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FULL PAPER

Synthesis and characterization of 2-pyridylalkoxide complexes of titanium, zirconium and tantalum. Crystal structures of $TiCp^*Me_2(OCMePy_2)$ and $TaCp^*Cl_3(OCPy_3)$ ($Cp^* = \eta^5$-C_5Me_5, $Py = C_5H_4N$)

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The methyltitanium derivative $TiCp^*Me_3$ ($Cp^* = \eta^5$-C_5Me_5) reacted with tris(2-pyridyl)methyl alcohol, $HOCPy_3$, to yield the alkoxide complex $TiCp^*Me_2(OCPy_3)$ **1**. The reaction of $TiCp^*Me_3$ with di-2-pyridyl ketone, Py_2CO, yielded, through an insertion process, the corresponding alkoxide derivative $TiCp^*Me_2(OCMePy_2)$ **2**. In order to establish the co-ordination mode of the alkoxide ligand, X-ray diffraction studies were carried out on complex **2**. Insertion of di-2-pyridyl ketone into a Ta–Me bond of $TaCp^*Me_4$ gave the corresponding alkoxide compound $TaCp^*Me_3(OCMePy_2)$ (**3**). Metathesis reaction of titanium and zirconium complexes MCp^*Cl_3 with the lithium alkoxide $LiOCRPy_2$ led to the corresponding derivatives $MCp^*Cl_2(OCRPy_2)$ [M = Ti, R = Me (**4**) or Py (**5**); M = Zr, R = Me (**6**) or Py (**7**)]. In an analogous way, tantalum derivatives $TaCp^*Cl_3(OCRPy_2)$ [R = Me (**8**) or Py (**9**)] can also be synthesized by reaction of $TaCp^*Cl_4$ with the appropriate lithium alkoxide $LiOCRPy_2$. The crystal structure of complex **9** has been determined by X-ray diffraction.

Introduction

The Lewis acidity of early transition metals in high oxidation states together with the co-ordinative and electronic unsaturation of their complexes are important characteristics for many catalytically active complexes.[1,2] These characteristics are the key features for obtaining any metal-centred reactivity.

Furthermore, mononuclear complexes are proposed to be the active species in many homogeneous catalytic systems[3] and can be stabilized by using sterically hindered ligands.[4] Very bulky ligands, however, can lower the activity of the catalyst[5] due to the fact that complexation of the substrates becomes sterically hindered. However, on the other hand, bulky ligands can protect the metal against deactivation and avoid undesired side reactions.

Alkoxide and aryl oxide ligands have been widely used to stabilize high oxidation states of early transition metals and numerous studies have been reported concerning the catalytic activity of their complexes in alkene metathesis[6] and, in particular, in alkene polymerization.[7,8]

On the other hand the immobilization of organometallic compounds on solid surfaces such as oxides and zeolites, or metals, is a vigorously growing branch of organometallic chemistry. This field is attracting the attention of chemists due to the highly active and selective surface species involved in the subsequent heterogeneous catalytic processes. However, the exact nature of these surface-bound species, the nature of the bonding, and the mechanism by which the metallic precursor reacts still remain unclear. In this context, the study of three-dimensional molecular model compounds can be envisaged as a useful tool in identifying more clearly the species present on a supported surface, and also in understanding the bonding between the metal and oxide surfaces and how these properties are related to the catalytic activity and selectivity.[9]

Herein we report the synthesis of several complexes of titanium, zirconium and tantalum with 2-pyridylalkoxide ligands as well as the crystal structure of two such compounds.

Results and discussion

Early transition metal alkyl complexes react with acidic reagents such as alcohols to yield the corresponding alkane and the alkoxide complex. A likely mechanism for the protonolysis process requires initial donation of an oxygen lone pair to the metal centre.[10] This methodology has been useful in our work aimed at the synthesis of alkyl alkoxide complexes of titanium and tantalum. In fact, the methyltitanium derivative $TiCp^*Me_3$ reacts in toluene with tris(2-pyridyl)methyl alcohol to give the complex $TiCp^*Me_2(OCPy_3)$ **1** (eqn. 1).

$$TiCp^*Me_3 + HOCPy_3 \longrightarrow \underset{\mathbf{1}}{TiCp^*Me_2(OCPy_3)} + MeH \quad (1)$$

Complex **1** was isolated as a yellow, air-sensitive solid that is very soluble in toluene or THF but less soluble in pentane or Et_2O. It was characterized by the usual spectroscopic techniques. The ^1H NMR spectrum shows, at room temperature, a singlet at δ 0.82 with a relative integral of 6 H, which is assigned to the two methyl groups bonded to the titanium atom. It can be inferred that the methyl ligands have equivalent chemical environments. The single resonance at δ 1.71 can be assigned to the protons of the Cp* group. In agreement with the equivalence of the methyl groups, the

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pyridyl moieties also have equivalent chemical environments and give rise to four multiplet signals centred at δ 6.47, 7.06, 8.05, and 8.30. According to these data, rotation around the O–C bond at room temperature and in solution is fast enough on the NMR timescale to allow equivalence of the methyl and the pyridyl groups. The ^{13}C NMR data are also consistent with this observation.

Another rather general method for the synthesis of alkoxide complexes consists of the insertion of ketones into metal–alkyl bonds. In this way, $TiCp^*Me_3$ reacts with di-2-pyridyl ketone, Py_2CO, in THF to yield the corresponding alkoxide complex $TiCp^*Me_2(OCMePy_2)$ **2** (eqn. 2). Complex **2** was isolated as a

$$TiCp^*Me_3 + Py_2CO \longrightarrow \underset{\mathbf{2}}{TiCp^*Me_2(OCMePy_2)} \quad (2)$$

yellow, air-sensitive solid that is soluble in THF or toluene but less soluble in pentane or Et_2O.

Suitable crystals of complex **2** were grown from a toluene–pentane solution and an X-ray diffraction study was carried out. An ORTEP[11] drawing is shown in Fig. 1 and relevant bond lengths and angles are given in Table 1. The structural analysis established a four-legged piano-stool co-ordination mode around the titanium atom. The pyridylalkoxide ligand is bonded through the oxygen atom and one of the nitrogen atoms of the pyridyl groups. It is noteworthy that the bond angle Ti(1)–O(2)–C(3) is very small [131.4(2)°] when compared to that in other analogous titanium alkoxide complexes.[12] This small bond angle, along with the rather long Ti–O bond distance [1.871(3) Å], points to a small O→Ti π donation in the Ti–O bond. It seems likely that the geometry around the oxygen atom is forced to allow co-ordination of one of the pyridinic nitrogen atoms, N(3), to the titanium centre. The titanium–nitrogen distance [2.307(3) Å] is rather long but does fall, albeit on the high side, within the expected range for titanium–nitrogen bonds.[8] The Ti–C bond *trans* to the pyridyl nitrogen atom is considerably shorter [Ti(1)–C(2) 2.139(4) Å] than that *trans* to the alkoxide [Ti(1)–C(1) 2.161(5) Å], a situation in contrast to that observed in the complex $TiCpCl_2(OCPr^i_2Py)$[8] for the titanium–chloride bond.

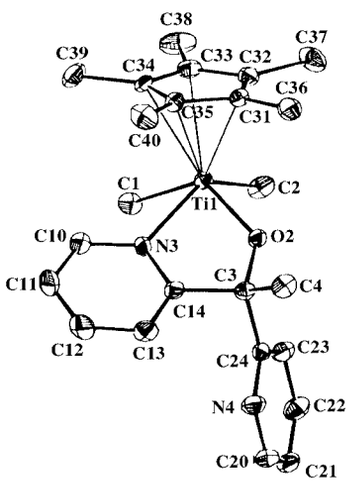


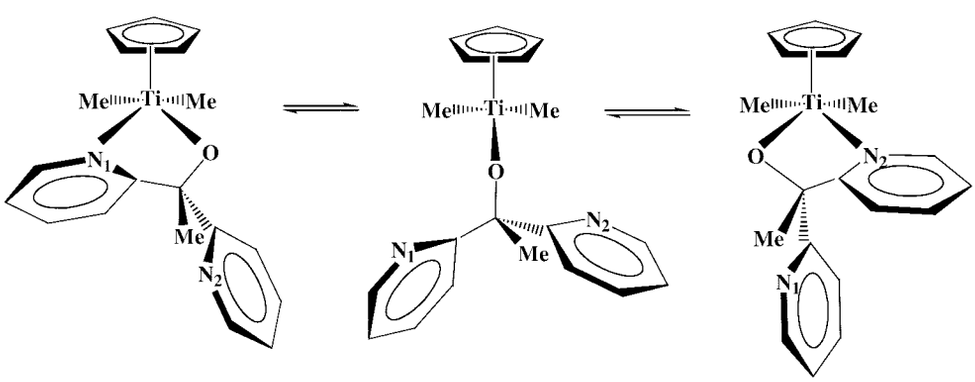
Fig. 1 Perspective ORTEP drawing of the molecular structure of complex **2**.

Table 1 Selected bond distances (Å) and angles (°) for complexes **2** and **9**

Complex **2**			
Ti(1)–O(2)	1.871(3)	Ti(1)–C(2)	2.139(4)
Ti(1)–N(3)	2.307(3)	Ti(1)–C(1)	2.161(5)
Ti(1)–C(31)	2.356(4)	Ti(1)–C(32)	2.394(4)
Ti(1)–C(33)	2.424(4)	Ti(1)–C(34)	2.446(4)
Ti(1)–C(35)	2.383(4)	O(2)–C(3)	1.390(4)
O(2)–Ti(1)–C(2)	88.51(15)	O(2)–Ti(1)–C(1)	125.57(16)
C(3)–O(2)–Ti(1)	131.4(2)	O(2)–Ti(1)–N(3)	72.54(12)
C(2)–Ti(1)–C(1)	83.13(19)	C(14)–N(3)–Ti(1)	114.2(3)
Complex **9**			
Ta(1)–O(5)	1.84(2)	Ta(1)–Cl(4)	2.594(6)
Ta(1)–N(36)	2.02(2)	Ta(1)–Cl(3)	2.703(6)
C(1)–O(5)–Ta(1)	124.6(15)	Cl(4)–Ta(1)–Cl(3)	102.4(2)
O(5)–C(1)–C(21)	105.1(18)	O(5)–Ta(1)–Cl(3)	75.8(5)

The ^1H and ^{13}C NMR spectra show that both pyridinic rings are equivalent in solution at room temperature. In fact, the ^1H NMR spectrum shows four multiplet signals centred at δ 6.47, 7.05, 8.06 and 8.44. In addition, two singlet signals at δ 0.77 and 1.84 are assigned to the two methyl groups bonded to the titanium atom and to the Cp* ligand, respectively (see Experimental section). This means that, under these experimental conditions, a rapid interchange between the two nitrogen atoms of the two pyridyl groups in the co-ordination sphere of the titanium centre is taking place. In order to explore this behaviour a ^1H VTNMR experiment was carried out. The results of this study show that at high temperature the methyl groups bonded to the titanium atom are equivalent and give rise to a single signal, but that when the temperature is lowered to 193 K coalescence takes place. At even lower temperatures until 183 K these two methyl groups become non-equivalent and their resonances appear as to two incompletely resolved singlet signals. Similar behavior was observed for the signals corresponding to the pyridyl moieties, which also become non-equivalent at 193 K.

Bearing in mind the above data, we can propose that in the solid state the nitrogen atom of one of the two pyridinic rings is co-ordinated to the titanium centre. In solution at room temperature, however, a fast interchange takes place between the two nitrogen atoms of the alkoxide ligand, making the two pyridinic rings equivalent (see Scheme 1).



Scheme 1

In order to gain a deeper insight into the co-ordination chemistry of the pyridylalkoxide ligands we extended the study to include analogous reactions with the monocyclopentadienyl tantalum complex $TaCp^*Me_4$, which exhibits a four-legged piano-stool structure with an empty orbital *trans* to the Cp* group. $TaCp^*Me_4$ reacts with di-2-pyridyl ketone in toluene, in a 1:1 molar ratio, to yield by the corresponding insertion process a tantalum alkoxide complex $TaCp^*Me_3(OCMePy_2)$ **3** (eqn. 3). Complex **3** was obtained as yellow, air-sensitive

$$TaCp^*Me_4 + Py_2CO \longrightarrow TaCp^*Me_3(OCMePy_2) \quad (3)$$
3

crystals that are soluble in toluene or THF but less soluble in pentane.

The ^1H and ^{13}C NMR spectra of complex **3** show that in solution, at room temperature, there are two different signals for the methyl groups bonded to the tantalum centre. A singlet is observed at δ 0.02, which is assigned to the methyl group *trans* to the alkoxide ligand (see Scheme 2), and another singlet is observed at −0.01, which corresponds to the methyl groups in *trans* position with respect to each other. Two singlet signals appear at δ 1.91 and 1.98 with integrals of 15 and 3 protons, respectively, and are assigned to the Cp* ligand and the methyl group of the alkoxide moiety. On the other hand, the two pyridinic rings give rise to four broad signals at δ 6.46, 6.91, 7.49 and 8.70 with integrals of two protons each. The broadness of these signals could be indicative of a fluxional process at this temperature. To clarify this point a VTNMR experiment was carried out. The results show that at high temperature (343 K) the signals are sharp and consistent with rapid interchange of the two nitrogen atoms in the co-ordination sphere of the tantalum centre. This interchange makes both pyridyl groups equivalent (Scheme 2). Coalescence takes place at 298 K and when the temperature is lowered to 253 K the interchange is slow and the two pyridyl groups become non-equivalent, giving rise in the ^1H NMR spectrum to eight multiplet signals with relative integrals of 1 H each. The coalescence temperature and the two site exchange equations[13] can be used to estimate that the value of $\Delta G^{\ddagger}$ for the exchange process is 14.0(1) kcal mol^{-1}. In addition, when interchange of the two nitrogen atoms in the co-ordination sphere is slow, all three methyl groups bonded to the tantalum atom have a different chemical environment. As a consequence, three signals are observed in the ^1H NMR spectrum for these protons at δ −0.06, 0.02 and 0.07.

Another general procedure to introduce alkoxide ligands into the co-ordination sphere of early transition metals is to use the corresponding lithium alkoxide. We have used this metathesis reaction to synthesize a new family of alkoxide derivatives of titanium, zirconium and tantalum. In this way, reaction of $TiCp^*Cl_3$ with $LiOCRPy_2$ (prepared "*in situ*" by reaction of di-2-pyridyl ketone with MeLi for complex **4** or PyLi for **5**) in a 1:1 molar ratio gives the corresponding mono-alkoxide complexes $TiCp^*Cl_2(OCMePy_2)$ **4** and $TiCp^*Cl_2(OCPy_3)$ **5** in high yields (eqn. 4). Complexes **4** and **5** were isolated as red, air-

$$MCp^*Cl_3 + LiOCRPy_2 \longrightarrow MCp^*Cl_2(OCRPy_2) + LiCl \quad (4)$$
M = Ti, R = Me (**4**) or Py (**5**)
M = Zr, R = Me (**6**) or Py (**7**)

sensitive solids that are very soluble in THF, dichloromethane and toluene, but only sparingly soluble in pentane or Et_2O. The ^1H and ^{13}C NMR spectra show that, in solution at room temperature, all pyridyl groups are equivalent.

As an example, the ^1H NMR spectrum of complex **4** shows two singlet signals at δ 1.63 and 2.01 with relative integrals of 3 and 15 protons, respectively, which are assigned to the methyl groups of the alkoxide and the Cp* ligands. On the other hand, there are four multiplet signals at δ 6.18, 6.40, 6.58 and 9.03 for the pyridinic protons. The ^{13}C NMR spectrum is consistent with the data provided by the ^1H NMR spectrum and shows singlet resonances at δ 13.4 and 20.9, which are assigned to the methyl groups of the Cp* and the alkoxide ligands, respectively. The signal due to the carbon atom bonded to the oxygen atom is observed at δ 90.3 and those due to the carbon atoms of the Cp* ring at δ 121.8. The aromatic carbon atoms of the pyridyl moiety resonate at δ 117.0, 121.7, 137.7 and 152.6 and the signal for the *ipso* carbon atom appears at δ 167.0.

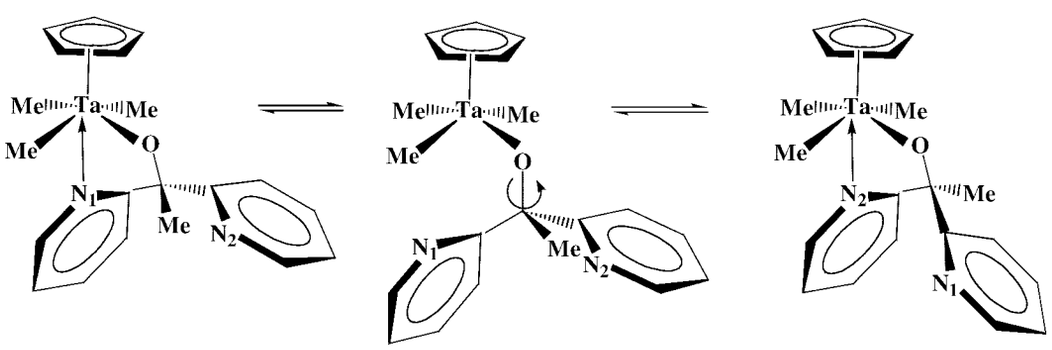
All the data described above indicate that if the pyridylalkoxide is co-ordinated in a bidentate manner a fluxional process that makes them equivalent should be active.

Similarly, reaction of $ZrCp^*Cl_3$ with the appropriate $LiOCRPy_2$ in a 1:1 molar ratio affords complexes $ZrCp^*Cl_2(OCMePy_2)$ **6** and $ZrCp^*Cl_2(OCPy_3)$ **7**. These were isolated as air-sensitive solids that are very soluble in CH_2Cl_2 and THF, less soluble in toluene and only sparingly soluble in pentane. The ^1H and ^{13}C NMR spectra of complex **6** indicate that, at room temperature, both pyridyl groups have a different chemical environment, probably due to the co-ordination of the nitrogen atom of one of them to the zirconium centre.

A VTNMR experiment for complex **6** showed that, upon raising the temperature, interchange of the nitrogen atoms of the pyridinic rings in the co-ordination sphere of the zirconium atom becomes quicker, with the coalescence temperature reached at 343 K. The calculated value of $\Delta G^{\ddagger}$ for the exchange process is 16.4(2) kcal mol^{-1}.[13]

The ^1H NMR spectrum of complex **7**, at room temperature, shows two sets of pyridyl signals, four with an integral of 1 H each and four with an integral of two protons each. These data indicate a co-ordination in which the nitrogen atom of a pyridyl group is in a *trans* position with respect to the Cp* ligand.

Finally, the pyridylalkoxide complexes of tantalum, $TaCp^*Cl_3(OCMePy_2)$ **8** and $TaCp^*Cl_3(OCPy_3)$ **9**, are readily synthesized following an analogous procedure to that used



Scheme 2

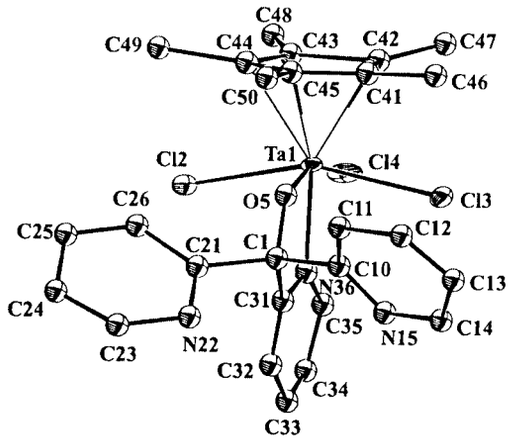


Fig. 2 Perspective ORTEP drawing of the molecular structure of complex **9**.

for the titanium and zirconium complexes (eqn. 5). Compounds **8** and **9** are isolated as colourless, air-sensitive solids that are soluble in toluene and THF but less soluble in pentane or Et_2O.

$$TaCp^*Cl_4 + LiOCRPy_2 \longrightarrow TaCp^*Cl_3(OCRPy_2) + LiCl \quad (5)$$

R = Me (**8**) or Py (**9**)

The ^1H NMR spectrum of complex **8** shows two singlet signals at δ 2.20 and 2.26, which are assigned to the methyl group of the alkoxide ligand and the methyl groups of the Cp* ring, respectively. The pyridinic ring protons give rise to eight multiplet signals at δ 6.27, 6.61, 7.04, 7.08, 7.32, 7.66, 8.38 and 10.13, indicating that in solution there are two different pyridinic rings, which suggests that the pyridyl alkoxide ligand is co-ordinated to the tantalum atom in a bidentate manner. The ^{13}C NMR data are consistent with this proposal. According to the ^1H and ^{13}C NMR data, the co-ordination mode of the alkoxide ligand in complex **9** is analogous to that proposed for **8**. In order to confirm the proposed structural disposition an X-ray diffraction study for **9** was carried out.

Crystals of complex **9**, which were unfortunately of poor quality, were grown from a toluene–pentane solution. An ORTEP drawing is shown in Fig. 2 and relevant bond lengths and angles are given in Table 1. The structural analysis established a distorted octahedral geometry around the tantalum atom where the alkoxide ligand is co-ordinated in a bidentate manner. The co-ordinated nitrogen atom is in a *trans* disposition with respect to the Cp* ligand. The Ta–O bond length [1.84(2) Å][14] is at the short end of the range expected for this type of complex while the C(1)–O(5)–Ta(1) bond angle [124.6(2)°] is small when compared to those in other tantalum alkoxide complexes. This may be the case in order to allow co-ordination of the nitrogen atom to the tantalum centre. The Ta–N bond length is rather short [2.02(2) Å] and comparable to that found in anionic nitrogen ligands.[15]

In conclusion, we would like to bring attention to the great potential offered by these versatile 2-pyridylalkoxide ligands, which enhance the stability of unsaturated compounds due to the assistance of the nitrogen donor function atom without preventing further reactivity. On the other hand, we have shown that it is possible to synthesize 2-pyridylalkoxide complexes by using different procedures such as protonolysis of metal–alkyl bonds, insertion of the ketone in the metal–alkyl bond or by a metathesis reaction. Further studies are in progress aimed at establishing the reactivity of these complexes as well as the synthesis of new complexes of early transition elements with these ligands.

Experimental

General procedures

The preparation and handling of all compounds described was performed with rigorous exclusion of air and moisture under a nitrogen atmosphere using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere.

The following reagents were prepared by literature procedures: $TiCp^*Cl_3$,[16] $TiCp^*Me_3$,[17] $TaCp^*Cl_4$,[18] $TaCp^*Me_4$,[19] $ZrCp^*Cl_3$[20] and $(2\text{-Py})_3COH$.[21] The commercially available compounds Cp*H, MeLi in diethyl ether, ^{n}BuLi, di-2-pyridyl ketone and 2-bromopyridine were used as received from Aldrich.

^1H and ^{13}C NMR spectra were recorded on a 200 Mercury Varian Fourier transform spectrometer. Trace amounts of protonated solvents were used as references and chemical shifts are reported in parts per million relative to $SiMe_4$.

Syntheses

$TiCp^*Me_2(OCPy_3)$ 1. To a solution of $TiCp^*Me_3$ (0.231 g, 1.012 mmol) in 6 mL of toluene was added $(2\text{-Py})_3COH$ (0.266 g, 1.012 mmol). The mixture was stirred at room temperature for 4 h. The solvent was removed under vacuum to give a yellow residue which was washed with *n*-pentane to give a yellow solid, characterized as complex **1** (0.380 g, 79%). IR (Nujol/PET (PET = polyethylene), cm^{-1}): 1585m, 1567w, 1299m, 1115m, 1075m, 755m and 746s. ^1H NMR (C_6D_6): δ 0.82 (s, 6 H, Ti–Me), 1.71 (s, 15 H, Cp*), 6.47 (m, 3 H, Ar), 7.06 (m, 3 H, Ar), 8.05 (m, 3 H, Ar) and 8.30 (m, 3 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 12.0 (Cp*), 56.3 (Ti–Me), 121.9 (C–O), 125.0 (Cp*), 122.0, 127.5, 136.2, 147.2 (s, C–H) and 168.1 (s, C_{ipso}). Found: C, 70.18; H, 6.68; N, 8.64. Calc. for $C_{28}H_{33}N_3OTi$: C, 70.73; H, 6.99; N, 8.84%.

$TiCp^*Me_2(OCMePy_2)$ 2. To a mixture of $TiCp^*Me_3$ (0.466 g, 2.041 mmol) and di-2-pyridyl ketone (0.376 g, 2.041 mmol) was added THF (10 mL). The mixture was stirred at room temperature for 1 h and the solvent removed under vacuum. The residue was stirred with pentane (10 mL) to give a yellow solid, characterized as complex **2** (0.442 g, 76%). IR (Nujol/PET, cm^{-1}): 1586m, 1568w, 1295m, 1153m, 1074m, 755m and 747s. ^1H NMR (C_6D_6): δ 0.77 (s, 6 H, Ti–Me), 1.84 (s, 15 H, Cp*), 2.13 (s, 3 H, C–Me), 6.47 (m, 2 H, Ar), 7.05 (m, 2 H, Ar), 8.06 (m, 2 H, Ar) and 8.44 (m, 2 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 12.2 (Cp*), 33.0 (C–Me), 55.6 (Ti–Me), 91.4 (O-C), 122.6 (Cp*), 121.9, 127.7, 137.0, 147.5, (s, C–H) and 170.0 (s, C_{ipso}). Found: C, 69.44; H, 7.84; N, 6.77. Calc. for $C_{24}H_{32}N_2OTi$: C, 69.89; H, 7.82; N, 6.79%.

$TaCp^*Me_3(OCMePy_2)$ 3. Toluene (10 mL) was added to a mixture of $TaCp^*Me_4$ (0.424 g, 1.127 mmol) and di-2-pyridyl ketone (0.207 g, 1.127 mmol) and heated at 50 °C for 4 h. The solution was evaporated to dryness and the residue washed with a mixture of *n*-pentane (8 mL) and diethyl ether (8 mL). The solution was cooled to −30 °C for 16 h to give a yellow crystalline solid, characterized as complex **3** (0.198 g, 32%). IR (Nujol/PET, cm^{-1}): 1584m, 1566s, 1297s, 1160s, 1077m, 1024m and 578m. ^1H NMR (C_6D_6, 18 °C): δ −0.01 (s, 6 H, Ta–Me), 0.02 (s, 3 H, Ta–Me), 1.91 (s, 15 H, Cp*), 1.98 (s, 3 H, C–Me), 6.46 (m, 2 H, Ar), 6.91 (m, 2 H, Ar), 7.49 (m, 2 H, Ar) and 8.70 (br, 2 H, Ar). ^1H NMR (toluene-d_8, 70 °C): δ 0.05 (s, 3 H, Ta–Me), 0.08 (s, 6 H, Ta–Me), 1.91 (s, 15 H, Cp*), 1.95 (s, 3 H, C–Me), 6.53 (m, 2 H, Ar), 6.97 (m, 2 H, Ar), 7.46 (m, 2 H, Ar) and 8.81 (m, 2 H, Ar). ^1H NMR (toluene-d_8, −20 °C): δ −0.06 (s, 3 H, Ta–Me), 0.02 (s, 3 H, Ta–Me), 0.07 (s, 3 H, Ta–Me), 1.95 (s, 15 H, Cp*), 2.02 (s, 3 H, C–Me), 6.39 (m, 1 H, Ar), 6.50 (m, 1 H, Ar), 6.73 (m, 1 H, Ar), 7.01 (m, 1 H, Ar), 7.34 (m, 1 H, Ar), 7.71 (m, 1 H, Ar), 8.41 (m, 1 H, Ar) and 9.26 (m, 1 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 11.5 (s, Cp*), 28.6 (s, OC*Me*), 37.6

(s, Ta–Me), 40.7 (s, Ta–Me), 90.7 (s, O–C), 117.1 (s, Cp*), 121.2, 122.9, 127.5, 136.2 (s, C-H) and 148.2 (s, C_{ipso}). Found: C, 53.46; H, 5.99; N, 4.93. Calc. for $C_{25}H_{35}N_2OTa$: C, 53.57; H, 6.29; N, 4.99%.

$TiCp^*Cl_2(OCMePy_2)$ 4. To a solution of di-2-pyridyl ketone (0.318 g, 1.726 mmol) in THF (15 mL) was added MeLi (1.079 mL, 1.726 mmol) at −78 °C. The mixture was stirred for 10 min and then $TiCp^*Cl_3$ (0.500 g, 1.726 mmol) added. The reaction mixture was allowed to reach room temperature and stirred for 30 min. After this time the solvent was removed under vacuum and the residue extracted with CH_2Cl_2 (16 mL). The solvent was partially evaporated and the solution cooled to −30 °C to yield red crystals of complex **4** (0.593 g, 78%). IR (Nujol/PET, cm^{-1}): 1598m, 1298s, 1167s, 1090m, 760s, 648s, 543m, 433m and 402w. ^1H NMR (C_6D_6): δ 1.63 (s, 3 H, Me–C), 2.01 (s, 15 H, Cp*), 6.18 (m, 2 H, Ar), 6.40 (m, 2 H, Ar), 6.58 (m, 2 H, Ar) and 9.03 (m, 2 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 13.4 (s, Cp*), 20.9 (s, Me–C), 90.3 (s, C–O), 121.8 (s, Cp*), 117.0, 121.7, 137.7, 152.6 (s, C–H) and 167.0 (s, C_{ipso}). Found: C, 58.07; H, 5.83; N, 5.99. Calc. for $C_{22}H_{26}Cl_2N_2OTi$: C, 58.30; H, 5.78; N, 6.18%.

$TiCp^*Cl_2(OCPy_3)$ 5. To a solution of 2-bromopyridine (0.329 mL) in THF (6 mL) was added ″BuLi (1.6 M, 2.1 mL) at −78 °C. After 10 min di-2-pyridyl ketone (0.636 g, 3.450 mmol) was added and the reaction mixture stirred at room temperature for 15 min. It was then cooled to −78 °C and $TiCp^*Cl_3$ (1.000 g, 3.450 mmol) added. The mixture was stirred at room temperature for 1 h, the solvent was removed under vacuum and the residue extracted with CH_2Cl_2 (16 mL). The solvent was evaporated to dryness and the residue washed with pentane to yield a red crystalline solid, which was characterized as complex **5** (1.409 g, 80%). IR (Nujol/PET, cm^{-1}): 1588s, 1569m, 1283m, 1116m, 1066s, 762s, 754s, 745m, 557m and 489m. ^1H NMR (C_6D_6): δ 2.05 (s, 15 H, Cp*), 6.34 (m, 3 H, Ar), 6.80 (m, 3 H, Ar), 8.02 (m, 3 H, Ar) and 8.90 (m, 3 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 13.7 (s, Cp*), 97.3 (s, C–O), 122.1 (s, Cp*), 128.3, 130.5, 137.0, 150.9 (s, C–H) and 164.3 (s, C_{ipso}). Found: C, 60.59; H, 5.05; N, 7.72. Calc. for $C_{26}H_{27}Cl_2N_3OTi$: C, 60.48; H, 5.27; N, 8.14%.

$ZrCp^*Cl_2(OCMePy_2)$ 6. To a solution of di-2-pyridyl ketone (0.111 g, 0.603 mmol) in THF (5 mL) was added, at −78 °C, MeLi (0.38 mL, 1.6 M in Et_2O). The mixture was stirred for 10 min and $ZrCp^*Cl_3$ (0.201 g, 0.603 mmol) added. The solution was allowed to reach room temperature and then stirred for 20 h. The solvent was evaporated under vacuum and the residue extracted with CH_2Cl_2 (5 mL). After filtration, the solvent was removed and the residue washed with pentane (6 mL) to yield a colourless solid, which was characterized as complex **6** (0.179 g, 60%). IR (Nujol/PET, cm^{-1}): 1599s, 1299m, 1169s, 1079m, 759s, 647s, 613vs, 537w and 421w. ^1H NMR (C_6D_6): δ 1.58 (s, 3 H, Me–C), 2.03 (s, 15 H, Cp*), 6.14 (m, 1 H, Ar), 6.16 (m, 1 H, Ar), 6.39 (m, 1 H, Ar), 6.41 (m, 1 H, Ar), 6.56 (m, 1 H, Ar), 6.60 (m, 1 H, Ar), 8.57 (m, 1 H, Ar) and 9.34 (m, 1 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 11.0 (s, Cp*), 19.6 (s, Me–C), 84.4 (s, C–O), 120.2 (s, Cp*), 115.0, 116.3, 119.7, 121.0, 126.4, 127.4, 135.9, 136.9 (s, C–H), 149.1 (s, C_{ipso}) and 151.1 (s, C_{ipso}). Found: C, 53.49; H, 5.05; N, 5.46. Calc. for $C_{22}H_{26}Cl_2N_2OZr$: C, 53.21; H, 5.28; N, 5.64%.

$ZrCp^*Cl_2(OCPy_3)$ 7. To a solution of 2-bromopyridine (0.091 mL, 0.961 mmol) in THF (7 mL), at −78 °C, was added ″BuLi (0.600 mL, 1.6 M in hexane). The mixture was stirred for 10 min and di-2-pyridyl ketone (0.177 g, 0.961 mmol) added. The solution was stirred for 15 min at room temperature, then cooled to −78 °C and $ZrCp^*Cl_3$ (0.320 g, 0.961 mmol) added. The solution was stirred at room temperature for 9 h, the solvent removed under vacuum and the residue extracted with CH_2Cl_2 (10 mL). After filtration, the solvent was evaporated and the residue washed with pentane (5 mL) to yield a solid, which was characterized as complex **7** (0.320 g, 60%). IR (Nujol/PET, cm^{-1}): 1586s, 1286w, 1118w, 1054m, 764vs, 746m, 676s, 553m and 482w. ^1H NMR (C_6D_6): δ 2.07 (s, 15 H, Cp*), 6.18 (m, 2 H, Ar), 6.50 (m, 1 H, Ar), 6.68 (m, 2 H, Ar), 7.71 (m, 1 H, Ar), 8.33 (m, 2 H, Ar), 8.50 (m, 1 H, Ar), 8.64 (m, 2 H, Ar) and 9.42 (m, 1 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 12.4 (s, Cp*), 89.9 (s, C–O), 119.4 (s, Cp*), 122.3, 123.2, 123.9, 137.4, 138.5, 147.5, 150.9, 153.0 (s, C–H), 161.4 and 165.6 (s, C_{ipso}). Found: C, 56.23; H, 4.70; N, 7.20. Calc. for $C_{26}H_{27}Cl_2N_3OZr$: C, 55.80; H, 4.86; N, 7.51%.

$TaCp^*Cl_3(OCMePy_2)\cdot 0.5C_6H_5Me$ $8\cdot 0.5C_6H_5Me$. To a solution of di-2-pyridyl ketone (0.154 g, 0.838 mmol) in THF (8 mL) was added, at −78 °C, MeLi (0.524 mL, 0.838 mmol). The mixture was stirred for 10 min and $TaCp^*Cl_4$ (0.384 g, 0.838 mmol) added. The reaction mixture was allowed to reach room temperature and stirred for 30 min. After this time the solvent was removed under vacuum and the residue extracted with toluene (10 mL). The toluene was partially evaporated and the solution cooled to −30 °C to yield a colourless solid, characterized as complex **8** (0.283 g, 55%). IR (Nujol/PET, cm^{-1}): 1598m, 1298s, 1167s, 1090m, 760s, 648s, 543m, 433m and 402w. ^1H NMR (C_6D_6): δ 2.04 (s, 1.5 H, toluene), 2.20 (s, 3 H, Me–C), 2.26 (s, 15 H, Cp*), 6.27 (m, 1 H, Ar), 6.61 (m, 1 H, Ar), 6.96 (m, 1.5 H, toluene), 7.03 (m, 1 H, toluene), 7.04 (m, 1 H, Ar), 7.08 (m, 1 H, Ar), 7.32 (m, 1 H, Ar), 7.66 (m, 1 H, Ar), 8.38 (m, 1 H, Ar) and 10.13 (m, 1 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 12.8 (s, Cp*), 25.2 (s, Me–C), 95.3 (s, C–O), 129.3 (s, Cp*), 122.2, 122.4, 122.6, 124.0, 136.3, 138.4, 148.7, 149.0 (s, C–H), 164.1, 167.2 (s, C_{ipso}), 121.4, 125.6, 128.1, 128.3 and 137.9 (s, toluene). Found: C, 45.50; H, 4.54; N, 4.23. Calc. for $C_{25.5}H_{30}Cl_3N_2OTa$: C, 45.86; H, 4.52; N, 4.19%.

$TaCp^*Cl_3(OCPy_3)$ 9. To a solution of 2-bromopyridine (0.183 mL, 1.923 mmol) in THF (9 mL), at −78 °C, was added ″BuLi (1.2 mL, 1.6 M). After 10 min of stirring, di-2-pyridyl ketone (0.354 g, 1.923 mmol) was added and the reaction mixture allowed to reach room temperature and stirred for 15 min. It was then was cooled to −78 °C and $TaCp^*Cl_4$ (0.881 g, 1.923 mmol) added. The mixture was stirred at room temperature for 1 h, the solvent removed under vacuum and the residue extracted with toluene (8 mL). The solvent was evaporated to dryness and the residue washed with pentane to yield a brown solid, characterized as complex **9** (0.539 g, 41%). IR (Nujol/PET, cm^{-1}): 1583s, 1569s, 1302m, 1158m, 1024m, 802s, 764s, 749s, 516w and 466m. ^1H NMR (C_6D_6): δ 2.27 (s, 15 H, Cp*), 6.37 (m, 1 H, Ar), 6.51 (m, 2 H, Ar), 6.75 (m, 1 H, Ar), 7.07 (m, 2 H, Ar), 7.09 (m, 1 H, Ar), 7.46 (m, 2 H, Ar), 8.02 (m, 1 H, Ar) and 8.26 (m, 2 H, Ar). ^{13}C-{^1H} NMR (C_6D_6): δ 12.9 (s, Cp*), 100.1 (s, C–O), 129.3 (s, Cp*), 122.3, 123.3, 124.5, 126.2, 135.5, 137.3, 148.5, 149.2 (s, CH), 163.2 and 163.8 (s, C_{ipso}). Found: C, 46.14; H, 4.07; N, 5.92. Calc. for $C_{26}H_{27}Cl_3N_3OTa$: C, 45.60; H, 3.97; N, 6.13%.

X-Ray structural determination of complexes 2 and 9

Crystal, data collection, and refinement parameters are collected in Table 2. Suitable crystals of these complexes were sealed in Lindemann capillary tubes under nitrogen and used for data collection. Reflections were collected at 25 °C on a NONIUS-MACH3 diffractometer equipped with a graphite monochromated radiation source ($\lambda = 0.71073$ Å).

The structures were solved by direct methods[22] and refinements on F^2 carried out by full-matrix least squares analysis.[23] The crystal of complex **9** was of poor quality and, unfortunately, no other crystal could be obtained. Although the X-ray structural determination of **9** was not accurate enough for an in-depth investigation of the parameters, it does show the

Table 2 Crystal data and structure refinement for complexes **2** and **9**

	2	**9**
Formula	$C_{24}H_{32}N_2OTi$	$C_{26}H_{27}Cl_3N_3OTa$
M	412.42	684.81
T/K	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a/Å	11.597(3)	15.369(6)
b/Å	15.2160(10)	16.6090(6)
c/Å	12.777(9)	12.455(6)
V/Å^3	2206.8(17)	3179(2)
Z	4	4
μ/cm^{-1}	4.04	3.73
$R1$	0.0585	0.0790
Reflections collected/ unique	5318/5318	3351/3351
$wR2$	0.1088	0.2214

overall structural features and hence has been included for this reason. Anisotropic thermal parameters were considered for all non-hydrogen atoms for **2**, while hydrogen atoms were included in calculated positions but not refined.

CCDC reference number 186/2080.

See http://www.rsc.org/suppdata/dt/b0/b002693j/ for crystallographic files in .cif format.

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