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A ligand influence on the stability of heterobimetallic complexes containing the Ti(μ -O)Al skeleton. Transformation of heterometallic systems to the homometallic Ti(IV) and Al(III) complexes†‡

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The influence of the ligands on the formation and stability of μ -oxo-bridged Ti(IV) complexes has been studied. Reaction of $LTiCl_3$ (1) and LAIMe(OLi) (L = HC(CMeN(2,6-*i*Pr₂C₆H₃))₂, "NacNac") afforded intermediate $LTiCl_2(\mu-O)AIMeL$ (5) in solution, which was converted to $LTiCl(\mu-O)_2TiClL$ (6) and LAIMeCl within 2 days. The decomposition of 5 was estimated to be thermodynamically favorable. The interaction of LTiMe₃ (3) and LAIMe(OH) yielded the intermediate LTiMe₃(μ -O)AlMeL (7). Complex 7 decomposes in solution giving the titanium oxo complex LTiMe(O) (8) and LAIMe₂. The calculated ΔG^{298} for this reaction is -128 kJ mol^{-1} . The degradation of LTiMe₂(μ -O)AlMeL is slow and follows first order kinetics with $k_2 = 4.09(7) \times 10^{-7} \text{ s}^{-1}$. The dimeric complex $LTiMe(\mu-O)_2TiMeL$ -toluene (9a) was isolated from the reaction of 3 with LAIMe(OH) in toluene and $LTiMe(\mu-O)_2TiMeL$ -hexane (9b) from hexane. The dimerization of 8 yielding $LTiMe(\mu-O)_2TiMeL$ (9) is marginally endothermic, with a calculated ΔG^{298} of +27 kJ mol⁻¹. The formation of the solid **9** is due to the lattice stabilization. The solid μ -oxo-bridged complex 9 and Mes₃Ga were obtained from the reaction of LTiMe₃ with [Mes₂Ga(OH)]₂-THF in toluene, and 9 was also isolated from the reaction of LTiMe₃ with 1 equiv. of H_2O in toluene. Compounds LTiCl₃ (1), LTiCl(μ -O)₂TiClL (6), 9a and 9b have been characterized by X-ray single crystal structure, NMR, IR, EI-MS and elemental analysis. Complexes 5, 7 and 8 have been characterized by NMR. Compounds 3, 6 and 9 possess moderate catalytic activity in the polymerization of ethylene.

Introduction

The preparation of new single-site olefin polymerization catalysts has attracted a great interest in both academia and industry in the last few decades.¹ Our interest has been focused on the preparation and characterization of oxo-bridged heterometallic complexes containing group 3 (Al, Ga) and group 4 (Ti, Zr, Hf) metals.² These compounds can serve as a model system for studying the polymerization of olefins and can be considered as effective single-site homogeneous catalysts possessing high catalytic activity and requiring a low ratio of cocatalyst to catalyst precursor, and allowing unprecedented control over the polymer microstructure, thus generating new polymers with improved properties.^{2e} In particular, the oxygen-bridged heterobimetallic complex Cp*₂ZrMe(μ -O)TiMe₂Cp* is highly active and produces linear low-density polyethylene.³

† Dedicated to Professor Ken Wade on the occasion of his 75th birthday. ‡ Electronic supplementary information (ESI) available: IR spectrum of LH, all experimental details and interpretation of NMR reactions *in situ*, NMR spectrum of complex **7**, NMR data for LAIMe₂ and LAIMe(OLi) in C_6D_6 at room temperature, atomic coordinates of the optimized molecules **7**, **8**, **9**, LAIMe₂, details of polymerization experiments. See DOI: 10.1039/b710470g

Although complexes containing the Al(μ -OR)Ti bond, including TiHal₂(salen)AlMe₂-AlMe₂Br (Hal = Cl, Br, SalenH₂ = N,Nbis(salicylidene)ethylenediamine),4 alkoxides,5 complexes supported by the (R)-H₈-BINOL ligand,⁶ or OSO-type ligands,⁷ are known, only three metallocene μ -oxo-bridged complexes containing the Ti(μ -O)Al group have been prepared, namely Cp2TiMe(µ-O)AlMeL,^{2b} Cp2Ti(SH)(µ-O)Al(SH)L and Cp2Ti(SH)(µ-O)Al(OH)L.2d These compounds were obtained using a building block strategy starting from organometallic hydroxide LAIMe(OH) and Cp₂TiMe₂, or a sulfide complex Cp₂Ti(µ-S)₂AlL and H₂O. All the reported complexes contain the cyclopentadienyl ligand. Therefore, an investigation was undertaken of the effect of various ligands on the stability and polymerization activity of heterobimetallic μ -oxo-bridged complexes containing the Ti(μ -O)Al skeleton. Here, we report the synthesis, characterization, and catalytic properties of oxygenbridged Ti(IV) complexes supported by the bulky β -diketiminato ligand (L = HC(CMeN(2,6-iPr₂C₆H₃))₂, "NacNac").

Results and discussion

Preparation and reactivity of complexes

The precursor used in this investigation, complex LTiCl₃ (1), was prepared in good yield by metathesis of TiCl₄ with LLi in toluene. Reaction in toluene yielded the major product 1 and minor amounts of $[C(CMeN(2,6-iPr_2C_6H_3))_2]_2H_2$ (2) (Scheme 1).⁸ Formation of 2 can be rationalized as a result of C–C coupling

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Table 1	(able 1 Calculated thermodynamic values (298 K) for the reactions in the system of LTiMe ₃ (3) with LAIMe(OH)						
	Reaction		ΔH^{298}	$\Delta G^{ m 298}$			
	(3)	LTiMe ₂ (μ -O)AlMeL \rightarrow LTiMe(O) + LAlMe ₂ 7 8	-51	-128			
	(2)	$LTiMe(O) \rightarrow LTiMe(\mu-O)_2TiMeL$	-73	27			
	(1)	$2LTiMe_2(\mu-O)AlMeL \rightarrow LTiMe(\mu-O)_2TiMeL + 2LAlMe_2$	-174	-229			

ulated th



of two ligands promoted by the Ti(IV) centre. Reaction of 1 with excess of MeLi produced the alkyl complex $LTiMe_3$ (3)⁹ (Scheme 1), while interaction of 1 with excess of KH in THF followed by the addition of toluene produced the Ti(III) complex $LTiCl_{2}^{10}$ (4), thus making 1 a potentially useful precursor for the preparation of Ti(IV) alkyl complexes and Ti(III) derivatives.

The reaction of 1 with LAIMe(OLi) was attempted in order to prepare the novel μ -oxo-bridged titanium–aluminium complex $LTiCl_2(\mu$ -O)AlClL (5). However, this reaction afforded LAIMeCl¹¹ and $LTiCl(\mu-O)_2TiClL$ (6), the latter being deposited from the solution. The intermediate complex 5 was observed by means of NMR, and its relative concentration was always small (see the ESI[‡]). The complete transformation of the starting material to 6 and LAIMeCl proceeded within 2 days at room temperature (Scheme 2).



Scheme 2

In order to explore the influence of the ligand on the stability of the μ -oxo-bridged titanium–aluminium system, the reaction of 3 with LAIMe(OH) was investigated. Similarly to the previous reaction LTiMe(µ-O)₂TiMeL (9) and LAlMe₂¹⁴ were isolated as final products at room temperature.¹² However, monitoring the reaction of 3 with 1 equiv. of LAIMe(OH) (see the ESI[‡]) by ¹H NMR spectroscopy revealed a series of products (LTiMe₂(μ -O)AlMeL (7), LTiMe(O) (8), 9, LAlMe₂ (Table 1) and CH₄) as shown in Scheme 3.



A maximum concentration of 7 was achieved from 7 to 36 hours after the beginning of the reaction (Fig. 1 and 2). However, within this time, complex 7 did not crystallize from the concentrated toluene or hexane solution,13 but slowly decomposed with deposition of $LTiMe(\mu-O)_2TiMeL$ (9) and formation of LAIMe₂¹⁴ (Scheme 3).

The formation of $\mathbf{9}$ and LAlMe₂ as the final reaction products implies migration of the methyl group from the Ti(IV) to the Al(III) and transfer of the oxygen atom from the Al(III) to the Ti(IV) centre, followed by dimerization of the intermediate 8. This can be regarded as a symmetrization of the system. In order to extend our study, we attempted the reaction of [Mes₂Ga(OH)]₂-THF and 3 in toluene at room temperature and 100 °C, which again results in the formation of 9, this time with Mes₃Ga (Scheme 4), confirming the oxygen metathesis. The formation of 9 was observed during the hydrolysis of 3 implying that 9 is highly stable, at least in the solid state, and that 9 is a final product of various reactions of the



Fig. 1 Concentration of complexes in the reaction system vs. time.



Fig. 2 Concentration of complexes in the reaction system vs. time.



Scheme 4

Ti(IV) alkyl complex **3** and compounds that are potential oxygen donors (*e.g.* hydroxides, water) (Scheme 5).



NMR, kinetic and thermodynamic study of the LTiMe₃-LAIMe(OH) system

The reaction of LTiMe₃ and LAIMe(OH) (ratio 1 : 1) was monitored in detail by ¹H NMR. In order to determine the concentration of a complex, the relative intensities of L (γ -H) or the protons of the Me-group (at the aluminium centre) were compared. We propose that the relaxation time of the protons in similar environments for different complexes would be similar, thus reducing the inaccuracy of the measurement.¹⁵ The decay of the initial species (LAIMe(OH), LTiMe₃) was found to follow second order kinetics (Fig. 3). A least squares fit of the linear plot of $1/c_3$ against time¹⁶ revealed the second order rate constant ($k_1 = 6.8(2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$).¹⁷ No other kinetic data are available for the interaction of alkyltitanium compounds with organometallic hydroxides. The reaction of (tBu_3PN)TiMe₃ with AlMe₃ was determined to be of second order ($k_1 = 3.9(5) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$).¹⁸ The decomposition of LTiMe₂(μ -O)AlMeL (7) with formation of LTiMe(O) (8) and LAlMe₂ was found to follow first order kinetics (ln(c(LAlMe₂)) vs. time and ln(c(7)) vs. time) (Fig. 4). The rate constant k_2 was determined as 4.09(7) $\times 10^{-7} \text{ s}^{-1}$.



Fig. 3 Representative data for the decay of LTiMe₃ (3) vs. time. Linear relationship 1/c(LTiMe₃) vs. time: $Y = 15.1(5) + 6.8(2) \times 10^{-3} \cdot X$.



Fig. 4 Representative data for the decay of $LTiMe_2(\mu$ -O)AlMeL (7) vs. time; the linear relationship between ln(c(7)) vs. time is $Y = -2.758(4)-4.09(7) \times 10^{-7} \cdot X$.

The decomposition of $LTiMe_2(\mu-O)AlMeL$ (7) resulted in the formation of LAIMe₂ and the titanium complex LTiMe(μ -O)₂TiMeL (9) according to the proton NMR spectrum. Calculated concentrations of complex 9 were always lower than those of LAIMe₂; this might be due to the observed resonance, which belongs to the monomeric complex LTiMe(O) 8. Its concentration initially was similar to that of LAIMe₂, and after about 33 to 35 $(\times 10^4)$ seconds the concentration of 8 starts to decrease relative to LAIMe₂ (see Fig. 1). This behavior of the concentration is common for monomeric species in dilute solutions, and oligomerization was induced by increasing the concentration. The additional resonances of γ -H (after 33 \times 10⁴ s at 5.42, 5.28 ppm), could be assigned to the oligomers, although deposition of 9 was not observed from the solution within the time of the experiment (0 to 80×10^4 s). Additionally, the rate of formation of 8 follows first order kinetics ($k_2 = 5.7(8) \times 10^{-7} \text{ s}^{-1}$), similar to that determined from $\ln(c(7))$ vs. time with linear regression. For that reason the presence of **8** in the solution seems feasible.

The results of the kinetic measurements imply the thermodynamic instability of LTiMe₂(μ -O)AlMeL (7). To get a more precise picture of the reaction involving compound 7, DFT calculations were carried out for all involved complexes without any simplifications, aiming at the determination of the reaction mechanism and reaction energetics. Transformation of 7 to LTiMe(O) (8) and LAlMe₂ or to complex LTiMe(μ -O)₂TiMeL (9) and LAlMe₂ is thermodynamically favored [eqn (1)–(3), Table 1]. The free energy of dimerization of 8 to 9 has a small positive value indicating thermodynamic instability of the dimeric complex in the gas phase [eqn (2)]. The solvation energies of the neutral molecules in solvents of low polarity such as benzene and toluene are small and, hence, we propose that dimerization of 8 is thermodynamically unfavorable in C₆D₆ and toluene solution. Obviously, compound 9 is lattice stabilized.

$$\Delta H_4 \approx 2E \text{ (Ti}(\mu\text{-O})) + 2E \text{ (Al-Me)} - 2E \text{ (Ti-Me)}$$
$$-2E(\text{Al}(\mu\text{-O})) \tag{4}$$

Alternatively, the enthalpy of this transformation can be estimated from the bond dissociation energies (BDE) [eqn (4)], provided that the BDEs of $Ti(\mu$ -O) are similar for the precursor and the reaction product. In fact, the calculated $Ti(\mu - O)$ distance in 7 (1.813 Å) is close to the Ti(μ -O) distance in LTiMe(μ -O)₂TiMeL– toluene (9a) and $LTiMe(\mu-O)_2TiMeL$ -hexane (9b) (1.843(2) and 1.8410(13) Å), implying similarity of the BDEs for $Ti(\mu-O)$ in both compounds.¹⁹ The experimentally determined BDEs have been collected from the literature; E(Ti-C) is 251 kJ mol⁻¹ for $Cp_2TiMe_2^{20,21}$ and 190–240 kJ mol⁻¹ for TiR₄²⁵ (mean *E*(Al–C) 255 kJ mol⁻¹²² and E(Al-O) is 424 kJ mol⁻¹²³). The Ti-O BDE strongly depends on the Ti-O bond length¹⁹ and varies from $670(\pm 9.6)$ kJ mol⁻¹ for [TiO]⁺²⁴ to E(Ti–OR) 466 kJ mol⁻¹ for $Ti(OR)_4$ (452 kJ mol⁻¹ for Cp₂Ti(OR)₂, R = C(O)Ph, C(O)CF₃).²⁵ Using various calorimetric reactions, the mean dissociation energies of Ti-O bonds in alkoxide complexes have been estimated as 431 kJ mol⁻¹.²⁶ The $E(Ti-OAIR^*)$ should be close to E(Ti-OR)since the Ti–O(Al) bond distances^{2,27} for the known μ -oxo-bridged $Ti(\mu$ -O)Al complexes are in the same range as those of the titanium alkoxides.²⁸ Using these values and eqn (4), the enthalpy of the reaction [eqn (3)] is estimated to lie in the range from -22 to

 Table 2
 Selected bond distances (Å) and angles (deg) for 1, 6, 9a and 9b^a

-92 kJ mol⁻¹, showing that the reaction is thermodynamically favorable.

Using this approach and bond dissociation energies Ti–Cl (388.3 kJ mol⁻¹²⁹ or 429.3 kJ mol^{-130,22}) and Al–Cl (430 kJ mol⁻¹³¹ or 420.7 \pm 10 kJ mol⁻¹²²), the enthalpy of the reaction [eqn (5)] was estimated to be between -71 and -193 kJ mol⁻¹. As a result, LTiCl₂(μ -O)AlMeL (5) is thermodynamically unstable and decomposed to give the thermodynamically favorable **6** and LAl(Me)Cl.

$$2 \text{LTiCl}_{2}(\mu \text{-O}) \text{AlMeL} \rightarrow \text{LTiCl}(\mu \text{-O})_{2} \text{TiClL} + 2\text{LAlMeCl}$$
(5)
5 6

Characterization of titanium complexes 1, 6, 7, 9a and 9b

The structure of LTiCl₃ (1) was determined in the space group *Pnma*; the structure is isotypic to that of LTiMe₃,⁹ arising from the comparable size of the Me group and Cl atom (Fig. 5). The geometry of the complex 1 is also similar to that of LZrCl₃,³² (L = β -diketiminato ligand N(SiMe₃)C(*t*Bu)CHC(Ph)N(SiMe₃)). The molecule displays crystallographic mirror symmetry. The Ti(IV) centre exhibits a distorted square pyramidal environment, with the Ti atom lying 0.51 Å out of the NNCICl plane. The Ti–N bond length in 1 is in the normal range³³ (Table 2).



Fig. 5 Molecular structure of 1 with selected labelled atoms. Ellipsoids represent 50% probability levels; carbon radii are arbitrary. "A" indicates atoms generated by mirror symmetry.

1		6		9a		9b	
Ti-N(1) Ti-Cl(1) Ti-Cl(2) N(1)-C(1) C(1)-C(2) N(1)-Ti-N(1) N(1)-Ti-Cl(2) N(1)-Ti-Cl(1)	2.062(3) 2.2531(17) 2.1893(19) 1.340(5) 1.391(5) 87.13(17) 99.81(10) 87.17(10)	Ti-O(B) Ti-O Ti-N(2) Ti-N(1) Ti-Cl O-Ti-O(B) O(B)-Ti-N(2) O-Ti-N(2)	1.8316(8) 1.8589(8) 2.1127(10) 2.1253(10) 2.2434(4) 81.78(4) 148.39(4) 88.78(4)	Ti-O Ti-C(1) Ti-N O(C)-Ti-O O-Ti-C(1) O-Ti-N C(1)-Ti-N N-Ti-N(D)	1.843(2) 2.092(5) 2.149(3) 82.83(16) 104.69(12) 91.35(11) 99.33(14) 84.54(16)	$\begin{array}{c} Ti-O \\ Ti-O(E) \\ Ti-C(1) \\ Ti-N(1) \\ Ti-N(2) \\ O-Ti-O(E) \\ O-Ti-C(1) \\ N(1)-Ti-N(2) \end{array}$	1.8410(13) 1.8514(13) 2.0808(19) 2.1568(14) 2.1591(15) 82.77(6) 104.89(7) 84.69(6)
Cl(2)-Ti-Cl(1)	107.84(7)	N(2)-Ti-N(1) O-Ti-Cl N(1)-Ti-Cl Ti(B)-O-Ti	85.47(4) 106.43(3) 100.01(3) 98.22(4)	Ti(C)–O–Ti	97.17(16)	O-Ti-N(1) O-Ti-N(2) C(1)-Ti-N(1)	155.27(6) 91.83(6) 99.83(7)

^{*a*} Symmetry transformations used to generate equivalent atoms A of 1: x, -y + 1/2, z; to generate equivalent atoms B of 6: -x + 1, -y + 1, -z + 1; C of 9a: -x + 1, -y, -z + 1; D of 9a: x, -y, z; E of 9b: -x + 1, -y, -z + 1.

The single crystal X-ray structures of 6 (Fig. 6), $LTiMe(\mu O_2$ TiMeL-toluene (9a) and LTiMe(μ -O)₂TiMeL-hexane (9b) (Fig. 7) have been determined by X-ray crystallographic methods.§ The structure of 7 was calculated and will be presented below. $LTiCl(\mu-O)_{2}TiClL$ (6) contained toluene of solvation. Compound 9 revealed two crystalline forms: 9a is a toluene and 9b a hexane solvate. Complexes 6, 9a and 9b display imposed crystallographic symmetries 1, 2/m and 1, respectively. The structures of **6** and 9 consist of two $LTi(Cl)(\mu-O)$ and $LTiMe(\mu-O)$ units containing Ti(IV) centres in a distorted square-pyramidal environment, formed by two nitrogen atoms, two bridging oxygen atoms and a carbon atom of the methyl group or chlorine atom. Mean deviation from the (NNOO) plane is 0.040 Å in 6, zero by symmetry in 9a, and 0.016 Å in 9b. The Ti atom lies 0.493, 0.413 and 0.409 Å above the (NNOO) plane in 6, 9a and 9b, respectively. The coordination environment of the Ti atom in $\{TiN_2(\mu-O)_2Me\}$ and $\{TiN_2(\mu-O)_2Cl\}$ has so far not been observed in the literature, although a distorted square-planar coordination was reported for the titanium atom {environment $TiN_2(\mu$ -OMe)₂Me} in the spirosiladiazatitanacyclobutane complex [(cyclo)Si(NtBu)₂Ti(µ-OMe)Me]₂³⁴ and {environment TiN₂(μ -OR)₂Me} in the chloride complexes [Ti(Cl)(NMe₂)(-OCH₂CH(CH₂Ph)N(R)-)]₂ (where R = iPr, cyclo-C₆H₁₁, 2-adamantyl),³⁵ [(cyclo)Si(NtBu)₂Ti(μ -OMe)Cl]₂.³⁴ All the bond distances in 6, 9a and 9b are in the normal range.^{33,36} The Ti(μ -O) bond lengths also fall in the range for Ti(IV) complexes with the Ti(μ -O)₂Ti unit.³⁷



Fig. 6 Molecular structure of **6** with selected atom labelling. Ellipsoids represent 50% probability levels. Carbon radii are arbitrary.

Although complexes 6 and 9 are slightly soluble in benzene and toluene (less than 1 mg in 1 ml), ¹H and ¹³C NMR spectra were measured. Based on thermodynamical and kinetic data an assumption was made (see the previous section) that 9 is lattice stabilized and monomer 8 might be present in the solution of 9. Hence, NMR resonances in the benzene solution of 9 have been assigned to the monomeric complex 8. Proton resonance of the methyl group attached to the titanium atom appears at 1.22 ppm and ¹³C resonances at 60.2 ppm for 8. The EI-MS of 9 exhibits View Article Online



Fig. 7 Molecular structure of 9b with selected atoms labelling. Ellipsoids represent 50% probability levels. Carbon radii are arbitrary.

the molecular ion for **9** and also a strong cation peak, which resulted from abstraction of the methyl group. The EI-MS of **6** contained strong cations of [LTiOCl]⁺ and of [LTi-2H]⁺. The ¹H and ¹³C NMR spectra of **6** are consistent either with **6** or with the monomer LTiCl(O); however, available data do not allow further detailed assignments.

The complexity of the molecules 6 and 9 prevents accurate assignment of the IR bands to the individual vibrations. Taking into account the calculated IR spectrum of 9, we were able to assign the Ti-Me and Ti- $(\mu$ -O) vibrations. Observed bands (321 and 340 cm^{-1} , calculated 330 and 352 cm⁻¹) were assigned to the out of plane vibrations of oxygen of the {MeTi(μ -O)₂TiMe} unit. A broad band at 564 cm⁻¹ (calculated 548, 554, 560 cm⁻¹) is attributed to the Ti-Me. Very strong overlapped bands with the energies 600 to 694 cm⁻¹ (calculated 585, 609, 620, 639, 642, 661, 664, 680, 693 cm⁻¹) were assigned to the modes of {MeTi(μ -O)₂TiMe} (inplane vibration of oxygen) and the ligand. The contribution of an in-plane Ti(μ -O)₂Ti vibration is most substantial for the calculated bands at 680 and 693 cm⁻¹. Similarly, very strong and overlapping bands within 620 to 690 cm^{-1} in the IR spectrum of **6** have been assigned to the modes with substantial contribution of $\{CITi(\mu -$ O₂TiCl} (in-plane vibrations of oxygen) and bands at 309 and 344 cm⁻¹ to the out of plane vibrations of oxygen in {CITi(μ - $O_{2}TiCl$.

The structure of LTiMe₂(μ -O)AlMeL (7) was calculated by DFT methods (Fig. 8). The Al–(μ -O) bond length (1.821 Å) in 7 is significantly longer than that in the μ -oxo-bridged titanium–aluminium complex Cp₂TiMe(μ -O)AlMeL^{2c} (1.715(3) Å) while the Ti–(μ -O) distance in 7 (1.813 Å) is similar to that in Cp₂TiMe(μ -O)AlMeL (1.808(3) Å), reflecting a higher Ti-(μ -O) bond strength (1.01 valence unit in terms of bond valence theory³⁸), than that of Al–(μ -O) (0.58 valence unit). The Ti1–O3–Al2 angle (160.1°) is also close to that in Cp₂TiMe(μ -O)AlMeL (151.7(2)°).^{2c}

The ¹H and ¹³C NMR spectra are in agreement with the proposed structure of 7. The proton resonances assigned to 7 have similar relative intensities in all NMR spectra at different reaction times (*in situ* reaction). In order to confirm the assignment, the NMR shifts were calculated with the Gauge-Independent

 $[\]S$ CCDC reference numbers 652772–652774. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b710470g



Fig. 8 Optimized geometry of LTiMe₂(μ -O)AlMeL (7), hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al2–O3 1.821, Al2–C8 1.981, Al2–N6 2.000, Al2–N4 2.011, Ti1–O3 1.813, Ti1–C9 2.092, Ti1–C10 2.089, Ti1–N7 2.090, Ti1–N5 2.416; O3–Al2–C8 111.95, O3–Al2–N6 116.60, C8–Al2–N6 106.40, C8–Al2–N4 107.32, N6–Al2–N4 94.73, O3–Ti1–C10 96.25, O3–Ti1–N7 108.48, O3–Ti1–C9 90.61, O3–Ti1–N5 166.44, C10–Ti1–N7 108.05, C10–Ti1–C9 121.32, C10–Ti1–N5 83.43, N7–Ti1–C9 124.54, C9–Ti1–N5 78.15, Ti1–O3–Al2 160.11.

Atomic Orbital (GIAO) method for 7.³⁹ Calculated ¹H (-0.21 to -0.11 ppm) and ¹³C (60.6 ppm) chemical shifts of the Ti–Me resonance are in good agreement with the observed values (0.53 and 56.6 ppm). The Me group at aluminium exhibits a proton resonance at -0.14 ppm and ¹³C resonance at -9.5 ppm. The calculated ¹³C chemical shift of Al–Me (-9.5 ppm) is in good agreement but the calculated proton shift fits less well (-1.34 ppm). The γ -H of each NC(Me)CHC(Me)N moiety showed resonances at 4.25 ppm (calcd 4.28) and 5.03 ppm (calcd 4.46). The upfield resonance is assigned to the NC(Me)CHC(Me)N attached to Al(III) and the downfield resonance to the Ti(IV) centre.

Polymerization experiments

The trialkyltitanium complex LTiMe₃ (**3**) and oxo-bridged complexes LTiCl(μ -O)₂TiClL (**6**) and LTiMe(μ -O)₂TiMeL–toluene (**9a**) showed low activity for polymerization of ethylene, although the activity of the oxo-bridged complexes **6** and **9a** was slightly higher at 80 °C than that at room temperature (Table 3). This result can be compared with the activity of LTiMe₂ complexes.⁴⁰ Budzelaar's Ti(III) alkyls were found to be inactive in toluene and displayed low to moderate activities in benzene upon activation with B(C₆F₅)₃. Additionally, all complexes were inactive for styrene polymerization even upon attempted activation with MAO in toluene at room temperature and 80 °C, and **3**, **6** and **9a** are inactive in combination with AlMe₃ for polymerization of ethylene. Increase of the cocatalyst to catalyst ratio did not increase the activities of **3** and **9a**. This behaviour is attributable to the instabilities of the active species, similarly to that of the LTiMe₂–B(C₆F₅)₃ system;⁴⁰ interaction of the complexes with MAO resulted in the formation of inactive species (see the ESI[‡]). The DSC measurements show that the melting points (T_m) of the polyethylene produced with **3**, **6** and **9a** at room temperature are in the range of 123.4 to 125.8 °C, similar to those (120 to 125 °C) produced with Cp*₂MeZr(μ -O)TiMe₂Cp*.³

Conclusions

Interaction of LTiMe₃ and LAlMe(OH) gives the target μ -oxo-bridged Ti(IV)–Al(III) complex LTiMe₂(μ -O)AlMeL (7). This reaction is determined to be a second order process. While the previously reported metallocene complex Cp₂TiMe(μ -O)AlMeL^{2c} was isolated and characterized, complex 7 is unstable and decomposes in solution giving the titanium oxo complex LTiMe(O) (8) and LAlMe₂. Decomposition of 7 is thermodynamically favorable and the estimated ΔG^{298} is -128 kJ mol⁻¹. Decomposition of LTiMe₂(μ -O)AlMeL (7) is slow and follows first order kinetics. The dimeric complex LTiMe(μ -O)₂TiMeL (9) was isolated from the reaction system. Dimerization of 8 to 9 is marginally endothermic (+27 kJ mol⁻¹) and formation of 9 is explained by lattice stabilization.

The chloride ligand at the Ti(IV) centre does not increase the stability of a μ -oxo-bridged Ti(IV)–Al(III) complex. The chloride complex LTiCl₂(μ -O)AlMeL (**5**) was observed only as a reaction intermediate and decomposed with deposition of solid LTiCl(μ -O)₂TiClL (**6**) and LAlMeCl. Decomposition of **5** is thermodynamically favorable; the estimated range of ΔH is -71to -193 kJ mol⁻¹.

Complex LTiMe(μ -O)₂TiMeL (9) was obtained by reaction of LTiMe₃ and [Mes₂Ga(OH)]₂-THF or alternatively by hydrolysis of LTiMe₃ (3) in toluene, thus confirming the oxygen transfer to the Ti(IV) centre by interaction of the titanium alkyl complex with group 13 hydroxides.

Taking the obtained results into account we have proved that the supporting ligands influence the stability of the μ -oxo-bridged

Table 3Ethylene polymerization data for the complexes 3, 4, 6 and 9a

Complex	Cocatalyst: MAO		AlMe ₃		$T_{\rm m}{}^d/{}^{\rm o}{\rm C}$	
	25 °C	85 °C	25 °C	80 °C	25 °C	85 °C
$LTiMe_3$ (3)	1×10^{3b}	c	Not active	Not active	123.7	_
$LTiCl_2$ (4) ^{<i>a</i>}	Not active	Not active	_	_		
$LTiCl(\mu-O)_2TiClL$ (6)	1×10^{3}	7×10^{3}	Not active	Not active	125.8	122.2
$LTiMe(\mu-O)_2TiMeL$ -toluene (9a)	$1-4 \times 10^{3}$	$4-8 \times 10^{3}$	Not active	Not active	123.4	119.9
TiBz4 ^e	1.4×10^{4}	1×10^4			126.2	123.5

^{*a*} LTiCl₃ (1) and 2 to 4 equiv. AlMe₃ formed LTiCl₂, therefore only LTiCl₂ (4) was tested. ^{*b*} Activity: g (polymer) mol (catalyst)⁻¹ h⁻¹ bar⁻¹, reproducibility is low as observed by different runs under the same conditions for **9a**. Conditions: time 1 h, pressure 1 bar, Al to Ti varied from 500 : 1 to 2000 : 1, volume 40 ml, 4.3–15.5 µmol of complex was used in different runs (see ESI† for details). ^{*c*} LTiMe₃ (3) decomposed on heating in solution thus preventing variable temperature study. ^{*d*} Determined by DSC. ^{*e*} TiBz₄ was studied as a reference under the same conditions. Polymerization of ethylene using TiBz₄ was studied in ref. 41. The reported activity of TiBz₄–AlEt₂Cl in *n*-heptane solution 7×10^3 g (polymer) mol (catalyst)⁻¹ h⁻¹ bar⁻¹.⁴²

Ti(IV)–Al(III) complexes. The alkyl complexes degrade more slowly than the corresponding chloride complexes. Moreover the investigated μ -oxo-bridged complexes supported by the NacNac ligand are unstable.

Complexes **3**, **6** and **9a** possess low catalytic activity in polymerization of ethylene. We explain these phenomena by the instability of the catalytically-active species.

Experimental

All operations were performed under an atmosphere of dry, O₂free N2 employing both Schlenk line techniques and an MBrown MB-150B inert atmosphere glove box. Solvents toluene, hexane and tetrahydrofuran were dried over Na/benzophenone and distilled under nitrogen prior to use. C₆D₆ was dried over K and degassed, H₂O was degassed under nitrogen. The compounds LH with the ligand $L = (2,6-iPr_2C_6H_3NC(Me))_2CH$, NacNac), LAIMe(OH), [Mes₂Ga(OH)]₂-THF were prepared by the known literature methods.^{2b,43,44,45} Complex LAIMe(OLi) was prepared from LAlMe(OH) and 1 equiv. of solid MeLi-(Et₂O)_{0.137} at room temperature in toluene, followed by crystallisation from hexane. Complex LTiMe₃ was prepared from LTiCl₃ and 4 equiv. of solid MeLi-(Et₂O)_{0.137} at 0 °C in toluene, followed by filtration, concentration and washing of the resulted product with n-hexane.9 The MeLi-Li(Et₂O)_{0.137} was prepared from the known amount (60 ml) of MeLi solution in Et₂O (1.6 M) by evaporation of Et₂O in a dynamic vacuum to constant weight. The amount of Et₂O was determined by the weight of the resulting solid and confirmed by ¹H NMR. The purity of all compounds was checked by ¹H and ¹³C NMR spectra. TiCl₄ (Aldrich 99%) was distilled prior to use in a dry and O₂-free N₂ atmosphere. Solutions of MeLi (1.6 M), nBuLi (1.6 M) (Acros Organics), MAO (10 wt.%) and AlMe₃ were used as received. ¹H and ¹³C NMR spectra were recorded using Bruker Avance DPX 200, Bruker Avance DRX 500 and Varian INOVA 600 spectrometers. Chemical shifts are reported in δ units downfield from Me₄Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 mass spectrometer, and elemental analyses were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were measured in sealed capillary tubes under nitrogen and are not corrected. Melting points of polymers were measured on Netzsch STA 409 PC spectrometer. For the preparation of 1, 2 see the ESI,‡ for 3 see ref. 9 and 4 see ref. 10. Compound $LTiCl_2(\mu$ -O)AlMeL (5) is unstable and was not isolated (see the ESI, p. 4[±]), complex $LTiMe_2(\mu-O)AlMeL$ (7) observed in solution and characterized by NMR (see ESI, p. 6–14[‡]), compound LTiMe(O) (8) was observed in solution of $LTiMe(\mu-O)_2TiMeL$ (9).

Preparation of LTiCl₃ (1)

Dry toluene (250 ml) was added to LH (14.69 g, 35.1 mmol) in a 500 ml Schlenk flask. The mixture was cooled to -78 °C and 22 ml of *n*BuLi solution in hexane (1.6 M, 35.1 mmol) was added drop by drop. The reaction solution was stirred for 1 h at -78 °C, allowed to warm to room temperature and stirred overnight at room temperature. This solution was cooled to -78 °C and a solution of TiCl₄ (3.9 ml, 6.71 g, 35.3 mmol) in toluene (20 ml) was added drop by drop by drop. The color of the solution immediately changed to

dark brown. Then, the reaction mixture was stirred 2 h at -78 °C and 16 h at room temperature. The resulting solution was filtered to remove LiCl and concentrated (10-20 ml), whereupon a black crystalline solid formed. The resulting mixture was filtered and the black crystals of 1 washed with *n*-hexane $(2 \times 10 \text{ ml})$. Yield of 1 12.80 g (65%). Anal. calcd (found) for $C_{29}H_{40}Cl_3N_2Ti$ (1): calcd C 60.85 (60.90); H 7.17 (7.20); N 4.90 (4.94). Mp 222-223 °C. EI-MS: m/z (%) = 571 (2.7) [M]⁺, 535 (100) [M⁺-Cl], 528 (5.4) [M⁺-C₃H₇], 498 (14.0) [M⁺–Cl₂], 418 (36.7) [L]. ¹H NMR (500.2 MHz, C_6D_6 , r.t.), δ_H (ppm) = 7.0–7.2 (m, 6 H, C_6H_3), 5.55 (s, 1H, C(CH₃)CHC(CH₃)), 3.14 (sept, 4H, J = 6.75 Hz, CHMe₂), 1.51 (s, 6H, C(CH₃)CHC(CH₃)), 1.42 (d, 12H, J = 6.7 Hz, CHMe₂), 1.10 $(d, 12H, J = 6.8 \text{ Hz}, CHMe_2)$. ¹³C NMR (125.76 MHz, toluene-d8, r.t.), $\delta_{\rm C}$ (ppm) = 170.6 (*C*(CH₃)CH*C*(CH₃)), 153.1 (*C*₆H₃), 140.3 (C₆H₃), 137.4 (C₆H₃), 107.7 (C(CH₃)CHC(CH₃), 29.1 (CHMe₂), 26.3 (C(CH₃)CHC(CH₃), 24.8 (CH₃), 24.5 (CH₃), assignment was done using ¹H¹³C correlation and available references.⁴⁶ IR (KBr, *cm*⁻¹, Nujol mull): 3071 (w), 3057 (w), 1933 (w), 1865 (w), 1797 (w), 1698 (w), 1587 (w), 1542 (vs), 1495 (s), 1464 (vs), 1450 (vs), 1384 (vs), 1361 (vs), 1346 (vs), 1313 (vs), 1282 (vs), 1254 (s), 1242 (vs), 1222 (s), 1178 (m), 1158 (m), 1097 (s), 1058 (m), 1040 (m), 1022 (s), 953 (w), 935 (s), 900 (w), 885 (w), 856 (s), 836 (w), 799 (vs), 763 (vs), 723 (m), 698 (m), 656 (w), 638 (w), 626 (m), 608 (w), 591 (w), 530 (m), 459 (vs), 435 (vs), 393 (vs), 368 (w), 352 (w).

Preparation of LTiCl(µ-O)₂TiClL (6)

Toluene (40 ml) was added to LAIMe(OLi) (0.50 g, 1.0 mmol) and LTiCl₃ (0.60 g, 1.0 mmol). The resulting solution was stirred for 10 min until all precursors dissolved and was left undisturbed for 3 days at room temperature. The red block-shaped crystals of 6 that deposited were filtered from the supernatant solution and LiCl through a coarse frit. Yield of 6 0.45 g (80%). An additional crop of 6 (0.1 g) can be obtained by crystallization of the concentrated (5-8 ml) supernatant solution. Anal. calcd (found) for C₆₅H₉₀Cl₂N₄O₂Ti₂: C 69.33 (69.17); H 8.00 (7.93); N 4.97 (4.96). Mp 229 °C decomp. EI-MS: m/z (%) = 536 (10) $[LTi_2O_2Cl-C_3H_9]^+$, 516 (15) $[M-2Cl-NiPr_2C_6H_3-iPr_2$ *i*Pr-MeCCHCMe]⁺, 498 (100) [LTiOOH or M-2Cl-N*i*Pr₂C₆H₃- $HiPr_2C_6H_3-HiPr-MeCCHCMe-CH_4]^+$, 480 (10) [LTiO-H]⁺. ¹H NMR (599.74 MHz, C₆D₆, r.t.), $\delta_{\rm H}$ (ppm) = 7.28, 7.17, 7.13– 6.99 (m, aryl), 5.19 (s, 2H, C(CH₃)CHC(CH₃)), 3.24 (sept, 4H, J = 6.70 Hz, CHMe₂), 2.85 (sept, 4H, J = 6.80 Hz, CHMe₂), 2.10 (s, 3H, toluene), 1.44 (d, 12H, J = 6.70 Hz, CHMe₂), 1.37 (s, 12H, C(CH₃)CHC(CH₃)), 1.18 (d, 12H, J = 6.70 Hz, $CHMe_2$), 0.91 (d, 12H, J = 6.70 Hz, $CHMe_2$), 0.85 (d, 12H, J = 6.80 Hz, CHMe₂). ¹³C NMR (125.707 MHz, C₆D₆, r.t.), $\delta_{\rm C}$ (ppm) = 167.9 (C(CH₃)CHC(CH₃)), 150.6 (C₆H₃), 141.9 (C₆H₃), 140.4 (C₆H₃), 126.8 (C₆H₃), 124.6 (C₆H₃), 124.3 (C₆H₃), 103.1 (C(CH₃)CHC(CH₃), 29.1 (CHMe₂), 28.1 (CHMe₂), 27.4 (CH₃), 26.1 (C(CH₃)CHC(CH₃), 25.2 (CH₃), 24.6 (CH₃), 24.5 (CH_3) , assignment was done using ¹H¹³C correlation and available reference.46

Preparation of LTiMe(µ-O)₂TiMeL-toluene (9a)

Toluene (40 ml) was added to LAlMe(OH) (0.38 g, 0.8 mmol) and LTiMe₃ (0.41 g, 0.8 mmol). The resulting solution was heated to 90 $^{\circ}$ C and kept at this temperature for 14 h, then filtered

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and slowly concentrated (over 5 h) under vacuum. The yellow block-shaped crystals of LTiMe(μ -O)₂TiMeL–toluene (**9a**) were contaminated with LAIMe₂ (NMR; see ref. 14), which deposited while concentrating the solution. The molar relative intensities of **9a** and LAIMe₂ are nearly 1 : 1. The precipitate was filtered and washed with toluene (4 × 5 ml) to give pure **9a** (NMR). Yield of **9a** 0.25 g (25%).

Preparation of LTiMe(µ-O)₂TiMeL-hexane (9b)

Alternatively, this reaction can be performed at room temperature over 14 h. Evaporation of toluene afforded an oily tar, which was soluble in *n*-hexane. Compound LTiMe(μ -O)₂TiMeL–hexane (**9b**) was deposited from a concentrated hexane solution together with LAIMe₂ (NMR, ref. 14) over 4 weeks at room temperature, also see ref. 13. **9b** was purified by washing with *n*-hexane (5 × 5 ml). Yield 0.42 g, 50%.

Reaction of LAlMe(OH) with 2 equiv. of LTiMe₃ in toluene afforded an oily intractable solid. The NMR spectrum of the resulting solid in C_6D_6 showed resonances of **9a**, LAlMe₂ and LAlMe(OH).

Compound 9a (LTiMe(μ -O)₂TiMeL-toluene). Anal. calcd (found) for C₆₇H₉₆N₄O₂Ti₂: C 74.17 (74.20); H 8.86 (8.81); N 5.17 (5.19). Mp 289 °C decomp. EI-MS: m/z (%) = 993 (2) [M]⁺, 978 (100) [M⁺–Me], 963 (2) [M⁺–C₂H₆]. ¹H NMR (500.2 MHz, C_6D_6 , r.t.), δ_H (ppm) = 7.31, 7.10–6.99 (m, aryl), 5.20 (s, 1H, $C(CH_3)CHC(CH_3)$, 2.99 (sept, 2H, J = 6.80 Hz, $CHMe_2$), 2.90 (sept, 2H, J = 6.80 Hz, CHMe₂), 2.10 (s, toluene), 1.47 (s, 6H, $C(CH_3)CHC(CH_3)$, 1.30 (d, 12H, J = 6.80 Hz, $CHMe_2$), 1.22 (d, 12H, J = 6.80 Hz, CHMe₂) overlapped with 1.22 (s, 3H, Ti-Me), 1.00 (d, 12H, J = 6.80 Hz, CHMe₂), 0.77 (d, 12H, J = 6.80 Hz, CHMe₂). ¹³C NMR (125.707 MHz, C₆D₆, r.t.), $\delta_{\rm C}$ $(ppm) = 167.6 (C(CH_3)CHC(CH_3)), 150.1 (C_6H_3), 142.8 (C_6H_3),$ 140.6 (C₆H₃), 137.8 (C₆H₃, toluene), 129.3 (C₆H₃, toluene), 126.2 (C₆H₃), 125.6 (C₆H₃, toluene), 124.3 (C₆H₃), 123.8 (C₆H₃), 100.5 (C(CH₃)CHC(CH₃), 60.2 (Ti-Me), 26.8 (CH₃), 25.6 (CHMe₂), 25.2 (CH₃), 24.5 (CH₃), 24.3 (CH₃), 21.4 (CH₃, toluene), assignment was performed using ¹H¹³C correlation and available references.⁴⁶ EI-MS and ¹H NMR of **9b** were similar to those of 9a.

Hydrolysis of LTiMe₃ (3)

LTiMe₃ (0.58 g, 1.1 mmol) was dissolved in toluene (40 ml). Then the solution was cooled to -79 °C and H₂O (20.4 µL, 1.1 mmol) was added with rigorous stirring over a period of 30 min. The resulting mixture was warmed to room temperature and stirred for 8 h. This dark green solution was filtered to remove the colourless solid (0.1 g) and all volatiles were removed in a dynamic vacuum. The oily residue was dissolved in *n*-hexane (20 ml), then the hexane solution concentrated (10 ml) and left undisturbed at room temperature for 1 d and then at +2 °C for 1 week, while **9b** deposited (0.06 g) (determined by NMR and EI-MS). The supernatant mixture was filtered from **9b** and concentrated (2– 3 ml) and left at +2 °C for 1 week. During this time crystals of **3** and LH deposited (determined by NMR and EI-MS, data for LH were identical to those in ref. 43). A mixture of LTiMe₃ (0.44 g, 0.86 mmol) and $[Mes_2Ga(OH)]_2$ -THF (0.62 g, 0.86 mmol) was dissolved in toluene (40 ml). The resulting solution was kept at 100 °C for 14 h under stirring and finally filtered hot. The solvent was removed under dynamic vacuum and the residue dissolved in hexane (40 ml). The hexane solution was concentrated (10 ml) and left at 2 °C for 5 d. During this time colourless and yellow crystals deposited from this solution. Melting point, NMR, EI-MS data for the colourless crystals were identical with Mes₃Ga, the NMR and EI-MS data for the yellow crystals were identical with those of **9b**.

X-Ray crystallography

The crystallographic data for 1, 6, 9a and 9b are summarized in Table 4.§ Intensities were collected on a Stoe-Siemens four-circle diffractometer for 1. A Bruker SMART 1000 CCD diffractometer was employed for 9a and 9b and a Bruker APEX2 CCD diffractometer for 6. The data were reduced (SAINT)⁴⁷ and corrected for absorption (SADABS).48 The structures were solved by direct methods, and refined against F^2 with non-hydrogen atoms anisotropic; hydrogen atoms were included using a riding model or rigid methyl groups. All calculations were carried out using SHELXTL software.49 Exceptions/special features: the toluene of compound 6 is disordered over an inversion centre and that of 9a over a mirror plane, corresponding to the stoichiometry of a mono- and disolvate, respectively, per molecule of the dinuclear complexes; the hexane of compound 9b is ordered (but with high U values) and lies across an inversion centre (monosolvate). Both forms of 9 diffracted weakly and were low-temperature sensitive; crystals (especially 9a) degraded by cracking during the data collections. The atoms of hexane 9a have very high U values and there is an improbably-short contact between C97 atoms of adjacent molecules, implying incomplete occupancy. However, a free refinement of the hexane occupancy led to a value of 0.91(1) Å. Nevertheless, the description as a single ordered site may be oversimplified. For the X-ray structure of [C(CMeN(2,6 $i \Pr_2 C_6 H_3)_2]_2 H_2$ (2) see ref. 8.

Density functional calculations

The B3LYP^{50,51} functional, as implemented in the Gaussian program package,⁵² was used throughout all the computations of the NMR-shifts and the thermodynamic data. Due to the atoms of the compound, a basis of type LANL2DZ⁵³ for Ti and a 6–31G(d',p') basis^{54,55} for the remaining atoms was used to achieve the needed precision. In the first step the compound was fully optimized to its equilibrium structure (coordinates are given in the ESI[‡]) and then, making use of analytical derivatives, the harmonic vibrational frequencies needed for the thermodynamic data were calculated. Error of calculation is less than 20 kJ mol⁻¹. For compound LTiMe₂(μ -O)AlMeL (7) itself the NMR shifts were calculated with the Gauge-Independent Atomic Orbital (GIAO) method³⁹ (see the ESI p. 29[‡]). Molecules LTiMe₂(μ -O)AlMeL (7), LTiMe(O) (8) and LAlMe₂ represent a true minimum on the potential energy surface without negative IR frequencies.

Table 4 Crystallographic data and structure refinement details[‡] for 1, 6, 9a and 9b^a

	1	6	9a	9b
Empirical formula	$C_{29}H_{40}Cl_3N_2Ti$	$C_{65}H_{90}Cl_2N_4O_2Ti_2$	$C_{74}H_{98}N_4O_2Ti_2$	C66H102N4O2Ti2
M	570.88	1126.11	1171.36	1079.32
Temperature/K	203(2)	100(2)	133(2)	193(2)
Radiation used $(\lambda)/\text{Å}$	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Μο Κα (0.71073)
Crystal size/mm	$1.00 \times 0.80 \times 0.20$	$0.22 \times 0.20 \times 0.06$	$0.18 \times 0.18 \times 0.12$	$0.5 \times 0.3 \times 0.3$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	Pnma	$P2_1/c$	C2/m	$P\overline{1}$
a/Å	13.678(6)	13.4999(18)	18.7080(17)	8.9759(11)
b/Å	21,795(14)	12.9944(16)	20.4316(18)	13.0850(16)
c/Å	9 9457(13)	17 350(2)	9.0082(8)	13 5178(16)
$a(^{\circ})$	90	90	90	88.349(4)
β (°)	90	101.761(5)	110.296(4)	79.207
γ (°)	90	90	90	80.387
$V/Å^3$	2965(2)	2979 6(6)	32.29 5(5)	1537 7(3)
Z	4	2	2	1
$\rho_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.279	1.255	1.205	1.166
μ/mm^{-1}	0.579	0.404	0.296	0.305
F (000)	1204	1204	1260	586
Scan range $\Theta(^{\circ})$	3.52 to 22.52	1.54 to 30.51	1.53 to 26.36	1.53 to 30.51
Completeness to Θ_{\max} (%)	97.0	100.0	100.0	99.2
Index ranges	$-14 \le h \le 8$	$-19 \le h \le 19$	$-23 \le h \le 23$	$-12 \le h \le 12$
	$0 \le k \le 23$	$-18 \le k \le 18$	$-25 \le k \le 25$	$-18 \le k \le 18$
	$-10 \le l \le 0$	$-24 \le l \le 24$	$-11 \le l \le 11$	$-19 \le l \le 19$
Total reflections	3227	157240	20806	32303
Unique reflections	1946	9104	3406	9307
<i>R</i> (int)	0.0425	0.0557	0.1551	0.0317
Data/restrains/parameters	1946/0/168	9104/105/390	3406/141/177	9307/1/330
Goodness-of-fit on F^2	1.047	1.033	1.041	1.043
$R1, wR2 [I > 2\sigma(I)]$	0.0546, 0.1367	0.0332, 0.0814	0.0760, 0.1920	0.0543, 0.1476
R1, wR2 (all data)	0.0682, 0.1493	0.0450, 0.0875	0.1165, 0.2132	0.0755, 0.1659
Maximum/minimum electron density/e A ⁻³	0.808, -0.698	0.598, -0.566	0.939, -0.634	1.151, -0.621

 ${}^{a} wR2 = \left(\sum [w(F_{\circ}^{2} - F_{\circ}^{2})^{2}] / \sum [F_{\circ}^{4}]\right)^{1/2}, R1 = \sum ||F_{\circ}| - |F_{\circ}|| / \sum |F_{\circ}|, weight = 1 / [\sigma^{2}(F_{\circ}^{2}) + (\mathbf{A}^{*} P)^{2} + (\mathbf{B}^{*} P)], where P = (\max(F_{\circ}^{2}, 0) + 2^{*} F_{\circ}^{2}) / 3; \text{ for } F_{\circ}^{2} + (\mathbf{A}^{*} P)^{2} + (\mathbf{A}^$ 1 A = 0.0767, B = 4.1667; for 6 A = 0.0373, B = 1.6762; for 9a A = 0.105, B = 10.00; for 9b A = 0.091, B = 1.03.

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