

Available online at www.sciencedirect.com



POLYHEDRON

Polyhedron 23 (2004) 2725-2731

Incorporation of polybasic aromatic amines into ruthenium(II) chloro complexes

Benjamin G. Harvey, Atta M. Arif, Richard D. Ernst *

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, UT 84112-0850, USA

Received 20 April 2004; accepted 14 May 2004 Available online 15 July 2004

Abstract

The reactions of $\text{RuCl}_2[P(C_6H_5)_3]_3$ with excesses of various aromatic amines led to six coordinate, pseudo-octahedral complexes. Thus, three equivalents of pyridazine or 3-methylpyridazine could be incorporated, or two equivalents of pyrazole or phthalazine, all as monodentate ligands. Reaction with 1,8-naphthyridine led to the incorporation of one bidentate ligand. X-ray structural data were obtained for the pyridazine, phthalazine and 1,8-naphthyridine complexes. © 2004 Elsevier Ltd. All rights reserved.

1. Introduction

The chemistry involving ruthenium complexes of aromatic amines such as pyridine, 2,2-bipyridine and pyrazine has been remarkably productive, yielding important contributions in a number of areas, including mixed valence compounds and photochemistry [1]. However, in the vast majority of these compounds, the ligand complements do not allow for direct Ru-Ru interactions, although these may easily be generated using a number of other ligands, such as the relatively simple acetate ion and various analogues [2]. We have therefore undertaken the preparations of ruthenium complexes containing aromatic polyamine ligands which could potentially lead to complexes with direct metal-metal interactions. In this study, we have examined reactions of $RuCl_2[P(C_6H_5)_3]_3$ with several relatively simple aromatic diamines, including pyridazine (1), 3-methylpyridazine (2), phthalazine (3), pyrazole (4) and 1,8naphthyridine (5).

* Corresponding author. Tel.: +8015818639.

E-mail address: ernst@chem.utah.edu (R.D. Ernst).



2. Experimental

All reactions were carried out under an atmosphere of nitrogen, using Schlenk techniques and apparatus. Solvents were dried and deoxygenated by distillation from CaH₂ (for CH₂Cl₂) or sodium benzophenone ketyl or by passing through columns of activated alumina, under a nitrogen atmosphere in each case. RuCl₂[P(C₆H₅)₃]₃ was prepared by a published procedure [3], while the diamines were all obtained from commercial sources. Elemental analyses were obtained from E&R Microanalytical Laboratories. NMR spectra were obtained as previously described [4].

2.1. Dichlorotris(pyridazine)(triphenylphosphine)ruthenium, $RuCl_2[P(C_6H_5)_3](C_4N_2H_4)_3$ (6)

To a magnetically stirred yellow-brown slurry of 1.0 g (1.0 mmol) RuCl₂(PPh₃)₃ in 20 ml THF were added 0.40 ml (5.5 mmol) of pyridazine via syringe. The solution rapidly changed color to a bright orange-red. The flask was swirled several times until all solids dissolved and then it was left undisturbed for 18 h. After several hours, bright red crystals began to precipitate from the solution. These crystals were isolated by removing the supernatant, washing with two 20 ml and one 10 ml portions of ether, and drying in vacuo. 0.56 g of product were isolated, corresponding to a yield of 80%. Monoclinic crystals suitable for a single crystal X-ray diffraction study were grown by layering a solution of the compound in CH₂Cl₂ with an equal volume of hexane. A similar procedure using a more concentrated solution led to orthorhombic crystals (space group *Pbca*, a = 10.2872(3), b = 23.6429(12), c = 33.5918(17) A at 293(1) K), having a higher solvent content, and yielding a similar, but less satisfactory, structural result.

¹H NMR (CD₂Cl₂ ambient): δ 10.74 (dt, 2H, H(1,9), J = 5.7, 1.4 Hz), 8.81 (dt, 1H, H5, J = 6.0, 1.4 Hz), 8.33 (m, 3H, H(4,8,12)), 7.55 (tt, 6H, H_o(PPh₃), J = 8.1, 1.2Hz), 7.43 (ddd, 2H, H(2,10), J = 8.1, 7.1, 2.1 Hz), 7.22 (ddd, 2H, H(3,11), J = 8.0, 6.5, 1.6 Hz), 7.12 (tq, 3H, H_p(PPh₃), J = 7.4, 1.5 Hz), 6.97 (td, 6H, H_m(PPh₃), J = 7.7, 1.8 Hz), 6.90 (ddd, 1H, H7, J = 8.0, 4.9, 1.5Hz), 6.45 (ddd, 1H, H6, J = 8.1, 6.0, 2.1 Hz).

Anal. Calc. for $C_{30}H_{27}Cl_2PN_6Ru$: C, 53.42; H, 4.03; N, 12.46. Found: C, 53.77; H, 4.02; N, 12.13%.

2.2. $Dichlorotris(3-methylpyridazine)(triphenylphos-phine)ruthenium, RuCl_2[P(C_6H_5)_3](3-CH_3C_4N_2H_3)$

To a stirred yellow-brown slurry of 0.50 g (0.52 mmol) RuCl₂(PPh₃)₃ in 20 ml of THF under nitrogen at ambient temperature were added 0.25 g (2.7 mmol) of 3-methylpyridazine via syringe. The reaction mixture rapidly converted to a bright red solution and was stirred overnight. After ca. 18 h, 50 ml of hexane were added with stirring to precipitate the product. The bright red-orange precipitate was collected on a medium frit, washed with 3×10 ml ether, and dried in vacuo. Yield: 285 mg, 75%.

¹H NMR (CDCl₃ ambient): δ 10.74 (d, 2H, H_o-Mepyd, J = 5.7 Hz), 8.52 (d, 1H, H_o-Mepyd, J = 5.7 Hz), 7.66 (t, 6H, H_m-PPh₃, J = 8.4 Hz), 7.26 (dd, 2H, H_m-Mepyd, J = 7.8, 6.0 Hz), 7.09 (t, 3H, H_p-PPh₃, J = 6.9 Hz), 7.02–6.90 (m, 8H, H_o-PPh₃ and H_p-Mepyd), 6.68 (d, 1H, H_p-Mepyd, J = 7.8 Hz), 6.48 (dd, 1H, H_m-Mepyd, J = 7.8, 6.0 Hz), 2.09 (s, 6H, Me), 1.90 (s, 3H, Me).

Anal. Calc. for C₃₃H₃₃PCl₂N₆Ru: C, 55.31; H, 4.64; N, 11.73. Found: C, 55.22; H, 4.53; N, 11.51%.

2.3. Dichlorobis(phthalazine)bis(triphenylphosphine)ruthenium, $RuCl_2[P(C_6H_5)_3]_2(C_8N_2H_6)_2$ (7)

To a stirred yellow-brown slurry of 0.50 g (0.52 mmol) RuCl₂(PPh₃)₃ in 20 ml THF under nitrogen at ambient temperature were added 0.15 g (1.1 mmol) of phthalazine as a solid. The mixture rapidly converted to a bright orange slurry. After 2 h of stirring, 50 ml of hexane were added and the reaction mixture was stirred for an additional 10 min. The resulting bright orange precipitate was collected on a medium frit, washed with 3×10 ml ether and dried in vacuo. The yield is virtually quantitative, with typical isolated yields greater than 90%. Crystals suitable for diffraction studies were grown in a closed system by slow diffusion of ether vapors into a concentrated CH₂Cl₂ solution of the product. A general description of a similar apparatus has been presented [5]; in this application, a solution of the complex was placed in one side and some ether was placed in the other side, thus leading to vapor phase transfer of each solvent to the other side. In other cases, simple evaporation of one solvent may be achieved by placing diphenylmethane in the other side.

Anal. Calc. for C₅₂H₄₂P₂Cl₂N₄Ru: C, 65.27; H, 4.42; N, 5.86. Found: C, 65.23; H, 4.82; N, 5.41%.

2.4. Dichloro(1,8-naphthyridine)bis(triphenylphosphine)ruthenium, $RuCl_2[P(C_6H_5)_3]_2(1,8-C_8N_2H_6)$ (**8**)

To a stirred yellow-brown slurry of 0.50 g (0.52 mmol) RuCl₂(PPh₃)₃ in 20 ml of THF under nitrogen at ambient temperature were added 80 mg (0.61 mmol) of 1,8-naphthyridine as a solid. A rapid color change to bright purple was followed by the precipitation of a purple solid. After stirring for approximately 10 min, the supernatant appeared virtually colorless. The purple precipitate was collected on a medium frit, washed with 3×10 ml ether and dried in vacuo. Yields for this reaction appeared quantitative, with isolated yields typically above 90%. Crystals suitable for diffraction studies were grown in a Schlenk tube by carefully layering hexane onto a concentrated solution of the compound in CH₂Cl₂.

Anal. Calc. for C₄₄H₃₆P₂Cl₂N₂Ru: C, 63.93; H, 4.39; N, 3.39. Found: C, 63.85; H, 4.53; N, 3.18%.

2.5. Dichlorobis(pyrazole)bis(triphenylphosphine)ruthenium, $RuCl_2[P(C_6H_5)_3]_2(C_3N_2H_4)_2$ (9)

To a magnetically stirred slurry of 0.50 g (0.52 mmol) RuCl₂(PPh₃)₃ in 20 ml THF were added 0.10 g (1.5 mmol) of pyrazole. A rapid color change to red was observed, followed by a slower (2–3 min) transition to yellow. The color change to yellow occurred much more rapidly if a large excess of pyrazole was used. The solution was stirred for 18 h and the solvent removed in

vacuo to yield a thick yellow oily solid. The solid was washed with 3×10 ml pentane and dried in vacuo. The powdery residue was extracted with 3×10 ml CH₂Cl₂ and filtered through a coarse frit with a Celite pad. The bright yellow filtrate was concentrated to ca. 10 ml and carefully layered with 50 ml hexane. After the flask had been left undisturbed for 24 h, yellow crystals were deposited on the sides of the flask. The supernatant was removed and the crystals were washed with 3×10 ml ether and dried in vacuo. 0.370 g of product were isolated, corresponding to a yield of 85%. Solutions of the product rapidly turn green upon exposure to air.

¹H NMR (chloroform-d₁, ambient): δ 11.70 (s, 2H, N–H), 8.13 (t, 4H, py–H(2,4), J = 1.5 Hz), 7.35 (t, 12H, H_o(PPh₃), J = 8.3 Hz), 7.17 (t, 6H, H_p(PPh₃), J = 7.4 Hz), 7.00 (q, 12H, H_m(PPh₃), J = 7.0 Hz), 5.94 (q, 2H, py–H3, J = 2.2 Hz).

Anal. Calc. for C₄₂H₃₈Cl₂P₂N₄Ru: C, 60.58; H, 4.60; N, 6.73. Found: C, 60.49; H, 4.76; N, 6.49%.

2.6. Crystallographic studies

Single crystals for X-ray diffraction study were fixed to glass fibers using Paratone oil and thereafter transferred to a Nonius Kappa CCD diffractometer for study. Structures were solved using direct method programs provided in the $s_{IR}-97$ or $s_{HELXL}-97$ program packages. All non-hydrogen atoms were subjected to anisotropic refinement. For **6**, the hydrogen atoms were refined isotropically, including those in a molecule of solvent CH_2Cl_2 . It can be noted that crystals having a higher CH_2Cl_2 content could also be obtained (see Section 2.1), but the solvent was poorly behaved, and a less satisfactory structure was obtained. The hydrogen atoms in 7 were also refined isotropically, except for those associated with the solvent molecules. These atoms were allowed to ride on their respective carbon atoms. Two CH_2Cl_2 molecules, one of half occupancy, were incorporated into this lattice. For 8, all but one hydrogen atom, H44, could be refined isotropically. That one was refined with a fixed thermal parameter. A summary of crystal and data collection parameters is given in Table 1, while pertinent bonding parameters for 6-8 are listed in Tables 2–4.

3. Results and discussion

The reactions of $RuCl_2[P(C_6H_5)_3]_3$ with excesses of pyridazine, 3-methylpyridazine, phthalazine, pyrazole and 1,8-naphthyridine in each case led to a six-coordinate ruthenium(II) complex, as summarized in Scheme 1. The reactions involving pyridazine or 3-methylpyridazine resulted in the incorporation of three equivalents of the ligand, together with expulsion of two phosphine ligands. In contrast, the reactions with phthalazine, pyrazole or 1,8-naphthyridine brought about the loss of only one phosphine ligand, leading only to the incorporation of two phthalazines, two pyrazoles or one (chelating) 1,8-naphthyridine ligand(s). The constitutions of these complexes have been established through analytical data, NMR spectroscopy when solubility permitted, and for 6-8, through single crystal X-ray diffraction studies. In each case where meaningful

Table 1

Crystallographic parameters for RuCl ₂	$_{2}[P(C_{6}H_{5})_{3}](C_{4}N_{2}H_{4})_{3}, R$	$uCl_2[P(C_6H_5)_3]_2(C_8N_2H_6)_2,$	and RuCl ₂ [P(C ₆ H ₅) ₃] ₂ (1,8-C ₈ N ₂ H ₆)
---	---	--------------------------------------	--

Empirical formula	C31H29Cl4N6PRu	$C_{53.5}H_{45}Cl_5N_4P_2Ru$	$C_{44}H_{36}Cl_2N_2P_2Ru$
Formula weight	759.44	1084.19	826.66
Temperature (K)	150(1)	150(1)	200(1)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	$\underline{P}2_1/\underline{c}$	<u>P</u> 1	<u>P</u> 1
Unit cell dimensions			
a (Å)	15.5365(3)	11.7277(1)	11.3392(3)
b (Å)	11.7054(3)	13.8433(2)	12.4477(3)
<i>c</i> (Å)	17.4477(3)	17.2485(3)	13.5955(4)
α (°)	90	87.2876(6)	90.0120(12)
β (°)	93.8557(13)	74.6044(6)	82.0268(12)
γ (°)	90	65.5332(10)	74.1443(11)
Volume (Å ³)	3165.87(12)	2451.10(6)	1826.64(8)
Ζ	4	2	2
$D_{ m calc}$	1.593	1.469	1.503
Absorption coefficient (cm ⁻¹)	9.17	6.99	6.99
θ Range (°)	3.8–27.5	3.5–27.5	2.5-27.9
Limiting indices	$-20 \leqslant h \leqslant 20,$	$-14 \leqslant h \leqslant 15,$	$-14 \leqslant h \leqslant 14,$
	$-14 \leqslant k \leqslant 15, \ -22 \leqslant l \leqslant 22$	$-17 \leq k \leq 17, -19 \leq l \leq 22$	$-16 \leqslant k \leqslant 15, \ -15 \leqslant l \leqslant 17$
Reflections collected	12360	17109	12433
Independent reflections; $n: I > n(I)$	7235; 2	10929; 2	8467; 2
R(F)	0.0289	0.0437	0.0469
$R_{\rm w}(F^2)$	0.0594	0.1052	0.0858
Maximum/minimum difference Fourier peak (eÅ ³)	0.41/-0.65	2.07/-1.29	0.64/-0.94

Table 2 Pertinent bonding parameters for $RuCl_2[P(C_6H_5)_3](C_4N_2H_4)_3$ (6)

Bond distances	(Å)		
Ru–N1	2.0760(17)	Ru–P1	2.2976(5)
Ru–N3	2.0735(17)	Ru–Cl1	2.4309(5)
Ru–N5	2.0604(16)	Ru–Cl2	2.4665(5)
Bond angles (°,)		
N1-Ru-N3	93.51(7)	N3–Ru–N5	87.33(7)
N1-Ru-N5	175.72(7)	N3–Ru–P1	97.06(5)
N1–Ru–P1	92.85(5)	N3–Ru–Cl1	172.44(5)
N1-Ru-Cl1	89.45(5)	N3-Ru-Cl2	85.56(5)
N1-Ru-Cl2	85.83(5)	P1-Ru-Cl1	89.73(2)
N5-Ru-P1	91.22(5)	P1-Ru-Cl2	177.14(2)
N5-Ru-Cl1	89.22(5)	Cl1-Ru-Cl2	87.72(2)
N5-Ru-Cl2	90.05(5)	Ru-P1-C19	115.48(7)
Ru-P1-C13	118.82(7)	Ru-P1-C25	116.23(7)

Table 3

Pertinent bonding parameters for $RuCl_2[P(C_6H_5)_3]_2(C_8N_2H_6)_2$ (7)

Bond distances	(Å)		
Ru–P1	2.4085(7)	Ru–P2	2.3855(7)
Ru–Cl1	2.4421(7)	Ru–Cl2	2.4661(7)
Ru–N1	2.055(2)	Ru–N2	2.057(2)
Bond angles (°)			
N1–Ru–N3	89.16(9)	N3–Ru–P1	95.80(7)
N1–Ru–P1	86.16(7)	N3–Ru–P2	88.17(7)
N1-Ru-P2	94.36(7)	N3-Ru-Cl1	177.21(7)
N1-Ru-Cl1	89.24(7)	N3-Ru-Cl2	87.70(7)
N1-Ru-Cl2	176.22(7)	P1-Ru-P2	176.01(3)
P1-Ru-Cl1	86.37(2)	P2-Ru-Cl1	89.67(2)
P1-Ru-Cl2	92.06(3)	P2-Ru-Cl2	87.65(3)
Cl1-Ru-Cl2	93.98(2)	Ru-P2-C35	112.79(9)
Ru-P1-C17	116.47(10)	Ru-P2-C41	116.23(10)
Ru-P1-C23	112.85(10)	Ru-P2-C47	120.68(10)
Ru-P1-C29	119.76(10)		

Table 4

Pertinent bonding parameters for $RuCl_2[P(C_6H_5)_3]_2(1,8-C_8N_2H_6)$ (8)

Bond distances (A)			
Ru–P1	2.2819(7)	Ru–P2	2.3040(8)
Ru–Cl1	2.4242(9)	Ru–Cl2	2.4050(9)
Ru–N1	2.217(3)	Ru–N2	2.222(2)
Bond angles (°))		
N1-Ru-N2	60.81(9)	N2-Ru-P1	160.60(7)
N1–Ru–P1	100.96(7)	N2–Ru–P2	101.17(7)
N1-Ru-P2	161.41(7)	N2-Ru-Cl1	86.35(8)
N1-Ru-Cl1	80.95(7)	N2-Ru-Cl2	81.53(7)
N1-Ru-Cl2	85.27(7)	P1-Ru-P2	97.45(3)
P1-Ru-Cl1	97.77(3)	P2-Ru-Cl1	94.09(3)
P1-Ru-Cl2	90.87(3)	P2-Ru-Cl2	97.06(3)
Cl1-Ru-Cl2	164.89(3)	Ru–P1–C9	108.74(9)
Ru–N1–C1	148.6(2)	Ru-P1-C15	125.39(11)
Ru–N1–C8	94.3(2)	Ru-P1-C21	117.42(10)
Ru–N2–C8	94.1(2)	Ru-P2-C27	106.79(11)
Ru–N2–C7	148.8(2)	Ru-P2-C33	124.08(10)
		Ru–P2–C39	119.71(10)

NMR data could be recorded, the spectral results were indicative of the presence of only one isomer, which was also consistent with the structural results.

The product of the reaction with excess pyridazine was found to adopt a mer, cis arrangement of ligands in a pseudooctahedral coordination environment (6). Fig. 1. A similar structure can be assumed for the 3-methylpyridazine complex, and this would be consistent with the NMR results which revealed two types of amine ligands in a 2:1 ratio. As would be expected, there is some evidence of inter-ligand steric repulsion involving the phosphine ligand, as the P-Ru-N angles all exceed 90° $(91.22(5)-97.06(5)^{\circ})$, thereby leading to generally acute N-Ru-Cl2 angles $(85.56(5)-90.05(5)^{\circ})$. While other angles also deviate from their ideal values, the presence of six aromatic rings in the complex can be expected to result in C–H/ π [6] and/or π/π [7] interactions, whether intramolecular or intermolecular [8], which could play an even larger role than the steric effects and therefore complicate further comparisons.

Although there seem to be no other examples of structurally characterized ruthenium complexes containing both phosphine and the simple pyridazine ligands, and just a few for transition metals generally [9], some comparisons may be made with various more common poly(amine) species. Thus, the Ru-N distances of 2.060(2)-2.076(2) A in 6 are similar to values of 2.049(2) and 2.084(3) Å in neutral pyridyl-substituted pyridazine complexes [10], as well as to those in a mixed valence Ru(II,III) complex [11], but longer than those in related cationic species (1.986(10)-2.031(7) A) [12], and shorter than Ru-N bonds in trimetallic carbonyl complexes in which pyridazine coordinates to two adjacent ruthenium(0) centers (2.11(1)-2.136(4) Å) [13]. Likewise, the Ru-Cl distances of 2.4309(5) and 2.4665(5) A are reasonably similar to values ranging from 2.392(1) to 2.431(1) A in the related cationic or carbonyl-containing complexes. The Ru–P distance of 2.2976(5) A may be compared to values in the range of 2.23–2.44 A found for two modifications of $RuCl_2[P(C_6H_5)_3]_3$ [14].

Notably, the reaction of $RuCl_2[P(C_6H_5)_3]_3$ with phthalazine led only to the incorporation of two equivalents of ligand, rather than three. As the resulting $RuCl_2[P(C_6H_5)_3]_2(C_8H_6N_2)_2$ complex contains an extra phosphine ligand compared to 6, the additional steric crowding may block access of a third amine ligand to the metal center; alternatively it could be that the lower solubility of this complex compared to its hypothetical pyridazine analogue led to 7's precipitation before a third incorporation could take place. Consequently, it could be possible to bring about the third incorporation using other solvents and/or more forcing conditions. A structural determination revealed the complex to have a cis, trans, cis pseudooctahedral geometry (Fig. 2), so the chloride ligands have remained cis to each other. The two $P(C_6H_5)_3$ ligands are located *trans* to each other, with one phenyl group from each pointed between the two chloride ligands. This results in the other phenyl groups being directed towards the phthalazine ligands,





presumably in order to optimize C–H/ π and π/π interactions. It seems quite possible that these interactions could play a role in stabilizing the observed *cis, trans, cis* isomer, and if the additional fused rings of the phthalazine ligands do not engage in any substantial stabilizing intermolecular interactions, such an arrangement could be found for the analogous pyridazine complex which would be a likely intermediate in the formation of **6**.

While there are no other structurally characterized (phthalazine)ruthenium complexes to compare with 7, and only a few transition metal complexes containing

both phosphine and phthalazine ligands [9c,15], one can note that the Ru–N distances for 7 are slightly shorter than those for **6**. The two Ru–P bonds are lengthened relative to the one in **6**, but are similar to the nearly *trans* Ru–P bonds in RuCl₂[P(C₆H₅)₃]₃ [14], whereas as noted before, the unique Ru–P bond in RuCl₂[P(C₆H₅)₃]₃ (ca. 2.23 Å) is similar to the Ru–P distance in **6**. The lengthening of the Ru–P bonds in **7** thus appears to be electronic in origin. The Ru–Cl bond distances for **6** and 7 are not significantly different from each other, but are longer than the values of ca. 2.38–2.39 Å in RuCl₂[P(C₆H₅)₃]₃.



Fig. 1. Perspective view and numbering scheme for RuCl2- $[P(C_6H_5)_3](C_4N_2H_4)_3$ (6).



Fig. 2. Perspective view and numbering scheme for $RuCl_2$ - $[P(C_6H_5)_3]_2(C_8N_2H_6)_2$ (7).



Fig. 3. Perspective view and numbering scheme for $RuCl_2$ - $[P(C_6H_5)_3]_2(1,8-C_8N_2H_6)$ (8).

The reaction of RuCl₂[P(C₆H₅)₃]₃ with 1,8-naphthyridine was unique in leading to the incorporation of only one ligand, at least under mild conditions, although a bidentate coordination mode was adopted in the product (8). Perhaps as a result of the smaller spatial requirements of the chelating diamine as compared to the two phthalazine ligands in 7, the phosphine ligands in 8 adopt a *cis* rather than *trans* orientation, with the chlorides becoming trans (Scheme 1, Fig. 3). Nonetheless, the marked asymmetry in the Ru–P–C angles (Table 3) seems to reveal the presence of some steric interactions between the phosphine ligands. In contrast, the Ru-P-C angles in the other complexes were more regular, although $RuCl_2[P(C_6H_5)_3]_3$ also displays a distortion [14]. In any event, this arrangement leads to an apparently favorable orientation for intramolecular C- H/π interactions between two of the naphthyridine hydrogen atoms and two of the phosphine phenyl groups [6]. The N1–Ru–N2 angle is of necessity quite small, at 60.81(9)°, thereby allowing for the P1-Ru-P2 angle to expand to $97.45(3)^{\circ}$. The chloride ligands are bent away from the phosphines toward the diamine, with a Cl1-Ru–Cl2 angle of 164.89(3)°. Presumably due to the lack of alignment between the nitrogen lone pairs and the metal center, the Ru–N distances in 8(2.217(3), 2.222(2))Å) are notably longer than those in 6 and 7. In turn, however, the opposite trend is observed for 8's Ru-Cl (2.4050(9), 2.4242(9) Å) and Ru-P bonds (2.2819(7), 2.3040(8) A).

Although there seem to be no structurally characterized examples of ruthenium complexes containing both phosphine and 1,8-naphthyridine ligands, two reports of chelating (naphthyridine)ruthenium complexes have appeared. The Ru–N distances in Ru(2,2'- $bpy)_2(1,8-C_8N_2H_6)^{2+}$ average 2.11(1) Å for the naphthyridine ligand [16], while in a more complicated, amino-substituted 1,8-naphthyridine complex [17], a highly asymmetric coordination is observed, with Ru-N distances of 2.066(6) and 2.377(7) A. More common than the observed monometallic chelating coordination mode are the monodentate bonding mode (with Ru-N distances to date of 2.078(9)-2.137(6) Å) [16,18] and a bridging mode in which the nitrogen centers are coordinated to different ruthenium centers which generally would be connected by a Ru-Ru bond [17,19,20]. In these cases, the Ru–N distances range from 2.00(3) to 2.21(3) A. Likewise, the monodentate coordination mode has been observed in phosphine-containing complexes of gold [21] and platinum [22], while the bridging mode has been observed in a dicopper phosphine complex [23].

The reaction of an excess of the five-membered ring ligand pyrazole with $RuCl_2[P(C_6H_5)_3]_3$ led only to the incorporation of two equivalents, and the expulsion of one phosphine ligand, analogous to the reaction involving phthalazine rather than to that of pyridazine. Attempts to incorporate a third equivalent of pyrazole using a large (10 equiv.) excess of pyrazole under reflux conditions did not lead to any observable change. The ¹H NMR spectrum demonstrated that the two phosphine ligands were equivalent, as were the two pyraz-The overall complex stoichiometery, oles. $RuCl_2[P(C_6H_5)_3]_2(C_3N_2H_4)_2$, again corresponds to a six-coordinate, pseudo-octahedral complex. A structural study has revealed that it adopts a different arrangement than that of 7 (Scheme 1) [24].

4. Summary

The complex $\operatorname{RuCl}_{2}[P(C_{6}H_{5})_{3}]_{3}$ has been found to be a useful starting material for the formation of polybasic aromatic amine complexes of ruthenium. Despite the potential abilities of pyridazine, pyrazole, phthalazine and 1,8-naphthyridine to bridge more than one metal center, none of the complexes involved such bridging, although the 1,8-naphthyridine ligand did chelate a single metal center. Each complex retained one or two of the triphenylphosphine ligands, whose steric bulk may have prevented the formation of dimetallic complexes. To some extent the product that was isolated was determined by solubility considerations, suggesting that additional incorporations could be achieved in some cases. Likewise, for at least pyrazole and pyridazine, it appears possible to limit the extent of incorporation through stoichiometry [24]. Notably, initial attempts to incorporate additional metal centers into the pyridazine complex have tended to lead instead to ligand exchange reactions [24], as has been seen for pyrazine complexes [25]. Possibly the use of less acidic metal centers or the deprotonation of coordinated pyrazole, which would lead to a more basic ligand that has been successfully employed for preparing heterobimetallic complexes [26], may be used to inhibit such exchanges. It is of final interest to note the recent report of a related Re(III) complex, ReCl₃[P(C₆H₅)₃] (C₃N₂H₄)₂ [27].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. 236487-236489 for compounds **8**, **7** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033) or email deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk.

Acknowledgements

Support for this research by the Research Corporation and the University of Utah is gratefully acknowledged.

References

- [1] (a) W. Keim, A. Klein, M. Glöckle, Acc. Chem. Res. 33 (2000) 755;
- (b) H. Durr, S. Bossmann, Acc. Chem. Res. 34 (2001) 905.
- [2] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metal Atoms, 2nd ed., Clarendon Press, Oxford, 1993.
- [3] T.D. Newbound, L. Stahl, M.L. Ziegler, R.D. Ernst, Organometallics 9 (1990) 2962.
- [4] P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Syn. 12 (1970) 237.
- [5] R.J. Neustadt, T.H. Cymbaluk, R.D. Ernst, F.W. Cagle Jr., Inorg. Chem. 19 (1980) 2375.
- [6] M. Nishio, M. Hirota, Y. Umezawa, The CH-π interaction, Wiley-VCH, New York, 1998.
- [7] (a) C.A. Hunter, K.R. Lawson, J. Perkins, C.J. Urch, J. Chem. Soc., Perkin Trans. 2 (2001) 651;
 (b) D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998)
- 1375; (c) C.A. Hunter, Chem. Soc. Rev. 23 (1994) 101.
- [8] (a) M. Scudder, I. Dance, J. Chem. Soc., Dalton Trans. (2000) 2909;
 - (b) G.R. Lewis, I. Dance, Inorg. Chim. Acta 306 (2000) 160;

(c) V. Kulsomphob, G.C. Turpin, K.-C. Lam, C. Youngkin, W. Trakarnpruk, P. Carroll, A.L. Rheingold, R.D. Ernst, J. Chem. Soc., Dalton Trans. (2000) 3086;

(d) G.C. Turpin, A.L. Rheingold, R.D. Ernst, J. Organometal. Chem. 672 (2003) 109.

[9] (a) A.S. Batsanov, M.J. Begley, M.W. George, P. Hubberstey, M. Munakata, C.E. Russell, P.H. Walton, J. Chem. Soc., Dalton Trans. (1999) 4251;
(b) X.-Y. Yu, M. Maekawa, T. Morita, H.-C. Chang, S. Kitagawa, G.-X. Jin, Polyhedron 21 (2002) 1613;
(c) J.T. Maeyer, T.J. Johnson, A.K. Smith, B.D. Borne, R.D. Pike, W.T. Pennington, M. Krawiec, A.L. Rheingold, Polyhedron 22 (2003) 419;
(d) H.-F. Klein, M. Helwig, U. Koch, U. Flörke, H.-J. Haupt, Z. Naturforsch. 48b (1993) 778;

(e) H.-F. Klein, M. Helwig, M. Karnop, H. König, B. Hammerschmitt, G. Cordier, U. Flörke, H.-J. Haupt, Z. Naturforsch. 48b (1993) 785.

- [10] G. De Munno, G. Denti, G. De Rosa, G. Bruno, Acta. Cryst. C 44 (1988) 1193.
- [11] A.N. Zhilyaev, I.V. Kuz'menko, T.A. Formina, G.N. Kuznetsova, I.B. Baranovskii, Russ. J. Inorg. Chem. 36 (1991) 1568.
- [12] (a) V.J. Catalano, R.A. Heck, A. Ohman, M.G. Hill, Polyhedron 19 (2000) 1049;
- (b) V.J. Catalano, R.A. Heck, C.E. Immoos, A. Öhman, M.G. Hill, Inorg. Chem. 37 (1998) 2150.
- [13] (a) J.A. Cabeza, R.J. Franco, A. Clamazares, V. Riera, C. Bois, Y. Jeannin, Inorg. Chem. 32 (1993) 4640;
 (b) F.A. Cotton, B.E. Hanson, J.D. Jamerson, J. Am. Chem. Soc. 99 (1977) 6588.
- [14] (a) S.J. La Placa, J.A. Ibers, Inorg. Chem. 4 (1965) 778;
 (b) R.D. Ernst, R. Basta, A.M. Arif, Z. Kristallogr. NCS 218 (2003) 49.
- [15] G.W. Bushnell, K.R. Dixon, Can. J. Chem. 56 (1978) 878.
- [16] H. Nakajima, H. Nagao, K. Tanaka, J. Chem. Soc., Dalton Trans. (1996) 1405.
- [17] M. Mintert, W.S. Sheldrick, J. Chem. Soc., Dalton Trans. (1995) 2663.
- [18] (a) T. Mizukawa, K. Tsuge, H. Nakajima, K. Tanaka, Angew. Chem. Int. Ed. 38 (1999) 362;
 (b) R.P. Thummel, D. Williamson, C. Hery, Inorg. Chem. 32 (1993) 1587;
 (c) S.M. Scott, A.K. Burrell, P.A. Cocks, K.C. Gordon, J. Chem. Soc., Dalton Trans. (1998) 3679.
- [19] (a) J.-P. Collin, A. Jouaiti, J.-P. Sauvage, W.C. Kaska, M.A. McLoughlin, N.L. Keder, W.T.A. Harrison, G.D. Stucky, Inorg. Chem. 29 (1990) 2238;
 (b) J.A. Cabeza, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans. (1988) 1437;
 (c) E. Binamira-Soriaga, N.L. Keder, W.C. Kaska, Inorg. Chem. 29 (1990) 3167;
 (d) C.S. Campos-Fernández, L.M. Thomson, J.R. Galán-Mascarós, X. Ouyang, K.R. Dunbar, Inorg. Chem. 41 (2002) 1523.
- [20] A.E.M. Boelrijk, M.M. van Velzen, T.X. Neenan, J. Reedijk, H. Kooijman, A.L. Spek, J. Chem. Soc., Chem. Commun. (1995) 2465.
- [21] M. Munakata, S.-G. Yan, M. Maekawa, M. Akiyama, S. Kitagawa, J. Chem. Soc., Dalton Trans. (1997) 4257.
- [22] G.W. Bushnell, K.R. Dixon, M.A. Khan, Can. J. Chem. 56 (1978) 450.
- [23] M. Maekawa, M. Munakata, S. Kitagawa, T. Kuroda-Sowa, Y. Suenaga, M. Yamamoto, Inorg. Chim. Acta 271 (1998) 129.
- [24] B.G. Harvey, A.M. Arif, R.D. Ernst, unpublished results.
- [25] M. Pizzotti, R. Ugo, C. Dragonetti, E. Annoni, F. Demartin, P. Mussini, Organometallics 22 (2003) 4001.
- [26] D. Carmona, J. Ferrer, J.M. Arilla, J. Reyes, F.J. Lahoz, S. Elipe, F.J. Modrego, L.A. Oro, Organometallics 19 (2000) 798.
- [27] B. Machura, M. Jaworska, R. Kruszynski, Polyhedron 23 (2004) 1819.