SYNTHESIS AND CHARACTERIZATION OF $Rh_2\{Ph(2-pyr)N\}_4$: A PRECURSOR TO A DIRHODIUM(III) DICATION CONTAINING AN Rh^2 Rh BOND

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Abstract— $Rh_2\{Ph(2-pyr)N\}_4$ has been prepared from hydrated rhodium trichloride and the sodium salt of 2-anilinopyridine in ethanol. The dark green air-stable compound has been characterized by analytical and spectroscopic measurements. The complex undergoes two facile one-electron oxidations at moderate potentials. The dication, $[Rh_2\{Ph(2-pyr)N\}_4]^{2+}$, formally contains two Rh(III) ions and a double Rh–Rh bond.

The one-electron oxidation of neutral binuclear Rh(II) compounds to the corresponding monocations, in which the mean oxidation state per Rh is 2.5, is well established¹⁻³ and results in a formal increase in Rh-Rh bond order from 1.0 to 1.5. The most extensively electrochemically studied series of dirhodium(II) complexes have been the tetracarboxylates $(Rh_2(O_2CR)_4L_2)^{4-14}$ Investigations into the electro-oxidation and electro-reduction reactions of Rh₂(O₂CR)₄ complexes in a number of solvents have shown that the midpoint potentials depended on the identify of both the carboxylate and the solvent.9 Carboxylates possessing electronwithdrawing substituents were more difficult to oxidize than those with electron-donating substituents and a linear relationship between oxidation potentials and Taft polar substituents constants has been observed. The potential for electrooxidation of a given Rh₂(O₂CR)₄ complex was inversely related to the solvent's donor ability.⁹ Investigations into the 1:1 and 1:2 Lewis base adducts 10,14 of Rh₂(O₂CR)₄ complexes have shown that the 1:2 adducts are more easily oxidized than the corresponding 1:1 adducts. The shifts in potential observed in these studies are in accord with expectations based on the model of Rh-Rh interactions put forth by Kawamura and Nakatsuji.

The impetus for this work was the observation

that, on replacing bridging carboxylate ions by amidates,¹⁵⁻¹⁹ that is changing the immediate coordination sphere about the $[Rh_2]^{4+}$ core from one of eight oxygen atoms to one comprising four oxygen and four nitrogen atoms, a shift in oxidation potentials to values which are 700-1000 mV less positive is observed. For example, the parent acetate complex Rh₂(O₂CCH₃)₄ undergoes a quasireversible one-electron oxidation at a potential of +1.17 V (SCE) in acetonitrile, while the amidate $Rh_2(HNC(O)CH_3)_4$ undergoes a corresponding oxidation at +0.15 V (SCE).¹⁹ Similar observations have been made for other pairs of dirhodium(II) compounds. In the two amidate-bridged compounds $Rh_2(C_6H_5NC(O)CH_3)_4$ and $Rh_2(HNC(O)CH_3)_4$ this shifting of oxidation potentials to less positive values is sufficiently dramatic that a second oxidation wave is brought into the available solvent range.^{18,19} These new one-electron oxidations occur at potentials >1.40 V (SCE), unfortunately too close to the solvent background for any further characterization of the doubly oxidized products to be feasible.

The substitution of a further four nitrogen atoms for the remaining four oxygens of the amidates ought to result in the further shifting of the oxidation potentials to less positive values and an increase in the relative stability of both the singly and doubly oxidized products. To test this hypothesis we have prepared a new dirhodium(II) complex, $Rh_2{Ph(2-pyr)N}_4$, in which the immedi-

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ate coordination sphere about the $[Rh_2]^{4+}$ core comprises eight nitrogen atoms. This complex undergoes two facile one-electron oxidations at moderate potentials. Although we have been unable to isolate the cations, $[Rh_2{Ph(2-pyr)N}_4]^{+/2+}$, they have been characterized spectroelectrochemically. This paper reports the synthesis and full characterization of the dirhodium(II) precursor and discusses its electron-transfer behaviour. A preliminary report of the redox behaviour of this compound has already appeared.²⁰

EXPERIMENTAL

Physical measurements

IR spectra were recorded in the region 4000–240 $\rm cm^{-1}$ on a Perkin–Elmer 983 spectrophotometer using Nujol mulls on CsI plates. The ¹H NMR spectrum was recorded on a Varian XL200 spectrometer. Electronic spectra were recorded in the range 1600–400 nm on a Varian 2390 spectrophotometer. Molecular weights were determined in acetone on a Perkin–Elmer Hitachi (model 115) osmometer calibrated with benzil. Mass spectra were by the University of London Intercollegiate Research Service at the School of Pharmacy.

Voltammetric studies employed a Metrohm E506 potentiostat interfaced with a Metrohm E505 cell-stand utilizing a three-electrode geometry. The working electrode consisted of either a dropping mercury electrode or a platinum wire electrode (Metrohm EA 285). A non-aqueous Ag-AgCl-Cl⁻, CH_2Cl_2 electrode, separated from the bulk of the solution by a fritted glass disk, was used as a reference electrode (Metrohm EA 441/5), and a platinum wire as an auxiliary electrode. Cyclic voltammetric (CV) measurements also employed a Metrohm E612 VA Scanner in conjunction with a Hewlett-Packard 7035B XY recorder. Currentvoltage curves were recorded at scan rates of 0.02- 0.50 V s^{-1} . The solvents used for the electrochemical measurements were CH2Cl2 and dimethylsulphoxide. The solvents contained 0.5 M tetra-n-butylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte. Deaeration of the solutions was carried out before commencing the experiment, and a stream of nitrogen was passed throughout. All potentials are reported with respect to the Ag-AgCl electrode, against which ferrocene is oxidized at a potential of +0.60 V. Spectroelectrochemistry was performed in an O.T.T.L.E. cell which had an optical path length of 0.10 cm. Time-resolved spectra were obtained using a Varian 2390 spectrophotometer.

Synthesis

Sodium metal (0.46 g, 20.0 mol) was added to a solution of 2-anilinopyridine (3.42 g, 20.0 mmol) in ethanol (50 cm³). The solution was stirred until all the sodium was dissolved (ca 15 min). To the homogeneous solution was added RhCl₃·3H₂O (0.50 g, 1.9 mmol). The resulting mixture was refluxed under N₂ for 3 h, after which time a microcrystalline dark green precipitate had formed. The precipitate was filtered off and recrystallized from MeOH. The final product was then extracted with the minimum volume of CH₂Cl₂ and then reprecipitated by addition of cold EtOH. The solid was dried in vacuo at room temperature. Yield 0.44 g (52%). Found : C, 59.4; H, 4.4; N, 12.7%. Calc. for Rh₂(C₁₁H₉N₂)₄: C, 59.8; H, 4.1; N, 12.7%. IR spectrum (Nujol mull, CsI plates); 1601 (s), 1584 (m), 1531 (w), 1508 (s), 1294 (s), 1229 (m), 1160 (w), 1015 (m), 858 (w), 743 (s), 709 (m), 529 (s), 506 (m), and 376 (w) cm^{-1} (s = strong, m = medium, w = weak). Electronic spectrum (1600-400 nm in CH₂Cl₂): 1015 ($\varepsilon = 2160 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$), 579 (770), and 476 (sh). ¹H NMR [CD₂Cl₂ solvent, $(CH_3)_4$ Si reference]: δ 6.5–8.5 ppm (complex multiplets). Mass spectrum : m/z 882, [Rh₂{Ph(2-713, $[Rh_2{Ph(2-pyr)N}_3]^+$; 544, $pyr)N_{4}^{+};$ $[Rh_{2}{Ph(2-pyr)N_{2}}^{+}; 441, [Rh{Ph(2-pyr)N_{2}}^{+};$ and 375, $[Rh_2{Ph(2-pyr)N}]^+$. Molecular weight (osmometrically in acetone): 864 (1.0×10^{-3}) , and 894 $(0.79 \times 10^{-3} \text{ mol } \text{dm}^{-3})$, calc. 882. The complex is soluble in a wide range of common organic solvents.

RESULTS AND DISCUSSION

The anion derived from 2-anilinopyridine has previously been observed to coordinate across both Mo and W quadruple bonds,²¹ across the Os-Os triple²² bond, in the complex $Os_2{Ph(2-pyr)N}_3Cl_3$, and across the $Ru^{2.5}_{-}Ru$ bond²³ in the complex Ru_{2} {Ph(2-pyr)N}₄Cl. The geometry of the last complex was unusual in that all four of the asymmetric ligands adopted the same orientation about the Ru^{2.5}Ru bond. Earlier attempts to prepare the Rh complex $Rh_2[Ph(2-pyr)N]_4$ by reaction of $RhCl_3 \cdot nH_2O$ with Na[Ph(2-pyr)N] were unsuccessful. When the reactants were combined in a 1:4 molar ratio a red solution was formed. Treatment of that solution with pyridine resulted in the deposition of orange crystals which were identified crystallographically as RhCl₂py₂[(C₆H₄)(2-pyr)NH].²⁴ In this complex the 2-anilinopyridinato ligand is not only coordinated through the pyridine nitrogen atom but also through an ortho carbon atom of

the phenyl group, thus forming a six-membered metallocyclic ring. However when RhCl₃·3H₂O and Na[Ph(2-pyr)N] are refluxed in EtOH, in a molar ratio of ca 1:10, for 2-3 h a dark green solution is formed, together with a dark precipitate. The recrystallization and subsequent extraction of this precipitate leads ultimately to the isolation of a complex with the empirical formula Rh{Ph(2pyr)N $_2$. The ¹H NMR spectrum in CD₂Cl₂ solvent only contains signals in the region δ 6.5–8.5 ppm. Considerable overlapping of these multiplets is observed and we have not attempted to assign the resonances to individual protons on the phenyl or pyridyl rings. Importantly no N-H resonance was observed in the range 0-20 ppm. The absence of a proton on the amine nitrogen atom is confirmed by the IR spectrum. The free ligand 2-anilinopyridine contains a v(N-H) stretching band at 3231 cm⁻¹, which is absent from the IR spectrum of the complex. The IR spectrum of the ortho-metallated complex, Rh₂Cl₂py₂[(C₆H₄)(2-pyr)NH], contained bands at 1522 and 1570 cm⁻¹ which were characteristic of the metallated phenyl ring.²⁴⁻²⁶ Analogous bands are absent from the spectrum of this complex, although several other strong bands do occur in the region 1500–1600 cm⁻¹. A strong band at 1604 cm^{-1} can be assigned to the skeletal vibrations of the pyridyl rings. Strong bands in the regions 700-850 and 500-540 cm⁻¹ are also characteristic of bridging 2-anilinopyridinato anions.^{22,23}

The binuclear nature of the product has been confirmed by a variety of techniques. The mass spectrum contains a strong parent-ion peak at m/z 882 corresponding to the binuclear cation $[Rh_2{Ph(2-pyr)N}_4]^+$. The successive loss of three of the bridging ligands, to give peaks at m/z 713, 544 and 375, is also observed, together with peaks due to the mononuclear fragment cations $[Rh{Ph(2-pyr)N}_3]^+$ and $[Rh{Ph(2-pyr)N}_2]^+$, at m/z 610 and 441, respectively. The complex was sufficiently soluble in acetone for its molecular weight to be determined by osmometry. Values obtained agree well with the proposed dimeric formulation (see Experimental). When four asymmetric ligands bridge a dimetal unit a total of four different geometric isomers are possible.²³ However, as we have observed that $Rh_2{Ph(2-pyr)N}_4$ does not readily form axial adducts, this suggests that a close approach to the sixth coordination site of each rhodium is not facile. It is likely that the presence of two pendant phenyl groups would be sufficient to block axial coordination and hence it appears reasonable to suggest that the molecule adopts structure 1 or 2. The former arrangement of bridging ligands has been observed for the Mo and W complexes M_2 {Ph(2-pyr)N}₄,²¹ while the *trans* dis-



position of two 2-anilinopyridine anionic ligands, both orientated in the same direction, has been observed in the mixed-ligand complex $Ru_2Cl(O_2C$ $CH_{3})_2\{Ph(2-pyr)N\}_2 \cdot Ph(2-pyr)NH.^{27}$

CV and linear alternating-current voltammetric (ACV) measurements were made in several solvents at a Pt electrode. Figure 1 shows the voltammetric



Fig. 1. Voltammetry of $Rh_2\{Ph(2-pyr)N\}_4$ in CH_2Cl_2 . Scan rate = 100 mV s⁻¹ (CV). Potentials vs Ag-AgCl reference electrode (against which ferrocene is oxidized at +0.60 V).

response of Rh_2 {Ph(2-pyr)N}₄ in CH₂Cl₂. Clearly the complex undergoes two oxidation processes in the potential range 0.0-0.8 V as well as being reduced at -1.13 V. The electrochemical oxidation of $Rh_2{Ph(2-pyr)N}_4$ to the cation $[Rh_2{Ph(2-pyr)N}_4]$ $pyr)N_{4}^{+}$ is straightforward and uncomplicated at $E_{1/2} = +0.07$ V. Diagnostic plots of $E_p - E_{p/2}$ and $E_p^a - E_p^c$ are in the range predicted for a one-electron transfer.²⁸ The peak current is proportional to the square root of the scan rate and $i_{p,a}/i_{p,c} = 1$, indicating a diffusion-controlled one-electron transfer. The second oxidation, the mid-point potential of which is +0.72 V, is chemically reversible, although apparently characterized by sluggish heterogeneous charge-transfer kinetics. Hence, although $i_{p,a}/i_{p,c} = 1.0$ at all scan rates, $\Delta E_p (E_p^a - E_p^c) = 100$ mV at v = 50 mV s⁻¹, and increases to 140 mV at 500 mV s^{-1} . In contrast to the oxidation behaviour of the dimer the reduction could be characterized as an irreversible process. A broad peak was obtained on the forward sweep and no peak was observed on the backward sweep. Neither scanning very rapidly nor recording the voltammograms at low temperatures improved the reversibility of this reduction wave. Analogous irreversible reduction waves have been reported for other dirhodium(II) complexes.9,29 The one-electron nature of both oxidation processes was indicated by the ACV peak widths at half height and confirmed by comparison of the diffusion-limited currents with that of a known quantity of ferrocene, as measured by stirred voltammetry. On the basis of the observed data, the following description is proposed for the oxidation/reduction of Rh_2 {Ph(2-pyr)N}₄:

$$\begin{array}{c} Rh_{2}\{Ph(2-pyr)N\}_{4} \xrightarrow{+e} [Rh_{2}\{Ph(2-pyr)N\}_{4}]^{-} \\ +e^{\dagger}|_{*} -e^{} \downarrow \\ [Rh_{2}\{Ph(2-pyr)N\}_{4}]^{+} \\ +e^{\dagger}|_{*} -e^{} \\ [Rh_{2}\{Ph(2-pyr)N\}_{4}]^{2+} \end{array}$$

Repeated attempts to isolate the mono- and dication, through chemical or electrochemical oxidation, have generally been unsuccessful. Hence we have of necessity characterized the cations $[Rh_2{Ph(2-pyr)N}_4]^{+/2+}$ in situ by controlled potential oxidation of $Rh_2{Ph(2-pyr)N}_4$ in an optically transparent cell sited in the beam of an electronic spectrophotometer.

The steady-state spectra obtained at potentials of -0.10, +0.20 and +0.85 V are illustrated in Fig. 2. These spectra (1, 2 and 3) correspond to Rh_2 {Ph(2 $pyr)N_{4}$, $[Rh_{2}{Ph(2-pyr)N_{4}}]^{+}$ and $[Rh_{2}{Ph(2-pyr)N_{4}}]^{+}$ $pyr)N_{4}^{2+}$, respectively, the band maxima and extinction coefficients of which are presented in Table 1. The transitions which occur upon sequential oxidation are totally reversible since the spectra obtained upon controlled potential reduction of the oxidized species were identical with those observed initially. The appearance of two isosbestic points in the time-resolved spectra obtained in carrying out reduction/oxidations is consistent with the 1:1 interconversions of reduced and oxidized forms of the complex. For completeness we have carried out a controlled-potential reduction, at -1.2 V, in the spectroeletrochemical cell. The steady-state spectrum obtained is illustrated by curve 4 in Fig. 2. A



Fig. 2. Steady-state electronic absorption spectra obtained at potentials of -0.10 V(1), +0.20 V(2), +0.85 V(3), and -1.20 V(4), in CH₂Cl₂-0.5 M TBABF₄.

Synthesis and characterization of Rh₂{Ph(2-pyr)N}₄

Complex	λ_{\max} of major peaks (nm) [ε (dm ⁻³ mol ⁻¹ cm ⁻¹)]
$Rh_{2}{Ph(2-pyr)N}_{4}$	1025 (2165), 579 (770), 476 (sh)
$[Rh_{2}{Ph(2-pyr)N}_{4}]^{+}$	1066 (5680), 525 (1235), 480 (sh)
$[Rh_{2}{Ph(2-pyr)N}_{4}]^{2+}$	1365 (7730), 500 (1545), 430 (sh)
" $[Rh_{2}{Ph(2-pyr)N}_{4}]^{1-}$ "	595 (700)

Table 1. Spectral characterization of $[Rh_2{Ph(2-pyr)N}_4]^n$ (n = -1, 0, 1 or 2) complexes

controlled-potential reoxidization did not result in the quantitative regeneration of the spectrum of the neutral molecule. This observation together with the absence of isosbestic points in the timeresolved spectra are consistent with our earlier deductions on the irreversible nature of this electrontransfer step.

The electronic spectrum of each of the species $[Rh_{2}{Ph(2-pyr)N}_{4}]^{0/+/2+}$ contains a moderate-tostrong band in the near-IR region of the electronic spectrum. The magnitude of the associated extinction coefficients suggests that these bands are due to a charge-transfer process, and we will not discuss them further. The electronic spectrum of each of the species in question contains a single distinct band in the visible portion of that spectrum together with a series of shoulders at higher energy. The neutral molecule is characterized by a band at 579 nm ($\varepsilon = 770 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$). Upon oxidation to the monocation that band moves to a higher energy, 525 nm, and increases in intensity. Further shifting and gain in intensity, to 500 nm and $\varepsilon = 1545$ dm⁻³ mol^{-1} cm⁻¹, accompanies the formation of the dication.

To attempt to make a detailed assignment of the electronic transitions for this complex, based upon extrapolation from the theoretical results^{13,30-34} obtained for the tetracarboxylates, $Rh_2(O_2CR)_4$, would be foolish. However, from the observations we have made, some useful general conclusions may be drawn. If the neutral dirhodium(II) complex, having no axial ligands, has the normal electronic ground state configuration $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*4}$, then the first electron to be removed by oxidation is likely to originate in the π^* molecular orbital. Thus the mono-oxidized product, $[Rh_2{Ph(2-pyr)N}_4]^+$, formally contains a Rh^{1.5}Rh bond, with the electronic configuration $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*3}$. In view of the smooth and reversible changes which occur in the electronic spectrum upon sequential oxidation, and which are consistent with the retention of the dimeric cage structure, we would suggest that the second electron removed also originated in the π^* molecular orbital. Hence the dication $[Rh_2{Ph(2-pyr)N}_4]^{2+}$ has the electronic configuration $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*2}$, and contains a Rh^{-2} -Rh bond.

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