

# Preparation and Characterization of *cis*- and *trans*- $[\text{Ir}(\text{tn})_2\text{Cl}_2]\text{CF}_3\text{SO}_3$ and of $[\text{Ir}(\text{tn})_3]\text{Cl}_3$ (tn = propane-1,3-diamine)

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Brorson, M., Galsbøl, F., Simonsen, K., Skov, L. K. and Søtofte, I., 1998. Preparation and Characterization of *cis*- and *trans*- $[\text{Ir}(\text{tn})_2\text{Cl}_2]\text{CF}_3\text{SO}_3$  and of  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$  (tn = propane-1,3-diamine). – Acta Chem. Scand. 52: 1017–1023. © Acta Chemica Scandinavica 1998.

Procedures are given for the preparation and isolation of *cis*- and *trans*- $[\text{Ir}(\text{tn})_2\text{Cl}_2]\text{CF}_3\text{SO}_3$  and of  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$ , (tn = propane-1,3-diamine). The compounds were prepared by the use of  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  (thtp = tetrahydrothiophene) as starting material, using either DMSO or neat tn as solvent. A procedure for the preparation of  $[\text{Rh}(\text{tn})_3]\text{Cl}_3$  in quantitative yield from  $\text{Rh}(\text{thtp})_3\text{Cl}_3$  is also given. The complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and by UV/VIS spectroscopy. The conformation of the six-membered chelate rings of  $[\text{Ir}(\text{tn})_3]^{3+}$  in the solid state was determined by single-crystal X-ray diffraction of  $[\text{Ir}(\text{tn})_3][\text{Co}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ . The three chelate rings all adopt the energetically favoured chair conformation; however, the overall idealized symmetry is *C*<sub>1</sub>. A comparative ligand field analysis, based on Gaussian resolution of the solution UV/VIS spectra for a number of homoleptic  $[\text{M}(\text{N}_6)]^{3+}$  (M = Co<sup>III</sup>, Rh<sup>III</sup>, Ir<sup>III</sup>) complexes, is also presented.

In comparison with other kinetically inert metal ions such as chromium(III), cobalt(III) and rhodium(III), the number of Werner-type amine complexes of iridium(III) reported in the literature is rather limited. This is most likely due to problems in their preparative chemistry. Amine complexes of iridium(III) are thus characterized by an extreme robustness, which makes the use of rather harsh reaction conditions, i.e. high temperatures and prolonged reaction times,<sup>1–4</sup> necessary. With the conventional starting materials,  $\text{IrCl}_3 \cdot \text{aq}$  and  $\text{K}_2\text{IrCl}_6$ , these conditions pose a serious problem, as many amines [e.g. propane-1,3-diamine (tn) and cyclic amines] cause a reduction of iridium to the metallic state. Recent preparations of iridium(III) complexes with the saturated macrocyclic amines 1,4,8,11-tetraazacyclotetradecane<sup>5,6</sup> (cyclam) and 1,4,7-triazacyclononane<sup>7,8</sup> (tacn) have only been possible because alternative iridium starting materials were used. In the present paper we report the preparation and characterization of *cis*- and *trans*- $[\text{Ir}(\text{tn})_2\text{Cl}_2]\text{CF}_3\text{SO}_3$  and of  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$ , all hitherto unknown compounds, by the use of  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  (thtp = tetrahydrothiophene) as starting material. The bis complexes were synthesized from  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  and tn by

using dimethyl sulfoxide (DMSO) as solvent, while the tris complex was prepared by the use of neat tn as solvent and addition of LiCl in the ratio Ir : LiCl = 1 : 3. A method for the preparation of  $[\text{Rh}(\text{tn})_3]\text{Cl}_3$  in quantitative yield, similar to that for  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$ , is also given.

The conformations of the three six-membered chelate rings in the tris complex were determined by crystal structure analysis of  $[\text{Ir}(\text{tn})_3][\text{Co}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$  and are compared with those known for other inert metal complexes. The electronic spectrum of  $[\text{Ir}(\text{tn})_3]^{3+}$  is discussed by a comparative ligand field analysis on homoleptic am(m)ine complexes based on Gaussian resolutions of the spectra.

## Experimental

**Materials.** The preparation of  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  has been described previously.<sup>5</sup>  $\text{Rh}(\text{thtp})_3\text{Cl}_3$  was prepared in a similar way using a reaction time of 2 h. All other chemicals were obtained commercially in analytical or reagent grade and were used without further purification.

**Instrumentation.** Absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-250 Fourier-transform spectrometer in D<sub>2</sub>O or DMSO-*d*<sub>6</sub> with dioxane as an internal reference. The chemical

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shifts,  $\delta$ , are given in ppm relative to TMS. Single-crystal X-ray data were collected at room temperature on an Enraf-Nonius CAD-4F diffractometer.

*Analyses.* C, H, N, Cl and S analyses were made by the Micro-analytical Laboratory at the H. C. Ørsted Institute, Copenhagen.

#### *Synthetic procedures.*

*cis- and trans-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub>.* 2.00 g of Ir(thtp)<sub>3</sub>Cl<sub>3</sub> (3.55 mmol) were placed in a 10-ml round-bottomed flask containing a magnetic stirring bar, and 4 ml of DMSO and 0.54 g of tn (7.28 mmol) were added. The flask was closed and the suspension heated in an oven at 140 °C with occasional stirring until a clear orange solution had formed (ca. 10 min). The heating was continued for 24 h, during which time yellow crystals precipitated and the colour of the solution turned lighter. The mixture was allowed to cool to room temperature, transferred with water to a beaker and then diluted to 400 ml. The yellow solution was filtered and applied on a column of SP-Sephadex C-25 (Li<sup>+</sup>-form, ca. 15 cm long and 2 cm in diameter). In order to remove the DMSO and thtp, the column was thoroughly washed with water. By elution with 0.1 M LiCl a yellow band consisting of *cis-* and *trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> developed, while some highly charged orange and pale-yellow species remained at the top of the column. The yellow eluate containing *cis-* and *trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> was collected and evaporated to a volume of 40 ml. The solution was then filtered, heated to near boiling and 10 ml of hot 1 M CF<sub>3</sub>SO<sub>3</sub>H were added. The mixture was allowed to stand for crystallization overnight at room temperature. The crystals were filtered off, washed with 3 ml of 1 M CF<sub>3</sub>SO<sub>3</sub>H, then with 96% ethanol and dried in air. Yield: 0.40 g (20%) of crude *trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub>.

To the mother liquor were added 20 ml of 1 M CF<sub>3</sub>SO<sub>3</sub>H, and the solution was evaporated to dryness. To the remanet was then added 96% ethanol, and the yellow crystals were isolated by filtration, washed with 96% ethanol until the filtrate was colourless, and dried in air. Yield: 0.70 g (35%) of crude *cis*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub>.

*trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub> was recrystallized by dissolving 1.00 g in 50 ml of boiling water followed by filtration. The filtrate was slowly cooled to room temperature on the turned-off hotplate and allowed to stand for crystallization overnight at room temperature. Crystals were isolated by filtration, washed with 3 ml of 1 M CF<sub>3</sub>SO<sub>3</sub>H, then with 96% ethanol and dried in air. Yield: 0.70 g (70%) of canary-yellow *trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub>. (Found: C 14.91, H 3.69, N 10.12, Cl 12.74, S 6.20. Calc. for IrC<sub>7</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>3</sub>SO<sub>3</sub>: C 15.00, H 3.60, N 10.00, Cl 12.65, S 5.72). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.68 (4 H, b, C-CH<sub>2</sub>-C),  $\delta$  2.69 (8 H, b, C-CH<sub>2</sub>-N) and 5.27 (8 H, b, C-NH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  28.27 (2 C, s, C-CH<sub>2</sub>-C) and  $\delta$  40.93 (4 C, s, -CH<sub>2</sub>-N).

*cis*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub> was recrystallized by dissol-

ving 1.00 g in 25 ml of boiling water followed by filtration and addition of 5 ml of 1 M CF<sub>3</sub>SO<sub>3</sub>H. The method for crystallization and isolation was similar to that described above for the *trans*-isomer. Yield: 0.79 g (79%) of lemon-yellow *cis*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]/CF<sub>3</sub>SO<sub>3</sub>. (Found: C 14.87, H 3.60, N 10.09, Cl 12.58, S 6.99. Calc. for IrC<sub>7</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>2</sub>F<sub>3</sub>SO<sub>3</sub>: C 15.00, H 3.60, N 10.00, Cl 12.65, S 5.72). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.44–1.59 (2 H, m, C-CH<sub>2</sub>-C),  $\delta$  1.70–1.76 (2 H, m, C-CH<sub>2</sub>-C), 2.73–2.77 (4 H, m, C-CH<sub>2</sub>-N), 5.09–5.12 (2 H, m, C-NH<sub>2</sub>), 5.29–5.34 (2 H, m, C-NH<sub>2</sub>) and 5.50 (4 H, b, C-NH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  27.63 (2 C, s, C-CH<sub>2</sub>-C),  $\delta$  41.29 (2 C, s, -CH<sub>2</sub>-N) and  $\delta$  41.42 (2 C, s, -CH<sub>2</sub>-N).

*[Ir(tn)<sub>3</sub>]/Cl<sub>3</sub>.* 1.00 g of Ir(thtp)<sub>3</sub>Cl<sub>3</sub> (1.78 mmol) and 0.22 g of LiCl (5.2 mmol) were placed in a 25-ml round-bottomed flask containing a magnetic stirring bar, and 15 ml of tn were added. The flask was closed and the suspension was heated in an oven at 140 °C with occasional stirring until a clear yellow solution had formed (ca. 2 h). The heating was continued for three weeks, during which white crystals precipitated and the colour of the solution became dark yellow. The mixture was then allowed to cool to room temperature, the crystals were isolated by filtration, washed thoroughly with 96% ethanol, then with diethyl ether and dried in air. Yield: 0.50 g (54%) of crude [Ir(tn)<sub>3</sub>]/Cl<sub>3</sub>.

[Ir(tn)<sub>3</sub>]/Cl<sub>3</sub> was recrystallized by dissolving 1.00 g in 6 ml of hot water. The solution was filtered, added to 100 ml of boiling 96% ethanol, and the mixture was set aside for crystallization, first at room temperature and then overnight at 5 °C. The crystals were isolated by filtration, washed with 96% ethanol, then diethyl ether and dried in air. Yield: 0.70 g (70%) of white [Ir(tn)<sub>3</sub>]/Cl<sub>3</sub>. (Found: C 20.82, H 5.91, N 16.43, Cl 20.16. Calc. for IrC<sub>9</sub>H<sub>30</sub>N<sub>6</sub>Cl<sub>3</sub>: C 20.75, H 5.80, N 16.13, Cl 20.42). <sup>1</sup>H NMR (D<sub>2</sub>O):  $\delta$  1.85–1.92 (6 H, m, C-CH<sub>2</sub>-C) and  $\delta$  2.75 (12 H, t, C-NH<sub>2</sub>). <sup>13</sup>C NMR  $\delta$  27.73 (3 C, s, C-CH<sub>2</sub>-C) and  $\delta$  42.21 (6 C, s, C-NH<sub>2</sub>).

*[Ir(tn)<sub>3</sub>]/[Co(CN)<sub>6</sub>]·5H<sub>2</sub>O.* This compound was prepared by addition of a slight excess of a dilute aqueous solution of K<sub>3</sub>[Co(CN)<sub>6</sub>] to a dilute aqueous solution of [Ir(tn)<sub>3</sub>]/Cl<sub>3</sub> followed by slow evaporation. The crystals were subjected to X-ray crystallographic investigations.

*[Rh(tn)<sub>3</sub>]/Cl<sub>3</sub>.* 1.00 g of Rh(thtp)<sub>3</sub>Cl<sub>3</sub> (2.11 mmol) and 0.27 g of LiCl (6.4 mmol) were placed in a 25 ml round-bottomed flask and 25 ml of tn were added. The suspension was stirred at 115 °C for 48 h during which a clear yellow solution was formed followed by precipitation of white crystals. The solution was allowed to cool to room temperature and the suspension was then transferred with 96% ethanol to a beaker, diluted to ca. 100 ml with ethanol and set aside for ca. 0.5 h in order to complete precipitation. The crystals were isolated by filtration, washed thoroughly with 96% ethanol, then diethyl ether and dried in air. The yield of white [Rh(tn)<sub>3</sub>]/Cl<sub>3</sub> is quantitative.

[Rh(tn)<sub>3</sub>]/Cl<sub>3</sub> was recrystallized in a similar manner as

described above for  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$ , giving the tetrahydrate. (Found: C 22.59, H 7.58, N 16.70, Cl 21.06. Calc. for  $\text{RhC}_9\text{H}_{38}\text{N}_6\text{Cl}_3\text{O}_4$ : C 21.46, H 7.60, N 16.68, Cl 21.12).

**Crystal structure determination of  $[\text{Ir}(\text{tn})_3][\text{Co}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ .** Crystal and experimental data for the compound are listed in Table 1. The unit-cell parameters were derived from a least-squares fit of refined diffractometer setting angles for 25 reflections. Four standards were measured for intensity and orientation control; no fading was observed. The intensities were corrected for Lorentz, polarization and absorption (Gaussian integration) effects. The structure was solved by the Patterson method with partial structure expansion and refined by the full-matrix least-squares technique. However, due to the size of the crystals, the reflecting power was rather poor, giving rise to a large  $wR(F^2)$ -value. One of the five oxygen atoms, O5, is disordered about two almost equally populated positions and refined isotropically, whereas all other non-hydrogen atoms were refined with anisotropic temperature factors. In the refinement the hydrogen atoms (except for the water molecules) were as calculated positions using a riding model with  $\text{N-H} = 0.90 \text{ \AA}$ ,  $\text{C-H} = 0.97 \text{ \AA}$  and fixed thermal parameters [ $U(\text{H}) = 1.2$  times  $U$  for attached C or N]. The structure refined well in the centrosymmetric space group  $P\bar{1}$ . Attempts to refine the structure in  $P1$  did not give any improvement in the definition of the O5 atom. There are two independent Co atoms in the asymmetric unit both situated at a centre of symmetry. The crystallographic computations were performed with SHELXS86<sup>9</sup> and SHELXL93.<sup>10</sup> The atomic scattering factors were taken from the literature.<sup>11</sup> The PLATON<sup>12</sup> program was used for molecular geometry calculations and the SHELXTL95 program<sup>13</sup> for the illustration.

Atomic coordinates and thermal parameters are listed in Table 2, and selected bond lengths and chelate angles around Ir are listed in Table 3. Tables of anisotropic thermal parameters, positional parameters for the hydrogen atoms, torsion angles, bond lengths, bond angles and calculated structure factors are available from one of the authors (I.S.) on request.

## Results and discussion

**Syntheses.** The complexes *cis*- and *trans*- $[\text{Ir}(\text{tn})_2\text{Cl}_2]\text{-CF}_3\text{SO}_3$  have been prepared by reaction of  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  with a stoichiometric amount of tn (propane-1,3-diamine) in DMSO at 140 °C. Unlike the reaction between  $\text{IrCl}_3 \cdot \text{aq}$  and tn in aqueous solution, no sign of reduction of iridium(III) to iridium metal was observed. However, formation of highly charged or oligomeric species was seen. The separation of the two geometrical isomers of dichlorobis(propane-1,3-diamine)-iridium(III) was achieved by fractional crystallization. Ion-exchange chromatography with SP-Sephadex C-25 did not give a satisfactory separation of the two isomers.

Attempts to prepare  $[\text{Ir}(\text{tn})_3]^{3+}$  by the above

Table 1. Crystal and experimental data for  $[\text{Ir}(\text{tn})_3][\text{Co}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$ .

Formula	$\text{C}_{15}\text{H}_{40}\text{N}_{12}\text{O}_5\text{CoIr}$
Formula weight	719.69
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions:	
$a/\text{\AA}$	8.467(3)
$b/\text{\AA}$	9.022(3)
$c/\text{\AA}$	18.303(5)
$\alpha/^\circ$	89.40(3)
$\beta/^\circ$	101.05(3)
$\gamma/^\circ$	99.20(3)
Unit-cell volume $V/\text{\AA}^3$	1354.3(8)
Formula units per unit cell, $Z$	2
$F(000)$	716
Calculated density $D_x/\text{g cm}^{-3}$	1.76
Radiation	Cu K $\alpha$
Wavelength, $\lambda/\text{\AA}$	1.5418
Linear absorption coefficient/ $\text{cm}^{-1}$	145.9
Temperature, $T/\text{K}$	296
Crystal description	Colourless
Crystal size/mm	$0.23 \times 0.07 \times 0.01$
Diffractometer	Enraf-Nonius CAD-4F
Unit-cell determination:	
No. of reflections used	25
$\theta$ -range/ $^\circ$	4.9–14.5
Intensity data collection:	
$\theta_{\text{max}}/^\circ$	68
Range of $h$	–10–10
Range of $k$	–11–11
Range of $l$	0–22
Scan mode	$\omega$
Scan range, $\Delta\omega$	$1.40 + 0.14 \tan \theta$
Total number of unique reflections	5544
No. of independent reflections, [ $I > 2\sigma(I)$ ]	2844
Corrections	Decay, Lorenz-polarization absorption
Transmission factors	0.1886–0.8104
Structure refinement:	
Minimization of	$\sum w( F_o ^2 -  F_c ^2)^2$
Anisotropic thermal parameters	All non-hydrogen atoms
Isotropic thermal parameters	Hydrogen atoms
No. of refined parameters	309
Weighting scheme	$[\sigma^2(F_o^2) + (0.1693P)^2 + 62.76P]^{-1}$ , $P = (F_o^2 + 2F_c^2)/3$
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.0887 (2837 reflections)
$wR2 = [\sum w( F_o ^2 -  F_c ^2)^2 / \sum wF_o^4]^{1/2}$	0.3308 (4852 reflections)
$S = [\sum w( F_o ^2 -  F_c ^2)^2 / (N_{\text{obs}} - N_{\text{var}})]^{1/2}$	1.09
Final $(\Delta/\sigma)_{\text{max}}$	0.47
Final $\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}/e \text{ \AA}^{-3}$	–4.74 and 2.98 (both within 1 $\text{\AA}$ from Ir)

mentioned procedure, i.e. by using a stoichiometric or excess amount of tn, only led to a decrease in the amount of dichloro complexes formed or to a dark brown solution that contained a small amount of impure  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$ , which was difficult to purify.

Reaction of  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  with neat tn only led to the

Table 2. Final positional and thermal parameters (in Å<sup>2</sup>) for [Ir(tn)<sub>3</sub>][Co(CN)<sub>6</sub>] · 5H<sub>2</sub>O.<sup>a</sup>

Atom	x/a	y/b	z/c	U <sub>eq</sub> <sup>b</sup>
Ir	0.18971(14)	0.41508(12)	0.24827(6)	0.0301(3)
N1	0.086(2)	0.431(2)	0.1359(10)	0.026(5)
N2	0.427(3)	0.469(3)	0.2259(11)	0.038(7)
N3	-0.042(3)	0.373(3)	0.2741(12)	0.042(7)
N4	0.192(3)	0.185(2)	0.2361(12)	0.038(7)
N5	0.191(2)	0.644(2)	0.2631(13)	0.041(7)
N6	0.301(2)	0.398(2)	0.3614(10)	0.029(6)
C1	0.180(4)	0.397(3)	0.0803(13)	0.049(9)
C2	0.346(3)	0.476(3)	0.0878(15)	0.045(9)
C3	0.468(4)	0.427(4)	0.1548(17)	0.056(11)
C4	-0.163(3)	0.247(3)	0.2380(16)	0.050(9)
C5	-0.106(4)	0.101(3)	0.2457(16)	0.047(9)
C6	0.036(4)	0.087(3)	0.2021(16)	0.045(9)
C7	0.175(3)	0.707(3)	0.3358(16)	0.045(9)
C8	0.309(4)	0.662(3)	0.3985(15)	0.052(10)
C9	0.274(4)	0.499(3)	0.4184(13)	0.050(10)
Co1	0.000	0.000	0.5000	0.0320(17)
N7	0.255(4)	0.061(3)	0.4074(17)	0.057(10)
N8	0.205(3)	0.212(3)	0.6223(16)	0.064(10)
N9	0.130(3)	-0.269(3)	0.5709(14)	0.053(8)
C10	0.163(4)	0.045(3)	0.4450(15)	0.040(9)
C11	0.131(3)	0.135(3)	0.5775(14)	0.038(8)
C12	0.088(3)	-0.168(3)	0.5442(13)	0.034(7)
Co2	0.500	0.000	0.000	0.0309(17)
N10	0.772(4)	0.262(3)	0.0458(16)	0.083(11)
N11	0.722(4)	-0.204(4)	0.0824(17)	0.074(11)
N12	0.373(5)	0.038(4)	0.137(2)	0.089(15)
C13	0.665(3)	0.162(3)	0.0281(14)	0.037(8)
C14	0.639(3)	-0.129(3)	0.0516(16)	0.042(9)
C15	0.425(4)	0.023(3)	0.0879(16)	0.045(9)
O1	0.506(3)	0.811(3)	0.2452(13)	0.073(9)
O2	0.658(3)	0.474(3)	0.3724(12)	0.062(8)
O3	0.056(3)	0.746(2)	0.1018(13)	0.064(8)
O4	0.827(3)	0.662(2)	0.2265(12)	0.056(7)
O5 <sup>c</sup>	0.539(7)	0.047(8)	0.344(3)	0.085(12)
O5' <sup>c</sup>	0.527(8)	0.136(10)	0.340(4)	0.085(12)

<sup>a</sup>The [Ir(tn)<sub>3</sub>]<sup>3+</sup> coordinates explicitly given correspond to the Δ enantiomer. <sup>b</sup>U<sub>eq</sub> = 1/3Σ<sub>i</sub>Σ<sub>j</sub>U<sub>ij</sub>a<sub>i</sub><sup>\*</sup>a<sub>j</sub><sup>\*</sup>a<sub>i</sub> · a<sub>j</sub>. <sup>c</sup>The population factors for O(5) and O(5') are 0.56(7) and 0.44(7), respectively.

Table 3. Ir–N bond distances (in Å) and N–Ir–N chelate bond angles (in °) for [Ir(tn)<sub>3</sub>]<sup>3+</sup>.

Ir–N1	2.09(2)	N1–Ir–N2	91.5(7)
Ir–N2	2.11(3)	N3–Ir–N4	91.3(10)
Ir–N3	2.08(3)	N5–Ir–N6	90.9(8)
Ir–N4	2.09(2)		
Ir–N5	2.08(2)		
Ir–N6	2.12(2)		

separation of an orange oil. However, the presence of 3 mol of LiCl per mol of iridium did successfully cause precipitation of the desired [Ir(tn)<sub>3</sub>]Cl<sub>3</sub>. (Reaction with the ratio LiCl:Ir = 1.5:1 also resulted in the appearance of an orange oil). The formation of [Ir(tn)<sub>3</sub>]Cl<sub>3</sub> was very slow, and the shorter reaction time than that prescribed gave decreased yields (e.g. 45% yield by heating for two weeks).

[Rh(tn)<sub>3</sub>]Cl<sub>3</sub> was synthesized analogously to [Ir(tn)<sub>3</sub>]Cl<sub>3</sub>; however, a lower temperature and a shorter reaction time successfully gave a quantitative yield.

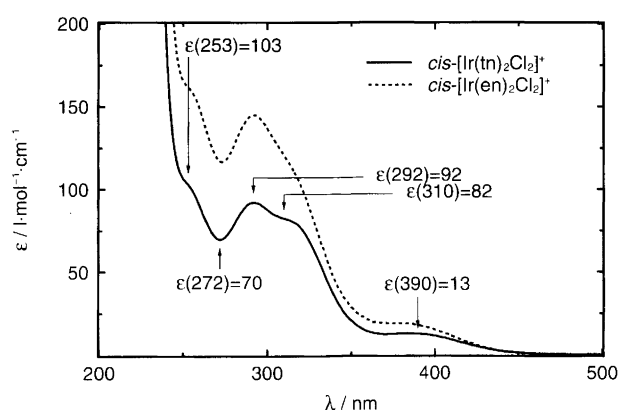


Fig. 1. Absorption spectra of *cis*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>CF<sub>3</sub>SO<sub>3</sub> and *cis*-[Ir(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>Cl · H<sub>2</sub>O in water.

**Configurational assignments.** The absorption spectra of *cis*- and *trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>CF<sub>3</sub>SO<sub>3</sub> are shown in Figs. 1 and 2, respectively. The geometric configurations of the two isomers were assigned by comparison with the

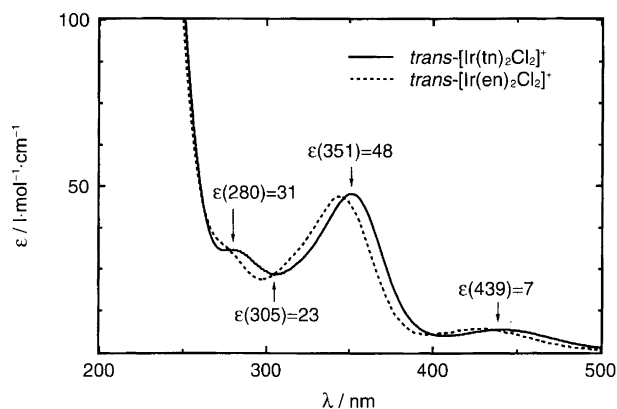


Fig. 2. Absorption spectra of  $\text{trans-[Ir(tn)}_2\text{Cl}_2\text{]CF}_3\text{SO}_3$  and  $\text{trans-[Ir(en)}_2\text{Cl}_2\text{]Cl} \cdot \text{H}_2\text{O}$  in water.

spectra of the analogous ethane-1,2-diamine (en) complexes (Ref. 3 and Figs. 1 and 2) and ammonia<sup>4</sup> complexes. These assignments are corroborated by the <sup>13</sup>C NMR spectra of *cis*- and *trans*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub>, which showed three and two resonances, respectively. The *cis* isomer has a C<sub>2</sub> axis that makes pairs of carbon atoms identical in a <sup>13</sup>C NMR spectrum. The *trans* isomer, on the other hand, has both a C<sub>2</sub> axis and a σ<sub>v</sub> mirror plane resulting in two inequivalent carbon atoms as in the free ligand. A similar <sup>13</sup>C NMR spectrum is, apart from the chemical shifts, observed for [Ir(tn)<sub>3</sub>]Cl<sub>3</sub> due to its pseudo-C<sub>3</sub> axis.

**Crystal structure.** The structure of [Ir(tn)<sub>3</sub>][Co(CN)<sub>6</sub>] · 5H<sub>2</sub>O consists of separate [Ir(tn)<sub>3</sub>]<sup>3+</sup> and [Co(CN)<sub>6</sub>]<sup>3-</sup> ions and water molecules linked together in a network of hydrogen bonds. In the [Co(CN)<sub>6</sub>]<sup>3-</sup> ion the Co–C bond lengths [av. 1.88(1) Å] and *cis* C–Co–C angles [in the range 88–93°] are quite ordinary and will not be discussed further. Figure 3 shows the iridium complex and Table 3 lists selected bond lengths and angles. The Ir–N bond lengths [av. 2.10(1) Å] are similar to those found in related compounds.<sup>6–8,14</sup> The six nitrogen atoms of the three tn ligands form an almost regular octahedral coordination sphere similar to that found<sup>15,16</sup> for [Co(tn)<sub>3</sub>]<sup>3+</sup>. While [Ir(tn)<sub>3</sub>]<sup>3+</sup> contains *six*-membered chelate rings, tris-bidentate complexes containing lesser flexible *five*-membered chelate rings, e.g. [M(en)<sub>3</sub>]<sup>3+</sup> (M = Co<sup>III</sup>, Rh<sup>III</sup> and Ir<sup>III</sup>), show much larger deviations from regular octahedral geometry, for example, in the form of a trigonal twist.<sup>17–19</sup>

The composition of the crystal was that of a racemate with Δ-[Ir(tn)<sub>3</sub>]<sup>3+</sup> and Λ-[Ir(tn)<sub>3</sub>]<sup>3+</sup> connected by the inversion symmetry. In Fig. 3 the Λ configuration is shown viewed down the octahedral pseudo-threefold axis. The three chelate rings all adopt the stable chair conformation. However, while two of the chair conformers fold in the same rotational direction, the third folds in the opposite direction, and the resulting overall symmetry is C<sub>1</sub>. The conformation of [Ir(tn)<sub>3</sub>]<sup>3+</sup> may therefore be described as (C<sub>1</sub>)-*chair*<sub>3</sub> (nomenclature of

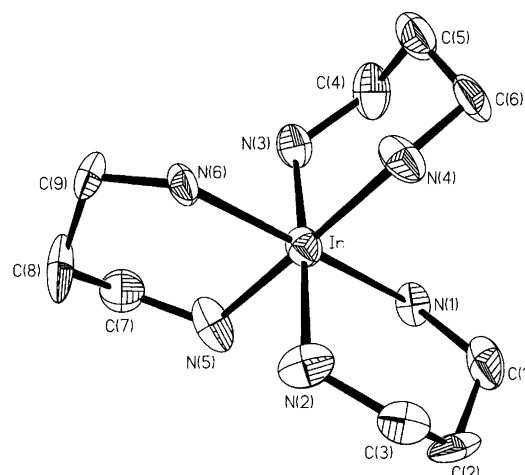


Fig. 3. Drawing<sup>13</sup> of the Λ-[Ir(tn)<sub>3</sub>]<sup>3+</sup> cation as viewed down a pseudo-threefold axis. All three six-membered chelate rings adopt a chair conformation but they fold differently. The overall conformation is (C<sub>1</sub>)-*chair*<sub>3</sub> (Refs. 20 and 21) or Λ*ppa* (Refs. 22 and 23).

Niketić and Woldbye)<sup>20,21</sup> or Λ*ppa* (Jurnak and Raymond).<sup>22,23</sup>

Sixteen different conformations are possible for each of the two optical isomers of a [M(tn)<sub>3</sub>]<sup>n+</sup> complex.<sup>20–22</sup> So far, five tris tn crystal structures are known for the robust metal ions chromium(III), cobalt(III) and iridium(III). In [Co(tn)<sub>3</sub>]Br<sub>3</sub> · H<sub>2</sub>O<sup>15</sup> and [Co(tn)<sub>3</sub>]Cl<sub>3</sub> · H<sub>2</sub>O<sup>16</sup> the conformation is (C<sub>3</sub>)-*chair*<sub>3</sub>, whereas the conformation in Co(tn)<sub>3</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · 2H<sub>2</sub>O<sup>24</sup> is *lel*<sub>3</sub>. In the chromium(III) compound [Cr(tn)<sub>3</sub>][Ni(CN)<sub>5</sub>] · 2H<sub>2</sub>O<sup>22,23</sup> the conformation is *syn-chair*<sub>2</sub>*lel* and in the present iridium(III) compound the conformation (C<sub>1</sub>)-*chair*<sub>3</sub> is found. Even though the presence of a particular conformation is likely to depend on the energy in the crystal lattice, e.g. hydrogen bonds, it is noticed that the conformations encountered are all among the most stable ones according to force-field calculations<sup>21</sup> performed after the appearance of the crystal structure of [Cr(tn)<sub>3</sub>][Ni(CN)<sub>5</sub>] · 2H<sub>2</sub>O.<sup>22,23</sup>

**Spectral properties.** The ligand-field absorption spectra of the present [Ir(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes are, as far as band energies and shapes are concerned, very similar to those of the analogous ethane-1,2-diamine<sup>3</sup> (cf. Figs. 1 and 2) and ammine<sup>4</sup> complexes. However, *cis*-[Ir(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> shows a higher molar absorptivity than *cis*-[Ir(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> and *cis*-[Ir(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>. A similar variation of the molar absorptivities is observed for the corresponding rhodium(III) complexes.<sup>25</sup> Whereas the *trans* isomers show similar intensities for all three complexes, the intensity order for the *cis* complexes is [Rh(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> > [Rh(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ≈ [Rh(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>. This is most likely due to a more rigid structure of the five-membered chelate ring in the *cis*-en complex than of the six-membered ring in the *cis*-tn complex, which makes a larger deviation from regular octahedral geometry in the *cis*-en complex likely.

The spectrum of  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$  is shown in Fig. 4. In accordance with previous work,<sup>26</sup> the two absorption bands at 251 ( $3.98 \mu\text{m}^{-1}$ ) and 224 nm ( $4.46 \mu\text{m}^{-1}$ ) are assigned as the two spin-allowed transitions  ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$ , respectively. The absorption at the low-energy foot of the first spin-allowed band is due to singlet  $\rightarrow$  triplet transitions that are relatively intense because of the large spin-orbit coupling of iridium(III).

*Gaussian resolution and ligand-field analysis of  $[\text{M}(\text{tn})_3]^{3+}$  ( $M = \text{Co}, \text{Rh}, \text{Ir}$ ) spectra.* Based on Gaussian resolution of the UV/VIS absorption spectra we have in a previous paper<sup>26</sup> discussed the variation of the spectrochemical parameter,  $\Delta = E(e_g) - E(t_{2g})$ , among complexes of the type  $[\text{M}^{\text{III}}(\text{N}_6)]^{3+}$  ( $\text{M}^{\text{III}} = \text{Co}, \text{Rh}$  and  $\text{Ir}$ ;  $\text{N}_6 = (\text{NH}_3)_6, (\text{en})_3, (\text{chxn})_3$  and  $(\text{tacn})_2$ }, ( $\text{chxn} = \text{trans-cyclohexane-1,2-diamine}$  and  $\text{tacn} = 1,4,7\text{-triazacyclononane}$ ). The new synthetic work of the present paper now allows us to extend this discussion with  $[\text{M}(\text{tn})_3]^{3+}$  complexes (cf. Figs. 4 and 5).

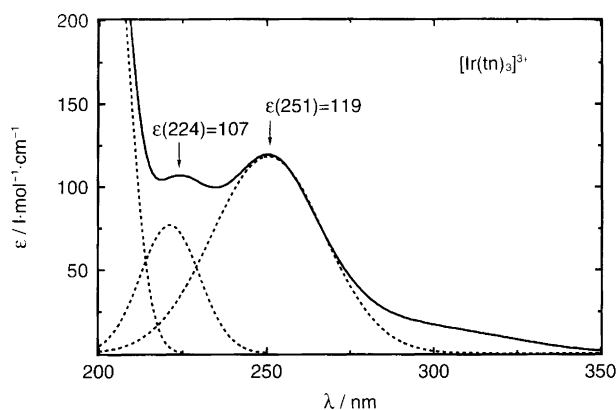


Fig. 4. Absorption spectrum of  $[\text{Ir}(\text{tn})_3]\text{Cl}_3$  in water and its Gaussian decomposition. The Gaussian fit was only optimized in the wavelength interval 205–269 nm, thus avoiding the problem of representing the spin-forbidden absorption bands by separate Gaussian functions.

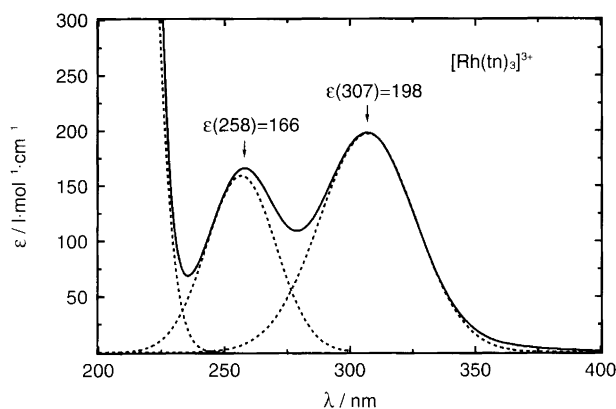


Fig. 5. Absorption spectrum of  $[\text{Rh}(\text{tn})_3]\text{Cl}_3$  in water and its Gaussian decomposition. The spectral minima are  $\epsilon(279) = 109$  and  $\epsilon(235) = 69$ . The Gaussian fit was optimized in the wavelength interval 230–337 nm.

Table 4 give the results of Gaussian resolution of the  $[\text{M}(\text{tn})_3]^{3+}$  complexes. Also given is the  $d^6$  model parameters<sup>27</sup> calculated on the basis of the Gaussian transition energies. The parameter  $\Delta/\Delta(\text{NH}_3)$  is particularly interesting as, for a given metal ion, it measures the field strength exerted by the  $(\text{tn})_3$  ligand sphere relative to that of the  $(\text{NH}_3)_6$  sphere. It was previously<sup>26</sup> found, with the exception of  $[\text{Co}(\text{chxn})_3]^{3+}$ , that  $\Delta/\Delta(\text{NH}_3)$  varies as  $\text{NH}_3 < \text{chxn} < \text{en} < \text{tacn}$  irrespective of the metal ion ( $\text{Co}^{\text{III}}, \text{Rh}^{\text{III}}$  or  $\text{Ir}^{\text{III}}$ ). The variation of  $\Delta/\Delta(\text{NH}_3)$  was thus  $\text{NH}_3 < \text{primary amine} < \text{secondary amine}$ , and this was interpreted<sup>26</sup> as reflecting the variation in the gas phase basicities of the amine ligands. The low value of  $\Delta/\Delta(\text{NH}_3)$  for  $[\text{Co}(\text{chxn})_3]^{3+}$  (cf. Fig. 6) was explained<sup>26</sup> as being due to steric crowding: The relative bulkiness of the  $\text{chxn}$  ligand is likely to result in somewhat elongated metal–nitrogen bonds, especially around small metal ions such as  $\text{Co}^{3+}$ . This in turn results in an effective donor strength of the ligand, expressed in terms of  $\Delta$ , which is less than what would be expected on the basis of the ligand's inherent basicity.

The trends seen in Fig. 6 for the  $\text{tn}$  complexes may be explained in similar terms to the  $[\text{Co}(\text{chxn})_3]^{3+}$  anomaly above: Whereas the other primary amines have five-membered chelate rings,  $\text{tn}$  has a six-membered chelate ring. This would tend to make steric crowding in  $\text{tn}$  complexes more pronounced. The  $\Delta/\Delta(\text{NH}_3)$  values of the  $\text{tn}$  complexes are accordingly in all cases smaller than those of the  $\text{chxn}$  and  $\text{en}$  complexes, and this is particularly pronounced for  $[\text{Co}(\text{tn})_3]^{3+}$  due to the small ionic radius<sup>27</sup> of  $\text{Co}^{3+}$  ( $R(\text{Co}^{3+}) = 0.55 \text{ \AA}$ ,  $R(\text{Rh}^{3+}) = 0.67 \text{ \AA}$  and  $R(\text{Ir}^{3+}) = 0.68 \text{ \AA}$ ).

The relative inaccuracy of metal–nitrogen bond lengths determined by X-ray crystallography makes it difficult to assess bond length elongation by this technique. The average  $\text{Ir}-\text{N}$  distances found in  $[\text{Ir}(\text{tn})_3]^{3+}$  ( $2.10(1) \text{ \AA}$ ),  $[\text{Ir}(\text{chxn})_3]^{3+}$  [ $2.093(6) \text{ \AA}$  for  $\text{ob}_3$  and  $2.087(6) \text{ \AA}$  for  $\text{lel}_3$ ],<sup>14</sup> and  $[\text{Ir}(\text{en})_3]^{3+}$  [ $2.081(8) \text{ \AA}$ ]<sup>19</sup> do, however, show the same trend as the  $\Delta$  values (cf. Fig. 6). The statistical significance of this correlation is, however, questionable.

Table 4. Energies of the  $d^6$  ligand-field transitions  ${}^1A_{1g} \rightarrow {}^1T_{1g}(E_1)$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}(E_2)$  obtained by Gaussian analysis of the UV/VIS spectra of  $[\text{M}(\text{tn})_3]^{3+}$  complexes (cf. Figs. 4 and 5), and corresponding calculated  $d^6$  model parameter values [Spectrochemical parameter  $\Delta = E(e_g) - E(t_{2g})$  measuring the  $d$  orbital splitting and Racah interelectronic repulsion parameter  $B$  (assuming  $C = 4B$ )].<sup>a</sup>

	$E_1/\mu\text{m}^{-1}$	$E_2/\mu\text{m}^{-1}$	$\Delta/\mu\text{m}^{-1}$	$B/\mu\text{m}^{-1}$	$\Delta/\Delta_{\text{NH}_3}$
$[\text{Co}(\text{tn})_3]^{3+}$	2.041 <sup>b</sup>	2.849 <sup>b</sup>	2.203	0.0597	0.963
$[\text{Rh}(\text{tn})_3]^{3+}$	3.257	3.897	3.395	0.0430	0.993
$[\text{Ir}(\text{tn})_3]^{3+}$	3.993	4.522	4.111	0.0347	1.004

<sup>a</sup>For details about the way the analysis was made, see Ref. 26. <sup>b</sup>The well separated  $\text{Co}^{\text{III}}$  bands makes Gaussian analysis unnecessary and the band energies given are those of the directly observed maxima (cf. Ref. 26).

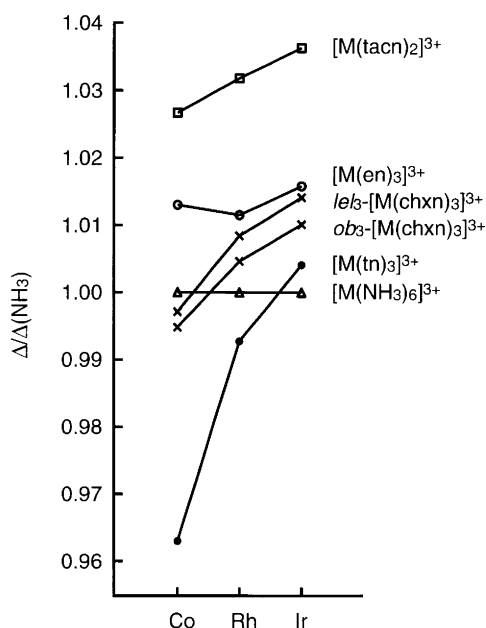


Fig. 6. Variation of the  $d^6$  model spectrochemical parameter  $\Delta = E(e_g) - E(t_{2g})$  determined on the basis of Gaussian resolutions of the ligand-field spectra. Values of  $\Delta$  have for each metal ion been normalized relative to  $\Delta$  of the  $[\text{M}(\text{NH}_3)_6]^{3+}$  complex. The general trend in  $\Delta/\Delta(\text{NH}_3)$  is  $\text{NH}_3 < \text{primary amine (tn, chxn, en)} < \text{secondary amine (tacn)}$ . However, for the sterically bulky amine ligands chxn and tn lower than expected  $\Delta/\Delta(\text{NH}_3)$  values are sometimes found. This may be explained in terms of M–N bond elongation, which leads to a decrease in  $\Delta$ .

## Conclusion

Attempts to prepare iridium(III) complexes of propane-1,3-diamine (tn) by using a method similar to that previously used for the preparation of rhodium(III) tn complexes<sup>25</sup> and iridium(III) complexes with ammonia<sup>4</sup> or ethane-1,2-diamine<sup>3</sup> complexes were not successful due to reduction of iridium(III) to iridium metal. However, when as in the preparation of cyclam complexes<sup>5</sup> of iridium(III),  $\text{Ir}(\text{thtp})_3\text{Cl}_3$  was used as starting material, tn complexes were obtained in reasonably good yield.

The two geometrical isomers *cis*- and *trans*- $[\text{Ir}(\text{tn})_2\text{Cl}_2]^+$  were separated by fractional crystallization of the triflate salts and their structural assignments were made from their ligand field and NMR spectra. The crystal structure of  $[\text{Ir}(\text{tn})_3][\text{Co}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$  established the identity of the tris-complex and showed the conformations of the six-membered chelate rings to be ( $C_1$ )-*chair*<sub>3</sub>.

On the basis of Gaussian resolution of the  $[\text{Ir}(\text{tn})_3]^{3+}$  electronic solution spectrum, the spectrochemical parameter  $\Delta = E(t_{2g}) - E(e_g) = 4.11 \mu\text{m}^{-1}$  has been determined. Its value is compared to those found for other homoleptic  $[\text{M}(\text{N}_6)]^{3+}$  ( $\text{M} = \text{Co}^{\text{III}}$ ,  $\text{Rh}^{\text{III}}$  and  $\text{Ir}^{\text{III}}$ ) complexes and for  $[\text{Co}(\text{tn})_3]^{3+}$  and  $[\text{Rh}(\text{tn})_3]^{3+}$  in particular.  $[\text{M}(\text{tn})_3]^{3+}$  complexes are found always to have smaller  $\Delta$  values than the corresponding  $[\text{M}(\text{en})_3]^{3+}$  ( $\text{en} = \text{ethane-}$

1,2-diamine) or  $[\text{M}(\text{chxn})_3]^{3+}$  (*trans*-cyclohexane-1,2-diamine) complexes. This is ascribed to the steric bulk of the tn ligand which has the potential of causing elongation of the metal–nitrogen bonds.

*Acknowledgement.* We thank Dr. Lene Mønsted for recording of the NMR spectra.

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Received December 12, 1997.