

REACTION OF TITANOCENE ALKYL WITH PYRIDINES; A NOVEL TYPE OF CYCLOMETALLATION REACTION

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Summary

Reaction of Cp_2TiR ($\text{R} = \text{alkyl}$) with 2-substituted-pyridines and with quinolines leads to α -metallation of these ligands with formation of triangular titanocycles containing Ti^{III} . Proof of the metallation at the α -position comes from reactions of the complexes formed with I_2 and $\text{D}_2\text{O}/\text{DCI}$ which yield the corresponding iodo- and deuterio-pyridine and -quinoline derivatives. Reaction of Cp_2TiR with the structurally related ligand benzalaniline leads to a side-on coordinated benzalaniline complex of titanocene. Reactions of this diamagnetic complex with I_2 , CO_2 and H_2 are described.

Introduction

The coordinatively unsaturated, thermally unstable compounds Cp_2TiR ($\text{R} = \text{alkyl}$) [1,2] show interesting reactivity towards a variety of organic substrates. Reagents such as isocyanides, isocyanates and carbon dioxide insert in the $\text{Ti}-\text{R}$ bond. Pinacol-type dimerisation reactions take place with ketones [2] and disproportionation to Cp_2TiR_2 and Cp_2TiCS_2 is observed with carbon disulfide [1]. In this paper we describe reactions of Cp_2TiR ($\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_4\text{H}_9$) with ligands formally containing the imine fragment $-\text{CH}=\text{N}-$ e.g. 2-substituted pyridines, quinolines and benzalaniline. The properties of the complexes formed and some characterisation reactions are described. A preliminary report on part of this study has appeared previously [3].

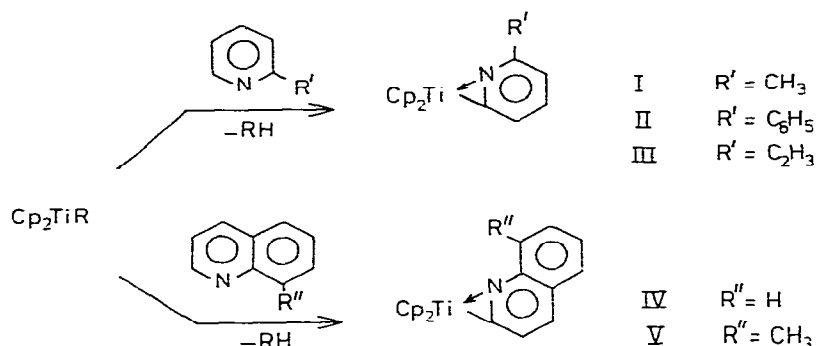
Results and discussion

Reactions with 2-substituted pyridines and quinolines

Reaction of Cp_2TiR ($\text{R} = \text{CH}_3$, $n\text{-C}_4\text{H}_9$) with the 2-substituted pyridines 2-methylpyridine, 2-phenylpyridine and 2-vinylpyridine and with quinoline and

8-methylquinoline yields, in a novel type of cyclometallation, the α -metallated products I–V, according to Scheme 1.

SCHEME 1



Addition of these heterocyclic bases to green ($\text{R} = \text{CH}_3$) or brown ($\text{R} = n\text{-C}_4\text{H}_9$) solutions of Cp_2TiR at -80°C results in a colour change to dark green or blue, indicating formation of the adduct $\text{Cp}_2\text{TiR} \cdot \text{L}$. On warming to room temperature a pronounced colour change to brown-purple is observed accompanied by evolution of RH , indicating metallation. The rate of metallation depends on the nitrogen base used. Under the conditions employed ($\sim 10^{-1} \text{ M}$ in ether) α -metallation starts at about -40°C for all ligands except for 2-vinylpyridine, for which it sets in at about 0°C . The products (I–V, Scheme 1) are purple crystalline solids, and are obtained in 10–60% yields. They were characterized by elemental analyses (Table 1), IR and molecular weight determination (monomeric, Table 1).

As shown in Fig. 1, the IR spectra of the complexes I–V show the characteristic $\eta^5\text{-C}_5\text{H}_5$ absorptions around 1010 cm^{-1} and 790 cm^{-1} and specific C–H out of plane deformation modes for the ligands.

The compounds are paramagnetic (EPR, Table 1) with 1 unpaired electron

TABLE I
ANALYTICAL AND PHYSICAL DATA FOR THE COMPOUNDS I–V
(for numbering see Scheme 1)

Compound	Yield (%)	Melting point ($^\circ\text{C}$)	Dec. Temp. ^a ($^\circ\text{C}$)	Mol. weight found (calcd.)	Analysis (found (calcd.) (%))		
					C	H	Ti
I ^c	40	120	133		71.04(71.12)	6.12(5.97)	17.94(17.73)
II	35	114	124		75.42(75.91)	5.79(5.46)	14.25(14.41)
III	10	129	148	250 (283)			16.66(16.97)
IV	40	118	122		73.51(74.52)	5.58(5.27)	16.45(15.64)
V ^d	60	118	137	288 (320)	74.80(75.00)	6.26(5.66)	14.45(14.96)

^a From DTA measurements. ^b Cryoscopically in benzene. ^c EPR (ether, 30°C , DPPH): $g = 1.990(\text{s})$.

^d $\mu_{\text{eff}} = 1.67 \text{ B.M.}$ (spin only-value expected for Ti^{III} 1.73 B.M.).

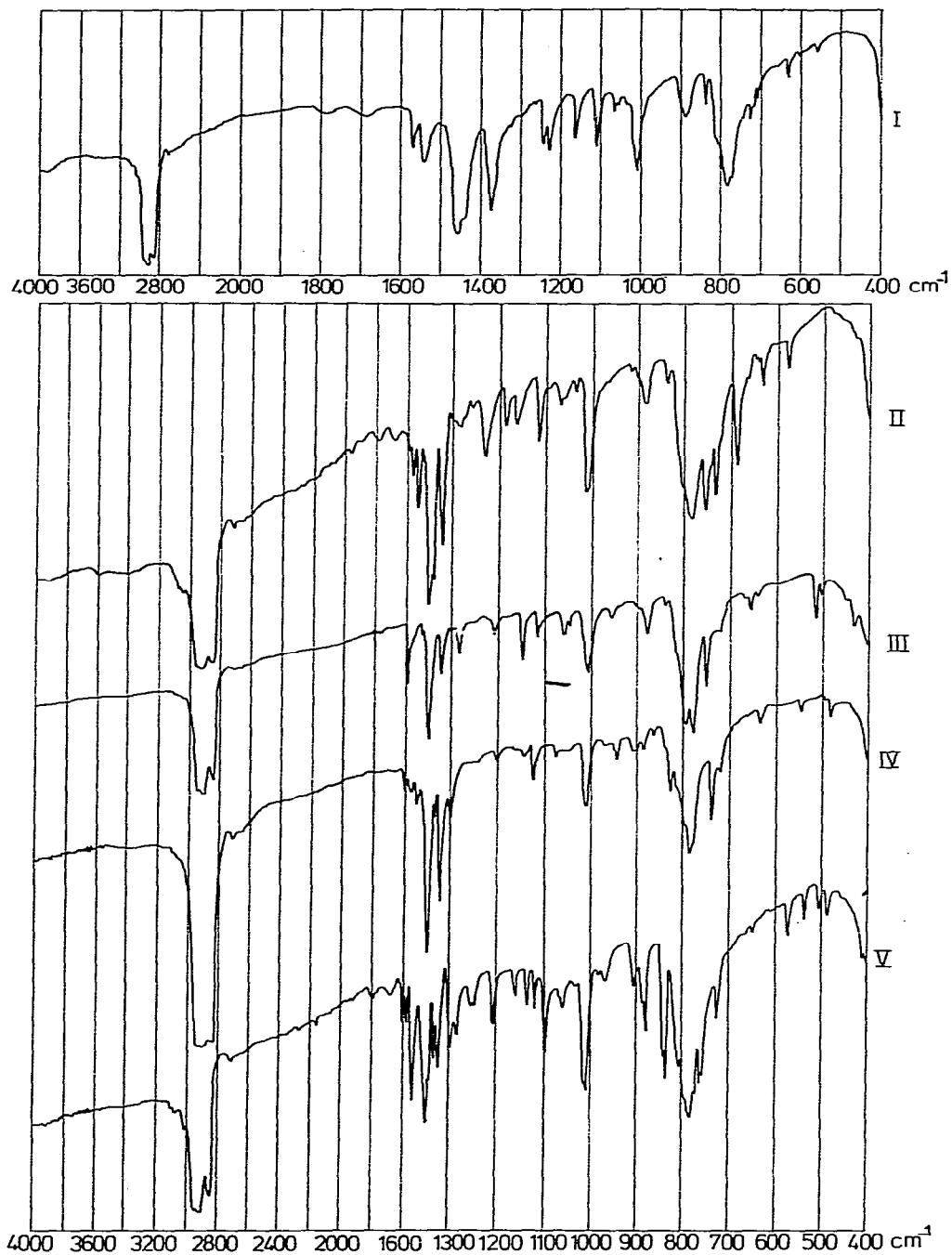
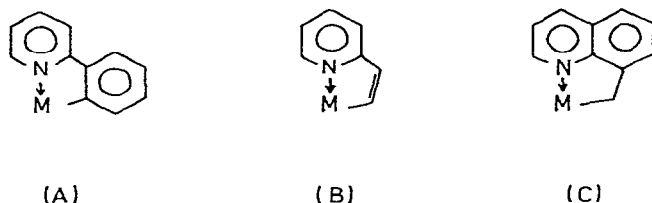


Fig. 1. IR spectra of the α -metallated complexes I–V (KBr, Nujol). For numbering see Scheme 1.

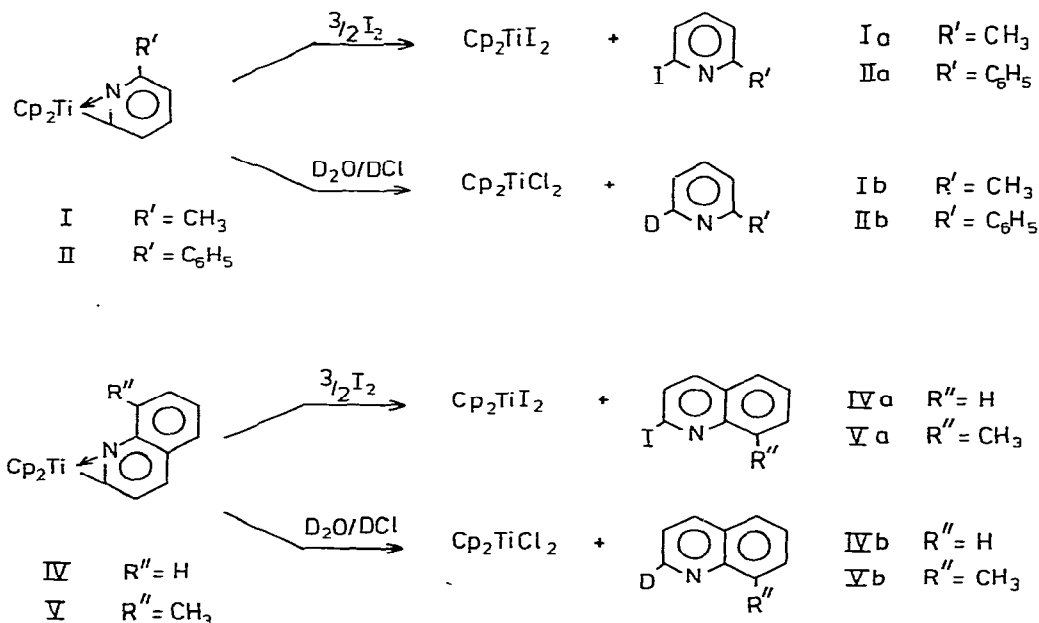
per Ti atom (Table 1), as expected for Ti^{III} compounds. They are thermally stable up to about $130^{\circ}C$ (Table 1), which indicates the presence of a coordinative Ti–N bond since coordinatively unsaturated compounds Cp_2TiR ($R = aryl$)

have a far lower thermal stability [4]. Internal coordination is also indicated by the fact that the complexes do not react with N_2 even at very low temperatures, in contrast to the complexes Cp_2TiR which form $(Cp_2TiR)_2N_2$ [5]. The formulation of the complexes (I–V) as triangular titanacycles in which the ligand is η^2 -coordinated to Ti corresponds to the structure of other titanocene complexes such as Cp_2Ti -acyl [6] and Cp_2Ti -iminoacyl [7] complexes in which the ligands are also η^2 -coordinated to Ti; it is consistent with the preference of early transition metals to form small metallocycles. The observed α -metallation is quite unusual, since normally metallation of this type of ligand gives five-membered metallocyclic rings with structures such as A, B and C [8–12].



The existence of a Ti–C bond at the 6-position in the pyridine complexes (I, II) and at the 2-position in the quinoline derivatives (IV, V) is demonstrated by reactions with I_2 or with D_2O/DCI , which yield the expected iodo- and deuterio-pyridines and -quinolines according to Scheme 2. Cp_2TiI_2 and Cp_2Ti -

SCHEME 2



Cl_2 were obtained almost quantitatively (80–95%), and were identified by IR, UV-vis and mass spectrometry. The pyridine and quinoline ligands formed (85–95%) were identified by IR, 1H NMR (Table 2) and mass spectrometry

TABLE 2

^1H NMR ^a (CHEMICAL SHIFTS δ IN PPM; COUPLING CONSTANTS J IN HZ) AND MASS SPECTRAL DATA (M^+ IN m/e) ^b FOR IODO- AND DEUTERIO-PYRIDINES AND -QUINOLINES

(for numbering see Scheme 1)

The numbering of the protons in the ligands is as follows:



Compound	$M^+(m/e)$	$\delta(\text{H}_4)$	$^3J(\text{H}_4, \text{H}_{3,5})$	$\delta(\text{H}_3, \text{H}_5)$	$\delta(\text{R}')$
Ia	219	7.50 (dd)	2.8 and 5.8	7.03–7.31(m)	$\delta(\text{CH}_3)$ 2.53(s)
Ib	94	7.47(t)	7.6 and 7.6	6.85–7.13(m)	$\delta(\text{CH}_3)$ 2.53(s)
IIb	156	7.95(dd)	3.0 and 8.0	^c	$\delta(\text{C}_6\text{H}_5)$ 7.05–7.75(m)
	$M^+(m/e)$	$\delta(\text{H}_4)$	$^3J(\text{H}_3, \text{H}_4)$	$\delta(\text{H}_3, \text{H}_5, \text{H}_6, \text{H}_7)$	$\delta(\text{R}'')$
IVa	255	7.97(d, br)	8.6	7.26–7.81(m)	^d
IVb	130	8.07(d)	8.2	7.15–7.85(m)	^d
Va	269	7.68(s, br)	—	7.60–7.72(m)	$\delta(\text{CH}_3)$ 2.75(d)
Vb	144	8.02(d)	8.0	7.08–7.72(m)	$\delta(\text{CH}_3)$ 2.73(s)

^a CDCl_3 , TMS, 35°C. ^b 100°C. ^c Coinciding with the phenyl absorptions. ^d $\delta(\text{H}_3)$ coinciding with $\delta(\text{H}_3, \text{H}_5, \text{H}_6, \text{H}_7)$.

(Table 2). As an example, Fig. 2 shows the ^1H NMR spectra of 2-methylpyridine and 2-methyl-6-deuteriopyridine (Ib). It can easily be seen that the characteristic H_6 signal in 2-methylpyridine disappears on deuteration, as, of course, does the coupling $^4J(\text{H}_4, \text{H}_6)$ (about 2 Hz in 2-methylpyridine).

It is remarkable that the α -metallation seems to be limited to ligands in which only one α -hydrogen is present. If two α -hydrogen atoms are present e.g. in pyridine itself or in 3- or 4-methylpyridine α -metallation does not take place. A plausible explanation could be that the presence of an α -substituent sterically forces the pyridine (or quinoline) ligand in the adduct stage in the yz plane of the molecule, in such a way that α -metallation with formation of RH is the favoured process (Fig. 3). In the absence of an α -substituent the ligand can rotate around the Ti–N bond out of the yz plane to a position where interaction of the π electron system on the ligand with “in plane” (the yz plane) orbitals on Ti [13] leads to a stabilisation. In this situation the α -hydrogen is shifted into a position unfavourable for RH formation and consequently α -metallation is unlikely.

Reactions with benzalaniline

In order to examine the scope of the α -metallation described above we treated Cp_2TiR ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) with another ligand containing the imine fragment $-\text{N}=\text{CH}-$ viz. benzalaniline, a ligand which is known to be easily *ortho*-metallated [14]. This reaction gave a side-on coordinated benzalaniline com-

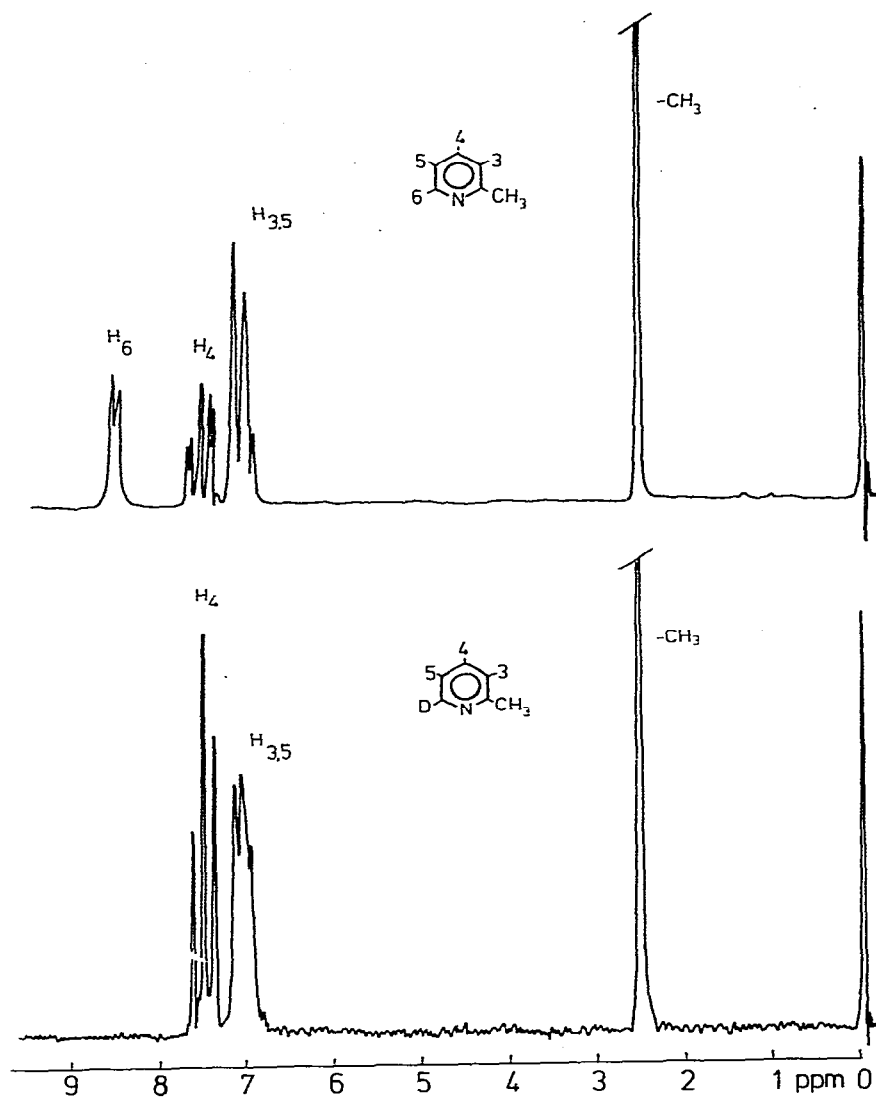
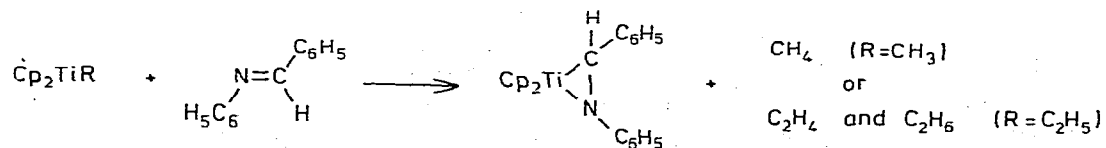


Fig. 2. ¹H NMR spectra of 2-methylpyridine (above) and 2-methyl-6-deuteriopyridine (Ib, below) (CCl₄, TMS, 35°C).

plex of titanocene, with formation of methane for R = CH₃ and a mixture of ethene and ethane (ratio 3 : 7) for R = C₂H₅, as shown in Scheme 3.

SCHEME 3



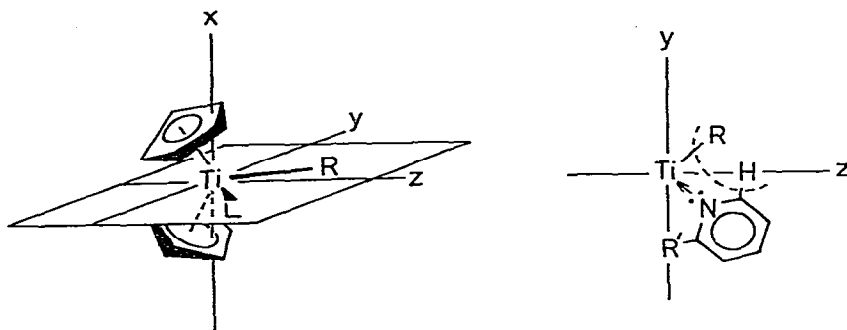


Fig. 3. Schematic view of the adduct system $\text{Cp}_2\text{TiR} \cdot \text{L}$ (left) and of the corresponding yz plane for $\text{Cp}_2\text{TiR} \cdot 2\text{-substituted pyridine}$ (right).

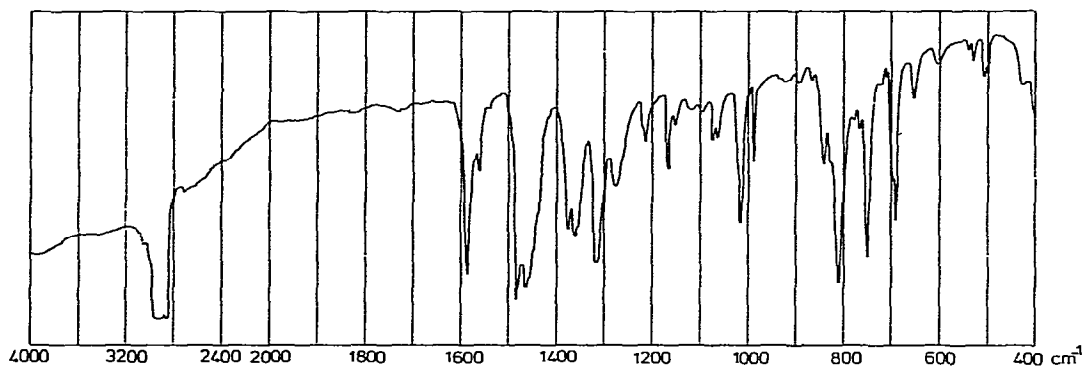


Fig. 4. IR spectrum of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ (KBr, Nujol).

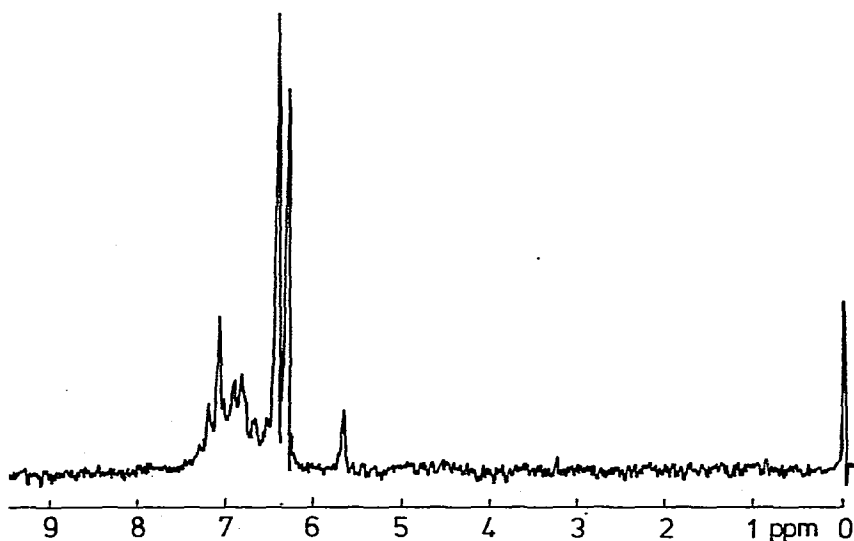


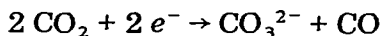
Fig. 5. ^1H NMR spectrum of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ (ether- d_{10} , TMS, 35°C ; solvent peaks are omitted).

The green complex formed was isolated in 45% yield. It is diamagnetic, thermally stable up to 130°C and monomeric. It was characterised by elemental analysis, IR (Fig. 4), ¹H NMR (Fig. 5) and ¹³C NMR.

As can be seen in Fig. 4, the IR spectrum of the compound shows the characteristic η^5 -C₅H₅ and phenyl absorptions, and a band at 1312 cm⁻¹ which is tentatively assigned to $\nu(\text{CN})$ (in benzalaniline $\nu(\text{CN})$ is found at 1627 cm⁻¹; in secondary aromatic amines in the range 1260–1340 cm⁻¹). The ¹H NMR spectrum (Fig. 5) consists of two singlets for the Cp ligands at δ 6.28 ppm and δ 6.40 ppm, a singlet for the imine hydrogen at δ 5.68 ppm (in the free ligand δ 8.38 ppm) and a multiplet at δ 6.50–7.40 due to the phenyl groups. The ¹³C NMR spectrum (ether-*d*₁₀; 35°C) shows the Cp carbon atoms at δ 120.5 ppm and δ 118.7 ppm, the imine carbon atom at δ 162.9 ppm (free ligand δ 162.3 ppm) and the phenyl carbons in the range δ 117.0–131.6 ppm. Both the IR and NMR data suggest a side-on coordination of the benzalaniline ligand to Ti and not an end-on coordination via the nitrogen lone pair, since this would not result in such a drastic lowering of $\nu(\text{CN})$ in the IR spectrum or such a large up-field shift in the ¹H NMR spectrum of the imine hydrogen resonance (Δ 2.70 ppm) compared to the free ligand [15,16].

Concerning the mechanism of the reaction as shown in Scheme 3, it must be noted that in the reaction with R = C₂H₅ a substantial amount of ethene is formed. This suggests a benzalaniline-induced homolysis of the Ti–R bond with formation of the complex described and alkyl radicals, which can abstract hydrogen atoms from the medium or disproportionate. This reaction resembles to some extent the reaction of Cp₂TiR (R = CH₃) with CS₂ to yield Cp₂TiCS₂ and Cp₂TiR₂ [1], but in the present case formation of Cp₂TiR₂ is not observed. Furthermore, it is evident that in contrast to the reactions with pyridines and quinolines, no α -metallation takes place. This difference in reactivity is probably related to the fact that benzalaniline has the *anti*-conformation [17]. Upon coordination to Cp₂TiR the adduct shown in Fig. 6 will first be formed. In this adduct the imine hydrogen is in an unfavourable position with respect to the Ti–R bond, in contrast to the adducts formed by 2-substituted pyridines (Fig. 3). Therefore, in the case of benzalaniline α -metallation does not take place for steric reasons. Due to the high reactivity of the Ti–R bond the adduct is not stable and decomposes via cleavage of the Ti–R bond to give the products described.

The question arises whether the complex Cp₂Ti · C₆H₅N=CHC₆H₅ should preferably be regarded as a formally Ti^{II} complex (with essentially *sp*² hybridised C and N and π -interaction between Ti and the ligand) or as a Ti^{IV} complex (a σ -bonded triangular metallocycle with *sp*³ C and N). The related azobenzene complex Cp₂Ti · C₆H₅N=NC₆H₅ was tentatively formulated as a Ti^{IV} complex mainly because hydrolysis yielded hydrazobenzene [18]. In order to get more insight in the bonding in our benzalaniline complex we carried out reactions with I₂, CO₂ and H₂, as shown in Scheme 4. In the reaction with I₂ Cp₂TiI₂ (81%) and free benzalaniline is formed (85%). Reaction with CO₂ gives the carbonato complex [(Cp₂Ti)₂(CO₃)₂] (76%) [19], CO and benzalaniline (90%); this reaction can be regarded as a two-electron disproportionation of CO₂:



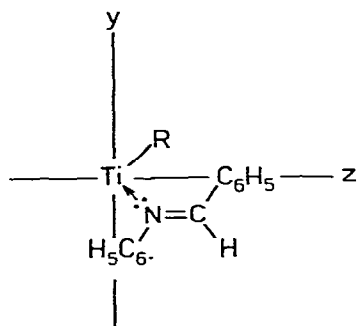
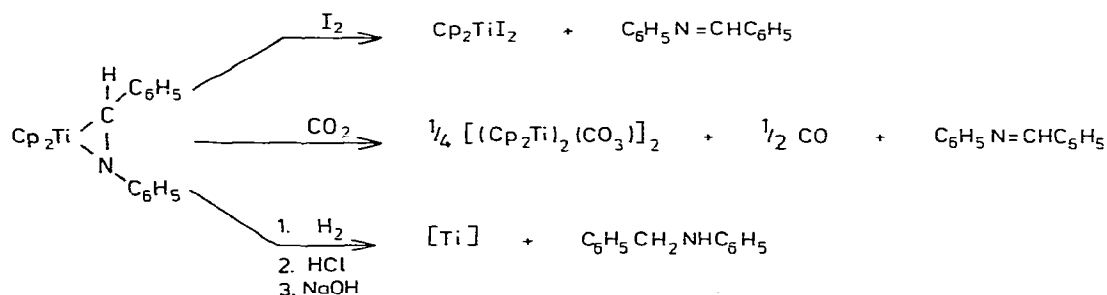
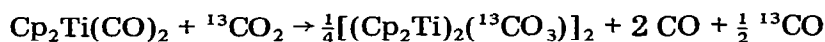


Fig. 6. Schematic view of the adduct system $\text{Cp}_2\text{Ti} \cdot \text{benzalaniline}$ in the yz plane of the molecule. The Cp ligands are omitted (see also Fig. 1).

SCHEME 4



A similar disproportionation was reported by Floriani et al. for $\text{Cp}_2\text{Ti}(\text{CO})_2$ [19]:



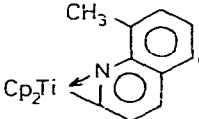
Reaction of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ with H_2 (and subsequent reaction with HCl and NaOH) gives benzyl(phenyl)amine (92%).

The results of these three reactions do not enable us to distinguish definitely between the limiting formulations of the complex as a formally Ti^{II} or Ti^{IV} complex. The results of the reactions with I_2 and CO_2 seem to favour a description as a divalent titanium complex, but the reaction with H_2 suggests a tetravalent Ti compound. The spectroscopic data as described above (IR, NMR) also do not allow a definite distinction to be made between the two limiting situations, although as mentioned before, the early transition metals seem to prefer to form small metallocycles.

Experimental

All experiments were carried out under argon. Solvents were distilled from benzophenoneketyl sodium under nitrogen. Compounds Cp_2TiR were prepared from Cp_2TiCl and RLi at -80°C according to ref. 2. The pyridines and quinolines were distilled before use and stored under nitrogen; commercially available benzalaniline was used without further purification. CO_2 and H_2 were pur-

chased from Gardner Cryogenics. Elemental analyses were performed in the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga. IR spectra were measured on a JASCO IRA-2 spectrophotometer (KBr/Nujol), ^1H NMR spectra were recorded on a Perkin-Elmer R-24B spectrometer and on a Varian XL-100 spectrometer. The EPR spectra were recorded on a Varian E3 X-band EPR spectrometer. Melting points and decomposition temperatures of solids were determined by differential thermal analysis (heating rate $1.5^\circ\text{C}/\text{min}$). Mass spectra were recorded by Mr. A. Kiewiet on an AEI-902 spectrometer at an ionizing voltage of 70 eV. GC experiments were performed on a Hewlett-Packard 428 GC apparatus on a Porapak Q column at 100°C .

Preparation of  (V, Scheme 1)

To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at -78°C 5.00 mmol of 8-methylquinoline were added. The dark green mixture was slowly warmed to room temperature (two hours) during which the colour changed to brown-purple and methane was evolved (from about -40°C ; GC). After being stirred at room temperature for 15 hours, the mixture was evaporated to dryness and extracted with 30 ml of n-pentane. On cooling the n-pentane extract to -78°C purple crystals of the title compound separated (2.40 mmol; 60%). The product is very air-sensitive and readily soluble in the common organic solvents. The other α -metallated compounds (I–IV) were prepared in the same way.

Reaction of V with I_2

To a solution of 0.30 mmol of the α -metallated product V in 5 ml of n-hexane at -78°C 0.45 mmol of I_2 was added. After warming to room temperature (two hours) a black precipitate of Cp_2TiI_2 (0.26 mmol; 87%) and a light yellow n-hexane solution had formed. Evaporation of this solution gave 2-iodo-8-methylquinoline (Va; 0.27 mmol; 90%). The reactions of the other α -metallated products (I–IV) with I_2 were carried out in the same way.

Reaction of V with $\text{D}_2\text{O}/\text{DCl}$

To a solution of 0.30 mmol of the α -metallated product V in 20 ml of ether at -78°C an eightfold excess of DCl in D_2O was added. After warming to room temperature (two hours) a red suspension (Cp_2TiCl_2) had formed. After addition of an excess of NaOH in 5 ml of D_2O and stirring for one hour a white aqueous layer and a light yellow ether layer had formed. Evaporation of the ether layer gave 2-deuterio-8-methylquinoline (Vb; 0.25 mmol; 83%). The reactions of the other α -metallated products (I–IV) with $\text{D}_2\text{O}/\text{DCl}$ were carried out in the same way.

Preparation of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$

To a solution of 4.00 mmol of Cp_2TiCH_3 in 30 ml of ether at -78°C 4.00 mmol of benzalaniline were added. The brown-green mixture was slowly warmed to room temperature (two hours) during which the colour changed to

green and methane was evolved (GC). After stirring at room temperature for two hours the mixture was evaporated to dryness and washed several times with 30 ml of n-pentane. The green product was recrystallized from 30 ml of ether to give green crystals of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ (1.80 mmol; 45%). The product is very air-sensitive and readily soluble in common organic solvents. Elemental analysis: C, 75.92; H, 6.25; Ti, 13.64. $\text{C}_{23}\text{H}_{21}\text{NTi}$ calcd.: C, 77.09; H, 5.63; Ti, 13.37%. Molecular weight (cryoscopically in benzene): found 354 (calcd. 359). Decomposition temperature (DTA): 129°C.

Reaction of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ with I_2

To a solution of 1.00 mmol of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ in 20 ml of ether at -78°C 1.00 mmol of I_2 was added. After warming to room temperature (two hours) a black precipitate of Cp_2TiI_2 (0.81 mmol; 81%; IR; mass spectrometry) and a light yellow ether solution had formed. Evaporation of this solution gave benzaniline (0.85 mmol; 85%; IR; ^1H NMR).

Reaction of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ with CO_2

A solution of 0.50 mmol of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ in 30 ml of n-pentane was connected to a gas burette filled with CO_2 . The reaction started immediately with formation of a green precipitate of $[(\text{Cp}_2\text{Ti})_2(\text{CO}_3)]_2$ (0.38 mmol; 76%; IR) and CO (GC), and was complete after 30 minutes. Evaporation of the light-yellow n-pentane solution gave benzaniline (0.45 mmol; 90%; IR; ^1H NMR).

Reaction of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ with H_2

A solution of 4.00 mmol of $\text{Cp}_2\text{Ti} \cdot \text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ in 30 ml of ether was connected to a gas burette filled with H_2 . The reaction started immediately with formation of a brown-purple solution and was complete after 30 minutes. The solution was cooled to -78°C and an eightfold excess of HCl in H_2O was added, and the solution turned green (Cp_2TiCl). After addition of an excess of NaOH in 5 ml of H_2O and stirring for one hour with warming to room temperature, a white aqueous layer and a light yellow ether layer had formed. Evaporation of the ether layer gave benzyl(phenyl)amine (3.68 mmol; 92%; IR; ^1H NMR; mass spectrometry).

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