Inorganica Chimica Acta, 31 (1978) L357–L360

Biscyclopentadienyl Compounds of Trivalent Vanadium with Vanadium Element Bonds

G. A. RAZUVAEV, V. N. LATYAEVA, E. N. GLADYSHEV*, E. V. KRASILNIKOVA, A. N. LINEVA, A. P. KOZINA

Institute of Chemistry, Academy of Sciences of the U.S.S.R., Gorky, U.S.S.R.

Received July 17, 1978

Among organometallic derivatives of trivalent vanadium $Cp_2VCH_2SiR_3$ compounds are fairly stable [1] and suitable as starting compounds for a number of syntheses**.

It was of interest to use their interaction with organoelement hydrides to obtain bimetallic organometallic compounds with V–Sn, V–Ge, V–Si, V–N, V–S bonds. Hydrides of the type R_3EH (where R = Et, i-Pr; E = Sn, Ge and Si) were primarily used for this purpose. Their reactivity decreases in the order: $R_3SnH > R_3GeH > R_3SiH$ [3].

It was found that $Cp_2VCH_2SiMe_3$ (I) readily reacts with Et_3SnH even when unfreezing the reaction mixture:

$$(I) + Et_3SnH \rightarrow Cp_2V\text{-}SnEt_3 + Me_4Si$$

Bimetallic organometallic compound $Cp_2V–SnEt_3$ was isolated as dark-blue crystals; some of its properties are presented in the Table.

Unlike the above compound triethylgermane reacts with the organovanadium compound only when heated:

$$(I) + Et_3GeH \xrightarrow{100\,^\circ C} Cp_2V–GeEt_3 + Me_4Si$$

The reaction products are obtained with high yields. The substitution of triethylgermane for $i\text{-}Pr_3GeH$ in this reaction does not afford a similar bimetallic organometallic isopropyl compound. Only the product of thermal decomposition of the starting compound, Cp_2V (75%) was observed among the reaction products after reacting for 3 hours at 110 °C. Therefore the synthesis of $Cp_2V–Ge(Pr\text{-}i)_3$ was achieved by an other route:

$$Cp_2VCl + i\text{-}Pr_3GeLi \rightarrow Cp_2V–Ge(Pr\text{-}i)_3 + LiCl$$

Physical properties of compounds obtained are presented in the Table. These are coloured crystalline solids, monomeric in benzene. Organosilicon hydride Et_3SiH has a lower reactivity and does not afford organosilylmetallic compounds with V–Si bond under the given conditions. When heating I with Et_3SiH at 110 °C during 4 hours the formation of Cp_2V and Me_4Si (the products of thermal decomposition of the starting organovanadium compound) was observed in analogy with the above reaction. Triethylsilane was isolated unreacted.

I interacts with hexamethyldisilazane similarly to its reactions with organoelement hydrides resulting in quantitative yield of $Cp_2V–N(SiMe_3)_2$ previously described [1]:

$$(I) + HN(SiMe_3)_2 \xrightarrow{60–70\,^\circ C} Cp_2V–N(SiMe_3)_2 + Me_4Si$$

The interaction of I with butyl mercaptane is analogous to the above reactions. The product obtained is a dark-brown oil of butyl mercaptan derivative (see Table):

$$(I) + HSC_4H_9 \xrightarrow[\text{hexane}]{70\,^\circ C,\ 2\ h} Cp_2V–SC_4H_9 + Me_4Si$$

The structure of the latter was proved by cleavage reaction with HCl affording Cp_2VCl_2 (80%) as well as by interaction with acetic acid according to:

$$Cp_2V–SC_4H_9 + 2CH_3COOH \rightarrow CpV(OCOCH_3)_2 + CpH + C_4H_9SH$$

The yields of $CpV(OCOCH_3)_2$, CpH and C_4H_9SH obtained from this reaction are 90,70 and 60%, respectively.

The interaction of $Cp_2VCH_2SiR_3$ with organogermanium hydrosulphides and hydroselenides takes place in comparatively moderate conditions resulting in the corresponding compounds $Cp_2V–SGeR_3$ and $Cp_2V–SeGeR_3$:

$$(I) + R_3GeXH \xrightarrow[\text{hexane}]{50\,^\circ C,\ 15\ min} Cp_2V–XGeR_3 + Me_4Si$$

R = Et, i-Pr; X = S, Se

The yields of reaction products are up to 70–95% and thus the method may be recommended to prepare new compounds. Sulphur- and selenium- containing compounds (Table) precipitated separately are dark-coloured crystalline solids. They are readily soluble in organic solvents and easily undergo hydrolysis and oxidation in the air. The structure of prepared

---

*To whom correspondence should be addressed.

**The formation of $(Cp_2V)_2(CHSiMe_3)_2$ as by-product in the synthesis of $Cp_2VCH_2SiMe_3$ from Cp_2V and Me_3SiCH_2Cl [2] was not confirmed.

TABLE. Reactions of Cp_2 V–R with R′–H.

No.	Starting Reagents, g(mmol)		Solvent (ml)	Reaction Conditions		$Cp_2V–R'$	Colour	Reaction Products[a]		Mol. wt. Found(Calc.)	Analysis % Found(Calc.)		
	$Cp_2V–R$	R′–H		Temp. (°C)	Time (min)			Mp °C	Yield, %		C	H	V
1.	R = CH_2SiMe_3 2.54 9.47	R′ = Et_3Sn 1.52 9.32	toluene 15	~20	2h	$Cp_2V–SnEt_3$	blue	57	88.4[b]		48.84 (49.66)	6.90 (6.51)	13.25 (13.16)
2.	R = CH_2SiMe_3 0.72 2.68	R′ = Et_3Ge 4.10 25.5		100	10–15	$Cp_2V–GeEt_3$	dark-violet	32[c]	91.0	310 (340)	56.40 (56.57)	7.45 (7.95)	14.75 (14.90)
3.	R = CH_2SiMe_3 0.88 3.28	R′ = Et_3GeS 1.53 6.36	pentane 10	50	10–15	$Cp_2V–SGeEt_3$	black	17–18	95.1	358 (373)			13.20 (13.69)
4.	R = CH_2SiMe_3 1.14 4.25	R′ = Et_3GeSe 3.28 13.66	hexane 20	50	10–15	$Cp_2V–SeGeEt_3$	dark-brown	58–59	80.5		46.02 (45.90)	5.52 (5.96)	
5.	R = CH_2SiMe_3 1.05 3.91	R′ = $(i\text{-}Pr)_3GeSe$ 2.69 9.57	hexane 20	50	10–15	$Cp_2V–SeGe(Pr\text{-}i)_3$	dark-brown	69–70	94.4	493 (462)	49.45 (49.94)	7.12 (6.72)	10.98 (11.06)
6.	R = $GeEt_3$ 0.98 2.88	R′ = Et_3GeS 0.80 4.14	hexane 10	~20	10–15	$Cp_2V–SGeEt_3$	black	17–18	78.4	358 (373)			13.36 (13.69)

[a] Me_4Si was obtained in reaction No. 1–5 with 59–94% yield. [b] Yield was computed on the basis of the quantity of initial Et_3SnH used. [c] Reported [4]: m.p. 32–34°.

compounds was determined by comprehensive methods, *i.e.* by cleavage with HCl, acetic acid and 1,2-dibromoethane.

Earlier it was shown that vanadium–germanium bond is less reactive as compared to V–C and V–N bonds in compounds of Cp_2VR type [4]. Our experiments proved that Cp_2VGeEt_3, $Cp_2VGe(Pr\text{-}i)_3$ and Cp_2VSnET_3 react when heated with hydrogen chloride to give Cp_2VCl and with cleavage of V–Ge, V–Sn bonds. In reactions with 1,2-dibromoethane Cp_2V-groupings are preserved and Cp_2VBr_2 is produced quantitatively. Yield of Et_3SnBr was 85%.

$$Cp_2V\text{–}SnEt_3 + 3/2\ BrCH_2CH_2Br \rightarrow Cp_2VBr_2 + 3/2CH_2{=}CH_2 + Et_3SnBr$$

Compounds containing V–S–Ge and V–Se–Ge groupings undergo heterolysis with HCl easier than those with V–Ge bond. For instance Cp_2VCl is produced in several minutes in almost quantitative yields. The second reaction product Et_3GeSH transforms into the corresponding chloride by the action of HCl in excess:

$$Cp_2V\text{–}SGeEt_3 + 2\ HCl \xrightarrow[\text{dioxane}]{20\,^{\circ}C} Cp_2VCl + Et_3GeCl + H_2S$$

In our view the exchange reaction of $Cp_2V\text{–}GeEt_3$ with hydrosulphide Et_3GeSH is of interest. The reaction is complete in several minutes at room temperature. These conditions lead to the formation of triethylgermane (81%) and $Cp_2V\text{–}SGeEt_3$ (80%).

$$Cp_2V\text{–}GeEt_3 + Et_3GeSH \rightarrow Cp_2V\text{–}SGeEt_3 + Et_3GeH$$

We managed to obtain a similar compound in the exchange reaction:

$$Cp_2VCl + i\text{-}Pr_3GeSeLi \rightarrow Cp_2V\text{–}SeGe(Pr\text{-}i)_3 + LiCl$$

as well as in insertion reactions of chalcogen in the V–Ge bond, the latter being more interesting.

Similar processes are well known in the chemistry of bimetallic organometallic compounds. For example sulphur and selenium under moderate conditions are inserted into Hg–Ge, Hg–Si bonds *etc.* [5]. Our experiments showed that sulphur and selenium are inserted into V–Ge bond in hexane solutions at ~20 °C. The yields of $Cp_2V\text{–}SGeR_3$ and $Cp_2V\text{–}SeGeR_3$ compounds were 75–80%:

$$Cp_2V\text{–}GeR_3 + S(Se) \xrightarrow[\text{hexane}]{20\,^{\circ}C} Cp_2V\text{–}SgeR_3\ (Cp_2V\text{–}SeGeR_3)$$

Sulphur and selenium-containing compounds were identical to those obtained according to the hydride method presented earlier.

Experimental

All reactions were carried out in evacuated sealed ampoules. Melting points were measured in evacuated sealed capillaries. GLC analyses of volatile products were carried out on a Tsvet-4 chromatograph with a catharometer detector using a 100 X 0.4 cm column packed with Silicone SE 30 (5%) on Chromaton N-AW-DMCS and with helium as the carrier gas. Typical experiments are given below.

Reaction of I with Triethyltin Hydride

2.54 g (9.47 mmol) of I was added to 1.92 g (9.32 mmol) of triethyltin hydride in 15 ml of toluene at liquid nitrogen temperatures. The mixture was heated to *ca.* 20 °C for 2 hours and the colour of the solution changed from dark-green to dark-blue. The solvent and Me_4Si (0.48 g, 59.1%) obtained were removed under vacuum. 15 ml of hexane were added to the residue (3.63 g); 3.19 g (88.4%) of bis(η^5-cyclopentadienyl)triethylstannylvanadium (m.p. 57°) were prepared by crystallization at –70 °C. Found: 48.84, H 6.90, V 13.25. Calcd. for $C_{16}H_{25}SnV$: C 49.66, H 6.51, V 13.16%.

Reaction of $Cp_2V\text{–}GeEt_3$ with Sulphur

0.20 g (6.25 mg-at) of fine sulphur powder were added to 1.67 g (4.90 mmol) of bis(η^5-cyclopentadienyl)triethylgermylvanadium in 20 ml of hexane. The colour of the solution gradually changed from violet to brown. The reaction mixture was shaken during 24 h at room temperature and then filtered. Black crystalline solid $Cp_2V\text{–}SGeEt_3$ precipitated from the filtrate cooled down to –78 °C. The yield was 1.39 g (3.68 mmol), 75.1% (m.p. 17–18°).

Reaction of Cp_2VCl with Triisopropylgermyllithium

2.90 mmol of $i\text{-}Pr_3GeLi$ in 15 ml of toluene were added to 0.63 g (2.91 mmol) of Cp_2VCl in 10 ml of THF. The colour of the reaction mixture changed from dark-blue to violet. Toluene and THF were removed under vacuum and 15 ml of hexane were added. Precipitated LiCl (2.75 mmol) (94.5%) was filtered off; 1.01 g (91.2%) of bis(η^5-cyclopentadienyl)triisopropylgermylvanadium (m.p. 100–101°) were separated from the mother liquor by low-temperature crystallization. Found: C 59.90, H. 8.56; mol. wt. (cryoscopy in benzene), 371. Calcd. for $C_{19}H_{31}GeV$: C 59.60, H 8.16, mol. wt., 382.8.

References

1 G. A. Razuvaev, V. N. Latyaeva, E. N. Gladyshev, A. N. Lineva, E. V. Krasilnikova, *Dokl. Akad. Nauk SSSR, 223,* 1144 (1975).

2 G. A. Razuvaev, V. N. Latyaeva, E. N. Gladyshev, A. N. Lineva, L. I. Vishinskaya, *Proc. VIIIth Intern. Conf. Organometal. Chem., Kyoto,* 1977, p. 149.

3 N. S. Vyazankin, O. A. Kruglaya, *Uspekhi Khim., 35,* 1388 (1966).

4 G. A. Razuvaev, V. T. Bychkov, L. I. Vishinskaya, V. N. Latyaeva, N. N. Spiridonova, *Dokl. Akad. Nauk SSSR, 220,* 854 (1975).

5 E. N. Gladyshev, N. S. Vyazankin, V. S. Andreevichev, A. A. Klimov, G. A. Razuvaev, *J. Organometal. Chem., 28,* C42 (1971).