# *cis*- and *trans*-Dichloro-derivatives of Six- and Seven-co-ordinate Zirconium and Hafnium bonded to Quadridentate Schiff-base Ligands. Crystal Structures of [Zr(acen)$Cl_2$(thf)], [M(salphen)$Cl_2$(thf)]·0.5thf, [M(acen)$Cl_2$], (M = Zr or Hf), and [Zr(msal)$Cl_2$] [acen = *N,N'*-ethylenebis(acetylacetoneiminate), salphen = *N,N'*-*o*-phenylenebis(salicylideneiminate), msal = *N*-methylsalicylideneiminate, and thf = tetrahydrofuran] †

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The reaction of $MCl_4$·2thf (thf = tetrahydrofuran) with the sodium salt of quadridentate Schiff bases [L = *N,N'*-ethylenebis(acetylacetoneiminate) (acen), *N,N'*-ethylenebis(salicylideneiminate) (salen), *N,N'*-ethylenebis(α-methylsalicylideneiminate) (dmsalen), or *N,N'*-*o*-phenylenebis(salicylideneiminate) (salphen)] yields the complexes [ML$Cl_2$(thf)]. *X*-Ray analyses showed for all of them that the metal ion is seven-co-ordinate with a pseudo-pentagonal bipyramidal geometry. Details of the structures of [Zr(acen)$Cl_2$(thf)] (**5**), [Zr(salphen)$Cl_2$(thf)]·0.5thf (**10**), and of the corresponding isostructural hafnium complex [Hf(salphen) $Cl_2$(thf)]·0.5thf (**11**) are reported. The equatorial plane of the bipyramid is defined by the $N_2O_2$ donor atoms and by the oxygen atom from thf, while the two chlorine atoms are *trans* to each other [Cl–Zr–Cl 169.1(1), (**5**); 165.2(1), (**10**); Cl–Hf–Cl 166.3(1)°, (**11**)]. Recrystallization of the seven-co-ordinate complexes from toluene removed the thf leading to six-co-ordinate complexes. The structural determination of the isostructural [Zr(acen)$Cl_2$] (**12**) and [Hf(acen)$Cl_2$] (**13**) showed the six-co-ordination of the metal with the two chlorines assuming a *cis* arrangement [Cl–Zr–Cl 87.2(1), (**12**); Cl–Hf–Cl 87.4(1)°, (**13**)]. Bond lengths within the co-ordination sphere are significantly shorter in the six-co-ordinate complexes. The *cis* and *trans* isomers do not interconvert in solutions of non-co-ordinating solvents, *i.e.* $C_6H_6$ or $CH_2Cl_2$, as shown by their distinctive $^1H$ n.m.r. spectra. In the absence of geometrical constraints zirconium(IV) prefers six-co-ordination and a *cis* arrangement of the chloride ligands. This was confirmed by synthesizing [Zr(msal)$_2$$Cl_2$] (**15**) (msal = *N*-methylsalicylideneiminate), [Cl–Zr–Cl 97.9(1)°] containing a bidentate Schiff-base ligand. Its crystallization from thf gave the unsolvated six-co-ordinated form. Crystallographic details: complex (**5**), space group $P\bar{1}$, $a$ = 8.401(1), $b$ = 15.987(2), $c$ = 7.805(1) Å, α = 98.41(1), β = 90.32(1), γ = 76.65(1)°, $Z$ = 2, and $R$ 0.042 for 3 713 observed reflections; (**10**), space group $P\bar{1}$, $a$ = 12.759(2), $b$ = 13.332(2), $c$ =7.587(1) Å, α = 91.60(2), β = 98.45(1), γ = 85.30(1)°, $Z$ = 2, and $R$ 0.033 for 3 813 observed reflections; (**11**), space group $P\bar{1}$, $a$ = 12.737(7), $b$ = 13.269(7), $c$ = 7.564(4) Å, α = 91.48(1), β = 98.56(1), γ = 85.26(1)°, $Z$ = 2, and $R$ 0.027 for 4 227 observed reflections; (**12**), space group $P2_1/n$, $a$ = 24.150(5), $b$ = 9.160(2), $c$ = 7.282(1) Å, β = 90.90(1)°, $Z$ = 4, and $R$ 0.034 for 1 894 observed reflections; (**13**), space group $P2_1/n$, $a$ = 24.096(10), $b$ = 9.161(4), $c$ = 7.262(3) Å, β = 90.87(1)°, $Z$ = 4, and $R$ 0.024 for 2 124 observed reflections; (**15**), space group $P\bar{1}$, $a$ = 13.024(3), $b$ = 14.522(3), $c$ = 9.797(2) Å, α = 90.10(1), β = 93.14(1), γ = 96.09(1)°, $Z$ = 4, and $R$ 0.044 for 3 294 observed reflections.

The chemical behaviour of a metal site or any functionality attached to it as a function of the co-ordination environment has not been adequately studied for Group 4 metals, in spite of their impact in organometallic chemistry and catalysis. Reactivity studies are largely limited to complexes containing cyclopentadienyl ligands,[1] and to a lesser extent alkoxo groups.[2] Quadridentate Schiff bases are a class of ancillary ligands particularly appropriate for affecting the chemical behaviour of the metal site and the chemistry of the related organometallic functionalities.[3] Of the Group 4 metals, few examples of appropriate complexes of titanium are available[4] for reactivity studies and practically none for zirconium and hafnium. Some rare reports concern complexes and adducts formed from $ZrCl_4$ and $Zr(OR)_4$ and Schiff-base ligands. However, neither the synthetic procedure is good, nor the chemical or structural characterization satisfactory.[5] Two structure determinations were reported for [Zr(salphen)$_2$] [salphen = *N,N'*-*o*-phenylenebis(salicylideneiminate)][6a] and [Zr(esal)$_4$] (esal = *N*-ethylsalicylideneiminate),[6b] which are, however, inappropriate for a reactivity study. We report here a general synthesis for [ML$Cl_2$] [M = Zr or Hf; L = *N,N'*-ethylenebis(salicylideneiminate) (salen), salphen, or *N,N'*-ethylenebis(acetylacetoneiminate) (acen)] complexes, which contain

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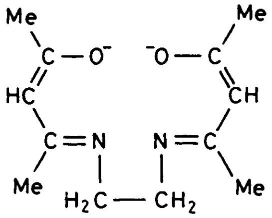
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

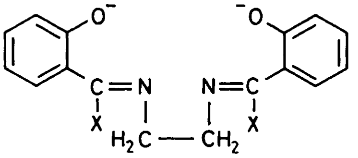
two reactive M–Cl bonds appropriate for introducing organometallic functionalities or for producing low oxidation states with co-ordination sites available on the metal. All compounds have been structurally characterized.

## Experimental

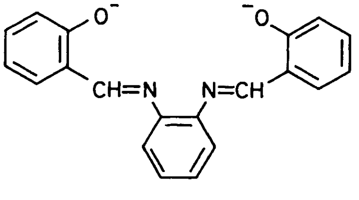
All the reactions were carried out under inert atmosphere. Solvents were dried and purified by standard techniques. The compounds $ZrCl_4$·2thf[7] and $HfCl_4$·2thf[7] were prepared by a reported procedure. The Schiff-base ligands were prepared by condensation of salicylaldehyde and acetylacetone with the corresponding diamine in EtOH. The sodium salts of Schiff bases were prepared by adding an equimolar amount of NaH to a thf solution or suspension of the Schiff-base ligand, then refluxing for 30 min the resulting solution or suspension. The sodium salt can be either used *in situ* or isolated as solid, and the content determined by a usual acid–base titration. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer, $^1H$ n.m.r. spectra with a 200 AC Bruker apparatus. Details will be given only for the preparations of the zirconium derivatives since the hafnium compounds were prepared by the same methods and showed very similar properties.



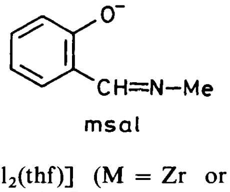
acen



X
salen H
dmsalen Me



salphen



msal

*Synthesis of* $[MLCl_2(thf)]$ (M = Zr or Hf; L = acen, salphen, salen, or dmsalen], (**5**)—(**11**).—The compound $ZrCl_4$·2thf (1.87 g, 4.96 mmol) was added to a thf suspension (70 $cm^3$) of $Na_2$(salphen) (4.90 mmol). The suspension was stirred until all the solids had dissolved, then the NaCl formed was removed by filtration. A yellow solid crystallized on standing for 48 h (yield *ca.* 70%). The synthesis of all the above complexes was performed using the same synthetic method. Yields ranged from 70 to 85%. The compounds showed similar solubility in various solvents except for the acen derivatives, which are much more soluble. The synthesis can be scaled up to ten times the reported amount with similar yields. In order to achieve an efficient separation from NaCl without using too much solvent, an extraction with thf is recommended.

$[Zr(salphen)Cl_2(thf)]$·0.5thf (**10**) (Found: C, 53.50; H, 4.25; Cl, 12.25; N, 4.90. $C_{26}H_{26}Cl_2N_2O_{3.5}Zr$ requires C, 53.40; H, 4.45; Cl, 12.15; N, 4.80%). I.r. (Nujol): ν(C=N) 1 608 $cm^{-1}$. Proton n.m.r. in $(CD_3)_2CO$: δ 8.83 (s, 2 H), 7.57 (m, 4 H), 7.37 (m, 4 H), 6.78 (t, 2 H), 6.64 (d, 2 H), 3.60 (m, 6 H), and 1.71 (m, 6 H).

$[Zr(salen)Cl_2(thf)]$ (**7**) (Found: C, 47.95; H, 4.35; Cl, 13.85; N, 5.50. $C_{20}H_{22}Cl_2N_2O_3Zr$ requires C, 48.00; H, 4.45; Cl, 14.15; N, 5.60%). The microanalysis was performed on a solid dried very well *in vacuo* in order to remove all the solvent of crystallization. I.r. (Nujol): ν(C=N) 1 615 $cm^{-1}$. Proton n.m.r. in $(CD_3)_2CO$: δ 8.64 (s, 2 H), 7.43 (m, 4 H), 6.78 (m, 4 H), 4.16 (s, 4 H), 6.64 (d, 2 H), 3.68 (m, 8 H), and 1.77 (m, 8 H).

$[Zr(dmsalen)Cl_2(thf)]$ (**9**) (Found: C, 49.60; H, 4.50; N, 5.00. $C_{22}H_{26}Cl_2N_2O_3Zr$ requires C, 50.00; H, 4.95; N, 5.30%). Proton n.m.r. in $(CD_3)_2CO$: δ 8.95 (m, 4 H), 7.77 (m, 2 H), 7.50 (m, 2 H), 4.15 (m, 4 H), and 2.63 (s, 6 H).

$[Zr(acen)Cl_2(thf)]$ (**5**) (Found: C, 42.20; H, 5.70; N, 6.10. $C_{16}H_{26}Cl_2N_2O_3Zr$ requires C, 42.10; H, 5.75; N, 6.15%). Proton n.m.r. in $(CD_3)_2CO$: δ 5.46 (s, 2 H), 3.82 (m, 4 H), 2.10 (s, 6 H), and 1.98 (s, 6 H).

$[Hf(salphen)Cl_2(thf)]$·0.5thf (**11**) (Found: C, 46.40; H, 3.80; Cl, 10.50; N, 4.15. $C_{26}H_{26}Cl_2HfN_2O_{3.5}$ requires C, 46.50; H, 3.90; Cl, 10.55; N, 4.15%). I.r. (Nujol): ν(C=N) 1 608 $cm^{-1}$. Proton n.m.r. in $(CD_3)_2CO$: δ 8.92 (s, 2 H), 7.64 (m, 4 H), 7.46 (m, 4 H), 6.83 (t, 2 H), 6.72 (d, 2 H), 3.62 (m, 6 H), and 1.80 (m, 6 H).

$[Hf(salen)Cl_2(thf)]$ (**8**) (Found: C, 40.75; H, 3.80; Cl, 12.15; N, 4.80. $C_{20}H_{22}Cl_2HfN_2O_3$ requires C, 40.85; H, 3.75; Cl, 12.05; N, 4.75%). The microanalysis was performed on a solid dried very well *in vacuo* in order to remove all the solvent of crystallization. I.r. (Nujol): ν(C=N) 1 615 $cm^{-1}$. Proton n.m.r. in $(CD_3)_2CO$: δ 8.64 (s, 2 H), 7.41 (m, 4 H), 6.76 (m, 4 H), 4.18 (s, 4 H), 3.69 (m, 8 H), and 1.77 (m, 8 H).

$[Hf(acen)Cl_2(thf)]$ (**6**) (Found: C, 35.10; H, 4.85; Cl, 12.85; N, 5.20. $C_{16}H_{26}Cl_2HfN_2O_3$ requires C, 35.35; H, 4.80; Cl, 13.05; N, 5.15%). Proton n.m.r. in $CD_2Cl_2$: δ 5.41 (s, 2 H), 3.82 (m, 4 H), 2.10 (s, 6 H), and 1.98 (s, 6 H).

*Synthesis of* $[M(acen)Cl_2]$ [M = Zr (**12**) or Hf (**13**)].—The compound $ZrCl_4$·2thf (2.29 g, 6.0 mmol) was added to a thf suspension (70 $cm^3$) of $H_2$acen (6.0 mmol). The suspension was stirred until the solid completely dissolved, then the NaCl formed was removed by filtration. The resulting solution was evaporated to dryness, then the residue was dissolved in hot toluene. A yellow solid crystallized from the resulting solution (yield *ca.* 71%).

$[Zr(acen)Cl_2]$ (Found: C, 37.25; H, 4.75; Cl, 18.40; N, 7.10. $C_{12}H_{18}Cl_2N_2O_2Zr$ requires C, 37.50; H, 4.70; Cl, 18.45; N, 7.30%). Proton n.m.r. in $CD_2Cl_2$; δ 5.51 (s, 2 H), 3.72 (s, 4 H), 2.12 (s, 6 H), and 2.03 (s, 6 H).

$[Hf(acen)Cl_2]$ (Found: C, 30.50; H, 3.75; Cl, 15.30; N, 5.95. $C_{12}H_{18}Cl_2HfN_2O_2$ requires C, 30.55; H, 3.85; Cl, 15.05; N, 5.95%). Proton n.m.r. $(C_6D_6)$: δ 4.98 (s, 2 H), 3.72 (m, 4 H), 1.72 (s, 6 H), and 1.32 (s, 6 H).

*Desolvation of Complex* (**10**); *Synthesis of* (**14**).—Complex (**10**) was suspended in toluene (150 $cm^3$), then refluxed for 2 h. The solid in suspension changed from light yellow to orange-yellow. The solid was filtered off and washed with toluene (*ca.* 95%) (Found: C, 50.25; H, 2.95; Cl, 14.80; N, 5.70; Zr, 19.00.

[Zr(salphen)Cl$_2$] (**14**), $C_{20}H_{14}Cl_2N_2O_2Zr$ requires C, 50.40; H, 2.95; Cl, 14.90; N, 5.90; Zr, 19.15%).

*Synthesis of* [Zr(msal)$_2$Cl$_2$] (**15**).—Sodium hydride (0.88 g, 36.9 mmol) was added to a thf solution (300 cm$^3$) of Hmsal (5.0 g, 36.9 mmol). A white precipitate formed suddenly. The suspension was then refluxed for 1 h, till complete evolution of hydrogen. The compound $ZrCl_4$·2thf (6.97 g, 18.45 mmol) was added. The two solids dissolved forming a light yellow solution, which was refluxed for 2 h. The NaCl formed was removed by filtration. Solvent was partially evaporated and on cooling at $-20$ °C a crystalline solid formed (*ca.* 63%) (Found: C, 44.70; H, 3.60; Cl, 16.35; N, 6.45. $C_{16}H_{16}Cl_2N_2O_2Zr$ requires C, 44.65; H, 3.75; Cl, 16.45; N, 6.50%). I.r. (Nujol): $\nu$ (C–N) 1 622 cm$^{-1}$. Proton n.m.r. ($CD_2Cl_2$): $\delta$ 3.40 (s, 3 H, Me), 3.41 (s, 3 H, Me), 7.02 (m, 4 H, Ph), 7.35 (m, 2 H, Ph), 7.55 (m, 2 H, Ph), and 8.17 (s, 2 H, CH).

*X-Ray Crystallography.*—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with data collection are given in Table 1. The reduced cells were obtained with use of TRACER.[8] Data were collected at room temperature (295 K) on a single-crystal four-circle diffractometer. For intensities and background the three-point technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[9] and the absolute scale was established by the Wilson method.[10] The crystal quality was tested by $\psi$ scans showing that crystal absorption effects could be neglected for complexes (**5**), (**12**), and (**15**). Data for complexes (**10**), (**11**), and (**13**) were corrected for absorption using a semiempirical method,[11] with maximum and minimum corrections of 1.000—1.089, 1.001—1.099, and 1.000—1.176 respectively. The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. Unit weights were used for complexes (**5**), (**10**), and (**11**) since these gave a satisfactory analysis of variance.[9] For complexes (**12**), (**13**), and (**15**) weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. At the end of the refinement the values for $k$ and $g$ were 1.0538 and 0.000 21 for (**12**), 1.1356 and 0.000 00 for (**13**), and 1.3375 and 0.000 13 for (**15**) respectively. Anomalous scattering corrections were included in all structure-factor calculations.[12b] Scattering factors for neutral atoms were taken from ref. 12*a* for non-hydrogen atoms and from ref. 13 for H. 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 isotropic, then anisotropic for non-H atoms, by full-matrix least squares. All the hydrogen atoms except those associated with the thf solvent molecule in complexes (**10**) and (**11**), which were ignored, were introduced in calculations as fixed contributors with isotropic $U$ values fixed at 0.08 Å$^2$. Most of the hydrogen atoms were located from difference maps, some others were placed in geometrically calculated positions. The thf solvent molecule [complexes (**10**) and (**11**)] was found to be disordered around a centre of symmetry, simulating a six-membered ring. This disorder was solved by considering the oxygen to be distributed over two centrosymmetric positions with a site occupation factor of 0.5. The final difference maps showed no unusual feature, with no significant peak above the general background of about 0.3 e Å$^{-3}$ for (**10**) and (**12**), 0.4 e Å$^{-3}$ for (**13**) and (**15**), and 0.6 e Å$^{-3}$ for (**5**) and (**11**).

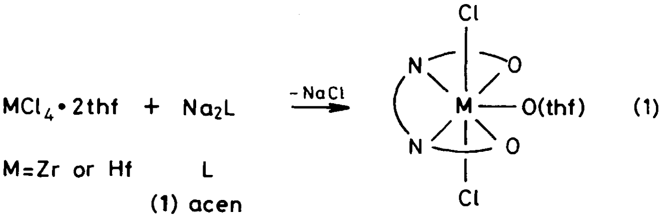
Final atomic co-ordinates are listed in Tables 2—7 for non-H atoms.

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

## Results and Discussion

The synthesis of Schiff-base complexes by using the alkali-metal salts of the ligand seems to have significant advantages over the other methods so far employed for early transition metals,[4,5] *i.e.* the control of the substitution degree of the chloride ligands in $MX_n$ halides, and the complete and easy substitution of all the protic hydrogens. This is the only way to get reducible and functionalizable complexes.

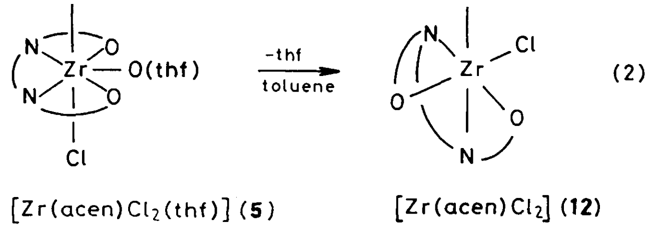
The reaction of $MCl_4$·2thf (M = Zr or Hf) with either a thf solution or suspension of the sodium salt of the quadridentate Schiff bases (**1**)—(**4**) gave complexes (**5**)—(**11**). The complexes can be made free from NaCl by extraction with thf. The 1:1 metal to ligand molar ratio must be strictly controlled since a slight excess of the Schiff base leads to the overall replacement of the chlorides and complexes analogous to [Zr(salphen)$_2$][6a] are obtained.



(**1**) acen
(**2**) salen
(**3**) dmsalen
(**4**) salphen

[M(acen)Cl$_2$(thf)]
M = Zr, (**5**); Hf, (**6**)
[M(salen)Cl$_2$(thf)]
M = Zr, (**7**); Hf, (**8**)
[Zr(dmsalen)Cl$_2$(thf)] (**9**)
[M(salphen)Cl$_2$(thf)]
M = Zr, (**10**); Hf, (**11**)

Complexes (**5**)—(**11**) are fairly soluble in organic solvents allowing a spectroscopic characterization by $^1$H n.m.r. spectroscopy. This solubility, which is an important prerequisite for studying their reactivity, is largely dependent on the quadridentate ligand, the acen derivatives being the most soluble. Complexes (**5**)—(**11**) are very sensitive to moisture and formation of oxo compounds has been observed. The C=N stretching vibrations and the resonances of the imino hydrogen which are affected by the acidity of the metal are a sort of spectroscopic probe. These parameters, however, do not change significantly with the nature of the metal, *i.e.* Ti$^{IV}$, Zr$^{IV}$, or Hf$^{IV}$, or its co-ordination number. These complexes have been isolated in solvated form with the metal achieving seven-co-ordination. This is supported by the *X*-ray analyses carried out on complexes (**5**) and (**9**)—(**11**). The hafnium compounds are isostructural with the corresponding zirconium derivatives. Details will be given only for complexes (**5**), (**10**), and (**11**). Recrystallization of complexes (**5**) and (**6**) from toluene gave the unsolvated form, equation (2).



[Zr(acen)Cl$_2$(thf)] (**5**)
[Hf(acen)Cl$_2$(thf)] (**6**)

[Zr(acen)Cl$_2$] (**12**)
[Hf(acen)Cl$_2$] (**13**)

**Table 1.** Experimental data for the *X*-ray diffraction studies on crystalline complexes (**5**), (**10**)—(**13**), and (**15**)[a]

| Complex | (**5**) | (**10**) | (**11**) | (**12**) | (**13**) | (**15**) |
|---|---|---|---|---|---|---|
| Formula | $C_{16}H_{26}Cl_2N_2O_3Zr$ | $C_{24}H_{22}Cl_2N_2O_3Zr\cdot 0.5C_4H_8O$ | $C_{24}H_{22}Cl_2HfN_2O_3\cdot 0.5C_4H_8O$ | $C_{12}H_{18}Cl_2N_2O_2Zr$ | $C_{12}H_{18}Cl_2HfN_2O_2$ | $C_{16}H_{16}Cl_2N_2O_2Zr$ |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ |
| Cell parameters at 295 K[b] | | | | | | |
| $a$/Å | 8.401(1) | 12.759(2) | 12.737(7) | 24.150(5) | 24.096(10) | 13.024(3) |
| $b$/Å | 15.987(2) | 13.332(2) | 13.269(7) | 9.160(2) | 9.161(4) | 14.522(3) |
| $c$/Å | 7.805(1) | 7.587(1) | 7.564(4) | 7.282(1) | 7.262(3) | 9.797(2) |
| $\alpha$/° | 98.41(1) | 91.60(2) | 91.48(1) | 90 | 90 | 90.10(1) |
| $\beta$/° | 90.32(1) | 98.45(1) | 98.56(1) | 90.90(1) | 90.87(1) | 93.14(1) |
| $\gamma$/° | 76.65(1) | 85.30(1) | 85.26(1) | 90 | 90 | 96.09(1) |
| $U$/Å$^3$ | 1 008.5(2) | 1 272.1(3) | 1 259.7(12) | 1 610.7(5) | 1 602.9(12) | 1 839.7(7) |
| $Z$ | 2 | 2 | 2 | 4 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.503 | 1.526 | 1.771 | 1.585 | 1.955 | 1.554 |
| $M$ | 456.5 | 584.6 | 671.9 | 384.4 | 471.7 | 430.4 |
| Crystal dimensions/mm | 0.26 × 0.40 × 0.53 | 0.18 × 0.32 × 0.63 | 0.20 × 0.30 × 0.58 | 0.11 × 0.35 × 0.48 | 0.18 × 0.29 × 0.47 | 0.25 × 0.35 × 0.65 |
| $\mu$/cm$^{-1}$ | 8.18 | 6.68 | 43.5 | 10.05 | 67.87 | 8.89 |
| Scan type | $\omega$ | $\omega$—2$\theta$ | $\omega$—2$\theta$ | $\omega$ | $\omega$—2$\theta$ | $\omega$—2$\theta$ |
| Scan width/° | 2.00 | 1.30 | 1.20 | 2.50 | 1.10 | 1.60 |
| 2$\theta$ range/° | 6—56 | 6—52 | 6—52 | 6—50 | 6—50 | 6—48 |
| Reflections measured | $\pm h, \pm k, l$ | $\pm h, \pm k, l$ | $\pm h, \pm k, l$ | $\pm h, k, l$ | $\pm h, k, l$ | $\pm h, \pm k, l$ |
| Unique total data | 4 858 | 4 995 | 4 905 | 2 829 | 3 017 | 5 749 |
| Unique obs. data, $N_o$, where $I > 3\sigma(I)$ | 3 713 | 3 813 | 4 227 | 1 894 | 2 124 | 3 294 |
| No. of variables, $N_v$ | 271 | 316 | 316 | 172 | 244 | 415 |
| Overdetermination ratio | 17.1 | 12.1 | 13.4 | 11.0 | 8.7 | 7.9 |
| Max. $\Delta/\sigma$ on last cycle | 0.1 | 0.1 | 0.1 | 0.3 | 0.4 | 0.2 |
| $R$[c] | 0.042 | 0.033 | 0.027 | 0.034 | 0.024 | 0.044 |
| $R'$[d] | | | | 0.034 | 0.023 | 0.044 |
| G.o.f.[e] | | | | 1.10 | 1.20 | 1.60 |

[a] Details in common: prismatic; Philips PW 1100 diffractometer; diffraction geometry, equatorial; scan speed 0.100° s$^{-1}$; graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.710 69 Å). [b] Obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space. [c] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $\Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$. [e] Goodness of fit $=[\Sigma w||F_o| - |F_c||^2/(N_o - N_v)]^{\frac{1}{2}}$.

**Table 2.** Fractional atomic co-ordinates ( × $10^4$) for complex (**5**)

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Zr | 1 099(0) | 2 373(0) | 4 798(0) | C(5) | 3 776(7) | 455(3) | 8 442(7) |
| Cl(1) | −1 199(2) | 3 007(1) | 6 941(2) | C(6) | 2 456(6) | 2 261(3) | 8 517(5) |
| Cl(2) | 3 724(2) | 1 833(1) | 3 105(2) | C(7) | 3 360(6) | 2 880(3) | 7 987(6) |
| O(1) | 857(4) | 1 129(2) | 4 013(4) | C(8) | 4 249(6) | 4 328(3) | 7 203(8) |
| O(2) | 803(4) | 3 441(2) | 3 540(4) | C(9) | 3 068(5) | 3 924(3) | 6 083(6) |
| O(3) | −1 190(4) | 2 418(2) | 2 983(5) | C(10) | 2 485(6) | 4 345(3) | 4 619(7) |
| N(1) | 2 273(4) | 1 645(2) | 6 968(4) | C(11) | 1 424(6) | 4 102(3) | 3 463(6) |
| N(2) | 2 619(4) | 3 242(2) | 6 457(4) | C(12) | 851(9) | 4 593(3) | 1 994(7) |
| C(1) | 1 519(7) | −357(3) | 2 748(7) | C(13) | −1 428(8) | 1 800(4) | 1 653(8) |
| C(2) | 1 726(5) | 348(2) | 4 147(6) | C(14) | −2 882(6) | 2 197(3) | 654(6) |
| C(3) | 2 719(6) | 181(3) | 5 489(6) | C(15) | −3 390(7) | 3 122(4) | 1 514(7) |
| C(4) | 2 880(5) | 816(3) | 6 924(5) | C(16) | −2 522(11) | 3 166(5) | 2 986(13) |

**Table 3.** Fractional atomic co-ordinates ( × $10^4$) for complex (**10**)

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Zr | 2 461(0) | 1 525(0) | 4 375(0) | C(12) | −742(3) | 2 429(3) | 1 028(5) |
| Cl(1) | 1 176(1) | 2 119(1) | 6 400(1) | C(13) | 195(3) | 1 892(3) | 1 793(4) |
| Cl(2) | 3 325(1) | 926(1) | 1 780(1) | C(14) | 1 359(3) | 3 046(3) | 1 135(5) |
| O(1) | 3 010(2) | 183(2) | 5 446(3) | C(15) | 2 233(3) | 3 669(3) | 1 383(5) |
| O(2) | 3 038(2) | 2 891(2) | 4 065(3) | C(16) | 2 251(4) | 4 428(3) | 135(6) |
| N(1) | 1 141(2) | 428(2) | 3 209(4) | C(17) | 3 034(4) | 5 094(4) | 366(7) |
| N(2) | 1 197(2) | 2 321(2) | 2 160(4) | C(18) | 3 800(4) | 5 026(3) | 1 875(7) |
| C(1) | 2 970(3) | −797(3) | 5 206(4) | C(19) | 3 796(3) | 4 305(3) | 3 133(6) |
| C(2) | 3 783(3) | −1 466(3) | 6 058(5) | C(20) | 3 021(3) | 3 599(3) | 2 890(5) |
| C(3) | 3 710(3) | −2 489(3) | 5 857(6) | O(3) | 3 773(2) | 1 804(2) | 6 792(3) |
| C(4) | 2 839(4) | −2 885(3) | 4 810(6) | C(21) | 4 613(3) | 1 077(3) | 7 592(5) |
| C(5) | 2 042(3) | −2 238(3) | 3 954(6) | C(22) | 5 393(3) | 1 712(4) | 8 732(6) |
| C(6) | 2 100(3) | −1 186(3) | 4 115(5) | C(23) | 4 720(4) | 2 612(3) | 9 258(6) |
| C(7) | 1 232(3) | −544(3) | 3 216(5) | C(24) | 3 857(5) | 2 743(4) | 7 782(8) |
| C(8) | 165(3) | 906(3) | 2 329(4) | O(1S) | 9 837(6) | 4 761(6) | 2 819(10) |
| C(9) | −797(3) | 447(3) | 2 022(5) | C(2S) | 9 249(7) | 4 579(7) | 4 346(11) |
| C(10) | −1 710(3) | 972(3) | 1 200(5) | C(3S) | 9 551(7) | 4 694(7) | 6 216(12) |
| C(11) | −1 686(3) | 1 968(3) | 722(5) | | | | |

**Table 4.** Fractional atomic co-ordinates ( × $10^4$) for complex (**11**)

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Hf | 2 448(0) | 1 522(0) | 4 365(0) | C(12) | −742(4) | 2 443(4) | 1 015(7) |
| Cl(1) | 1 178(1) | 2 114(1) | 6 380(2) | C(13) | 187(4) | 1 898(4) | 1 796(6) |
| Cl(2) | 3 332(1) | 927(1) | 1 820(2) | C(14) | 1 359(4) | 3 039(4) | 1 134(7) |
| O(1) | 2 998(3) | 182(2) | 5 458(5) | C(15) | 2 232(4) | 3 667(4) | 1 376(7) |
| O(2) | 3 034(3) | 2 891(3) | 4 085(5) | C(16) | 2 255(5) | 4 433(5) | 130(9) |
| N(1) | 1 140(3) | 430(3) | 3 207(5) | C(17) | 3 035(7) | 5 102(5) | 373(11) |
| N(2) | 1 198(3) | 2 320(3) | 2 156(5) | C(18) | 3 802(6) | 5 030(5) | 1 876(11) |
| C(1) | 2 962(4) | −798(4) | 5 218(6) | C(19) | 3 794(5) | 4 298(4) | 3 137(9) |
| C(2) | 3 774(4) | −1 465(4) | 6 089(8) | C(20) | 3 018(4) | 3 587(4) | 2 882(7) |
| C(3) | 3 701(5) | −2 509(4) | 5 879(9) | O(3) | 3 743(3) | 1 792(3) | 6 776(5) |
| C(4) | 2 853(5) | −2 891(4) | 4 825(9) | C(21) | 4 604(4) | 1 081(4) | 7 543(7) |
| C(5) | 2 048(4) | −2 239(4) | 3 940(8) | C(22) | 5 376(5) | 1 723(6) | 8 680(9) |
| C(6) | 2 093(4) | −1 187(4) | 4 119(7) | C(23) | 4 698(6) | 2 606(5) | 9 230(10) |
| C(7) | 1 233(4) | −546(4) | 3 212(7) | C(24) | 3 810(7) | 2 738(6) | 7 767(12) |
| C(8) | 161(4) | 905(4) | 2 323(6) | O(1S) | 9 844(8) | 4 763(8) | 2 797(14) |
| C(9) | −800(4) | 452(4) | 2 029(7) | C(2S) | 9 235(10) | 4 581(11) | 4 346(16) |
| C(10) | −1 707(4) | 981(4) | 1 191(7) | C(3S) | 9 539(10) | 4 697(10) | 6 212(19) |
| C(11) | −1 684(4) | 1 974(5) | 715(8) | | | | |

**Table 5.** Fractional atomic co-ordinates ( × $10^4$) for complex (**12**)

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Zr | 1 184(0) | 1 974(0) | 2 394(1) | C(4) | 2 267(2) | 1 607(5) | −7(6) |
| Cl(1) | 1 215(1) | 4 471(1) | 3 716(2) | C(5) | 2 737(2) | 2 129(6) | −1 153(7) |
| Cl(2) | 1 706(1) | 1 160(2) | 5 144(2) | C(6) | 1 771(2) | 3 892(5) | −445(7) |
| O(1) | 1 337(1) | −44(3) | 1 341(4) | C(7) | 1 190(2) | 3 878(6) | −1 301(7) |
| O(2) | 393(1) | 1 532(4) | 2 783(5) | C(8) | 101(3) | 3 621(9) | −2 542(9) |
| N(1) | 1 853(2) | 2 470(4) | 439(5) | C(9) | 280(2) | 2 973(6) | −731(7) |
| N(2) | 797(2) | 3 067(4) | −142(5) | C(10) | −141(2) | 2 251(8) | 263(9) |
| C(1) | 1 816(2) | −2 291(5) | 1 219(8) | C(11) | −91(2) | 1 593(6) | 1 891(8) |
| C(2) | 1 819(2) | −664(5) | 1 030(7) | C(12) | −564(2) | 903(9) | 2 864(9) |
| C(3) | 2 272(2) | 103(5) | 512(7) | | | | |

**Table 6.** Fractional atomic co-ordinates ( × $10^4$) for complex (**13**)

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|---|---|---|---|
| Hf | 1 189(0) | 2 013(0) | 2 388(0) | C(4) | 2 266(3) | 1 628(7) | 1(8) |
| Cl(1) | 1 214(1) | 4 489(2) | 3 713(3) | C(5) | 2 742(3) | 2 147(8) | −1 136(10) |
| Cl(2) | 1 702(1) | 1 198(2) | 5 131(3) | C(6) | 1 766(3) | 3 917(7) | −440(11) |
| O(1) | 1 333(2) | −2(5) | 1 339(6) | C(7) | 1 195(3) | 3 895(8) | −1 306(10) |
| O(2) | 398(2) | 1 555(6) | 2 830(7) | C(8) | 100(4) | 3 667(13) | −2 529(12) |
| N(1) | 1 858(2) | 2 505(5) | 460(7) | C(9) | 292(3) | 2 962(9) | −725(9) |
| N(2) | 807(2) | 3 089(6) | −125(7) | C(10) | −133(3) | 2 216(11) | 251(12) |
| C(1) | 1 813(3) | −2 254(8) | 1 188(11) | C(11) | −86(3) | 1 598(9) | 1 935(11) |
| C(2) | 1 811(3) | −624(7) | 1 037(9) | C(12) | −547(3) | 877(13) | 2 920(14) |
| C(3) | 2 265(3) | 123(7) | 522(10) | | | | |

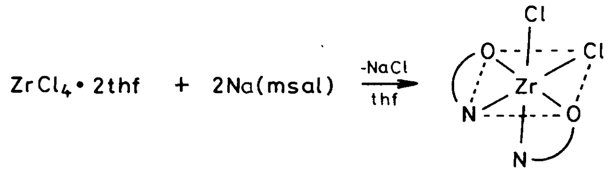
**Table 7.** Fractional atomic co-ordinates ( × $10^4$) for complex (**15**)

| | Molecule A | | | Molecule B | | |
|---|---|---|---|---|---|---|
| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | *X*/*a* | *Y*/*b* | *Z*/*c* |
| Zr | 966(1) | 2 318(1) | 1 716(1) | 6 084(1) | 2 377(1) | 3 498(1) |
| Cl(1) | 1 393(2) | 821(1) | 927(2) | 7 717(2) | 3 355(2) | 3 775(2) |
| Cl(2) | 2 583(2) | 3 210(2) | 1 163(2) | 6 627(2) | 969(2) | 4 514(2) |
| O(1) | 1 357(4) | 2 174(3) | 3 671(4) | 5 452(4) | 2 797(3) | 5 167(4) |
| O(2) | 124(4) | 2 631(4) | 52(4) | 6 257(4) | 2 076(4) | 1 555(4) |
| N(1) | −516(4) | 1 511(4) | 2 496(5) | 5 231(4) | 3 621(4) | 2 674(5) |
| N(2) | 289(4) | 3 658(4) | 2410(6) | 4 502(4) | 1 538(4) | 2 879(6) |
| C(1) | 1 023(6) | 1 823(5) | 4 861(6) | 4 742(6) | 3 306(5) | 5 614(7) |
| C(2) | 1 675(6) | 1 931(6) | 6 069(7) | 4 454(6) | 3 235(5) | 6 975(7) |
| C(3) | 1 340(7) | 1 532(7) | 7 295(8) | 3 693(7) | 3 735(6) | 7 401(8) |
| C(4) | 381(8) | 1 049(6) | 7 336(8) | 3 211(6) | 4 327(6) | 6 525(10) |
| C(5) | −267(6) | 947(5) | 6 164(8) | 3 529(6) | 4 449(5) | 5 213(9) |
| C(6) | 58(6) | 1 340(5) | 4 916(7) | 4 283(5) | 3 920(5) | 4 723(8) |
| C(7) | −673(5) | 1 195(5) | 3 721(8) | 4 592(6) | 4 060(5) | 3 328(8) |
| C(8) | −1 371(6) | 1 257(6) | 1 476(8) | 5 416(6) | 3 929(6) | 1 249(7) |
| C(11) | −569(6) | 3 178(6) | −438(7) | 5 780(7) | 1 687(5) | 413(7) |
| C(12) | −1 024(7) | 3 019(6) | −1 745(8) | 6 311(7) | 1 676(6) | −796(8) |
| C(13) | −1 760(8) | 3 589(7) | −2 226(9) | 5 795(11) | 1 254(8) | −1 963(9) |
| C(14) | −2 031(7) | 4 314(7) | −1 449(10) | 4 786(11) | 845(7) | −1 948(10) |
| C(15) | −1 579(7) | 4 464(6) | −159(9) | 4 266(8) | 865(6) | −750(9) |
| C(16) | −829(6) | 3 912(6) | 370(8) | 4 750(7) | 1 282(5) | 447(7) |
| C(17) | −367(6) | 4 125(5) | 1 737(8) | 4 215(6) | 1 225(5) | 1 671(8) |
| C(18) | 628(7) | 4 049(6) | 3 796(8) | 3 759(7) | 1 359(6) | 3 994(9) |

The loss of solvent is relatively easy in spite of the high affinity of zirconium for oxygen. The desolvation of complexes (**5**) and (**6**) occurs with a rearrangement of the co-ordination geometry around the metal. The metal becomes six-co-ordinated in complexes (**12**) and (**13**), and the two chloride ligands move from a nearly *trans* to a *cis* arrangement. The structure depicted for (**12**) and (**13**) is based on an *X*-ray analysis. The answer to the question of whether both forms or only one, eventually, exist in solution can be obtained from the distinctive $^1H$ n.m.r. spectra in $C_6D_6$. The conversion from the six- into the seven-co-ordinate form, that is from the *cis* to the *trans* form, is determined by the presence of a co-ordinating solvent. The *cis* arrangement of the two chlorines requires a significant distortion of the Schiff-base ligand from its more natural planar co-ordination geometry. When a quadridentate ligand much more rigid than acen, like salphen, is employed, such a *cis-trans* arrangement may be more difficult. Thermal desolvation of complex (**10**) containing the rigid ligand salphen produces (**14**), for which, due to its insolubility, we were unable to establish the stereochemistry for the chloride ligands, either by an *X*-ray or a spectroscopic analysis. The i.r. spectrum in the M–Cl stretching region is too complex to allow an assignment for the *cis* or *trans* isomer.

$$\underset{(\mathbf{10})}{[\mathrm{Zr(salphen)Cl_2(thf)}]} \xrightarrow[\text{toluene}]{-\text{thf}} \underset{(\mathbf{14})}{[\mathrm{Zr(salphen)Cl_2}]} \qquad (3)$$

Titanium [4] and molybdenum [14] having an ionic radius of *ca.* 0.68 Å in the +4 oxidation state form complexes [$MLCl_2$] with acen and salphen having a rigorous octahedral co-ordination and with the two chlorine ligands *trans* to each other. In the case of zirconium and hafnium the preferred geometry of the [$MLX_2$] complexes is *cis*, unless a co-ordinating solvent forces the two Cl ligands to be *trans* in a seven-co-ordinate geometry. Using a bidentate Schiff-base ligand [reaction (4)] which does not have geometrical constraints the *cis* isomer is the only one obtained even in the presence of a co-ordinating solvent.



(4)

(**15**)

The structure of complex (**15**) has been confirmed by an *X*-ray analysis. Dichloro derivatives of $Ti^{IV}$ (ref. 15) and $Mo^{IV}$ (ref. 16) with the same bidentate ligand have a *trans* arrange-

**Table 8.** Selected bond distances (Å) and angles (°) for complexes (**5**), (**10**), (**12**), and (**15**)

| | | | | (**15**) | |
|---|---|---|---|---|---|
| | (**5**) | (**10**) | (**12**) | Molecule A | Molecule B |
| Zr–Cl(1) | 2.488(1) | 2.447(1) | 2.482(1) | 2.435(2) | 2.430(3) |
| Zr–Cl(2) | 2.485(1) | 2.477(1) | 2.465(1) | 2.440(3) | 2.431(2) |
| Zr–O(1) | 2.050(3) | 2.015(2) | 2.037(3) | 1.972(4) | 1.993(5) |
| Zr–O(2) | 2.057(3) | 2.051(3) | 1.977(3) | 1.996(5) | 1.983(4) |
| Zr–N(1) | 2.286(3) | 2.378(3) | 2.217(4) | 2.317(5) | 2.341(6) |
| Zr–N(2) | 2.348(3) | 2.361(3) | 2.287(4) | 2.335(6) | 2.329(5) |
| Zr–O(3) | 2.376(1) | 2.338(2) | | | |
| Cl(1)–Zr–Cl(2) | 169.1(1) | 165.2(1) | 87.2(1) | 96.9(1) | 98.8(1) |
| N(1)–Zr–N(2) | 71.9(1) | 68.8(1) | 71.6(1) | 86.4(2) | 82.6(2) |
| O(2)–Zr–N(2) | 76.9(1) | 75.9(1) | 79.7(1) | 77.9(2) | 78.2(2) |
| O(2)–Zr–N(1) | 148.8(1) | 144.4(1) | 148.1(1) | 87.9(2) | 86.3(2) |
| O(1)–Zr–N(2) | 145.4(1) | 143.8(1) | 99.6(1) | 85.1(2) | 88.2(2) |
| O(1)–Zr–N(1) | 76.8(1) | 76.0(1) | 78.8(1) | 78.2(2) | 77.8(2) |
| O(1)–Zr–O(2) | 132.4(1) | 137.6(1) | 92.8(1) | 158.7(2) | 160.3(2) |
| Cl(2)–Zr–N(2) | 82.3(1) | 83.0(1) | 170.2(1) | 91.2(2) | 87.9(2) |
| Cl(2)–Zr–N(1) | 88.7(1) | 84.3(1) | 102.4(1) | 173.6(1) | 168.3(2) |
| Cl(2)–Zr–O(2) | 85.4(1) | 86.8(1) | 107.7(1) | 97.5(2) | 98.4(2) |
| Cl(2)–Zr–O(1) | 82.7(1) | 85.6(1) | 86.4(1) | 95.6(1) | 95.2(1) |
| Cl(1)–Zr–N(2) | 87.5(1) | 84.0(1) | 85.4(1) | 171.1(2) | 170.8(2) |
| Cl(1)–Zr–N(1) | 84.5(1) | 84.4(1) | 92.4(1) | 85.9(2) | 91.4(2) |
| Cl(1)–Zr–O(2) | 96.0(1) | 97.0(1) | 99.0(1) | 97.3(1) | 94.4(2) |
| Cl(1)–Zr–O(1) | 104.0(1) | 100.8(1) | 167.8(1) | 97.7(1) | 97.5(2) |
| O(2)–Zr–O(3) | 71.1(1) | 71.5(1) | | | |
| O(1)–Zr–O(3) | 71.1(1) | 71.9(1) | | | |
| Cl(2)–Zr–O(3) | 111.6(1) | 109.1(1) | | | |
| Cl(1)–Zr–O(3) | 79.0(1) | 85.7(1) | | | |

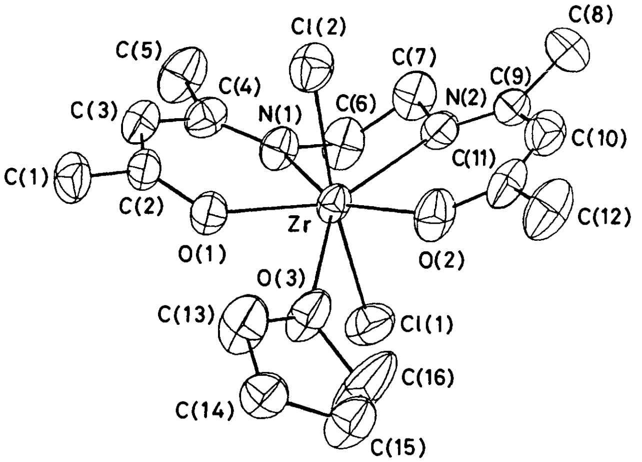


**Figure 1.** An ORTEP drawing for complex (**5**) (45% probability ellipsoids)

ment of the two chlorides. On that basis we can assume that the controlling parameter of the *cis-trans* geometry is, very probably, for reasonably flexible ligands, the metal-ion size. We would emphasize that the mutual position and its control by the ligand, solvent, and metal are very important in the perspective of using such compounds for functionalization and, in general, for reactivity studies. Structural studies have been carried out on the related complexes (**5**), (**10**)—(**12**), and (**15**).

Compound (**5**) consists of discrete [Zr(acen)$Cl_2$(thf)] molecules where the metal is seven-co-ordinated in a pseudo-pentagonal bipyramid (Figure 1), the equatorial plane being roughly defined by the donor atoms of the acen ligand and by the oxygen atom from a thf molecule. The apices are occupied by two chlorine atoms in a significantly bent arrangement [Cl(1)–Zr–Cl(2) 169.1(1)°]. The O(1)–Zr–O(2) angle [132.4(1)°] is unusually large[17,18] allowing the approach of the O(3) atom to the $N_2O_2$ core which appears to be tetrahedrally distorted [from −0.111(3) to 0.109(3) Å]. The Zr and O(3) atoms are 0.203 9(4) and 1.101(4) Å respectively from the mean plane through the $N_2O_2$ core. The two six-membered chelation rings have a half-chair conformation, zirconium being 0.608 7(4) Å from the mean plane through O(1)C(3)N(1), and 0.203 9(4) Å from the nearly perfect O(2)C(3)N(2) plane. The dihedral angle between these planes is 44.3(2)°, indicating an umbrella conformation for the acen ligand.[17–19] The two ZrNO planes are, as usual for Schiff-base derivatives, approximately coplanar, the dihedral angle they form being 15.6(1)°. The five-membered chelation ring shows an envelope conformation with C(6) 0.673(5) Å from the ZrN(1)N(2)C(7) plane. Bond distances and angles in the co-ordination sphere of complexes (**5**), (**10**), (**12**), and (**15**) are compared in Table 8 and will be discussed below. Table 9 lists bond distances and angles for complexes (**11**) and (**13**).

Compounds (**10**) (M = Zr) and (**11**) (M = Hf) were found to be isomorphous. They consist of discrete [M(salphen)-$Cl_2$(thf)] molecules and disordered thf solvent molecules in a 2/1 molar ratio. Bond distances and angles in (**10**) and (**11**) are very similar as a consequence of the similar ionic radii of the two metals. Values in square brackets refer to complex (**11**). The co-ordination around the metal atoms, exhibiting a *trans* arrangement of the chlorine atoms (Figures 2 and 3), is very similar to that in complex (**5**), the differences observed being probably due to the difference in steric hindrance of the two Schiff bases (Table 8). The equatorial plane of the bipyramid is provided by the $N_2O_2$ core of salphen, the enlargement of the O(1) ··· O(2) bite {O(1)–M–O(2) 137.6(1) [137.0(1)]°} allowing the accommodation of the O(3) atom from a thf molecule at 0.827(3) [0.808(4)] Å from the $N_2O_2$ plane. The two chlorines

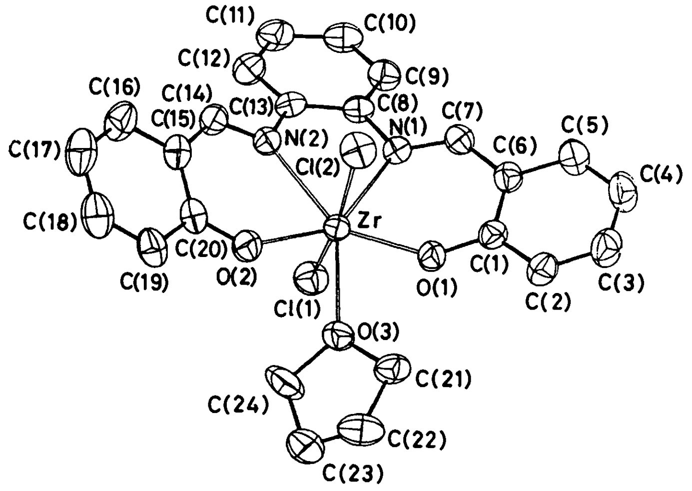


Figure 2. An ORTEP drawing for complex (**10**) (48% probability ellipsoids)

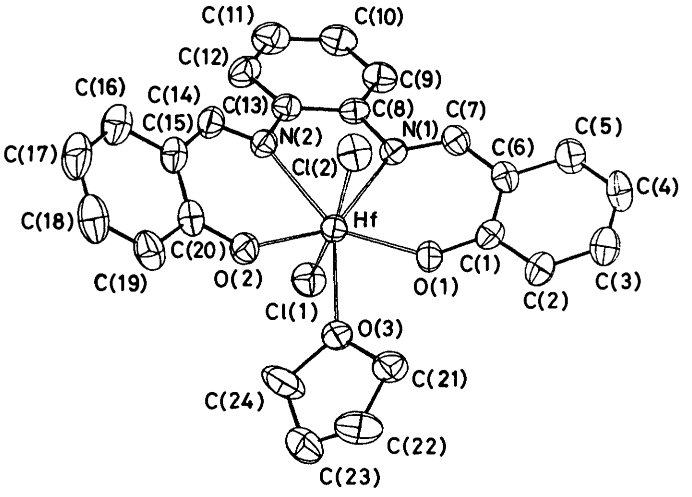


Figure 3. An ORTEP drawing for complex (**11**) (48% probability ellipsoids)

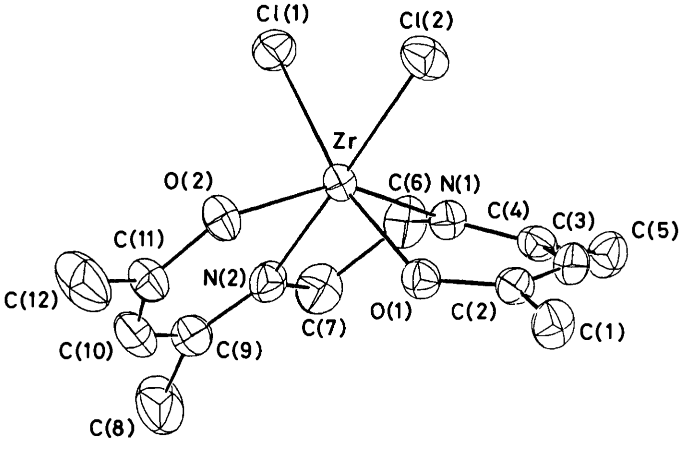


Figure 4. An ORTEP drawing for complex (**12**) (48% probability ellipsoids)

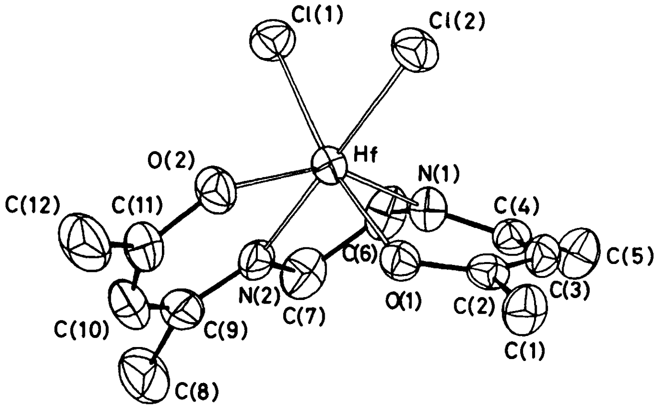


Figure 5. An ORTEP drawing for complex (**13**) (48% probability ellipsoids)

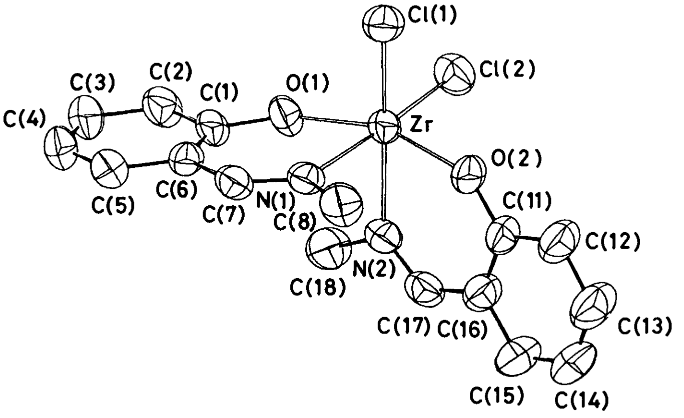


Figure 6. An ORTEP drawing for molecule A in complex (**15**) (48% probability ellipsoids)

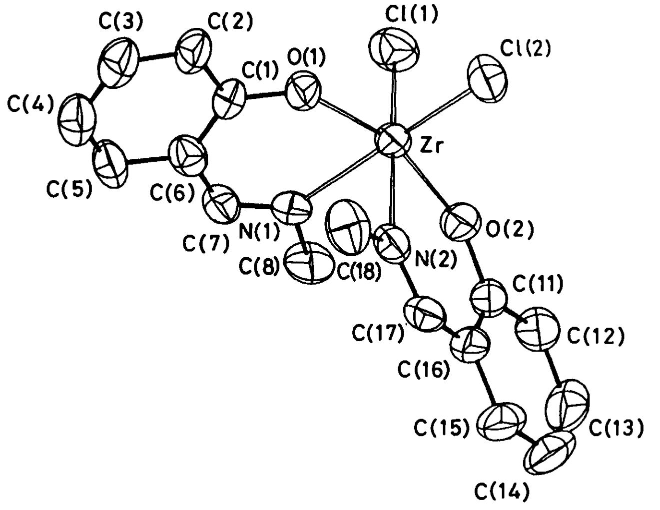


Figure 7. An ORTEP drawing for molecule B in complex (**15**) (48% probability ellipsoids)

are nearly *trans* to each other: 165.2(1) [166.3(1)]°. The salphen ligand assumes an umbrella conformation.[17–19] The two six-membered chelation rings adopt a half-chair conformation with the metal at 0.403(1) [0.410(1)] and 0.535(1) [0.547(1)] Å from the planes through N(1)C(3)O(1) and N(2)C(3)O(2) respectively. They are folded to form a dihedral angle of 42.1(1) [34.6(1)]°. The five-membered chelation ring is enveloped with the metal at 0.682(1) [0.685(1)] Å from the $N_2C_2$ plane. In complexes (**5**), (**10**), and (**11**) the *trans* arrangement of the

**Table 9.** Selected bond distances (Å) and angles (°) for complexes (**11**) and (**13**)

| | (**11**) | (**13**) | | (**11**) | (**13**) |
|---|---|---|---|---|---|
| Hf–Cl(1) | 2.453(2) | 2.464(2) | Hf–N(1) | 2.354(4) | 2.198(5) |
| Hf–Cl(2) | 2.453(2) | 2.445(2) | Hf–N(2) | 2.339(4) | 2.258(5) |
| Hf–O(1) | 2.008(3) | 2.029(5) | Hf–O(3) | 2.312(4) | |
| Hf–O(2) | 2.048(4) | 1.983(5) | | | |
| Cl(1)–Hf–Cl(2) | 166.3(1) | 87.4(1) | Cl(2)–Hf–O(1) | 85.6(1) | 86.6(1) |
| N(1)–Hf–N(2) | 69.9(1) | 71.9(2) | Cl(1)–Hf–N(2) | 84.3(1) | 85.5(2) |
| O(2)–Hf–N(2) | 76.2(2) | 80.9(2) | Cl(1)–Hf–N(1) | 84.5(1) | 92.6(1) |
| O(2)–Hf–N(1) | 145.0(2) | 149.6(2) | Cl(1)–Hf–O(2) | 96.7(1) | 98.6(2) |
| O(1)–Hf–N(2) | 144.3(2) | 99.4(2) | Cl(1)–Hf–O(1) | 100.5(1) | 168.8(2) |
| O(1)–Hf–N(1) | 76.2(2) | 79.4(2) | O(2)–Hf–O(3) | 71.1(2) | |
| O(1)–Hf–O(2) | 137.0(1) | 92.2(2) | O(1)–Hf–O(3) | 71.3(2) | |
| Cl(2)–Hf–N(2) | 83.7(1) | 170.6(2) | Cl(2)–Hf–O(3) | 108.4(1) | |
| Cl(2)–Hf–N(1) | 85.0(1) | 102.4(1) | Cl(1)–Hf–O(3) | 85.3(1) | |
| Cl(2)–Hf–O(2) | 86.9(1) | 106.2(2) | | | |

chlorine atoms causes an enlargement of the $N_2O_2$ cavity to allocate the seven-co-ordinate metal.

Complexes (**12**) (M = Zr) and (**13**) (M = Hf) are isostructural. They consist of discrete [M(acen)$Cl_2$] units (Figures 4 and 5) where the two chlorine atoms are *cis* around the six-co-ordinate metal atoms {Cl(1)–M–Cl(2), 87.2(1) [87.4(1)]°}. The acen ligand is not planar, the two six-membered chelation rings being twisted to form a dihedral angle of 60.1(2) [61.6(2)]°. This indicates the inability of the $N_2O_2$ cavity to allocate in its usual square-planar configuration the large zirconium or hafnium atoms. Therefore, the acen ligand is forced to rotate around the ethylene bridge to bring the O(1) atom from an equatorial to an axial position, thus imposing a *cis* arrangement of the chlorine atoms. The O(2) $\cdots$ N(2) chelation ring is still planar with M at 0.206(1) [0.246(1)] Å, while the N(1) $\cdots$ O(1) one is significantly distorted with the metal at 0.869(1) [0.858(1)] Å. The five-membered chelation ring does not have the usual *gauche* conformation, but it is folded along the N(1) $\cdots$ N(2) line, C(6) and C(7) being out of the N–M–N plane by 0.870(5) [0.855(8)] and 0.423(5) [0.408(8)] Å respectively on the same side.

In the asymmetric unit of complex (**15**) there are two independent molecules A and B (Figures 6 and 7) having nearly the same geometry. In each of them zirconium is surrounded in a nearly octahedral environment by the donor atoms of two bidentate Schiff bases and two chlorine atoms in a *cis* arrangement [Cl(1)–Zr–Cl(2), 96.9(1) and 98.8(1)° for A and B respectively]. Bond distances and angles in the co-ordination sphere are close to those observed in complexes (**5**), (**10**), (**12**), and in [Zr(esal)$_4$] [6b] (Table 8). The Zr–Cl, Zr–O, or Zr–N bond distances are similar, though the Zr–Cl and Zr–O bond distances are shorter and the Zr–N bond distances longer than those found in the strictly related complex (**12**). This is certainly a consequence of less strain imposed by the two bidentate ligands with respect to the quadridentate one, allowing the co-ordinated ligand to arrange in a more symmetrical fashion. The chlorines are *trans* to nitrogen atoms, while in complex (**12**) they are forced to be *trans* to the oxygen and nitrogen atoms respectively. The msal ligands [6b] are nearly planar with zirconium significantly displaced, at 0.040(2) and 0.302(2) Å for molecule A and B respectively, from the plane through O(1),C(1) $\cdots$ C(7),N(1) and at 0.169(2) and 0.075(2) Å for molecule A and B respectively from the plane through O(2),C(11) $\cdots$ C(17),N(2). Their mutual orientations in the two independent molecules are different, the dihedral angle they form being 83.8(1) and 72.8(1)° for A and B respectively.

A careful examination of the structural parameters for such a homogeneous series of compounds gives an idea as to how the stereochemistry at the metal is controlled by the size of the $N_2O_2$ cavity available in the quadridentate ligand and by the metal-ion radius. The mutual arrangement of the functionalizable or reactive sites is a crucial molecular property for the reactivity pathways of the metal.

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## References

1 M. Bottrill, P. D. Gavens, and J. McMeeking, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 3, ch. 22.2, p. 281; ch. 22.3, p. 232; D. J. Cardin, M. F. Lappert, C. L. Raston, and P. I. Riley, *ibid.*, ch. 23.2, p. 559.

2 M. T. Reetz, *Top. Curr. Chem.*, 1982, **106**, 1; T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1985, **107**, 701; A. K. McMullen, I. P. Rothwell, and J. C. Huffman, *ibid.*, p. 1072; S. L. Latesky, A. K. McMullen, G. P. Niccolai, and I. P. Rothwell, *Organometallics*, 1985, **4**, 902, 995; J. L. Kerschner, P. E. Fanwick, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1987, **109**, 5840 and refs. therein; L. R. Chamberlain, J. L. Kerschner, A. P. Rothwell, I. P. Rothwell, and J. C. Huffman, *ibid.*, p. 6471; A. W. Duff, R. A. Kamarudin, M. F. Lappert, and R. J. Norton, *J. Chem. Soc., Dalton Trans.*, 1986, 489.

3 J. M. Pratt and P. J. Craig, *Adv. Organomet. Chem.*, 1973, **11**, 404; J. A. Streeky, D. G. Pillsbury, and D. H. Busch, *Inorg. Chem.*, 1980, **19**, 3148; J. A. Switzer and J. F. Endicott, *J. Am. Chem. Soc.*, 1980, **102**, 1181.

4 M. Mazzanti, J-M. Rosset, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1989, 953 and refs. therein.

5 R. C. Fay, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, ch. 32, pp. 434—439 and refs. therein; R. C. Fay, *Coord. Chem. Rev.*, 1983, **52**, 285.

6 (*a*) R. D. Archer, R. O. Day, and M. L. Illingsworth, *Inorg. Chem.*, 1979, **18**, 2908. (*b*) D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *Chem. Commun.*, 1970, 368.

7 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135.

8 S. L. Lawton and R. A. Jacobson, TRACER, a cell reduction program, Ames Laboratory, Iowa State University of Science and Technology, 1965.

9 G. Sheldrick, SHELX 76, System of Crystallographic Computer Programs, University of Cambridge, Cambridge, 1976.

10 A. J. C. Wilson, *Nature (London)*, 1942, **150**, 151.

11 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 9, (*b*) p. 149.

13 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

14 G. Pennesi, F. Corazza, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Res.*, 1989, (*S*) 86 and refs. therein.

15 C. Floriani, unpublished work.

16 J. E. Davies and M. B. Gatehouse, *J. Chem. Soc., Dalton Trans.*, 1974, 184.

17 M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1972–1973, **9**, 311; M. Calligaris, G. Nardin, and L. Randaccio, *ibid.*, 1972, **7**, 385.

18 M. Calligaris and L. Randaccio, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 20.1, p. 715.

19 F. Corazza, C. Floriani, and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 1987, 709.

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