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AN UNUSUAL REACTION OF TETRAPHENYLCYCLOPENTADIENYL DERIVATIVES OF THE GROUP IVA ELEMENTS WITH ISOPROPYLIDENETRIPHENYLPHOSPHORANE

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Summary

Reactions of the compounds of the $R_2R'EC_{29}H_{21}$ type (R = Alk; R'Alk,Cl; E = Si,Ge,Sn; $C_{29}H_{21}$ = 1,2,3,4-tetraphenylcyclopentadiene-5-yl) with $Ph_3P{=}CMe_2$ were carried out. As was shown for $Me_3GeC_{29}H_{21}$ by ^{13}C and ^{31}P NMR spectroscopy, the reactions proceed in the direction of demetallation (kinetic control) and deprotonation (thermodynamic control); the salts $[R_2E(C_{29}H_{20})Cl]^-[Ph_3PCHMe_2]^+$ were isolated.

Interaction of η^1-cyclopentadienyl and 9-fluorenyl derivatives of the Group IVA elements with alkylidenetriphenylphosphoranes proceeds by deprotonation with the formation of carbanions with a phosphonium counter ion [1–6]. It turned out that the reaction of $Ph_3P{=}CMe_2$ with compounds of the general formula $R_2R'EC_{29}H_{21}$ (R = Alk; R' = Alk,Cl; $C_{29}H_{21}$ = 1,2,3,4-tetraphenylcyclopentadiene-5-yl; E = Si,Ge,Sn) (Ia–e) is an unusual one. The reaction was studied in detail by ^{13}C and ^{31}P NMR spectroscopy for tetraphenylcyclopentadienyltrimethylgermane $Me_3GeC_{29}H_{21}$ (Ia). Just after mixing Ia with $Ph_3P{=}CMe_2$ in tetrahydrofuran (THF) an organometallic substituent is abstracted and the salt $[C_{29}H_{21}]$ $[Ph_3PCMe_2GeMe_3]$ (IIa) is formed. After 24 hours (evacuated NMR tube), along with IIa, the product of deprotonation, $[Me_3Ge(C_{29}H_{20})][Ph_3PCHMe_2]$ (IIIa) was detected in a IIa:IIIa ratio equal to 3:1; after 10 days the content of IIIa increases and becomes predominant (IIa:IIIa = 1:3).

In studying the reaction of $Ph_3P{=}CMe_2$ with compounds Ib–e the ^{13}C and ^{31}P NMR spectra were not investigated thoroughly but the general trend of corresponded to that observed for Ia. Therefore, we propose for these reactions Scheme 1 involving not only deprotonation (compounds IIIb–e were isolated in a crystalline state) but also demetallation.

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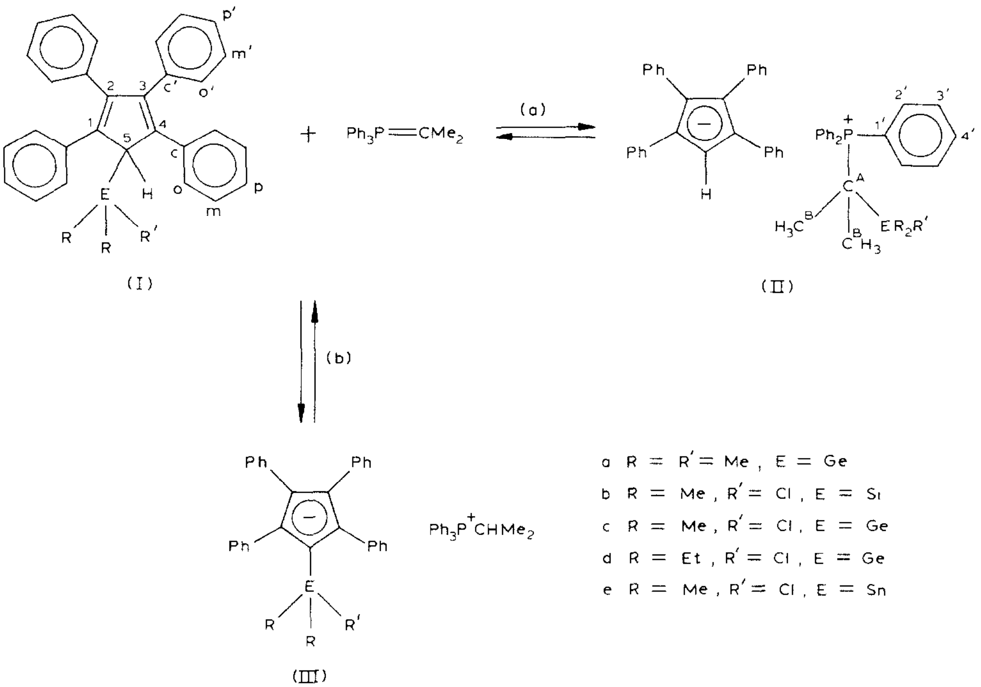


SCHEME 1

Thus, in reactions of tetraphenylcyclopentadienyl derivatives of Group IVA elements with $Ph_3P{=}CMe_2$ two reversible processes take place. Salts II are formed under kinetic control and salts III are formed under thermodynamical control.

Deprotonation (reaction b) refers to a typical acid-base equilibrium whose position is determined by the relative strength (pK_a) of the corresponding CH acids. Earlier we have shown [1–6] that in reactions of phosphorus ylides with CH acids ($pK_a \sim \leqslant 20$) the equilibrium of deprotonation is almost completely shifted towards the corresponding phosphonium salts.

Reactions of reversible demetallation (a) have not been reported. However, taking into account the polarity of the $E{-}C_{29}H_{21}$ bond, one can see a similarity between reaction (a) and the well-known [7] addition of organohalides of the Group IVA elements to phosphorus ylides, which can be considered as a nucleophilic substitution at the element atom (Scheme 2).

$$R_3GeX + Ph_3P{=}CMe_2 \rightleftarrows [R_3GeCMe_2PPh_3]X$$
$$X = Cl;\ C_{29}H_{21}$$

SCHEME 2

It was shown for Ia that both forward and reverse reactions (a) proceed rather fast. This is revealed by a typical broadening of the resonance signals of IIa in the ^{13}C NMR spectrum at room temperature. The signals of salt IIIa in this case are not broadened (Fig. 1).

Attempts to isolate salt IIa in a pure form failed; it exists in solution only together with IIIa. Salts IIIa–e were obtained as orange-red solids sensitive to traces of oxygen and atmospheric moisture, readily soluble in aprotic bipolar solvents, and insoluble in hexane. For compounds Ib–d, containing the R_2ECl group, the forma-

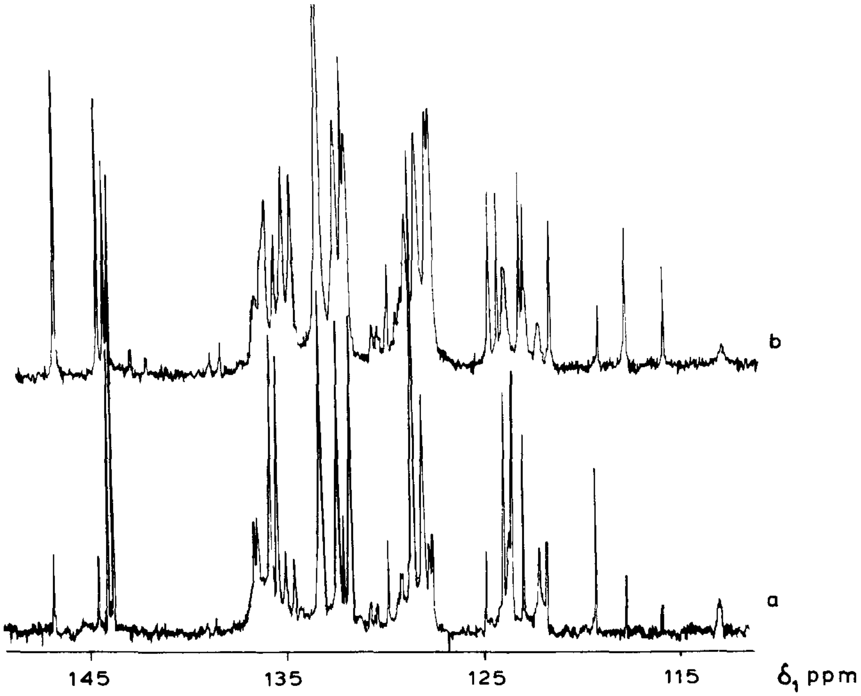


Fig. 1. ^{13}C NMR spectra of a reaction mixture of tetraphenylcyclopentadienyltrimethylgermane (Ia) with isopropylidenetriphenylphosphorane: (a) 24 hours after mixing of the reagents; (b) 10 days after mixing.

tion of salts III is much faster than for Ia. In about day after mixing the reagents, compounds IIIb–d were isolated from the solution in 40–50% yields. Under similar conditions, according to ^{13}C NMR data, only ~ 25% of salt IIIa is present in the solution.

The resonance signals of C(1,4) and C(2,3) of the cyclopentadienyl ring in the ^{13}C NMR spectra of compounds I (Table 1), IIa, and III (Table 2) were assigned by comparison with the spectrum of tetraphenylcyclopentadiene (IV), its deuterium derivative, and their isopropyltriphenylphosphonium salts V (Tables 1, 2). In this case the values of the isotopic H/D substitution effects observed on ^{13}C chemical shifts were used.

The assignment of the ^{13}C NMR resonance signals of the phenyl substituents was performed with the use of the off-resonance technique, relative intensities of resonance signals, and characteristic values of chemical shifts.

The difference in chemical shifts of C^B in the phosphonium fragments of the demetallation product IIa (23.88 ppm) and of the deprotonation product IIIa (16.77 ppm) deserves attention. In addition, $^1J(^{31}P-^{13}C)$ changes from 32.2 to 47.3 Hz. These facts can be used for rapid analysis of mixtures of compounds formed in demetallation-deprotonation reactions.

TABLE 1

^{13}C NMR SPECTRAL PARAMETERS OF TETRAPHENYLCYCLOPENTADIENE AND ITS ORGANOSILICON AND ORGANOGERMANIUM DERIVATIVES (I)

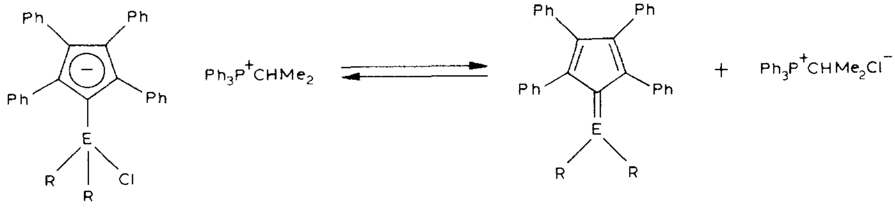
	C(1,4)	C(2,3)	C(5)	C(*c*,*c*′)	C(*o*,*o*′)	C(*m*,*m*′)	C(*p*,*p*′)	C-Me
Ia	142.84	142.19	54.65	138.54	131.38	129.75	126.90	−2.17
				138.02	128.51	128 29	126.90	
Ib	145.48	141.71	55.23	137.98	131.12	130.24	127.28	1.29
				137.67	128.48	128.27	127.10	
Ic	144.74	140.73	56.65	137.93	131.12	129.91	127 33	3.32
				137.09	128.56	128.35	127.19	
Id [a]	143.79	139.72	54.69	135.86	130.15	128.91	126.64	8.16
				136.71	127.83	127.61	126.43	
IV	145.16	140.88	45 73	137.71	130.62	128.71	127.33	–
				137.39	128.71	128.56	127.01	

[a] Ge–CH_2 10.83 ppm.

When passing from compounds I to their salts III, as well as in the case of other cyclopentadienyl compounds, the typical upfield shifts of C(1,4) and C(2,3) resonance signals by 19–20.5 and 8.3–10.9 ppm, respectively are observed. This is accompanied with a simultaneous downfield shift of C(5) signals by 53–59 ppm.

It should be noted that the additive scheme proposed earlier for metallated cyclopentadienes [8] is unsuitable for calculation of ^{13}C chemical shifts of organometallic tetraphenylcyclopentadiene derivatives. The greatest deviations are observed for the C(5) atom.

We believe that compounds IIIb–e are in equilibrium with tetraphenylcyclopentadienylides of the Group IVA elements just as in the case of the corresponding fluorenyl derivatives [5,9] (Scheme 3).



(III b–e)

SCHEME 3

In the reaction of $Me_2Sn(C_{29}H_{21})Cl$ with $Ph_3P{=}CMe_2$ salt V and salt VI of composition $Cl^-Ph_3P^+CMe_2SnMe_2Cl$ were isolated along with compounds IIIe.

$$\underset{\text{(IIe)}}{[C_{29}H_{21}][Ph_3PCMe_2SnMe_2Cl]} + [Ph_3PCHMe_2]Cl \rightleftarrows$$

$$\underset{\text{(V)}}{[C_{29}H_{21}][Ph_3PCHMe_2]} + \underset{\text{(VI)}}{[Ph_3PCMe_2SnMe_2Cl]Cl}$$

SCHEME 4

The formation of V and VI may be due to counterion exchange (Scheme 4) between IIe and isopropyltriphenylphosphonium chloride according to Scheme 3 which also

TABLE 2

^{13}C AND ^{31}P NMR SPECTRAL PARAMETERS OF SALTS II, III, AND V (J(C–P) ARE GIVEN IN PARENTHESES IN Hz)

	C(1,4)	C(2,3)	C(5)	C(c,c')	C(o,o')	C(m,m')	C(p,p')	C(A)	C(B)	C(1′)	C(2′)	C(3′)	C(4′)	C-Me
IIa	122.04	122.54	111.32	144.71	132.52	127.75	122.22	23.42	23.38	119.52	135.22	131.20	135.84	−0.34
				144.63	127.62	127.06	120.43	(32.2)	(2.6)	(81.5)	(8.8)	(11.7)	(3.2)	
IIIa	123.44	131.26	113.79	147.01	132.57	132.57	122.97	21.27	16.77	118.00	134.39	131.41	135.62	3.68
				144.69	126.75	126.57	121.72	(46.8)	(2.0)	(82.9)	(9.0)	(12.2)	(3.4)	
IIIb	124.87	132.76	108.54	146.29	132.96	132.69	123.19	22.01	16.59	118.19	134.53	131.40	135.80	6.31
				144.07	126.74	126.57	121.99	(47.6)	(1.80)	(83.0)	(9.2)	(12.2)	(3.2)	
IIIc	124.42	131.03	112.25	145.39	132.81	132.61	122.99	22.76	16.62	118.24	134.52	131.41	135.88	7.79
				144.07	126.94	126.61	122.20	(47.6)	(2.2)	(82.8)	(9.5)	(11.8)	(3.0)	
IIId[a]	124.78	131.34	109.75	145.54	132.78	132.78	123.31	21.96	16.62	118.04	134.36	131.27	135.77	13.27
				144.06	126.91	126.72	122.25	(48.3)	(2.1)	(83.0)	(9.2)	(12.1)	(3.4)	
IIIe	–[b]	–[b]	109.09	145.89	–[b]	–[b]	–[b]	–[b]	16.73	118.33	134.51	131.30	135.89	1.3
				143.70	–[b]	–[b]	–[b]	–[b]	(2.2)	(82.9)	(9.2)	(12.2)	(2.7)	
V	121.78	122.85	110.69	144.50	132.66	127.79	122.41	21.22	16.76	118.27	134.52	131.17	135.30	–
				144.29	127.42	127.14	120.51	(47.3)	(2.2)	(82.9)	(9.3)	(12.0)	(2.0)	

[a] Ge–CH$_2$ 9.38; ^{31}P NMR in ppm from 85% H_3PO_4 for IIa 37.33, for IIIa 30.91 (accuracy ±0.5 ppm). [b] Overlap of signals prevents assignments.

testifies to the reversible demetallation of organostannane Ie in the reaction with isopropylidenetriphenylphosphorane and to the equilibrium between salt IIIe and dimethyltin tetraphenylcyclopentadienylide.

Experimental

The spectra were measured on a Jeol FX-100 (48 k memory) and Varian FT-80A (16 k memory) instruments on degassed solutions of the samples in THF. ^{13}C NMR chemical shifts are given in ppm relative to $SiMe_4$, and are accurate to ±0.05 ppm; J(C–P) values, in Hz, are accurate to ±0.1 Hz.

All reactions were carried out in a dry argon atmosphere or on vacuum line (10^{-4} mmHg). Tetraphenylcyclopentadiene (IV) was used as the starting material and was prepared as described in ref. 10. It was purified by transformation into tetraphenylcyclopentadienyllithium [10], followed by quenching with aqueous HCl in THF solution and recrystallization from CCl_4/hexane (1/1 v/v). After quenching with D_2O/HCl and repeated treatment by MeLi and D_2O/HCl, the deuterium derivative of tetraphenylcyclopentadiene (4.93 at.% D) was obtained. Isopropylidenetriphenylphosphorane was prepared according to the method given in ref. 11. The isopropyltriphenylphosphonium salt of tetraphenylcyclopentadiene (V) and its deuterium derivative were prepared by mixing equimolar quantities of $Ph_3P{=}CMe_2$ and tetraphenylcyclopentadiene in THF in vacuo (10^{-4} mmHg).

Synthesis of tetraphenylcyclopentadienyl derivatives of germanium and tin

A typical preparative procedure involved gradually adding a suspension of tetraphenylcyclopentadienyllithium (10 mmol) in 80 ml benzene to a stirred solution of the organogermanium or organotin chloride (15 mmol) in 30 ml benzene and then refluxing for 3 h. The precipitate was filtered off and solvents were removed in vacuo. The residue was washed with cold hexane and dried at 2×10^{-2} mmHg until its weight was constant. The yields, melting points and analytical data for the products are shown in Table 3.

TABLE 3

YIELDS, ANALYTICAL DATA AND MELTING POINTS FOR TETRAPHENYLCYCLOPENTADIENYL DERIVATIVES OF GERMANIUM AND TIN

Compound	Yield (%)	Analysis (Found (calcd.) (%))				M.p. [a] (°C)
		C	H	Cl	Ge(Sn)	
Ia	36	78.93 (78.89)	6.27 (6.21)	–	14.78 (14.90)	128–129
Ic	50	73.51 (73.53)	5.28 (5.36)	7.09 (6.98)	14.23 (14.30)	146–147
Id	61	74.01 (73.99)	5.71 (5.83)	6.53 (6.62)	13.89 (13.55)	107–108
Ie	58	67.31 (67.24)	5.09 (4.92)	6.43 (6.40)	21.18 (21.44)	117–118

[a] In a sealed capillary.

Reactions of tetraphenylcyclopentadienyl derivatives of Group VIA elements with isopropylidenetriphenylphosphorane

Generally, stoichiometric quantities of the reagents were mixed in THF. The dark red-orange solution was stirred for about day at room temperature and solvent was removed in vacuo. Benzene (50–60 ml) was condensed onto residue in vacuo (8×10^{-4} mmHg), and the upper layer was decanted. After removing the benzene from the lower layer and washing the residue with hexane, isopropyltriphenylphosphonium salts of tetraphenylcyclopentadienyl derivatives of Group IVA elements (IIIb–d) were obtained as fluffy red-orange powders. In this way were prepared: IIIb (from 2.02 g Ib in 40 ml THF and 1.33 g ($Ph_3P{=}CMe_2$ in 30 ml THF, yield 55%. Found: Cl, 4.53. $C_{52}H_{48}ClPSi$ calcd.: Cl, 4.61%); IIIc (from 4.74 g Ic in 70 ml THF and 2.84 g $Ph_3P{=}CMe_2$ in 50 ml THF; yield 47%. Found: Cl, 4.53. $C_{52}H_{48}ClGeP$ calcd.: Cl, 4.37%); IIId (from 3.31 g Id in 30 ml THF and 1.88 g $Ph_3P{=}CMe_2$ in 70 ml THF; yield 44%. Found: Cl, 4.31. $C_{54}H_{53}ClGeP$ calcd.: Cl, 4.22%).

A different procedure was used for reaction of organotin compound Ie with $Ph_3P{=}CMe_2$. A mixture of 4.17 g Ie and 2.57 g $Ph_3P{=}CMe_2$ was stirred in 100 ml THF for 2 h. The solvent was removed in vacuo until crystallization. The precipitate was filtered off, washed with benzene and dried, to give 1.29 g $[Ph_3PCMe_2SnMe_2Cl]Cl$ (VI). Found: C, 52.15; H, 5.31; Cl, 13.17. $C_{23}H_{27}Cl_2PSn$ calcd.: C, 52.71; H, 5.19; Cl, 13.53%. A crystalline orange product was obtained after removal of the solvent from the filtrate and washing of the residue with benzene in vacuo. It was identified as $[Ph_3PCHMe_2][C_{29}H_{21}]$ (V) on the basis of its NMR spectra (Table 2). Removal of the solvent from the remaining benzene solution gave 1.99 g (35%) of IIIe. Found: Cl, 3.87. $C_{52}H_{48}ClPSn$ calcd.: Cl, 4.13%. A THF solution of V is unstable.

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