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A NEW METHOD FOR THE SYNTHESIS OF ORGANOMETALLIC DERIVATIVES OF THE TRANSITION METALS IN THEIR LOWEST OXIDATION STATES

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Summary

The exchange reactions of organotitanium(IV) compounds with alkyllithiums have been investigated; tris(trimethylsilylmethyl)titanium and tribenzyltitanium have been synthesized. It is shown that this method may be used for the synthesis of compounds of the transition metals in their lowest oxidation states, and excludes the stage of organometal halide formation.

Sufficiently stable R_4Ti compounds are formed by the reaction of $TiCl_4$ with organometallic compounds of Groups I—III elements, whose organic radical does not contain hydrogen in the β-position to the metal [1,2]. The corresponding organotitanium(IV) halides R_nTiCl_{4-n} (n = 1—3, R = trimethylsilylmethyl, benzyl, etc.) with a Ti—C σ-bond are also frequently obtained in quantitative yields [3,4].

The reactions of the compounds of Groups I—III metals with $TiCl_3$ do not give the corresponding R_3Ti compounds. Thus, tribenzyltitanium cannot be obtained by the reaction of $TiCl_3$ with $C_6H_5CH_2MgCl$. As has been shown in refs. 5 and 6, the primary products of the reaction of $TiCl_3$ with $LiCH_2SiMe_3$ ($RTiCl_2$ and R_2TiCl) undergo disproportionation with quantitative formation of R_2Ti^{II} and R_4Ti^{IV}.

The method of preparation of organometallic compounds of the transition metals studied in the present work excludes the stage of organometal halide formation and may be used both for the synthesis of compounds with a carbon—metal σ-bond and for the synthesis of π-allyl derivatives. Alkyl derivatives of transition metals are usually unstable and rapidly decompose with reduction of the metal and disproportionation of the alkyl residues (R_{-H} and R_{+H}).

The proposed method is based on exchange reactions of MR_{n+1} compounds (R is an organic radical that does not contain a hydrogen atom in the β-position to the metal or a π-allyl group with alkyllithiums.

$$\begin{array}{l} MR_{n+1} + R^1Li \overset{1}{\rightleftharpoons} [MR_nR^1] + RLi \\ \qquad\qquad\qquad\qquad\quad \downarrow 2 \\ \qquad\qquad\qquad\qquad MR_n + 0.5\ R^1_{+H} + 0.5\ R^1_{-H} \end{array}$$

Exchange reaction 1 leads to transition of the alkyl group of the organolithium compounds (R^1) to the metal of variable valence. The unstable compound formed decomposes according to reaction 2 to give the products of disproportionation and an organometallic compound with the metal in a lower oxidation state. Similar results are obtained with R_nMHal:

$$R_nMHal + R^1Li \rightarrow LiHal + R_nMR^1 \rightarrow R_nM + 0.5\,R^1_{+H} + 0.5\ R^1_{-H}$$

As an illustration of this method we describe the synthesis of the new titanium(III) σ-compounds, $Ti(CH_2SiMe_3)_3$ and $Ti(CH_2C_6H_5)_3$, and the synthesis of $(\pi\text{-}R)_2Cr$.

Tris(trimethylsilylmethyl)titanium

Interaction of tetrakis(trimethylsilylmethyl)titanium (prepared as described in ref. 2) with C_2H_5Li (synthesized according to ref. 7) was carried out under vacuum in a glass reactor equipped with a magnetic stirrer and a manometer in a toluene solution or a mixture of hexane and toluene, at 23°C. Variations of the pressure in the system were measured. The reaction terminated after 80—120 minutes. The gaseous products were analyzed chromatographically, the amount of titanium in solution was determined photocolorimetrically and the amount of lithium by titration with acid. Data of chromatographic analysis are given in Table 1. As can be seen, at a Ti/Li ratio of 1 or 2 the amount of ethane formed is 90—100% of the theoretically possible yield and that of ethylene is 4—14%. The low yield of ethylene is probably due to its polymerisation in the presence of titanium(IV) compounds. It was established that a new portion of ethylene was consumed during the reaction, while ethylene added after termination of the reaction was not consumed.

Along with titanium(III) compounds, $LiCH_2SiMe_3$ is also formed. These compounds may form a complex:

$$Ti(CH_2SiMe_3)_3 + LiCH_2SiMe_3 \rightleftharpoons Li^+[Ti(CH_2SiMe_3)_4]^-$$

To isolate TiR_3 it is necessary to precipitate the organolithium compound without affecting the TiR_3.

TABLE I

INTERACTION OF $Ti(CH_2SiMe_3)_4$ WITH LiEt (23°C, toluene, during 2 h)

N	Initial amount of TiR_4 (mmol)	Molar ratio Ti/Li	The amount of gas formed (% as against theory)	
			C_2H_6	C_2H_4
1	0.24	1	90	4
2	0.24	1	94	6
3	0.21	2	100	14
4	0.21	1	90	6

Of the several methods studied the best results were obtained by treating a solution of the complex with carbon dioxide at −78°C. After such treatment and subsequent filtration a light yellow lithium-free solution was obtained. The yield of $Ti(CH_2SiMe_3)_3$ was 70% with respect to the initial TiR_4. Addition of $LiCH_2SiMe_3$ to a toluene solution of this compound at a ratio of Li/Ti 1/1 gives the same dark brown solution of $Li^+[Ti(CH_2SiMe_3)_4]^-$ complex. Tris(trimethyl)-titanium is stable in a hexane/toluene mixture at room temperature and in the dark for several weeks. At room temperature it is a viscous liquid and is distilled at 55°C at residual pressure of 10^{-4} mmHg.

Toluene solutions of TiR_3 and I_2 interact at 20°C according to the equation:

$TiR_3 + 3\ I_2 \rightarrow TiI_3 + 3\ RI$,

It was established that 3.1 mol of iodine are consumed per mol of the organotitanium compound.

Hydrolysis of $Ti(CH_2SiMe_3)_3$ with subsequent volumetric and chromatographic analyses showed that tetramethyl silane (RH) is formed in the quantity given by the ratio RH/Ti 3.0.

IR analysis showed CH_2D groups in the products of $Ti(CH_2SiMe_3)_3$ by D_2O, but no CHD_2 or CD_3 groups have been found.

Fig. 1a shows the IR spectrum of tris(trimethylsilylmethyl)titanium in the 200—700 cm^{-1} region recorded in a vaseline oil suspension on UR-20 and Perkin—Elmer 457 spectrometers. Bands at 700 and 615 cm^{-1} apparently belong to out-of-plane CH_2 bending vibrations and the band at 1420 cm^{-1} to in-plane bending vibrations. The very intensive band at 850 cm^{-1} and the less intensive band at 750 cm^{-1} correspond to antisymmetrical and fully symmetrical Si—C vibrations (ν(Si—C)), respectively. The three low-frequency bands at 250, 285 and 500 cm^{-1} may be assigned to vibrations of the Ti—C bond. The presence of three absorption bands of the metal—carbon bond suggests a D_{3h} symmetry of the ligand arrangement at the metal atom.

Tris(trimethylsilylmethyl)titanium gave no ESR signal, the mixture of it with $LiCH_2SiMe_3$, and TiR_4, having ESR spectra with *g*-factor 2. It has been established that NMR spectra of this compound were identical with that for TiR_4. This fact

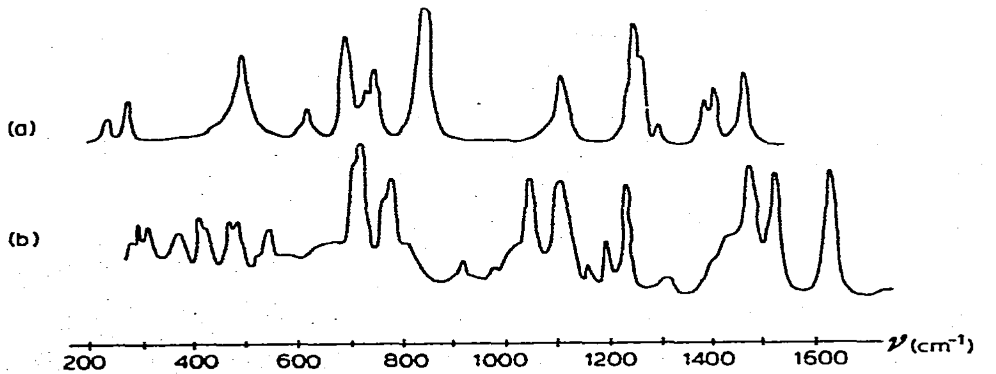

Fig. 1. IR spectra of organotitanium(III) compounds. Suspension in vaseline oil (a) $Ti(CH_2SiMe_3)_3$. (b) $Ti(CH_2C_6H_5)_3$.

is rather peculiar and the detailed study of TiR_4 and TiR_3 with ^1H, ^{29}Si, ^{13}C NMR is now in progress.

Tribenzyltitanium

Tributyltitanium was obtained at 0°C in a xylene solution by interaction of tetrabenzyltitanium (prepared according to ref. 1) with ethyllithium for 2 h. The dissolved part of the benzyllithium formed was precipitated by carboxylation at —78°C. $Ti(CH_2C_6H_5)_3$ solution was obtained after filtration in 65% yield with respect to the initial TiR_4.

Reaction of iodine with a xylene solution of tribenzyltitanium requires 3.02 mol of I_2 for every mole of TiR_3

Chromatographic analysis (using an internal standard) established toluene (RH) in the quantity given by the ratio RH/Ti 3.1 in the products of tribenzyltitanium decomposition with a diluted aqueous solution of 2 *N* sulfuric acid.

The complete set of bands belonging to a benzyl ligand was observed in the IR spectrum of tribenzyltitanium (Fig. 1b). The absorption band at 540 cm^{-1} may apparently be assigned to Ti—C vibrations. However, the presence of several low-frequency bands that should include bands characterising deformation of the phenyl ring make a reliable assignment impossible.

The NMR spectrum of tribenzyltitanium recorded in $C_6H_5CD_3$ at TiR_3 concentration of 4 wt.% showed the chemical shift of the methylene protons to be 2.095 ppm. For tetrabenzyltitanium under the same conditions $\delta(CH_2)$ 2.79 ppm, is in agreement with published data [1]. Tribenzyltitanium hardly decomposes at all during storage for several weeks at 20°C, whereas at 50°C 10% of it decomposes after 15 h.

Di-π-allylchromium

Di-π-allylchromium was obtained by allowing tri-π-allylchromium, prepared according to ref. 9, to react for 1 h with ethyllithium at 20°C. The precipitated allyllithium was filtered off. The yield of di-π-allylchromium was 95% with respect to the initial chromium compound.

The synthesized compounds in combination with protonic and Lewis acids act as catalysts of diene polymerization.

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