Synthesis, Characterization and Structure of the Salicylate Salt of $[RuH(terpy)(PPh_3)_2]^+$ (terpy = 2,2′:6′,2″-terpyridine)†

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The complex $[RuH(terpy)(PPh_3)_2][C_7H_5O_3]$ **1** has been synthesised from 2,2′:6′,2″-terpyridine (terpy) and $[RuH(C_7H_5O_3)(PPh_3)_3]$ where $C_7H_5O_3$ is salicylate. It shows ν(RuH) at 1960 cm^{-1} and a hydridic ^1H triplet at δ −6.30, $J = 26.2$ Hz. The crystal structure of **1** has been determined: space group *Pnam*, $a = 14.705(7)$, $b = 15.380(6)$, $c = 22.667(9)$ Å, and $Z = 4$. The PPh_3 ligands are mutually *trans* about the Ru atom which, with the terpy ligand, lies on a mirror plane. The Ru–N distance *trans* to the hydride ligand is relatively long. The salicylate ion is internally hydrogen bonded. The complex displays a metal-to-ligand charge transfer transition (480 nm) and an irreversible metal oxidation $Ru^{II} \longrightarrow Ru^{III}$ at *ca.* 0.6 V.

The strong affinity of 2,2′:6′,2″-terpyridine (terpy) for ruthenium has been known for more than five decades.[1] During the last few years ruthenium terpy chemistry has received considerable attention.[2–6] Here we describe the synthesis, structure and properties of the first hydridoruthenium complex incorporating terpy, $[RuH(terpy)(PPh_3)_2]^+$, isolated as the salicylate ($C_7H_5O_3^-$).

Results and Discussion

The starting material used was $[RuH(C_7H_5O_3)(PPh_3)_3]$.[7] In warm benzene terpy displaces the salicylate ion and a PPh_3 ligand and red crystals of $[RuH(terpy)(PPh_3)_2][C_7H_5O_3]$ **1** are deposited in excellent yield. The complex absorbs strongly in the visible region with a metal-to-ligand charge transfer (m.l.c.t.) band[6a] $t_2(Ru) \longrightarrow \pi^*(terpy)$ at 480 nm (ε 3945 $dm^3\ mol^{-1}\ cm^{-1}$) associated with a shoulder at 345 nm (ε 8415 $dm^3\ mol^{-1}\ cm^{-1}$). Other bands are observed at 310 (ε 29 140) and 280 nm (ε 22 070 $dm^3\ mol^{-1}\ cm^{-1}$) [Fig. 1(*a*)].

The presence of co-ordinated hydride in complex **1** is revealed by the IR and ^1H NMR spectra. The Ru–H stretch occurs as a sharp and strong band at 1960 cm^{-1} in dichloromethane solution. In $CDCl_3$ solution the hydridic proton signal occurs at δ −6.30 as a symmetrical triplet with $J = 26.2$ Hz [Fig. 1(*b*)]. The hydride ligand is thus coupled to two equivalent PPh_3 donors suggesting a *trans* geometry for the $Ru(PPh_3)_2$ fragment.

A view of the crystal structure of the cation of complex **1** is shown in Fig. 2. Selected bond distances and angles are listed in Table 1. The metal and the terpy ligand are situated on a crystallographic mirror plane. The hydridic hydrogen atom could not be directly located. It has been fixed at a distance of 1.7 Å (ref. 8) from the metal in a position *trans* to N(2). This completes an approximately octahedral co-ordination about the Ru atom.

The Ru–N(2) distance of 2.011(7) Å in complex **1** is significantly longer than those in $[Ru(H_2O)(terpy)(PEt_3)_2][ClO_4]_2\cdot 2H_2O$[6b] and $[Ru(NO_2)(terpy)(PMe_3)_2][ClO_4]$,[6a] 1.952(9) and 1.985(5) Å respectively. The stronger *trans* influence of the hydride ligand[8b] is a plausible reason for this. The P–Ru–P angle in **1**, 162.5(1)°, is less obtuse than those in the other two phosphine complexes (≈176°).[6]

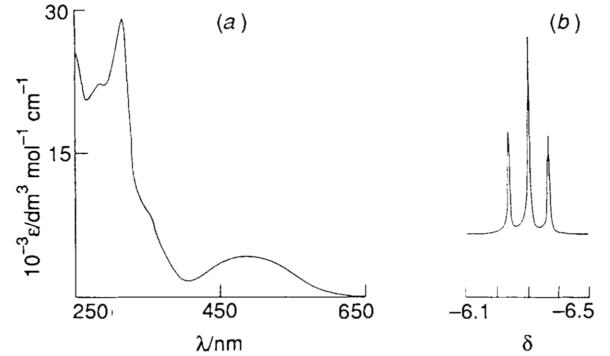

Fig. 1 (*a*) Electronic spectrum of complex **1** in dichloromethane solution. (*b*) Proton NMR spectrum of the hydridic proton of **1** in $CDCl_3$

Table 1 Selected bond lengths (Å) and angles (°) for $[RuH(terpy)(PPh_3)_2][C_7H_5O_3]$

Ru–P(1)	2.331(2)	Ru–N(2)	2.011(7)
Ru–N(1)	2.072(9)	Ru–N(3)	2.107(7)
P(1)–Ru–N(1)	94.2(1)	N(1)–Ru–N(2)	78.2(3)
P(1)–Ru–N(2)	98.2(1)	N(1)–Ru–N(3)	155.4(3)
P(1)–Ru–N(3)	89.3(1)	N(2)–Ru–N(3)	77.2(3)
P(1)–Ru–P(1A)	162.5(1)		

The salicylate ion is disordered, occupying one or other of a pair of sites related by the crystallographic mirror plane. The two carboxylate C–O distances are 1.23(2) and 1.31(2) Å. The presence of internal hydrogen bonding between the latter carboxylic oxygen and phenolic oxygen is indicated. The ^1H NMR signal of the acidic proton accordingly appears as a broad feature strongly shifted downfield to δ 16.31; it disappears upon shaking with D_2O.

Complex **1** displays an irreversible one-electron anodic cyclic voltammetric peak at 0.56 V *vs.* saturated calomel electrode (SCE) in MeCN (0.59 V in CH_2Cl_2). The complex $[RuCl(terpy)(PPh_3)_2][PF_6]$ is known to display a reversible Ru^{III}–Ru^{II} couple at 0.89 V in MeCN.[3a] In the case of **1** the anodic response is assigned to the $Ru^{II} \longrightarrow Ru^{III}$ oxidation. Rapid decomposition of the hydridic ruthenium(III) species so formed can account for the irreversible nature of the voltammogram.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Atomic coordinates (× 10^4) for $[RuH(terpy)(PPh_3)_2][C_7H_5O_3]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	939(1)	1021(1)	2500	C(20)	3510(5)	894(7)	4165(4)
P(1)	945(1)	1251(1)	3517(1)	C(21)	2682(5)	1264(6)	4007(4)
N(1)	−302(6)	379(6)	2500	C(22)	993(5)	2363(4)	3813(3)
N(2)	1328(5)	−232(5)	2500	C(23)	1033(6)	3085(4)	3452(3)
N(3)	2369(5)	1112(5)	2500	C(24)	1031(6)	3919(5)	3690(4)
C(1)	−1153(8)	726(8)	2500	C(25)	1012(6)	4025(6)	4288(4)
C(2)	−1930(9)	254(11)	2500	C(26)	979(7)	3303(6)	4659(4)
C(3)	−1873(9)	−632(9)	2500	C(27)	965(7)	2492(5)	4416(3)
C(4)	−1011(9)	−1030(8)	2500	C(28)	−59(5)	834(4)	3905(3)
C(5)	−261(7)	−490(8)	2500	C(29)	−34(11)	150(10)	4311(8)
C(6)	667(6)	−852(6)	2500	C(30)	−817(13)	−59(11)	4590(8)
C(7)	904(9)	−1726(6)	2500	C(31)	−1641(7)	272(7)	4442(5)
C(8)	1842(9)	−1935(7)	2500	C(32)	−1634(12)	1050(12)	4054(8)
C(9)	2483(8)	−1309(6)	2500	C(33)	−838(13)	1304(11)	3835(10)
C(10)	2211(7)	−458(6)	2500	C(34)	291(18)	7374(14)	3929(8)
C(11)	2798(7)	322(6)	2500	C(35)	810(13)	6607(9)	3605(7)
C(12)	3726(7)	248(7)	2500	C(36)	1621(12)	6455(10)	3792(8)
C(13)	4256(6)	999(8)	2500	C(37)	2087(17)	6811(15)	4219(12)
C(14)	3825(7)	1787(8)	2500	C(38)	1689(17)	7412(14)	4533(9)
C(15)	2895(7)	1819(6)	2500	C(39)	821(16)	7699(11)	4384(9)
C(16)	1943(5)	757(5)	3859(3)	C(40)	421(13)	6284(11)	3068(9)
C(17)	2048(6)	−147(6)	3880(4)	O(1)	−564(8)	7509(8)	3742(6)
C)18)	2881(7)	−504(6)	4039(4)	O(2)	−374(8)	6593(8)	2913(7)
C(19)	3614(6)	29(7)	4188(4)	O(3)	826(9)	5730(9)	2778(6)

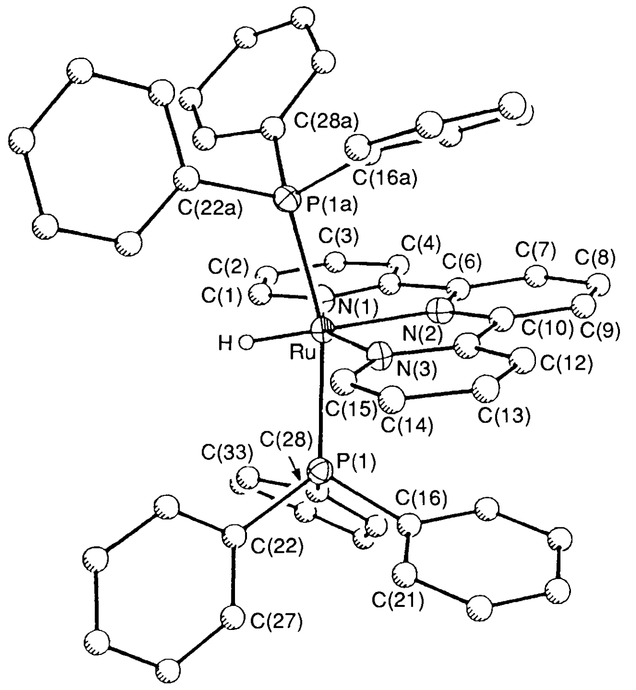

Fig. 2 Perspective view and atom labelling scheme for the cation of complex **1**

Experimental

Material.—The complex $[RuH(C_7H_5O_3)(PPh_3)_3]$ was prepared in excellent yield by a modification {heating $[Ru(PPh_3)_3Cl_2]$,[9] $C_7H_6O_3$ and NEt_3 in ethanol} of the reported method.[7] 2,2′:6′,2″-Terpyridine was purchased from Aldrich. The preparation of tetraethylammonium perchlorate and the purification of solvents for electrochemical and spectroscopic work were as before.[10]

Physical Measurements.—Spectroscopic data were obtained with the following spectrometers: electronic, Hitachi 330; IR, Perkin-Elmer 783; ^1H NMR ($CDCl_3$), Bruker 400 MHz FT. Electrochemical and microanalytical measurements were done as before.[10]

Preparation of Hydrido(2,2′:6′,2″-*terpyridine*)*bis*(*triphenylphosphine*)*ruthenium Salicylate*, $[RuH(terpy)(PPh_3)_2][C_7H_5O_3]$.—To a nitrogen-flushed solution of $[RuH(C_7H_5O_3)(PPh_3)_3]$ (100 mg, 0.09 mmol) in benzene (20 cm^3) was added 2,2′:6′,2″-terpyridine (25 mg, 0.11 mmol). The red solution was stirred and warmed under nitrogen for 2 h, then cooled to room temperature. The deposited crystals were collected by filtration, washed thoroughly with benzene and finally dried *in vacuo* over P_4O_{10}. Yield 90% (Found: C, 70.10; H, 4.65; N, 4.20. Calc. for $C_{58}H_{47}N_3O_3P_2Ru$: C, 69.85; H, 4.70; N, 4.20%). ^1H NMR ($CDCl_3$): δ −6.30 (t, H, Ru–H), 7.88 (d, 2 H, $H^{3,3''}$), 8.03 (d, 2 H, $H^{3',5'}$) and 16.309 (s, H, acidic salicylate proton):[6a,11] other aromatic signals (δ 7.48–6.45) not assigned due to overlap.

X-Ray Structure Determination.—Single crystals were grown by slow diffusion of a dichloromethane solution of complex **1** into hexane.

Crystal data. $C_{58}H_{47}N_3O_3P_2Ru$, $M = 996.1$, orthorhombic, space group *Pnam*, $a = 14.705(7)$, $b = 15.380(6)$, $c = 22.667(9)$ Å, $U = 5126(4)$ Å^3 (by least-squares fit of diffractometer angles for 25 automatically centred reflections), $Z = 4$, $D_c = 1.289$ g, cm^{-3}, dark brown prism (0.20 × 0.32 × 0.50 mm), μ(Mo-Kα) = 4.04 cm^{-1}, $\lambda = 0.710\,73$ Å, $F(000) = 2048$, 22 °C.

Data collection and processing. Nicolet R3m/V diffractometer, ω-scan method ($2 \leqslant 2\theta \leqslant 55°$), graphite-monochromated Mo-Kα radiation. 6430 Unique reflections, 3438 observed [$F > 6\sigma(F)$], corrected for Lorentz polarization effects; semiempirical absorption correction (transmission 0.863–0.792). Three standard reflections monitored showed no significant variations.

Solution and refinement. The structure was solved by direct methods and subsequently refined by full-matrix least-squares procedures. All non-hydrogen atoms were made anisotropic. The hydrogen atoms of the terpy moiety were located in a ΔF map and the rest were added in calculated positions with U values (isotropic thermal parameters) of 0.08 Å^2. The salicylate anion was disordered with respect to the terpy plane and its atoms were refined with a site occupation factor of 0.5. The final residuals R and R' were 0.0654 and 0.0669 respectively. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. The maximum and minimum residual electron densities in the final ΔF map were 0.79 and −0.69 e Å^{-3} respectively. Positional parameters for the non-hydrogen atoms are collected in Table 2.

Computations were carried out on a MicroVAX II computer using the SHELXTL-Plus program package.[12]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

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