Photochemical incorporation of *N*-benzylidene(phenyl)amine into the complex [{Ti(η^5-C$_5$Me$_5$)(η-O)}$_3$(μ_3-CH)] as a model of the titanium oxide surface†

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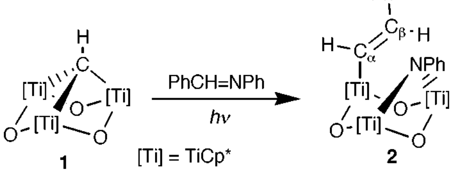
The photochemical incorporation of PhCH=NPh to the metal oxide model [{TiCp*(μ-O)}$_3$(μ_3-CH)] (Cp* = η^5-C$_5$Me$_5$) occurs by breaking of the C=N imine bond and formation of μ-imido and σ-alkenyl groups on the [Ti$_3$O$_3$] core; the crystal structure of the obtained product, [{TiCp*(μ-O)}$_3$(μ-NPh)(CH=CHPh)], was determined by X-ray diffraction.

Ti$_3$O$_3$(μ_3-CR) systems are surface models suitable for examination of both the cooperative interaction between metal centres maintained in close proximity and the chemistry of alkylidyne groups on a metallic oxide support. Recently we have described that the reactions under mild conditions of carbon monoxide and isocyanides with [{TiCp*(μ-O)}$_3$(μ_3-CR)] complexes proceed *via* insertion into the μ_3-alkylidyne units.[1] However, the incorporation of ketones follows other pathways and the experimental data support the insertion of carbonyl groups, R$_2$C=O, into the Ti–H bond of the *in situ* formed [{TiCp*(μ-O)}$_3$(μ-C=CH$_2$)(H)] intermediate to give alkoxide–vinylidene derivatives [{TiCp*(μ-O)}$_3$(μ-C=CH$_2$)(OCHR$_2$)].[2] Here, we present the preliminary result observed from the photochemical treatment of the trinuclear titanium derivative [TiCp*(μ-O)}$_3$(μ_3-CH)] **1**[3] with *N*-benzylidene(phenyl)amine.

When a solution of **1** and PhCH=NPh in hexane was irradiated for 45 h the alkenylimido complex [{TiCp*(μ-O)}$_3$(CH=CHPh)(μ-NPh)] **2** (Scheme 1) was obtained in good yield.‡ The ^{1}H NMR spectrum of compound **2** shows two signals in a 2 : 1 ratio for the Cp* ligands in accord with C_s symmetry in solution, and supports the presence of a *trans*-styryl group ($^3J_{HH}$ 18.3 Hz).‡ This ligand is σ-bonded to the titanium atom in accord with the observation in the ^{13}C NMR spectrum of a doublet of doublets at δ 190.4 (^1J 126.0, ^2J 2.5 Hz) and a doublet of multiplets at δ 140.2 (^1J 154.4 Hz) corresponding to C$_\alpha$ and C$_\beta$ resonances, respectively. A band of medium intensity at 1581 cm^{-1} in the IR spectrum is assigned to the alkenyl carbon–carbon double bond.



Scheme 1

An X-ray diffraction study of **2** reveals (Fig. 1)§ a *trans*-alkenyl group on one titanium atom and a phenyl imido moiety bridging the other two titanium atoms in a *syn–syn* disposition.

The styrene environment is planar with a Ti(2)–C(41) bond length of 2.127(9) Å, similar to those observed for Ti–C(sp^3) bonds in alkyl titanium complexes [TiCp*Me$_3$] (av. 2.10 Å),[4a] [{TiCp*Me}$_3$(μ-O)$_3$] (av. 2.09 Å),[4b] [{Ti$_4$Cp*$_4$Me$_2$}(μ-O)$_5$] (2.11 Å),[4c] [{TiCp*(μ-O)}$_3$(μ_3-CMe)] (av. 2.11 Å),[4d] [{TiCp*(μ-O)}$_3$(CH$_2$CH=CHMe)$_3$] (av. 2.13 Å)[4e] or Ti–C(sp^2) in alkenyl biscyclopentadienyl derivatives.[5] Within the styryl group, the C(41)–C(42) bond length [1.320(12) Å] is within the range for a C=C double bond.[6]

On the opposite side of the molecule, the Ti(1), Ti(3), N(13) and O(13) atoms form a distorted square (see Fig. 1), almost perpendicular to the Ti(1)–Ti(2)–Ti(3) and phenyl [C(51)–C(56)] planes. The N(13) atom shows a planar environment with Ti–N distances of 1.957(6) and 1.948(6) Å, close to the value of 1.91 Å (av.) found in [TiCp*(NMe$_2$)$_3$][7] and also to that of 1.939 Å reported in the cubane structure [{Ti$_4$Cp*$_4$}(μ_3-N)$_4$].[8] The average Ti–O bond distance (1.84 Å)[9] and Ti–ring centroid distance (2.06 Å) are comparable to those in the literature for the titanium organometallic oxides [{TiCp*(μ-O)}$_3$X$_3$] (X = Me,[4b] Cl,[10] Br[11]).

A reasonable proposal for this reaction (Scheme 2) involves imine insertion into one of the three titanium–carbon(alk-

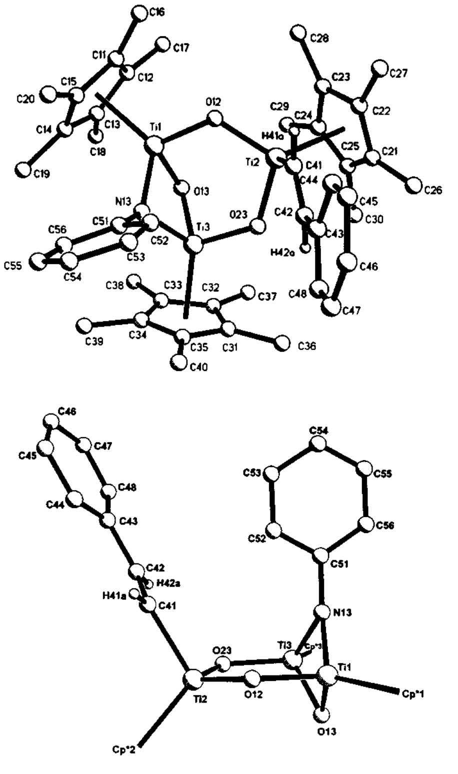


Fig. 1 Molecular structure of [{Ti(η^5-C$_5$Me$_5$)(μ-O)}$_3$(CH=CHPh)(μ-NPh)] **2**. Selected lengths (Å) and angles (°): Ti–Cp* 2.06(av.), Ti–O 1.84(5)(av.), Ti(2)–C(41) 2.127(9), C(41)–C(42) 1.32(1), Ti(1)–N(13) 1.957(6), Ti(3)–N(13) 1.948(6); O(12)–Ti(1)–O(13) 102.4(2), O(12)–Ti(1)–N(13) 101.4(2), O(13)–Ti(1)–N(13) 84.8(2), O(12)–Ti(2)–O(23) 106.6(2), O(12)–Ti(2)–C(41) 105.4(3), O(23)–Ti(2)–C(41) 100.2(3); O(13)–Ti(3)–O(23) 100.7(2), O(13)–Ti(3)–N(13) 84.5(2), O(23)–Ti(3)–N(13) 102.5(3), Ti(1)–N(13)–Ti(3) 88.7(3), Ti(2)–O(12)–Ti(1) 122.7(3), Ti(1)–O(13)–Ti(3) 95.6(2), Ti(2)–O(23)–Ti(3) 123.7(3). Cp* is the centroid of the C$_5$Me$_5$ ring.

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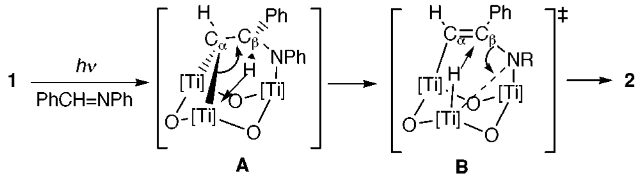
† Dedicated to Alexander von Humboldt on the occasion of his commemorative year 1999.



Scheme 2

ylidyne) bonds to generate the species **A** which was not detected. β-Hydrogen elimination[2] would then give a hydride–enamine intermediate **B** while subsequent carbon–nitrogen bond rupture, transfer of hydrogen from titanium to the β-carbon and formation of a nitrogen–titanium bond, would afford the σ-alkenyl-μ-imido complex **2**. However, we can not exclude the possibility that the conversion of **A** to **2** could occur directly by a concerted pathway.

To our knowledge, this observed behaviour is comparable only to the alkylidene/imine metathesis-like reactions reported by Rocklage and Schrock,[12] and by Cantrell and Meyer[13] for mononuclear niobium, tantalum and molybdenum alkylidene complexes. In our case the metathesis-like process occurs on the Ti_3O_3 surface with the cooperative participation of the three metal atoms and opens new perspectives in trinuclear titanium chemistry. Further studies of this process with other imines are in progress and the results will be published in due course.

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Notes and references

‡ *Preparation* of **2**: *N*-benzylidene(phenyl)amine (0.356 g, 197 mmol) was added to a solution of **1** (1.0 g, 164 mmol) in 60 mL of hexane. The reaction mixture was irradiated at room temp. for 45 h with a UV lamp. The final reddish solution was concentrated and cooled to obtain red crystals of **2**. Yield: 0.90 g (*ca*. 75%). Anal. Calc. for $C_{44}H_{57}NO_3Ti_3$, (M = 791.64): C, 66.76; H, 7.26; N, 1.77. Found: C, 67.28; H, 7.69; N, 1.72%. Selected NMR data (δ, J/Hz): ^{1}H (500 MHz, C_6D_6, 25 °C, TMS): 1.95 (s, 30H, C_5Me_5), 2.09 (s, 15H, C_5Me_5), 8.04 (d, 1H, ^3J 18.3, –C*H*=CHPh), 6.84 (d, 1H, ^3J 18.3, –CH=C*H*Ph); ^{13}C{^{1}H} (125 MHz, C_6D_6, 25 °C, TMS): 11.7, 12.20 (C_5*Me*$_5$), 122.6, 122.5 (*C*$_5$Me$_5$), 140.2 (dm, ^1J 154.4, –CH=*C*HPh), 158.9, (C_{ipso}, μ-NPh), 190.4 (dd, ^1J 126.0, ^2J 2.5, –*C*H=CHPh). IR (KBr, cm^{-1}): ν 3052w, 2913s, 1581m, 1542w, 1488w, 1440s, 1375s, 1245s, 1024m, 898s, 759w, 729s, 688s, 397s. EI mass spectrum *m/z* 792 (M^+, 11%).

§ Single crystals of **2** were obtained by slow cooling of a hexane solution. *Crystal data* for **2**: $C_{44}H_{57}NO_3Ti_3$, M = 791.61, triclinic, space group $P\bar{1}$, a = 11.4865(1), b = 12.559(1), c = 16.049(1) Å, α = 87.64(1), β = 89.82(1), γ = 82.87(1)°, V = 2295.3(3) Å^3, Z = 2, D_c = 1.145 g cm^{-3}; $F(000)$ = 836. λ = 0.71073 Å, μ(Mo-Kα) = 0.544 mm^{-1}. The data were collected on an Enraf Nonius CAD4 diffractometer. Intensity measurements were performed by ω–θ scans in the range $6 < 2\theta < 44°$ at 19 °C on a crystal of dimensions 0.45 × 0.40 × 0.38 mm. Of the 5916 measured reflections, 5577 were independent; largest minimum and maximum in the final difference Fourier synthesis: −0.415 and 1.422 e Å^{-3}, $R1$ = 0.077 and $wR2$ = 0.251 [for 4025 reflections with $F > 4\sigma(F)$]. The structure was solved by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97). CCDC 182/1374. See http://www.rsc.org/suppdata/cc/1999/1839/ for crystallographic data in .cif format.

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