Reactivity of New Azido-complexes of Titanium and Vanadium

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Mono- and bis-azido-complexes of Ti^{IV} and V^{V} have been prepared in good yield from chloro- or alkoxo-derivatives of the transition metal, using $SiMe_3(N_3)$ as azide source. The stable azides $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$, $[Ti(OPr^i)_2(N_3)_2]$, $[TiCl(OPr^i)_2(N_3)]$, $[VO(OPr^i)(N_3)_2]$, and $[VO(OCH_2Bu^t)(N_3)_2]$ have been isolated and characterized. The azido-group can be displaced by reaction with protic reagents and HN_3 is eliminated. The compounds also react with phosphines to form phosphiniminato-complexes, with N_2 elimination.

It has been known for several years that azido-complexes of the early transition metals can be prepared using sodium or halogen azides and the metal halides and in this way $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$,[1] $[VOCl_2(N_3)]$, and $[VCl_3(N_3)]$,[2] $[TiCl_3(N_3)]$, and $[TiBr_2(N_3)_2]$ [3] have been isolated. Recently, the reaction of $SnBu_3(N_3)$ with $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ leading to $[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$ has also been reported.[4] In contrast, the use of trimethylsilyl azide $SiMe_3(N_3)$ as azide source has received little attention.

In a previous paper [5] we described the synthesis of some azido-complexes of Ti^{IV} by metathetical reaction between a metal–chlorine bond and $SiMe_3(N_3)$. We now propose, as an extension of this process, the reaction between a metal–alkoxide bond and $SiMe_3(N_3)$ to give mixed azido- and alkoxy-derivatives of Ti^{IV} and V^{V}. The reactivity of the azido-ligand towards alcohols and phosphines is also described.

RESULTS AND DISCUSSION

Synthesis.—Reaction of d^0 chlorides of Ti^{IV}, such as $[Ti(\eta\text{-}C_5H_5)Cl_3]$, with $SiMe_3(N_3)$ leads cleanly to the corresponding azido-complexes [5] [equation (1)]. Starting

$$[M]Cl + SiMe_3(N_3) \longrightarrow [M]N_3 + SiMe_3Cl \quad (1)$$

from $ZrCl_4$, $[ZrCl_3(N_3)]$ can be prepared as a white solid which cannot be purified [$\nu(N_3)$ at 2 180, 2 140, and 1 325 cm^{-1}]. But use in this way of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and $[V(\eta\text{-}C_5H_5)_2Cl_2]$ was unsuccessful even in refluxing toluene, whereas $[Ti(\eta\text{-}C_5H_5)_2Cl]$ did not give the expected titanium(III) azide but the titanium(IV) derivative $[Ti(\eta\text{-}C_5H_5)_2Cl(N_3)]$ which has been prepared by another method.[5] Significantly, use of $[Ti(\eta\text{-}C_5H_5)_2Cl]$ and $Na[N_3]$ also failed.[1]

As an extension of reaction (1), treatment of d^0 alkoxides of Ti^{IV} or V^{V} with $SiMe_3(N_3)$ leads cleanly to the corresponding azido-complexes with the elimination of alkoxotrimethylsilane [equation (2)]. In the case of

$$[M]OR + SiMe_3(N_3) \longrightarrow [M]N_3 + SiMe_3(OR) \quad (2)$$

$Ti(OPr^i)_4$, $[VO(OPr^i)_3]$, and $[VO(OCH_2Bu^t)_3]$ only disubstitution occurred whatever the amounts of $SiMe_3(N_3)$; $[Ti(OPr^i)_2(N_3)_2]$, $[VO(OPr^i)(N_3)_2]$, and $[VO(OCH_2Bu^t)(N_3)_2]$ were so obtained.

With mixed derivatives such as $[TiCl(OR)_3]$, where there may be competition between chloride and alkoxide as leaving group, an alkoxy-group is lost upon monosubstitution while in disubstitution one alkoxy-group and the chloride atom are eliminated. For example, 1 equivalent of $SiMe_3(N_3)$ with $[TiCl(OPr^i)_3]$ yields $[TiCl(OPr^i)_2(N_3)]$ as the main product, while 2 (or more) equivalents yield $[Ti(OPr^i)_2(N_3)_2]$. The compound $[VO(OCH_2Bu^t)(N_3)_2]$ can also be prepared by a similar disubstitution starting from $[VOCl(OCH_2Bu^t)_2]$.

Characterization and Spectroscopic Data.—All these species are insoluble in benzene and other cryoscopic solvents which prevents molecular-weight measurements. Their insolubility together with their thermal and mechanical stability suggests a polymeric structure.[6,7]

Characteristic i.r bands (cm^{-1}) of azido-groups in some titanium and vanadium complexes

Compound		ν_{asym}	ν_{sym}
$[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$		2 115—2 090	1 260
$[Ti(\eta\text{-}C_5H_5)Cl(N_3)(NEt_2)]$		2 100—2 080	1 270
$[Ti(OPr^i)_2(N_3)_2]$		2 120—2 080	1 280
$[TiCl(OPr^i)_2(N_3)]$		2 120	1 290
$[VO(OPr^i)(N_3)_2]$		2 100—2 080	1 260
$[TiCl_3(N_3)]$	ref. 2	2 185—2 135	1 230
$[VOCl_2(N_3)]$	ref. 2	2 130, 2 095, 2 045	1 250
$[Ti(\eta\text{-}C_5H_5)_2(N_3)_2]$	ref. 1	2 070—2 040	1 330

In the i.r. spectra the expected N_3 bands were observed, namely ν_{asym} in the 2 070—2 120 cm^{-1} range and ν_{sym} in the 1 250—1 330 cm^{-1} range (Table), but these data cannot establish definitely the mode of attachment (terminal or bridged) of the N_3 group, as was stressed in a recent paper.[8]

The ^1H n.m.r. spectra of many of these compounds cannot be recorded due to their poor solubility. Yet, it was possible to compare the shielding of the cyclopentadienyl group for various complexes and the azido-ligand exhibited nearly as marked an electron-withdrawing ability as chloride. For example, for $[Ti(\eta\text{-}C_5H_5)Cl_2X]$ $\delta(C_5H_5) = 7.18$ when $X = Cl$, 7.02 when $X = N_3$, and 6.83 when $X = OR$; for $[Ti(\eta\text{-}C_5H_5)Cl_{2-x}(N_3)_x]$ $\delta(C_5H_5) = 6.55$ when $x = 0$, 6.50 when $x = 1$, and 6.50 when $x = 2$ (in tetrahydrofuran solvent).

Reactivity.—The reactivity of titanium and vanadium azides is still virtually unexplored since the previously reported derivatives $[TiCl_3(N_3)]$ and $[VOCl_2(N_3)]$ are explosive and cannot be handled easily. In contrast, the azido-complexes reported herein and in an earlier paper are quite stable and their chemical behaviour has been investigated.

Substitution reactions involving transition-metal azides have been little studied. We recently published some results on the replacement of N_3 by Cl in reactions with HCl or CH_3COCl[5] [equations (3) and (4)].

$$[M]N_3 + HCl \longrightarrow [M]Cl + HN_3 \tag{3}$$

$$[M]N_3 + CH_3COCl \longrightarrow [M]Cl + CH_3NCO + N_2 \tag{4}$$

In the present work the azido-complexes were found to react cleanly with alcohols to give the corresponding alkoxy-complexes [equation (5)]. For example $[Ti(\eta\text{-}C_5H_5)Cl_2(OCH_2CF_3)]$, $[Ti(OPr^i)_2(OCH_2CF_3)_2]$, and

$$[M]N_3 + ROH \longrightarrow [M]OR + HN_3 \tag{5}$$

$[VO(OPr^i)(OCH_2CF_3)_2]$ were obtained by action of CF_3CH_2OH on $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$, $[Ti(OPr^i)_2(N_3)_2]$, and $[VO(OPr^i)(N_3)_2]$ respectively. They were characterized by ^1H n.m.r. and i.r. data and by comparison with authentic samples.[9,10]

Such processes are of synthetic interest since $[Ti(\eta\text{-}C_5H_5)Cl_2(OCH_2CF_3)]$ cannot be prepared from $[Ti(\eta\text{-}C_5H_5)Cl_3]$ neither by action of CF_3CH_2OH nor by $Li(OCH_2CF_3)$, and attempts to prepare $[VO(OPr^i)(OCH_2CF_3)_2]$ from $[VO(OPr^i)_3]$ and CF_3CH_2OH failed. Furthermore, it was of interest to treat these azido-complexes with diols with the aim of preparing new binuclear titanium (or vanadium) derivatives bearing diolato-bridging groups.

When $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$ was treated with a diol, for example with *cis*-butene-1,4-diol, either mononuclear $[Ti(\eta\text{-}C_5H_5)Cl_2(OCH_2CH{=}CHCH_2OH)]$ or binuclear diolato-bridged $[Cl_2(\eta\text{-}C_5H_5)Ti(OCH_2CH{=}CHCH_2O)Ti(\eta\text{-}C_5H_5)Cl_2]$ was obtained depending on the temperature. The binuclear complex is monomeric in dioxan. With pyrocatechol (two OH functions in *ortho* positions) disubstitution involving N_3 and a chloride leads to mononuclear $[Ti(\eta\text{-}C_5H_5)Cl(O_2C_6H_4)]$.

In the reaction of $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$ with a secondary amine $NHEt_2$ we observed that the $Ti{-}N_3$ bond is not cleaved, instead cleavage of the Ti–Cl bond with elimination of HCl gives $[Ti(\eta\text{-}C_5H_5)Cl(NEt_2)(N_3)]$. This product is not obtained pure but ^1H n.m.r. and i.r. data are in agreement with this formula. Other protonic reagents, such as C_5H_6 and $PhC{\equiv}CH$, do not react with the $Ti{-}N_3$ bond, in contrast with the behaviour of $Ti{-}NR_2$ bonds.[11,12]

N_2 *Elimination*. Some azido-complexes of Rh, Ir,[8,13] and Pd[14] have been found to react with CO to give isocyanato-complexes [equation (6)]. In this study, no similar reactions were obtained with carbon monoxide at atmospheric pressure, but methyl isocyanate is obtained from CH_3COCl as mentioned above.

By contrast, some azido-derivatives of Si and Sn were

$$[M]N_3 + CO \longrightarrow [M]NCO + N_2 \tag{6}$$

found to react with phosphines to give phosphinimines[15-18] [equation (7)]. We previously reported the formation of $[Ti(\eta\text{-}C_5H_5)Cl_2(N{=}PPh_3)]$ by this route.[5] This was extended to the phosphines PMe_3 and PMe_2Ph,

$$[M]N_3 + PR_3 \longrightarrow [M]N{=}PR_3 + N_2 \tag{7}$$

and $[Ti(\eta\text{-}C_5H_5)Cl_2(N{=}PMe_3)]$ and $[Ti(\eta\text{-}C_5H_5)Cl_2(N{=}PMe_2Ph)]$ were prepared. They were isolated and characterized by i.r. data [disappearance of $\nu(N_3)$ and appearance of $\nu(P{=}N)$ at 1 150 and 1 140 cm^{-1} respectively], ^1H n.m.r. spectra [$(\eta\text{-}C_5H_5)$: Me intensity ratio], and comparison with authentic samples obtained from $[Ti(\eta\text{-}C_5H_5)Cl_3]$ and $SiMe_3(N{=}PR_3)$.[19] It is interesting that the ^1H n.m.r. cyclopentadienyl signal is markedly shifted towards high fields when the basicity of the phosphine increases: $\delta(C_5H_5) = 6.80, 6.42$, and 6.20 with PMe_3, PMe_2Ph, and PPh_3 respectively.

No analogous reaction between $[Ti(OPr^i)_2(N_3)_2]$ and $[VO(OPr^i)(N_3)_2]$ with PMe_3 was observed, even in refluxing toluene, probably due to their association by bridging N_3. Moreover, attempts to obtain similar reactions with $P(OMe)_3$ and $AsPh_3$ on $[M]N_3$ were unsuccessful.

EXPERIMENTAL

Trimethylsilyl azide was used as purchased from Merck. All manipulations were carried out under argon in conventional Schlenk-type apparatus using solvents dried by usual procedures. The i.r. spectra were recorded as Nujol mulls on KBr discs, and ^1H n.m.r. spectra were run on a Perkin-Elmer R12 spectrophotometer using tetramethylsilane as internal standard. Microanalyses were carried out by the Service Central de Microanalyse du CNRS. The compounds $Ti(OPr^i)_4$, $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$, $ZrCl_4$, and $[V(\eta\text{-}C_5H_5)_2Cl_2]$ were purchased from Alfa; $[VO(OPr^i)_3]$, $[VO(OCH_2Bu^t)_3]$, $[VOCl(OCH_2Bu^t)_2]$, $[TiCl(OPr^i)_3]$, and $[Ti(\eta\text{-}C_5H_5)_2Cl]$ were prepared by literature methods.[20-23]

General Procedure for the Preparations of Bis(azido)-complexes.—(*a*) An excess (at least 2 equivalents) of $SiMe_3(N_3)$ was added to 1 equivalent of $Ti(OPr^i)_4$ {or $[VO(OPr^i)_3]$, $[VO(OCH_2Bu^t)_3]$, $[TiCl(OPr^i)_3]$, or $[VOCl(OCH_2Bu^t)_2]$} in solution in pentane and stirred at room temperature for 5 d. A solid precipitated, which was filtered off and washed with pentane: $[Ti(OPr^i)_2(N_3)_2]$, white solid (yield 70%) (Found: C, 28.8; H, 5.6; Ti, 19.6. Calc. for $C_6H_{14}N_6O_2Ti$: C, 28.8; H, 5.6; Ti, 19.2%); $[VO(OPr^i)(N_3)_2]$, yellow solid (yield 50%) (Found: C, 17.4; H, 3.5; V, 24.0. Calc. for $C_3H_7N_6O_2V$: C, 17.1; H, 3.3; V, 24.3%); $[VO(OCH_2Bu^t)(N_3)_2]$, yellow-brown (yield 20%) (Found: C, 25.2; H, 4.6; V, 20.4. Calc. for $C_5H_{11}N_6O_2V$: C, 25.2; H, 4.6; V, 21.4%).

All these compounds are soluble in tetrahydrofuran but insoluble in other common solvents.

(*b*) One equivalent (or less) of $SiMe_3(N_3)$ was added to 1 equivalent of $Ti(OPr^i)_4$ {or $[VO(OPr^i)_3]$} in solution in pentane and stirred at room temperature for 5 d; $[Ti(OPr^i)_2(N_3)_2]$ {or $[VO(OPr^i)(N_3)_2]$} was isolated.

Azido(chloro)di(η-cyclopentadienyl)titanium(IV).—Trimethylsilyl azide (1.0 g, 8.7 mmol) was added to a green solution of $[Ti(\eta\text{-}C_5H_5)_2Cl]$ (0.8 g, 3.7 mmol) in tetrahydrofuran (10 cm^3) at room temperature. An exothermic reaction immediately occurred and a red colour developed After stirring for 2 h the volume of the solution was reduced and pentane added until precipitation of a brown-red solid was complete. The product was filtered off, washed with pentane, and characterized as $[Ti(\eta\text{-}C_5H_5)_2Cl(N_3)]$ by ^1H n.m.r. and i.r. data and by comparison with authentic samples.[5]

Reaction with Alcohols.—(*a*) 2,2,2-*Trifluoroethanol*. An excess (2.0 g, 20.0 mmol) of CF_3CH_2OH was added to a solution of $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$ (1.10 g, 4.86 mmol) in tetrahydrofuran (10 cm^3). The solution turned brown-yellow. The volume of the mixture was reduced and pentane added. A yellow-green precipitate was obtained, filtered off, and washed with pentane, giving $[Ti(\eta\text{-}C_5H_5)Cl_2(OCH_2CF_3)]$ (yield 95%) (Found: C, 29.0; H, 2.4; Cl, 26.2; Ti, 17.3. Calc. for $C_7H_7Cl_2F_3OTi$: C, 29.6; H, 2.5; Cl, 25.0; Ti, 16.9%). Proton n.m.r. data (p.p.m.) in CCl_4 solvent: $\eta\text{-}C_5H_5$, 6.85 (s); OCH_2CF_3, 4.75 (q).

In a separate experiment, CF_3CH_2OH in excess was added to a solution of $[Ti(OPr^i)_2(N_3)_2]$ {or $[VO(OPr^i)(N_3)_2]$} in benzene. After stirring for 2 h, the clear solution was evaporated under reduced pressure and the liquid left was $[Ti(OPr^i)_2(OCH_2CF_3)_2]$ {or $[VO(OPr^i)(OCH_2CF_3)_2]$}, characterized by comparison of its ^1H n.m.r. and i.r. spectra with those of an authentic sample.[9,10]

(*b*) cis-*Butene*-1,4-*diol*. The diol (0.67 g, 7.5 mmol) was added at −50 °C to a solution of $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$ (1.7 g, 7.5 mmol) in tetrahydrofuran (10 cm^3). After stirring for 2 h, the solution was allowed to warm to room temperature and a yellow-green colour developed. Partial evaporation of the solution and addition of pentane gave yellow-green $[Ti(\eta\text{-}C_5H_5)Cl_2(OCH_2CH{=}CHCH_2OH)]$ (yield 20%) (Found: C, 39.1; H, 4.1; Cl, 27.3; Ti, 18.2. Calc. for $C_9H_{12}Cl_2O_2Ti$: C, 39.9; H, 4.0; Cl, 26.2; Ti, 17.7%). This product is insoluble in CCl_4, $CHCl_3$, and C_6H_6. Proton n.m.r. data (p.p.m.) in tetrahydrofuran solvent: $\eta\text{-}C_5H_5$, 6.83 (s); other unresolved peaks, 5.75 and 5.30; $\nu(OH)$ at 3 300 cm^{-1}.

In another experiment, $HOCH_2CH{=}CHCH_2OH$ (0.52 g, 6.0 mmol) was added at room temperature to a solution of $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$ (1.35 g, 6.0 mmol) in tetrahydrofuran (5 cm^3). The solution turned brown-yellow. The solvent was evaporated and pentane added. An orange precipitate was obtained, filtered off, and washed with pentane to give $[Cl_2(\eta\text{-}C_5H_5)Ti(OCH_2CH{=}CHCH_2O)Ti(\eta\text{-}C_5H_5)Cl_2]$ (yield 40%) (Found: C, 37.2; H, 3.6; Cl, 30.8; Ti, 20.5. Calc. for $C_{14}H_{16}Cl_4O_2Ti_2$: C, 37.0; H, 3.5; Cl, 31.3; Ti, 21.1%). This product is soluble in CH_2Cl_2, insoluble in CCl_4 and C_6H_6, and monomeric in dioxan by cryoscopic measurements [*M* 410 (calc. 454)]. Proton n.m.r. data (p.p.m.) in tetrahydrofuran solvent: $\eta\text{-}C_5H_5$, 6.88 (s); other unresolved peaks, 5.8 and 5.35.

(*c*) *Pyrocatechol*. The compound $C_6H_4(OH)_2$ (0.10 g, 1.0 mmol) was added to a solution of $[Ti(\eta\text{-}C_5H_5)Cl_2(N_3)]$ (0.47 g, 2.0 mmol) in tetrahydrofuran (10 cm^3) and stirred for 12 h. The red-brown solution was partially evaporated and diethyl ether added to give brown $[Ti(\eta\text{-}C_5H_5)Cl(O_2C_6H_4)]$ (yield 95%) (Found: C, 50.7; H, 3.5; Cl, 15.8; Ti, 18.3. Calc. for $C_{11}H_9ClO_2Ti$: C, 51.4; H, 3.5; Cl, 13.8; Ti, 18.7%). Proton n.m.r. data (p.p.m.) in CH_2Cl_2 solvent: $\eta\text{-}C_5H_5$, 6.53 (s); $C_6H_4O_2$, *ca.* 7.0 (unresolved peaks).

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REFERENCES

[1] R. S. P. Coutts and P. C. Wailes, *Austral. J. Chem.*, 1971, **24**, 1075.

[2] K. Dehnicke, *J. Inorg. Nuclear Chem.*, 1965, **27**, 809.

[3] K. Dehnicke, *Angew. Chem. Internat. Edn.*, 1979, **18**, 507.

[4] E. Rudolfo de Gil, M. de Burguera, A. V. Rivera, and P. M. Axfield, *Acta Cryst.*, 1977, **B33**, 578.

[5] R. Choukroun, D. Gervais, and J. R. Dilworth, *Transition Metal Chem.*, 1979, **4**, 249.

[6] Z. Dori and R. Z. Ziolo, *Chem. Rev.*, 1973, **73**, 3, 247.

[7] K. Dehnicke, *Angew. Chem. Internat. Edn.*, 1967, **6**, 3, 240.

[8] W. Rigby, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, *J.C.S. Dalton*, 1979, 371.

[9] M. Basso-Bert and D. Gervais, *Inorg. Chim. Acta*, 1979, **34**, 191.

[10] R. Choukroun, A. Dia, and D. Gervais, *Inorg. Chim. Acta*, 1979, **34**, 211.

[11] A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Organometallic Chem.*, 1970, **23**, 165.

[12] R. Choukroun and D. Gervais, *Synth. React. Inorg. Metal. Org. Chem.*, 1978, **8**, 137.

[13] M. Kubota and T. G. Chappel, *J.C.S. Dalton*, 1979, 406.

[14] W. Beck, W. P. Fehlhammer, P. Pollmann, and H. Schachl, *Chem. Ber.*, 1969, **102**, 1976.

[15] H. Schmidbaur, *Adv. Organometallic Chem.*, 1970, **9**, 259.

[16] S. S. Washburne and W. R. Peterson, *J. Organometallic Chem.*, 1971, **33**, 153.

[17] J. I. G. Cadogan, I. Gosney, E. Henry, T. Naisby, B. Nay, N. J. Stewart, and N. J. Tweddle, *J.C.S. Chem. Comm.*, 1979, 189.

[18] J. C. Wilburn, P. Wisian-Neilson, and R. H. Neilson, *Inorg. Chem.*, 1979, **18**, 1429

[19] J. R. Dilworth, H. J. de Liefde Meijer, and J. H. Teuben, *J. Organometallic Chem.*, 1978, **159**, 47.

[20] H. Funk, W. Weis, and M. Zeising, *Z. anorg. Chem.*, 1958, **296**, 36.

[21] M. Hecht, G. Jander, and M. Schlapmann, *Z. anorg. Chem.*, 1947, **254**, 255.

[22] N. M. Cullinane, S. J. Chard, G. F. Price, and B. B. Millward, *J. Appl. Chem.*, 1952, 250.

[23] L. E. Manzer, *J. Organometallic Chem.*, 1976, **110**, 291.

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