

Reactions of vanadocene with benzyl bromide

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Abstract

The formation of bibenzyl in the reaction of vanadocene with benzyl bromide is explained in terms of an initial oxidative addition of benzyl bromide and subsequent free radical reactions. ESR evidence is presented for the V^{IV} intermediate.

Introduction

Studies of reactions of low valent transition metal salts or low valent organotransition metal complexes with organic halides have a long history [1]. As early as 1923 it was reported that the reaction of vanadium(II) chloride with xanthenol in the presence of hydrochloric acid gave bixanthy [2]. A number of synthetically useful applications have resulted from these and similar investigations [1]. Our interest in this area derived from the potential use of these reactions in formation of new carbon–carbon bonds, one of the fundamental processes of organic chemistry. One of our studies was concerned with the reaction of chromium(II) compounds with organic halides in non-aqueous solution [3], and it has recently been established [4] that (as for the reactions in aqueous solution) the products are formed by free radical pathways.

Reductive coupling of aralkyl halides by vanadium(II), with dichloro-tetra-pyridinevanadium [5] or vanadocene [5,6] has been reported. Mechanistic studies of these reactions showed that free radicals are not involved in the coupling reaction, even though they may be involved in the initial reaction of the aralkyl halides with vanadium(II). In a study of the addition of benzyl halides to vanadocene [6], evidence for the formation of benzyl-bis-cyclopentadienevanadium and halogeno-bis-cyclopentadienevanadium was presented. It was suggested that the first step in these reactions might be oxidative addition to a tetravalent vanadium compound (eq. 1), although no evidence was presented for this proposal. With an excess of



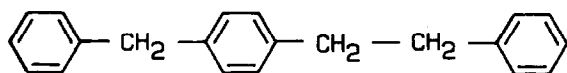
vanadocene this intermediate should give halogenovanadocene and aralkylvanadocene (eq. 2). The latter was shown to react with an excess of benzyl halide to give bibenzyl and halogeno vanadocene (eq. 3).

We describe below a detailed mechanistic study of the reaction of vanadocene with benzyl bromide. The study is an extension of earlier work [6] in which the conclusions were based mainly on the results of UV spectroscopic studies and where a number of mechanistic questions remained open.

Results and Discussion

Product studies

Vanadocene was treated in diethyl ether with an equimolar amount of benzyl bromide for 3 h at room temperature. Bromovanadocene was isolated in 88% yield, and after removal of the solvent unchanged benzyl bromide (5.9%), bibenzyl (61.5%) and non-volatile material (24%) were obtained by distillation. The non-volatile material was investigated by MS ($M^+ = 272$) and ^1H NMR spectroscopy. The fragmentation pattern, with the most intense peaks at $181\ m/e$ ($M^+ - \text{C}_7\text{H}_7$) and $m/e = 91$, considered together with the appearance of 14 aromatic and 6 aliphatic (ratio 4/2) protons in the ^1H NMR spectrum, indicates a trimeric benzyl system to which we ascribe structure 1. However, a non-linear structure cannot be ruled out.



(1)

Having established an almost quantitative product balance we investigated the reaction under various conditions; in each case product analyses were carried out by GLC. As vanadocene and bromovanadocene have low solubilities in diethyl ether, we used tetrahydrofuran (THF) as solvent for the mechanistic studies in order to ensure a homogeneous solution.

Aliquots of solutions of known concentration in THF of vanadocene and of benzyl bromide, containing cumene as internal standard, were mixed at various temperatures. Before the addition of benzyl bromide the solution of vanadocene was kept in the thermostat at the appropriate temperature for at least 10 min. At appropriate times (Table 1) samples were taken for the GLC analysis by syringe through a septum that protected the solution against air. All experiments were carried out under argon. It was observed that, whatever the reaction temperature, after 1–2 min about 50% of the benzyl bromide had reacted with the vanadocene. At 0°C 6% of bibenzyl could be seen after this time and smaller amounts at lower temperatures. The main product after hydrolysis with concentrated hydrochloric acid was toluene, amounting to 40–45% after 1 min. With time there was a decrease in the amount of toluene and an increase in that of bibenzyl. The reaction was almost complete after 180 min, at 0°C but very little reaction took place in this time at -50°C .

The results indicate that 50% of the benzyl bromide is consumed in an initial fast reaction even at -50°C . It is therefore not surprising that in a similar reaction of vanadocene with half an equivalent of benzyl bromide even after 2 min at room

Table 1

Variation with time of the composition of the products of the reaction of equimolar amounts of benzyl bromide and vanadocene in THF at various temperatures ^a

<i>T</i> (°C)	<i>t</i> (min)	C ₆ H ₅ CH ₃ (%)	C ₆ H ₅ CH ₂ Br (%)	(C ₆ H ₅ CH ₂) ₂ (%)	Product balance (%)
0	1	41.6	46.8	6.6	95.0
	6	38.6	44.5	16.4	99.5
	10	37.2	42.6	20.2	100.0
	56	29.9	36.5	33.8	100.2
	180	6.5	10.5	73.7	90.7
-20	2	45.3	44.8	2.0	92.1
	10	46.0	42.6	3.9	92.5
	90	39.7	39.8	12.5	92.0
	150	32.4	31.0	22.2	85.6
-50	2	44.0	50.4	0.5	94.9
	10	41.6	50.0	0.7	92.3
	90	39.2	38.5	7.2	88.7
	150	37.8	38.5	12.7	89.0

^a Product analyses by GLC after hydrolysis with concentrated aqueous HCl.

temperature 97% of benzyl bromide had reacted. GLC analysis of the mixture after hydrolysis showed that it contained 95% of toluene and ca. 2% of bibenzyl. The product composition of this product mixture remained unchanged even after 23 h at room temperature except that the residual benzyl bromide had disappeared. The green and stable solution formed in the reaction pointed to the presence of an organometallic product, and this was identified as benzylvanadocene, in line with the results of work by De Liefde Meijer et al. [6]. On hydrolysis with concentrated hydrochloric acid it yielded toluene and chlorovanadocene. In the presence of additional benzyl bromide, benzylvanadocene reacted in a subsequent slow process to give bibenzyl.

In order to confirm these conclusions we analysed tetrahydrofuran solutions of independently prepared benzylvanadocene. When the solution was hydrolyzed prior to the GLC analysis a high yield of toluene (85%) and small amounts of benzylcyclopentadiene (3%) were found. When the original solution was injected into the GLC apparatus a sizable amount of bibenzyl was detected indicating a thermolysis in the injection system. When an equimolar amount of benzyl bromide was added to the dark green solution of benzylvanadocene in THF the colour changed within 3 h to dark blue, indicating the presence of bromovanadocene. GLC analysis of this solution after hydrolysis revealed the presence of 4.5% of toluene, 4.3% of benzyl bromide, 76.4% of bibenzyl, and ca. 3% of benzylcyclopentadiene and benzyl trimers. Thus the behaviour was as expected from the information in the literature. Bibenzyl is the product of a slow reaction of benzylvanadocene with benzyl bromide.

ESR-spectroscopical studies

So far our observations are in keeping with those made by De Liefde Meijer et al. in their UV spectroscopic investigations. In order to gain further insight, particu-

Table 2

ESR parameters of selected complexes of structure $\text{Cp}_2\text{VRR}'$

R	R'	<i>g</i> -value	<i>a_V</i> (mT)	Reference
CH ₃	CH ₃	1.9915	6.30	8
C ₂ H ₅	C ₂ H ₅	1.9920	6.27	8,9
C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	1.9910	6.40	8
Br	Br	2.0212	6.60	7
Br	Cl	2.0005	7.00	7
Cl	Cl	1.9821	7.40	7
CH ₃	Cl	1.9900	6.92	10

larly into the first step of the reaction of vanadocene with benzyl bromide and into the step forming bibenzyl, we carried out ESR spectroscopic studies.

De Liefde Meijer [6] postulated for the initial fast reaction of benzyl bromide with vanadocene an oxidative addition to a vanadium(IV) compound (eq. 1), which then would react with an excess of vanadocene to give bromovanadocene and benzylvanadocene (eq. 2).

Vanadium(IV) complexes have been characterized and isolated in the form of dihalovanadocene [7] (halogens and pseudohalogens). Dialkylvanadocene complexes have also been reported, although dimethylvanadocene seems to be the only thermally stable complex of this type [8]. At the beginning of our investigation only (chloro)(methyl)vanadocene was known as a stable vanadium(IV) complex of vanadocene containing an alkyl group and a halogen atom [10].

Vanadium in the formal oxidation state four contains one unpaired *d*-electron, and so can be characterized by ESR spectroscopy. Because of its nuclear spin of 7/2, splitting of the ESR signal into 8 equidistant lines of equal intensity is observed. In Table 2 we show ESR data of vanadium(IV) complexes. The coupling constant of the vanadium nucleus ranges from 6.3 to 7.4 mT, with the values for the dialkyl complexes on the lower side and those for the dihalo complexes at the upper end. The mixed (chloro)(methyl)vanadocene shows intermediate behaviour. A similar trend is also observed for the *g*-value of (chloro)(methyl)vanadocene. It seemed likely that the coupling parameters would enable identification of an initial product of oxidative addition of benzyl bromide to vanadocene if it could be detected.

First we tried to detect a vanadium(IV) species by injecting a THF solution of benzyl bromide to an equimolar solution of vanadocene in an ESR tube in the cavity of the ESR spectrometer. From room temperature down to -50°C we could not find the expected vanadium(IV) species. Either it was not formed or its stationary concentration was too low. We therefore constructed a special cell that allowed mixing of THF solutions of vanadocene and benzyl bromide in the cavity of the ESR spectrometer under conditions of slow flow (0.5 ml/min). The continuous regeneration of a possible reactive intermediate led at -23.5°C to the identification of a spectrum that was a superposition of two signals with 8 lines each. The signal A had a *g*-value of 1.9860 and a vanadium coupling constant of *a_V* of 6.37 mT, and the signal B had a *g*-value of 2.0041 and *a_V* of 6.68 mT (see Fig. 1).

Signal A was also seen when solutions of independently prepared benzylvanadocene were examined by ESR spectroscopy even though vanadium(III) is not ESR active. It was shown by quantitative determination of the spin concentration that in

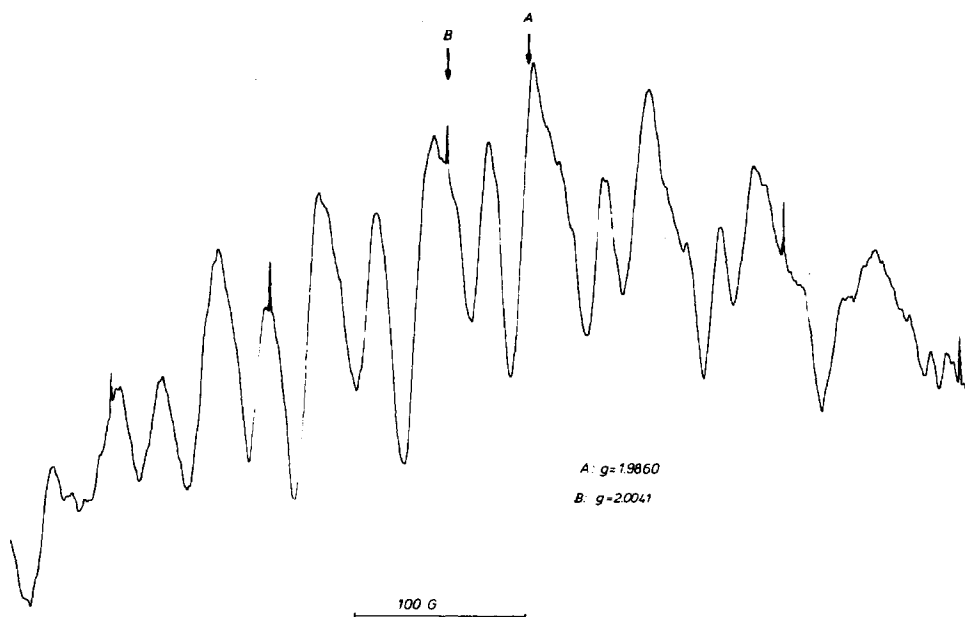
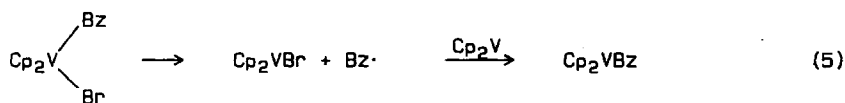
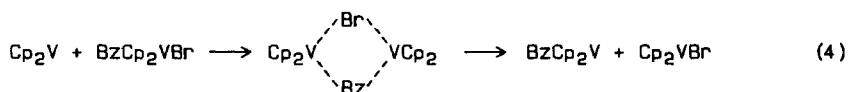


Fig. 1. ESR spectrum obtained from the reaction of vanadocene with benzyl bromide in a flow experiment.

this case the signal was due to only 0.2% of the benzylvanadocene present. Its occurrence can be accounted for in terms of the easy oxidation of vanadium(II or III) by oxygen to its formal oxidation state IV, and as expected, the intensity of the persistent signal with $g = 1.9860$ and $a_V = 6.37$ mT was increased considerably upon exposure of the solution to air. We thus attribute the presence of this signal in our flow experiment to the effect of traces of oxygen.

Signal B, on the other hand, disappears immediately if the flow of the two solutions is stopped or if the temperature is raised above -18°C , and so is due to a short-lived reactive intermediate. From its g -value, which is the mean of that for dibromovanadocene and that of dibenzylvanadocene, and from the magnitude of a_V , which is also in the expected range, we attribute this signal to (benzyl)(bromo)-vanadocene.

How does the reaction of (benzyl)(bromo)vanadocene with vanadocene to give the stable products benzylvanadocene and bromovanadocene take place? Two processes can be envisaged (eqs. 4 and 5):



Eq. 4 represents a bimolecular process in which a molecule of vanadocene reacts

with (benzyl)(bromo)vanadocene. In eq. 5 the products are formed in a two-step process, the unimolecular decomposition of (benzyl)(bromo)vanadocene being followed by the trapping of the benzyl radical by the excess of vanadocene. The latter reaction might seem unlikely since no benzyl radicals were detected in the ESR experiment described above and almost no bibenzyl is formed in the initial fast reaction of benzyl bromide with vanadocene. However, these objections can be countered by reference to the reaction conditions. The initial concentration of vanadocene in our experiments is $10^{-2} M$, and the concentration of benzyl radicals, if they are formed must be less than 10^{-8} , which is approximately the concentration limit of detection by ESR. If the reaction of vanadocene with benzyl radicals to form benzylvanadocene is fast, then the formation of bibenzyl cannot compete. If the rate constant for reaction of chromous complexes with radicals to form σ -alkylchromium(III) compounds [11], viz. $4 \times 10^7 M^{-1} s^{-1}$ at $0^\circ C$, is taken as reference the almost exclusive formation of benzylvanadocene is understandable even though the dimerization of benzyl radicals is diffusion controlled [12,13]. We thus favor a unimolecular decomposition of (benzyl)(bromo)vanadocene to bromovanadocene and benzyl radicals (see also below).

Reaction of alkylvanadocene with benzyl bromide

It was shown above that benzylvanadocene reacts with benzyl bromide to give bibenzyl and bromovanadocene. Two mechanisms can be considered for this process. Benzylvanadocene, as a 16-electron complex, might undergo oxidative addition (eq. 6), and reductive elimination could then yield bibenzyl and bromovanadocene. Another possibility, indicated in eq. 7, is an S_H2 process (eq. 7), involving the transition state shown in brackets, which would yield benzyl radicals and (benzyl)(bromo)vanadocene. The latter would then break down to bromovanadocene and additional benzyl radicals, and dimerization of these would give bibenzyl.

In order to test these possibilities we carried out cross-over experiments. Equation 6 requires that the reaction of benzylvanadocene with a substituted benzyl bromide gives solely unsymmetrical coupling products. The process shown in eq. 7,

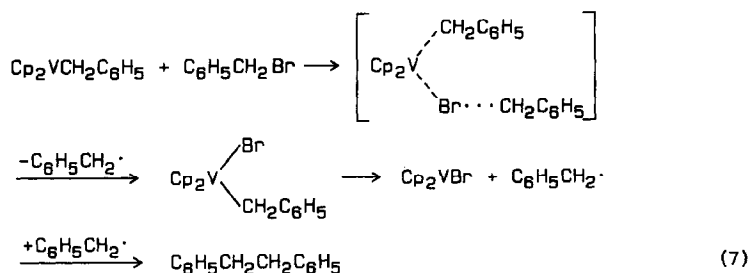
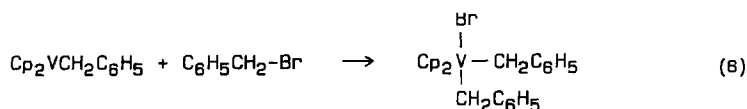


Table 3

Variation with time of the products of the reaction of benzylvanadocene with *o*-xylyl bromide ^a

<i>t</i> (min)	C ₆ H ₅ CH ₃ (%)	<i>o</i> -CH ₃ C ₆ H ₄ CH ₂ Br (%)	Dimers (%)	Bz-Bz/Bz'- Bz/Bz'-Bz' ^b	Product balance (%)
7	17.2	27.8	47.5	1.4/2.4/1.0	92.5
14	8.4	21.3	57.9	1.0/2.0/1.1	87.6
160	5.2	16.0	66.6	1.0/1.9/1.1	87.6
48 h	5.3	15.0	67.1	1.0/2.1/1.2	87.4

^a GLC analyses after hydrolysis with concentrated aqueous HCl. ^b Bz = C₆H₅CH₂-; Bz' = *o*-CH₃C₆H₄CH₂-.

on the other hand, should give three different dimers, two symmetrical and one unsymmetrical.

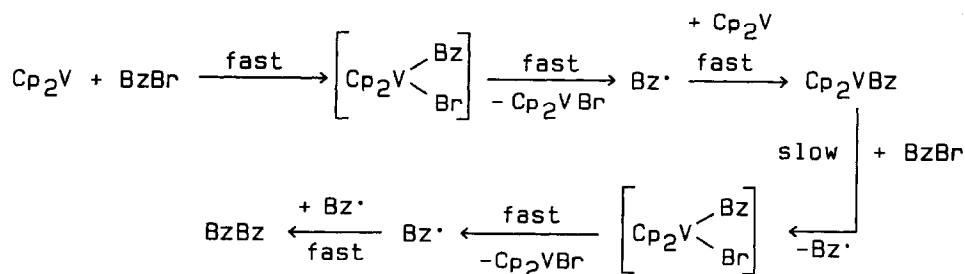
In Table 3 we show the results of a reaction of benzylvanadocene with *o*-xylyl bromide. Within the accuracy of the GLC determination we found a ratio of 1/2/1 for bibenzyl/1-(2-methyl-phenyl)-2-phenyl ethane/1,2-di-(2-methylphenyl)ethane. This can only be accounted for on the assumption that benzyl and *o*-methylbenzyl radicals are formed simultaneously and combine statistically. It excludes the pathway shown in eq. 6 if a concerted reductive elimination is assumed. However, it does not rule out the possibility that the vanadium(V) intermediate decomposes to bromovanadocene and two benzyl radicals.

In order to gain more insight we treated methylvanadocene with benzyl bromide. As (chloro)(methyl)vanadocene is reported to be a stable compound, we expected, if the process shown in eq. 7 operates, that (bromo)(methyl)vanadocene and bibenzyl would be formed as products. Equimolar amounts of methylvanadocene and benzyl bromide in THF were allowed to react for 3 h and the mixture was then analysed by GLC, and shown to contain 4% of toluene, 3% of benzyl bromide, 13% of benzylcyclopentadiene, and 73% of bibenzyl. No product of coupling methyl and benzyl radicals, i.e. ethylbenzene, was detected. For the identification of the organometallic product a second experiment was carried out in which methylvanadocene, partly dissolved in petroleum ether was treated with a 1.5 molar excess of benzyl bromide. After 2 h at room temperature the solution was cooled to -18°C and the precipitated solid was isolated, and found to be (bromo)(methyl)vanadocene (87%), which had $g = 2.0120$ and $a_V = 6.62$ mT, the expected ESR parameters. This observation shows that a vanadium(IV) species is formed in the reaction of alkylvanadocene with benzyl bromide. In the case of benzylvanadocene this intermediate is unstable and eliminates benzyl radicals. There is still doubt about the initial formation of a vanadium(V) compound (eq. 6), because such a species might decompose in two steps, the first giving one benzyl radical and then, when benzyl is the second alkyl group subsequently losing another benzyl radical in a fast step. With methyl as the second group the vanadium(IV) complex would not decompose. Although we can not exclude this possibility, we favor the process shown in eq. 7.

Conclusions

The ESR spectroscopic study has shown that the reaction of vanadocene with benzyl bromide involves initial fast oxidative addition to give (benzyl)(bromo)vana-

docene, and a subsequent fast reaction gives benzylvanadocene and bromovanadocene. From the results of our experiments we favor a unimolecular decomposition of (benzyl)(bromo)vanadocene to give bromovanadocene and benzyl radicals, which are trapped in a fast reaction by vanadocene. The rate-determining step in the reaction sequence is the attack of benzyl bromide on benzyl vanadocene. From the cross-over experiments we conclude that free radical coupling yields bibenzyl. The isolation of benzyl trimers also supports the free radical pathway. Taking account also of the results of the reaction of methylvanadocene with benzyl bromide, the total reaction sequence is as shown in Scheme 1.



Scheme 1

It is important to note that the initial reaction of vanadocene with benzyl bromide does not involve an outer sphere electron transfer from vanadocene to benzyl bromide by dissociative electron capture which would lead directly to benzyl radicals and bromide ions. The difference in the half-wave oxidation potential of vanadocene ($E_{1/2}$ vs. SCE = -0.60 V) and the reduction potential of benzyl bromide ($E_{1/2}$ vs. SCE = -1.24 V) would not preclude such a process a priori. In other systems, such as the reaction of chromium(II) with benzyl halide, this is the preferred pathway [1,4].

Experimental

Analytical instruments

^1H and ^{13}C NMR spectra (internal standard TMS): Varian XL 200 and EM 360 A. Mass spectra: Finnigan MAT 312/188. IR spectra: Perkin-Elmer 397. UV spectra: Cary-219 spectrometer. ESR spectra: Bruker ER 420. GLC analysis: Varian 3700 with CDS 111 data system. Columns: OV 101 10%, glass-capillary column (60 m) and SE 30 10%, glass column (6 m $\times$ 1/4 cm). Melting points: Büchi 510 (under argon); uncorrected. Elementary analysis: Heraeus EA-301.

Solvents

Diethyl ether and tetrahydrofuran were refluxed for several hours over sodium/potassium alloy in the presence of 4-phenylbenzophenone and then distilled. All solvents were stored over 4 Å molecular sieves and saturated for 2 h with argon.

Reactions under inert conditions

All operations with organometallic vanadium compounds were carried out under argon 5.0, which was purified further to remove traces of oxygen. Glass vessels were heated under vacuum (ca. 1.3 Pa) with hot air (300°C) and filled with argon. This procedure was repeated twice.

Vanadium compounds. Vanadocene was prepared as described by Koehler and Prössdorf [14]; purification of the crude product by sublimation under vacuum as described in ref. 14 gave vanadocene in 22% yield (m.p. 168–169°C). A better procedure involves stirring the isolated crude product with n-hexane for several hours at r.t., then filtering the dark violet solution and evaporating it to dryness. This gives vanadocene in 55% yield with a purity identical with that of sublimed material. Dichlorovanadocene [15], chlorovanadocene [6], bromovanadocene [6], benzylvanadocene [6], and methylvanadocene [6] were prepared by published methods.

Vanadocene and benzyl bromide. To 0.98 g (5.41 mmol) vanadocene in 50 ml diethyl ether was added benzyl bromide (0.91 g, 5.31 mmol). After stirring at r.t. dark blue crystals had separated. n-Hexane (10 ml) was added and the suspension stirred for another 30 min then filtered. The solid isolated was washed with n-hexane then dried and shown to be bromovanadocene (1.22 g, 88%, based on benzyl bromide). The remaining blue solution was treated with 15 ml of 10% hydrochloric acid and the organic layer was washed twice with 10 ml of 10% hydrochloric acid then dried over magnesium sulfate, and the solvent was then removed under vacuum. The slightly yellow oil (0.40 g), was purified by bulb-to-bulb distillation at 2000 Pa; 0.35 g of the oil gave 20.7 mg (5.9%) of benzyl bromide at 95–96°, 220 mg (62%) bibenzyl at ca. 120°C and left 84 mg of a solid residue, which was identified by MS and ¹H NMR as a benzyl trimer.

MS (70 eV): *m/e* 272 (*M*⁺, 12%). 181(100), 167(15), 166(37), 165(46), 105(12), 91(53), 77(12), 65(18), 51(9), 39(11). ¹H NMR (CDCl₃): δ 2.7–2.8 (d, 4H), 3.9 (s, 2H), 7.0–7.1 (d, 14H). The components of the yellow oil plus the bromovanadocene account for a product balance of 86%.

GLC-analysis of the products of the reaction of vanadocene with benzyl bromide

The reactions were carried out in THF. Vanadocene (for amounts see Table 4) was dissolved in 5 ml THF in a Schlenk vessel and the vessel was sealed with a rubber septum. In order to remove traces of oxygen which might have entered during the manipulations the vessel was evacuated until the solvent started to boil and then filled with argon. Two procedures were followed: (a) benzyl bromide and the internal standard were added from a syringe and the amounts determined by weighting; (b) benzyl bromide and (the internal standard) cumene were dissolved in

Table 4

Conditions used for the reaction of vanadocene with benzyl bromide. For the results of the GLC analysis see Tables 1 (exp. 4–6) and Table 2 (exp. 1–3)

No.	Cp ₂ V (g/mmol)	C ₆ H ₅ CH ₂ Br (g/mmol)	<i>T</i> (°C)	Column
1.	0.285/1.65	0.294/1.72	22	OV 101 ^a
2.	0.313/1.73	0.648/3.50	22	OV 101 ^a
3.	0.263/1.45	0.123/0.72	22	SE 30 ^b
4.	0.262/1.45	0.249/1.46	0	SE 30 ^b
5.	0.197/1.09	0.186/1.09	–20	SE 30 ^b
6.	0.230/1.27	0.218/1.27	–50	SE 30 ^b

^a Direct GLC analysis. ^b GLC analyses after hydrolysis.

Table 5

Reactions of benzylvanadocene with benzyl bromide and *o*-methylbenzyl bromide ^a

Cp ₂ V (g/mmol)	C ₆ H ₅ CH ₂ Br (g/mmol)	<i>o</i> -CH ₃ C ₆ H ₄ CH ₂ Br (g/mmol)	<i>T</i> (°C)	Column
0.208/0.76	0.128/0.75	—	22	OV 101
0.109/0.40	—	0.070–0.40	22	SE 30

^a GLC analyses after hydrolysis with hydrochloric acid.

THF and aliquots of this solution were added to the THF solution of vanadocene from a syringe.

For the GLC analysis samples of the reaction mixture were taken out by syringe and injected either directly or after hydrolysis of 0.1 ml samples with 0.05 ml of concentrated hydrochloric acid. Before the reactants were added at 0, –20 or at –50 °C the solution of vanadocene was kept at the reaction temperature for at least 10 min.

GLC-analysis of the products of the reaction of benzylvanadocene with benzyl bromide and o-methylbenzylbromide

The procedure was identical to that described above. The coupling products 1-(2-methylphenyl)-2-phenylethane, 1,2-di-(2-methylphenyl)ethane, and bibenzyl were identified by their MS spectra in a GC-MS analysis. For these compounds the GLC response factor used for bibenzyl was used. Table 5 shows the results of the experiments.

Reaction of methylvanadocene with benzyl bromide

To a suspension of methylvanadocene (0.43 g; 2.19 mmol) in 30 ml of n-hexane at room temperature was added 0.3 ml (ca. 0.433 g = 2.53 mmol) of benzyl bromide. The solution soon became yellow-brown. After 90 min, 10 ml of n-hexane were distilled off under vacuum and the reaction vessel was cooled to –78 °C. (Bromo)(methyl)vanadocene (0.5269; 87%) isolated by filtration (m.p. 191–194 °C) ESR spectrum: $g = 2.0120$, $a_V = 6.62$ mT. Analysis. Found: C, 47.62; H, 4.46; Br, 29.31. C₁₁H₁₃VBr (276.09) calc: C, 47.86; H, 4.75; Br, 28.95%.

The amount of bibenzyl formed was determined by GLC in a different experiment with cumene as internal standard.

ESR experiments

The flow experiments were carried out in a special flat cell (inner diameter 0.5 mm) which allowed measurements at variable temperatures. Efficient mixing of the reactant solutions was achieved by placing quartz wool at the entrance of the two separate reagent solutions into the flat region of the cell. 1.5×10^{-2} M solutions (75 ml) of the reactants in THF were prepared and then connected by tubes to the cell. The flow rate was ca. 0.5 ml/min. Cell and tubing were purged thoroughly by argon before use.

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