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SYNTHESIS AND MOLECULAR STRUCTURE OF NIOBOCENE—(TRICARBONYL)(π-CYCLOPENTADIENYL)MOLYBDENUM WITH METAL—METAL BOND AND UNUSUAL COORDINATION OF CARBONYL GROUPS

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Summary

$(C_5H_5)_2NbBH_4$ reacts with $C_5H_5M(CO)_3Me$ in toluene solution in the presence of Et_3N to give binuclear complexes $(C_5H_5)_2Nb—M(CO)_3C_5H_5$ where M is Mo or W (IV and V, respectively). The structure of IV has been studied by X-ray diffraction (the crystals are orthorhombic, a 12.748(5), b 16.745(6), c 14.314(7) Å; $Z = 8$, space group $Pbca$, automatic difractometer Syntex $P2_1$, λ(Mo-K_α), 1382 reflections, $R = 0.056$, $R_w = 0.058$). Molecule IV contains a wedge-like sandwich $(\pi\text{-}C_5H_5)_2Nb$ (Nb—C 2.37—2.48, C—C (av) 1.42 Å, angle between ring planes 49°) linked with the $(\pi\text{-}C_5H_5)Mo(CO)$ fragment by a direct Nb—Mo bond (3.073 Å) and two bridging CO groups, one nonsymmetrically bonded through the carbon atom only (C—O 1.17, Nb—C 2.53, Mo—C 2.02 Å) and the other σ-bonded to Mo (Mo—C 1.944 Å) and π-bonded to Nb (C—O 1.22, Nb—C 2.22, Nb—O 2.26 Å). Three types of carbonyl groups present in IV give rise to strong IR bands at 1870, 1700 and 1560 cm^{-1} assigned to the terminal, μ-bridging and σ,π-bridging CO groups respectively. Complex V has a similar structure. The electronic structure of IV and its dissociation across the Nb—Mo bond are discussed.

Introduction

Among a vast number of binuclear transition metal complexes involving M—M bonds [1] only a few are known to contain sandwich groups $(C_5H_5)_2M$ [2,3]. The accessibility of metal atoms in such structures depends strongly on the correspondence between the spacial and electronic characteristics of a binuclear system and a reagent. Therefore such complexes are very promising for the development of stereoselective catalysts.

Electron deficient and coordinatively unsaturated complexes of the types $Cp_2Ti—Cr(CO)_3Cp$ (I), $Cp_2V—Cr(CO)_3Cp$ (II) [2] and also $Cp_2Ti—Mo(CO)_3Cp$ (III) [3] ($Cp = \pi\text{-}C_5H_5$) should be particularly reactive. These are obtained by the reactions:

$$2\,Cp_2M + [CpCr(CO)_3]_2 \rightarrow 2\,Cp_2M—Cr(CO)_3Cp \qquad (M = Ti, V)$$

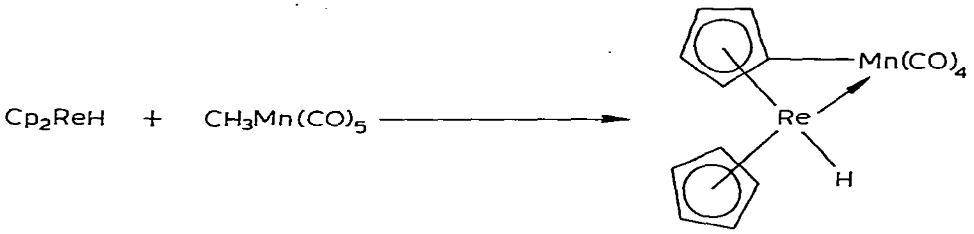
$$\left.\begin{array}{l}[Cp_2TiCl]_2 + 2\,NaMo(CO)_3Cp \\ [Cp_2TiNMe_2]_2 + 2\,HMo(CO)_3Cp\end{array}\right] \longrightarrow 2\,Cp_2Ti—Mo(CO)_3Cp$$

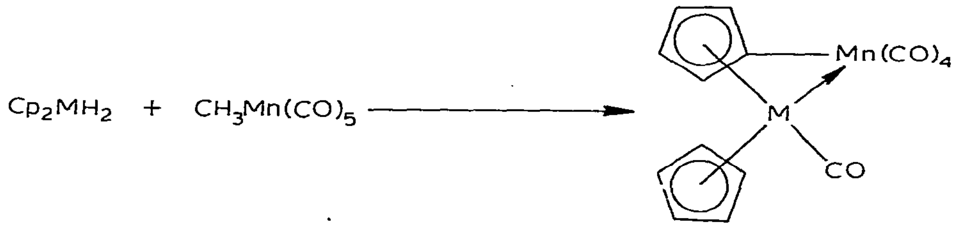
Complexes I and II are pyrophoric, very soluble in benzene (unlike salt-like complexes $Cp_2M^+\ CpCr(CO)_3^-$ of the same composition where M is Cr or Co [2]. Compound II is a selective hydrogenation catalyst [2].

In this work we describe the synthesis, structures and some properties of the complexes $Cp_2NbM(CO)_3Cp$ containing Nb—Mo and Nb—W bonds (IV and V, respectively).

Results and discussion

Earlier Kaesz et al. [4] demonstrated the possibility of the formation of metal—metal bonds in reactions between hydride complexes Cp_2ReH and Cp_2MH_2 (M = Mo, W) and methylcarbonylmanganese complex in benzene:





(M = Mo, W)

The reactions involve manganation of the ring with formation of the Mn—C σ-bond and Re → Mn or M → Mn donor—acceptor bonds.

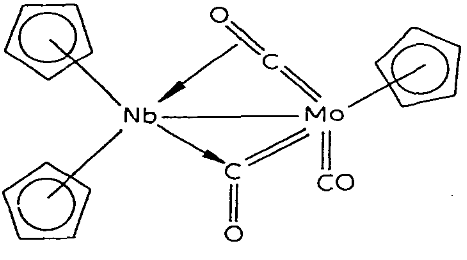
We have found that the reaction of niobocene tetrahydroborate with cyclopentadienyltricarbonylmethyl complexes of Mo and W in toluene in the presence of triethylamine, i.e. the reaction which is formally analogous to those described by Kaesz, proceeds in another direction:

$$Cp_2NbBH_4 + Et_3N + CH_3M(CO)_3Cp \xrightarrow{110^\circ C} Cp_2NbM(CO)_3Cp$$

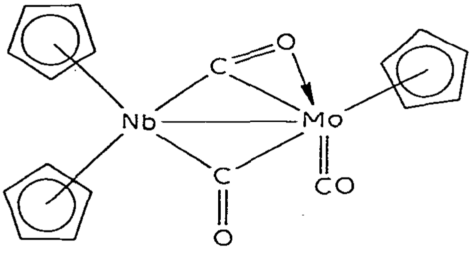
$$(IV, M = Mo; V, M = W)$$

The system Cp_2NbBH_4/Et_3N prepared previously is expected to generate Cp_2NbH as follows from the results reported in [5], where this system has been shown to react with cyclooctatetraene to give $Cp_2Nb(\eta^3\text{-}C_8H_9)$, the product of insertion of C_8H_8 in the Nb—H bond.

Complexes IV and V are noticeably more stable in air than I, II and III containing Ti—Cr, V—Cr and Ti—Mo bonds respectively, and also differ by an unusual coordination of the carbonyl ligands. In fact, the IR spectra of pyrophoric complexes I and II show CO stretching bands at 2020, 1930, 1870 and 2020, 1928, 1840 cm^{-1} respectively [2], and that of paramagnetic complex III has bands at 1956, 1928, and 1903 cm^{-1} [3]. On the contrary, complex IV is a brown-green solid consisting of prismatic crystals stable in air (however, solutions of IV in THF decompose rapidly). The mass spectrum of IV has no molecular ion peak (P); the heaviest ion corresponds to the elimination of one CO group (P — CO, m/e 440). The ion P — 3 CO and the products of dissociation at the Nb—Mo band, viz. Cp_2Nb^+ (m/e 223) and $CpMo(CO)_3$ (m/e 245), are also present. The ^1H NMR spectrum in THF contains two singlets from $(C_5H_5)_2Nb$ (δ 5.37 ppm) and C_5H_5Mo (δ 4.92 ppm) with a peak area ratio of 10/5. The IR spectrum of IV contains bands of the cyclopentadienyl ligand (820 s, doublet; 1008 m, 1420 m, 3100 m cm^{-1}) and three isolated intense bands (1870, 1700 and 1560 cm^{-1}) in the carbonyl region. The first two bands undoubtedly arise from terminal and bridging CO ligands. The terminal CO group has to be at the Mo atom because, in the presence of the Nb—Mo bond, coordination of this CO ligand to the Nb atom would lead to its rare gas electronic configuration which is inconsistent with bridging by yet another CO group. The unusually low frequency of the third CO band (1560 cm^{-1}) can be explained only by bridging coordination with additional O → Nb or O → Mo bonding (formulae A and B, respectively):



(A)



(B)

The tungsten compound V has a similar IR spectrum: cyclopentadienyl ligand bands at 816, 828, 1011, 1420 and 3113 cm^{-1} and CO stretching bands at 1865, 1698, and 1560 cm^{-1}.

This unusual type of CO coordination has only recently been reported for binuclear $Mn_2(CO)_5(Ph_2PCH_2CH_2PPh_2)$ [6], where the bridging ligand frequency

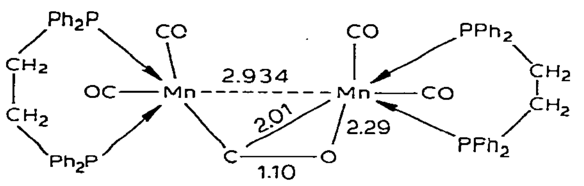
TABLE 1

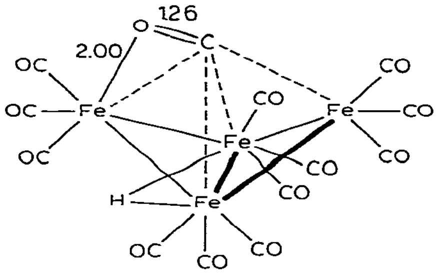
ATOMIC COORDINATES (X 10^4) AND ANISOTROPIC TEMPERATURE FACTORS (X 10) IN THE FORM

$T = \exp[-1/40\ (B_{11}h^2a^{*2} + \ldots + 2\ B_{12}hka^*b^*)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	657(1)	1911(1)	4135(1)	13.0(5)	11.8(3)	16.9(4)	1.8(4)	0.0(4)	−0.6(3)
Nb	1304(1)	460(1)	3002(1)	20.4(5)	13.7(4)	17.6(4)	4.3(4)	0.4(4)	0.2(4)
O(1)	1471(7)	1417(5)	6038(5)	20(5)	20(4)	18(4)	−1(3)	−2(3)	0(3)
O(2)	−351(7)	246(4)	3514(5)	17(5)	10(3)	25(4)	−5(3)	−2(3)	−5(3)
O(3)	2851(7)	1996(5)	3392(4)	7(5)	20(4)	28(4)	−7(3)	5(3)	0(3)
C(1)	1134(10)	1579(6)	5334(8)	14(6)	11(4)	10(5)	−6(4)	2(5)	−4(4)
C(2)	−42(10)	870(7)	3858(6)	18(7)	10(5)	16(5)	9(5)	13(5)	−1(4)
C(3)	2007(12)	1781(7)	3591(8)	19(8)	11(5)	20(5)	8(5)	−5(5)	1(4)
C(4)	1790(9)	−160(6)	4435(8)	0(6)	10(5)	21(5)	3(4)	−2(4)	6(4)
C(5)	2728(10)	130(7)	4040(8)	13(7)	13(5)	22(5)	5(4)	−4(5)	−1(4)
C(6)	2952(10)	−216(7)	3210(8)	13(7)	12(5)	22(6)	5(4)	−4(5)	5(4)
C(7)	2148(10)	−826(6)	3059(8)	14(7)	11(4)	18(5)	0(4)	5(5)	9(4)
C(8)	1473(10)	-791(7)	3838(8)	24(7)	14(5)	18(5)	1(5)	−2(5)	2(4)
C(9)	646(11)	172(7)	1490(8)	21(8)	15(5)	13(5)	3(5)	4(5)	0(4)
C(10)	289(11)	967(7)	1694(7)	28(8)	17(5)	3(4)	−4(5)	−3(4)	4(4)
C(11)	1190(11)	1465(7)	1737(7)	23(7)	24(5)	4(4)	−3(6)	0(4)	5(4)
C(12)	2094(11)	987(7)	1589(8)	21(7)	30(	15(5)	3(5)	2(5)	8(4)
C(13)	1748(11)	192(7)	1412(8)	19(8)	14(5)	11(5)	4(4)	3(5)	−2(4)
C(14)	−503(11)	2757(7)	3175(9)	15(7)	10(4)	32(6)	11(5)	−10(5)	1(4)
C(15)	480(11)	3100(7)	3329(8)	17(7)	8(4)	27(5)	6(5)	−9(5)	3(4)
C(16)	561(10)	3309(6)	4308(8)	14(6)	7(4)	17(5)	3(4)	−2(5)	−3(3)
C(17)	−367(10)	3013(6)	4766(9)	10(7)	4(4)	39(6)	7(4)	3(5)	−7(4)
C(18)	−1006(10)	2669(7)	4045(10)	16(7)	12(5)	43(7)	5(5)	−10(6)	−1(5)

is diminished to 1645 cm^{-1}, and for the tetranuclear anion $[Fe_4(CO)_{13}H]^-$ [7]:





On the other hand, a large decrease of the ν(CO) frequency (down to 1600 cm^{-1}) is observed in the IR spectra of adducts of substituted carbonylmetal compounds with Lewis aids coordinated to the oxygen atom of a carbonyl group [8] and so a possibility of an intermolecular coordination in the crystal could not be excluded. For an unequivocal estimation of the structure of IV we have carried out the X-ray study. The results have shown crystals of IV to be built of discrete molecules with intermolecular distances exceeding the sums of Van der Waals radii. The molecule has structure A rather than B although the latter previously seemed to be more probable as in it the Nb atom interacts with only three atoms in the bisector plane similar to Cp_2NbH_3 [9]. On the contrary in structure A the Nb atom is bonded to two planar cyclopentadienyl rings (average C—C 1.42, Nb—C(C_5H_5) 2.37—2.48 Å), Mo atom (the Nb—Mo bond length 3.073 Å), and also O(2), C(2), and C(3). The three latter atoms together with the Nb and Mo atoms are situated in the same bisector plane. The Nb—O(2) and Nb—C(2) distances are practically identical (2.26 and 2.22 Å, respectively) and close to Nb—C distances 2.18 and 2.19 Å with the coordinated diphenylacetylene in $Cp_2Nb(OOCCMe_3)(\pi\text{-}PhC{\equiv}CPh)$ studied by us recently [10] and to 2.299 Å with coordinated ethylene in $Cp_2Nb(C_2H_5)(C_2H_4)$ [11]. On the other hand, the Nb—C(3) distance 2.53 Å is the largest of the known Nb—C distances [12] exceeding the ordinary Nb—Et bond length (2.316 Å) and Nb—C(C_5H_5) 2.402 Å in $Cp_2NbEt(C_2H_4)$ [11], and the longest Nb—C(C_5H_5) distance 2.48 Å in IV. At the same time, the direct Nb—C(3) bond certainly exists and leads to a decrease of the MoC(3)O(3) angle to 154.7°. The MoC(1)O(1) angle involving a non-bridging CO ligand is equal to 176.8°.

The bonding of Nb with C(3), Mo and the C(2)O(2) group can probably be described within a MO pattern similar to that proposed for Cp_2TiH^+ in ref. 13 and for Cp_2VCl in ref. 14 on the assumption of the C_{2v} symmetry for the Cp_2NbX fragment where X = Mo(CO)Cp. In this case the doubly occupied 1 a_1 orbital at the Nb atom is directed along the y axis in the bisector plane and can overlap with the antibonding π^*-orbitals of the carbonyl bridge C(3)O(3). On the other hand, the lowest vacant orbital b_2 can accept the π-electron pair of the C(2)O(2) bond which thus behaves similar to the olefin in the Zeise salt. Finally the higher vacant orbital 2 a_1 localized in the z direction will overlap with the filled σ-orbital of Mo forming an ordinary Nb—Mo bond.

The presence of the strong four-electron donor bridge C(2)O(2) can be responsible for some shortening of the Nb—Mo bond (3.073 Å) in comparison with the sum of covalent radii (3.16—3.25 Å) determined from the length of the ordinary

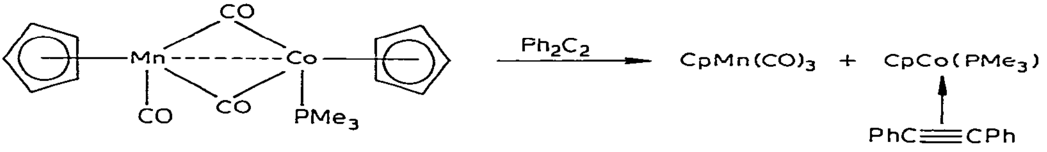
Mo—Mo bond in $[CpMo(CO)_3]_2$ (3.222 Å) [15] and Nb—Nb bond in dimeric niobocene $[CpNb(C_5H_4)H]_2$ (3.10 Å) [16] or that taken from ref. 17 (r_{Nb} 1 1.66 Å, r_{Mo} 1.58 Å).

The presence of four atoms O(2), C(2), Mo and C(3) bonded to Nb and situated in the bisector plane leads to some opening of the angle between the C_5H_5 ring planes to 49° in comparison with complexes $Cp_2Nb(CO)H$ (37°) [18] and $Cp_2Nb(CO)SH$ (45°) [19].

The distances between Mo and C(2) and C(3) atoms of the carbonyl bridges are shorter than those formed by Nb. This is consistent with the greater strength of Mo—CO bonds which remain intact when the Nb—Mo bond dissociates under electron impact to give Cp_2Nb^+ and $CpMo(CO)_3^+$ fragment ions. A similar conclusion can be drawn from attempts to replace the terminal carbonyl group with diphenylacetylene in refluxing toluene. This reaction gives a quantitative yield of the $[CpMo(CO)_3]_2$ (the destiny of the niobocene moiety has not yet been studied):

$$\text{IV} + PhC{\equiv}CPh \rightarrow [CpMo(CO)_3]_2 + \{Cp_2Nb \cdot Ph_2C_2\}$$

Such "nonsymmetric" cleavage of carbonyl bridges has recently been observed in the reaction between tolane and complex VI containing the Mn—CO bond [20] (ν(CO) 1902, 1757 cm^{-1}):



(VI)

With PMe_3 under heating complex VI reacts in a similar manner forming $CpCo(PMe_3)_2$ and $CpMn(CO)_3$. However, the photochemical reaction with PMe_3 leads to symmetrical dissociation of this complex to give $CpMn(CO)(PMe_3)_2$ and $CpCo(CO)PMe_3$ [20]. On the other hand, complex IV remains intact under UV irradiation in the presence of PPh_3 in THF for 1 h. It is likely that the steric strain in IV prevents an entry of a ligand bulkier than CO into the coordination sphere, while the Nb—Mo bond is stronger than the Co—Mn bond which hinders photodissociation.

In conclusion, it is to be noted that IV and V are interesting examples of cyclopentadienylcarbonyl complexes involving both wedge-like and half-sandwich types of M—CO coordination and all possible types of M—CO coordination (terminal, two-electron μ-bridge, and four-electron σ,π bridge).

Experimental

All chemical operations were carried out under pure argon. Toluene, benzene, heptane and triethylamine were distilled over sodium metal dispersion in argon flow. The IR spectra (KBr pellets) were obtained with an UR-20 instrument in the range 400—3500 cm^{-1}. Melting points (uncorrected) were determined in capilleries sealed under vacuum. The ^1H NMR spectra were recorded with a Perkin—Elmer instrument (60 MHz) using $(Me_3Si)_2O$ as internal standard.

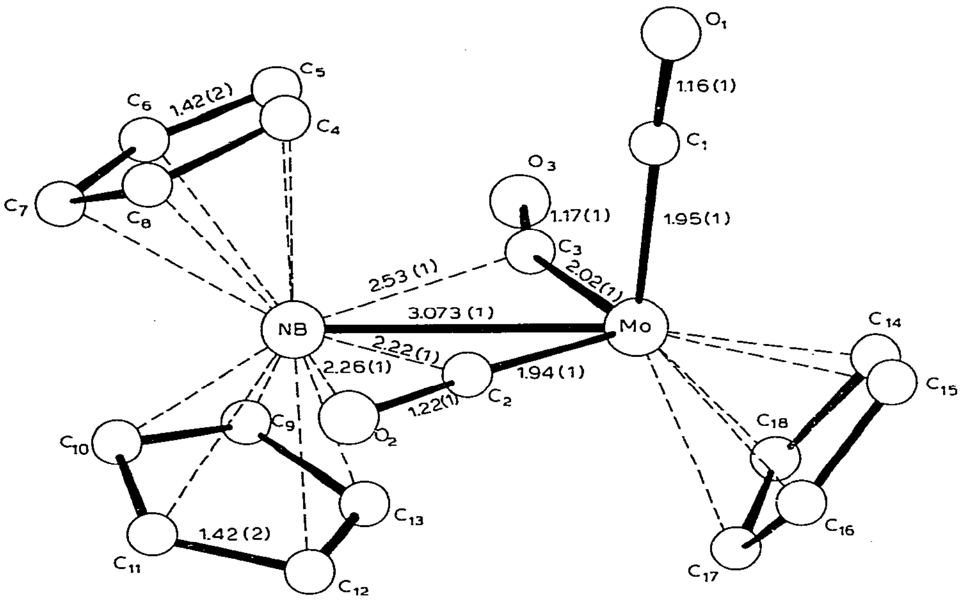


Fig. 1. Structure of $(\pi\text{-}C_5H_5)_2Nb(\mu\text{-}CO)(\sigma,\pi\text{-}CO)Mo(CO)(\pi\text{-}C_5H_5)$ [*Nb*—*Mo*].

The mass spectra were obtained with an AEI MS 30 instrument equipped with a DS-50 data processing system. The experimental conditions were: direct inlet system temperature 100°C, ionizing electron energy 70 eV.

The X-ray diffraction data were collected with a Syntex $P2_1$ automatic difractometer, λ (Mo-K_α), $\theta/2\theta$ scan, 1382 reflections. The structure was solved by the heavy atom method and refined by the full matrix anisotropic least squares to $R = 0.056$, $R_w = 0.058$. Crystals are orthorhombic, a 12.748(5), b 16.745(6), c 14.314(7) Å, $Z = 8$, d_{meas} 2.00, $d_{\text{calc.}}$ 2.02 g cm^{-3}, space group *Pbca*.

Preparation of $Cp_2NbMo(CO)_3Cp$ (IV) and $Cp_2NbW(CO)_3Cp$ (V)

Triethylamine (10 ml) was added to a dark-green solution of Cp_2NbBH_4 [5] (1.00 g, 4.2 mmol) in 25 ml of toluene. The solution was heated to 60°C and then cooled, whereupon it became brownish in colour. A solution of $CpMo(CO)_3Me$ (1.08 g, 4.2 mmol) or $CpW(CO)_3Me$ (1.47 g, 4.2 mmol) in 10 ml of toluene was added to the mixture obtained. After refluxing for 30 min and cooling to room temperature, dark brown-green crystals were isolated by decantation, washed with benzene/heptane (1/1) and dried under high vacuum at 20°C. The yield was 0.95 for IV and 1.10 g for V (~50%).

IV: m.p. 245—247°C (dec.). Found: C, 46.87; H, 3.57; Mo, 20.45; Nb, 19.80. $C_{18}H_{15}MoNbO_3$ calcd.: C, 46.17; H, 3.23; Mo, 20.49; Nb, 19.84%.

V: m.p. 230°C (dec.). Found: C, 39.17; H, 2.88; Nb, 16.50; W, 32.65. $C_{18}H_{15}NbO_3W$ calcd.: C, 38.87; H, 2.72; Nb, 16.70; W, 33.06%.

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