Electron-transfer processes with substituted group 5 metal carbonyls. Synthesis, crystal and molecular structure of $Ag_3M_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$, M = Nb, Ta, the first structurally characterized carbonyl derivatives of niobium(0) and tantalum(0)

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Abstract

Some new tetracarbonyl derivatives of tantalum(I), $TaI(CO)_4LL$ (LL = tmeda, dppm, 2,2'-dipy), have been obtained by diiodine oxidation of $[Ta(CO)_6]^-$ in the presence of the bidentate ligand.

Dicyclopentadienylcobalt(II) does not react with the tetracarbonyl dppe derivatives of niobium(I) and tantalum(I), $MI(CO)_4dppe$, whereas the corresponding pentamethyl substituted complex, $CoCp_2^*$, carries out the two-electron transfer to form $[CoCp_2^*][M(CO)_4dppe]$. Finally, oxidation of the $[M(CO)_4dmpe]^-$ anion, M = Nb, Ta, with the silver(I) salts $AgNO_2$ and $AgBF_4$ gave the hexanuclear mixed metal clusters $Ag_3M_3(CO)_{12}(dmpe)_3$, which were studied by X-ray diffraction methods. Crystals of $Ag_3Nb_3(CO)_{12}(dmpe)_3$ are rhombohedric, space group $R\bar{3}c$, hexagonal setting, No. 167, a 14.323(1), c 44.772(4) Å, V 7954.6 Å^3, $Z = 6$, D_{calc} 1.739 g cm^{-3}, $\mu(Cu-K_\alpha)$ 162.93 cm^{-1}, $F(000) = 4068$; $R = 0.044$. Crystals of the tantalum derivative are isotypic: a 14.274(5), c 44.55(3) Å, V 7860.6 Å^3, $Z = 6$, D_{calc} 2.095 g cm^{-3}, $\mu(Mo-K_\alpha)$ 78.82 cm^{-1}, $F(000) = 4644$, $R = 0.029$. The coordination geometry around the group 5 metal may be described as a distorted square antiprism, the coordination sites being filled with the four carbonyl groups, the two

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silver atoms and the two phosphorous atoms of the bidentate ligand. The central core of the clusters is constituted by two almost regular interpenetrated equilateral triangles of silver and niobium (or tantalum) atoms. Both metal clusters react with dry hydrogen iodide giving silver metal and $MI(CO)_4(dmpe)$.

Introduction

Early transition elements of groups 5 and 4 are rather reluctant to form uncharged carbonyl complexes of the zerovalent metal. Among group 5 metals, hexacarbonylvanadium is well established [1], whereas the corresponding derivatives of niobium(0) and tantalum(0) are unknown, or metastable species have been reported by metal vaporization techniques [2]. As far as group 4 metals are concerned, the same situation applies. On the other hand, anionic hexacarbonyl derivatives are known for vanadium($-$I) [3], niobium($-$I) [4] and tantalum($-$I) [4] and improved procedures have recently been published [5] for the syntheses of these compounds. Relevant acquisitions in this field are the reports by Ellis and co-. workers concerning the preparation of the hexacarbonyl derivatives of zirconium($-$II) [6] and titanium($-$II) [7]. The oxidation of the hexacarbonyl metalates appeared therefore to be the appropriate route to the zerovalent complexes. In earlier papers on this subject, it has been shown, however, that oxidation normally gives the niobium(I) and tantalum(I) heptacoordinate carbonyl species such as $[M_2(\mu\text{-}X)_3(CO)_8]^-$ [8], $M(acac)(CO)_4(THF)$ [9] or $MX(CO)_{4-n}$(tertiary-phosphine)$_n$ [10].

In this paper we report the preparation of some new heptacoordinated tetra-carbonyl complexes of niobium(I) and tantalum(I), the attempts to reduce them to the zerovalent state and, finally, the successful oxidation of the tertiary phosphine substituted tetracarbonyl species $[M(CO)_4(dmpe)]^-$, dmpe = 1,2-bis(dimethylphos-phino)ethane, with AgX ($X = NO_2^-$, BF_4^-) to give mixed metal carbonyl clusters of formally zerovalent niobium and tantalum. A preliminary account of this work has appeared [11].

Experimental

Infrared spectra were recorded with a Perkin Elmer Mod. 283 instrument equipped with grating on solutions or Nujol mulls prepared under rigorous exclusion of air and moisture. Gas analyses were performed with a Dani Mod. 3200 gas chromatograph. Photolytic reactions were performed with a 125 W Philips HPK mercury lamp.

Unless otherwise stated, all operations were carried out under argon in prepurified solvents, the latter being dried by conventional methods.

1,2-Bis(diphenylphosphino)methane, dppm; 1,2-bis(dimethylphosphino)ethane, dmpe; 1,2-bis(diphenylphosphino)ethane, dppe; 2,2'-bipyridine, 2,2'-dipy, were commercial products used as received. N,N,N',N'-tetramethylethylenediamine, tmeda, was distilled from sodium before use. 2,2'-Bipyridinium diiodide, $[2,2'\text{-di-}pyH_2]I_2$ was prepared by treating 2,2'-dipy with gaseous HI in n-heptane as solvent followed by filtration of the colourless solid and drying in vacuo. The hexacarbonyl

metalates($-$I) of vanadium [12], niobium [5a] and tantalum [5a], cobaltocene [13a], CoCp$_2$, decamethylcobaltocene [13b], CoCp$_2^*$ and silver nitrite [14], AgNO$_2$, were prepared according to literature procedures.

Synthesis of substituted derivatives of Ta^I, TaI(CO)$_4$LL, LL = tmeda, 2,2'-dipy, dppm

(1) LL = tmeda

A suspension of tmeda (0.1 g, 0.88 mmol) and Na(THF)$_2$[Ta(CO)$_6$] (0.48 g; 0.93 mmol) in THF (25 ml) was treated at ca. $-78°$C with diiodine (0.23 g, 0.9 mmol). Immediate reaction with gas evolution and formation of a red suspension were observed. The solvent was removed in vacuo and toluene (25 ml) was added. After filtration, n-heptane (50 ml) was layered over the toluene solution. After two days, TaI(CO)$_4$tmeda crystallized in the form of large red crystals stable in air for short periods of time (0.3 g, 66% yield). Anal. Found: C, 23.0; H, 2.8; N, 5.4. C$_{10}$H$_{16}$IN$_2$O$_4$Ta calcd.: C, 22.4; H, 3.0; N, 5.2%. Infrared spectrum in the carbonyl stretching region: 2006s, 1913m, 1875vs and 1865sh cm^{-1} (THF); 2009s, 1920m, 1880vs and 1865s cm^{-1} (toluene).

(2) LL = 2,2'-dipy

(a) From Na[Ta(CO)$_6$] by diiodine oxidation in the presence of 2,2'-dipy. A solution of 2,2'-dipy (0.23 g, 1.5 mmol) in THF (25 ml) was treated with Na(THF)$_2$[Ta(CO)$_6$] (0.75 g, 1.5 mmol). After cooling to about $-78°$C, diiodine (0.4 g, 1.6 mmol) was added as a solid. In a few minutes, a dark red suspension was formed. Once at room temperature, the suspension was filtered and the solid was washed with water to dissolve NaI and then dried in vacuo over P$_4$O$_{10}$ overnight to give 0.66 g (78% yield) of TaI(CO)$_4$(2,2'-dipy) in the form of a violet solid stable in air for short periods of time. Anal. Found: C, 29.5; H, 1.6; N, 4.7. C$_{14}$H$_8$IN$_2$O$_4$Ta calcd.: C, 29.2; H, 1.4; N, 4.9%. Infrared spectrum in the carbonyl stretching region: 2009s, 1925m, 1889vs and 1881sh cm^{-1} (THF); 2016s, 1926m, 1893vs cm^{-1} (CH$_2$Cl$_2$).

(b) From Na[Ta(CO)$_6$] and [2,2'-dipyH$_2$]I$_2$. A suspension of Na(THF)$_2$[Ta-(CO)$_6$] (0.38 g; 0.74 mmol) in THF (25 ml) was treated at room temperature with [2,2'-dipyH$_2$]I$_2$ (0.32 g, 0.78 mmol). Immediate reaction with evolution of H$_2$ and CO (by gas chromatography) was observed. After 4 h stirring at room temperature, the solvent was evaporated in vacuo and the residue was suspended in water (10 ml), filtered, washed with water (8 × 5 ml) and dried in vacuo over P$_4$O$_{10}$. TaI(CO)$_4$(2,2'-dipy) was obtained in 83% yield and identified by its infrared spectrum (THF) and CO analysis.

(3) LL = dppm

A suspension of Na(THF)$_2$[Ta(CO)$_6$] (0.50 g; 0.98 mmol) in THF (30 ml) was treated with diiodine (0.28 g, 1.1 mmol) at ca. $-78°$C. Evolution of gas and formation of a red solution took place upon mixing the reagents. When the temperature was ca. $-50°$C, dppm (0.39 g, 1 mmol) was added. After 1 h stirring at room temperature, the solvent was removed in vacuo, the residue was suspended in toluene (25 ml) and filtered, to obtain a red solution. By treatment with n-heptane (50 ml) TaI(CO)$_4$dppm (0.55 g, 69% yield) was formed as an orange microcrystalline solid. Anal. Found: C, 44.0; H, 2.8. C$_{29}$H$_{22}$IO$_4$P$_2$Ta calcd.: 43.3; H, 2.7%. Infrared

spectrum in the carbonyl stretching region: 2019s, 1941m, 1905vs and 1892s cm^{-1} (THF); 2019s, 1947m, 1909vs and 1891s cm^{-1} (toluene).

Reduction of MI(CO)$_4$dppe with CoL$_2$

(a) M = V; L = Cp. A suspension of Na[V(CO)$_6$] (1.42 g, 5.9 mmol) in THF (100 ml) was treated with diiodine (1.51 g, 5.9 mmol) at about −78°C. Gas evolution and formation of a red solution took place upon mixing the reagents. When the temperature was about −50°C, dppe (2.4 g, 6 mmol) was added and the mixture was slowly warmed up to −10°C and kept at this temperature for 1 h. An infrared spectrum in the carbonyl stretching region revealed that VI(CO)$_4$dppe [10a] was the only carbonyl species in solution. The red solution was treated with CoCp$_2$ (1.1 g, 5.8 mmol) which caused the formation of a yellow solid in a red solution. After 15 h, the solvent was removed in vacuo and the residue was dissolved in toluene (100 ml) and filtered. The solid (2.6 g) consisted of a mixture of NaI and CoCp$_2$I. The volume of the solution was reduced to 20 ml and n-heptane was added (50 ml) in order to precipitate V(CO)$_4$dppe in the form of a brown-green micro-crystalline solid [15] (2.72 g, 82% yield) which gave satisfactory (C, H) elemental analysis. The infrared spectrum in the carbonyl stretching region (1994s, 1904m-sh, 1869vs cm^{-1}, toluene) is consistent with that reported in the literature [15].

(b) M = Ta; L = C$_5$Me$_5$ (Cp).* A solution of TaI(CO)$_4$dppe (0.28 g, 0.34 mmol) in THF (25 ml) was treated at about −30°C with CoCp$_2^*$ [16*] (0.12 g, 0.35 mmol). Immediate reaction with separation of a yellow solid was observed. After 1 h stirring at room temperature, an infrared spectrum in the carbonyl stretching region revealed absorptions due to the starting material [10a] (2016s, 1943m, 1896vs, 1880m-s cm^{-1}) and to the [Ta(CO)$_4$dppe]$^-$ anion. Addition of 0.12 g (0.33 mmol) of CoCp$_2^*$ caused the absorption of the starting material to disappear from the IR spectrum while the absorptions due to the [Ta(CO)$_4$dppe]$^-$ anion increased their intensity. Filtration of the suspension afforded CoCp$_2^*$I (0.13 g, 95% yield) and a brown solution which, upon addition of n-heptane (25 ml) afforded 0.18 g (63% yield) of CoCp$_2^*$[Ta(CO)$_4$dppe] in the form of a microcrystalline brown solid. Anal. Found: C, 58.7; H, 5.3. C$_{50}$H$_{54}$CoO$_4$P$_2$Ta calcd.: C, 58.8; H, 5.3%. Infrared spectrum: 1903s, 1786vs, 1760s cm^{-1} (THF); 3050w, 1901s, 1780vs, 1750vs, 1610w, 1435m, 1185w, 1155w, 1090m-w, 1025m, 815w, 810m, 750m, 740m, 695s, 665m and 515m cm^{-1} (Nujol mull).

Synthesis of NEt$_4$[M(CO)$_4$dmpe], M = Nb, Ta. Only the preparation of NEt$_4$-[Nb(CO)$_4$dmpe] is described in detail, the tantalum compound being prepared in a similar way. A solution of NEt$_4$[Nb(CO)$_6$] (1.74 g, 4.5 mmol) in THF (100 ml) was photolyzed in the presence of dmpe (0.81 g, 5.4 mmol) for 2 h in a stream of argon at 20°C [17]. The red solution was filtered and the solvent was removed in vacuo at room temperature. The residue was suspended in n-heptane (25 ml) and filtered affording NEt$_4$[Nb(CO)$_4$dmpe] (1.71 g, 79% yield) in the form of a red-orange microcrystalline solid stable in air for short periods of time. Anal. Found: C, 44.3; H, 7.8; N, 2.9. C$_{18}$H$_{36}$NNbO$_4$P$_2$ calcd.: C, 44.5; H, 7.5; N, 2.9%. Infrared spectrum in the carbonyl stretching region: 1898s, 1780vs, 1735sh cm^{-1} (THF).

By operating in a similar way, NEt$_4$[Ta(CO)$_4$dmpe] was obtained in 80% yield

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* Reference number with asterisk indicates a note in the list of references.

after 10–12 h photolysis at 20 °C in a stream of argon. Anal. Found: C, 37.9; H, 6.6; N, 2.8. $C_{18}H_{36}NO_4P_2Ta$ calcd.: C, 37.7; H, 6.3; N, 2.4%. Infrared spectrum in the carbonyl stretching region: 1892s, 1775vs, 1740sh cm^{-1} (THF).

Reaction of NEt$_4$[M(CO)$_4$dmpe] with AgX. Synthesis of Ag$_3$M$_3$(CO)$_{12}$(dmpe)$_3$.

(a) X = NO$_2^-$. Only the preparation of the tantalum derivative is reported in detail, the niobium-silver cluster being obtained under similar experimental conditions. A solution of NEt$_4$[Ta(CO)$_4$(dmpe)] (0.471 g; 0.82 mmol) in THF (300 ml) was treated at room temperature with AgNO$_2$ (0.257 g, 1.67 mmol) * under argon. The reaction mixture was warmed to 45 °C for 30 min, cooled to room temperature and filtered. The solvent was partially removed in vacuo at 0 °C until some red-orange solid began to separate. When the volume of the solvent was reduced to ca. 30 ml, the solid was filtered and dried in vacuo at room temperature (0.164 g). The filtered solution was cooled to −30 °C to give a second crop (0.02 g) of Ag$_3$Ta$_3$(CO)$_{12}$(dmpe)$_3$ (40% total yield with respect to tantalum) as red-orange crystals. Anal. Found: C, 21.5; H, 3.0. $C_{30}H_{48}Ag_3O_{12}P_6Ta_3$ calcd.: C, 21.8; H, 2.9%. Infrared spectrum in the carbonyl stretching region: 1923s, 1832vs cm^{-1} (Nujol mull); 1928s, 1843vs (THF); 1928s, 1840vs cm^{-1} (CH$_3$CN). χ_M corr: +876 × 10^{-6} cgsu at 20 °C; diam. corr. −892 × 10^{-6} cgsu (for the entire cluster). In the case of the niobium-silver cluster the following results were obtained: Anal. Found: C, 26.0; H, 3.5. $C_{30}H_{48}Ag_3Nb_3O_{12}P_6$ calcd.: C, 25.9; H, 3.5%. Infrared spectra in the carbonyl stretching region: 1935s, 1840vs cm^{-1} (Nujol mull); 1930s, 1842vs cm^{-1} (THF); 1931s, 1844vs cm^{-1} (CH$_3$CN).

(b) X = BF$_4^-$. A solution of AgBF$_4$ (0.07 g, 0.36 mmol) in THF (100 ml) was treated with NEt$_4$[Ta(CO)$_4$(dmpe)] (0.193 g; 0.34 mmol) at about −60 °C. Immediate formation of a red solution and precipitation of a dark-brown solid were observed. An IR spectrum of the solution at room temperature revealed the absorptions due to Ag$_3$Ta$_3$(CO)$_{12}$(dmpe)$_3$ (1928s, 1840vs cm^{-1}), together with other absorptions of lower intensity due to unidentified products. The suspension was filtered and the volume of the solution was reduced to 10 ml in vacuo at room temperature. After cooling at about −30 °C for 15 h, the red-orange solid was filtered, washed with toluene (3 × 5 ml) and dried in vacuo affording 0.072 g (38% yield) of Ag$_3$Ta$_3$(CO)$_{12}$(dmpe)$_3$ identified by infrared spectra and elemental analysis. The preparation of the niobium cluster was performed similarly.

Structure determination of Ag$_3$M$_3$(CO)$_{12}$(dmpe)$_3$. The X-ray studies were performed on an Enraf–Nonius CAD4 four-circle diffractometer equipped with a graphite monochromator.

M = Nb. A red transparent crystal with dimensions (mm) 0.3 × 0.3 × 0.2 was sealed under argon in a Lindeman capillary. The Cu-K_α radiation (λ 1.5418 Å) was used for the determination of cell constants (least-squares procedure for 25 accurately centred reflections) and for subsequent intensity data collection. The space group was $R\bar{3}c$, No. 167 [18]; the hexagonal setting was chosen. Crystal data: a 14.323(1), c 44.772(4) Å, V 7954.6 Å^3, $Z = 6$, D_{calc} 1.739 g cm^{-3}, μ(Cu-K_α) 162.93 cm^{-1}, $F(000) = 4068$. At 20 °C, 7946 reflections were collected in the scan range

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* This corresponds to a 2/1 Ag/M molar ratio, while the stoicheiometry of eq. 5 requires a 1/1 ratio. When the 1/1 ratio was used unreacted starting material was found in the reaction mixture, due to further oxidation of the metal cluster by AgNO$_2$.

Table 1a

Fractional atomic coordinates of $Ag_3Ta_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$; estimated standard deviations in parentheses refer to the least significant digit

Atom	x	y	z	B ($\overset{\circ}{A}{}^2$) [a]
Ag	0.1149(1)	0.000	0.250	4.82(3)
Ta	− 0.23366(4)	0.000	0.250	3.03(1)
P	0.0510(2)	− 0.3485(2)	0.28271(8)	4.46(7)
O1	0.2483(8)	− 0.129(1)	0.2270(3)	8.5(4)
O2	0.154(1)	0.119(1)	0.1856(2)	11.2(5)
C1	0.157(1)	− 0.165(1)	0.2357(3)	5.0(3)
C2	0.178(1)	0.152(1)	0.2094(3)	6.7(5)
C3	− 0.005(1)	− 0.4834(9)	0.2670(3)	7.3(4)
C4	0.195(1)	− 0.306(1)	0.2852(4)	7.9(5)
C5	0.010(1)	− 0.372(1)	0.3218(3)	7.9(5)
H31	− 0.0808	− 0.5223	0.2699	8
H32	0.0249	− 0.5214	0.2784	8
H41	0.2283	− 0.2914	0.2658	8
H42	0.2337	− 0.2422	0.2973	8
H43	0.2050	− 0.3620	0.2944	8
H51	− 0.0668	− 0.3942	0.3237	8
H52	0.0198	− 0.4264	0.3306	8
H53	0.0485	− 0.3066	0.3335	8

[a] Hydrogen atoms were not refined, but included in the structure factor calculations. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$.

Table 1b

Fractional atomic coordinates of $Ag_3Nb_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$; estimated standard deviations in parentheses refer to the least significant digit.

Atom	x	y	z	B ($\overset{\circ}{A}{}^2$) [a]
Ag	0.11457(7)	0.000	0.250	4.44(2)
Nb	− 0.23280(6)	0.000	0.250	2.64(2)
P	0.0513(2)	− 0.3482(2)	0.28258(6)	4.16(6)
O1	0.2469(6)	− 0.1280(7)	0.2267(2)	8.2(3)
O2	0.154(1)	0.1178(8)	0.1853(2)	11.0(4)
C1	0.1591(8)	− 0.1617(8)	0.2356(2)	5.0(3)
C2	0.175(1)	0.149(1)	0.2095(3)	7.0(4)
C3	− 0.003(1)	− 0.4828(7)	0.2664(3)	6.7(3)
C4	0.1944(9)	− 0.306(1)	0.2852(3)	7.4(3)
C5	0.010(1)	− 0.372(1)	0.3215(3)	7.7(4)
H31	− 0.0797	− 0.5204	0.2684	8
H32	0.0255	− 0.5204	0.2766	8
H41	0.2259	− 0.2895	0.2663	8
H42	0.2292	− 0.2410	0.2975	8
H43	0.2026	− 0.3598	0.2947	8
H51	− 0.0639	− 0.3944	0.3227	8
H52	0.0241	− 0.4243	0.3293	8
H53	0.0507	− 0.3056	0.3321	8

[a] Hydrogen atoms were not refined, but included in the structure factor calculations. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$.

$8^\circ < \theta < 69^\circ$ (ω-scan), of which 5091 showed $I > 3\sigma(I)$. An empirical absorption correction according to the ψ-scan method [19] was applied. After merging the equivalent reflections, 1211 independent observations with $I > 3.5\sigma(I)$ were used in structure solution and refinement [20]. The structure was solved by Patterson synthesis and subsequent difference Fourier syntheses. In the final full-matrix refinement, with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atoms in calculated position were included into the structure factor calculation and a correction for secondary extinction [21] was applied on F_c. Refinement converged at $R = 0.044$, $R_w = 0.057$ [$w = 1/\sigma^2(F_o)$]. In Table 1a, atomic coordinates and isotropic thermal parameters are listed [22*].
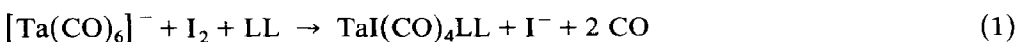
M = Ta. Crystal dimensions (mm) $0.2 \times 0.2 \times 0.2$, Mo-$K_\alpha$ radiation (λ 0.7107 Å) was used. Crystal data: space group: $R\bar{3}c$, hexagonal setting, No. 167 [18]; a 14.274(5), c 44.55(3) Å, V 7860.6 Å^3, $Z = 6$, D_{calc} 2.095 g cm^{-3}, μ(Mo-K_α) 78.82 cm^{-1}, $F(000) = 4644$. At 20°C, 6411 reflections were measured, 3372 were considered in the scan $4^\circ < \theta < 25^\circ$ and an empirical absorption correction was applied. Since preliminary Gandolfi photographs showed that the niobium and the tantalum compounds are isotypic, fractional coordinates of the former were used as a first model in structure solution for the latter, substituting atomic scattering factors for niobium by those for tantalum. The final R values obtained were $R = 0.029$, $R_w = 0.037$ for 984 independent intensities and 84 parameters. Table 1b gives atomic coordinates and isotropic thermal parameters [22].

Reactions of Ag$_3$M$_3$(CO)$_{12}$(dmpe)$_3$ with dry HI. Only the reaction for M = Ta is described in detail, the other being performed in a similar way. A suspension of Ag$_3$Ta$_3$(CO)$_{12}$(dmpe)$_3$ (0.15 g, 0.9 mmol) in toluene (25 ml) was treated with dry HI (0.28 mmol) at about -78°C. Immediate reaction was observed at low temperature. The mixture was allowed to warm slowly at room temperature and at about -40°C evolution of gas (H$_2$ by gas chromatography; some CO was present; gas phase previously washed with aqueous NaOH solution to eliminate excess HI) was observed. At room temperature an orange solution in the presence of a black precipitate was present. The mixture was filtered and the orange solution was dried in vacuo at room temperature to give 0.064 g (42% yield) of TaI(CO)$_4$(dmpe) in the form of an orange microcrystalline solid. Anal. Found: C, 21.8; H, 2.9. C$_{10}$H$_{16}$IO$_4$P$_2$Ta calcd.: C, 21.1; H, 2.8%. Infrared spectrum (toluene): 2019s, 1943m, 1897vs and 1875m-s cm^{-1}. The insoluble solid was dried in vacuo, dissolved in HNO$_3$ and found to give AgCl by treatment with NaCl in aqueous solution.
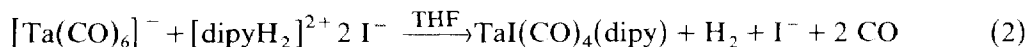
In the case of niobium, NbI(CO)$_4$(dmpe) was formed which was identified by IR spectroscopy in the carbonyl stretching region: 2021s, 1948m, 1900vs and 1876m-s cm^{-1} (toluene).

Results and discussion

Tetracarbonyliodo derivatives of tantalum(I) with the bidentate ligands tmeda, 2,2'-dipy and dppm have been prepared by oxidation of the [Ta(CO)$_6$]$^-$ anion with diiodine in the presence of the bidentate ligand or with the diprotonated bipyridinium cation, according to eq. 1 and 2, respectively.

$$[\text{Ta(CO)}_6]^- + \text{I}_2 + \text{LL} \rightarrow \text{TaI(CO)}_4\text{LL} + \text{I}^- + 2\,\text{CO} \tag{1}$$

(LL = tmeda, dppm, 2,2′-dipy)

$$[Ta(CO)_6]^- + [dipyH_2]^{2+} 2\ I^- \xrightarrow{THF} TaI(CO)_4(dipy) + H_2 + I^- + 2\ CO \qquad (2)$$

These compounds are new members of a well established class of non-cyclopentadienyl heptacoordinated tetracarbonyl derivatives of tantalum(I) [8,9,10,23]. Of considerable interest is the reaction with the diprotonated bipyridinium cation, eq. 2, which occurs readily at room temperature with di-hydrogen evolution. This reaction is somewhat reminiscent of the electron-transfer processes observed for the hexacarbonyl vanadates(−I) of protonated nitrogen bases [24]. It is possible that the hexacarbonyl tantalate $[dipyH_2][Ta(CO)_6]_2$ is an intermediate of reaction 2, then readily undergoing the redox process in the presence of the iodide ion to give the final product.

The tetracarbonyl derivatives of vanadium(I), niobium(I) and tantalum(I), $MI(CO)_4(dppe)$, have been treated with dicyclopentadienylcobalt(II), which has been used earlier in these laboratories for the reduction of $TiCp_2X_2$ [25], $FeI_2(CO)_4$ [25], $MnI(CO)_5$ [25] and $V(CO)_6$ [9]. In this case, only the vanadium compound gave the already known [15] zerovalent complex, see eq. 3, whereas the niobium(I)

$$VI(CO)_4(dppe) + CoCp_2 \rightarrow V(CO)_4(dppe) + CoCp_2I \qquad (3)$$
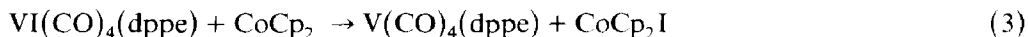
and the tantalum(I) species did not react under similar conditions. The use of the stronger reducing agent bis(pentamethylcyclopentadienyl)cobalt(II), $CoCp_2^*$ [26], led to the reduction of $MI(CO)_4(dppe)$, M = Nb, Ta, to the (−I) oxidation state, as indicated by eq. 4. This shows once again that in the case of niobium and tantalum, the zerovalent state is not readily accessible, presumably because it is adjacent to the exceedingly more stable states +I and −I.

$$MI(CO)_4(dppe) + 2\ CoCp_2^* \xrightarrow{THF} [CoCp_2^*][M(CO)_4(dppe)] + CoCp_2^*I \qquad (4)$$
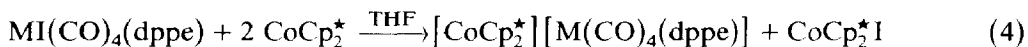
(M = Nb, Ta)

Earlier work [9] from these laboratories had shown that the reaction of the hexacarbonylmetalate(−I) anions with silver halides leads to the formation of the halo-bridged dimeric anions $[M_2(\mu\text{-}X)_3(CO)_8]^-$, with corresponding reduction to silver metal. The use of silver salts containing poorly coordinating anions, such as $AgNO_2$ and $AgBF_4$ as oxidizing agents for the tertiary phosphine substituted $[M(CO)_4(dmpe)]^-$ anions led to retention of silver in the final product and the mixed niobium- and tantalum-silver cluster compounds of eq. 5 were thus formed.

$$3\ NEt_4[M(CO)_4(dmpe)] + 3\ AgX \rightarrow Ag_3M_3(CO)_{12}(dmpe)_3 + 3\ NEt_4X \qquad (5)$$

(M = Nb, Ta; X = NO_2, BF_4)

The new niobium and tantalum complexes are slightly soluble in THF, which is the solvent used for their preparation. The IR spectra in the carbonyl stretching region suggest that the electronic situation around the metal has drastically changed during the conversion from the tetracarbonyl tertiary phosphine substituted metalates(−I) to the final product. In fact, while the $[Ta(CO)_4(dmpe)]^-$ anion has IR absorptions (THF) at 1898s, 1780vs and about 1735s cm^{-1}, the corresponding mixed metal cluster substantially shows two main bands at 1928m and 1843vs cm^{-1}. Thus, the increased wavenumber values suggest an increased oxidation state of the group 5 metal in the cluster. The rather simple spectra obtained for these clusters
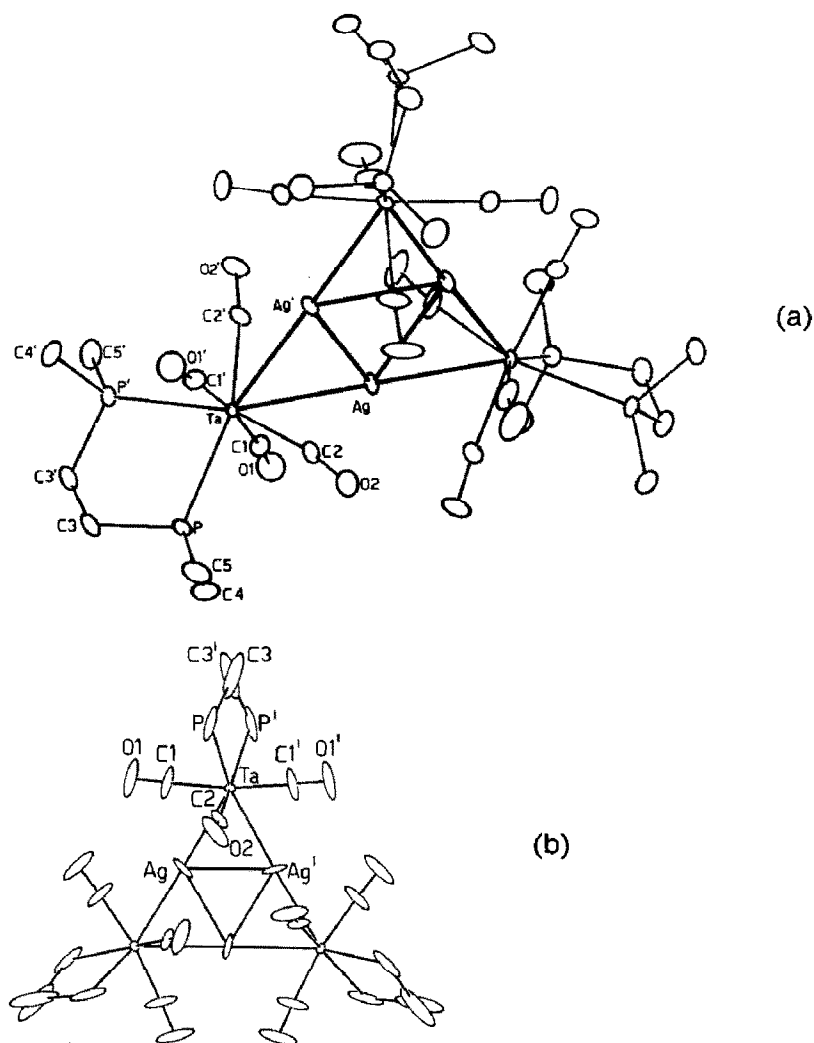
Fig. 1. (a) ORTEP view of $Ag_3Ta_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$ (thermal ellipsoids are drawn at 10% probability); (b) ORTEP view of $Ag_3Ta_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$ along the ternary axis of symmetry. The methyl carbon atoms C4 and C5 and their symmetry related atoms and three of the six carbonyl groups made up by C2 and O2 and their symmetry related atoms have been omitted for clarity.

are indicative of a considerable degree of symmetry. Moreover, the observed IR spectrum is that expected for local C_{4v} symmetry of the $M(CO)_4$ moiety for which two carbonyl stretching vibrations ($A_1 + E$) are expected.

Since the niobium and tantalum complexes did not contain formally charged ligands and in view of the interest for zerovalent complexes of niobium and tantalum, it was decided to carry out a crystal structure study of these compounds by X-ray diffraction methods.

The molecules of $Ag_3M_3(CO)_{12}(dmpe)_3$ (for M = Ta, see Fig. 1) show D_3 point symmetry. The metal atoms occupy special positions 18e in the hexagonal setting of space group $R\bar{3}c$ (No. 167), i.e., they are situated on a twofold crystallographic axis. Interatomic distances and angles are reported in Tables 2 and 3, respectively. For reasons of symmetry, the metal atoms build up a planar heterometallic raft.

Table 2

Selected interatomic distances (Å) in $Ag_3M_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$; estimated standard deviations in parentheses refer to the least significant digit.

	M = Nb	M = Ta
Ag–Ag	2.8424(5)	2.8418(8)
Ag–C1	2.767(4)	2.784(4)
Ag–C2	2.593(4)	2.614(5)
Ag–C2'	2.931(4)	2.937(5)
M–Ag	2.8879(2)	2.8884(2)
M–C1	2.080(4)	2.049(4)
M–C2	2.103(4)	2.082(4)
M–P	2.5726(8)	2.556(1)
P–C3	1.829(4)	1.816(4)
P–C4	1.828(4)	1.834(5)
P–C5	1.816(5)	1.813(4)
C1–O1	1.169(5)	1.200(5)
C2–O2	1.152(5)	1.143(5)
C3–C3'	1.471(7)	1.518(8)

Since the metallic radii of Ag (1.44 Å [27]) and Nb or Ta (both 1.47 Å [27]) are very similar, the heterometallic core of our cluster compounds shows an arrangement similar to a (111) plane in a close-packed layer of a metal structure. In the clusters, the intramolecular Ag–Ag distance of 2.842 Å is slightly shorter than in silver metal, 2.883 Å [27]. A very short Ag–Ag distance (2.810 Å) has been reported [28] for the cubic Laves phase $NaAg_2$ that contains a network of corner-connected Ag_4 tetrahedra, whereas a longer Ag–Ag distance (2.968–2.998 Å) has been observed by Venanzi et al. [29] in the heterometallic raft-like cluster cation $\{Rh_3Ag_3H_9-[CH_3C(CH_2PPh_2)_3]_3\}^{3+}$. Another example of a similar arrangement is the hexanuclear Os–Cu cluster, $Cu_3Os_3H_9(PMe_2Ph)_9$, in which the inner triangular core is formed once again by the group 11 metal [30].

Table 3

Selected interatomic angles (degrees) in $Ag_3M_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$; (estimated standard deviations in parentheses refer to the least significant digit).

	M = Nb	M = Ta
Ag–Ag'–Ag	60.0	60.0
Ag–Ag'–M	60.520(8)	60.53(1)
M–Ag–M'	178.97(1)	178.93(2)
Ag–M–Ag'	58.97(1)	58.93(2)
Ag–M–P	124.20(2)	124.13(3)
Ag–M–P'	143.68(2)	143.47(2)
P–M–P'	76.45(4)	76.79(5)
C3–P–C4	101.0(3)	101.4(3)
C3–P–C5	104.7(2)	104.3(2)
C4–P–C5	101.8(2)	102.0(2)
P–C3–C3'	112.0(2)	110.9(3)
M–C1–O1	175.6(3)	177.6(5)
M–C2–O2	169.4(3)	172.1(4)
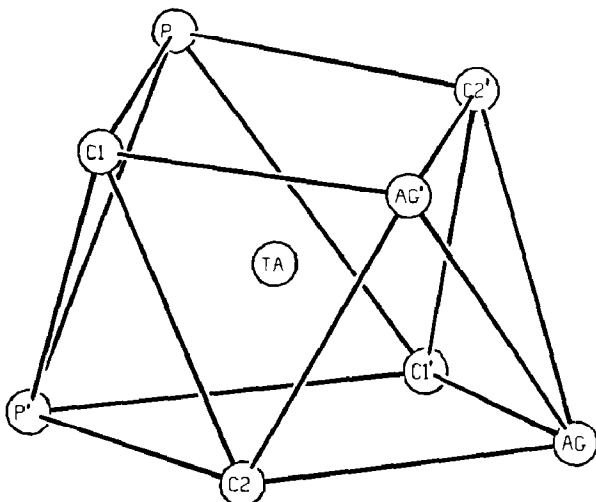
Fig. 2. Coordination polyhedron of the tantalum atom in $Ag_3Ta_3(CO)_{12}(Me_2PCH_2CH_2PMe_2)_3$ (arbitrary atomic radii).

The shortest contacts between group 5 metal atoms and silver atoms in our compounds amount to 2.888 Å and might be compared to the sum of the metallic radii, 2.91 Å [27], of the same elements.

The M–C–O groups are not exactly linear. The M–C2–O2 group shows the largest deviation from linearity with 169.4(3)° for M = Nb and 172.1(4)° for M = Ta. A similar bonding situation as in our cluster has been found in two other heterometallic compounds, namely $CpW(CO)_3AuPPh_3$ [31] and $(\eta^3-C_3H_5)Fe(CO)_3$-$AuPPh_3$ [32]. These heterometallic carbonyl compounds have been classified as "type 3 bent semibridging" by Crabtree and Lavin [33].

The coordination polyhedron of the group 5 metal atoms may be described as a distorted square antiprism (Fig. 2), the symmetry being lowered to C_2 by elongation along the twofold crystallographic axis passing through the central metal atom.

On the basis of the established molecular structure of our compounds, it is possible to explain the IR spectra in THF or CH_3CN solutions. The four carbonyl groups of each $M(CO)_4LL$ fragment are related by the virtual C_2 axis intersecting the Ag–Ag bond. From the viewpoint of the carbonyl groups, the local symmetry of the $M(CO)_4$ group is thus close to C_{4v} which agrees with the simplicity of the experimentally observed IR spectrum.

The structural and spectroscopic data suggest that the assignment of a zerovalent oxidation state to niobium and tantalum in these complexes is the best approximation to the actual electronic situation within the cluster. The observation that the Ag–Ag distance is similar to that in the metal is also consistent with this interpretation. Furthermore, the chemical behaviour is also in agreement with the presence of substantially zerovalent metals. The hexanuclear complexes show signs of decomposition in solution at low temperature over extended periods of time, with separation of silver metal. Even more interesting is the reaction with gaseous HI giving Ag metal and the iodo derivative of niobium(I) or tantalum(I), with hydrogen evolution, see eq. 6.

$$Ag_3M_3(CO)_{12}(dmpe)_3 + 3 \, HI \rightarrow 3Ag + 3MI(CO)_4(dmpe) + \tfrac{3}{2}H_2 \qquad (6)$$
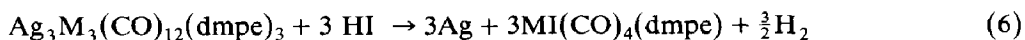
It is quite remarkable that the alternative products, AgI and $MH(CO)_4(dmpe)$ are not observed, especially considering that tertiary phosphine-substituted hydrido complexes of tantalum(I) corresponding to that formulation are known [10a,34]. This observation is again essentially in agreement with the presence of bare silver atoms in the cluster structure, which simply undergo M–Ag bond fission under the influence of HI.

Acknowledgements

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