Synthesis and Reactivity of Mixed Arene Halides of Niobium(I). Crystal and Molecular Structure of Nbmes$_2$ and [Nbmes$_2$(CO)][Nb$_2$(μ-I)$_3$(CO)$_8$]

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Bis(mesitylen)niobium(0), Nbmes$_2$, prepared via the NbCl$_5$/Al/AlCl$_3$/mes system by exaustive reduction in the presence of 1,2-dimethoxyethane or tetrahydrofuran as previously reported, has been studied by X-ray diffraction methods. The sandwich molecule has parallel, substantially planar, aromatic rings, in an eclipsed conformation. Nbmes$_2$ is oxidized to Nbmes$_2$X by reaction with 1,1'-dimethyl-4,4'-bipyridinium halides [methylviologen halides, mvX$_2$ (X = Cl, I)]. The reaction of both halo compounds with CO yielded the niobium(I) derivatives [Nbmes$_2$(CO)] [Nb$_2$(μ-X)$_3$(CO)$_8$]. In the case of X = I an IR study at low temperature has shown the presence of intermediate carbonyl compounds, presumably Nbmes$_2$I(CO) and [Nbmes$_2$(CO)]$^+$. The ionic iodide derivative was shown by X-ray diffraction methods to consist of discrete [Nbmes$_2$(CO)]$^+$ cations and [Nb$_2$(μ-I)$_3$(CO)$_8$]$^-$ anions. The two mesitylene groups in the cation are bent and in an eclipsed conformation.

Recently, we reported that the reaction of NbX$_5$ with Al/AlX$_3$ in mesitylene followed by low-temperature treatment of the reaction mixture with 1,2-dimethoxyethane and/or tetrahydrofuran afforded the bis-mesitylene derivative of niobium(0), Nbmes$_2$. The reactivity of this compound has been investigated: the niobium(0) derivative is prone to oxidation to niobium(I) and can be easily reduced to niobium(−I), especially in the presence of carbon monoxide[1].

In the framework of our studies concerning the low-valent derivatives of group 5 metals, we now report on the crystal and molecular structure of the parent compound, Nbmes$_2$, the preparation of mixed halide-arene derivatives of niobium(I) and their reaction with CO affording the dinuclear anion [Nb$_2$(μ-I)$_3$(CO)$_8$]$^-$ as the [Nbmes$_2$(CO)]$^+$ derivative.

Results and Discussion

After several attempts, large red crystals of the paramagnetic [μ_{eff} (21 °C) = 1.87 BM] Nbmes$_2$ were grown from pentane at −30 °C, and the structure of the compound was solved. It consists of a sandwich molecule where the niobium atom is bound to two almost parallel (dihedral angle, 2.9°) and planar (maximum deviation of the carbon atoms from the least-squares plane 0.007 Å) mesitylene rings (Figure 1). The methyl substituents, which are in an eclipsed conformation (Figure 2) show only small deviations from the ring plane, the value of 0.104 Å being the maximum deviation. The central niobium atom exhibits distances of 1.849(1) and 1.850(1) Å from the ring planes, the Nb−C mean distance ranging from 2.305(5) to 2.362(5) Å. The mean C−C distances within the aromatic rings are 1.410(7) and 1.508(7) Å.

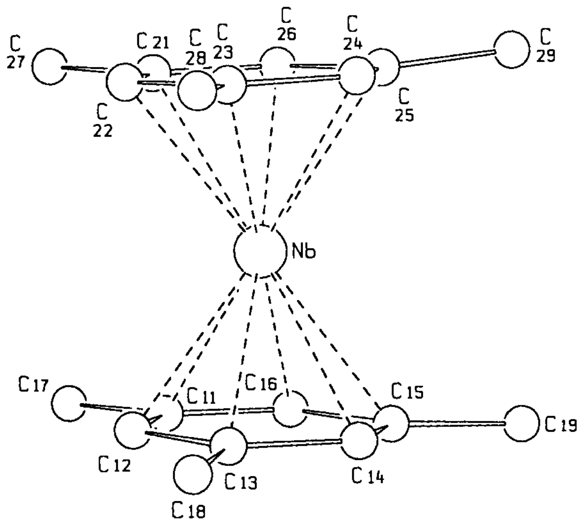


Figure 1. Molecular structure of Nb(mes)$_2$

Several zerovalent bis(arene)metal complexes, mainly concerning chromium, have been structurally characterized[2]. It is interesting to note that most of them show planar and parallel aromatic rings[2a,b,d−n] and adopt an eclipsed conformation both for benzene and alkylbenzene complexes[2a−e,h,m]: the niobium derivative as well as a recently described[2d] vanadium complex follow the same trend. Although in the niobium complex the interatomic repulsion is certainly lower than in 3d systems due to the larger size of the central metal atom, the eclipsed conformation in both the neutral and the cationic [Nbmes$_2$(CO)]$^+$ complex (vide infra) is somewhat surprising. This problem, which is outside the scope of this paper, certainly deserves further attention.

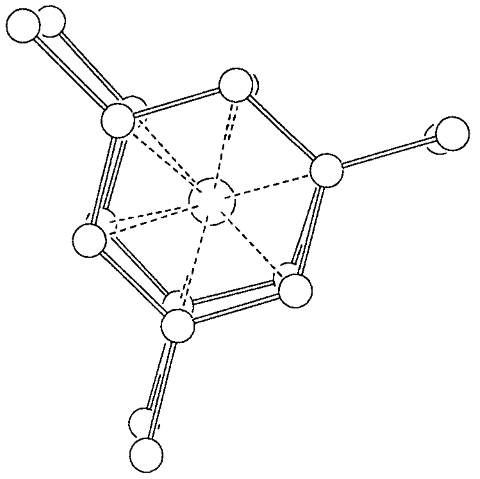


Figure 2. View of the $Nb(mes)_2$ molecule perpendicular to the (ring 1)–Nb–(ring 2) vector

The reaction of $Nbmes_2$ with methylviologen halides, mvX_2, proceeds smoothly in THF or toluene at room temperature, affording deep colored solutions of $Nbmes_2X$ according to equation (1). The corresponding bis(toluene)niobium halides (X = Br, I) have been reported by Green and coworkers[3] to be formed by reaction of $Nb(\eta^6\text{-toluene})_2$ with allyl halides at low temperature. The mesitylene derivatives have been characterized by elemental analyses and ^1H-NMR spectroscopy.

$$Nbmes_2 + mvX_2 \longrightarrow Nbmes_2X + mvX \quad (1)$$

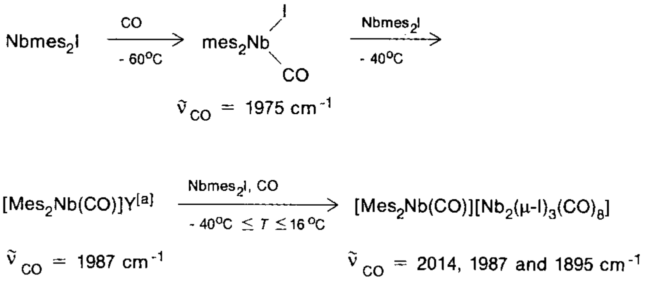
mv = methylviologen = 1,1'-dimethyl-4,4'-bipyridinium

$$3\ Nbmes_2X + 9\ CO \longrightarrow [Nbmes_2(CO)][Nb_2(\mu\text{-}X)_3(CO)_8] + 4\ mes \quad (2)$$

Due to their solubility in nonpolar solvents, an ionic structure such as $[Nbmes_2]X$ can be excluded; moreover, such an ionic compound would give $[Nbmes_2(CO)]X$ upon reaction with CO, as the salt $[Nbmes_2]BPh_4$ does[1]. In contrast, the reaction of $Nbmes_2X$ with CO in toluene or THF proceeds with absorption of 3 mol of CO per mol of niobium to afford the products of equation (2). The formation of the halide-bridged dinuclear anion[4] is quite unexpeted and corresponds to the complete loss of the arene ligands from two niobium atoms.

It was expected that, by performing the reaction at low temperature, some intermediate species could be detected on the way to the products of reaction (2). When a cold (about −60°C) solution of $Nbmes_2I$ in THF was treated with CO, the IR spectrum of the solution revealed an absorption at 1975 cm^{-1} which gradually shifted to 1987 cm^{-1} by increasing the temperature to about −30°C (with the chloride derivative $Nbmes_2Cl$, no intermediate IR absorptions other than those of the final compound $[Nbmes_2(CO)][Nb_2(\mu\text{-}Cl)_3(CO)_8]$ were observed). At about −10°C the absorption at 1975 cm^{-1} was completely substituted by the band at 1987 cm^{-1} attributable to the $[Nbmes_2(CO)]^+$ cation[1]. At about 16°C, the absorption at 1895 cm^{-1} due to the dinuclear anion was observed and after 2 h at this temperature the pattern of the spectrum in the carbonyl stretching region was superimposable to that of $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$ with bands at 2018 and 1985 cm^{-1} attributable to the $[Nb_2(\mu\text{-}I)_3(CO)_8]^-$ anion[4]. These observations are summarized in Scheme 1.

Scheme 1



[a] The nature of the Y anion is not known: as the IR spectrum shows the 1987 cm^{-1} carbonyl band only, typical of the cation. A possible formulation for the anion is $[Nbmes_2I_2]^-$.

The presence of detectable concentrations of $Nbmes_2(CO)I$ may be related to a more efficient metal-to-carbon monoxide π-back donation with respect to the chloro derivative. A similar situation was encountered in the case of the carbonylation of $[TiCp_2X]_2$[5].

Table 1. Bond distances [Å] and angles [°] of $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8] \cdot 0.5\ C_7H_8$ (estimated standard deviations in parentheses refer to the least significant digit)

I1	Nb1	2.9895(8)	Nb1	I1	Nb2	83.21(3)
I1	Nb2	2.9821(8)	Nb1	I2	Nb2	83.64(2)
I2	Nb1	2.9684(8)	Nb1	I3	Nb2	84.17(3)
I2	Nb2	2.9781(7)	I1	Nb1	I2	80.36(3)
I3	Nb1	2.9522(8)	I1	Nb1	I3	81.50(2)
I3	Nb2	2.9637(8)	I2	Nb1	I3	79.45(2)
Nb1	C11	2.023(9)	I1	Nb2	I2	80.32(3)
Nb1	C12	2.014(8)	I1	Nb2	I3	81.42(3)
Nb1	C13	2.039(8)	I2	Nb2	I3	79.11(2)
Nb1	C14	2.036(9)	C11	Nb1	C12	71.8(4)
Nb2	C21	2.046(8)	C11	Nb1	C13	111.2(3)
Nb2	C22	2.070(9)	C11	Nb1	C14	75.1(4)
Nb2	C23	2.031(8)	C12	Nb1	C13	69.4(3)
Nb2	C24	2.035(9)	C12	Nb1	C14	113.2(3)
Nb3	C31	2.088(7)	C13	Nb1	C14	71.5(4)
O11	C11	1.164(9)	C21	Nb2	C22	70.6(3)
O12	C12	1.151(9)	C21	Nb2	C23	109.8(3)
O13	C13	1.153(9)	C21	Nb2	C24	69.5(3)
O14	C14	1.179(9)	C22	Nb2	C23	74.5(3)
O21	C21	1.144(8)	C22	Nb2	C24	111.0(3)
O22	C22	1.143(9)	C23	Nb2	C24	69.6(3)
O23	C23	1.154(9)	Nb1	C11	O11	177.9(8)
O24	C24	1.168(9)	Nb1	C12	O12	177.7(9)
O31	C31	1.153(8)	Nb1	C13	O13	175.6(8)
			Nb1	C14	O14	179.6(9)
			Nb2	C21	O21	179.1(6)
			Nb2	C22	O22	177.6(8)
			Nb2	C23	O23	178.1(8)
			Nb2	C24	O24	178.7(8)
			Nb3	C31	O31	178.1(7)

The increase of the wavenumber values for the CO stretching vibration on going from Nbmes$_2$I(CO) to [Nbmes$_2$(CO)]$^+$ is in agreement with the decrease of electron density at the niobium center due to the positive charge.

Single crystals of [Nbmes$_2$(CO)][Nb$_2$(μ-I)$_3$(CO)$_8$] were grown and an X-ray diffraction study was undertaken in view of both the still limited number of crystallographically characterized bis-arene carbonyl compounds of transition metals and the possibility to compare the structural parameters of the anion with those of the corresponding chloro derivative published earlier[4].

The complex [Nbmes$_2$(CO)][Nb$_2$(μ-I)$_3$(CO)$_8$] is an ionic derivative built up of [Nbmes$_2$(CO)]$^+$ cations and [Nb$_2$(μ-I)$_3$(CO)$_8$]$^-$ anions. Selected bond distances and angles are listed in Table 1.

Within the cation (see Figure 3) the niobium atom is coordinated by one CO molecule and two η^6-mesitylene ligands. The latter are in an eclipsed orientation (Figure 4) with an interplanar angle of 32.2°. The distance of the Nb atom from the ring plane of 1.923(1) Å is slightly longer than in Nbmes$_2$, which can be explained by the increase of the coordination number and a steric repulsion of the tilted mesitylene ligands. The aromatic rings are almost planar with a maximum deviation of 0.004 Å from the least-squares plane. The methyl groups are slightly bent outside the ring plane, the deviation being 0.107(2)–0.341(2) Å. The Nb–C$_{ring}$ distances in the range 2.330(7)–2.450(7) Å are similar to that observed in the same cation of the BPh$_4^-$ salt[1]. The distance Nb–C$_{carbonyl}$ of 2.088(7) Å as well the C–O distance of 1.153(8) Å and the Nb–C–O angle of 178.1(7)° are in the expected range of values for carbonyl derivatives of Nb(I)[1,4,6]. The mean C–C distances within the aromatic ring are 1.41(2) and 1.40(2) Å.

As far as the anion is concerned (see Figure 5) the two niobium atoms of the dinuclear unit are bridged by iodide atoms located at the vertices of an approximately equilateral triangle, on a plane perpendicular to the Nb–Nb vector (see Figure 6). The coordination of the niobium atoms is completed by four CO groups to form a sevenfold coordination polyhedron, which can be classified according to Muetterties and Wright[7] as a "square base-trigonal cap" of C_s symmetry. As expected from the 18-electron counting, no Nb–Nb interaction is present, the metal-metal distance being 3.965(1) Å compared with 3.631 Å in the case of the bridging chloride anionic dinuclear compound[4]. The iodide bridges are symmetrical with Nb–I distances ranging from 2.9522(8) to 2.9895(8) Å, i.e. longer than the sum of the covalent radii of 2.67 Å[8].

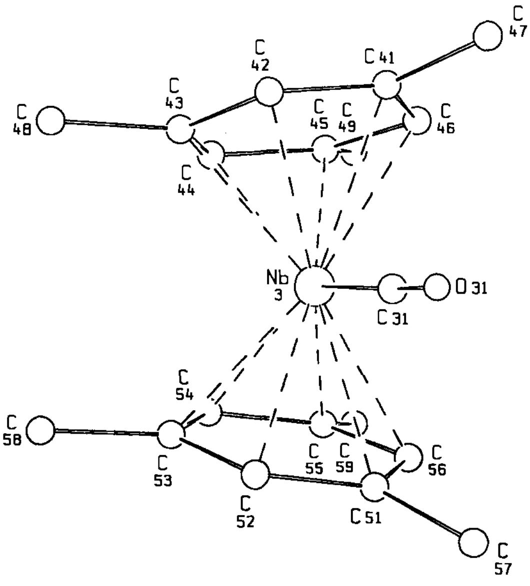


Figure 3. View of the [Nb(mes)$_2$CO]$^+$ cation in [Nbmes$_2$(CO)][Nb$_2$(μ-I)$_3$(CO)$_8$]

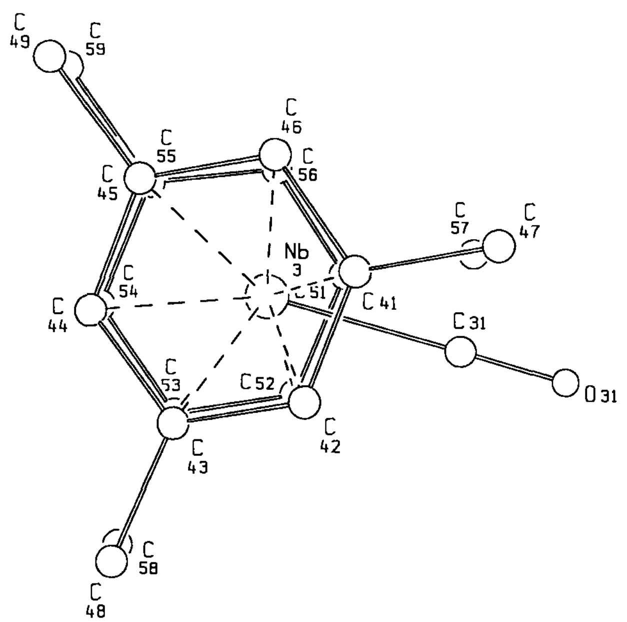


Figure 4. View of the [Nb(mes)$_2$CO]$^+$ cation along the (ring 1)–Nb–(ring 2) vector

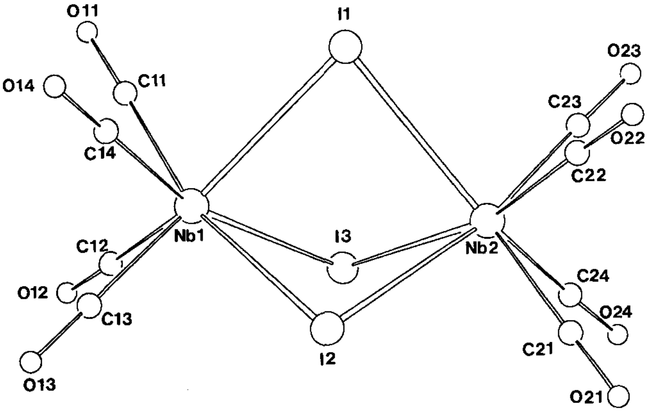


Figure 5. View of the [Nb$_2$(μ-I)$_3$(CO)$_8$]$^-$ anion in [Nbmes$_2$(CO)][Nb$_2$(μ-I)$_3$(CO)$_8$]

[Nbmes$_2$(CO)][Nb$_2$(μ-I)$_3$(CO)$_8$] reacts with 1,2-bis(diphenylphosphanyl)ethane, diphos, to give the new iododicarbonyl compound NbI(CO)$_2$(diphos)$_2$ in high yields according to equation (3). Dicarbonyl halo complexes with bidentate tertiary phosphanes of the general formula MX-

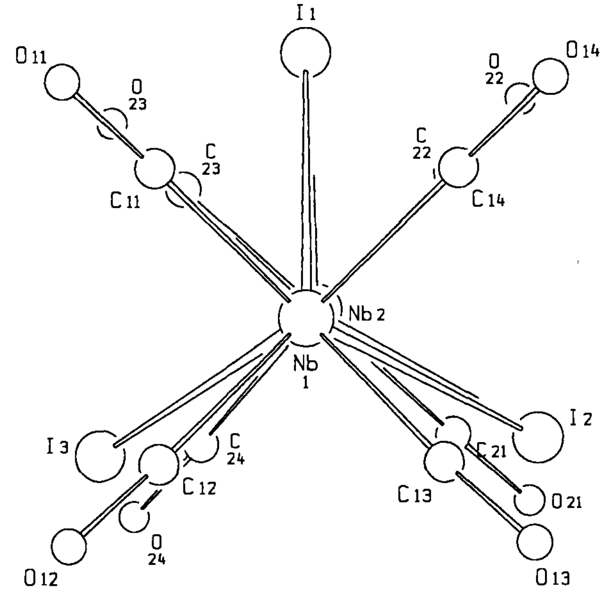


Figure 6. View of the $[Nb_2(\mu\text{-}I)_3(CO)_8]^-$ anion along the Nb−Nb vector

$(CO)_2(P-P)_2$ (X = Cl, Br; M = Nb, Ta) have been reported[6b,9] and used[10] for the reductive coupling of carbon monoxide.

$$[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8] + 4\ \text{diphos} \longrightarrow 2\ NbI(CO)_2(\text{diphos})_2 + \text{"}Nbmes_2I(CO)\text{"} + 4\ CO \quad (3)$$

There was no direct observation of the carbonyl derivative $Nbmes_2I(CO)$, but it was noticed that one third of niobium was lost as a black pyrophoric material: the latter probably originates from the unstable carbonyl iodide of niobium(I). It has to be noticed that the reaction of $[Nbmes_2(CO)]BPh_4$ with LiI in THF *under argon* causes rapid evolution of CO and separation of unidentified niobium-containing solids.

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Experimental

Unless stated otherwise, all operations were carried out under prepurified nitrogen or argon. Solvents were dried by conventional methods prior to use. – IR: Perkin-Elmer FT/1725X instrument, solutions or nujol and/or poly(chlorotrifluoroethylene) mulls, prepared with rigorous exclusion of moisture and air. As far as the low-temperature experiments are concerned, the cold solution was transferred by using a cannula into an IR cell (SPECAC, England) equipped with 0.1-mm CaF_2 windows, precooled at about −60 °C.

$NbCl_5$ was a commercial product (Fluka) sublimed prior to use. 1,1′-dimethyl-4,4′-bipyridinium dichloride trihydrate, $mvCl_2 \cdot 3\ H_2O$, (Fluka) was heated at 90 °C/0.05 Torr for 4 h and stored under argon. 1,1′-Dimethyl-4,4′-bipyridinium diiodide, mvI_2[11], and bis(1,3,5-trimethylbenzene)niobium(0), $Nbmes_2$[1], were prepared according to literature procedures.

X-ray Diffraction Experiments performed on $Nbmes_2$ and $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$[12]: Single crystals of the complexes were grown from pentane at −30 °C and from toluene at 18 °C, respectively. X-ray data collection was performed on crystals mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator at room temperature. Crystal data and summary of data collection and structure refinement are listed in Table 2.

Table 2. Crystal data and summary of data collection and structure refinement for $Nb(mes)_2$ and $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$

		$Nbmes_2$	$[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]\cdot 0.5\ C_7H_8$
Formula		$C_{18}H_{24}Nb$	$C_{27}H_{24}Nb_3I_3O_9 . 0.5\ C_7H_8$
Molecular weight		333.30	1197.99
Crystal size (mm)		0.6 x 0.5 x 0.5	0.35 x 0.35 x 0.3
Crystal system		triclinic	triclinic
Space group		$P\bar{1}$	$P\bar{1}$
Lattice constants (Å or degrees)	a	9.796(1)	12.227(3)
	b	10.822(1)	14.417(6)
	c	8.724(1)	11.956(3)
	α	107.64(1)	106.35(3)
	β	113.77(1)	108.00(2)
	γ	91.49(1)	80.95(3)
Cell volume (Å^3)	V	794.8	1917.6
Temperature of data collection (°C)		18	18
Formula unit	Z	2	2
F(000)		346	565
Density (g cm^{-3})	ρ_x	1.393	2.075
Radiation		CuK_α	MoK_α
Absorption coefficient (cm^{-1})	μ	61.623	32.871
Scan type		ω/θ	ω/θ
Range of data collection (degrees)	θ	4-75	3-26
Range of data collection (h,k,l)		-12,12; -13,13; 0,10	-15,15; 17,17; 0,14
No. of measured reflections		3328	7884
No. of independent observed reflections with $I > 3\sigma(I)$		3058	5153
No. of parameters		173	395
Absorption correction		DIFABS 12	DIFABS 12
Minimum, maximum correction		0.704, 1.584	0.604, 1.573
Extinction coefficient	g	6.4755×10^{-6}	6.4755×10^{-6}
R-values	R	0.065	0.042
	R_w	0.084	0.049

$Nbmes_2$: A crystal of $Nbmes_2$ was mounted on a glass rod, sealed with a thin layer of varnish and used for the X-ray experiment. The lattice parameters of the triclinic compound with the space group $P\bar{1}$ were refined on the single crystal diffractometer by using 25 automatically centered reflections in the Θ range 15–31°. During the measurement, a small loss of intensity of 0.2% per hour was observed and consequently corrected with the program DECAY[13]. The position of the niobium atom was obtained from a Patterson synthesis[13]. A difference Fourier synthesis showed the carbon atoms of the mesitylene ligands. Refinement with isotropic temperature parameters converged to $R = 0.144$. An empirical absorption correction with the program DIFABS[14] improved the R value to 0.082. Then anisotropic temperature parameters were assigned to the niobium and carbon atoms resulting in $R = 0.074$. With the calculated position of the hydrogen atoms taken into account during the structure factor calculation and after refinement of the extinction coefficient g[15], the final R_w value of 0.084 was obtained. The fractional coordinates are reported in Table 3.

$[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$ crystallizes as toluene solvate with 0.5 C_7H_8. Due to the sensitivity of the compound to oxygen, the selected crystal was sealed under argon in a glass capillary. The lattice parameters were refined by using 25 automatically centered reflections between Θ = 11.5 and 14.9°. During the measurement

Table 3. Fractional atomic coordinates for $Nb(mes)_2$ (estimated standard deviations in parentheses refer to the least significant digit). Anisotropically refined atoms are given with the isotropic equivalent displacement parameters defined as $4/3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab\cos\gamma B_{1,2} + ac\cos\beta B_{1,3} + bc\cos\alpha B_{2,3}]$

Atom	X	Y	Z	B(Å^2)
Nb	0.28278(6)	0.26412(5)	0.10491(6)	1.22(1)
C11	0.2828(9)	0.0698(8)	-0.1030(9)	2.4(2)
C12	0.2446(8)	0.0382(7)	0.022(1)	2.2(2)
C13	0.3420(9)	0.0869(7)	0.2044(9)	2.2(2)
C14	0.4784(8)	0.1716(7)	0.2629(9)	2.2(2)
C15	0.5222(8)	0.2060(7)	0.1437(9)	2.1(2)
C16	0.4190(8)	0.1536(8)	-0.0416(9)	2.2(2)
C17	0.183(1)	0.012(1)	-0.300(1)	4.0(3)
C18	0.304(1)	0.045(1)	0.336(1)	4.4(2)
C19	0.668(1)	0.290(1)	0.203(1)	3.4(2)
C21	0.0769(9)	0.3446(8)	-0.060(1)	2.5(2)
C22	0.0454(9)	0.3155(8)	0.069(1)	2.7(2)
C23	0.1456(9)	0.3731(8)	0.252(1)	2.5(2)
C24	0.2769(9)	0.4617(8)	0.303(1)	2.6(2)
C25	0.3123(9)	0.4925(7)	0.1748(9)	2.3(2)
C26	0.209(1)	0.4330(7)	-0.008(1)	2.6(2)
C27	-0.033(1)	0.286(1)	-0.258(1)	4.2(3)
C28	0.108(1)	0.345(1)	0.391(1)	4.2(2)
C29	0.446(1)	0.5942(9)	0.230(1)	3.8(2)

the crystal showed a total loss of intensity of 33.6%, which was corrected with the program DECAY[13]. Direct methods[16] revealed the structural skeleton including the niobium, iodine, and carbon atoms. Refinement with isotropic temperature parameters converged to $R = 0.157$. A difference Fourier synthesis showed the carbon atoms of a toluene molecule being disordered on a center of symmetry. Additional refinement and an empirical absorption correction[14] improved the R value to 0.105. With anisotropic temperature parameters for the nonhydrogen atoms of $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$ an R value of 0.044 was obtained. By taking into account the calculated positions of the hydrogen atoms (with fixed isotropic temperature parameters) for the calculation of the structure factors F_c we obtained a final R value of 0.042. The extinction coefficient g was not refined. The fractional coordinates are reported in Table 4.

Synthesis of $Nbmes_2X$ (X = Cl, I): Only the preparation of $Nbmes_2I$ is described in detail, the chloro derivative being obtained in a similar way. – A suspension of mvI_2 (1.15 g, 2.61 mmol) in toluene (40 ml) was treated with $Nbmes_2$ (0.87 g, 2.6 mmol). A reaction took place upon mixing the reagents. After stirring at room temp. for 5 h, the brown suspension was filtered and the volume of the solution was reduced to about 10 ml. Addition of heptane (20 ml) caused the precipitation of a black, microcrystalline solid which was filtered off and dried in vacuo at room temp. to afford 1.11 g (93%) of $Nbmes_2I$. – ^1H NMR ($[D_6]$benzene, TMS internal standard): $\delta = 7.11$ (s, 6H), 2.07 (s, 18H).

$C_{18}H_{24}INb$ (460.2) Calcd. C 47.0 H 5.3 I 27.6 Nb 20.2
Found C 45.2 H 4.9 I 27.2 Nb 19.8

The chloro derivative *$Nbmes_2Cl$* was obtained as a brown microcrystalline solid from $Nbmes_2$ and $mvCl_2$ in 87% yield. – ^1H NMR ($[D_6]$benzene, TMS internal standard): $\delta = 7.08$ (s, 6H), 2.05 (s, 18H).

$C_{18}H_{24}ClNb$ (368.7) Calcd. C 58.6 H 6.6 Cl 9.6 Nb 25.2
Found C 57.2 H 6.0 Cl 9.7 Nb 25.0

Table 4. Fractional atomic coordinates for $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8] \cdot 0.5\ C_7H_8$ (estimated standard deviations in parentheses refer to the least significant digit). Starred atoms were refined isotropically. Anisotropically refined atoms are given as in Table 3

Atom	X	Y	Z	B(Å^2)
I1	0.75039(7)	0.85999(6)	0.21130(8)	6.37(2)
I2	0.83376(6)	0.64138(6)	0.35307(6)	5.07(2)
I3	0.56532(6)	0.63864(6)	0.08880(7)	5.39(2)
Nb1	0.62199(8)	0.77567(7)	0.33058(8)	4.40(2)
Nb2	0.80829(8)	0.65227(7)	0.10109(8)	4.37(2)
Nb3	0.26556(8)	0.74073(7)	0.67220(8)	4.07(2)
O11	0.4404(9)	0.9564(8)	0.292(1)	11.7(4)
O12	0.3719(8)	0.7227(9)	0.310(1)	11.3(4)
O13	0.634(1)	0.7178(8)	0.5708(8)	10.4(3)
O14	0.719(1)	0.9492(9)	0.562(1)	12.2(4)
O21	0.9988(7)	0.4757(6)	0.1321(8)	7.4(2)
O22	1.0561(7)	0.7169(8)	0.126(1)	9.5(3)
O23	0.7874(9)	0.7074(8)	-0.1450(8)	9.7(3)
O24	0.7411(9)	0.4709(8)	-0.1279(9)	8.8(3)
O31	0.3886(8)	0.8733(7)	0.5751(8)	8.1(3)
C11	0.508(1)	0.8912(9)	0.306(1)	6.9(4)
C12	0.463(1)	0.741(1)	0.320(1)	7.1(4)
C13	0.625(1)	0.738(1)	0.482(1)	6.8(3)
C14	0.683(1)	0.886(1)	0.477(1)	7.3(4)
C21	0.930(1)	0.5385(9)	0.1201(9)	5.3(3)
C22	0.968(1)	0.6951(9)	0.120(1)	6.3(3)
C23	0.793(1)	0.688(1)	-0.056(1)	6.2(3)
C24	0.766(1)	0.536(1)	-0.043(1)	6.3(3)
C31	0.343(1)	0.8266(8)	0.608(1)	5.7(3)
C41	0.438(1)	0.7992(8)	0.833(1)	5.7(3)
C42	0.4690(9)	0.7115(8)	0.7601(9)	4.7(3)
C43	0.415(1)	0.6281(8)	0.7394(9)	4.9(3)
C44	0.328(1)	0.6342(8)	0.799(1)	5.6(3)
C45	0.294(1)	0.7229(9)	0.872(1)	6.1(3)
C46	0.345(1)	0.8080(9)	0.885(1)	6.1(3)
C47	0.501(1)	0.888(1)	0.862(1)	8.2(4)
C48	0.460(1)	0.531(1)	0.677(1)	8.6(5)
C49	0.222(1)	0.727(1)	0.954(1)	9.2(5)
C51	0.121(1)	0.8003(8)	0.513(1)	5.5(3)
C52	0.1692(9)	0.7100(8)	0.4593(9)	5.1(3)
C53	0.1697(9)	0.6278(8)	0.495(1)	4.9(3)
C54	0.1156(9)	0.6382(8)	0.588(1)	5.5(3)
C55	0.067(1)	0.7281(9)	0.644(1)	5.6(3)
C56	0.074(1)	0.8108(9)	0.608(1)	5.8(3)
C57	0.112(1)	0.891(1)	0.466(1)	8.2(4)
C58	0.211(1)	0.529(1)	0.429(1)	8.0(4)
C59	-0.011(1)	0.736(1)	0.723(1)	8.4(4)
C61	-0.0465	-0.0295	0.0461	15.0(6)*
C62	0.1506	0.0217	0.0771	15.0(8)*
C63	0.0819	-0.0199	0.1311	15.0(9)*
C64	0.1660	-0.0429	0.2500	25(4)*

Reaction of $Nbmes_2I$ with CO: Synthesis of $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$: A solution of $Nbmes_2I$ (0.32 g, 0.69 mmol) in toluene (50 ml) was exposed to CO for 15 h. The black solid which formed was filtered off, washed with toluene (2 × 5 ml) and dried in vacuo at room temp. to afford 0.238 g (88%) of $[Nbmes_2(CO)][Nb_2(\mu\text{-}I)_3(CO)_8]$ as dark red microcrystalline solid. The filtrate, after standing at room temp. for several days, gave black crystals (0.025 g) suitable for an X-ray diffraction study. – IR (THF): $\tilde{\nu} = 2014$ m, 1987 w, 1895 vs cm^{-1}.

$C_{27}H_{24}I_3Nb_3O_9$ (1151.9) Calcd. CO 21.9 Nb 24.2 I 33.0
Found CO 21.5 Nb 24.1 I 33.2

A gas volumetric control of the reaction showed that $Nbmes_2I$ absorbed CO at 24.6°C up to a CO/Nb molar ratio of 3.1.

The chloro complex *[$Nbmes_2(CO)$][$Nb_2(\mu\text{-}Cl)_3(CO)_8$]* was identified spectroscopically [IR (THF): $\tilde{\nu}$ = 2007 m, 1987 w, 1906 vs cm^{-1}] to be formed in the reaction of $Nbmes_2Cl$ with CO under the same experimental conditions as used for the iodo derivative.

Reaction of $Nbmes_2X$ (X = Cl, I) with CO at Low Temperature: A solution of $Nbmes_2I$ (0.25 g, 0.54 mmol) in THF (25 ml) was treated with CO at ca. −78°C. While the temp. of the reaction mixture was slowly increased, samples of the solution were examined by IR spectroscopy, the IR cell being cooled at ca. −60°C. The following absorptions (cm^{-1}) were observed in the carbonyl stretching region (temperatures, °C, of the cell in parenthesis): $\tilde{\nu}$ = 1975 (−50); 1987 and 1975 (−40); 1987 (−40, 0); 1987 and 1895 (0). After 2 h at 16°C the absorptions typical of [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}I)_3(CO)_8$] were observed at $\tilde{\nu}$ = 2014 m, 1987 w and 1895 vs cm^{-1}.

When the reaction was repeated with the chloro derivative, no absorption was observed in the carbonyl stretching region but those of the final compound [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}Cl)_3(CO)_8$] at $\tilde{\nu}$ = 2007 m, 1987 w and 1906 vs cm^{-1}.

Reaction of [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}I)_3(CO)_8$] with diphos: Synthesis of $NbI(CO)_2(diphos)_2$: A suspension of [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}I)_3(CO)_8$] (0.14 g, 0.12 mmol) in toluene (10 ml) was treated with 1,2-bis(diphenylphosphanyl)ethane (0.29 g, 0.73 mmol). Within 2 h a red solution and a black solid were obtained with evolution of CO. The reaction mixture was separated from a black, pyrophoric material by filtration and the volume of the solution was reduced to 5 ml. Addition of heptane (5 ml) caused the separation of an orange-red solid which was identified as $NbI(CO)_2(diphos)_2$ {0.25 g, 97% yield with respect to [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}I)_3(CO)_8$]}. – IR (toluene): $\tilde{\nu}$ = 1850 vs and 1775 s cm^{-1}; (THF) 1847 vs and 1773 s cm^{-1}.

$C_{54}H_{48}NbIO_2P_4$ (1072.7)	Calcd.	C 60.5	H 4.5
	Found	C 60.1	H 4.8

CAS Registry Numbers

diphos: 1663-45-2 / mvI_2: 1983-60-4 / $mvCl_2$: 1910-42-5 / $Nbmes_2$: 68088-96-0 / $Nbmes_2I$: 139130-81-7 / $Nbmes_2Cl$: 139130-82-8 [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}I)_3(CO)_8$]: 139130-84-0 / [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}I)_3(CO)_8$] · 0.5 C_7H_8: 139130-90-8 / [$Nbmes_2(CO)$][$Nb_2(\mu\text{-}Cl)_3(CO)_8$]: 139130-85-1 / $Nbmes_2I(CO)$: 139130-86-2 / [$Nbmes_2(CO)$]-[$Nbmes_2I_2$]: 139130-88-4 / $NbI(CO)_2(diphos)_2$: 139130-89-5

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[1] F. Calderazzo, G. Pampaloni, L. Rocchi, J. Strähle, K. Wurst, *J. Organomet. Chem.* **1991**, *413*, 91.

[2] [2a] $Ti(\eta^6\text{-}C_6H_6)_2$: G. G. Tairova, E. F. Kvashina, O. N. Krasochka, G. A. Kichigina, Yu. A. Shvetsov, E. M. Lisetsky, L. O. Atovmyan, Yu. G. Borod'ko, *Nouv. J. Chim.* **1981**, *5*, 603. – [2b] $Ti(\eta^6\text{-}C_6H_5Me)_2$: G. G. Tairova, O. N. Krasochka, V. I. Ponomaryov, E. F. Kvashina, Yu. A. Shvetsov, E. M. Lisetsky, D. P. Kiryukhin, L. O. Atovmyan, Yu. G. Borod'ko, *Trans. Met. Chem.* **1982**, *7*, 189. – [2c] $V[\eta^6\text{-}(1,4\text{-}C_6H_4F_2)]_2$: L. J. Radonovich, E. C. Zuerner, H. F. Efner, K. J. Klabunde, *Inorg. Chem.* **1976**, *15*, 2976. – [2d] $V[\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)]_2$: D. Braga, P. Sabatino, *Acta Crystallogr., Sect. C*, **1990**, *46*, 2308. – [2e] $Cr(\eta^6\text{-}C_6H_6)_2$: F. Jellinek, *J. Organomet. Chem.* **1963**, *1*, 43; F. A. Cotton, W. A. Dollase, J. S. Wood, *J. Am. Chem. Soc.* **1963**, *85*, 1543; J. A. Ibers, *J. Chem. Phys.* **1964**, *40*, 3129; E. Keulen, F. Jellinek, *J. Organomet. Chem.* **1966**, *5*, 490. – [2f] $Cr(\eta^6\text{-}C_{10}H_8)_2$: Ch. Elschenbroich, R. Möckel, W. Massa, M. Birkhahn, U. Zenneck, *Chem. Ber.* **1982**, *115*, 334. – [2g] $Cr(\eta^6\text{-tetralone})_2$: H. Brunner, J. Ernst, T. Wischert, *J. Organomet. Chem.* **1987**, *328*, 331. – [2h] $Cr(\eta^6\text{-}C_6H_5CF_3)_2$: S. B. Larson, C. M. Seymour, J. J. Lagowski, *Acta Crystallogr., Sect. C*, **1987**, *43*, 1624. – [2i] $Cr\{\eta^6\text{-}[1,4\text{-}C_6H_4(CF_3)_2]\}_2$, $Cr\{\eta^6\text{-}[1,3\text{-}C_6H_4(CF_3)_2]\}_2$, $Cr\{\eta^6\text{-}[1\text{-}Cl\text{-}3\text{-}(CF_3)C_6H_4]\}_2$: M. W. Eyring, E. C. Zuerner, L. J. Radonovich, *Inorg. Chem.* **1981**, *20*, 3405. – [2j] $Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6F_5PPh_2)$: R. Faggiani, N. Hao, C. J. L. Lock, B. G. Sayer, M. J. McGlinchey, *Organometallics* **1983**, *2*, 96. – [2k] $Mo(\eta^6\text{-}C_6H_5Me)_2$: F. M. Miao, *Cryst. Struct. Commun.* **1982**, *11*, 153. – [2l] $Mo(\eta^6\text{-}C_6H_5CH_2CH{=}CH_2)_2$: M. L. H. Green, I. Treurnicht, J. A. Bandy, A. Gourdon, K. Prout, *J. Organomet. Chem.* **1986**, *306*, 145. – [2m] $W(\eta^6\text{-}C_6H_5Me)_2$: K. Prout, A. Gourdon, C. Couldwell, B. Meunier, F. M. Miao, J. Woolcock, *Acta Crystallogr., Sect. B*, **1982**, *38*, 456. – [2n] $M[\eta^6\text{-}1,3,5\text{-}C_6H_3(tBu)_3]_2$, M = Gd, Y: J. G. Brennan, F. G. N. Cloke, A. A. Sameh, A. Zalkin, *J. Chem. Soc., Chem. Commun.* **1987**, 1668.

[3] M. L. H. Green, D. O'Hare, J. G. Watkin, *J. Chem. Soc., Chem. Commun.* **1989**, 698; M. L. H. Green, D. O'Hare, P. Mountford, J. G. Watkin, *J. Chem. Soc., Dalton Trans.* **1991**, 1705.

[4] F. Calderazzo, M. Castellani, G. Pampaloni, P. F. Zanazzi, *J. Chem. Soc., Dalton Trans.* **1985**, 1989.

[5] P. Biagini, F. Calderazzo, G. Pampaloni, P. F. Zanazzi, *Gazz. Chim. Ital.* **1987**, *117*, 27.

[6] [6a] W. A. Herrmann, W. Kalcher, H. Biersack, I. Bernal, M. Creswick, *Chem. Ber.* **1981**, *114*, 3558. – [6b] C. Felten, J. Richter, W. Priebsch, D. Rehder, *Chem. Ber.* **1989**, *122*, 1617.

[7] E. L. Muetterties, C. M. Wright, *Quart. Rev.* **1967**, *21*, 109.

[8] L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, **1960**.

[9] S. Datta, S. S. Wreford, *Inorg. Chem.* **1977**, *16*, 1134; J. D. Brown, S. Datta, J. K. Kouba, L. K. Smith, S. S. Wreford, *ibid.* **1978**, *17*, 729; R. J. Burt, G. J. Leigh, D. L. Hughes, *J. Chem. Soc., Dalton Trans.* **1981**, 793.

[10] P. A. Bianconi, I. D. Williams, M. P. Engeler, S. J. Lippard, *J. Am. Chem. Soc.* **1986**, *108*, 311; P. A. Bianconi, R. N. Vrtis, Ch. P. Rao, I. D. Williams, M. P. Engeler, S. J. Lippard, *Organometallics* **1987**, *6*, 1968; R. N. Vrtis, Ch. P. Rao, S. G. Bott, S. J. Lippard, *J. Am. Chem. Soc.* **1988**, *110*, 7564; R. N. Vrtis, S. Liu, Ch. P. Rao, S. G. Bott, S. J. Lippard, *Organometallics* **1991**, *10*, 275; R. N. Vrtis, S. G. Bott, R. L. Rardin, S. J. Lippard, *ibid.* **1991**, *10*, 1364; J. D. Protasiewicz, S. J. Lippard, *J. Am. Chem. Soc.* **1991**, *113*, 6564.

[11] *Beilsteins Handbuch der Organischen Chemie*, 4th Ed., vol. XXIII, p. 211.

[12] Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56019, the names of the authors and the journal citation.

[13] B. A. Frenz in H. Schenk, R. Olthof-Hazekamp, R. van Konigsveld, G. C. Bassi, *The Enraf-Nonius CAD4-SDP. – A Real Time System for Concurrent X-Ray Data Collection and Crystal Structure Refinement*, in Computing in Crystallography, Delft University Press, Delft, Holland, **1978**, p. 64.

[14] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, **1983**, *39*, 158.

[15] W. H. Zachariasen, *Acta Crystallogr.* **1963**, *16*, 1139.

[16] G. M. Sheldrick, *SHELXS 86, Program for Solution of Crystal Structures from Diffraction Data*, University of Göttingen, **1986**.

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