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Synthesis and reactivity of η^6-arene derivatives of niobium(II), niobium(I), and niobium(0) *

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Abstract

The primary reduction products in the Al/AlX$_3$/NbX$_5$/arene system, namely Nb(η^6-arene)(AlX$_4$)$_2$, X = Cl, arene = benzene, hexamethylbenzene; X = Br, arene = hexamethylbenzene, have been isolated. Tetrahydrofuran at room temperature reacts with Nb(η^6-hexamethylbenzene)(AlBr$_4$)$_2$, to give the aluminium-free complex Nb$_2$(η^6-hexamethylbenzene)$_2$Br$_4$, whose crystal structure was determined by X-ray diffraction methods. In the presence of tetrahydrofuran or dimethoxyethane, the η^6-mesitylene-tetrahaloaluminato complexes are further reduced by aluminium to bis-mesityleneniobium(0), Nb(mes)$_2$, which undergoes: a) disproportionation with CO to [Nb(mes)$_2$(CO)]$^+$[Nb(CO)$_6$]$^-$, b) oxidation by V(CO)$_6$ or (4,4′-dimethyl-2,2′-dipyridyl)(BPh$_4$)$_2$ under carbon monoxide to [Nb(mes)$_2$(CO)]X, X = [V(CO)$_6$]$^-$ or BPh$_4$$^-$. The structure of [Nb(mes)$_2$(CO)] BPh$_4$ has been determined by X-ray diffraction methods. In the presence of CO, Nb(mes)$_2$ is reduced by CoCp$^\star_2$ [Cp* = η^5-C$_5$(CH$_3$)$_5$] to [Nb(CO)$_6$]$^-$, which was isolated as its CoCp$^{\star+}_2$ derivative; it efficiently deoxygenates CO$_2$ to CO in the presence of carbon monoxide acceptors such as the [Nb(mes)$_2$(THF)]$^+$ cation.

Introduction

The reactions of metal halides with the Al/AlX$_3$ system in the parent aromatic hydrocarbon as medium, introduced by Fischer and Hafner in 1955 [1], have been widely used for the synthesis of η^6-arene derivatives of *d* transition metals, lanthanides [2], actinides [3] and Main Group elements [4].

It is noteworthy that the Fischer–Hafner reducing system affords different products depending on the metal. Typical transition *d* metals [5] and vanadium [6] give bis-arene complexes of general formula [(η^6-arene)$_2$M]$^{n+}$, $n = 0$–2. On the other hand, early and late transition elements, namely titanium [7], palladium [8],

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* Dedicated to Professor P.L. Pauson in recognition of his contributions to organometallic chemistry.

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copper [9] and silver [10], produce mono-arene complexes with bridging tetrahaloaluminato groups.

The work-up procedure is also important in establishing the nature of the reaction products. Thus, it is known [11] that the treatment with water of the primary reaction product arising from the $MCl_n/Al/AlCl_3$/hexamethylbenzene (HMB), M = Ti, Zr, $n = 4$; M = Nb, Ta, $n = 5$) system gives η^6-HMB trinuclear clusters of general formula $[M_3(\eta^6\text{-HMB})_3Cl_6]^{n+}$ (M = Ti, Zr, Nb, Ta; X = Cl, Br; $n = 1, 2$). In this connection, we have recently shown [11d] that the primary product of the reaction between $ZrCl_4$ and $Al/AlCl_3$/HMB is $Zr(\eta^6\text{-HMB})(AlCl_4)_2$, which undergoes oxidation to $[Zr_3(\eta^6\text{-HMB})_3Cl_6]^+$ upon treatment with water.

In this paper we report the identification of the primary reaction products in the $NbX_5/Al/AlX_3$/arene system and the first synthesis of a niobium(0) bis-arene complex by conventional methods (not involving the use of the metal vapour technique) and some new chemistry of $Nb(1,3,5\text{-trimethylbenzene})_2$, $Nb(mes)_2$. A preliminary account of this work has appeared [12].

Experimental

Unless otherwise stated, all operations were carried out under purified argon. The reaction vessels were oven-dried before use. Solvents were dried by conventional methods.

Infrared spectra were recorded with a Perkin–Elmer Model 283 instrument equipped with grating for solutions or for Nujol mulls of the compounds prepared with rigorous exclusion of moisture and oxygen. Gaschromatographic analyses were performed with a Dani Model 8400 instrument equipped with a Carbowax 20 M column.

Niobium pentachloride, $NbCl_5$ (Fluka), aluminium trichloride, $AlCl_3$ (Carlo Erba), and aluminium tribromide, $AlBr_3$ (Fluka), were commercial products and were sublimed in vacuo prior to use. Niobium pentabromide, $NbBr_5$, was prepared from $NbCl_5$ and isopropyl bromide [13]. *N,N'*-Dimethyl-4-4'-dipyridylium tetraphenylborate, methylviologen [14] tetraphenylborate, $mv(BPh_4)_2$, was prepared by reaction of $[mv]I_2$ [15] and $NaBPh_4$ in water. Ferricinium tetraphenylborate, $FeCp_2[BPh_4]$ [16], vanadium hexacarbonyl, $V(CO)_6$ [17], vanadium bis(1,3,5-trimethylbenzene), $V(mes)_2$ [6b], and decamethylcobaltocene, $CoCp^\star_2$ [18] were prepared by published methods.

X-ray diffractometric experiments on $Nb_2(\eta^6\text{-HMB})_2Br_4$ and $[Nb(mes)_2(CO)]BPh_4$

Single crystals of $Nb_2(\eta^6\text{-HMB})_2Br_4$ and $[Nb(mes)_2(CO)]BPh_4$ were obtained by recrystallization from THF and a THF/diethyl ether mixture, respectively. The X-ray data collection was performed on crystals sealed in 0.3 mm capillary tubes and mounted on a Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo-K_α radiation. All the calculations were carried out on a MicroVAX II computer using the SHELXS [19] and VAXSDP [20] structure determination program packages.

Crystal data and a summary of data collection and structure refinement are listed in Table 1.

The niobium and the bromine atoms of the $Nb_2(\eta^6\text{-HMB})_2Br_4$ molecule were located by direct methods, the carbon atoms by difference Fourier syntheses. The

Table 1

Crystal data and summary of data collection and structure refinement for [Nb(mes)$_2$CO]BPh$_4$ and Nb$_2$(η^6-HMB)$_2$Br$_4$

Compound	Nb$_2$(η^6-HMB)$_2$Br$_4$	[Nb(mes)$_2$CO]BPh$_4$
Formula	$C_{24}H_{36}Br_4Nb_2$	$C_{43}H_{44}BNbO$
Formula weight (g/mol)	830.0	680.6
Space group	$I4_1/a$ (88) (origin choice 2)	$P2_1/c$ (14)
Cell constants		
a (Å)	25.564(4)	15.008(3)
b (Å)	25.564(4)	10.963(2)
c (Å)	8.826(3)	21.680(3)
α (degrees)	90	90
β (degrees)	90	98.62(3)
γ (degrees)	90	90
Cell volume (Å^3)	5768(4)	3527(2)
Z	8	4
D_{calc} (g cm^{-3})	1.91	1.28
Crystal size (mm)	0.5 × 0.25 × 0.25	0.25 × 0.3 × 0.15
μ(Mo-K_α) (cm^{-1})	62.6	3.5
F(000)	3216	1424
Radiation (λ, Å)	Mo-K_α (0.71069)	Mo-K_α (0.71069)
Temperature (K)	213	273
Data collection range, 2θ (degrees)	10–52	10–52
Scan technique	ω	ω
No. of measured reflections	2255	5974
No. of unique reflections having $F_o^2 > 3\sigma(F_o^2)$	1040	3072
No. of refined parameters	136	415
Max./Min. absorption correction	1.37/0.84	1.22/0.77
R	0.046	0.046
R_w	0.054	0.050
Largest peak (e/Å^3)	0.86	0.41

Table 2

Fractional atomic coordinates for Nb$_2$(η^6-HMB)$_2$Br$_4$

Atom	x	y	z	B (Å^2) [a]
Nb	0.54480(5)	0.52440(5)	0.0513(2)	2.01(3)
Br1	0.54303(7)	0.47555(7)	−0.2163(2)	3.25(4)
Br2	0.47358(7)	0.57731(6)	−0.1114(2)	3.26(4)
C1	0.6364(6)	0.5329(7)	0.011(2)	3.2(4)
C2	0.6066(6)	0.5797(6)	−0.024(2)	2.8(4)
C3	0.5841(6)	0.6072(6)	0.100(2)	3.1(4)
C4	0.5788(6)	0.5840(6)	0.238(2)	2.6(4)
C5	0.5945(6)	0.5278(6)	0.254(2)	2.5(4)
C6	0.6298(6)	0.5069(6)	0.148(2)	2.0(3)
C11	0.6740(7)	0.5115(8)	−0.114(2)	4.2(4)
C22	0.6126(7)	0.6068(8)	−0.179(2)	4.0(4)
C33	0.5684(8)	0.6648(7)	0.076(2)	4.3(5)
C44	0.5567(7)	0.6117(7)	0.376(2)	3.7(4)
C55	0.5888(8)	0.5015(8)	0.411(2)	4.5(5)
C66	0.6602(7)	0.4577(7)	0.187(2)	4.2(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3 \cdot (a^2 \cdot B_{1,1} + b^2 \cdot B_{2,2} + c^2 \cdot B_{3,3})$.

Table 3

Fractional atomic coordinates for $[Nb(mes)_2CO]BPh_4$ (estimated standard deviations in parentheses refer to the least significant digit)

Atom	x	y	z	B (Å^2) [a]	Atom	x	y	z	B (Å^2) [a]
Nb	0.71058(4)	0.18935(5)	0.09334(3)	3.102(9)	C32	0.1214(4)	0.2741(6)	0.0164(3)	4.0(1)
O1	0.5048(6)	0.095(1)	0.0678(8)	22.5(5)	C33	0.1075(5)	0.2820(6)	−0.0479(3)	4.6(2)
C1	0.5790(6)	0.125(1)	0.0760(8)	14.5(5)	C34	0.1775(5)	0.3184(7)	−0.0789(3)	4.7(2)
C11	0.7075(5)	−0.0249(6)	0.1220(3)	4.3(1)	C35	0.2590(5)	0.3478(6)	−0.0444(3)	4.1(2)
C12	0.7593(4)	−0.0130(6)	0.0737(3)	3.8(1)	C36	0.2720(4)	0.3390(6)	0.0201(3)	3.9(1)
C13	0.8357(4)	0.0626(6)	0.0814(3)	3.6(1)	C41	0.2253(4)	0.1304(6)	0.1351(3)	3.7(1)
C14	0.8561(4)	0.1271(6)	0.1368(3)	4.1(1)	C42	0.3008(5)	0.0666(7)	0.1210(3)	5.1(2)
C15	0.8009(5)	0.1213(6)	0.1847(3)	4.2(2)	C43	0.3040(6)	−0.0607(7)	0.1183(3)	6.1(2)
C16	0.7269(5)	0.0441(6)	0.1759(3)	4.8(2)	C44	0.2302(6)	−0.1271(7)	0.1299(3)	6.3(2)
C17	0.6310(6)	−0.1186(8)	0.1162(4)	7.3(2)	C45	0.1543(6)	−0.0699(7)	0.1420(3)	5.4(2)
C18	0.9004(5)	0.0564(7)	0.0341(3)	5.0(2)	C46	0.1527(5)	0.0580(6)	0.1444(3)	4.3(2)
C19	0.8279(6)	0.1843(9)	0.2474(3)	6.8(2)	C51	0.1382(4)	0.3350(6)	0.1631(3)	3.5(1)
C21	0.6173(4)	0.3375(6)	0.0310(3)	4.3(2)	C52	0.1312(4)	0.3018(7)	0.2252(3)	4.7(2)
C22	0.6985(4)	0.3238(6)	0.0069(3)	4.0(1)	C53	0.0682(5)	0.3542(8)	0.2578(3)	5.6(2)
C23	0.7802(4)	0.3496(5)	0.0440(3)	3.5(1)	C54	0.0080(5)	0.4392(8)	0.2306(3)	5.3(2)
C24	0.7801(4)	0.3802(6)	0.1068(3)	3.4(1)	C55	0.0134(4)	0.4755(7)	0.1706(3)	4.7(2)
C25	0.7007(4)	0.3859(6)	0.1349(3)	3.6(1)	C56	0.0769(4)	0.4225(7)	0.1379(3)	4.0(1)
C26	0.6192(4)	0.3674(6)	0.0945(3)	4.4(2)	C61	0.3106(4)	0.3491(6)	0.1624(3)	3.7(1)
C27	0.5291(5)	0.3273(9)	−0.0132(4)	7.3(2)	C62	0.3786(4)	0.2966(8)	0.2045(3)	5.1(2)
C28	0.8649(5)	0.3620(7)	0.0153(3)	4.8(2)	C63	0.4525(5)	0.3649(9)	0.2335(4)	6.5(2)
C29	0.7009(5)	0.4403(8)	0.1993(3)	5.7(2)	C64	0.4598(5)	0.4873(9)	0.2214(4)	6.8(2)
C31	0.2038(4)	0.3026(6)	0.0534(3)	3.4(1)	C65	0.3932(5)	0.5422(8)	0.1803(4)	6.0(2)
					C66	0.3206(5)	0.4748(7)	0.1523(3)	4.8(2)
					B	0.2186(5)	0.2787(7)	0.1296(3)	3.4(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3 \cdot (a^2 \cdot B_{1,1} + b^2 \cdot B_{2,2} + c^2 \cdot B_{3,3} + ac \cdot (\cos\beta) \cdot B_{1,3})$.

fractional atomic coordinates for $Nb_2(\eta^6\text{-HMB})_2Br_4$ are shown in Table 2. There is half molecule in the asymmetric unit and the other atoms are produced by an inversion centre. All non-hydrogen atoms were refined anisotropically to $R = 0.046$ and $R_w = 0.054$.

In the case of $[Nb(mes)_2CO]BPh_4$, the structure was solved by the heavy-atom technique. Several Fourier maps revealed all the non-hydrogen atoms. Hydrogen atoms were placed in their calculated positions. The fractional atomic coordinates for $[Nb(mes)_2CO]BPh_4$ are reported in Table 3. Full-matrix least-squares refinements with anisotropic thermal parameters for all non-hydrogen atoms were carried out and the refinements converged to $R = 0.046$ and $R_w = 0.050$.

For both structures, absorption correction was applied to the unmerged data set with the program DIFABS [21].

Preparation of $Nb(\eta^6\text{-HMB})(AlX_4)_2$ *(X = Cl, Br)*

A suspension of aluminium powder (0.32 g, 11.9 mmol) and HMB (1.95 g, 12.0 mmol) in benzene (50 ml) was treated with $AlBr_3$ (1.15 g, 4.3 mmol) and $NbBr_5$ (1.97 g, 4.0 mmol). After 12 h stirring at room temperature and refluxing for 2 h, the mixture consisted of two liquid layers, the lower having a deep-brown colour. The mixture was filtered and the filtrate, after partial evaporation of the solvent *in vacuo* at room temperature, was treated with n-heptane (50 ml). The brown solid which formed was filtered off, dried *in vacuo* at room temperature, and transferred into a sublimation apparatus where it was heated at 50 °C/0.05 mmHg for 2 h. The residue was identified as $Nb(\eta^6\text{-HMB})(AlBr_4)_2$ (0.875 g, 23%). Anal. Found: Al, 5.9, Br, 67.1, Nb, 10.2. $C_{12}H_{18}Al_2Br_8Nb$ calc.: Al, 5.7; Br, 67.4, Nb, 9.8%.

The tetrachloroaluminato derivative, $Nb(\eta^6\text{-HMB})(AlCl_4)_2$, was isolated in 20% yield by the same procedure except for the reflux period, which was increased to 20 h. Anal. Found: Al, 8.9, Cl, 46.8, Nb, 15.3. $C_{12}H_{18}Al_2Cl_8Nb$ calc.: Al, 9.1; Cl, 47.8, Nb, 15.7%.

Preparation of $Nb_2(\eta^6\text{-HMB})_2Br_4$

(a) From $Nb(\eta^6\text{-HMB})(AlBr_4)_2$. $Nb(\eta^6\text{-HMB})(AlBr_4)_2$ (0.89 g, 0.94 mmol) was dissolved in THF (50 ml) at room temperature. After filtration to remove the insoluble solid, the brown clear filtrate was cooled at about −30 °C for some days. The black-brown crystals which separated out (0.12 g, 31% yield) were isolated, briefly dried *in vacuo* at room temperature, and identified as $Nb_2(\eta^6\text{-HMB})_2Br_4$. Anal. Found: C, 34.9, H, 4.4. $C_{24}H_{36}Br_4Nb_2$ calc.: C, 34.7, H, 4.4%.

(b) from $NbBr_5/Al/AlBr_3/HMB$. A suspension of aluminium powder (0.43 g, 15.9 mmol) and HMB (1.78 g, 11.0 mmol) in benzene (50 ml) was treated with $AlBr_3$ (1.57 g, 5.9 mmol) and $NbBr_5$ (2.69 g; 5.5 mmol). After 8 h of reflux, the mixture was filtered hot, cooled down to ca. 0 °C, and treated dropwise with THF (50 ml). After stirring at room temperature for 12 h, the resulting brown solid was filtered off, and dried *in vacuo* at room temperature to afford 0.55 g (24% yield) of $Nb_2(\eta^6\text{-HMB})_2Br_4 \cdot 0.25THF$ in the form of oxygen and moisture-sensitive brown microcrystalline solid. Anal. Found: Br, 36.0, Nb, 21.4. $C_{25}H_{38}Br_4Nb_2O_{0.25}$ calc.: Br, 37.7, Nb, 21.9%.

Treatment of η^6*-HMB niobium(II) complexes with water*

(a) $Nb(\eta^6\text{-HMB})(AlCl_4)_2$/water at room temperature. $Nb(\eta^6\text{-HMB})(AlCl_4)_2$ (0.173 g, 0.29 mmol) was treated with water (9 ml) in a gas-volumetric apparatus at

24.8 °C. Vigorous evolution of gas (identified as H_2 by gas-chromatography) was observed upon mixing the reagents. The H_2/Nb molar ratio was 1.24.

(b) $Nb(\eta^6\text{-HMB})(AlBr_4)_2$/water at room temperature. In a similar procedure $Nb(\eta^6\text{-HMB})(AlBr_4)_2$ (0.56 g, 0.59 mmol) evolved H_2 upon contact with water (9 ml) up to a H_2/Nb molar ratio of 1.05.

(c) $Nb(\eta^6\text{-HMB})(AlBr_4)_2$/water at ca. −40 °C. A mixture of water (30 ml) and CH_2Cl_2 (50 ml) was cooled to ca. −40 °C and treated with $Nb(\eta^6\text{-HMB})(AlBr_4)_2$ (3.5 g, 3.7 mmol). Gas was evolved. The mixture was allowed to warm to room temperature, the brown organic layer was separated from the aqueous one, and the latter washed with CH_2Cl_2 (2 × 20 ml). The organic extracts were combined, dried over Na_2SO_4, and filtered. The brown solution was evaporated to dryness to give 0.79 g (48.5% yield) of analytically (Nb, Br) pure $[Nb_3(\eta^6\text{-HMB})_3Br_6]Br$ [11b].

(d) $Nb_2(\eta^6\text{-HMB})_2Br_4$/water at room temperature. In the procedure described under (a), $Nb_2(\eta^6\text{-HMB})_2Br_4$ (0.344 g, 0.41 mmol) evolved H_2 upon contact with water (8.1 ml) up to a H_2/Nb molar ratio of 0.45.

(e) $Nb_2(\eta^6\text{-HMB})_2Br_4$/aqueous HBr at room temperature. In the procedure described under (a), $Nb_2(\eta^6\text{-HMB})_2Br_4$ (0.46 g, 0.55 mmol) evolved H_2 upon contact with a hydrobromic solution (9 mmol of concentrated HBr solution in 9 ml of H_2O) up to a H_2/Nb molar ratio of 0.99.

Preparation of $Nb(mes)_2$

A suspension of Al powder (5.7 g, 211.3 mmol), $AlCl_3$ (4.69 g, 35.2 mmol) and $NbCl_5$ (9.45 g, 35.0 mmol) in mesitylene (40 ml) was stirred at room temperature for 15 h and at 120–130 °C for 4 h. The reaction mixture consisted of two brown liquid layers. With *vigorous* mechanical stirring, DME (50 ml) was slowly added (30 min) to the mixture cooled to −15 °C. After the addition was complete, n-heptane (50 ml) was added and the deep-red suspension was stirred at room temperature for 15 h. After filtration to remove insoluble materials, the red filtrate was evaporated at 30–40 °C/10^{-2} mmHg, and the residue was extracted with n-heptane (50 ml) and the extract filtered. The filtrate was dried *in vacuo* at room temperature and the residue extracted with n-heptane (5 ml). The extract was cooled to −78 °C, $Nb(mes)_2$ (5.03 g, 43% yield) was obtained as a dark brown microcrystalline compounds. The compound, which gave the correct elemental (C,H,Nb) analysis, is readily oxidized by air and dissolves in the common organic ethereal and hydrocarbon solvents. The IR spectrum (Nujol and polychlorotrifluoroethylene [22*] mulls) with bands at 3020m, 2960m, 2920m-s, 2870m, 1610m-s, 1470m-w, 1380m, 1260w, 1140w, 1020m-s, 985m, 810m-s and 440s cm^{-1}, is very similar to that of $V(mes)_2$.

Reaction of $AlCl_3$ with 1,2-dimethoxyethane (DME)

1,2-Dimethoxyethane (30 ml), cooled at about −30 °C, was treated with $AlCl_3$ (3.89 g, 29.2 mmol), and colourless solid was formed. After 15 h stirring at room temperature, the solid was filtered off, washed with 1,2-dimethoxyethane (2 × 5 ml), and dried *in vacuo* to give 5.93 g (91% yield) of $AlCl_3(DME)$ in the form of a moisture-sensitive, microcrystalline solid insoluble in aliphatic hydrocarbons but

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[*] Reference number with an asterisk indicates a note in the list of references

slightly soluble in aromatic hydrocarbons and ethers. Anal. Found: Al, 12.2; Cl, 47.3. $C_4H_{10}AlCl_3O_2$ calc.: Al, 12.1; Cl, 47.6%.

Reaction of Nb(mes)$_2$ with CO: synthesis of [Nb(mes)$_2$(CO)][Nb(CO)$_6$]

A solution of Nb(mes)$_2$ (1.02 g, 3.1 mmol) in n-heptane (100 ml) was placed in a glass autoclave (Büchi, Uster, CH) and stirred for 24 h under CO at a pressure of 5 atm. The bright-green solid formed was filtered off, dried *in vacuo* at room temperature, and identified as [Nb(mes)$_2$(CO)][Nb(CO)$_6$] (0.64 g, 67% yield). Anal. Found: CO, 31.1; Nb, 28.9. $C_{25}H_{24}Nb_2O_7$ calc.: CO, 31.5; Nb, 29.9%. IR spectrum (THF): 1990m, 1889m-sh, 1859vs cm^{-1}.

Attempted reaction of V(mes)$_2$ with CO

A solution of V(mes)$_2$ (0.38 g, 1.3 mmol) in n-heptane (100 ml) was placed in a glass autoclave and stirred for 48 h under CO at a pressure of 5 atm. No solid was formed and 95% of the V(mes)$_2$ was recovered.

Reaction of Nb(mes)$_2$ with V(CO)$_6$: synthesis of [Nb(mes)$_2$(CO)][V(CO)$_6$]

A solution of V(CO)$_6$ (0.32 g, 1.5 mmol) in n-heptane (50 ml) was treated under an atmosphere of carbon monoxide with a solution of Nb(mes)$_2$ (0.48 g, 1.4 mmol) in n-heptane (50 ml). Immediate reaction with gas absorption and precipitation of a bright-green solid was observed. The solid was filtered off, washed with n-heptane (2 × 10 ml), and dried *in vacuo* at room temperature to give 0.53 g (63% yield) of [Nb(mes)$_2$(CO)][V(CO)$_6$] as a bright-green microcrystalline solid, which was recrystallized from THF/Et$_2$O to give dark-green crystals. Anal. Found: CO, 33.5, Nb, 15.8, V, 8.7. $C_{25}H_{24}NbO_7V$ calc.: CO, 33.8; Nb, 16.0, V, 8.8%. IR spectrum: THF: 1990m, 1891m-sh, 1856vs cm^{-1}.

When the same reaction was repeated in a gas-volumetric apparatus at 19.9 °C absorption of CO corresponding to a CO/Nb molar ratio of 1.04 was observed.

Reaction of V(mes)$_2$ with V(CO)$_6$ under CO

A solution of V(CO)$_6$ (0.294 g, 1.34 mmol) in n-heptane (50 ml) was treated with V(mes)$_2$ (0.39 g, 1.34 mmol) under a CO atmosphere. Immediate reaction occurred without gas absorption, but with precipitation of a brown solid, which was filtered off, washed with n-heptane (2 × 5 ml), and dried *in vacuo* to give 0.59 g (86% yield) of analytically (CO) pure [V(mes)$_2$][V(CO)$_6$] [6b].

Reaction of Nb(mes)$_2$ with mv(BPh$_4$)$_2$

(a) Under CO. Synthesis of [Nb(mes)$_2$(CO)]BPh$_4$. A solution of Nb(mes)$_2$ (0.392 g, 1.2 mmol) in THF (50 ml) was treated at 19.9 °C with mv(BPh$_4$)$_2$ (0.99 g, 1.2 mmol) under a CO atmosphere in a gas-volumetric apparatus. The immediate formation of a violet solid suspended in a green solution was accompanied by CO absorption (CO/Nb molar ratio 0.99 in about 3 min). The suspension was filtered and the filtrate was reduced in volume to about 10 ml *in vacuo* at room temperature and then kept at about −30 °C for some days, to give 0.10 g of dark-green crystals. Another crop of crystals (0.61 g, 89% of total yield) was obtained by addition of n-heptane to the solution followed by cooling at −30 °C for some hours. The compound was identified as [Nb(mes)$_2$(CO)]BPh$_4$. Anal. Found: C, 75.5, H, 6.0. $C_{43}H_{44}BNbO$ calc.: C, 75.9, H, 6.5%. IR spectrum: THF: 1987 cm^{-1} (1942 cm^{-1}

for $Nb(mes)_2{}^{13}CO^+$). ^{1}H-NMR spectrum (THF-d_8, values in ppm referred to TMS as internal standard (multiplicity)): 7.28–6.78 (26H, m); 2.11 (18H, s).

(b) Under dinitrogen: synthesis of $[Nb(mes)_2(THF)]BPh_4$. A solution of $Nb(mes)_2$ (0.4 g, 1.2 mmol) in THF (20 ml) was treated at 19.9 °C with $mv(BPh_4)_2$ (1.0 g, 1.2 mmol) under a dinitrogen atmosphere in a gasvolumetric apparatus. No gas uptake was observed and a violet solid in a brown solution was obtained. After filtration, the solution was concentrated up to 5 ml *in vacuo* at room temperature and n-heptane (25 ml) was added. Immediate formation of a brown solid took place and this was filtered off and dried *in vacuo* at room temperature to give 0.51 g (58.6% yield) of $[Nb(mes)_2(THF)]BPh_4$ as a solid extremely sensitive to moisture. No reproducible elemental analyses for this compound were obtained. IR spectrum (Nujol mull): 3060w, 3040w, 1580w, 1430w, 1030s, 860s, 740s, 700vs and 610s cm^{-1}. Upon exposure to air, the absorptions at 1030 and 860 cm^{-1} disappeared and a broad absorption in the range 3500–3100 cm^{-1} became evident. ^{1}H-NMR spectrum (THF-d_8, values in ppm referred to TMS as internal standard (multiplicity)): 7.29–6.79 (26H, m); 3.61 (4H, t); 2.21 (18H, s); 1.76 (4H, t).

Reaction of $Nb(mes)_2$ with $[FeCp_2]BPh_4$

A suspension of $[FeCp_2]BPh_4$ (0.68 g, 1.35 mmol) in toluene (30 ml) was treated with $Nb(mes)_2$ (0.47 g, 1.41 mmol). After 24 h stirring at room temperature, a brown solid in a orange solution was obtained. The solid was filtered off and dried *in vacuo* to give 0.72 g (82% yield) of $[Nb(mes)_2]BPh_4$ as a pyrophoric brown solid. This solid was found to absorb CO in toluene at 22.4 °C up to a CO/Nb molar ratio of 0.92 to give $[Nb(mes)_2(CO)]BPh_4$, identified from its IR spectrum in THF solution.

From the orange filtrate, after evaporation to dryness, $FeCp_2$ was obtained by sublimation *in vacuo* (77% yield).

Reaction of $Nb(mes)_2$ with $CoCp^\star{}_2$

A solution of $CoCp^\star{}_2$ (0.46 g, 1.4 mmol) in toluene (50 ml) was treated under argon with $Nb(mes)_2$ (0.45 g, 1.35 mmol). After 24 h stirring at room temperature the system was unchanged. After evacuation and introduction of CO, an orange solid slowly (7 days) formed. This was filtered off, washed with toluene (2 × 5 ml), and dried *in vacuo* at room temperature to give 0.6 g (75% yield) of $CoCp^\star{}_2[Nb(CO)_6]$ as an orange microcrystalline solid, stable in air for short periods of time. Anal. Found: C, 51.4, H, 5.2. $C_{26}H_{30}CoNbO_6$ calc.: C, 52.9, H, 5.1%. IR spectrum (Nujol and polychlorotrifluoroethylene mulls): 2960w, 2920w, 2880w, 1845vs, 1580w, 1375m, 1360w, 1020m-s, 570s, 440m and 380m-w cm^{-1}. IR spectrum (THF): 1885m-sh and 1860vs cm^{-1}.

Reaction of $[Nb(mes)_2(CO)]BPh_4$ with $CoCp^\star{}_2$

$[Nb(mes)_2(CO)]BPh_4$ (0.3 g, 0.44 mmol) in THF (30 ml) was treated at 21.3 °C with $CoCp^\star{}_2$ (0.15 g, 0.46 mmol) under argon in a gas-volumetric apparatus. Immediate evolution of gas up to a CO/Nb molar ratio of 0.97 was observed and a yellow solid in a red solution was formed. After filtration and washing of the solid with THF (2 × 10 ml) the solution was evaporated to dryness *in vacuo* at room temperature and the residue was treated with n-heptane then filtered. The yellow solid (0.26 g, 91% yield) was identified as $[CoCp^\star{}_2]BPh_4$ from its IR spectrum as a

Nujol mull. The filtrate was evaporated to small volume and cooled to about −78 °C to give red crystals of $Nb(mes)_2$ (0.12 g, 82% yield).

Reaction of $Nb(mes)_2$ with CO_2 in the presence of $[Nb(mes)_2(THF)]BPh_4$

A solution of $Nb(mes)_2$ (0.6 g, 1.8 mmol) in THF (50 ml) was treated with $mv(BPh_4)_2$ (0.74, 0.9 mmol) under argon. After 1 h stirring at room temperature, the suspension was filtered and the solution exposed to CO_2 at atmospheric pressure. The formation of a black solid in a green solution was observed within 1 h. The black pyrophoric solid (0.25 g) was filtered off and the filtrate was evaporated to dryness. The green solid (0.545 g; 45% yield) was identified as $[Nb(mes)_2(CO)]BPh_4$ from its spectroscopic (IR) and analytical data (CO, Nb).

When a solution of $Nb(mes)_2$ (1.34 g, 4.0 mmol) in n-heptane (50 ml) was treated with CO_2 (5 atm) pressure in a 250 ml glass autoclave at room temperature a black solid in a colourless solvent was present after 15 h. Carbon monoxide was present in the gas phase (as indicated by gas chromatography). The solid recovered by filtration consisted of a pyrophoric material of unidentified composition. This reaction was repeated several times, black solids of unreproducible elemental analyses being obtained.

Results and discussion

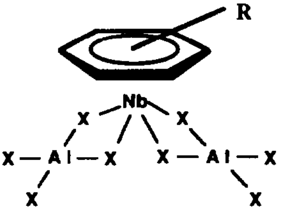
The reduction of NbX_5 (X = Cl, Br) by aluminium powder in benzene as solvent in the presence of AlX_3/HMB affords the tetrahaloaluminato complexes $Nb(\eta^6\text{-HMB})(AlX_4)_2$ in 20–25% yields, according to equation 1. The low yields are mainly

$$NbX_5 + Al + AlX_3 + HMB \rightarrow Nb(\eta^6\text{-HMB})(AlX_4)_2 \qquad (1)$$

$$(X = Cl, Br)$$

due to the low solubility of the η^6-HMB complexes in the aromatic hydrocarbon.

The tetrahaloaluminato derivatives of niobium(II) are dark microcrystalline solids, sensitive to oxygen and moisture, and reactive towards Lewis bases such as acetone, THF and DME (*vide infra*). Single crystals of the products of equation 1 could not be obtained and so their structure could not be established conclusively. However, it is believed that the tetrahaloaluminato complexes have the atom connectivity shown below, i.e., with a symmetrically bonded arene ligand and bridging halides, similar to the bonding situation already found [7] for the corresponding titanium(II) complexes:



Support for this suggestion comes from the observation that in the case of the HMB-bromo derivative decomplexation of the $AlBr_3$ moiety occurred on treatment

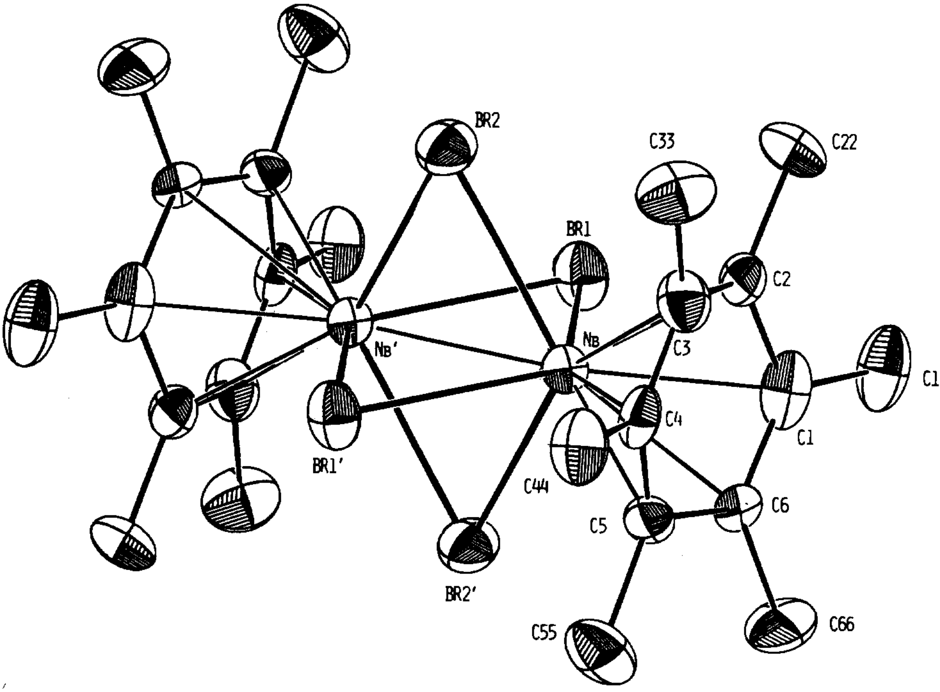


Fig. 1. Molecular structure of $Nb_2(\eta^6\text{-HMB})_2Br_4$ (thermal ellipsoids are drawn at 50% probability level).

with THF (equation 2) and the $Nb_2(\eta^6\text{-HMB})_2Br_4$ compound was isolated in ca. 30% yield.

$$2\ Nb(\eta^6\text{-HMB})(AlBr_4)_2 + 4x\text{THF} \rightarrow Nb_2(\eta^6\text{-HMB})_2Br_4 + 4\ AlBr_3(\text{THF})_x \quad (2)$$

The Nb^{II} derivative, $Nb_2(\eta^6\text{-HMB})_2Br_4$, is a black-brown crystalline solid sensitive to oxygen and moisture which can be recrystallized from THF at low temperature.

The dimeric niobium(II) derivative was studied by X-ray diffractometry at low temperature (213 K) and found to have the centrosymmetric molecular structure shown in Fig. 1, i.e., with four bridging bromides and one HMB ligand per niobium atom. Bond distances and angles are listed in Tables 4 and 5.

Table 4

Selected bond distances (Å) in $Nb_2(\eta^6\text{-HMB})_2Br_4$ (estimated standard deviations in parentheses refer to the least significant digit. Dashed atoms $= 1-x,\ 1-y,\ -z$).

Nb'-Nb	2.761(2)	Nb-C5	2.19(2)	C3-C4	1.37(2)
Nb-Br1	2.671(2)	Nb-C6	2.38(1)	C3-C33	1.54(2)
Nb-Br1'	2.676(2)	C1-C2	1.45(2)	C4-C5	1.50(2)
Nb-Br2	2.684(2)	C1-C6	1.39(2)	C4-C44	1.52(3)
Nb-Br2'	2.695(2)	C1-C11	1.56(3)	C5-C6	1.41(2)
Nb-C1	2.38(2)	C2-C3	1.42(2)	C5-C55	1.55(2)
Nb-C2	2.22(2)	C2-C22	1.53(3)	C6-C66	1.52(2)
Nb-C3	2.38(2)				
Nb-C4	2.41(2)				

Table 5

Selected bond angles (degrees) in $Nb_2(\eta^6\text{-HMB})_2Br_4$ (estimated standard deviations in parentheses refer to the least significant digit. Dashed atoms $= 1-x,\ 1-y,\ -z$)

Nb'-Nb-Br1	59.00(6)	Br2-Nb-C2	90.0(4)	C2-C1-C6	121(1)
Nb'-Nb-Br1'	58.84(6)	Br2-Nb-C3	86.3(5)	C2-C1-C11	117(2)
Nb'-Nb-Br2	59.31(5)	Br2-Nb-C4	107.0(4)	C6-C1-C11	121(1)
Nb'-Nb-Br2'	58.93(5)	Br2-Nb-C5	143.9(4)	C1-C2-C3	117(2)
Nb'-Nb-C1	144.1(4)	Br2-Nb-C6	155.1(4)	C1-C2-C22	121(1)
Nb'-Nb-C2	141.1(5)	Br2'-Nb-C1	106.8(4)	C3-C2-C22	121(1)
Nb'-Nb-C3	144.2(4)	Br2'-Nb-C2	142.8(5)	C2-C3-C4	121(1)
Nb'-Nb-C4	144.1(4)	Br2'-Nb-C3	153.6(4)	C2-C3-C33	118(2)
Nb'-Nb-C5	139.9(4)	Br2'-Nb-C4	122.6(4)	C4-C3-C33	121(2)
Nb'-Nb-C6	142.3(4)	Br2'-Nb-C5	88.8(4)	C3-C4-C5	118(1)
Br1-Nb-Br1'	117.84(7)	Br2'-Nb-C6	84.7(4)	C3-C4-C44	124(1)
Br1-Nb-Br2	75.61(7)	C1-Nb-C2	36.6(6)	C5-C4-C44	118(1)
Br1-Nb-Br2'	73.75(7)	C1-Nb-C3	62.1(6)	C4-C5-C6	118(1)
Br1-Nb-C1	85.8(4)	C1-Nb-C4	71.9(5)	C4-C5-C55	118(1)
Br1-Nb-C2	92.5(5)	C1-Nb-C5	63.1(6)	C6-C5-C55	119(1)
Br1-Nb-C3	125.6(4)	C1-Nb-C6	33.9(5)	C1-C6-C5	118(1)
Br1-Nb-C4	155.1(4)	C2-Nb-C3	35.8(6)	C1-C6-C66	122(1)
Br1-Nb-C5	138.4(4)	C2-Nb-C4	63.1(6)	C5-C6-C66	119(1)
Br1-Nb-C6	104.1(4)	C2-Nb-C5	78.9(6)		
Br1'-Nb-Br2	73.84(7)	C2-Nb-C6	65.0(5)		
Br1'-Nb-Br2'	75.35(7)	C3-Nb-C4	33.1(6)		
Br1'-Nb-C1	155.1(4)	C3-Nb-C5	64.8(7)		
Br1'-Nb-C2	139.4(4)	C3-Nb-C6	73.6(5)		
Br1'-Nb-C3	104.8(4)	C4-Nb-C5	37.7(6)		
Br1'-Nb-C4	86.1(4)	C4-Nb-C6	63.0(6)		
Br1'-Nb-C5	92.4(5)	C5-Nb-C6	35.6(5)		
Br1'-Nb-C6	124.9(4)	Nb-Br1-Nb	62.16(6)		
Br2'-Nb-Br2	118.25(7)	Nb'-Br2-Nb	61.75(6)		
Br2-Nb-C1	122.8(4)				

The HMB rings (see the lateral view of the molecule in Fig. 2) are not planar (the dihedral angle between the C2-C1-C6-C5 plane and the C2-C3-C4-C5 plane is 19.9(2)°). This folding results in a "boat" structure in which two carbon atoms (C2 and C5) make a closer approach to the niobium atom (Nb-C2 = 2.22(2) Å and Nb-C5 = 2.19(2) Å) than the other carbon atoms (C1,C3,C4 and C6) of the ring (Nb-C1 = Nb-C3 = Nb-C6 = 2.38(2) Å and Nb-C4 = 2.41 Å). This situation is frequently encountered in other structurally characterized "bent arenes" [23]. The mean plane of the aromatic ring is 1.85 Å from niobium.

Another peculiarity of the molecule is the slight asymmetry of the bromide bridge. Although two of the Nb-Br distances are very similar (Nb-Br1 = 2.671(2) Å and Nb-Br1' = 2.676(2) Å), the other two are significantly different, being 2.684(2) Å for Nb-Br2 and 2.695(2) for Nb-Br2'.

The distance between the two niobium atoms is 2.761(2) Å. A few dimeric niobium(II) complexes have been reported previously [24] and the values of the Nb-Nb distances vary from 2.632(1) Å in the $[Nb_2Cl_6(\mu\text{-}SC_4H_8)_2]^{2+}$ cation [24c] to 3.056(1) and 3.072(1) Å in $Cp_2Nb_2(CO)_4(\mu\text{-}Cl)_2$ and $Cp_2Nb_2(PhCCPh)_2(\mu\text{-}Cl)_2$, respectively [24b]. A Nb-Nb distance of 3.361(1) Å has been found [24d] in $Cp_2Nb_2(\text{butadiene})_2(\mu\text{-}Cl)_2$. The observed metal-metal distance in our dimeric

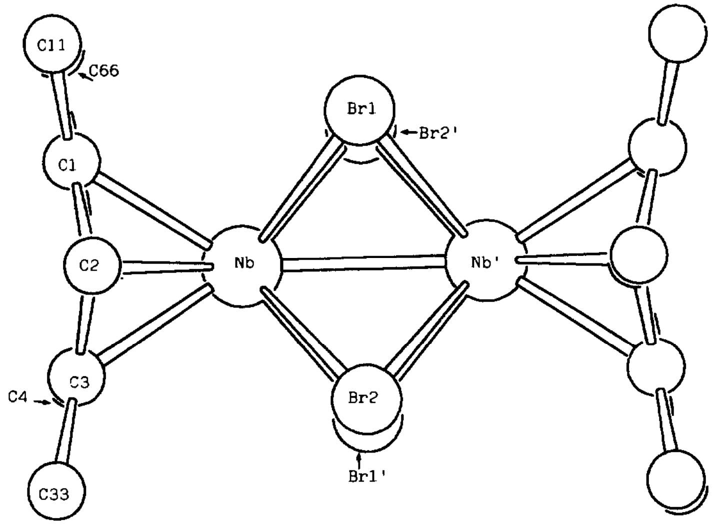
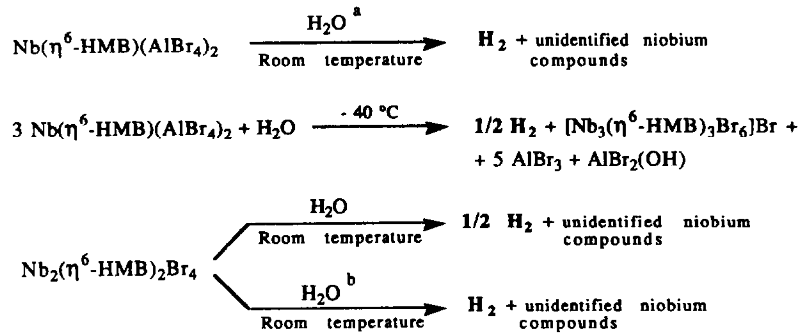


Fig. 2. A view of the $Nb_2(\eta^6\text{-HMB})_2Br_4$ molecule perpendicular to the Nb–Nb′ vector.

compound is not inconsistent with the presence of a single niobium-niobium bond, which is also in agreement with a total count of 18 valence electrons for the central metal atom.

In their pioneering work on the $NbCl_5/Al/AlCl_3$/HMB system, Fischer and Röhrscheid [11a] described a chloro-derivative of the same stoicheiometry as that of equation 2, obtained in low yields (9%) after treatment with water at 0 °C of the crude reaction mixture, the major component (26% yield) being the trinuclear compound $[Nb_3(\eta^6\text{-HMB})_3Cl_6]$ Cl.

Owing to the availability of the niobium(II) tetrabromoaluminato complex, $Nb(\eta^6\text{-HMB})(AlBr_4)_2$, and of the dimer $Nb_2(\eta^6\text{-HMB})_2Br_4$, the reaction of these compounds with water was investigated in some detail (Scheme 1). Both compounds evolve dihydrogen on treatment with water up to a H_2/Nb molar ratio of 1 for the aluminato derivative and up to a H_2/Nb molar ratio of 0.45 in the case of $Nb_2(\eta^6\text{-HMB})_2Br_4$. In the case of the bridged bromide complex, the H_2/Nb molar ratio was 0.99 when an aqueous solution of HBr at pH about zero was used instead of water. On the other hand, the low temperature (about −40 °C) treatment of



Scheme 1. [a] pH ca zero after decomposition of $Nb(\eta^6\text{-HMB})(AlBr_4)_2$. [b] pH ca zero by addition of hydrobromic acid.

$Nb(\eta^6\text{-HMB})(AlBr_4)_2$ with water afforded a 49% yield of $[Nb_3(\eta^6\text{-HMB})_3Br_6]Br$ [11b] (Scheme 1).

From the data presented here it is clear that the oxidation of the niobium(II) complexes brought about by water depends on both the concentration of H^+ in solution and the temperature: the low temperature treatment with water prevents extensive decomposition of the niobium(II) arene derivative. We can therefore conclude that the original reaction mixture obtained by Fischer and Röhrscheid contained the tetrachloroaluminato derivative of niobium(II), which underwent both partial $AlCl_3$ decomplexation to $Nb_2(\eta^6\text{-HMB})_2Cl_4$ and oxidation to the trinuclear Nb(II)-Nb(II)-Nb(III) complex in the presence of water. A similar situation was found [11d] for the $ZrCl_4/Al/AlCl_3$/HMB/water system.

In the case of the $NbCl_5/Al/AlCl_3$/1,3,5-trimethylbenzene system, the initial reaction product was not isolated, but the crude reaction mixture, still containing unreacted aluminium, was treated with tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) at temperatures as low as −15 °C. Under these conditions further reduction occurs, and $Nb(mes)_2$ was obtained in 30–50% yields (see equation 3) after recrystallization from n-pentane at −78°C. It was found that DME is

$$NbCl_5 \xrightarrow[\text{2) DME, } -15\,^\circ\text{C}]{\text{1) Al/AlCl}_3\text{/mes}} Nb(mes)_2 \qquad (3)$$

preferable to THF owing to the low solubility of the $AlCl_3$ adduct $AlCl_3(DME)$ [25*] which makes the separation of $Nb(mes)_2$ easier. This is the first synthesis of a zero-valent bis-arene complex of niobium not requiring the use of the vapour-metal technique.

The availability of a Nb^0 derivative in gram quantities allowed a study of its reactions, especially that with carbon monoxide, to be carried out. Although a silver-niobium mixed metal cluster of formula $Ag_3Nb_3(CO)_{12}(dmpe)_3$, dmpe = 1,2-bis(dimethylphosphino)ethane, has recently been described [26], no experimental evidence of stable binary carbonyl species of niobium(0) has been reported yet [27*]. It was therefore of interest to use $Nb(mes)_2$ as a possible starting material for the preparation of zerovalent niobium carbonyl derivatives by substitution reactions.

We found that a smooth reaction occurs between CO and $Nb(mes)_2$ at room temperature and atmospheric pressure, and more readily under higher pressures of CO. The reaction of equation 4, is formally similar to that observed [28] with $V(mes)_2$, except that the redox carbonylation of niobium(0) occurs more readily. In

$$2\,Nb(mes)_2 + 7\,CO \rightarrow [Nb(mes)_2CO][Nb(CO)_6] + 2\,mes \qquad (4)$$

comparative experiments carried out at room temperature and at 5 atm of CO pressure, the vanadium system is substantially unaffected by CO. The ionic $[V(mes)_2][V(CO)_6]$ can only be obtained by carbonylation of $V(mes)_2$ under more drastic conditions [28].

The different behaviour between $V(mes)_2$ and $Nb(mes)_2$ in their reactions with CO can be compared with the reductive carbonylation systems of vanadium and niobium, **A** and **B**, respectively, shown below. While high temperatures and pressures are required for reductive carbonylation of vanadium to $[V(CO)_6]^-$, $NbCl_5$ is

A: $VCl_3/Mg/Zn/pyridine/CO \rightarrow [V(CO)_6]^-$ [29]

B: $NbCl_5/Mg/Zn/pyridine/CO \rightarrow [Nb(CO)_6]^-$ [30]

converted into $[Nb(CO)_6]^-$ under much milder conditions (room temperature and atmospheric pressure). The systems **A** and **B** involve different metal substrates and therefore cannot be directly compared. Different rates may in fact be involved in the preliminary redox steps of the reaction. On the other hand, the results obtained with $M(mes)_2$ suggest that low-valent niobium has generally easier kinetic pathways for the access of carbon monoxide to its coordination sphere. This is a further example of the well-established [31] higher kinetic lability of the 4*d* transition metal systems compared with their 3*d* analogues.

The products of equation 4 are believed to be formed by gradual displacement of the arene ligand from the coordination sphere of niobium, followed by the electron transfer between a carbonyl-containing zerovalent niobium complex as electron acceptor and $Nb(mes)_2$ still present in solution. In view of the previously mentioned unavailability of the carbonyl derivative of niobium(0), this suggestion could not be directly validated. However, $V(CO)_6$ does in fact react with $Nb(mes)_2$ as expected, namely according to equation 5.

$$V(CO)_6 + Nb(mes)_2 + CO \rightarrow [Nb(mes)_2CO][V(CO)_6] \qquad (5)$$

The tendency to form $[Nb(mes)_2CO]$ $[V(CO)_6]$ is so high that the ionic derivative is formed even in the absence of CO (i.e. under argon), partial decomposition of $V(CO)_6$ being probably the source of carbon monoxide. To further confirm the occurrence of fast one-electron transfer reactions between bis-arene and hexacarbonyl derivatives of group 5 metals and in order to compare the behaviour of $Nb(mes)_2$ with that of $V(mes)_2$, we treated the latter with $V(CO)_6$. The formation of the ionic derivative of equation 6 was observed. However, in contrast to the behaviour of $Nb(mes)_2$, even when the reaction was carried out under carbon monoxide, no addition of CO to the bismesitylenevanadium(I) cation took place. It should be noted that the ionic species formed in equation 6 had been obtained earlier [6b] by a reaction similar to 6 carried out under dinitrogen, or, as mentioned above, by carbonylation of $V(mes)_2$ [28] at high temperature and pressure.

$$V(CO)_6 + V(mes)_2 \rightarrow [V(mes)_2][V(CO)_6] \qquad (6)$$

As far as the redox properties of $Nb(mes)_2$ are concerned, this compound can be oxidized to the $[Nb(mes)_2CO]^+$ cation by methylviologen tetraphenylborate, $mv(BPh_4)_2$, in THF or toluene under carbon monoxide (equation 7). If the reaction is performed under argon or nitrogen in THF the cation $[Nb(mes)_2(THF)]^+$ is obtained (equation 8), and this promptly reacts with CO to give the carbonyl cation $[Nb(mes)_2CO]^+$ (equation 9).

$$Nb(mes)_2 + mv(BPh_4)_2 + CO \rightarrow [Nb(mes)_2CO]BPh_4 + mv(BPh_4) \qquad (7)$$

$$Nb(mes)_2 + mv(BPh_4)_2 + THF \rightarrow [Nb(mes)_2(THF)]BPh_4 + mv(BPh_4) \qquad (8)$$

$$[Nb(mes)_2(THF)]BPh_4 + CO \rightarrow [Nb(mes)_2CO]BPh_4 + THF \qquad (9)$$

In an attempt to isolate the 16-electrons species $[Nb(mes)_2]^+$, a toluene solution of $Nb(mes)_2$ was treated with $[FeCp_2]BPh_4$ at room temperature. A smooth reaction took place with formation of $[Nb(mes)_2]BPh_4$ and $FeCp_2$ (equation 10), which were easily separated owing to the low solubility of $[Nb(mes)_2]BPh_4$ in the reaction

$$Nb(mes)_2 + [FeCp_2]BPh_4 \rightarrow [Nb(mes)_2]BPh_4 + FeCp_2 \qquad (10)$$

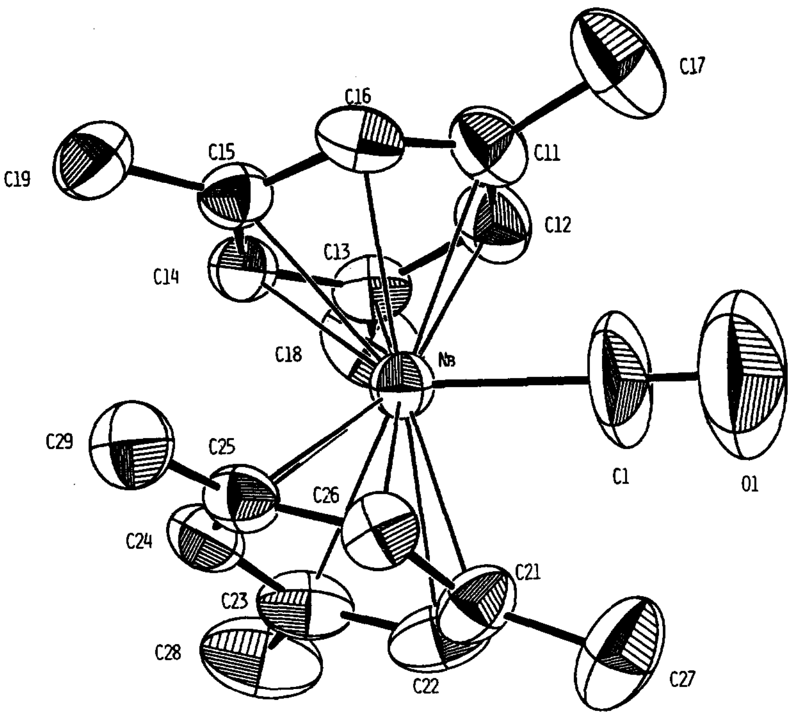


Fig. 3. View of the $[Nb(mes)_2CO]^+$ cation in $[Nb(mes)_2CO]BPh_4$ (thermal ellipsoids are drawn at 50% probability level).

medium. $[Nb(mes)_2]BPh_4$ is very sensitive to moisture and air and no correct C, H elemental analyses were obtained. Nevertheless the existence of this cation was confirmed by its reaction with CO in toluene: absorption of carbon monoxide up to CO/Nb molar ratio of 0.92 was observed, to give $[Nb(mes)_2(CO)]BPh_4$.

It is to be noted that when the ferricinium hexafluorophosphate, $[FeCp_2]PF_6$, was used instead of $[FeCp_2]BPh_4$ a pyrophoric compound which did not react with CO was obtained; this suggests that the coordination sphere of niobium(I) may be saturated by a fluoride ion of the anion. Recently, Cloke and coworkers [32] reported that $Nb(1,3,5\text{-}^tBuC_6H_3)_2$, obtained by low-temperature co-condensation of niobium atoms with 1,3,5-tri-t-butylbenzene, reacts with $AgBF_4$ in toluene at $-78\,°C$ to give a compound formulated as $[Nb(1,3,5\text{-}^tBuC_6H_3)_2]BF_4$.

The bis-mesitylene carbonyl niobium(I) cation, as tetraphenylborato derivative, has been studied by X-ray diffraction methods and it has been found to have the structure shown in Fig. 3. Bond distances and angles are shown in Tables 6 and 7.

The niobium atom exhibits a distorted trigonal coordination geometry with the centroids of the two mesitylene rings and the carbonyl carbon lying coplanar with niobium. The two aromatic rings adopt a nearly eclipsed conformation and are inclined at 147.7° to leave the necessary room for the carbonyl group. The perpendicular metal-ring plane separations are 1.912 and 1.938 Å. In a similar complex, $[Nb(\eta^6\text{-toluene})_2(PMe_3)]BF_4$ [33], containing the more bulky trimethylphosphine ligand, the two toluene ligands are inclined at 142.3°. The methyl groups deviate by 0.17 (C17), 0.20 (C18) and 0.13 (C19) Å from the plane of one aromatic

Table 6

Selected bond distances (Å) in $[Nb(mes)_2CO]BPh_4$ (estimated standard deviations in parentheses refer to the least significant digit)

Nb–C1	2.075(9)	C21–C27	1.52(1)	C51–C52	1.411(9)
Nb–C11	2.432(6)	C22–C21	1.403(9)	C51–C56	1.384(9)
Nb–C12	2.393(7)	C22–C23	1.391(8)	C51–B	1.62(1)
Nb–C13	2.381(6)	C23–C24	1.401(9)	C52–C53	1.39(2)
Nb–C14	2.346(6)	C23–C28	1.50(1)	C53–C54	1.37(2)
Nb–C15	2.347(6)	C24–C25	1.418(9)	C54–C55	1.38(2)
Nb–C16	2.380(7)	C25–C24	1.418(9)	C55–C56	1.40(1)
Nb–C21	2.419(6)	C25–C26	1.408(8)	C61–C62	1.389(9)
Nb–C22	2.369(6)	C25–C29	1.52(1)	C61–C66	1.41(2)
Nb–C23	2.378(6)	C26–C21	1.41(1)	C61–B	1.647(9)
Nb–C24	2.337(6)	C31–C32	1.404(8)	C62–C63	1.40(2)
Nb–C25	2.349(6)	C31–C36	1.395(9)	C63–C64	1.37(1)
Nb–C26	2.388(7)	C31–B	1.653(9)	C64–C65	1.37(2)
C1–O1	1.15(1)	C32–C33	1.381(9)	C65–C66	1.38(2)
C11–C12	1.41(1)	C33–C34	1.39(2)		
C11–C16	1.386(9)	C34–C35	1.37(1)		
C11–C17	1.54(2)	C35–C36	1.386(8)		
C12–C11	1.41(1)	C41–C42	1.40(2)		
C12–C13	1.404(9)	C41–C46	1.39(1)		
C13–C14	1.389(9)	C41–B	1.63(1)		
C13–C18	1.51(1)	C42–C43	1.40(1)		
C14–C15	1.42(1)	C43–C44	1.38(1)		
C15–C16	1.39(2)	C44–C45	1.36(1)		
C15–C19	1.53(1)	C45–C46	1.40(2)		
C21–C22	1.403(9)	C46–C41	1.39(1)		
C21–C26	1.41(1)				

ring and by 0.17 (C27), 0.25 (C28) and 0.22 (C29) Å from the plane of the other one away from the metal. It is noteworthy that the larger deviations from the planes of the aromatic rings are observed for the methyl groups far away from the carbonyl ligand (C18, C19, C28, C29), their non-bonding distances are 3.41 (C18 ··· C28) and 3.46 (C19 ··· C29) Å. The carbonyl ligand is almost linear (Nb–C1–O1 = 176(1)°) with Nb–C1 and C1–O1 distances of 2.075(9) and 1.15(1) Å, respectively. Mean values for Nb–C bond distances of 2.055, 2.134 and 2.260 Å have been found in other Nb^I derivatives, namely the $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$ anion [34], $CpNb(CO)_4$ [35], and $NbCl(CO)_2(dmpe)_2$ [36], respectively.

The infrared spectrum of the $[Nb(mes)_2CO]^+$ cation varies slightly with the anion: the CO stretching vibration (THF solution) was found at 1990 and 1987 cm^{-1} for the hexacarbonylmetalates(−I), M = V, Nb, and the tetraphenylborate derivatives, respectively, and is consistent with the oxidation number +1 of the metal. Carbon monoxide stretching vibrations at 2068m and 1984vs cm^{-1} have been found for $[Nb(\eta^6\text{-mesitylene})(CO)_4]Al_2Br_6Cl$ in CH_2Cl_2 solution [34] suggesting that the substitution of 3 CO groups by one mesitylene ring does not greatly modify the electronic density at the metal.

$Nb(mes)_2$ is not reduced by decamethylcobaltocene in toluene under argon during 24 h. On the other hand, a smooth reaction takes place under CO, with

Table 7

Selected bond angles (degrees) in $[Nb(mes)_2CO]BPh_4$ (estimated standard deviations in parentheses refer to the least significant digit)

C1-Nb-C11	70.5(4)	C13-Nb-C22	104.2(2)	C23-Nb-C26	72.1(2)
C1-Nb-C12	87.9(4)	C13-Nb-C23	88.7(2)	C24-Nb-C25	35.2(2)
C1-Nb-C13	121.8(4)	C13-Nb-C24	101.1(2)	C24-Nb-C26	60.8(2)
C1-Nb-C14	141.0(4)	C13-Nb-C25	132.3(3)	C25-Nb-C26	34.6(3)
C1-Nb-C15	117.3(5)	C13-Nb-C26	160.3(2)	Nb-C1-O1	176(1)
C1-Nb-C16	84.1(5)	C14-Nb-C15	35.4(2)	C12-C11-C17	119.7(6)
C1-Nb-C21	70.8(4)	C14-Nb-C16	61.2(2)	C16-C11-C17	119.7(7)
C1-Nb-C22	96.3(5)	C14-Nb-C21	147.7(2)	C12-C13-C18	119.3(6)
C1-Nb-C23	129.6(4)	C14-Nb-C22	117.1(2)	C14-C13-C18	121.9(6)
C1-Nb-C24	136.1(3)	C14-Nb-C23	87.2(2)	C14-C15-C19	121.6(6)
C1-Nb-C25	105.5(4)	C14-Nb-C24	80.8(2)	C16-C15-C19	120.0(6)
C1-Nb-C26	75.3(3)	C14-Nb-C25	102.8(2)	C22-C21-C27	118.8(7)
C11-Nb-C12	33.7(2)	C14-Nb-C26	137.3(2)	C26-C21-C27	121.4(6)
C11-Nb-C13	60.6(2)	C15-Nb-C16	34.1(2)	C22-C23-C28	120.4(6)
C11-Nb-C14	70.7(2)	C15-Nb-C21	153.8(2)	C24-C23-C28	120.3(5)
C11-Nb-C15	60.5(2)	C15-Nb-C22	146.2(2)	C24-C25-C29	121.8(6)
C11-Nb-C16	33.5(2)	C15-Nb-C23	112.2(2)	C26-C25-C29	120.6(6)
C11-Nb-C21	139.4(2)	C15-Nb-C24	89.4(2)	C21-C26-C25	122.0(6)
C11-Nb-C22	143.2(2)	C15-Nb-C25	91.7(2)	C32-C31-C36	114.8(5)
C11-Nb-C23	148.7(2)	C15-Nb-C26	120.8(2)		
C11-Nb-C24	149.2(3)	C16-Nb-C21	148.8(2)		
C11-Nb-C25	141.6(2)	C16-Nb-C22	176.1(2)		
C11-Nb-C26	138.9(2)	C16-Nb-C23	146.1(2)		
C12-Nb-C13	34.2(2)	C16-Nb-C24	120.8(2)		
C12-Nb-C14	60.7(2)	C16-Nb-C25	109.3(2)		
C12-Nb-C15	72.7(2)	C16-Nb-C26	122.2(3)		
C12-Nb-C16	60.9(2)	C21-Nb-C22	34.1(2)		
C12-Nb-C21	133.6(3)	C21-Nb-C23	60.6(2)		
C12-Nb-C22	115.2(2)	C21-Nb-C24	71.3(3)		
C12-Nb-C23	116.0(2)	C21-Nb-C25	62.2(3)		

formation of $CoCp^{\star}_2[Nb(CO)_6]$ after 168 h stirring at room temperature (equation 11).

$$Nb(mes)_2 + CoCp^{\star}_2 + 6\ CO \rightarrow CoCp^{\star}_2[Nb(CO)_6] + 2\ mes \qquad (11)$$

Our findings are in agreement with those by Green and coworkers [33], who reported that the potassium reduction of $Nb(mes)_2$ under CO affords $K[Nb(CO)_6]$; moreover, the same authors reported that the anion $[Nb(mes)_2]^-$ can be obtained by potassium reduction of $Nb(mes)_2$ in the presence of a crown ether. The more negative redox potential of potassium with respect to $CoCp^{\star}_2$ may explain the observed difference in reactivity.

When a n-heptane solution of $Nb(mes)_2$ was exposed to carbon dioxide under pressure (5 atm), a slow reaction took place with formation of CO (as shown by gas chromatography of the gas phase) and niobium was oxidized to an unidentified, black, pyrophoric compound. The deoxygenation of CO_2 to CO was faster when a carbon monoxide acceptor such as $[Nb(mes)_2(THF)]^+$ was present in the reaction mixture. By treating a 1 : 0.5 mixture of $Nb(mes)_2$ and $mv(BPh_4)_2$ in THF with CO_2 at atmospheric pressure, formation of a black solid in a green solution ($\tilde{\nu}(CO) = 1987$

cm^{-1}, typical of $[\mathrm{Nb(mes)_2(CO)}]\mathrm{BPh_4}$, *vide infra*) was observed 1 h after mixing of the reagents and no carbon monoxide was present in the gas phase (equation 12).

$$2\ \mathrm{Nb(mes)_2} + \mathrm{mv(BPh_4)_2} + \mathrm{CO_2} \rightarrow$$
$$[\mathrm{Nb(mes)_2(CO)}]\mathrm{BPh_4} + \text{unidentified niobium-containing product} \qquad (12)$$

Work in progress in this field is aimed at improving our knowledge of the low-valent tantalum organometallics, which appear to be the most difficult to obtain.

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