Bis(arene)vanadium Anions, a New Class of Organovanadium Complexes: Syntheses, Reactivity towards Carbon Oxides, and Electron Spin Resonance Investigation

Giovanni Fochi* and Xu Runjuan
Scuola Normale Superiore, Pisa and Dipartimento di Chimica e Chimica Industriale dell'Università, Sezione di Chimica Inorganica, Via del Risorgimento 35, I-56126 Pisa, Italy
Arturo Colligiani
Istituto di Chimica Industriale, Università di Messina, I-98100 Sant'Agata (ME), Italy

Reduction of bis(arene)vanadium(O) complexes (**1**) with potassium in co-ordinating ether solvents gives solutions of the corresponding bis(arene)vanadate(-I) derivatives (**2a**; arene = benzene) and (**2b**; arene = mesitylene). Solvated potassium salts were isolated in yields depending on the arene ligands and the type of procedure required. The e.s.r. spectra of the reduction mixtures both in 1,2-dimethoxyethane and hexamethylphosphoramide are discussed. Solutions of $K[V(C_6H_6)_2]$ (**2a**) in tetrahydrofuran are quickly reoxidized by both carbon mono- and di-oxide to give the vanadium(O) complex (**1a**); C_1 and C_2 products are formed, the relative yields depending on the concentrations of the reactants.

The organometallic chemistry of Group 5 elements in their $-$I oxidation state is very rich, though restricted to the hexacarbonylmetalate anions and their substituted derivatives. A preliminary report of a non-carbonyl organovanadium($-$I) species, $[V(C_6H_6)_2]^-$, appeared in 1975;[1] however, in spite of its interest, this observation has not been developed further. More recently the existence of bis(naphthalene)metalates of niobium and tantalum[2a] and of the bis(mesitylene)niobium anion[2b] has been suggested.

It appeared important to use bis(arene) anionic derivatives of Group 5-metals as electron-rich reagents, whose electron density and hence chemical properties could in principle be different from those of carbonylmetalates, due to the different π acidities of the ligands.

This paper reports experimental procedures for the preparations of two different bis(arene)vanadium anions as solvated potassium salts, the e.s.r. spectrum of bis(benzene)-vanadium (**1a**) after reduction, and the reaction of potassium bis(benzene)vanadate (**2a**) with both carbon monoxide and carbon dioxide in tetrahydrofuran (thf) solution. Parts of this work have been described in preliminary communications,[3,4] including a structural investigation of potassium bis(mesitylene)-vanadate (**2b**).[3]

Experimental

Unless otherwise stated, all operations were carried out under an atmosphere of prepurified nitrogen or argon. Carbon mono- and di-oxide were prepurified gases. Solvents were carefully dried by conventional methods prior to use. I.r. spectra were measured with a Perkin-Elmer model 283 instrument equipped with grating. Quantitative spectrophotometric analyses were carried out at 572 nm with a Varian Techtron 635 instrument. E.s.r. spectra were registered on an ER-200 D-SRC Bruker spectrometer operating in the X band and provided with a TM_{110} cavity. The static magnetic field H_0 was modulated at 100 kHz.

G.c. analyses of gaseous samples were performed with a DANI 3200 gas chromatograph equipped with either 5A molecular sieve or Porapack Q packed columns and a hot-wire detector; argon or helium was the carrier gas. Liquid samples were analysed with a DANI 8400 gas chromatograph, equipped with either 10% OV-101 or 10% Carbowax 20 M on Chromosorb W-HP (100—120 mesh) or Porapack PS packed columns, and a flame ionization detector; helium was the carrier gas.

Alkalimetric titrations utilized 0.1 mol dm^{-3} HCl and were followed potentiometrically.

Compound (**1a**)[5] and bis(mesitylene)vanadium(O) (**1b**)[6] were prepared by known procedures. Potassium sand was prepared in hot n-heptane by means of a Vibro-Mixer equipped with a perforated plate immersed in the molten metal.

Preparation of Solvated Potassium Bis(benzene)vanadate (**2a**).—Tetrahydrofuran (100 cm^3) was added to compound (**1a**) (2.71 g, 13.1 mmol) and potassium sand (0.54 g, 13.9 mmol). The initially red-brown mixture was stirred for 4 h; then the unreacted potassium was filtered off, washed with two portions (25 cm^3) of thf, dissolved in a few cm^3 of ethanol, and diluted with water. Titration gave 0.88 mmol of hydroxide, thus showing that 1 mol of potassium per mol of vanadium complex had reacted, within experimental error.

The dark violet mother-liquor was concentrated *in vacuo* to *ca.* 60 cm^3 and diethyl ether (100 cm^3) was added. After standing at -40 °C overnight, black-violet needles were collected by filtration [3.01 g, 68.5% as (**2a**)·1.25 thf] [Found: K, 11.8 (alkalimetrically); V, 15.5 (redox titration with 0.1N $KMnO_4$ after dissolution in H_2SO_4–HNO_3 and reduction with SO_2); (**1a**), 61.3 [gravimetrically after hydrolysis of (**2a**)]. (**2a**)·1.25 thf requires K, 11.6; V, 15.1; (**1a**), 61.6%].

Reduction of Bis(mesitylene)vanadium (**1b**).—Tetrahydrofuran (100 cm^3) was added to compound (**1b**) (1.97 g, 6.76 mmol) and potassium sand (0.37 g, 9.51 mmol). The initially red-brown mixture was stirred for 4 h, then the unreacted potassium was treated and analysed as described above: 2.95 mmol of potassium had not been solubilized during the reduction of (**1b**), and hence a 97.0% yield was evaluated for the reaction between (**1b**) and potassium. Diethyl ether (200 cm^3) was added to the black-brown mother-liquor. The initial red-brown colour was immediately restored, while very fine silvery platelets of potassium separated. These were treated as described above and titrated (3.55 mmol, corresponding to 54.1% of the potassium reacted). The mother-liquor was dried *in vacuo* and n-heptane (100 cm^3) was added; after filtration, the liquid was dried again, yielding 1.72 g of compound (**1b**) (87.3% based on the initial reactant). The heptane-insoluble residue reacted violently with water, giving a strongly alkaline solution.

Preparation of Solvated Potassium Bis(mesitylene)vanadate (**2b**).—Tetrahydrofuran (50 cm^3) was added to compound (**1b**) (3.25 g, 11.2 mmol), and potassium sand (0.49 g, 12.5 mmol). The mixture was stirred at room temperature for 4 h and then cooled to −40 °C. After standing at low temperature overnight the product (**2b**) was collected by filtration and dried *in vacuo* [1.07 g, 20.1% as (**2b**)·2 thf] [Found: K, 8.0 (alkalimetrically). $C_{26}H_{40}KO_2V$ requires K, 8.2%].

Reaction of a Tetrahydrofuran Solution of Potassium Bis(benzene)vanadate (**1a**) *with an Atmosphere of* CO_2.—Tetrahydrofuran (100 cm^3) was added to compound (**1a**) (3.92 g, 18.9 mmol), and potassium sand (0.89 g, 22.7 mmol). The mixture was stirred for 4 h and then filtered; 4.0 mmol of unreacted potassium were determined as described above, and hence compound (**2a**) was formed in 98.9% yield. The filtrate was brought into contact with an atmosphere of CO_2; an immediate reaction took place and the mixture turned to the red-brown colour of (**1a**) while a very fine solid precipitated and a slight increase in temperature was noticed. Neither CO nor acetylene could be detected (g.c.) in the gas phase. After filtration, the thf-insoluble brownish product (3) was washed with four portions (25 cm^3) of thf, dried *in vacuo* (1.6 g) and finally homogenized carefully.

Compound (**1a**) was recovered (3.64 g, 92.9%) by evaporating the mother-liquor, which on i.r. inspection revealed the absence of any metal carbonyls.

The following determinations were carried out on compound (3). G.c. analysis after dissolution in water showed thf to be practically absent.

A 0.334-g sample was dissolved in degassed 10% aqueous H_2SO_4 (30 cm^3). The gas evolved was slowly bubbled, with the aid of a nitrogen flux, through a 0.332N solution (30 cm^3) of $Ba(OH)_2$. The excess of hydroxide was then titrated using 80.1 cm^3 of 0.1 mol dm^{-3} HCl: 1.95 mequivalents of CO_2 were therefore evolved corresponding to 0.25 mol of CO_2 precursors in compound (3) per mol of (**1a**).

A 0.237-g sample was treated with degassed water and the oxalate ions were precipitated with excess of calcium acetate. The insoluble solid was washed with degassed water, dissolved in 10% aqueous H_2SO_4, and finally titrated with 12.8 cm^3 of a 0.1114N solution of $KMnO_4$: the content in oxalate precursors of compound (3) was then evaluated to be 4.81 mmol [0.25 mol per mol of (**1a**)].

A 0.258-g sample was dissolved in 10% H_2SO_4 and titrated with 25.8 cm^3 of a 0.1114N solution of $KMnO_4$. In compound (3) the total equivalents of species capable of reducing acidic permanganate were thus close to the number of moles of (**2a**) (95%).

A 0.148-g sample was dissolved in 30% H_2SO_4 and the resulting solution was diluted to 25.0 cm^3 with water. A 0.5-cm^3 amount was then kept at 100 °C for 30 min together with 5% aqueous 4,5-dihydroxynaphthalene-2,7-disulphonic acid (disodium salt, dihydrated) (0.5 cm^3) and concentrated H_2SO_4 (5 cm^3). By comparison with a calibration curve obtained for authentic samples, the A_{572} value (0.527) corresponded to 5.7×10^{-2} mmol of glycolic acid in compound (3)

Concentrated HCl (1 cm^3) was carefully added to a 0.355-g sample suspended in diethyl ether (50 cm^3). The mixture was dried by azeotropic distillation in a Dean–Stark apparatus during a 27-h reflux. After addition of BF_3–CH_3OH (Supelco) and 1,4-dioxane as internal standard, g.c. on Porapack PS showed 0.15 mmol of methyl formate and 0.32 mmol of dimethyl oxalate.*

Reaction of Solid $K[V(C_6H_6)_2]\cdot 1.25$ thf, (**2a**)·1.25 thf, *with* CO_2*-saturated Tetrahydrofuran.*—A flask with a heavy-bottomed fragile ampoule containing compound (**2a**)·1.25 thf (2.2 g, 6.5 mmol) was connected in a stream of CO_2 to another flask with CO_2-presaturated thf (300 cm^3) through a piece of glass tubing with ground joints. The solvent was transferred over the ampoule and slightly cooled. The ampoule was broken with the aid of a Teflon-covered magnetic bar. The reaction was very fast and the mixture looked similar to the one described above. On applying the procedures described above the following results were obtained: compound (**1a**) was recovered in 83% yield; the thf-insoluble product (4) was ascertained to contain precursors of CO_2 [0.29 mol per mol of (**2a**)·1.25 thf], oxalate (0.15), and glycolate (0.0020).

Results and Discussion

Syntheses.—Bis(arene)vanadium anions consistute a class of extremely air-sensitive vanadium(−I) complexes, which are synthetically attainable provided extraordinary care is taken in handling them both in solution and even as solids. They are formed according to Scheme 1, as already observed by Elschenbroich and Gerson.[1]

$$\underset{(\mathbf{1a}),\,(\mathbf{1b})}{[V(\text{arene})_2]} + K \xrightarrow{\text{thf}} \underset{(\mathbf{2a}),\,(\mathbf{2b})}{K[V(\text{arene})_2]}$$

Scheme 1. Arene = C_6H_6 (**a**) or $C_6H_3Me_3$-1,3,5 (mesitylene) (**b**)

When either compound (**1a**) or (**1b**) is mixed with an excess of potassium sand in thf or 1,2-dimethoxyethane (dme) dark solutions result. In the case of (**1a**), after filtration of the unreacted potassium and addition of diethyl ether or n-heptane, a black microcrystalline solid precipitates in about 70% yield and analyses as (**2a**)·1.25 thf. On the other hand, dilution of a filtered thf solution of (**2b**) by either of the same solvents causes immediate decomposition to (**1b**) (*ca.* 90%), elemental potassium (*ca.* 50%) and untractable alkaline products. The stability difference between (**2a**) and (**2b**) could be explained by different electronic situations in (**1a**) and (**1b**): the electron-donating methyl substituents render (**1b**) the electron-richer system and therefore the more difficult to accept an extra electron.

To isolate (**2b**) in the solid state a concentrated thf solution must be prepared and cooled to −40 °C. A dark microcrystalline solid then precipitates in low yield (*ca.* 20%), having a potassium content consistent with the formula (**2b**)·2thf.

The observed decomposition of compound (**2b**) when thf is diluted with non-co-ordinating solvents reveals the role of solvation energy in the delicate thermodynamic balance for this system, as confronted with the ionization potential of the alkali metal. Consistent with this is the observation that sodium sand does not react with (1) even over prolonged reflux.

Reactions with Carbon Monoxide and Carbon Dioxide.—The

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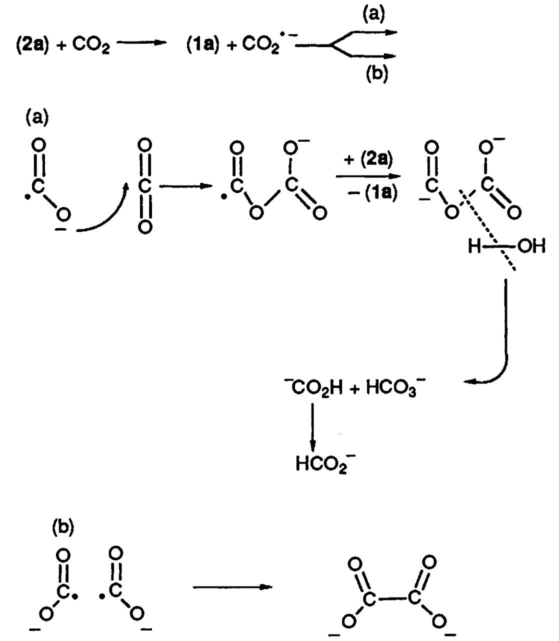
* Conversion into methyl esters, with either diazomethane or BF_3–methanol, after extraction of the acids was not a viable method, due to their considerable solubilities in water. Better results were obtained by dehydrating an ether suspension of the hydrolysis mixture by azeotropic distillation; nevertheless, control experiments carried out on weighed authentic samples of potassium formate and oxalate showed that considerable loss could not be avoided, so that final g.c. examination gave only qualitative results.

Table. Yields of the hydrolysis products of compounds (**3**) and (**4**)

Product	Mol per mol of (**2a**) (**3**)	 (**4**)
CO_3^{2-} and/or HCO_3^-	0.25	0.29
$^-O_2C{-}CO_2^-$ and/or $HO_2C{-}CO_2^-$	0.25	0.15
$HOCH_2CO_2^-$	0.0030	0.0020
CO, H_2, C_2H_2 in the gas phase	Absent	—



Scheme 2. Formation of HCO_2^-, HCO_3^-, and $C_2O_4^{2-}$

reactivity of compound (**2a**) towards carbon oxides in thf shows a general trend towards one-electron oxidation: (**1a**) can be recovered in yields greater than 80% in all cases.

The solid products derived from carbon oxides have i.r. spectra of little diagnostic value and are not completely analysable by chemical methods. However, upon hydrolysis they gave carbonate, oxalate, and formate. For the determination of carbonate, oxalate,[7] and glycolate,[7] reliable results were obtained by standard semimicroanalytical methods or procedures already adopted for products of similar reactions. On the contrary, for formate determination, application of g.c. to the methyl ester, prepared from the hydrolysis mixtures, gave only qualitative information (see Experimental section). The complexity of the analytical problem has led us to correct some of the results reported preliminarily.[4]

Reduction of carbon mono- and di-oxide by alkali metals requires drastic conditions,[8] unless the metal is activated by either dissolution in liquid ammonia,[9] amalgam formation,[10] or addition of naphthalene[11] or crown ethers.[12] Dissolving potassium in thf containing (**1a**) can be considered a novel method of activating the alkali metal.

When carbon monoxide is brought into contact with a thf solution of compound (**2a**) a rapid reaction takes place (*ca.* 15 min) and (**1a**) is formed in 95% yield. The analysis of the thf-insoluble highly pyrophoric brownish product is still an unsolved problem, because in the hydrolysis mixture no species where carbon is more reduced than in CO have been detected. As a hypothesis, we suggest that some cyclic oligomers[8b,12] derived from the CO radical anion could be present.

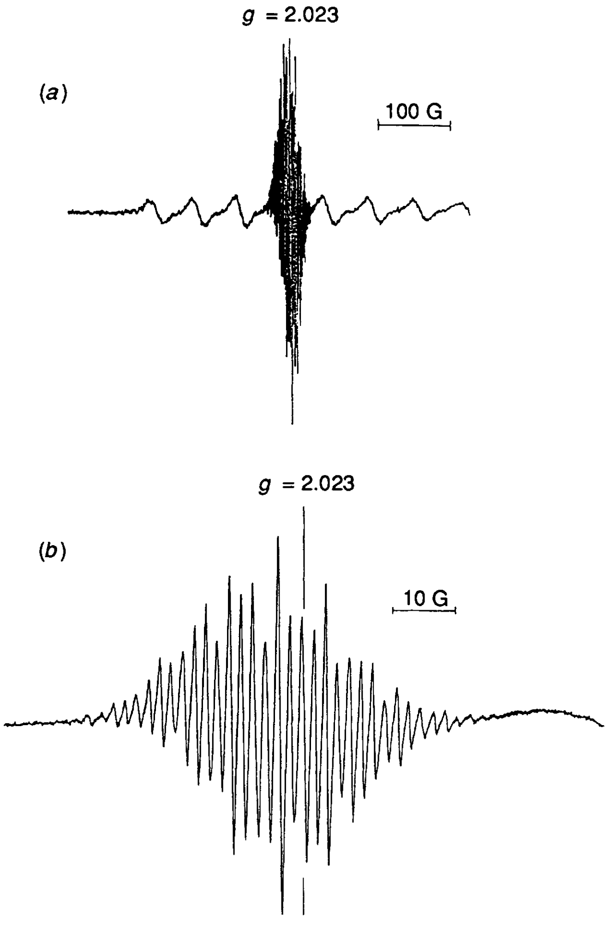


Figure. *X*-Band e.s.r. spectra of a solution of compound (**1a**) in hmpa in the presence of potassium sand. Microwave frequency = 9.82 GHz. Amplitude of the H_0 modulation = 0.25 G (G = 10^{-4} T). (*a*) Whole spectrum, (*b*) detail of the finely structured feature. The spectra were calibrated with respect to diphenylpicrylhydrazyl. Compound (**1b**) gave rise to very similar spectra under the same conditions

Carbon dioxide reacts instantly with filtered dark blue 0.05—0.13 mol dm^{-3} thf solutions of (**2a**) at room temperature and atmospheric pressure; the liquid turns red-brown, while a very fine solid separates. No CO can be detected chromatographically in the gas phase. Vacuum evaporation of the mother-liquor, the i.r. inspection of which reveals the absence of metal carbonyls, gives (**1a**) in 95% yield. The thf-insoluble brownish powder (**3**), after hydrolysis, reveals the presence of carbonate, oxalate, glycolate (see Table), and formate (see Experimental section and above in this paragraph).

From the ascertained yields of carbonates and oxalates the overall stoicheiometry (4) can be suggested.

$$\underset{(\mathbf{2a})}{4(K)} + 3CO_2 + 2H_2O \longrightarrow 4K^+ + HCO_2^- + HC_2O_4^- + 2HO^- \quad (1)$$

$$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O \quad (2)$$

$$CO_3^{2-} + HC_2O_4^- \rightleftharpoons HCO_3^- + C_2O_4^{2-} \quad (3)$$

$$\underset{(\mathbf{2a})}{4(K)} + 4CO_2 + H_2O \longrightarrow 4K^+ + HCO_2^- + HCO_3^- + C_2O_4^{2-} \quad (4)$$

While the 1:1 formation of formate and acid carbonate resembles the electrochemical reduction of CO_2 in aqueous media,[13] thus suggesting that these two hydrolysis products could have a common precursor in (**3**), oxalate is likely to be already present in (**3**) as the consequence of the dimerization of the CO_2 radical anion[13] (see Scheme 2). The hypothesis of a competition between pathways (a) and (b) seems to be supported by the analysis of (**4**), the thf-insoluble product of the reaction of solid (**2a**)·1.25 thf with CO_2-saturated thf. The yield of carbonate is higher than in the former case, while the opposite occurs for oxalate (see Table). This could be explained by the different ratios of $CO_2^{\bullet -}$ and CO_2 in the two cases. When CO_2 diffuses into a solution of compound (**2a**) it is rapidly consumed by the vanadium reagent, so that $CO_2^{\bullet -}$ experiences a low local CO_2 concentration and hence pathway (b) is favoured. On the contrary, in the second case the $CO_2^{\bullet -}$ generated by (**2a**) comes immediately into contact with a high concentration of CO_2, thus favouring pathway (a).

E.S.R. Spectra.—The reaction of bis(arene)vanadium(0) complexes, having one unpaired electron, with potassium metal should lead to the formation of species possessing formally 18 valence electrons and thus being diamagnetic. Indeed, at room temperature the disappearance of the characteristic eight-line e.s.r. spectrum of the paramagnetic unreduced species (**1a**) has been reported.[1]

By taking the preliminary crystallographic analysis[3] as a starting point, we wanted to verify the possibility that also in solution two molecules might interact through a K^+ ion: the interaction of the two respective *d* electrons might result in the formation of a triplet state, detectable by e.s.r. spectroscopy only at low temperature. Therefore we planned e.s.r. measurements of frozen solutions, because this could help to clarify to what extent the added electron is actually located on vanadium.

In dme, room-temperature reduction of both bis(benzene)- and bis(mesitylene)-vanadium(0) by excess of potassium sand was incomplete even after 1 week of very efficient stirring, as shown by the only partial disappearance of the eight-line spectra characteristic of the unreduced species. Besides, in hexamethylphosphoramide, hmpa, e.s.r. spectroscopy revealed that the vanadium(0) reagents were consumed in a few minutes, but at the same time a very strong one-line e.s.r. absorption arose which, within a few hours, evolved a very finely structured feature (see Figure), while the original eight-line spectra reappeared.

As we could never observe flat spectra at room temperature, it was impossible to verify our triplet-state hypothesis on freezing the mixtures. In future, we will try to explain the origin of the observed e.s.r. behaviour, probably due to massive solvent involvement.

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