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Addition and Substitution Complexes of 2-Pyrrolidinone with Chloro and Alkoxo Titanium(IV) Derivatives

R. CHOUKROUN and D. GERVAIS

Laboratoire de Chimie de Coordination du CNRS, BP 4142, 31030 Toulouse Cedex, France

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When the γ lactam 2-pyrrolidinone (=LH) is reacted with members of the series $TiCl_{4-x}(OR)_x$ *where R = isopropyl or ethyl, either addition or substitution may occur depending on the value of x. The adducts* $TiCl_4\cdot LH$, $TiCl_4\cdot 2LH$, $TiCl_2(OR)_2\cdot LH$ *and* $TiCl_2(OR)_2\cdot 2LH$ *corresponding to x values of 0 and 2 may be isolated. In contrast, when x = 3 or 4 the N-substituted products* $TiCl(OR)_2L$ *and* $Ti(OR)_3L$ *are obtained.*

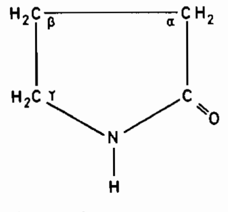
Infra-red and NMR (^1H *and* ^{13}C) *data are consistent with the involvement of the carbonyl group in the adduct formation and also possibly in dimerization of the substitution derivatives.*

The efficiency of, titanium Lewis acids as NMR shift reagents for lactams has been re-confirmed.

Introduction

Very little work has been so far reported on the reactions of lactams with titanium derivatives. Very recently, however, Jain [1] obtained 1,1 and 1,2 adducts of $TiCl_4$ with 1-methyl-2 pyrrolidinone and Bose used $TiCl_4$ as shift-reagent for ^{13}C and ^1H NMR spectroscopy of β-lactams [2, 3].

The present investigation describes the synthesis and structure of a series of chloro and alkoxo-titanium(IV) complexes with the γ-butyrolactam, 2-pyrrolidinone (=LH).



According to previously reported investigations, on reacting 2-pyrrolidinone with various derivatives of boron, cobalt, nickel, copper [4, 5] adducts were regularly obtained and the site of coordination was the oxygen of the carbonyl group. However, an example of substitution of hydrogen of the NH group was reported resulting in N-trimethylsilylation when 2-pyrrolidinone reacts with trimethylsilyl chloride. This was explained by the electron donating ability of the trimethylsilyl group [6].

In the series of chloro and alkoxo titanium compounds $TiCl_{4-x}(OR)_x$, the Lewis acidity was shown to vary considerably. The shielding of the titanium is markedly increased when a chlorine atom is replaced by an alkoxy group and, consequently, the ability to form Lewis complexes is decreased [7–9].

In the present work, it was found interesting to study the action of 2-pyrrolidinone on the series $TiCl_{4-x}(OR)_x$ and to determine the type of reaction involved: either formation of adducts or substitution of hydrogen with formation of the Ti–N bond.

Results and Discussion

Reaction of 2-Pyrrolidinone (LH) with $TiCl_4$ *and* $Ti(OR)_4$

With $TiCl_4$, the formation of adducts occurred. Depending upon experimental conditions (see below), $TiCl_4\cdot LH$ and $TiCl_4\cdot 2LH$ may be obtained as practically insoluble yellow solids, in good agreement with previously reported results for the action of 1 methyl 2-pyrrolidinone on $TiCl_4$ [1].

In contrast, by reaction with $Ti(OR)_4$ (R = isopropyl) a substitution reaction is observed which is unique in transition metal chemistry and is probably due to the lowering of Lewis acidity when chlorine is totally replaced by alkoxy group in the environment of the titanium atom. Moreover, only monosubstitution is possible and the compound $\llcorner\overline{(CH_2)_3C(O)N}Ti(OR)_3$ is obtained even when a large excess of 2-pyrrolidinone is employed. It is noteworthy that a Ti–O bond is replaced by a Ti–N bond in this process while the opposite is generally observed – as in the case of the action of ROH on $Ti(NR_2)_4$ [10, 11] – so that it appears that the Ti–N bond is much more stable in pyrrolydinyl derivatives than in alkylamido NR_2 analogues. This conclusion is also supported by the fact that we found it possible to substitute NR_2 by pyrrolydinyl; when 2-pyrrolidinone was reacted on $Ti(OR)_3(NR)_2$, HNR_2 was evolved. Moreover, as would be expected, the substitution can also be obtained from methyl titanium compounds such as $\mathrm{CH_3Ti(OR)_3}$ with evolution of $\mathrm{CH_4}$.

To summarize, the substituted derivative $\mathrm{Ti(OR)_3L}$ may be obtained according to the general scheme

$$\mathrm{XTi(OR)_3} + \overline{\mathrm{(CH_2)_3C(O)N}}\mathrm{H\ (=LH)} \longrightarrow \overline{\mathrm{(CH_2)_3C(O)N}}\mathrm{Ti(OR)_3\ (=Ti(OR)_3L) + XH} \quad (1)$$

with X = OR, $\mathrm{NR_2}$, $\mathrm{CH_3}$ (but not with X = Cl as will be seen later).

$\mathrm{Ti(OR)_3L}$, a soluble colourless solid, was characterized by elemental analysis and by identification of XH. Cryoscopically, it was found monomeric but a tendency to dimerize was observed in the more concentrated solutions.

Reaction of LH with $TiCl_{4-x}(OR)_x$ (x = 1–3)

The situation is a little more complicated in the case of these mixed derivatives because disproportionation can possibly occur. This is well exemplified by $\mathrm{TiCl(OR)_3}$ (R = isopropyl) for which either substitution or disproportionation takes place depending upon the experimental conditions.

When benzene is used as solvent, the substitution of an alkoxy group by pyrrolidinyl occurs with evolution of alcohol in a way very similar to scheme 1 for $\mathrm{Ti(OR)_4}$. It is noteworthy that in this process the TiOR bond is more easily cleaved than the TiCl one, according to the scheme

$$\mathrm{TiCl(OR)_3 + LH} \begin{array}{ll} \nearrow \mathrm{Ti(OR)_3L + HCl} & (2) \\ \searrow \mathrm{TiCl(OR)_2L + ROH} & (3) \end{array}$$

The same product $\mathrm{TiCl(OR)_2L}$ can also be prepared by reacting acetyl chloride with $\mathrm{Ti(OR)_3L}$ as indicated by the following equation:

$$\mathrm{Ti(OR)_3L + CH_3C(O)Cl} \longrightarrow \mathrm{TiCl(OR)_2L + CH_3C(O)OR} \quad (4)$$

$\mathrm{TiCl(OR)_2L}$, a yellow viscous product, was characterized by elemental analysis and by identification of the alcohol (3) and the acetate (4). Cryoscopically, it was found to be a dimer.

On the other hand, when the reaction is carried out in $\mathrm{CH_2Cl_2}$, precipitation occurs on addition of pentane, owing to the formation $\mathrm{TiCl_2(OR)_2{\cdot}2LH}$, according to the sehcme

$$\mathrm{2TiCl(OR)_3 + 2LH} \longrightarrow \mathrm{TiCl_2(OR)_2{\cdot}2LH + Ti(OR)_4} \quad (5)$$

$\mathrm{TiCl_2(OR)_2{\cdot}2LH}$, obtained as colourless crystals, soluble in usual solvents ($\mathrm{C_6H_6}$, $\mathrm{CHCl_3}$ but not in pentane) was characterized analytically.

As may be expected from the above results, formation of adducts occurred with derivatives with more than one chlorine bonded to titanium. So, with $\mathrm{TiCl_2(OR)_2}$ (R = isopropyl) an adduct was prepared, $\mathrm{TiCl_2(OR)_2{\cdot}LH}$, as a glassy solid.

Finally, with $\mathrm{TiCl_3(OR)}$ (R = ethyl) a disproportionation still took place:

$$\mathrm{2\,TiCl_3(OR) + 2LH} \longrightarrow \mathrm{TiCl_4{\cdot}2LH + TiCl_2(OR)_2} \quad (6)$$

The insoluble adduct $\mathrm{TiCl_4{\cdot}2LH}$ was precipitated and analytically characterized while $\mathrm{TiCl_2(OR)_2}$ was identified in the filtrate.

In conclusion, 1,1 and 1,2 adducts were obtained in the case of $\mathrm{TiCl_4}$ and $\mathrm{TiCl_2(OR)_2}$ and the substitution of one alkoxy group was obtained in the case of $\mathrm{Ti(OR)_4}$ and $\mathrm{TiCl(OR)_3}$.

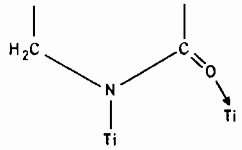
Infrared Spectra (Table II)

Of adducts

As previously reported, the formation of adducts of 2-pyrrolidinone [4, 5] and 1-methyl-2pyrrolidinone [1] is accompanied by a shift of the CO carbonyl stretching vibration toward lower energies, consistent with the assumption that oxygen is the donor atom. For example, in the case of 1,1 and 1,2 adducts of $\mathrm{TiCl_4}$ with 1-methyl-2-pyrrolidinone [1] the shift is *ca.* 70 $\mathrm{cm^{-1}}$ (from 1688 $\mathrm{cm^{-1}}$ for the free ligand to 1620 $\mathrm{cm^{-1}}$). In this work, very similar results were obtained for $\mathrm{TiCl_4{\cdot}LH}$ as well as for $\mathrm{TiCl_4{\cdot}2LH}$; the CO peak was found at 1620 $\mathrm{cm^{-1}}$ (shift 70 $\mathrm{cm^{-1}}$) while in the case of 1,1 and 1,2 adducts of $\mathrm{TiCl_2(OR)_2}$, the shift is slightly less (50 $\mathrm{cm^{-1}}$) and the peak is found at 1640 $\mathrm{cm^{-1}}$.

Of substitution products

$\mathrm{Ti(OR)_3L}$ in dilute solutions, either in dichloromethane or in benzene, may be studied in monomeric form. The CO stretching vibration is found unchanged at 1690 $\mathrm{cm^{-1}}$. But as the concentration of the solution is progressively increased, another band appears and gains intensity at 1655 $\mathrm{cm^{-1}}$. This new band is thought to be due to the dimerization of the complex by coordination of the free carbonyl of the pyrrolidinyl ligand of a substituted molecule with the titanium atom of another molecule and we tentatively suggest the bridged structure:



Very similar results were obtained and similar interpretations are proposed in the case of $\mathrm{TiCl(OR)_2L}$ which is almost completely dimerized: two bands are

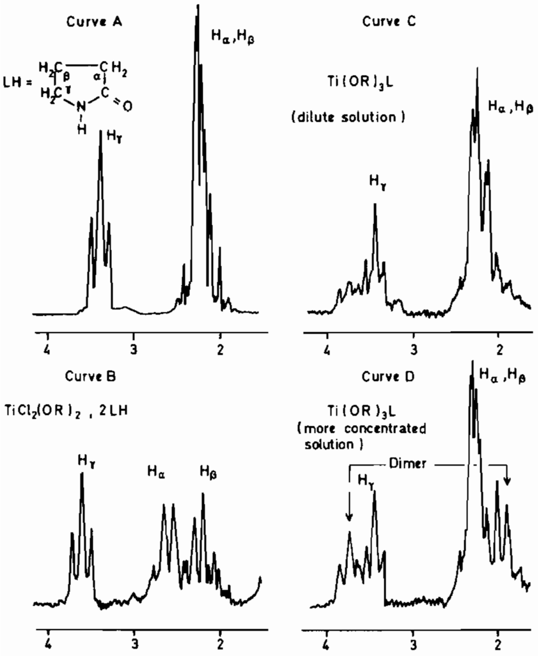


Figure 1. ^{1}H resonance of α, β and γ CH_2 groups of 2-pyrrolidinone (=LH). Curve A: free ligand; curve B: 1,2 adduct with $TiCl_2(OR)_2$ (R = isopropyl); curves C and D: N-substituted derivative (obtained from $Ti(OR)_4$) either monomer (C) or partially dimerized (D).

observed at 1700 and 1650 cm^{-1} and the latter one is the more intense. Furthermore, it is noteworthy that in these cases, absorptions appeared at 1570, 1545 cm^{-1} for $Ti(OR)_3L$ and 1560, 1535 cm^{-1} for $TiCl(OR)_2L$, which are not easily assigned by comparison with the spectra of the reacting species. We tentatively assign them to the CN bond stretching mode which is consistent with its higher multiplicity and an increased delocalization in substitution complexes, specially in the dimeric ones.

^{13}C NMR Spectra (Table III)

Of adducts

NMR spectra of adducts of $TiCl_4$ could not be recorded, due to their very poor solubility. In the spectra of the adducts of $TiCl_2(OR)_2$ the ^{13}C resonance of the carbonyl group is shifted downfield (4.5 ppm) slightly less markedly than the $TiCl_4$ induced shifts observed by Bose [3] for β-lactams (8.3 to 5.0 ppm). α, β and γ-CH_2 carbon resonances are also shifted downfield but not to such a large extent (1.0 to 4.2 ppm).

Of substitution derivatives

For $Ti(OR)_3L$ monomer, the carbonyl peak is found practically unchanged at 177.4 ppm. More surprisingly, only very slight shifts are observed for the CH_2 carbons (in the literature, there are no available data for the comparison). For $TiCl(OR)_2L$ dimer, the downfield shifts are similar to our previous observations for adducts, in good agreement with the assumption that dimerization occurs through bridging carbonyl groups.

^{1}H NMR Spectra (Table IV)

Of adducts

In $TiCl_2(OR)_2 \cdot LH$ and $TiCl_2(OR)_2 \cdot 2LH$, ^{1}H resonance of NH was found at 8.40 and 8.65 ppm, respectively (7.84 in the free ligand). The γ-CH_2 resonance appeared as a triplet at *ca.* 3.63 and 3.60 ppm (3.40 in the free ligand). The α and β-CH_2 which gave an unresolved multiplet (2.25–2.15 ppm) in the free ligand are more distinctly separated in the complexes so that we can assign for the 1,1 adduct 2.70 (Hα) and 2.20 (Hβ) and for the 1.2 adduct 2.58 (Hα) and 2.18 (Hβ) (Figure 1, curve B *versus* curve A).

There are some analogies between our results and those reported by Dini [12] in the case of adducts of ε-caprolactams with $PtCl_2$ and $RhCl_3$. Moreover, the $TiCl_2(OR)_2$ induced shifts of the γ protons of 2-pyrrolidinone are similar (although slightly lower) to those induced by $TiCl_4$ on those of β-lactams (0.50 to 0.60 ppm) [2]. We think that, for γ-lactam, a further interest in using titanium derivatives as shift reagents lies in their ability to separate the α and β methylene resonances which are superimposed in the free ligand.

Of substitution derivatives.

For $Ti(OR)_3L$ monomer, except for the expected absence of the NH peak, the spectrum is not very different from that of LH: Hγ at 3.42 ppm (3.40 in LH), Hα and Hβ at *ca.* 2.30–2.20 (2.25–2.15 in LH). By progressively increasing the concentration in $Ti(OR)_3L$, we were able to attribute some new peaks to the dimer $[Ti(OR)_3L]_2$ (Figure 1. Curves C and D). The more striking feature of the new spectra is a marked downfield shift peak of the Hγ in the dimer (3.72 ppm). This value is very similar to the result obtained for the adducts (curve B), consistent with the involvement of the carbonyl group in dimerization. Equally consistent with this assumption, the spectrum of $TiCl(OR)_2L$ dimer exhibited a downfield shifted peak (3.57 ppm) for Hγ. We also note, in good agreement with this interpretation, that for both the dimeric species the separation of Hα and Hβ is clearly greater than for the free ligand and is observed between 1.8 and 2.5 ppm, instead of the narrow multiplet at 2.30 ppm.

General Comments

In the series $TiCl_{4-x}(OR)_x$, the decreasing acidity of the Lewis acid as x is increased from x = 0 ($TiCl_4$) to x = 4 ($Ti(OR)_4$) is well illustrated when studying

TABLE I. Analytical Data of Complexes of LH (2-Pyrrolidinone) with $TiCl_{4-x}(OR)_x$.

Compound	From Reaction	% C exp (theor.)	% H exp (theor.)	% N exp (theor.)	% Cl exp (theor.)	% Ti exp (theor.)
$Ti(OR)_3L$	$Ti(OR)_4$ + LH	50.2 (50.3)	8.8 (8.7)	4.2 (4.5)		15.6 (15.5)
$Ti(OR)_3L$	$CH_3Ti(OR)_3$ + LH	46.5 (50.3)	8.5 (8.7)	4.5 (4.5)		15.5 (15.5)
$TiCl(OR)_2L$	$TiCl(OR)_3$ + LH	42.0 (42.0)	7.3 (7.0)	4.7 (4.9)	12.3 (12.4)	16.2 (16.7)
$TiCl(OR)_2L$	$Ti(OR)_3L + CH_3COCl$	42.3 (42.0)	7.4 (7.0)	4.5 (4.9)	12.5 (12.4)	
$TiCl_2(OR)_2 \cdot LH$	$TiCl_2(OR)_2$ + LH	35.9 (37.3)	6.3 (6.5)	4.9 (4.3)	22.1 (22.0)	15.4 (14.9)
$TiCl_2(OR)_2 \cdot 2LH$	$TiCl(OR)_3$ + LH	41.0 (41.3)	6.9 (6.9)	6.9 (6.9)	17.1 (17.4)	11.9 (11.8)
$TiCl_4 \cdot LH$	$TiCl_4$ + LH	17.5 (17.5)	2.5 (2.5)	5.0 (5.0)	51.4 (51.7)	17.4 (17.4)
$TiCl_4 \cdot 2LH$	$TiCl_4$ + 2LH	27.2 (26.6)	3.9 (3.9)	7.8 (7.8)	38.7 (39.4)	13.3 (13.3)
$TiCl_4 \cdot 2LH$	$TiCl_3OEt$ + LH	27.4 (26.6)	4.0 (3.9)	7.7 (7.8)	36.2 (39.4)	13.4 (13.3)

the action of the γ-butyrolactam, 2-pyrrolidinone. As a matter of fact, formation of adducts (involving oxygen of the carbonyl group) is only possible with $x \leqslant 2$, while with $x = 3, 4$ substitution occurs – quite an original result in transition metal chemistry. Moreover, the coordination insaturation of these substituted derivatives results in a tendency to dimerize much more markedly for the chloro derivative $TiCl(OR)_2L$ than for the trialkoxo derivative $Ti(OR)_3L$. The spectroscopic data can be interpreted assuming that dimerization involves the carbonyl group.

Furthermore, $TiCl_2(OR)_2$ may be used as an effective shift reagent in the study of γ-lactams by NMR as $TiCl_4$ was found to be useful as reagent for β-lactams.

Experimental

Starting Materials

The ligand 2-pyrrolidinone, from Eastman, was used without further purification. $TiCl_4$ and $Ti(Oi\text{-}Pr)_4$, from Fluka A.G., were purified by distillation. $TiCl_{4-x}(OR)_x$ (with R = isopropyl or ethyl), $(CH_3)Ti(Oi\text{-}Pr)$ and $Ti(OiPr)_3(NEt_2)$ were prepared and purified according to the literature methods [17–19].

All solvents (benzene, toluene, dichloromethane) were dried by means of sodium wire or molecular sieve.

Syntheses, purifications and manipulations were carried out under dry dinitrogen atmosphere.

Physical Measurements

Infrared data were obtained in the range 4000–400 cm^{-1}, using a Perkin–Elmer spectrophotometer (model 557) and KBr plates. Spectra were determined as Nujol mulls or as solutions in dichloromethane or benzene, depending on the solubility of the product.

Proton NMR spectra were obtained from a Perkin–Elmer R12 spectrophotometer at 33 °C, using deuterochloroform solutions with TMS as the internal standard.

^{13}C NMR spectra were obtained from a Fourier transform spectrometer (Bruker WH90), operating at room temperature, with complete noise decoupling of the protons. All the spectra were registered for deuterochloroform solutions and are referenced to TMS, considering the ^{13}C resonance of $CDCl_3$ at 76.9 ppm.

Molecular weight determinations were made cryoscopically in benzene and cyclohexane.

Conductivity measurements were obtained from benzene solutions, with a Philips PW950 conductivity bridge and a conductivity cell with platinum electrodes.

C, H, N, Cl, Ti analyses were performed by the Service Central de Microanalyse du CNRS (Thiais, France).

TABLE II. Infrared Data of Complexes of LH (2-Pyrrolidinone) with $TiCl_{4-x}(OR)_x$.

$LH^{a,b}$	$Ti(OR)_3L$	$TiCl(OR)_2L$	$TiCl_2(OR)_2 \cdot LH$	$TiCl_2(OR)_2 \cdot 2LH$	$TiCl_4 \cdot LH$	$TiCl_4 \cdot 2LH$	Assignment
3224			3340	3300	3320	3300	$\nu(NH)^{a,b}$
1692	1690	1700	1640	1640	1620	1620	$\nu(C{=}O)^{a,b}$
	$(1655)^c$	1650					
	1570	1560					$\nu(C\text{---}N)$?
	1550	1550–1535					

[a] According to ref. 4. [b] In good agreement with ref. 13. [c] Found for concentrated solutions.

Preparation of the Complexes

The analytical data are listed in Table I.

Preparation of $Ti(OR)_3L$

Reaction between $Ti(OisoPr)_4$ and LH. a) in stoichiometric quantities: to $Ti(OisoPr)_4$ (5.40 g, 19 mmol) in 15 ml CH_2Cl_2 was added LH (1.61 g, 19 mmol) in 5 ml CH_2Cl_2, at room temperature. After 1 hour stirring, the solution was left overnight at −30 °C. White crystals were isolated by filtration and dried under reduced pressure. Evolved isoPrOH was trapped and characterized by ^1H NMR. Three crystallizations from CH_2Cl_2 at −30 °C were necessary to give a pure product. Yield: 60%. $Ti(OisoPr)_3L$ is soluble in solvents such as benzene, pentane but less soluble in carbon tetrachloride. Molecular weight data (over a wide concentration range: 40–200 m*M*) show a degree of association of $1 < n < 1.3$ in benzene and $1.2 < n < 1.6$ in cyclohexane. The complex was found to be a non-electrolyte.

b) using an excess of LH: a mixture of $Ti(OisoPr)_4$ (1 equiv) and LH (2 or 3 equiv) under the conditions described above, still led to white crystalline $Ti(OisoPr)_3L$.

Reaction between $CH_3Ti(OisoPr)_3$ and LH: to $CH_3Ti(OisoPr)_3$ (2.58 g, 10.7 mmol) in 5 ml CH_2Cl_2 was added LH (0.91 g, 10.7 mmol) in 5 ml CH_2Cl_2 at room temperature. Elimination of the methyl group as methane was observed. After 1 hour stirring, the yellow solution was cooled to −30 °C overnight and $Ti(OisoPr)_3L$ appeared as white crystals.

Reaction between $Ti(OisoPr)_3(NEt_2)$ and LH: to a solution of $Ti(OisoPr)_3(NEt_2)$ (1.22 g, 4.5 mmol) in 5 ml CH_2Cl_2 at −30 °C, was added LH (0.35 g, 4.5 mmol) in 2 ml CH_2Cl_2. A red colour developed and then turned yellow when room temperature is reached. The solvent was removed and trapped, under reduced pressure, and diethylamine was characterized by ^1H NMR spectra. $Ti(OisoPr)_3L$ was obtained as white crystals by crystallization of the residue in 5 ml CH_2Cl_2 at −30 °C.

Preparation of $TiCl(OisoPr)_2L$

Reaction between $TiCl(OisoPr)_3$ and LH: to $TiCl(OisoPr)_3$ (5.7 g, 20 mmol) in 20 ml C_6H_6 was added 1.85 g LH (20 mmol). The bright yellow solution was stirred for 1 hour and the solvent removed under reduced pressure (isoPrOH was characterized by ^1H NMR spectra). The yellow viscous paste obtained was washed with hexane and dried at 60 °C under reduced pressure. Yield: 90%. $TiCl(OisoPr)_2L$ was found to be soluble in benzene and dichloromethane. Molecular weight data in benzene (concentration range: 40–100 m*M*) and conductivity measurement showed a constant degree of association $n \cong 1.8$ and the product to be non-ionic.

Reaction between $Ti(OisoPr)_3L$ and CH_3COCl: to $Ti(OisoPr)_3L$ (3.35 g, 10.8 mmol) in 10 ml C_6H_6, cooled at 0 °C, was added CH_3COCl (0.85 g, 10.8 mmol) in 5 ml C_6H_6. After 1 hour stirring, the solution was allowed to warm to room temperature. The solvent was removed and trapped: iso-propyl acetate was characterized by ^1H NMR spectra. The yellow viscous product left was washed with hexane and dried *in vacuo*. Yield: 90%.

Preparation of $TiCl_2(OisoPr)_2 \cdot LH$

Reaction between $TiCl_2(OisoPr)_2$ and LH: to $TiCl_2(OisoPr)_2$ (6.85 g, 28.9 mmol) in 10 ml CH_2Cl_2 was added LH (2.45 g, 28.9 mmol) in 5 ml CH_2Cl_2 at room temperature. Eliminating the solvent, a yellow viscous product was obtained, washed twice with hexane, dried *in vacuo* at 60 °C and transformed into a glassy yellow solid. Yield: 90%. This complex is soluble in benzene, dichloromethane, but insoluble in hexane. This compound is associated in benzene with $1.2 < n < 1.8$ (concentration range 20–90 m*M*) and non-ionic.

Preparation of $TiCl_2(OisoPr)_2 \cdot 2LH$

Disproportionation reaction between $TiCl(OR)_3$ and LH: to $TiCl(OisoPr)_3$ (5.27 g, 20.2 mmol) in 10 ml CH_2Cl_2 was added at room temperature LH (1.7 g, 20.2 mmol) in 5 ml CH_2Cl_2. After 1 hour stirring, the solvent was removed: a yellow viscous product was obtained. This product was soluble in pentane and transformed into a white precipitate in cooling.

TABLE III. NMR Data: ^{13}C Chemical Shifts of Complexes of LH (2-Pyrrolidinone) with $TiCl_{4-x}(OR)_x$[a].

Compound	LH				R = iso-propyl[c]	
	C=O	C_α	C_β	C_γ	CH	CH_3
LH[b]	177.6	28.2	18.4	40.0	–	–
$Ti(OR)_3L$	177.3	28.4	19.0	40.4	60.5	24.8
$TiCl(OR)_2L$	181.5	31.4	20.4	44.1	d	25.3
$TiCl_2(OR)_2 \cdot LH$	182.0	30.7	19.3	44.1	d	23.7
$TiCl_2(OR)_2 \cdot 2LH$	182.0	31.0	20.0	43.8	80.0	25.1

[a] δ in ppm downfield from TMS, in $CDCl_3$ solvent. [b] In good agreement with [14]. [c] For comparison in $Ti(OiPr)_4$: CH = 76.2, CH_3 = 26.5 according to [15]. [d] Not clearly apparent.

TABLE IV. NMR Data: ^{1}H Chemical Shifts of Complexes of LH (2-Pyrrolidinone) with $TiCl_{4-x}(OR)_x$[a].

Compound	LH		H_γ Triplet	NH(b)	R = iso-propyl	
	H_α	H_β			CH Septuplet	CH_3 Doublet
LH[c]	(2.25–2.15)[d]		3.40	7.84		
$Ti(OR)_3L$[e, f]	(2.30–2.20)[d]		3.42[e]	–	4.53[e]	1.24
$TiCl(OR)_2L$	2.60	2.25	3.57	–	4.88	1.33
$TiCl_2(OR)_2 \cdot LH$	2.70	2.20	3.63	8.40	5.05	1.43
$TiCl_2(OR)_2 \cdot 2LH$	2.58	2.18	3.60	8.65	5.15	1.35

[a] δ in ppm downfield from TMS, in $CDCl_3$ solvent. [b] Broad singlet. [c] In good agreement with the literature data [16]. [d] Unresolved narrowish multiplet. [e] Values in the table are for the monomer; in more concentrated solutions, we obtained for the dimer: septuplet 4.90; H_γ 3.72 and an upfield shifted H_α H_β multiplet at *ca.* 2.20. [f] For comparison in $Ti(OR)_3(NR_2)$: septuplet 4.50, doublet 1.22.

The precipitate was isolated by filtration and dried *in vacuo*. Crystallization of the white precipitate in pentane gave colorless crystals.

Preparation of $TiCl_4 \cdot LH$

Reaction between $TiCl_4$ and LH: to an excess of $TiCl_4$ (5.1 g, 26.8 mmol) in 20 ml of 1.1 mixture of C_6H_6–CH_2Cl_2 at 0 °C was added 1.5 g LH (17 mmol). A yellow solid was obtained. After 2 hours stirring, the precipitate was isolated by filtration, washed with C_6H_6 and dried under reduced pressure. This compound is insoluble in common organic solvents.

Preparation of $TiCl_4 \cdot 2LH$

Reaction between $TiCl_4$ and LH: to $TiCl_4$ (4.66 g, 24.5 mmol) dissolved in 10 ml toluene and cooled at 0 °C was added 2 LH (4.16 g, 49 mmol) in 5 ml toluene. A gummy product was obtained which was transformed, when agitated with a spatula, into a yellow powder. The solid was isolated by filtration, washed with toluene and dried *in vacuo*. The complex which is slightly soluble in dichloromethane, is insoluble in benzene, toluene and pentane.

Disproportionation reaction between $TiCl_3OEt$ and LH: to $TiCl_3OEt$ (2.29 g, 11.4 mmol) in 50 ml C_6H_6 at 0 °C was added LH (1.45 g, 11.4 mmol) in 10 ml C_6H_6: After 3 hours stirring, a yellow precipitate was obtained, isolated by filtration, washed with benzene and dried *in vacuo*. Yield: 70% ($TiCl_2(OEt)_2$ was characterized by ^{1}H NMR in the filtrate).

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