

THE STRUCTURE AND FORMATION OF NIOBOCENE CARBONYL HETERONUCLEAR DERIVATIVES. THE MOLECULAR STRUCTURES OF $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})\text{Mn}(\text{CO})_4$, $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Ni}(\text{CO})_3$ AND $[\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})]_2\text{Mo}(\text{CO})_4$

Yu. V. SKRIPKIN, A. A. PASYNSKII*, V. T. KALINNIKOV, M. A. PORAI-KOSHITS,
L. Kh. MINACHEVA, A. S. ANTYSYSHKINA and V. N. OSTRIKOVA

*The N.S. Kurnakov Lenin Order Institute of General and Inorganic Chemistry, Academy of
Sciences of the USSR, Leninskii Prospekt 31 Moscow V-71 (U.S.S.R.)*

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Summary

The heteronuclear $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})\text{Mn}(\text{CO})_4$ (I), $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Ni}(\text{CO})_3$ (II) and $[\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})]_2\text{M}(\text{CO})_4$ (III, M = Mo; IV, M = W) complexes were prepared by reaction of $\text{Cp}_2\text{NbBH}_4/\text{Et}_3\text{N}$ with $\text{Mn}_2(\text{CO})_{10}$ in refluxing toluene, direct reaction of Cp_2NbBH_4 with $\text{Ni}(\text{CO})_4$ in ether, and reaction of $\text{Cp}_2\text{NbBH}_4/\text{Et}_3\text{N}$ with $\text{M}(\text{CO})_5 \cdot \text{THF}$ complexes (M = Mo or W) in THF/benzene mixture. An X-ray investigation of compounds I–III was performed. It is established that in I the bonding between $\text{Mn}(\text{CO})_5$ and $\text{Cp}_2\text{Nb}(\text{CO})$ (with the angle (α) between the ring planes being $44.2(5)^\circ$) fragments takes place via a direct Nb–Mn bond ($3.176(1) \text{ \AA}$) and a highly asymmetric carbonyl bridge (Mn–C_{CO} $1.837(5) \text{ \AA}$, Nb–C_{CO} $2.781(5) \text{ \AA}$). On the other hand, in complex II the sandwich $\text{Cp}_2\text{Nb}(\text{CO})\text{H}$ molecule (angle $\alpha = 37.8^\circ$) is combined with the $\text{Ni}(\text{CO})_3$ group generally via a hydride bridge (Nb–H $1.83 \text{ \AA}$, Ni–H $1.68 \text{ \AA}$, NbHNi angle 132.7°) whereas the large Nb...Ni distance, $3.218(1) \text{ \AA}$, shows the weakening or even absence of the direct Nb–Ni bond. Similarly, in complex III two $\text{Cp}_2\text{Nb}(\text{CO})\text{H}$ molecules (with α angles equal to 41.4 and 43.0° , respectively) are joined to the $\text{Mo}(\text{CO})_4$ group via the hydride bridges (Nb–H 1.83 and $1.75 \text{ \AA}$ and Mo–H 2.04 and $2.06 \text{ \AA}$) producing a *cis*-form. The direct Nb–Mo bonds are probably absent, since the Nb...Mo distances are rather long (3.579 and $3.565 \text{ \AA}$). The effect of electronic and steric factors on the structure of heteronuclear niobocene carbonyl derivatives is discussed.

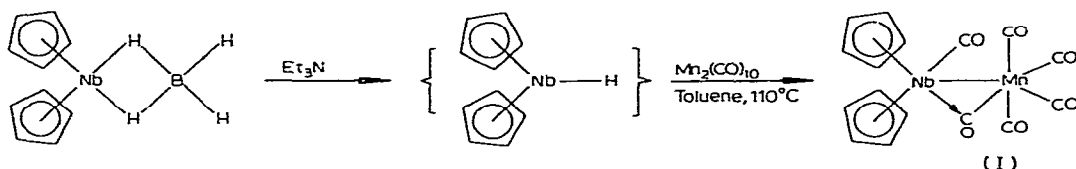
Introduction

Recently, bi- and polynuclear complexes with direct metal–metal bonds have been discussed as spatially strained systems in which a repulsion between the

ligands joined to different metal atoms significantly lengthens the M—M bonds [1–4]. This effect should be most pronounced when one of the metals is part of a bulky sandwich Cp_2M group and the other ligands (including the second metal atom) are in a bisecting plane of the angle between the rings (in view of theoretical models [5]). On the other hand, such systems could be less hindered sterically when some of the terminal ligands become bridged (CO, H etc.) or transfer from one to the other metal and produce novel, often unexpected, structures. In the search for such transformations we have carried out a series of studies on the heteronuclear derivatives based on dicyclopentadienyl compounds of niobium and other Group IV–VII transition elements. The synthesis and structures of $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Zn}(\text{BH}_4)_2$ [2,3], $\text{Cp}_2\text{NbH}(\mu\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2$ [4] and $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})(\sigma,\pi\text{-CO})\text{Mo}(\text{CO})\text{Cp}$ [6] have been reported. The present work is concerned with the synthesis and molecular structures of the new heteronuclear complexes $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})\text{Mn}(\text{CO})_4$ (I), $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Ni}(\text{CO})_3$ (II) and *cis*- $[\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})]_2\text{M}(\text{CO})_4$, here M = Mo or W (III and IV, respectively).

Results

The synthesis of I was carried out by reaction of niobocene hydride, generated in the $\text{Cp}_2\text{NbBH}_4/\text{Et}_3\text{N}$ system, with $\text{Mn}_2(\text{CO})_{10}$ refluxed in toluene:



Complex I was isolated in the form of dark red crystals, m.p. 180°C (decomp), stable in air for a day and readily oxidized in solution. I is well soluble in the common (except aliphatic) organic solvents.

The IR spectrum of I shows the stretching modes of the terminal carbonyls on the Mn atom (1874 , 1982 and 2048 cm^{-1}), the bridged CO (1842 cm^{-1}) as well as the terminal CO group at the Nb atom (1940 cm^{-1}), assigned analogously to the 1940 cm^{-1} band in the spectrum of $\text{Cp}_2\text{Nb}(\text{CO})\text{Cl}$ [7]. The mass spectrum of I contains the molecular ion ($m/e\ 446$) and the peaks of its stepwise decarbonylation and decomposition products along Nb—Mn bond.

The structure of the complex is established by its X-ray analysis (details of the structure, crystallographic constants, atomic coordinates and other structural parameters were given previously [8], Tables 1 and 2 repeat the principal interatomic distances and bond angles). The crystal structural elements are binuclear molecular complexes with sandwich $\text{Cp}_2\text{Nb}(\text{CO})$ fragments and pentacarbonyl $\text{Mn}(\text{CO})_5$ groups. The bis-cyclopentadienyl fragments have an eclipsed conformation with a wedge angle of $44.2(5)^\circ$. The structural fragments are combined directly via Nb—Mn interaction ($3.176(1)\text{ \AA}$) and another carbonyl bridge ($\text{C}(13)\text{O}(3)$) with the Mn—C(13) distance being $1.837(5)\text{ \AA}$ and Nb—C(13) being $2.781(5)\text{ \AA}$ (Fig. 1). Although this latter distance is significantly longer than the Nb—C(O) bond ($2.061(4)\text{ \AA}$), it is still shorter than intermole-

TABLE 1

BOND LENGTHS IN THE STRUCTURE $(C_5H_5)_2Nb(CO)(\mu-CO)Mn(CO)_4$

Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)
Nb—Mn	3.176(1)	C(14)—O(4)	1.145(7)
Nb—C	2.061(4)	C(15)—O(5)	1.146(6)
Nb—C(1)	2.441(5)	C(1)—C(2)	1.394(6)
Nb—C(2)	2.418(5)	C(2)—C(3)	1.420(6)
Nb—C(3)	2.385(4)	C(3)—C(4)	1.396(6)
Nb—C(4)	2.364(5)	C(4)—C(5)	1.431(6)
Nb—C(5)	2.375(5)	C(5)—C(1)	1.416(6)
Nb—C(6)	2.445(4)	C(6)—C(7)	1.395(6)
Nb—C(7)	2.430(5)	C(7)—C(8)	1.415(7)
Nb—C(8)	2.374(5)	C(8)—C(9)	1.405(7)
Nb—C(9)	2.359(5)	C(9)—C(10)	1.420(7)
Nb—C(10)	2.375(5)	C(10)—C(6)	1.421(6)
Nb—C(13)	2.781(5)	C(1)—H(1)	1.04
Mn—C(11)	1.820(4)	C(2)—H(2)	1.08
Mn—C(12)	1.794(5)	C(3)—H(3)	1.04
Mn—C(13)	1.837(5)	C(4)—H(4)	1.04
Mn—C(14)	1.843(5)	C(5)—H(5)	1.09
Mn—C(15)	1.839(5)	C(6)—H(6)	1.09
C—O	1.137(5)	C(7)—H(7)	1.05
C(11)—O(1)	1.145(5)	C(8)—H(8)	1.09
C(12)—O(2)	1.147(5)	C(9)—H(9)	1.04
C(13)—O(3)	1.156(6)	C(10)—H(10)	1.05

cular contact. The MnC(13)O(3) angle reduces to 164.2(4)°, unlike MnCO angles for the terminal carbonyl groups, which are close to 180°. Finally, the NbMnC(13) angle is contracted to 60.6(2)°, against the 91.2° NbMnC angles with other equatorial CO groups. Thus the Nb and Mn atoms, the CO group bonded to Nb, the terminal carbonyl groups C(12)O(2), C(14)O(4) and the

TABLE 2

BOND ANGLES IN THE STRUCTURE $Cp_2Nb(CO)(\mu-CO)Mn(CO)_4$

Angle	ω (°)	Angle	ω (°)
CNbMn	81.2(1)	C(14)MnC(15)	88.0(2)
MnNbC(13)	35.1(1)	MnC(11)O(1)	174.2(4)
CNbC(13)	116.3(1)	MnC(12)O(2)	178.1(5)
NbMnC(11)	91.5(2)	MnC(13)O(3)	164.2(4)
NbMnC(12)	161.1(2)	MnC(14)O(4)	176.1(4)
NbMnC(13)	60.6(2)	MnC(15)O(5)	177.4(4)
NbMnC(14)	94.7(2)	C(1)C(2)C(3)	108.6(4)
NbMnC(15)	91.8(2)	C(2)C(3)C(4)	108.2(4)
C(11)MnC(12)	90.8(2)	C(3)C(4)C(5)	107.4(4)
C(11)MnC(13)	93.0(2)	C(4)C(5)C(1)	107.4(4)
C(11)MnC(14)	85.6(2)	C(5)C(1)C(2)	107.8(5)
C(11)MnC(15)	173.7(2)	C(6)C(7)C(8)	107.6(5)
C(12)MnC(13)	100.5(2)	C(7)C(8)C(9)	108.5(4)
C(12)MnC(14)	104.2(2)	C(8)C(9)C(10)	108.8(4)
C(12)MnC(15)	87.9(2)	C(9)C(10)C(11)	107.2(4)
C(13)MnC(14)	155.3(2)	C(10)C(11)C(12)	108.3(5)
C(13)MnC(15)	93.3(2)		

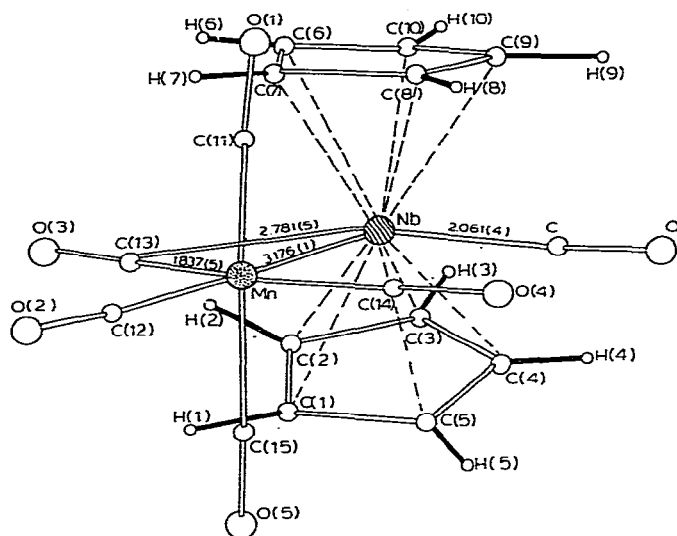
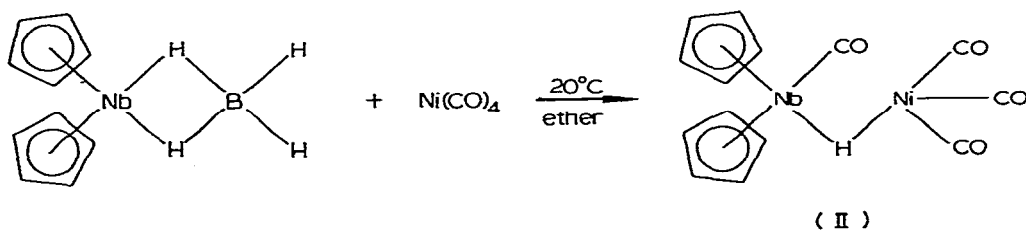


Fig. 1. Molecular structure of $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})\text{Mn}(\text{CO})_4$.

bridged $\text{C}(13)\text{O}(3)$ group bonded to Mn are all in a bisector plane of the angle between the rings. In the structural fragment $(\mu\text{-CO})\text{Mn}(\text{CO})_4$ the Mn atom has a distorted octahedral coordination. The Mn—CO bond lengths are identical (the mean value is $1.835(5)$ Å), with the exception of the somewhat shorter Mn— $\text{C}(12)\text{O}(2)$ bond ($1.794(5)$ Å) located *trans*, with respect to Nb. The short $\text{C}_{\text{C}_5\text{H}_5} \cdots \text{C}_{\text{CO}(\text{equatorial})}$ contacts, $3.08\text{--}3.13$ Å, should be noted.

Complex II was obtained by reaction of niobocene borohydride with $\text{Ni}(\text{CO})_4$ in ether at room temperature without addition of triethylamine:



Complex II was isolated in the form of dark red crystals, unstable in the air, particularly in solutions. II is well soluble in organic (including aliphatic) solvents. The IR spectrum of II in toluene contains two stretching bands of the three terminal carbonyl groups at Ni atom (1985 and 2063 cm^{-1}), typical of an almost C_{3v} symmetry. The terminal CO group at Nb shows a band at 1947 cm^{-1} , assigned analogously to the 1940 cm^{-1} band in the spectrum of $\text{Cp}_2\text{Nb}(\text{CO})\text{Cl}$ [7]. The band at 1919 cm^{-1} may be due to the stretching vibrations of the Nb—H—Ni bridge. The composition and structure of complex II were established on the basis of an X-ray analysis described in a separate publication [17]. Interatomic distances and bond angles are given in Tables 3 and 4. The structure of the complex is shown in Fig. 2: it includes the molecular $\text{Cp}_2\text{Nb}(\text{CO})\text{H}$ and

TABLE 3

BOND LENGTHS IN THE STRUCTURE $(C_5H_5)_2Nb(CO)(\mu-H)Ni(CO)_3$

Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)
Nb—Ni	3.218(1)	C(1)—H(1)	1.10
Nb—C	2.061(8)	C(2)—H(2)	1.10
Nb—H	1.83	C(3)—H(3)	1.08
		C(4)—H(4)	1.09
Ni—C(11)	1.780(11)	C(5)—H(5)	1.09
Ni—C(12)	1.752(11)	C(6)—H(6)	1.09
Ni—C(13)	1.754(10)	C(7)—H(7)	1.11
Ni—H	1.68	C(8)—H(8)	1.09
		C(9)—H(9)	1.11
		C(10)—H(10)	1.09
C—O	1.126(10)		
C(11)—O(1)	1.152(13)		
C(12)—O(2)	1.141(15)		
C(13)—O(3)	1.184(13)		
C(1)—C(2)	1.427(13)		
C(2)—C(3)	1.436(12)		
C(3)—C(4)	1.444(13)		
C(4)—C(5)	1.478(13)		
C(5)—C(1)	1.450(13)		
C(6)—C(7)	1.420(14)		
C(7)—C(8)	1.492(16)		
C(8)—C(9)	1.456(15)		
C(9)—C(10)	1.427(14)		
C(10)—C(6)	1.397(15)		

TABLE 4

BOND ANGLES IN THE STRUCTURE $(C_5H_5)_2Nb(CO)(\mu-H)Ni(CO)_3$

Angle	ω (°)	Angle	ω (°)
NiNbC	74.6(2)	C(2)C(3)H(3)	125.8
NiNbH	22.6(2)	C(4)C(3)H(3)	125.5
HNbC	97.1	C(3)C(4)H(4)	126.8
NbNiH	24.7	C(5)C(4)H(4)	125.9
NbNiC(11)	113.5(3)	C(1)C(5)H(5)	126.3
NbNiC(12)	103.2(3)	C(4)C(5)H(5)	126.9
NbNiC(13)	100.6(3)		
C(11)NiC(12)	117.1(5)		
C(11)NiC(13)	108.3(5)	C(6)C(7)C(8)	107.0(9)
C(11)NiH	97.0(3)	C(7)C(8)C(9)	107.1(9)
C(12)NiC(13)	112.3(5)	C(8)C(9)C(10)	106.0(9)
C(12)NiH	96.6(3)	C(9)C(10)C(6)	111.0(9)
C(13)NiH	124.5(3)	C(10)C(6)C(7)	108.8(9)
NbHNi	132.7		
NiC(11)O(1)	179.1(9)		
NiC(12)O(2)	176.9(9)	C(7)C(6)H(6)	124.9
NiC(13)O(3)	172.4(9)	C(10)C(6)H(6)	126.3
NbCO	173.9(7)	C(6)C(7)H(7)	126.6
		C(8)C(7)H(7)	126.3
C(1)C(2)C(3)	108.6(7)	C(7)C(8)H(8)	125.8
C(2)C(3)C(4)	108.5(7)	C(9)C(8)H(8)	127.1
C(3)C(4)C(5)	107.4(7)	C(8)C(9)H(9)	126.8
C(4)C(5)C(1)	106.9(7)	C(10)C(9)H(9)	127.9
C(5)C(1)C(2)	108.7(8)	C(6)C(10)H(10)	123.9
		C(9)C(10)H(10)	125.1
C(2)C(1)H(1)	124.9		
C(5)C(1)H(1)	126.9		
C(1)C(2)H(2)	125.9		
C(3)C(2)H(2)	125.5		

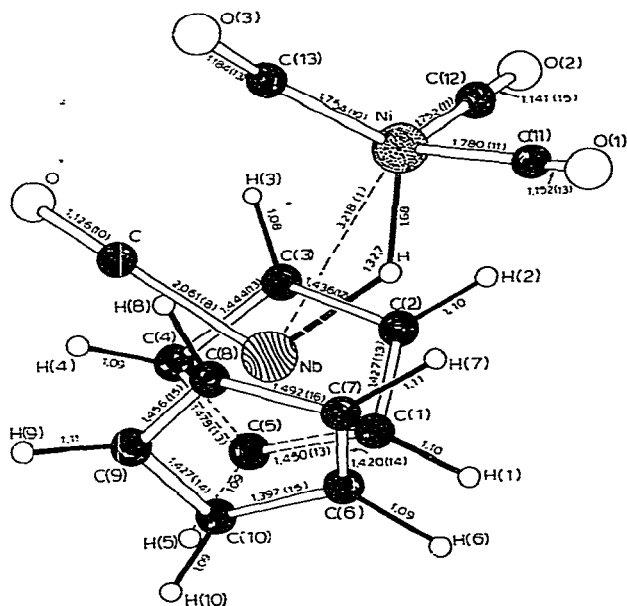
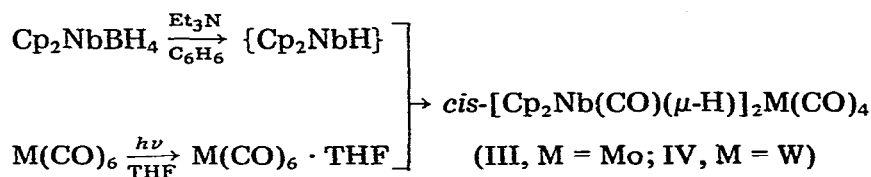


Fig. 2. Molecular structure of $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Ni}(\text{CO})_3$.

$\text{Ni}(\text{CO})_3$ fragments combined via a hydride bridge (Nb-H 1.83 Å, Ni-H 1.68 Å, NbHNi angle 132.7°). The $\text{Nb}\cdots\text{Ni}$ distance, 3.218(1) Å, is 0.25 Å longer than the sum of the covalent radii of Nb and Ni atoms ($1.66 + 1.30 = 2.96$ Å) [9], and is practically nonbonding. The Ni atom has a tetrahedral environment consisting of the three carbonyl groups and the bridge H. The mean $\text{Ni-C}(\text{CO})$ distance is equal to 1.762 ± 0.011 Å with a mean bond length C-O of 1.155 ± 0.015 Å; the mean NiCO angles are $176.1(9)^\circ$. The $\text{C}(11)\text{O}(1)$ and $\text{C}(12)\text{O}(2)$ carbonyls are located almost symmetrically to the bisector plane, which is also a plane of symmetry in the nickel polyhedron.

The bisector plane of the dihedral angle between the rings ($\alpha = 37.8^\circ$) contains the atoms Nb, Ni, H and C (the CNbH angle is 97° , Nb-C 2.061(8), C-O 1.126(10) Å. The NbCO angle is 173.9° . The $\text{C}(13)\text{O}(3)$ group bonded to Ni is close to this plane and produces a short $\text{C}(13)\cdots\text{C}$ contact (3.057(13) Å) with the carbonyl C atom bonded to Nb.

Complexes III and IV were prepared by consecutive reactions of Cp_2NbBH_4 with Et_3N in benzene and with $\text{M}(\text{CO})_5 \cdot \text{THF}$ adducts ($\text{M} = \text{Mo}$ and W), obtained under UV-irradiation of $\text{M}(\text{CO})_6$ in THF:



Complexes III and IV were isolated in the form of red-brown crystals, stable in the air for a day and practically insoluble in organic solvents. The IR spec-

TABLE 5

BOND LENGTHS IN THE STRUCTURE $[(C_5H_5)_2NbH(CO)]_2Mo(CO)_4$

Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)
Mo—C(1)	2.023(13)	C(7)—C(8)	1.394(23)	C(7)—H(7)	1.02
Mo—C(2)	1.904(14)	C(8)—C(9)	1.431(23)	C(8)—H(8)	1.01
Mo—C(3)	1.908(14)	C(9)—C(10)	1.426(24)	C(9)—H(9)	1.04
Mo—C(4)	1.995(13)	C(10)—C(11)	1.360(24)	C(10)—H(10)	1.03
Mo—H(1)	2.04	C(11)—C(7)	1.396(24)	C(11)—H(11)	1.03
Mo—H(2)	2.06				
C(1)—O(1)	1.163(16)	C(12)—C(13)	1.398(18)	C(12)—H(12)	1.05
C(2)—O(2)	1.191(17)	C(13)—C(14)	1.411(21)	C(13)—H(13)	1.02
C(3)—O(3)	1.185(17)	C(14)—C(15)	1.388(20)	C(14)—H(14)	1.02
C(4)—O(4)	1.160(16)	C(15)—C(16)	1.416(21)	C(15)—H(15)	1.00
Nb(1)—H(1)	1.752	C(16)—C(12)	1.452(19)	C(16)—H(16)	1.00
Nb(1)—C(5)	2.062(14)				
C(5)—O(5)	1.152(17)	C(17)—C(18)	1.410(26)	C(17)—H(17)	0.99
Nb(2)—H(2)	1.827	C(18)—C(19)	1.392(25)	C(18)—H(18)	1.03
Nb(2)—C(6)	2.023(14)	C(19)—C(20)	1.428(27)	C(19)—H(19)	1.02
C(6)—O(6)	1.159(17)	C(20)—C(21)	1.392(24)	C(20)—H(20)	1.02
		C(21)—C(17)	1.369(26)	C(21)—H(21)	1.05
Mo—Nb(1)	3.579(2)	C(22)—C(23)	1.407(25)	C(22)—H(22)	1.05
Mo—Nb(2)	3.565(2)	C(23)—C(24)	1.394(26)	C(23)—H(23)	1.00
		C(24)—C(25)	1.351(24)	C(24)—H(24)	1.03
		C(25)—C(26)	1.390(24)	C(25)—H(25)	1.05
		C(26)—C(22)	1.368(24)	C(26)—H(26)	1.01

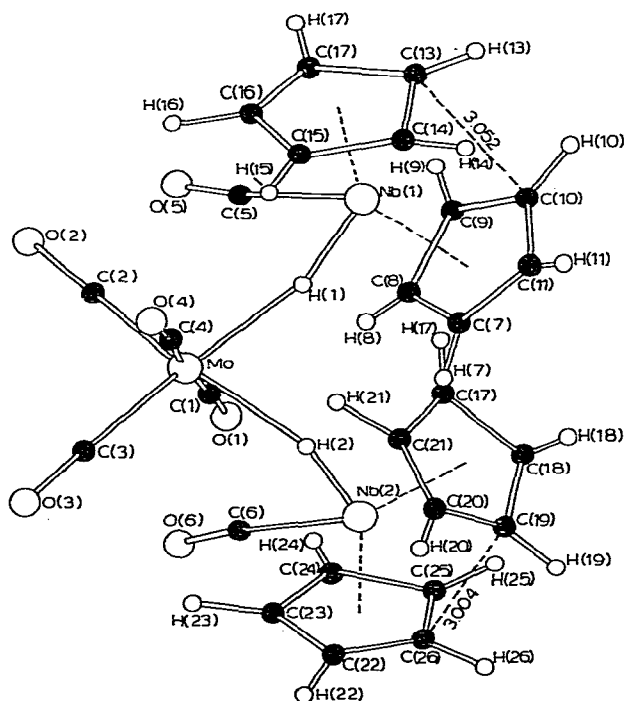
Fig. 3. Molecular structure of $[Cp_2Nb(CO)(\mu-H)]_2Mo(CO)_4$.

TABLE 6

BOND ANGLES IN THE STRUCTURE $[(C_5H_5)_2NbH(CO)]_2Mo(CO)_4$

Angle	ω ($^\circ$)	Angle	ω ($^\circ$)
C(1)MoC(2)	89.2(6)	C(8)C(7)C(11)	108.1(14)
C(1)MoC(3)	87.5(6)	C(8)C(7)H(7)	127.8
C(1)MoC(4)	175.1(6)	C(11)C(7)H(7)	124.1
C(1)MoH(1)	96.0	C(7)C(8)H(8)	124.2
C(1)MoH(2)	81.6	C(7)C(8)C(9)	107.6(14)
C(2)MoC(3)	88.4(6)	C(9)C(8)H(8)	128.2
C(2)MoH(2)	167.9	C(8)C(9)C(10)	106.2(14)
C(2)MoH(1)	96.7	C(8)C(9)C(9)	126.4
C(3)MoH(2)	99.0	C(10)C(9)H(9)	127.4
C(3)MoH(1)	173.8	C(9)C(10)C(11)	108.5(14)
C(4)MoC(2)	87.5(6)	C(9)C(10)H(10)	125.1
C(4)MoC(3)	88.7(6)	C(11)C(10)H(10)	126.4
C(4)MoH(2)	102.2	C(7)C(11)H(11)	126.2
C(4)MoH(1)	87.9	C(10)C(11)H(11)	124.3
H(1)MoH(2)	76.6	C(10)C(11)C(7)	109.5(14)
MoC(1)O(1)	176.3(2)		
MoC(2)O(2)	178.1(2)	C(13)C(12)C(16)	106.9(12)
MoC(3)O(3)	178.4(2)	C(13)C(12)H(12)	126.9
MoC(4)O(4)	177.6(2)	C(16)C(12)H(12)1	126.9
MoH(1)Nb(1)	141.0	C(12)C(13)C(14)	109.1
MoH(2)Nb(2)	133.1	C(12)C(13)H(13)	125.9
		C(14)C(13)H(13)	124.4
C(5)Nb(1)H(1)	97.6	C(13)C(14)C(15)	108.2(13)
Nb(1)C(5)O(5)	177.1(12)	C(13)C(14)H(14)	124.5
H(2)Nb(2)C(6)	100.3	C(15)C(14)H(14)	127.3
Nb(2)C(6)O(6)	175.1(13)	C(14)C(15)C(16)	109.0(13)
		C(14)C(15)H(15)	122.6
		C(16)C(15)H(15)	128.4
		C(12)C(16)C(15)	106.8(12)
		C(12)C(16)H(16)	126.7
		C(15)C(16)H(16)	126.4
C(18)C(17)C(21)	105.6(15)	C(26)C(22)C(23)1	108.2(15)
C(21)C(17)H(17)	130.9	C(26)C(22)H(22)	123.5
C(18)C(17)H(17)	123.5	C(23)C(22)H(22)	128.3
C(17)C(18)C(19)	110.4(15)	C(22)C(23)C(24)	106.2(15)
C(17)C(18)H(18)	123.4	C(22)C(23)H(23)	130.4
C(19)C(18)H(18)	126.3	C(24)C(23)H(23)	123.3
C(20)C(19)C(18)	106.0(15)	C(25)C(24)C(23)	109.0(16)
C(20)C(19)H(19)	129.1	C(25)C(24)H(24)	123.5
C(18)C(19)H(19)	124.9	C(23)C(24)H(24)	127.4
C(21)C(20)C(19)	106.8(14)	C(26)C(25)C(24)	108.6(15)
C(18)C(20)H(20)	124.3	C(24)C(25)H(25)	127.6
C(21)C(20)H(20)	128.9	C(26)C(25)H(25)	123.8
C(25)C(26)H(17)	111.2(15)	C(25)C(26)C(22)	107.9(15)
C(20)C(21)H(21)	125.4	C(25)C(26)H(26)	123.6
C(17)C(21)H(21)	123.4	C(22)C(26)H(26)	128.5

trum of III (in KBr) contains the stretching modes of the terminal carbonyl group at Nb (1939 cm^{-1}) and the terminal carbonyl groups on the Mo atom as well as the Nb—H—Mo bridge vibrations (these bands appear at 1805, 1850, 1875, 1898 and 2006 cm^{-1} , their precise assignment has not been performed, however). The stretching vibrations of the cyclopentadienyl ligands appear in the form of split bands at 811, 823, 1008, 1019, 1425 and 1438 cm^{-1} .

The exact composition and structure of complex III, and in particular its

tri-nuclear composition were detected only after a thorough X-ray analysis which is to be published in a separate communication. For interatomic distances and bond angles see Tables 5 and 6. The projection on the MoH(1)H(2) plane of the complex is shown in Fig. 3. In this complex one may draw a two-fold axis along a bisector of the H(1)MoH(2) angle. The two $\text{Cp}_2\text{Nb}(\text{CO})\text{H}$ molecules and the $\text{Mo}(\text{CO})_4$ fragment are combined only via the hydride bridges (the mean Nb—H bond length is 1.79(1) Å, Mo—H is 2.05(1) Å; MoH(1)Nb(1) and MoH(2)Nb(2) angles are 141 and 133°, respectively). Both $\text{Cp}_2\text{Nb}(\text{CO})$ fragments produce an eclipsed configuration typical of the wedge-shaped sandwiches, with dihedral angles (α) between the C_5H_5 planes being 41.4 and 43.0° in fragments.

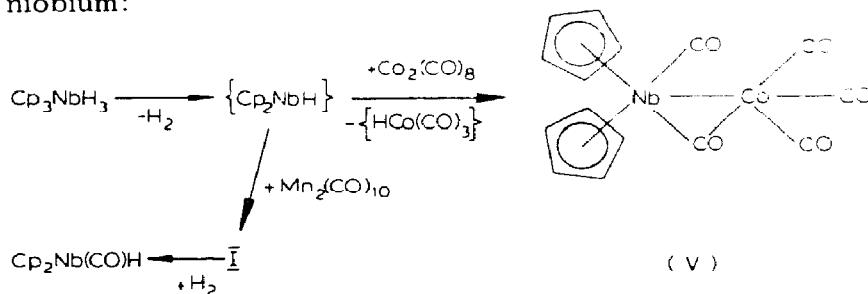
The Nb—CO and Nb—H bonds are almost in a bisector plane of the cyclopentadienyl wedge. The lengths of the Nb—C(O) bonds are 2.06(1) and 2.02(1) those of C—O are 1.15(2) and 1.16(2) Å, the NbCO angle is equal to 177(2) and 175(2)°. The mean Nb— C_{5H_5} distances are 2.37 and 2.38 Å.

The Mo...Nb(1) and Mo...Nb(2) distances (3.579 and 3.565 Å) may show the absence of direct Nb—Mo interaction. Thus the Mo coordination polyhedron is a distorted octahedron with *cis*-located bridging hydrogens (the mean Mo—C(O) bond length is 1.95 Å).

Discussion

It is interesting to compare the conditions of formation and structure of complex I to those of the known complex $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})\text{Co}(\text{CO})_3$ (V) [10] and also the properties of complexes II and III to those of the complex $\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Fe}(\text{CO})_4$ (VI) [11].

Analogously to complex I, complex V was generated in the reaction of niobocene hydride (from CpNbH_3) and binuclear cobalt carbonyl with elimination of a $\text{HCo}(\text{CO})_3$ fragment and transfer of a carbonyl group from cobalt to niobium:



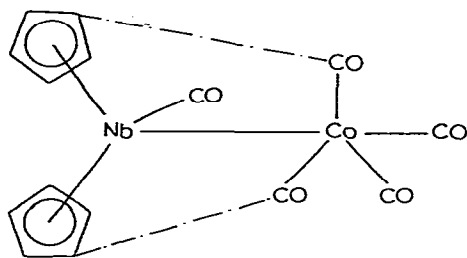
Note that under the same conditions the reaction of Cp_2NbH_3 with $\text{Mn}_2(\text{CO})_{10}$ gives only $\text{Cp}_2\text{Nb}(\text{CO})\text{H}$ instead of complex I [12]. This could be explained by the splitting action of H_2 on generating the Nb—Mn bond in I, whereas our reaction of Cp_2NbH formation from Cp_2NbBH_4 and Et_3N involves only generation of the adduct $\text{Et}_3\text{N} \cdot \text{BH}_3$ which is inactive towards the Nb—Mn bond.

The structure of complex V is similar to that of I: it has one asymmetric carbonyl bridge with a short Co—C bond, 1.792(4) Å, and a long Nb—C bond, 2.531(4) Å, as well as the direct Nb—C bond of 2.992(1) Å. However, signifi-

cant difference between V and I is the presence of only three terminal carbonyl groups on the Co atom which, being oriented from the niobium atom, do not participate in short contacts with carbons of the C_5H_5 rings and CO at niobium and do not hinder the Nb—Co contact close to the sum of two covalent metal radii ($1.66 + 1.29 = 2.95 \text{ \AA}$ [9]).

On the other hand, in complex I three of the four carbonyl groups at Mn are in an equatorial plane with short contacts with C_5H_5 carbons (3.08 and $3.13 \text{ \AA}$). This may hinder a contact between Nb and Mn close to the sum of covalent radii ($1.66 + 1.38 = 3.04 \text{ \AA}$ [9]). Thus the Nb—Mn bond is elongated to $3.176(1) \text{ \AA}$. Steric hindrance may be a reason also for the elongated bridged Nb—C bond, $2.781(5) \text{ \AA}$ compared to $2.531(4) \text{ \AA}$ in V. The stronger bonding of niobocene carbonyl and metal carbonyl fragments in V may explain its greater stability in the presence of H_2 compared to I.

The carbonyl bridges in complexes I and V are due to the lone electron pair of Nb^{III} in the a_1 orbital in the bisector plane of the angle between the rings [5] overlapping with the π^* orbital of the carbonyl bonded to Mn or Co in the same plane. Thus, not only a Nb—C(bridged) bond energy gain is produced but the interligand nonvalent interactions require less energy as well. In particular, in complex I (structure A) in the absence of bridging one would observe short contacts between CO groups in the equatorial plane of the Co atom and the ring carbons of Nb, which could reduce the strength of the Nb—Co bond:



(A)

Thus in complexes I and V, with similar electronic properties of the carbonyl bridge and direct metal—metal bond formation, the bond length and complex geometry in general are defined essentially by steric factors.

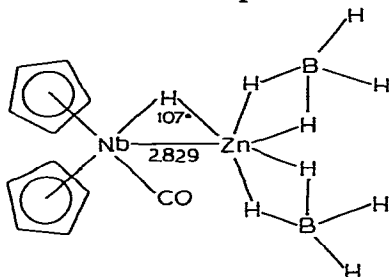
On the other hand, comparing complex I to $Cp_2Nb(CO)(\mu-H)Fe(CO)_4$ (VI) [11] means a replacement of the greater Mn atom ($r 1.38 \text{ \AA}$) and a longer CO bridge by the smaller Fe atom ($r 1.34 \text{ \AA}$) and the shorter hydride bridge. Hence one could expect a decrease of the Nb—Fe distance in VI with respect to Nb—Mn in I, and stronger short contacts between the ligands bonded to the metal neighbours. In fact in the structure of VI there are no short contacts [11] and the Nb—Fe distance ($3.318 \text{ \AA}$) is longer than the sum of Nb and Fe covalent radii ($1.66 + 1.34 = 3.00 \text{ \AA}$ [9]) and even longer by $0.14 \text{ \AA}$ than the Nb—Mn bond in I.

This paradox may be explained by the change in electronic properties caused by the formation of the direct Nb—M bond on going from I to VI. In the latter complex the $Fe(CO)_4$ fragment, with a 16-electron metal valence shell has one vacant low energy orbital which may accept an electron pair either from the Nb—H bond (producing two-electron three-center bonding) or directly from

the Nb^{III} atom. In this case the hydride bridge formation is more favourable when the Nb—Fe coupling is weak (or even absent), which may explain the larger NbHFe angle (141°). Similarly in our complex Cp₂Nb(CO)(μ-H) · Ni(CO)₃ (II) the bonding between metal-containing fragments takes place also via the bridging hydride atom (NbHNi angle 132.7°) while the Nb...Ni distance (3.218(1) Å) observed far exceeds the sum of Nb and Ni covalent radii (1.66 + 1.30 = 2.96 Å [9]). Analogously to VI, complex II contains a 16-electron Ni(CO)₃ fragment with one low energy vacant orbital occupied by the Nb—H electron pair rather than by the Nb^{III} lone electron pair. Thus metal atom coupling is generally antibonding and their approach is unfavourable particularly at short C(O)_{Nb}...C(O)_{Ni} contacts (3.057(13) Å).

Recently, longer nonbonding Nb...M distances have been observed in similar complexes with a single hydride bridge: 3.453 Å for Cp₂Nb(CO)(μ-H)Cr(CO)₅ and 3.758 Å for Cp₂Nb(CO)(μ-H)Nb(CO)₃Cp [13].

We expected a simultaneous formation of the hydride bridge and the direct metal—metal bond in reaction products of niobocene hydride with M(CO)₅ · THF complexes (M = Mo or W) containing readily replaceable THF molecule. It was assumed that the hydride bridge would replace THF analogously to the formation of Cp₂Mo(μ-H)₂ · M(CO)₅ complexes [14]. Further transfer of the carbonyl from M(CO)₅ to the Nb atom should afford another vacant orbital on the M atom which could accept the Nb^{III} lone electron pair producing direct donor-acceptor Nb → Mo bonding. In this case, however, this orbital is more favourable for addition of the second Cp₂Nb(CO)H fragment (VII) via the hydride bridge at the *cis* position to the initially coordinated VII molecule (described in ref. 15). It is as expected that according to the X-ray analysis of complex III the Nb...Mo distances (3.579 and 3.565 Å) far exceed the sum of Nb and Mo covalent radii (1.66 + 1.58 = 3.24 Å [9]). The values of the NbHMo angles are large (141 and 133°, respectively) and identical to those at the hydride bridges, NbHFe (141°) in VI and NbHNi (132.7°) in II, in which the metal—metal bonds are weak or even absent. On the other hand these angles greatly exceed the NbHZn angle (107°) in the complex Cp₂Nb(CO)(μ-H)Zn(BH₄)₂ · 0.5 C₆H₆ (VIII) [2,3]. In VIII the Nb—Zn distance (2.829(2) Å) is less than the sum of Nb and Zn covalent radii (1.66 + 1.34 = 3.00 Å [9]), and may correspond to a direct donor-acceptor Nb—Zn bond supplemented with a hydride bridge:



Experimental

1. Synthesis of complexes

All operations during the synthesis and isolation of complexes I—IV were carried out under a pure argon atmosphere using absolute solvents saturated

with argon. Cp_2NbBH_4 was obtained by a reported method [16]. The commercial carbonyls $\text{Mn}_2(\text{CO})_{10}$, $\text{Ni}(\text{CO})_4$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$ were distilled before use, or sublimed. Triethylamine was distilled over sodium. The IR spectra were taken in KBR pellets on a UR-20 instrument.

$\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-CO})\text{Mn}(\text{CO})_4$ (I). 3 ml of Et_3N was added to a dark green solution of 1.1 g (4.62 mmol) of Cp_2NbBH_4 in 40 ml of toluene; the solution had a brown tinge. 0.9 g (2.32 mmol) of $\text{Mn}_2(\text{CO})_{10}$ in 15 ml of toluene was added to the solution. The reaction solution was refluxed for 1 h and its colour changed to dark red. The solvent was removed under vacuo and the residue recrystallized from benzene/heptane mixture to give 1.68 g (81%) of dark red crystals. Found: C, 43.12; H, 2.36. $\text{C}_{16}\text{H}_{10}\text{O}_6\text{NbMn}$, calcd.: C, 43.07; H, 2.36%.

IR spectrum (cm^{-1}): 444w, 458w, 497w, 525w, 600w, 650s, 667vs, 677s, 811m, 825m, 1008w, 1023w, 1071w, 1421w, 1445w, 1842s, 1874s, 1940vs, 1982s, 2048s, 3150m.

$\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})\text{Ni}(\text{CO})_3$ (II). 0.86 g (5.04 mmol) of $\text{Ni}(\text{CO})_4$ in 10 ml of ether was added dropwise to a stirred dark green solution of 1.2 g (5.04 mmol) of Cp_2NbBH_4 in 40 ml of ether at room temperature. By the end of addition the reaction mixture had become red-brown. The solution was evaporated to dryness, the residue extracted with 50 ml of pentane and the extract concentrated to 20 ml. The dark-red crystals precipitated on cooling to -20°C were separated from mother liquid by decanting, washed with cold pentane and dried under vacuo. Yield 0.45 g (23%).

IR spectrum (cm^{-1} , in toluene): 1947, 1985, 2063 (CO); 1919 (Nb—H—Ni).

$[\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})]_2\text{Mo}(\text{CO})_4$ (III). 3 ml of Et_3N was added to a dark-green solution of 0.6 g (2.52 mmol) of Cp_2NbBH_4 in 30 ml of benzene and the mixture was heated to 50°C . The solution became brown. A solution of $\text{Mo}(\text{CO})_5 \cdot \text{THF}$ prepared by UV-irradiation of 0.35 g (1.32 mmol) of $\text{Mo}(\text{CO})_6$ in 30 ml of THF for 2 h was added to the reaction mixture. The colour changed to red-brown and dark-red crystals precipitated after 10 min at 40°C . After separation from the solution the crystals were washed with benzene/heptane (1/1) mixture and dried under vacuo. Yield 0.3 g (33%) cf. Cp_2NbBH_4 . Found: C, 43.80; H, 3.26. $\text{C}_{26}\text{H}_{22}\text{MoNb}_2\text{O}_6$ calcd.: C, 43.82; H, 3.08%.

IR spectrum (cm^{-1}): 450m, 484m, 561w, 581m, 594w, 611w, 636w, 688w, 810s, 825s, 900w, 1008m, 1019m, 1069w, 1110w, 1369w, 1422w, 1437w, 1805s, 1849s, 1877s, 1898s, 1938vs, 2005s, 2070w, 3130m.

$[\text{Cp}_2\text{Nb}(\text{CO})(\mu\text{-H})]_2\text{W}(\text{CO})_4$ (IV). This was prepared analogously to III from 0.5 g (2.10 mmol) of Cp_2NbBH_4 in 25 ml of benzene with addition of 3 ml of Et_3N and a $\text{W}(\text{CO})_5 \cdot \text{THF}$ solution obtained by UV irradiation of 0.37 g (1.05 mmol) of $\text{W}(\text{CO})_6$ in 25 ml of THF. Dark red crystals of IV were obtained, (0.32 g, 38% cf. Cp_2NbBH_4). Found: C, 39.12; H, 2.91. $\text{C}_{26}\text{H}_{22}\text{Nb}_2\text{O}_6\text{W}$ calcd.: C, 39.00; H, 2.75%.

IR spectrum (cm^{-1}): 448m, 482m, 580m, 607w, 618w, 678m, 742w, 810s, 825s, 1005m, 1119m, 1245w, 1368w, 1418m, 1431m, 1793s, 1837s, 1858s, 1882s, 1931s, 1996s, 2065w, 3121m.

2. Determination of the structures of complexes I–III

Crystallographic data, atomic coordinates and anisotropic thermal vibration constants of I have been given previously [8].

The crystals of complex II are monoclinic. The elementary cell parameters are $a = 7.754(2)$, $b = 16.056(4)$, $c = 12.036(3)$ Å, $\beta = 99.24(2)^\circ$, $V = 1479.0(7)$. Space group $P2_1/c$; $Z = 4$. The intensities of 3784 independent non-zero reflections were measured on an automatic diffractometer Syntex $P2_1$, with a Mo- K_α source and a graphite monochromator using the scanning method of $\theta/2\theta$ ($2\theta_{\max} 60^\circ$). The structures were decoded by Patterson, simple and differential Fourier and least squares methods in isotropic and anisotropic versions. The final value of R was 0.053. The bridging H atom was localized by differential Fourier synthesis, and cyclopentadienyl hydrogens were detected by means of HPOSN program. H atoms were not corrected. The constants of isotropic temperature parameters were equal to 10 Å^2 . All structural calculations were performed using XTL-Syntex programs on a NOVA-1200 computer.

The crystals of complex III belong to the monoclinic system. The elementary cell parameters: $a = 11.9987(2)$, $b = 14.948(4)$, $c = 15.191(3)$ Å, $\beta = 110.75(2)^\circ$, $Z = 4$; $\rho(\text{X-ray}) = 1.20 \text{ g/cm}^3$. Space group $P2_1/n$.

The set of experimental data was obtained on an automatic Syntex $P2_1$ diffractometer by standard procedures ($\lambda(\text{Mo-}K_\alpha)$, graphite monochromator, θ - 2θ scanning) using a faceted crystal. The absorption correction was performed using experimental azimuthal scanning curves over four reflections (111, 232, 046, 463). The structural calculations (with XTL programs on a NOVA-1200 computer) were based on 2440 reflections with $I > 1.96 \sigma T$ ($2\theta_{\max} = 52^\circ$).

The structure was solved by heavy atom techniques with three-dimensional Patterson-Fourier syntheses. After three least-squares iterations of position and isotropic thermal parameters of all non-hydrogen atoms the differential Fourier synthesis was evaluated which localized all hydrogens. In the final calculations, however, the cyclopentadienyl ring hydrogen coordinates were used, which were estimated in terms of standard bond lengths and angles of sp^2 carbons. The structural iteration was carried out in an anisotropic approximation by the block-diagonal least-squares method to R equal to 0.065. The hydrogen atoms were not iterated.

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