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Review

METAL CARBONYL COMPLEXES OF GROUP VB METALS

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Introduction

Binary metal carbonyls of Group VB metals represent an interesting area of research in several respects: (a) the hexacarbonyl complexes are known for vanadium(0), $V(CO)_6$, and vanadium(−I), $[V(CO)_6]^-$, and for niobium(−I) and tantalum(−I), $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$; (b) the neutral species for niobium(0) and tantalum(0) have not yet been reported; (c) the neutral species for vanadium(0), is unique in that it has an odd valence electron count and yet there is no metal–metal bond formation; thus the $V(CO)_6/[V(CO)_6]^-$ redox couple is similar to several others such as $\frac{1}{2}$ $Mn_2(CO)_{10}/[Mn(CO)_5]^-$ or $\frac{1}{2}$ $Co_2(CO)_8/[Co(CO)_4]^-$ with the notable exception that, in contrast with what happens with manganese and cobalt, for which the monomeric $Mn(CO)_5$ and $Co(CO)_4$ are unstable, $V(CO)_6$ is a 17-electron long-lived radical and the study of its redox couple is considerably simplified. Most of the chemistry and the physical properties of Group VB metals is characterized by unusual features compared with those for more typical metal carbonyl systems. Some aspects will be outlined here in the light of recent investigations carried out in these and other laboratories.

Hexacarbonylvanadium(0) was discovered in 1959 [1] and its monomeric nature both in the solid state [1] and in solution [2] (as proved by magnetic susceptibility measurements which showed it to be paramagnetic at room temperature) was soon recognized. Although the crystal [1,3] and the molecular structure [3] of $V(CO)_6$ is that expected for a mononuclear compound of octahedral geometry, there is an unusual temperature dependence of the magnetic susceptibility, a drastic fall in the magnetic moment being observed at around 60 K [4,5]. The compound is deeply coloured, whereas its solutions in inert solvents (only saturated hydrocarbons can be regarded as unreactive towards $V(CO)_6$) and in the isostructural $Mo(CO)_6$ are yellow to orange [6]. Saturated hydrocarbon solutions of $V(CO)_6$ show a single strong band at 1973 cm^{-1} (in n-heptane), which is shifted to 1934 cm^{-1} by ^{13}CO labeling [7], again in agreement with an octahedral structure of the compound. The deep green-black colour of $V(CO)_6$ has recently been attributed to light excitation to a $[V(CO)_6]^+[V(CO)_6]^-$ state [8]. In view of the unusual properties of this compound, an X-ray diffraction study below 60 K would be justified, and work in progress is aimed at this. In view of the 17e → 18e conversion in conjunction with the low oxidation state of the metal, $V(CO)_6$ can behave as both an oxidizing agent (being reduced to the closed-shell 18e system of the $[V(CO)_6]^-$ anion of d^6 configuration) and a reducing agent.

The hexacarbonylmetalates of niobium(−I) and tantalum(−I) are also rather unique in that only the two-electron redox processes have so far been observed, leading to formation of the substituted niobium(I) and tantalum(I) carbonyl complexes of the unknown 18e $[M(CO)_7]^+$ cation of d^4 configuration. The latest results in this field are considered below, and an attempt is made to rationalize the known facts. A reasonably good understanding of the reactions undergone by the vanadium-carbonyl system has been reached, and the first attempts aimed at clarifying aspects of the niobium and tantalum systems have been made and will be discussed below.

Synthetic procedures

Contrary to what usually happens in the case of metal carbonyl derivatives of other transition elements, for which the usual synthetic procedures lead to the zerovalent complexes (e.g., the hexacarbonyl of chromium(0), molybdenum(0) and tungsten(0)) directly or to an easily decomposed hydride (e.g., the formation of $CoH(CO)_4$ from cobalt(II) salts with the CO/H_2 mixture, the hydride being unstable with respect to $Co_2(CO)_8$ and H_2 [9] at room temperature), the reductive carbonylations of vanadium salts are bound to give derivatives of the $[V(CO)_6]^-$ anion. Only carbonylation of vapourized metal in a matrix at about 20 K gives $V(CO)_6$ directly [10]. The original [11] method of preparation of $[V(CO)_6]^-$ required the use of both Mg and Zn as electropositive metals and pyridine as reaction medium: this system gave pyridine solutions of $Mg[V(CO)_6]_2$. The reaction was carried out at superatmospheric pressures of carbon monoxide at elevated temperature, and a somewhat elaborate isolation procedure has to be used for $V(CO)_6$; we shall come back to this point later. The other reducing systems were sodium metal in diglyme [12], and an electrochemical reduction of the vanadium salts [13] in an electrolytic cell operating under CO pressure with an aluminium anode. Recently a method for preparing the $[V(CO)_6]^-$ anion has been described which involves reduction of anhydrous VCl_3 [14] or its tetrahydrofuran adduct, $VCl_3 \cdot 3$ THF [6], with sodium in tetrahydrofuran in the presence of cyclooctatetraene: this method applies under atmospheric pressure and at [6] or slightly above [14] room temperature, and it appears to be the best route to the vanadium(−I) compound currently available.

In order to form $V(CO)_6$ from $[V(CO)_6]^-$ oxidation is required. The original method of isolating $V(CO)_6$ invariably consisted of treating the salts containing the $[V(CO)_6]^-$ anion with a mineral acid in the presence of a dehydrating agent (H_3PO_4/P_4O_{10} was most used [13b,15]). Our original method [11] involved treating $[V(CO)_6]^-$ with proton donors in aqueous solution, followed by the extraction of the precursor to $V(CO)_6$ in diethyl ether, drying the organic phase with a conventional solid drying agent, and concentrating the ether solution to a small volume: at this point molecular hydrogen evolution was observed, accompanied by the formation of $V(CO)_6$ which was isolated by sublimation at reduced pressure. Recent work has enabled us to elucidate the nature of the "precursor" to $V(CO)_6$ present in the organic phase which has come into contact with water (hereafter called "precursor II") and, consequently, to devise a better method of preparing $V(CO)_6$ involving reactions in hydrocarbon solvents rather than water. It has been shown [16] that $Na[V(CO)_6]$ reacts with dry HCl in saturated hydrocarbons at temperatures as low as about −78°C to give "precursor I", which rapidly decomposes to molecular hydrogen and $V(CO)_6$. Further, it has been shown that "precursor I" is also produced in rigorously anhydrous diethyl ether, and is immediately converted by the small amounts of water deliberately added into "precursor II", characterized by IR absorptions at 1910m, 1872s and 1812w cm^{-1}, typical of $[V(CO)_6]^-$ anion undergoing distortion from the octahedral symmetry to some lower one due to interaction with a countercation in solution (ion-pair formation in solution of carbonyl metalates is now well established [17]). The established experimental facts can thus be rationalized in terms of the following sequence:

$$[V(CO)_6]^- + HCl_{(solv)} \xrightarrow{\text{sat. hydrocarbon}} \underset{\text{"precursor I"}}{C_6HO_6V} + Cl^- \qquad (1)$$

$$C_6HO_6V \xrightarrow{\text{sat. hydrocarbon}} \tfrac{1}{2}\,H_2 + V(CO)_6 \qquad (2)$$

$$C_6HO_6V + H_2O \xrightarrow{Et_2O} \underset{\text{"precursor II"}}{[H_3O]^+[V(CO)_6]^-} \qquad (3)$$

The new method of preparation which has now been adopted in our laboratories is based on eq. 2, if water is rigorously excluded, $V(CO)_6$ crystallises out from the saturated hycrocarbon solution and can be filtered off.

Observation of reaction 3 was of interest since it implies that whatever is the structure [18,19] of "precursor I" it must be a very strong acid. Possible reasons for the observed increase in acid strength of $MH(CO)_n$ species in water in the sequence $MnH(CO)_5 < CoH(CO)_4 < VH(CO)_6$ has been discussed and a thermodynamic cycle including the rupture of the M–H bond and the energy related to the electron addition to the resulting $M(CO)_n$ fragment has been presented [18,20].

The nature of "precursor I" is still uncertain and we discuss later some further indirect experimental evidence related to this problem. As for "precursor II" this is certainly an onium derivative, as indicated in eq. 3. The formation of $V(CO)_6$ may therefore be visualized as an electron transfer from $[V(CO)_6]^-$ to a proton with formation of molecular hydrogen, according to eq. 4. Several examples of such electron transfer processes have been found recently, and are discussed in a subsequent section.

$$[H_3O]^+[V(CO)_6]^- \rightarrow \tfrac{1}{2}\,H_2 + H_2O + V(CO)_6 \qquad (4)$$

Efficient syntheses of the hexacarbonylmetalates of niobium(−I) and tantalum(−I) have been described only very recently [21,22]. In spite of the fact that these complexes have been known since 1961 [12], their preparations were difficult and sometimes accompanied by erratic results. Since the starting materials were the pentahalides of niobium(V) and tantalum(V), the reducing system used in the original preparation was sodium suspended in diglyme. The reported yield of $[Ta(CO)_6]^-$ was 32%, while $[Nb(CO)_6]^-$ was identified only spectroscopically. An improvement involved use of iron carbonyls and sodium/potassium alloy in a high pressure synthesis of both $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ (14% yield) [23]. A considerable improvement in the preparation of $[Nb(CO)_6]^-$ was obtained when it was found [21] that the Mg/Zn/pyridine system, which had been used for the carbonylation of the vanadium(III) salts to $[V(CO)_6]^-$, would work even better, at atmospheric pressure of CO and at room temperature, with niobium, as shown in eq. 5.

$$NbCl_5 \xrightarrow[p(CO)\ 1\ \text{atm, pyridine}]{\text{Mg/Zn/py, r.t.}} [Nb(CO)_6]^- \tag{5}$$

The essential prerequisite for a successful carbonylation of niobium(V) to niobium(−I) is the use of extremely well purified reagents. It has been shown [21] that, as expected, magnesium acts as the predominant reductant in this system, although the presence of zinc is required for reasonable rates. It has been suggested [21] that since the radical anion of pyridine is probably involved in the electron transfer, a better chemisorption of pyridine on zinc might facilitate the subsequent electron-transfer process. $TaCl_5$ is carbonylated by the same system, but the yields from both the carbonylation and the work up procedure are substantially lower than those for niobium. The hexacarbonylniobate(−I) can now be prepared in yields as high as 50% [24] based on $NbCl_5$ used, and quantities of $Na[Nb(CO)_6]$ as large as 20 g can be prepared in a single run.

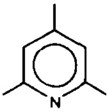
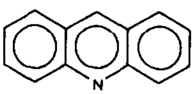
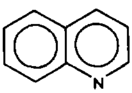
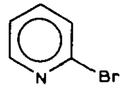
Electron-transfer processes

A. With $[V(CO)_6]^-$. Mention has been made earlier that treatment of $Na[V(CO)_6]$ with dry HCl in a saturated hydrocarbon or in diethyl ether produces $V(CO)_6$ and molecular hydrogen (eq. 2), and that the ethereal solutions containing $[H_3O]^+[V(CO)_6]^-$ also give $V(CO)_6$ upon concentration, (eq. 4). Dilute solutions of $[H_3O]^+[V(CO)_6]^-$ are indefinitely stable at room temperature, which shows that if the hydrated proton is separated from $[V(CO)_6]^-$ by the solvent no electron transfer can occur. Further recent work on protonated nitrogen base derivatives of the $[V(CO)_6]^-$ anion has thrown some light on both the nature of the "precursor I" of eq. 1 and the electron transfer to protons [19]. Although chemical [25] and photochemical [26,27] cleavage of M–H bonds of metal carbonyl hydrides $MH(CO)_n$ are well established, it is believed that eq. 1 does not involve such cleavage. Peripheral evidence suggests that "precursor I" does not contain a V–H bond and thus its ground state structure is not that of a hydride. A carbyne type structure, $(CO)_5V{\equiv}COH$, is preferred, although only indirect experimental evidence is available to support this hypothesis. It is interesting, however, to note that for the corresponding compound of cobalt, $CoH(CO)_4$, a recent calculation [28] has suggested that the carbyne type structure, $(CO)_3Co{\equiv}COH$, should be 7 kcal more stable than the formyl structure, $(CO)_3Co{-}C(O)H$, the hydrido structure containing a Co–H bond of course being the ground state, as shown by electron diffraction studies [29]. Some years ago, the pyridinium derivatives $[C_5H_5NX]^+[V(CO)_6]^-$ ($X = H$, Me) were prepared according to eq. 6 [30]. The pyridinium derivative with $X = H$ has now been studied by X-ray diffraction methods [19]. Coordination at vanadium is octahedral. The most important feature of the crystal structure is the interaction of the proton attached to nitrogen with the four equatorial carbonyl groups of the $[V(CO)_6]^-$ anion. The two axial carbonyl groups are not involved in this interaction but do interact with the pyridine π-electron density.

$$[C_5H_5NX]^+ + [V(CO)_6]^- \rightarrow [C_5H_5NX]^+[V(CO)_6]^- \tag{6}$$

TABLE 1

COLOUR AND PROPERTIES OF HEXACARBONYL DERIVATIVES OF PROTONATED HETEROCYCLIC NITROGEN BASES, $BH^+[V(CO)_6]^-$

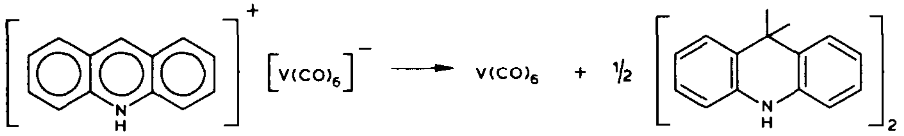
B				
pK_a	7.43	5.60	4.94	0.90
Colour	Brick-red	Green	Black	Brown
Chemical properties [a]	Stable	Reductive C–C coupling	Stable	$\frac{1}{2}H_2 + V(CO)_6$

[a] Thermal stability at room temperature.

The pyridinium derivatives obtained by reaction 6 are brown to orange substances, and the compound with X = H can be sublimed at about 70°C under reduced pressure. This shows that, as is confirmed by the X-ray investigation, we are dealing with a small lattice energy due to the large size of both the anion and the cation, and that the additional cation–anion interactions are mainly of the hydrogen-bonding type, i.e. rather weak. Several other protonated nitrogen base adducts of the $[V(CO)_6]^-$ anion have recently been prepared [19] and they range in colour from the yellow-orange of the 2,6-di-t-butyl pyridinium derivative to the black of the quinolinium compound as indicated in Table 1.

It is relevant to note that electron-transfer processes have been observed with the 2-bromopyridinium derivative and with the acridinium complex, according to eq. 7 and 8, respectively.

$$BH^+[V(CO)_6]^- \rightarrow \tfrac{1}{2}H_2 + V(CO)_6 + B \qquad (7)$$
$$(B = \text{2-bromopyridine})$$



(8)

It is noteworthy that formation of molecular hydrogen occurs rapidly with the pyridinium derivative which has the lowest pK_a, suggesting that the strength of the N–H bond is the dominant feature in this reaction. For species with rather high pK_a values, on the other hand, the electron-transfer process also occurs, as shown in eq. 8, although in this case no rupture of the N–H bond takes place, and reductive carbon–carbon coupling in the 9-position of the acridine ring occurs, with formation of 9,9′-biacridan.

B. Electron-transfer processes to protons with $[M(CO)_6]^-$ *(M = Nb, Ta).* Following the unsuccessful attempts to isolate the product of the reaction of $[V(CO)_6]^-$ with HCl in saturated hydrocarbon solution (which appeared to offer the best conditions for intercepting "precursor I"), we based our approach on the knowledge that on descending a vertical sequence of metals the strength of the M–H bond usually increases, as indicated, for example, by the considerably higher stability of

$OsH_2(CO)_4$ than of its iron and ruthenium analogues, and by some other peripheral information [18]. Thus, we thought that treatment of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ anions with HCl might enable isolation of hydrido complexes and permit a study of their thermal decomposition, which would have led finally to the neutral binary carbonyl of the metals, which, as mentioned above, have not yet been described. However, we soon discovered that (a) no formation of any hydrogen containing species was observable [31], and (b), one equivalent of the hexacarbonylmetalate would be capable of reducing two protons, and, in addition to one mol of H_2 per mol of metal, compounds containing niobium(I) and tantalum(I) were obtained. The first of these products to be isolated was the tetrahydrofuran-stabilized derivative $H(THF)_2[Nb_2Cl_3(CO)_8]$, whose X-ray structure showed the presence of the chloro-bridged dimeric anion, each heptacoordinated niobium atom being surrounded by three bridging chlorides and by four terminal carbonyl groups [31]. It is noteworthy that the dimeric anion can formally be thought as derived from the replacement of three carbonyl groups of $[Nb(CO)_7]^+$ to give $[NbCl_3(CO)_4]^{2-}$, followed by recombination with a $[Nb(CO)_4]^+$ fragment to give the final anion. Similar reactions to that just described for niobium(−I) have been shown also to occur with tantalum. The overall stoicheiometry of the redox process can be written as in eq. 9. The niobium(I) dimeric complexes are discussed in one of the later sections; the dimeric carbonyl anions of niobium(I) and tantalum(I) have considerable stability, as shown by the fact that several redox processes result in their formation.

$$2[M(CO)_6]^- + 4\,HCl \rightarrow 2\,H_2 + Cl^- + [M_2Cl_3(CO)_8]^- + 4\,CO \qquad (9)$$

On the other hand, the products obtained by reaction 9 are particularly useful materials for preparing other derivatives of niobium(I) and tantalum(I), which may be otherwise difficult to obtain. Among them are the cationic η^6-arene derivatives $[M(CO)_4(\eta^6\text{-arene})]^+$, obtained from dinuclear anions [32] by the aluminium bromide promoted ligand exchange reaction shown in eq. 10.

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

The cationic η^6-arene complexes in eq. 10 can be regarded as substitution products of the hypothetical $[M(CO)_7]^+$ cation. The recent preparation of the arene complexes of niobium(I) and tantalum(I) [32] completes the series of the cationic η^6-arene complexes of Group VB metals, which was initiated several years ago with the synthesis of the complexes of vanadium(I), obtained by the disproportionation reaction of $V(CO)_6$ promoted by aromatic hydrocarbons [33,34] (see eq. 11). We have not been able to prepare the derivatives of $[M(CO)_4(\eta^6\text{-arene})]^+$ containing an anion other than the halodialuminate; attempts to bring about exchange with another anion failed due to unfavourable solubility properties. Thus, we are not really able to comment, even qualitatively, on the stabilities of the vanadium arene complexes relative to those of the niobium and tantalum analogues. In the case of Group VIB arene complexes of formula $M(CO)_3(\eta^6\text{-arene})$, there are indications that the stability increases from chromium to molybdenum and tungsten [35].

$$2\,V(CO)_6 + \text{arene} \rightarrow [V(CO)_4(\eta^6\text{-arene})][V(CO)_6] + 2CO \qquad (11)$$

C. Oxidations of $[M(CO)_6]^-$, M = V, Nb and Ta. Oxidations of $[V(CO)_6]^-$ have not yet been studied in great detail. It is known that iodine oxidation produces VI_3 [30]. On the other hand, $Na[V(CO)_6]$ does not undergo oxidative additions easily: no reaction occurred when a sample of Na[$V(CO)_6$] was left for several hours in neat acetyl chloride. Nevertheless, as discussed above, reaction between Na[$V(CO)_6$] and HCl occurs rapidly even at dry-ice temperature. In our opinion, this is further strong evidence that the attack of the proton is not at the metal centre, but rather at the carbonyl oxygen of the $[V(CO)_6]^-$ anion, to produce "precursor I", to which the carbyne type structure was tentatively assigned.

In contrast, oxidations of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ have been extensively studied. The motivation for this extensive study was the possibility of obtaining the neutral binary carbonyls of these two metals. As it is very often the case with second and third row transition elements, the metal carbonyls gave derivatives of the metals in low oxidation states, still containing bonded carbon monoxide. A typical example is the reaction with I_2; whereas as mentioned above, the hexacarbonylvanadate gives VI_3 directly, $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ gave the dimeric $[M_2I_3(CO)_8]^-$ anions [32], according to eq. 12. This resembles the behaviour of Group VIB metal carbonyls, in that whereas $Cr(CO)_3(\eta^6\text{-arene})$ gives CrI_3 [36] with I_2, the corresponding molybdenum(0) and tungsten(0) complexes give the $[MI(CO)_3(\eta^6\text{-arene})]^+$ cations [37].

$$2[M(CO)_6]^- + 2\,I_2 \rightarrow [M_2I_3(CO)_8]^- + I^- + 4\,CO \tag{12}$$

Oxidations of the hexacarbonylmetalates of niobium(−I) and tantalum(−I) to the dimeric halide-bridged anions have been successfully carried out with a number of oxidizing agents, such as $FeCl_3$, AgX, $HgCl_2$, $CuCl_2$, CuCl, CuBr and CuI [7]. The general oxidation process can be written as in eq. 13 for the niobium derivative (most of the available data are for $[Nb(CO)_6]^-$).

$$2[Nb(CO)_6]^- + 3\,X^- \rightarrow [Nb_2X_3(CO)_8]^- + 4e^- + 4\,CO \qquad (X = Cl, Br, I) \tag{13}$$

The reaction of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ with the acetylacetonato complexes of nickel(II) and iron(III) also led to the acetylacetonato derivatives of niobium(I) and tantalum(I), which were isolated as their tetrahydrofuran adducts, $M(acac)(CO)_4THF$ (see eq. 14).

$$[M(CO)_6]^- + acac^- + THF \xrightarrow{THF} M(acac)(CO)_4THF + 2e^- + 2CO \tag{14}$$

In the case of bis(acetylacetonato)nickel(II), the two electrons in eq. 14 are transferred to nickel with formation of $Ni(CO)_4$, whereas the oxidation by tris(acetylacetonato)iron(III) leads to formation of the corresponding iron(II) complex. From a preparative point of view the nickel(II) reaction is preferable, whereas from a mechanistic viewpoint the iron(III) reaction is more interesting because of the absence of side reactions. It has been shown that the reaction between $Fe(acac)_3$ and $[Nb(CO)_6]^-$ is completely inhibited in dimethylformamide as solvent. Moreover, with THF as solvent but in the presence of one molar equivalent of dibenzo-18-crown-6, no reaction was observed even over long periods. This was attributed to a specific function of the alkali cation associated to $[Nb(CO)_6]^-$ in the electron-transfer process [38].

The structure of the acetylacetonato complex $Ta(acac)(CO)_4THF$, was solved by X-ray diffraction and shown to consist of a heptacoordinated tantalum atom surrounded by the bidentate acetylacetonato group, four carbon monoxide ligands, and the oxygen atom of the THF ligand [38].

D. $V(CO)_6$ as an oxidizing agent. The strong tendency of $V(CO)_6$ to undergo reduction to the $[V(CO)_6]^-$ anion had been established earlier. For example, VCp_2 is oxidized by $V(CO)_6$ to give in n-heptane as solvent and under atmospheric pressure of CO the $[VCp_2(CO)_2]^+$ cation [39]. Moreover, the reaction [40] of $V(\eta^6\text{-arene})_2$ with CO to give $V(CO)_6$ was shown [41] to lead to $[V(\eta^6\text{-arene})_2]^+[V(CO)_6]^-$, the formation of $V(CO)_6$ requiring the oxidation of $[V(CO)_6]^-$ or its reaction with protons, see eq. 4. Furthermore the formal disproportionation (eq. 11) of $V(CO)_6$ with aromatic hydrocarbons [33] was interpreted as being due to the rate-determining partial substitution of carbonyl groups in $V(CO)_6$ to give η^2- or η^4-bonded arene derivatives, followed by oxidation of the latter by the excess $V(CO)_6$ to give the observed final products. It has now been shown that the redox processes triggered by $V(CO)_6$ are quite general, and are not limited to systems containing carbocyclic ligands, such as cyclopentadienyls and arenes [38]. The reaction of $V(CO)_6$ with the carbonylmetalates of cobalt(–I), manganese(–I) and Group VIB metals in the zero or in the (–I) oxidation states are shown in equations 15–18. Like the reactions with the species containing the carbocyclic ligands, these fast redox processes are selective, as revealed by the IR spectra in the carbonyl stretching region. In one of these reactions, that shown in eq. 17, in which CO absorption occurs, it was possible to

$$2\,V(CO)_6 + 2[Co(CO)_4]^- \rightarrow Co_2(CO)_8 + 2[V(CO)_6]^- \qquad (15)$$

$$2\,V(CO)_6 + 2[Mn(CO)_5]^- \rightarrow Mn_2(CO)_{10} + 2[V(CO)_6]^- \qquad (16)$$

$$2\,V(CO)_6 + [M_2(CO)_{10}]^{2-} \xrightarrow{CO} 2\,M(CO)_6 + 2[V(CO)_6]^- \qquad (17)$$

$$2\,V(CO)_6 + 2[MCp(CO)_3]^- \rightarrow M_2Cp_2(CO)_6 + 2[V(CO)_6]^- \qquad (18)$$

$$(M = Cr, Mo, W)$$

establish by monitoring the gas absorption that the process is complete in a few minutes, and is probably diffusion-controlled. The reactions take place in an aromatic hydrocarbon as solvent (toluene) and provide rather rare examples of redox processes occurring in an organic solvent of such a low polarity [42]. The carbonylmetalate anions were introduced into the reaction as their partially soluble tetrabutylammonium derivatives. The outer-sphere mechanism suggested by some peripheral information for these processes was definitely established for the $[Mn(CO)_5]^-/V(CO)_6$ system by using ^{13}CO-labelled $V(CO)_6$ and showing that no labelling was present in $Mn_2(CO)_{10}$, and that $[V(^{13}CO)_6]^-$ was the product of the reaction ($\tilde{\nu}$(CO) 1808 cm^{-1} in toluene solution). It is believed that these redox processes occur within the coordination sphere of the metal, thus involving the intermediacy of the carbonyl groups, without the requirement of M–CO bond breaking at any stage of the reaction, as suggested by the labeling experiment and by the fact that substitution reactions of $V(CO)_6$, in spite of being much faster than those of the corresponding d^6 $M(CO)_6$ complexes of Group VIB metals [43], are considerably slower than those in reactions 15–18. It is interesting to note that light-promoted production of the excited $[V(CO)_6]^+[V(CO_6]^-$ state for $V(CO)_6$ [8] and the molecular hydrogen production in the $H^+/[V(CO)_6]^-$ system or the reductive C–C coupling in the acridine-$H^+/[V(CO)_6]^-$ system, are believed to be closely related processes, in which carbonyl-mediated electron-transfers may occur.

E. Hexacarbonylvanadium(0) as a reducing agent. Hexacarbonylvanadium(0) can also behave as a reducing agent, which is not surprising in view of its zero oxidation state. However, what is less usual, is the high selectivity of the processes observed [38]. Hexacarbonylvanadium(0) was found to reduce the cyclopentadienyl derivatives of nickel(II) and manganese(II), giving $Ni(CO)_4$ and $MnCp(CO)_3$, respectively, as in eq. 19 and 20, the oxidation product being $VCp(CO)_4$. Reaction 19 occurs even

$$2\ V(CO)_6 + NiCp_2 \rightarrow 2\ VCp(CO)_4 + Ni(CO)_4 \qquad (19)$$

$$V(CO)_6 + MnCp_2 + CO \rightarrow VCp(CO)_4 + MnCp(CO)_3 \qquad (20)$$

under an atmosphere of dinitrogen and a gasvolumetric experiment has shown that no absorption of gas occurs. These observations indicate that the formation of $VCp(CO)_4$ and $Ni(CO)_4$ probably occurs via a concerted process, within an intermediate involving bridging Cp and/or bridging CO groups.

Concluding remarks

The recent experimental results have revealed some interesting features of the hexacarbonyl derivatives of Group V transition metals. Hexacarbonylvanadium(0) undergoes two main types of reaction: (a) substitution processes; (b) electron-transfer processes. Whereas the substitution processes have been shown [43] to have some unique features (especially high second-order rate constants) attributed to the nature of long-lived radicals typical of $V(CO)_6$, the electron-transfer involving hexacarbonylvanadium(0) always involves one electron transfer to or from $V(CO)_6$, corresponding to oxidizing or reducing properties of this species. Both types of electron-transfer occur readily at room temperature or below in hydrocarbon solvents. In the case of the $[Mn(CO)_5]^-/V(CO)_6$ system, an outer-sphere process was suggested by labelling with $V(^{13}CO)_6$. Electron-transfer through metal-coordinated CO groups appears to occur rather readily in these vanadium-based processes.

In contrast to the $V(CO)_6/[V(CO)_6]^-$ system, for which the one-electron transfer process to $V(CO)_6$ to give the 18-electron complex $[V(CO)_6]^-$ is the predominant feature, no evidence has been gathered for such a one-electron process for the $[M(CO)_6]^-$ anions of niobium(−I) and tantalum(−I). With two-electron transfer being the predominant feature, complexes of niobium(I) and tantalum(I) resulted from the interaction with a number of oxidizing agents. Isolation of the neutral species of niobium(0) and tantalum(0) is still to come, and more sophisticated preparative procedures must be considered in order to reach this goal.

The most recent results with niobium and tantalum have revealed that substitution products of the hypothetical $[M(CO)_7]^+$ cation, such as $[M(CO)_4(\eta^6\text{-arene})]^+$, $M(acac)(CO)_4THF$, acac = $C_5H_7O_2$, and $[M_2(\mu\text{-}X)_3(CO)_8]^-$ are readily accessible. It is of interest to compare these results with those for the still hypothetical isoelectronic species $Ti(CO)_7$, whose substitution product, $Ti(CO)_3(dppe)_2$, was recently reported [44].

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