Journal of Organometallic Chemistry, 330 (1987) 47–59
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Reactions of hexacarbonyl derivatives of group 5 metals (V, Nb, Ta) with 9,10-phenanthrenequinone *

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(Received January 20th, 1987)

Abstract

9,10-Phenanthrenequinone (PQ) derivatives of vanadium, niobium and tantalum of formula $V(C_{14}H_8O_2)_3$ and $Na[M(C_{14}H_8O_2)_3]$ (M = V, Nb, Ta) have been prepared: (a) by reaction with PQ of the carbonyl derivatives $V(CO)_6$ and $Na[M(CO)_6]$ (M = V, Nb, Ta) and (b) by reaction of the anhydrous metal chlorides VCl_3 and M_2Cl_{10} (M = Nb, Ta) with the mono- or the di-anion of PQ. Reaction of $Na[M(C_{14}H_8O_2)_3]$ (M = Nb, Ta) with hydrogen chloride has given the protonated species $H[M(C_{14}H_8O_2)_3]$ in good yields.

Treatment of $V(C_{14}H_8O_2)_3$ or $Na[V(C_{14}H_8O_2)_3]$ with sodium sand in THF gave the reduced derivatives of formula $Na_n[V(C_{14}H_8O_2)_3]$ ($n = 1, 2, 3$) which were isolated and identified by elemental analysis and IR spectroscopy. Oxidation of the anionic species by silver ions was examined.

The reduced species $Na_3[M(C_{14}H_8O_2)_3]$ (M = V, Nb, Ta) react with benzyl chloride or triphenylmethylchloride in THF to give dibenzyl and hexaphenylethane, respectively.

Introduction

Low-valent metal carbonyl derivatives are useful starting materials for the preparation of coordination compounds. This aspect of the reactivity of metal carbonyls has been considered previously [1] in connection with its application to the synthesis of metal-quinone complexes [2]. These compounds are of interest because both the metal centre and the quinone ligand can be redox-active [2]. It is known [1] that 9,10-phenanthrenequinone (PQ, $C_{14}H_8O_2$) can bind to a transition

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* Dedicated to Professor Luigi Sacconi in recognition of his important contribution to inorganic and organometallic chemistry.

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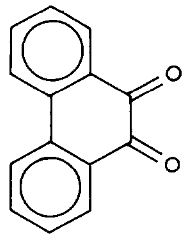
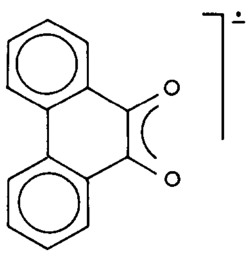


(A)



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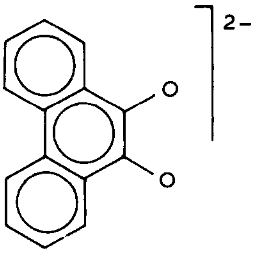

(C)

metal as the oxidized quinone (**A**) [3,4] or as the semiquinone anion (**B**) [5–11], or as the fully reduced diolate dianion (**C**) [1,5,12,13].

The $C_{14}H_8O_2$ ligand is a highly delocalized electron system, and as such can undergo chemical and electrochemical reduction [2], either when free or when coordinated to a transition element [1]. An example of such a redox ability has been observed in the phenanthrene semiquinone derivative of chromium(III), $Cr(C_{14}H_8O_2)_3$, which shows a reversible or quasi-reversible redox series corresponding to $Cr(quinone)_3^n$ complexes, where n ranges from 3 + to 3 − [14]. As far as the previous studies on these systems are concerned, relatively little is known about derivatives of 4*d* and 5*d* transition elements, except for some molybdenum complexes of formula $Mo(PQ)_3$ and $Mo_2O_5(PQ)_2$, prepared from the hexacarbonyl [8,12].

As part of our work [15] on hexacarbonyl derivatives of Group 5 metals (V, Nb, Ta), we have studied the reactions of $V(CO)_6$, $[V(CO)_6]^-$, $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ with 9,10-phenanthrenequinone, and obtained some new derivatives. A recent report [16] on vanadium derivatives of the same type prompted us to publish our results. In this paper we deal with the isolation of vanadium, niobium and tantalum complexes containing the $C_{14}H_8O_2$ ligand, and their reduction with sodium. Some of these products were also prepared from the anhydrous metal chlorides.

Experimental

Unless otherwise stated, all operations were carried out under prepurified nitrogen or argon. Solvents were carefully dried by conventional methods prior to use. Hexacarbonylvanadium(0) [17], sodium hexacarbonylvanadate(−I) [18], niobate (−I) [19] and tantalate(−I) [19] were prepared by literature methods. Nb_2Cl_{10} and Ta_2Cl_{10} (Fluka) were purified by refluxing in $SOCl_2$, evaporation to dryness of the resulting red (Nb) or pink (Ta) solutions, and sublimation at 100–110 °C/10^{-2} Torr to give yellow Nb_2Cl_{10} and colourless Ta_2Cl_{10}. 9,10-Phenanthrenequinone (Fluka) was purified by sublimation or by recrystallization from boiling tetrahydrofuran (THF). The monoanion, $C_{14}H_8O_2^{\dot{-}}$, as its sodium derivative, was prepared by reduction of 9,10-phenanthrenequinone with one equivalent of sodium sand in THF at room temperature. The suspension of the slightly soluble sodium derivative thus obtained was used for the further reactions with VCl_3. The infrared spectrum of the sodium derivative, isolated as a green microcrystalline solid analysing as $NaC_{14}H_8O_2$ after drying in vacuo, shows a very strong IR absorption at 1410 cm^{-1} attributed to the C–O stretching vibration.

IR spectra were recorded with a Perkin–Elmer model 283 instrument in solutions or as Nujol or halocarbon mulls of the complexes prepared with rigorous exclusion of air and moisture. Magnetic susceptibilities were measured with a magnetic balance equipped for the Faraday method and calibrated with $CuSO_4 \cdot 5H_2O$.

The amount of solvent retained by the products described in this paper was determined by heating the compound at $160\,°C/5 \times 10^{-2}$ Torr followed by weighting of the volatile products collected in a cold trap. The nature of the condensed product was established by IR or ^1H NMR spectroscopy.

Preparation of $Na_2(C_{14}H_8O_2)$

A solution of 3.22 g (15.5 mmol) of PQ in THF (200 ml) was treated with 0.69 g (30.0 mmol) of sodium sand. The orange solution initially became a green suspension, and after 10 h an orange-brown solution was obtained. No sodium was left. After filtration, the volume of the filtrate was reduced in vacuo until an orange microcrystalline solid formed. The precipitation of the solid was completed by addition of n-heptane (100 ml). The solid was filtered and dried in vacuo, to give 3.96 g (81% yield) of $Na_2(THF)[C_{14}H_8O_2]$ as an orange solid, which turns green immediately upon contact with air. Anal. Found: C, 66.0; H, 4.9. $C_{18}H_{16}Na_2O_3$ calcd.: C, 66.3, H, 4.9%.

Preparation of $V(C_{14}H_8O_2)_3$ (1)

(a) From $V(CO)_6$. A suspension of PQ (1.6 g; 7.7 mmol) in toluene (50 ml) was treated at about $-78\,°C$ with $V(CO)_6$ (0.53 g; 2.42 mmol). The mixture was then allowed to warm up and when the temperature was about $-40\,°C$, the orange suspension became dark-green and vigorous evolution of gas was observed. When the gas evolution had ceased (1 h), the solid formed was filtered off, washed with toluene (2 × 10 ml), and dried in vacuo, to give 1.75 g (69% yield) of $V(C_{14}H_8O_2)_3 \cdot$ 4toluene as a microcrystalline black-green solid, stable in air for a short time. Anal. Found: C, 81.0, H, 5.0, toluene, 36.5; $C_{70}H_{56}O_6V$ calcd.: C, 80.5, H, 5.4, toluene, 35.3%. $\chi_V^{corr} = +1500 \times 10^{-6}$ cgsu; (diamagnetic correction -625×10^{-6} cgsu); $\mu_{eff}(17.2\,°C)$ 1.87 BM. IR spectrum (Nujol mull): 3060vw, 1595m, 1545w, 1490vs, 1315s, 1260m, 1225m, 1160w, 1120m, 1115m, 935m, 760m, 755m-s, 720m, 710m, 690w, 670w, 540m-w and 430m-w cm^{-1}; (polychlorotrifluoroethylene mull): 3060vw, 2980vw, 2880vw, 1595m, 1545w, 1490vs, 1450w, 1390m-s, 1355w and 1315 m-s cm^{-1}.

Gas-volumetric monitoring of the reaction showed that on treatment of 0.17 mmol of $V(CO)_6$ with 0.53 mmol of PQ in toluene (10 ml) at $20\,°C$, 0.99 mmol of CO were evolved, corresponding to a CO/V molar ratio of 5.82.

(b) From VCl_3. Anhydrous VCl_3 (0.49 g; 31 mmol) was added to a suspension of $NaC_{14}H_8O_2$ obtained by treating a solution of PQ (1.92 g; 9.2 mmol) in THF (150 ml) with sodium sand (0.22 g; 9.6 mmol). After 10 h stirring at room temperature, the suspension was heated and filtered when hot. The filtrate was cooled to $-30\,°C$, and 0.114 g of crystalline product, identified as $V(C_{14}H_8O_2)_3 \cdot n$ THF from its IR spectrum in (Nujol) were obtained.

Preparation of $Na[V(C_{14}H_8O_2)_3]$ *(2)*

(a) From $Na[V(CO)_6]$. A solution of PQ (2.42 g; 11.6 mmol) in THF (100 ml) was treated at about −78 °C with $Na[V(CO)_6]$ (0.88 g; 3.6 mmol). The mixture was allowed to warm up and at about −50 °C, a vigorous evolution of gas took place and the colour of the solution changed from orange to dark-green, with precipitation of a solid. The mixture was stirred for 1 h at room temperature, and the solid then filtered off and dried in vacuo, to give 2.29 g (75% yield) of $Na(THF)_2[V(C_{14}H_8O_2)_3]$ * as a dark-green microcrystalline solid stable in air for a short time. Anal. Found: C, 70.8, H, 5.1. $C_{50}H_{40}NaO_8V$ calcd.: C, 71.2, H, 4.7%. $\chi_V^{corr} = +333 \times 10^{-6}$ cgsu (diamagnetic correction -476×10^{-6} cgsu); μ_{eff} (19 °C) 0.88 BM. IR spectrum (Nujol mull): 3060vw, 1605w, 1550m, 1500s, 1490sh, 1140m, 1405w, 1300vs, 1290vs, 1230vs, 1195s, 1155s, 1120w, 1060m-s, 1035w, 935w, 765s, 720s and 490s cm^{-1}; (polychlorotrifluoroethylene mull): 3060vw, 2980vw, 2880vw, 1605m, 1510s, 1490m-w, 1465w, 1410m, 1400s, 1350m-w and 1300m cm^{-1}.

Gas-volumetric monitoring of the reaction showed that on treatment of 0.14 mmol of $Na[V(CO)_6]$ with 0.44 mmol of PQ in toluene (10 ml) at 20 °C, 0.85 mmol of CO were evolved, corresponding to a CO/V molar ratio of 6.07.

(b) By sodium reduction of ***1***. A suspension of sodium sand (0.02 g; 0.87 mmol) in THF (30 ml) was treated at room temperature with **1** as its toluene solvate (0.85 g, 0.81 mmol). After 10 h stirring no sodium was left. The reaction was filtered and the dark-green solid (0.58 g, 86% yield) was dried in vacuo and identified as the monosodium derivative (IR spectrum). The yield was determined from THF analysis of the product.

One- and two-electron reduction of 2

A suspension of $Na(THF)_2[V(C_{14}H_8O_2)_3]$ (0.36 g; 0.43 mmol) in THF (25 ml) was treated with sodium sand (0.01 g; 0.43 mmol). After 3 h stirring at room temperature the mixture was filtered and the volume of the filtrate reduced to 10 ml. Addition of n-heptane (20 ml) caused slow precipitation of $Na_2(THF)_2$-$[V(C_{14}H_8O_2)_3]$ (0.26 g; 70% yield) as black-green cyrstals, which were filtered off and dried in vacuo. χ_V^{corr} $+1298 \times 10^{-6}$ cgsu (diamagnetic correction -342×10^{-6} cgsu); μ_{eff} (19 °C) 1.74 BM. Anal. Found: C, 68.0, H, 4.9, THF, 16.8. $C_{50}H_{40}Na_2O_8V$ calcd.: C, 69.4, H, 4.6, THF, 16.6%. IR spectrum (Nujol mull): 3070w, 1605m, 1565w, 1490w, 1420w, 1340m, 1290w, 1230w, 1115m-s, 1060s, 1030s, 935m, 790mw, 750s, 720m-s, 685w, 585s and 490 m-w cm^{-1}.

Reaction **2** with two equivalents of sodium sand in THF and operating as described above gave the trianion $[V(C_{14}H_8O_2)_3]^{3-}$, as its sodium salt (see subsequent section) in 85% yield.

Preparation of $Na_3[V(C_{14}H_8O_2)_3]$

A solution of PQ (3.27 g; 15.7 mmol) in THF (300 ml) was treated with sodium sand (0.86 g; 37.4 mmol). The orange red suspension was treated at room temperature with VCl_3 (0.82 g; 5.23 mmol) and the mixture was stirred for 10 h at room temperature, then filtered. After partial evaporation of the solvent in vacuo, the

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* The solid crystallizes out with variable amounts of sodium-coordinated solvent, depending on the conditions used for drying. The same is true for the other derivatives reported in this paper.

residue was treated with n-heptane (200 ml), which induced precipitation of an orange-brown microcrystalline solid (1.31 g) which was filtered off and dried in vacuo. The filtrate, after cooling down to −30 °C, yielded another crop of solid (2.09 g) for a total yield of 71% of $Na_3(THF)_{2.4}[V(C_{14}H_8O_2)_3]$. The product even as solid turns green immediately upon exposure to air. $\chi_V^{corr} = +3445 \times 10^{-6}$ cgsu (diamagnetic correction -495×10^{-6} cgsu); μ_{eff} (17 °C) 2.83 BM. Anal. Found: V, 5.4, THF, 18.8. $C_{51.6}H_{43.2}Na_3O_{8.4}V$ calcd.: V, 5.6, THF, 18.9%. IR spectrum (Nujol mull): 3060vw, 1600m, 1570ms, 1510w, 1485m-s, 1225w, 1175w, 1110m-s, 1065s, 1025s, 930m, 785s, 750v-s, 720v-s, 680m, 580m, 565m, 540m-s and 430 cm^{-1}; (polychlorotrifluoroethylene mull): 3060vw, 2980vw, 2880vw, 1600m, 1570m-s, 1510w, 1485m-s, 1410m, 1360m-s and 1330m cm^{-1}.

The trianion $[V(C_{14}H_8O_2)_3]^{3-}$ was also obtained in high yield by reduction of $V(C_{14}H_8O_2)_3$ with three equivalents of sodium sand in THF at room temperature.

Reaction of $Na_n[V(C_{14}H_8O_2)_3]$ with $n = 1–3$, with $AgBF_4$

Only the reaction for $n = 3$ is described in detail, the others being performed similarly.

A solution of $Na_3(THF)_{2.4}[V(C_{14}H_8O_2)_3]$ (0.85 g; 0.93 mmol) in THF (50 ml) was treated at room temperature with a solution of $AgBF_4$ (0.28 g; 0.95 mmol) in THF (20 ml). Immediate reaction took place, as evidenced by the precipitation of a solid and formation of a silver mirror. After 1 h stirring at room temperature, the suspension was filtered and the volume of the filtrate was reduced to 20 ml. Addition of n-heptane (50 ml) caused precipitation of a green microcrystalline solid (0.72 g, 97% yield), identified as the disodium derivative from its IR spectrum in Nujol. For $n = 2$ and $n = 1$, the reaction with one equivalent of silver tetrafluoroborate in THF gave the corresponding oxidized products in 62 and 25% yields, respectively. Yields were determined from the THF analysis of the products.

Reaction of $Na_3[V(C_{14}H_8O_2)_3]$ with RCl ($R = PhCH_2$, Ph_3C)

A solution of $Na_3(THF)_3[V(C_{14}H_8O_2)_3]$ (0.74 g; 0.77 mmol) in THF (30 ml) was treated with $PhCH_2Cl$ (0.10 ml, 0.87 mmol) and the mixture was stirred overnight at room temperature. The suspended solid (predominantly consisting of NaCl) in the green suspension was filtered off and the filtrate evaporated to dryness in vacuo. The residue was sublimed at 40 °C/10^{-2} Torr to give 0.06 g (85% yield) of dibenzyl, identified from its IR spectrum. The sublimation residue was the disodium derivative (0.59 g, 88%) (IR spectrum in Nujol and THF analysis). The solid initially filtered off was dissolved in water, and the chloride content was found to correspond to a Cl^-/V molar ratio of 0.94.

When the trianion was treated with Ph_3CCl, there was immediate reaction with formation of $Na_2(THF)_{1.7}[V(C_{14}H_8O_2)_3]$ (IR spectrum and THF analysis), NaCl (Cl^-/V molar ratio 1.1) and hexaphenylethane (IR spectrum, 90% yield).

*Preparation of $Na[M(C_{14}H_8O_2)_3]$ ($M = Nb$, **3**; $M = Ta$, **4**)*

Only the preparation of the niobium derivative, **3**, is described in detail, the tantalum compound, **4**, being prepared similarly.

(a) From $Na[Nb(CO)_6]$. A solution of $Na(THF)[Nb(CO)_6]$ (0.95 g, 2.7 mmol) in Et_2O (50 ml) was treated with PQ (1.77 g, 8.5 mmol) at about −78 °C. The mixture was allowed to warm up, and at about −40 °C the orange colour changed to

blood-red and vigorous evolution of gas took place, with separation of a microcrystalline solid. When the gas evolution ceased (3h), the mixture was filtered and the solid washed with Et_2O (2 × 25 ml) and dried in vacuo to give 1.86 g (79% yield) of $Na(Et_2O)_{1.8}[Nb(C_{14}H_8O_2)_3]$ (**3**) as a dark-red microcrystalline solid, stable in air for a short time. The tantalum derivative $Na(Et_2O)_{1.2}[Ta(C_{14}H_8O_2)_3]$, (**4**) was obtained analogously in 79% yield. Anal. Found for M = Nb: C, 66.7, H, 4.5, Et_2O, 14.8. $C_{49.2}H_{42}NaNbO_{7.8}$ calcd.: C, 67.6, H, 4.8, Et_2O, 15.3%. Anal. Found for M = Ta: C, 60.9, H, 3.2, Et_2O, 10.0. $C_{46.8}H_{36}NaO_{7.2}Ta$ calcd.: C, 61.6, H, 4.0, Et_2O, 9.7%. $\chi_{Nb}^{corr} = +366 \times 10^{-6}$ cgsu (diamagnetic correction -477×10^{-6} cgsu); μ_{eff} (17 °C) 0.92 BM; $\chi_{Ta}^{corr} = +366 \times 10^{-6}$ cgsu (diamagnetic correction -460×10^{-6} cgsu); μ_{eff} (17 °C) 0.92 BM.

Gas-volumetric monitoring of the reaction showed that on treatment of 0.24 mmol of $[Nb(CO)_6]^-$ (0.17 mmol of $[Ta(CO)_6]^-$) with 0.78 mmol (Ta, 0.62 mmol) of PQ in THF (20 ml) at 20 °C, 1.43 (Ta, 1.03) mmol of CO were evolved, corresponding to a CO/M molar ratio of 5.96 for M = Nb and 6.06 for M = Ta.

(b) From Nb_2Cl_{10}. A solution of PQ (5.62 g; 27 mmol) in THF (500 ml) was treated with sodium sand (1.13 g, 49 mmol). After 5 h stirring at room temperature the orange-red solution was cooled to −78 °C and treated with a solution of freshly sublimed Nb_2Cl_{10} (2.42 g, 4.5 mmol) in toluene (50 ml). After 10 h stirring at room temperature, the mixture was filtered, evaporated to 50 ml under reduced pressure, and treated with n-heptane (200 ml). This caused the separation of a dark-red microcrystalline solid, which was filtered off and dried in vacuo, to give 7.75 g (97% yield) of $Na(THF)_{1.7}[Nb(C_{14}H_8O_2)_3]$.

The tantalum derivative, $Na(THF)_{1.1}[Ta(C_{14}H_8O_2)_3]$ (**4**) was obtained analogously as an orange solid in a 82% yield. Anal. Found for M = Nb: C, 66.7, H, 4.5, THF, 14.1; $C_{48.8}H_{37.6}NaNbO_{7.7}$ calcd.: C, 67.9, H, 4.4, THF 14.2%; Anal. Found for M = Ta: C, 60.8, H, 4.1, THF, 8.7. $C_{46.4}H_{32.8}NaO_{7.1}Ta$ calcd.: C, 61.4, H, 3.6, THF, 8.7%. IR spectrum (Nujol mull): M = Nb: 3060w, 1600sh, 1590w, 1490w, 1340ms, 1285m, 1105m-s, 1055s, 1030s, 930m-w, 790m, 750s, 720m-s, 688m and 590m cm^{-1}. M = Ta: 3070vw, 1620w, 1595m, 1485w, 1340m-s, 1285w, 1115m, 1055s, 1030s, 930w, 788m, 752s, 720s, 685m-w, 640w and 585 cm^{-1}. IR spectrum (polychlorotrifluoroethylene mull): M = Nb: 3060vw, 2980vw, 2880vs, 1600m-w, 1580m-w, 1490w, 1450mw, 1420m, 1360s and 1340ms cm^{-1}; M = Ta: 3070vw, 2985vw, 2885vw, 1620m, 1610m, 1590m, 1495m, 1450m, 1420w, 1370s and 1340m-s cm^{-1}.

Treatment of 3 and 4 with dry HCl. Preparation of $H[M(C_{14}H_8O_2)_3]$ (M = Nb, 5; M = Ta, 6)

(a) In n-heptane / CH_2Cl_2. A suspension in n-heptane (100 ml) of $Na[Nb(C_{14}H_8O_2)_3]$ (1.93 g; 2.60 mmol), obtained from **3** by heating at 140 °C in vacuo, was treated at about −50 °C with 2.60 mmol of dry HCl. The mixture was stirred for 30 min at low temperature and then allowed to warm to room temperature and filtered. The solid was extracted with CH_2Cl_2 (2 × 50 ml) and the brown extract was filtered and its volume was reduced to 30 ml. Addition of n-heptane (100 ml) caused separation of a red microcrystalline solid, which was filtered off and dried in vacuo to give 1.02 g (54% yield) of $H[Nb(C_{14}H_8O_2)_3]$ (**5**). Anal. Found: H (as H_2) *, 0.13, Nb, 13.0. $C_{42}H_{25}NbO_6$ calcd.: H (as H_2), 0.14, Nb, 12.9%. IR spectrum (Nujol mull): 3070vw, 1600m, 1500m, 1380m-s, 1340m-s, 1290w, 1120m-s,

1060vs, 1031s, 930w, 920w, 800m, 750vs, 695m, 652m, 595s and 425w cm^{-1}; (polychlorotrifluoroethylene mull); 3070vw, 1600m, 1500m, 1450m, 1380m-s and 1340m-s cm^{-1}. The tantalum derivative H[Ta($C_{14}H_8O_2$)$_3$)] (**6**) was obtained analogously in 64% yield. Anal. Found: H (as H_2) *, 0.11, Ta, 22.6; $C_{42}H_{25}O_6Ta$ calcd.: H (as H_2), 0.12, Ta, 22.4%. IR spectrum (Nujol mull): 3080vw, 1620w, 1595m, 1520m, 1490m, 1340s, 1290m, 1115s, 1060s, 1030s, 930w, 810w, 785m, 750s, 720s, 685m, 590m and 435w cm^{-1}; (polychlorotrifluoroethylene mull): 3080vw, 1620m, 1595m, 1490m-w, 1450s, 1390w, 1370s and 1340m cm^{-1}.

(b) In n-heptane followed by treatment with water. A suspension in n-heptane (50 ml) of Na[Nb($C_{14}H_8O_2$)$_3$] (0.501 g; 0.68 mmol) obtained from **3** by heating at 140 °C in vacuo, was treated at about −50 °C with 0.83 mmol of dry HCl. The mixture was stirred at low temperature for 1 h and then allowed to warm to room temperature. The solid was filtered off, washed with water (6 × 5 ml) and dried overnight in vacuo over P_4O_{10} to give 79% yield of H(H_2O)$_3$[Nb($C_{14}H_8O_2$)$_3$] (**5**) as a red microcrystalline solid. Anal. Found: C, 65.6, H, 3.7; $C_{42}H_{31}NbO_9$ calcd.: C, 65.3; H, 4.0%. IR spectrum (Nujol mull): 3400s-br, 3070vw, 1620m-s, 1600m-s, 1490w, 1340m-s, 1290w, 1185m, 1115s, 1060s, 1030s, 930w, 835m, 780s, 750vs, 720m-s, 685m and 587m-s cm^{-1}.

A similar procedure gave the tantalum derivative, H(H_2O)$_3$[Ta($C_{14}H_8O_2$)$_3$] (**6**) in 72% yield. Anal. Found: C, 58.7, H, 3.3; $C_{42}H_{31}O_9Ta$ calcd.: C, 58.6, H, 3.6%. IR spectrum (Nujol mull): 3380s-br, 3070 vw, 1595m-s, 1520w, 1340s, 1290w, 1115s, 1060s, 1030s, 930w, 785w, 763s, 720m, 685m-w, 595m and 430m cm^{-1}.

(c) In THF. A solution of Na(THF)$_{1.7}$[Nb($C_{14}H_8O_2$)$_3$] (1.44 g; 1.67 mmol) in THF (150 ml) was treated at about −50 °C with 2.2 mmol of dry HCl. When the mixture had warmed to room temperature, it was filtered, and the filtrate was evaporated to about 50 ml and treated with n-heptane (100 ml). The solid which separated was filtered off and dried in vacuo, to give 0.82 g (58% yield) of H(THF)$_{1.6}$ [Nb($C_{14}H_8O_2$)$_3$] as a red-brown microcrystalline very hygroscopic solid. Anal. Found: H (as H_2), 0.12, Nb, 11.0, THF, 13.3; $C_{48.4}H_{37.8}NbO_{7.6}$ calcd.: H (as H_2), 0.12, Nb, 11.1, THF, 13.8%. IR spectrum (Nujol mull): 3190m-br, 3070vw, 1600m, 1500m, 1380m-s, 1340m-s, 1290m, 1120m-s, 1060s, 1030s, 930w, 805m, 790m, 755vs, 720m-s, 710m-s, 698m, 652w, 595s and 425w cm^{-1}.

The tantalum analogue, H(THF)$_{1.6}$[Ta($C_{14}H_8O_2$)$_3$], was obtained analogously in 64% yield. Anal. Found: H (as H_2), 0.10, Ta, 19.2, THF, 12.8; $C_{48.4}H_{36.8}O_{7.6}Ta$ calcd.: H (as H_2), 0.11, Ta, 19.6, THF, 12.5%. IR spectrum (Nujol mull): 3180m-br, 3080vw, 1625m, 1530m, 1500m, 1343m-s, 1300w, 1295w, 1195m, 1129m, 1120m-w, 1060w, 1030s, 930m, 920w, 880m, 795m, 785vs, 753m, 722m, 710m-w, 685m-w and 595m-s cm^{-1}.

Reduction of Na[M($C_{14}H_8O_2$)$_3$], (3 and 4) with sodium and reaction of the reduced species with $PhCH_2Cl$ and Ph_3CCl

Only the reduction of the tantalum compound is described in detail, that of the niobium compound being similar.

A solution of **4** as Na(THF)[Ta($C_{14}H_8O_2$)$_3$] (1.69 g; 1.9 mmol) in THF (100 ml) was treated with sodium sand (0.1 g; 4.3 mmol). After 4 h stirring at room

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* This is the hydrogen content evolved as H_2 by reaction with sodium in THF (1 mmol of compound with an excess of sodium; dihydrogen measured gas-volumetrically in a thermostated gas burette).

temperature the dark brown solution was separated from the unreacted sodium metal by filtration and the filtrate treated with $PhCH_2Cl$ (0.5 ml, 4.3 mmol). After 14 h stirring at room temperature, the orange-brown mixture was filtered, the filtrate was dried in vacuo, and the residue sublimed at 40 °C/10^{-2} Torr to give 0.24 g (69% yield with respect to tantalum) of dibenzyl, identified from its IR spectrum. The residue from the sublimation consisted of 1.5 g of $Na(THF)_n[Ta(C_{14}H_8O_2)_3]$ as judged from its IR spectrum in Nujol. The solid isolated by the first filtration was treated with water and found to contain a Cl^-/Ta molar ratio of 1.89.

When two equivalents of Ph_3CCl were used, an immediate reaction was observed and $Na(THF)_n[Ta(C_{14}H_8O_2)_3]$, NaCl ($Cl^-/Ta$ molar ratio 2.0) and hexaphenylethane (95% yield) were found as products.

*Reaction of $Na[M(C_{14}H_8O_2)_3]$ (M = Nb, **3**; M = Ta, **4**) with dioxygen*

In a gas-volumetric apparatus, a solution of $Na(THF)_n[M(C_{14}H_8O_2)_3]$ ($M = Nb$, $n = 1.7$, 0.68 g, 0.79 mmol; $M = Ta$, $n = 1$, 0.67 g, 0.74 mmol) in THF (25 ml) was treated with dry O_2 at 19.6 °C giving an adsorbed O_2/M molar ratio of 1.53 (within 4 h) for $M = Nb$ and 1.46 (within 15 h) for $M = Ta$. The IR spectrum of the yellow-orange solution showed an intense absorption at 1686 cm^{-1} typical of free PQ in THF solution.

Results and discussion

The preparation of the neutral quinone derivative of vanadium of formula $V(C_{14}H_8O_2)_3$ was carried out starting from hexacarbonylvanadium(0) in toluene as solvent, as shown in eq. 1. The reaction was very fast under these conditions, and

$$V(CO)_6 + 3\ PQ \xrightarrow{\text{toluene}} \underset{\mathbf{(1)}}{V(C_{14}H_8O_2)_3} + 6\ CO \qquad (1)$$

the product was obtained in good yield as the tetra-solvent adduct, $V(C_{14}H_8O_2) \cdot 4C_6H_5CH_3$. The isolated product is sufficiently pure (as judged from the analytical data) to be used for further reactions and for magnetic measurements. It is noteworthy that in an earlier study [9], difficulties were encountered in the isolation of the product of the reaction between $V(CO)_6$ and PQ. In our hands, the vanadium derivative is stable at room temperature for indefinite periods of time under an inert atmosphere. Owing to its low solubility, no molecular weight determination could be carried out. The magnetic moment at room temperature is 1.87 BM, corresponding approximately to one unpaired electron per molecular formula. In addition, the IR spectrum shows a strong absorption at 1490 cm^{-1}, which has been attributed [5,7] to the presence of the semiquinone unit $C_{14}H_8O_2^{\cdot -}$ (**B**) as a ligand, thus corresponding to the transfer of one electron per quinone from vanadium. The magnetic moment is in agreement with this view when account is taken of the fact that the d^2 system of vanadium(III) shows strong antiferromagnetic coupling with the three unpaired electrons on the partially reduced quinone ligands.

To confirm the nature of the vanadium complex, it was made by an alternative procedure. Anhydrous vanadium(III) chloride was found to react in THF as solvent with three equivalents of $NaC_{14}H_8O_2$ to give the same product as was obtained from $V(CO)_6$ (see eq. 2). Once difficulties connected with the preparation of

$$VCl_3 + 3\ Na + 3\ PQ \xrightarrow{THF} V(C_{14}H_8O_2)_3 + 3\ NaCl \qquad (2)$$

$V(CO)_6$ are overcome [17,18], the reaction shown in eq. 1 appears to provide the best route to compound **1**, in view of the fact that no separation from other products is necessary, in contrast to the situation when the method starting from VCl_3 is used.

In view of the considerable electron delocalization in PQ as ligand, it was expected that the vanadium complex would undergo chemical reduction, similar to that encountered for the corresponding chromium(III) derivative [14]. It was found that compound **1** is indeed readily reduced by one electron if the strictly stoicheiometric amount of sodium is used (vide infra, see eq. 3).

$$\mathbf{1} + Na \xrightarrow{THF} \underset{(\mathbf{2})}{Na[V(C_{14}H_8O_2)_3]} \qquad (3)$$

Compound **2** crystallizes as a green THF-solvated microcrystalline solid, and is stable indefinitely under an inert atmosphere. In agreement with the formulation previously given for compound **1**, the product obtained from reaction 3 has a strongly reduced magnetic moment. The IR spectrum does not show the strong absorption at 1490 cm^{-1} typical of **1**, in agreement with the addition of one electron to the system, which results in a lowering of the C–O stretching frequency.

Compound **2** was also obtained from $Na[V(CO)_6]$ and PQ in THF as solvent (eq. 4). It is noteworthy that the reaction is very fast even in toluene, in which the sodium hexacarbonylvanadate(−I) is practically insoluble. This is even more remarkable when it is recalled that the 18-electron species $[V(CO)_6]^-$ shows a low reactivity, especially with respect to CO substitution and only under photochemical activation, is it possible to bring about CO substitution [20]. It therefore seems that the reason for the lability of $[V(CO)_6]^-$ with respect to CO substitution by PQ must originate in a preliminary electron-transfer from the metal to PQ, vanadium(−I) thus being converted into a much more labile oxidation state of the metal. We thus believe that this is another possible case of rate enhancement by electron-transfer, several examples of which have been reported [21].

$$Na[V(CO)_6] + 3\ PQ \xrightarrow{THF} Na[V(C_{14}H_8O_2)_3] + 6\ CO \qquad (4)$$

The PQ ligand coordinated to vanadium is prone to further reduction by sodium. Products corresponding to a two- and a three-electron reduction of $V(C_{14}H_8O_2)_3$ were obtained by the action of sodium in THF (see eq. 5). The reduced products can be oxidized by one-electron by $AgBF_4$ in tetrahydrofuran solution.

$$Na[V(C_{14}H_8O_2)_3] + n\ Na \xrightarrow{THF} Na_{n+1}[V(C_{14}H_8O_2)_3] \qquad (5)$$

$(n = 1, 2)$

The sodium derivatives obtained by reactions 4 and 5 presumably always contain sodium-coordinated THF. Possible structures for these compounds may be based on the solid state data obtained by Pierpont and coworkers [12] for the 9,10-phenanthrenequinone derivative of molybdenum, $Mo(PQ)_3$. This compound is essentially monomeric, with pairs of molecules strongly interacting through a charge-transfer type of bonding. If such a basic structure is considered valid for the vanadium derivative $V(PQ)_3$, it is not difficult to envisage that the sodium cation can interact with the structure by coordination to the oxygen atoms of the bonded quinone ligand, the coordination requirements of the sodium cation being presumably completed by THF. It is reasonable to assume that the insertion of sodium cation into the structure of $V(PQ)_3$ with consequent reduction of the system, will help to relieve the steric intra- and/or inter-molecular strain. The ready reduction by sodium of the vanadium-quinone system can therefore be understood in terms of both strain relief and contribution for lattice and sodium-coordination energies which compensates for the ionization of the alkali metal. It is interesting to note that cathecolato complexes of vanadium(III) have been reported with $NH_2Et_2{}^+$ and K^+ as counterions. The X-ray structure of $K_3[V(C_6H_4O_2)_3]\cdot 1.5H_2O$ showed pseudooctahedral coordination for vanadium, with oxygen-coordinated potassium ions [22].

It was of interest to investigate the behaviour of the hexacarbonylmetalates($-$I) of niobium and tantalum towards 9,10-phenanthrenequinone for the reasons explained in the Introduction, and also in an attempt to use a potentially mild oxidizing agent to synthesize low-valent carbonyl derivatives of the metals containing the quinone as additional ligand.

Reaction of $[M(CO)_6]^-$ ($M = Nb$, Ta) with three equivalents of 9,10-phenanthrenequinone led (even at ca. $-40\,^\circ C$) to fast and complete generation of carbon monoxide and formation of the sodium derivatives $Na[M(C_{14}H_8O_2)_3]$ (**3** and **4**) (see eq. 6). If one equivalent of PQ is used, one third of the $[M(CO)_6]^-$ is converted into **3** or **4**. The predominantly diamagnetic compounds of niobium and tantalum have

$$Na[M(CO)_6] + 3\ PQ \xrightarrow{Et_2O} \underset{\substack{(\mathbf{3}:\ M = Nb,\\ \mathbf{4}:\ M = Ta)}}{Na[M(C_{14}H_8O_2)_3]} + 6\ CO \qquad (6)$$

red to orange colours and their IR spectra are substantially identical (see Fig. 1b and 1c). Moreover these IR spectra and colours are very similar to those of the $Na_3[V(C_{14}H_8O_2)_3]$ species (Fig. 1a), suggesting that we are dealing with analogous structures and electron distributions in the organic ligand. The best description of the bonding arrangement in the niobium and tantalum species is therefore that of three diolato ligands (**C** in the Introduction) bonded to d^0 centres of formally Nb^V and Ta^V. The similarity of the spectra thus suggests that in the case of $Na_3[V(C_{14}H_8O_2)_3]$ we are dealing with diolato ligands bonded to a formally vanadium(III) metal ion. This way of regarding the bonding in these systems finds support from the fact that the higher oxidation states are more stable for the 4*d*-5*d* elements than for their 3*d* congeners [23]. In keeping with this view, while the sodium derivative $Na_3[V(C_{14}H_8O_2)_3]$ is extremely sensitive to oxygen, the niobium and tantalum compounds, **3** and **4**, react slowly with oxygen, 4 and 15 h, respectively, being required for the oxidation of the complexes to the corresponding oxides and free PQ.

The niobium and tantalum derivatives **3** and **4**, can also be prepared from the pentachlorides by reaction with the dianion of PQ, according to eq. 7.

$$M_2Cl_{10} + 12\ Na + 6\ PQ \xrightarrow{THF} 2\ \underset{\substack{(\mathbf{3}:\ M = Nb,\\ \mathbf{4}:\ M = Ta)}}{Na[M(C_{14}H_8O_2)_3]} + 10\ NaCl \qquad (7)$$

The sodium derivatives of niobium and tantalum appeared, in view of the stable nature of the metals in their higher oxidation states, to be good candidates for an

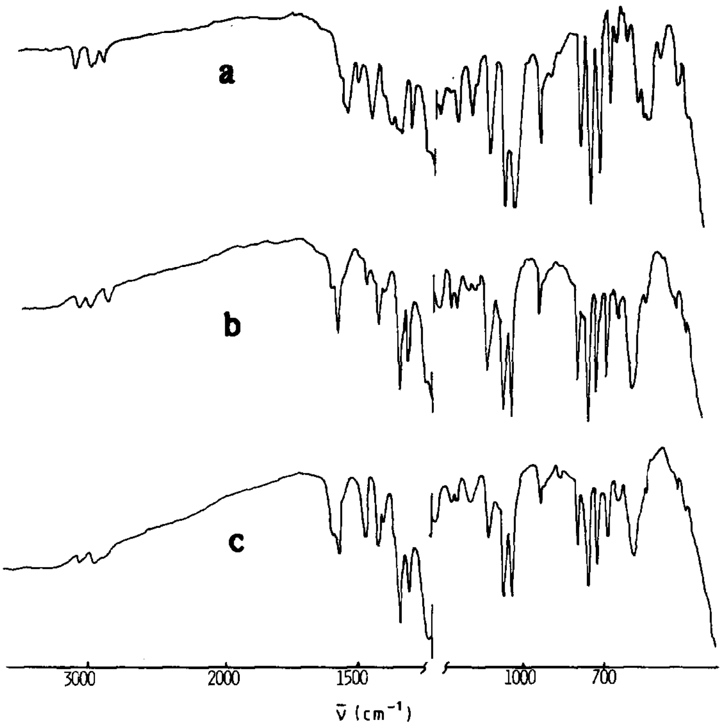

Fig. 1. IR spectra of (a) $Na_3(THF)_{2.4}[V(C_{14}H_8O_2)_3]$, (b) $Na(THF)_{1.7}[Nb(C_{14}H_8O_2)_3]$ and (c) $Na(THF)_{1.1}[Ta(C_{14}H_8O_2)_3]$. (Polychlorotrifluoroethylene (4000–1300 cm^{-1}) and Nujol mulls (1300–400 cm^{-1})).

attempt to prepare systems having protons instead of sodium cations in the presumably ionic extended structure. The unsolvated $Na[M(C_{14}H_8O_2)_3]$ compounds were found to react immediately with dry hydrogen chloride at low temperature to afford new protonated derivatives (see eq. 8). Pre-treatment of the solvated sodium

$$Na[M(C_{14}H_8O_2)_3] + HCl \rightarrow \underset{\substack{(\mathbf{5}:\ M = Nb,\\ \mathbf{6}:\ M = Ta)}}{H[M(C_{14}H_8O_2)_3]} + NaCl \qquad (8)$$

derivatives in vacuo to remove the presumably sodium-coordinated solvents, and the use for reaction 8 of a non-coordinating medium (CH_2Cl_2 or n-heptane), were required in order to avoid the presence of external Lewis bases and permit binding of the proton to the metal-coordinated oxygen atoms of the quinone ligand. The presence of the oxygen-coordinated proton is evidenced by the following observations: (a) molecular hydrogen is quickly formed when **5** and **6** are treated with sodium metal; (b) the derivatives have an acid reaction in contact with water. The IR spectrum does not show any strong band between 4000 and 3000 cm^{-1} which can be assigned to an OH stretching vibration; however, an OH stretching of this type could be weak and not easily observable and, for example, the OH stretching vibration of the OH-bridged dimer $Fe_2(CO)_6(PR_2)OH$ [24] was reported to be at 3550 cm^{-1} and easily overlooked because of its low intensity. Noteworthy is the fact that the IR spectra of **5** and **6** are substantially identical to those of the starting sodium derivatives, apart from absorptions around 1050 and 900 cm^{-1} due to coordinated THF in the sodium compounds.

The sodium derivatives **3** and **4** do not react with $PhCH_2Cl$ and Ph_3CCl unless they are previously reduced with two equivalents of sodium * (see eq. 9) after further reduction the products of reductive carbon–carbon coupling of the organic moiety are obtained (see eq. 10). This is consistent with the increase of electron density at the metal following the reduction with sodium, which may trigger the required electron transfer to the carbocation.

$$Na[M(C_{14}H_8O_2)_3] + 2\ Na \rightarrow Na_3[M(C_{14}H_8O_2)_3] \tag{9}$$

$$Na_3[M(C_{14}H_8O_2)_3] + 2\ RCl \rightarrow Na[M(C_{14}H_8O_2)_3] + 2\ NaCl + RR \tag{10}$$

$$(M = Nb, Ta;\ R = PhCH_2,\ Ph_3C)$$

Acknowledgements

The authors thank the Consiglio Nazionale delle Ricerche (CNR, Roma) and the Ministero della Pubblica Istruzione for financial support.

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* The products of $Na[M(C_{14}H_8O_2)_3]$ reduction were not isolated, but prepared in situ and used in solution for the reaction with RCl.

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