

# Synthesis and characterization of two new “pincer” complexes of zinc(II). The X-ray crystal structures of the five coordinate complexes $[\text{ZnCl}_2\{\eta^3\text{-}NN'\text{-}2,6\text{-(R}_2\text{NCH}_2)_2\text{C}_5\text{H}_3\text{N}\}]$ (R = *n*-Bu or Me)

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**Abstract:** The potentially terdentate *NN'* donor ligand 2,6-bis[di-(*n*-butyl)aminomethyl]pyridine (**1**) does not form a stable, isolable Ru complex using any standard Ru starting materials. This is in contrast to the dimethylamino derivative **2**. In the presence of Zn metal as a reducing agent, the treatment of hydrated ruthenium trichloride with **2** leads instead to the isolation of a diamagnetic Zn(II) complex (**3**) of general formula  $[\text{ZnCl}_2(\mathbf{1})]$ . Analysis of **3** (NMR, X-ray) reveals the complex to be a mononuclear Zn halide compound containing ligand **1** in an  $\eta^3\text{-}NN'$  bonding motif. The Zn atom is found to be five-coordinate and in a geometry best described as midway between trigonal bipyramidal and square pyramidal in structure. Similar experiments using **2** produce an analogous Zn species (**4**) which has likewise been fully characterized (NMR, X-ray) and found to be similar to **3** although the metal is in a distinctly square pyramidal environment. These compounds are viewed as relatives of the class of Zn “pybox” catalysts.

*Key words:* pincer complexes, zinc(II) compounds, X-ray crystal structure.

**Résumé :** Lorsqu'on le met en présence de dérivés du ruthénium appropriés, le ligand donneur, potentiellement terdentate *NN'*, 2,6-bis[di(butyl)aminométhy]pyridine (**1**) ne forme aucun complexe stable ou isolable du Ru. Ceci est en opposition avec le comportement du dérivé diméthylamino, **2**. En présence de Zn métallique comme agent de réduction, le traitement du trichlorure de ruthénium hydraté avec du produit **2** conduit plutôt à un complexe diamagnétique de Zn(II), de formule générale  $[\text{ZnCl}_2(\mathbf{1})]$  que l'on peut isoler. L'analyse de ce complexe (**3**) par RMN et diffraction des rayons X indique que le complexe est un composé mononucléaire d'halogénure de zinc contenant un ligand **1** dans un motif de liaison  $\eta^3\text{-}NN'$ . On a observé que le zinc est pentacoordonné et qu'une structure intermédiaire entre une bipyramide trigonale et une pyramide à base carrée est la meilleure façon de décrire sa géométrie. Des expériences semblables avec le complexe **2** conduisent à la formation d'une espèce analogue contenant du zinc (**4**) que l'on a aussi caractérisée par RMN et diffraction des rayons X; on a trouvé que ce complexe est semblable à **3**, même si le métal se trouve dans un environnement à pyramide à base carrée bien caractérisée. On considère que ces composés sont apparentés aux catalyseurs de la classe « pybox ».

*Mots clés :* complexes en forme de pince, composés du Zn(II), structure cristalline par diffraction des rayons X.

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## Introduction

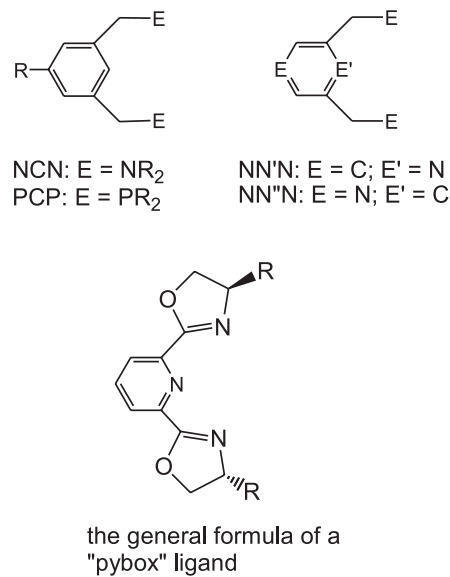
The use of multidentate ligands in the stabilization of transition metal fragments is an important aspect of modern inorganic and organometallic synthesis. Of the large number of ligands that are currently known, the group of potentially terdentate ligands referred to as the “pincer” class of ligands (Fig. 1) has been yielding a rich body of interesting and novel chemistry (1). In particular, pincer complexes of the platinum group metals have been used in a number of diverse applications which include molecular sensor technology (1, 2) and in the modelling of reaction intermediates (1, 3). Several other properties, many of which have direct industrial relevance, have also been reported for metal complexes containing a pincer ligand. These aspects include a number of catalytic organic transformations involving C—C (4), C—N (5), and C—halogen bond formation (6), in addition to the polymerization of activated olefins via ROMP<sup>3</sup> or ATRP<sup>4</sup>. One of our areas of interest revolves around the inorganic chemistry of Ru containing a neutral, potentially terdentate *NN'N*-donor ligand derived from 2,6-bis(aminomethyl)pyridine (**1**: R = *n*-Bu; **2**: R = Me, Fig. 1). We have previously shown that **2** can be used to produce a number of useful Ru containing starting materials and reagents for the catalytic and stoichiometric activation of a variety of substrates including olefins, amines, and sulphur containing compounds (5, 7–10). We wished to expand our investigations to include Ru pincer complexes containing **1**. However, our attempts to coordinate this particular pincer ligand to a Ru metal centre have instead led to the isolation of a new *NN'N* complex of Zn(II). The incorporation of a Zn metal atom was the result of a failed attempt to produce a reactive source of Ru(II) (i.e., Ru(III) reduced via Zn) in situ in the presence of **1**. From this result, we have expanded this Zn chemistry and have fully characterized (NMR, X-ray) two novel Zn complexes, incorporating ligands **1** or **2**. In contrast to the plenitude of work involving platinum group metal pincer compounds (1–3, 5–9), relatively little is known about the Group XII transition metal chemistry of these ligands (1). This work has obvious relevance to Zn pybox (Fig. 1) complexes and their derivatives (pybox = [2,6-bis{oxazolin-2-yl}pyridine]) (11*a*). Several halide and pseudohalide complexes of Zn(II) in the presence of a pybox ligand are known to be potent enantioselective catalysts (e.g., Diels–Alder, aldol reactions, etc.) (11*b*, 11*c*) and surmised to have the general formula [ZnX<sub>2</sub>(η<sup>3</sup>-*NN'N*-pybox)]. In addition, complexes of this general class have recently been used as models for hydrolytic metallo-enzymes (11*d*).

## Experimental section

### General

All synthetic manipulations were carried out under inert atmosphere (Schlenk) techniques. Solvents were dried and degassed by standard methods. Diethyl ether was predried with NaOH and distilled from sodium–benzophenone; halocarbons were distilled from CaH<sub>2</sub> and hydrocarbon solvents and tetrahydrofuran (THF) was distilled from sodium–

Fig. 1.



benzophenone. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P) were recorded on a Bruker AC-200 or AC-300 spectrometer at RT (RT = room temperature). Chemical shifts (<sup>1</sup>H and <sup>13</sup>C) are reported in ppm referenced to external SiMe<sub>4</sub> (δ<sub>H or C</sub> = 0.00) and coupling constants (*J*) are given in Hz. Elemental analyses were performed by Kolbe Microanalytisches Laboratorium, Mülheim, Germany. The compounds [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (**12**), [RuCl<sub>2</sub>(nbd)]<sub>n</sub> (nbd = 1,5-norbornadiene) (**13**), and 2,6-bis(dimethylaminomethyl)pyridine (**2**) (**14**) were synthesized according to previously published procedures. All other reagents and solvents were used as received from commercial sources.

### Synthesis of 2,6-bis(di-*n*-butylaminomethyl)pyridine (**1**)

A sample of HBr (0.210 L, 48% in water) was added dropwise to a precooled solution (0°C) of 2,6-pyridinedimethanol (15.99 g, 43.0 mmol) in 500 mL of acetic anhydride. After addition was complete, the flask was removed from the ice bath and the mixture stirred overnight at 100°C. The resulting brown solution was cooled again to 0°C and a white precipitate formed. The solid was filtered, washed with ethylacetate (2 × 50 mL), and then dried under reduced pressure to give 29.0 g (73%) of a white solid presumed to be the HBr salt of 2,6-bis(bromomethyl)pyridine. A 150 mL portion of di-*n*-butylamine was added to a 15.0 g (4.44 mmol) portion of the above salt suspended in 150 mL of benzene. The mixture was then heated to reflux temperature for 48 h. Pentane was then added to the resulting light brown suspension to precipitate any salts. The solid was removed by filtration and washed with ether (3 × 20 mL). Volatile components of the combined organic fractions were then removed under reduced pressure to give 10.9 g (69%) of **1** which was deemed to be of sufficient purity (>95%: NMR) for further use. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.45 (t, 1H, py-H,

<sup>3</sup>ROMP = Ring Opening Metathesis Polymerization (7*a*).

<sup>4</sup>ATRP = Atom Transfer Radical Polymerization (6*b*, 7*b*).

$J = 7.6$ ), 7.23 (d, 2H, py-*H*), 3.56 (s, 4H, CH<sub>2</sub>), 2.37–2.32 (m, 8H, NCH<sub>2</sub>), 1.38–1.29 (m, 8H, CH<sub>2</sub>), 1.24–1.14 (m, 8H, CH<sub>2</sub>), 0.77–0.72 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 160.1 (*o*-C, py), 136.4 (*m*-C, py), 120.5 (*p*-C, py), 60.9 (NCH<sub>2</sub>), 54.3 (CH<sub>2</sub>), 29.6 (CH<sub>2</sub>), 20.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>).

### Synthesis of [ $\{\eta^3\text{-}NN'N\text{-}2,6\text{-bis}(\text{di-}n\text{-butylaminomethyl})\text{pyridine}\}$ zinc(II) chloride] (**3**)

#### Method A

A solution of hydrated ruthenium trichloride (0.35 g, 3.44 mmol) and **1** (1.64 g, 4.54 mmol) was dissolved in EtOH (25 mL) and heated to 40°C in the presence of excess Zn powder for a period of 48 h. The resulting black suspension was centrifuged, the green-brown layer was then removed, and a black solid portion was isolated. This material was dissolved in 30 mL of dichloromethane, filtered, and the solution concentrated to a volume of about 5–10 mL. Pentane (10 mL) was then added and the resulting precipitated solid was collected and dried in vacuo to afford crude **3** in the form of a brown-grey solid (1.51 g, 88%).

#### Method B

A solution of anhyd zinc dichloride (0.13 g, 0.95 mmol) and **1** in EtOH (25 mL) was stirred at RT for 12 h. The liquid layer was removed from the resulting white suspension and the remaining solid was then dried under reduced pressure. The white solid thus obtained was dissolved in 5 mL of dichloromethane and filtered. The resulting light grey solution was mixed with 10 mL of pentane to precipitate **3** in the form of a white solid (yield: 0.30 g, 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.88 (t, 1H, py-*H*,  $J = 7.2$ ), 7.27 (d, 2H, py-*H*), 3.86 (s, 4H, CH<sub>2</sub>), 2.80–2.72 (m, 8H, NCH<sub>2</sub>), 1.59–1.43 (m, 8H, CH<sub>2</sub>), 1.33–1.15 (m, 8H, CH<sub>2</sub>), 0.92–0.84 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 158.6 (*o*-C, py), 141.1 (*m*-C, py), 122.4 (*p*-C, py), 57.5 (NCH<sub>2</sub>), 52.5 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 21.0 (CH<sub>2</sub>), 14.3 (CH<sub>3</sub>). Anal. calcd. for C<sub>23</sub>H<sub>43</sub>N<sub>3</sub>Cl<sub>2</sub>Zn (497.89): C 55.48, H 8.71, N 8.44; found: C 55.39, H 8.65, N 8.39.

### Synthesis of [ $\{\eta^3\text{-}NN'N\text{-}2,6\text{-bis}(\text{dimethylaminomethyl})\text{pyridine}\}$ zinc(II) chloride] (**4**)

#### Method A

A solution of hydrated ruthenium trichloride (0.52 g, 5.12 mmol) and **2** (1.61 g, 8.33 mmol) was dissolved in EtOH (25 mL) and stirred at RT in the presence of excess Zn powder for a period of 12 h. The resulting black suspension was centrifuged, the brown-black layer was then removed and a black solid portion was isolated. This material was dissolved in 30 mL of dichloromethane, filtered, and the solution concentrated to a volume of about 5–10 mL. Pentane (10 mL) was then added and the resulting precipitated solid was collected and dried in vacuo to afford crude **4** in the form of a light yellow solid (0.31 g, 17%).

#### Method B

A solution of zinc dichloride (0.41 g, 3.0 mmol) and **2** in EtOH (25 mL) was stirred at RT for 12 h. The yellow liquid layer was removed from the resulting suspension and the remaining solid was then dried under reduced pressure. The white solid thus obtained was dissolved in 5 mL of dichloro-

methane and the yellow solution was filtered thereafter. The mixture was then treated with a 10 mL portion of pentane to precipitate **4** in the form of a white solid (yield: 0.37 g, 37%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.92 (t, 1H, py-*H*,  $J = 7.9$ ), 7.29 (d, 2H, py-*H*), 3.77 (s, 4H, CH<sub>2</sub>), 2.49 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 155.5 (*o*-C, py), 141.5 (*m*-C, py), 122.8 (*p*-C, py), 65.2 (NCH<sub>2</sub>), 46.5 (CH<sub>3</sub>). Anal. calcd. for C<sub>11</sub>H<sub>19</sub>N<sub>3</sub>Cl<sub>2</sub>Zn (329.57): C 40.09, H 5.81, N 12.75; found: C 40.15, H 5.75, N 12.66.

## Crystal structure determinations

### General

Intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å) at a temperature of 150 K. The structures were solved with direct methods (SHELXS-97 (15)) and refined with the program SHELXL-97 (16) against  $F^2$  of all reflections up to a resolution of  $(\sin \theta/\lambda)_{\text{max}} = 0.65$  Å<sup>-1</sup>. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined freely with isotropic parameters. The drawings, calculations, and checking for higher symmetry were performed with the PLATON package (17).

### Crystal structure determination of **3**

Formula: C<sub>23</sub>H<sub>43</sub>Cl<sub>2</sub>N<sub>3</sub>Zn; fw = 497.87; colourless-brownish plate, 0.25 × 0.25 × 0.11 mm<sup>3</sup>; monoclinic,  $C2/c$  (no. 15),  $a = 13.1705(1)$  Å,  $b = 9.1163(1)$  Å,  $c = 21.7754(2)$  Å,  $\beta = 92.0916(6)^\circ$ ,  $V = 2612.75(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho = 1.266$  g cm<sup>-3</sup>, analytical absorption correction (PLATON (17),  $\mu = 1.158$  mm<sup>-1</sup>, 0.73–0.88 transmission). Measured reflections = 27 704, 3003 unique reflections ( $R_{\text{int}} = 0.0466$ ),  $R$  ( $I > 2\sigma(I)$ ):  $R1 = 0.0188$ ,  $wR2 = 0.0507$ .  $R$  (all data):  $R1 = 0.0195$ ,  $wR2 = 0.0512$ .  $S = 1.040$ .  $-0.218 < \Delta\rho < 0.278$  e Å<sup>-3</sup>.

### Crystal structure determination of **4**

Formula: C<sub>11</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>3</sub>Zn; fw = 329.56; yellow block, 0.63 × 0.28 × 0.28 mm<sup>3</sup>; tetragonal,  $P4_12_12$  (no. 92),  $a = b = 10.5893(1)$  Å,  $c = 25.9157(3)$  Å,  $V = 2906.01(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho = 1.507$  g cm<sup>-3</sup>, analytical absorption correction (PLATON (17),  $\mu = 2.041$  mm<sup>-1</sup>, 0.30–0.60 transmission). Measured reflections = 19 719, 3323 unique reflections ( $R_{\text{int}} = 0.0316$ ),  $R$  ( $I > 2\sigma(I)$ ):  $R1 = 0.0183$ ,  $wR2 = 0.0484$ .  $R$  (all data):  $R1 = 0.0186$ ,  $wR2 = 0.0486$ .  $S = 1.071$ .  $-0.364 < \Delta\rho < 0.609$  e Å<sup>-3</sup>.

## Results and discussion

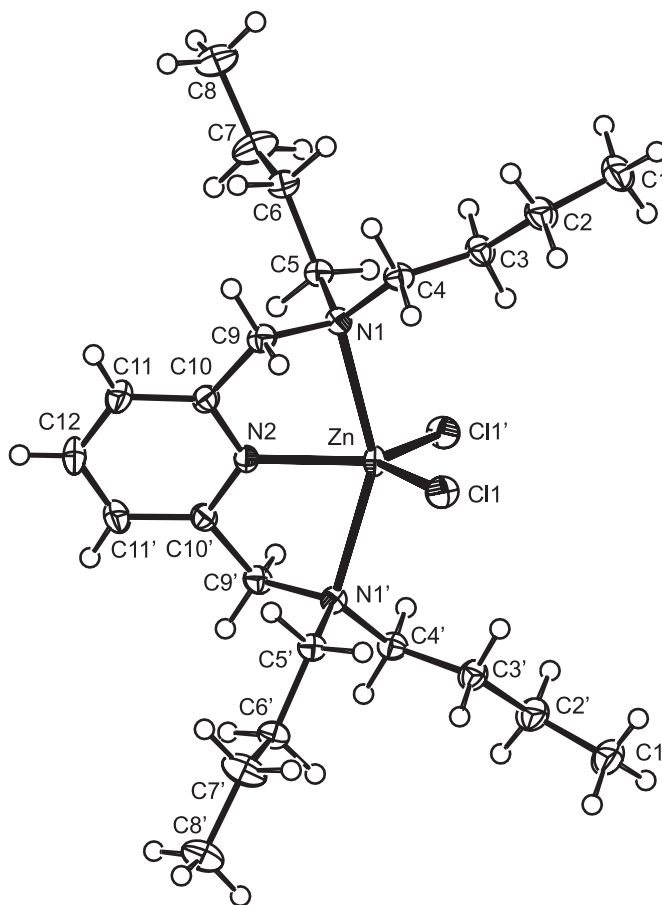
Our desire to use a Bu derivative of the  $NN'$  ligand (i.e., **1**) was a direct consequence of the observation that several of our catalysts containing ligand **2** have low-solubility characteristics in organic solvents. Thus, derivative **1** was synthesized to evaluate its potential as a ligand for metal complexation where the resulting species will ideally present more favourable solubility properties. In addition, the trialkyl *N*-donor atoms of **1** are expected to have a stronger (Lewis) basic character when compared with the analogous *N*-atoms of **2**. Thus, one can evaluate the effect of increased ligand basicity on complexation behaviour, stability, and catalytic performance. Ligand **1** was produced according to a

modified version of a simple two-step procedure (18). The treatment of 2,6-pyridinedimethanol with aq HBr, followed by heating in the presence of excess  $\text{HNBU}_2$ , gives **1** in 51% overall yield (see Experimental section).

The typical synthesis of Ru complexes containing **2** involves the reaction of the ligand with 1 equiv of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in a halocarbon solvent. However, the treatment of **1** with this Ru precursor ( $\text{CH}_2\text{Cl}_2$  or  $\text{C}_2\text{H}_4\text{Cl}_2$  as solvent) gave no reaction at RT (NMR). Heating of these mixtures to reflux temperature gave a complicated mixture of products (NMR) including both starting materials, free  $\text{PPh}_3$ , and a number of other phosphine containing complexes in an inseparable mixture. The use of a hydrocarbon solvent such as toluene gave only starting materials at both RT and upon addition of heat. We then attempted the use of the polymeric form of  $[\text{RuCl}_2(\text{nbd})]$  as the Ru starting material. Unfortunately, this also gave a complex mixture upon treatment with **1**, using either toluene or THF as solvent. Following these failures, we attempted the use of hydrated  $\text{RuCl}_3$  as the source of Ru under reducing conditions (Zn metal in EtOH) in the presence of **1**. To our surprise, a new complex was formed which appeared to contain the reducing agent (i.e., Zn) and not a Ru metal centre. Elemental analysis indicated a formula which corresponds to  $[\text{ZnCl}_2(\mathbf{1})]$  (i.e., **3**). Although the yield of **3** was low, heating of the mixture to  $40^\circ\text{C}$  gave **3** in over 88% isolated yield. Complex **3** can also be produced in moderate yield from anhyd zinc dichloride (EtOH, reflux, 12 h) in the absence of ruthenium halide source. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** indicates a high degree of molecular symmetry and the diamagnetic nature of this inorganic Zn complex. The  $^1\text{H}$  NMR spectrum reveals a singlet resonance assigned to the benzylic methylene protons of the  $NN'N$  ligand fragment ( $\delta_{\text{H}} = 3.86$  ppm) and a corresponding  $^{13}\text{C}$  resonance for the corresponding benzylic carbon ( $\delta_{\text{C}} = 57.5$  ppm). These results cannot distinguish between an  $\eta^3\text{-}NN'N$ , or  $\eta^1\text{-}N_{\text{py}}$  binding motif of **1** to the metal centre nor the possibility that a multinuclear complex has been formed.

Therefore, a single crystal X-ray structure determination of **3** was carried out to confidently assign the structural properties of this compound. A suitable crystal was obtained by the slow evaporation of a dichloromethane solution of the complex which had been layered by a blanket of pentane and THF. The solid-state molecular structure of **3** is depicted in Fig. 2. The list of relevant bond lengths and angles appears in Table 1. The coordination sphere around the Zn atom is best described as midway between trigonal bipyramidal (TBP) and square pyramidal (SQP) in structure. The  $\tau$ -value for estimating the distortion from these two extremes was found to be 0.47 (the  $\tau$ -values range from 1.0 for a true trigonal bipyramidal geometry to 0.0 for an idealized square pyramidal structure. See ref. 19). However, the compound is not on a true Berry pseudo-rotation pathway between these two ideal geometries. Thus, a numerical description such as the  $\tau$ -value is very approximate (19). Since complex **3** has an exact  $C_2$  symmetry plane in the solid-state, the Zn atom is in the plane formed by the three N atoms. The bond lengths between the metal and the N and halogen ligands are typical for a complex that is formally Zn(II) and can be compared with that of other Zn complexes containing the  $3N\text{-}2X$  ( $X = \text{halogen or pseudo-}$

Fig. 2. Representation of the solid-state structure of **3**.



halogen) ligand set. These include such complexes as  $[\text{ZnCl}_2(\eta^3\text{-terpy})]$  (terpy = 2,6,2',2''-terpyridine) (20a) and others (crystallographically characterized examples of the general formula  $[\text{ZnX}_2(\eta^3\text{-}NN'N'')]$  can be found in ref. 20b–20j; for a discussion of the bond length properties of coordination complexes, including Zn(II) compounds, see ref. 21; for a general discussion on the coordination properties of zinc(II) ions see ref. 22). Complex **3** may also be viewed as an analogue of compounds having the general formula  $[\text{ZnX}_2(\eta^3\text{-pybox})]$ . Such complexes have recently found application in a variety of Lewis acid-catalyzed asymmetric organic transformations including Diels–Alder reactions (11b), aldol (Mukaiyama) reactions (11b), and for the enantioselective addition of enol silanes to ketomalonate (11c).

The robust nature of **3** was demonstrated by the following experiments. No reaction was observed (NMR) when a solution of **3** was heated to reflux temperature under a nitrogen atmosphere in a  $\text{CCl}_4$  (12 h), acetonitrile (12 h), benzene (48 h), or toluene (48 h) solution. No spectral changes were observed when a RT solution of **3** is treated with a basic trialkyl phosphine (e.g.,  $\text{PMe}_3$ ) or a phosphite (e.g.,  $\text{P}[\text{OMe}]_3$ ), even in the presence of excess  $\text{AgBF}_4$ . However, treatment of **3** with an ether solution of HCl resulted in some decomposition of the material (a black precipitate was noted). Compound **3** was also found to be unstable to the presence

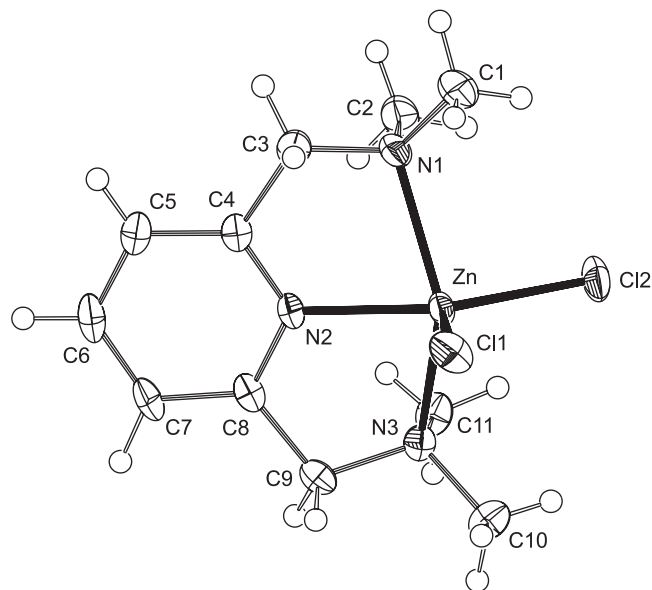
**Table 1.** Important bond lengths (Å) and angles (deg) for complexes **3** and **4**.<sup>a</sup>

Bond length	Complex <b>3</b>	Complex <b>4</b>
Zn—Cl(1)	2.2293(3) <sup>b</sup>	2.2636(4)
Zn—Cl(2)	n.a. <sup>c</sup>	2.2882(5)
Zn—N(1)	2.3883(8)‡	2.2554(13)
Zn—N(2)	2.0498(12)	2.0980(12)
Zn—N(3)	n.a.	2.2512(14)
Bond and torsion angles		
Cl(1)—Zn—N(1)	95.35(2)	135.63(4)
Cl(1)—Zn—N(2)	119.10(1)	103.54(4)
Cl(1)—Zn—Cl(1A)	121.81(1)	n.a.
Cl(1)—Zn—Cl(2)	n.a.	108.94(2)
Cl(1)—Zn—N(1A)	99.07(2)	n.a.
Cl(1)—Zn—N(3)	n.a.	109.57(4)
N(1)—Zn—Cl(1A)	150.11(3)	n.a.
Cl(2)—Zn—N(1)	n.a.	95.06(4)
Cl(2)—Zn—N(2)	n.a.	147.50(5)
Cl(2)—Zn—N(3)	n.a.	94.28(4)
N(2)—Zn—Cl(1A)	119.10(1)	n.a.
N(1)—Zn—N(2)	n.a.	74.89(5)
N(1)—Zn—N(3)	n.a.	138.17(5)
N(2)—Zn—N(3)	n.a.	75.52(5)
N(2)—Zn—N(1A)	75.06(2)	n.a.
Cl(1A)—Zn—N(1A)	95.35(2)	n.a.
N(1)—C(9)—C(10)—N(2)	35.68(11)	n.a.
N(1)—C(3)—C(4)—N(2)	n.a.	27.54(19)
N(2)—C(8)—C(9)—N(3)	n.a.	-21.33(18)

<sup>a</sup>Standard deviations are given in parenthesis.<sup>b</sup>Also the Zn—Cl(1A) or Zn—N(1A) bond length.<sup>c</sup>n.a. = not applicable.

of sulphur dioxide or phenylacetylene<sup>5</sup> when a silver salt was present (AgBF<sub>4</sub> or AgOTf). Under these conditions, the bis HX salt (X = BF<sub>4</sub> or OTf) of ligand **1** can be isolated from the reaction mixture<sup>6</sup>.

Despite our failure to produce the desired Ru complexes by the above route, we were intrigued as to the possibility of forming the related Zn(II) complex using the prototypical NN'N ligand **2** described earlier. Thus, treatment of a solution of anhyd zinc dichloride with a solution of **2** in EtOH solution gave complex **4** in 37% isolated yield. Interestingly, treatment of a solution of **2** with Zn metal in the presence of hydrated ruthenium trichloride under a nitrogen atmosphere leads to the formation of both **4** (17%) and the known complex [RuCl<sub>2</sub>(NN'N)]<sub>2</sub>(μ-N<sub>2</sub>) (15%; NMR) (**5b**). Thus, it appears that the higher nucleophilicity of the nitrogen atoms in **1**, when compared with ligand **2**, may be detrimental to forming stable Ru(II) species.

**Fig. 3.** Representation of the solid-state structure of **4**.

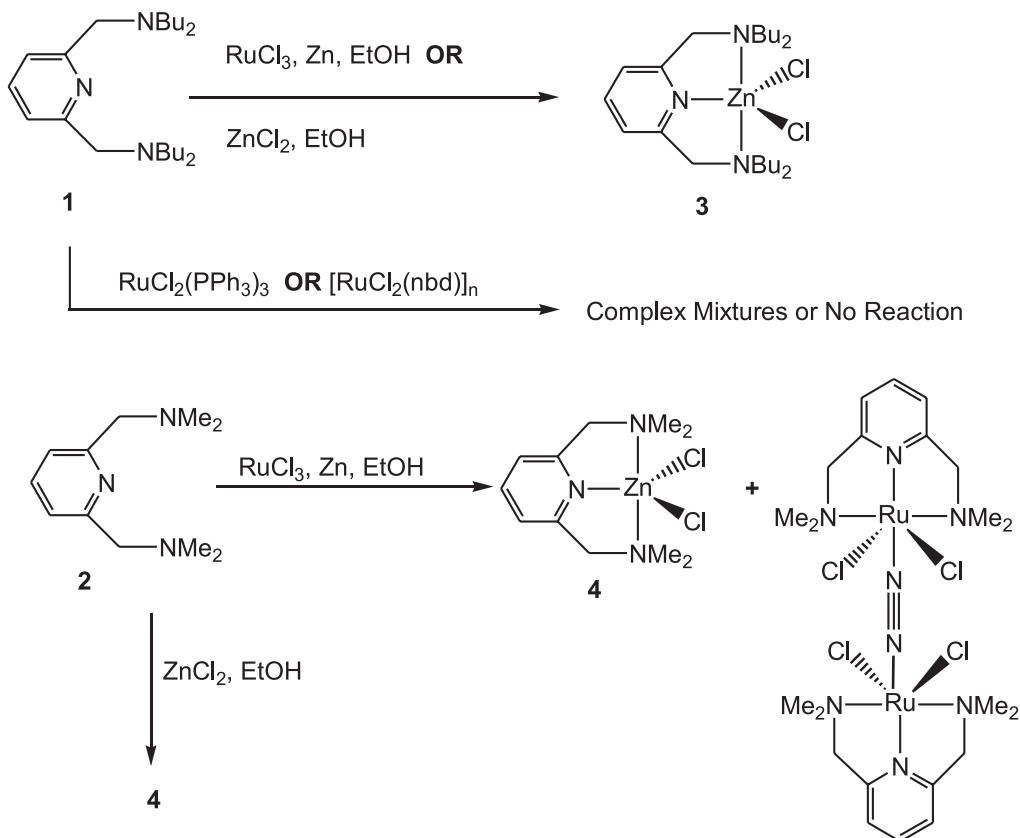
As in the case of **3**, an X-ray structural determination of **4** was also carried out. The compound has a somewhat similar molecular structure when compared with **3** (i.e., a mononuclear complex (Fig. 3)). However, the Zn atom in **4** is more accurately described as being in a slightly distorted square pyramidal environment ( $\tau = 0.16$  (19)). Also, compound **4** has an approximate, non-crystallographic *C<sub>s</sub>* (mirror) symmetry and hence the Zn atom, unlike in **3**, is not in the plane formed by the three N atoms (a deviation of 0.726(1) Å). The important bond lengths and angles for complex **4** can be found in Table 1. The NN'N pincer ligand is in a typical geometry (5*b*–5*c*, 7*b*, 8–10). Compound **4** was also found to be stable to prolonged heating (12 h) under a nitrogen atmosphere in CCl<sub>4</sub> solution.

## Conclusions

Attempts to synthesise Ru complexes under standard conditions (5*b*, 5*c*) with the basic NN'N ligand **1** leads to complex mixtures or a complete absence of any reaction. The former result may be due to the more basic nature of the trialkylamine donor atoms when compared with the complementary ligand **2**. Treatment of hydrated RuCl<sub>3</sub> with **1** in the presence of Zn metal in EtOH solution leads to a thermally stable compound (**3**), which is an NN'N complex of Zn(II). Complex **3** and its methyl analogue **4** can also be produced in moderate yields using anhyd zinc chloride as the metal source (Scheme 1). Both **3** and **4** have been characterized by elemental analysis, NMR, and by a single crystal X-ray structure determination.<sup>7</sup> The latter results show that both

<sup>5</sup>Our interest in the activation of SO<sub>2</sub> and PhC≡CH stems from earlier work (2, 8, 10).<sup>6</sup>Compound **1**·2(HBF<sub>4</sub>)·0.5(H<sub>2</sub>O): Selected data: <sup>1</sup>H NMR ([CD<sub>3</sub>]<sub>2</sub>CO): 11.54 (s, 2H, NH), 8.13 (t, 1H, *J* = 7.8, py-*H*), 7.73 (d, 2H, py-*H*), 4.87 (d, 4H, CH<sub>2</sub>), 3.49–3.43 (m, 8H, NCH<sub>2</sub>), 1.92–1.81 (m, 8H, CH<sub>2</sub>), 1.44–1.31 (d, 8H, CH<sub>2</sub>), 0.94–0.85 (m, 12H, CH<sub>3</sub>). <sup>19</sup>F NMR ([CD<sub>3</sub>]<sub>2</sub>CO): 145.3 (s, BF<sub>4</sub>). Anal. calcd. for C<sub>23</sub>H<sub>46</sub>N<sub>3</sub>B<sub>2</sub>F<sub>4</sub>O<sub>0.5</sub> (527.24): C 50.57, H 8.49, N 7.69; found: C, 50.51, H 8.32, N 7.09.<sup>7</sup>Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada ([http://www.nrc.ca/cisti/irm/unpub\\_e.shtml](http://www.nrc.ca/cisti/irm/unpub_e.shtml) for information on ordering electronically). Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and hydrogen coordinates for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Centre. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Scheme 1.



compounds are mononuclear, five coordinate Zn species but the geometry about the metal is notably different between the two species. Compound **3** is best described as midway between TBP and SQP geometry while compound **4** has a slightly distorted SQP geometry about the metal centre. These results clearly emphasize that subtle changes in ligand structure can have a large effect on metal geometry, even with the two closely related cases of pincers **1** and **2**. This observation may have a profound impact on catalytic applications, especially as both **3** and **4** may be viewed as simple relatives to the Zn pybox systems which are known to be mediators of regio- and enantio-selective organic reactions (11*a*–11*c*).

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## References

- (a) G. van Koten. *Pure Appl. Chem.* **61**, 1681 (1989), and refs. therein; (b) M.H.P. Rietveld, D.M. Grove, and G. van Koten. *New J. Chem.* **21**, 751 (1997), and refs. therein; (c) P. Steenwinkel, R.A. Gossage, and G. van Koten. *Chem. Eur. J.* **4**, 759 (1998), and refs. therein; (d) B. Rybtchinski and D. Milstein. *Angew. Chem. Int. Ed.* **38**, 870 (1999), and refs. therein; (e) C.M. Jensen. *Chem. Commun.* 2443 (1999), and refs. therein.
- (a) M. Albrecht, R.A. Gossage, A.L. Spek, and G. van Koten. *Chem. Commun.* 1003 (1998); (b) M. Albrecht and G. van Koten. *Adv. Mater.* **11**, 171 (1999).
- (a) J.A.M. van Beek, G. van Koten, W.J.J. Smeets, and A.L. Spek. *J. Am. Chem. Soc.* **108**, 5010 (1986); (b) G. van Koten. *Pure Appl. Chem.* **62**, 1155 (1990); (c) A.J. Canty and G. van Koten. *Pure Appl. Chem.* **28**, 406 (1995); (d) P. Dani, T. Karlen, R.A. Gossage, W.J.J. Smeets, A.L. Spek, and G. van Koten. *J. Am. Chem. Soc.* **119**, 11317 (1997); (e) R.A. Gossage, A.D. Ryabov, A.L. Spek, D.J. Stufkens, J.A.M. van Beek, R. van Eldik, and G. van Koten. *J. Am. Chem. Soc.* **121**, 2488 (1999); (f) M. Albrecht, R.A. Gossage, A.L. Spek, and G. van Koten. *J. Am. Chem. Soc.* **121**, 11898 (1999); (g) A. Vigalok, B. Rybtchinski, L.J.W. Shimon, Y. Ben-David, and D. Milstein. *Organometallics*, **18**, 895 (1999).
- J.G. Donkervoort, J.L. Vicario, J.T.B.H. Jastrzebski, R.A. Gossage, G. Cahiez, and G. van Koten. *J. Organomet. Chem.* **558**, 61 (1998).
- (a) Q. Jiang, D. van Plew, S. Murtuza, and X. Zhang. *Tetrahedron Lett.* **37**, 797 (1996); (b) R.A.T.M. Abbenhuis, I. del Río, M.M. Bergshoef, J. Boersma, N. Veldman, A.L. Spek, and G. van Koten. *Inorg. Chem.* **37**, 1749 (1998); (c) R.A.T.M. Abbenhuis, J. Boersma, and G. van Koten. *J. Org. Chem.* **63**, 4282 (1998).
- (a) J.W.J. Knapen, A.W. van der Made, J.C. de Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, and G. van Koten. *Nature (London)*, **372**, 659 (1994); (b) R.A. Gossage, L.A. van de Kuil, and G. van Koten. *Acc. Chem.*

- Res. **31**, 423 (1998); (c) R.A. Gossage, J.T.B.H. Jastrzebski, J. van Ameijde, S.J.E. Mulders, A.J. Brouwer, R.M.J. Liskamp, and G. van Koten. *Tetrahedron Lett.* **40**, 1413 (1999); (d) G. van Koten and J.T.B.H. Jastrzebski. *J. Mol. Catal. A: Chem.* **146**, 317 (1999); (e) A.W. Kleij, R.A. Gossage, J.T.B.H. Jastrzebski, J. Boersma, and G. van Koten. *Angew. Chem. Int. Ed.* **39**, 176 (2000).
7. (a) I. del Río and G. van Koten. *Tetrahedron Lett.* **40**, 1401 (1999); (b) I. del Río and G. van Koten. *Organometallics*, **19**, 361 (2000).
  8. I. del Río, R.A. Gossage, M. Lutz, A.L. Spek, and G. van Koten. *Inorg. Chim. Acta*, **287**, 113 (1999).
  9. I. del Río, R.A. Gossage, M. Lutz, A.L. Spek, and G. van Koten. *J. Organomet. Chem.* **583**, 69 (1999).
  10. I. del Río, R.A. Gossage, M.S. Hannu, M. Lutz, A.L. Spek, and G. van Koten. *Organometallics*, **18**, 1097 (1999).
  11. (a) M. Gómez, G. Muller, and M. Rocamora. *Coord. Chem. Rev.* **193–195**, 769 (1999) and refs. therein; (b) D.A. Evans, M.C. Kozlowski, and J.S. Tedrow. *Tetrahedron Lett.* **37**, 7481 (1996); (c) F. Reichel, X. Fang, S. Yao, M. Ricci, and K.A. Jørgensen. *Chem. Commun.* 1505 (1999); (d) P. Molenveld, W.M.G. Stikvoort, H. Kooijman, A.L. Spek, J.F.J. Engbersen, and D.N. Reinhoudt. *J. Org. Chem.* **64**, 3896 (1999).
  12. R. Holm, Jr. *Inorg. Synth.* **12**, 238 (1970).
  13. E.W. Abel, M.A. Bennett, and G. Wilkinson. *J. Chem. Soc.* 3178 (1959).
  14. B.M. Markies, P. Wijkens, H. Kooijman, N. Veldman, A.L. Spek, J. Boersma, and G. van Koten. *Organometallics*, **13**, 3244 (1994).
  15. G.M. Sheldrick. *SHELXS-97*. Program for crystal structure solution. University of Göttingen, Göttingen, Germany. 1997.
  16. G.M. Sheldrick. *SHELXL-97*. Program for crystal structure refinement. University of Göttingen, Göttingen, Germany. 1997.
  17. A.L. Spek. *PLATON*, a multipurpose crystallographic tool. Utrecht University, The Netherlands. 1999.
  18. J.A.M. van Beek, G. van Koten, G.P.C.M. Dekker, E. Wissing, M.C. Zoutberg, and C.H. Stam. *J. Organomet. Chem.* **394**, 659 (1990).
  19. A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, and G.C. Verschoor. *J. Chem. Soc. Dalton Trans.* 1349 (1984).
  20. (a) M. Vlasse, T. Rojo, and D. Beltran-Porter. *Acta Crystallogr. Sect. C: Struct. Commun.* **C39**, 560 (1983); (b) P.J.M.W.L. Birker, A.J. Schierbeek, G.C. Verschoor, and J. Reedijk. *J. Chem. Soc. Chem. Commun.* 1124 (1981); (c) G.A. Nicholson, J.L. Petersen, and B.J. McCormick. *Inorg. Chem.* **21**, 3274 (1982); (d) H. Plenio and D. Burth. *Organometallics*, **15**, 4054 (1998); A. Abufarang and H. Vahrenkamp. *Inorg. Chem.* **34**, 2207 (1995); (e) A. Hazell, C.J. McKenzie, and L.P. Nielsen. *J. Chem. Soc. Dalton Trans.* 1751 (1998); (f) M. Graf, B. Greaves, and H. Stoeckli-Evans. *Inorg. Chim. Acta*, **204**, 239 (1993); (g) E. Amadei, M. Carcelli, S. Ianelli, P. Cozzini, P. Pelagatti, and C. Pelizzi. *J. Chem. Soc. Dalton Trans.* 1025 (1998); (h) A.L. Vance, N.W. Alcock, J.A. Heppert, and D.H. Busch. *Inorg. Chem.* **37**, 6912 (1998); (i) H.W. Smith. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **B31**, 2701 (1975); (j) J. Wirbser and H. Vahrenkamp. *Z. Naturforsch. B: Chem. Sci.* **47B**, 962 (1992).
  21. A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, and R. Taylor. *J. Chem. Soc. Dalton Trans.* S1 (1989).
  22. (a) C.W. Bock, A.K. Katz, and J.P. Glusker. *J. Am. Chem. Soc.* **117**, 3754 (1995); (b) Y.-H. Chiu, O. dos Santos, and J.W. Canary. *Tetrahedron*, **55**, 12069 (1999).