Inorg. Chem. **2008**, *47*, 9042−9049

Inorganic Chemistry
Article

Comparisons between Yttrium and Titanium N-Heterocyclic Carbene Complexes in the Search for Early Transition Metal NHC Backbonding Interactions

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Received June 6, 2008

The d^0 yttrium N-heterocyclic carbene compound YL$_3$ (L = OCMe$_2$CH$_2$[C{N(CHCH)NPr^i}]) has been made and structurally characterized. It adopts a mer configuration of the three bidentate ligands. A comparison of this with the isostructural d^1 titanium complex TiL$_3$ is made in order to seek experimental evidence of a π-bonding contribution to the M−C bond. This has been augmented by DFT calculations. Experimentally, the metal radius-corrected Ti−C distance is shorter than the Y−C distance, suggesting a π-bonding contribution in the d^1 complex, but the computational data suggest that a shorter σ bond might simply be formed by the more strongly polarizing titanium cation. From the potassium reduction of TiL(OPr^i)$_3$, only a byproduct arising from silicone grease activation was isolable, identified as a mixed-valent, multinuclear, d^0/d^1 cluster [Ti^{III}L$_2${Pr^{i}OSiMe$_2$O}K$_2$OTi^{IV}(OPr^i)$_4$]$_2$ in which the carbene ligands are bound to the Ti^{III} centers in preference to Ti^{IV}, with longer Ti−C distances than those found in TiL$_3$.

Introduction

An enormous range of synthetic studies of metal N-heterocyclic carbene (NHC) complexes has been reported in the past decade; these strongly basic σ-donor ligands now enjoy widespread use as supporting ligands in late-transition metal-based homogeneous catalysis, and increasing use in early transition metal/lanthanide metal-based catalysis.[1] The desire to understand and design better catalysts, combined with increasingly frequent reports of unanticipated NHC ligand chemistry such as alkyl migration[2] and metal binding through the heterocycle backbone carbon,[3] reinforces the need for a clear picture of the metal−NHC carbon bond.

The current consensus on the metal−carbon bonding in the M−NHC moiety is that the carbenes form stronger metal−ligand bonds than phosphines,[4] through a very polar, dative/electrostatic interaction. The formulation of an accurate theoretical picture of this M−C bond is still under discussion.[5] Detailed studies support the existence of up to 30% π-backbonding from electron-rich metals

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10.1021/ic801046u CCC: $40.75

into the carbene carbon-based π orbital in molecules such as Cp*(NHC)Ir=PMes (NHC = $C\{NPr^iCMe\}_2$),[6] MX-(NHC) and $M(NHC)_2X$ (M = Cu, Ag, Au; X = F−I; NHC = $C\{NHCH\}_2$),[7] and $[Ag_3(TIME^{Me})_2](PF_6)_3$ [$TIME^{Me}$ = (1,1,1-tris(3-methylimidazol-2-ylidene)[methyl]ethane)].[8]

Experimental evidence was sought *via* a careful database study of the crystal structures of late transition-metal complexes; this demonstrated that the M−NHC bond is on average 4% shorter than a standard M−C single bond.[9] From Gaussian 98 computational analyses, the authors attribute this to a change in hybridization of the carbenoid C to include more p character.

In *cis*-dicarbene complexes of Pt^{II}, a backbonding π contribution from the NHC has been calculated at approximately 10%, using a combination of multinuclear spectroscopy and X-ray diffraction to differentiate between the σ and π components of the bonding; these findings were also supported by computational analyses.[10] Fourier transform infrared spectroscopic and crystallographic studies were used to analyze π backbonding in (NHC)RhCl(cod) and $(NHC)RhCl(CO)_2$ complexes.[11]

Subtraction of the Shannon radii values from the Cu−C distance in pairs of related Cu^I and Cu^{II} complexes of NHC ligands, such as $[Cu\{OCPh(CH_2\{1\text{-}C[NCHCHNBu^t])_2\}]_2$ and $(\mu\text{-}O)[CuCl\{OCPh(CH_2\{1\text{-}C[NCHCHNBu^t])\}]_2$,[12] yielded a shorter corrected Cu−C distance for the lower oxidation state metal, while the complex $Cu\{CN(2,6\text{-}Pr^iC_6H_3)CHCHN(2\text{-}NC_5H_4)\}Br$, which is geometrically constrained to disfavor π-backbonding interactions, contained shorter Cu−C bonds than in related unconstrained Cu^I complexes.[13]

For more electropositive metal systems, fewer computational studies exist. One computational study of M−NHC bonding in complexes with d-orbital occupancies that range from d^0 to d^{10} suggested that the π system of the NHC is able to act as a π donor in d^0 metal systems,[14] and a similar scenario is proposed for the metallated 14-electron Rh complex $Rh(CH_2CMe_2[C\{N(CHCH)NBu^t\}])_2$.[15] Another interesting alternative to the traditional metal backbonding interaction has also been suggested in d^0 Ti^{IV} and V^V halide complexes, which are formally incapable of backbonding interactions. The single-crystal molecular structures of the complexes $VOCl_3(NHC)$ and $TiCl_2(NMe_2)_2(NHC)_2$ (NHC = $C\{NMesCH\}_2$)[16] showed close interactions between the flat NCN aromatic plane of the carbene and π-donor ligands in the cis position. The possibility of a stabilizing interaction between the cis-π-donor ligand and the formally empty C(2p) orbital of the NHC was supported by a visual inspection of DFT-generated Kohn−Sham orbitals in these complexes and has since been suggested for Re^V and Sn^{IV} NHC adducts.[17] Similar close contacts were also observed in other Ti^{IV} complexes of the form $Ti(L)(OPr^i)_n(Br)_{3-n}$ ($n = 1-3$, L = $NBu^tCH_2CH_2[C\{N(CHCH)NBu^t\}]$), but these were attributed to electrostatic repulsions between the large ligands. DFT calculations, backed up by Wiberg bond-order analyses, provided the same geometric result as found in the experimental systems with no measurable cis-ligand backbonding.[18]

Since then, DFT computational studies on four different samarium carbenes of the form $[carbene]SmCl_3$ were reported ([carbene] = $C\{NMeCH\}_2$, $C\{NMeCH_2\}_2$, and similar variants); these predicted strong coordination energies ($\Delta G < -35$ kJ mol^{-1}) and concluded that there was a strong σ Sm−C bond with no evidence for π-back-donation from the carbene to the Sm, or from the chloride to the Sm.[19]

Vibrational spectroscopy, which monitors the strength of the stretch of the O=U=O moiety in the uranyl $[UO_2]^{2+}$ NHC complexes $UO_2(NBu^tCH_2CH_2[C\{N(CHCH)NR\}])_2$ (R = Bu^t, mesityl), has been used to demonstrate that the U−C bond strength in uranyl-bound NHCs is not influenced by a bend of the NHC away from the U−NHC plane.[20]

However, experimental details that might show the possibility for straightforward backbonding interactions in early transition metal complexes have yet to appear.

We recently reported the synthesis of the d^1 complex TiL_3 (L = $OCMe_2CH_2[C\{N(CHCH)NPr^i\}]$), to confirm the synthetic utility of $TiCl_3(THF)_3$ (THF = tetrahydrofuran) as made from the low-cost Ti^{III} precursor $3TiCl_3\cdot AlCl_3$.[21]

Interested by the wide variation in titanium−carbene distances, we have sought to make some comparable d^0 and d^1 complexes, so that we might look for experimental evidence of straightforward backbonding in carbene com-

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plexes in this area of the periodic table. Herein, we present the first experimental study of the presence of backbonding in early transition-metal complexes, alongside the description of new yttrium and titanium N-heterocyclic complexes, and a silicone-grease activation product.

Experimental Section

General Methods. All manipulations of oxygen- or moisture-sensitive materials used standard Schlenk techniques (rotary pump for vacuum 10^{-3} mbar) or a glovebox (Mbraun Unilab or Labstar, Vacuum Atmospheres) under dry dinitrogen. NMR spectra were recorded on a Bruker DPX 300 spectrometer, at an operating frequency of 300 MHz (^{1}H) or 75 MHz (^{13}C{^{1}H}), or a Bruker DPX 360 spectrometer, with the variable-temperature unit set to 298 K unless otherwise stated; ^{29}Si NMR was performed on a Bruker AMX500 spectrometer. Chemical shifts are reported in parts per million and referenced internally to residual solvent proton resonance, and externally to tetramethylsilane. Elemental analyses were determined by Stephen Boyer at London Metropolitan University. All solvents used were degassed by N_2 purge and evacuation−refill cycles and were purified prior to use either by passage through activated alumina towers or by distillation from the appropriate drying agent under dinitrogen. NMR spectroscopic-grade d_6-benzene was dried over potassium metal, degassed by the freeze−thaw method, and vacuum-transferred before use. The compounds $YCl_3(THF)_3$,[22] [KL],[23] and [TiL(OPr^i)$_3$][24] were prepared according to literature methods. All other reagents were purchased from Aldrich.

Preparation of YL$_3$, 1. To a Schlenk tube charged with $YCl_3(THF)_3$ (1.029 g, 2.5 mmol) and KL (1.595 g, 7.25 mmol) was added cold THF (80 mL, −78 °C), and the resulting mixture was allowed to warm to room temperature overnight with stirring. The pale beige-colored solution was separated from the colorless powder of KCl by filtration and evaporated to dryness. Extraction with hexane (2 × 30 mL), followed by evaporation of the combined hexane extracts, gave YL$_3$ **1** as a light cream-colored solid (0.945 g, 1.50 mmol, 62%). Anal. calcd for $C_{30}H_{51}N_6O_3Y$: C, 56.95; H, 8.13; N, 13.28. Found: C, 56.94; H, 7.85; N, 12.93. MS(EI): *m*/*z* = 632 (M$^+$).^{1}H NMR (C_6D_6, 298 K, 360 MHz): δ 6.341 (d, $^3J_{HH}$ = 19.40 Hz, 1H, *i*-PrNC(H)C(*H*)N), 6.337 (d, $^3J_{HH}$ = 19.37 Hz, 1H, *i*-PrNC(*H*)C(H)N), 5.74 (sept, $^3J_{HH}$ = 6.78 Hz, 1H, C*H*(CH$_3$)$_2$), 3.90 (s, 2H, NC*H*$_2$C(CH$_3$)$_2$O), 1.26 (s, 6H, NCH$_2$C(C*H*$_3$)$_2$O), 1.08 (d, $^3J_{HH}$ = 6.79 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 62.9 MHz): 197.28 (d, $^1J_{CY}$ = 31.32 Hz, N*C*N), 122.34 (*i*-PrNC(H)*C*(H)N), 112.96 (*i*-PrN*C*(H)C(H)N), 71.65 (NCH$_2$*C*-(CH$_3$)$_2$O), 65.91 (N*C*H$_2$C(CH$_3$)$_2$O), 50.99 (*C*H(CH$_3$)$_2$), 31.39 (NCH$_2$C(*C*H$_3$)$_2$O), 24.40 (CH(*C*H$_3$)$_2$). X-ray-quality crystals were deposited from the concentrated C_6D_6 solution of **1** upon standing for 24 h.

Preparation of [Ti^{III}L$_2${Pr^{i}OSiMe$_2$O}K$_2$OTi^{IV}(OPr^i)$_4$]$_2$, 3. A Schlenk was charged with TiL(O^{i}Pr)$_3$ (2.8 g, 6.89 mmol) and K (0.29 g, 6.89 mmol) in toluene (25 cm^3) and warmed to 70 °C for 16 h. After this time, the mixture had turned dark green and was filtered *via* filter cannula. After evaporation to dryness of the filtrate, the resulting green solid was extracted with hexanes. Cooling the green solution to −30 °C yielded a red solid identified as [Ti^{III}L$_2${Pr^{i}OSiMe$_2$O}K$_2$OTi^{IV}(OPr^i)$_4$]$_2$, **3** (0.16 g, 5%). Anal. calcd for $C_{74}H_{150}K_4N_8O_{18}Si_2Ti_4$: C, 48.19; H, 8.20; N, 6.08%. Found: C, 48.06; H, 8.36; N, 5.98%. ^{29}Si NMR (C_6D_6, 500 MHz): δ −9.05 (s, 1Si, TiO*Si*(CH$_3$)$_2$OK). Resonances in the ^{1}H NMR spectra were broadened and paramagnetically shifted.

An ampule was charged with TiL(O^{i}Pr)$_3$ (0.850 g, 2 mmol) and K (0.082 g, 2 mmol) with toluene (25 cm^3). The resulting mixture was heated to 70 °C for 16 h. Removal of the volatiles under reduced pressure afforded an intractable green-brown solid.

An ampule was charged with TiL(O^{i}Pr)$_3$ (0.850 g, 2 mmol) and K (0.164 g, 4 mmol) with toluene (25 cm^3). The resulting mixture was heated to 70 °C for 16 h. Removal of the volatiles under reduced pressure afforded an intractable brown solid.

Red block-shaped single crystals were grown from toluene that were suitable for a single-crystal structure analysis. M = 1844.20, monoclinic, space group $P2(1)/c$, a = 11.4228(10) Å, b = 16.3048(14) Å, c = 26.637(2) Å, β = 101.052(2)°, V = 4869.0(7) Å^3, Z = 2, T = 150(2) K, μ(Mo Kα) = 0.573, 4976 measured reflections.

Thermal Stability of KL. A Youngs tap-equipped NMR tube was charged with KL (16 mg, 0.06 mmol) and benzene-d_6 (0.7 cm^3), and the resulting pale yellow solution warmed to 80 °C for 10 days. After six days, the solution began to turn orange, and by 10 days, the solution was an orange/red color. ^{1}H spectra were recorded at the start, t = 0 h, and at t = 3 days, 6 days, and 10 days. ***t* = 0 h.** ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ 6.66 (s, 1H, Im*H*), 6.48 (d, ^4J = 1.5 Hz, 1H, Im*H*), 4.46 (septet, ^3J = 6.6 Hz, 1H, C*H*(CH$_3$)$_2$), 3.93 (s, 2H, C*H*$_2$), 1.25 (d, ^3J = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (s, 6H, OC(C*H*$_3$)$_2$). ***t* = 3 days.** No change was observed. ***t* = 6 days.** Less than 5% decomposition (by integration). ***t* = 10 days.** Approximately 12% conversion to a new soluble product. ^{1}H NMR (250 MHz, C_6D_6, 25 °C): δ 7.29 (m, 1H, Im*H*), 7.22 (m, 1H, Im*H*), 6.52 (m, 1H, Im*H*), 6.46 (m, 1H, Im*H*), 3.50 (septet, ^3J = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 3.39 (septet, ^3J = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 2.10 (s, 4H, NC*H*$_2$), 1.07 (d, ^3J = 6.7 Hz, 6H, C(C*H*$_3$)$_2$), 1.05 (d, ^3J = 6.7 Hz, 6H, C(C*H*$_3$)$_2$).

Treatment of KL with Silicone Grease. A Youngs tap-equipped NMR tube was charged with KL (16 mg, 0.06 mmol) and Dow Corning high-vacuum silicone grease (5.0 mg, 0.6 mmol assuming an empirical formula of OSiMe$_2$) and benzene-d_6 (0.7 cm^3). The pale yellow solution was warmed to 80 °C for 10 days. After three days, the solution turned dark red, and over the course of the next 7 days, a red solid was slowly deposited. ^{1}H NMR spectra obtained at the same intervals (3 days, 6 days, 10 days) showed that the decomposition to what appears to be the same compound as above is nearly complete after six days; that is, decomposition is faster in the presence of grease. ***t* = 3 days.** Broadening of the KL resonances to fwhm = 25 Hz. Less than 5% decomposition (by integration). ***t* = 6 days.** Ligand resonances are no longer observable. Resonances from two new compounds and "grease" are the only resonances present. ***t* = 10 days.** Virtually unchanged from 6 days.

Crystallographic Details. Crystallographic X-ray data were collected using Mo Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD area detector diffractometer using ω scans. Structure solution and refinement were carried out using the SHELXTL suite of programs.[25] The standard uncertainties on the average values of bond distances were calculated using Model B and the semiweighted method of Taylor and Kennard.[26]

Computational Details. The DFT calculations were performed using the hybrid functional B3LYP with the package Gaussian 03,

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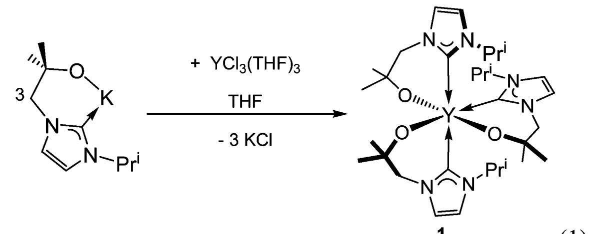
revision E.01.[27] Both calculations employed the LanL2DZ basis set.[28,29] The model geometries **1a** and **2a** were optimized without any constraints. A harmonic frequency calculation (using the same method/basis set) was performed at the optimized geometry for both **1a** and **2a** and yielded no imaginary frequencies in either case, confirming that the geometry of each is a true minimum on the potential energy surface. The Kohn−Sham orbital representations and the slices through the isosurfaces of the Y−C and Ti−C bonds were visualized in JMOL.[30]

Results and Discussion

Comparison of Tris(Alkoxy Carbene) Adducts of Y d^0 and Ti d^1 ML_3 Complexes. Treatment of $YCl_3(THF)_3$ with 3 equiv of KL, $K[OCMe_2CH_2(1\text{-}C\{NCHCHNPr^i\})]$, in cold THF affords a pale beige-colored solution, and a colorless precipitate of KCl. From the solution, colorless crystals of YL_3 **1** may be isolated in good (62%) yield, eq 1. Complex **1** is pale-cream in color and soluble in aprotic solvents including hexanes.

Complex **1** is diamagnetic, and benzene-d_6 solutions of **1** show a $^1J_{Y-C}$ coupling of 31 Hz in the ^{13}C NMR spectrum. The carbene carbon chemical shift is at 197.3 ppm (d, $^1J_{CY}$ = 31.32 Hz), which is at the high end of the range of frequencies of chemical shifts exhibited by yttrium NHC complexes reported to date. Known yttrium-bound carbene chemical shifts fall in the range 186−194 ppm in benzene-d_6,[24,31] that for **1** is closest to the shift of 199.9 ppm reported for $Y(O\text{-}4,6\text{-}Bu^t_2\text{-}C_6H_2\text{-}2\text{-}CH_2\text{-}[C\{N(CHCH)NPr^i\}])_3$.[32] Interestingly, the ^1H NMR spectrum contains a single set of equivalent ligand resonances, indicating that either the complex has overall C_3 symmetry in the bulk or, on the NMR time scale, the ligands are sufficiently mobile to equilibrate the resonances.



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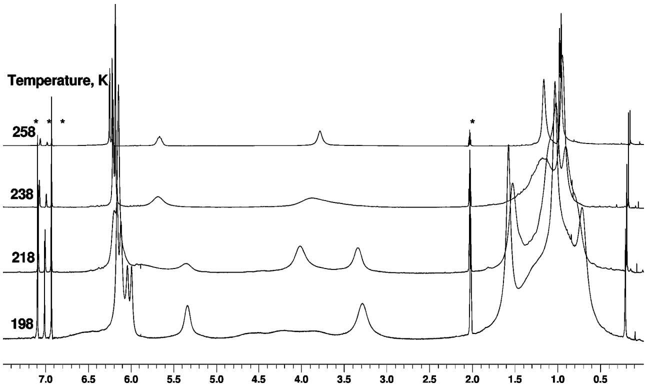

Figure 1. Variable low-temperature NMR spectroscopic study of YL_3 **1** in toluene d_8. * = solvent resonances.

A variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectroscopic experiment was undertaken to identify whether there was any dynamic equilibrium process occurring in solution that renders the ligand resonances equivalent for YL_3 at ambient temperature, or whether the solid-state molecular structure determined was not representative of the bulk material. Figure 1 shows a series of ^1H NMR spectra measured in toluene-d_8 over the temperature range 258 to 198 K (−15 to −75 °C). At and above room temperature, one set of ligand resonances is observed, with minimal changes in chemical shift with the temperature measured. The carbene carbon chemical shift is 194.8 ppm at 258 K with a $^1J_{YC}$ coupling constant of 32 Hz. Upon cooling, the most obvious change in the spectra occurs as the ligand backbone CH_2 singlet resonance, at 3.8 ppm and 258 K, first broadens at 238 K, then splits into two broad resonances by 218 K which appear to be similar in size. However, further cooling of the solution to 198 K shows a further splitting of only the higher-frequency resonance of this pair (at 4 ppm), into two resonances. One other broad singlet of a similar integral is also visible at this temperature, suggesting that a second pair of H atoms have become inequivalent. Therefore, the lower symmetry of the data at temperatures below 238 K confirm that the bulk material does also possess *meridionally*-disposed ligands, as in the crystal structure. If the bulk complex possessed C_3 symmetry, upon cooling, a maximum of two resonances due to the diastereotopic backbone CH_2 protons would be observed.

Molecular Structure of YL_3. Single crystals suitable for an X-ray crystallographic study were grown from a concentrated benzene solution at room temperature. The molecular structure, Figure 2, is *pseudo*-octahedral about the central yttrium atom but not C_3-symmetric; the ligands are disposed such that the three alkoxides (or the three carbenes) of each

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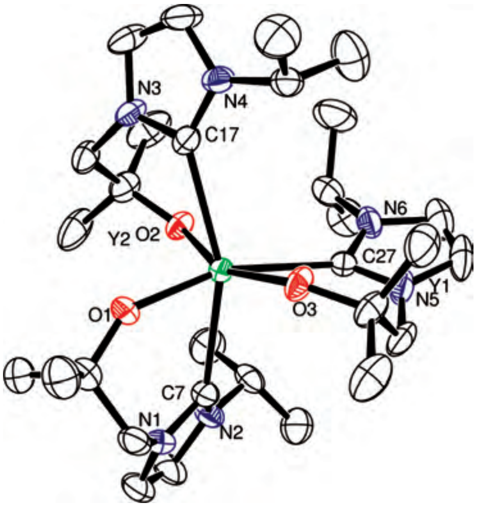

Figure 2. Displacement ellipsoid drawing (50% probability) of the molecular structure of **1**. Lattice solvent and hydrogen atoms omitted for clarity. Λ-*mer* isomer shown.

bidentate ligand are *meridionally* rather than *facially* situated, contrary to that anticipated from the NMR spectral data. Selected distances and angles are reported in Table 1. The asymmetric unit of **1** contains two independent molecules, both of which are the Λ-*mer* isomer.

The geometry of this d^0 complex **1** is the same as that of the d^1 titanium complex TiL_3 **2** which we recently reported.[21] This allows us to compare the six metal carbene bonds in the two systems. Selected distances (Å) and angles (deg) for **1** are collected in Table 1, alongside metrics for the Ti analogue **2**.

There are two molecules of **1** in the asymmetric unit. The semiweighted mean of the six $Y-C_{carbene}$ bond lengths in **1** is 2.588(12) Å, with a range of 2.561(4)−2.644(4) Å. (The semiweighted mean is used since environmental effects are not considered negligible in the variation of the bond distances.[26]) That for the six $Ti-C_{carbene}$ bond lengths in **2** is 2.279(2) Å, with a range of 2.252(4)−2.300(5) Å. The semiweighted averages of the Y−O and Ti−O bond distances are 2.147(10) Å and 1.971(1) Å, respectively.

Table 1 also shows these average distances after normalization by subtraction of the covalent radius for the six-coordinate metal. These radii are 0.810 Å for Ti^{III} and 1.04 Å for Y^{III}.[33] We chose to use the reported covalent radii data since we are concerned with subtlety in a soft carbon ligand,[34] but the data for the ionic radii for these two cations would have produced corrected values with exactly the same Δ values. The difference in the average N−C distance in the NHC group between YL_3 and TiL_3 is within the standard uncertainties.

The normalized data show that the Ti−C bonds are shorter than the Y−C bonds, which could be taken as evidence of a higher bond order, and thus the involvement of π-back-donation from the carbene carbon. The data also show that the Y−O bonds are shorter than the Ti−O bonds, as might be expected for a more electropositive metal center.

Thus, on the basis of experiment alone, it is tempting to suggest that there is a backbonding interaction present in the d^1 Ti system **2** which accounts for a shorter Ti−C bond than in the d^0 Y complex **1**. This analysis is unable to support any π-donating character in the Y−C bond (see above). We note that the electron paramagnetic resonance spectrum of the d^1 complex **2** was relatively broad and showed no evidence of hyperfine coupling to the six nitrogen atoms of the NHC rings.

Computation Analyses of Y d^0 and Ti d^1 ML_3. Preliminary DFT calculations were also performed on molecules **1** and **2**, to provide a computational picture of the differences in the bonding. Geometry optimizations on both structures proceeded smoothly to completion and reproduce successfully the principal features of the structures as determined by X-ray crystallography; the discrepancy in observed and calculated M−C distances ranges between 0.0 and 0.04 Å, Table 2, with smaller discrepancies in the values for **2**, and almost all distances erring to a longer calculated bond distance. Thus, it is likely that the electronic structure and M−C bonds of the calculated **1** and **2** complexes provide good models for those of **1** and **2**. Table 2 also contains the average values for the M−C and M−O distances, and two average values, to identify any bond length differences between ligand groups that are trans disposed toward either a carbene group or an alkoxide group.

On first inspection of the data, it appears that M−C bonds trans to a carbene are shorter than those trans to an alkoxide for both metals. This is the opposite of the situation that one would expect if π-donation to the NHC was present; that is, better π-donation from a trans alkoxide would shorten the M−C trans to M−O more. However, the difference between the M−C distances for trans to C or O are not significant within the 3σ threshold for either **1** or **2**.

The calculated distances again present shorter Ti−C than Y−C bonds, after subtraction of the covalent radius of each metal, and shorter Y−O than Ti−O bonds again, as were seen in the crystal structures.

If there is backbonding in the Ti−C bonds of the Ti complex, or indeed if there is π-donation in the Y−C bonds of the Y complex, this should be visible in the Kohn−Sham representations of the orbitals calculated by DFT. Inspection of the data for **1a** and **2a** shows no evidence of any significant π-symmetry overlap in either system. However, inspection of the total electron density plot shows a better σ-overlap between the Ti and carbon atoms than between the yttrium and carbon atoms. An isosurface electron density plot for the plane containing the metal and the two *trans*-carbene carbon atoms was generated for both **1a** and **2a**; these are shown in Figure 3.

The contours in these plots show a better overlap of the electron density in the Ti−C σ bonds, suggesting that the relative shortness of the bond may simply be due to an increased interaction between the two atoms arising from the smaller, more strongly polarizing Ti center.

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Table 1. Selected Distances (Å) and Angles (deg) for **1** and **2** and Normalized Average Distances (Corrected for the Covalent Radii of the Six-Coordinate Metal Cation)

distance (Å)/angle (deg)		ligand trans	value (obsd)[a]	distance (Å)/angle (deg)		ligand trans	value (obsd)[a]	Δ(Y−Ti) corr[b]
Y1	C7	C	2.594(4)	Ti1	C7	C	2.263(5)	
Y1	C27	O	2.644(4)	Ti1	C27	O	2.299(4)	
Y	C	*average*	2.588(12)	Ti	C	*average*	2.279(2)	
Y	C	*avg. corr.**	1.548	Ti	C	*avg. corr.**	1.461	0.087
Y1	O2	O	2.179(3)	Ti1	O2	O	1.948(3)	
Y1	O1	C	2.118(3)	Ti1	O1	C	1.994(3)	
Y	O	*average*	2.150(11)	Ti	O	*average*	1.971(1)	
Y	O	*avg. corr.**	1.109	Ti	O	*avg. corr.**	1.157	−0.048
C7	N1		1.364(5)	C7	N1		1.361(5)	
C7	N2		1.359(5)	C7	N2		1.361(5)	
N1−C7−N2		C	103.0(4)	N1−C7−N2		C	102.9(4)	

[a] obsd: Observed in X-ray diffraction experiment. [b] corr: Distance corrected for M(III) radius, 0.810 Å for Ti and 1.04 Å for Y. * average corrected.

Table 2. Comparison of Selected Observed versus Computed Distances (Å) and Angles (deg) for **1** and **2**, from the X-Ray Diffraction Experiments and DFT Geometry Optimization Calculations, Respectively

bond (Å)/angle (deg)		ligand trans	obsd	calcd	Δ (calcd − obsd)	bond (Å)/angle (deg)		ligand trans	obsd	calcd	Δ (calcd − obsd)
Y1	C7	C	2.594(4)	2.63	0.04	Ti1	C7	C	2.263(5)	2.29	0.027
Y1	C17	C	2.570(4)	2.57	0	Ti1	C17	C	2.252(4)	2.27	0.018
Y2	C37	C	2.562(4)			Ti2	C47	C	2.274(4)		
Y2	C47	C	2.561(4)			Ti2	C37	C	2.286(4)		
Y1	C27	O	2.644(4)	2.66	0.02	Ti1	C27	O	2.299(4)	2.32	0.021
Y2	C57	O	2.594(4)			Ti2	C57	O	2.300(5)		
Y	C	*average*	2.588(12)	2.62	0.032	Ti	C	*average*	2.279(2)	2.30	0.021
Y	C	*avg. with C trans*	2.571(7)	2.60	0.049	Ti	C	*avg. with C trans*	2.269(2)	2.28	0.011
Y1	O2	O	2.179(3)	2.21	0.031	Ti1	O2	O	1.948(3)	1.95	0.002
Y1	O3	O	2.143(3)	2.19	0.076	Ti1	O3	O	1.958(3)	1.97	0.012
Y2	O5	O	2.177(3)			Ti2	O5	O	2.014(3)		
Y2	O6	O	2.161(3)			Ti2	O6	O	1.945(3)		
Y1	O1	C	2.118(3)	2.15	0.032	Ti1	O1	C	1.994(3)	1.99	−0.004
Y2	O4	C	2.115(3)			Ti2	O4	C	1.972(3)		
Y	O	*average*	2.150(11)	2.18	0.03	Ti	O	*average*	1.971(1)	1.97	−0.001
Y	O	*avg. with O trans*	2.165(6)	2.20	0.035	Ti	O	*avg. with O trans*	1.966(1)	1.96	−0.006
C7	N2		1.359(5)	1.39	0.031	N1	C7		1.361(5)	1.39	0.029
C7	N1		1.364(5)	1.39		N2	C7		1.361(5)	1.39	
C	N	*average*	1.360(2)	1.39		N	C	*average*	1.359(2)	1.39	
N1−C7−N2		C	103.0(4)	103.1	0.1	N1−C7−N2		C	102.9(4)	103.2	0.3
N3−C17−N4		C	103.5(3)	103.5	0.0	N3−C17−N4		C	102.6(4)	103.4	0.8
N5−C27−N6		O	103.0(4)	103.0	0.0	N5−C27−N6		O	102.9(4)	102.5	0.4

[a] C: NHC group in trans position. O: $OCMe_2$ group in trans position. [b] obsd: Data from X-ray crystallographic study. calcd: Data from geometry optimization in DFT calculations.

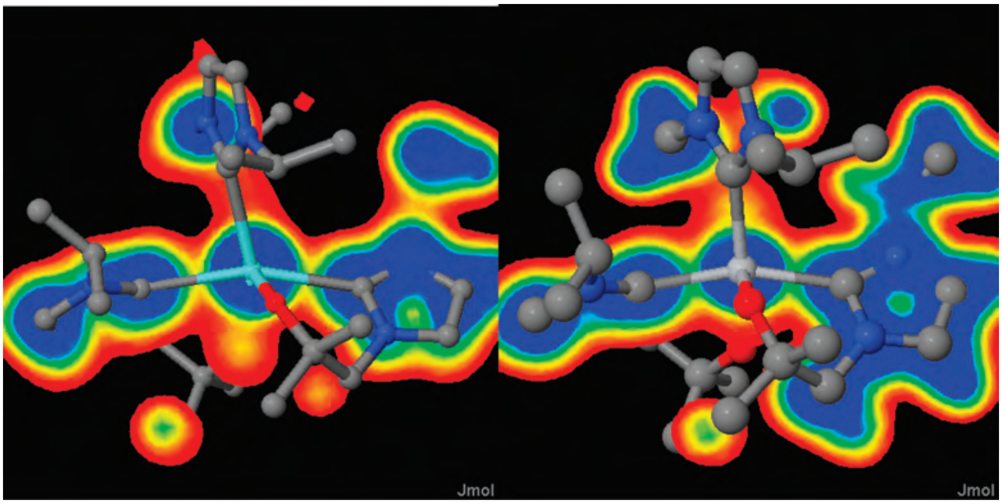
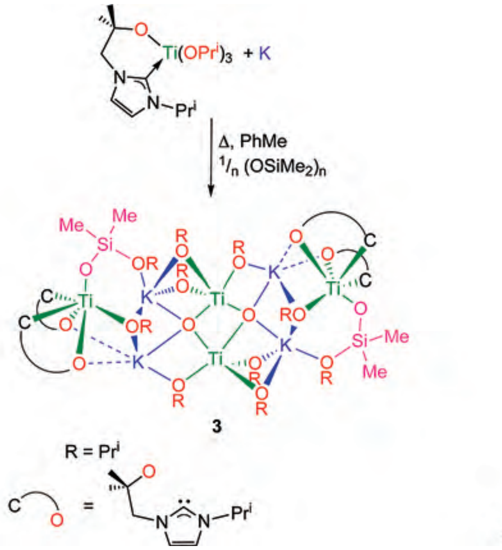


Figure 3. Computed isosurface electron density plots for **1a** (Y, left) and **2a** (Ti, right).

Comparison of Alkoxy Carbene Adducts of Ti d^0 and Ti d^1 Complexes. We anticipated that reduction of the previously made carbene complex TiL(OPr^i)$_3$[24] to a Ti^{III} carbene complex would provide a simple complex for further structural comparisons in a d^0 and d^1 system, but the reaction did not afford a simple reduction product in our hands. Treatment of a solution of TiL(OPr^i)$_3$ with elemental potassium in toluene at 70 °C for 16 h resulted in a color change of the solution from brown to dark green. After removal of the volatiles from the crude mixture, and extraction with diethyl ether, the only isolable product from the reaction was determined to be the bimetallic, mixed-valent potassium−titanium complex **3**, $[Ti^{III}L_2\{Pr^iOSiMe_2O\}K_2OTi^{IV}(OPr^i)_4]_2$, which was identified by a single-crystal X-ray diffraction study. The yield of complex **3** is poor, 5%, but no other tractable material could be isolated from the oily product mixture. Two control experiments, heating solutions of KL alone and with grease, resulted only in a varied amount of decomposition in each case; this suggests that the siloxane cleavage chemistry is mediated by a titanium (III) center.



(2)

Upon cooling a solution of **3** in diethyl ether to −30 °C, single crystals suitable for X-ray structural analysis grew; the molecular structure is shown in Figure 4.

The molecular structure of **3** is composed of a dimeric assembly of two $Ti^{III}K^I_2Ti^{IV}$ clusters. All eight metal cations are assembled into an alkoxide-bridged chain with *iso*-propoxide ligands bridging the metal centers. Also, the structure contains an equivalent of $[OSiMe_2]$, a fragment of the cyclic siloxanes which constitute the silicone grease used to render the glassware airtight. The two outermost titanium cations are assigned as Ti^{III}, and the two central titanium cations as Ti^{IV}. This is because of two points. First, the carbene ligands have rearranged such that the softer Ti^{III} cation is coordinated by two L carbene ligands, which cap the cluster structure, while the harder Ti^{IV} centers are entirely oxygen-coordinated in this formalism. Second, the $Ti-O_{alkoxide}$ distances are significantly longer for the softer Ti(1) than Ti(2). A comparison of the terminal alkoxides shows that Ti(1)−O(9) (1.970(2) Å) is longer than Ti(2)−O(6) (1.873(2) Å). A comparison of the μ_2-bridging alkoxides shows three values for Ti(1)−O of 1.990(2), 2.036(2), and 2.039(2) Å and two values for Ti(2)−O of 1.886(1) and 1.927(2) Å.

Ti(1) is formally trivalent, and pseudo-octahedrally six-coordinate, with the two carbene groups in a cis configuration. One of its four oxygen donor ligands is the $OSiMe_2O$ group derived from grease activation. The two Ti−C carbene distances of 2.306(4) and 2.308(3) Å are significantly longer than those in **2** (average 2.279 Å), and in the other Ti(III) NHC complex, $[Ti\{C(N[-(CH_2)_2\text{-9-fluorenyl}]N[2,6\text{-}Pr^i_2C_6H_3]\text{-}CH_2)_2\}(NMe_2)Cl]$, in which it is 2.221(2) Å.[35] For comparison, there is a wide range of $Ti^{IV}-C_{carbene}$ distances for the 13 extant structurally characterized complexes, 2.194(7)−2.313(5) Å, but the average $Ti^{IV}-C$ distance is 2.230 Å.[18,24,36] Other distances to the Ti^{III}, Ti^{IV}, and the five-coordinate K^I cations are within the conventional range.[33]

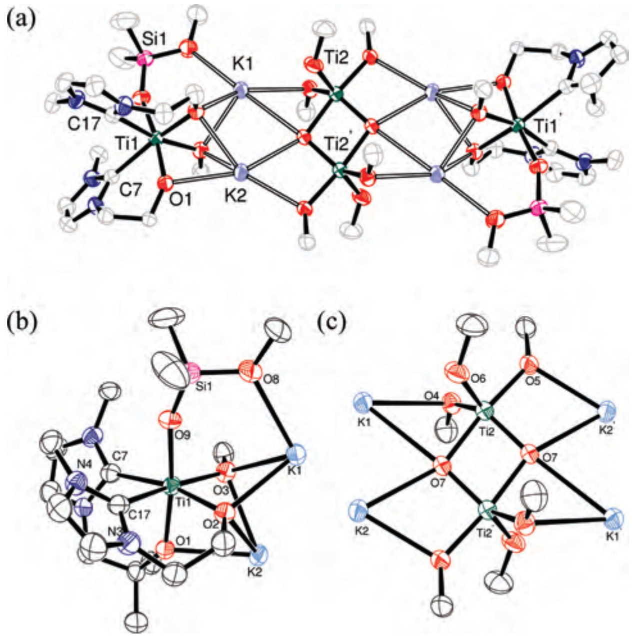


Figure 4. Displacement ellipsoid drawing (50% probability) of the molecular structure of **3**. (a) molecule with all hydrogens and carbon-bound methyl groups omitted for clarity. (b) coordination sphere of Ti1. (c) Coordination sphere of Ti2. Selected distances (Å) and angles (deg): Ti1−C7 2.308(3), Ti1−C17 2.306(4), Ti1−O1 1.990(2), Ti2−O6 1.873(2), O8−Si1 1.656(3), O9−Si1 1.583(2), O9−Ti1−C17 86.35(11), C17−Ti1−C7 90.35(12).

Conclusions

The isostructural complexes YL_3 **1** and TiL_3 **2** differ in that, after subtraction of the metal's covalent radius, the Y−C bonds are longer than the Ti−C bonds, and the Y−O bonds are shorter than the Ti−O bonds. This could be taken as experimental evidence of a π-backbonding interaction in the titanium complex, but comparison of the computed total electron density for the two complexes suggests that the shortening may in fact simply be due to the increased electrostatic interaction caused by the smaller titanium center. The only tractable complex isolable from the reduction of the mono(ligand) complex $TiL(OPr^i)_3$ with elemental potassium was a mixed-valent, multinuclear, d^0 and d^1 cluster, $[Ti^{III}L_2\{Pr^iOSiMe_2O\}K_2OTi^{IV}(OPr^i)_4]_2$, **3**. Structural analysis shows that the carbene ligands are bound to the Ti^{III} centers in preference to Ti^{IV}. The Ti−C distances in **3** are significantly longer than those found in TiL_3.

A survey of the available distances in titanium N-heterocyclic carbene complexes in the literature shows that the distances span a very wide range, and the $Ti^{III}-C$

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[35] Downing, S. P.; Danopoulos, A. A. *Organometallics* **2006**, *25*, 1337.

distances overlap with those for $Ti^{IV}-C$, but it should be noted that the size of the data set is still small. There are now nine $Ti^{III}-C_{carbene}$ distances in the range 2.221(2)−2.308(3) Å, with the average $Ti^{III}-C$ being 2.279 Å, and 13 $Ti^{IV}-C_{carbene}$ distances in the range 2.194(7)−2.313(5) Å, with the average $Ti^{IV}-C$ being 2.230 Å.

Acknowledgment. We thank the Leverhulme Trust, the Alexander von Humboldt Foundation, the Royal Society, the EPSRC, the Universities of Edinburgh and Nottingham for financial support, Dr. Andrew Turner for help with the computational analysis, Dr. Anna Collins for help with calculation of the crystallographic means, Professor Ullrich Englert for helpful discussions, and Professor Simon Parsons for the use of the diffractometer. This work has made use of the resources provided by the EaStCHEM Research Computing Facility (http://www.eastchem.ac.uk/rcf). This facility is partially supported by the eDIKT initiative (http://www.edikt.org).

Supporting Information Available: Crystallographic data files for complexes **1** (690293) and **3** (690294) (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org. These are also available online at http://www.ccdc.cam.ac.uk/.

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