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Exchange of Organoimido Groups at a Mononuclear Titanium Centre and a Crystallographic Evaluation of the Relative Structural Influences of the NBu^t, NC_6H_4Me-4 and $NC_6H_4NO_2$-4 Ligands

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The *tert*-butylimido complex [Ti(NBu^t)Cl$_2$(py)$_3$] **1a** (py = pyridine) undergoes exchange reactions of the NBu^t ligand with arylamines RNH$_2$ to form the arylimido derivatives [Ti(NR)Cl$_2$(py)$_3$] (R = C$_6$H$_4$Me-4 **1b**, C$_6$H$_4$NO$_2$-4 **1c** or C$_6$H$_3$Me$_2$-2,6 **1d**); comparison of the crystal structures of **1a**–**1c** gave a direct evaluation of N-substituent effects in d^0, six-co-ordinated organoimido complexes.

An important feature of the organoimido ligand (NR, R = alkyl or aryl) is that the physical and chemical properties of complexes containing this functional group may be significantly and systematically tuned by modifying the N-bound group R.[1,2] We have recently shown that a diverse range of new reactive *tert*-butylimido titanium derivatives are available from the versatile and easily prepared precursors [Ti(NBu^t)Cl$_2$(4Bu^t-py)$_2$] (py = pyridine)[3] or *trans,mer*-[Ti(NBu^t)Cl$_2$(py)$_3$] **1a**.[4] These include mono- and bis-cyclopentadienyl, indenyl, tris(pyrazolyl)hydroborate, azamacrocyclic, cyclooctatetraenyl and alkoxide supported *tert*-butylimido titanium derivatives.[3,4] Clearly arylimido analogues of these synthons and their derivatives are highly desirable targets and here we outline their synthesis *via* the first *tert*-butylimido ligand–arylamine exchange reactions of any Group 4 transition metal, together with the crystal structures of the *tert*-butyl-, 4-methylphenyl- and 4-nitrophenyl-imido titanium derivatives [Ti(NR)Cl$_2$(py)$_3$] which provide a direct evaluation of N-substituent effects in organoimido complexes.

The arylimido complexes *trans,mer*-[Ti(NR)Cl$_2$(py)$_3$] (R = C$_6$H$_4$Me-4 **1b**, C$_6$H$_4$NO$_2$-4 **1c** or C$_6$H$_3$Me$_2$-2,6 **1d**) are readily formed on addition of one equivalent of the appropriate RNH$_2$ to a dichloromethane solution of [Ti(NBu^t)Cl$_2$(py)$_3$] **1a**[4] at room temperature and allowing the solution to stand for 2–6 h. Removal of solvent and *tert*-butylamine under reduced pressure generally afforded good yields of the desired product in a sufficiently pure form for immediate use in further synthetic studies [equation (1)].† There is literature precedent for *tert*-butylimido–arylamine exchange reactions for later transition metals[5–7] but our reactions are the first reported examples of the application of this method for an early transition metal. Only the formation of [Ti(NC$_6$H$_4$NO$_2$-4)Cl$_2$(py)$_3$] **1c** proceeds in low yield with several unidentified side-products. This is probably due to the electron-withdrawing nature of the *p*-NO$_2$ substituent (rather than to the absence of *ortho* substituents) since the *p*-tolyl analogue **1b** is formed in satisfactory yield.

$$\textit{trans,mer}\text{-}[\mathrm{Ti(NBu^t)Cl_2(py)_3}] + \mathrm{RNH_2} \longrightarrow \textit{trans,mer}\text{-}[\mathrm{Ti(NR)Cl_2(py)_3}] + \mathrm{Bu^tNH_2} \quad (1)$$

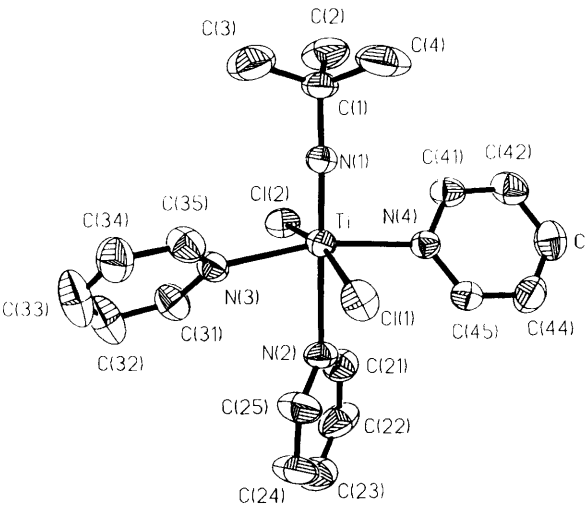

Fig. 1 Thermal ellipsoid plot for one of the two crystallographically independent molecules of [Ti(NBu^t)Cl$_2$(py)$_3$] **1a**. Hydrogen atoms omitted for clarity. Average bond lengths (Å) and angles (°): Ti–N(1) 1.705(3), Ti–Cl 2.438(1), Ti–N(py$_{trans}$) 2.445(3), Ti–N(py$_{cis}$) 2.253(3), N(1)–C(1) 1.450(5); C(1)–N(1)–Ti 173.3(3), N(1)–Ti–Cl(1) 97.33(12), N(1)–Ti–N(2) 176.09(13), N(1)–Ti–N(3) 96.61(13)

Compounds **1a**–**1c** form a homologous series of organoimido complexes in which the identity of the N-substituent alone has been systematically modified, and which thus offers the opportunity to evaluate directly the structural effects of different NR groups for six-co-ordinate, d^0 complexes. There has been considerable debate concerning the origin and quantification of the *trans* influence of multiply bonded ligands in transition-metal complexes.[1,8–11] Although it is clear that the broad order

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† Typical preparation (*e.g.* of **1d**). A solution of **1a** (485 mg, 1.13 mmol) in dichloromethane (30 cm^3) at room temperature was treated with 2,6-dimethylaniline (0.14 cm^3, 1.14 mmol). The initially orange solution became dark red over 2 h. Volatiles were removed under reduced pressure to afford a red-brown powder which was washed twice with pentane (2 × 15 cm^3) and dried *in vacuo* to yield **1d** (yield 86%). The product obtained in this way is >95% pure (by ^{1}H NMR spectroscopy) Found (calc.): **1a** C, 52.6 (52.4); H, 5.9 (5.7); N, 12.9 (13.1); **1b** C, 50.7 (51.2); H, 3.9 (3.9); N, 14.2 (14.2); **1c** C, 57.1 (57.1); H, 4.9 (5.0); N, 12.2 (12.2); **1d** C, 58.5 (58.1); H, 5.2 (5.1); N, 12.1 (11.8%).

of *trans* influence among different types of multiply bonded ligands is nitrido > oxo > imido,[12] there are still very few systematic structural data [1,2] concerning the effects of modifying the organoimido N-substituent, even though the electronic characteristics of the NR ligand could be crucial to the properties of the resultant complex. The most important imido N-substituents are the *tert*-butyl and aryl (and 2,6-disubstituted analogues) groups. Therefore, the crystal structures of $[Ti(NBu^t)Cl_2(py)_3]$ **1a**, $[Ti(NC_6H_4Me\text{-}4)Cl_2(py)_3]$ **1b** and $[Ti(NC_6H_4NO_2\text{-}4)Cl_2(py)_3]$ **1c** were determined (Figs. 1–3).*

The structures confirm the pseudo-octahedral nature of these complexes which feature mutually *trans* chloride and pyridine ligands, the remaining pyridine being *trans* to the NR ligand. Compound **1c** is only the second structurally characterised 4-nitrophenylimido complex.[15] Importantly, **1b** and **1c** are free of *ortho*-aryl non-hydrogen-atom substituents so that steric contributions to structural features will therefore be minimised as far as possible. In **1b** and **1c** the aryl rings are rotated out of the TiCl(1)Cl(1a)N(1)N(2) plane by *ca.* 30 and 32° respectively and so may interact to some extent with both of the imido nitrogen p_π orbitals. A detailed bonding analysis of these and related model oxo, sulfido and nitrido analogues is underway.

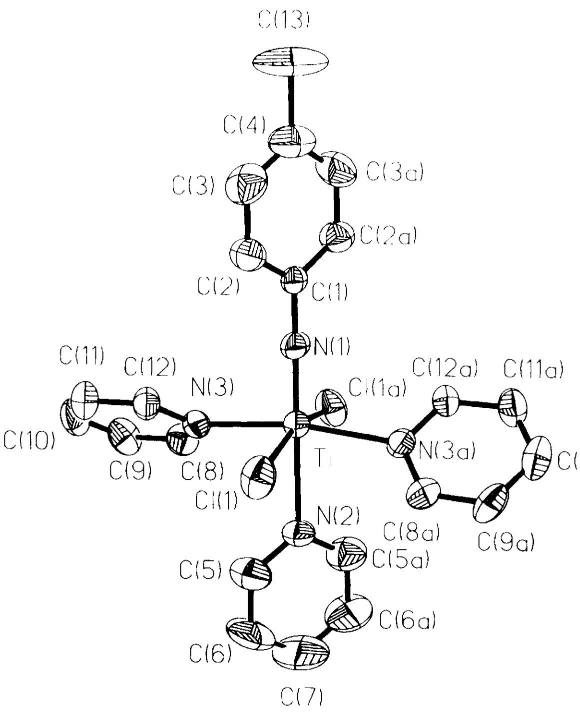

Fig. 2 Thermal ellipsoid plot for $[Ti(NC_6H_4Me\text{-}4)Cl_2(py)_3]$ **1b**. Hydrogen atoms omitted for clarity. Atoms labelled 'a' are related to their counterparts by a crystallographic two-fold axis. Bond lengths (Å) and angles (°): Ti–N(1) 1.705(4), Ti–Cl(1) 2.3942(13), Ti–N(2) 2.428(4), Ti–N(3) 2.227(2), N(1)–C(1) 1.378(6); C(1)–N(1)–Ti 180.0, N(1)–Ti–Cl(1) 98.65(3), N(1)–Ti–N(2) 180.0, N(1)–Ti–N(3) 95.35(7)

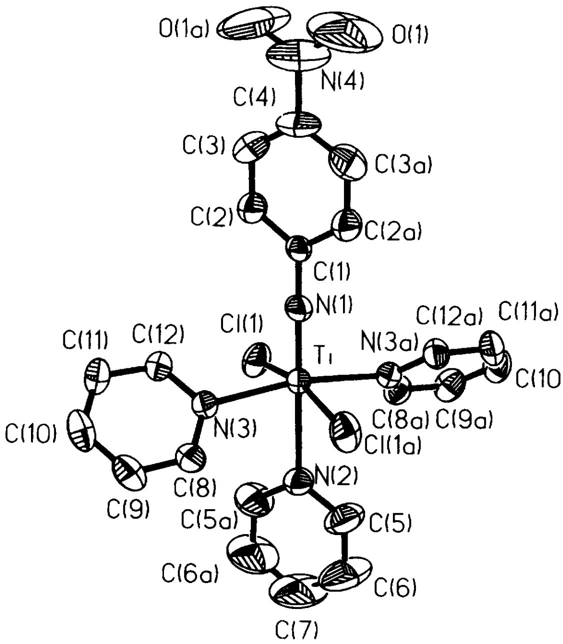

Fig. 3 Thermal ellipsoid plot for $[Ti(NC_6H_4NO_2\text{-}4)Cl_2(py)_3]$ **1c**. Hydrogen atoms omitted for clarity. Atoms labelled 'a' are related to their counterparts by a crystallographic two-fold axis. Bond lengths (Å) and angles (°): Ti–N(1) 1.722(3), Ti–Cl(1) 2.3800(13), Ti–N(2) 2.428(3), Ti–N(3) 2.228(3), N(1)–C(1) 1.359(4); C(1)–N(1)–Ti 180.0, N(1)–Ti–Cl(1) 97.66(2), N(1)–Ti–N(2) 180.0, N(1)–Ti–N(3) 95.33(5)

Although the Ti=NR bond lengths in $[Ti(NBu^t)Cl_2(py)_3]$ **1a** and $[Ti(NC_6H_4Me\text{-}4)Cl_2(py)_3]$ **1b** are identical, the structural influence of NBu^t is significantly greater than that of NC_6H_4Me-4. Thus there is a substantial and general lengthening of the Ti–Cl bonds and the *cis* and *trans* Ti–N(py) bonds in **1a** compared to **1b**. There is no clear trend in the N(imido)–Ti–Cl or N(imido)–Ti–N(py_{cis}) angles. The formal *trans* influence, however, of NBu^t and NC_6H_4Me-4 [*i.e.*, the *difference* between the average *cis* Ti–N(py) and *trans* Ti–N(py) bond lengths which is 0.193(4) and 0.201(4) Å for **1a** and **1b** respectively] is probably identical within experimental precision. Note well that the pyridine ligands are (essentially) σ-only ligands and any conclusions concerning the *trans* influence of the organoimido group should bear this in mind.

The structure of $[Ti(NC_6H_4NO_2\text{-}4)Cl_2(py)_3]$ **1c** is also very interesting. The Ti=N bond length in **1c** is significantly longer

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* Crystal data. $C_{19}H_{24}Cl_2N_4Ti$ **1a**, M = 427.22, triclinic, space group $P\bar{1}$, T = 153 K, a = 11.766(2), b = 13.278(3), c = 14.361(3) Å, α = 93.06(3), β = 93.96(3), γ = 92.92(3)°, U = 2231.7(8) Å^3, crystal size 0.30 × 0.18 × 0.11 mm, Z = 4, D_c = 1.272 g cm^{-3}, $F(000)$ = 888, graphite-monochromated Mo-Kα radiation, λ = 710 69 Å, μ = 6.3 cm^{-1}. The intensities of 8858 reflections [5931 independent, R(int) = 0.1221] were measured using a FAST area-detector diffractometer.[13] The structure was solved by direct methods (SHELXS 86)[14a] and refined in anisotropic approximation (475 parameters, H atoms isotropic in riding model) by full-matrix least squares (SHELXL 93)[14b] against F_o^2 for all reflections to $R1$ = 0.0749 [to $R1$ = 0.0523 for 4084 reflections with $I > 2\sigma(I)$].

$C_{22}H_{22}Cl_2N_5Ti$ **1b**, M = 461.24, monoclinic, space group $C2/c$, T = 293 K, a = 8.356(2), b = 22.542(5), c = 12.596(3) Å, β = 103.74(3)°, U = 2304.7(9) Å^3, crystal size 0.60 × 0.15 × 0.15 mm, Z = 4, D_c = 1.329 g cm^{-3}, $F(000)$ = 952, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 6.18 cm^{-1}. The intensities of 2012 reflections [1865 independent, R(int) = 0.0593] were measured on an Enraf-Nonius CAD4 diffractometer (ω–2θ scan, 1.81 < θ < 24.94°). The structure was solved by Patterson methods (SHELXS 86)[14a] and refined in anisotropic approximation (137 parameters, H atoms isotropic in riding model) by full-matrix least squares (SHELXL 93)[14b] against F_o^2 for all reflections to $R1$ = 0.238 [to $R1$ = 0.0339 for 751 reflections with $I > 2\sigma(I)$].

$C_{21}H_{19}Cl_2N_5O_2Ti$ **1c**, M = 492.21, monoclinic, space group $C2/c$, T = 293 K, a = 8.296(5), b = 23.251(5), c = 12.590(5) Å, β = 105.310(5)°, U = 2342(2) Å^3, crystal size 0.80 × 0.20 × 0.20 mm, Z = 4, D_c = 1.396 g cm^{-3}, $F(000)$ = 1008, graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å, μ = 6.20 cm^{-1}. The intensities of 2202 reflections [2054 independent, R(int) = 0.0428] were measured on an Enraf-Nonius CAD4 diffractometer (ω–2θ scan, 1.75 < θ < 24.94°). The structure was solved by direct methods (SHELXS 86)[14a] and refined in anisotropic approximation (144 parameters, H atoms isotropic in riding model) by full-matrix least squares (SHELXL 93)[14b] against F_o^2 for all reflections to $R1$ = 0.1899 [to $R1$ = 0.030 for 1074 reflections with $I > 2\sigma(I)$].

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

[by 0.017(5) Å] than that in **1b**. The imido nitrogen to aryl ring *ipso* carbon bond lengths in **1c** and **1b** are also somewhat different [difference 0.019(7) Å]. The changes in Ti=NR and N–C_{ipso} bond lengths provide convincing evidence for a greater delocalisation of the imido nitrogen π electrons away from titanium and out onto the aromatic ring in **1c**. We were therefore surprised to find that, despite the significant difference in Ti=N bond lengths, the structural influence of the $C_6H_4NO_2$-4 group (in **1c**) is *identical* to that of NC_6H_4Me-4 (in **1b**) as far as the σ-donor pyridine substituents are concerned. However, the weakly π-donating chloride ligands do bind a little more tightly to the titanium centre in **1c** than they do in **1b**, presumably taking advantage of the diminished π donation from the arylimido ligand. Despite the different Ti=NR bond lengths, there is no apparent difference in the NR ligand *trans* influence between **1c** and **1b**, the difference between the *cis* and *trans* Ti–N(py) bond lengths being 0.200(4) and 0.201(4) Å respectively.

In summary, we have demonstrated the first *tert*-butylimido ligand–arylamine exchange reactions for any Group 4 transition metal. The combined structural data for the complexes **1a**–**1c** show, for the first time, the different influences of the NR ligand in a systematically modified, substitutionally diverse, series of six-co-ordinate, d^0 organoimido complexes. There is no experimental relationship between the Ti=NR bond length and the ability of an NR group to distort other titanium–ligand bonds present. Furthermore, the *tert*-butyl-, 4-methylphenyl- and 4-nitrophenyl-imido ligands appear to have essentially the same *trans* influence according to the experimental data. We are currently investigating the consequences of these changes in the N substituent on the reactivity of imido titanium complexes.

Acknowledgements

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