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# RADICAL IONS

## XXXII *. ALKYL LIGAND EXCHANGE IN BIS(CYCLOPENTADIENYL)DIALKYLTITANIUM(III) RADICAL ANIONS

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## Summary

Bis(cyclopentadienyl)dialkyltitanium(IV) derivatives containing $\beta$-silylalkyl groups, such as $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_3)_2$, can be reduced electrolytically or using potassium to their radical anions. The resolved ESR spectra of the $Ti^{III}$ species ($g$ values 1.983 to 1.985) have been assigned by computer simulation, and exhibit coupling constants $a_H$ 0.27—0.448 mT (4 H) and $a^{47}{}_{Ti} \sim a^{49}{}_{Ti}$ 1.01—1.05 mT. The radical anions can also be generated at low temperatures with an excess of LiR′ and so are presumably involved in the alkylation of $(\eta^5\text{-}C_5H_5)_2TiCl_2$. At higher temperatures, a novel alkyl ligand exchange $Cp_2TiR_2 + 2\ LiR' \rightarrow Cp_2TiR'_2 + 2\ LiR$ is observed.

## Introduction

Bis(cyclopentadienyl)titanium(III) complexes, which are of considerable interest, e.g. as Ziegler-type catalysts for low-pressure ethylene polymerization [2,3] or as reducing reagents for molecular nitrogen [2,4,5], have been much studied by ESR-techniques [2,5—7]. However, all the investigations concerned only rather complex reaction mixtures of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ or $(\eta^5\text{-}C_5H_5)_2TiCl$ with organometallic compounds, and there is no direct evidence for one-electron transfer during these reactions. On the other hand, low-lying vacant orbitals are

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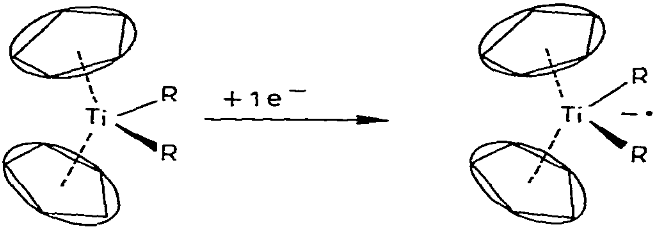
* For Part XXXI see ref. 1a. Also Part 122 of Chemistry of Organosilicon Compounds, for Part 121 see ref. 1b.

available in $d^0Ti^{IV}$ complexes and, therefore, one-electron reduction should yield the corresponding radical anions $d^1Ti^{III-\cdot}$, which would be isoelectronic [8] with the well-known [8,9] neutral paramagnetic $d^1V^{IV}$ complexes.

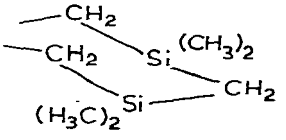
Recently, the thermal and air-stable $d^0Ti^{IV}$ compounds I, II and III with organosilicon ligands were synthesized [10], and these can be reduced to their radical anions (eq. 1). Their identification by fully resolved ESR spectra is discussed below, the study has also led to detection of a novel alkyl ligand exchange between the radical anions (eq. 1) and lithium alkyls.



(1)

R = $CH_2Si(CH_3)_3$ ,

(I)



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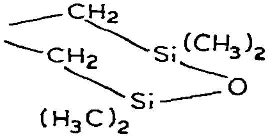


(III)

## One-electron reduction and assignment of the ESR spectra

Potassium metal reduces the bis(cyclopentadienyl)titanium(IV) derivatives (1) at 190 K in complexing ether solvents, such as a 1/1 mixture of DME and THF, to their radical anions $I^{-\cdot}$, $II^{-\cdot}$, $III^{-\cdot}$. Under the specified conditions, the radical anions are rather persistent; e.g. the half-life time of $I^{-\cdot}$ exceeds 20 min even at 300 K. The ESR spectrum of $I^{-\cdot}$ (Fig. 1) consists of a pentet due to 4 equivalent methylene protons with a $g$ factor of 1.9852. At increased sensitivity, hyperfine structures become resolved, which are attributed to the coupling of the isotopic nuclei $^{47}Ti$ ($I$ 5/2, $\gamma$ −0.3148, 7.28%) and $^{49}Ti$ ($I$ 7/2, $\gamma$ −0.3149, 5.51%) by computer simulation (Fig. 1). No coupling interaction is observed between the cyclopentadienyl ring protons and K metal. Electrolytic reduction of the titanium(IV) complexes (eq. 1) in DME/THF containing $n\text{-}Bu_4N^+ClO_4^-$ also produces the radical anions $I^{-\cdot}$, $II^{-\cdot}$ and $III^{-\cdot}$, but with somewhat shorter half-life times under the above conditions, e.g. less than 1 min for $I^{-\cdot}$ at 230 K.

The ESR data are summarized in Table 1 together with those of the n-butyl derivative, which will be mentioned later (Fig. 3). All the bis(cyclopentadienyl)-titanium(III) dialkyl radical anions exhibit similar general features (cf. also ref. 2). On silasubstitution, small but significant differences are observed: the $g$ values decrease and titanium coupling constants increase (Table 1). This trend is expected from the linear correlation between $a_{Ti}$ and $g_{av}$ found by Kenworthy et al. [6]. According to their argument, however, and contrary to the generally accepted donor properties of $R_3SiCH_2$ groups, the electron donor effect is expected to be

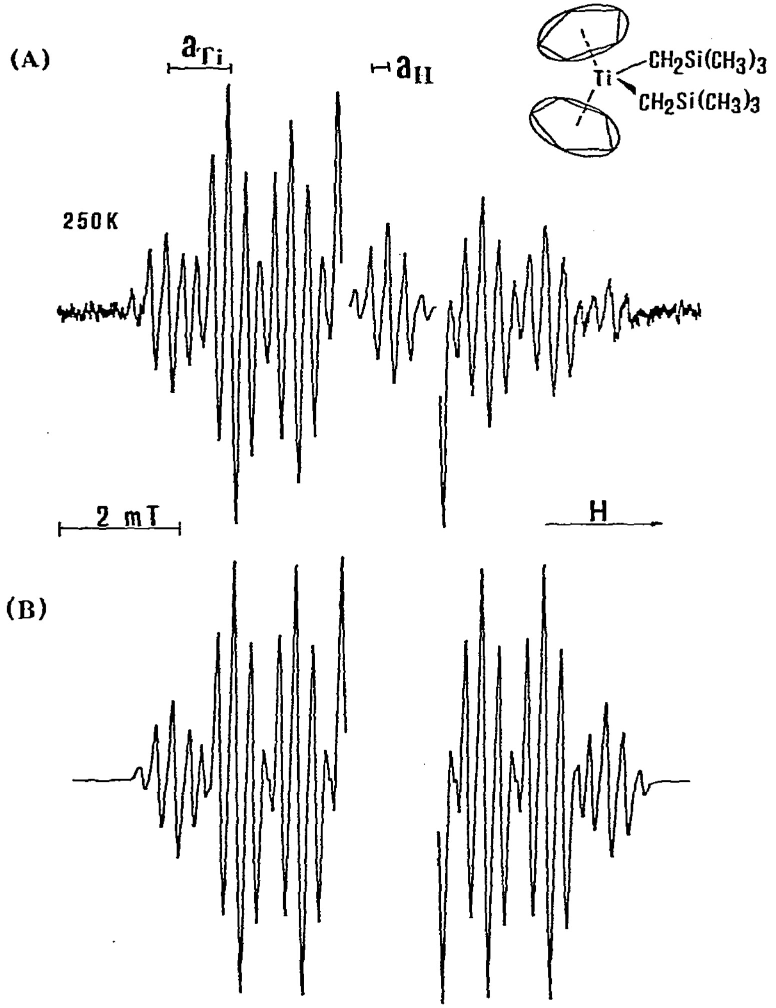
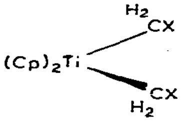
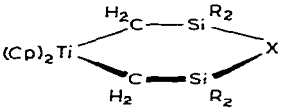


Fig. 1. (A) ESR spectrum of ($\eta^5$ — $C_5H_5)_2Ti(CH_2Si(CH_3)_3)_2^{-\cdot}$ ($I^{-\cdot}$) at 250 K in 1/1 DME/THF. The satellite signals are amplified 100 fold relative to the central pentet. (B) Computer simulation for the satellite signals.

smaller than that of alkyl substituents. It is interesting to note that all the trends observed in the ESR parameters of the $Cp_2TiR_2^{-\cdot}$ derivatives (Table 1) have also been found in the corresponding series of isoelectronic vanadium complexes, $(\eta^5\text{-}C_5H_5)_2VR_2$ [9]: the sila-substituted one again displays a smaller $g$ value and a larger $a_V$ coupling constant. Within the radical anions $I^{-\cdot}$, $II^{-\cdot}$ and $III^{-\cdot}$, only the hydrogen coupling constants $a_H^{CH_2}$ (Table 1) differ significantly, with spin delocalization considerably increasing on ring fixation of the 2 substituents. Although the mechanism of the spin delocalization to the $CH_2$ protons has not yet been unravelled, presumably the geometrical distortions induced by the bulky methylsilyl groups are more important than electronic effects (cf. Table 1: $II^{-\cdot}$ and $III^{-\cdot}$). The singly occupied orbital [8] in $Cp_2TiX_2^{-\cdot}$ is localized predominantly in the $TiX_2$ plane between the $\sigma$(TiX) bonds (cf. ref.

TABLE 1

| $M^{-\cdot}$ | X | $g$ | $a_H$ | $a_{^{47}Ti}/a_{^{49}Ti}$ |
|---|---|---|---|---|
|  | $CH_2CH_2CH_3$ [a] | 1.988 | 0.250 | 0.91 |
| | $Si(CH_3)_3$ [b] | 1.985 | 0.270 | 1.01 |
|  | $CH_2$ | 1.983 | 0.388 | 1.02 |
| | O | 1.983 | 0.448 | 1.05 |

[a] At 290 K. [b] Temperature dependent: at 230 K $g$ = 1.9847, $a_{Ti}$ = 1.03 mT and $a_H^{CH_2}$ = 0.275 mT.

8) for 10 $a_1$ of $Cp_2TiCl_2$: 69.5% $d_{z^2}$(Ti) and 16.1% $p$(X), and thus should be especially sensitive to changes in the angle XTiX. This model also explains why the cyclopentadienyl ring proton coupling in the radical anions $I^{-\cdot}$, $II^{-\cdot}$ and $III^{-\cdot}$ is too small to be resolved in the ESR spectra.

## Alkyl ligand exchange with lithium alkyl

The successful one-electron reduction of $d^0Ti^{IV}$ complexes suggests that the formation of $Ti(\eta^5\text{-}C_5H_5)_2R_2^{-\cdot}$ $M^+$ (M = MgX, Li, Na, etc.) during reactions of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ with excess RM [2,5,6] may also involve one-electron transfer from RM reagents to intermediate $d^0Cp_2TiR_2$ compounds. The corresponding radical anions were indeed detected by ESR spectroscopy in reaction mixtures of I, II or III with alkyllithiums: for instance, after treating a solution of III in DME/THF with an excess of n-butyllithium in n-hexane at low temperature (cf. Experimental), the ESR spectrum of $III^{-\cdot}$ (Fig. 2B) appears. With $Li^+$ as counterion, the $g$ value 1.9833 and the coupling constants $a_H^{CH_2}$ 0.416 mT and $a_{Ti}$ 1.05 mT are observed at 230 K. However, on warming the solution to 290 K the ESR signals of $III^{-\cdot}$ start to disappear and become superimposed by those of a new paramagnetic species. The spectrum is shifted a little to lower field ($g$ 1.988) and exhibits a pentet hyperfine splitting due to 4 equivalent protons with $a_H^{CH_2}$ 0.250 mT (Fig. 3). By comparison with the ESR parameters of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2CH_3)_2^{-\cdot}$ [2] it can be assigned to the closely related radical anion $(\eta^5\text{-}C_5H_5)_2Ti(CH_2CH_2CH_2CH_3)_2^{-\cdot}$.

One possible mechanism of this novel alkyl ligand exchange is a dissociative substitution at the titanium centre with a $Ti^{III\cdot}$ species as a key intermediate.

$$Ti^{IV}CH_2SiR_3 + R^- \rightarrow [Ti^{III}CH_2SiR_3]^{-\cdot} + R^\cdot \quad (2)$$

$$[Ti^{III}CH_2SiR_3]^{-\cdot} \underset{+^-CH_2SiR_3}{\overset{-^-CH_2SiR_3}{\rightleftharpoons}} [Ti^{III}]^\cdot \underset{-R^-}{\overset{+R^-}{\rightleftharpoons}} [Ti^{III}R]^{-\cdot} \quad (3)$$

Very recently, Russell and Lamson [11] observed ESR spectra of alkyl

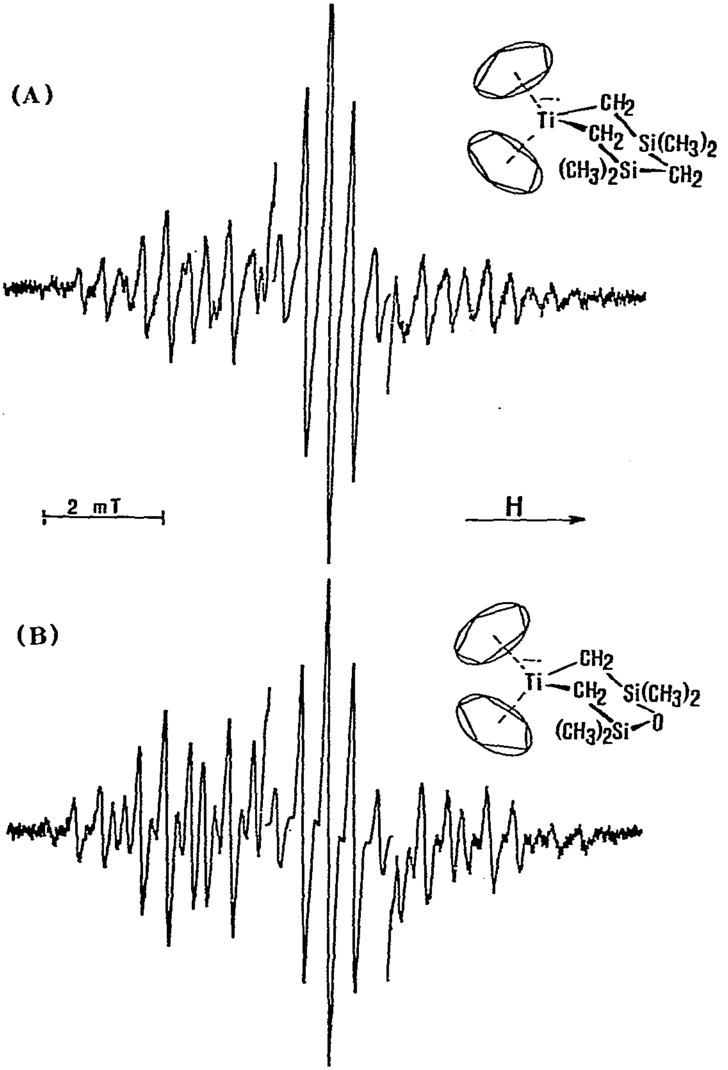


Fig. 2. ESR spectra of the bis(cyclopentadienyl)titanium dialkyl radical anions $II^{-\cdot}$ and $III^{-\cdot}$ at 230 K in 1/1 DME/THF.

radicals immediately after mixing benzene solutions of RLi with $TiCl_4$ in a flow system. They have suggested a single electron transfer from RLi to $TiCl_4$ followed by dissociation of $Cl^-$, although they have no evidence for the formation of $[TiCl_4]^{-\cdot}$ or $[R_4Ti]^{-\cdot}$.

$$RLi + TiCl_4 \rightarrow R^{\cdot} + [TiCl_4]^{-\cdot} \quad (4)$$

$$[TiCl_4]^{-\cdot} \rightarrow [TiCl_3]^{\cdot} + R^- \quad (5)$$

In the present system, dissociation of an alkyl anion from the $[Cp_2TiR_2]^{-\cdot}$ species occurs undoubtedly more slowly than the cleavage of $Cl^{-\cdot}$ from $[TiCl_4]^{-\cdot}$ and related systems, and therefore $[Cp_2Ti^{III}R_2]^{-\cdot}$ species can be detected successfully by ESR. Reaction 3 would be essentially reversible, but in the situation

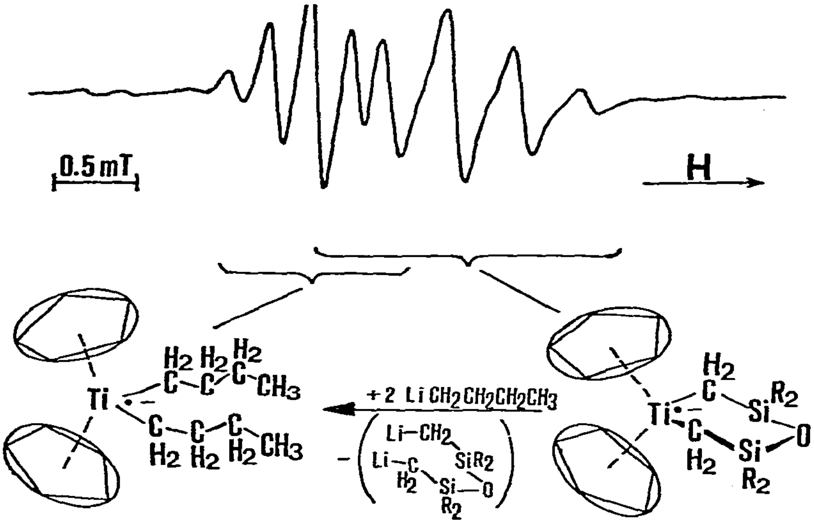


Fig. 3. ESR spectrum of the reaction mixture of $Cp_2Ti(CH_2Si(CH_3)_2)_2O$ with $LiCH_2CH_2CH_2$-$CH_3$ at 260 K in DME/THF/n-hexane.

that excess alkyllithium reagents subsist in the mixture, $[Ti^{III}R]^{-\cdot}$ species are likely the dominant product. At the same time, however, we can point out the fact that silyl-substituted carbanions, $(Me_3Si)_nH_{3-n}C^-$ are more stabilized than alkyl anions by delocalization of a negative charge involving interaction of the non-bonding electrons with an acceptor orbital on silicon [12,13]. Therefore, in the present system, methylsilyl carbanions are better leaving groups as actually observed.

Another possible factor to determine the direction in equilibrium 3 is the electronic effect of the silyl group to destabilize the anion radical species. The rates of the alkylligand exchange reaction of titanium(IV) complexes (Fig. 3) with butyllithium depend strongly on the alkyl ligand structure: whereas $II^{-\cdot}$ and $III^{-\cdot}$ react only slowly, the conversion of I is too fast even at 200 K to detect the ESR spectrum of the intermediate radical anion $I^{-\cdot}$. Obviously, methylsilyl groups are more effective electron donors than alkyl substituents and, therefore, do not stabilize radical anions as well. Only, if the ligand possesses a cyclic chelating structure, the alkyl ligand exchange is slow enough to detect the intermediate $Cp_2Ti(CH_2SiR_2)_2X^{-\cdot}$ by ESR spectroscopy.

## Experimental

*Alkali metal reduction* was carried out in DME/THF by the standard procedure using sublimed K under high vacuum. The clear yellow solutions of the titanium(IV) compounds were not visibly changed after contact with K at 190 K but gave strong ESR signals.

*Electrochemical reduction* of the titanium(IV) compounds could be achieved in DME/THF using $n$-$Bu_4N^+$ $ClO_4^-$ as a supporting electrolyte in an ESR tube with a Pt electrode (diameter 3 mm) designed for low temperature electrolysis in an ESR cavity.

*The reaction of $Cp_2TiR_2$ with alkyllithium* was investigated repeatedly using the following procedure: 0.05 ml of commercially available n-butyllithium in hexane (ca. 1.5 *N*) is mixed with ca. 1 mg of $Cp_2Ti(CH_2SiR_2)_2O$ in 0.2 ml of DME/THF under vacuum at —90°C in an ESR tube designed for alkali metal reduction. After insertion into the ESR cavity, the mixture immediately gave a strong signal of the corresponding radical anion. At 180 K the signal remained unchanged even after 2 h, whereas at 300 K it disappeared in 10 min, and a new signal assigned to $Cp_2TiBu_2^{-\cdot}$ was observed.

*Electron spin resonance spectra* were recorded with Varian E9 equipment (frequency 9.5 GHz, 330 mT magnetic field, and 100 kHz field modulation), and calibrated with perylene radical anion in DMR [14] ($a_H$ 0.04503, 0.30473 and 0.34934 mT; $g$ 2.002657).

## References

1 (a) H. Nöth, W. Winterstein, W. Kaim and H. Bock, Chem. Ber., 112 (1979) in press; (b) H. Sakurai, A. Shirahata and A. Hosomi, Angew. Chem., 91 (1979) 178; Intern. Ed., 18 (1979) 163.
2 H.H. Brintzinger, J. Amer. Chem. Soc., 89 (1967) 6871, and references cited therein.
3 K. Clauss and H. Bestian, Liebigs Ann. Chem., 654 (1962) 8.
4 E.E. van Tamelen, Acc. Chem. Res., 3 (1970) 361 and references cited therein.
5 G. Henrici-Olivé and S. Olivé, Angew. Chem. Int. Ed., 7 (1968) 398, 796; J. Organometal. Chem., 19 (1969) 309; ibid., 23 (1970) 155.
6 J.G. Kenworthy, J. Myatt and P.F. Todd, J. Chem. Soc. (B), (1970) 791; J.G. Kenworthy, J. Myatt and M.C.R. Symons, J. Chem. Soc. (A), (1971) 1020, 3428.
7 L.E. Manzer, Inorg. Chem., 15 (1976) 2567.
8 J.Z. Petersen, D.L. Lichtenberger, R.F. Fenske and L.F. Dahl, J. Amer. Chem. Soc., 97 (1975) 6433 and references cited therein.
9 Cf. e.g. A.G. Evans, J.C. Evans, D.J.C. Espley, P.H. Morgan and J. Mortimer, J. Chem. Soc. Dalton, (1978) 57, who report an ESR study on $(\eta^5\text{-}C_5H_5)_2V(CH_2R)_2$ with R = $CH_3$, $Si(CH_3)_3$.
10 H. Sakurai and H. Umino, J. Organometal. Chem., 142 (1977) C49; cf. also M.R. Collier, M.F. Lappert and R. Pearce, J. Chem. Soc. Dalton Trans., (1973) 445.
11 G.A. Russell and D.W. Lamson, J. Organometal. Chem., 156 (1978) 17.
12 M.A. Cook, C. Eaborn, A.E. Jukes and D.R.M. Walton, J. Organometal. Chem., 24 (1970) 529.
13 H. Sakurai, K. Nishiwaki and M. Kira, Tetrahedron Lett., (1973) 4193.
14 J.R. Bolton, J. Phys. Chem., 71 (1967) 3702.