DALTON
FULL PAPER

Synthesis and characterization of mono- and bi-metallic derivatives of Groups 4 and 5 with 2,5-dimethoxy-1,4-benzoquinone

Fausto Calderazzo,[a] **Ulli Englert,**[b] **Guido Pampaloni** *[a] **and Vincenzo Passarelli**[a,c]

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy. E-mail: pampa@dcci.unipi.it*
[b] *Institute für Anorganische Chemie der RWTH Aachen, Professor-Pirlet-Strasse 1, D-52074 Aachen, Germany*
[c] *Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy*

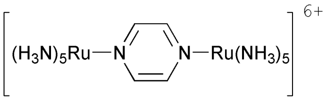
Received 6th April 2001, Accepted 20th July 2001
First published as an Advance Article on the web 17th September 2001

The ligating properties of 2,5-dimethoxy-1,4-benzoquinone, $C_8H_8O_4$ **1** towards metallic Lewis acids and organometallics in low oxidation states has been investigated. The title compound reacts with Group 4 tetrahalides to give adducts of formula $MCl_4(C_8H_8O_4)$ (M = Ti **4a**; M = Zr **4b**) and $(TiCl_4)_2(C_8H_8O_4)$ **5**. Moreover, bis-cyclopentadienyl derivatives of titanium(II) ($TiCp_2L_2$; L = CO, PMe_3) and vanadium(II) (VCp_2) react with **1** affording both 1 : 1 and 2 : 1 derivatives of general formula $MCp_2(C_8H_8O_4)$ (M = Ti **10**; M = V **7**), $(MCp_2)_2(C_8H_8O_4)$ (M = Ti **11**; M = V **6**). The molecular structure of **6** has been determined by X-ray diffraction showing the presence of bimetallic units, with two [VCp_2] fragments bonded to a quinonoid oxygen atom of a bridging 2,5-dimethoxy-1,4-benzenedialcoholato. The derivatives $[(MCp_2)_2(C_8H_8O_4)][BPh_4]_n$ (M = Ti, V; *n* = 1 **12a**, **b**; *n* = 2 **12c**, **d**) have been prepared by oxidation of $(MCp_2)_2(C_8H_8O_4)$ (M = Ti **11**; M = V **6**) with a stoichiometric amount of $[FeCp_2][BPh_4]$. The reaction of the vanadium derivative $VCp_2(C_8H_8O_4)$ **7** with $TiCl_4$ affords the heterobimetallic compound $VCp_2(C_8H_8O_4)TiCl_4$ **8**. The magnetic properties of the 1 : 1 and 2 : 1 species are reported.

Introduction

Recent studies[1] on the synthesis and characterization of bimetallic compounds have shown that their electrochemical,[1] spectroscopic[1] and magnetic[2,3] properties depend on the interactions between the metals operated by appropriate organic bridges. Molecules containing oxygen and nitrogen as donor atoms (namely, quinonoid and/or amino functionalities) have been largely and successfully used[1] for this purpose.

The first example of an interaction between two metal centres was reported by Creutz and Taube[4] for the $\{[Ru(NH_3)_5]_2(pyrazine)\}^{6+}$ cation containing pyrazine as a bridging ligand. This example was followed[1] by a large number of studies aimed at clarifying how structural modifications in the bridge affect the degree of intermetallic interaction.



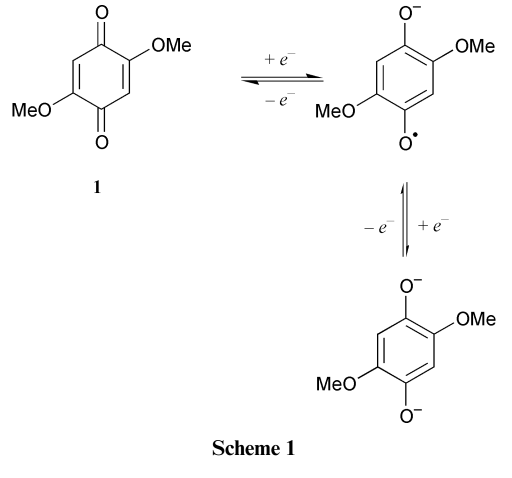
Recently,[1,2] quinonoid compounds have been shown to be excellent starting materials for the synthesis of bimetallic derivatives. In addition, the magnetic properties of the bimetallic derivative $[Fe(salen)]_2$(2,5-dihydroxy-1,4-benzoquinone) have been investigated[2] and discussed in terms of antiferromagnetic coupling through the bridging organic component.

The methoxy derivative, 2,5-dimethoxy-1,4-benzoquinone, which has the advantage of preventing intermolecular hydrogen bonding, has never been used as a precursor for bimetallic derivatives. Therefore, in the framework of our research on the interaction of quinonoid compounds with early transition elements, we decided to investigate the coordinating ability of 2,5-dimethoxy-1,4-benzoquinone towards titanium, zirconium and vanadium compounds and to study the properties of the magnetically active derivatives.

Results and discussion

Reduction of 2,5-dimethoxy-1,4-benzoquinone

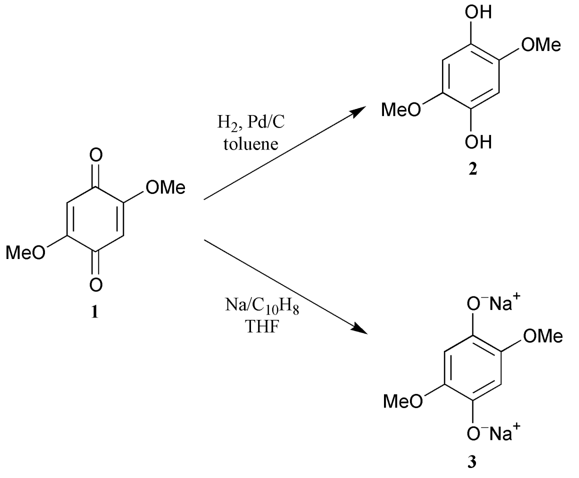
Due to the presence of the quinonoid functionality, 2,5-dimethoxy-1,4-benzoquinone **1** is an electroactive species undergoing two reversible monoelectronic reductions at 0.43 and 0.97 V (*vs.* Ag/AgCl electrode in DMF)[5] affording (Scheme 1) the semiquinonato radical anion and the dianionic dialcoholato species, respectively.



Scheme 1

As prepared by reduction of **1** with $SnCl_2$/HCl,[6] 2,5-dimethoxy-1,4-dihydroxybenzene **2** has been known for many years. We have found that **1** is easily reduced either by dihydrogen (in the presence of Pd/C, similar reductions have been successfully carried out on 9,10-phenanthrenequinone, *p*-benzoquinone and 3,5-di-*tert*-butyl-*o*-benzoquinone) or by sodium–naphthalene (Na/**1** molar ratio = 2). In both cases the quinonoid functionality is reduced by two electrons affording

DOI: 10.1039/b103144a



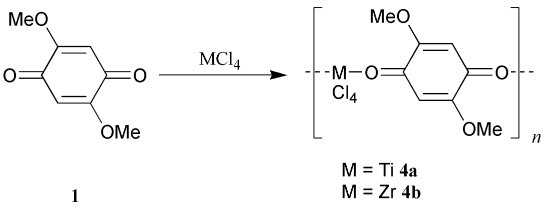
Scheme 2

2 or the corresponding disodium derivative Na$_2$[C$_8$H$_8$O$_4$] **3** (Scheme 2, solid Na$_2$[C$_8$H$_8$O$_4$] may contain variable amounts of THF depending on the amount of time it is left drying *in vacuo* at room temperature).

The IR spectra of **2** and **3** show no strong absorptions at about 1665 cm^{-1} typical of compound **1**, thus confirming the reduction of the quinonoid functionality; strong absorptions in the 1200–1000 cm^{-1} region, characteristic of C–O–C stretching (symmetric and asymmetric) of aryl-alkyl ethers, are indicative† of the bielectronic character of the observed reductions (**2**: 1024, 1191 cm^{-1}; **3**: 1030, 1175 cm^{-1}). Moreover, the strong bands (the coupling of the O–H bending and the C(annular)–O stretching in phenols produces two bands in the 1180–1260 and 1330–1390 cm^{-1} regions)[7] at 1242 and 1349 cm^{-1} and the broad one at 3367 cm^{-1} (O–H stretching) in the IR spectrum of **2** suggest the presence of the phenolic functionality. The C–O stretching of the deprotonated phenolic functionality in **3** produces a strong band at 1208 cm^{-1}. The ^{1}H-NMR spectrum of **2** consists of three singlets (3.7, 6.5, 7.0 ppm), the resonance at 7.0 ppm disappearing on addition of D$_2$O, thus confirming its assignment to the phenolic protons.

Coordination compounds of 2,5-dimethoxy-1,4-benzoquinone, 1

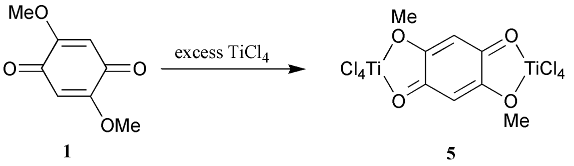
The reaction of MCl$_4$ (M = Ti, Zr) with **1** (**1**/MCl$_4$ molar ratio = 1) affords 1 : 1 adducts of general formula [MCl$_4$-(C$_8$H$_8$O$_4$)]$_n$ (M = Ti **4a**; M = Zr **4b**) [eqn. (1)]. The IR spectra are useful for the elucidation of compounds **4a** and **4b**. A strong absorption is observed at 1555 cm^{-1} (M = Zr) or at 1553 cm^{-1} (M = Ti), while the band at about 1665 cm^{-1} typical of **1** is absent. This observation suggests the coordination of both quinonoid oxygens to the metal centres. When the quinonoid functionality interacts with a metal centre, the C=O stretching vibration is observed at lower wavenumbers, the shift depending on the nature of the ligand. For example, the C=O stretching vibration of 9,10-phenanthrenequinone or 1,10-phenanthroline-5,6-dione undergoes a shift of 100 or 55 cm^{-1} respectively, to lower wavenumbers upon coordination to Group 4 tetrachlorides.[8,9] On the other hand, it must be noted that the absorptions assigned to the stretching vibrations associated with the ether function (998, 1206, 1230 cm^{-1}) of **1** are only slightly affected by addition of the tetrachloride fragment (**4a**: 981, 1224, 1245, 1263 cm^{-1}; **4b**: 979, 1236, 1248 cm^{-1}).



(1)

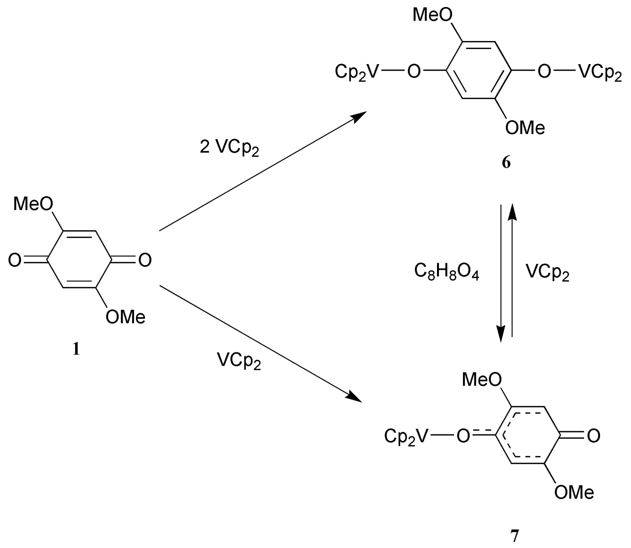
In addition, the polynuclear nature of the 1 : 1 adducts is postulated by considering that *both* quinonoid oxygens are involved in the coordination and that MCl$_4$ (M = Ti, Zr) usually forms hexacoordinate adducts with Lewis bases.[10] Similar polynuclear derivatives are already known: some years ago, Handa and coworkers reported the synthesis and structural characterization of inorganic polymers containing trifluoroacetato-bridged [Mo(II)]$_2$ units connected by *p*-quinones such as anthraquinone and 2,6-dimethylbenzoquinone.[11]

The 2 : 1 derivative (TiCl$_4$)$_2$(C$_8$H$_8$O$_4$) **5** [eqn. (2)] has been obtained by reacting **1** with an excess of TiCl$_4$. The analogous reaction between **1** and ZrCl$_4$, even after prolonged heating, does not give (ZrCl$_4$)$_2$(C$_8$H$_8$O$_4$) but mixtures of the 1 : 1 adduct ZrCl$_4$(C$_8$H$_8$O$_4$) **4b** and ZrCl$_4$. The polynuclear nature of ZrCl$_4$[12] together with the low basicity of **1** may explain this experimental observation. The IR spectrum of **5** shows no band due to uncoordinated **1** (1665 cm^{-1}), but a strong absorption at 1538 cm^{-1} is present, due to the stretching of the titanium-coordinated quinonoid bond [a decrease of the wavenumber of *ca.* 100 cm^{-1} with respect to the free quinone is observed in the TiCl$_4$(9,10-phenanthrenequinone) adduct[8]]. Moreover, the spectral pattern in the 1300–1100 cm^{-1} region is strongly affected by coordination, thus suggesting that also the ethereal function interacts with titanium.



(2)

The reaction of **1** with VCp$_2$ affords two different products, namely (VCp$_2$)$_2$(C$_8$H$_8$O$_4$) **6** or VCp$_2$(C$_8$H$_8$O$_4$) **7**, depending on the molar ratio between the reagents, the latter one requiring longer reaction times to be obtained in a pure state (Scheme 3).



Scheme 3

The absence of strong IR absorptions at about 1665 cm^{-1} and the presence of intense bands at 1016, 1194 (symmetric and asymmetric C–O–C stretching vibrations) and 1220 cm^{-1} (C–O stretching vibration) suggest that **1** has been bielectronically reduced to give **6**. Moreover, the IR spectrum of **7** shows

---

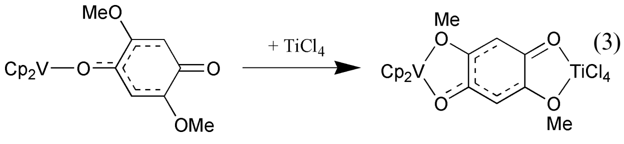
† The symmetric and asymmetric stretching of the C–O–C fragment in aryl-alkyl ethers are IR-active vibration modes of elevated intensity at about 1230 cm^{-1} and 1050 cm^{-1}, respectively. Moreover, the C–O stretching of a phenolic system is observed at about 1250 cm^{-1}.[7]

absorptions at 1665 cm^{-1} and 1595 cm^{-1}, due to vibrations of the C=O and C–C bonds, respectively; moreover, strong absorptions at 1030, 1194 and 1215 cm^{-1} associated with C–O and C–O–C groups (*vide supra*) are present. These spectral data suggest that **7** contains a semiquinonato anion, *i.e.* the quinonoid functionality of **1** has undergone a formal mono-electronic reduction.

Compounds **6** and **7** readily interconvert by addition of the appropriate reagent; on addition of **1** to a solution of $(VCp_2)_2(C_8H_8O_4)$ in toluene, slow precipitation of **7** is observed; on the other hand, **6** is promptly formed by adding VCp_2 to $VCp_2(C_8H_8O_4)$, see Scheme 3.

Due to their reactivity towards oxygen and/or moisture both in solution or in the solid state, we had difficulties in obtaining single crystals suitable for an X-ray diffraction study. After several attempts, small single crystals of compound **6** were obtained by layering heptane on a toluene solution and cooling it at *ca.* 4 °C. The low quality of the crystals prevented an accurate solution of the structure, nevertheless the connectivity has been established, showing that the structure of compound **6** consists of bimetallic units, with two $[VCp_2]$ fragments bonded to a quinonoid oxygen atom of a bridging 2,5-dimethoxy-1,4-benzenedialcoholato.‡ The compound crystallizes in the space group $P\bar{1}$ with two independent molecules both located on crystallographic inversion centres (Fig. 1). The main differences between the two molecules are the values of the dihedral angles V(1)–O(10)–C(4)–C(3) [molecule A: −38(2)°] and V(2)–O(20)–C(7)–C(6) [molecule B: 167(1°)] and the dihedral angles C(1)–O(1)–C(3)–C(4) [molecule **A**: 158(2)°] and C(2)–O(2)–C(6)–C(7) [molecule **B**: 69(2)°].

The addition of $TiCl_4$ to the 1 : 1 species $VCp_2(C_8H_8O_4)$ **7** affords the heterobimetallic compound $VCp_2(C_8H_8O_4)TiCl_4$ **8**, see eqn. (3). The IR spectrum of **7** is not much modified by the addition of $TiCl_4$, the main differences being the shift of the quinonoid stretching vibration from 1665 to 1574 cm^{-1} and the presence of a single strong band at 1220 cm^{-1} in the region where two strong absorptions (1194, 1215 cm^{-1}) are observed for **7**. As in the case of the bimetallic titanium derivative $(TiCl_4)_2(C_8H_8O_4)$ **5**, we propose that the addition of $TiCl_4$ to **7** involves both quinonoid and ethereal oxygens and that the second methoxy functionality is coordinated to vanadium(III), reasonably due to an electronic redistribution.



(3)

7 **8**

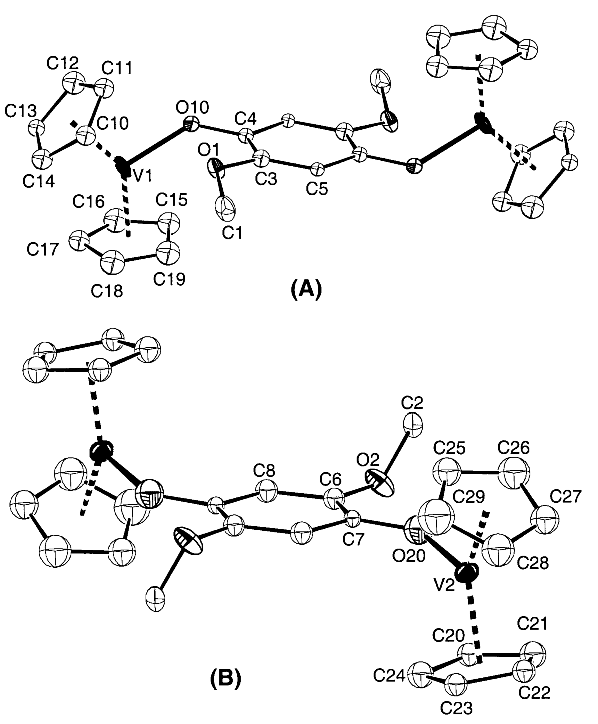
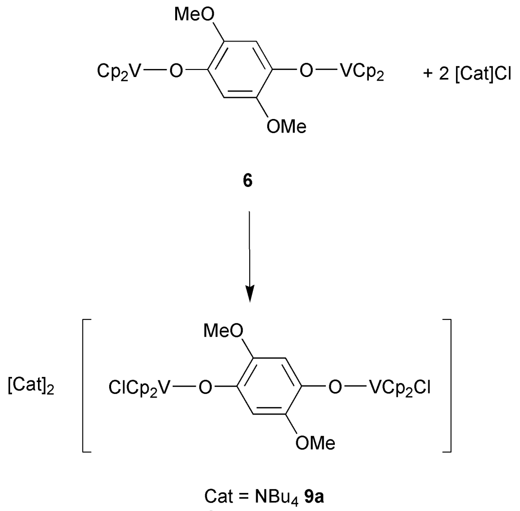


Fig. 1 Displacement ellipsoid plot (30%) of the molecular structure of the two independent molecules (**A** and **B**) of $(VCp_2)_2(C_8H_8O_4)$, **6**, with the numbering scheme used.[15] Some selected parameters are: V–C(cyclopentadienyl): 2.28, average; V1–O10: 1.935(9), V2–O20: 1.929(11); V1 ··· O1: 3.06, V2 ··· O2: 4.65 Å; Cp–V–Cp: 140°, average.

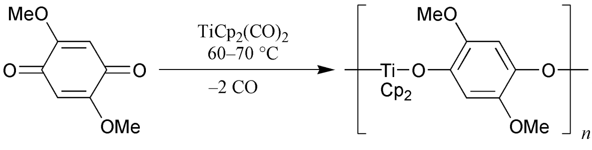
The coordinatively unsaturated bimetallic derivative $(VCp_2)_2(C_8H_8O_4)$ **6** (a 16 valence electron species) reacts with two equivalents of chloride yielding the $[(VCp_2Cl)_2(C_8H_8O_4)]^{2-}$ anion, isolated as both the tetrabutylammonium and bis(triphenylphosphine)iminium salts, $[Cat]_2[(VCp_2Cl)_2(C_8H_8O_4)]$ ($[Cat]^+ = [NBu_4]^+$ **9a**; $[Cat]^+ = [PPN]^+$ **9b**), see eqn. (4). The IR spectra of **9a**,**b** show the absorptions characteristic of the bielectronically reduced quinone (**9a**: 1026, 1193, 1201 cm^{-1}; **9b**: 1026, 1194, 1233 cm^{-1}). Moreover, intense bands at 601, 693, 724, 1115 and 1261 cm^{-1} are observed in the IR spectrum of **9b**, due to the bis(triphenylphosphine)iminium cation.



(4)

Cat = NBu4 **9a**
Cat = PPN **9b**

The reaction of $TiCp_2(CO)_2$ with **1** affords the sparingly soluble derivative $TiCp_2(C_8H_8O_4)$, see eqn. (5). IR monitoring



(5)

1 **10**

---

‡ Crystal data: $(VCp_2)_2(C_8H_8O_4)$ **6**: triclinic, space group $P\bar{1}$, $a = 8.062(1)$, $b = 11.084(2)$, $c = 14.896(2)$ Å, $\alpha = 68.13(1)$, $\beta = 78.57(1)$, $\gamma = 77.24(1)°$, $V = 1194.8(3)$ Å^3, $Z = 2$, $D_C = 1.49$ g cm^{-3}, $\mu = 0.797$ mm^{-1}, $F(000) = 548$. The crystals were transferred into thin-wall glass capillaries and sealed off under an atmosphere of argon. All single crystals tested were relatively small, showing broad reflections and hence only low diffraction intensity. Intensity data were collected with Mo-Kα radiation with an ENRAF-Nonius CAD4 diffractometer equipped with a graphite monochromator, $\lambda = 0.71073$ Å at 228 K on a crystal of approximate dimensions 0.28 × 0.20 × 0.12 mm. In view of the modest linear absorption coefficient and the small crystal size no absorption correction was applied. After merging, 4169 independent reflections remained for structure solution by direct methods.[13] The structure model was completed by Fourier difference syntheses and refined with full-matrix least-squares on F^2.[14] Convergence was reached for 4169 reflections and 169 variables at agreement factors of $wR2 = 0.1786$ (all data), $R1 = 0.1699$ [observations with $I > 2\sigma(I)$].

(see Experimental) of the reaction has shown that no reaction takes place between $TiCp_2(CO)_2$ and **1** after 24 h stirring at room temperature. At *ca.* 60 °C, gas evolution is observed, the carbonyl species gradually disappears from the solution and the brown $TiCp_2(C_8H_8O_4)$ **10** is formed. The IR spectrum of **10** in the 1200–1000 cm^{-1} region (1036, 1196, 1215 cm^{-1}) is similar to that of $(VCp_2)_2(C_8H_8O_4)$ **6** (1016, 1194, 1220 cm^{-1}), thus suggesting that **1** has undergone a formal bielectronic reduction to the diolato species. Due to the low solubility and to the tendency of 1,4-benzoquinone to give polynuclear compounds,[16] we propose a polynuclear structure for **10**, with a bridging dianion $[C_8H_8O_4]^{2-}$ between two $[TiCp_2]$ moieties.

The thermal reaction of **1** with two equivalents of $TiCp_2(CO)_2$ does not afford the pure 2 : 1 species $(TiCp_2)_2(C_8H_8O_4)$ probably due to the competing thermal decomposition of the dicarbonyl derivative. This fact prompted us to use the bis-trimethylphosphine derivative $TiCp_2(PMe_3)_2$ which has been shown[17] to undergo easy substitution of the coordinated phosphine. As a matter of fact, $TiCp_2(PMe_3)_2$ quickly reacts with **1** affording the bimetallic species $(TiCp_2)_2(C_8H_8O_4)$ **11** (Scheme 4). Alternatively, **11** can be obtained by reacting $[TiCp_2Cl]_2$ with the disodium derivative **3** (Scheme 4).

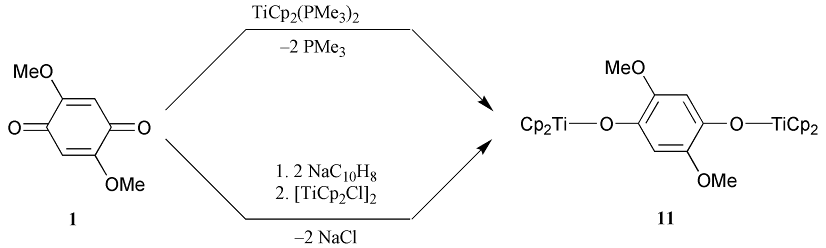
The IR spectrum of **11** is similar to that of the vanadium derivative $(VCp_2)_2(C_8H_8O_4)$ **6**, showing the characteristic absorptions of the bielectronically reduced quinonoid functionality (1019, 1198, 1221 cm^{-1}).

The bimetallic derivatives $(MCp_2)_2(C_8H_8O_4)$ (M = Ti **11**; M = V **6**) can be oxidized by one or two electrons affording cationic complexes of general formula $[(MCp_2)_2(C_8H_8O_4)]^{n+}$ which have been isolated as the tetraphenylborato salts: $[(MCp_2)_2(C_8H_8O_4)][BPh_4]_n$ ($n = 1$, M = Ti **12a**; $n = 1$, M = V **12b**; $n = 2$, M = Ti **12c**; $n = 2$, M = V **12d**) (Scheme 5). The IR spectra of compounds **12a**–**12d** do not show the absorption at 1665 cm^{-1} typical of **1**; thus suggesting that the coordinated dianion $[C_8H_8O_4]^{2-}$ has not undergone oxidation to quinone **1**; moreover, the strong absorptions in the region between 1200 and 1000 cm^{-1} suggest the presence of the coordinated dianion $[C_8H_8O_4]^{2-}$.

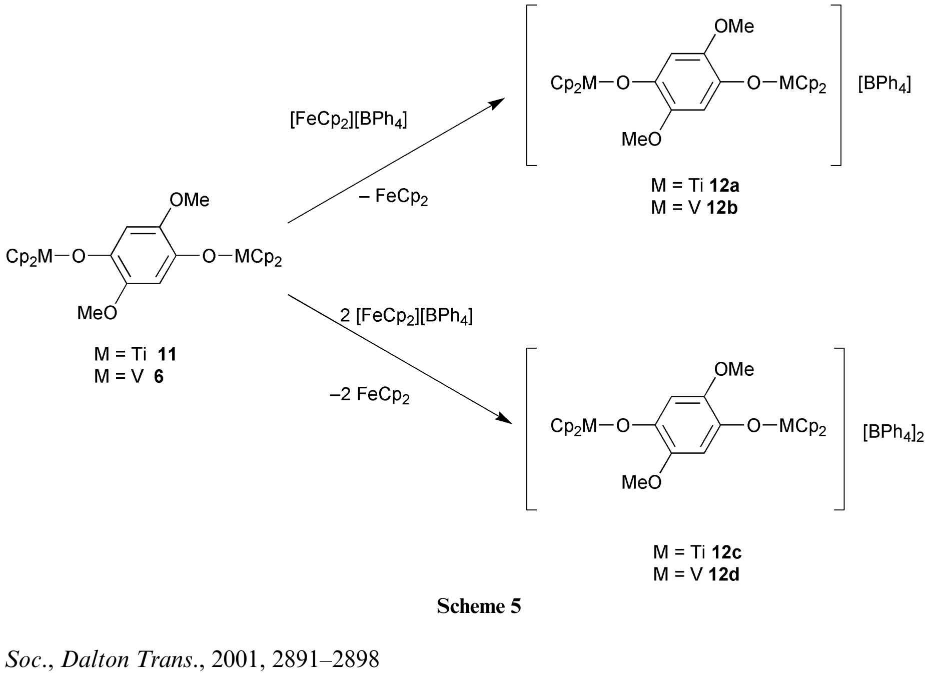
The quantitative monoelectronic oxidation of $(MCp_2)_2(C_8H_8O_4)$ (M = Ti, **11**; M = V, **6**) to the mixed-valence derivatives **12a** and **12c** suggests that the two metal centres in **6** and **11** undergo oxidation at two different potentials, and that probably we are dealing with a system containing two electronically interacting metal centres.[1] A similar situation is observed in the Creutz–Taube cation and related systems. Further evidence is reported below.

Magnetic measurements

The monometallic species $MCp_2(C_8H_8O_4)$ (M = Ti **10**; M = V **7**) possess different magnetic properties. Compound **10** is diamagnetic (at 298 K), thus confirming the spectroscopically (IR) established presence of a bielectronically reduced quinonoid functionality and the formal oxidation state +IV of the titanium centre. On the other hand, the vanadium(III) derivative $VCp_2(C_8H_8O_4)$ **7** is paramagnetic with a magnetic moment of 2.77 μ_B at room temperature. This value suggests the occurrence of antiferromagnetic coupling between the metal-centred unpaired electrons and that centred on the organic ligand, 3.32 μ_B being the spin-only expected value for a vanadium(III) ion of d^2 electronic configuration and the semiquinonato radical anion. In order to clarify this observation, variable-temperature magnetic measurements (70–298 K) have been carried out on **7** (Fig. 2): the molar susceptibility follows the Curie–Weiss law ($C = 0.948$ cgsu K, $\theta = -81.3$ K). The negative non-zero value of θ suggests[18] the occurrence of antiferromagnetic interactions. As far as the coupling mechanism is concerned, a literature survey[19] has shown that antiferromagnetic coupling is common in the field of quinonoid derivatives of transition metals and that the mechanism of this phenomenon can be



Scheme 4



Scheme 5

Table 1 Magnetic data for compounds **6**, **11**, **12b** and **12d**

Compound	μ_{eff}/μ_B (298 K)	g	J/cm^{-1}	$N\alpha$/cgsu (×10^5)	$\lvert J\rvert S_1S_2{}^a$/cm^{-1}
$(TiCp_2)_2(C_8H_8O_4)$ **11**	1.10[b]	1.3	7.0	7.2	1.8
$(VCp_2)_2(C_8H_8O_4)$ **6**	2.54[b]	1.8	4.3	13.2	4.3
$[(VCp_2)_2(C_8H_8O_4)][BPh_4]$ **12b**	2.69[c]	1.7	4.0	105.4	2.0
$[(VCp_2)_2(C_8H_8O_4)][BPh_4]_2$ **12d**	2.06[b]	2.1	7.3	29.5	1.8

[a] S_i = Total electronic spin number of the i-th ion. [b] Per metal centre. [c] Calculated per bimetallic unit.

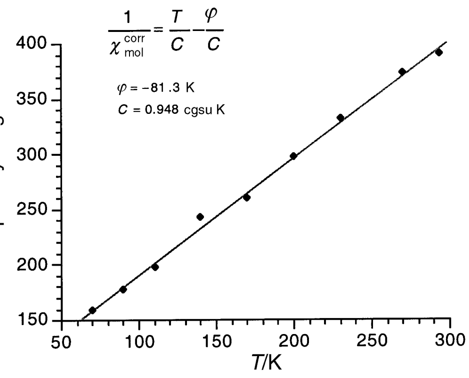


Fig. 2 Magnetic behaviour of $VCp_2(C_8H_8O_4)$. The solid line represents the calculated plot (Curie–Weiss law, $C = 0.948$ cgsu K; $\theta = -81.3$ K).

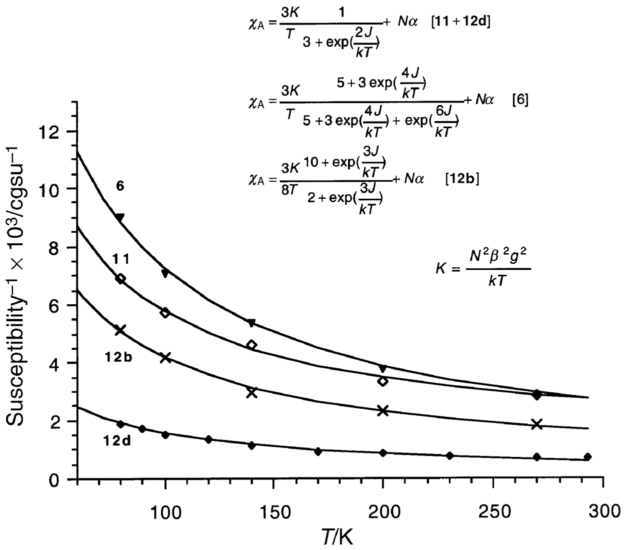


Fig. 3 Magnetic susceptibility of compounds **6**, **11**, **12b** and **12d**. The solid lines represent the calculated plots.

inter- and/or intra-molecular. Since we have no detailed structural information on **7**, no definite conclusion can be drawn about the mechanism of the observed antiferromagnetic coupling.

The bimetallic derivatives $(MCp_2)_2(C_8H_8O_4)$ (M = Ti **11**; M = V **6**), $[(MCp_2)_2(C_8H_8O_4)][BPh_4]_n$ (M = Ti, n = 1 **12a**; M = V, n = 1 **12b**; M = Ti, n = 2 **12c**; M = V, n = 2 **12d**) contain a bi-electronically reduced quinonoid functionality (*vide supra*) and metal centres with different electronic configurations depending on the nature of the metal centres and of the total charge of the $[(MCp_2)_2(C_8H_8O_4)]$ unit. Due to the diamagnetism of the $[C_8H_8O_4]^{2-}$ dianion, the metal ions only are expected to contribute mostly to the magnetic properties of these compounds.

The tetraphenylborato derivative **12c** is diamagnetic in agreement with the presence of two titanium(IV) ions. On the other hand, the mixed valence titanium(III)/titanium(IV) monocation **12a** is paramagnetic with an effective magnetic moment of 1.70 μ_B (at 298 K) per bimetallic unit, as expected for a titanium(III) (d^1 electronic configuration) derivative. The neutral titanium derivative **11** is paramagnetic with an effective magnetic moment of 1.10 μ_B per titanium centre (1.59 μ_B per bimetallic unit), thus suggesting antiferromagnetic coupling. Variable-temperature magnetic measurements on **11** have confirmed this suggestion, the molar susceptibility fitting the van Vleck equation for a d^1–d^1 coupled system (Fig. 3). Fitting parameters (g-factor and the exchange coupling constant J) are reported in Table 1.

The vanadium derivatives $(VCp_2)_2(C_8H_8O_4)$ **6**, $[(VCp_2)_2(C_8H_8O_4)][BPh_4]$ **12b** and $[(VCp_2)_2(C_8H_8O_4)][BPh_4]_2$ **12d** are paramagnetic, the magnetic moments at room temperature being reported in Table 1. By fitting the experimental data (susceptibility *vs.* temperature) with the appropriate van Vleck equation (Fig. 3), the parameters reported in Table 1 have been determined.

In order to compare the titanium and vanadium derivatives, the stabilisation energy $\lvert J\rvert S_1S_2$, S_i = total electronic spin number of the i-th ion, see Table 1, has been calculated. The neutral bimetallic titanium derivative **11** shows a degree of interaction lower than the vanadium analogue **6**, reasonably due to a less efficient overlap between the metal and the bridging ligand frontier orbitals. A decreasing interaction is observed on going from $(VCp_2)_2(C_8H_8O_4)$ **6** to $[(VCp_2)_2(C_8H_8O_4)][BPh_4]$ **12b** and $[(VCp_2)_2(C_8H_8O_4)][BPh_4]_2$ **12d**: we propose that the increase in the nuclear charge on going from **6**, to **12b** or **12d** reduces the overlap between frontier orbitals and consequently the interaction between the metal centres.

The observed value of 2.1 for the g-factors of **12d** is substantially the spin-only g-factor expected for a metallic ion. The observed values lower than 2 observed for **6**, **12b** and **11** are reasonably due to the occurrence of different spin–orbit coupling for each metallic ion.

The tetrabutylammonium **9a** and bis(triphenylphosphine)iminium **9b** salts of the complex anion $[(VCp_2Cl)_2(C_8H_8O_4)]^{2-}$ are paramagnetic with comparable values of χ_{mol}^{corr} at room temperature. The magnetic moments resulting from the Curie law are 2.33 and 2.42 μ_B (298 K) per metallic centre, respectively, suggesting a similar degree of interaction between the two paramagnetic vanadium(III) ions of d^2 electronic configuration.

Conclusions

2,5-Dimethoxy-1,4-benzoquinone has been shown to produce 1 : 1 and 2 : 1 derivatives. The basicity of the quinonoid and ethereal oxygens and the redox activity of the quinonoid functionality make **1** reactive towards metal centres both in high and low oxidation states.

The presence of differently hybridized oxygen atoms (sp^2 for the quinonoid functionality and sp^3 for the ethereal one) within the same molecule has allowed the Lewis basicity of the two sets of donor atoms to be compared. The observed primary addition of MCl_4 (M = Ti **4a**; M = Zr **4b**) to the quinonoid oxygens and the further addition of the second equivalent of $TiCl_4$ to afford the bimetallic derivative $(TiCl_4)_2(C_8H_8O_4)$ **5** clearly indicate that the quinonoid oxygens are the sites of stronger Lewis basicity. In addition, the absence of reaction between $ZrCl_4(C_8H_8O_4)$ **4b** and $ZrCl_4$ confirms that the ethereal oxygen atoms are less basic than the quinonoid ones, the former being unable to cause the fragmentation of the polynuclear structure of $ZrCl_4$.[12] Moreover, the fact that the methoxylic oxygen is not coordinated to the metal centres in the organometallic derivatives **6**, **7**, **10**, **11** and **12a**–**d** further underlines the poor Lewis basicity of the ethereal function in **1**.

Variable-temperature magnetic measurements on the bimetallic derivatives **6**, **11**, **12b** and **12d**, have evidenced the ability of the bridging $C_8H_8O_4$ unit to establish antiferromagnetic coupling between metal centres.

Experimental

All the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use.

IR spectra were recorded with a FT-1725X instrument on Nujol mulls prepared under rigorous exclusion of moisture and air, using KBr windows, or on solutions, using 0.1 mm cells (CaF_2 windows). ^1H- and ^{13}C-NMR spectra (200 MHz for ^1H, TMS as reference) were measured with a Varian Gemini 200BB instrument. Magnetic susceptibilities were measured with a magnetic balance (balance Sartorius 4104, electromagnet Varian V 2900) according to the Faraday method (using $CuSO_4{\cdot}5H_2O$ for calibration) at three different field strengths (9400, 10200 and 10800 G) and averaging the observed values. Diamagnetic corrections were calculated using Pascal contributions.[20] The compounds examined were crystallized twice from the appropiate solvent mixtures before being used for the magnetic measurements.

$TiCl_4$ (Merck) was distilled and used as a solution in heptane. $ZrCl_4$ (Fluka) was treated with boiling $SOCl_2$; the solution was partially evaporated under reduced pressure, and heptane was added for precipitation. The solid was recovered by filtration and dried *in vacuo*. Pd/C (Pd 3% w/w) (Aldrich) was contacted with dihydrogen (1 atm, 298 K) for 12 h and stored in sealed vials under argon. [PPN]Cl (Aldrich) was dried *in vacuo* in the presence of P_4O_{10} for 12 h. $[NBu_4]Cl$ was dried by dissolving the commercial product in benzene and distilling the H_2O–benzene azeotropic mixture. Naphthalene (Aldrich) was used as received. Finely divided sodium was prepared by suspending the commercial product (Aldrich, 50% w/w in paraffinic wax) in toluene and recovering the solid by filtration, washing with heptane and drying *in vacuo*. 2,5-Dimethoxy-1,4-benzoquinone **1**,[21] VCp_2,[22] $TiCp_2$,[23] $TiCp_2(PMe_3)_2$,[24] $[TiCp_2Cl]_2$[25] and $[FeCp_2][BPh_4]$[26] were prepared according to literature procedures.

Reduction of 2,5-dimethoxy-1,4-benzoquinone. *(a) With dihydrogen.* A suspension of **1** (513 mg, 3.05 mmol) and 69 mg (19 μmol of Pd) of Pd/C (3%) in toluene (25 ml) was contacted with dihydrogen (1 atm) and stirred for 7 h, dihydrogen pressure being maintained at 1 atm. The suspension was filtered and the hydrogenated product was separated from the Pd/C mixture by extraction with boiling toluene. The extract was evaporated, the residue suspended in heptane and the resulting suspension filtered. The solid was dried *in vacuo* and identified as 2,5-dimethoxy-1,4-dihydroxybenzene **2** (colourless, 410 mg, 80% yield). IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3367s, 1603vw, 1533s, 1520s, 1465s, 1349s, 1242ms, 1191s, 1167m, 1024s, 853m, 830s, 723m, 670m, 589m, 448m. ^1H-NMR ($CDCl_3$): δ 3.7 (6H), 6.5 (2H), 7.0 (2H; disappears upon adding D_2O and a new resonance is observed at about 4.5 ppm, due to water). ^{13}C-NMR ($CDCl_3$): δ 57.2 (CH_3), 102.5 (CH), 140.2 (C=O or C–O), 142.2 (C–O or C=O).

(b) With sodium–naphthalene. Finely divided sodium (210 mg, 913 mmol) was added to a suspension of **1** (769 mg, 4.58 mmol) in THF (50 ml) containing naphthalene (1.17 g, 9.10 mmol). The suspension was stirred for 12 h, then filtered and the solid washed with heptane (3 × 20 ml), dried *in vacuo* and identified as $Na_2[C_8H_8O_4]{\cdot}0.7$ THF **3** (green-brown, air sensitive, 714 mg, 60% yield). Found: C, 48.9, H, 5.2. $C_{10.8}H_{13.6}Na_2O_{4.7}$ requires: C, 49.0; H, 5.2%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 1521s, 1495s, 1319mw, 1208s, 1175s, 1164m, 1052m, 1030s, 882ms, 848ms, 722m, 687m, 598m, 453m.

Reaction of 1 with MCl_4 (M = Ti, Zr) (1 : 1 molar ratio). Only the procedure for M = Ti is reported, that for M = Zr being substantially the same, except for the fact that the tetrachloride was added as a solid. A 0.833 M solution of $TiCl_4$ (5 ml, 4.16 mmol) in heptane was added to a suspension of **1** (703 mg, 4.18 mmol) in CH_2Cl_2 (50 ml). The suspension was stirred for 12 h, filtered and the solid was finally dried *in vacuo* and identified as $TiCl_4(C_8H_8O_4)$ **4a** (green-brown, air sensitive, 774 mg, 52% yield). Found: C, 26.1; H, 2.4; Ti, 13.8. $C_8H_8Cl_4O_4Ti$ requires C, 26.9; H, 2.2; Ti, 13.4%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3076w, 1592ms, 1553s, 1367s, 1299w, 1263s, 1245s, 1224s, 981m, 840s, 774w, 723mw, 573mw.

$ZrCl_4(C_8H_8O_4)$ **4b** (violet, air sensitive, 78% yield). Found: C, 23.5; H, 2.1; Zr, 22.1. $C_8H_8Cl_4O_4Zr$ requires: C, 24.0; H, 2.0; Zr, 22.7%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3130w, 1613m, 1555s, 1394m, 1312mw, 1248s, 1236s, 979m, 883w, 838s, 723m, 641mw, 599mw.

Reaction of 1 with excess $TiCl_4$. A 0.768 M solution of $TiCl_4$ (15 ml, 11.5 mmol) in heptane was added to a suspension of **1** (485 mg, 2.88 mmol) in CH_2Cl_2 (50 ml). The suspension was stirred for 12 h, filtered and the solid was finally dried *in vacuo* and identified as $(TiCl_4)_2(C_8H_8O_4)$ **5** (brown, air sensitive, 1.014 g, 64% yield). Found: C, 17.0; H, 1.5; Ti, 17.2. $C_8H_8Cl_8O_4Ti_2$ requires: C, 17.6; H, 1.5; Ti, 17.5%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3065w, 1582s, 1538s, 1394s, 1289w, 1260mw, 1214s, 1180mw, 1101w, 1026w, 953mw, 839s, 584w, 432m.

Reaction of 1 with VCp_2 (1 : 2 molar ratio). Vanadocene (541 mg, 2.99 mmol) was added to a suspension of **1** (250 mg, 49 mmol) in toluene (50 ml). The solid promptly dissolved and the solution became deep brown. The solution was stirred for 30 min, evaporated and the residue was suspended in 50 ml of heptane. The suspension was filtered and the solid dried *in vacuo* and identified as $(VCp_2)_2(C_8H_8O_4)$ **6** (brown, air sensitive, 554 mg, 70% yield). Found: C, 64.0; H, 5.1; V, 19.0. $C_{28}H_{28}O_4V_2$ requires: C, 63.4; H, 5.3; V, 19.2%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3070w, 1490s, 1483s, 1390ms, 1220s, 1194s, 1169m, 1016m, 874m, 802s, 722w, 589mw, 452m. Magnetic measurement (per metallic centre, 70–298 K, diamagnetic correction = -1.44×10^{-4} cgsu): T (K), $\chi_{\mathrm{mol}}^{\mathrm{corr}} \times 10^3$ (cgsu): 70, 9.78; 80, 9.01; 90, 8.00; 100, 7.09; 120, 6.24; 140, 5.35; 170, 4.49; 200, 3.72; 230, 3.36; 270, 2.86; 298, 2.86; μ_{eff}(298 K) = 2.62 μ_{B}.

Reaction of 1 with VCp_2 (1 : 1 molar ratio). Vanadocene (399 mg, 2.20 mmol) was added to a suspension of **1** (371 mg, 2.21 mmol) in toluene (50 ml). Part of the solid promptly dissolved and the solution became deep brown. The suspension was stirred for 3 days until the supernatant liquid became colourless. The suspension was filtered and the deep blue solid dried *in vacuo* and identified as $VCp_2(C_8H_8O_4)$ **7** (air sensitive, 654 mg, 85% yield). Found: C, 61.1; H, 5.1; V, 14.8. $C_{18}H_{18}O_4V$ requires: C, 61.9; H, 5.2; V, 14.6%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3100w, 1665m, 1595ms, 1493s, 1444s, 1324w, 1269m, 1215s, 1194s, 1165m, 1030m, 953w, 884s, 803s, 731m, 593m. Magnetic measurement (70–298 K, diamagnetic correction = -1.89×10^{-4} cgsu): T (K), $\chi_{\mathrm{mol}}^{\mathrm{corr}} \times 10^3$ (cgsu): 70, 6.25; 90, 5.61; 110, 5.06; 140, 4.11; 170, 3.84; 200, 3.36; 230, 3.01; 270, 2.68; 298, 2.63; μ_{eff} = 2.77 μ_{B}.

Reaction of $VCp_2(C_8H_8O_4)$ with $TiCl_4$. A 0.768 M soluion of $TiCl_4$ (1.33 ml, 1.02 mmol) in heptane was added to a suspension of $VCp_2(C_8H_8O_4)$ (355 mg, 1.02 mmol) in CH_2Cl_2 (25 ml). A dark solid promptly precipitated out. The suspension was stirred for 6 h and then filtered. The solid was dried *in vacuo* and identified as $VCp_2(C_8H_8O_4)TiCl_4$ **8** (dark-brown, 408 mg, 74% yield, air sensitive). Found: C, 39.8; H, 3.3. $C_{18}H_{18}Cl_4TiV$ requires; C, 40.1; H, 3.4%. IR (Nujol mull): $\tilde{\nu}$/cm^{-1} 3100w, 1574s, 1292mw, 1220s, 1182mw, 1100mw, 990m, 852s, 722s, 594m.

Reaction of $(VCp_2)_2(C_8H_8O_4)$ with $C_8H_8O_4$. A suspension of **1** (0.083 g, 0.49 mmol) in toluene (30 ml) was treated with $(VCp_2)_2(C_8H_8O_4)$ (259 mg, 0.488 mmol). The suspension was stirred for 3 days; the solid was recovered by filtration, dried *in vacuo* and analytically and spectroscopically (IR) identified as $VCp_2(C_8H_8O_4)$ (**7**) (252 mg, 74% yield).

Reaction of $VCp_2(C_8H_8O_4)$ with VCp_2. $VCp_2(C_8H_8O_4)$ (153 mg, 0.438 mmol) was added to a solution of VCp_2 (77 mg, 0.43 mmol) in toluene (30 ml). The solid promptly dissolved. The solution was stirred for 30 min and the solvent removed *in vacuo*. The residue was added to heptane (30 ml) and the resulting suspension filtered. The solid was dried *in vacuo* and analytically and spectroscopically (IR) identified as $(VCp_2)_2(C_8H_8O_4)$ **6** (120 mg, 52% yield).

Reaction of $(VCp_2)_2(C_8H_8O_4)$ with [Cat]Cl ($[Cat]^+ = [NBu_4]^+$, $[PPN]^+$). Only the procedure for $[Cat]^+ = [NBu_4]^+$ is reported, that for $[Cat]^+ = [PPN]^+$ being analogous. $(VCp_2)_2(C_8H_8O_4)$ (304 mg, 0.573 mmol) was added to a solution of $[NBu_4]Cl$ (318 mg, 1.14 mmol) in THF (50 ml). The solution was stirred at room temperature for 12 h. The suspension was filtered, the deep violet solid was dried *in vacuo* and identified as $[NBu_4]_2[(VCp_2Cl)_2(C_8H_8O_4)]$ **9a** (air sensitive, 400 mg, 64% yield). Found: C, 65.3; H, 9.1; N, 2.6; V, 9.5. $C_{60}H_{100}Cl_2N_2O_4V_2$ requires: C, 66.3; H, 9.3; N, 2.6; V, 9.4%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3098w, 1488s, 1444s, 1387m, 1261w, 1201s, 1193s, 1153m, 1064w, 1026ms, 882s, 799s, 722m, 596m. Magnetic measurement (per metallic centre): diamagnetic correction = -3.77×10^{-4} cgsu, $\chi_{mol}^{corr} = 2.26 \times 10^{-3}$ cgsu, μ_{eff} (298 K) = 2.33 μ_B.

$[PPN]_2[(VCp_2Cl)_2(C_8H_8O_4)]$ **9b** (gray-green, air sensitive, 80% yield). Found: C, 7.10; H, 5.0; N, 1.4; V, 6.0%. $C_{100}H_{88}Cl_2N_2O_4P_4V_2$ requires: C, 71.6; H, 5.3; N, 1.7; V, 6.1%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3100w, 1487s, 1442s, 1269s, 1233s, 1194s, 1159ms, 1115s, 1026ms, 882s, 810s, 724s, 693s, 601m. Magnetic measurement (per bimetallic unit): diamagnetic correction = -0.53×10^{-4} cgsu, $\chi_{mol}^{corr} = 2.44 \times 10^{-3}$ cgsu, μ_{eff}(298 K) = 2.42 μ_B.

Reaction of 1 with $TiCp_2(CO)_2$. $TiCp_2(CO)_2$ (0.69 g, 2.95 mmol) was added to a suspension of **1** (496 mg, 2.95 mmol) in toluene (50 ml). The suspension was stirred for 3 h without lowering of the concentration of the carbonylic complex being observed by IR [the IR spectrum of $TiCp_2(CO)_2$ dissolved in toluene shows two strong carbonyl stretching bands at 1968 cm^{-1} ($\varepsilon = 1637\ M^{-1}\ cm^{-1}$) and 1884 cm^{-1} ($\varepsilon = 2209\ M^{-1}\ cm^{-1}$).] The mixture was heated at 60 °C for 6 h, until complete disappearance of $TiCp_2(CO)_2$ (IR). The suspension was filtered and the solid dried *in vacuo* and identified as $TiCp_2(C_8H_8O_4)$ **10** (brown, air sensitive, 845 mg, 83% yield, diamagnetic at 298 K). Found: C, 6.20; H, 5.4; Ti, 14.2. $C_{18}H_{18}O_4Ti$ requires: C, 6.24; H, 5.2; Ti, 13.8%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3080w, 1600w, 1495s, 1386m, 1262w, 1215s, 1196s, 1103w, 1036m, 902ms, 811s, 722mw, 669w, 600m, 455m.

Reaction of $Na_2[C_8H_8O_4]$ with $[TiCp_2Cl]_2$. Sodium sand (100 mg, 4.35 mmol) was added to a suspension of **1** (369 mg, 2.19 mmol) and naphthalene (0.648 g, 5.05 mmol) in THF (50 ml). The suspension was stirred for 12 h and then 933 mg, (4.37 mmol of titanium) of $[TiCp_2Cl]_2$ were added. The solution promptly turned brown and an abundant solid formed. The solvent was removed *in vacuo* and the residue was extracted with boiling toluene. The extract was evaporated, the residue suspended in heptane (50 ml) and recovered through filtration. The chloride-free solid was dried *in vacuo* and identified as $(TiCp_2)_2(C_8H_8O_4)$ **11** (brown, air sensitive, 359 mg, 47% yield). Found: C, 64.0; H, 5.2; Ti, 18.4. $C_{28}H_{28}O_4Ti_2$ requires: C, 64.2; H, 5.4; Ti, 18.3%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3109w, 1495s, 1445s, 1398ms, 1260mw, 1221s, 1198s, 1170m, 1019ms, 904m, 807s, 722mw, 669mw, 595m, 452m. Magnetic measurement (per bimetallic unit, 70–298 K, diamagnetic correction = -2.86×10^{-4} cgsu): T (K), $\chi_{mol}^{corr} \times 10^3$ (cgsu): 67, 2.23; 70, 2.21; 75, 2.03; 80, 1.90; 85, 1.78; 90, 1.69; 95, 1.60; 100, 1.52; 110, 1.43; 120, 1.35; 140, 1.14; 170, 0.89; 200, 0.84; 230, 0.75; 270, 0.68; 298, 0.67; μ_{eff}(298 K) = 1.27 μ_B.

Reaction of 1 with $TiCp_2(PMe_3)_2$. A suspension of **1** (81 mg, 0.48 mmol) in toluene (15 ml) was treated with 320 mg (0.969 mmol) of $TiCp_2(PMe_3)_2$. The resulting suspension was stirred for 12 h; the volatiles were evaporated *in vacuo* and the residue was suspended in heptane (50 ml). The solid was recovered by filtration, dried *in vacuo* and analytically and spectroscopically (IR) identified as $(TiCp_2)_2(C_8H_8O_4)$ **11** (171 mg, 68% yield).

Oxidation of $(MCp_2)_2(C_8H_8O_4)$ (M = Ti, V) with $[FeCp_2][BPh_4]$. Only the procedures for M = Ti are reported, those for M = V being similar.

(a) Ti : Fe molar ratio = 2. $(TiCp_2)_2(C_8H_8O_4)$ (297 mg, 0.566 mmol) was added to a suspension of $[FeCp_2][BPh_4]$ (289 mg, 0.566 mmol) in toluene (50 ml). The suspension was stirred for 12 h and filtered. The solid was washed with heptane (2 × 20 ml), dried *in vacuo* and identified as $[(TiCp_2)_2(C_8H_8O_4)][BPh_4]$ **12a** (red-brown, air sensitive, 290 mg, 61% yield). Found: C, 73.6; H, 5.7; Ti, 11.3. $C_{52}H_{48}BO_4Ti_2$ requires: C, 74.0; H, 5.7; Ti, 11.4%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3112w, 3056w, 1578w, 1494s, 1444s, 1388m, 1260w, 1214s, 1196s, 1172w, 1140w, 1068w, 1018m, 908m, 882w, 820s, 754w, 734s, 706s, 612m, 552w, 492w. Magenetic measurement (per metallic centre): diamagnetic correction = -4.97×10^{-4} cgsu, χ_{mol}^{corr} (298 K) = 1.20×10^{-3} cgsu, μ_{eff}(298 K) = 1.70 μ_B.

$[(VCp_2)_2(C_8H_8O_4)][BPh_4]$ **12b** (blue-green, air sensitive, 73% yield). Found: C, 74.0; H, 5.7; V, 12.2. $C_{52}H_{48}BO_4V_2$ requires: C, 73.51; H, 5.7; V, 12.2%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3108w, 3056w, 1580w, 1494s, 1444s, 1388m, 1263w, 1217s, 1196ms, 1145mw, 1031w, 1014m, 908sh, 884m, 832s, 754w, 736s, 707s, 611m, 552w, 492mw. Magnetic measurement (per bimetallic unit, 70–298 K, diamagnetic correction = -4.95×10^{-4} cgsu): T (K), $\chi_{mol}^{corr} \times 10^3$ (cgsu): 70, 7.58; 75, 7.31; 80, 6.90; 90, 6.22; 100, 5.71; 110, 5.29; 120, 5.11; 140, 4.60; 170, 3.85; 200, 3.30; 230, 3.03; 270, 2.86; 298, 2.85; μ_{eff}(298 K) = 2.62 μ_B.

(b) Ti : Fe molar ratio = 1. $(TiCp_2)_2(C_8H_8O_4)$ (137 mg, 0.261 mmol) was added to a suspension of $[FeCp_2][BPh_4]$ (267 mg, 0.528 mmol) in toluene (30 ml). The suspension was stirred for 12 h and filtered. The resulting solid was washed with heptane (2 × 20 ml), dried *in vacuo* and identified as $[(TiCp_2)_2(C_8H_8O_4)][BPh_4]_2$ **12c** (brown, air sensitive, 185 mg, 61% yield, diamagnetic at 298 K). Found: C, 79.0; H, 5.6; Ti, 8.3. $C_{76}H_{68}B_2O_4Ti_2$ requires: C, 78.5; H, 5.9; Ti, 8.4%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3102w, 3056w, 1578w, 1494s, 1456s, 1340m, 1262w, 1216s, 1196ms, 1170w, 1145w, 1018m, 908w, 882w, 814s, 754w, 734s, 704s, 612m, 552w, 492w.

$[(VCp_2)_2(C_8H_8O_4)][BPh_4]_2$ **12d** (blue-green, air sensitive, 65% yield). Found: C, 78.5; H, 5.9; V, 9.0. $C_{76}H_{68}B_2O_4V_2$ requires: C, 78.1; H, 5.9; V, 8.7%. IR (Nujol mull): $\tilde{\nu}/cm^{-1}$ 3104w, 3054w, 1580w, 1494s, 1456s, 1340m, 1268mw, 1217s, 1195ms, 1145m, 1012m, 882m, 832s, 754w, 735s, 706s, 611m, 542w, 487w. Magnetic measurement (per bimetallic unit, 70–298 K, diamagnetic correction = -7.02×10^{-4} cgsu): T (K), $\chi_{mol}^{corr} \times 10^3$ (cgsu): 67, 5.93; 70, 5.65; 75, 5.33; 80, 5.12; 90, 4.59; 100, 4.19; 120, 3.74; 140, 2.95; 170, 2.54; 200, 2.30; 230, 2.08; 270, 1.82; 293, 1.68; μ_{eff} = 2.01 μ_B.

Acknowledgements

The authors wish to thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Roma), Programma di Ricerca Scientifica di Notevole Interesse Nazionale, Cofinanziamento MURST 2000–2001, for financial support.

References

1 M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121 and references therein.

2 F. Lloret, M. Julve, J. Faus, X. Solans, Y. Journaux and I. Morgenstern-Badarau, *Inorg. Chem.*, 1990, **29**, 2232.

3 M. D. Ward, *Inorg. Chem.*, 1996, **35**, 1712.

4 C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1973, **21**, 1086.

5 J. Q. Chambers, in *The Chemistry of Quinonoid Compounds*, S. Patai, ed., J. Wiley, New York, 1974, vol. 2, p. 737.

6 R. Nietzki and F. Rechberg, *Ber. Dtsch. Chem. Ges.*, 1900, **23**, 1211.

7 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectroscopic Identification of Organic Compounds*, 5th edn., J. Wiley, New York, 1991.

8 C. Floriani, R. Henzi and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 1972, 2640.

9 F. Calderazzo, F. Marchetti, G. Pampaloni and V. Passarelli, *J. Chem. Soc., Dalton Trans.*, 1999, 4389.

10 C. A. McAuliffe and D. S. Barratt, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, eds., Pergamon, Oxford, 1987, vol. 3, p. 323.

11 M. Handa, H. Matsumoto, D. Yoshioka, R. Nukada, M. Mikuriya, I. Hiromitsu and K. Kasuga, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1811.

12 B. Krebs, *Z. Anorg. Allg. Chem.*, 1970, **378**, 263.

13 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.

14 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

15 A. L. Spek, PLATON98, Utrecht University, Utrecht, The Netherlands, 1998.

16 R. R. Burch, *Chem. Mater.*, 1990, **2**, 633.

17 M. Bochmann, in *Comprehensive Organometallic Chemistry*, E. W. Abel, F. G. A. Stone and G. Wilkinson, eds., Pergamon, Oxford, 1995, vol. 4, p. 230.

18 A. E. Earnshaw, *An Introduction to Magnetochemistry*, Academic Press, London, 1968.

19 C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331 and references therein.

20 E. König, in *Landoldt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, 6th edn., Springer, Berlin, 1966, vol. 2, p. 16.

21 J. B. Conant and L. F. Fieser, *J. Am. Chem. Soc.*, 1924, **46**, 1865.

22 C. E. Zybill, in *Synthetic Methods of Organometallic and Inorganic Chemistry*, W. A. Herrmann, ed., Georg Thieme, Stuttgart, 1997, vol. 8, p. 5.

23 D. J. Sikora, K. J. Moriarty and M. D. Rausch, *Inorg. Synth.*, 1986, **24**, 147.

24 L. B. Kool, M. D. Rausch, H. G. Alt, M. Herberhold, U. Thewalt and B. Wolf, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 394.

25 L. E. Manzer, *Inorg. Synth.*, 1990, **28**, 261.

26 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.