	707(3)	3.3(3)	4.2(3)	3.5(4)	−0.2(2)	1.1(2)	0.0(2)
O(1)	1438(3)	−602(5)	1296(3)	6.4(3)	2.1(2)	10.7(4)	0.3(2)	2.9(3)	−0.4(2)
O(2)	442(3)	3340(6)	253(2)	6.4(3)	8.4(3)	3.8(2)	0.3(2)	−1.2(2)	0.6(2)

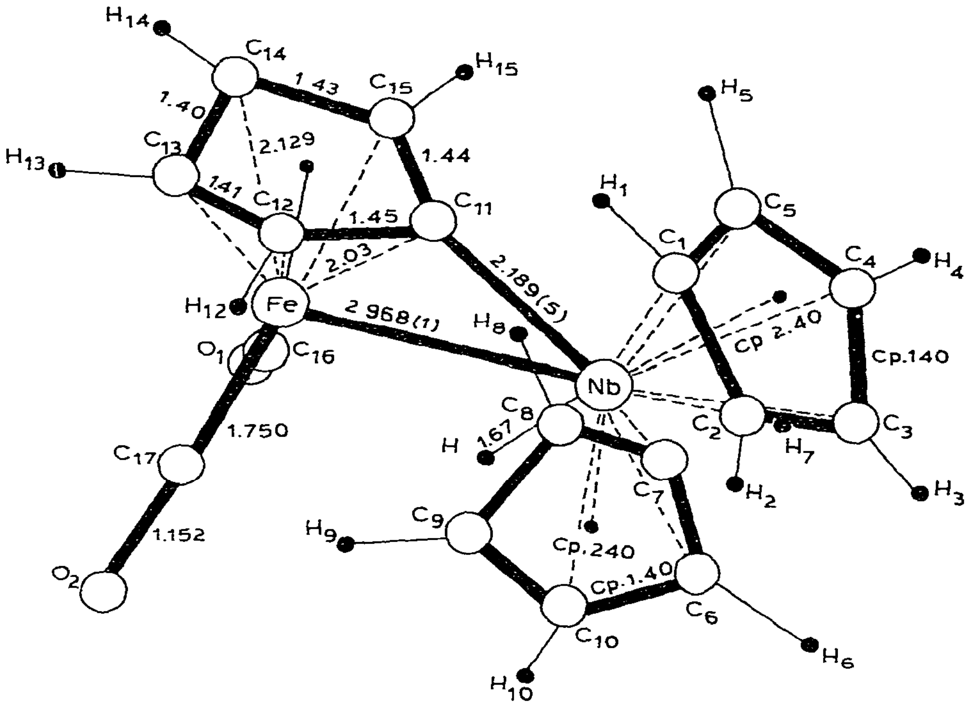


Fig. 1. The structure of $(C_5H_5)_2Nb(H)(\sigma,\pi\text{-}C_5H_4)Fe(CO)_2$.

(1780 cm^{-1}). The mass spectrum contains the molecular ion (*m*/*e* 400) and the ions formed in its step-wise decarbonylation followed by the dissociation of the Nb—Fe bond. The complex structure (Fig. 1) has been determined by X-ray diffraction. Table 1 contains non-hydrogen atom coordinates together with the anisotropic temperature factors. The hydrogen coordinates are given in Table 2.

TABLE 2

HYDROGEN ATOM COORDINATES

	x	*y*	*z*
H(1)	0.317(4)	0.086(7)	0.186(2)
H(2)	0.375(4)	0.079(7)	0.083(3)
H(3)	0.487(4)	0.301(7)	0.084(2)
H(4)	0.487(4)	0.442(7)	0.185(3)
H(5)	0.375(3)	0.302(7)	0.346(3)
H(6)	0.423(4)	0.525(7)	0.020(2)
H(7)	0.416(4)	0.699(7)	0.114(2)
H(8)	0.270(4)	0.752(7)	0.134(2)
H(9)	0.173(3)	0.602(7)	0.046(2)
H(10)	0.271(4)	0.451(7)	−0.010(3)
H(12)	0.366(4)	0.125(7)	0.356(2)
H(13)	0.021(4)	0.483(7)	0.194(2)
H(14)	0.082(3)	0.253(7)	0.250(2)
H(15)	0.236(4)	0.244(7)	0.244(3)
H	0.257(3)	0.273(6)	0.073(2)

TABLE 3

BOND LENGTHS, d (Å), IN COMPLEX III

Bond		Bond		Bond	
Nb—Fe	2.968(1)	C(1)—C(2)	1.41(1)	C(1)—H(1)	0.92(6)
Nb—H	1.67(5)	C(2)—C(3)	1.39(1)	C(2)—H(2)	0.95(6)
Nb—C(1)	2.406(6)	C(3)—c(4)	1.41(1)	C(3)—H(3)	0.99(6)
Nb—C(2)	2.404(6)	C(4)—C(5)	1.40(1)	C(4)—H(4)	0.92(6)
Nb—C(3)	2.406(5)	C(5)—C(1)	1.39(1)	C(5)—H(5)	1.03(6)
Nb—C(4)	2.398(6)	C(6)—C(7)	1.40(1)	C(6)—H(6)	0.98(6)
Nb—C(5)	2.427(6)	C(7)—C(8)	1.40(1)	C(7)—H(7)	0.88(6)
Nb—C(6)	2.412(6)	C(8)—C(9)	1.40(1)	C(8)—H(8)	0.99(6)
Nb—C(7)	2.396(7)	C(9)—C(10)	1.40(1)	C(9)—H(9)	1.03(6)
Nb—C(8)	2.420(6)	C(10)—C(6)	1.38(1)	C(10)—H(10)	0.93(6)
Nb—C(9)	2.410(6)	C(11)—C(12)	1.45(1)	C(12)—H(12)	1.00(6)
Nb—C(10)	2.405(6)	C(12)—C(13)	1.41(1)	C(13)—H(13)	0.95(6)
Nb—C(11)	2.189(5)	C(13)—C(14)	1.40(1)	C(14)—H(14)	0.88(6)
Fe—C(11)	2.030(5)	C(14)—C(15)	1.43(1)	C(15)—H(15)	0.88(6)
Fe—C(12)	2.062(5)	C(15)—C(11)	1.44(1)		
Fe—C(13)	2.133(5)	C(16)—O(1)	1.167(7)		
Fe—C(14)	2.129(6)	C(17)—O(2)	1.521(7)		
Fe—C(15)	2.074(5)				
Fe—C(16)	1.733(6)				
Fe—C(17)	1.750(6)				

Table 3 includes interatomic distances and Table 4 valence angle values. The complex contains dinuclear molecules $Cp_2\overline{NbH(C_5H_4)Fe}(CO)_2$ as structural units. The niobocene fragment has the usual eclipsed ring conformation. The Nb atom is linked with three atoms (C(11), Fe, and H) lying in the bisector plane of the dihedral angle φ (46.8°) between the rings. The most important

TABLE 4

VALENCE ANGLES (°) IN COMPLEX III

Angle	
C(11)NbH	101(1.5)
C(11)NbFe	43.1(1)
FeNbH	58.0(1.5)
C(16)FeC(17)	92.7(3)
C(1)C(2)C(3)	107.5(5)
C(2)C(3)C(4)	108.1(6)
C(3)C(4)C(5)	108.0(5)
C(4)C(5)C(1)	107.7(5)
C(5)C(1)C(2)	108.6(5)
C(6)C(7)C(8)	108.3(6)
C(7)C(8)C(9)	107.5(5)
C(8)C(9)C(10)	107.7(5)
C(9)C(10)C(6)	109.0(6)
C(10)C(6)C(7)	107.6(6)
C(11)C(12)C(13)	111.0(5)
C(13)C(14)C(15)	108.0(5)
C(14)C(15)C(11)	110.8(5)
C(15)C(11)C(12)	102.9(4)
FeC(16)O(1)	178.2(5)
FeC(17)O(2)	178.3(5)

TABLE 5

FACTORS OF AX + BX + CZ + D EQUATIONS OF PLANAR FRAGMENTS AND OUT-OF-PLANE DISPLACEMENT OF CERTAIN ATOMS

Atoms	I	II	III	IV	V	Angles (°) between the planes	
C(1)	0.005			−2.381			
C(2)	0.001			−1.981		I : II	46.8
C(3)	−0.007			−1.517		I : III	90.1
C(4)	0.010			1.611		II : III	90.6
C(5)	−0.009			−2.172		I : IV	23.0
C(6)		0.006		1.495		II : IV	23.8
C(7)		−0.008		1.577		I : V	−65.9
C(8)		0.008		2.152		II : V	68.7
C(9)		−0.004		2.390		III : IV	90.4
C(10)		−0.001		−1.986		III : V	77.2
C(11)			0.023	0			
C(12)			−0.017				
C(13)			0.004				
C(14)			0.011				
C(15)			−0.022				
Nb	2.0931	−2.0953		0			
Fe			1.6942	0	−0.010		
C(16)				−1.259	0.013		
C(17)				1.260	0.012		
O(1)				−2.110	−0.008		
O(2)				2.100	−0.007		
H				0.01			
A	−0.6826	0.0622	−0.0947	−0.3451	0.8996		
B	0.6193	0.7973	−0.6028	0.7702	0.0603		
C	−0.3879	−0.6004	−0.7922	−0.5364	−0.4326		
	−4.2860	3.4183	−5.8177	0.5067	0.5046		

planar fragments of the molecule and the dihedral angle values are listed in Table 5. On the whole, the complex geometry is rather regular; its symmetry is near C_s. The C_5H_4 moiety lies in the plane perpendicular to the principal structural planes of the niobocene fragment (two C_5H_5 rings and the bisector plane between them). The C(11)NbFe and $Fe(CO)_2$ planes are also practically perpendicular to each other.

The centres of both π-C_5H_5 ligands are equally (to within 0.002 Å) removed from the Nb atom. The C_5H_5 planes are, however, not strictly perpendicular to the Nb—ring centre directions. Thus, the C(5) and C(8) atoms of the two rings positioned symmetrically with respect to Nb are the furthest from the Nb atom, whereas the distances between Nb and C(4) and C(7) are the shortest Nb—C distances.

The Fe—C_5H_4 distances are also nonequivalent: the shortest distance is between Fe and C(11) which forms the σ-bond with Nb. The furthest ring atoms are C(13) and C(14).

The C—C distances in the π-C_5H_5 rings are identical within experimental error. Conversely, the distances in the C_5H_4 σ,π-ligand are not equivalent. The distances between C(11) and its neighbours, C(12) and C(15), are the longest (av. 1.445 Å), the adjacent bonds are somewhat shorter (av. 1.42 Å), and the locking bond, C(14)—C(13), is the shortest one (1.40 Å). The C—C bonds in

TABLE 6

THE MOST IMPORTANT NONBONDED DISTANCES (Å) IN COMPLEX III

Distance		Distance	
C(3)...C(6)	3.01(1)	C(15)...C(16)	2.93(1)
H(3)...H(6)	2.48(8)	C(14)...C(16)	3.01(1)
C(4)...C(7)	3.19(1)	C(12)...C(17)	2.94(1)
C(2)...H	2.45(5)	C(13)...C(17)	3.07(1)
C(1)...H	2.75(6)	H...Fe	2.52(5)
H(2)...H	2.44(8)	C(16)...Nb	3.79(1)
C(10)...H	2.44(5)	C(17)...Nb	3.75(1)
C(9)...H	2.76(5)	C(16)...C(10)	3.44(1)
H(10)...H	2.39(7)	C(17)...C(9)	3.43(1)
C(5)...C(11)	2.99(1)	C(16)...H	2.84(5)
C(1)...C(11)	3.19(1)	C(17)...H	2.77(5)
C(1)...C(15)	3.13(1)		
C(5)...C(15)	3.13(1)		
C(1)...H(15)	2.72(6)		
C(5)...H(15)	2.75(6)		
H(5)...H(15)	2.24(8)		
C(8)...C(11)	3.02(1)		
C(9)...C(11)	3.21(1)		
C(9)...C(12)	3.14(1)		
C(8)...C(12)	3.19(1)		
C(9)...H(12)	2.79(6)		
C(8)...H(12)	2.41(8)		

this ring are on average longer by 0.026 Å than the C—C bonds in the two other rings. The difference between the Nb—C_5H_5 (centre) and Fe—C_5H_4 (centre) distances amount to 0.40 Å which is larger by 0.1 Å than the difference between the accepted values of Nb (1.66 Å) and Fe (1.34 Å) covalent radii in cyclopentadienyl compounds [3].

The C_5H_5 intracycle angles in the niobocene fragment are the same to within the uncertainties, whereas the C_5H_4 angles are noticeably distorted: the intracycle angle at C(11), σ-bonded with Nb (102.9(4)°), is markedly smaller than other intracycle angles whose mean values (for pairs of symmetrical angles) are 110.9(8) and 108.9(5)°. The C_5H_5 ligand planes make a dihedral angle of 46.8° which results in short C(3)···C(6) (3.01 Å) and C(4)···C(7) (3.19 Å) nonbonded distances. Other short distances between C_5H_5 and C_5H_4, and also between C_5H_4 and CO are listed in Table 6. Most of these, e.g. C(5)···C(11), C(8)···C(11), C(1)···C(15), C(9)···C(12), appear because of the contracting action of the Nb—Fe bond whose length (2.968 Å) approaches the sum of the Nb and Fe covalent radii (1.66 + 1.34 = 3.00 Å) [3] and might probably be even less but for those short contacts. The considerable shortening of the Nb—C_5H_4 σ-bond, 2.189(5) Å compared with ca. 2.3 Å in other σ-bonded niobocene derivatives (Table 7), is seemingly also due to the presence of the Nb—Fe bond. A similar phenomenon was observed in the titanocene derivative Cp_2-Ti(σ,π-C_5H_4)TiCp(C_4H_8O) (IV) [4] where the formation of the ordinary Ti—Ti bond 3.336 Å long results in shortening of the Ti—$C_{C_5H_4}$ distance to 2.19 Å.

The hydride hydrogen atom is only linked with niobium (Nb—H 1.67(5) Å) whereas the carbonyl groups are attached to Fe, unlike in I and II. The short contacts, C(16)···H (2.84 A) and C(17)···H (2.76), between the carbonyl

TABLE 7

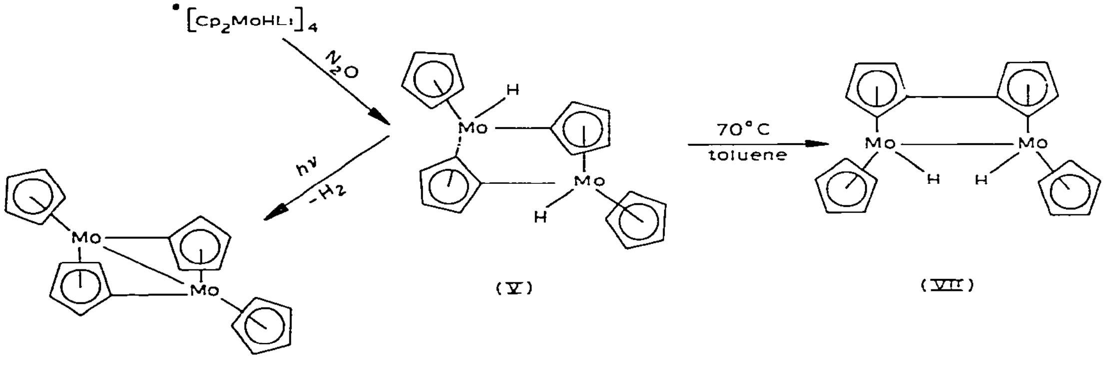
SOME STRUCTURAL CHARACTERISTICS OF NIOBIUM DICYCLOPENTADIENYL COMPLEXES CONTAINING σ-BONDED CARBON ATOMS

Formula	Cp_2Nb fragment conformation	Nb—ring centre distance,	$Nb—C_{Cp}$ (av.) (Å)	C—C (av.) (Å)	σ-bonded Nb—C, Å	α, (°)	$(C...C)_{min}$ Cp_2Nb—sandwich, (Å)	Ref.
$[(\pi\text{-}C_5H_5)(\pi,\sigma\text{-}C_5H_4)NbH]_2$	eclipsed	2,05	2,398	1,418	2,296	39,6	3,16	1
$[(\pi\text{-}C_5H_5)_2Nb(C_4H_9)]_2O$	eclipsed	2,12	2,44	1,39	2,32	46,0	3,07	10
$(\pi\text{-}C_5H_5)_2Nb(CS_2)(C_3H_5)$	eclipsed	—	2,43	—	2,309	49,7	—	11
$(\pi\text{-}C_5H_5)_2Nb(C_2H_5)(CH_2{=}CH_2)$	eclipsed	2,06	2,402	1,406	2,316	46,6	—	12
$(\pi\text{-}C_5H_5)_2NbH(\pi,\sigma\text{-}C_5H_4)Fe(CO)_2$	eclipsed	2,09	2,408	1,40	2,189	46,8	3,02	this work

groups and the hydride ion seemingly hinder elongation of the C(16)···C(14), C(15) and C(17)···C(12), C(13) distances as they do not allow bending of the carbonyl groups in the direction of Nb.

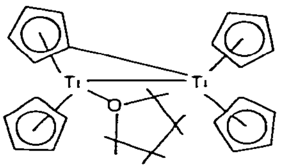
Discussion

The formation of the σ,π-cyclopentadienylidene bridge observed in III is not unusual with wedge-like sandwich complexes. This is, as a rule, the result of inclusion of a "carbene-like" Cp_2M fragments [5] into an active $H—C_5H_4M$ bond of the second Cp_2M fragment, as e.g. in the case of the structurally studied niobocene dimer and its tantalum analogue [6]. A similar mode of coordination occurs in molybdenocene dimer (V) [7] and its dehydrogenation product (VI) [8]. The formation of the stable fulvalene structure of molybdenocene dimer (VII) involves a complex of this type as intermediate [7]:

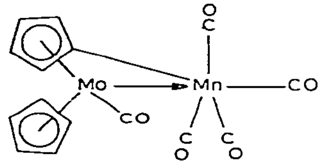


(VI) (V) (VII)

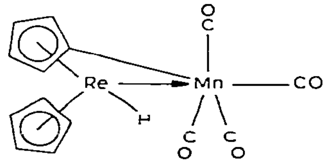
The titanocene dimer is probably formed in a similar way [9,10]. Lastly, the complexes involving the Ti—Ti (IV) [4], Mo—Mn (VIII) and Re—Mn (IX) bonds each contain one cyclopentadienyl bridge:



(IV)



(VIII)

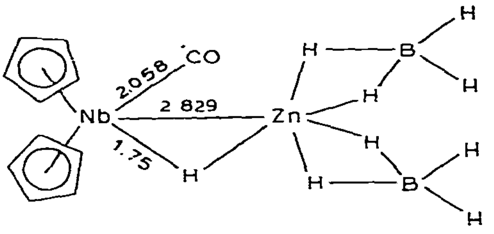


(IX)

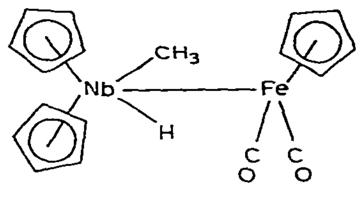
The formation of the latter two complexes, VIII and IX, from Cp_2MoH_2 (or Cp_2ReH) and $MeMn(CO)_5$ very much resembles the formation of complexes I to III: in all these reactions methane is evolved and an M—M′ bond is formed. The difference is in the source of hydrogen: with I and II, the hydride Nb—H hydrogen is involved, VIII and IX are formed by elimination of a sandwich system proton, and the formation of III proceeds with the displacement of a monocyclopentadienyl fragment proton.

To understand why those reactions follow different paths it would be worthwhile to consider the mutual effects by the Nb—M′ bond and ligand environment at the atom M′ linked with the niobocene fragment in the niobocene heterobinuclear derivatives studied, in accordance with what has been said in the Introduction.

Recently, we have studied the complex, $\overline{Cp_2Nb(CO)(\mu\text{-}H)Zn}$—$(BH_4)_2 \cdot$ 0.5 C_6H_6 (X) [12]. The latter contains the Nb—Zn bond, and the ligand environment at Nb it is almost the same as in III and the presumed intermediate A:



(X)

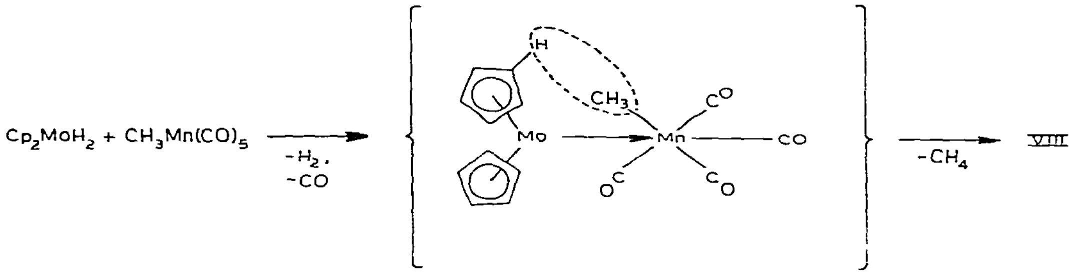


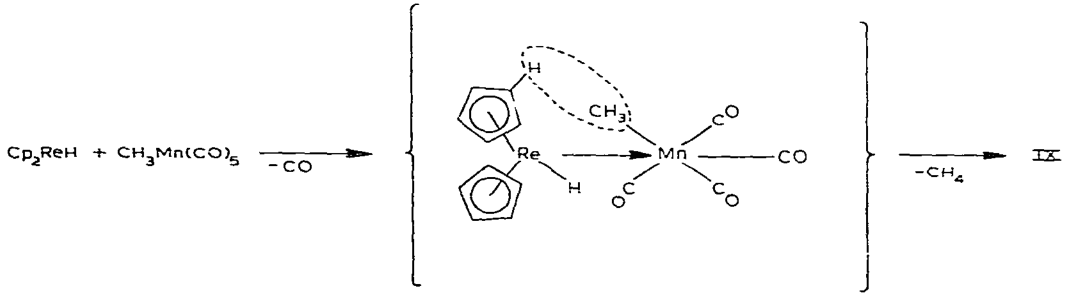
(A)

The bisector plane contains the bridging H atom, the Zn atom and the carbonyl group C atom. The angle, φ, between the outer ligands, H—Nb—C(CO) (102.8°), practically coincides with the H—Nb—C(C_5H_4) angle (101.5°) in III. Unlike in III, the ligands at Zn, the tetrahydroborate hydrogen atoms, however, lie in the base of a tetragonal pyramid and the Zn—H bonds are bent in the direction opposite to the Nb atom. The formation of the Nb—Zn bond, therefore, causes no steric strain (the dihedral angle, φ, between the rings in X is only 39.3° against 46.8° in III). The former value is close to the angle value, 37°, characterizing the initial $Cp_2Nb(CO)H$ structure [13]. The ligands at M′ should be bent likewise in such niobocene derivatives containing Nb—M bonds as $Cp_2Nb(H)_2AlR_2$, $Cp_2Nb(H)_2Hf(CH_2Ph)_3$ [14] and $Cp_2Nb(EPh)_2 \cdot Fe(CO)NO$, $Cp_2Nb(EPh)_2 \cdot Co(CO)_2$ (E = S, Se, Te) [15]. A similar structural feature was observed in $[Cp_2Nb(SMe)_2Ni(MeS)_2NbCp_2]^{2+}$ [16] (Ni—Nb 2.78 Å).

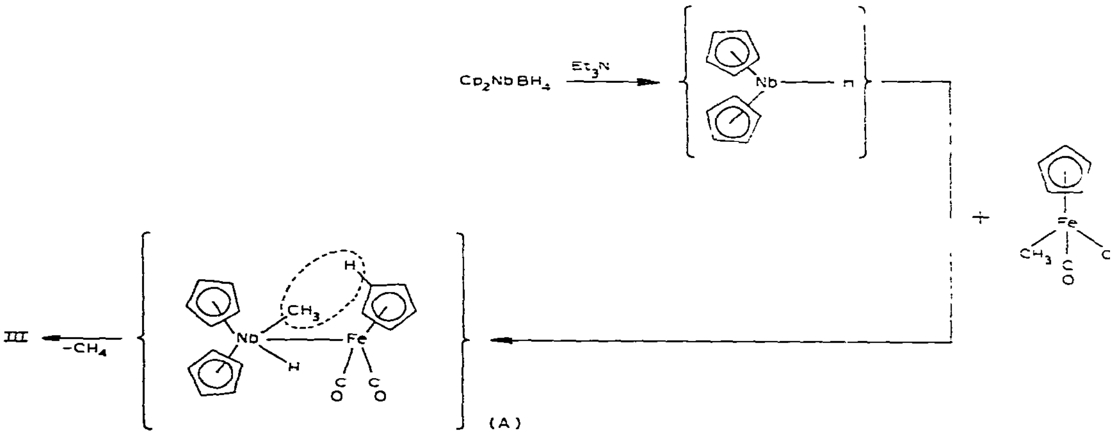
On the other hand, $Cp_2Nb(CO)(\mu\text{-}H)Fe(CO)_4$ (XI) described recently [17,18] contains an Fe atom whose ligand environment (the bridge H atom excluded) is a trigonal bipyramid, the equatorial plane of which is perpendicular to the Nb···Fe axis [18]. Repulsion between the equatorial CO-groups and the ligands attached to Nb (CO and/or C_5H_5) hinders approach of the Fe and Nb atoms to each other. Accordingly, the fragments are linked by the hydride bridge in this adduct and Nb—Fe bond suggested by the authors [17] either does not exist or is sufficiently weakened. This follows from the large Nb—Fe distance (3.324 Å) which exceeds the Nb—Fe distance in III by 0.356 Å, and from the large hydride bridge angle value which is equal to 141° (against 107° in the adduct with $Zn(BH_4)_2$). In addition to that, the Nb—H bond in VII 1.91(3) Å is elongated strongly from VI (1.75 Å) where the hydride bridge is supplemented with the Nb—Zn bond.

Finally, the direct Cp_2M—$M'L'_n$ bond may prove sufficiently stable if steric strain is removed by conversion of terminal ligands to bridging groups. Thus, steric strain arising from the proximity of the wedge-like sandwich moiety and the $M'L'_n$ fragment, in which at least some of the ligands lie in the plane perpendicular to the Cp_2M—M′ bond, is probably the driving force of the processes leading to methane elimination and formation of bonds between manganese and sandwich rings in reactions of formation of complexes IV and V [11] following the schemes:

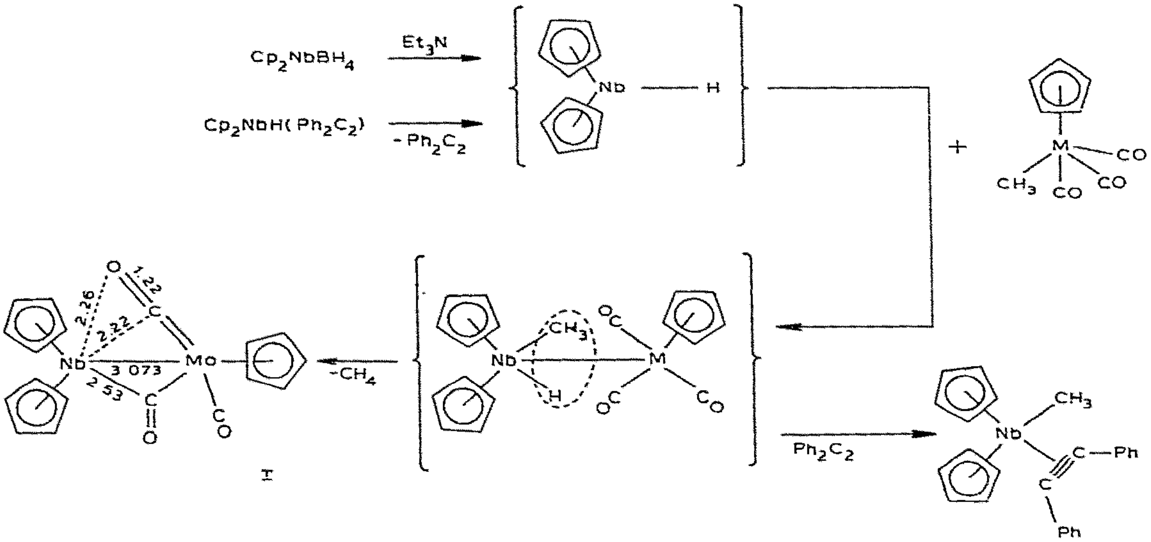




Proximity of C_5H_5 at Fe and CH_3 at Nb in intermediate A, formed by insertion of Cp_2NbH into the CH_3—$Fe(CO)_2Cp$ bond during the synthesis of III, leads to the same effect. The steric strain in that case is removed by formation of CH_4 from $CH_3(Nb)$ and $H—C_5H_4(Fe)$ and of the σ,π-bonded C_5H_4 bridge:



Lastly, the addition of the carbonyl group to the metal carbonyl fragment on going to the corresponding Mo and W complexes (syntheses of I and II) leads to intermediate B in which the carbonyl ligands are in the vicinity of the ligands at Nb. As a result, steric strain is removed by combination of H and CH_3 to form methane in the niobium coordination sphere, methane is eliminated and two carbonyl groups form coordination bonds with niobium [2]:



Methyl group shift from Mo to Nb was proved by the isolation of niobocene methyltolane derivative VIII from the same reaction with $Cp_2NbH(Ph_2C_2)$ as starting material ($[CpMo(CO)_3]_2$ is formed simultaneously) [19]. This is indicative of the ease of dissociation of the Nb—Mo bond, (probably weakened by steric strain) in B.

Conclusion

The study of III reported here and comparison of the results obtained with the data on other heterobinuclear derivatives of sandwich complexes show that nonbonded interactions play an important, perhaps determining, part in the structural and chemical behaviour of clusters containing bulky ligands. The major effect of the formation of the $Cp_2M—M'(L')_n$ bond is the approach of molecule fragments to each other which results in steric strain. This explains the formation of unusual clusters and, to a certain extent, makes it possible to predict product structures and carry out intended syntheses.

Experimental

The synthesis of III was carried out under pure argon using absolute solvents saturated with Ar. $CpFe(CO)_2Me$ was made as recommended in ref. 21 and Cp_2NbBH_4 as described in ref. 20. M.p.'s were measured using capillaries filled under vacuum and are uncorrected. The IR spectra were recorded on a UR-20 instrument (KBr pellets). The mass spectrum was obtained on a DS-50 instrument.

Crystals III are monoclinic, a 15.812(4), b 8.206(2), c 22.521(5) Å; β 95.75(2)°, $Z = 8$; $\rho_{calc.}$ 1.90 g/cm³, Space group C^2/c.

The integral intensities were measured for a faceted crystal of nearly cubic form of ca. 0.25 mm edge on dimension using an automatic Syntex diffractometer (Mo-K_α, $\theta/2\theta$ scan). 2180 independent nonzero reflections were collected in the θ range 0 to 50°. The structure was solved by the heavy atom method and refined by the full matrix LSQ procedure using the anisotropic approximation for thermal motions. All the hydrogen atoms for which position parameters only were refined were located from differential synthesis. B_H for all the hydrogen atoms was assumed to be equal to 4.5 Å. The calculations were made using Synthex-XTL programmes on a Nova-1200 computer. The final R factor was equal to 0.034.

Preparation of $Cp_2\overline{Nb(H)(\sigma,\pi\text{-}C_5H_4)Fe}(CO)_2$

Triethylamine (5 ml) was added to a dark-green solution of Cp_2NbBH_4 (0.8 g, 3.36 mmol) in 30 ml toluene upon which the solution turned brownish. A yellow solution of $CpFe(CO)_2Me$ (0.65 g, 3.36 mmol) in 10 ml toluene was added to it. In 5 minutes, the reaction mixture became brown-red coloured. It was then allowed to stay at 50°C for an hour, the red-brown crystals precipitated were separated by decantation, washed with 1 : 1 benzene/heptane, and dried under vacuum. The yield was 0.48 g (35.8%), m.p. 164—165°C (decomposes). Found: C, 50.94; H, 5.63; Nb, 23.32; Fe, 13.58%. $C_{17}H_{15}O_2NbFe$ calcd. C, 51.01; H, 3.78; Nb, 23.21; Fe, 13.99%.

IR spectrum (cm^{-1}): 425w, 495m, 585m, 600m, 652m, 688m, 795s, 823s, 852m, 860m, 888w, 1014m, 1030m, 1075m, 1113w, 1162w, 1336w, 1378m, 1438m, 1780m, 1880vs, 1951vs, 2940w, 3100w, 3120w, 3128w.

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