Redox Reactions in the Formation of Titanium Complexes with Aromatic Schiff's Bases

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Reaction of $TiCl_3$,3thf (thf = tetrahydrofuran) with potentially quadridentate Schiff's bases gives the complexes trichloro[*NN'*-ethylenebis(salicylideneimine)]tetrahydrofurantitanium(III), (I), dichloro[*NN'*-ethylenebis(salicylideneiminato)]titanium(IV), (II), dichloro[*NN'*-*o*-phenylenebis(salicylideneiminato)]titanium(IV), (III), and trichloro[*NN'*-(*o*-hydroxybenzylamino-*o*-phenylene)salicylideneiminato]tetrahydrofurantitanium(IV), (IV). Hydrogenation of one of the C=N bonds of the Schiff's base occurs in formation of complex (IV).

ALTHOUGH there are several reports [1-4] of complex formation between *N*-substituted salicylaldimines and quadrivalent titanium, analogous reactions of tervalent titanium do not appear to have been studied. Our interest in Schiff's base complexes of tervalent titanium stems from their potential as precursors of organotitanium(III) compounds in which the Ti–C bond might be stabilized by the Schiff's base ligand. Such a stabilizing effect has been observed for some organometallic complexes of tervalent iron [5] and rhodium.[6]

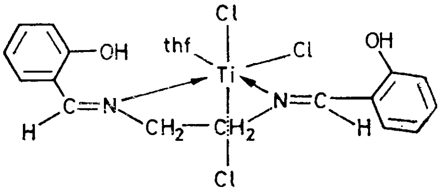
EXPERIMENTAL

All operations were carried out in an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran (thf) was dried over sodium diphenyl ketyl. *NN'*-Ethylenebis(salicylideneimine) ($salenH_2$), *NN'*-*o*-phenylenebis(salicylideneimine) ($salpnH_2$), and $TiCl_4$,2thf were prepared by established procedures. The thf was distilled and the solid ligands were sublimed *in vacuo* directly into reaction vessels.

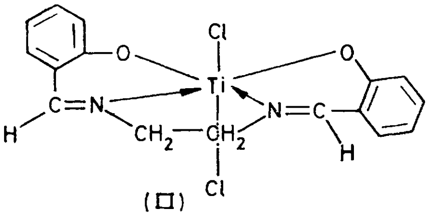
Reactions of $TiCl_3$,3thf.—(a) *With* $salenH_2$. A solution of $salenH_2$ (1·05 g, 5·6 mmol) in thf (10 cm^3) was added to a stirred solution of $TiCl_3$,3thf (2·00 g, 5·4 mmol) in thf (80 cm^3) at room temperature. A green precipitate formed immediately. This was filtered off, washed with a little thf, and dried *in vacuo* to yield green *trichloro*[NN'-*ethylenebis*(*salicylideneimine*)*tetrahydrofurantitanium*(III) (I) (0·82 g, 31%) (Found: C, 48·1; H, 4·4; Cl, 21·5; N, 5·3; Ti, 9·7. Calc. for $C_{20}H_{24}Cl_3N_2O_3Ti$: C, 48·6; H, 4·8; Cl, 21·6; N, 5·7; Ti, 9·7%).

When the reaction was allowed to proceed without isolation of the green complex, the mixture slowly turned red (*ca.* 3 h). The red solid was filtered off, washed with thf, and dried *in vacuo* to yield red crystals of *dichloro*[NN'-*ethylenebis*(*salicylideneiminato*)]*titanium*(IV) (II) (0·9 g, 43%) (Found: C, 50·1; H, 3·8; Cl, 18·4; N, 7·1; Ti, 12·7. Calc. for $C_{16}H_{14}Cl_2N_2O_2Ti$: C, 49·8; H, 3·6; Cl, 18·4; N, 7·3; Ti, 12·4%).

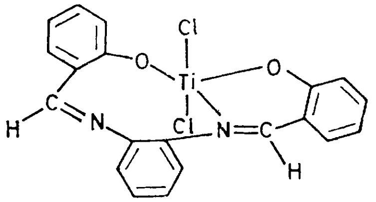
(b) *With* $salpnH_2$. With this Schiff's base, a transient green colour formed; this rapidly changed to red-brown and a dark brown solid was deposited. The solid was filtered off, washed with thf, and dried *in vacuo* to yield *dichloro*[NN'-o-*phenylenebis*(*salicylideneiminato*)]*titanium*(IV) (III) (47%) (Found: C, 55·7; H, 3·5; Cl, 16·0; N, 6·3; Ti, 10·9. Calc. for $C_{20}H_{14}Cl_2O_2Ti$: C, 55·5; H, 3·2; Cl, 16·3; N, 6·5; Ti, 11·1%). The red filtrate was concentrated to low bulk and cooled to −10 °C; an orange-red solid formed which was filtered off, washed with a little cold thf, and dried *in vacuo* to yield orange air-stable crystals of *trichloro*[NN'-(o-*hydroxybenzylamino*-o-*phenylene*)-*salicylideneiminato*]*titanium*(IV) (IV) (51%) (Found: C, 53·4; H, 4·7; Cl, 20·1; N, 5·5; Ti, 8·9. Calc. for $C_{23}H_{23}Cl_3N_2O_3Ti$: C, 53·2; H, 4·25; Cl, 19·7; N, 5·2; Ti, 8·85%).



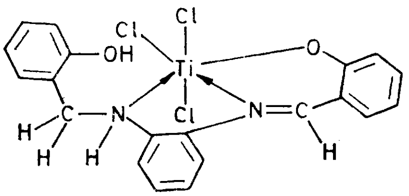
(I)



(II)



(III)



(IV)

The complexes [(salen)$TiCl_2$] and [(salpn)$TiCl_2$] were also prepared from $TiCl_4$,2thf and the appropriate Schiff's base when heated under reflux in thf.

U.v. and visible diffuse-reflectance (against magnesium oxide), solution, and i.r. spectra were recorded with Optica

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[1] V. A. Kogan, O. A. Osipov, V. I. Minkin, V. P. Sodolov, *Russ. J. Inorg. Chem.*, 1965, **10**, 45.

[2] V. P. Sokolov, V. A. Kogan, O. A. Osipov, L. G. Kolomin, *Russ. J. Inorg. Chem.*, 1969, **14**, 1260.

[3] N. S. Biradar and V. H. Kulkarni, *Rev. Roumaine Chim.*, 1970, **15**, 1993.

[4] N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3847.

[5] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1971, 3665.

[6] R. J. Cozens, K. S. Murray, and B. O. West, *Chem. Comm.*, 1970, 1262.

C4DR, Unicam SP 700, and Perkin-Elmer 621 spectrophotometers, respectively. Magnetic susceptibilities were measured on powdered samples by the Faraday method. Titanium was determined colorimetrically using hydrogen peroxide. Carbon, hydrogen, nitrogen, and chlorine were determined by standard microanalytical techniques.

RESULTS AND DISCUSSION

The reactions of Schiff's bases with transition-metal compounds can lead to three types of complex. The most common of these is the inner-chelate complex in which the ligand is bonded to the metal *via* the oxygen atoms of its deprotonated hydroxy-groups and the nitrogen atoms of its –C=N groups.[7] In some instances, notably with transition-metal halides, the base co-ordinates *via* the nitrogen atoms only. This behaviour has been observed in, *e.g.*, molybdenum(V)[8] and titanium(IV) halides.[1] A third alternative, so far only observed with hexacarbonylmolybdenum, involves hydrogenation of the –C=N groups and formation of an inner-chelate complex between the secondary amine ligand and the metal in a higher oxidation state.[9] In the work reported here, all three co-ordination types have been observed.

I.r. spectra: [a] band maxima (cm^{-1}) and assignments [b]

Compound	ν(OH)	ν(C=N)	ν(C–O)	δ(O–H)	ν_{sym}(C–O–C)	ν_{sym}(C–O–C)	ν(Ti–Cl)
salenH_2	2 660— 2 730m	1 635s	1 284m	1 270m			
$TiCl_3$,3thf					1 009s	850s	353, 327, 293m [c]
[(salenH_2)$TiCl_3$(thf)] (I)	3 080m	1 647s		1 285s	1 020s	875s	345, 300, 283m [d]
[(salen)$TiCl_2$] (II)		1 610s	1 330ms				347s
salpnH_2	2 600— 2 740wm	1 611s	1 276ms	1 260m			
[(salpn)$TiCl_2$] (III)		1 595s	1 330m		*f*		334vs
[(salpnH_3)$TiCl_3$(thf)] (IV) [e]	3 050m	1 593s	1 280m 1 333ms	1 256m			345, 300, 283m

[a] In Nujol mulls. [b] L. J. Bellamy, 'Advances In Infrared Group Frequencies,' Methuen, London, 1968. [c] ν(TiCl) 360, 331, and 300 cm^{-1} (R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 1963, 379). [d] Assignments based on comparisons with Ti^{III} complexes with *N*-donor ligands (D. Ferguson, Ph.D. Thesis, U.M.I.S.T., 1973). [e] ν(N–H) 3 223m, δ(N–H) 1 605s. [f] See text this page.

The green complex (I) which is the initial product of the reaction between $TiCl_3$,3thf and salenH_2 is extremely unstable; it decomposes instantly in air and slowly even under an atmosphere of nitrogen or *in vacuo*. This suggests that the redox reaction leading to [(salen)$TiCl_2$] *vide infra* can occur, albeit slowly, in the solid state. Despite its instability, complex (I) was characterized as [(salenH_2)$TiCl_3$(thf)] by elemental analysis, i.r. and visible spectroscopy, and by magnetic-susceptibility measurements.

An apparent magnetic moment μ_{eff} (295 K) of 1·3 B.M. confirmed the paramagnetism of (I) but is substantially lower than the spin-only value (μ_{eff} 1·73 B.M.) for Ti^{III}. This low value is attributed to partial oxidation of the solid which occurs even with rigorous exclusion of oxygen and water. Visible spectra of the green solution, obtained by filtering the reaction mixture after *ca.* 5 min, and the green solid are very similar showing a broad, low-intensity absorption at 13·7 kK [$\varepsilon \simeq 20$ l mol^{-1} cm^{-1} (solution spectrum)] with a shoulder at 14·7 kK; this is characteristic of Ti^{III} complexes. Intense absorption, presumably charge transfer in origin, occurred above 18 kK. When the green solution was exposed to air it instantly turned orange-red. The oxidized solution had no absorption maxima in the region 13—17 kK. The co-ordination of the salenH_2 ligand in (I) *via* the azomethine nitrogen atoms only was supported by its i.r. spectrum (Table). A shift of ν(C=N) of the free base to higher frequencies is characteristic of this mode of co-ordination.[1,3] The magnitude of the shift, 12 cm^{-1}, compared with 35—40 cm^{-1} observed for a series of titanium(IV) complexes [$TiCl_4(LH_2)$] (LH_2 = bidentate Schiff's base),[1] reflects the lower Lewis acidity of Ti^{III}. If the reaction between $TiCl_3$,3thf and salenH_2 was allowed to proceed for several hours, the green solid and solution slowly turned red. This change was accompanied by the liberation of *ca.* 0·5 mol HCl per titanium atom. The i.r. spectrum of the diamagnetic red solid (Table) is identical to that of [$TiCl_2$(salen)] which has been shown to have the inner-chelate structure (II) by *X*-ray crystallography.[10]

The possibility that the titanium(IV) complex (II) had been formed *via* oxidation of complex (I) by adventitious oxygen was excluded on the grounds that deliberate exposure of (I) to dry air did not afford (II). Instead an orange solid was produced. Its i.r. spectrum is very similar to that of (I) except that absorption in the region *ca.* 3 000 cm^{-1} is broader. The spectra are identical in the region 1 000—1 700 cm^{-1}; below this, bands in the two spectra differ in intensity rather than in position. This indicates that aerial oxidation of (I) has left the ligand environment of the titanium atom substantially unchanged. The nature of the orange complex is currently under investigation.

Oxidation to a titanium(IV) complex also occurred in the reaction between salpnH_2 and $TiCl_3$,3thf. The oxidation was much faster than in the salenH_2 reaction; a transient green colouration formed, probably due to the salpnH_2 analogue of (I), but no titanium(III) species

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[7] R. H. Holm and G. W. Everett, *Progr. Inorg. Chem.*, 1966, **7**, 83.

[8] F. L. Bowden, C. A. McAuliffe, and B. J. Sayle, unpublished work.

[9] P. C. H. Mitchell and D. A. Parker, *J.C.S. Dalton*, 1972, 1828.

[10] R. L. Beddoes, D. W. J. Cruickshank, G. Gilli, and O. S. Mills, *Acta Cryst.*, 1972, **B28**, 1889.

could be isolated. The insoluble dark brown diamagnetic product was shown to be [(salpn)$TiCl_2$], (III), by elemental analysis and i.r. spectroscopy (Table). A *trans* structure is suggested for the complex by analogy with [(salen)$TiCl_2$]. A second diamagnetic complex, (IV), was isolated from the filtrate. Elemental analysis of (IV) established the presence of one organic ligand molecule, three chlorine atoms, and one molecule of thf per titanium atom, but it could not distinguish between the various possible stages of protonation or reduction of the organic ligand. The i.r. spectrum of (IV) (Table), however, showed that partial hydrogenation of the Schiff's base ligand had occurred and that the partially hydrogenated ligand was co-ordinated *via* a phenolic-oxygen atom, and the nitrogen atoms of an azomethine group and an aliphatic amine group. In the i.r. spectrum of complex (IV) there are bands at 3 223 and 1 605 cm^{-1} which we assign to vibrations of NH in the co-ordinated amine group. Bands at 3 050 and 1 256 cm^{-1} are assigned to vibrations of OH. Thus at least one OH group of the ligand is not bonded to titanium in complex (IV). Stretching vibrations of the chelated Schiff's base part of the ligand gave strong bands at 1 593 (C=N) and 1 330 (C–O) cm^{-1}. The spectrum in the region 800—1 100 cm^{-1} is very complex and it is not possible to ascertain whether the thf is co-ordinated. In view of the strong preference of titanium for octahedral co-ordination, it is probable that the thf is present as thf of solvation.

Formation of complex (IV) involves hydrogenation of only one of the –C=N groups of the Schiff's base ligand; it is accompanied by oxidation of Ti^{III} to Ti^{IV} and is the first example of partial hydrogenation of a Schiff's base ligand. If, as seems probable, the hydrogen required for this hydrogenation is provided by reduction of protons released when the OH groups of the base react with the tervalent titanium, then a maximum yield of 50% of complex (IV) is to be anticipated. This is very close to the experimental yield of 47%. The rest of the titanium now present as Ti^{IV} can appear in the non-hydrogenated analogue of complex (IV) or *via* HCl elimination as the inner-chelate complex (III). Evidently the latter possibility is preferred. The overall stoicheiometry of the reaction is therefore as in equation (1).

$$2LH_2 + 2TiCl_3,3thf \longrightarrow [TiCl_2(L)] + [TiCl_3(LH_3)(thf)] + HCl \quad (1)$$

Hydrogenation of the –C=N groups of Schiff's bases requires powerful reducing agents, *e.g.* hydrogen 1 500 p.s.i. and a rhodium–carbon catalyst,[9] and presumably, co-ordination activates this group towards hydrogenation in the reaction with $TiCl_3$,3thf. It has been suggested that the orientation of the OH and –C=N groups in the Schiff's base complex may facilitate direct hydrogen transfer between these groups. However, this could account for the uptake of only one hydrogen atom per –C=N group. If on the other hand the reduction of protons produces hydrogen, the latter can hydrogenate the –C=N group or be liberated as molecular hydrogen. In the latter event the principal if not exclusive metal-containing product would be the inner-chelate complex of the metal in a higher oxidation state. In this connection it is interesting to note that the major product (*ca.* 97%) from the reaction between VCl_3,3thf and salpnH_2 is [VCl_2(salpn)].[11]

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[11] D. Ferguson, personal communication.