Dichloro(diphosphine)(2-pyridyl-ketone)ruthenium(II) complexes[1]

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Abstract: Described are the synthesis and characterization of Ru(II) complexes of the type $RuCl_2L_2$(N-O), where L_2 is either 1,4-bis(diphenylphosphino)butane (dppb) or $(PPh_3)_2$, and N-O represents chelated 2-benzoylpyridine (2-bzpy) or 2-acetylpyridine (2-acpy); the Ru presursors used were $[RuCl_2(dppb)]_2(\mu$-dppb) or $RuCl_2(PPh_3)_3$. The crystal structure of *cis*-$RuCl_2$(dppb)(2-bzpy) is presented, and three other $RuCl_2L_2$(N-O) complexes with cis-chlorines are isolated and characterized spectroscopically; of the trans-dichloro species, $RuCl_2(PPh_3)_2$(N-O) complexes are isolated, while the corresponding dppb species are characterized in situ. In all cases, thermodynamically stable cis-complexes are formed from initially formed trans-species.

Key words: ruthenium, phosphines, 2-benzoylpyridine, 2-acetylpyridine, X-ray structures.

Résumé : On décrit la synthèse et la caractérisation de complexes du Ru(II) du type $RuCl_2L_2$(N-O) dans lesquels L_2 = 1,4-bis(diphénylphosphino)butane (dppb) ou $(PPh_3)_2$ et N-O = 2-benzoylpyridine (2-bzpy) ou 2-acétylpyridine (2-acpy) chélatées; les complexes de Ru utilisés sont le $[RuCl_2(dppb)]_2(\mu$-dppb) ou $RuCl_2(PPh_3)_3$. On a déterminé la structure cristalline du *cis*-$RuCl_2$(dppb)(2-bzpy) et on a isolé trois autres complexes du $RuCl_2L_2$(N-O) portant des atomes de chlore en cis et on les a caractérisés de façon spectroscopique; des espèces trans-dichlorées, les complexes $RuCl_2(PPh_3)_2$(N-O) ont été isolés alors que les espèces correspondantes du dppb ont été caractérisées in situ. Dans tous les cas, les complexes cis thermodynamiquement stables se forment à partir des espèces trans obtenues initialement.

Mots clés : ruthénium, phosphines, 2-benzoylpyridine, 2-acétylpyridine, structures par diffraction des rayons X.

[Traduit par la Rédaction]

Introduction

Some 25 years ago, one of our groups published a paper (1) that questioned a reported synthesis of $[RuCl_2(PPh_3)_2]_2$ from $RuCl_2(PPh_3)_3$ using catalytic amounts of the 2-pyridylketones, C_5H_4N-COR (R = H, Me, Ph) (2). The reported synthesis using 2-acetylpyridine (2) was repeated (1), and the product was identified as $RuCl_2(PPh_3)_2(C_5H_4N$-COMe) containing an η^2-*N*,*O*-bonded pyridylketone; the complex was identified by C, H, N, and Cl analysis, molecular weight, ^{1}H and ^{31}P NMR, and IR data in the ν(CO) and ν(Ru-Cl) regions: the $^{31}P\{^1H\}$ NMR AB pattern required the complex to have cis-phosphines, while trans-chlorines were "favoured slightly" based on the dominance of a single 325 cm^{-1} band in the 400–250 cm^{-1} IR region (1). An X-ray analysis of the supposed $[RuCl_2(PPh_3)_2]_2$ complex was reported "to be underway" (2); no X-ray structure was ever published, but the authors of ref. 2 did agree that their product was certainly not $[RuCl_2(PPh_3)_2]_2$.[4]

This present paper reports on the synthesis and structural characterization of the complex, *cis*-$RuCl_2$(dppb)(2-benzoylpyridine), where dppb = 1,4-bis(diphenylphosphino)butane; data on the corresponding trans-isomer, and on the analogous 2-acetylpyridine species, are presented also. The bis(triphenylphosphine) complexes containing these 2-pyridylketones are also described. It should be noted that 2-benzoylpyridine (2-bzpy) is also called 2-pyridylphenylketone (3); we use the former-type nomenclature throughout this paper.

2-Pyridylketone complexes of transition metals have been known since the 1960s, particularly the 2-bzpy ligand systems (4). More recent interest in such ligands has generally focussed on bioinorganic model systems or their hemi-labile character for use in catalysis. Structural work describing bidentate, *N*,*O*-bonded 2-bzpy includes that on mono- and

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Dedicated to John Harrod, a close friend and colleague of one of us (BRJ) for 43 years; John physically handed me my first sample of $RuCl_3{\cdot}3H_2O$ in Jack Halpern's laboratory at UBC in 1960.

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bis-(2-bzpy) complexes of Zn(II) in relation to models for alcohol-dehydrogenases (3), and that on Cu(I) complexes (5), while the first structural work involving Ru species was that describing an η^2-*N*,*O*-bonded 2-pyridylketone moiety of an ONNS-bonded thiosemicarbazone of 2,6-diacetylpyridine bonded to Ru(II) (6). Very recent reports on Ru complexes have described the structures of $[Ru(PMe_3)_2(CO)(COMe)(2\text{-bzpy})]BPh_4$ (7), $[Ru(2,2'\text{-bipyridine})_2(2\text{-bzpy})][PF_6]_2$ (8), and $RuCl_2(DMSO)_2$(2-acpy), where 2-acpy is 2-acetylpyridine (9). Complexes such as $[Ru(NH_3)_4(N\text{-}O)][BF_4]_2$, where N-O = 2-bzpy or 2-acpy, have been isolated and characterized spectroscopically (10). Structurally characterized complexes of other platinum metals containing 2-pyridylketones have been reported, for example, $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(2\text{-bzpy})]BF_4$ (11), and several cationic chlororhodium(III) complexes containing 2-bzpy (4).

More generally, our earlier collaborative studies have developed methods for synthesizing *cis*- and *trans*-$RuCl_2(dppb)L_2$ and the corresponding bis(triphenylphosphine) complexes, where L = a N-donor or L_2 = a bidentate, *N*,*N*-donor, with a basic interest in their potential as hydrogenation catalysts (12, 13), and so extension to *N*,*O*-donor systems allows us also to obtain a broader data base for such complexes, as well as to comment more definitively on the nature of the $RuCl_2(PPh_3)_2$(2-acetylpyridine) species isolated in 1978 (1).

Experimental

General

Synthetic procedures were performed using standard Schlenk techniques under dry Ar because solutions of the precursor complexes $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ (14, 15) and $RuCl_2(PPh_3)_3$ (16) are air-sensitive. Common chemicals used were of reagent grade quality (Aldrich). Tetrabutylammonium perchlorate (TBAP) from Fluka was recrystallized from EtOH–H_2O, and dried under vacuum at 80 °C (caution!). Reagent grade solvents (Merck) were appropriately distilled, dried, and stored over Linde 4 Å molecular sieves.

IR spectra (in cm^{-1}) were recorded as CsI pellets on a Bomen–Michelson 102 instrument, and UV–vis spectra in CH_2Cl_2, given as λ_{max} or sh = shoulder in nm (ε, in M^{-1} cm^{-1}), on an HP 8452A spectrophotometer. NMR spectra were recorded on a Bruker 400 MHz spectrometer (400 MHz for ^1H, 100.6 MHz for ^{13}C, 162 MHz for ^{31}P) at room temperature (r.t., ~20 °C) in CH_2Cl_2 or CD_2Cl_2. Residual solvent proton, solvent carbon, or external $P(OMe)_3$ (^{31}P, δ 141.00 relative to 85% aq. H_3PO_4) were used as references. Cyclic and differential pulse voltammetries were carried out at r.t. in freshly distilled CH_2Cl_2 containing 0.1 M TBAP, using a PAR model 273A potentiostat/galvanostat with an EG&G/PARC model 175 universal programmer as a sweep generator. A three-electrode system with resistance compensation was used throughout, the working and auxiliary electrodes being a stationary Pt foil and a Pt wire, respectively. The reference electrode was Ag/AgCl in a Luggin capillary in the CH_2Cl_2 medium, in which ferrocene is oxidized at 0.43 V (Fc^+/Fc); all potentials are reported with respect to the Ag/AgCl electrode. Elemental analyses were performed at the Institute of Chemistry of the University of São Paulo.

cis-$RuCl_2$(dppb)(2-bzpy) (*cis*-**1**)

cis-**1** was prepared by stirring $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ (97 mg, 0.06 mmol) and 2-bzpy (60 mg, 0.32 mmol) in C_6H_6 (8 mL) at r.t. for 2 h. The resulting blue solution was reduced in volume to ~1 mL, when Et_2O was added to precipitate a blue solid that was collected, washed with hexanes and Et_2O, and dried under vacuum. Yield: 70%. UV–vis: 300 (9685), 620 (3370), 720 sh (2010). Anal. calcd. for $C_{40}H_{37}NOP_2Cl_2Ru$: C 62.47, H 4.87, N 1.83; found: C 62.8, H 5.1, N, 1.5. Crystals suitable for X-ray analysis were grown by evaporation of a CH_2Cl_2–Et_2O–MeOH solution of the complex. *trans*-**1** was generated in situ in a NMR tube in C_6D_6 from a rapid reaction of $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ with excess 2-bzpy (see *Results and discussion*).

cis-$RuCl_2$(dppb)(2-acpy) (*cis*-**2**)

cis-**2** was made by refluxing $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ (97 mg, 0.06 mmol) and 2-acpy (0.1 mL, 0.89 mmol) in C_6H_6 (8 mL) for 48 h. The resulting purple precipitate was collected, washed with Et_2O, and dried under vacuum. Yield: 75%. UV–vis: 340 sh (2780), 557 (3175), 655 sh (1690). Anal. calcd. for $C_{35}H_{35}NOP_2Cl_2Ru$: C 58.41, H 4.91, N 1.95; found: C 57.9, H 4.9, N, 1.8. *trans*-**2** was generated in situ as described for *trans*-**1**, but using excess 2-acpy (see *Results and discussion*).

trans-$RuCl_2(PPh_3)_2$(2-acpy) (*trans*-**3**)

trans-**3** was prepared by dissolving $RuCl_2(PPh_3)_3$ (100 mg, 0.10 mmol) and 2-acpy (0.014 mL, 0.12 mmol) in CH_2Cl_2 (5 mL) at r.t. The solution immediately changed from brown to blue, when the volume was rapidly reduced to ~1 mL; hexanes was then added to precipitate a blue solid that was collected, washed with hexanes, and dried under vacuum. Yield: 68%. UV–vis: 376 (1705), 604 (1970). Anal. calcd. for $C_{43}H_{37}NOP_2Cl_2Ru$: C 63.16, H 4.56, N 1.71; found: C 62.4, H 5.0, N 1.3.

cis-$RuCl_2(PPh_3)_2$(2-acpy) (*cis*-**3**)

cis-**3** was prepared by stirring $RuCl_2(PPh_3)_3$ (50 mg, 0.05 mmol) and 2-acpy (0.014 mL, 0.12 mmol) in CH_2Cl_2 (5 mL) for 12 h at r.t. The volume of the resulting purple solution was reduced to ~1 mL and hexanes was added to precipitate a purple solid that was collected, washed with Et_2O, and dried under vacuum. Yield: 70%. UV–vis: 346 sh (4900), 554 (5200), 680 sh (2250). Anal. calcd. for $C_{43}H_{37}NOP_2Cl_2Ru$: C 63.16, H 4.56, N 1.71; found: C 62.8, H 4.7, N 1.8.

trans-$RuCl_2(PPh_3)_2$(2-bzpy) (*trans*-**4**)

trans-**4** is formed immediately on mixing $RuCl_2(PPh_3)_3$ (200 mg, 0.20 mmol) and 2-bzpy (57.2 mg, 0.31 mmol) in CH_2Cl_2 (5 mL) at r.t. The volume of the blue solution was reduced to ~1 mL, and Et_2O was added to give a blue solid that was collected, washed with Et_2O, and dried under vacuum. Yield: 62%. UV–vis: 280 sh (2520), 670 (5025). Anal. calcd. for $C_{48}H_{39}NOP_2Cl_2Ru$: C 65.53, H 4.47, N 1.59; found: C 65.15, H 4.6, N 1.6.

Table 1. $^{31}P\{^{1}H\}$ NMR, electrochemical, and IR data for complexes **1**–**4**.

Complex	δ_A and δ_X	$^{2}J_{AX}$ (Hz)	$E_{1/2}$ (V)	ν(CO), ν(Ru-Cl) (cm^{-1})
$RuCl_2$(dppb)(2-bzpy) (*trans*-(**1**))	51.1, 43.3	43.70		
$RuCl_2$(dppb)(2-bzpy) (*cis*-(**1**))	44.7, 40.1	38.47	0.70	1591, 256 and 227
$RuCl_2$(dppb)(2-acpy) (*trans*-(**2**))	50.0, 43.0	44.00		
$RuCl_2$(dppb)(2-acpy) (*cis*-(**2**))	46.3, 41.1	38.55	0.68	1580, 262 and 235
$RuCl_2(PPh_3)_2$(2-acpy) (*trans*-(**3**))	48.4, 39.5	35.60	0.60	1617, 325
$RuCl_2(PPh_3)_2$(2-acpy) (*cis*-(**3**))	45.5, 40.1	33.54	0.68	1575, 250 and 224
$RuCl_2(PPh_3)_2$(2-bzpy) (*trans*-(**4**))	49.1, 39.1	35.28	0.60	1588, 329
$RuCl_2(PPh_3)_2$(2-bzpy) (*cis*-(**4**))	43.8, 39.2	34.17	0.68	1589, 314 and 281

cis-$RuCl_2(PPh_3)_2$(2-bzpy) (*cis*-4)

cis-**4** was prepared as described for *trans*-**4**, but the reactant solution was left for 6 h at r.t. Yield: 65%. UV–vis: 292 (10 900), 604 (4045), 720 sh (2350). Anal. calcd. for $C_{48}H_{39}NOP_2Cl_2Ru$: C 65.53, H 4.47, N, 1.59; found: C 65.5, H 4.6, N 1.7.

The $^{31}P\{^{1}H\}$ NMR, IR, and electrochemical data for complexes **1**–**4** are summarized in Table 1; ^{1}H and ^{13}C NMR data spectra were measured, and the more significant findings are presented in the *Results and discussion* text.

X-ray crystallography of *cis*-$RuCl_2$(dppb)(2-bzpy) (*cis*-1)

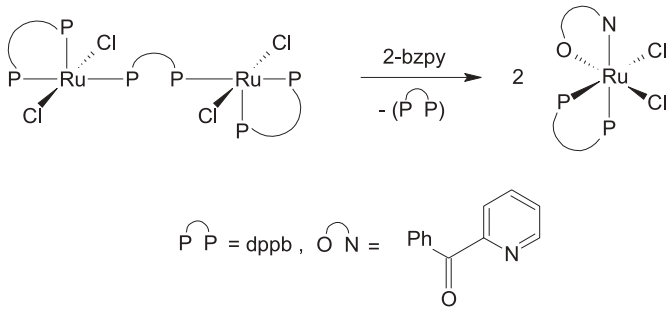
A prismatic crystal was used in the single-crystal, X-ray diffraction experiment, measurements being made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Crystal and structure refinement data for *cis*-**1** are summarized in Table 2.[5] One standard reflection measured every 30 min was used to apply a decay correction, the maximum decay being 1%. The data collection and reduction were performed with the programs CAD-4 (17) and XCAD-4 (18), respectively.

The structure was solved by direct methods with SHELXS-86 (19), and the model refined by full-matrix least-squares on F^2 by means of SHELXL-97 (20). After inclusion of the complete complex in the refinement, the difference Fourier map showed two peaks that were interpreted as a MeOH solvent. All the H atoms were stereochemically positioned and refined with the riding model (20), with the C—H bond lengths in the aromatics rings, CH_2 and CH_3 groups, being set equal to 0.93, 0.97, and 0.96 Å, respectively. Once the complete isotropic model was obtained, an empirical absorption correction (21) was applied (minimum and maximum transmission factors were 0.9039 and 0.8469, respectively), after which all non-H atoms were refined anisotropically. The H atoms of the aromatic rings and CH_2 were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the C atom to which each one is bonded; this percentage was set to 50% for the H atoms of the Me group. The atomic scattering factors were taken from ref. 22.

Results and discussion

The $RuCl_2$(dppb)(2-bzpy) complex (**1**) is isolated from a simple, 2 h, r.t. reaction of excess 2-bzpy with $[RuCl_2(dppb)]_2$(μ-dppb), as outlined in eq. [1]. The structure of **1**, presented as an ORTEP in Fig. 1 (23), reveals the Ru(II) ion in a distorted octahedral environment, with cis-chlorines, one trans to a P atom of chelated dppb, and one trans to the O atom of chelated 2-bzpy, whose N atom is trans to the second P atom. The asymmetric unit consists of one molecule of *cis*-**1** and a MeOH solvent. Throughout the paper, the cis- and trans-nomenclature refers to the arrangement of chlorine ligands.

[1]



Relevant interatomic distances and angles are listed in Table 3. The Ru—Cl (avg 2.427 Å), Ru—N (2.126 Å), and Ru—P (avg 2.289 Å) bond lengths observed are within the normal, well-established range for those in Ru(II) complexes (12, 13, 24). The Ru—N bond is ~0.07 Å shorter than that in $[Ru(PMe_3)_2(CO)(COMe)(2\text{-bzpy})]^+$ where the N atom is trans to CO (7), but is ~0.08 Å longer than that in [Ru(2,2′-bipyridine)$_2$(2-bzpy)]$^{2+}$ where the N atom is trans to a bipyridine-N (8); the expected trans influence (8, 25) is evident. The Ru—O bond length of 2.035(3) Å is the shortest found in the three Ru-(2-bzpy) complexes: trans to the COMe group in the monocation, the Ru—O length is 2.226(4) Å (7), while trans to a bipyridyl-N the value is 2.058 Å (8). Ru—N and Ru—O bond distances in *trans*-$RuCl_2(DMSO)_2$(2-acpy), where both N and O are trans to S-bonded DMSO, are 2.122(3) and 2.084(3) Å, respectively

[5] Supplementary data (full crystal data and details on data collection and refinement have been deposited along with tables of atomic coordinates, anisotropic thermal parameters, all bond lengths and angles, and torsion angles) 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 for information on ordering electronically). CCDC 208536 contains the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit @ccdc.cam.ac.uk).

Table 2. Crystal data and structure refinement for $RuCl_2$(dppb)(2-bzpy).

Empirical formula	$C_{40}H_{37}Cl_2NOP_2Ru{\cdot}CH_3OH$
Formula weight	813.66
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.917(2)
b (Å)	11.446(2)
c (Å)	15.667(3)
α (°)	86.06(1)
β (°)	74.41(1)
γ (°)	80.93(1)
Volume (Å^3)	1861.3(7)
Z	2
Density (calculated) (Mg m^{-3})	1.452
Absorption coefficient (mm^{-1})	0.687
F(000)	836
Crystal size (mm^3)	0.25 × 0.19 × 0.15
θ range for data collection (°)	$1 \le \theta \le 25$
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $0 \le l \le 17$
Decay of standard	±1
Reflections collected	6237
Independent/observed reflections	6237 (R(int) = 0.00)/4424 ($I > 2\sigma(I)$)
Completeness to θ = 25° (%)	95.4
Data/parameters	6237/444
Goodness-of-fit on F^2	1.041
SHELXL-97 weight parameters	0.0750, 0.0
Final R indices ($I > 2\sigma(I)$)	$R1$ = 0.0453, $wR2$ = 0.1199
R indices (all data)	$R1$ = 0.0770, $wR2$ = 0.1317
Extinction coefficient	0.0002(6)
Largest diff. peak and hole[a] (e Å^{-3})	0.915 and –1.040

[a]At ~1 Å from the Ru atom.

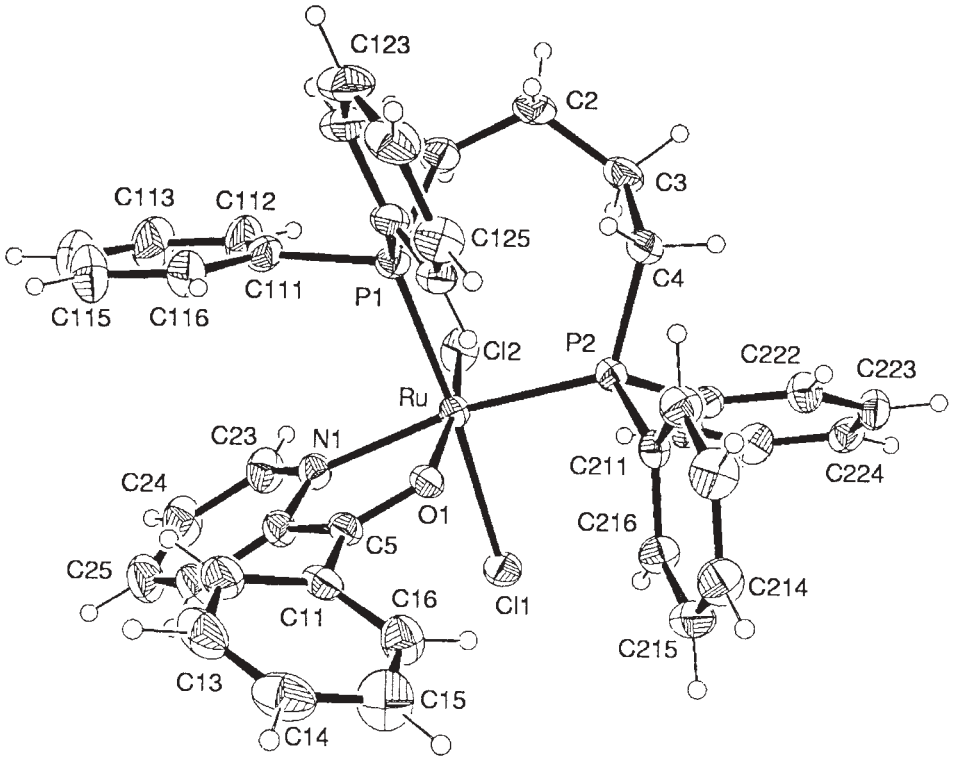
(9). The Ru—O bond in *cis*-**1** is also shorter than that found for the acetylpyridine moiety of an ONNS-bonded thiosemicarbazone at Ru(II) (2.232 Å) (6) and for the coordinated acetone of $RuCl_2(CO)(PPh_3)_2$(acetone), 2.194 Å (26); the small value is readily rationalized in that in *cis*-**1**, the coordinated ketone moiety is trans to chloride, a π-donor, while in the other systems the ketone group is trans to PPh_3 (26) and an imine N atom (6), both π-acceptors. The bite angle of the benzoylpyridine ligand in *cis*-**1** (76.7(1)°) is close to those found, for example, in the other Ru-(2-bzpy) (7, 8) and Ru-(2-acpy) (9) complexes; the essential planarity of the five-membered chelate ring, with an approximate 45° twist of the benzoyl-phenyl from the planarity, is similar to those noted for the other two 2-bzpy complexes (7, 8). The structure of the "*cis*-$RuCl_2$(dppb)" component of *cis*-**1** is very similar to that in *cis*-$RuCl_2$(dppb)(N-N) complexes, where N-N = 2,2′-bipyridine or 1,10-phenanthroline (12).

Table 1 lists some spectroscopic and electrochemical data for *cis*-**1** and the other 2-pyridylketone complexes studied in this work. The solution NMR data imply the solid state structure is maintained in solution: the $^{31}P\{^1H\}$ NMR AX pattern does not itself distinguish between *cis*-**1** and *trans*-**1** (see below), but two strong ν(Ru-Cl) bands in the IR spectrum are consistent with cis-geometry. We have recently established for Ru(II)-dppb species (with 18 data points) an inverse dependence of the ^{31}P shifts on Ru—P bond length (12); the data for *cis*-**1** fit well with this correlation and imply that the δ values of 44.7 and 40.1 refer to P(1) and P(2), respectively. ^{1}H NMR data confirm the presence of one bzpy ligand per dppb, while the coordination shift of the H^N atom adjacent to the N atom (δ 8.68 → 9.03) and that of ν(C=O) (1668 → 1591 cm^{-1}) again show both *O*- and *N*-coordination of bzpy. The lower ν(C=O) value in the Ru(II) species vs. values for the Zn(II) complexes (~1620 cm^{-1}) (3) is consistent with the presence of significant Ru → carbonyl π-backbonding (27). A coordination shift of the ^{13}C resonance of the C=O group (δ 193.8 → 206.1) is also evident.

The blue colour of *cis*-**1** is manifested in an absorption maximum at 620 nm with a shoulder at 720 nm, while the CV reveals a reversible redox process ($i_{pa}/i_{pc} \cong 1$) with $E_{1/2}$ = 0.70 V, the process being confirmed by differential pulse voltammetry. The Ru^{III}/Ru^{II} couple is ~10 mV more positive that for the structurally similar *cis*-$RuCl_2$(dppb)(bipy) (12), showing relative stabilization of the lower valence state by substitution of a 2-pyridyl by a benzoyl moiety.

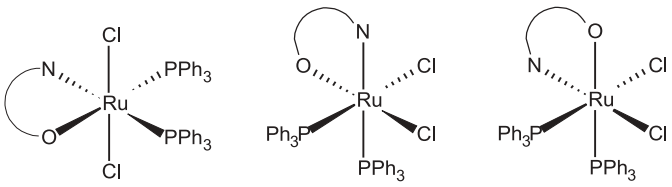
Synthesis of the 2-acetylpyridine (2-acpy) analogue (*cis*-**2**) is as for *cis*-**1**, but requires the use of reflux conditions. The NMR and IR spectroscopic data and CV data (Table 1) are very similar to those of *cis*-**1**, and the structure is assumed to be the same (type **II** as in Fig. 1, see below and

Fig. 1. ORTEP view of *cis*-$RuCl_2$(dppb)(2-bzpy) (**1**), showing the atom labeling, with 30% probability ellipsoids.



also rxn. [1]). The Me resonance of the coordinated acetyl group is seen at δ 2.10 (upfield shifted from that of the free ligand at δ 2.71), while there is again a downfield shift (δ 8.68 → 8.85) for H^N. In contrast with *cis*-**1**, *cis*-**2** is purple and the solution spectrum shows an absorption maximum at 557 nm.

As described in the *Experimental* section, two complexes with the formulation $RuCl_2(PPh_3)_2$(2-acpy) (**3**) were isolated from the same reaction precursor $RuCl_2(PPh_3)_3$ but using different timescales. A blue solid is obtained after a few minutes, while a 12 h reaction time generates a purple solid, and the complexes have different spectroscopic properties. Three structural formulations are possible for the bis(triphenylphosphine) species: **I** (with trans chlorines), and **II** and **III** (with cis chlorines). The more stable, purple complex has ^{31}P NMR, IR, and CV data (Table 1) close to those found for *cis*-**1** and *cis*-**2**, and is thus assigned the cis-dichloro geometry **II** (cf. rxn. [1]). The ^{1}H NMR data (as for *cis*-**2**) show an upfield shift for the Me (δ 2.71 → 2.41) and a downfield shift for H^N (δ 8.68 → 9.51). The ^{31}P NMR data of a solution of the blue complex show about a 9 ppm difference between the δ_A and δ_X values vs. ~5 ppm for the cis-complexes, and the ν(Ru-Cl) region shows a single, sharp band at 325 cm^{-1}, findings that imply that the blue species is *trans*-**3**. Of note, the ^{1}H NMR shift for the Me is now slightly downfield (δ 2.71 → 2.79), while that for H^N is now slightly upfield (δ 8.68 → 8.60). These shifts are the reverse of those seen for the cis-complexes, and presumably reflect that the acetyl is now trans to the π-acceptor PPh_3 (structure **I**) vs. the π-donor chloride ligand (structure **II**). Further, the $E_{1/2}$ value of *trans*-**3** is 8–10 mV lower than those of the cis-species, again consistent with the trans formulation, as a trans-dichloro species of this type invariably has a lower reduction potential than that of a corresponding *cis*-formulation (12, 28, 29). Of note, a solution of the blue *trans*-**3** isomerizes over time to the purple cis-species, a process that can be readily monitored by CV (30) (cf. Fig. 2, $t_{1/2}$ ~ 30 min at r.t.), ^{31}P or ^{1}H NMR, or by UV–vis spectroscopy. *trans*-**3** shows UV–vis absorption maxima at 376 and 604 nm, while *cis*-**3** has a maximum at 554 and a shoulder at ~680 nm.



cis- and *trans*-$RuCl_2(PPh_3)_2$(2-bzpy)$_2$ (**4**) are made similarly to the 2-acpy analogues (**3**), the initially formed kinetic product being the blue, trans-isomer, this then transforming to an isolable, purple cis-isomer (Table 1). Whether *cis*-**4** has geometry **II** or **III** is unclear; the ^{31}P NMR data are close to those of the other cis species (of structure **II**), but the ν(Ru-Cl) IR data are significantly different and may indicate structure **III**.

cis-$RuCl_2$(dppb)$_2$(2-bzpy) (*cis*-**1**) was isolated after a 2 h reaction time at r.t. (see above), but initially when the reactants are mixed, the trans-isomer is detected by in situ ^{31}P NMR (see Fig. 3 and Table 1). Corresponding behaviour is seen for the isolated *cis*- and in situ formed *trans*-

Fig. 2. Differential pulse voltammogram of *cis*- and *trans*-$RuCl_2(PPh_3)_2$(2-acpy) (**3**).

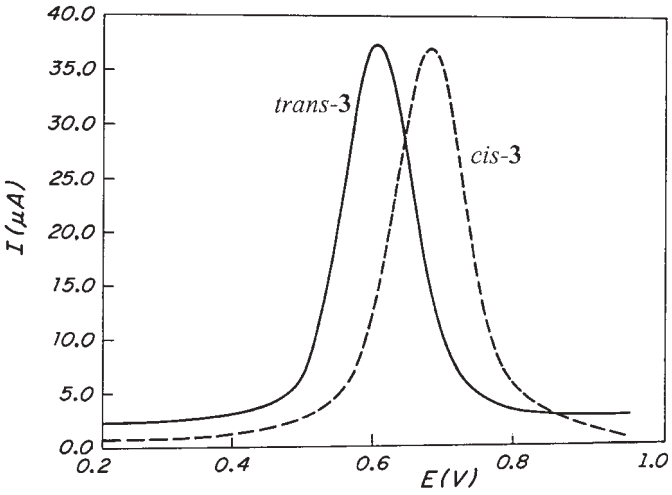
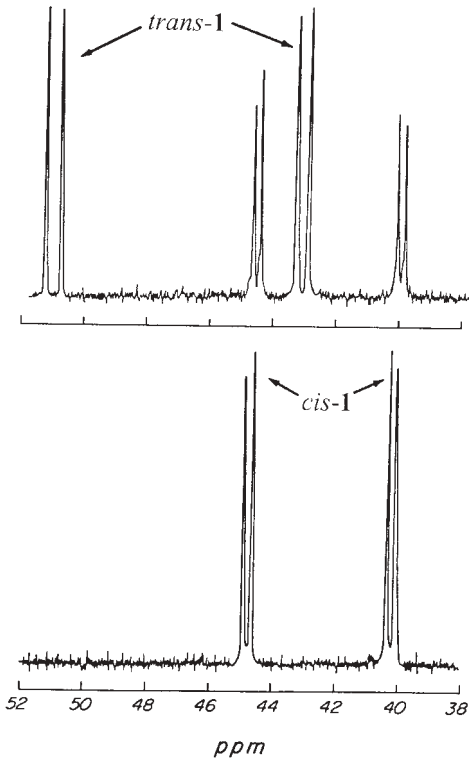


Fig. 3. $^{31}P\{^1H\}$ NMR in C_6H_6 of a mixture of *cis*- and *trans*-$RuCl_2$(dppb)(2-bzpy) (**1**): top, "immediately" after mixing $[RuCl_2(dppb)]_2$(μ-dppb) and 2-benzoylpyridine; bottom, after 25 min when just *cis*-**1** is seen.



$RuCl_2(dppb)_2$(2-acpy) (**2**) species (Table 1). The trans → cis isomerization process is faster for all the systems in the presence of sunlight; details of possible isomerization mechanisms (31) for these chelated six-coordinate complexes remain to be elucidated.

Reevaluation of the 1978 data for the reported $RuCl_2(PPh_3)_2$(2-acpy) complex **3** in this current paper (see *Introduction*) can now be made. The previously reported r.t. $^{31}P\{^1H\}$ NMR (δ_A 43.6, δ_X 38.8; J = 35 Hz) and ^1H NMR data (δ_{Me} 2.40; δ_H 9.54, H adjacent to N) in $CDCl_3$, and the purple colour (1), are all consistent with a *cis*-**3** formulation (see Table 1). The only contrary evidence is the reported single ν(Ru-Cl) value of 325 cm^{-1} (1) that pertains to *trans*-**3**. It is evident that the spontaneous trans/cis isomerization process was not recognized in the early work, and the data reported in this current paper, especially with the X-ray analysis for *cis*-**1**, characterize more completely the nature of these Ru(II) 2-pyridylketone complexes.

Table 3. Selected bond lengths (Å) and angles (°) for $RuCl_2$(dppb)(2-bzpy), esds in parentheses.

Bond lengths (Å)			
Ru—O(1)	2.035(3)		
Ru—N(1)	2.126(4)		
Ru—P(1)	2.286(1)		
Ru—P(2)	2.292(1)		
Ru—Cl(2)	2.397(1)		
Ru—Cl(1)	2.458(1)		
O(1)—C(5)	1.251(5)		
N(1)—C(23)	1.327(6)		
N(1)—C(21)	1.370(6)		
Bond angles (°)			
O(1)-Ru-N(1)	76.7(1)	C(121)-P(1)-Ru	119.8(2)
O(1)-Ru-P(1)	95.19(9)	C(111)-P(1)-Ru	110.4(2)
N(1)-Ru-P(1)	92.4(1)	C(1)-P(1)-Ru	119.1(2)
O(1)-Ru-P(2)	91.99(9)	C(221)-P(2)-C(211)	100.7(2)
N(1)-Ru-P(2)	167.3(1)	C(221)-P(2)-C(4)	100.1(2)
P(1)-Ru-P(2)	94.47(5)	C(211)-P(2)-C(4)	102.7(2)
O(1)-Ru-Cl(2)	170.15(9)	C(221)-P(2)-Ru	120.7(1)
N(1)-Ru-Cl(2)	93.6(1)	C(211)-P(2)-Ru	110.3(1)
P(1)-Ru-Cl(2)	86.66(5)	C(4)-P(2)-Ru	119.5(2)
P(2)-Ru-Cl(2)	97.52(5)	C(5)-O(1)-Ru	119.0(3)
O(1)-Ru-Cl(1)	87.15(9)	C(23)-N(1)-C(21)	117.2(4)
N(1)-Ru-Cl(1)	82.4(1)	C(23)-N(1)-Ru	128.5(4)
P(1)-Ru-Cl(1)	173.64(4)	C(21)-N(1)-Ru	113.9(3)
P(2)-Ru-Cl(1)	91.35(4)	O(1)-C(5)-C(21)	117.6(4)
Cl(2)-Ru-Cl(1)	90.04(5)	O(1)-C(5)-C(11)	118.1(4)
C(121)-P(1)-C(111)	102.5(2)	N(1)-C(21)-C(26)	122.1(5)
C(121)-P(1)-C(1)	102.6(2)	N(1)-C(21)-C(5)	112.6(4)
C(111)-P(1)-C(1)	99.4(2)	N(1)-C(23)-C(24)	121.8(6)

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