New Carbonyl Derivatives of Niobium(I) and Tantalum(I)†

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The hexacarbonylmetalates(1 –) of niobium and tantalum are oxidised by H^+ and halogens to give the $[M_2X_3(CO)_8]^-$ anions (X = Cl, Br, or I). By exchange reactions, the μ-acetato- and μ-methoxo-complexes (X = O_2CMe or OMe) were also obtained. The crystal and molecular structure of $[H(thf)_2][Nb_2Cl_3(CO)_8]$ was investigated by *X*-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with $a = 16.283(3)$, $b = 9.293(2)$, $c = 9.050(2)$ Å, $\alpha = 113.01(2)$, $\beta = 96.56(2)$, $\gamma = 98.39(2)°$, $U = 1\ 224.7$ Å^3, $D_c = 1.792$ g cm^{-3} ($Z = 2$), μ(Mo-K_α) = 12.2 cm^{-1}. The two niobium atoms of the dimeric anion are bridged by three chlorides located at the vertices of an approximately equilateral triangle perpendicular to the niobium-niobium vector [Nb ··· Nb 3.631(1) Å]. The seven-co-ordination of niobium is completed by four carbonyl groups. The dimeric chloride-bridged complexes of niobium(I) and tantalum(I) undergo the following reactions: (*a*) reduction by sodium to the hexacarbonylmetalate(1 –); (*b*) chloride substitution by $C_5H_5^-$ to the cyclopentadienyl derivatives $[M(\eta^5\text{-}C_5H_5)(CO)_4]$ in good yields and by arenes in the presence of aluminium bromide to the new cationic complexes $[M(\eta^6\text{-arene})(CO)_4]^+$ as their hexa(bromo)chlorodialuminate derivatives.

We have recently developed new preparative procedures for the hexacarbonylmetalates(1 –) of vanadium,[1] niobium,[2] and tantalum.[2] The availability of these complexes in relatively large quantities has allowed the study of their chemistry, which is still largely unexplored especially for niobium and tantalum, to be made. The oxidation state zero is unknown for binary carbonyl derivatives of niobium and tantalum and the oxidation state 1 + was until recently exemplified by the cyclopentadienyl derivatives $[Nb(\eta^5\text{-}C_5H_5)(CO)_4]$[3] and $[Ta(\eta^5\text{-}C_5H_5)(CO)_4]$[4] only and by some of their substitution products. We have recently shown[5] that the hydrido-complex of vanadium $[VH(CO)_6]$ is not stable and that stoicheiometric amounts of water promote its ionic dissociation to $[H_3O]^+$-$[V(CO)_6]^-$. In attempts to isolate hydrido-complexes of niobium and/or tantalum, acidification of the corresponding hexacarbonylmetalates was carried out. However, no hydrido-species were observed and the halide-bridged species of niobium(I) and tantalum(I), $[M_2X_3(CO)_8]^-$, were unexpectedly formed,[6] by an unusual two-electron transfer process from metal(1 –) to protons.

This paper reports some further extension of the work on the halide–carbonyl complexes, the full details of the *X*-ray investigation of the niobium derivative with chloride bridges, and the use of the halide–carbonyl complexes as intermediates for the synthesis of the new η^6-arene–tetracarbonyl complexes of niobium(I) and tantalum(I), $[M(\eta^6\text{-arene})(CO)_4]^+$, and of the already known cyclopentadienyl derivatives.

Experimental

Unless otherwise stated, all of the operations involving the preparation and manipulation of the metal complexes were carried out under an atmosphere of prepurified argon in strictly anhydrous solvents, the latter dried by conventional methods prior to use. Infrared spectra were measured with a Perkin-Elmer 283 instrument equipped with a suitable grating. The hexacarbonylmetalates of niobium(1 –) and tantalum(1 –) were prepared as previously described[2] and products with variable contents of tetrahydrofuran (thf) were obtained, depending on the drying procedure used.

Oxidation of $[M(CO)_6]^-$ (M = Nb *or* Ta).—(*a*) *By protons: preparation of* $[H(thf)_2][M_2Cl_3(CO)_8]$. The hexacarbonylniobate(1 –) anion, as $Na[Nb(CO)_6]$·thf (2.036 g, 5.72 mmol), was suspended in n-heptane (100 cm^3) and treated with dry HCl (19.0 mmol) introduced into the cold (*ca.* –70 °C) suspension with a syringe through a rubber stopper. The colour of the suspension turned immediately to red and the temperature of the mixture was allowed to rise slowly; at *ca.* –40 °C, a vigorous evolution of gas (dihydrogen and CO) took place. After *ca.* 1 h, when the temperature was substantially at ambient, the solvent was evaporated under reduced pressure and the solid residue was treated with dichloromethane (100 cm^3). The red-brown solution was concentrated to *ca.* 10 cm^3 and n-heptane was added, which caused the separation of the brown compound (1.1 g, 58% yield). Analytical and spectroscopic data are in Tables 1 and 2, respectively.

The corresponding tantalum derivative was prepared similarly in 50% yield.

Preparation of $[Na(thf)_2][Nb_2Cl_3(CO)_8]$. The hexacarbonylniobate(1 –) anion, as $Na[Nb(CO)_6]$·0.25thf (1.903 g, 6.3 mmol), was dissolved in thf (80 cm^3) and treated with dry HCl (12.4 mmol) at dry-ice temperature. By slowly raising the temperature, at –40 °C the colour turned to red-brown and evolution of gas (dihydrogen and CO) was observed. The solution, maintained at room temperature for *ca.* 30 min, was filtered. After partial evaporation of the solvent (to *ca.* 5 cm^3) under reduced pressure, n-heptane (100 cm^3) was added and the ochre solid so obtained was collected by filtration and dried *in vacuo* (58% yield).

The similar treatment of $Na[Ta(CO)_6]$·thf in thf did not lead to the isolation of a pure product by operating with either HCl

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† *Supplementary data available* (No. SUP 56231, 5 pp.): thermal parameters, full bond distances and angles, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Analytical data for carbonyl derivatives of niobium(I) and tantalum(I)

(*a*) Halide complexes

	Analysis^a (%)				
	C	H	CO	Halogen	Other
$[H(thf)_2][Nb_2Cl_3(CO)_8]$	28.6 (29.0)	2.5 (2.6)	33.2 (33.9)	16.2 (16.1)	
$[Na(thf)_2][Nb_2Cl_3(CO)_8]$	27.2 (28.1)	2.4 (2.4)	32.1 (32.1)	14.5 (15.6)	
$[N(PPh_3)_2][Nb_2Cl_3(CO)_8]$	50.0 (50.1)	2.8 (2.9)		10.1 (11.1)	N: 1.2 (1.2)
$Na[Nb_2Br_3(CO)_8]$			33.4 (33.3)	35.4 (35.6)	
$Na[Nb_2I_3(CO)_8]$			27.1 (27.5)	46.1 (46.8)	
$Na[Nb_2(O_2CMe)_3(CO)_8]$	27.6 (27.5)	2.0 (1.5)			
$Na[Nb_2(OMe)_3(CO)_8]$			42.3 (42.6)		
$[H(thf)_2][Ta_2Cl_3(CO)_8]$	22.7 (22.9)	1.9 (2.0)	26.2 (26.7)	8.4 (8.5)	
$[N(PPh_3)_2][Ta_2Cl_3(CO)_8]$	42.1 (42.9)	2.5 (2.5)			N: 1.2 (1.3)

(*b*) Arene complexes

	Analysis^a (%)	
	CO	Halogen^b
$[Nb(\eta^6\text{-}C_6H_4Me_2\text{-}p)(CO)_4][Al_2Br_6Cl]$	13.0 (12.7)	56.8 (58.5)
$[Nb(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_4][Al_2Br_6Cl]$	12.6 (12.6)	56.9 (57.6)
$[Nb(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)(CO)_4][Al_2Br_6Cl]$	12.6 (12.3)	55.3 (56.7)
$[Nb(\eta^6\text{-}C_6Me_6)(CO)_4][Al_2Br_6Cl]$	11.8 (12.0)	54.2 (55.0)
$[Ta(\eta^6\text{-}C_6H_5Me)(CO)_4][Al_2Br_6Cl]$	11.4 (11.7)	54.0 (54.0)
$[Ta(\eta^6\text{-}C_6H_4Me_2\text{-}p)(CO)_4][Al_2Br_6Cl]$	11.5 (11.6)	51.7 (53.2)
$[Ta(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_4][Al_2Br_6Cl]$	11.3 (11.4)	50.9 (52.4)
$[Ta(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)(CO)_4][Al_2Br_6Cl]$	11.1 (11.2)	50.9 (51.7)
$[Ta(\eta^6\text{-}C_6Me_6)(CO)_4][Al_2Br_6Cl]$	10.9 (10.9)	50.2 (50.3)

[a] Calculated values are given in parentheses. [b] $\dfrac{100 \times \text{Equivalents of halogen } (6 \times 79.9 + 35.45)}{7 \times \text{g of sample}}$.

or HI. The i.r. spectrum in the carbonyl stretching region is reported in Table 2. Attempts to isolate the compound by partial evaporation of the solvent under reduced pressure failed, due to interaction of the octacarbonyl complex with thf, presumably *via* CO dissociation.

(*b*) *Oxidation of* $[Nb(CO)_6]^-$ *by Halogens: preparation of* $Na[Nb_2X_3(CO)_8]$ (X = Cl, Br, *or* I). A solution of $PhI{\cdot}Cl_2$[7] (0.210 g, 0.76 mmol) in thf (30 cm^3) was treated at *ca.* −60 °C with $Na[Nb(CO)_6]{\cdot}1.8thf$ (0.302 g, 0.74 mmol). By warming up to room temperature, a brown-orange suspension was obtained, which was stirred for *ca.* 10 min and then filtered. Partial evaporation of the solvent under reduced pressure and addition of n-heptane (30 cm^3) gave an orange-brown solid, which was collected by filtration and dried *in vacuo* (23% yield), and identified by its i.r. spectrum and elemental analysis as $Na[Nb_2Cl_3(CO)_8]{\cdot}0.4thf$. The similar treatment of $Na[Ta(CO)_6]{\cdot}1.7thf$ (0.438 g, 0.88 mmol), suspended in n-pentane (50 cm^3) at −60 °C, with $PhI{\cdot}Cl_2$ (0.260 g, 0.95 mmol) gave a brown suspension after stirring for 20 h at room temperature. The solid was filtered off and its i.r. spectrum in dichloromethane solution showed the bands (2 013m and 1 891vs cm^{-1}) typical of the $[Ta_2Cl_3(CO)_8]^-$ anion (see Table 2).

The hexacarbonylniobate(1−) anion, as $Na[Nb(CO)_6]{\cdot}1.9thf$ (0.555 g, 1.32 mmol), was suspended in n-pentane (50 cm^3) and treated dropwise with bromine (1.41 mmol) dissolved in the same solvent (25 cm^3) at about −78 °C. The colour of the suspension changed rapidly from yellow to brown. The solvent was removed under reduced pressure and the brown residue was treated with dichloromethane to dissolve the dimeric $Na[Nb_2Br_3(CO)_8]$. After filtration and reduction to small volume, the dimeric complex was precipitated by addition of n-heptane, and dried *in vacuo* (35% yield). The compound was identified spectroscopically and analytically (Br, CO). By operating in the same manner with I_2 in n-pentane, the dimer $Na[Nb_2I_3(CO)_8]$ was obtained in 39% yield and identified spectroscopically and analytically (I, CO).

Preparation of Bis(triphenylphosphine)iminium Derivatives of the $[M_2Cl_3(CO)_8]^-$ (M = Nb *or* Ta) *Anions.*—The sodium derivative $[Na(thf)_2][Nb_2Cl_3(CO)_8]$ (0.40 g, 0.58 mmol) dissolved in dichloromethane (10 cm^3) was treated with 0.401 g (0.70 mmol) of $[N(PPh_3)_2]Cl$. The brown-orange solution was stirred for *ca.* 30 min and then, after partial evaporation of the solvent under reduced pressure, diethyl ether was added to precipitate the orange-brown $[N(PPh_3)_2]^+$ derivative, which was collected by filtration and dried *in vacuo* (0.43 g, 70% yield).

The tantalum derivative was similarly obtained by treatment of $[H(thf)_2][Ta_2Cl_3(CO)_8]$ with the stoicheiometric amount of $[N(PPh_3)_2]Cl$ in dichloromethane (76% yield).

Collection and Reduction of X-Ray Data for the Complex $[H(thf)_2][Nb_2Cl_3(CO)_8]$.—A crystal of approximate dimensions 0.31 × 0.23 × 0.15 mm was sealed in a glass capillary under argon and mounted on a Philips PW 1 100 four-cycle automatic diffractometer. The crystals are triclinic, $C_{16}H_{17}Cl_3Nb_2O_{10}$ M = 661.5; lattice parameters, as resulting from the least-squares method applied to the angular setting values of 25 reflections, are a = 16.283(3), b = 9.293(2), c = 9.050(2) Å, α = 113.01(2), β = 96.56(2), γ = 98.39(2)°, U = 1 224.7 Å^3, $F(000)$ = 652. The space group $P\bar{1}$, assumed on the basis of the intensity statistics, was later confirmed by the structural analysis. A cell content of two formula units yielded a calculated density of 1.792 g cm^{-3}; experimental measurement of the density was not possible due to the low stability of the compound towards air and moisture.

The intensity data were measured with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Scans of 1.6°(ω) were made in the ω–2θ mode, at a speed of 0.05° s^{-1}. A periodic

Table 2. Infrared spectroscopic data for metal(I) complexes of Group 5A in the carbonyl stretching region

(*a*) $M'[M_2X_3(CO)_8]$ complexes

			$\nu_{CO}/cm^{-1\,a}$	
M′	X	Medium	M = Nb	M = Ta
H	Cl	Toluene	2 023, 1 910	2 010, 1 895
H	Cl	Et_2O	2 007, 1 907	2 005, 1 892
H	Cl	thf	2 014, 1 904	*b*
H	Cl	CH_2Cl_2	2 015, 1 910	2 014, 1 895
H	Cl	H_2O	—	2 017, 1 890
H	Cl	Acetone	—	2 000, 1 870
Na	Cl	Toluene	2 023, 1 910	—
Na	Cl	Et_2O	2 008, 1 907	—
Na	Cl	thf	2 007, 1 906	*b*
Na	Cl	CH_2Cl_2	2 017, 1 909	—
Na	Cl	H_2O	2 022, 1 902	—
Na	Br	Toluene	2 022, 1 913	—
Na	Br	Et_2O	2 019, 1 912	—
Na	Br	thf	2 019m, 1 924w, 1 888vs	—
Na	Br	CH_2Cl_2	2 023, 1 909	—
Na	I	Toluene	2 020, 1 913	—
Na	I	Et_2O	2 018, 1 913	—
Na	I	thf	2 014m, 1 930w, 1 895vs	—
Na	I	CH_2Cl_2	2 016, 1 907	—
$N(PPh_3)_2{}^c$	Cl	Et_2O	2 012, 1 910	2 005, 1 895
$N(PPh_3)_2$	Cl	thf	2 007, 1 904	*b*
$N(PPh_3)_2$	Cl	CH_2Cl_2	2 012, 1 912	2 010, 1 893
$N(PPh_3)_2$	Cl	Acetone	—	2 000, 1 874
Na	O_2CMe	thf	2 008, 1 879	—
Na	O_2CMe	CH_2Cl_2	2 015, 1 892	—
Na	O_2CMe	$(C_2ClF_3)_n$	2 010, 1 873	—
Na	OMe	thf	1 987, 1 862	—
Na	OMe	Acetone	1 988, 1 863	—

(*b*) $[M(\eta^5\text{-}C_5H_5)(CO)_4]^c$

M = V	M = Nb	M = Ta
2 027, 1 933	2 031, 1 935	2 025, 1 922

(*c*) $[M(\eta^6\text{-arene})(CO)_4][Al_2Br_6Cl]^d$

Arene	M = V	M = Nb	M = Ta
C_6H_5Me	—	2 073, 1 992^e	2 069, 1 981
$C_6H_4Me_2$-*p*	—	2 071, 1 990	2 069, 1 980
$C_6H_3Me_3$-1,3,5	2 065, 1 986^f	2 068, 1 984	2 063, 1 974
$C_6H_2Me_4$-1,2,4,5	2 063, 1 987^f	2 065, 1 982	2 061, 1 972
C_6Me_6	2 062, 1 989^f	2 057, 1 973	2 055, 1 964

[a] The relative intensities of the two bands are medium and very strong respectively. [b] The complex reacts with the medium. [c] In n-heptane. [d] In dichloromethane, in CaF_2 cells. [e] Not isolated. [f] As $[V(CO)_6]^-$ derivative.

check of three standard reflections showed no significant intensity variation. A total of 2 271 independent reflections were measured in the range $2 \leqslant \theta \leqslant 20°$; 506 reflections having $I \leqslant 3\sigma(I)$ were rejected.* 1 765 Reflections were corrected for Lorentz-polarisation and absorption effects and used in subsequent calculations. The absorption correction (μ = 12.2 cm^{-1} for Mo-K_α) was applied according to a semiempirical method[8] based on the ψ scans of some reflections; correction factors on the intensity were in the range 1.00—1.35.

The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares program of the SHELX-76 package.[9] The C–O carbonyl distance was constrained to 1.16 ± 0.03 Å. Anisotropic thermal parameters were refined for Nb, Cl, and carbonyl oxygens. The H atoms of thf were introduced at calculated positions and were refined maintaining the geometry of the methylene groups (C–H 1.08 Å). Their common isotropic thermal parameter refined to U = 0.16(1) Å^2. In the final stages of the refinement (when R = 0.05), a difference Fourier map revealed a residual electronic density maximum of 1.5 e Å^{-3}, located at *ca.* 1 Å from the oxygen atom of a thf unit. This position was assigned to the residual H atom of the chemical formula, and its contribution was included in the calculation of the last cycle, by constraining the O–H distance to 1.00 ± 0.05 Å. The final R value [$R = \Sigma(F_o - F_c)/\Sigma F_o$] decreased to 0.046 for 1 765 reflections and 191 parameters {R' = 0.059; the quantity minimised in the least-squares refinement was $\Sigma w(F_o - F_c)^2$, where $w = 1/[\sigma(F_o) + aF^2]$; a assumed the value 0.0308 in the last cycle}. The maximum residual density on the difference map was 0.7 e Å^{-3}. Atomic scattering factors corrected for real and imaginary parts of anomalous dispersion were taken from the library of the SHELX-76 system of programs for Cl, O, C, and H, and from ref. 10 for Nb. Table 3 gives the fractional atomic co-

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* Standard deviations on intensities were computed as $\sigma(I) = [P + 0.25(T_P/T_B)^2(B_1 + B_2) + (0.02I)^2]^{\frac{1}{2}}$, where P is the total peak count in a scan of time T_P, B_1 and B_2 are the background counts each in a time T_B, and I is the intensity, equal to $P - 0.5(T_P/T_B)(B_1 + B_2)$.

Table 3. Fractional atomic co-ordinates for non-hydrogen atoms of $[H(thf)_2][Nb_2Cl_3(CO)_8]$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Nb(1)	0.2262(1)	1.2441(1)	0.2046(1)
Nb(2)	0.2714(1)	0.9093(1)	−0.1294(1)
Cl(1)	0.2681(1)	0.9758(1)	0.1775(1)
Cl(2)	0.1385(1)	1.0365(1)	−0.0800(1)
Cl(3)	0.3368(1)	1.2137(1)	0.0160(1)
O(1)	0.2087(1)	1.2543(11)	0.5560(10)
O(2)	0.0423(1)	1.2970(11)	0.2747(11)
O(3)	0.3607(1)	1.5381(10)	0.4862(12)
O(4)	0.2004(1)	1.5731(11)	0.1922(13)
O(5)	0.2951(1)	0.5763(11)	−0.1210(11)
O(6)	0.1359(1)	0.6170(11)	−0.4120(11)
O(7)	0.2946(1)	0.8969(13)	−0.4833(10)
O(8)	0.4560(1)	0.8539(14)	−0.1902(12)
C(1)	0.2139(1)	1.2504(13)	0.4275(15)
C(2)	0.1070(1)	1.2767(13)	0.2498(14)
C(3)	0.3130(1)	1.4298(15)	0.3853(14)
C(4)	0.2067(1)	1.4518(15)	0.1905(14)
C(5)	0.2849(1)	0.6981(15)	−0.1251(14)
C(6)	0.1817(1)	0.7220(15)	−0.3094(15)
C(7)	0.2845(1)	0.9043(14)	−0.3559(15)
C(8)	0.3921(1)	0.8759(15)	−0.1635(15)
O(9)	−0.0188(1)	0.6241(10)	0.0732(11)
C(9)	0.0490(1)	0.7658(14)	0.1218(14)
C(10)	0.0589(11)	0.8533(20)	0.2993(20)
C(11)	−0.0096(13)	0.7724(24)	0.3527(25)
C(12)	−0.0545(10)	0.6272(20)	0.2143(19)
O(10)	0.4893(10)	0.8667(17)	0.4297(18)
C(13)	0.5505(10)	0.7711(18)	0.4498(18)
C(14)	0.5347(11)	0.6368(21)	0.2844(21)
C(15)	0.4737(1)	0.6500(18)	0.1724(18)
C(16)	0.4442(11)	0.7964(22)	0.2539(21)

Table 4. Relevant bond distances (Å) and angles (°) in $[H(thf)_2]$-$[Nb_2Cl_3(CO)_8]$ with estimated standard deviations in parentheses

Nb(1)–Cl(1)	2.608(3)	Nb(1)–C(2)	2.069(11)
Nb(1)–Cl(2)	2.620(3)	Nb(1)–C(3)	2.051(12)
Nb(1)–Cl(3)	2.592(3)	Nb(1)–C(4)	2.050(12)
Nb(2)–Cl(1)	2.607(3)	Nb(2)–C(5)	2.028(12)
Nb(2)–Cl(2)	2.614(3)	Nb(2)–C(6)	2.077(12)
Nb(2)–Cl(3)	2.600(3)	Nb(2)–C(7)	2.069(12)
Nb(1)–C(1)	2.021(21)	Nb(2)–C(8)	2.073(12)
Cl(1)–Nb(1)–Cl(2)	76.4(1)	Cl(1)–Nb(2)–Cl(2)	76.5(1)
Cl(1)–Nb(1)–Cl(3)	76.9(1)	Cl(1)–Nb(2)–Cl(3)	76.8(1)
Cl(2)–Nb(1)–Cl(3)	77.2(1)	Cl(2)–Nb(2)–Cl(3)	77.2(1)
C(1)–Nb(1)–Cl(3)	79.6(3)	C(5)–Nb(2)–Cl(1)	80.1(3)
C(1)–Nb(1)–Cl(2)	127.3(3)	C(5)–Nb(2)–Cl(2)	126.1(3)
C(1)–Nb(1)–Cl(3)	140.1(3)	C(5)–Nb(2)–Cl(3)	141.7(3)
C(1)–Nb(1)–C(2)	69.6(4)	C(5)–Nb(2)–C(6)	69.2(4)
C(1)–Nb(1)–C(3)	69.3(4)	C(5)–Nb(2)–C(7)	109.6(5)
C(1)–Nb(1)–C(4)	110.7(4)	C(5)–Nb(2)–C(8)	70.9(5)
C(2)–Nb(1)–Cl(1)	118.5(3)	C(6)–Nb(2)–Cl(1)	119.5(3)
C(2)–Nb(1)–Cl(2)	82.0(3)	C(6)–Nb(2)–Cl(2)	81.5(3)
C(2)–Nb(1)–Cl(3)	150.3(3)	C(6)–Nb(2)–Cl(3)	149.1(3)
C(2)–Nb(1)–C(3)	107.8(4)	C(6)–Nb(2)–C(7)	70.6(4)
C(2)–Nb(1)–C(4)	70.7(4)	C(6)–Nb(2)–C(8)	110.2(5)
C(3)–Nb(1)–Cl(1)	108.8(3)	C(7)–Nb(2)–Cl(1)	168.6(3)
C(3)–Nb(1)–Cl(2)	163.4(3)	C(7)–Nb(2)–Cl(2)	101.1(3)
C(3)–Nb(1)–Cl(3)	88.5(3)	C(7)–Nb(2)–Cl(3)	91.8(3)
C(3)–Nb(1)–C(4)	72.1(4)	C(7)–Nb(2)–C(8)	72.3(4)
C(4)–Nb(1)–Cl(1)	168.7(3)	C(8)–Nb(2)–Cl(1)	106.7(3)
C(4)–Nb(1)–Cl(2)	99.6(3)	C(8)–Nb(2)–Cl(2)	162.7(3)
C(4)–Nb(1)–Cl(3)	91.9(3)	C(8)–Nb(2)–Cl(3)	86.9(3)
Nb(1)–Cl(1)–Nb(2)	88.2(1)	Nb(1)–C(1)–O(1)	179(1)
Nb(1)–Cl(2)–Nb(2)	87.8(1)	Nb(1)–C(2)–O(2)	179(1)
Nb(1)–Cl(3)–Nb(2)	88.8(1)	Nb(1)–C(3)–O(3)	178(1)
		Nb(1)–C(4)–O(4)	175(1)
		Nb(2)–C(5)–O(5)	178(1)
		Nb(2)–C(6)–O(6)	176(1)
		Nb(2)–C(7)–O(7)	177(1)
		Nb(2)–C(8)–O(8)	176(1)

ordinates with estimated standard deviations. Relevant interatomic bond distances and bond angles are in Table 4. The Figure shows the $[Nb_2Cl_3(CO)_8]^-$ anion with the atom numbering scheme used.

Preparation of the μ-*Acetato Derivative*, $Na[Nb_2(O_2CMe)_3(CO)_8]$.—The sodium derivative $[Na(thf)_2][Nb_2Cl_3(CO)_8]$ (0.158 g, 0.23 mmol) was treated with an aqueous HO_2CMe–O_2CMe^- buffer solution (2 mol dm^{-3}, 5 cm^3). Dissolution with partial decomposition (CO evolution) was observed. The aqueous solution was extracted with diethyl ether and the ether layer was evaporated to dryness. The solid residue was dissolved in thf (3 cm^3) and the acetato-complex, which was then precipitated by addition of n-heptane (50 cm^3), was collected by filtration and dried *in vacuo* (30% yield). Carboxylic vibrations were observed in $(C_2ClF_3)_n$ at 1 556 and 1 466 cm^{-1}.

Preparation of the μ-*Methoxo Derivative*, $Na[Nb_2(OMe)_3(CO)_8]$.—The μ-Cl derivative $[H(thf)_2][Nb_2Cl_3(CO)_8]$ (0.410 g, 0.62 mmol) was treated at *ca.* −50 °C with sodium methoxide (0.171 g, 3.17 mmol) in thf (50 cm^3). The colour changed from brown-yellow to red and after *ca.* 30 min the reaction was over. The reaction mixture was filtered at room temperature, the solution was concentrated to *ca.* 10 cm^3 by evaporation under reduced pressure, and n-heptane (30 cm^3) was added to precipitate the μ-methoxo-derivative, which was collected by filtration and dried *in vacuo* (0.232 g, 71% yield). Analytical and spectroscopic data are in Tables 1 and 2, respectively.

Reduction of $[M_2Cl_3(CO)_8]^-$ *with Sodium.*—The sodium derivative $[Na(thf)_2][Nb_2Cl_3(CO)_8]$ (0.308 g, 0.45 mmol) dissolved in thf (50 cm^3) was treated with sodium sand (0.052 g, 2.2 mmol) under an argon atmosphere. Within a few minutes a yellow solution was formed, together with some black solid. The latter was filtered off and from the solution sodium hexacarbonylniobate(1 −) was obtained in 69% yield, after concentration and cooling to dry-ice temperature, followed by filtration and drying *in vacuo*.

In the case of the corresponding tantalum derivative, $[H(thf)_2][Ta_2Cl_3(CO)_8]$, the reaction occurred similarly and the hexacarbonyltantalate(1 −) was isolated in 80% yield, by operating under an atmosphere of carbon monoxide. The reduction in the case of niobium was shown to operate under carbon monoxide, with increased yields with respect to those obtained under argon.

Reaction of $[M_2Cl_3(CO)_8]^-$ *with Lithium Cyclopentadienide.*—The sodium derivative $[Na(thf)_2][Nb_2Cl_3(CO)_8]$ (0.832 g, 1.22 mmol) in thf (50 cm^3) was treated at 0 °C with lithium cyclopentadienide (0.342 g, 4.75 mmol) under an argon atmosphere and the resulting solution was stirred for *ca.* 1 h, while the temperature was slowly raised. After evaporation of the solvent under reduced pressure, the residue was sublimed at 105 °C (*ca.* 10^{-2} mmHg) obtaining 0.60 g (92% yield) of $[Nb(\eta^5-C_5H_5)(CO)_4]$.

The corresponding tantalum derivative $[Ta(\eta^5-C_5H_5)$-

$(CO)_4]$ was similarly obtained in 80% yield by sublimation of the solid residue from the treatment of $[H(thf)_2][Ta_2Cl_3(CO)_8]$ with $Li(C_5H_5)$ in a 20% excess with respect to the required stoicheiometry. The i.r. data in the carbonyl stretching region of the $[M(\eta^5\text{-}C_5H_5)(CO)_4]$ complexes are in Table 2.

Preparation of the $[M(CO)_4(\eta^6\text{-arene})]^+$ (M = Nb *or* Ta) *Cations*.—The cations were prepared from the $[M_2Cl_3(CO)_8]^-$ anions by reaction with $AlBr_3$ in the neat aromatic hydrocarbon, or in dichloromethane as solvent in the case of solid aromatic hydrocarbons, at room temperature.

(*a*) *Neat aromatic hydrocarbon.* The octacarbonyl derivative of niobium(I), $[H(thf)_2][Nb_2Cl_3(CO)_8]$ (0.618 g, 0.93 mmol) was reacted with 1,3,5-trimethylbenzene (30 cm^3) under carbon monoxide at atmospheric pressure in the presence of $AlBr_3$ (1.534 g, 5.75 mmol). The colour of the suspension became rapidly dark upon mixing the reagents and an oily brown layer separated out. The mixture was stirred overnight at room temperature, then filtered, and the solid product on the filter was washed with the aromatic hydrocarbon. It was then dissolved in dichloromethane (50 cm^3); the solution, after filtration, was concentrated to small volume (10 cm^3) by evaporation under reduced pressure and n-heptane (*ca.* 50 cm^3) was added to complete the precipitation of the red arene complex. The latter was recovered by filtration and drying *in vacuo* (32% yield). The preparations of the *p*-xylene derivative (M = Nb) and of the toluene, *p*-xylene, and 1,3,5-trimethylbenzene (M = Ta) complexes (see Table 1) were carried out similarly.

(*b*) *In dichloromethane solution.* The niobium derivative $[H(thf)_2][Nb_2Cl_3(CO)_8]$ (0.680 g, 1.03 mmol) dissolved in dichloromethane (50 cm^3) was treated at 0 °C with $AlBr_3$ (1.49 g, 5.58 mmol) and 1,2,4,5-tetramethylbenzene (1.79 g, 13.4 mmol). The temperature was slowly allowed to rise, and after *ca.* 30 min at room temperature the i.r. spectrum of the solution did not show any absorption due to the starting niobium derivative. The red arene complex (only partially soluble in dichloromethane) was present as a precipitate; the latter was filtered off, washed with dichloromethane, and dried *in vacuo* (58% yield). By similar procedures were prepared the 1,2,4,5-tetramethyl- (M = Ta) and hexamethyl-benzene derivatives (M = Nb or Ta) reported in Tables 1 and 2.

The arene complexes are very sensitive to both air and moisture. They have little solubility in saturated hydrocarbons, and with aromatic hydrocarbons they usually give a bilayer system; they are slightly soluble in halogenated solvents but the less methyl-substituted derivatives rapidly react with them. Thermal decomposition occurred more easily as the degree of methyl substitution on the ring decreased. The 1,3,5-trimethylbenzene derivative $[Nb(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_4][Al_2Br_6Cl]$ was heated at *ca.* 70 °C (*ca.* 10^{-2} mmHg): rapid decomposition took place under these conditions, and the aromatic hydrocarbon was recognised as one of the volatile products by i.r. spectroscopy.

Arene Exchange Reactions.—Due to the low solubility of the complexes in other solvents, the exchange reaction of the arene derivatives was studied in dichloromethane: competitive reaction with the solvent was generally present, except in the case of the more stable hexamethylbenzene complex. The 1,3,5-trimethylbenzene–niobium complex (0.121 g, 0.135 mmol) was dissolved in dichloromethane (10 cm^3) and hexamethylbenzene (0.220 g, 1.36 mmol) was added to the solution, while the temperature of the stirred solution was maintained at 20.0 °C in the dark. After 5 h, the i.r. carbonyl bands of the starting complex had completely disappeared and the new bands of the hexamethylbenzene derivative had appeared (see Table 2). The newly formed hexamethylbenzene complex was precipitated by addition of n-heptane and found to analyse correctly for the formulation expected, namely $[Nb(\eta^6\text{-}C_6Me_6)(CO)_4][Al_2Br_6Cl]$.

Results and Discussion

This paper deals with the treatment of the hexacarbonylmetalates(1 –) of niobium and tantalum with protons and with the discovery that they undergo a two-electron oxidation to carbonyl derivatives of niobium(I) and tantalum(I), equation (1). Carbonylmetalates may perform, at least in principle,

$$2[M(CO)_6]^- + 4H^+ + 3Cl^- \longrightarrow 2H_2 + 4CO + [M_2Cl_3(CO)_8]^- \quad (1)$$

several modes of reactivity with protons, as follows. (*a*) Attack at the metal with formation of metal carbonyl hydrido-complexes. This is normally the case of complexes containing strong metal–hydrogen bonds with weak acidity in water,[5] such as $[MnH(CO)_5]$ being prepared by protonation[11] of $[Mn(CO)_5]^-$. (*b*) Base-catalysed proton transfer, such as in the case of the acidification of $[Co(CO)_4]^-$ and $[V(CO)_6]^-$, in the presence of nitrogen bases[12] or water,[5] to give $[NHR_3]^+[Co(CO)_4]^-$ and $[H_3O]^+[V(CO)_6]^-$, respectively. This is typical of protonated carbonylmetalates behaving as strong acids in water. In this connection, it is interesting to note that $[MnH(CO)_5]$ in hydrocarbon solution is unaffected by tertiary amines,[13] contrary to $[CoH(CO)_4]$.[12] (*c*) One-electron transfer to proton, such as in the protonation of $[V(CO)_6]^-$ with dry HCl in anhydrous ethers or hydrocarbon solvents, under which conditions H_2 and $[V(CO)_6]$ are the products.[5] (*d*) Protonation of the carbonyl oxygen, especially in the case of triply bridging[14] or doubly bridging[15] carbonyl groups. (*e*) Protonation of the carbonyl carbon to give a formyl group, M–C(O)H, a case still unobserved.

Reaction (1) was carried out both under anhydrous conditions and in aqueous solution, making sure that the pH was not too low. An appropriate medium is a 1 mol dm^{-3} solution of pyridine and HCl (1 : 1) (hydrolytic pH corresponding to 2.7 pH units).

Strictly connected with the problem of the two-electron transfer process is the lability of the intermediate arising from the primary attack of the proton to $[M(CO)_6]^-$. It has already been pointed out in earlier publications[5] that acidification of anhydrous and solvent-free $Na[V(CO)_6]$ leads to the formation of a thermally unstable precursor to $[V(CO)_6]$, $\{C_6HO_6V\}$, which rapidly evolves dihydrogen, according to equation (2).

$$\{C_6HO_6V\} \longrightarrow \tfrac{1}{2}H_2 + [V(CO)_6] \quad (2)$$

In the case of niobium and tantalum, the second electron transfer to proton is presumably taking place from a hydrido-complex (not isolated or even observed) reacting with HCl, equations (3) and (4). The main difference between the vanadium system and niobium and tantalum is that, while with vanadium the intermediate arising from the proton attack to $[V(CO)_6]^-$ is not hydridic in nature,[5b] the corresponding products of niobium and tantalum may have a certain hydridic character, such that they undergo fast attack by excess HCl. Consistent with this interpretation is the general qualitative observation[5b] that the stability of metal carbonyl hydrido-complexes increases by descending a vertical sequence of

$$[M(CO)_6]^- + H^+ \longrightarrow \{C_6HO_6M\} \quad (3)$$

$$\{C_6HO_6M\} + HCl \longrightarrow H_2 + \{MCl(CO)_6\} \longrightarrow \text{Products} \quad (4)$$

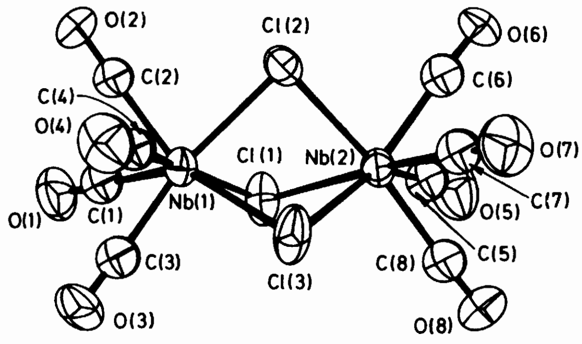

Figure. View of the $[Nb_2Cl_3(CO)_8]^-$ anion along a direction approximately perpendicular to the Nb–Nb vector

elements, although quantitative data concerning this point are still lacking.*

A second method of preparation of the dinuclear anions of niobium(I) and tantalum(I) is the oxidation of the hexacarbonylmetalates with halogens, according to the stoicheiometry of equation (5) (X = Cl, Br, or I). The chloro-carbonyl of

$$2[M(CO)_6]^- + 2X_2 \longrightarrow [M_2X_3(CO)_8]^- + X^- + 4CO \quad (5)$$

niobium(I), $[H(thf)_2][Nb_2Cl_3(CO)_8]$, has been studied by *X*-ray diffraction methods. The Figure shows the molecular structure of the anion. The two niobium atoms of the dimer are bridged through three chlorides located at the vertices of an approximately equilateral triangle, on a plane perpendicular to the Nb–Nb vector. This plane is a nearly perfect mirror plane relating the two halves of the complex. Another pseudo-mirror plane perpendicular to this one passes through Cl(1), two Nb atoms and four carbonyl groups [C(1), C(4), C(5), and C(7) and the oxygen atoms linked to them]. An approximate two-fold axis passing through Cl(1), along the intersection of these planes completes the idealised C_{2v} symmetry assumed by the anion. The Nb$\cdots$Nb non-bonding separation is 3.631(1) Å. The niobium–chloride distances average 2.607 Å, in the range 2.592(3)—2.620(3) Å. The Cl–Nb–Cl angles average 76.8°, in the range 76.4(1)—77.2(1)°. The mean Nb–Cl–Nb angle is 88.3°. Each Nb atom is bonded to four carbonyl groups. The mean niobium–carbon distance is 2.05 Å, in the range 2.02(1)—2.08(1) Å, close to the values found[2,16] in other carbonyl derivatives of niobium. The packing may be described as a stacking of alternate layers of dimers and tetrahydrofuran molecules parallel to the (100) plane.

The i.r. spectra in the carbonyl stretching region (see Table 2) are in agreement with the C_{4v} symmetry of the tetracarbonyl moiety of the dimeric anion, for which two i.r.-active bands ($A_1 + E$) are expected. As mentioned above, the dimeric anion has approximately C_{2v} symmetry, but this should require five bands ($3A_1 + B_1 + B_2$), thus suggesting that coupling of the vibrations along the chloride bridges is virtually non-existent.

The halide bridge of the niobium dimer can be substituted by other bridging ligands (Y), such as O_2CMe and OMe, equation (6). Based on the i.r. spectra in solution (see Table 2), the same

$$[Nb_2X_3(CO)_8]^- + Y^- \longrightarrow X^- + [Nb_2Y_3(CO)_8]^- \quad (6)$$

overall geometry as that of the halide complexes is assigned to these compounds.

The niobium(I) dinuclear compounds appear to be more stable than the corresponding tantalum derivatives. Yields of the latter are usually lower and carbonyl substitution was noted in solvents such as tetrahydrofuran. Spectral changes in the carbonyl stretching region were observed under argon for $[Ta_2Cl_3(CO)_8]^-$ in thf, which could be reversed, although incompletely, under carbon monoxide.

The halide complexes of niobium(I) and tantalum(I) are readily reduced by sodium in thf to give the hexacarbonylmetalate, equation (7). The tendency to form the hexacarbonylmetalate under these conditions is so high that even in the absence of CO, ligand redistribution occurred with partial decomposition to unidentified low-valent metal complexes, $[NbL_n]^-$, equation (8).

$$[M_2X_3(CO)_8]^- + 4Na + 4CO \longrightarrow 2Na[M(CO)_6] + 2NaX + X^- \quad (7)$$

$$3[Nb_2X_3(CO)_8]^- + 12Na \xrightarrow{nL} 4Na[Nb(CO)_6] + 8NaX + X^- + 2[NbL_n]^- \quad (8)$$

The niobium(I) and tantalum(I) halide derivatives are the first halide carbonyl complexes of Group 5A elements to be reported in the literature and they are useful for the preparation of other complexes of these metals. The halide ligands can be displaced, for example, by the cyclopentadienide anion and the corresponding η^5-C_5H_5 complexes were obtained, equation (9).

$$[M_2X_3(CO)_8]^- + 2C_5H_5^- \longrightarrow 3X^- + 2[M(\eta^5\text{-}C_5H_5)(CO)_4] \quad (9)$$

The η^5-cyclopentadienyl derivatives are usually prepared[3,4] by the reductive carbonylation at high temperature and pressure of halide–cyclopentadienyl complexes in good (Nb) or moderate (Ta) yields. Since the hexacarbonylniobate(1–) anion can be prepared at atmospheric pressure of CO and room temperature, reaction (9) can be suggested as an alternative route to the cyclopentadienyl derivative. The i.r. spectra of the $[M(\eta^5\text{-}C_5H_5)(CO)_4]$ complexes (Table 2) show that the three η^5-cyclopentadienyl derivatives are isostructural with a C_{4v} local symmetry ($A_1 + E$) of the four carbonyl groups. The crystal and molecular structure of $[V(\eta^5\text{-}C_5H_5)(CO)_4]$ has appeared.[17] Moreover, the wavenumber values of the carbonyl stretching vibrations decrease in the sequence Nb > V > Ta. This is typical of families of compounds in a vertical sequence of metals, in which the 4*d* element is believed to have the lowest degree of π back donation.

Halide displacement by aluminium bromide was found to promote the formation of the η^6-arene–tetracarbonyl complexes, equation (10). Comparison of the i.r. spectra of the arene

$$[M_2X_3(CO)_8]^- + 4AlBr_3 + 2(\text{arene}) \longrightarrow 2[M(\eta^6\text{-arene})(CO)_4][Al_2Br_6X] + X^- \quad (10)$$

complexes of the three metals (V, Nb, Ta) shows again that the compounds are isostructural. The crystal and molecular structure of one of the vanadium(I) derivatives was recently

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* Pertinent to this point are the quantitative data concerning deprotonation of metal carbonyl hydrides as a function of the metal in vertical sequences of the Periodic Table: B. V. Lokshin and A. A. Pasinskj, *J. Organomet. Chem.*, 1973, **55**, 315; D. C. Harris and H. B. Gray, *Inorg. Chem.*, 1974, **14**, 1215; A. Nakamura and S. Otsuka, *J. Mol. Catal.*, 1976, **1**, 285; H. W. Walker, C. T. Kresge, P. C. Ford, and R. G. Pearson, *J. Am. Chem. Soc.*, 1979, **101**, 7428; R. F. Jordan and J. R. Norton, *J. Am. Chem. Soc.*, 1982, **104**, 1255; 'Mechanistic Aspects of Inorganic Reactions,' A.C.S. Symposium Series No. 198, 1982, pp. 403—423; R. G. Pearson and P. C. Ford, *Comments Inorg. Chem.*, 1982, **1**, 279; H. W. Walker, R. G. Pearson, and P. C. Ford, *J. Am. Chem. Soc.*, 1983, **105**, 1179.

solved[18] and shown to contain the planar six-membered ring symmetrically bonded to vanadium together with the four carbonyl groups in an arrangement of local C_{4v} symmetry. The i.r. spectra in solution of the niobium and tantalum derivatives are in agreement with this geometry. Again, also in this case, similar to the cyclopentadienyl complexes, the 4*d* element has the highest wavenumber value of the CO stretching vibrations.

While the η^6-arene cationic complexes of vanadium(I) are produced[18,19] by disproportionation of $[V(CO)_6]$, the unavailability of the zero-valent niobium and tantalum carbonyl complexes made the $AlBr_3$–$[M_2X_3(CO)_8]^-$ system the only possible route to the η^6-arene complexes of these metals. The latter complexes show a rather low stability, both thermal and chemical. For example, heating the compounds at *ca.* 70 °C *in vacuo* led to complete decomposition with evolution of CO and arene. The arene ligands are also readily displaced by oxygenated solvents and halide ions: *e.g.* as in equation (11).

$$2[M(\eta^6\text{-arene})(CO)_4]^+ + 3X^- \longrightarrow [M_2X_3(CO)_8]^- + 2(\text{arene}) \quad (11)$$

The formation of the dinuclear halide complexes was observed spectroscopically. The η^6-arene ligands are so labile with respect to their displacement by halides that reaction (11) occurred even during spectral measurements upon contact with the KBr windows of the i.r. cells. The decomposition by the oxygenated solvents is also presumably induced by the X^- anions resulting from the interaction of the solvent with the $[Al_2Br_6Cl]^-$ counteranion of the complexes. Attempts to substitute the $[Al_2Br_6Cl]^-$ anions with others, such as $[BPh_4]^-$, $[PF_6]^-$, or $[V(CO)_6]^-$ failed, because of unfavourable solubility properties of the reagents.

The arene complexes reported in this paper are the first arene–carbonyl complexes of niobium and tantalum to be reported in the literature. However, some η^6-arene derivatives of these metals, both mononuclear and polynuclear have been reported previously, containing one arene per metal atom[20] and two arenes per metal atom.[21] The i.r. data of Table 2 show a decrease of the carbonyl wavenumber values with increasing methyl substitution on the ring. This is a well known[22] phenomenon for η^6-arene carbonyl derivatives of Group 6A metals, which is usually attributed to a higher basicity of the ligand and to a corresponding higher degree of π back donation. Thus, increasing methyl substitution is expected to increase the stability of the complex, which is substantiated by thermochemical measurements on $[M(\eta^6\text{-arene})(CO)_3]$ complexes of Group 6A metals.[23] Consistent with these data, our arene complexes underwent arene exchange, the more methyl-substituted product being favoured, equation (12). Because of

$$[M(\eta^6\text{-arene})(CO)_4]^+ + \text{arene}' \longrightarrow [M(\eta^6\text{-arene}')(CO)_4]^+ + \text{arene} \quad (12)$$

solubility problems, dichloromethane had to be used as solvent of reaction (12) and some decomposition due to the solvent was observed with the less methyl-substituted products. In the case of the more stable trimethyl- and hexamethyl-benzene complexes of niobium, the exchange reaction was exclusively observed and C_6Me_6 was found to displace the trimethylbenzene ligand completely.

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