DALTON

Syntheses and crystal structures of phenyl(2-pyridyl)amido complexes of zirconium(IV), niobium(V) and tantalum(V)

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Di-μ-chloro-dichlorotetrakis[phenyl(2-pyridyl)amido]dizirconium(IV), trichlorobis[phenyl(2-pyridyl)amido]niobium(V) and trichlorobis[phenyl(2-pyridyl)amido]tantalum(V) have been synthesized in a direct reaction between 2-(phenylamino)pyridine and the appropriate metal halide under reflux in toluene. The use of butyllithium was rejected because of the formation of the unreactive ligand adduct bis[2-(phenylamino)pyridine]bis[phenyl(2-pyridyl)amido]dilithium. Single-crystal structures were determined for all four compounds. The niobium and tantalum complexes are monomeric in the solid state, whereas the zirconium complex is a dimer with two bridging chloride ligands. The amide is didentate with one σ- and one π-donor bond. The chelate rings formed have narrow N–M–N angles, around 60°. The co-ordination spheres around the transition metals are pseudo-pentagonal bipyramids.

Three decades after the discovery of metallocenes of Group 4 metals[1] their activation by methylaluminoxane led to increased study of the homogeneous olefin polymerisation catalysts.[2,3] The fact that metallocenes have been thoroughly studied and protected by a large number of patents was a motivating factor for our study on alternative catalyst systems. Up to the present study we have concentrated on syntheses of dialkylamido and alkylimido complexes.[4–7] However, because monodentate ligands are not able to perform metallocene-like rigidity we started to use chelating ligands, particularly substituted 2-aminopyridines.

Although the complexation of 2-pyridylamines has not been extensively studied it is known that they are able to form complexes with a variety of bonding modes. In [tris(3,5-dimethylpyrazolyl)hydroborato]nitrosylbis[(2-pyridyl)amido]tungsten[8] the amidopyridine ligand is monodentate and the heterocyclic nitrogens are unco-ordinated. In contrast, late transition metals seem to co-ordinate through the pyridine nitrogen only, as for example in the bis(2-aminopyridine)dichloropalladium(II)[9] and di{iodobis[bis(2-pyridyl)amine]copper(II)} iodide perchlorate.[10] It has also been reported that 2-aminopyridines can behave as a bridge over a multiple metal–metal bond, as in trichlorotris[phenyl(2-pyridyl)amido]diosmium(III),[11] tetrakis[phenyl(2-pyridyl)amido]ditungsten(II)[12] and an analogous molybdenum complex.[12] The most closely related structures to the complexes presented in this paper are, however, bis[methyl(2-pyridyl)amido](*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine)vanadium(II)[13] and bis[phenyl(2-pyridyl)amido]tris(triphenylphosphine)ruthenium(II)[14] which have similar amidopyridine bonding patterns.

Amido complexes are usually prepared from lithiated ligand precursors. Our results showed, however, that direct reactions between 2-(phenylamino)pyridine and transition-metal halides give more easily the desired bis(amidopyridine) complexes.

Results and Discussion

Since the synthesis of tetrakis(diethylamido)uranium(IV)[15] was reported, lithium amides have widely been used in the preparation of amido complexes. In our experiments 2-(phenylamino)pyridine which was treated with an equimolar amount of butyllithium [titrated using benzhydrol (Ph_2CHOH) as an indicator] did not form any isolable complexes with Group 4 metal(IV) halides. Several experiments were carried out and finally colourless crystals were isolated from the mixture obtained upon reaction of 2 molar equivalents of lithiated 2-(phenylamino)pyridine with zirconium(IV) chloride. On single-crystal determination the compound was characterised as [2-(phenylamino)pyridine] [phenyl(2-pyridyl)amido]lithium. The compound, which crystallises as a dimer, is only partially lithiated: two of the four secondary amine protons are left.

When Barr *et al.*[16] studied the reaction of lithiated 2-(phenylamino)pyridine with butyllithium hexamethylphosphoramide [$LiBu{\cdot}P(NMe_2)_3O$] they isolated monomeric [2-(phenylamino)pyridine][phenyl(2-pyridyl)amido]lithium crystals, however these were obtained, due to slight a LiBu deficiency, as a minor species together with stoichiometric [phenyl(2-pyridyl)amido]lithium–hexamethylphosphoramide. According to this it seemed likely that [$Li_2(NC_5H_4NHPh\text{-}2)_2(NC_5H_4NPh\text{-}2)_2$] is formed after the complexation attempt, during the purification. After isolation of this side product we increased the reaction times in both steps. Butyllithium was allowed to react for 3 h with vigorous reflux in diethyl ether and the toluene suspension of the lithium amide was refluxed with the metal halide ($HfCl_4$) in toluene for 10 h. The reaction mixture was then filtered. According to unit-cell measurements [$Li_2(NC_5H_4NHPh\text{-}2)_2(NC_5H_4NPh\text{-}2)_2$] was obtained.†

In the next stage we examined the direct reaction between 2-(phenylamino)pyridine and transition-metal halides. First zirconium(IV) chloride was added to a cooled toluene solution of 2-(phenylamino)pyridine. The reaction mixture turned gradually to intense orange. Additional heating did not cause any observed changes. After filtration large orange crystals started to grow immediately from the filtrate and precipitation was complete in an hour. According to single-crystal analysis the dimeric complex di-μ-chloro-dichlorotetrakis[phenyl(2-pyridyl)amido]dizirconium(IV) was obtained. This result indicated that monomeric zirconium complexes would be co-ordinatively unsaturated and monomeric complexes might be obtained with higher-oxidation-state metals, therefore niobium(V) and tantalum(V) were studied. The standard procedure was heating of the ligand precursor and metal halide in toluene, which gave highest yields when 2 equivalents or a slight excess of the pro-ligand was used. When the ligand to metal molar

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† a = 11.563(8), b = 10.405(8), c = 8.752(14) Å, α = 91.12(11), β = 93.951(11), γ = 63.16(4)°.

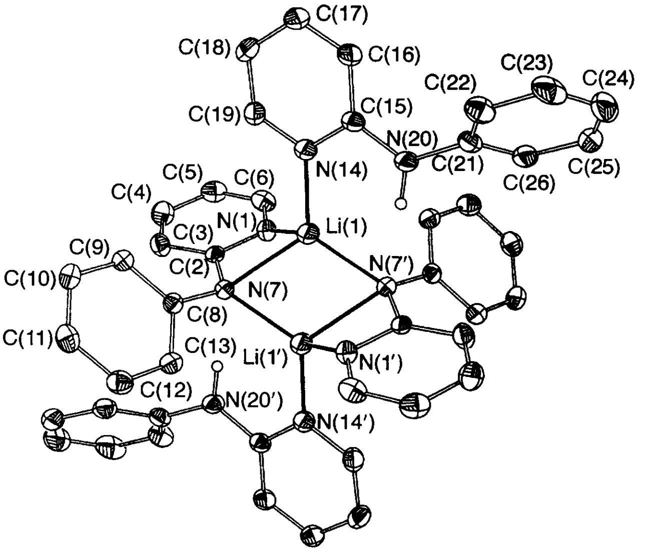

Fig. 1 Molecular structure of [Li$_2$(NC$_5$H$_4$NHPh-2)$_2$(NC$_5$H$_4$NPh-2)$_2$]. Displacement ellipsoids are drawn at the 30% probability level and CH hydrogen atoms are omitted for clarity

ratio was higher, *e.g.* 6 : 1, the crystallisation of the complex became more difficult apparently due to the increased number of toluene-soluble species. It seems likely that the metal halide is involved in adduct formation and species such as [NC$_5$H$_4$NH$_2$-Ph][MCl$_6$] are formed.

In [Li$_2$(NC$_5$H$_4$NHPh-2)$_2$(NC$_5$H$_4$NPh-2)$_2$] (Fig. 1) the co-ordination sphere of the metal is a very distorted tetrahedron. The N–Li–N angles range between 65.5(2) for N(1)–Li(1)–N(7) and 120.7(3)° for N(7)–Li(1)–N(14). Two of the 2-(phenylamino)pyridines co-ordinate to lithium *via* the pyridine nitrogen atoms only, while in the other two ligands there is a bridging amido bond between two lithium ions and a π-donor bond from the heterocyclic nitrogen atom. The bridges have different Li–N distances of 2.023(7) and 2.192(7) Å. The molecule has weak intramolecular hydrogen bonding where N(20) is a donor to Li and N(7'); the pattern is highly similar to that found in [Li(NC$_5$H$_4$NHPh-2)(NC$_5$H$_4$NPh-2)]·P(NMe$_2$)$_3$O. The important geometric features for [Li$_2$(NC$_5$H$_4$NHPh-2)$_2$(NC$_5$H$_4$-NPh-2)$_2$] are presented in Table 1 and the hydrogen-bonding pattern in Table 2.

Table 1 Interatomic distances (Å) and angles (°) in [Li$_2$(NC$_5$H$_4$NHPh-2)$_2$(NC$_5$H$_4$NPh-2)$_2$]

Li(1)–N(1)	2.034(7)	Li(1)–N(14)	2.009(7)
Li(1)–N(7)	2.192(7)	Li(1) · · · Li(1')	2.399(12)
Li(1)–N(7')	2.023(7)		
N(1)–Li(1)–N(7)	65.5(2)	N(7)–Li(1)–N(14)	120.7(3)
N(1)–Li(1)–N(7')	118.4(3)	N(7')–Li(1)–N(14)	118.4(3)
N(7)–Li(1)–N(7')	110.7(3)	Li(1)–N(7)–Li(1')	69.3(3)
N(1)–Li(1)–N(14)	112.4(3)		

Primed atoms are related to unprimed ones by the symmetry operation $-x + 1, -y, -z + 1$.

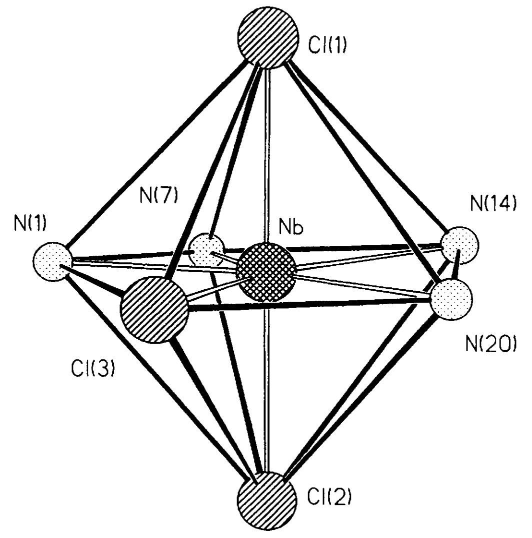

Fig. 2 Pseudo-pentagonal-bipyramidal co-ordination sphere of [NbCl$_3$(NC$_5$H$_4$NPh-2)$_2$]

Although the bond lengths and angles are similar in all the studied transition-metal complexes, the general appearance of the complexes is different. The zirconium complex dimerises to adopt a similar seven-co-ordination sphere as those of the Group 5 metals. In the monomeric niobium and tantalum complexes the ligands adopt different orientations: in the niobium case the phenyl(2-pyridylamido) ligands are in *anti*-like conformation (Fig. 4), whereas in the tantalum complex (Fig. 5) the ligand arrangement is more symmetric and similar to that found in the zirconium complex (Fig. 3.). The co-ordination spheres of all three transition-metal complexes can be regarded as pseudo-pentagonal bipyramids (Fig. 2). The dimeric zirconium complex can be considered as a two pseudo-pentagonal-bipyramid structure where the polyhedra share vertices *via* Cl(1) and Cl(1') atoms. Two chloride ligands occupy the axial positions of the polyhedra and the pentagonal plane is formed from two pairs of nitrogen atoms and the third chloride ligand, which is in the case of the zirconium complex symmetry equivalent to the axial chloride ion.

The rigid pyridylamido ligand induces distortions from ideal symmetry in the pentagonal angles: nitrogen–metal–nitrogen angles in the chelate ring are small, *ca* 60° compared to the ideal 72°. Small chelate angles lead to wider equatorial Cl–M–N angles and N–M–N angles where the nitrogen atoms originate from different ligands. The widest pentagonal *cis* angles are N–M–N angles between amido nitrogen atoms which are in the *cis* position in the zirconium and tantalum complexes, 86.25(12)° for N(7)–Ta–N(20) and 84.68(14)° for N(7)–Zr(1)–N(20). The axial Cl(1)–M–Cl(2) angle is nearly

Table 2 Hydrogen-bonding geometry (Å, °) in [Li$_2$(NC$_5$H$_4$NHPh-2)$_2$(NC$_5$H$_4$NPh-2)$_2$] and comparison to [Li(NC$_5$H$_4$NHPh-2)(NC$_5$H$_4$NPh-2){P(NMe$_2$)$_3$O}].[14]

	Type	[Li$_2$(NC$_5$H$_4$NHPh-2)$_2$(NC$_5$H$_4$NPh-2)$_2$]	[Li(NC$_5$H$_4$NHPh-2)(NC$_5$H$_4$NPh-2){P(NMe$_2$)$_3$O}][14]
N(20)–H(20)	D–H	0.90(4)	0.86
N(7')–H(20)	A–H	2.30(4)	2.11(6)
N(20)–N(7')	D–A	3.193(4)	2.963
Li(1)–H(20)	A–H	2.59(4)	2.52
N(20)–Li(1)	D–A	3.163(7)	3.075
N(20)–H(20)–N(7')	D–H–A	170(3)	173
N(20)–H(20)–Li(1)	D–H–A	122(3)	124

D = Donor, A = acceptor. Symmetry operation as in Table 1.

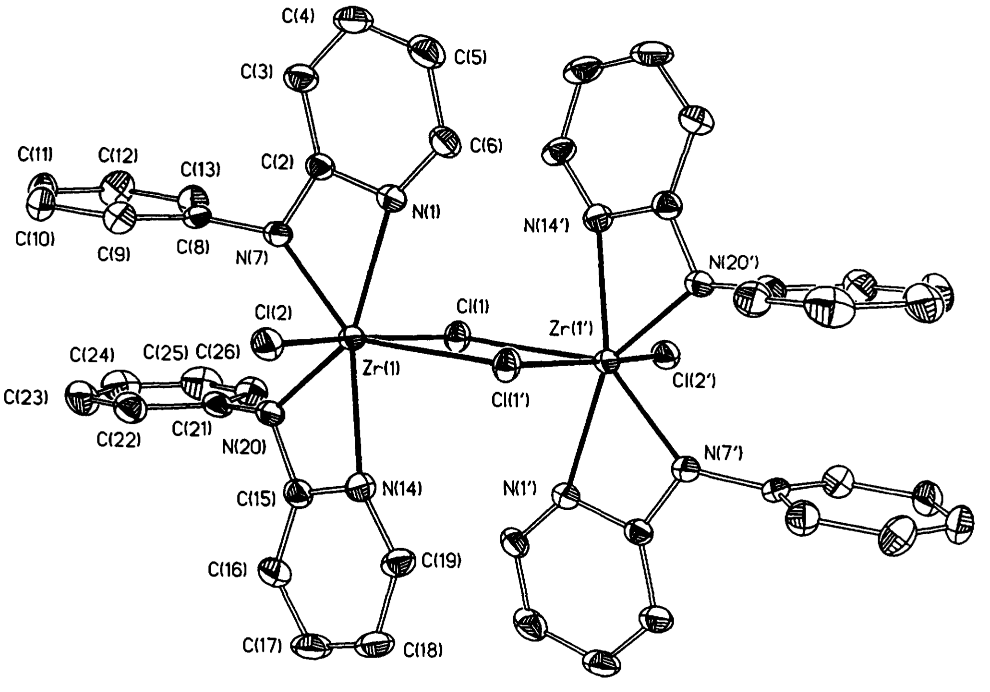

Fig. 3 Molecular structure of [$Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4$]. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity

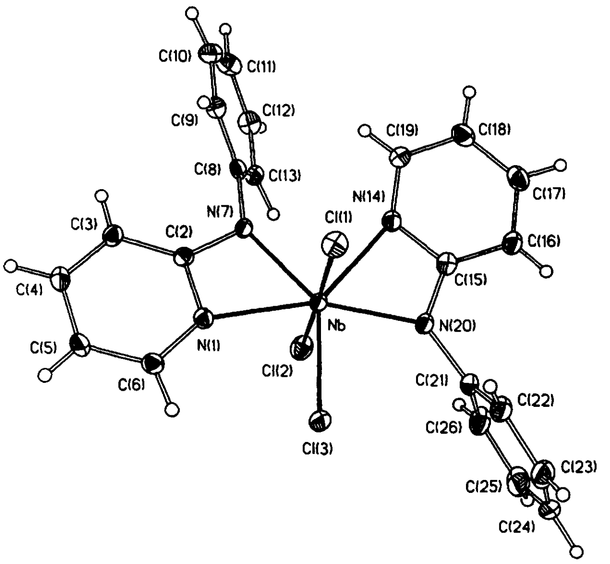

Fig. 4 Molecular structure of [$NbCl_3(NC_5H_4NPh\text{-}2)_2$]. Displacement ellipsoids are drawn at the 30% probability level

linear in the niobium complex, namely 176.39(4)°, and quite similar around tantalum 174.94(4)°, in the zirconium complex the bridging Cl(1) atom is bent towards Zr(1') leading to an axial angle of 168.90(4)°.

In each of the present transition-metal complexes the M–N bond lengths differ from literature values. All amido bonds are slightly longer than those previously reported. In [$Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4$] $M\text{–}N_{amido}$ distances are 2.154(4) and 2.155(4) Å, whereas in dichlorobis(dimethylamido)bis(tetrahydrofuran)zirconium(IV)[17] values of 2.030(2) and 2.034(4) Å have been found. In the [$NbCl_3(NC_5H_4NPh\text{-}2)_2$] complex $M\text{–}N_{amido}$ bond lengths are 2.067(3) and 2.102(3) Å, whereas in pentakis(dimethylamido)niobium(V) and an analogous pyrrolidine complex the $M\text{–}N_{amido}$ distance range is 1.977(17)–2.056(13) Å.[18] Similarly in [$TaCl_3(NC_5H_4NPh\text{-}2)_2$] the values of 2.094(3) and 2.106(3) Å are longer than the related amido bond lengths, 1.954(5) and 1.963(5) Å, in trichlorobis(dimethylamido)(dimethylamine)tantalum(V).[19]

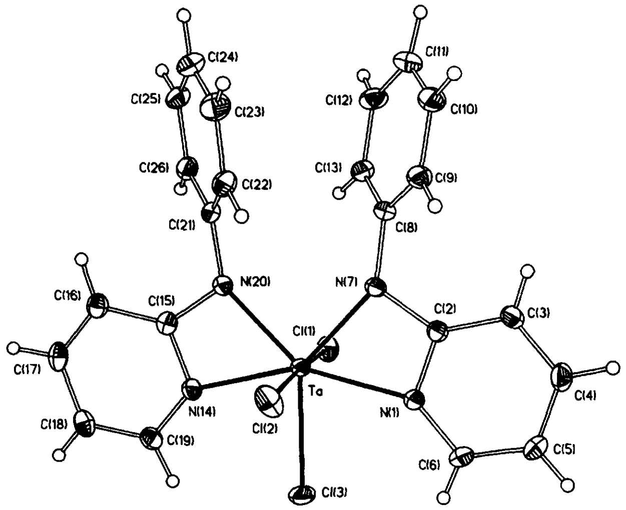

Fig. 5 Molecular structure of [$TaCl_3(NC_5H_4NPh\text{-}2)_2$]. Displacement ellipsoids are drawn at the 30% probability level

In contrast $M\text{–}N_{pyridine}$ π-donor bonds seem to be shorter in the present complexes than previously known ones: in [$Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4$] $M\text{–}N_{pyridine}$ distances are 2.291(4) and 2.293(4) Å, whereas in trichloro(dimethyldithiocarbamato)bis(pyridine)zirconium(IV) the $Zr\text{–}N_{pyridine}$ distances vary between 2.374(5) and 2.393(5).[20] The $M\text{–}N_{pyridine}$ bonds of this type are also shorter in [$NbCl_3(NC_5H_4NPh\text{-}2)_2$] [2.225(3) and 2.284(4) Å] and [$TaCl_3(NC_5H_4NPh\text{-}2)_2$] [2.204(3) and 2.206(3) Å] than the corresponding distances in [$Nb(NBu^t)Cl_4(py)$]$^-$ (py = pyridine) anion[21] [2.479(4) Å] and 2,2'-bipyridyldichlorotrimethyltantalum(V)[22] [2.29(2) Å].

The M–Cl bonding patterns found in this work are highly similar to those previously known for complexes of Zr,[20] Nb[21] and Ta.[19] The important geometric features for the complexes are presented in Table 3.

Conclusion

Direct reaction of 2-(phenylamino)pyridine and niobium(V) chloride or tantalum(V) chloride in toluene gives monomeric

Table 3 Selected bond lengths (Å) and angles (°) in $[Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4]$, $[NbCl_3(NC_5H_4NPh\text{-}2)_2]$ and $[TaCl_3(NC_5H_4NPh\text{-}2)_2]$

	M = Zr	Nb	Ta
M–Cl(1)	2.5935(13)	2.3618(11)	2.3646(14)
M–Cl(2)	2.4203(13)	2.3900(11)	2.3673(14)
M–Cl(3)		2.3974(12)	2.431(2)
M–Cl(1′)	2.6497(13)		
M–N(1)	2.293(4)	2.225(3)	2.204(3)
M–N(7)	2.155(4)	2.102(3)	2.106(3)
M–N(14)	2.291(4)	2.284(4)	2.206(3)
M–N(20)	2.154(4)	2.067(3)	2.094(3)
Cl(1)–M–Cl(2)	168.90(4)	176.39(4)	174.94(4)
Cl(1)–M–Cl(3)		92.16(4)	87.01(5)
Cl(1)–M–Cl(1′)	78.89(4)		
Cl(2)–M–Cl(3)		91.28(4)	87.98(4)
Cl(2)–M–Cl(1′)	90.01(4)		
N(1)–M–N(7)	59.88(14)	60.03(11)	60.39(14)
N(1)–M–N(14)	156.28(14)	141.06(10)	152.86(12)
N(1)–M–N(20)	144.14(14)	158.96(11)	146.43(12)
N(7)–M–N(14)	143.81(14)	81.43(11)	146.52(12)
N(7)–M–N(20)	84.68(14)	140.80(11)	86.25(12)
N(14)–M–N(20)	59.45(14)	59.97(11)	60.70(12)
N(1)–M–Cl(3)		77.54(8)	76.57(9)
N(1)–M–Cl(1′)	78.51(10)		
N(7)–M–Cl(3)		137.47(8)	136.94(9)
N(7)–M–Cl(1′)	137.86(10)		
N(14)–M–Cl(3)		141.08(8)	76.37(8)
N(14)–M–Cl(1′)	78.07(10)		
N(20)–M–Cl(3)		81.47(9)	136.78(9)
N(20)–M–Cl(1′)	135.33(10)		
M–Cl(1)–M′	101.11(4)		

Primed atoms are related to unprimed ones by the symmetry operation $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

compounds in reasonable yield. The reaction also occurs with zirconium(IV) chloride, but a crystalline complex is significantly harder to obtain because of the co-ordinatively unsaturated nature of the monomeric complex. Depending on the method used, the zirconium complex could easily form side products with LiCl, ligand hydrochlorides or form chain structures. However, it is possible that lithiated ligand precursors can be successfully used to synthesize monomeric 2-(phenylamido)pyridine complexes, especially with Group 5 metals. This method would need careful optimisation of the reaction conditions. Instead, direct reaction gives rapid and simple access to these new amido complexes.

Experimental

All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques. Yields are estimated for homomorphous crystalline material only. Mass spectra was recorded using a JEOL JMS-SX102 spectrometer.

Preparations

$[Li_2(NC_5H_4NHPh\text{-}2)_2(NC_5H_4NPh\text{-}2)_2]$. (2-Phenylamino)pyridine (2.10 g, 2 mol equivalent), was dissolved in diethyl ether (20 cm^3) and cooled to −78 °C. An equimolar amount of butyllithium (2 mol dm^{-3}, in hexane) was added dropwise. The solution was warmed slowly to 50 °C and kept at this temperature for 60 min. The ether was then vaporised and the precipitate dissolved in toluene. The solution was cooled to −20 °C and zirconium chloride (1 equivalent) was added. The temperature of the continuously stirred suspension was allowed to rise to room temperature in 60 min. The solution was then refluxed for 1–4 h depending on the experiment. It was filtered and left at −15 °C for crystallisation. A colourless crystalline precipitate was obtained overnight. The second experiment with hafnium(IV) chloride was undertaken in the same manner.

$[Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4]$. 2-(Phenylamino)pyridine (9.32 g, 54.8 mmol) was suspensed in toluene (100 cm^3) and cooled to −50 °C. Zirconium(IV) chloride (6.20 g, 26.8 mmol) was added to the suspension. The temperature of the continuously stirred suspension was allowed to rise to room temperature in 60 min. The mixture which started to turn orange was then refluxed for 45 min. The orange solution was separated from the viscous, amorphous precipitate and filtered. Large orange crystals were obtained in 2 h. Yield *ca.* 10%. Electron-impact (EI) mass spectrum: *m*/*z* 500 $[ZrCl_2(NC_5H_4NPh\text{-}2)_2{}^+]$ and 463 $[ZrCl(NC_5H_4NPh\text{-}2)_2{}^+]$.

$[NbCl_3(NC_5H_4NPh\text{-}2)_2]$. 2-(Phenylamino)pyridine (7.30 g, 42.9 mmol) was suspensed in toluene (70 cm^3). Niobium(V) chloride (3.72 g, 13.8 mmol) was added to the suspension. The solution which rapidly turned to intense purple was heated for 60 min at 90 °C, toluene (50 cm^3) was added and solution was stirred for 2 h at room temperature. Again part of the product was amorphous and insoluble in toluene. The solution was filtered and purple prismatic crystals were obtained in 15 h. Yield 2.3 g (31%). EI Mass spectrum: *m*/*z* 536 $[NbCl_3(NC_5H_4NPh\text{-}2)_2{}^+]$ and 367 $[NbCl_3(NC_5H_4NPh\text{-}2)^+]$.

$[TaCl_3(NC_5H_4NPh\text{-}2)_2]$. 2-(Phenylamino)pyridine (2.88 g, 16.9 mmol) was suspensed in toluene (70 cm^3) and cooled to −50 °C. Tantalum(V) chloride (3.03 g, 8.46 mmol) was added to the suspension. The temperature was raised to 90 °C in 2 h. At −10 °C the solution began to change to red. After heating for 90 min it was filtered. Dark red crystals started to grow in 12 h. Yield 2.9 g (54%). EI Mass spectrum: *m*/*z* 624 $[TaCl_3(NC_5H_4NPh\text{-}2)_2{}^+]$, 589 $[TaCl_2(NC_5H_4NPh\text{-}2)_2{}^+]$ and 457 $[TaCl_3(NC_5H_4NPh\text{-}2)^+]$.

X-Ray crystallography

In each case a portion of air-sensitive but thermally stable crystals were transferred to perfluoroether. The crystal selected for the X-ray measurements was mounted on a glass fibre using the oil-drop method.[23] In the case of $[Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4]$ the crystals suffered from twinning, probably because of their rapid growth. The crystal employed was changed several times before indexing was successful. All X-ray diffraction data sets were collected at −80 °C. Intensity data sets were recorded on an automated four-circle Rigaku AFC-7S diffractometer using graphite-monochromatised Mo-Kα radiation (λ = 0.710 73 Å). Reflection intensities over background were collected using 2θ–ω scans. The intensities of the three standard reflections, recorded after every 200 intensity scans, showed only standard fluctuations or minor decay (< 2.5%) in all measurements. For all data sets ψ scans were used for absorption correction. In the case of $[Li_2(NC_5H_4NHPh\text{-}2)_2(NC_5H_4NPh\text{-}2)_2]$ and $[Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4]$ absorption correction had no effect on data quality. The data set was compressed to reflection files with the TEXSAN software.[24]

Structure determination and refinement. Structures were solved with the SHELXTL PC 4.1 program package[25] using direct methods which showed the positions of the non-hydrogen atoms. Further refinement with full-matrix least squares on F^2 was carried out with SHELXL 93[26] using all collected reflections. In each case non-hydrogen atoms were refined anisotopically. In all compounds the hydrogen atoms were found from the Fourier-difference map and refined. The crystallographic data are presented in Table 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/252.

Table 4 Crystallographic data

	$[Li_2(NC_5H_4NHPh\text{-}2)_2\text{-}(NC_5H_4NPh\text{-}2)_2]$	$[Zr_2Cl_4(NC_5H_4NPh\text{-}2)_4]$	$[NbCl_3(NC_5H_4NPh\text{-}2)_2]$	$[TaCl_3(NC_5H_4NPh\text{-}2)_2]$
Colour	Colourless	Orange	Deep purple	Black-red
Formula	$C_{44}H_{38}Li_2N_8$	$C_{44}H_{36}Cl_4N_8Zr_2$	$C_{22}H_{18}Cl_3N_4Nb$	$C_{22}H_{18}Cl_3N_4Ta$
M	792.70	1001.04	537.66	625.70
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P\bar{1}$
a/Å	8.742(3)	16.531(8)	15.210(9)	8.680(3)
b/Å	10.408(6)	18.609(7)	9.111(6)	10.831(5)
c/Å	11.562(6)	14.182(8)	15.732(6)	12.777(6)
α/°	116.62(3)			65.830(3)
β/°	92.76(4)	97.33(5)	99.86(4)	83.960(4)
γ/°	91.07(4)			83.250(4)
U/Å^3	938.4(8)	4327(4)	2147.9(8)	1086.1(9)
Z	2	8	4	2
D_c/g cm^{-3}	1.226	1.537	1.663	1.913
Crystal dimensions/mm	0.25 × 0.25 × 0.25	0.40 × 0.40 × 0.35	0.30 × 0.25 × 0.25	0.25 × 0.20 × 0.15
$F(000)$	364			
μ/mm^{-1}	0.074	2016	1088	604
Transmission range	0.9569–1.0000	0.771	0.951	5.446
2θ Range/°	5–53	0.9807–1.0000	0.7298–1.0000	0.6370–1.0000
Reflections refined	3288	5–50	5–50	5–50
Parameters	320	3648	3591	3783
Observed reflections	2000	334	343	343
R	0.0799	3401	3271	3686
$wR2$	0.1617	0.0457	0.0375	0.0218
S (Goodness of fit, F^2)	1.028	0.1107	0.0948	0.0538
Residual electron density/e Å^{-3}	0.178, −0.230	1.176	1.078	1.064
		0.532, −0.427	0.966, −0.584	0.943, −1.061

$R = \Sigma\|F_o| - |F_c\|/|F_o|$ with $F > 4\sigma(F)$, function minimised; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)]^{\frac{1}{2}}$; $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)]^{\frac{1}{2}}$.

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References

1 G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, 1954, **76**, 4281.

2 M. Bochmann, *J. Chem. Soc., Dalton. Trans.*, 1996, 225.

3 G. Fink, R. Mülhaupt, and H. H. Brintzinger, (Editors), *Ziegler Catalysts*, Springer V, Berlin, Heidelberg, 1995.

4 M. Polamo, I. Mutikainen and M. Leskelä, *Acta Crystallogr., Sect. C*, 1996, **52**, 1082.

5 M. Polamo, I. Mutikainen and M. Leskelä, *Acta Crystallogr., Sect. C*, 1996, **52**, 1348.

6 M. Polamo, I. Mutikainen and M. Leskelä, *Z. Kristallogr.*, 1996, **211**, 641.

7 M. Polamo and M. Leskelä, *Acta Crystallogr., Sect. C*, 1996, **52**, 1631.

8 N. A. Obaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, *J. Chem. Soc., Dalton Trans.*, 1987, 1063.

9 M. C. Navaro Ranninger, S. Martinez-Carrera and S. Carcia-Blanco, *Acta Crystallogr., Sect. C*, 1984, **41**, 21.

10 J. E. Johnson and R. A. Jacobson, *J. Chem. Soc., Dalton Trans.*, 1973, 580.

11 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem.*, 1984, **23**, 4693.

12 A. R. Chakravarty, F. A. Cotton and E. S. Shamshoun, *Inorg. Chem.*, 1984, **23**, 4216.

13 J. J. H. Edema, S. Gambarotta, A. Meetsma, A. L. Spek and N. Veldman, *Inorg. Chem.*, 1991, **30**, 2062.

14 A. R. Chakravarty, F. A. Cotton and E. S. Shamshoun, *Inorg. Chim. Acta*, 1984, **86**, 5.

15 R. G. Jones, G. Karmas, G. A. Martin and H. Gilman, *J. Am. Chem. Soc.*, 1956, **78**, 4285.

16 D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 469.

17 S. Brenner, R. Kempe and P. Arndt, *Z. Anorg. Allg. Chem.*, 1995, **621**, 2021.

18 C. Heath and M. B. Hursthouse, *Chem. Commun*, 1971, 143.

19 M. H. Chisholm, J. C. Huffman and L.-S. Tan, *Inorg. Chem.*, 1981, **20**, 1859.

20 H. W. Roesky, B. Meller-Rehbein and M. Noltemeyer, *Z. Naturforsch., Teil B*, 1991, **46**, 1117.

21 W. Clegg, R. J. Errington, D. C. R. Hockless and C. Redshaw, *Polyhedron*, 1991, **10**, 1959.

22 M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1973, 1830.

23 T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615.

24 TEXSAN Single Crystal Structure Analysis Software, Version 1.6, Molecular Structure Corporation, The Woodlands, TX, 1993.

25 G. M. Sheldrick, SHELXTL PC., Release 4.1, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.

26 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.

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