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Niobium(I) and tantalum(I) tetracarbonyl derivatives containing nitrogen ligands[1]

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Abstract

Diamino derivatives of niobium(l) and tantalum(l) of general formula $MX(CO)_4(NN)$, M = Nb, Ta; X = Cl, 1; NN = ethylendiamine (en), *N,N'*dimethylethylendiamine (dmen), *N,N,N',N'*-tetramethylethylendiamine (tmen), 2,2-dipyridyl (2,2'-dipy), 4,4'-dipyridyl (4,4'-dipy), have been prepared by oxidation of the $[M(CO)_6]^-$ anions with either 1,1'-dimethyl-4,4'-dipyridilium diiodide (methylviologen, mvI_2) in the presence of the diamine or the diprotonated salt of the corresponding diamine, $[(NN)H_2]Cl_2$. Alternatively, these derivatives have been obtained by amine exchange reactions on $[MCl(CO)_4(4,4\text{-dipy})]_n$ or by chloride substitution on the dinuclear anion $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$. The $MX(CO)_4(NN)$ derivatives have been characterized by analytical, spectroscopic and, in the case of $TaI(CO)_4$ (tmen), also by single crystal diffractometry. Crystal data. $TaI(CO)_4$(tmen), monoclinic, space group $P2_1/c$ (No. 14); $a = 16.222$ (5); $b = 12.855$ (3); $c = 16.452$ (6) Å, $\beta = 117.67$ (2)°, $M = 536.10$ g mol^{-1}; $V = 3038.4$ (1) Å^3; $Z = 8$; $D_c = 2.344$ g cm^{-3}; $\lambda = 0.7107$ Å; $T = 203$ K; $\mu = 91.71$ cm^{-1}; $F(000) = 1984$; $R = 0.045$; $Rw = 0.048$.

Keywords: Niobium; Tantalum; Carbonyls; Nitrogen ligands

1. Introduction

The hexacarbonylmetalates(-I) of Group 5 elements, $[M(CO)_6]^-$, M = V, Nb, Ta, were first prepared in the early sixties [1] by carbonylaton of Group 5 metal halides [1,2]; these compounds could, at least in principle, be used as starting materials for preparing the neutral metal carbonyls by oxidation reactions. Up to now, this goal has been achieved only in the case of $V(CO)_6$, see Eq. (1) ([2] a, b, g, i, [3]), the oxidation of $[M(C0)_6]^-$, M = Nb, Ta, being a two-electron transfer reaction to the metal(I) derivatives [4], see Eq. (2). This suggests that niobium(I) and tantalum(I) complexes of nd^4 configuration are particularly stable [5].

$$[V(CO)_6]^- \rightarrow V(CO)_6 + e^- \qquad (1)$$

$$M(\text{-I}) \rightarrow M(I) + 2e^-;\ M = Nb, Ta \qquad (2)$$

Work by several research groups has shown many interesting features of the substituted carbonyl derivatives of general formula $MX(CO)_{4-n}L_n$, M = Nb, Ta, X = halogen, L = isocyanide, tertiary phosphine [6].

At the best of our knowledge, only a few reports deal with carbonyl derivatives of niobium and tantalum containing additional ligands different from tertiary phosphines [7]. Moreover, no carbonyl derivatives of niobium(I) with nitrogen-containing ligands have been reported in the literature. The paucity of data about nitrogen-containing systems of low-valent Group 5 elements, may be related to the lability of the M–N bond when M is in a reduced state (I or lower). As a matter of fact, the use of $[Ta(CO)_5(NH_3)]^-$ has recently provided a convenient and non photolytic route to substi-

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tuted pentacarbonyltantalates(-I) $[Ta(CO)_5(L)]^-$, L = RNC, POR_3, AsR_3, SbR_3 ([7]a) and highly reduced carbonyl derivatives such as $Na_4[M(CO)_4]$, M = Cr, Mo, W, have been obtained by Ellis and coworkers by using the tmen-substituted metal carbonyl derivatives $M(CO)_4(tmen)$ [8].

This paper describes the synthesis of carbonyl derivatives of niobium(I) and tantalum(I) containing nitrogen ligands and reports the first X-ray crystallographic study of an adduct of tantalum(I) with a nitrogen donor ligand.

2. Results and discussion

2.1. Synthetic procedure

2.1.1. Redox reactions

The hexacarbonylmetalates of niobium(-I) and tantalum(-I) react with methylviologen iodide, mvI_2, in toluene in the presence of bidentate nitrogen bases to give the corresponding derivatives of formula $MI(CO)_4(NN)$, Eq. (3), in yields of about 20%.

$$NaM(CO)_6 + 2\ mvI_2 + NN \rightarrow MI(CO)_4(NN) + 2\ mvI + NaI + 2CO;\ M = Nb,\ Ta;\ NN = dmen,\ tmen \qquad (3)$$

The reaction medium is important in determining the yield of reaction (3); no expected organometallics being formed in THF.

By taking into consideration that $NaM(CO)_6$ promptly reacts with mvI_2 ([4]a) to give the $[M_2(\mu\text{-}I)_3(CO)_8]^-$ anions according to Eq. (4) and that $[M_2(\mu\text{-}Cl)_3(CO)_8]^-$ quantitatively gives $MCl(CO)_4(NN)$ by treatment with NN (vide infra),

$$2NaM(CO)_6 + 4\ mvI_2 \rightarrow Na[M_2(\mu\text{-}I)_3(CO)_8] + 4\ mvI + NaI + 4CO;\ M = Nb,\ Ta \qquad (4)$$

the relatively low yields are probably due to a parasitic reaction between the oxidant and the diamine [9], which is much more pronounced in THF than in toluene.

Some of us and other groups have reported the oxidation of the hexacarbonylmetalates of Group 5 elements by HX ([4]a, [10]) or ammonium salts ([4]a, [11]). Accordingly, $TaI(CO)_4(2,2'\text{-dipy})$ was obtained by reaction of $NaTa(CO)_6$ with $(2,2'\text{-dipyH}_2)I_2$ [12], see Eq. (5).

$$NaTa(CO)_6 + (2,2'\text{-dipyH}_2)I_2 \rightarrow TaI(CO)_4(2,2'\text{-dipy}) + H_2 + NaI + 2CO \qquad (5)$$

By this route $TaCl(CO)_4(dmen)$ and $[MCl(CO)_4(4,4'\text{-dipy})]_n$ have been obtained in good yields from $NaM(CO)_6$ and the diprotonated nitrogen bases $(dmenH_2)Cl_2$ or $(4,4'\text{-dipyH}_2)Cl_2$ [see Eqs. (6) and (7)].

$$NaTa(CO)_6 + (dmenH_2)Cl_2 \rightarrow TaCl(CO)_4(dmen) + H_2 + NaCl + 2CO \qquad (6)$$

$$n\ NaM(CO)_6 + n\ (4,4'\text{-dipyH}_2)Cl_2 \rightarrow [MCl(CO)_4(4,4'\text{-dipy})]_n + n\ H_2 + n\ NaCl + 2n\ CO;\ M = Nb,\ Ta \qquad (7)$$

Reactions (6) and (7) are reminiscent of the electron-transfer processes observed for the hexacarbonylmetalates(-I) of vanadium, niobium and tantalum of protonated nitrogen bases ([4]a, [13]). It is therefore conceivable that compounds of general formula $[BH_2][M(CO)_6]_2$ are intermediates in reactions (6) and (7), undergoing the redox process in the presence of the chloride ion and the diamine.

The 4,4′-dipy derivative deserves some comment: due its low solubility and to the nature of the 4,4′-dipy ligand, these compounds are expected to have an oligonuclear nature containing the heterocyclic base as a bridging group, vide infra. Examples of 4,4′-dipy behaving as bridging ligands to give dinuclear [14] or polynuclear [15] species have been reported.

2.1.2. Substitution reactions

$[MCl(CO)_4(4,4'\text{-dipy})]_n$ was considered to be an appropriate starting material for the preparation of other niobium(I) and tantalum(I) derivatives. In fact, it was reckoned that diamines having chelating properties could easily displace the bridging ligand. As shown in Eq. (8), this expectation has been verified, reactions going to completion in a few minutes.

$$[MCl(CO)_4(4,4'\text{-dipy})]_n + nNN \rightarrow nMCl(CO)_4(NN) + n4,4'\text{-dipy};\ M = Nb,\ Ta;\ NN = en,\ dmen,\ tmen,\ 2,2'\text{-dipy} \qquad (8)$$

Another synthetic procedure based on a substitution reaction uses the chloride-bridged dinuclear anion of niobium(I), $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$, as starting material, Eq. (9). Reactions are fast and proceed with quantitative conversion of the starting material into the desired product.

$$Na(THF)_n[Nb_2(\mu\text{-}Cl)_3(CO)_8] + NN \rightarrow 2NbCl(CO)_4(NN) + NaCl + n\ THF;\ NN = en,\ dmen,\ tmen,\ 2,2'\text{-dipy},\ 4,4'\text{-dipy} \qquad (9)$$

It is interesting to note that, at variance with what observed with bidentate phosphines ([4]a), [Eq. (10)], the formation of the dicarbonyl derivative $NbCl(CO)_2(NN)_2$ has never been observed, thus confirming the higher π-donor properties of the phosphorous ligand with respect to the nitrogen one.

Table 1
Infrared spectra (0.1 mm, CaF_2) of $MX(CO)_4(NN)$ in the carbonyl stretching region

$\tilde{\nu}_{CO}$ (cm^{-1})							
THF				Toluene			
en	dmen	tmen	2,2′-dipy	4,4′dipy	dmen	tmen	2,2′-dipy
X = Cl							
M = Nb							
2016m-s		2017s	2019s	2018s			
1920m-s		1909m-s	1935m-s	1925sh			
1883vs		1886vs	1894vs	1893vs			
1875sh		1880sh	1886sh	1884sh			
M = Ta							
2014m-s	2012s		2013s	2012s	2017s	2014s	2015s
1912m-s	1908s		1920m	1904sh	1918s	1918m	1928m
1876vs	1873vs		1883vs	1878vs	1878vs	1873vs	1886vs
1870sh	1868sh		1876sh	1871sh	1871sh	1870sh	1874sh
X = I							
M = Nb							
	2018m-s				2022s	2017s	
	1933m-s				1940m-s	1934s	
	1981vs				1895vs	1893vs	
	1883sh				1880sh	1882sh	
M = Ta							
	2012m-s	2006s	2009s		2016m-s	2013m-s	
	1913m	1913m	1925m		1923m	1922m-s	
	1878s	1875s	1889s		1883s	1880s	
	1866s	1865sh	1881sh		1867s	1871sh	

$$\mathrm{Na(THF)}_n[\mathrm{Nb_2}(\mu\text{-Cl})_3(\mathrm{CO})_8] + 2\mathrm{PP} \rightarrow 2\mathrm{NbCl(CO)_2(PP)_2} + \mathrm{NaCl} + n\mathrm{THF} + 4\mathrm{CO};\ \mathrm{PP} = \mathrm{dmpe,\ dppe} \quad (10)$$

Reactions described by Eqs. (8) and (9) represent the only synthetic pathway to the ethylenediamino-substituted derivatives of niobium(I) and tantalum(I). In fact, these derivatives cannot be prepared by the oxidation routes described in Section 2.1.1, due to the fact that the reaction of the ammonium salt of en [16] with $NaM(CO)_6$ is extremely slow.

2.2. Characterization of the diamino adducts of niobium(I) and tantalum(I)

The infrared spectra of the $MX(CO)_4(NN)$ derivatives are characterized by the absorptions typical of the amine ligand [bands due to the N–H stretching vibrations are observed at 3287, 3240 and 3127 cm^{-1} for $NbCl(CO)_4(en)$, at 3312, 3205 and 3123 cm^{-1} for $TaCl(CO)_4(en)$ and at 3255 and 3220 cm^{-1} for $TaCl(CO)_4(dmen)$]. As far as the carbonyl stretching region is concerned, four absorptions are observed ($3A' + A''$), see Table 1, in agreement with a C_s symmetry of the molecule and with the results of the crystallographic work on $TaI(CO)_4(tmen)$, vide infra.

The positions of the absorption maxima depend on the nature of the diamine and on the metal. In agreement with general experience [17], the bands are shifted to lower wavenumbers on going from niobium to tantalum.

As far as the influence of the amine is concerned, the data reported in Table 1 show an decrease of the $\tilde{\nu}_{CO}$ on going from the aromatic to the aliphatic diamines, suggesting a certain degree of electronic delocalization involving the π-system of the dipyridyl ligand.

Compound $TaI(CO)_4(tmen)$ has been studied by X-ray crystallography [18]. The asymmetric unit contains two independent molecules of similar conformation which significantly differ as far as metal-ligand parameters are concerned [19]. Relevant interatomic distances and angles for both molecules are compiled in Table 2. Fig. 1 shows a PLATON view of the two molecules, and a schematic drawing of the coordination polyhedron of the tantalum atom in molecule **1** is in Fig. 2. The coordination geometry at the metal atom is that of a capped trigonal prism with the iodine atom capping the rectangular face defined by C2, C3, N1 and N2; the Ta–I bond is almost perpendicular to that plane. This type of coordination may be expected to show considerable flexibility, and indeed the angles at the metal subtended by iodine and by the atoms at the capped face sites are different in the two molecules: they comprise values between 76.3 (3) and 88.0 (2)° for molecule **1**, and between 72.4 (2) and 102.6 (3)° for molecule **2**.

Table 2
Selected bond distances (Å) and angles (°) in TaI(CO)$_4$(tmen)

Molecule 1				Molecule 2			
Tal	I1	2.9621(7)		Ta2	I2	2.9513(8)	
Tal	N1	2.394(7)		Ta2	N3	2.426(8)	
Tal	N2	2.450(7)		Ta2	N4	2.396(7)	
Tal	C1	2.05(1)		Ta2	C5	2.07(1)	
Tal	C2	2.047(9)		Ta2	C6	2.06(1)	
Tal	C3	2.064(8)		Ta2	C7	2.06(1)	
Tal	C4	2.041(9)		Ta2	C8	2.04(1)	
O1	C1	1.16(1)		O5	C5	1.13(1)	
O2	C2	1.16(1)		O6	C6	1.16(1)	
O3	C3	1.15(1)		O7	C7	1.15(1)	
O4	C4	1.16(1)		O8	C8	1.16(1)	
N1	C11	1.48(1)		N3	C31	1.51(1)	
N1	C12	1.49(1)		N3	C32	1.50(1)	
N1	C13	1.50(1)		N3	C23	1.50(2)	
N2	C21	1.49(1)		N4	C41	1.49(1)	
N2	C22	1.48(1)		N4	C42	1.49(1)	
N2	C23	1.49(1)		N4	C43	1.50(1)	
C11	C21	1.50(2)		C31	C41	1.50(2)	
I1	Tal	N1	85.4(2)	I2	Ta2	N3	89.6(2)
I1	Tal	N2	88.0(2)	I2	Ta2	N4	85.1(2)
I1	Tal	C1	134.0(3)	I2	Ta2	C5	173.4(3)
I1	Tal	C2	76.3(3)	I2	Ta2	C5	173.4(3)
I1	Tal	C3	87.3(3)	I2	Ta2	C7	102.6(3)
I1	Tal	C4	155.2(3)	I2	Ta2	C8	115.1(3)
N1	Tal	N2	73.7(3)	N3	Ta2	N4	74.3(3)
N1	Tal	C1	133.8(4)	N3	Ta2	C5	88.8(3)
N1	Tal	C2	158.0(3)	N3	Ta2	C6	147.1(4)
N1	Tal	C3	97.1(3)	N3	Ta2	C7	88.8(3)
N1	Tal	C4	85.6(3)	N3	Ta2	C8	144.4(4)
N2	Tal	C1	83.3(3)	N4	Ta2	C5	100.6(3)
N2	Tal	C2	117.0(3)	N4	Ta2	C6	129.1(3)
N2	Tal	C3	170.0(3)	N4	Ta2	C7	161.4(4)
N2	Tal	C4	111.5(3)	N4	Ta2	C8	82.4(3)
C1	Tal	C2	68.1(4)	C5	Ta2	C6	105.9(4)
C1	Tal	C3	106.3(4)	C5	Ta2	C7	71.0(4)
C1	Tal	C4	66.1(4)	C5	Ta2	C8	69.3(4)
C2	Tal	C3	70.2(4)	C6	Ta2	C7	69.5(4)
C2	Tal	C4	106.0(3)	C6	Ta2	C8	68.1(4)
C3	Tal	C4	71.0(4)	C7	Ta2	C8	108.7(4)
Tal	N1	C11	108.2(5)	Ta2	N3	C31	109.7(6)
Tal	N1	C12	113.3(5)	Ta2	N3	C32	111.3(7)
Tal	N1	C13	113.3(6)	Ta2	N3	C33	112.0(8)
C11	N1	C12	106.7(8)	C31	N3	C32	107.(1)
C11	N1	C13	108.5(7)	C31	N3	C33	108.3(9)
C12	N1	C13	106.6(8)	C32	N3	C33	108.(1)
Tal	N2	C21	108.9(6)	Ta2	N4	C41	107.9(6)
Tal	N2	C22	113.2(6)	Ta2	N4	C42	117.0(6)
Tal	N2	C23	112.0(6)	Ta2	N4	C43	110.1(6)
C21	N2	C22	108.3(8)	C41	N4	C42	106.9(8)
C21	N2	C23	108(1)	C41	N4	C43	109.5(8)
C22	N2	C23	107(1)	C42	N4	C43	105.3(8)
Tal	C1	O1	177.(1)	Ta2	C5	O5	176.3(8)
Tal	C2	O2	178.4(8)	Ta2	C6	O6	178.8(8)
Tal	C3	O3	178.9(8)	Ta2	C7	O7	179.(1)
Tal	C4	O4	176.1(8)	Ta2	C8	O8	178.2(8)
N1	C11	C21	109.4(8)	N3	C31	C41	111.0(9)
N2	C21	C11	113.1(8)	N4	C41	C31	111.1(9)

Estimated standard deviations in parentheses refer to the least significant digit.

The major differences between the two independent molecules are observed in the geometry of the M(CO)$_4$ fragment which assumes different orientations with respect to the tmen ligand in the two molecules: in molecule **1** (Fig. 1), the angles N1–Tal–(carbonyl groups) and N2–Tal–(carbonyl groups) are comprised between 83.3 (3) and 170.0 (3)°; on the other hand, in molecule **2**, the angles N3–Ta2–(carbonyl groups) and N4–Ta2–(carbonyl groups) are between 88.8(3) and 161.4 (4)°. Moreover, the Ta–N bond distances are different within each molecule, for example Tal–N1 = 2.394 (7) Å and Tal–N2 = 2.450 (7) Å.

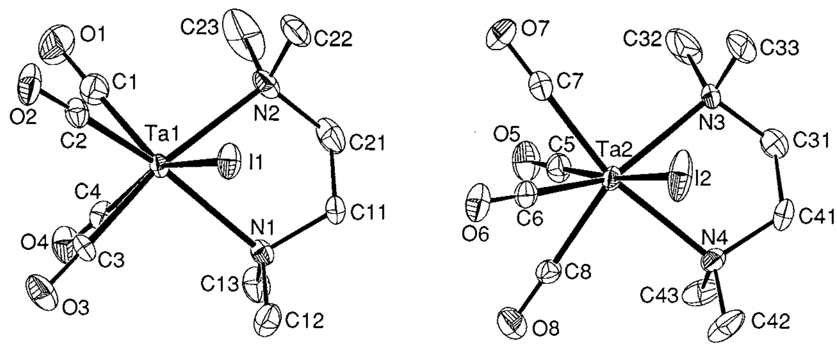
The five-membered ring Ta1–N1–C11–C21–N2 assumes an envelope conformation and is conformationally stable at low temperature; the C11–C12 distance is found to be 1.50 Å which is typical of a C–C single bond [21]. Once the covalent radii of the metals are considered [22], the Ta–N bond distance is rather similar to that observed in other crystallographically studied compounds [23–26]. The Ta–CO bond distances in Ta(CO)$_4$(tmen) should be compared with those observed in other structurally characterized tantalum(I) carbonyl derivatives ([4]a, [27–31]).

Although the structure of TaI(CO)$_4$(tmen) is rather similar to that of TaI(CO)$_4$(dppe) ([4]a), the Ta–I [2.962 (1) Å in TaI(CO)$_4$(tmen) and 2.819 (2) in the phosphino derivative] and the Ta–CO bond distances [2.050 (av.) Å in TaI(CO)$_4$(tmen) and 1.950 (av.) in TaI(CO)$_4$(dppe)] are longer in the amino derivative. Moreover, once the Ta–P distance [2.572 (6) Å, av.] in TaI(CO)$_4$(dppe) is decreased by the covalent radius of phosphorus (1.10 Å) and increased by that of nitrogen (0.70 Å), the resulting separation between the atoms (2.172 Å) is smaller than the Ta–N distance in the amino-carbonyl derivative (2.422 Å, average). These data suggest a lower stability of the amine-containing carbonyl derivatives with respect to the phosphine substituted ones.

3. Conclusions

Diamino derivatives of niobium(I) and tantalum(I) of general formula MX(CO)$_4$(NN), M = Nb, Ta; X = Cl, I; NN = ethylendiamine (en), *N*,*N*′-dimethylethylendiamine (dmen), *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (tmen), 2,2′-dipyridyl (2,2′-dipy), 4,4′-dipyridyl (4,4′-dipy), have been prepared and fully characterized, see Scheme 1.

The similarities observed in the IR carbonyl stretching region (3A′ + A″ symmetry) suggest that the MX(CO)$_4$(NN) derivatives have similar structures, i.e. a capped trigonal prismatic geometry around the metal atom with the halide in the capping position, as verified crystallographically in the case of TaI(CO)$_4$(tmen).



Molecule 1 Molecule 2

Fig. 1. PLATON [20] plot of the molecular structure of the two independent molecules TaI(CO)$_4$(tmen), with the atom numbering used. Ellipsoids are drawn at 30% probability.

4. Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were measured with a Perkin-Elmer FT-1725X instrument on solutions or on nujol and/or polychlorotrifluoroethylene (PCTFE) mulls prepared under rigorous exclusion of moisture and air.

^{1}H-NMR spectra (200 MHz, reference, TMS) were measured with a Varian Gemini 200 BB instrument.

2,2′-dipyridyl (2,2′-dipy), 4,4′-dipyridyl (4,4′-dipy), were used as received. Ethylendiamine, en, *N*,*N*′-dimethylethylendiamine, dmen, *N*,*N*,*N*′,*N*′-tetramethylethylendiamine, tmen, were distilled from sodium at atmospheric pressure. Na(THF)$_n$[M(CO)$_6$], M = Nb, Ta ([2]k), Na(THF)$_n$[Nb$_2$(μ-Cl)$_3$(CO)$_8$] [10], and [4,4′-dipyMe$_2$]I$_2$, mvI$_2$ [32], were prepared according to literature. The ammonium salts of 4,4′-dipy and amen, [4,4′-dipyH$_2$]Cl$_2$ and [dmenH$_2$]Cl$_2$ were prepared by reaction of the diamine with hydrogen chloride in heptane. The colourless solid was filtered, washed with heptane and dried in vacuo.

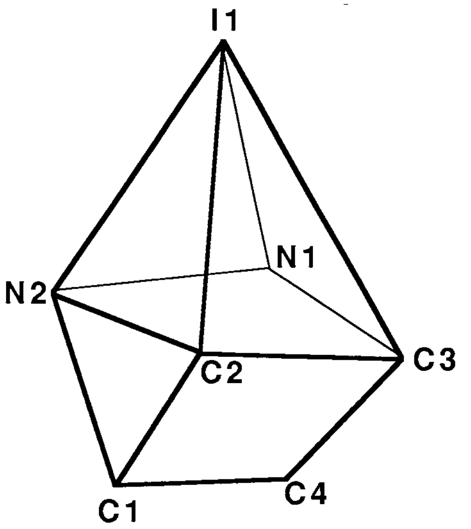


Fig. 2. Schematic representation of the coordination polyhedron of tantalum in TaI(CO)$_4$(tmen), molecule 1.

4.1. Preparation of MX(CO)$_4$(NN) by oxidation of [M(CO)$_6$]$^-$

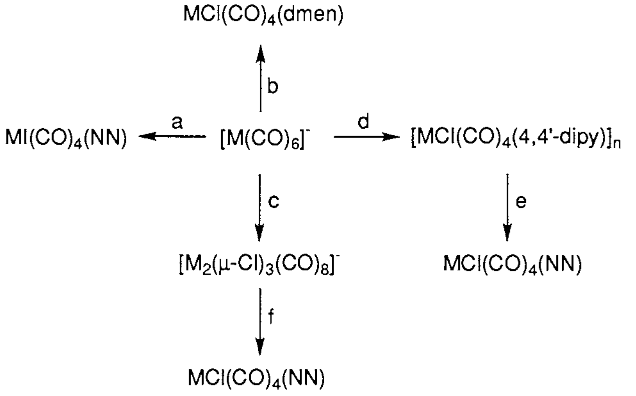
4.1.1. mvI$_2$, NN = dmen, tmen; M = Nb, Ta; X = I

In the following only the preparation of NbI(CO)$_4$(tmen) is described in detail, the other preparations being similar. A suspension of Na(THF)$_{4.2}$ [Nb(CO)$_6$] (0.55 g, 0.94 mmol) in toluene (30 ml) was treated with tmen (0.108 g, 0.93 mmol) and after cooling at ca. − 70°C, solid mvI$_2$ (0.82 g, 1.86 mmol) was added. No reaction was observed. The mixture was allowed to warm to room temperature and evolution of gas and formation of a dark solid in a red–orange solution was observed. After filtration, the volume of the solution was reduced to ca. 2 ml and heptane (10 ml) was added. The brick-red solid was collected by filtration and dried in vacuo at room temperature obtaining 0.089 g (21% yield) of NbI(CO)$_4$(tmen). Anal. Found: C, 26.2; H, 3.4; N, 6.2. Calcd. for C$_{10}$H$_{16}$IN$_2$NbO$_4$: C, 26.8; H, 3.6; N, 6.2%. Solution IR spectra are in Table 1. ^{1}H-NMR (200 MHz, C$_6$D$_6$, 25°C): $\delta = 2.03$(s, 6H), 2.62 (s, 4H).

NbI(CO)$_4$(dmen): 10%, red, Anal. Found: C, 22.3; H, 2.4; N, 6.1. Calcd. for C$_8$H$_{12}$IN$_2$NbO$_4$: C, 22.9; H, 2.9; N, 6.7%. Solution IR spectra are in Table 1.

TaI(CO)$_4$(tmen): 14%, red, Anal. Found: C, 21.7; H, 2.5; N, 4.8. Calcd. for C$_{10}$H$_{16}$IN$_2$O$_4$Ta: C, 22.4; H, 3.0; N, 5.2%. Solution IR spectra are in Table 1.

TaI(CO)$_4$(dmen): the compound was prepared similarly and identified spectroscopically: Solution IR spectra are in Table 1.



[a] NN / mvI$_2$ / toluene; M = Nb, Ta; NN = dmen, tmen; [b] (dmenH$_2$)Cl$_2$ /THF; M = Ta; [c] CuCl / THF; M = Nb; [d] (4,4'-dipyH$_2$)Cl$_2$ /THF; M = Nb, Ta; [e] NN / THF; M = Nb, Ta; NN = en, dmen, tmen, 2,2'-dipy; [f] NN / THF; M = Nb, Ta; NN = en, dmen, tmen, 2,2'-dipy, 4,4'-dipy; .

Scheme 1.

4.1.2. [(NN)H$_2$]Cl$_2$, NN = dmen, M = Ta, X = Cl; NN = 4,4′-dipy, M = Nb, Ta; X = Cl

TaCl(CO)$_4$(dmen): a suspension of Na(THF)$_2$[Ta(CO)$_6$] (1.024 g, 1.98 mmol) in THF (60 ml) was treated at room temperature with [dmenH$_2$]Cl$_2$ (0.391 g, 2.4 mmol). After 5 days stirring at ca. 40°C, the orange suspension was filtered and the volume of the solution was reduced to ca. 2 ml. After addition of heptane (10 ml) the red–orange solid was filtered and dried in vacuo at room temperature affording 0.517 g (63% yield) of TaCl(CO)$_4$ (dmen) as a microcrystalline orange solid. Anal. Found: C, 21.8; H, 2.5; N, 5.9. Calcd. For C$_8$H$_{12}$ClN$_2$O$_4$Ta: C, 23.1; H, 2.9; N, 6.7%. IR (nujol): $\tilde{\nu}$ = 3255m, 3220m-s, 2011vs, 1928s, 1865vs, 1839vs cm^{-1}. Solution IR spectra are in Table 1.

By operating in a similar way the following compounds were isolated:

[NbCl(CO)$_4$(4,4′-dipy)]$_n$ from Na(THF)$_{4.2}$[Nb(CO)$_6$] and [4,4′-dipyH$_2$]Cl$_2$ in THF, 2 h, room temperature, 40% yield, red–brown microcrystalline solid. Anal. Found: C, 42.0; H, 1.9; N, 7.0. Calcd. for C$_{14}$HgClN$_2$NbO$_4$: C, 42.4; H, 2.0; N, 7.1%. Solution IR spectra are in Table 1.

[TaCl(CO)$_4$(4,4′-dipy)]$_n$ from Na(THF)$_2$[Ta(CO)$_6$] and [4,4′-dipyH$_2$]Cl$_2$ in THF, 2 days, room temperature, 38% yield, red–brown microcrystalline solid. Anal. Found: C, 35.9; H, 2.6; N, 5.2. Calcd. for C$_{14}$HgClN$_2$O$_4$Ta: C, 34.7; H, 1.7; N, 5.8%. Solution IR spectra are in Table 1.

4.2. Preparation of MCl(CO)$_4$(NN), by substitution reactions

4.2.1. From [MCl(CO)$_4$(4,4′-dipy)]$_n$ by amine substitution; M = Nb, Ta; NN = en, dmen, tmen, 2,2′-dipy

NbCl(CO)$_4$(en): a suspension of [NbCl(CO)$_4$(4,4′-dipy)]$_n$ (0.222 g, 0.56 mmol) in THF was treated with en (0.047 ml, 0.793 mmol). Immediate formation of a orange–red suspension was observed. After 5 h stirring at room temperature, the solvent was removed in vacuo at room temperature and the residue washed with toluene (3 × 5 ml) and dried in vacuo at room temperature. NbCl(CO)$_4$(en) (0.11 g, 65% yield) was obtained as a red microcrystalline solid. Anal. Found: C, 23.9; H, 2.6; N, 8.9. Calcd. for C$_6$H$_8$ClN$_2$NbO$_4$: C, 24.0; H, 2.7; N, 9.3%. IR (nujol): $\tilde{\nu}$ = 3287m, 3240m-s, 3127m-s, 2023vs, 1926s, 1725s, 1801vs cm^{-1}; solution IR spectra are in Table 1.

By operating in a similar way, the following compounds were isolated:

TaCl(CO)$_4$(NN), NN = dmen, tmen, identified spectroscopically (IR spectra in toluene and THF).

TaCl(CO)$_4$(en): red, microcrystalline, 45%; Anal. Found: C, 18.0; H, 2.5; N, 7.3. Calcd. for C$_6$H$_8$ClN$_2$O$_4$Ta: C, 18.5; H, 2.1; N, 7.2%. IR (nujol): V = 3312m, 3205m-s, 3123ms, 1995m, 1914s, 1844s, 1800vs cm^{-1}; solution IR spectra are in Table 1.

TaCl(CO)$_4$(2,2′-dipy): violet, microcrystalline, 50%; Anal. Found: C, 35.5; H, 1.9; N, 6.5. Calcd. for C$_{14}$HgClN$_2$O$_4$Ta: C, 34.7; H, 1.7; N, 5.8%. Solution IR spectra are in Table 1.

4.2.2. From Na(THF)$_n$[Nb$_2$(μ-Cl)$_3$(CO)$_8$] by chloride substitution; NN = en, tmen, 2,2′-dipy, 4,4′-dipy

Only the preparation of NbCl(CO)$_4$ (en) is reported in detail, the other compounds being identified in solution by IR spectroscopy.

A solution of Na(THF)$_n$[Nb$_2$(μ-Cl)$_3$(CO)$_8$] (from Na(THF)$_{4.2}$[Nb(CO)$_6$] (0 29 g, 0.49 mmol) and CuCl in THF, $\tilde{\nu}$ = 2018s, 1903vs cm^{-1}} in THF (20 ml) was treated with en (0.031 g, 0.5 mmol). Immediate reaction

Table 3
Atomic coordinates for $TaI(CO)_4(tmen)$

Atom	x	y	z	$U_{eq}(Å^2)$
Tal	0.16082(2)	0.38769(3	0.37706(2)	0.02444(9)
I1	0.01896(4)	0.54457(5)	0.35730(4)	0.0417(2)
O1	0.3787(6)	0.4025(9)	0.4366(6)	0.079(3)
O2	0.2118(5)	0.5833(6)	0.2877(5)	0.061(2)
O3	0.0578(6)	0.3707(7)	0.1572(5)	0.064(3)
O4	0.2371 (5)	0.1911 (6)	0.3134(5)	0.054(2)
N1	0.0648(5)	0.2670(6)	0.4055(4)	0.030(2)
N2	0.2143(6)	0.3911(7)	0.5429(5)	0.040(2)
C1	0.3002(7)	0.395(1)	0.4159(7)	0.048(3)
C2	0.1936(6)	0.5134(8)	0.3212(6)	0.036(3)
C3	0.0941(7)	0.3759(8)	0.2358(5)	0.037(3)
C4	0.2105(6)	0.2605(8)	0.3395(6)	0.037(3)
C11	0.0630(7)	0.2983(9)	0.4912(6)	0.042(3)
C12	−0.0339(7)	0.266(1)	0.3318(7)	0.050(3)
C13	0.0988(7)	0.1569(8)	0.4159(7)	0.048(3)
C21	0.1608(8)	0.312(1)	0.5659(6)	0.054(4)
C22	0.2019(8)	0.4935(9)	0.5766(6)	0.057(4)
C23	0.3149(9)	0.364(1)	0.5961(8)	0.100(6)
Ta2	0.32881 (2)	−0.10031 (3)	0.61478(2	0.02865(9)
I2	0.42126(5	0.07610(7)	0.57549(5	0.0746(2)
O5	0.2485(5)	0.2881 (6)	0.6846(5)	0.057(2)
O6	0.2914(5	0.1030(6)	0.7066(4)	0.053(2)
O7	0.4377(6)	0.1165(8)	0.8345(5)	0.065(3)
O8	0.1127(5)	0.0695(7)	0.5546(5)	0.060(3)
N3	0.4429(5)	0.2175(8)	0.6084(5)	0.048(3)
N4	0.2715(5)	0.1426(7)	0.4558(5)	0.035(2)
C5	0.2767(7)	0.2236(8)	0.6574(6)	0.041(3)
C6	0.3049(6	0.0305(9)	0.6728(6)	0.040(3)
C7	0.3992(7)	0.1095(9)	0.7557(6)	0.046(3)
C8	0.1909(6)	0.0798(8)	0.5751(6)	0.036(3)
C31	0.4072(8)	0.259(1)	0.5123(7)	0.065(4)
C32	0.4603(9)	0.309(1)	0.6709(9)	0.098(5)
C33	0.5344(8)	0.164(2)	0.6352(9)	0.093(6)
C41	0.3517(7)	0.179(1)	0.4427(6)	0.060(4)
C42	0.225(1)	0.057(1)	0.3881 (7)	0.067(5)
C43	0.2004(8)	0.228(1)	0.4290(8)	0.057(4)

Estimated standard deviations in parentheses refer to the least significant digit.

Anisotropically rcfincd atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a^2*\beta(1,1)+b^2*\beta(2,2)+c^2*\beta(3,3)+ab(\cos\gamma)*\beta(1,2)+ac(\cos\beta)*\beta(1,3)+bc(\cos\alpha)*\beta(2,3)]$.

was observed and a colourless solid formed. An IR spectrum of the solution in the carbonyl stretching region had absorptions at 2017s, 1920m, 1883vs, 1875sh cm^{-1}.After filtration, the solution was evaporated to dryness, the residue washed with heptane (2 × 5 ml) and dried in vacuo affording 0.047 g (32% yield) of $NbCl(CO)_4(en)$. Anal. Found: C, 23.9; H, 2.6; N, 8.9. Calcd. for $C_6H_8ClN_2NbO_4$: C, 24.0; H, 2.7; N, 9.3%. Solution IR spectra are in Table 1.

4.3. *$TaI(CO)_4(tmen)$: Crystal structure solution and refinement [33]*

Red crystals of $TaI(CO)_4(tmen)$ were obtained by slow diffusion of heptane into a toluene solution of the compound at room temperature. Crystal data: space group $P2_1/c$ (No. 14); $a = 16.222$ (5); $b = 12.855$ (3); $c = 16.452(6)$ Å; $\beta = 117.67$ (2); $M = 536.10$ g mol^{-1}; $V = 3038.4$ (1) $Å^3$; $Z = 8$; $D_c = 2.344$ g cm^{-3}, $\lambda = 0.7107$ Å; $\mu = 91.71$ cm^{-1}; $F(000) = 1984$. Note that at room temperature a unit cell with half of the above volume is found [34].

Data collection was performed at 203 K on a crystal with approximate dimensions 0.19 × 0.16 × 0.1 mm. Data were collected with a ENRAF NONIUS CAD4 diffractometer in the ω-mode, using graphite-monochromated Mo-K_α radiation. During data collection, no significant variation in intensities of three standard reflections was observed. In the range $3.0° < \theta < 27.0°$, 6817 reflections were measured; 4795 unique reflections with $I > 1.0\sigma(I)$ were used for further computations. An empirical absorption correction based on Ψ-scans [35] was applied. Structure solution was by direct methods [36]. Full-matrix least-squares refinement [37] was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Calculations were performed using the SDP system of programs [36]. Refinement converged with 325 parameters using a statistical weighting scheme $w = 1/[\Sigma^2(F_o)]$ to $R = 0.045$ and $Rw = 0.048$ with a goodness of fit of 1.341. The fractional coordinates of the non-hydrogen atoms are listed in Table 3.

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[19] A referee of this paper encouraged us to comment on the statistically significant differences between the two symmetrically independent molecules. Obviously, such differences may be either due to systematic errors not reflected in the estimated standard deviations, or to differences in the crystalline environment [see, e.g. J. Bernstein, in: A. Domenicano, I. Hargitai (Eds.), Accurate Molecular Structures, Oxford University, New York, 1992, pp. 469–497]. The latter are often referred to as 'packing effects': recent results indicate that in the case of metal complexes such packing effects are accompanied by changes in bond angles [T. Wagner, U. Englert, Struct. Chem., in press] and even in bond distances [A. Martin, A.G. Orpen, J. Am. Chem. Soc. 118 (1996) 1464]. Based on data from the Cambridge Structural Database, Martin and Orpen have obtained a standard deviation in the order of magnitude of 0.01 Å for the case of metal–chlorine bonds.

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[34] The preliminary set of data collected at room temperature gave the following results: space group $P2_1/n$ (No. 14); $a = 8.484$ (4); $b = 12.980$ (3); $c = 14.028$ (2) Å, $\beta = 90.37$ (3)°, $V = 1544$ (1) Å^3; $Z = 4$; $D_c = 2.304$ g cm^{-3}.

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