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ORGANOMETALLIC COMPLEXES AS CATALYSTS IN IONIC POLYMERIZATIONS*

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Abstract—The syntheses and properties of some organometallic complexes containing titanium and aluminium, which have been isolated by us in the pure state by crystallization from solvents, are here described. Whereas some of these complexes contain bridge chlorine atoms between titanium and aluminium, others do not contain halides in their molecules.

The catalytic properties exhibited by these complexes for the polymerization of ethylene and of α-olefins, are described.

Finally the nature of the co-ordinated anionic polymerizations and the causes of the stereospecificity in the polymerization of the vinyl monomers are discussed.

DURING the previous Symposium on the Chemistry of Co-ordination Compounds in Rome[1] we had given a report on the importance assumed by certain catalytic systems containing transition metals and metal–organic bonds, acting by a mechanism which has been defined by us as anionic co-ordinated.[2]

As it is known, the catalysts discovered by Ziegler belonging to that class had enabled him to prepare low-pressure linear polyethylene.[3] Working with Ziegler type catalysts, our School succeeded in discovering sterically differentiated polymers of α-olefins[4] and of diolefins.[5] Later we discovered highly stereospecific catalysts which enabled us to obtain crude polymers having a high content of crystallizable macromolecules.[6]

Several authors have given an interpretation of the mechanism of ethylene polymerizations, as well as of the stereospecific polymerizations of propylene based on the hypotheses of the structure of the catalytic complexes. These hypotheses, however, were not supported by direct, experimental proofs of the structure of the catalytic complexes. Some of these authors were only partially acquainted with our previous work.

It is, therefore, useful to report here on the structure and catalytic activity of several complexes having a well defined composition, containing titanium and aluminium, and isolated in the pure state by crystallization from solutions.

In papers already published or in press in Italian journals we describe in more detail their preparation, chemical properties and structure.

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* This communication was presented in a summarized form at the International Conference on Co-ordination Chemistry held in London, April 1959.

[1] G. Natta, *La Ricerca Scientifica* Suppl. **28**, (1958).

[2] G. Natta, *Experientia* Suppl. VII, 21 (1957).

[3] K. Ziegler, *Angew. Chem.* **67**, 426 (1955).

[4] G. Natta, P. Pino, P. Corradini, F. Danusso, G. Mazzanti, E. Mantica and G. Moraglio, *J. Amer. Chem. Soc.* 77, 1708 (1955); G. Natta, *Atti Accad. Naz. Lincei* **4**, (8), 61 (1955); G. Natta, P. Pino and G. Mazzanti, *Chim. e Industr.* **37**, 927 (1955).

[5] G. Natta and P. Corradini, *J. Polymer Sci.* **20**, 251 (1956); G. Natta, P. Corradini and L. Porri, *Rend. Accad. Naz. Lincei* **20**, (8), 728 (1956); G. Natta, L. Porri, P. Corradini and D. Morero, *Rend. Accad. Naz. Lincei* **20**, (8), 560 (1956).

[6] G. Natta, P. Pino and G. Mazzanti, *Brevetto Ital.* 526. 101; G. Natta, P. Pino, G. Mazzanti and P. Longi, *Gazz. Chim. Ital.* **87**, 570 (1957).

I. *Crystallizable Complexes Containing Titanium and Aluminium*

(a) *Complexes having the general formula* $(C_5H_5)_2TiCl_2AlR_1R_2$ *in which* R_1 *and* R_2 *are chlorine atoms or ethyl groups*

We have prepared three different complexes belonging to this class.[7] In Table 1 their overall formulae and physical properties are indicated. All complexes are highly soluble in aromatic solvents and can be crystallized from n-heptane. The three complexes referred to above were prepared by us in two different ways:

TABLE 1. PHYSICAL PROPERTIES OF COMPLEXES OF THE GENERAL FORMULA $(C_5H_5)_2TiCl_2AlR_1R_2$ WHERE R_1 AND R_2 ARE CHLORINE ATOMS OR ETHYL GROUPS)

Complex	Melting temperature (°C)	Magnetic moment B.M.
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	126–130	1·70
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	88–92	1·57
$(C_5H_5)_2TiCl_2AlCl_2$	155–160	1·72

(1) By reacting *bis*(cyclopentadienyl) titanium dichloride with an excess of aluminium alkyl compound,(7) according to the following:

$$(C_5H_5)_2TiCl_2 + Al(C_2H_5)_3 \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)_2 + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6$$

$$(C_5H_5)_2TiCl_2 + Al(C_2H_5)_2Cl \rightarrow (C_5H_5)_2TiCl_2AlC_2H_5Cl + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6$$

$$(C_5H_5)_2TiCl_2 + AlC_2H_5Cl_2 \rightarrow (C_5H_5)_2TiCl_2AlCl_2 + \tfrac{1}{2}C_2H_4 + \tfrac{1}{2}C_2H_6$$

(2) By reacting *bis*(cyclopentadienyl) titanium monochloride respectively with diethyl-aluminium-monochloride, ethyl-aluminium-dichloride or aluminium-trichloride,[8] as follows:

$$(C_5H_5)_2TiCl + ClAl(C_2H_5)_2 \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)_2$$

$$(C_5H_5)_2TiCl + ClAl(C_2H_5)Cl \rightarrow (C_5H_5)_2TiCl_2Al(C_2H_5)Cl$$

$$(C_5H_5)TiCl + AlCl_3 \rightarrow (C_5H_5)_2TiCl_2AlCl_2$$

The study of the chemical properties of these complexes and the X-ray examination of their lattice structure carried out on single crystals, enabled us to conclude that the two cyclopentadienyl nuclei are bound to the titanium atom, while the latter is bound to aluminium through two bridge chlorine atoms.

From all the above-mentioned complexes it is possible, by treatment with anhydrous hydrochloric acid, to recover *bis*(cyclopentadienyl) titanium dichloride[7] in high yield.

The presence of chlorine bridges, similar to those existing in other electron-deficient molecules, e.g. Al_2Cl_6 molecules, is confirmed by the reaction with trimethylamine.

If an excess of this compound is reacted, in heptane, with the complex $(C_5H_5)TiCl_2Al(C_2H_5)_2$, a precipitate is obtained which is formed by *bis*(cyclopentadienyl) titanium monochloride; after removal of the solvent by evaporation, the

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[7] G. Natta, P. Pino, G. Mazzanti and U. Giannini, *J. Amer. Chem. Soc.* **79**, 2975 (1957); G. Natta, P. Pino, G. Mazzanti and U. Giannini, *La Ricerca Sci.* Suppl. **28**, (1958).

complex of trimethylamine with Al-diethyl-monochloride $(CH_3)_3N \rightarrow Al(C_2H_5)_2Cl$ can be isolated by distillation (0·5 mm Hg; 79–80°).[8]

The structure of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ has been confirmed by the determination of its crystalline structure by X-ray examination.[9] As indicated in Fig. 1, the Ti–Al distance is about 3·54 Å, the Cp–Ti–Cp angles are 130° and the Ti–Cl–Al angles are about 90°. The unit cell constants are as follows:

$$a = 15{\cdot}77\ \text{Å};\ b = 14{\cdot}24\ \text{Å};\ c = 7{\cdot}54\ \text{Å}$$

space group P_{nma}

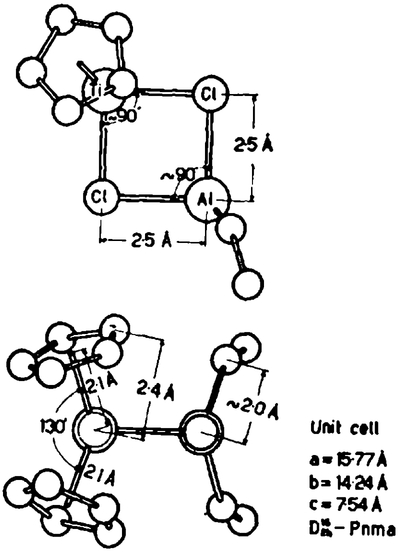

FIG. 1. Spatial model of the complex having formula: $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

X-ray investigations, for the other complexes of this class, confirm the existence of chlorine bridges in the molecule.

(b) *Complex* $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$

By reacting *bis*(cyclopentadienyl) titanium monochloride in benzene at 80° with aluminium triethyl in excess, a red solid product is obtained after removal of benzene, which can be purified by crystallization from n-heptane.[10]

The purified product (tabular crystals) is very soluble in aromatic hydrocarbons, melts (dec) at 169–171° and is diamagnetic.

The results of chemical analysis and the determination of molecular weight are in agreement with the formula $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$.[10]

The two cyclopentadienyl nuclei are bound to titanium. In fact, by treating an ether solution of this complex with HCl and chlorine, *bis*(cyclopentadienyl) titanium dichloride is recovered in good yields (95–97%). The X-ray examination on single crystals of this complex enabled us to establish that the molecule possesses a binary

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[8] G. Natta, P. Pino, G. Mazzanti and U. Giannini, In press.

[9] G. Natta, P. Corradini and I. W. Bassi, *J. Amer. Chem. Soc.* **80**, 755 (1958).

[10] G. Natta, G. Mazzanti, P. Corradini, U. Giannini and S. Cesca, *Atti Accad. Naz. Lincei* (8), **26**, 150 (1959).

axis of symmetry and that the Ti–Ti distance is 3·07 Å, while the Ti–Al distance is 2·83 Å. The Ti–Ti–Al angle is 91°40′ and the angle between the two Ti–Ti–Al planes is 100°30′/(Fig. 2).

(c) *Complexes* $Al_2TiCl_8C_6H_5$ *and* $AlTiCl_5C_6H_5$

A solid crystalline, violet complex, containing titanium and aluminium was isolated by a Friedel–Crafts reductive reaction on $TiCl_4$. The conditions adopted were similar to those used by Fischer for the preparation of transition metal complexes, in which the metal is bound to aromatic nuclei by means of bonds of the π-type.

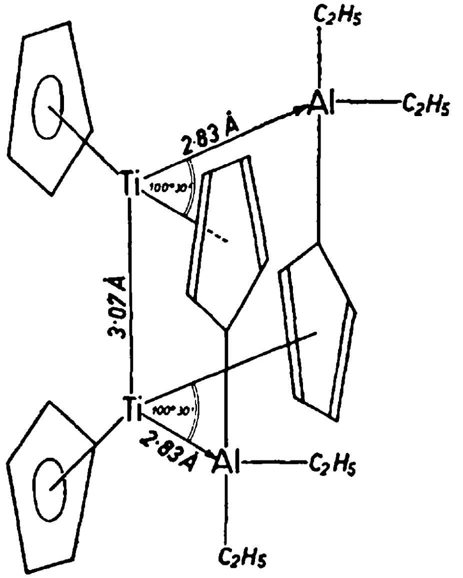

FIG. 2. Spatial model of the complex having formula: $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$

When the reaction was carried out between $TiCl_4$, $AlCl_3$, Al and benzene at 80° for several hours, a complex having an overall formula $Al_2TiCl_8C_6H_5$[11] was obtained. From Table 2, it can be seen that the composition of this product does not change when varying, within rather wide limits, the ratios between the moles of the various reactants used in its preparation. This complex melts at 110–115° (dec.) and is very soluble in benzene and toluene and only slightly soluble in aliphatic hydrocarbons. It undergoes a rapid change in presence of oxygen and moisture, giving hydrochloric acid and phenol.

It reacts exothermally with water in absence of oxygen yielding benzene. This behaviour agrees with the presence of phenyl groups bound to a metal by σ bonds.

By decomposition with dilute hydrochloric acid and titration with ferric sulphate it was established that titanium is present in the trivalent form.

When treating this complex, at room temperature or lower, with compounds containing lone electron pairs, such as e.g. tetrahydrofurane, dibutyl ether, pyridine

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[11] G. Natta, G. Mazzanti and F. Pregaglia, *Gazz. Chim. Ital.* In press.

or trimethylamine elimination of one molecule of $AlCl_3$ takes place. This fact might prove the presence in the complex of one $AlCl_3$ molecule linked in a labile way, in agreement with a formula of the type: $[AlTiCl_5C_6H_5]\cdot AlCl_3$.

If the reaction with tetrahydrofurane is carried out at higher temperature (50–60°C) and for longer time, the above mentioned complex undergoes considerable decomposition and, besides the tetrahydrofuranate of aluminium trichloride ($AlCl_3\cdot 2C_4H_8O$), it is possible to isolate a crystalline, green precipitate which proved to be a tetrahydrofuranate of titanium trichloride having the formula $TiCl_3\cdot 3C_4H_8O$.[11] By treatment of a toluene solution of $[AlTiCl_5C_6H_5]\cdot AlCl_3$ at $-60°$ with tetrahydrofurane, a microcrystalline precipitate is obtained, dark-red in colour, insoluble in aromatic and aliphatic hydrocarbons.

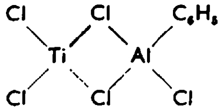
TABLE 2. COMPOSITION OF THE PRODUCT OBTAINED BY REACTING $TiCl_4$, Al, $AlCl_3$ AND BENZENE, AT 80°

Starting reagents					Time (hr)	Product obtained			
$TiCl_4$ (moles)	$AlCl_3$ (moles)	Al (moles)	C_6H_6 (moles)	Molar ratio $Ti/AlCl_3/Al/C_6H_6$		(1) Yields %	Al %	Ti %	Cl %
0·09	0·09	0·27	1·4	1 : 1 : 3 : 15	13	60	11·77 —	10·25 —	60·65 60·60
0·06	0·06	0·12	1·2	1 : 1 : 2 : 20	6	20	11·67 11·64	10·30 10·50	60·80 —
0·09	0·117	0·180	1·8	1 : 1·3 : 2 : 20	20	92	11·60 11·47	10·38 —	60·90 —
0·03	0·06	0·09	0·51	1 : 2 : 3 : 17	18	80	—	—	61·40
0·05	0·03	0·40	1	1 : 0·6 : 8 : 20	15	25	11·90	10·30	61·10
Calculated for $Al_2TiCl_8C_6H_5$							11·67	10·35	61·30

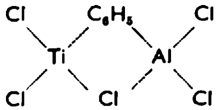
(1) = referred to $TiCl_4$

When operating with a deficiency of the electron donor reactant in respect to the amount of $AlCl_3$ the precipitate corresponds to the formula $TiAlCl_5C_6H_5$.[11]

Analytical results and chemical behaviour of these complexes agree with both the structural formulae:



(a)



(b)

Formula (a) appears to be much more probable, at least in the normal state, than (b) as the bridges are symmetrical in respect to the axis passing through the titanium and aluminium atoms.

In formula (a) titanium is bound to aluminium by means of chlorine bridges, similar to those already found in the crystallizable complexes having general formula $(C_5H_5)_2TiCl_2AlR_1R_2$.

II. *Nature of Complexes Containing Titanium and Aluminium*

Titanium generally presents a lower tendency to form complexes in comparison with the heavier transition metals belonging to the same period. Therefore it may be of interest to discuss the nature of the complexes prepared by us. Most correspond to lower degree of oxidation than the maximum; some of which are rather unusual for titanium. Certain titanium complexes, containing only one metal atom having a degree of oxidation 4, were already known, but the chief interest, from the viewpoint of catalysis, is shown by the complexes containing more than one metal atom in their molecule. A degree of oxidation 4 is found in the compound $(C_5H_5)_2TiCl_2$ which, by itself, does not behave as a catalyst acting with an anionic co-ordinated mechanism. Assuming that titanium having a degree of oxidation 4 receives six electrons from each cyclopentadienyl group and two electrons from each chlorine ion, the number of electrons given by the ligand groups is 16 and the total number of electrons is 34. The number of electrons of krypton is therefore approached, without being reached. A similar electronic configuration should be presented by the complex $(C_5H_5)_2Ti(C_6H_5)_2$ as the bonds between phenyl groups and titanium are of the σ type, in contrast with the cyclopentadienyl groups which are bound to titanium by means of σ–π bonds.

When the degree of oxidation of titanium decreases, a tendency appears to form complexes containing more than one metal atom. $TiCl_3$ and $TiCl_2$ as distinct from $TiCl_4$ (which is a liquid, non-ionic compound), have high melting points. Their known crystalline modifications are all characterized by a co-ordination number 6. They exhibit an ionic nature, greater than $TiCl_4$, though the large force fields due to the presence of ions of a strong electro-positive metal, having a low valence and small diameter, do cause a close co-ordination of chlorine ions and their compact packing (mostly hexagonal compact). Owing to the large diameter of chlorine atoms, such a packing exhibits voids in which titanium atoms can find place (in the different modifications of $TiCl_3$ and in $TiCl_2$).[12]

Only the titanium atoms on the edge of each layer formed by packing of one plane of Ti atoms between two planes of Cl atoms, are not completely co-ordinated and can bind themselves with other groups. This may explain an epytactic adsorption of aluminium alkyls or chloroalkyls, by which the electro-negative groups complete the co-ordination of peripheral titanium atoms, while the aluminium atoms (having a small diameter) can epytactically occupy the positions of the metal corresponding to a peripheral growth of the lattice of $TiCl_3$.[1]

Titanium complexes having a degree of co-ordination 6 are more stable in the solid state owing to the force fields of the crystal. Crystalline complexes stable even in solution, having a degree of co-ordination 8, are those corresponding to the general formula $(C_5H_5)_2TiCl_2AlR_1R_2$.

As already pointed out, the X-ray examination revealed the presence of bridge bonds between Ti and Al, a tetrahedral pattern for the four groups co-ordinated to Al and also a slightly distorted tetrahedral configuration of the two cyclopentadienyl groups together with the two chlorine atoms in relation to titanium. The 3-centre bridge bonds allow aluminium to assume an sp^3, and titanium a d^4sp^3 hybridization. Trivalent titanium possesses only one (unpaired) electron on d-orbitals, and this is the reason for paramagnetic properties shown by complexes of this type.

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[12] G. Natta, P. Corradini, I. W. Bassi and L. Porri, *Rend. Accad. Naz. Lincei* **24**, (8), 121 (1958).

The red complex $[CpTiCpAlR_2]_2$ appears to be of rather unusual structure. This is the very first case of a titanium complex corresponding to a degree of oxidation 1. The X-ray examination demonstrates the existence of two types of cyclopentadienyl groups: two of them, belonging to one type, are bonded by σ–π bonds to the Ti atoms, while the two others are linked to Al by means of σ–σ bonds (Fig. 2).

The position of the latter two cyclopentadienyl groups suggests that they may be bridge-linked both to titanium and to aluminium and furthermore are bonded by π bonds to titanium. The complex is diamagnetic owing to a probable Ti–Ti bond, confirmed by the small distance (3·1 Å) between the two Ti atoms. Furthermore, one can suppose that each Ti atom gives an electron pair to an Al atom, thus forming a bond of dative type.

A deeper X-ray study is being undertaken in our Institute; this study will better elucidate the structure of this complex, which also appears to be electron deficient.

III. *Catalytic Properties of Crystallizable Complexes Containing Titanium and Aluminium*

Table 3 shows that benzene solutions of the three complexes corresponding to the general formula $(C_5H_5)_2TiCl_2AlR_1R_2$ are able to promote, by themselves, ethylene polymerization yielding polymers of high molecular weight. However, the complex containing no alkyl groups exhibits an extremely low activity.

TABLE 3. CATALYTIC ACTIVITY OF COMPLEXES OF THE GENERAL FORMULA $(C_5H_5)_2TiCl_2AlR_1R_2$ (R_1 AND R_2 BEING —Cl OR $—C_2H_5$) IN THE POLYMERIZATION OF ETHYLENE AT 95° AND 40 ATM

Catalyst		Solvent		Time (hr)	Crystalline polyethylene (g)	Terminal groups found in the polymer
Type	moles	Type	cm³			
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	0·003	*n*-heptane	40	8	7	$—C_6H_5$
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	0·0035	*n*-heptane	40	8	8	$—C_6H_6$
$(C_5H_5)_2TiCl_2AlCl_2$	0·0046	toluene	50	21	3	$—C_5H_5$

In the case of complexes containing ethyl groups, it has been found, using C^{14} labelled alkyls, that each polymeric chain contains one of the ethyl groups initially present in the complex. On the other hand, in the case of the complex containing 4 chlorine atoms per molecule, we were able to establish, using C^{14} labelled cyclopentadienyl groups, the presence of these groups linked to the polymeric chains.[13] Ethylene polymerization by means of these complexes might, therefore, take place according to a mechanism similar to the one observed with catalysts acting by means of an anionic co-ordinated mechanism, by insertion of the monomeric molecules on a metal-organic bond which can be of the Al–C type or even of the Ti–C type.

However as far as it is known we cannot exclude that the polymerization of ethylene, by means of the above complexes, takes place only after the complex has been transformed into an activated form in which one bridge chlorine atom has

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[13] G. Natta, G. Mazzanti, U. Giannini, G. Pajaro and S. Cesca, In press.

been substituted by an alkyl group or by a cyclopentadienyl group. In this way the relatively low activity shown by these complexes could be explained.

The possibility that the chain growth in anionic co-ordinated polymerization takes place through insertion of a polarized monomeric molecule on a bridge of an electron deficient molecule containing alkyl bridge bonds, had been already considered by Natta.*

Later, a mechanism of this type was proposed also by other authors.[14] The lower activity of the complex not containing alkyl groups could be explained by the much higher energy of activation required for a bridge-like arrangement of the cyclopentadienyl nucleus (linked by π–σ bonds to titanium, in the non-activated state) between titanium and aluminium.

TABLE 4. CATALYTIC ACTIVITY OF COMPLEXES OF THE GENERAL FORMULA $(C_5H_5)_2TiCl_2AlR_1R_2$ (WHERE R_1 AND R_2 ARE —Cl OR —C_2H_5) IN THE POLYMERIZATION OF ISOBUTYL-VINYL-ETHER, IN TOLUENE SOLUTION, AT −78°

Catalyst	Monomer/catalyst molar ratio	Time (hr)	Conversion of the monomer (%)	[η]	Properties of the polymer
$(C_5H_5)_2TiCl_2AlCl_2$	400	2	97	2·03	91% insoluble in acetone; highly crystalline at X-rays.
$(C_5H_5)TiCl_2AlC_2H_5Cl$	300	3	34	2·15	55% insoluble in acetone, highly crystalline at X-rays.
$(C_5H_5)_2TiCl_2Al(C_3H_5)_2$	35	10	0	—	—

[η] = intrinsic viscosity in toluene at 30°

The hypothesis that catalytic activity is connected with an activated form of this type could explain the lack of catalytic activity of other titanium *bis*(cyclopentadienyl) compounds which are not able to form bridges in the molecule, such as *bis*(cyclopentadienyl) titanium dichloride, *bis*(cyclopentadienyl) titanium diphenyl or dimethyl, which do not alone promote ethylene polymerization.

By decreasing the number of alkyl groups in the complexes having the general formula $(C_5H_5)_2TiCl_2AlR_1R_2$, a cationic activity arises in these compounds, which enables them to promote, e.g. stereospecific polymerization of vinyl ethers (Table 4)[15]. In this case, contrary to what happens in ethylene polymerization, neither alkyl nor cyclopentadienyl groups initially bound to the catalytic complex, can be found in the polymer.

The complex $(C_5H_5)_2TiCl_2AlClC_2H_5$ is an interesting example of a catalyst able to promote stereospecific polymerisation through two different mechanisms, either cationic or anionic, depending on the ability of the monomers to polymerize by one or by the other mechanism.

The complex free of halogen atoms $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ can promote the polymerization of ethylene.[10]

As shown in Table 5, the polyethylenes contain high molecular weight fractions which, by X-ray examination prove to be highly crystalline and also low molecular weight fractions according to a wide dispersion in molecular weights.

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* Opening Lecture of the Congress of Pure and Applied Chemistry, Paris, July (1957);[1] and Lecture given in Rome at the Symposium on the Chemistry of Co-ordination Compounds.[1]

[14] F. Patat and H. Sinn, *Angew. Chem.* **70**, 496 (1958).

[15] G. Natta, G. Dall'Asta, G. Mazzanti, U. Giannini and S. Cesca, *Angew. Chem.* **71**, 205 (1959).

TABLE 5. CATALYTIC ACTIVITY OF THE COMPLEX $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ IN THE POLYMERIZATION OF ETHYLENE, IN THE PRESENCE AND IN THE ABSENCE OF $TiCl_3$, USING TOLUENE AS SOLVENT OF THE MONOMER

Organometallic compounds		$TiCl_3$ moles . 10^3	Polymerization conditions			Poly-ethylene (g)	Fractionation of the polymer					
Type	moles . 10^3		Tempera-ture (°C)	Pressure (atm)	Time (hr)		Ether extractable fraction (%)	Boiling heptane extractable fraction		Residue		
								(%)	[η]	(%)	[η]	Crystal-linity (%)
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	2·8	0	90	10	19	6·25	55	14·5	0·11	30·5	1·87	86
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	2·2	0	90	40	8	11·3	13·3	13·9	0·12	72·8	2·75	85
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	3·4	1·95	80	3	5	67·2	0·3	0·8	—	98·9	8·90	81
$Al(C_2H_5)_3$	6·5	2·08	80	3	5	82	0	1·4	—	98·6	8·45	84

[η] = intrinsic viscosity in tetraline at 135°

The $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$-$\alpha TiCl_3$ catalytic system polymerizes ethylene, yielding polymers having very high molecular weight and crystallinity (Table 5).

The same catalytic system promotes propylene polymerization at rates comparable with those obtained with the typical catalysts $Al(C_2H_5)_3$-$\alpha TiCl_3$, yielding polymers remarkably richer in isotactic macromolecules (not extractable by boiling n-heptane) (Table 6). These isotactic fractions possess higher molecular weights.[10]

The higher stereospecificity and higher degree of polymerization can be ascribed to the fact that chain transfers between the growing polymeric chains and the alkyl groups present in solution in the catalytic system, occur to a more limited extent in comparison with polymerization by means of the $Al(C_2H_5)_3$-$TiCl_3$ catalytic system. In fact, this reduced alkyl-transfer should be accompanied by a lower probability of inversion in steric configuration of the monomeric units entering the growing chain.[16]

TABLE 6. PROPYLENE POLYMERIZATION IN THE PRESENCE OF THE CATALYTIC SYSTEMS $TiCl_3$-$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$ AND $TiCl_3$-$Al(C_2H_5)_3$—POLYMERIZATION CONDITIONS: TEMPERATURE 75°C; PROPYLENE CONSTANT PRESSURE 5 ATM; TIME 7 HOURS

Catalyst			Solvent		Poly-propylene (g)	Average rate of polymerization $\frac{g\ C_3H_6}{g\ TiCl_3 . h}$	Isotactic polymers not extractable with boiling heptane	
Organometallic compounds		$TiCl_3$ moles $.10^3$	Type	cm^3			(%)	$[\eta]$
Type	moles $.10^3$							
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	4·15	3·7	toluene	250	20·9	5·7	94·5	3·96
$Al(C_2H_5)_3$	9·0	4·1	toluene	250	68·6	15·5	83·1	2·58
$[(C_5H_5)_2TiAl(C_2H_5)_2]_2$	2·45	2·6	n-heptane	300	45·6	16·2	93·0	6·99
$Al(C_2H_5)_3$	8·4	4·2	n-heptane	500	97	21·3	85·2	4·17

$[\eta]$ = intrinsic viscosity in tetraline at 135°C

TABLE 7. CATALYTIC ACTIVITY OF THE COMPLEX $[AlTiCl_5C_6H_5]\cdot AlCl_3$ IN THE POLYMERIZATION OF ETHYLENE—POLYMERIZATION CONDITIONS: TEMPERATURE 80°, INITIAL PRESSURE 25 ATM, TIME: 14 HOURS

$[AlTiCl_5C_6H_5]\cdot AlCl_3$ moles	Solvent		Polyethylene (g)	Fractionation of the polymer					
	Type	cm^3		Waxy polymers extractable with boiling acetone (%)	Boiling heptane extractable fraction		Residue		
					(%)	$[\eta]$	(%)	$[\eta]$	Crystallinity (%)
0·007	benzene	100	12·6	28·0	6·4	0·14	65·0	1·28	85
0·003	heptane	100	15·5	26·1	23·4	0·15	49·4	0·90	86

$[\eta]$ = intrinsic viscosity in tetraline at 135°C

The complex having the formula $(AlTiCl_5C_6H_5)\cdot AlCl_3$, dissolved in benzene or suspended in heptane, promotes ethylene polymerization yielding waxy, low molecular weight polymers together with solid polymers containing high molecular weight fractions, crystalline under X-ray examination[11] (Table 7).

In the I.R. spectra of the polyethylenes thus obtained, an absorption band at 14·33 μ, attributable to phenyl groups bound to the polymeric chains, is easily detectable. Although the formation of linear polyethylenes, in which at least a part of the chains contains, as terminal groups, the phenyl group initially bound in the

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[16] G. Natta, *Rend. Accad. Naz. Lincei* **24**, (8), 246 (1958).

complex, is to be ascribed to a polymerization mechanism of anionic type, the complex $(AlTiCl_5C_6H_5)\cdot AlCl_3$ exhibits also an acidic character. It can promote fast polymerization of propylene, yielding oily polymers, similar to the products of the polymerization of this monomer by means of $AlCl_3$ or $TiCl_4$. In this low molecular weight polypropylenes no phenyl group can be detected by I.R. analysis.

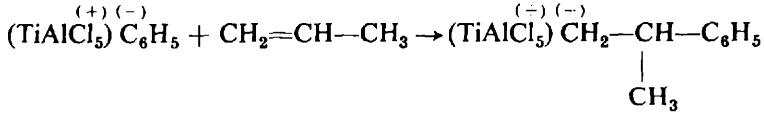
The solid, microcrystalline complex $AlTiCl_5C_6H_5$ promotes ethylene polymerization at a rate much higher than that observed with the complex $(AlTiCl_5C_6H_5)\cdot AlCl_3$, yielding polymers which are free of oily, low molecular weight fractions (Table 8).

In the I.R. spectra of fractions having the lower molecular weights (extractable by heptane), it was possible to detect the presence of phenyl groups bound to the polymeric chains.

This complex promotes the polymerization of propylene[11] (Table 8) but with an activity much lower than that of the most typical stereospecific catalysts[6] yielding linear polymers containing fractions made up of atactic macromolecules, stereoblock[17] fractions and fractions consisting of isotactic macromolecules.[4]

In the I.R. spectra of fractions having lower molecular weights (extractable by ether or by n-heptane) the presence of bands at 13, 16 and 14·33 μ was detected, attributable to benzylidene groups.

The initiation growth of the first polypropylene chains in the presence of complex $TiAlCl_5C_6H_5$ could therefore occur by addition of a monomeric molecule according to a reaction of the following type:



$$\overset{(+)}{(TiAlCl_5)}\,\overset{(-)}{C_6H_5} + CH_2{=}CH{-}CH_3 \rightarrow \overset{(+)}{(TiAlCl_5)}\,\overset{(-)}{CH_2}{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}C_6H_5$$

Transfer reactions with the monomer[18] may successively originate other polymeric chains, according to an anionic mechanism, as proposed by us for other catalysts acting in the stereospecific polymerization of propylene.[19]

IV. *Nature of Anionic, Co-ordinated Polymerization*

Already in previous papers we had exposed our points of view on the nature of anionic co-ordinated catalysis.

We shall limit ourselves to point out here the contribution brought by the study of the catalytic properties of the new metallorganic complexes of definite composition.

All catalytically active complexes contain in their molecule two metal atoms. When comparing these results with those obtained using the most typical catalysts of the Ziegler type, for which complexes of defined composition have not so far been isolated in a pure crystallizable form, it can be assumed that, also for these catalysts, the active components are formed by electron deficient metallorganic complexes, containing in their molecules at least two metal atoms.

Whereas ethylene polymerization can take place also with catalysts soluble in the polymerization medium, anionic co-ordinated polymerization of alpha-olefines takes place only with catalysts acting in the presence of a heterogeneous solid phase. In

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[17] G. Natta, G. Mazzanti, G. Crespi and G. Moraglio, *Chim. e Industr.* 39, 275 (1957).

[18] G. Natta, I. Pasquon, E. Giachetti and F. Scalari, *Chim. e Industr.* 40, 103 (1958).

[19] G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti and M. Peraldo, *Chim. e Industr.* 38, 124 (1956.)

TABLE 8. CATALYTIC ACTIVITY OF THE COMPLEX $AlTiCl_5C_6H_6$ IN THE POLYMERIZATION OF ETHYLENE AND OF PROPYLENE

$AlTiCl_5C_6H_6$ moles	Monomer	Polymerization conditions			Polymer (g)	Fractionation of the polymer						
						Ether extractable fraction (%)	Boiling heptane extractable fraction			Residue		
		Temperature (°C)	Pressure (atm)	Time (hr)			(%)	[η]	Crystallinity (%)	(%)	[η]	Crystallinity (%)
0·007	ethylene	85	20	3	114	0·25	1·1	0·11	80	98·65	9·0	87
0·004	propylene	110	25	16	24	80·3	10·85	0·89	45	10·15[a]	3·90	72

[a] In the case of polypropylene the residue after heptane extraction consists of isotactic macromolecules.

order that this polymerization results stereospecific, it is necessary that in the catalysts a crystalline structure or molecular aggregate having an ordered structure is present.

In catalysts containing titanium and aluminium, the same types of bridge bonds between the two metals are present, being the Ti atom either part of a soluble complex or present on the surface of a crystalline lattice.

In the latter case the initially incomplete co-ordination of titanium in certain peripheral regions of the lattice facilitates chemisorption of metal-organic compounds of strongly electropositive metals, having a small ionic radius (Al, Be, Mg).

Some authors,[20] stated that in polymerizations occurring in the presence of typical Ti–Al catalytic systems, the polymeric chains grow on titanium. According to these authors[20] we could not have foreseen this possibility and our statement referring to the growth of the polymeric chains on aluminium should be considered as incorrect. The possibility of existence of catalytic systems containing only titanium compounds had been previously demonstrated by us in preparing catalysts for the polymerization of ethylene and propylene by reacting *bis*(cyclopentadienyl) titanium diphenyl with $TiCl_4$. It can be assumed that, by means of this reaction, complexes containing at least two Ti atoms are formed.[21] In such cases the polymeric chain grows on a titanium atom (probably on the one which is more electropositive), or on a bridge between two Ti atoms. These catalysts have poor activity. A low activity is shown also by the catalysts obtained from methyl-titanium trichloride.[22] In order to have catalysts showing a high activity, the presence of another metal in the complex seems to be necessary.

The hypothesis that also in the case of catalysts prepared from titanium halides and Al–trialkyls the polymeric chain grows on a titanium–alkyl bond, disagrees with the following experimental results:

(1) The presence of phenyl groups, bound to the polymeric chains, has been ascertained in the case of ethylene polymerization by catalysts prepared from Al-triphenyl and $(C_5H_5)TiCl_2$. Terminal phenyl groups are not present in polyethylenes prepared with catalysts obtained from $(C_5H_5)_2Ti(C_6H_5)_2$ and Al-triethyl.[23]

(2) Investigations adsorbing $Al(C_2H_5)_3$ containing ^{14}C labelled alkyls on $TiCl_3$ and then polymerizing in the presence of non-labelled $Al(C_2H_5)_3$ proved that practically all the alkyl groups bound to aluminium previously adsorbed on α-$TiCl_3$ are found as terminal groups in polymeric chains. On the other hand it cannot be considered that all these alkyl groups were initially engaged in titanium alkylation.[24] Furthermore, at the polymerization end the major part of all the polymeric chains produced remain chemically bound to aluminium[25] as indicated by the chemical analysis of the polymerization products. This is probably due to a dissociation of each catalytic complex, in two parts, one containing the titanium atom, the other one containing alkyl groups (including polymeric chains) bound to aluminium. This dissociation is followed by an association involving other aluminium alkyls from the solution.

As previously mentioned, when dealing with the activity of complexes having

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[20] D. B. Ludlum, A. W. Anderson and C. E. Ashby, *J. Amer. Chem. Soc.* **80**, 1380 (1958); E. J. Badin, *Ibid.* **80**, 6545 (1958); D. S. Breslow and N. R. Newburg, *J. Amer. Chem. Soc.* **81**, 81 (1959).

[21] G. Natta, P. Pino, G. Mazzanti and R. Lanzo, *Chim. e Industr.* **39**, 1032 (1957).

[22] Belg. Pat. 553, 477.

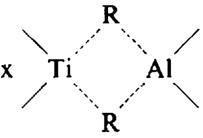
[23] G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *J. Polymer Sci.* **26**, 120 (1957).

[24] G. Natta, G. Pajaro, I. Pasquon and V. Stellacci, *Rend. Accad. Naz. Lincei* **24**, (8), 479 (1958).

[25] G. Natta, L. Giuffre' and I. Pasquon, *Rend. Accad. Naz. Lincei* **25**, (8), 417 (1958).

general formula $(C_5H_5)_2TiCl_2AlR_1R_2$, we cannot exclude that in the case of Ti–Al catalytic systems the polymerization occurs by insertion of the monomeric molecules into a bridge in which alkyl groups link Ti to Al by means of 3-centre bonds.

In such a case it is difficult to distinguish whether the chain grows on Ti or on Al.

It may be assumed that the partial ionic dissociation of a complex  takes place as indicated in Fig. 3.

A first step of association of the monomer with the transition metal, caused by the high electronic density of the double bond and by the electron deficiency of the transition metal, is admissible. Kinetic data with α-$TiCl_3$–$Al(C_2H_5)_3$ catalytic systems agree with this hypothesis. In this way an explanation is available for the fact that the rate of certain transfer processes and the rate of growing process are both of the same order in respect to the monomer concentration,[26] as they were two parallel reactions following the same intermediate state. This step should be followed by a polarization of the double bond, of the entering monomeric unit as indicated in Fig. 3.

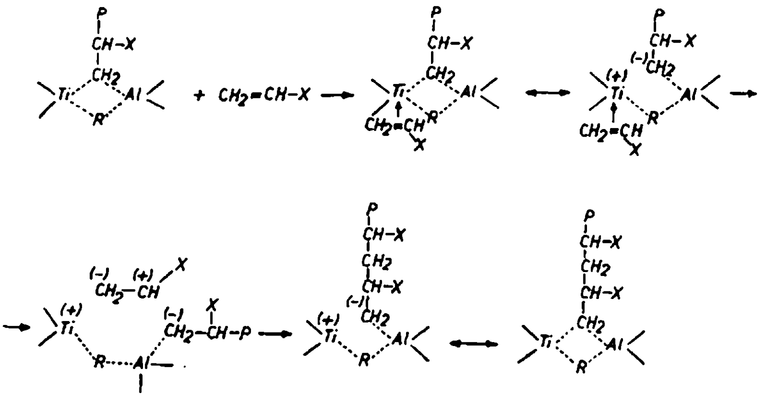


FIG. 3.

The chain growth must be ascribed to the neutralisation of the charge on the CHR group, belonging to the new monomeric unit, with the terminal CH_2 group of the polymeric chain, whilst it can be foreseen that the CH_2 group of the new monomeric unit links itself to the more electropositive metal, which is aluminium.

V. *Stereospecificity in Ionic Co-ordinated Polymerizations*

Many authors have interpreted our statement that stereospecific polymerization of alpha-olefines takes place only on catalysts acting in heterogeneous phase, should be extended also to the polymerization of other monomers.

It must be considered that our School was the first to obtain isotactic and syndiotactic polymers from diolefines and that these sterically regular polymers were prepared by means of soluble catalysts.[27] Furthermore, we have extended the

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[26] G. Natta, I. Pasquon and E. Giachetti, *Makrom. Chem.* **24**, 258 (1957).

[27] G. Natta, L. Porri and G. Zanini, *Chim. e Industr.* In press.

stereospecific polymerizations of vinyl ethers to some soluble catalysts[15] different from those proposed by Schildknecht.[28]

When the monomer contains two groups rich in electrons (two double bonds in diolefines or one double bond and one oxygen with a lone electron pair in the case of vinyl ethers) an association of the monomeric molecules with the electron deficient catalyst should be possible before the addition to the growing polymeric chains, even if the catalyst does not contain a heterogeneous phase, able to adsorb the monomer. In such cases a stereospecific polymerization can take place through soluble catalytic complexes.

In fact, soluble catalysts are the reaction product between chromium-acetylacetonate and Al-trialkyls used by us for the synthesis of isotactic and syndiotactic polymers of diolefines.[27]

Also soluble are the compounds having a weak cationic activity and able to form etherates [$(AlClR_2)_2$; $(AlCl_2R)_2$; $TiCl_2(OR)_2$] used by us for the cationic stereospecific polymerization of alkyl-vinyl-ethers.[15] Therefore, excluding the case of the polymerizations of α-olefines, stereospecific polymerizations are not necessarily connected with the presence of insoluble catalysts acting from the beginning of the polymerization in hererogeneous phase.

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[28] C. E. Schildknecht, A. O. Zoss and C. McKinley, *Industr. Engng. Chem.* **39**, 180 (1947); C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert and A. O. Zoss, *Ibid.* **40**, 2104 (1948); C. E. Schildknecht, A. O. Zoss, G. Grasser, *Ibid.* **41**, 2891 (1949).