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1,1-DICYCLOPENTADIENYL-3,3-DIMETHYLVANADA(IV)CYCLOBUTANE

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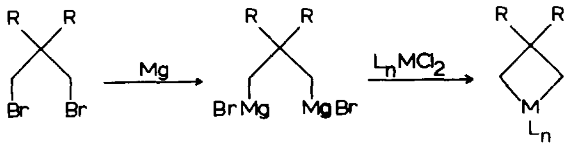
Summary

The reaction of 1,3-bis(bromomagnesio)-2,2-dimethylpropane (**1b**) with dichlorodicyclopentadienylvanadium(IV) (**5**) gave 1,1-dicyclopentadienyl-3,3-dimethylvanada(IV)cyclobutane (**4**) in 30% yield, contaminated with dicyclopentadienylneopentylvanadium(III) (**12**). Attempts to purify **4** were only partially successful due to its limited stability ($t_{1/2} = 4$ h at 25 °C in cyclopentane). Identification of **4** is therefore based on its having sufficient thermal stability for isolation, on its reaction with bromine to give 1,3-dibromo-2,2-dimethylpropane (**2b**), and especially on its ESR and ^{1}H NMR spectra. The reaction of **4** with cyclohexanone (**15**) gave **17** and **18** as the main products; **17** is the aldol dimer of **15**, while **18** may be derived from either **4** or **12**. Because methylenecyclohexane (**16**) is not one of the reaction products, it is concluded that **4** does not have a pronounced tendency to fragment to give a metallacarbene (**20**).

Introduction

The direct synthesis of the 1,3-di-Grignard reagents **1a** [1] and **1b** [2] from the corresponding dibromides **2a** and **2b** made these valuable synthetic reagents available for a number of applications in organic [3] and organometallic chemistry. Particularly promising, is the use of **1** for the synthesis of metallacyclobutanes, **3**. Metallacyclobutanes are at present the subject of intensive investigation, and the preparation depicted in Scheme 1 gives, in principle, a rather general route to this interesting class of compounds.

SCHEME 1



2a: R=H
2b: R=Me

1a: R=H
1b: R=Me

3

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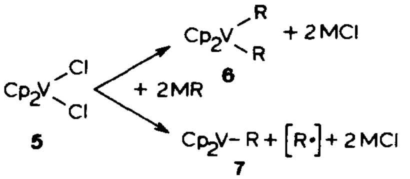
We are engaged in a systematic study of the applicability of compounds **1** for this purpose and we have already reported the synthesis of metallacyclobutanes of tin [4], titanium, zirconium and hafnium [5]; compounds which, with the exception of titanacyclobutanes, are so far not accessible by other routes. We now report on the synthesis and some reactions of 1,1-dicyclopentadienyl-3,3-dimethylvanada(IV) cyclobutane, **4**.

Results and discussion

The synthesis of the title compound, **4**, presented a challenge for several reasons. In the first place, vanadacyclobutanes were not reported in the literature, and, more seriously, compounds containing a vanadium–carbon σ-bond are often rather unstable thermally and are sensitive to moisture and oxygen [6].

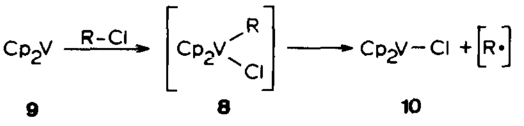
In contrast to the corresponding compounds of the Group IVB elements, the reaction of two equivalents of organolithium or Grignard reagents with dichlorodicyclopentadienylvanadium(IV) (**5**) does not normally lead to stable dialkyldicyclopentadienylvanadium(IV) compound (**6**) [7]. Instead, by a radical decomposition, the monoalkyldicyclopentadienylvanadium(III) species (**7**) are obtained (Scheme 2).

SCHEME 2



It is assumed that the reduction of vanadium(IV) compounds is a consequence of steric hindrance, the atomic radius of vanadium (1.22 Å) being smaller than that of, e.g., titanium (1.32 Å). Especially in compounds such as **6**, which contain two bulky cyclopentadienyl groups, vanadium apparently cannot sustain the tetracoordinate state [7]. In the reaction of **5** with two equivalents of a Grignard reagent, it is even likely that reduction occurs before the stage which gives **6** is reached. An intermediate in this reaction, which is formed after substitution of the first chlorine atom of **5** by an alkyl group, is the alkylchlorodicyclopentadienylvanadium(IV) species **8** (Scheme 3). It has been shown that **8**, when formed by a different route, i.e., by the oxidative addition of an alkyl halide to dicyclopentadienylvanadium(II) (**9**), is quantitatively reduced to the vanadium(III) species **10** [8] (Scheme 3). Consequently,

SCHEME 3

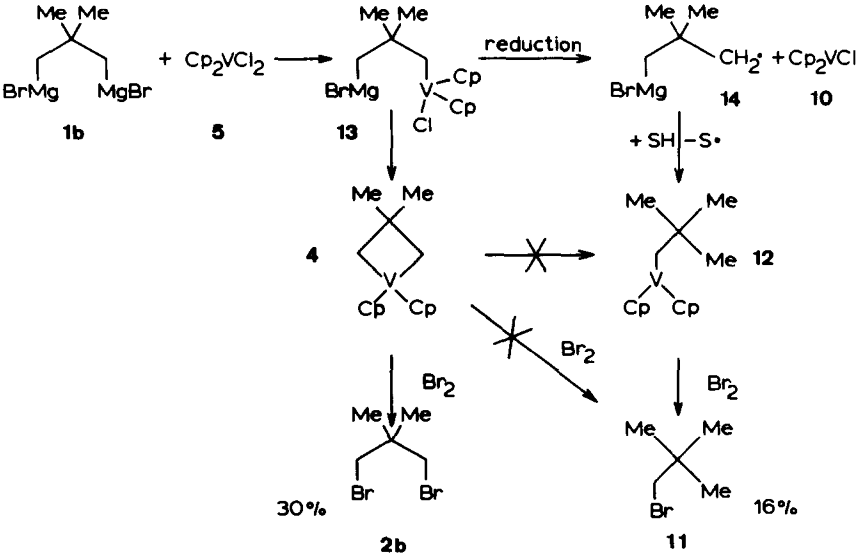


8 might be expected to decompose in the same fashion when it is formed from **5** (Scheme 2). Only when the groups are very small or are electron-withdrawing, have compounds of type **6** been obtained [7].

In view of these unfavourable facts, the synthesis of **4** from **5** did not look too promising, except for the fact that a four-membered ring might be regarded as a "small" substituent on the metal.

Our experience with Group IVB metallacyclobutanes had taught us that unsubstituted four-membered rings, such as those obtained from **1a**, are usually formed in much lower yield than the 3,3-dimethyl-substituted ones derived from **1b**; there are indications that the low yields are not so much a consequence of the instability of the end products, but are due rather to side reactions at intermediate stages [5]. We therefore concentrated our efforts on the 3,3-dimethyl-substituted vanadacyclobutane **4** (Scheme 4).

SCHEME 4



The reaction of **1b** in diethyl ether with one mol equivalent of **5** at −20 °C was slow, presumably because of the low solubility of **5**. After 3 h, titration of an aliquot with HCl indicated that 15% of **1b** had not reacted; after 7 h, only 2% of **1b** was left. At the same time, a white precipitate (presumably of magnesium salts) formed in an intensely purple-blue solution. Treatment of the clear supernatant solution with an excess of bromine gave **2b** (30%) and neopentyl bromide (**11**) (16%); in this reaction, a green precipitate was formed which, according to its IR spectrum [9], was dibromodicyclopentadienylvanadium(IV).

As **1b** was absent from the final reaction mixture (i.e. there was no residual starting material vide supra), the formation of **2b** may be taken as evidence for the formation of monomeric **4** (vide infra). It is not known whether the reaction of **4** with bromine is quantitative for the reaction of titanacyclobutanes with iodine has been shown to give rise to cyclopropanes [10]. The yield of 30% of **4**, as determined by the bromination reaction, must therefore be considered as a lower limit.

Neopentyl bromide (**11**) is probably formed from the neopentylvanadium(III) species **12** and not from **4**. This is concluded from the observation that when the original reaction mixture was allowed to stand, **4** decomposed (as shown by a decrease in the yield of **2b** on bromination) while the amount of **11** (and thus that of **12**) remained constant. It also follows that **12** cannot be formed from the decomposition of **4**. Rather, it is likely that **12** is formed only during the initial phase of the reaction between **1b** and **5**.

We rationalize these results as follows (Scheme 4). The first step of the reaction between **1b** and **5** involves the replacement of one chlorine atom at vanadium by carbon, with the formation of **13**. Compound **13** is the critical intermediate in this reaction, because it belongs to the category of alkylchlorodicyclopentadienylvanadium(IV) species, **8** (see Scheme 3) which may be expected to be reduced rapidly to **10** and to the organomagnesium radical **14**; the latter then abstracts hydrogen from the solvent (SH) to give **12**. This reductive cleavage of **13** represents serious competition with its ring closure to **4**; it is presumably the relatively favourable entropy of formation of a four-membered ring to which the success of obtaining any **4** at all must be attributed. Alternatively, **13** might react in an intermolecular fashion by dimerization, which would furnish the eight-membered analogue of **4**, or by polymerization; the products would, however, be of the structural type **6** (Scheme 2), the substituents R in this case being neopentyl-like ($R = CH_2CMe_2CH_2V$) and thus very large. Consequently, such intermolecular condensation products would not be thermally stable and would decompose to give vanadium(III) species. The low yield of soluble vanadium species (in the bromination reaction: **4** + **12** = 40%) may be caused by the availability of such decomposition pathways.

The purification and identification of **4** was hampered by its (thermal) instability. In the reaction mixture (solvent Et_2O), the decomposition of **4** was monitored by reacting it with an excess bromine to give **2b**, which was determined by quantitative GLC. The decomposition followed a clean first-order process (correlation coefficient 0.9992) with a half life of 2.5 h at 25 °C; at −80 °C, the half life was approximately 27 d. In contrast to Group IVB metallacyclobutanes, **4** has very low solubility in cyclopentane (< 1 mM at -20 °C, as determined by reaction with bromine). The decomposition of **4** in these cyclopentane solutions was also first order, with a half life of 4 h at 25 °C (correlation coefficient 0.997). Thus, **4** has a thermal stability at 25 °C which is comparable to that of its zirconium analogue ($t_{1/2} = 3$ h in toluene) and slightly higher than that of its titanium analogue ($t_{1/2} = 1$ h in cyclopentane) [5].

We tried to isolate **4** by evaporation of the clear supernatant solution from the reaction mixture, and extraction of the residue with a hydrocarbon. Unfortunately, **4** was insufficiently soluble in cyclopentane, a solvent which gave pure metallacyclobutanes of the Group IVB series [5], and so toluene had to be used. Compound **4** could be dissolved in this solvent but it proved impossible to remove all the magnesium bromide and **12**. Accordingly, the elemental analyses were somewhat variable (see Experimental).

The proposed identity of **4** was consistent with its ESR and ^1H NMR spectra, which were measured in toluene-d_6 solutions obtained as described in the previous paragraph. The ESR spectrum (Fig. 1) shows the expected eight line pattern caused by ^{51}V ($I = 7/2$). Both the g-factor (2.00) and the hyperfine coupling constant A (60×10^{-4} cm^{-1}) characterize the compound as a tetraorganovanadium(IV) species

TABLE 1

ESR DATA FOR ORGANOMETALLIC COMPOUNDS OF VANADIUM IN DIFFERENT OXIDATION STATES

Compound	g-factor	A [10^{-4} cm^{-1}]	Multiplicity	Ref.
4	2.00	60	8	This work
5	1.99	67	8	11
$V(CH_2C_6H_5)_4$	1.99	54	8	12,13
$Cp_2V(CH_2C_6H_5)_2$	1.99	52	8	13
7 ($R = C_6H_5$)	2.13	[a]	1 [a]	11
9	2.00	24	8	14

[a] Hyperfine coupling not detectable because of line width.

(Table 1); dicyclopentadienylvanadium(II) (**9**) shows the same g-factor and multiplicity, but has a smaller value for A; vanadium(III) species (**7**) have a different g-factor and do not show the eight line pattern because of their extreme line width. Couplings with protons [12] could not be observed for **4**; this was also the case in, e.g., Cp_2VEt_2 [13].

Valuable information on the identity and stoichiometry of **4** was derived from its ^1H NMR spectrum (in toluene-d_8, 250 MHz, −30 °C). In the "normal" range (0–10 ppm), only broad signals were observed due to the paramagnetic species present; these signals were from traces of toluene-d_7 and unidentified impurities. However, Köhler and his coworkers have reported that the ^1H NMR resonances of vanadium(II) and vanadium(III) species can spread over a range of several hundred ppm [15]. Similarly, we found the signals for the four protons on the metallacyclobutane ring at δ 385 ppm, with a large line width ($W_{1/2} = 5000$ Hz); the chemical shift and line width become progressively smaller as the distance to the metal increases and so the values for the cyclopentadienyl protons are δ 150 ppm (10 H, $W_{1/2}$ 2500 Hz) and for the methyl protons, δ −0.7 ppm (6 H, $W_{1/2}$ 250 Hz). We were not able to observe ^{13}C NMR signals, probably because the concentration was too small and the lines were too broad.

An aspect which deserved careful scrutiny was the identity of the species responsible for the ESR and for the NMR spectra. In view of the extreme sensitivity

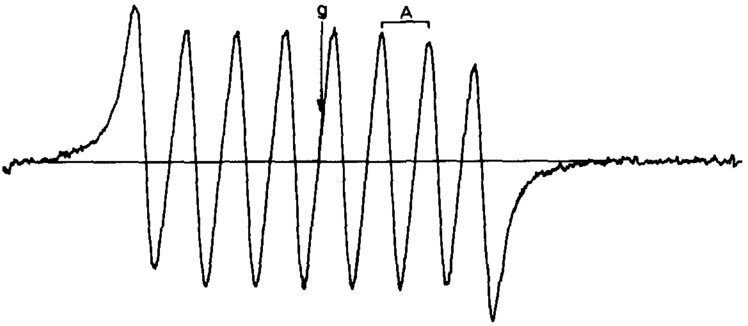


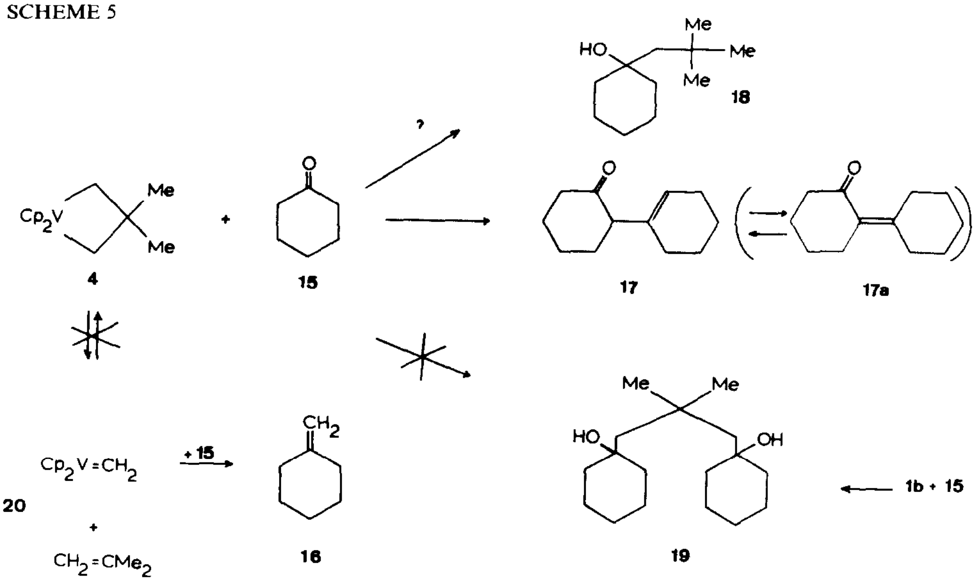
Fig. 1. ESR spectrum of **4** in toluene-d_8 at −30 °C in the X-band, obtained with a Varian V 4502-12 spectrometer; g 2.00, A 60×10^{-4} cm^{-1}.

of the ESR method, and the lack of quantitative information from it, it was conceivable that the ESR spectrum was indeed related to **4**, present only in minute quantities, while the NMR spectrum was produced by a different vanadium species, e.g., by **12** (Scheme 4). We therefore took great care in determining accurately the integral ratios in the ^{1}H NMR spectrum of **4**; repeated measurements on different preparations gave consistent ratios for $CH_2:CH_3:C_5H_5$ of 4.0 : 5.8 : 10.2. These ratios exclude **12** and are compatible only with **4**. When taken in combination with the results of the elemental analysis, we may conclude that all the spectral measurements refer to the same species, namely **4**. It is of interest to note that with respect to the proton chemical shifts, **4** resembles vanadium(II) and vanadium(VIII) species [15].

In the reaction of the three Group IVB metallacyclobutanes with cyclohexanone (**15**) we had previously observed interesting differences in reaction products [5]. The results could be interpreted by invoking the well-known tendency of titanacyclobutanes to fragment into a titanium-methylene complex [16], which then converts **15** into methylenecyclohexane (**16**), while the zircona- and hafna-cyclobutanes behave more like a normal organometallic reagent and give nucleophilic addition to the carbonyl group [5]. It was therefore of interest to investigate the analogous reaction of **4**.

When treated with **15**, **4** gave, after hydrolysis, the aldol-dimer **17**, together with a small amount of its isomer **17a** [17], and the mono-adduct **18** [5]; neither the di-adduct **19** [5] nor the methylene derivative **16** were detected (Scheme 5).

SCHEME 5



The formation of **17** shows that **4** acted as a base rather than as a nucleophile; the origin of **18** is uncertain as it could be derived either from **4** or from **12**, the latter also being present in the reaction mixture. The absence of **16** indicates either that **4** does not fragment to give **20** or at least that the tendency is not as pronounced as with titanacyclobutanes [16]. It may, however, be that the fragmentation is obscured in the reaction with **15** because it is slower than other processes, such as that yielding

17. Therefore, further experiments, e.g., reactions with olefins, are required to clarify this point. It may be relevant, however, that vanadium compounds have not to our knowledge been reported to be efficient catalysts in olefin metathesis [18].

Finally, it should be emphasized that the absence of **19** from the products of the reaction of **4** with **15** furnishes additional proof (cf., also the results of the base titration, vide supra) of the absence of **1b**, because reaction of **1b** with **15** gives **19** (Scheme 5).

Conclusion

1,1-Dicyclopentadienyl-3,3-dimethylvanada(IV)cyclobutane, **4**, has been prepared from dichlorocyclopentadienylvanadium, **5**, and 1,3-bis(bromomagnesio)-2,2-dimethylpropane, **1b**, in 30% yield. Although it was not possible to isolate **4** in a pure form because of its limited stability, the very fact that it is isolable at room temperature, its ESR and ^{1}H NMR spectral data, and its reaction with bromine (to give 1,3-dibromo-2,2-dimethylpropane, **2b**), clearly establish its identity.

Experimental

Because of the extreme sensitivity of **1b** and of the vanadium compounds to oxygen and moisture, the purification of the starting materials and the solvents, and all reactions, were carried out in fully sealed and evacuated glass apparatus [19].

All solvents were distilled from sodium-potassium alloy before use. The magnesium was sublimed twice and used as a coarse crystalline powder. 1,3-Dibromo-2,2-dimethylpropane, **2b**, was prepared by literature procedures [20]. Dichlorodicyclopentadienylvanadium(IV), **5**, was supplied by Ventron, Karlsruhe. Bromine and cyclohexanone were freshly distilled before use and sealed in glass tubes.

The ^{1}H NMR spectra were measured with a Bruker WM-250 spectrometer at 250 MHz. The GC-MS analyses were performed on a Finnigan 4000 mass spectrometer.

1,3-Bis(bromomagnesio)-2,2-dimethylpropane, 1b

The dihalide **2b** (16.1 g, 70 mmol) was added at room temperature over 48 h to magnesium (24.3 g, 1 mol) in diethyl ether (1.8 l) [2]. The progress of the reaction was followed by taking samples via ampoules sealed to the glass apparatus. After hydrolysis of the sample, the amount of **1b** was determined by titration with 0.1 *M* HCl and with complexon (EDTA).

1,1-Dicyclopentadienyl-3,3-dimethylvanada(IV)cyclobutane, 4

Dichlorodicyclopentadienylvanadium, **5**, (373 mg, 1.48 mmol), contained as a powder in an ampoule sealed to the evacuated glass apparatus was added at −20 °C to a solution of **1b** (1.48 mmol) in diethyl ether (200 ml). After it had been stirred for 7 h at −20 °C, the reaction mixture consisted of a purple-blue solution (in some preparations it was nearly black) above a white powder of (presumably) magnesium salts. Titration (see above) showed that the clear supernatant solution contained less than 2% starting material (**1b**). Dioxane was added to the reaction mixture, and the resulting mixture was filtered. The filtrate was evaporated to dryness and toluene (15 ml) was added to the purple-black residue. Filtration of this mixture gave a filtrate which was used directly for the reaction with cyclohexanone and, after evaporation to dryness, for the elemental analysis. For ESR and NMR spectroscopy, this toluene solution was evaporated to dryness and the residue dissolved in toluene-d_8; the measurements were performed at $-30\,^\circ$C.

The elemental analyses were performed by Mr. A.F. Hamminga, Rijksuniversiteit Groningen, Afdeling Centrale Microanalyse. Anal.: Found: C, 59.35, 61.12, 57.05; H, 6.98, 5.95, 7.07; Br, 12.1; Cl, 0; V, 12.1. $C_{15}H_{20}V$ (**4**) calcd.: C, 71.70; H, 8.02; V, 20.27%. The C : H ratio found (8.89) corresponds well with that calcd. (8.94). A contamination by 0.2 mol $MgBr_2$ per mol of **4** can be calculated from the bromine value; this combination of **4** and $MgBr_2$ accounts for 98.9% of the analyzed sample.

*Reaction of **4** with bromine*

The yields of **4** and **12** were determined immediately after the reaction of **1b** with **5** by adding, at $-20\,^\circ$C, an excess of bromine to the clear supernatant layer. GC-MS, using standard solutions of the products **2b** and **11**, showed that **2b** and **11** were formed in 30% and 16% yield, respectively, based on the amount of **1b** used.

*Reaction of **4** with cyclohexanone, **15***

Cyclohexanone, **15**, (98 mg, 1 mmol) was added at $-20\,^\circ$C to 40 ml of the freshly prepared toluene solution of **4** (vide supra). After it had been stirred for 1 h at $-20\,^\circ$C, the solution was warmed to room temperature and water was added. The organic layer was separated, dried ($MgSO_4$) and analysed by GC-MS. The main peak was due to **18** [5] and its dehydration product, neopentylidenecyclohexane, (the amount of the latter increased on standing) and **17** [17] (^{1}H NMR spectrum (90 MHz, $CDCl_3$): δ 4.71 (bs, 1H, =CH), 2.67–2.4 (m, 7H, allylic H and H α to C=O), 2.38–1.73 ppm (m, 10H, other CH_2). Mass spectrum, m/z (rel. intensity in %): 178(42) $\mathbf{17}^{+\cdot}$, 149(34), 135(66), 107(36), 91(43), 79(88), 41(100)). Some minor peaks were obtained of which only **17a** [17] was tentatively identified by its mass spectrum [m/z (rel. intensity in %): 178(24) $\mathbf{17a}^{+\cdot}$, 149(75), 135(24), 107(22), 91(48), 79(99), 41(100)].

Acknowledgements

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