

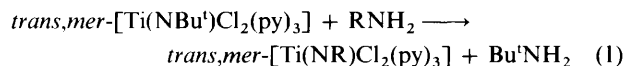
Dalton Communications

Exchange of Organoimido Groups at a Mononuclear Titanium Centre and a Crystallographic Evaluation of the Relative Structural Influences of the NBu^t , $\text{NC}_6\text{H}_4\text{Me-4}$ and $\text{NC}_6\text{H}_4\text{NO}_2\text{-4}$ LigandsPhilip E. Collier, Simon C. Dunn, Philip Mountford,* Oleg V. Shishkin and Daniel Swallow
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The *tert*-butylimido complex $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **1a** (py = pyridine) undergoes exchange reactions of the NBu^t ligand with arylamines RNH_2 to form the arylimido derivatives $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ (R = $\text{C}_6\text{H}_4\text{Me-4}$ **1b**, $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$ **1c** or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$ **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 $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(4\text{Bu}^t\text{-py})_2]$ (py = pyridine)³ or *trans,mer*- $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **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 $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ which provide a direct evaluation of N-substituent effects in organoimido complexes.

The arylimido complexes *trans,mer*- $[\text{Ti}(\text{NR})\text{Cl}_2(\text{py})_3]$ (R = $\text{C}_6\text{H}_4\text{Me-4}$ **1b**, $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$ **1c** or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$ **1d**) are readily formed on addition of one equivalent of the appropriate RNH_2 to a dichloromethane solution of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **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*-



[†] Typical preparation (*e.g.* of **1d**). A solution of **1a** (485 mg, 1.13 mmol) in dichloromethane (30 cm³) at room temperature was treated with 2,6-dimethylaniline (0.14 cm³, 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 cm³) and dried *in vacuo* to yield **1d** (yield 86%). The product obtained in this way is >95% pure (by ¹H 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%).

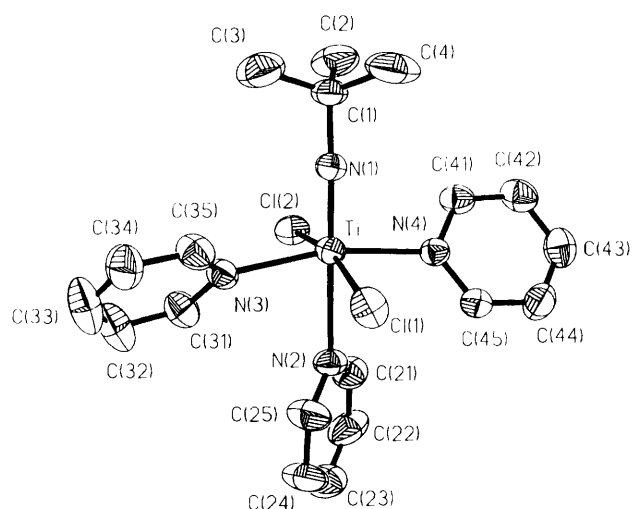


Fig. 1 Thermal ellipsoid plot for one of the two crystallographically independent molecules of $[\text{Ti}(\text{NBu}^t)\text{Cl}_2(\text{py})_3]$ **1a**. Hydrogen atoms omitted for clarity. Average bond lengths (Å) and angles (°): Ti–N(1) 1.705(3), Ti–Cl 2.438(1), Ti–N(py_{trans}) 2.445(3), Ti–N(py_{cis}) 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)

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 $[\text{Ti}(\text{NC}_6\text{H}_4\text{NO}_2\text{-4})\text{Cl}_2(\text{py})_3]$ **1c** proceeds in low yield with several unidentified side-products. This is probably due to the electron-withdrawing nature of the *p*-NO₂ substituent (rather than to the absence of *ortho* substituents) since the *p*-tolyl analogue **1b** is formed in satisfactory yield.

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

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')Cl₂(py)₃] **1a**, [Ti(NC₆H₄Me-4)Cl₂(py)₃] **1b** and [Ti(NC₆H₄NO₂-4)Cl₂(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.

Although the Ti=NR bond lengths in [Ti(NBu')Cl₂(py)₃] **1a** and [Ti(NC₆H₄Me-4)Cl₂(py)₃] **1b** are identical, the structural influence of NBu' is significantly greater than that of NC₆H₄Me-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' and NC₆H₄Me-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

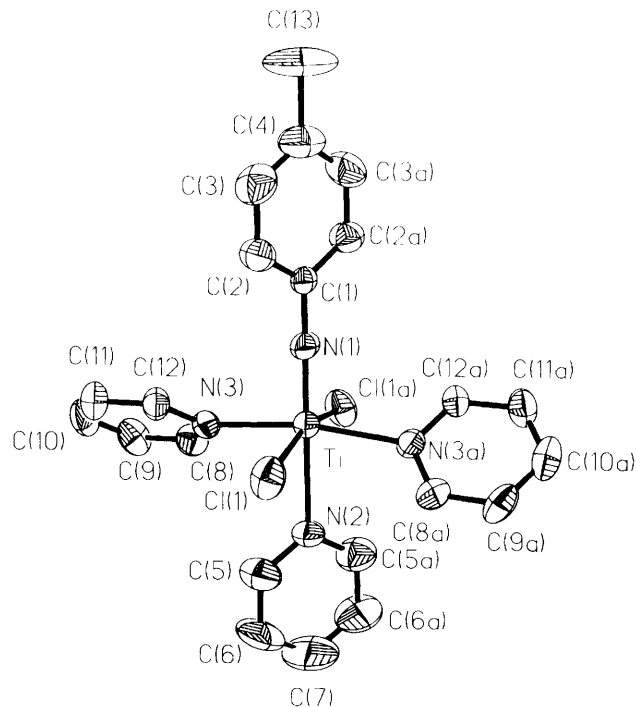


Fig. 2 Thermal ellipsoid plot for [Ti(NC₆H₄Me-4)Cl₂(py)₃] **1b**. Hydrogen atoms omitted for clarity. Atoms labelled 'a' are related to their counterparts by a crystallographic two-fold axis. Bond lengths (Å) and angles (°): Ti–N(1) 1.705(4), Ti–Cl(1) 2.3942(13), Ti–N(2) 2.428(4), Ti–N(3) 2.227(2), N(1)–C(1) 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)

* Crystal data. C₁₉H₂₄Cl₂N₄Ti **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) Å³, crystal size 0.30 × 0.18 × 0.11 mm, *Z* = 4, *D_c* = 1.272 g cm⁻³, *F*(000) = 888, graphite-monochromated Mo-K α 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 *R*1 = 0.0749 [to *R*1 = 0.0523 for 4084 reflections with *I* > 2 σ (*I*)].

C₂₂H₂₂Cl₂N₅Ti **1b**, *M* = 461.24, monoclinic, space group *C*2/*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) Å³, crystal size 0.60 × 0.15 × 0.15 mm, *Z* = 4, *D_c* = 1.329 g cm⁻³, *F*(000) = 952, graphite-monochromated Mo-K α 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 -2 θ 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 *R*1 = 0.238 [to *R*1 = 0.0339 for 751 reflections with *I* > 2 σ (*I*)].

C₂₁H₁₉Cl₂N₅O₂Ti **1c**, *M* = 492.21, monoclinic, space group *C*2/*c*, *T* = 293 K, *a* = 8.296(5), *b* = 23.251(5), *c* = 12.590(5) Å, β = 105.310(5)°, *U* = 2342(2) Å³, crystal size 0.80 × 0.20 × 0.20 mm, *Z* = 4, *D_c* = 1.396 g cm⁻³, *F*(000) = 1008, graphite-monochromated Mo-K α 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 -2 θ 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 *R*1 = 0.1899 [to *R*1 = 0.030 for 1074 reflections with *I* > 2 σ (*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.

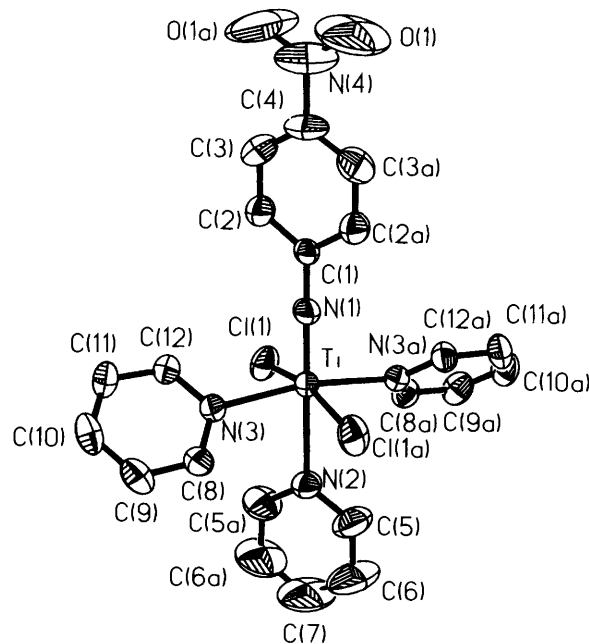


Fig. 3 Thermal ellipsoid plot for [Ti(NC₆H₄NO₂-4)Cl₂(py)₃] **1c**. Hydrogen atoms omitted for clarity. Atoms labelled 'a' are related to their counterparts by a crystallographic two-fold axis. Bond lengths (Å) and angles (°): Ti–N(1) 1.722(3), Ti–Cl(1) 2.3800(13), Ti–N(2) 2.428(3), Ti–N(3) 2.228(3), 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)

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(NC₆H₄NO₂-4)Cl₂(py)₃] **1c** is also very interesting. The Ti=N bond length in **1c** is significantly longer

[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 C₆H₄NO₂-4 group (in **1c**) is *identical* to that of NC₆H₄Me-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-coordinate, d⁰ 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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