

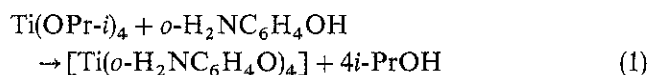
Communication

o-Aminophenoxytitanium complexes

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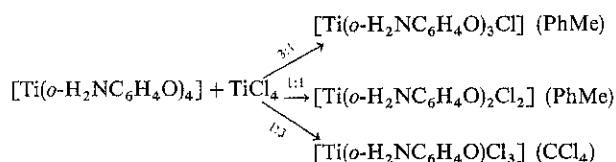
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In connection with related studies on alkyl alkoxytitanium complexes we tried to obtain chelated phenoxy compounds using *o*-aminophenol. Many methods have been used for the preparation of similar compounds⁽¹⁾. New $[\text{Ti}(o\text{-NH}_2\text{C}_6\text{H}_4\text{O})_{4-n}\text{Cl}_n]$ ($n = 1, 2$ and 3) *o*-aminophenoxytitanium complexes have been isolated by redistribution reactions of different molar ratios of TiCl_4 and $[\text{Ti}(o\text{-NH}_2\text{C}_6\text{H}_4\text{O})_4]$ obtained from $[\text{Ti}(\text{OPr-}i)_4]$ and *o*-aminophenol. We found that the totally substituted *o*-aminophenoxytitanium derivative can be readily obtained by alcohol exchange in boiling toluene between stoichiometric amounts of $[\text{Ti}(\text{OPr-}i)_4]$ and the phenol, as shown in Equation (1).



$[\text{Ti}(o\text{-H}_2\text{NC}_6\text{H}_4\text{O})_4]$ is an orange microcrystalline solid, partially soluble in toluene, and can be manipulated in air for short periods.

Redistribution reactions between $[\text{Ti}(o\text{-H}_2\text{NC}_6\text{H}_4\text{O})_4]$ and different molar ratios of TiCl_4 led to the haloalkoxy complexes mentioned in Scheme 1. The reactions were carried out in boiling toluene or CCl_4 to give microcrystalline orange-brown to red-black almost insoluble solids.



Scheme 1

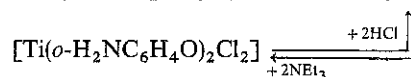
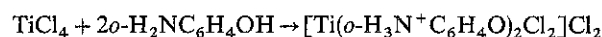
The redistribution of π -donor alkoxy groups between the two metal centres is favoured on electronic and steric grounds^(2,3) and almost quantitative yields have been found in most cases.

The *o*-aminophenoxytitanium complexes, which are soluble in tetrahydrofuran, dimethylsulphoxide and methanol but insoluble in non-polar solvents, were characterized by analysis (see Table 1), i.r. and ^1H n.m.r. spectroscopy. They show $\nu(\text{N-H})$ i.r. absorptions at $3250\text{--}3400\text{ cm}^{-1}$ (Nujol) and one broad signal due to NH_2 protons at $5.00\text{--}5.45$ ppm in $\text{DMSO-}d_6$, in which they must be monomeric. The amino groups are probably not coordinated.

These compounds cannot be obtained by reaction of TiCl_4 with the phenol because the HCl evolved protonates the amino group to give the species shown in Scheme 2.

Table 1. Analytical data obtained for titanium complexes

Compound	Found (Calcd.)%			
	C	H	N	Ti
$[\text{Ti}(o\text{-H}_2\text{NC}_6\text{H}_4\text{O})_4]$	59.8(60.0)	5.1(5.0)	11.1(11.6)	9.9(10.0)
$[\text{Ti}(o\text{-H}_2\text{NC}_6\text{H}_4\text{O})_3\text{Cl}]$	52.2(53.0)	4.2(4.4)	9.5(10.3)	
$[\text{Ti}(o\text{-H}_2\text{NC}_6\text{H}_4\text{O})_2\text{Cl}_2]$	42.3(43.0)	3.7(3.6)	7.7(8.3)	
$[\text{Ti}(o\text{-H}_2\text{NC}_6\text{H}_4\text{O})\text{Cl}_3]$	28.1(27.6)	2.9(2.3)	5.4(5.3)	
$[\text{Ti}(o\text{-H}_3\text{NC}_6\text{H}_4\text{O})_2\text{Cl}_2]\text{Cl}_2$	35.0(35.3)	3.6(3.5)	6.4(6.9)	



Scheme 2

The cationic complex is a brown solid which can be alternatively obtained by reaction of the diphenoxydihalocomplex with HCl . It is thermally stable at 100°C *in vacuo* but is reversibly transformed into the neutral complex by reaction with a stronger Lewis base such as NEt_3 . It is also insoluble in nonpolar solvents and soluble in THF and DMSO. The i.r. spectrum shows $\nu(\text{N-H})$ i.r. absorptions at $3220, 3280\text{ cm}^{-1}$ and a broad signal is observed in the ^1H n.m.r. spectrum at 10.20 ppm due to the $-\text{NH}_3^+$ protons.

We have no data to assign the structure and molecularity of these *o*-aminophenoxyhalotitanium compounds, but with reference to the monomeric nature of $[\text{Ti}(\text{OPh})_2\text{Cl}_2]$ in benzene and its phenoxy bridged dimeric structure⁽⁴⁾ in the solid, we may suggest that solutions in polar solvents contain monomeric species, whereas di- or polymeric structures must be present in solids.

Acknowledgement

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References

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