Tetrahedron Letters,Vol.25,No.45,pp 5191-5192,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

A VERSATILE METHOD FOR THE SYNTHESIS OF 1,3-METALLATITANACYCLOBUTANES

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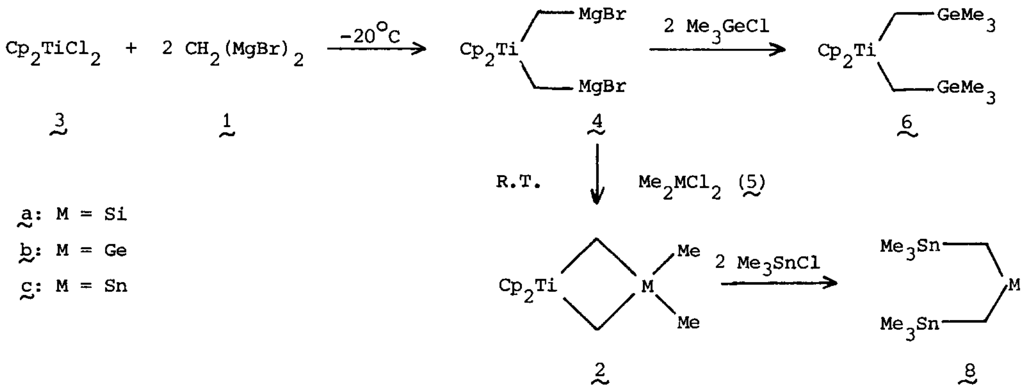
Abstract: The reaction of Cp_2TiCl_2 with two moles of $CH_2(MgBr)_2$ gave $Cp_2Ti(CH_2MgBr)_2$ which with Me_2MCl_2 (M = Si,Ge,Sn) was converted to the corresponding 1,3-metallatitanacyclobutanes.

There is currently considerable interest in metallacyclobutanes of transition metals, and a considerable number with a variety of metals as heteroatoms has been synthesized.[1] Much less is known about four-membered rings containing two metal and two carbon atoms, in particular when at least one of the heteroatoms is a transition metal.[2] The successful preparation of metallacyclobutanes via the 1,3-di-Grignard route[1b,c] and the demonstrated usefulness of the 1,1-di-Grignard reagent $CH_2(MgBr)_2$ (1) as an organometallic synthon[3] inspired us to combine the two strategies, as illustrated in the synthesis of the 1,3-metallatitanacyclobutanes 2.



a: M = Si
b: M = Ge
c: M = Sn

In an evacuated and sealed glass vessel at -20°C, Cp_2TiCl_2 (3) was reacted with two moles of 1 in ether/benzene (1:1) solution. After stirring for one hour, a practically insoluble, dark red, viscous precipitate had been formed which contained ca. 40% of 4. Structural identity and yield of 4 were determined by its conversion with chlorotrimethylgermane to 6, which was identical with a compound obtained by Lappert et al.[4] along a different route. Similarly, on addition of 5 to 4 and warming to room temperature, the insoluble red precipitate slowly dissolved to yield a brownish red solution of 2; a white powder remained (presumably MgBrCl). The isolation of 2 was achieved by evaporation of the reaction mixture to dryness, extraction of the residue with benzene, followed by filtration and evaporation of the filtrate; the residue thus obtained consisted, respectively, of practically pure 2a (100% yield relative to 4 by ^1H NMR analysis), while 2b (75% yield) and especially 2c (15% yield) contained $Cp_2\underline{TiCH_2Ti}(Cp_2)CH_2$ (7)[2b,5] (for 2c ca. 7%).

Table 1. Spectral Data of 2a, 2b and 2c

Compound	^{1}H NMR [a]			^{13}C NMR [b]			HRMS
	C_5H_5	CH_2	CH_3	C_5H_5	CH_2	CH_3	(calc.)
2a	5.57	2.52	0.13	110.2 (d; 173)	70.6 (t; 130)	1.0 (q; 119)	264.0803 [c] (264.0814)
2b	5.43	2.75	0.26	108.6 (d; 174)	71.5 (t; 134)	-0.2 (q; 125)	310.0250 [d] (310.0260)
2c	5.39	2.93	0.19	[e]	[e]	[e]	[e]

[a] 90 MHz, δ[ppm]; in C_6D_6 (C_6HD_5 as internal standard at 645 Hz; integrals in agreement with the number of protons). [b] 62.89 MHz (C_6D_6), δ[ppm] (multiplicity; ^1J(CH) [Hz]). [c] $2a^{+\cdot}$: 31% [d] $2b^{+\cdot}$: 27%; expected isotope pattern. [e] Not yet determined due to instability of 2c.

The structure assignments of 2 are based on the spectral data (Table 1). The monomeric structure of 2a, obtained by different routes[2d,e], has been unambiguously established.[2e] Monomeric structures are supported by the mass spectra, in which the $2^{+\cdot}$ ions are prominent. Typical for the strained, four-membered rings are the relatively low field proton chemical shifts[1b] of the Me_2M groups, and the low field shifts of both nuclei of the CH_2 group; the latter are, as expected,[4] slightly shifted upfield in comparison to the carbon analogue 2d (2, M = C).[1a,c] The large ^1J(CH) > 130 Hz of the CH_2 groups is also indicative of a four-membered ring (compare e.g. 2b, ^1J(CH) = 134 Hz; 6: $\delta(^{13}C)$ = 65 ppm, ^1J(CH) = 118 Hz). Contrary to 2d,[1a,c] 2a and 2b are stable in solution at room temperature; in C_6D_6, no decomposition was observed after two months. This probably indicates the inability of 2a and 2b to fragment[1a] into $Cp_2Ti{=}CH_2$ and $Me_2M{=}CH_2$, as the tendency to form the latter is clearly lower for M ≠ C. Only 2c decomposed within a few days; this is presumably due to another effect, i.e. the wellknown instability of small tin heterocycles.[1b]

Chemical corroboration of the structures of 2 was achieved by reaction with chlorotrimethylstannane to give 8. This illustrates that Ti-C bonds react readily with Cl-Sn bonds; similar (side) reactions between 2c and 5c are probably responsible for the low yield obtained of 2c.

The new approach to 1,3-dimetallacyclobutanes is in principle also applicable to metal dihalides other than 3 and 5. The investigation of its scope, and of the reactions of 2, is in progress.

References and Notes

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5. Compound 7 was not formed by decomposition of the intermediate $Cp_2Ti(Cl)CH_2MgBr$[3]; its mode of formation will be the subject of a forthcoming publication.

(Received in UK 24 August 1984)