

Reduction of (-)-Ie with $\text{NaBH}_4\text{-AlCl}_3$ to (-)-If (m.p. 95–97°, $[\alpha]^{27\text{D}} -25^\circ$ (EtOH); found: C, 62.0; H, 4.2; N, 10.3), followed by hydrogenation over Pd/C, afforded (-)-Ia (m.p. 153–158°, $[\alpha]^{26\text{D}} -49^\circ$ (EtOH)). The melting point, 232–233°, of the diacetamide, $[\alpha]^{30\text{D}} +134^\circ$ (EtOH), was undepressed by admixture of authentic⁶ diacetamide, m.p. 233–235°, $[\alpha]^{26\text{D}} +128^\circ$ (EtOH), prepared from authentic⁶ (-)-Ia, m.p. 156–158°, $[\alpha]^{24\text{D}} -47^\circ$ (EtOH), $+34^\circ$ (N HCl).⁷

(-)-Ia and (+)-DNDBCH-6-one have thus been correlated *via* (-)-Ie; (-)-Ia therefore⁴ has the S-configuration. It would appear that the assumptions underlying the theoretical treatment^{1,2} deserve re-examination.

The absolute configurations of the many common hindered biphenyls related⁸ to Ia and Ib will be listed in future publications.

(6) J. Meisenheimer and M. Höring, *Ber.*, **60**, 1425 (1927).

(7) The sign of rotation of Ia is pH dependent (F. A. McGinn, unpublished results).

(8) Cf. also K. Mislow, *Trans. N.Y. Acad. Sci.*, [2] **19**, 298 (1957).

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LEWIS ACID CHARACTER OF TELLURIUM HEXAFLUORIDE

Sir:

In a previous communication,¹ the formation of fluorotellurate salts from tellurium hexafluoride and certain alkali metal fluorides was described. We have now found that tellurium hexafluoride will react exothermally with tertiary amines to form stable adducts of the composition $\text{TeF}_6\text{-}2\text{R}_3\text{N}$. Analysis of the n-m-r data suggests that geometrical isomers are present in solutions of the trimethylamine complex.

Trimethyl- and triethylamines were added to tellurium hexafluoride in a vacuum system. The trimethylamine adduct was a white solid, but the ethyl analog had a dark color that apparently was due to minor secondary reactions. The pressure-volume relationships indicated a stoichiometry of two molecules of amine for one of the hexafluoride and analysis of the trimethylamine complex confirmed the indicated composition (*Anal.* Calcd. for $\text{TeF}_6\text{-}2\text{N}(\text{CH}_3)_3$: C, 20.0; H, 5.04; F, 31.7. Found: C, 19.56; H, 5.10; F, 29.14). Pyridine formed a complex that was highly dissociated at 25°, but amides, ethers and nitriles did not absorb tellurium hexafluoride at this temperature. This low acceptor strength and the previously cited¹ low stability of fluorotellurate salts indicate that tellurium hexafluoride is a relatively weak Lewis acid.

The F¹⁹ magnetic resonance spectrum of the molten trimethylamine adduct showed only one sharp peak; amine exchange through simple dissociation of the complex was therefore indicated. A dimethylformamide solution of the trimethylamine adduct gave a single broad resonance at 25°,

(1) E. L. Muetterties, *THIS JOURNAL*, **79**, 1004 (1957).

and at higher temperatures, the peak sharpened and shifted in the direction of the tellurium hexafluoride resonance. The amide solution was cooled to a glass that at $\sim -180^\circ$ displayed three broad resonances of approximate intensities 1:1:0.4. On warming above -180° , these three peaks broadened rapidly (but at different rates) and finally merged into a single peak. It should be noted that the weak doublet due to spin-spin coupling of fluorine with the Te¹²⁵ isotope persisted at 25° (masked at low temperatures by the broad resonances), and therefore no fluorine exchange was taking place in this system.

The n-m-r data are consistent with the behavior of an octavalent complex which has geometrical isomers and which undergoes amine exchange through simple dissociation of the complex. At $\sim -180^\circ$, the three fluorine resonances may be ascribed to the three possible isomers. On steric grounds, the two peaks of relative intensity 1 probably arise from the 1,8- and 1,3-isomers, and the peak of relative intensity 0.4 from the 1,2-isomer. Above $\sim -180^\circ$, slight dissociation of the complexes leads to amine exchange and this occurs at different rates for the three isomers. At higher temperatures the three isomers are indistinguishable in the n-m-r spectrum because of fast amine exchange. At temperatures above 25°, the complex is highly dissociated in solution and the position of resonance is a measure of the equilibrium constant for the dissociation. Without supporting data, these conclusions cannot be considered rigorously established. Unfortunately, the rapid amine exchange will not permit isolation of the postulated isomers by conventional techniques.

CONTRIBUTION No. 418

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A CRYSTALLIZABLE ORGANOMETALLIC COMPLEX CONTAINING TITANIUM AND ALUMINUM

Sir:

Following our previous researches¹ concerning the nature of the catalytic agent promoting the α -olefins polymerization, we have isolated a crystallizable compound containing titanium, aluminum and organometallic bonds, which causes the polymerization of ethylene.

By treating 0.01 mole of bis-(cyclopentadienyl)-titanium dichloride² suspended in 50 ml. of *n*-heptane with 0.025 mole of triethylaluminum at 70°, in the absence of air and of moisture, a slow gas evolution takes place, the titanium compound is dissolved and the solution becomes dark blue. By cooling the solution at -50° , a blue crystalline solid has been obtained in good yield.

The macroscopic blue needles of the compound, recrystallized four times from *n*-heptane, melt at 126–130° without appreciable decomposition.

(1) G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti and M. Peraldo, *La Chimica e l'Industria*, **38**, 124 (1956); G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *ibid.*, **39**, 19 (1957).

(2) G. Wilkinson and G. M. Birmigam, *THIS JOURNAL*, **76**, 4281 (1954).

The blue compound contains titanium, aluminum, chlorine and organic groups; from the elementary quantitative analysis a ratio Ti:Al:Cl = 1:1:2 has been found.

The values 331 and 339 have been calculated for the molecular weight of the blue compound from two different cryoscopic measurements in benzene.

By treating the blue product with 2-ethylhexanol, ethane is evolved; a quantitative gas volumetric determination shows that two moles of ethane are evolved per mole of compound.

By treating the product with anhydrous hydrochloric acid in ether solution bis-(cyclopentadienyl)-titanium dichloride is formed in almost quantitative yield (more than 90%).

The analytical data and the chemical behavior agree very well with a formula $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$, as shown in the table for $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

	Calcd.	Found	
Cl, %	21.22	21.02 ^a	20.78 ^a
Al, %	8.073	7.92	7.90 ^b
Ti, %	14.33	14.34	14.55 ^b
-C ₂ H ₅ , %	17.40	16.07	17.67 ^b
Mol. weight	334	331	339 ^a

It seems probable that, in the complex, both C₅H₅- groups are bound to the titanium atom and that both C₂H₅- groups are bound to the aluminum atom.

By polymerizing ethylene in heptane solution in the presence of 0.6 g. of the Ti-Al complex at 40 atm. and 95° after a reaction time of 20 hours, 8.4 g. of white polymer has been obtained, which has been fractionated by boiling solvent extraction (acetone extractable fraction 10.1%; ether extractable fraction 1.8%, carbon tetrachloride extractable fraction 17.20%, residue 70.9% having intrinsic viscosity in tetralin at 135° = 1.55 × 100 ml./g.).

As it is reported in the next table, $(C_5H_5)_2TiCl_2$ alone is completely inactive for the ethylene polymerization; $Al(C_2H_5)_3$, accordingly with previously published data,⁷ does not give solid polyethylene in the reaction conditions, but only low molecular weight oily polymers. Comparative experiments were carried out at 95° and 40 atm.

Soluble catalyst Type	Moles	Solvent Type	Cc.	Re-talline ac-poly-ethylation time, hours	ene, g.	Oily polymers, g.
$(C_5H_5)_2TiCl_2$	0.005	Benzene	100	20	0	0
$Al(C_2H_5)_3$.05	n-Heptane	300	8	0	11.07 ^a
$(C_5H_5)_2TiCl_2$ - $Al(C_2H_5)_3$.003	n-Heptane	40	8	7	0.4

^a 66% of the product consists of hydrocarbons lower than decane.

(3) Decomposition of the complex by H₂SO₄ 5%; titanium has been determined as titanium cupferrate, aluminum as 8-oxyquinoline, chlorine by gravimetric determination (I. Ubaldini and F. Capizzi, *Chimica e Industria*, **37**, 779 (1955)).

(4) Decomposition of the complex by Na₂O₂; chlorine has been determined by the Volhard titration.

(5) By gas volumetric determination.

(6) By cryoscopic determination in benzene solution.

(7) G. Natta, P. Pino, and M. Farina, *Supplemento Ric. Scient.*, **25**, 120 (1955).

Although the complex is a catalyst for the ethylene polymerization, less active than the catalyst prepared from TiCl₄ and Al(C₂H₅)₃, the composition of the complex strongly supports the hypothesis that the Ziegler type catalysts⁸ for the polymerization of ethylene are, generally, bimetallic complexes containing organometallic bonds.

(8) K. Ziegler, Belgian Patent 533,362; K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

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A NOVEL REARRANGEMENT IN THE 5-NITRONORBORNENE SERIES

Sir:

The failure of salts of 5-nitronorbornenes (Ia, R = H¹; Ib, R = CH₃²; Ic, R = C₆H₅^{3,4}; shown in the aci form) to undergo the Nef reaction⁵ has been attributed⁶ to homoallylic⁷ resonance stabilization (I ↔ II) of the aci forms. We find, however, that, although a ketone is not obtained, Ia does yield a nitrogen-containing transformation product under Nef reaction conditions.

Addition of an ice-cold aqueous methanolic slurry of the sodium salt of Ia to 8.5% (by wt.) hydrochloric acid at -20 to -10° gave in 30-37% yields a rearrangement product (VI), m.p. 104.5-106.5°, isomeric with 5-nitronorbornene. *Anal.* Calcd. for C₇H₉NO₂ (139.15): C, 60.42; H, 6.52; N, 10.07. Found: C, 60.71; H, 6.63; N, 10.04; mol. wt. (Rast) 150. γ_{NH} 3380, 3150; $\gamma_{C=O}$ 1667; γ_{C-C-H} 3040; $\gamma_{C=C}$ 1616 (shoulder) cm.⁻¹ in CHCl₃. As is true with hydroxamic esters,⁸ VI and VII do not give a color test with ferric chloride and are weakly acidic; they can be extracted with ether from 10% sodium bicarbonate solution but not from 20% sodium hydroxide; they are regenerated upon acidification.

Hydrogenation of pure VI over platinum oxide at 2 atm. consumed 1.00 mole of hydrogen and gave in 96% yield a dihydro derivative (VII), m.p. 43-46°, n_D^{20} 1.5065 (on the supercooled liquid). *Anal.* Calcd. for C₇H₁₁NO₂: C, 59.55; H, 7.85; N, 9.93. Found: C, 59.41; H, 7.79; N, 9.68. γ_{NH} 3180; $\gamma_{C=O}$ 1668 cm.⁻¹. Dichromate oxidation of VII and VIII gave glutaric acid.

Hydrogenation of VI over Raney nickel catalyst at 2 atm. (92% yield) or reduction of VII with iron powder and aqueous ethanolic ammonium chloride solution⁹ yielded a tetrahydro derivative

(1) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

(2) E. E. Van Tamelen and R. J. Thiede, *THIS JOURNAL*, **74**, 2615 (1952).

(3) W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).

(4) W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

(5) W. E. Noland, *Chem. Revs.*, **55**, 137 (1955).

(6) W. C. Wildman and D. R. Saunders, *J. Org. Chem.*, **19**, 381 (1954).

(7) M. Simonetta and S. Winstein, *THIS JOURNAL*, **76**, 18 (1954).

(8) H. L. Yale, *Chem. Revs.*, **33**, 231 (1943).

(9) (a) V. O. Lukashevich and M. A. Voroshilova, *Compt. rend. acad. sci. U.R.S.S.*, **2**, 394 (1935); *Org. Chem. Ind. (U.S.S.R.)*, **4**, 253 (1937), *C. A.*, **32**, 2091 (1938); Russian Patent 51,050, May 31, 1937;