# Transition Metal–Carbohydrate Chemistry. Part 2.† Homoleptic Diacetoneglucose Complexes of Aluminium and Group 4 Metals‡

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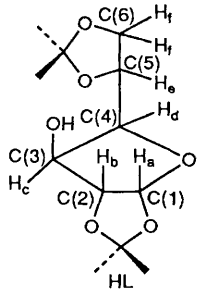
The synthesis of homoleptic 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL) complexes of aluminium and Group 4 metals (Ti, Zr or Hf) was achieved by ligand displacement from $AlEt_3$ and $[M(PhCH_2)_4]$ (M = Ti, Zr or Hf) with HL. The products were characterized by $^1H$ and $^{13}C$ NMR, which showed the sugar ligands to be equivalent and free to rotate about the M–O bond, even at 193 K. Pyridine adducts of all the complexes were obtained and the crystal structures of two of them, $[AlL_3(py)]$ and $[ZrL_4(py)_2]$, determined. The reaction of $[AlL_3]$ with two equivalents of 4,4'-bipyridine (4,4'-bipy) led to the formation of the one-to-one adduct $[AlL_3(4,4'\text{-bipy})]$. Complexation of $[TiL_4]$ by 1,10-phenanthroline (phen) gave the Lewis-base adduct $[TiL_4(phen)]$ which shows a strong steric effect of the base and a clear differentiation of the sugar ligands *cis* and *anti* to the N donor atoms. Optical rotatory power values $[\alpha]_D$ were measured for all the complexes. Crystallographic details: $[AlL_3(py)]$, trigonal, space group *R*3, $a = b = c = 10.639(2)$ Å, $\alpha = \beta = \gamma = 93.18(2)°$, $Z = 1$ and $R = 0.049$ for 2154 independent observed reflections; $[ZrL_4(py)_2]$, triclinic, space group *P*1, $a = 13.843(1)$, $b = 12.682(1)$, $c = 10.942(1)$ Å, $\alpha = 87.73(1)$, $\beta = 73.32(1)$, $\gamma = 66.96(1)°$, $Z = 1$ and $R = 0.057$ for 3336 independent observed reflections.

Transition metals can be used to assemble sugars in novel architectures. The molecules so formed take advantage of the intrinsic properties of both sugar and metal. (*i*) Sugars are natural chiral ligands;[2] (*ii*) sugar–metal complexes should have pronounced three-dimensional characteristics, like receptor cavities; (*iii*) they represent an unprecedented version of the metal–alkoxy chemistry;[3] (*iv*) their oxygen-rich periphery may serve as a binding area for cations, hydrogen-binding species and as a simulation of a solvation sphere; (*v*) such complexes may have an interesting use as Lewis acids, precursors of metal aggregates, and as functionalizable species in organometallic chemistry.

The monosaccharide we used for this purpose was the diacetoneglucose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL). So far, only one other homoleptic sugar compound has been reported,[1] although Riediker and co-workers have found an interesting use for some diacetoneglucose derivatives in metal-assisted enantioselective synthesis.[4]




Here we report the synthesis and full characterization of $[AlL_3]$ and $[ML_4]$ (M = Ti, Zr or Hf) and their pyridine adducts. The structure of two of these species has been determined by an X-ray structure analysis.

## Results and Discussion

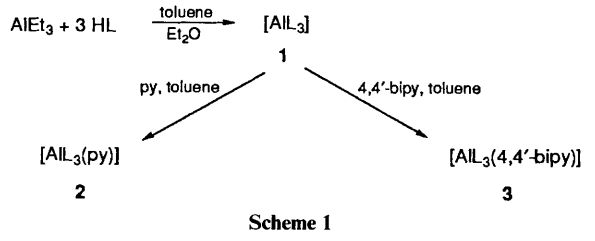
The monoprotic 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL) was used to make homoleptic complexes of aluminium and Group 4 metals. Our approach for the synthesis of such species is depicted in equation (1).

$$MR_n + n\,HL \longrightarrow ML_n + n\,RH \qquad (1)$$

Despite the fact that the preparation of alkyl derivatives of transition metals is often laborious and essentially limited to early transition metals, this synthetic route has the advantage of being clean and the only by-products of the reactions are hydrocarbons. An alternative method of synthesis, *i.e.* the metathetic exchange of an alkali-metal derivative of the protected sugar with the transition-metal chlorides, even if more simple, leads to a successive difficult separation of the final product from the alkali chlorides. The oxygen-rich periphery of the complex can act as a binding site for the alkali cation, solubilizing the salts even in hydrocarbon solvents.

The complex $[AlL_3]$ **1** is a white oily solid which can be recrystallized from cold *n*-hexane. Recrystallization from toluene containing one equivalent of pyridine (py) gives colourless cube crystals of $[AlL_3(py)]$ **2** (Scheme 1). The $^1H$ and $^{13}C$ NMR spectra do not reveal a single sugar conformation

† Ref. 1 may be regarded as Part 1 of the series.
‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.




**Scheme 1**

even at low temperature, or discrete differences in the three diacetoneglucose ligands. Detailed spectral data are given in the Experimental section. Recrystallization of complex **1** from toluene in presence of 4,4'-bipyridine (4,4'-bipy) was carried out in an attempt to obtain a dimeric unit of the Lewis acid **1**. The stoichiometric ratio of the isolated product **3**, however, was found to be only one aluminium per bipyridine. The fact that the monomeric complexation is preferred over the formation of the expected dimer is almost certainly due to the steric hindrance of the sugar ligands. Some useful information on this can be obtained from the crystal structure of the pyridine adduct **2**. The three methyl groups [C(8), see Fig. 1] of the 1,2-isopropylidene moieties of the three sugars in this molecule are pointing in the direction of the pyridine ring, building a $C_3$ cavity where the ligand lies. From a space-filling representation of the molecule **2**, it can be seen that these methyl groups rise beyond the limit of the aromatic ring. In the case of the bipyridine adduct **3**, this disposition of the methyl groups is probably responsible for the failure of a second molecule of $AlL_3$ to attack and for the formation of the one-to-one adduct.

X-Ray structural analysis of complex **2** shows it to be monomeric with three diacetoneglucose ions co-ordinated to the aluminium through the O(4) oxygens (Fig. 1). The co-ordination geometry is best described as a trigonal pyramid, the aluminium atom lying on a three-fold axis of the *R*3 space group. The apex of the pyramid is occupied by a pyridine molecule which is required to be statistically distributed around the $C_3$ axis. The metal atom is displaced by 0.405(7) Å from the basal plane running through the co-ordinated oxygen atoms [O(4), O(4') and O(4'')].

The Al–O(4) distance [1.706(2) Å, Table 1] is in very good agreement with the value of 1.706(4) Å found for the aryloxide Al–O distance in [AlMe(dbmp)(bhmap)] (Hdbmp = 2,6-di-*tert*-butyl-4-methylphenol, Hbhmap = 3-*tert*-butyl-2-hydroxy-5-methylacetophenone).[6] By contrast the Al–O(4)–C(4) angle is narrower [130.6(2) *vs.* 158.0(4)°] and the O(4)–C(4) corresponding distance significantly longer [1.402(4) *vs.* 1.363(7)° Å]. This suggested some $sp^2$-hybridization character for the O(4) oxygen, hence a degree of multiple bonding between oxygen and aluminium.

The torsion angles of the freely rotating C(2)–C(3) single bond in one independent carbohydrate ligand do not differ considerably from those observed in *cis*-$[ZrL_4(py)_2]$ and in $[VL_3(py)_2]$[1] (Table 2). The C(1), C(2), O(2), C(7), O(1) dioxolane rings are pushed upwards to face the pyridine ring in such a way that the C(2)–C(3) bonds are nearly perpendicular to the basal plane [dihedral angle 85.6(2)°], *i.e.* the ligand is disposed with its elongation axis nearly perpendicular to the basal plane. A conformational analysis carried out using the program MOBY[7] and restricted to the torsion angle O(4')–Al–O(4)–C(4) showed the ability of the ligand to rotate freely in a range of about 270° without any change of potential energy. This situation is completely different from that observed in $[VL_3(py)_2]$[1] where the carbohydrate ligands, arranged with their elongation axis nearly parallel to the equatorial plane, are prevented from rotating. It can therefore be concluded that, in spite of being chirotropic the aluminium atom is not stereogenic.

Bond distances and angles within the carbohydrate ligands are typical of this genre and the O–C distances are not significantly different, except for O(3)–C(3) and O(3)–C(6) (Table 1).

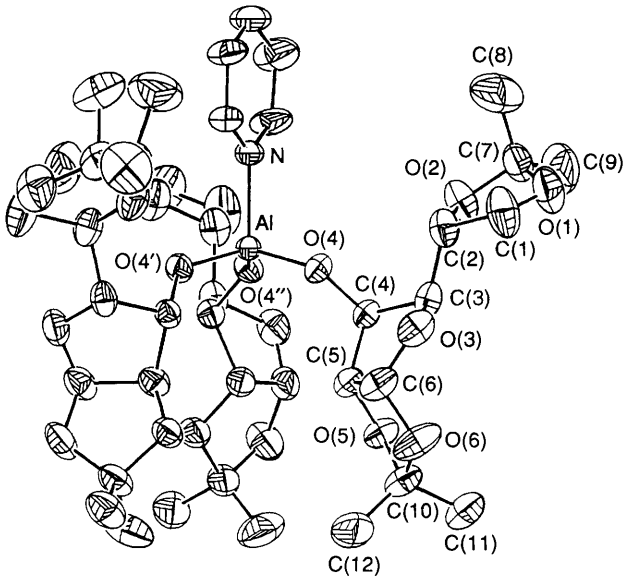



**Fig. 1** ORTEP[5] drawing of complex **2** (30% probability ellipsoids). Primed and double-primed atoms denote transformations of *z*, *x*, *y* and *y*, *x*, *z* respectively

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

| | | | |
|---|---|---|---|
| Al–O(4) | 1.706(2) | O(5)–C(5) | 1.421(4) |
| Al–N(1) | 1.942(2) | O(5)–C(10) | 1.434(5) |
| O(1)–C(1) | 1.352(9) | O(6)–C(6) | 1.412(5) |
| O(1)–C(7) | 1.407(8) | O(6)–C(10) | 1.427(7) |
| O(2)–C(2) | 1.430(5) | C(1)–C(2) | 1.521(8) |
| O(2)–C(7) | 1.407(7) | C(2)–C(3) | 1.503(6) |
| O(3)–C(3) | 1.440(5) | C(3)–C(4) | 1.533(5) |
| O(3)–C(6) | 1.369(5) | C(4)–C(5) | 1.510(4) |
| O(4)–C(4) | 1.402(4) | C(5)–C(6) | 1.543(6) |
| O(4)–Al–N(1) | 103.7(1) | Al–O(4)–C(4) | 130.6(2) |
| O(4)–Al–O(4') | 114.5(1) | | |

Symmetry operator for primed atom: *z*, *x*, *y*.

Complex **1** is an interesting starting material not only for its acidic properties but also for its possible use in organometallic chemistry and as a precursor of polyaluminoxane.

The synthesis of Group 4 metal–diacetoneglucose derivatives makes use of the corresponding well known $[M(CH_2Ph)_4]$ compounds [equation (2)]. The major technical difficulty in

$$[M(CH_2Ph)_4] \xrightarrow[-PhCH_3]{Et_2O} [ML_4] \xrightarrow[\text{toluene}]{py} cis\text{-}[ML_4(py)_2] \quad (2)$$

| | | |
|---|---|---|
| + | M | M |
| 4 HL | **4** Ti | **7** Ti |
| | **5** Zr | **8** Zr |
| | **6** Hf | **9** Hf |

the preparation of complexes **4**–**6** is their purification *via* crystallization. Their extremely high solubility limits the number of usable solvents and crystals suitable for an X-ray structural analysis are hard to grow. The $^1H$ NMR spectra of these compounds show a close correlation between the titanium and zirconium derivatives; the hafnium complex is fluxional even at low temperature. In the two former cases a single set of sugar protons was observed, which, even upon cooling down to 193 K (either in $[^2H_8]$toluene or $[^2H_2]$-methylene chloride) did not decoalesce but showed only signal

**Table 2** Comparison of relevant torsional angles within the diacetoneglucose ligands

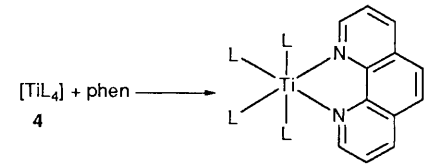
| | | *cis*-$[ZrL_4(py)_2]$ **8**[a] | | | | $[VL_3(py)_2]$[b] | | | $[TiL_2(Cl)(\eta\text{-}C_5H_5)]$[c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $[AlL_3(py)]$ **2**[a] | Molecule A | Molecule B | Molecule C | Molecule D | Unprimed | Primed | Double primed | Unprimed | Primed |
| M–O(4)–C(4)–C(3) | 162.3(2) | 148.0(15) | −170.8(9) | 176.2(14) | −178.6(8) | 148.5(6) | 159.2(5) | 137.9(6) | 160.9 | 120.9 |
| M–O(4)–C(4)–C(5) | −86.6(3) | −99.7(19) | −61.0(15) | −73.1(20) | −70.9(14) | −102.6(8) | −91.3(7) | −110.7(6) | −89.0 | −130.8 |
| C(10)–O(5)–C(5)–C(4) | 137.2(3) | 131.5(10) | 137.0(10) | 134.8(10) | 141.7(13) | 137.0(7) | 135.4(7) | 127.4(7) | 130.5 | 144.5 |
| C(10)–O(6)–C(6)–O(3) | −127.6(4) | −124.7(11) | −125.0(10) | −116.8(11) | −120.8(16) | −122.2(7) | −119.5(7) | −88.6(9) | −136.8 | −117.1 |
| O(2)–C(2)–C(3)–O(3) | 176.2(3) | 174.6(9) | 168.4(9) | 173.1(9) | 179.5(10) | 173.3(6) | 170.6(6) | 179.5(7) | 79.7 | −179.2 |
| C(1)–C(2)–C(3)–C(4) | 175.9(4) | 177.9(11) | 168.7(10) | 175.5(11) | −172.3(12) | 175.3(7) | 173.4(7) | 179.8(9) | 84.6 | −174.3 |
| C(2)–C(3)–C(4)–O(4) | −37.4(4) | −37.2(14) | −43.5(13) | −38.8(14) | −43.2(15) | −45.7(8) | −45.3(9) | −38.9(9) | −41.2 | −42.8 |
| O(3)–C(3)–C(4)–O(4) | 80.4(3) | 78.5(12) | 75.7(10) | 78.1(11) | 76.3(12) | 71.8(7) | 74.0(7) | 80.5(7) | 82.3 | 76.5 |
| O(4)–C(4)–C(5)–O(5) | 157.1(3) | 154.6(9) | 161.4(9) | 160.1(9) | 161.0(10) | 165.5(6) | 161.8(6) | 167.1(6) | 149.7 | 163.0 |
| O(4)–C(4)–C(5)–C(6) | −90.7(3) | −94.5(11) | −87.0(11) | −88.3(11) | −87.9(12) | −86.3(7) | −87.2(7) | −82.6(7) | −100.7 | −85.2 |
| O(5)–C(5)–C(6)–O(3) | 109.9(3) | 111.0(10) | 109.1(10) | 103.8(10) | 103.5(13) | 106.0(7) | 104.7(7) | 93.8(7) | 117.7 | 100.3 |
| C(4)–C(5)–C(6)–O(6) | −126.0(3) | −123.7(10) | −125.7(10) | −129.4(10) | −128.2(13) | −128.4(7) | −128.4(6) | −141.2(7) | −111.3 | −132.8 |

[a] Present work. [b] Ref. 1. [c] Ref. 4(*d*).

broadening. The $[\alpha]_D$ values for complexes **4–9** are not significantly different from the value obtained for diacetoneglucose, but show a uniform decreasing trend from titanium to zirconium and hafnium. This fact, despite the variety in the co-ordination numbers and, in accord with the nature of the various metal centres in the complexes cited above, could be rationalized in terms of longer bond distances and thus free rotation around the metal–oxygen bonds, as inferred from the $^1H$ NMR spectra. Complexes **4–6** are very sensitive to air, as expected for homoleptic $M(OR)_4$ alkoxo derivatives of Group 4 metals. The controlled hydrolysis of these complexes is currently being studied, in an effort to prepare metal–oxo aggregates.[8a] Their use as Lewis acids may be of considerable interest. Their Lewis acidity has been proven by their reaction with pyridine and the complexes so formed are much easier to handle in terms of crystallization.

The pyridine adducts are obtained by addition of a stoichiometric amount of pyridine to the toluene solution of compounds **4–6**. Complexes **7–9** have been isolated as crystalline solids, and elemental analysis has shown them to contain two pyridine molecules per metal atom. The *cis* geometry reported is essentially derived from the crystal structure of complex **8** and from the normal stereochemistry of $MX_4$ adducts in the Group 4 metal series.[8b,9] A regular significant variation in the proton chemical shifts was observed in the $^1H$ NMR spectra of the pyridine adducts **7–9**. This time, the enhanced rigidity due to the presence of the pyridine molecules allows the hafnium derivative to show a single set of signals instead of the fluxional behaviour of compound **6**. A differentiation of the sugar molecules on the basis of NMR spectra could not however be obtained, even with low-temperature studies, where again signal broadening but no decoalescence was noticed. The $[\alpha]_D$ value is rather low for all the compounds and close to that of diacetoneglucose.

Another example of the *cis* co-ordination in titanium complexes was obtained by the reaction of complex **4** with 1,10-phenanthroline (phen) [equation (3)]. This Lewis base possesses




(3)

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a blocked planar three aromatic-ring skeleton in which the nitrogen atoms are forced to co-ordinate in a *cis* fashion. The more powerful steric demand, compared with pyridine, of this molecule was expected to induce a differentiation between the sugar ligands in *cis* and *trans* positions with respect to the co-ordinated nitrogen atoms. Indeed, on the basis of the $^1H$ and $^{13}C$ NMR spectra, such a differentiation could be demonstrated. The resonances of the protons belonging to the furanoside skeleton are split into two different, easily recognisable sets. One of these series of signals, particularly the protons $H_d$, $H_e$ and the two $H_f$, as well as two of the singlets due to the methyl groups of the isopropylidene moieties, are shifted to higher fields, compared to the same signals in the related homoleptic complex **4** and pyridine adduct **7**. This upfield shift probably indicates a fairly strong shielding by the aromatic ring on these protons. The $[\alpha]_D$ value for this molecule is definitely different from those obtained for complexes **4** and **7**, thus indicating a different disposition of the sugar ligands around the metal centre which is strongly affected by the presence of the bulky rigid ligand.

Complex **8** is monomeric. Co-ordination around the zir-

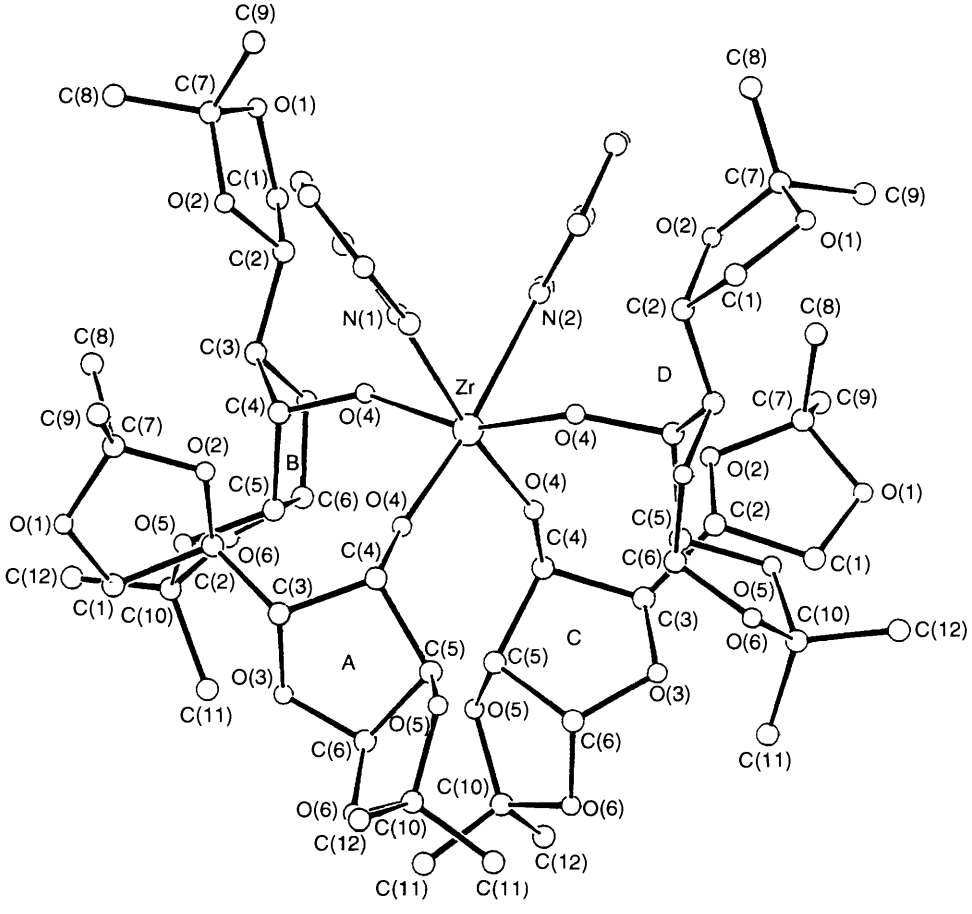


**Fig. 2** SCHAKAL[10] drawing of complex **8**

conium is pseudo octahedral involving four carbohydrate and two pyridine ligands in a *cis* configuration (Fig. 2). The best equatorial plane runs through the O(4A), O(4C), N(1), N(2) and Zr atoms. The complex possesses a pseudo-$C_2$ local symmetry, with the local $C_2$ axis lying on that plane intersecting the N(1)–Zr–N(2) angle. Bond distances and angles around zirconium reflect this symmetry. The Zr–O(4A) and Zr–O(4C) bond distances [mean value 1.949(9) Å] are not significantly different from each other but are significantly shorter than the Zr–O(4B) and Zr–O(4D) distances [mean value 2.020(9) Å] (Table 3). The former correspond to the largest Zr–O(4)–C(4) angles [mean values 156.4(8)° for A and C *vs.* 143.2(10)° for B and D] in agreement with those observed in zirconium enolates.[11] The relatively high estimated standard deviations prevent a correlation with the corresponding O(4)–C(4) bond distances.

The carbohydrate molecules are oriented in such a way that the directions of the C(2)–C(3) bonds form dihedral angles of 36.2(6) (A), 37.3(5) (C), 80.2(6) (B) and 85.6(7)° (D) with the normal to the best equatorial plane, confirming the pseudo-$C_2$ local symmetry. Conformational analysis carried out using the program MOBY[7] and restricted to rotations around individual Zr–O(4) bonds showed that the ligands were not free to rotate for more than 60 and 30° for A and C, respectively, around the equilibrium positions. Rotation over 360° of the B ligand around the Zr–O(4B) bond shows two minima in the ranges 330–30° and 170–230° separated by strong energy barriers. The corresponding rotations carried out for ligand D show a similar trend with two minima in the ranges 340–20° and 130–300°. From the torsion-angle data quoted in Table 2, it appears that in spite of the freely rotating C(2)–C(3) single bond, the carbohydrate ligand maintains nearly the same conformation as the unprimed molecule in $[TiL_2(Cl)(\eta\text{-}C_5H_5)]$.[4f]

On removing the two pyridine ligands in complex **8** a $C_2$ cavity available for a variety of small molecules remains. In addition, the oxygen-rich periphery should bind any cation accompanying the nucleophilic or basic species.

**Table 3** Selected bond distances (Å) and angles (°) for complex **8**

(*a*) In the zirconium co-ordination sphere

| | | | |
|---|---|---|---|
| Zr–O(4A) | 1.945(7) | Zr–O(4C) | 1.952(10) |
| Zr–O(4B) | 2.022(6) | Zr–O(4D) | 2.017(6) |
| Zr–N(1) | 2.411(11) | Zr–N(2) | 2.421(7) |
| N(1)–Zr–N(2) | 84.3(3) | O(4A)–Zr–N(2) | 171.9(3) |
| O(4D)–Zr–N(2) | 81.8(3) | O(4A)–Zr–N(1) | 87.6(3) |
| O(4D)–Zr–N(1) | 82.4(3) | O(4A)–Zr–O(4D) | 97.1(3) |
| O(4C)–Zr–N(2) | 88.9(3) | O(4A)–Zr–O(4C) | 99.2(3) |
| O(4C)–Zr–N(1) | 173.1(3) | O(4A)–Zr–O(4B) | 98.5(3) |
| O(4C)–Zr–O(4D) | 95.6(3) | Zr–O(4A)–C(4A) | 157.0(7) |
| O(4B)–Zr–N(2) | 80.8(3) | Zr–O(4B)–C(4B) | 146.3(6) |
| O(4B)–Zr–N(1) | 84.3(3) | Zr–O(4C)–C(4C) | 155.8(8) |
| O(4B)–Zr–O(4D) | 159.0(3) | Zr–O(4D)–C(4D) | 140.1(7) |
| O(4B)–Zr–O(4C) | 95.6(3) | | |

(*b*) In the diacetoneglucose ligands

| | A | B | C | D |
|---|---|---|---|---|
| O(1)–C(1) | 1.411(26) | 1.396(20) | 1.337(17) | 1.327(18) |
| O(1)–C(7) | 1.372(20) | 1.424(20) | 1.407(24) | 1.359(20) |
| O(2)–C(2) | 1.442(20) | 1.357(19) | 1.403(15) | 1.417(16) |
| O(2)–C(7) | 1.391(19) | 1.393(20) | 1.435(16) | 1.371(16) |
| O(3)–C(3) | 1.444(17) | 1.445(17) | 1.445(15) | 1.453(15) |
| O(3)–C(6) | 1.397(15) | 1.389(15) | 1.396(11) | 1.398(23) |
| O(4)–C(4) | 1.385(14) | 1.367(10) | 1.394(18) | 1.420(14) |
| O(5)–C(5) | 1.425(13) | 1.405(11) | 1.396(15) | 1.406(17) |
| O(5)–C(10) | 1.419(16) | 1.415(18) | 1.423(17) | 1.452(24) |
| O(6)–C(6) | 1.399(14) | 1.435(12) | 1.410(18) | 1.389(24) |
| O(6)–C(10) | 1.391(16) | 1.459(15) | 1.368(15) | 1.374(32) |

## Conclusion

This is the first report on the preparation of homoleptic diacetoneglucose complexes, in relatively high yield. Metal–sugar complexes are potentially very interesting starting materials as novel versions of metal–alkoxo species. Their characteristics reside in the presence of chiral ligands, which generate cavities for complexation, and an oxygen-rich periphery for hydrogen bonding or electrostatic complexation.[12]

## Experimental

*General Procedures.*—All manipulations of air- and/or moisture-sensitive materials were performed on a vacuum–nitrogen atmosphere line using Schlenk and cannula techniques, or in a nitrogen-filled glove-box. Infrared spectra were recorded on a Perkin Elmer 883 spectrophotometer and $^1H$ (200, 13 MHz) and $^{13}C$ (50.32 MHz) NMR spectra on a Bruker AC200 spectrometer. The following chemicals were obtained commercially and used as received unless stated otherwise: $ZrCl_4$ (Fluka), $TiCl_4$ (Fluka, distilled), $LiBu^n$ (1.6 mol $dm^{-3}$ in hexane, Fluka), 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (Fluka, Aldrich), pyridine (Fluka, distilled), $AlEt_3$. The synthesis of $[M(CH_2Ph)_4]$ (M = Ti,[13] Zr[14] or Hf[15]) has been performed as reported in the literature.

*Syntheses.*—$[AlL_3]$ **1**. Triethylaluminium (3.5 $cm^3$, 25.6 mmol) was added dropwise to a stirring suspension of HL (20.00 g, 76.8 mmol) in diethyl ether (200 $cm^3$) over 1 h, in a nitrogen-atmosphere glove-box. On addition of $AlEt_3$ there was an immediate reaction, the evolution of gas, and a colourless solution was formed, which was stirred for a further 3 h. The volatiles were removed under reduced pressure and the resultant white oily solid washed with cold pentane (*ca.* 40 $cm^3$) to afford crude white $[AlL_3]$, which was dried *in vacuo* (15.8 g, 78%). The product can be recrystallized from cold hexane (Found: C, 53.95; H, 7.80. $C_{36}H_{57}AlO_{18}$ requires C, 53.75; H, 7.80%). IR (Nujol, KBr): 1375vs, 1248vs, 1216vs, 1166vs, 1072vs(br), 943m, 843s, 807m, 729m, 694w, 636w, 510w and 464w $cm^{-1}$. $^1H$ NMR: fluxional species even at low temperature. $[\alpha]_D^{30}$ [tetrahydrofuran (thf), 75.5 g $dm^{-3}$] = −11.3°.

$[AlL_3(py)]$ **2**. Pyridine (0.28 g, 3.50 mmol) was added dropwise to a stirred solution of $[AlL_3]$ (2.787 g, 3.46 mmol) in toluene (80 $cm^3$). The resultant solution was allowed to stir for 12 h to afford a pale yellow solution. The solvent was removed under reduced pressure and the white solid washed with hexane (20 $cm^3$) and dried *in vacuo* (2.2 g, 72%). Colourless cubes of $[AlL_3(py)]$ can be grown from a concentrated toluene solution (Found: C, 50.20; H, 7.25; N, 0.20. $C_{41}H_{62}AlNO_{18}$ requires C, 55.70; H, 7.05; N, 1.60%). NMR: $^1H$ (200 MHz, $C_6D_6$, 298 K), δ 1.20 (s, 9 H, Me), 1.32 (s, 9 H, Me), 1.46 (s, 18 H, Me), 4.14 (m, 3 H, $H_f$), 4.28 (m, 3 H, $H_f$), 4.45 (d of d, 3 H, $J_{H_dH_c}$ = 8.6, $J_{H_dH_c}$ = 2.6, $H_d$), 4.64 (m, 3 H, $H_e$), 4.80 (d, 3 H, $J_{H_bH_a}$ = 3.6, $H_b$), 4.93 (d, 3 H, $J_{H_cH_d}$ = 2.4, $H_c$), 6.18 (d, 3 H, $J_{H_aH_b}$ = 3.4, $H_a$), 6.53 (t, 2 H, $J_{H_bH_i}$ = 6.7, $H_h$), 6.76 (t, 1 H, $J_{H_iH_h}$ = 6.7, $H_i$) and 8.70 (d, 2 H, $J_{H_gH_h}$ = 6.7 Hz, $H_g$); $^{13}C$ (50 MHz, $CD_2Cl_2$, 298 K), δ 26.1, 26.7, 27.4, 27.5, 68.2, 73.7, 75.9, 83.6, 88.1, 106.2, 109.5, 112.0, 126.3, 142.1 and 149.2. $[\alpha]_D^{30}$ (thf, 43.4 g $dm^{-3}$ = −16.1°).

$[AlL_3(4,4'\text{-bipy})]$ **3**. Toluene (80 $cm^3$) was added to a solid mixture of $[AlL_3]$ (3.87 g, 4.81 mmol) and 4,4'-bipyridine (0.76 g, 4.81 mmol). The resultant yellow solution was allowed to stir for 12 h during which time a white precipitate was formed. The suspension was filtered to afford a pale yellow solution. The solvent was removed under reduced pressure to yield a white powder which was washed with hexane (20 $cm^3$) and dried *in vacuo* (3.68 g, 79%) (Found: C, 56.65; H, 7.15; N, 2.65. $C_{46}H_{65}AlN_2O_{18}$ requires C, 57.50; H, 6.80; N, 2.90%). $^1H$ NMR (200 MHz, $C_6D_6$, 298 K): δ 1.22 (s, 9 H, Me), 1.47 (s, 18 H, Me), 4.14 (m, 3 H, $H_f$), 4.28 (m, 3 H, $H_f$), 4.53 (d of d, 3 H, $J_{H_dH_c}$ = 8.6, $J_{H_dH_c}$ = 2.6, $H_d$), 4.73 (m, 3 H, $H_e$), 4.86 (d, $J_{H_bH_a}$ =

3.2, $H_b$), 5.02 (d, 3 H, $J_{H_cH_d}$ = 2.0, $H_c$), 6.23 (d, 3 H, $J_{H_aH_b}$ = 3.2, $H_a$), 6.70 (t, 4 H, $J_{H_bH_g}$ = 5.4, $H_h$) and 8.68 (d, 4 H, $J_{H_gH_h}$ = 5.4 Hz, $H_g$). $[\alpha]_D^{30}$ (thf, 26.5 g dm$^{-3}$) = −18.1°.

[$TiL_4$] **4**. Diacetoneglucose (10.00 g, 38.42 mmol) in diethyl ether (120 cm$^3$) was added dropwise *via* cannula to a stirred chilled (−20 °C) solution of freshly prepared [$Ti(CH_2Ph)_4$] (3.98 g, 9.61 mmol) in diethyl ether (50 cm$^3$) over 15 min. The mixture was allowed to warm to room temperature and stirred for a further 12 h, during which time the solution changed from red to yellow. The volatiles were removed under reduced pressure to yield an oily brown solid, which was dissolved in hexane (50 cm$^3$). The resultant cloudy solution was filtered and cooled to *ca.* −78 °C to yield off-white crystals of [$TiL_4$], which were collected at low temperature, and dried *in vacuo* (7.1 g, 68%) (Found: C, 53.35; H, 7.25. $C_{48}H_{76}O_{24}Ti$ requires C, 53.15; H, 7.05%). NMR: ($C_6D_6$, 298 K): $^1$H (200 MHz), δ 1.11 (s, 12 H, Me), 1.36 (s, 12 H, Me), 1.41 (s, 12 H, Me), 1.46 (s, 12 H, Me), 4.15 (d, 8 H, $J_{H_fH_e}$ = 5.0, 2 $H_f$), 4.28 (d of d, 4 H, $J_{H_dH_e}$ = 9.0, $J_{H_dH_c}$ = 2.4, $H_d$), 4.69 (m, 4 H, $H_e$), 4.76 (d, 4 H, $J_{H_bH_a}$ = 4.0, $H_b$), 5.32 (d, 4 H, $J_{H_cH_d}$ = 2.4, $H_c$) and 6.10 (d, 4 H, $J_{H_aH_b}$ = 3.6 Hz, $H_a$); $^{13}$C (50 MHz), δ 26.2, 27.1, 27.8, 27.9, 68.6, 73.7, 86.6, 86.9, 88.9, 106.5, 110.5 and 112.7. $[\alpha]_D^{30}$ (thf, 89.0 g dm$^{-3}$) = −41.6°.

[$ZrL_4$] **5**. Diacetoneglucose (14.40 g, 55.32 mmol) in diethyl ether (150 cm$^3$) was added dropwise *via* cannula to a stirred chilled (−20 °C) solution of [$Zr(CH_2Ph)_4$] (6.30 g, 13.82 mmol) in diethyl ether (100 cm$^3$) over 15 min. The mixture was allowed to warm to room temperature and stirred for a further 6 h to afford a pale yellow solution. The volatiles were removed under reduced pressure to yield an oily white solid, which was washed with cold hexane (50 cm$^3$) and dried *in vacuo* to afford crude product (11.8 g, 76%). The product can be purified by recrystallization from hexane (Found: C, 51.75; H, 7.15. $C_{48}H_{76}O_{24}Zr$ requires C, 51.10; H, 6.80%). NMR ($C_6D_6$, 298 K): $^1$H (200 MHz), δ 1.15 (s, 12 H, Me), 1.41 (s, 12 H, Me), 1.49 (s, 12 H, Me), 4.07 (m, 8 H, $H_f$), 4.37 (d of d, 4 H, $J_{H_dH_e}$ = 8.6, $J_{H_dH_c}$ = 2.8, $H_d$), 4.62 (m, 4 H, $H_e$), 4.66 (d, 4 H, $J_{H_bH_a}$ = 3.6, $H_b$), 5.03 (d, 4 H, $J_{H_cH_d}$ = 3.0, $H_c$) and 6.06 (d, 4 H, $J_{H_aH_b}$ = 3.6 Hz, $H_a$); $^{13}$C (50 MHz): δ 25.9, 27.1, 27.8, 27.9, 68.6, 75.3, 82.3, 84.0, 87.9, 106.7, 112.1 and 112.5. $[\alpha]_D^{30}$ (thf, 59.4 g dm$^{-3}$) = −28.4°.

[$HfL_4$] **6**. Diacetoneglucose (7.51 g, 28.85 mmol) in diethyl ether (80 cm$^3$) was added dropwise *via* cannula to a stirred chilled (−20 °C) solution of [$Hf(CH_2Ph)_4$] (3.92 g, 7.21 mmol) in diethyl ether (40 cm$^3$). The mixture was allowed to warm to room temperature, during which time a reaction ensued with the formation of a cloudy pale yellow solution. The mixture was stirred for a further 6 h, then the volatiles were removed *in vacuo* to afford an oily white solid. The solid was extracted into hexane and the cloudy solution filtered to remove unreacted sugar. The resultant colourless solution was cooled to *ca.* −20 °C to yield a crystalline white solid which was collected while cold and dried *in vacuo* (4.9 g, 56%) (Found: C, 46.95; H, 6.35. $C_{48}H_{76}HfO_{24}$ requires C, 47.45; H, 6.30%). IR (Nujol, KBr): 1376vs, 1257m, 1216s, 1165s, 1071vs, 1016vs, 951m, 884m, 843m, 810m, 735w, 637w, 608w, 512w and 464w cm$^{-1}$. $^1$H NMR: fluxional species even at low temperature. $[\alpha]_D^{30}$ (thf, 82.6 g dm$^{-3}$) = −10.63°.

[$TiL_4(py)_2$] **7**. Pyridine (0.37 g, 4.67 mmol) was added dropwise to a stirred solution of [$TiL_4$] (24.74 g, 2.28 mmol) in hexane (80 cm$^3$). There was an immediate reaction and formation of a white precipitate and colourless solution. The mixture was stirred for a further 6 h, then the solid was isolated by filtration and dried *in vacuo* (2.1 g, 74%). A crop of [$TiL_4$] crystals can be obtained by layering a saturated toluene solution with octane (ratio 1:2) and cooling slowly to *ca.* −10 °C (Found: C, 56.05; H, 7.15; N, 1.60. $C_{58}H_{86}N_2O_{24}Ti$ requires C, 56.05; H, 6.95; N, 2.25%). NMR ($C_6D_6$, 298 K): $^1$H (200 MHz), δ 1.16 (s, 12 H, Me), 1.37 (s, 12 H, Me), 1.41 (s, 12 H, Me), 1.48 (s, 12 H, Me), 4.19 (m, 8 H, $H_f$), 4.34 (d of d, 4 H, $J_{H_dH_e}$ = 9.6, $J_{H_dH_c}$ = 2.6, $H_d$), 4.61 (m, 4 H, $H_e$), 4.89 (d, 4 H, $J_{H_bH_a}$ = 3.6, $H_b$), 5.46 (d, 4 H, $J_{H_cH_d}$ = 2.4, $H_c$), 6.07 (d, 4 H, $J_{H_aH_b}$ = 3.4, $H_a$), 6.67 (t, 4 H, $J_{HH}$ = 8.2, $H_h$), 6.89 (t, 2 H, $J_{HH}$ = 7.6, $H_i$) and 8.71 (d, 4 H, $J_{HH}$ = 7.6 Hz, $H_g$); $^{13}$C (50 MHz), δ 26.4, 27.1, 27.7, 28.0, 68.6, 73.8, 83.9, 87.3, 88.3, 106.5, 112.5, 137.0 and 150.6. $[\alpha]_D^{30}$ (thf, 29.4 g dm$^{-3}$) = −38.2°.

[$ZrL_4(py)_2$] **8**. Pyridine (0.60 g, 7.54 mmol) was added dropwise to a stirred solution of [$ZrL_4$] (4.25 g, 3.76 mmol) in hexane (80 cm$^3$). The mixture was stirred for 12 h, after which the volatiles were removed under reduced pressure and the resultant oily yellow solid washed with cold pentane (20 cm$^3$) and dried *in vacuo* (3.4 g, 70%). The crude white product can be recrystallized from hexane (Found: C, 54.00; H, 7.00; N, 1.95. $C_{58}H_{86}N_2O_{24}Zr$ requires C, 54.15; H, 6.75; N, 2.15%). NMR ($C_6D_6$, 298 K): $^1$H (200 MHz), δ 1.23 (s, 24 H, Me), 1.41 (s,

**Table 4** Experimental data for the X-ray diffraction studies on complexes **2** and **8**

| Complex | **2** | **8** |
|---|---|---|
| Formula | $C_{41}H_{62}AlNO_{18}$ | $C_{58}H_{86}N_2O_{24}Zr$ |
| *M* | 883.9 | 1286.5 |
| Space group | *R*3 (no. 146) | *P*1 (no. 1) |
| *a*/Å | 10.639(2) | 13.843(1) |
| *b*/Å | 10.639(2) | 12.682(1) |
| *c*/Å | 10.639(2) | 10.942(1) |
| α/° | 93.18(2) | 87.73(1) |
| β/° | 93.18(2) | 73.32(1) |
| γ/° | 93.18(2) | 66.96(1) |
| *U*/Å$^3$ | 1198.4(4) | 1687.6(3) |
| *Z* | 1 | 1 |
| $D_c$/g cm$^{-3}$ | 1.225 | 1.266 |
| *F*(000) | 472 | 680 |
| *T*/°C | 22 | 22 |
| λ/Å | 1.541 78 | 0.710 69 |
| μ/cm$^{-1}$ | 9.33 | 2.30 |
| crystal dimensions/mm | 0.35 × 0.35 × 0.39 | 0.18 × 0.28 × 0.40 |
| Transmission coefficient | 0.962–1.000 | 0.968–1.000 |
| *R** | 0.049 [0.051] | 0.057 [0.057] |
| *R'** | 0.056 [0.058] | 0.058 [0.059] |
| $R_G$* | 0.071 [0.074] | 0.066 [0.067] |

* $R = \Sigma||\Delta F|/\Sigma|F_o|$. $R' = [\Sigma(w)^{\frac{1}{2}}|\Delta F|/\Sigma(w)^{\frac{1}{2}}|F_o|]$. $R_G = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. The values in square brackets refer to the 'inverted' structure.

**Table 5** Fractional atomic coordinates (× 10$^4$) for complex **2**

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Al | 1179(—) | 1179(—) | 1179(—) |
| O(1) | 5224(5) | −1906(4) | −1881(5) |
| O(2) | 3820(4) | −1528(3) | −462(3) |
| O(3) | 5083(3) | 1700(3) | −480(3) |
| O(4) | 2603(2) | 1111(2) | 523(2) |
| O(5) | 5381(2) | 2064(3) | 2527(2) |
| O(6) | 6401(3) | 2909(4) | 953(4) |
| N(1) | 61(2) | 61(2) | 61(2) |
| C(1) | 4968(7) | −693(7) | −2044(5) |
| C(2) | 4126(4) | −347(4) | −984(4) |
| C(3) | 4700(3) | 542(4) | 67(4) |
| C(4) | 3806(3) | 948(3) | 1076(3) |
| C(5) | 4429(3) | 2204(3) | 1563(3) |
| C(6) | 5154(4) | 2658(4) | 440(4) |
| C(7) | 4233(6) | −2495(5) | −1267(5) |
| C(8) | 3140(13) | −2932(12) | −2181(9) |
| C(9) | 4732(9) | −3500(7) | −528(11) |
| C(10) | 6444(4) | 2890(4) | 2295(5) |
| C(11) | 7614(5) | 2311(6) | 2738(7) |
| C(12) | 6311(6) | 4173(6) | 2878(10) |
| C(21)* | 463(10) | −975(9) | −507(11) |
| C(22)* | −297(10) | −1830(14) | −1268(17) |
| C(23) | −1525(4) | −1525(4) | −1525(4) |
| C(24)* | −1954(11) | −452(19) | −904(25) |
| C(25)* | −1120(8) | 376(17) | −184(16) |

* Site occupation factor is 0.3333.

12 H, Me), 1.43 (s, 12 H, Me), 4.25 (m, 8 H, $H_f$), 4.33 (d of d, 4 H, $J_{H_dH_e}$ = 9.0, $J_{H_dH_c}$ = 2.4, $H_d$), 4.64 (m, 4 H, $H_e$), 4.89 (d, 4 H, $J_{H_bH_a}$ = 3.6, $H_b$), 4.96 (d, 4 H, $J_{H_cH_d}$ = 1.6, $H_c$), 6.24 (d, 4 H, $J_{H_aH_b}$ = 3.6, $H_a$), 6.76 (t, 4 H, $J_{HH}$ = 7.2, $H_h$), 6.92 (t, 2 H, $J_{HH}$ = 7.4, $H_i$) and 8.93 (d, 4 H, $J_{HH}$ = 4.8 Hz, $H_g$); $^{13}C$ (50 MHz): δ 26.4, 27.1, 27.9, 28.0, 68.9, 73.7, 82.1, 84.4, 88.0, 106.7, 109.9, 112.0, 124.8, 138.9 and 151.5. $[\alpha]_D^{30}$ (thf, 29.4 g $dm^{-3}$) = −24.5°.

$[HfL_4(py)_2]$ **9**. Pyridine (0.27 g, 3.41 mmol) was added dropwise *via* a syringe to a stirred solution of $[HfL_4]$ (2.03 g, 1.66 mmol) in hexane (80 $cm^3$). An immediate reaction ensued with the formation of a crystalline white solid and colourless solution. The mixture was left to stir at room temperature for 12 h. Filtration yielded white crystalline $[HfL_4(py)_2]$ (1.3 g, 57%). A further sample of $[HfL_4(py)_2]$ can be obtained by cooling the mother-liquor to *ca.* 0 °C (Found: C, 49.80; H, 6.15; N, 1.65. $C_{58}H_{86}HfN_2O_{24}$ requires C, 50.70; H, 6.30; N, 2.05%). IR (Nujol, KBr): 1605w (sp), 1378vs, 1214s, 1165s, 1148s, 1069vs, 1041s, 1012s, 953m, 880m, 850m, 803m, 758w, 708w, 698w, 575w, 532w and 420w $cm^{-1}$. NMR ($C_6D_6$, 298 K): $^1H$ (200 MHz), δ 1.17 (s, 12 H, Me), 1.23 (s, 12 H, Me), 1.41 (s, 24 H, 2 Me), 4.23 (m, 8 H, $H_f$), 4.36 (d of d, 4 H, $J_{H_dH_e}$ = 9.0, $J_{H_dH_c}$ = 2.2, $H_d$), 4.59 (m, 4 H, Me), 4.93 (br s, 8 H, $H_b$, $H_c$), 6.27 (br s, 4 H, $H_a$), 6.75 (t, 4 H, $J_{HH}$ = 6.8, $H_h$), 6.94 (t, 2 H, $J_{HH}$ = 6.9 Hz, $H_i$) and 8.85 (br s, $H_g$); $^{13}C$ (50 MHz), δ 26.7, 27.0, 27.8, 28.0, 69.0, 73.7, 81.9, 84.5, 88.0, 106.7, 109.7, 124.6 and 151.3. $[\alpha]_D^{30}$ (thf, 45.2 g $dm^{-3}$) = −8.62°.

$[TiL_4(phen)]$ **10**. The complex $[TiL_4]$ (2.86 g, 2.6 mmol) was added in one portion to a solution of dry and degassed 1,10-phenanthroline (0.41 g, 2.3 mmol) in toluene (80 $cm^3$). The resulting colourless limpid solution was stirred at room temperature overnight. The solvent was then evaporated *in vacuo* and hexane (70 $cm^3$) was added to the solid residue. The resulting white suspension was stirred for 30 min and the solid was collected on a filter and dried *in vacuo* (2.37 g, 82%) (Found: C, 57.05; H, 7.10; N, 2.45. $C_{60}H_{84}N_2O_{24}Ti$ requires C, 56.95; H, 6.70; N, 2.20%). IR (Nujol, KBr): 1518m, 1339m, 1250s, 1216s, 1165s, 1125s, 1061vs, 1016s, 950w, 882m, 838m, 728m, 623m, 536w, 482w and 444w $cm^{-1}$. NMR ($C_6D_6$, 298 K): $^1H$ (200 MHz), δ 0.55 (s, 6 H, Me), 0.77 (s, 6 H, Me), 1.23 (s, 6 H, Me), 1.27 (s, 6 H, Me), 1.29 (s, 6 H, Me), 1.33 (s, 6 H, Me), 1.56 (s, 6 H, Me), 3.29 (d of d, 2 H, $J_{H_fH_{e'}}$ = 2, $J_{H_fH'_{f'}}$ = 8.6, $H_{f'}$), 3.55 (m, 2 H, $H_{e'}$), 3.80 (d of d, 2 H, $J_{H_dH_{c'}}$ = 2.6, $J_{H_dH_{e'}}$ = 8.2, $H_{d'}$), 3.91 (d of d, 2 H, $J_{H'_fH_f}$ = 8.6, $J_{H'_fH_{e'}}$ = 3.8, $H'_{f'}$), 4.30 (m, 4 H, $H_f$), 4.32 (d, 2 H, $J_{H_cH_{d'}}$ = 2.6, $H_{c'}$), 4.50 (d of d, 2 H, $J_{H_dH_e}$ = 11.2, $J_{H_dH_c}$ = 2.6, $H_d$), 5.2 (m, 2 H, $H_e$), 5.21 (d, 2 H, $J_{H_bH_{a'}}$ = 3.4, $H_{b'}$), 5.47 (d, 2 H, $J_{H_bH_a}$ = 3.6, $H_b$), 5.82 (d, 2 H, $J_{H_cH_d}$ = 2.6, $H_c$), 6.25 (d, 2 H, $J_{H_aH_{b'}}$ = 3.4, $H_{a'}$), 6.38 (d, 2 H, $J_{H_aH_b}$ = 3.6, $H_a$), 7.18 (s, 2 H, $H_j$, $H_k$), 7.39 (d of d, 2 H, $J_{H_hH_g}$ = 8, $J_{H_hH_j}$ = 4.8, $H_h$), 7.60 (d, 2 H,

**Table 6** Fractional atomic coordinates ( × $10^4$) for complex **8**

| Atom | X/a | Y/b | Z/c | Atom | X/a | Y/b | Z/c |
|---|---|---|---|---|---|---|---|
| Zr | 0(—) | 0(—) | 0(—) | C(4B) | −1785(8) | 366(8) | 2796(9) |
| O(1A) | −5093(9) | 3419(11) | 1444(13) | C(5B) | −1664(9) | 1323(9) | 3411(11) |
| O(2A) | −3542(6) | 2207(8) | 130(10) | C(6B) | −1000(9) | 739(9) | 4375(11) |
| O(3A) | −2258(6) | 4009(6) | 746(7) | C(7B) | −2519(13) | −2756(13) | 3697(14) |
| O(4A) | −928(6) | 1569(6) | −199(7) | C(8B) | −3585(24) | −2527(24) | 4608(26) |
| O(5A) | −998(7) | 3864(6) | −2250(7) | C(9B) | −2265(15) | −3538(16) | 2553(18) |
| O(6A) | −1669(8) | 5222(6) | −614(8) | C(10B) | −2512(11) | 2397(11) | 5355(13) |
| O(1B) | −1702(8) | −3287(7) | 4330(8) | C(11B) | −2032(13) | 3317(14) | 5173(15) |
| O(2B) | −2418(8) | −1736(6) | 3306(9) | C(12B) | −3529(14) | 2643(14) | 6483(17) |
| O(3B) | −950(6) | −377(6) | 4412(6) | C(1C) | 4529(12) | −715(13) | −572(14) |
| O(4B) | −901(6) | −169(6) | 1754(6) | C(2C) | 3362(10) | −599(10) | 63(11) |
| O(5B) | −2667(6) | 2108(6) | 4210(7) | C(3C) | 2661(9) | 471(10) | 917(11) |
| O(6B) | −1650(7) | 1368(7) | 5594(7) | C(4C) | 1462(9) | 651(9) | 1485(11) |
| O(1C) | 5194(7) | −1793(8) | −474(13) | C(5C) | 894(9) | 1969(9) | 1715(10) |
| O(2C) | 3508(6) | −1525(6) | 836(9) | C(6C) | 1659(9) | 2382(9) | 663(11) |
| O(3C) | 2629(7) | 1422(7) | 135(9) | C(7C) | 4577(15) | −2391(16) | 229(18) |
| O(4C) | 1073(6) | 305(6) | 598(8) | C(8C) | 4497(21) | −3208(22) | −632(24) |
| O(5C) | 953(7) | 2333(6) | 2869(7) | C(9C) | 5068(21) | −2939(22) | 1171(25) |
| O(6C) | 1840(7) | 3163(7) | 1359(9) | C(10C) | 1265(10) | 3283(10) | 2628(13) |
| O(1D) | 2801(13) | −3014(11) | −6012(10) | C(11C) | 309(13) | 4387(14) | 2922(15) |
| O(2D) | 2148(8) | −2755(7) | −3887(8) | C(12C) | 2053(15) | 3167(16) | 3379(18) |
| O(3D) | 1631(8) | 234(8) | −4463(8) | C(1D) | 1944(14) | −2010(14) | −5736(16) |
| O(4D) | 929(6) | −414(6) | −1844(6) | C(2D) | 1656(10) | −1649(12) | −4295(12) |
| O(5D) | 3241(8) | 301(8) | −3055(9) | C(3D) | 2156(10) | −882(11) | −4018(12) |
| O(6D) | 2568(12) | 1386(11) | −4517(12) | C(4D) | 2016(10) | −636(9) | −2619(11) |
| N(1) | −1183(7) | −617(7) | −757(8) | C(5D) | 2118(10) | 507(10) | −2675(11) |
| N(2) | 986(7) | −2033(6) | 135(8) | C(6D) | 1731(13) | 1079(14) | −3786(15) |
| C(1A) | −4302(13) | 3665(13) | 1814(14) | C(7D) | 2760(12) | −3555(13) | −4913(15) |
| C(2A) | −3196(10) | 2772(10) | 935(12) | C(8D) | 2377(23) | −4441(24) | −4820(27) |
| C(3A) | −2546(9) | 3329(9) | −2(11) | C(9D) | 3912(23) | −4001(24) | −4834(27) |
| C(4A) | −1452(9) | 2484(10) | −832(11) | C(10D) | 3352(18) | 1185(17) | −3901(20) |
| C(5A) | −793(8) | 3251(9) | −1169(10) | C(11D) | 3188(17) | 2237(18) | −3139(20) |
| C(6A) | −1351(10) | 4180(10) | −50(11) | C(12D) | 4450(22) | 637(22) | −4859(25) |
| C(7A) | −4640(13) | 2400(13) | 699(14) | C(21) | −1349(8) | −294(8) | −1897(10) |
| C(8A) | −4706(15) | 1416(16) | 1524(19) | C(22) | −2096(9) | −512(9) | −2313(11) |
| C(9A) | −5132(16) | 2410(17) | −274(19) | C(23) | −2665(9) | −1115(10) | −1596(11) |
| C(10A) | −1241(11) | 5034(11) | −1940(13) | C(24) | −2452(10) | −1508(10) | −474(12) |
| C(11A) | −252(15) | 5272(16) | −2348(17) | C(25) | −1744(10) | −1215(10) | −48(11) |
| C(12A) | −2119(14) | 5739(14) | −2514(16) | C(31) | 1233(9) | −2817(10) | −796(11) |
| C(1B) | −1326(10) | −2480(11) | 4613(12) | C(32) | 1763(10) | −4002(11) | −653(13) |
| C(2B) | −1535(9) | −1656(9) | 3535(10) | C(33) | 2101(11) | −4317(12) | 393(14) |
| C(3B) | −1795(9) | −429(9) | 3919(10) | C(34) | 1908(10) | −3492(11) | 1299(12) |
| | | | | C(35) | 1326(9) | −2385(9) | 1150(11) |

$J_{H_gH_h}$ = 8, $H_g$) and 9.96 (d, 2 H, $J_{H_jH_h}$ = 4.8 Hz, $H_j$); $^{13}C$ (50 MHz): δ 25.6, 26.7, 26.9, 27.4, 27.6, 27.7, 28.0, 67.7, 69.7, 73.2, 73.9, 83.4, 84.3, 84.7, 86.6, 87.3, 87.8, 106.5, 108.2, 111.4, 112.2, 125.0, 127.2, 129.7, 138.3, 144.7 and 152.0. $[\alpha]_D^{30}$ (thf, 29.3 g $dm^{-3}$) = +23.2°.

*X-Ray Crystallography for Complexes* **2** *and* **8**.—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Crystal data and details are given in Table 4. The reduced cells were obtained with the use of TRACER.[16] The data were collected at room temperature on a single-crystal four-circle diffractometer. For intensities and background individual reflection profiles were analysed.[17] The structure amplitudes were obtained after the usual Lorentz and polarization corrections[18] and the absolute scale was established by the Wilson method.[19] Data reduction, structure solution and refinement were carried out on a GOULD 32/77 computer. The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected for complex **2**. The related intensity data were then corrected for absorption using ABSORB.[20] The function minimized during the full-matrix least-squares refinement was $\Delta w|\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. Scattering factors for neutral atoms were taken from ref. 21(*a*) for non-hydrogen and from ref. 22 for hydrogen atoms. Anomalous scattering corrections were included in all structure-factor calculations.[21b] Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first done isotropically, then anisotropically for all non-H atoms in complex **2**. For complex **8** only the Zr, O and N atoms were allowed to vary anisotropically. The pyridine molecule in complex **2** was found to be disordered around the three-fold axis running through the nitrogen and C(23) carbon atoms, so the C(21), C(22), C(24), C(25) 'partial' atoms have been refined with a site-occupation factor of 0.3333. The N–C and C–C bond distances within this molecule were constrained to be 1.34(1) and 1.39(1) Å respectively. The hydrogen atoms of complex **2**, excluding those associated with pyridine, which were ignored, were directly located from a difference map and introduced into the calculations as fixed contributors prior to the last stage of refinement ($U_{iso}$ = 0.10 $Å^2$). For complex **8** all the hydrogen atoms were put in geometrically calculated positions and introduced into the refinement as fixed contributors ($U_{iso}$ = 0.08 $Å^2$). Since the space groups of the two complexes are polar all the coordinates were inverted ($x, y, z \rightarrow -x, -y, -z$) and the structures were refined to convergence once again. The resulting final $R_G$ values (Table 4) indicated the original choice should be considered the correct one.

Final atomic coordinates are listed in Tables 5 and 6 and selected bond distances and angles in Tables 1 and 3 for complexes **2** and **8** respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

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## References

1 J. Ruiz, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1991, 2467.
2 Y. Shigenobu, *Coord. Chem. Rev.*, 1988, **23**, 113 and refs. therein; T. Tanase, K. Kurihara, S. Yano, K. Kobayashi, T. Sakurai, S. Yoshikawa and M. Hidai, *Inorg. Chem.*, 1987, **26**, 3134 and refs. therein; M. J. Adam and L. D. Hall, *Can. J. Chem.*, 1982, **60**, 2229; S. J. Angyal, *Chem. Soc. Rev.*, 1980, **9**, 415.
3 M. L. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 15.3 and refs. therein.
4 (*a*) M. Riediker and R. O. Duthaler, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 494; (*b*) R. O. Duthaler, P. Herold, W. Lottenbach, K. Oertle and M. Riediker, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 495; (*c*) G. Bold, R. O. Duthaler and M. Riediker, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 497; (*d*) M. Riediker, A. Hafner, U. Piantini, G. Rihs and A. Togni, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 499; (*e*) M. Riediker, R. W. Lang, P. Herold, K. Oertle and G. Bold, *Eur. Pat.*, Appl. EP 0254 685 A2, 1988; (*f*) R. O. Duthaler, A. Hafner and M. Riediker, in *Organic Synthesis via Organometallics*, eds. K. H. Dötz and R. W. Hoffmann, Vieweg, Braunschweig, 1991, p. 285.
5 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
6 M. B. Power, S. G. Bott, E. J. Bishop, K. D. Tierce, J. L. Atwood and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1991, 241.
7 MOBY, Molecular Modelling on the PC, Version 1.4, Springer, Heidelberg, 1992.
8 C. A. McAuliffe, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, ch. 31, (*a*) p. 333; (*b*) p. 354.
9 W. Oppolzer, I. Rodriguez, J. Blagg and G. Berardinelli, *Helv. Chim. Acta*, 1989, **72**, 123; T. Roll, J. O. Metter and G. Helmchen, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 112; H. Kunz, B. Muleer and D. Schanzenbach, *Angew. Chem., Int. Ed. Engl.*, 1987, **86**, 867; J. P. Benner, G. B. Gill, S. J. Parrot and B. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 1984, 291; J. K. Whitesell, S. W. Madley, J. D. Kelly and E. R. Bacon, *J. Org. Chem.*, 1985, **50**, 4144; A. Hosomi, T. Imai, M. Endo and H. Sakurai, *J. Organomet. Chem.*, 1985, **285**, 95; P. A. Bartlett, W. S. Johnson and D. J. Elliott, *J. Am. Chem. Soc.*, 1983, **105**, 2088; C. H. Heathcock, S. Kydoka and D. A. Blumenkoff, *J. Org. Chem.*, 1984, **49**, 4214; S. J. Danishefsky, W. H. Pearson and D. F. Harvey, *J. Am. Chem. Soc.*, 1984, **106**, 2455; S. J. Danishefsky, W. H. Pearson and D. C. Miles, *J. Am. Chem. Soc.*, 1987, **109**, 862; T. Mukaiyama, K. Narasaka and K. Banno, *J. Am. Chem. Soc.*, 1974, **96**, 7503; C. Gennari, A. Bernardi, L. Colombo and C. Scolastico, *J. Am. Chem. Soc.*, 1985, **107**, 5812; M. T. Reetz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 556; C. H. Heathcock, S. K. Davidsen, K. T. Hug and L. A. Flippin, *J. Org. Chem.*, 1986, **51**, 3027.
10 P. K. Keller, SCHAKAL, Program for graphic representation of molecular and crystallographic models, University of Freiburg, 1987.
11 P. Veya, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1991, **10**, 2991; *J. Chem. Soc., Chem. Commun.*, 1991, 1166.
12 U. Piarulli, C. Floriani, G. Gervasio and D. Viterbo, unpublished work.
13 U. Giannini and U. Zucchini, *Chem. Commun.*, 1968, 940.
14 U. Zucchini, U. Giannini, E. Albizzati and R. D'Angelo, *Chem. Commun.*, 1969, 1174.
15 J. J. Felten and W. P. Anderson, *J. Organomet. Chem.*, 1972, **36**, 87; 1974, **82**, 375.
16 S. L. Lawton and R. A. Jacobson, TRACER, a cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, Ames, IA, 1965.
17 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
18 G. Sheldrick, SHELX 76, System of Crystallographic Computer Programs, University of Cambridge, 1976.
19 A. J. C. Wilson, *Nature (London)*, 1942, **150**, 151.
20 F. Ugozzoli, ABSORB, a Program for $F_o$ Absorption Correction, *Comput. Chem.*, 1987, **11**, 109.
21 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 99; (*b*) p. 149.
22 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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