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Redox Reactions with Metal Carbonyls of Group V

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The carbonylmetalates of cobalt(-I), manganese(-I), chromium(-I), molybdenum(-I), tungsten(-I), and the anionic carbonyl cyclopentadienyl derivatives of the zerovalent Group VI metals ($[MCp(CO)_3]^-$, M = Cr, Mo, W) are readily oxidized by hexacarbonylvanadium(0) to give the neutral metal carbonyls. In the case of the $V(CO)_6/[Mn(CO)_5]^-$ system, by ^{13}CO-labeling of the oxidizing agent $V(CO)_6$, it is shown that the redox reaction occurs *via* an outer-sphere mechanism. On the other hand, hexacarbonylvanadium(0) behaves as a reducing agent towards $NiCp_2$ and $MnCp_2$, the reduced products being $Ni(CO)_4$ and $MnCp(CO)_3$, respectively. The hexacarbonylmetalates of niobium(-I) and tantalum(-I) are oxidized by a number of oxidizing agents, exclusively by a two-electron transfer process to niobium(I) and tantalum(I). When the acetylacetonato complexes of nickel(II) and iron(III) are used as oxidizing agents, the $M(acac)(CO)_4THF$ complexes (M = Nb, Ta) were obtained, the oxidation by nickel(II) being the preferred one from a preparative point of view. The crystal and molecular structure of the tantalum complex, $Ta(acac)(CO)_4THF$, has been solved by *X*-ray diffraction methods. Crystals are orthorhombic, space group $P2_12_12_1$, a = 15.347(3), b = 12.227(3), c = 8.642(3) Å, V = 1621.6 Å^3, D_c = 1.900 g · cm^{-3}, Z = 4. The tantalum atom is heptacoordinated, being surrounded by the bidentate acetylacetonato ligand, by four carbon monoxide groups, and by the oxygen atom of the THF ligand. The THF ligand of the complexes is easily substituted, together with one of the carbonyl groups, by isocyanides, and a bidentate tertiary phosphane, while with the monodentate triphenylphosphane a substitutional equilibrium is established.

Redox-Reaktionen von Metallcarbonylen der Gruppe V

Die Carbonylmetallate von Cobalt(-I), Mangan(-I), Chrom(-I), Molybdän(-I), Wolfram(-I) und die anionischen Carbonyl(cyclopentadienyl)-Derivate der nullwertigen Metalle der Gruppe VI ($[MCp(CO)_3]^-$, M = Cr, Mo, W) werden durch Hexacarbonylvanadium leicht zu den neutralen Metallcarbonylen oxidiert. Im Falle des $V(CO)_6/[Mn(CO)_5]^-$-Systems wird durch ^{13}CO-Markierung des oxidierenden Agens $V(CO)_6$ gezeigt, daß die Redox-Reaktion über einen "Outer-sphere"-Mechanismus erfolgt. Auf der anderen Seite wirkt Hexacarbonylvanadium(0) gegenüber $NiCp_2$ und $MnCp_2$ als Reduktionsmittel unter Bildung von $Ni(CO)_4$ bzw. $MnCp(CO)_3$. Die Hexacarbonylmetallate von Niobium(-I) und Tantal(-I) werden durch eine Anzahl oxidierender Agentien ausschließlich durch eine Zweielektronen-Übertragung zu Niobium(I) und Tantal(I) oxidiert. Mit den Acetylacetonato-Komplexen von Nickel(II) und Eisen(III) als oxidierenden Agentien wurden die Komplexe $M(acac)(CO)_4$ THF (M = Nb, Ta) erhalten, wobei die Oxidation mit Nickel(II) aus präparativer Sicht günstiger ist. Die Kristall- und Molekülstruktur von $Ta(acac)(CO)_4THF$ wurde durch Rönt-

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genstrukturanalyse ermittelt. Die Kristalle sind orthorhombisch, Raumgruppe $P2_12_12_1$, a = 15.347(3), b = 12.227(3), c = 8.642(3) Å, V = 1621.6 Å^3, D_c = 1.900 g·cm^{-3}, Z = 4. Das Tantal-Atom ist heptacoordiniert und wird umgeben vom zweizähnigen Acetylacetonato-Liganden, von vier CO-Gruppen und durch den Sauerstoff des THF-Liganden. Der THF-Ligand wird, zusammen mit einer der Carbonylgruppen, leicht durch Isocyanide und ein zweizähniges tertiäres Phosphan substituiert, während sich mit einem einzähnigen Phosphan ein Substitutionsgleichgewicht bildet.

Since its discovery[1)], hexacarbonylvanadium(0), a long-lived 17-electron species, has attracted considerable interest under several respects. Although its crystal and molecular structure is that expected for a mononuclear compound of octahedral geometry[2)], it has unusual magnetic properties in the solid state[3)], a drastic reduction of the magnetic moment being observed starting from about 60 K. In addition, the deep black-green colour in the solid state has been explained[4)] with a light excitation to a $[V(CO)_6]^+[V(CO)_6]^-$ state. Recent work from these Laboratories[5)] has shown that the closed shell $[V(CO)_6]^-$ anion of d^6 electronic configuration can function as a reducing agent in protonated nitrogen base adducts of formula $BH^+[V(CO)_6]^-$. Electron-transfer and charge-transfer processes mediated by carbonyl groups appear to be particularly facile with the $V(CO)_6$/$[V(CO)_6]^-$ couple, which is unique among metal carbonyl redox couples $M(CO)_n$/$[M(CO)_n]^-$ since no metal-metal bond is present in the oxidized species.

A preliminary communication[6)] has indicated that $V(CO)_6$ can behave as an oxidizing agent in outer-sphere redox processes towards the anions of manganese(-I), cobalt(-I), chromium(-I), molybdenum(-I), tungsten(-I), and the anionic cyclopentadienyl derivatives of zerovalent Group VI metals. Moreover, in the reductions of bis(cyclopentadienyl) derivatives of nickel(II) and manganese(II) promoted by $V(CO)_6$, the distribution of products and their nature is such to be typical of inner-sphere processes. On the other hand, hexacarbonylniobate(-I) undergoes oxidation by several oxidants via a 2-electron process[6)]. This paper reports the full details of the redox processes with hexacarbonyl derivatives of Group V metals, and the crystal and molecular structure of one of the products obtained via a reductive ligand transfer process between acetylacetonato complexes of iron(III) or nickel(II) and $[M(CO)_6]^-$, M = Nb, Ta.

Experimental

Unless otherwise stated, all of the operations were carried out under prepurified nitrogen or argon. Solvents were carefully dried by conventional methods prior to use. Cuprous halides were prepared according to literature methods[7)]. Anhydrous copper(II) and iron(III) chlorides were prepared by treating the hydrates with refluxing $SOCl_2$, followed by filtration, washing with n-heptane and drying under reduced pressure at 90°C for several hours. Anhydrous nickel(II) acetate was obtained by warming the hydrate at 100°C/ca. 10^{-2} Torr for about 10 h. Silver halides were prepared by precipitation from $AgNO_3$ aqueous solutions with the appropriate halide, followed by filtration, washing with water, EtOH and Et_2O in that order and drying in vacuo at room temperature. Anhydrous bis(acetylacetonato)-nickel(II) was prepared by heating the hydrate[8)] at 100°C under reduced pressure. Tris-

(acetylacetonato)iron(III) was obtained according to the literature method[9] and recrystallized from toluene/*n*-hexane. The tetraethylammonium derivatives, $[NEt_4]_2[M_2(CO)_{10}]$ (M = Cr, Mo, W), the tetrabutylammonium salts, $NBu_4[M(CO)_n]$ (M = Mn, n = 5; M = Co, n = 4), and $NBu_4[MCp(CO)_3]$ (M = Cr, Mo, W; Cp = η^5-C_5H_5) were prepared by reacting the appropriate ammonium bromide with the sodium salt of the complex anion[10-12] in water or alcohol as solvent.

The hexacarbonylmetalates(-I) of vanadium[13], niobium[14], and tantalum[14] and $V(CO)_6$[15] were prepared as previously described.

Preparation of $V(^{13}CO)_6$: The method, carried out at atmospheric pressure of CO and at room temperature, allowed the preparation of labelled $[V(^{13}CO)_6]^-$ without dilution of the commercially available (Merck Sharp & Dohme, Canada, 90% enriched) ^{13}CO and with the maximum possible utilization of the available volume of gas. A suspension of anhydrous VCl_3 (1.11 g, 7.05 mmol) in tetrahydrofuran (THF, 200 ml) contained in a 250 ml flask was treated at −78 °C with sodium sand (0.66 g, 28.7 mmol) and cyclooctatetraene (0.37 g, 3.56 mmol) in an atmosphere of ^{13}CO. The gas was introduced in the reaction flask from a burette, connected alternatively with the ^{13}CO reservoir. The temperature was raised slowly to the ambient value and after 48 h the reaction mixture was filtered and the volume of the solution containing the $[V(^{13}CO)_6]^-$ anion was reduced to ca. 50 ml by evaporation under reduced pressure. The solution was then cooled to dry-ice temperature and the yellow crystalline $Na[V(^{13}CO)_6]$ was collected by filtration and dried at 60°C/ca. 10^{-2} Torr (40% yield). – IR (THF): νCO 1844 sh, 1816 vs and 1783 w cm^{-1}; (acetone): 1817 cm^{-1}. – Hexacarbonylvanadium(0), $V(^{13}CO)_6$, νCO(*n*-heptane): 1934 cm^{-1} (1973 cm^{-1} for the unlabelled compound), was obtained as previously reported[15].

Reaction of $V(CO)_6$ with $CoCp_2$: A solution of $CoCp_2$ (0.323 g, 1.71 mmol) in toluene (30 ml) was treated with $V(CO)_6$ (0.381 g, 1.74 mmol) at −50 °C. While the reaction mixture was warming up to room temp., the formation of a violet solid was observed. The solid was filtered, washed with toluene, and dried in vacuo: 0.584 g (84%) of $[CoCp_2][V(CO)_6]$ after recrystallization from THF/Et_2O. – IR (THF): νCO 1892 m and 1856 vs; (acetone): 1859; (nujol mull): 3120 m, 1832 vs br, 1415 m, 1115 w, 1055 w, 1020 s, 860 s, 645 vs and 450 s cm^{-1}.

$C_{16}H_{10}CoO_6V$ (408.1) Calcd. C 47.1 H 2.5 Found C 47.0 H 2.4

Reaction of $V(CO)_6$ with $NBu_4[M(CO)_n]$ (M = Mn, n = 5; M = Co, n = 4): Only the reaction with the manganese complex is described in detail, the other being carried out under similar conditions. Tetrabutylammonium pentacarbonylmanganate(-I) (0.19 g, 0.43 mmol) was partially dissolved in toluene (25 ml) and treated at about −50 °C with $V(CO)_6$ (0.089 g, 0.41 mmol). An immediate colour change took place. The temp. of the reaction mixture was raised and the IR spectrum of the solution, measured at room temp., showed the carbonyl absorptions due to $Mn_2(CO)_{10}$ (2045 m, 2006 vs and 1981 cm^{-1}) and to $[V(CO)_6]^-$ (1852 cm^{-1}). When the reaction was carried out by using labelled $V(^{13}CO)_6$, the IR spectrum showed the presence of $Mn_2(^{12}CO)_{10}$ and $[V(^{13}CO)_6]^-$ (2045 m, 2006 vs and 1981 cm^{-1}; 1808 cm^{-1}) exclusively. In all cases, the reaction appeared to go to completion within few min from the time of mixing of the reagents.

Reaction of $V(CO)_6$ with $[NEt_4]_2[M_2(CO)_{10}]$ (M = Cr, Mo, W): The reaction with the chromium derivative is described in detail. The chromium complex (0.102 g, 0.18 mmol) in toluene (20 ml) was treated at about −50 °C with $V(CO)_6$ (0.080 g, 0.36 mmol) under carbon monoxide at atmospheric pressure. A fast gas absorption was noted and the IR spectrum of the solution, measured at room temp., showed the absorption at 1983 cm^{-1}

due to $Cr(CO)_6$. In a gasvolumetric control experiment, it was found that the absorption of CO was quantitative and it was complete in about 10 min, thus suggesting that the rate-determining step is probably the diffusion of the gas in the solution.

Reaction of $V(CO)_6$ with $NBu_4[MCp(CO)_3]$ (M = Cr, Mo, W): Only the reaction with the molybdenum complex is reported in detail, the others being carried out under similar conditions. A solution of the molybdenum derivative (0.257 g, 0.53 mmol) in toluene (20 ml) was treated with $V(CO)_6$ (0.125 g, 0.57 mmol) at −50°C. An immediate colour change occurred upon mixing the reagents: the reaction mixture was brought to room temp. and the IR spectrum showed the presence of the carbonyl stretching absorptions of $Mo_2Cp_2(CO)_6$ at 2011 w, 1954 vs and 1911 vs and that of $[V(CO)_6]^-$ at 1852 cm^{-1}.

Reaction of $V(CO)_6$ with $NiCp_2$: Bis(cyclopentadienyl)nickel(II) (0.243 g, 1.29 mmol) in toluene (30 ml) was treated with $V(CO)_6$ (0.566 g, 2.58 mmol) at −50°C. After 14 h stirring at room temp., the IR spectrum of the solution showed absorptions due to $Ni(CO)_4$ (2040 cm^{-1}) and to $VCp(CO)_4$ (2023 m and 1920 vs cm^{-1}). The volatile products were removed in vacuo and the IR spectrum of the condensed liquid showed the presence of $Ni(CO)_4$. The residue was sublimed at 50°C/ca. 10^{-2} Torr affording 0.57 g (96% yield) of pure $VCp(CO)_4$. A gasvolumetric control of the reaction showed that no significant volume change accompanied the reaction of $NiCp_2$ (0.33 mmol) with 0.66 mmol of $V(CO)_6$ in 10 ml of toluene.

Reaction of $V(CO)_6$ with $MnCp_2$: Bis(cyclopentadienyl)manganese(II) (0.257 g, 1.44 mmol) in toluene (50 ml) was treated with $V(CO)_6$ (0.315 g, 1.44 mmol) at −50°C under an atmosphere of carbon monoxide. The temp. was raised to the ambient value and the mixture was stirred for about 5 h. A spectrophotometric control of the solution showed no significant amounts of unreacted $V(CO)_6$. After filtration to eliminate a small amount of a yellow-orange solid, the solution was evaporated to dryness under reduced pressure and the residue was sublimed at 50°C/ca. 10^{-2} Torr to yield 0.43 g of a mixture of $MnCp(CO)_3$ and $VCp(CO)_4$, as shown by the IR spectrum in the carbonyl stretching region.

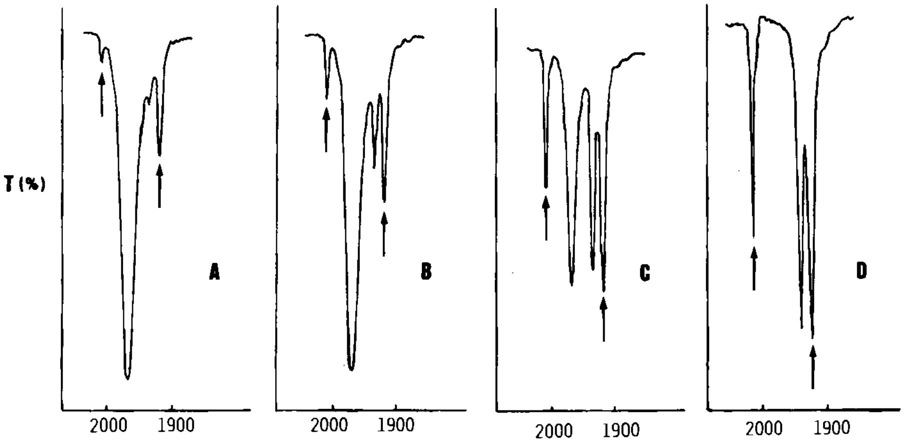

Fig. 1. Reaction between $V(CO)_6$ and $MnCp_2$ in *n*-heptane as solvent at room temperature. (A) 10 min from mixing. (B) After 40 min. (C) After 150 min. (D) After 15 h. The bands marked with an arrow are due to $VCp(CO)_4$. The band at 2027 cm^{-1} is common to both compounds

The reaction was carried out in *n-heptane* as solvent at room temp. and followed spectroscopically, as shown in Fig. 1, at different times. The final spectrum, measured after 15 h, had the bands due to $VCp(CO)_4$ and $MnCp(CO)_3$, as confirmed by an IR spectrum measured under the same conditions with authentic samples of the two substances ($VCp(CO)_4$: 2027 m, 1933 vs; $MnCp(CO)_3$: 2027 m, 1945 vs cm^{-1}.

Furthermore, a gasvolumetric control of the reaction showed that 0.19 mmol of $V(CO)_6$, when reacted with 0.19 mmol of $MnCp_2$ in 10 ml of toluene at 24.3 °C under an atmosphere of carbon monoxide, caused the absorption of 0.19 mmol of CO in about 40 min, corresponding to a CO/V molar ratio of 1.0.

Oxidation of $Na[Nb(CO)_6]$ *with CuX. Formation of* $Na[Nb_2(\mu\text{-}X)_3(CO)_8]$*:* Only the reaction with X = Cl is reported in detail, the others being carried out under similar conditions. A suspension of $Na[Nb(CO)_6] \cdot 0.5$ THF[16] (6.266 g, 19.6 mmol) in THF (150 ml) was treated at −50°C with CuCl (3.958 g, 39.98 mmol) under nitrogen. While the temp. was being raised towards the ambient value, the suspension turned brown, a copper mirror was formed, and a vigorous evolution of carbon monoxide took place. The brown suspension was stirred until no more gas evolution was noticed (4 h), then it was filtered and the clean brown solution was evaporated to dryness under reduced pressure. The residue was treated with *n*-heptane (50 ml), filtered, washed with *n*-heptane, and dried in vacuo affording 4.43 g (72%) of $Na[Nb_2(\mu\text{-}Cl)_3(CO)_8] \cdot 1.2$ THF in the form of a brown microcrystalline solid. It was identified analytically (Cl, CO) and by spectroscopic comparison with an authentic sample prepared as previously described[17,18].

Similar reactions, carried out with CuBr and CuI, afforded the corresponding bromo and iodo derivatives, which were identified analytically (halogen, CO) and spectroscopically by comparison with authentic samples obtained[18] by oxidation of $Na[Nb(CO)_6]$ with Br_2 and I_2, respectively.

Reaction of $Na[Nb(CO)_6]$ *with* $CuCl_2$*:* By operating as described in the preceding section, the μ-Cl anion was obtained by treating the hexacarbonylniobate(-I) (0.857 g, 1.73 mmol) with the stoichiometric amount of $CuCl_2$ (0.245 g, 1.8 mmol) in THF (30 ml) as solvent (68% yield). In a control gasvolumetric experiment, 0.25 mmol of $Na[Nb(CO)_6]$, treated with 0.29 mmol of anhydrous $CuCl_2$ in THF (10 ml) at 24.3 °C, caused the evolution of 0.495 mmol of CO, corresponding to a CO/Nb molar ratio of 1.98.

Similar oxidations of $Na[Nb(CO)_6]$ were carried out with anhydrous $FeCl_3$, AgX, $HgCl_2$. In all cases, fast reactions were observed at room temp., although the mixing of the reagents was initially carried out at −50°C. In the case of $FeCl_3$, the usual work up of the reaction mixture was modified as follows: the solvent (THF) was removed in vacuo and dichloromethane was added; after filtration, the clear solution was partially evaporated under reduced pressure and the dimeric anion was precipitated by addition of *n*-heptane (80% yield). In the other cases, the $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$ anion was identified spectroscopically in the crude reaction mixture.

Oxidation of $Na[Nb(CO)_6]$ *with* $NbCl_5$ *and Subsequent Reaction with LiCp:* A solution of $Na[Nb(CO)_6] \cdot 2$ THF (1.052 g, 2.12 mmol) in dimethoxyethane (30 ml) under CO was treated dropwise at −40 °C with a solution of $NbCl_5$ (1.62 mmol) in the same solvent (45 ml). Immediate reaction was observed; the temp. was allowed to raise slowly. The IR spectrum of the solution which had been stirred at room temp. for 30 min, showed the carbonyl stretching vibrations at 2017 m and 1903 vs cm^{-1} typical of the $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$ anion. This solution was then cooled to 0°C and 3.22 mmol of LiCp dissolved in dimethoxyethane (35 ml) was added dropwise in 30 min. The IR spectrum of the resulting solution had bands at 1860 and at 2029 m, 1917 vs cm^{-1} due to $[Nb(CO)_6]^-$ and to $NbCp(CO)_4$, respectively. The solvent was removed under reduced pressure and the residue was sublimed at 70°C/ca. 10^{-2} Torr affording 0.44 g (51%) of $NbCp(CO)_4$ as dark red crystals.

Reaction of Na[Nb(CO)$_6$] with Bis(acetato)nickel(II): Anhydrous bis(acetato)nickel(II) (0.271 g, 1.53 mmol) was suspended in THF (50 ml) and treated with $Na[Nb(CO)_6] \cdot 1.8$ THF (0.304 g, 0.74 mmol) under carbon monoxide. After 68 h stirring at room temp., the IR spectrum of the solution showed the carbonyl stretching bands at 2040 cm^{-1} due to $Ni(CO)_4$ and at 2015 m and 1879 vs cm^{-1} due to the $[Nb_2(\mu\text{-}MeCO_2)_3(CO)_8]^-$ anion[18]. The suspension was filtered and the solution was evaporated to 10 ml under reduced pressure. Addition of *n*-heptane caused the precipitation of the acetato complex $Na[Nb_2(\mu\text{-}MeCO_2)_3(CO)_8] \cdot 2$ THF (0.094 g; 34%). Spectroscopic properties and analytical data were in

Table 1. Carbonyl stretching vibrations (cm^{-1}) of niobium(I) and tantalum(I) acetylacetonato carbonyl complexes

	Nb	Ta
$M(acac)(CO)_4THF$		
n-heptane	2017 m, 1920 vw, 1907 s, 1892 s	2011 m, 1913 s, 1879 s
toluene	2014 m, 1890 s	2004 m, 1875 vs
THF	2011 m, 1882 br, vs	2006 m, 1885 w, 1871 vs
dichloromethane	2012 m, 1894 br, vs	2006 m, 1875 br, vs
dimethoxyethane	2011 m, 1868 vs	2001 m, 1858 vs
nujol	2011 m, 1877 vs	2001 m, 1867 vs
$M(acac)(CO)_3(PPh_3)_2$		
toluene	1934 s, 1840 vs, 1826 m	1923 s, 1816 vs
nujol	1929 s, 1838 vs, 1809 vs	1916 s, 1816 vs
$M(acac)(CO)_3(\widehat{PP})$[a]		
toluene	1960 s, 1865 s, 1818 m	1947 s, 1853 s, 1813 m
nujol	1997 w, 1923 s, 1827 br, vs	1998 w, 1914 s, 1813 vs
$M(acac)(CO)_3(CyNC)_2$		
toluene[b]	1952 m, 1867 vs, 1823 w	1954 m, 1935 w, 1855 vs
nujol[b]	1945 vw, 1865 br, vs	1932 vw, 1854 br, vs
$M(acac)(CO)_4(PPh_3)$		
toluene	–	2001 m, 1875 vs[c]

[a] $\widehat{PP}$ = 1,2-bis(diphenylphosphino)ethane. – [b] $\tilde{\nu}_{N=C}$ (M = Nb): 2119 m, 2000 w cm^{-1} (toluene); 2114 mw, 2000 w cm^{-1} (nujol). $\tilde{\nu}_{N=C}$ (M = Ta): 2119 m, 2000 w cm^{-1} (toluene); 2096 mw, 1999 w cm^{-1} (nujol). – [c] Spectroscopically identified.

Table 2. ^{1}H-NMR spectra in C_6D_6 of $M(acac)(CO)_4THF$ (M = Nb, Ta) (δ-values in ppm referred to TMS as internal standard)

	Nb	Ta
CH (acac)	5.00 (1H, s)	5.07 (1H, s)
2,5-CH_2 (THF)[a]	3.28 (4H, m)	3.35 (4H, m)
CH_3 (acac)	1.62 (6H, s)	1.62 (6H, s)
3,4-CH_2 (THF)[a]	1.13 (4H, m)	1.13 (4H, m)

[a] Uncomplexed THF, in C_6D_6 as solvent, shows these resonances at 3.60 and 1.45 ppm, respectively.

agreement with those of the same compound obtained either by reaction of $Na[Nb(CO)_6]$ with acetic acid[17] or by ligand exchange from the chloro derivative[18].

Reaction of Na[M(CO)$_6$], M = Nb, Ta, with Bis(acetylacetonato)nickel(II). Preparation of M(acac)(CO)$_4$ THF: The reaction with the niobium derivative is reported in detail, the tantalum case being very similar. A solution of $Ni(acac)_2$ (5.73 g, 22.3 mmol) in THF (100 ml) was treated at room temp. with $Na[Nb(CO)_6] \cdot 5.2$ THF (7.39 g, 11.2 mmol). The yellow suspension was stirred overnight under CO at atmospheric pressure. The solvent was then removed in vacuo and the residue was dissolved in 100 ml of boiling pentane. After filtration the filtered solution was evaporated up to initial crystallization and then cooled to about −30°C to afford 3.03 g (71%) of $Nb(acac)(CO)_4THF$ as red crystals.

$C_{13}H_{15}NbO_7$ (376.2) Calcd. CO 29.8 Nb 24.7 Found CO 30.0 Nb 23.5

The corresponding tantalum derivative was obtained in 67% yield as red-orange crystals, by reacting $Na[Ta(CO)_6]$ with bis(acetylacetonato)nickel(II) in the 1:2 ratio in THF as solvent.

$C_{13}H_{15}O_7Ta$ (464.2) Calcd. CO 24.1 Ta 39.0 Found CO 24.3 Ta 39.0

The crystals for the *X*-ray diffractometric study of the tantalum derivative were obtained by recrystallization at about −30°C from a pentane solution.

The spectroscopic data of the acetylacetonato complexes of niobium(I) and tantalum(I) are in Tables 1 and 2.

Ta(acac)(CO)$_4$ THF: X-ray Data Collection and Reduction[19]: A crystal with dimensions $0.17 \times 0.10 \times 0.10$ mm^3 was mounted on a computer controlled Philips PW 1100 single-crystal diffractometer, equipped with graphite monochromatized Mo-K_α radiation, λ = 0.71069 Å. The crystals are orthorhombic. The cell dimensions, determined by a least-squares calculation based on the setting angles of 25 reflections with 2ϑ angles ranging between 10 and 20°, are: a = 15.347(3), b = 12.227(3), c = 8.642(3) Å, V = 1621.6 Å^3. The space group is $P2_12_12_1$ (from systematic extinctions). The calculated density for four $Ta(C_5H_7O_2)(CO)_4(C_4H_8O)$ molecules in the unit cell is 1.900 g · cm^{-3}, the absorption coefficient for the Mo-K_α is μ = 66.93 cm^{-1}, F(000) = 888.

The intensities of *hkl* and $\bar{h}kl$ reflections were collected up to $2\vartheta \leqslant 50°$; the ω-2ϑ scan technique was employed, the scan range being 1.4° and the speed 0.05° s^{-1}. Totally, 3180 reflections were measured. Owing to the presence of anomalous dispersion, the intensities of pairs of reflections are sensibly different and were merged and averaged only in the *hk*0, *h*0*l* and 0*kl* zones to obtain a total of 2896 reflections, 1328 of which, having $I \leqslant 2\sigma(I)$, were considered as "unobserved" and excluded from the refinement. Three standard reflections which were measured periodically, showed no apparent variation in the intensity during data collection. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of *North* et al.[20]; the transmission factors were in the range 0.98−0.69. The data were corrected for Lorentz and polarization factors.

The structure was solved by Patterson method and refined by the full-matrix least-squares method with SHELX-76[21] package of programs. Anisotropic thermal parameters were refined for the tantalum atom. The hydrogen atoms (with the exception of those of the methyl groups) were included at the calculated positions (C−H = 1.08 Å) with overall isotropic parameter U = 0.10 Å^2. The methyl groups were refined as rigid groups starting from the staggered position. The refinement converged to R(unweighted) = 0.029 and R(weighted) = 0.031 for 99 parameters and 1568 observed reflections [$R_w = (\Sigma w(|F_o| - |F_c|)^2)^{1/2}/$

$(\Sigma w F_o^2)^{1/2}$, $w = (\sigma^2(F_o) + 0.0017 F_o^2)^{-1}$]. The atomic scattering factors were taken from ref.[21] for O, C and H and from ref.[22] for Ta; the correction for anomalous dispersion was included. At the end of the refinement all the positional parameters were inverted and several least-squares cycles were performed: the R index raised to 0.036 (R_w = 0.039), confirming that the results here reported concern the exact absolute configuration of the structure. The atomic coordinates are listed in Table 3.

Table 3. Fractional atomic coordinates of $Ta(C_5H_7O_2)(CO)_4(C_4H_8O)$. Estimated standard deviations in parentheses refer to the last digit

Atom	x/a	y/b	z/c
Ta	0.44349(4)	0.18869(4)	0.02234(5)
O(1)	0.5730(7)	0.2990(10)	-0.2278(12)
O(2)	0.5550(9)	0.0038(11)	-0.1500(15)
O(3)	0.3108(8)	0.0199(9)	-0.1386(13)
O(4)	0.3285(8)	0.3071(11)	-0.2417(13)
O(5)	0.4164(5)	0.0999(7)	0.2298(9)
O(6)	0.5408(6)	0.2556(7)	0.1701(9)
O(7)	0.3646(6)	0.3101(10)	0.1712(10)
C(1)	0.5222(10)	0.2624(12)	-0.1387(17)
C(2)	0.5132(10)	0.0694(13)	-0.0794(18)
C(3)	0.3573(9)	0.0824(12)	-0.0826(16)
C(4)	0.3694(11)	0.2601(13)	-0.1460(20)
C(5)	0.4444(11)	0.1130(11)	0.3708(15)
C(6)	0.3990(10)	0.437(13)	0.4871(21)
C(7)	0.5102(9)	0.1837(13)	0.4110(16)
C(8)	0.5536(9)	0.2494(10)	0.3122(13)
C(9)	0.6276(10)	0.3176(15)	0.3752(17)
C(10)	0.2733(13)	0.2931(17)	0.2246(24)
C(11)	0.2500(15)	0.3902(18)	0.3206(28)
C(12)	0.3118(13)	0.4758(17)	0.2736(24)
C(13)	0.3900(13)	0.4260(17)	0.1881(23)

Reaction of Na[Nb(CO)$_6$] with Fe(acac)$_3$: A solution of Fe(acac)$_3$ (1.523 g, 4.32 mmol) was treated with Na[Nb(CO)$_6$] · 1.8 THF (0.854 g, 2.08 mmol) at −50°C. The originally orange-red suspension became red-brown and gas evolution was observed when the temperature was gradually increased to the ambient value. An IR spectrum of the solution showed absorptions due to Nb(acac)(CO)$_4$THF. However, a pure product could not be isolated, mainly due to the comparable solubilities with the reduction product, Fe(acac)$_2$. A gasvolumetric control of the reaction showed that by reacting 0.31 mmol of Na[Nb(CO)$_6$] with 0.61 mmol of Fe(acac)$_3$ in dimethoxyethane (10 ml) at 24°C, 0.63 mmol of CO were evolved in a few min, corresponding to a CO/Nb molar ratio of 2.03.

A solution of Fe(acac)$_3$ (0.115 g, 0.32 mmol) and dibenzo-18-crown-6 (0.056 g, 0.16 mmol) in THF (20 ml) was treated with Na[Nb(CO)$_6$] · 1.8 THF (0.061 g, 0.15 mmol) at room temperature. The IR spectrum of the solution measured 20 h after mixing of the reagents showed that no carbonyl species other than [Nb(CO)$_6$]$^-$ was present.

A solution of Fe(acac)$_3$ (0.048 g, 0.14 mmol) in dimethylformamide (10 ml) was treated with Na[Nb(CO)$_6$] · 1.8 THF (0.025 g, 0.060 mmol) at room temperature. The IR spectrum of the solution in the carbonyl stretching region, measured after 20 h did not show any carbonyl compound other than $[Nb(CO)_6]^-$.

Reactions of M(acac)(CO)$_4$THF

a) *Substitution Reactions*

Preparation of M(acac)(CO)$_3$(PPh$_3$)$_2$, M = Nb, Ta: A solution of PPh_3 (0.690 g, 2.63 mmol) in toluene (25 ml) was stirred under reduced pressure with $Nb(acac)(CO)_4THF$ (0.198 g, 0.53 mmol) for 1 h. The resulting red solution was concentrated to about 10 ml and *n*-heptane was added. The orange precipitate of the triphenylphosphane derivative was filtered, washed with warm *n*-heptane (6 x 20 ml) and dried in vacuo (0.253 g, 60%).

$C_{44}H_{37}NbO_5P_2$ (800.6) Calcd. C 66.0 H 4.7 CO 10.5 Found C 65.7 H 4.3 CO 10.4

By operating in a similar manner, the tantalum analogue was prepared in a 53% yield.

$C_{44}H_{37}O_5P_2Ta$ (888.7) Calcd. C 59.5 H 4.2 CO 9.5 Found C 58.9 H 4.0 CO 9.0

A gasvolumetric experiment carried out with 0.36 mmol of $Nb(acac)(CO)_4THF$ and triphenylphosphane (2.15 mmol) in toluene (25 ml) at 24.5°C under CO at atmospheric pressure, gave CO evolution corresponding to 0.22 mmol, for a CO/Nb molar ratio of 0.61. In the course of an analogous experiment with tantalum, the CO evolution corresponded to a CO/Ta molar ratio of 0.5. Moreover, a solution of the bis(triphenylphosphane) derivative $Ta(acac)(CO)_3(PPh_3)_2$ (0.193 g, 0.217 mmol) in toluene (20 ml) maintained under carbon monoxide at atmospheric pressure at 23.5°C was found to absorb 0.35 mmol of CO per mol of tantalum, and the IR spectrum of the solution showed new carbonyl absorption bands at 2001 m and 1875 vs cm^{-1}, see Table 1, attributed to the tetracarbonyl compound $Ta(acac)(CO)_4(PPh_3)$.

Preparation of M(acac)(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$): A solution of $Nb(acac)(CO)_4THF$ (0.146 g, 0.40 mmol) in toluene (30 ml) was treated with one equivalent of 1,2-bis(diphenylphosphino)ethane. An immediate change of colour took place accompanied by CO evolution. After about 1 h, the volume of the solvent was decreased under reduced pressure and *n*-heptane was added. This caused the precipitation of the diphos complex as a red-orange microcrystalline solid, which was collected by filtration and dried in vacuo (72% yield).

$C_{34}H_{31}NbO_5P_2$ (674.5) Calcd. C 60.5 H 4.6 Found C 60.5 H 4.3

By a similar procedure, the tantalum analogue was prepared in 77% yield as a red-orange microcrystalline solid.

$C_{34}H_{31}O_5P_2Ta$ (762.5) Calcd. C 53.6 H 4.1 Found C 53.6 H 4.8

A gasvolumetric control of the reaction under carbon monoxide at 24.2°C in toluene as solvent showed that the tetracarbonyl-tetrahydrofuran complexes of niobium (0.404 mmol) and tantalum (0.32 mmol) treated with diphos (0.427 and 0.33 mmol, respectively) evolved CO in a CO/metal molar ratio of 1.0 in both cases: the CO evolution was substantially complete five min after mixing the reagents.

Preparation of M(acac)(CO)$_3$(CyNC)$_2$: A solution of $Nb(acac)(CO)_4THF$ (0.264 g, 0.57 mmol) in toluene (25 ml) was treated with cyclohexyl isocyanide (0.15 ml, 1.22 mmol). The solution turned promptly red-brown with evolution of gas. After 20 min stirring, the solution was evaporated to about 10 ml under reduced pressure and *n*-heptane was added. After cooling down to about −30°C, the red-brown cyclohexyl isocyanide complex was collected by filtration and dried in vacuo (0.106 g, 38%).

$C_{22}H_{29}N_2NbO_5$ (494.4) Calcd. C 53.4 H 5.9 N 5.7 Found C 53.0 H 5.8 N 5.2

By a similar procedure, the red-brown tantalum derivative was obtained in about the same yield.

$C_{22}H_{29}N_2O_5Ta$ (582.4) Calcd. C 45.4 H 5.0 N 4.8 Found C 44.8 H 5.1 N 4.6

Metathetical Reactions

Reaction with Dry HCl: A solution of $Nb(acac)(CO)_4THF$ (0.475 g, 1.26 mmol) in THF (30 ml) was treated with 1.30 mmol of dry HCl at −80°C. The IR spectrum of the resulting supernatant solution revealed the absorptions due to the $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$ anion and unreacted starting material. After cooling again to −80°C, 2.6 mmol of dry HCl was added, which caused the absorptions of the starting material to disappear from the IR spectrum. After filtration, the solution was partially evaporated under reduced pressure to about 5 ml and by addition of *n*-heptane, the analytically and spectroscopically pure $H(THF)_2[Nb_2(\mu\text{-}Cl)_3(CO)_8]$[17,18] was isolated in 92% yield.

The analoguous reaction was carried out between $Ta(acac)(CO)_4THF$ and dry HCl (1:3 molar ratio), with the exception that *n*-heptane was used as solvent instead of THF, due to the instability of the $[Ta_2(\mu\text{-}Cl)_3(CO)_8]^-$ anion in the latter solvent[17]. The IR spectrum in dichloromethane of the isolated product was superimposable to that of an authentic sample of the dimeric anion[18].

Reaction with NaOMe: A solution of $Nb(acac)(CO)_4THF$ (0.602 g, 1.6 mmol) in THF (50 ml) was treated with sodium methoxide (0.15 g, 2.6 mmol) at room temperature. The IR spectrum of the solution, measured 10 min after mixing the reagents, showed that no starting material was present. The mixture was evacuated to dryness at room temp. and the residue was dissolved in dichloromethane. After filtration the solution was treated with *n*-heptane (50 ml), which caused the separation of $Na[Nb_2(\mu\text{-}OMe)_3(CO)_8]$[18], analytically and spectroscopically pure.

Reaction with Lithium Cyclopentadienide, LiCp: A solution of $Nb(acac)(CO)_4THF$ (0.630 g, 1.67 mmol) in THF (30 ml) was treated with LiCp (0.122 g, 1.69 mmol) at room temperature. The IR spectrum of the solution measured 2 h after mixing the reagents showed the absorption due to $NbCp(CO)_4$ (2029 m and 1915 vs cm^{-1}) and to $[Nb(CO)_6]^-$ (1856 cm^{-1}). The solvent was evaporated to dryness under reduced pressure and the solid residue was sublimed at 100°C/ca. 10^{-2} Torr affording 0.305 g (65%) of spectroscopically pure $NbCp(CO)_4$.

Similar results were obtained in the case of the tantalum derivative ($TaCp(CO)_4$, 54% yield).

c) *Reduction*

Reduction of M(acac)(CO)₄THF with Sodium: A solution of $Nb(acac)(CO)_4THF$ (0.494 g, 1.31 mmol) in THF (50 ml) was treated with sodium sand (0.101 g, 4.4 mmol) under carbon monoxide at room temperature. The colour of the solution turned dark with absorption of gas. The IR spectrum of the solution after 10 h stirring revealed the presence of the absorption at 1856 cm^{-1} due to the $[Nb(CO)_6]^-$ anion. An analoguous result was obtained by operating under nitrogen and by using 1 mol of sodium per niobium.

The corresponding tantalum acetylacetonato complex was reduced by sodium to give the hexacarbonyltantalate(-I) anion.

Results and Discussion

Metal carbonyl derivatives of Group V transition elements are unique since the oxidized counterpart of $[V(CO)_6]^-$, $V(CO)_6$, has no metal-metal bond, contrary to what happens for other mononuclear carbonylmetalates (e.g., $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$) and, furthermore, the oxidized counterparts of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ have not been prepared as yet[23]. Thus, the study of redox processes for these systems is particularly facile (for vanadium) and attractive (for niobium and tantalum) since it is hoped that suitable conditions may be found to stabilize the neutral species. Moreover, when tetraalkylammonium cations are used, a moderate solubility is obtained for the carbonylmetalates in hydrocarbon solvents: thus, this allowed us to study redox processes in media of low polarity, which has not been done before to a great extent[24]. Redox processes involving $V(CO)_6$ in hydrocarbon solvents were carried out earlier[25], and the bis(cyclopentadienyl) cation $[VCp_2(CO)_2]^+$ could be isolated from the reaction of $V(CO)_6$ with VCp_2 in *n*-heptane as solvent under an atmosphere of carbon monoxide. Moreover, the reaction[26] of bis(arene)vanadium(0) complexes with CO to give $V(CO)_6$ was in fact shown[27] to lead to $[V(\eta^6\text{-arene})_2][V(CO)_6]$, the formation of $V(CO)_6$ from the latter ionic compound requiring the oxidation of $[V(CO)_6]^-$ or its treatment with protons.

Also the reaction of $V(CO)_6$ with aromatic hydrocarbons to give[28] $[V(CO)_4(\eta^6\text{-arene})][V(CO)_6]$ (the *X*-ray investigation of the 1,2,4,5-tetramethyl derivative has recently appeared[29]) was interpreted[28] as being due to the rate-determining partial substitution of carbonyl groups in $V(CO)_6$ to give η^2- or η^4-bonded vanadium(0) complexes, followed by electron transfer to still unreacted $V(CO)_6$ present in solution.

The results reported in this paper definitely establish that electron-transfer processes with the $V(CO)_6/[V(CO)_6]^-$ couple are quite general, are not limited to systems containing carbocyclic ligands, such as cyclopentadienyls and arenes, and that, beside behaving as an oxidizing agent, $V(CO)_6$ can also act as a reducing agent, if the appropriate counterpart is provided.

The oxidation of bis(cyclopentadienyl)cobalt(II) by $V(CO)_6$ belongs to the category of reactions already observed in the past, see equation (1).

$$V(CO)_6 + CoCp_2 \longrightarrow [CoCp_2][V(CO)_6] \qquad (1)$$

The product obtained from reaction (1) is substantially insoluble in the reaction medium (toluene or *n*-heptane) and has IR carbonyl stretching bands typical of the $[V(CO)_6]^-$ anion; there is, therefore, little doubt that the product has to be formulated as an ionic derivative containing the cobalticinium cation. In this case the driving force of the reaction is the large stability of both components of the product of equation (1), the cation and anion being both low-spin d^6 systems.

The reaction of $V(CO)_6$ with the carbonylmetalates of cobalt(-I), manganese(-I), and the others are less expected. The reactions shown in equations (2)–(5) have been carried out in toluene, where the tetraalkylammonium derivatives of the reagents are at least partially soluble.

$$V(CO)_6 + [Co(CO)_4]^- \longrightarrow 1/2\ Co_2(CO)_8 + [V(CO)_6]^- \tag{2}$$

$$V(CO)_6 + [Mn(CO)_5]^- \longrightarrow 1/2\ Mn_2(CO)_{10} + [V(CO)_6]^- \tag{3}$$

$$V(CO)_6 + 1/2\ [M_2(CO)_{10}]^{2-} \xrightarrow{CO} M(CO)_6 + [V(CO)_6]^- \tag{4}$$

$$V(CO)_6 + [MCp(CO)_3]^- \longrightarrow 1/2\ M_2Cp_2(CO)_6 + [V(CO)_6]^- \tag{5}$$

(M = Cr, Mo, W)

Similar to the reactions with the carbocyclic ligand containing species, also reactions (2) – (5) are clean and fast, as established by the IR spectra in the carbonyl stretching region. In one of them, equation (4), absorption of carbon monoxide is necessary: gasvolumetric measurements of the CO uptake established that the reaction is over in about ten minutes at room temperature and it is presumably diffusion-controlled. It is interesting noting that high reaction rates have been observed not only with the partially soluble tetrabutylammonium derivatives but also with sodium carbonylmetalates which are substantially insoluble in the reaction medium used (toluene). In this case we are dealing with an heterogeneous process occurring between the surface of the carbonylmetalate and dissolved $V(CO)_6$. Several outer-sphere processes are characterized[24)] by elevated reaction rates; the assumption was therefore that we are dealing here with this type of reaction. The outer-sphere mechanism for the reaction between $V(CO)_6$ and $[Mn(CO)_5]^-$ was definitely established by using ^{13}CO-labelled $V(CO)_6$ and showing, see Experimental Section, that no labeling was present in the manganese species and that only the reduced product of vanadium, $[V(^{13}CO)_6]^-$, was labelled, as shown by the IR data in the carbonyl stretching region. The question may then arise now how the electron-transfer process is actually taking place between the reduced and the oxidized carbonyl complexes. Although assistance by alkali ion has been suggested for redox processes involving the $C_{10}H_8/C_{10}H_8^-$ system[30)] and the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple[31)], we do not believe that the tetraalkylammonium cation plays any major role beside that of providing solubility to the reagents. On the other hand, the electron-transfer is believed to occur within the coordination sphere of the metals, thus by intermediacy of the carbonyl groups. It is interesting to note, in this connection, that the light excitation process to $[V(CO)_6]^+[V(CO)_6]^-$ suggested earlier[4)] and the molecular hydrogen evolution or the reductive C–C coupling process observed with protonated nitrogen base derivatives containing the $[V(CO)_6]^-$ anion[5)] are closely related processes to those reported in this paper.

On the other hand, reduction by $V(CO)_6$ have also been evidenced in this work. Treatment of $V(CO)_6$ with the bis(cyclopentadienyl) complexes of nickel(II) and manganese(II) lead to nickel(0) and manganese(I) carbonyl complexes, the latter containing the cyclopentadienyl ligand, according to equations (6) and (7).

$$2\,V(CO)_6 + NiCp_2 \longrightarrow 2\,VCp(CO)_4 + Ni(CO)_4 \tag{6}$$

$$V(CO)_6 + MnCp_2 + CO \longrightarrow VCp(CO)_4 + MnCp(CO)_3 \tag{7}$$

In the case of the nickel reaction, the driving force is presumably the formation of tetracarbonylnickel(0). It is interesting to note that a recent paper[32)] has pointed out the possibility of electroreducing $NiCp_2$ to $Ni(CO)_4$ under carbon monoxide, an intermediate $[NiCp(CO)]^-$ anion being presumably formed before loss of Cp^- and complete carbonylation can occur. Our reaction (6) occurs even under nitrogen atmosphere and, of course, a gasvolumetric control has shown that no CO absorption occurs during the reaction. These observations show that the formation of $VCp(CO)_4$ and $Ni(CO)_4$ according to reaction (6) is very selective, thus suggesting that we are dealing with a concerted process, in which the ligands are transferred from one metal centre to the other in such a way as to allow the exclusive formation of the observed products. In view of the fact that a ligand exchange process is occurring and that the reaction is slower than those shown in equation (2)–(5), we suggest that an inner-sphere process is involved. The same conclusions apply to reaction (7) also. When it was decided to carry out the reaction between $V(CO)_6$ and $MnCp_2$, the possibility was envisaged that this could lead to an electron-transfer process to $V(CO)_6$, leading to the formation of the still unknown $[MnCp_2(CO)]^+$ cation, isoelectronic with $[VCp_2(CO)_2]^+$. Apart from the similar electron counting with vanadium, the existence of manganese(III) carbonyl derivatives is a possibility: as a matter of fact, recently a manganese(III) carbonyl complex with a tetradentate Schiff base was reported[33)]. Absorption of carbon monoxide is necessary in order to obtain the final products of equation (7): this was ascertained by gasvolumetric measurement of the CO uptake (Exp. Section). Also in this case, no products other than those indicated in equation (7) were observed, thus showing the high selectivity of the process. The IR spectral data concerning this reaction are in Fig. 1 in the Experimental Section.

An interesting point concerning reactions (6) and (7) is that they show a substantial solvent effect. Although no quantitative data are available to substantiate this point, it has been noted that in toluene as solvent, reaction (7) is faster than in *n*-heptane: this can also be verified by comparing the reaction times reported in the Experimental Section for the redox process between $V(CO)_6$ and $MnCp_2$ on a preparative scale, as compared with those indicated in Fig. 1 for the spectroscopic study of the same reaction.

Turning now our attention to the hexacarbonylmetalates of niobium(-I) and tantalum(-I) it has been already pointed out that a common feature of the redox processes involving these species is the two-electron transfer to yield niobium(I) and tantalum(I) carbonyl derivatives[6,17,18)]. Hexacarbonylniobate(-I) can be oxidized to the known halo-bridged $[Nb_2(\mu\text{-}X)_3(CO)_8]^-$ anions by Cu(I), Cu(II), Fe(III), Ag(I), and Hg(II) halides, the reactions being usually run in THF as solvent. The generalized equation for the oxidation of the $[Nb(CO)_6]^-$ anion can therefore be written as in (8).

$$2\ [Nb(CO)_6]^- + 3\ X^- \longrightarrow [Nb_2(\mu\text{-}X)_3(CO)_8]^- + 4\ e^- + 4\ CO \qquad (8)$$

$(X = Cl, Br, I)$

Of importance is the case of the oxidation of $[Nb(CO)_6]^-$ by the pentachloride of niobium, since this reaction could be useful in the preparation of the dimeric octacarbonyl derivative. Although we have shown that the oxidation by niobium(V) takes place and that the chloro-bridged dimer $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$ is obtained in the solution, as evidenced by IR data in the carbonyl stretching region of the crude reaction mixture, the reaction is complicated by the formation of byproducts, presumably due to the further oxidation of Nb(I) by Nb(V). On the other hand, the occurrence of the synproportionation (9) was definitely established by the isolation of $NbCp(CO)_4$ by addition of LiCp to the solution containing the spectroscopically detected dimeric anion of niobium(I). This second metathetical step was accompanied by some reduction of niobium(I) to niobium(-I), as evidenced by the formation of some $[Nb(CO)_6]^-$ beside the main component, $NbCp(CO)_4$.

$$2\ NbCl_5 + 4\ [Nb(CO)_6]^- \longrightarrow 3\ [Nb_2(\mu\text{-}Cl)_3(CO)_8]^- + Cl^- \qquad (9)$$

Of particular interest are the reactions of the $[M(CO)_6]^-$ anions with the acetylacetonato complexes of nickel(II) and iron(III). They both lead to the tetracarbonyl-acetylacetonato complexes of niobium(I) and tantalum(I), according to the stoichiometry of equation (10).

$$[M(CO)_6]^- + acac^- + THF \xrightarrow{THF} M(acac)(CO)_4THF + 2\ e^- + 2\ CO \qquad (10)$$

$(M = Nb, Ta)$

In the case of nickel(II) as oxidizing agent, $Ni(CO)_4$ was detected as the resulting nickel-containing reduced product, whereas in the case of iron(III), the reduction to the corresponding iron(II) acetylacetonato complex was verified. From a preparative point of view, the reaction with nickel(II) is preferred since the reduced product is easily eliminated from the reaction mixture. On the other hand, as it is specified in the Experimental Section, an excess of the nickel(II) complex is necessary in order to convert all of the hexacarbonylmetalate(-I); this is probably due to further reaction of the metal(I) acetylacetonato complex with nickel(II). The acetylacetonato complex of niobium(I) and the dimeric chloro-bridged complex of niobium(I) have been shown to undergo oxidation by nickel(II), the latter being reduced to $Ni(CO)_4$.

From a mechanistic point of view, the reaction of the β-diketonato complex of iron(III) is more interesting, due to the good solubility of both the oxidizing agent and its reduced product and to the fact that the oxidation of Nb(-I) by Fe(III) takes place without any side-reaction. By gasvolumetric control of the evolved carbon monoxide, it was possible in fact to establish that the cited reaction is clean (CO/Nb molar ratio 2.03) and complete in a few minutes. On the other hand, substituting THF with dimethylformamide as solvent suppressed the reaction completely. The suggestion was therefore made that dimethylformamide, being a solvent of elevated dielectric constant (36.7[34]), could in fact solvate $Na[Nb(CO)_6]$ somehow interfering with the electron- and ligand transfer processes. In order to confirm this hypothesis, we decided to carry out a reaction in THF, to which one mol of dibenzo-18-crown-6 was added (with respect to the sodium ion present). Also this experiment was followed by no change of the $[Nb(CO)_6]^-$ anion, thus confirming that the sodium ion is involved in the process. An obvious function of the sodium ion is to bring the $[Nb(CO)_6]^-$ anion and the iron(III) complex close together, by complexation to the carbonyl and acetylacetonato oxygens of the coordinated structures of the two interacting species. Coordination of alkali metal ions to carbonylmetalates is well known[35] and interaction of transition metal coordinated oxygens with alkali ions is also well established[36].

In view of the still limited number of acetylacetonato-carbonyl derivatives of transition metals existing in the literature (the derivatives of rhodium(I)[37], iridium(I)[38], manganese(I)[39], ruthenium(II)[40] have been reported), we studied the product of reaction (10) by *X*-ray diffraction methods by using the tantalum de-

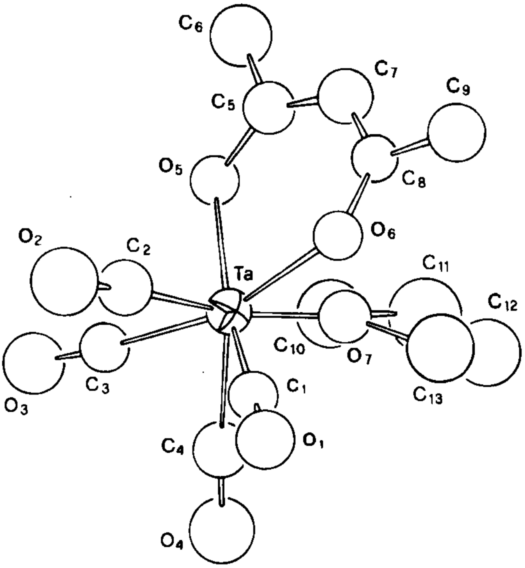

Fig. 2. View of $Ta(acac)(CO)_4$ THF, with the numbering scheme used in the text

rivative, which gave more suitable crystals. The monomeric nature of the compounds was definitely established. The dimeric formulation reported[6] in the preliminary communication should therefore by regarded as untenable, although it cannot be excluded that a monomeric-dimeric equilibrium may exist in solution under certain conditions. The molecular structure of the acetylacetonato complex is shown in Fig. 2.

The tantalum atom is heptacoordinated to four carbonyl groups, the two oxygen atoms of the acetylacetonato group and the oxygen atom of the tetrahydrofuran ligand. It can be roughly described as a square pyramid with the acetylacetonato and tetrahydrofuran groups coordinated about the axis. As a matter of fact, see Table 4, the angles at tantalum between adjacent carbonyl groups are comprised between 66.4 and 73.1°, whereas the angles between opposite carbonyl groups are 107.1 and 110.8°. This is a situation rather similar to that encountered[29] in the $[V(CO)_4(1,2,4,5\text{-}C_6H_2Me_4)]^+$ cation. Thus, the carbonyl groups can be regarded to possess an approximately C_{4v} local symmetry. According to this view, two bands (A_1 + E) would be expected to be IR-active, in agreement with the spectra in most solvents, see Table 1. On the other hand, in *n*-heptane, which usually displays a much higher resolution, the low wavenumber band around 1900 cm^{-1} is split in two bands. The molecule of the tantalum(I) complex possesses an idealized plane of symmetry passing through the acetylacetonato methine, the tantalum atom, the oxygen atom of the THF ligand, and two opposite carbonyl groups.

Table 4. Bond distances (Å) and angles (°) in $Ta(acac)(CO)_4THF$

Ta - O(5)	2.137(8)	O(5) - Ta - O(6)	80.1(3)	Ta - O(5) - C(5)	131.2(9)
Ta - O(6)	2.128(9)	O(5) - Ta - O(7)	75.9(3)	Ta - O(6) - C(8)	132.7(9)
Ta - O(7)	2.307(10)	O(5) - Ta - C(1)	155.1(5)	Ta - O(7) - C(10)	125.2(9)
Ta - C(1)	2.051(15)	O(5) - Ta - C(2)	95.8(5)	Ta - O(7) - C(13)	122.3(9)
Ta - C(2)	2.011(16)	O(5) - Ta - C(3)	85.6(4)	C(10) - O(7) - C(13)	110.6(12)
Ta - C(3)	2.064(14)	O(5) - Ta - C(4)	133.0(5)	Ta - C(1) - O(1)	174.4(13)
Ta - C(4)	2.042(17)	O(6) - Ta - O(7)	77.7(3)	Ta - C(2) - O(2)	174.8(13)
O(1) - C(1)	1.184(18)	O(6) - Ta - C(1)	79.9(5)	Ta - C(3) - O(3)	177.5(12)
O(2) - C(2)	1.195(21)	O(6) - Ta - C(2)	99.7(5)	Ta - C(4) - O(4)	176.3(14)
O(3) - C(3)	1.152(18)	O(6) - Ta - C(3)	162.8(3)	O(5) - C(5) - C(6)	114.1(14)
O(4) - C(4)	1.187(21)	O(6) - Ta - C(4)	130.8(5)	O(5) - C(5) - C(7)	123.8(14)
O(5) - C(5)	1.302(16)	O(7) - Ta - C(1)	113.9(5)	C(6) - C(5) - C(7)	122.1(14)
O(6) - C(8)	1.246(14)	O(7) - Ta - C(2)	171.6(5)	C(5) - C(7) - C(8)	125.3(14)
O(7) - C(10)	1.490(22)	O(7) - Ta - C(3)	108.3(4)	O(6) - C(8) - C(7)	125.6(13)
O(7) - C(13)	1.477(24)	O(7) - Ta - C(4)	80.2(5)	O(6) - C(8) - C(9)	116.1(12)
C(5) - C(6)	1.488(22)	C(1) - Ta - C(2)	73.1(6)	C(7) - C(8) - C(9)	118.2(13)
C(5) - C(7)	1.374(21)	C(1) - Ta - C(3)	110.8(6)	O(7) - C(10) - C(11)	106.7(16)
C(7) - C(8)	1.348(19)	C(1) - Ta - C(4)	69.9(6)	C(10) - C(11) - C(12)	105.0(18)
C(8) - C(9)	1.510(21)	C(2) - Ta - C(3)	72.1(6)	C(11) - C(12) - C(13)	110.8(17)
C(10) - C(11)	1.492(31)	C(2) - Ta - C(4)	107.1(6)	O(7) - C(13) - C(12)	102.8(14)
C(11) - C(12)	1.470(30)	C(3) - Ta - C(4)	66.4(6)		
C(12) - C(13)	1.535(29)				

An interesting aspect ist that the crystal which was chosen for the crystal structure determination was in fact one of the two enantiomers[41]. The compound in fact crystallizes in the $P2_12_12_1$ space group, which is one of the enantiomeric space groups. The relevant point here is that the crystal chosen for the *X*-ray determination was grown from *n*-pentane at $-30\,^{\circ}\mathrm{C}$. As expected, dissolution of the crystals of the compound did not lead to any appreciable optical activity, thus showing that no asymmetric induction had occurred at any stage of the reaction between bis(acetylacetonato)nickel(II) and $[\mathrm{Ta(CO)_6}]^-$.

Tetrahydrofuran adducts of low valent metal complexes such as those of manganese(I)[42], rhenium(I)[43], and chromium(0)[44] are generally labile. It was therefore expected that fast loosening of the THF ligand from the complex would lead to difficulties of crystallization. This was not observed, although, of course, the crystals were grown at $-30\,^{\circ}\mathrm{C}$, at which temperature the equilibrium between coordinated and free THF would be frozen. ^{1}H NMR data show that coordinated THF in $\mathrm{Ta(acac)(CO)_4THF}$ undergoes a relatively fast exchange with external THF at room temperature in $\mathrm{C_6D_6}$ as solvent (the exchange being practically complete in about 30 min).

The ^{1}H NMR spectrum of the acetylacetonato complex of tantalum(I) shows two singlets at 5.07 and 1.62 ppm due to the methine and methyl protons of the acetylacetonato ligand, respectively. The niobium(I) complex behaves similarly. The observed equivalence of the acetylacetonato methyl groups confirms that the solid state structure maintains in solution. The ^{1}H NMR data are in Table 2 including the resonances due to the THF ligand. For the latter it is interesting to note that the signals of the protons are shifted to higher fields on complexation, see Table 2, contrary to what had been found earlier[43] for a THF adduct of rhenium(I).

Relevant to the point of the rather high lability of the THF ligand in the niobium(I) and tantalum(I) acetylacetonato complexes, it is believed that the substitution reactions in $\mathrm{M(acac)(CO)_4THF}$ probably occur via a mechanism of THF dissociation. The reaction, see equation (11), is, for example, fast with the bidentate 1,2-bis(diphenylphosphino)ethane for which semiquantitative data of the time required for the CO displacement from the complex are available, based on gasvolumetric measurements. Also, it has been shown that, while with the bidentate tertiary phosphane, reaction (11) goes to completion even under carbon monoxide, with the monodentate triphenylphosphane an equilibrium situation was operating involving both CO and displaced THF, see equation (12). Moreover, preformed $\mathrm{Ta(acac)(CO)_3(PPh_3)_2}$ was found to absorb CO, thus showing that also equilibrium (13) is operating.

$$\mathrm{M(acac)(CO)_4THF} + \overset{\frown}{\mathrm{L\;\;L}} \longrightarrow \mathrm{M(acac)(CO)_3}(\overset{\frown}{\mathrm{L\;\;L}}) + \mathrm{CO} + \mathrm{THF} \qquad (11)$$

$$\mathrm{M(acac)(CO)_4THF} + 2\,\mathrm{PPh_3} \rightleftharpoons \mathrm{M(acac)(CO)_3(PPh_3)_2} + \mathrm{CO} + \mathrm{THF} \qquad (12)$$

$$\mathrm{Ta(acac)(CO)_3(PPh_3)_2} + \mathrm{CO} \rightleftharpoons \mathrm{Ta(acac)(CO)_4(PPh_3)} + \mathrm{PPh_3} \qquad (13)$$

The acetylacetonato ligand of the tetracarbonyl complex is rather labile, as shown by the facile metathetical reactions that it can undergo with hydrogen chloride, sodium methoxide, and lithium cyclopentadienide, see equations (14)–(16). It is believed that the labilization of the acetylacetonato ligand is probably triggered by the proton of HCl or by the alkali ions of the other reagents.

$$2\ \mathrm{M(acac)(CO)_4THF} + 3\ \mathrm{HCl} \longrightarrow \mathrm{H(THF)_2[M_2(\mu\text{-}Cl)_3(CO)_8]} + 2\ \mathrm{acacH} \tag{14}$$

$$2\ \mathrm{Nb(acac)(CO)_4THF} + 3\ \mathrm{NaOMe} \longrightarrow \mathrm{Na[Nb_2(\mu\text{-}OMe)_3(CO)_8]} + 2\ \mathrm{THF} + 2\ \mathrm{Na(acac)} \tag{15}$$

$$\mathrm{M(acac)(CO)_4THF} + \mathrm{LiCp} \longrightarrow \mathrm{MCp(CO)_4} + \mathrm{THF} + \mathrm{Li(acac)} \tag{16}$$

The acetylacetonato derivatives of niobium(I) and tantalum(I) are easily reduced by sodium in THF at room temperature to give the hexacarbonylmetalate(-I) anions, according to equation (17).

$$\mathrm{M(acac)(CO)_4THF} + 2\ \mathrm{Na} + 2\ \mathrm{CO} \longrightarrow \mathrm{Na[M(CO)_6]} + \mathrm{Na(acac)} + \mathrm{THF} \tag{17}$$

$$(\mathrm{M} = \mathrm{Nb, Ta})$$

The tendency to form the hexacarbonylmetalates is so high that, even in the absence of carbon monoxide, ligand redistribution occurs with partial decomposition of the starting carbonyl derivative.

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