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Syntheses, Molecular Structures and Electrochemical Behavior of Two Isomeric Ru(PhNpy)$_2$(PPh$_3$)$_2$ Complexes

AKHIL R. CHAKRAVARTY, F. ALBERT COTTON* and EDWAR S. SHAMSHOUM

Department of Chemistry, Texas A&M University, College Station, Tex. 77843, U.S.A.

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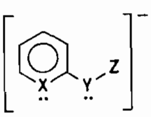
The title compounds, isomers of Ru(PhNpy)$_2$(PPh$_3$)$_2$ (PhNpy = the anion of 2-(N-anilino)-pyridine), having C_1 and C_2 symmetry, were prepared by reacting RuCl$_2$(PPh$_3$)$_3$ with LiPhNpy in toluene. The crystal and molecular structures of these compounds have been determined from three-dimensional X-ray study. Both compounds crystallize in the monoclinic space group $P2_1/c$ with the following unit cell dimensions: C_1-isomer: $a = 13.852(3)$, $b = 18.872(3)$, $c = 18.206(3)$, $\beta = 84.32(5)$, $V = 4736(2)$ and $Z = 4$. C_2-isomer: $a = 11.166(9)$, $b = 20.404(8)$, $c = 20.716(16)$, $\beta = 97.14(7)$, $V = 4683(10)$ and $Z = 4$. The structures were refined to $R = 0.053$ ($R_w = 0.083$) for the C_1-isomer and $R = 0.055$ ($R_w = 0.063$) for the C_2-isomer. In the C_1-isomer, the coordinating atoms N-py, N-Ph and PPh$_3$ are all in cis-*arrangement. In the C_2-isomer, the py-rings are* trans *to each other. The complexes are six-coordinate with four-membered chelate rings. The N–Ru–N angle in the chelate rings is* ca. *62° in each case. The Ru–P bond lengths lie in the range 2.286(3)–2.337(1) Å. The average Ru–N(py), and Ru–N(Ph) bond lengths are 2.083 Å and 2.171 Å, respectively. Dichloromethane solutions of the C_1 and C_2 isomers display two quasireversible oxidation waves at 0.480, 1.175 V and 0.290, 1.040 V, respectively. The responses have one-electron stoichiometry and are assignable to Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples.*

Introduction

In recent times, monoanionic ligands of the type *1* and *2* have been extensively used to form complexes with various transition metals. In many cases such ligands bridge metal atoms and facilitate in the formation of dinuclear or polynuclear species with metal–metal multiple bonding [1].



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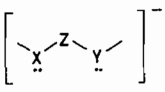

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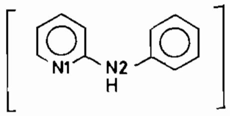

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Other modes of ligation can be either unidentate coordination or bidentate chelation to a single metal atom. The reactivity of such ligands has been well studied with various transition metals, *viz.*, Cr, Mo, W, Re, *etc.*, but only a few ruthenium species are known to exist. In the course of our studies of ruthenium chemistry we have chosen 2-(N-anilino)-pyridine, (PhNH(2-pyridyl), *3*, as a ligand whose chemistry is expected to be similar to that of 2-aminopyridine and other ligands of class *1*. The anion of *3* [PhN(2-pyridyl)]$^-$ displays two coordination modes. It acts as a bridging ligand [2] in Mo and W complexes, but, as shown here, it can form a stable, four-membered chelate ring with ruthenium-(II).

In this paper we describe the synthesis of two isomeric products, each having the formula Ru(PhNpy)$_2$(PPh$_3$)$_2$. The molecular structures of these new complexes have been determined by single crystal X-ray studies. The electron transfer behavior of the complexes is also reported.

Experimental

Chemicals

RuCl$_3$·3H$_2$O and PhNHpy were purchased from Aldrich Chemical Company. The starting material Ru(PPh$_3$)$_3$Cl$_2$ was made by following the literature method [3].

Measurements

Electronic spectra were recorded with a Cary 17D spectrophotometer. Electrochemical data were obtained from a Beckman Electroscan 30 analytical system. Dichloromethane and 0.1 *M* tetrabutylammonium perchlorate (TBAP) were used as solvent and supporting electrolyte, respectively. Experiments

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*Author to whom correspondence should be addressed.

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were done in a three-electrode cell which includes a planar Beckman model 39273 Platinum-inlay working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE). The solutions were deoxygenated by passing nitrogen gas through them. All measurements were made at room temperature (*ca.* 298 K) and are uncorrected for junction potentials.

Preparation of Ru(PhNpy)$_2$(PPh$_3$)$_2$

Under argon atmosphere, 340 mg (2.0 mmol) of 2-(N-anilino)pyridine (PhNHpy) was dissolved in 10 ml of toluene. To this 0.25 ml of n-butyllithium (1.2 mmol) was added slowly. The initially yellow solution became greenish yellow after the addition. This solution was then added to a solution of 480 mg (0.5 mmol) of Ru(PPh$_3$)$_3$Cl$_2$ in 10 ml toluene. The mixture was stirred at –20 °C for one hour and then allowed to warm slowly to room temperature, where it was stirred for 16 hours; a yellow-brown color was obtained. The solution was then filtered into a Schlenk tube and covered with a layer of hexane. Orange crystals (25% yield) and yellow crystals (15% yield) were obtained.

X-ray Crystallographic Procedures

The structures of the two complexes were obtained using the same general procedures as have been described elsewhere [4, 5]. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material from FAC.

Results and Discussion

RuCl$_2$(PPh$_3$)$_3$ reacts smoothly with the lithium salt of 2-(N-anilino)pyridine in toluene to give two Ru(PhNpy)$_2$(PPh$_3$)$_2$ isomers which are obtained in crystalline form by slow diffusion of hexane into toluene solution. The colors of the crystals obtained are yellow and orange. Both compounds are stable in the solid state but labile in solution. Electronic spectra of the complexes in dichloromethane display a sharp band at 305 nm with a shoulder near 400 nm.

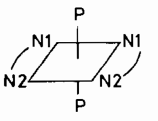
Molecular Structures

Since PhNpy$^-$ is an unsymmetrical bidentate ligand, there are five possible geometrical isomers of the molecular formula Ru(PhNpy)$_2$(PPh$_3$)$_2$, *4–8*. Of these, *6–8* exist in enantiomers. We have obtained two of the five isomers and characterized both of them by X-ray crystallography. The orange and yellow isomers each contain a pseudooctahedral arrangement of two PPh$_3$ ligands *cis* to each other, and two chelating PhNpy-ligands. The molecular unit of each isomer is shown in Figs. 1 and 2; the phenyl rings of the PPh$_3$ ligands have been omitted to

TABLE I. Crystallographic Parameters.

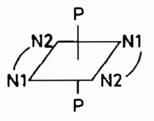
Compound	C_1-Ru(PhNpy)$_2$(PPh$_3$)$_2$	C_2-Ru(PhNpy)$_2$(PPh$_3$)$_2$
Formula	$RuP_2N_4C_{58}H_{48}$	$RuP_2N_4C_{58}H_{48}$
Formula weight	964.07	964.07
Space group	P2$_1$/c (No. 14)	P2$_1$/c (No. 14)
a, Å	13.852(3)	11.166(9)
b, Å	18.872(3)	20.404(8)
c, Å	18.206(3)	20.716(16)
β, degrees	84.32(5)	97.14(7)
V, Å^3	4736(2)	4683(10)
Z	4	4
d_{calc}, g/cm^3	1.352	1.367
Crystal size, mm	0.5 × 0.2 × 0.2	0.4 × 0.4 × 0.3
μ(Mokα), cm^{-1}	37.06	4.37
Data collection instrument	Syntex P$\bar{1}$	CAD-4
Radiation	Cu	Mo
Scan method	$\omega-2\theta$	$\omega-2\theta$
Data collection range	6–115°	4–50°
No. unique data,	5093	5317
$F_o^2 \geqslant 3\sigma(F_o^2)$	5069	3152
Number of parameters refined	586	586
R[a]	0.053	0.055
R_w[b]	0.083	0.063
Quality-of-fit indicator[c]	2.18	1.52
Largest shift/esd, final cycle	0.12	0.01

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.



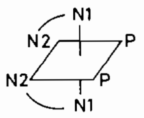
C_{2v}

4



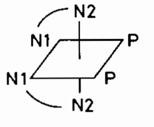
C_{2h}

5



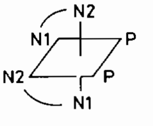
C_2

6



C_2

7



C_2

8

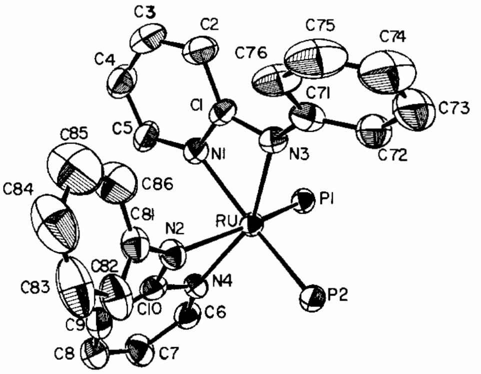


Fig. 1. An ORTEP drawing of C_1-Ru(PhNpy)$_2$(PPh$_3$)$_2$ molecule. Atoms are represented by thermal vibration ellipsoids at the 40% level and the atomic labeling scheme is defined. The phenyl rings of the PPh$_3$ are removed for clear view.

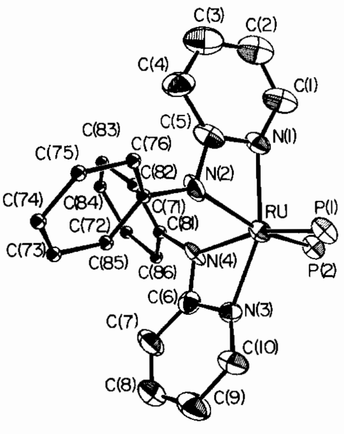


Fig. 2. A perspective view of the C_2-Ru(PhNpy)$_2$(PPh$_3$)$_2$ molecule with atoms represented by thermal vibration ellipsoids at the 40% level. The phenyl rings of the PPh$_3$ are excluded to clearly show the coordination sphere.

provide an unencumbered view of the more essential features of the structures. Complete drawings defining the labels for all atoms are available as supplementary material. The orange isomer is of type *8*, where the molecule has molecular symmetry C_1. The yellow compound contains an isomer of type *6* or *7* which has C_2 molecular symmetry. We did not isolate the other C_2 isomer. In RuCl$_2$(Azpy)$_2$, only one isomer is known [6] to exist and it is also the C_2 isomer that has the pyridine rings *trans* to each other (Azpy = 2-(phenylazo)-pyridine). The near coplanarity required of the two py rings in the other C_2 isomer may be responsible for its being relatively unstable.

The atomic coordinates and equivalent isotropic thermal vibration parameters of the C_2 and C_1 isomers are listed in Tables II and III, respectively. Important bond distances and bond angles are in Tables IV and V, respectively.

TABLE II. Table of Positional Parameters and Their Estimated Standard Deviations in C_2-Ru(PhNpy)$_2$(PPh$_3$)$_2$.[a]

Atom	*x*	*y*	*z*	*B(A2)*
Ru	0.25362(7)	0.25195(5)	0.10525(4)	2.07(1)
P1	0.2510(3)	0.1402(1)	0.1122(1)	2.54(6)
P2	0.0722(3)	0.2757(1)	0.0428(1)	2.50(6)
N1	0.3678(6)	0.2487(5)	0.0329(3)	2.6(2)
N2	0.4454(6)	0.2553(5)	0.1356(3)	2.8(2)
N3	0.1918(7)	0.2785(4)	0.1910(4)	2.2(2)
N4	0.2551(7)	0.3555(4)	0.1314(3)	2.2(2)
C1	0.3690(9)	0.2485(6)	−0.0317(5)	3.6(2)
C2	0.473(1)	0.2617(5)	−0.0582(5)	4.2(3)
C3	0.579(1)	0.2774(6)	−0.0177(6)	4.8(3)
C4	0.580(1)	0.2749(5)	0.0505(6)	3.9(3)
C5	0.4720(8)	0.2585(5)	0.0738(4)	2.8(2)
C6	0.2187(9)	0.3448(5)	0.1880(5)	2.4(2)
C7	0.209(1)	0.3871(8)	0.2405(5)	3.7(3)
C8	0.174(1)	0.3613(6)	0.2965(5)	4.3(3)
C9	0.146(1)	0.2935(6)	0.3010(6)	4.5(3)
C10	0.1582(8)	0.2536(6)	0.2464(4)	3.3(2)
C11	0.125(1)	0.1003(5)	0.1470(5)	2.9(3)
C12	0.017(1)	0.1337(5)	0.1465(5)	3.3(3)
C13	−0.081(1)	0.1057(6)	0.1738(6)	4.5(3)
C14	−0.068(1)	0.0431(7)	0.2027(6)	4.8(3)
C15	0.042(1)	0.0099(6)	0.2029(6)	4.6(3)
C16	0.141(1)	0.0368(5)	0.1750(5)	3.7(3)
C21	0.268(1)	0.0902(5)	0.0396(5)	3.2(3)
C22	0.175(1)	0.0470(5)	0.0145(5)	3.9(3)
C23	0.191(1)	0.0105(6)	−0.0404(6)	5.1(3)
C24	0.297(1)	0.0159(6)	−0.0706(6)	5.3(4)
C25	0.388(1)	0.0601(6)	−0.0445(6)	5.2(3)
C26	0.372(1)	0.0978(5)	0.0110(5)	3.9(3)
C31	0.376(1)	0.1058(5)	0.1710(5)	3.1(3)
C32	0.438(1)	0.0486(6)	0.1556(6)	4.7(3)
C33	0.520(1)	0.0207(7)	0.2047(6)	6.3(4)
C34	0.538(1)	0.0479(7)	0.2679(6)	5.5(4)
C35	0.477(1)	0.1050(6)	0.2795(6)	4.9(3)
C36	0.393(1)	0.1351(6)	0.2320(5)	3.6(3)
C41	−0.0270(9)	0.2116(5)	0.0045(5)	2.6(2)
C42	−0.148(1)	0.2042(6)	0.0180(6)	4.1(3)
C43	−0.222(1)	0.1551(6)	−0.0168(7)	4.9(3)
C44	−0.172(1)	0.1173(6)	−0.0636(6)	4.7(3)
C45	−0.053(1)	0.1252(6)	−0.0756(6)	4.4(3)
C46	0.022(1)	0.1714(5)	−0.0408(5)	3.2(3)
C51	0.0038(9)	0.3225(5)	−0.0308(5)	2.6(2)

(continued overleaf

TABLE II *(continued)*

Atom	*x*	*y*	*z*	*B(A2)*
C52	0.198(1)	0.3604(5)	−0.0325(5)	3.2(3)
C53	0.214(1)	0.3963(5)	−0.0896(5)	3.9(3)
C54	0.125(1)	0.3954(6)	−0.1432(6)	5.0(3)
C55	0.018(1)	0.3598(6)	−0.1397(6)	4.6(3)
C56	0.002(1)	0.3228(5)	−0.0837(5)	3.7(3)
C61	−0.0313(9)	0.3300(5)	0.0813(5)	2.7(2)
C62	−0.065(1)	0.3903(6)	0.0512(6)	4.4(3)
C63	−0.143(1)	0.4304(6)	0.0817(7)	5.4(4)
C64	−0.184(1)	0.4134(6)	0.1398(6)	5.2(3)
C65	−0.152(1)	0.3539(6)	0.1690(6)	4.6(3)
C66	−0.072(1)	0.3110(5)	0.1390(6)	3.6(3)
C71	0.5347(9)	0.2602(5)	0.1901(5)	3.1(2)
C72	0.514(1)	0.3034(6)	0.2396(5)	4.0(3)
C73	0.600(1)	0.3062(7)	0.2944(6)	5.1(3)
C74	0.699(1)	0.2668(7)	0.3014(6)	5.4(4)
C75	0.717(1)	0.2228(7)	0.2530(6)	6.0(4)
C76	0.635(1)	0.2188(6)	0.1962(6)	5.0(3)
C81	0.294(1)	0.4186(5)	0.1126(5)	3.0(3)
C82	0.409(1)	0.4239(6)	0.0943(6)	4.1(3)
C83	0.451(1)	0.4837(6)	0.0729(6)	5.9(4)
C84	0.373(1)	0.5390(7)	0.0666(6)	5.9(4)
C85	0.255(1)	0.5327(6)	0.0853(6)	6.5(4)
C86	0.213(1)	0.4712(6)	0.1101(6)	5.0(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)*-[a2*B(1.1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B-(1.2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2.3)].

TABLE III. Table of Positional Parameters and Their Estimated Standard Deviations in C$_1$-Ru(PhNpy)$_2$(PPh$_3$)$_2$.[a]

Atom	*x*	*y*	*z*	*B(A2)*
Ru	0.21274(3)	−0.03789(2)	0.20285(2)	2.356(8)
P1	0.2311(1)	−0.09289(6)	0.08877(7)	2.64(3)
P2	0.1672(1)	−0.12889(7)	0.28621(7)	2.65(3)
N1	0.2806(3)	0.0531(2)	0.1550(2)	2.89(9)
N2	0.1592(4)	0.0377(2)	0.2882(2)	3.03(9)
N3	0.3665(3)	−0.0255(2)	0.2105(2)	3.07(9)
N4	0.0710(3)	−0.0024(2)	0.2032(2)	2.61(8)
C(1)	0.3686(4)	0.0393(2)	0.1771(3)	2.8(1)
C(2)	0.4482(5)	0.0880(3)	0.1604(3)	4.1(1)
C(3)	0.4259(5)	0.1509(3)	0.1274(4)	4.7(1)
C(4)	0.3330(5)	0.1651(3)	0.1090(3)	4.5(1)
C(5)	0.2610(5)	0.1155(3)	0.1233(3)	3.6(1)
C(6)	−0.0083(4)	−0.0069(3)	0.1672(3)	3.2(1)
C(7)	−0.0912(5)	0.0339(3)	0.1879(4)	4.1(1)
C(8)	−0.0870(5)	0.0839(3)	0.2451(3)	4.1(1)
C(9)	−0.0058(4)	0.0901(3)	0.2821(3)	3.6(1)
C(10)	0.0756(4)	0.0448(2)	0.2605(3)	2.7(1)
C11	0.2540(4)	−0.0261(3)	0.0140(3)	2.9(1)
C12	0.1794(5)	0.0210(3)	0.0034(3)	3.9(1)
C13	0.1919(5)	0.0719(3)	−0.0535(3)	4.6(1)
C14	0.2794(6)	0.0761(3)	−0.0973(3)	5.0(2)
C15	0.3532(6)	0.0302(3)	−0.0865(4)	5.3(2)
C16	0.3409(5)	−0.0205(3)	−0.0305(3)	4.2(1)
C21	0.1259(4)	−0.1376(2)	0.0539(3)	2.6(1)
C22	0.0613(4)	−0.1756(3)	0.1018(3)	3.5(1)
C23	−0.0145(5)	−0.2151(3)	0.0770(3)	4.1(1)
C24	−0.0255(4)	−0.2145(3)	0.0018(4)	4.2(1)
C25	0.0364(5)	−0.1763(3)	−0.0470(3)	4.3(1)
C26	0.1127(5)	−0.1373(3)	−0.0201(3)	3.8(1)
C31	0.3273(4)	−0.1584(3)	0.0616(3)	2.8(1)
C32	0.4223(5)	−0.1441(3)	0.0797(3)	3.9(1)
C33	0.4980(5)	−0.1904(3)	0.0607(4)	4.8(1)
C34	0.4795(5)	−0.2545(3)	0.0253(3)	4.6(1)
C35	0.3861(5)	−0.2688(3)	0.0066(3)	3.8(1)
C36	0.3111(5)	−0.2209(3)	0.0250(3)	3.4(1)
C41	0.0387(4)	−0.1560(3)	0.2970(3)	3.0(1)
C42	0.0079(4)	−0.2250(3)	0.2822(3)	3.5(1)
C43	−0.0907(5)	−0.2420(3)	0.2857(4)	4.6(1)
C44	−0.1611(5)	−0.1894(4)	0.3039(4)	5.4(2)
C45	−0.1309(5)	−0.1219(3)	0.3200(4)	4.8(1)
C46	−0.0318(4)	−0.1048(3)	0.3173(3)	3.5(1)
C51	0.2301(4)	−0.2158(3)	0.2778(3)	2.8(1)
C52	0.2622(5)	−0.2497(3)	0.3387(3)	4.3(1)
C53	0.3117(5)	−0.3154(3)	0.3290(4)	4.9(1)
C54	0.3303(5)	−0.3437(3)	0.2598(3)	4.0(1)
C55	0.3000(5)	−0.3099(3)	0.1990(3)	4.0(1)
C56	0.2494(5)	−0.2456(3)	0.2088(3)	3.5(1)
C61	0.1844(4)	−0.1054(3)	0.3822(3)	3.2(1)
C62	0.2656(5)	−0.0646(3)	0.3958(3)	3.9(1)
C63	0.2830(5)	−0.0484(3)	0.4691(4)	4.6(1)
C64	0.2197(5)	−0.0722(4)	0.5268(3)	4.9(2)
C65	0.1401(6)	−0.1124(4)	0.5151(3)	5.5(2)
C66	0.1218(5)	−0.1298(3)	0.4422(3)	4.4(1)
C71	0.4380(4)	−0.0492(3)	0.2536(3)	3.6(1)
C72	0.4544(5)	−0.1227(3)	0.2580(3)	4.7(1)
C73	0.5226(6)	−0.1484(4)	0.3027(4)	6.7(2)
C74	0.5747(6)	−0.1026(5)	0.3440(4)	8.0(2)
C75	0.5569(6)	−0.0300(5)	0.3406(5)	7.5(2)
C76	0.4912(4)	−0.0020(4)	0.2957(3)	4.9(1)
C81	0.1859(4)	0.0800(3)	0.3460(3)	3.6(1)
C82	0.1326(5)	0.0793(3)	0.4159(3)	4.8(1)
C83	0.1613(6)	0.1205(4)	0.4729(4)	6.7(2)
C84	0.2406(6)	0.1610(5)	0.4632(5)	8.1(2)
C85	0.2960(7)	0.1642(5)	0.3925(5)	9.4(2)
C86	0.2673(6)	0.1228(4)	0.3354(4)	6.3(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)*-[a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1 2).

Actually, it is quite an idealization to describe either of these structures as octahedral. In the yellow (C$_2$) isomer, the P1–Ru–P2 angle, 103.2°, is much greater than the ideal angle of 90°. The expansion of this angle must be due mainly to the demands of two bulky PPh$_3$ ligands in *cis* positions. In Ru(HCS$_2$)$_2$(PPh$_3$)$_2$, the P–Ru–P angle is known [7] to be 101.3°. In other ruthenium(II) complexes of the type Ru(AB)$_2$(PPh$_3$)$_2$ (where AB is a chelating ligand of type *1* or *2*) the PPh$_3$ ligands are known to have the *trans*-configuration.

The expansion of the P–Ru–P angle is abetted by the small chelate angles N1–Ru–N2 and N3–Ru–

TABLE IV. Some Bond Distances and Angles in C_2-Ru(PhNpy)$_2$(PPh$_3$)$_2$.

Bond Distances, Å			
Ru–P(1)	2.286(3)	P(2)–C(51)	1.840(9)
Ru–P(2)	2.307(3)	P(2)–C(61)	1.860(9)
Ru–N(1)	2.086(6)	N(1)–C(1)	1.340(9)
Ru–N(2)	2.156(6)	N(1)–C(5)	1.366(10)
Ru–N(3)	2.068(7)	N(2)–C(5)	1.352(9)
Ru–N(4)	2.182(7)	N(2)–C(71)	1.414(10)
P(1)–C(11)	1.850(10)	N(3)–C(6)	1.390(10)
P(1)–C(21)	1.846(10)	N(3)–C(10)	1.340(10)
P(1)–C(31)	1.870(9)	N(4)–C(6)	1.306(11)
P(2)–C(41)	1.834(9)	N(4)–C(81)	1.427(11)
Bond Angles, Deg.			
P(1)–Ru–P(2)	103.21(1)	Ru–N(4)–C(6)	93.8(6)
P(1)–Ru–N(1)	91.6(3)	Ru–N(2)–C(71)	144.2(6)
P(1)–Ru–N(2)	91.9(3)	Ru–N(4)–C(81)	143.1(6)
P(1)–Ru–N(3)	101.4(2)	Ru–P(1)–C(11)	118.6(3)
P(1)–Ru–N(4)	162.0(2)	Ru–P(1)–C(21)	119.8(3)
P(2)–Ru–N(1)	99.9(2)	Ru–P(1)–C(31)	113.6(3)
P(2)–Ru–N(2)	157.4(2)	Ru–P(2)–C(41)	122.4(3)
P(2)–Ru–N(3)	93.9(2)	Ru–P(2)–C(51)	112.6(3)
P(2)–Ru–N(4)	85.1(2)	Ru–P(2)–C(61)	115.8(3)
N(1)–Ru–N(2)	62.4(2)	C(1)–N(1)–C(5)	120.4(7)
N(1)–Ru–N(3)	158.4(3)	N(1)–C(5)–C(4)	122.0(8)
N(1)–Ru–N(4)	102.9(3)	C(5)–N(2)–C(71)	122.5(7)
N(2)–Ru–N(3)	99.6(3)	C(6)–N(3)–C(10)	120.0(8)
N(2)–Ru–N(4)	85.4(3)	N(3)–C(6)–C(7)	121.2(9)
N(3)–Ru–N(4)	61.6(3)	C(6)–N(4)–C(81)	122.3(8)
Ru–N(1)–C(5)	95.7(5)	N(4)–C(6)–N(3)	107.8(8)
Ru–N(2)–C(5)	93.0(5)	N(1)–C(5)–N(2)	108.0(7)
Ru–N(3)–C(6)	96.3(6)		

TABLE V. Some Bond Distances and Angles in C_1-Ru(PhNpy)$_2$(PPh$_3$)$_2$.

Bond Distances, Å			
Ru–P(1)	2.313(1)	P(2)–C(51)	1.856(4)
Ru–P(2)	2.337(1)	P(2)–C(61)	1.842(4)
Ru–N(1)	2.105(3)	N(1)–C(1)	1.347(5)
Ru–N(2)	2.185(3)	N(1)–C(5)	1.351(5)
Ru–N(3)	2.161(3)	N(2)–C(10)	1.316(5)
Ru–N(4)	2.073(3)	N(2)–C(81)	1.399(5)
P(1)–C(11)	1.861(4)	N(3)–C(1)	1.364(5)
P(1)–C(21)	1.849(4)	N(3)–C(71)	1.397(5)
P(1)–C(31)	1.849(4)	N(4)–C(6)	1.337(5)
P(2)–C(41)	1.844(4)	N(4)–C(10)	1.378(5)
Bond Angles, deg.			
P(1)–Ru–P(2)	104.59(3)	Ru–N(2)–C(10)	92.4(2)
P(1)–Ru–N(1)	89.42(9)	Ru–N(4)–C(10)	95.6(2)
P(1)–Ru–N(2)	158.64(9)	N(2)–C(10)–N(4)	109.5(3)
P(1)–Ru–N(3)	94.91(9)	Ru–N(3)–C(71)	139.5(3)
P(1)–Ru–N(4)	99.65(8)	Ru–N(2)–C(81)	144.2(3)
P(2)–Ru–N(1)	161.66(9)	Ru–P(1)–C(11)	110.4(1)
P(2)–Ru–N(2)	88.09(9)	Ru–P(1)–C(21)	119.5(1)
P(2)–Ru–N(3)	104.02(9)	Ru–P(1)–C(31)	123.5(1)
P(2)–Ru–N(4)	92.31(8)	Ru–P(2)–C(41)	118.0(1)
N(1)–Ru–N(2)	82.4(1)	Ru–P(2)–C(51)	120.1(1)
N(1)–Ru–N(3)	62.3(1)	Ru–P(2)–C(61)	112.8(1)
N(1)–Ru–N(4)	97.0(1)	C(1)–N(1)–C(5)	121.6(4)
N(2)–Ru–N(3)	98.6(1)	N(1)–C(1)–C(2)	120.5(3)
N(2)–Ru–N(4)	62.1(1)	C(1)–N(3)–C(71)	123.5(4)
N(3)–Ru–N(4)	154.6(1)	C(6)–N(4)–C(10)	120.9(3)
Ru–N(1)–C(1)	95.7(2)	N(4)–C(10)–C(9)	119.9(4)
Ru–N(3)–C(1)	92.7(3)	C(10)–N(2)–C(81)	122.6(3)
N(1)–C(1)–N(3)	109.1(3)		

N4, which are *ca.* 62°. The N1–C5–N2 and N4–C6–N3 angles are *ca.* 108° which is much lower than the ideal 120° angle for an sp^2 carbon. This deviation is due, of course, to the requirement of the four-membered chelate rings. The N1–Ru–N3 angle is *ca.* 158°, which means that the pyridine nitrogen atoms are not strictly *trans*. This decrease is attributable to the presence of two bulky PPh$_3$ ligands in the *cis*-positions. Bond lengths in this isomer are in the range: Ru–P, 2.28–2.31 Å; Ru–N, 2.06–2.19 Å, P–C, 1.83–1.87 Å. The Ru–P bond distances are short compared to those in other known complexes. In Ru(HCS)$_2$(PPh$_3$)$_2$, [7] Ru(PhCOO)(CO)Cl(PPh$_3$)$_2$, [8] Ru(OAc)(*p*–MeC$_6$H$_4$NCH)(CO)(PPh$_3$)$_2$ [9] and Ru(mhp)$_2$(PPh$_3$)$_2$ [10] the average Ru–P bond distances are 2.346 Å, 2.394 Å, 2.379 Å and 2.367 Å, respectively (where mhp = 6-methyl-2-pyridinolato). The shorter Ru–P bond length would permit an increase in the π-backbonding. Both here and in Ru(HCS$_2$)$_2$(PPh$_3$)$_2$ the Ru–P bonds are shorter than those in compounds where the PPh$_3$ are in *trans*-configuration, and, of course, the metal to phosphine π-donation is more effective in *cis* stereochemistry than in a *trans*-arrangement.

In the C_1 isomer, the P1–Ru–P2 angle is again large, *viz.*, 104.59°, and the chelate angles N1–Ru–N3 and N2–Ru–N4 are again *ca.* 62°, the same as in the other isomer. The difference between the two isomers is in the relative disposition of the PhNpy ligands. The N3–Ru–N4 angle is 154.6° compared to the corresponding N4–Ru–N3 angle of 158.4° for the other isomer. The decrease in the N3–Ru–N4 angle seems to be related to the relative increase in the P1–Ru–P2 angle. The angles N1–Ru–N4 and N2–Ru–N3 are *ca.* 98°. The angles N1–Ru–N2 is 82.4°. This is much lower than the corresponding angle N2–Ru–N4 which is 85.4°, in the C_2 isomer. The angle N1–Ru–N4 (97°) is less than N2–Ru–N3 (98.6°). This may be due to steric repulsion between two N–Ph groups. The N1–C1–N3 and N2–C10–N4 angles, 109.1° and 109.5°, respectively, show large deviations from the ideal 120° to make chelate ring formation possible. The O–C–N angles in Ru(mhp)$_2$(PPh$_3$)$_2$ [10] are 108.4° which is comparable to the N–C–N angles observed in the two molecules studied here. In the C_1 isomer, the Ru–P distances, 2.31–2.34 Å, are greater than that found in the other isomer. The Ru–N bond distances are the same in both isomers within the experimental error. However the Ru–N(py) bond lengths (average value 2.083 Å) are shorter than the Ru–N(Ph) bond lengths (average value, 2.171 Å). The Ru–d(π) → py–N–p(π) interaction seems to be greater than the Ru–d(π)–Ph–Np(π) interaction. While the acyclic nitrogen atom acts primarily as a σ-donor, the pyridine nitrogen atom is expected to behave as a σ-donor and π-acceptor. Though detailed structural information is not available the reported results on $Ru(Azpy)_2Cl_2$ shows [6a] that in these complexes the Ru–N(azo) bond lengths (2.049 Å) are shorter than Ru–N(pyridine) (1.980 Å); thus, the azo function in Azpy is an even better π-acceptor than the pyridine nitrogen atom. The observed [6b] high Ru^{III}/Ru^{II} formal potentials in these species are due to strong π-interaction between ruthenium and azpy (azpy = 2-(phenylazo)pyridine). The present isomers display the same couple at near zero potentials (*vide infra*) because they have chelating ligands which are poorer π-acceptors and good σ-donors.

The bite angle in the four membered rings in $Ru(PhNpy)_2(PPh_3)_2$ can be compared with other reported [7–14] complexes (Table VI). The extent of the compression of the chelate angle follows the order: MeCOO > PhCOO > mhp > PhNpy > SO_4-Ph_2PPy > CHS_2 ~ $Ph_2PCH_2PPh_2$ > S_2PEt_2. This trend shows the effect of the relative size of the coordinating atoms on the bite angle.

Electrochemistry

The electrochemical behavior of both complexes was studied by cyclic voltammetry using platinum as a working electrode, saturated calomel as the reference electrode (SCE) and platinum wire as an auxiliary electrode. Dichloromethane and 0.1 *M* tetrabutylammonium perchlorate were used as solvent and supporting electrolyte, respectively. The concentration of the complex was *ca.* 10^{-3} *M* and potentials were measured versus SCE at 298 K. Cyclic voltammograms are shown in Fig. 3. Electrochemical data are presented in Table VII.

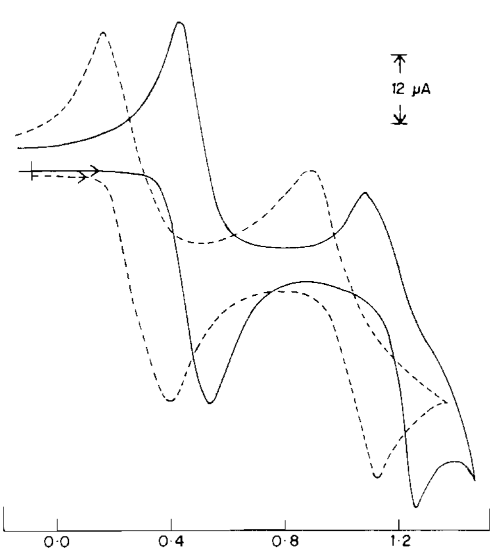


Fig. 3. Cyclic voltammograms of C_1-$Ru(PhNpy)_2(PPh_3)_2$ (solid line) and C_2-$Ru(PhNpy)_2(PPh_3)_2$ (dashed line). Both were taken in CH_2Cl_2 solution (concentration 1×10^{-3} *M*) with a platinum electrode and 0.1 *M* tetrabutyl ammonium perchlorate as supporting electrolyte. Scan rate was 40 mVs^{-1} and scan direction is shown by arrow sign.

Each complex exhibits two one-electron waves, near 0.4 and 1.1 V. Constant potential electrolysis occurred freely at a potential higher than the anodic peak potentials (E_{pa}) but no significant electrolysis takes place at potentials lower than the cathodic peak potentials (E_{pc}). This means that the complexes only undergo oxidation and not reduction. The one-electron stoichiometry of the electron transfer process was determined from the peak current measurements of these CV-grams and the one of the known [15] species $Os_2(\mu\text{-}O)(\mu\text{-dppm})_2Cl_6$.

The couple which appears at 0.48 V and 0.29 V in the C_1 and C_2 isomers, respectively, is due to oxidation of ruthenium(II) to ruthenium(III) (eqn. 1). The peak to peak separations (ΔEp) are 120 and 240 mV in C_1 and C_2 isomers,

TABLE VI. Chelate Angles in $Ru(PhNpy)_2(PPh_3)_2$ and Related Complexes.

Complex	X–Ru–Y	Angle, deg.	Ref.
$Ru(CO)(MeCOO)(p\text{-}MeC_6H_4NCH)(PPh_3)_2$	X = O, Y = O	58.7	9
$Ru(CO)Cl(PhCOO)(PPh_3)_2$	X = O, Y = O	61.0	8
$Ru(mhp)_2(PPh_3)_2$[a]	X = N, Y = O	61.8	10
C_2-$Ru(PhNpy)_2(PPh_3)_2$	X = N, Y = N	62.0	This work
C_1-$Ru(PhNpy)_2(PPh_3)_2$	X = N, Y = N	62.4	This work
$Ru(CO)_2(SO_4)(PPh_3)_2$	X = O, Y = O	66.8	14
$Ru(Ph_2Ppy)(CO)_2Cl_2$	X = N, Y = P	68.7	11
$Ru(HCS_2)_2(PPh_3)_2$	X = S, Y = S	71.0	7
$Ru(Ph_2PCH_2PPh_2)_2Cl_2$	X = P, Y = P	71.0	13
$Ru(S_2PEt_2)_2(PMe_2Ph)_2$	X = S, Y = S	77.5	12

[a] Mhp = 6-methyl-2-pyridinolato anion.

TABLE VII. Electrochemical Data[a] of $Ru(PhNpy)_2(PPh_3)_2$ in CH_2Cl_2 Solution (concentration 10^{-3} *M*) with 0.1 *M* TBAP as supporting electrolyte.

	C_2-Ru(PhNpy)$_2$-(PPh$_3$)$_2$	C_1-Ru(PhNpy)$_2$-(PPh$_3$)$_2$
Ru^{III}/Ru^{II} couple		
E_{pa}, V	0.540	0.420
E_{pc}, V	0.420	0.160
ΔE_p, mV	120	260
E°_{298}, V	0.480	0.290
V, mVs^{-1}	40	40
i_{pa}/i_{pc}	1.05	1.10
Ru^{IV}/Ru^{III} couple		
E_{pa}, V	1.270	1.180
E_{pc}, V	1.080	0.900
E°_{298}, V	1.175	1.040
ΔE_p, mV	190	280
V, mVs^{-1}	40	40

[a] E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively. ΔE_p is the peak to peak separation. E°_{298} is the formal redox potential and $E^\circ_{298} = (E_{pa} + E_{pc})/2$. V is the scan rate. i_{pa} and i_{pc} are the anodic and cathodic peak currents respectively.

$$Ru^{III}(PhNpy)_2(PPh_3)_2{}^+ + e^- \longrightarrow Ru^{II}(PhNpy)_2(PPh_3)_2 \quad (1)$$

respectively at 40 mVs^{-1}. This indicates that the electron-transfer process is quasi-reversible. The reversible ruthenium(II)–ruthenium(III) couple of $Ru(bpy)_3(ClO_4)_2$ in CH_2Cl_2 is known [6b] to have $\Delta Ep = 115$ mV. The anodic and cathodic peak current (i_{pa} and i_{pc} respectively) heights are approximately equal at scan rates 40–200 mVs^{-1}, and there is no peak current and peak potential shift on repeated scans.

The cyclic voltammetric response near 1.1 V is assignable to a ruthenium(III)–ruthenium(IV) couple (eqn. 2). The peak to peak separations

$$Ru^{IV}(PhNpy)_2(PPh_3)_2{}^{2+} + e^- \longrightarrow Ru^{III}(PhNpy)_2(PPh_3)_2{}^+ \quad (2)$$

are 190 and 280 mV for C_1 and C_2 isomers, respectively. The i_{pa}/i_{pc} ratio again approximately equals unity. It seems that the electron-transfer process is faster in the couple(1) than in the couple(2).

The electrochemical behaviour of closely similar compounds has not been reported in the literature and the best comparison we can make is with *cis*-$Ru(dppm)_2Cl_2$ (where dppm = diphenylphosphinomethane), where the Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples are known [16] to appear at 0.79 and >1.9 V, respectively, and the Ru^{IV}/Ru^{III} couple is irreversible, and with *cis*-$Ru(bpy)_2Cl_2$, where the couples appear [16] at 0.32 and 1.9 V. The presence of arylphosphines in a complex is expected to make the oxidation of the metal more difficult because they will help to stabilize the t_{2g} electrons. Comparisons of the formal potentials of Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples in the present compounds and for *cis*-$Ru(bpy)_2Cl_2$ and *cis*-$Ru(dppm)_2Cl_2$ confirm the weak π-acceptor ability of the PhNpy$^-$ ligand. To our knowledge, these are the lowest Ru^{III}/Ru^{II} and Ru^{IV}/Ru^{III} couples in ruthenium complexes having chelating aromatic nitrogenous ligands with a $Ru(NN)_2(P)_2$ coordination environment. Comparison between the formal potentials for C_1 and C_2 isomers suggests that the C_1 isomer is more stable than the C_2-one, which is in accord with the relative yields of the complexes. Similar observations are reported [6] in $Ru(Azpy)_2Cl_2$ complexes where the C_1 isomer is more stable than the C_2 one. Thermal isomerization of the C_2 to C_1 in high boiling solvents is known [6b] to occur in $Ru(Azpy)_2Cl_2$ species.

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