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A monomeric ruthenium thiolato complex with a chelated η^6-arene ligand. The preparation and structure of $[Ru\{2\text{-}(\eta^6\text{-}Ph)\text{-}6\text{-}PhC_6H_3S\}(2,6\text{-}Ph_2C_6H_3S)(PPh_3)]$

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Abstract

Reaction of $[RuCl_2(PPh_3)_3]$ with the 2,6-diphenylthiophenolate anion (DPT) gives the complex $[Ru(\eta^6\text{-}DPT)(DPT)(PPh_3)]$, with one thiol phenyl substituent η^6-bonded to the ruthenium. The X-ray crystal structure reveals a distorted piano stool type of geometry. Crystal data: space group $P2_1/c$, $a=14.204(4)$, $b=9.503(5)$, $c=31.680(9)$ Å, $\beta=97.40(3)°$, $Z=4$. The η^6-arene ligand is labile and can readily be replaced by CO and 1,2-bis(diphenylphosphino)ethane.

Introduction

The ruthenium chemistry associated with 2,6-dialkyl and fluoro-substituted thiophenolate ligands has recently received considerable attention [1–4]. The dominant feature of the coordination chemistry of these complexes is the formation of four or five coordinate complexes, and since such complexes are formally electronic deficient, some of them exhibit weak interactions of the metals with *ortho*-alkyl hydrogens or *ortho*-fluoro groups [4]. We have recently reported the synthesis of the molybdenum complex $[Mo(\eta^6\text{-}DPT)(DPT)(CO)]$ [5, 6], and other workers have described the synthesis of the η^1- and η^6-bonded complexes $[Mo(\eta^1\text{-}DPP)(DPP)(NHMe_2]$ and $[MoH(\eta^6\text{-}DPP)(PMePh_2)_2]$ by reaction of 2,6-diphenylphenol (DPPH) with appropriate molybdenum precursors [7]. We have now attempted to extend this chemistry to generate analogous thiolato complexes of the platinum group metals. It has already been shown [6] that $RhCl_3$ reacts with DPT to give a binuclear complex with a bridging thiolate ligand also σ-bonded via a phenyl substituent, rather than an Rh η^6-arene complex. Here we report the preparation and structure of a monomeric 18-electron thiolato complex of ruthenium(II) containing a chelated η^6-arene ligand in which the η^6-arene group is readily displaced by a range of ligands.

Experimental

Syntheses of complexes and ligands were routinely carried out under N_2 using standard Schlenk line techniques, and solvents freshly distilled over suitable drying agents prior to use. $[RuCl_2(PPh_3)_3]$ and the ligand DPT were synthesized by the literature methods [6, 8].

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a EX-270 JEOL spectrometer (270 MHz) in $CDCl_3$ solutions; IR spectra were recorded on a Perkin-Elmer 1330 spectrophotometer using Nujol mulls between KBr discs; UV–Vis spectra on a PU-8730 UV–Vis scanning spectrophotometer for CH_2Cl_2 solutions using quartz cells having a path length of 1 cm. Elemental analyses are by courtesy of MEDAC Ltd. using either CEC 240xA or Carlo Erba 1106 instruments.

Cyclic voltammetric measurements were made on an EG and G PAR model 362 scanning potentiostat. This was interfaced via an A/D converter to an Opus 3 microcomputer. The CV data was analysed using the CONDECON software programme [9]. A three-electrode cell configuration was used with a platinum-wire working electrode and platinum-wire secondary electrode, with silver wire as a pseudo-reference electrode.

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Synthesis of the title compound (I)

To a suspension of $[RuCl_2(PPh_3)_3]$ (0.12 g, 0.12 mmol) in methanol (25 ml), was added four mole equivalents of 2,6-diphenylthiophenol (0.13 g, 0.49 mmol) and about an equivalent amount of triethylamine (0.15 ml). The suspension was heated under reflux for 3 h. A red precipitate was generated which was collected by filtration and washed with methanol and ether. Yield 0.10 g, 90%. *Anal.* Calc. for $C_{54}H_{41}PS_2Ru$: C, 73.2, H, 4.7. Found, C, 72.5, H, 4.5%. Absorption spectrum (CH_2Cl_2): λ_{max} 315.2.

Reaction of title compound with CO

CO gas was bubbled through a toluene solution of the η^6-arene complex (0.04 g) for about 15 min at 45 °C to give a yellow solution. The solvent was evaporated under reduced pressure to produce a green residue which became yellow on standing in air or under dinitrogen.

Reaction of title compound with 1,2-bis(diphenylphosphino)ethane (dppe)

Excess dppe (0.1 g) was added to a red solution of the title complex (0.04 g) in toluene. After heating under reflux for 3 h, a yellow solution was produced. The solvent was removed under reduced pressure and the resulting yellow oil triturated with diethyl ether. The small amount of yellow product was filtered off and dried *in vacuo*.

X-ray data collection and structure determination

The crystal measured 0.5 × 0.3 × 0.2 mm. Crystal data: $C_{54}H_{41}PRuS_2$, monoclinic, space group $P2_1/c$, $a=14.204(4)$, $b=9.503(5)$, $c=31.680(9)$ Å, $\beta=97.40(3)°$, $U=4241$ Å^3, $Z=4$, $D_c=1.39$ g cm^{-3}, $F(000)=1824$, $T=23$ °C, (Mo Kα) = 0.71069 Å, $2\theta_{max}=50.1°$, RIGAKU/MSC diffractometer, $\omega/2\theta$ scan, the minimax scan rate 16° min^{-1} (in ω), scan width 0.798° + 0.350tanθ. The structure analysis is based on 2953 observed reflections with $I>3\sigma(I)$; the intensities were corrected for absorption using empirical scan data, and for Lorentz and polarization factors. The structure was solved by direct methods and was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-H atoms (523 variables). Final $R=0.073$, $R_w=0.087$, $S=1.70$, $(\Delta/\sigma_{max}=0.27$. The final difference electron density synthesis showed maximum features of 1.01 and −0.99 e Å^{-3}. All calculations were performed on a Micro VAX II computer using the TEXSAN program. The scattering factors were taken from the International Tables. Atomic coordinates and thermal parameters are listed in Table 1; selected bond lengths and angles are given in Table 2.

TABLE 1. Atomic coordinates

Atom	x	y	z	B_{eq}
Ru	0.7554(1)	0.1951(1)	0.84852(4)	3.08(5)
S(1)	0.7523(3)	−0.0523(5)	0.8324(1)	3.8(2)
S(2)	0.6163(3)	0.1535(5)	0.8814(1)	3.9(2)
P	0.8457(3)	0.1301(5)	0.9125(1)	3.0(2)
C(11)	0.968(1)	0.179(2)	0.9130(4)	3.1(6)
C(12)	1.014(1)	0.272(2)	0.9432(5)	4.7(9)
C(13)	1.108(1)	0.312(3)	0.9414(5)	7(1)
C(14)	1.155(1)	0.272(3)	0.9097(7)	7(1)
C(15)	1.114(1)	0.175(3)	0.8795(6)	7(1)
C(16)	1.019(1)	0.138(2)	0.8806(4)	4.3(8)
C(21)	0.812(1)	0.198(2)	0.9627(4)	3.0(6)
C(22)	0.758(1)	0.316(2)	0.9632(4)	4.1(8)
C(23)	0.732(1)	0.372(2)	1.0009(5)	4.6(8)
C(24)	0.763(1)	0.305(2)	1.0387(5)	4.9(8)
C(25)	0.819(1)	0.193(2)	1.0401(4)	5.0(8)
C(26)	0.844(1)	0.138(2)	1.0018(4)	3.6(7)
C(31)	0.854(1)	−0.060(2)	0.9242(4)	2.8(6)
C(32)	0.772(1)	−0.123(2)	0.9337(5)	5(1)
C(33)	0.778(1)	−0.267(2)	0.9443(5)	5(1)
C(34)	0.858(1)	−0.341(2)	0.9460(5)	4.8(9)
C(35)	0.938(1)	−0.276(2)	0.9362(6)	6(1)
C(36)	0.935(1)	−0.135(2)	0.9264(5)	4.4(8)
C(41)	0.737(1)	−0.069(2)	0.7752(4)	4.6(8)
C(42)	0.814(1)	−0.092(2)	0.7540(5)	4.7(9)
C(43)	0.804(2)	−0.098(2)	0.7094(5)	7(1)
C(44)	0.713(2)	−0.079(3)	0.6870(5)	8(1)
C(45)	0.638(1)	−0.053(3)	0.7066(5)	7(1)
C(46)	0.645(1)	−0.051(2)	0.7517(5)	5(1)
C(51)	0.911(2)	−0.120(3)	0.7765(6)	6(1)
C(52)	0.929(2)	−0.225(2)	0.8070(6)	7(1)
C(53)	1.024(2)	−0.244(4)	0.8245(8)	11(2)
C(54)	1.098(2)	−0.177(5)	0.8154(8)	12(2)
C(55)	1.082(2)	−0.068(4)	0.7866(8)	10(2)
C(56)	0.987(2)	−0.042(3)	0.7672(6)	7(1)
C(61)	0.558(1)	−0.035(2)	0.7713(5)	5(1)
C(62)	0.528(1)	−0.113(2)	0.8017(5)	6(1)
C(63)	0.440(2)	−0.100(2)	0.8164(5)	6(1)
C(64)	0.378(2)	0.009(3)	0.7991(9)	10(2)
C(65)	0.406(2)	0.090(3)	0.7669(9)	8(2)
C(66)	0.492(1)	0.070(2)	0.7541(6)	5(1)
C(71)	0.576(1)	0.331(2)	0.8849(5)	4.4(9)
C(72)	0.503(2)	0.359(3)	0.9106(6)	6(1)
C(73)	0.481(2)	0.500(4)	0.9160(8)	9(2)
C(74)	0.526(2)	0.609(3)	0.8970(8)	9(2)
C(75)	0.596(2)	0.578(2)	0.8717(8)	8(1)
C(76)	0.617(2)	0.436(3)	0.8660(6)	6(1)
C(81)	0.459(1)	0.252(3)	0.9334(6)	7(1)
C(82)	0.455(1)	0.254(3)	0.9777(6)	9(1)
C(83)	0.417(2)	0.151(4)	1.0002(7)	12(2)
C(84)	0.375(2)	0.039(4)	0.9779(9)	12(2)
C(85)	0.373(2)	0.031(4)	0.9345(9)	11(2)
C(86)	0.414(1)	0.133(3)	0.9132(7)	9(2)
C(91)	0.699(1)	0.938(2)	0.8384(5)	3.8(8)
C(92)	0.791(1)	0.419(2)	0.8525(5)	4.1(8)
C(93)	0.861(1)	0.354(2)	0.8305(5)	5(1)
C(94)	0.832(1)	0.269(2)	0.7952(5)	6(1)
C(95)	0.736(2)	0.266(2)	0.7799(5)	5(1)
C(96)	0.670(1)	0.328(2)	0.7997(5)	5(1)

TABLE 2. Selected bond distances (Å) and bond angles (°)

Ru–C(91)	2.10(2)	Ru–C(92)	2.19(2)
Ru–C(93)	2.25(1)	Ru–C(94)	2.23(2)
Ru–C(95)	2.26(1)	Ru–C(96)	2.23(1)
Ru–P	2.337(4)	Ru–S(1)	2.405(5)
Ru–S(2)	2.383(4)	S(1)–C(41)	1.80(1)
S(2)–C(71)	1.79(2)	P–C(11)	1.79(1)
P–C(21)	1.83(1)	P–C(31)	1.84(2)
P–Ru–S(2)	88.3(1)	P–Ru–S(1)	85.3(1)
S(2)–Ru–S(1)	86.4(2)	C(71)–C(76)–C(91)	118(2)
S(2)–C(71)–C(76)	121(2)	S(2)–C(71)–C(72)	118(2)
C(71)–S(2)–Ru	99.3(7)	C(91)–Ru–S(2)	84.1(5)

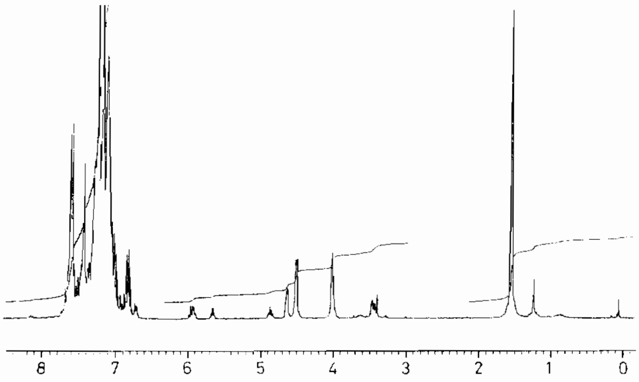

Fig. 1. ^1H NMR spectrum ($CDCl_3$) of title complex.

Results and discussion

The synthesis of the η^6-arene complex [Ru(η^6-DPT)(DPT)(PPh_3)] was achieved by the reaction of [$RuCl_2(PPh_3)_3$] [8] with four equivalents of 2,6-diphenylthiophenol [6] and triethylamine in methanol under reflux. The complex was isolated as a red powder by filtration, then recrystallized from $CHCl_3$/ether in 80–90% yield. Elemental analysis suggested the formulation [$Ru(DPT)_2(PPh_3)$].

Spectroscopy

The ^1H NMR data was diagnostic of an η^6-arene interaction with the most striking feature of the NMR spectrum [6] being the appearance of five multiplet resonances in the 3–6 ppm region (Fig. 1), each integrating as one proton (δ 6.72 (d, *ortho*-H), 5.66 (t, *meta*-H), 4.85 (t, *meta*-H), 4.50 (d, *ortho*-H), 3.44 (t, *para*-H)). These are assigned to the phenyl protons of an η^6-coordinated arene ligand. Complete assignment of the η^6-arene resonances was possible using proton decoupling procedures. The chemical shifts for the η^6-arene ligand lie in the range 3–7 ppm and the coupling constant values are about 6 Hz. Both parameters are of the same order of magnitude as found for other similar η^6-arene complexes [5, 6]. Other chelated η^6-arene ligand complexes of Cr and Mo are reported to exhibit, at most, three resonances. The five proton resonances seen for the complex arises from the lower overall symmetry within the molecule. The *para*-proton resonance for the η^6-arene group is shifted to significantly higher fields than the *ortho*- and *meta*-protons.

The ^{13}C NMR shows four resonances in the 70–120 region (δ 78.5, 79.0, 87.5 and 111.4 ppm; *p*-, *m*-, *o*- and *ipso*-carbon atoms of the η^6-C_6H_5 ring) which are assigned to the phenyl carbons of the η^6-coordinated arene ligand [6].

The ^{31}P NMR spectrum shows one resonance at 36.9 ppm assigned to a single bound PPh_3 ligand. The IR spectrum of the complex shows sharp bands at 510 and 531 cm^{-1}, which also indicates the presence of a PPh_3 ligand in the compound.

X-ray structure

A perspective view of the structure of the title complex is shown in Fig. 2, and a further view with most of the phenyl groups omitted for the sake of clarity appears in Fig. 3. The dominant feature of the structure is the presence of an η^6-arene ligand moiety from an *o*-phenyl substituent of one of the thiolate ligands which is also bound via sulfur. The overall geometry about Ru is a distorted variant of the 'three-legged piano stool' structure commonly found for mono-η^6-arene complexes.

The three angles S(1)–Ru–S(2), S(1)–Ru–P and S(2)–Ru–P are almost the same (86.4, 85.3 and 88.3, respectively), and there is only slight inequivalence among the three bond lengths (Ru–S(1) = 2.41, Ru–S(2) = 2.38, Ru–P = 2.34 Å), so that the plane of the η^6-arene group and the plane which is formed by the atoms S(1), S(2) and P are almost parallel (the interplanar angle is 171°). Thus we could regard the complex to have approximately C_3 symmetry when we consider only the donor atom framework of the complex. This is significantly different from the previous reported

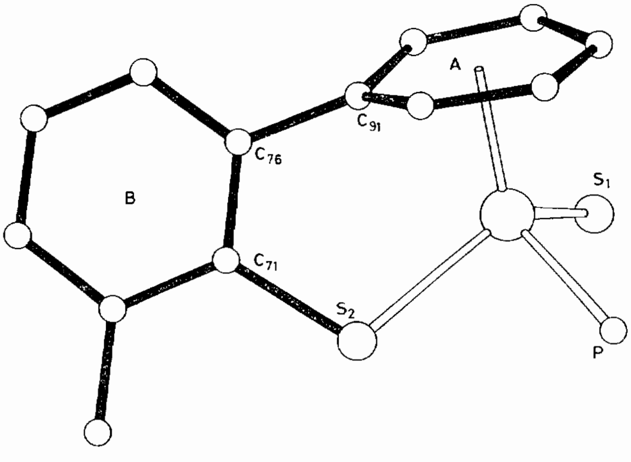

Fig. 2. Perspective view of the molecule [Ru(η^6-DPT)(DPT)(PPh_3)], showing the atom-numbering scheme.

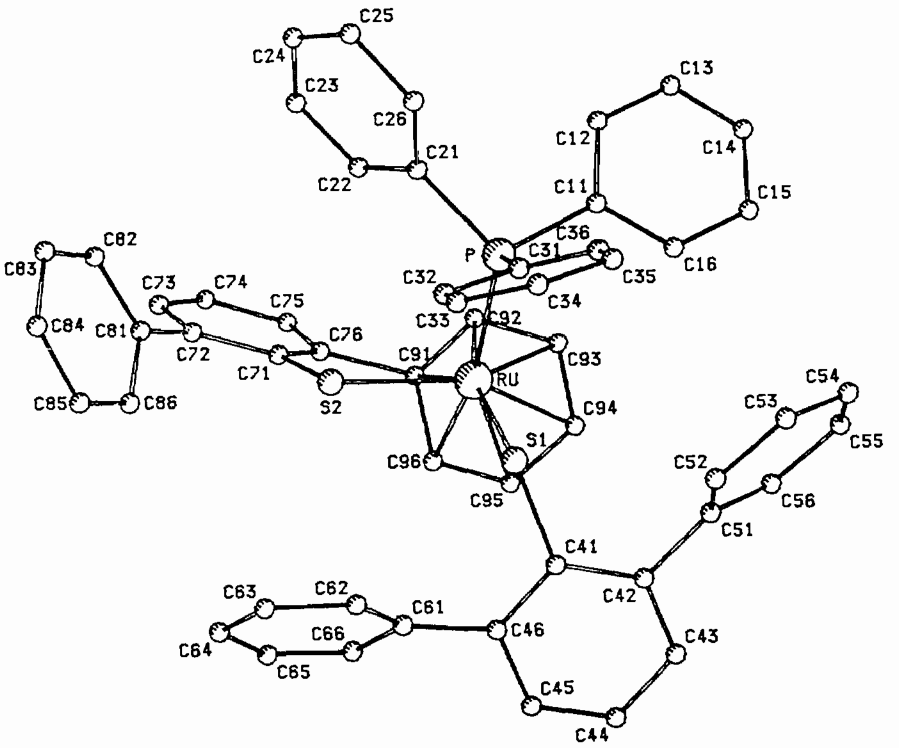

Fig. 3. An ORTEP view of the title complex with the majority of the phenyl groups omitted for clarity.

complex of Mo, in which the steric interactions between the two thiolato ligands cause considerable variations among these three angles [5, 6]. Presumably in this case the steric bulk of the PPh_3 ligand prevents any increase in the S(1)–Ru–S(2) angle.

The plane of the non-coordinated *o*-phenyl ring, C (Fig. 3) lies at 53° to the thiophenol phenyl ring B. η^6-Coordination of the *o*-phenyl ring, A, causes an increase of this interplanar angle to 71°. The rotation of ring A relative to B accompanies a displacement of the ruthenium atom from the plane of the chelate ring atoms C(91), C(76), C(71), S(2) (Fig. 2), but the Ru atom also achieves a position on the normal through the centre of ring A. The six carbon atoms are located in a plane with the centroid of the ring 1.72 Å from the Ru atom. However, only C(91) is closer to the Ru than the other five C atoms (Ru–C(91) = 2.10, Ru–C_{other} = 2.19–2.26 Å) which causes some distortion in the η^6-arene ring. These distances nevertheless all lie within the range found for other Ru η^6-arene complexes [10]. A similar distortion was observed in the Mo η^6-DPT complex.

Reactivity

As with other η^6-arene complexes the π-bonded phenyl group is readily displaced by a variety of two-electron-donor ligands.

The complex readily reacts with CO at atmospheric pressure in toluene to give a yellow solution, which shows some unexpected properties. On attempting to remove solvent under vacuum, the solution turns green immediately, and when exposed to the atmosphere the solution in the flask immediately became yellow again. When the above experiment was repeated, but this time the flask was opened to either N_2 or argon, the same behaviour was observed. Finally, the solution was evaporated to dryness and a green solid was isolated. When N_2 was passed into the flask, the solid turned to yellow after a few minutes. The IR of the yellow solid displayed two sharp bands at 1975 and 2010 cm^{-1}, indicating that more than one CO ligand is bonded to Ru. The ^1H NMR now showed no evidence for an η^6-arene ligand. These reactions have been followed by using solution IR and ^{31}P NMR spectroscopy; the initial yellow product, following green product and subsequent yellow product all showed the same IR and ^{31}P NMR spectra (δ_P = 29.16 ppm). For the NMR spectra $CDCl_3$ was used as solvent and the same sequence of colour changes was observed. These data suggest that the three products are in fact substantially the same complex, formulated as the sixteen electron species $[Ru(DPT)_2(CO)_2(PPh_3)]$. We are not at present able to provide an entirely convincing explanation for the colour changes that occur, although they do so completely reproducibly. The spectroscopy is consistent with the presence of a small amount of a highly coloured species. Despite repeated attempts, we were not able to obtain satisfactory elemental analyses for the carbonyl

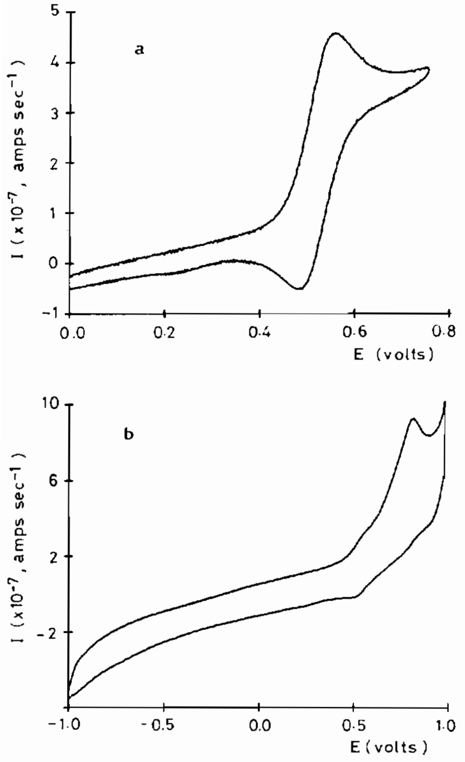

Fig. 4. (a) Cyclic voltammogram of title complex, at scan rate 0.5 V s^{-1}, platinum electrode, 0.3 mol dm^{-3} [NBU$_4$][BF$_4$] in CH$_2$Cl$_2$. (b) After CO bubbled for 15 min.

complex. The analogous Mo complex also forms an unstable carbonyl complex on treatment with carbon monoxide [6].

The complex reacted with excess dppe, when heated under reflux in toluene, to give a yellow solution. The ^{1}H NMR spectrum shows the η^6-arene is missing; the ^{31}P NMR spectrum exhibits a sharp single peak at $\delta_P = 35.54$ ppm which shows the existence of only one phosphorous environment. This is consistent with the displacement of the PPh$_3$ ligand to give the complex [Ru(DPT)$_2$(dppe)$_2$] where the bulky thiolate ligands are assigned to *trans*-sites. However, attempts to characterize the product were not successful.

Disappointingly the title complex shows no sign of any reactions with H$_2$ or diphenylacetylene in toluene at room temperature.

Electrochemistry

The redox behaviour of the red η^6-arene complex was studied at a platinum-wire electrode in 0.3 mol dm^{-3} [NBu$^n{}_4$][BF$_4$]–CH$_2$Cl$_2$ under an atmosphere of N$_2$. The resulting cyclic voltammogram is shown in Fig. 4. There is a reversible oxidation at $E_{1/2} = +0.53$ V, but no discernible reduction process. The reversibility of the oxidation couple is indicated by the near-unity value for the ratio i_{pa}/i_{pc} over the scan range 0.02–0.5 V s^{-1} and the symmetry of the plot of current function (dI/dt) with potential. However the I_1 convolution of the process [9] indicated that it is not entirely reversible and that there is some chemical decomposition of the [Ru(η^6-DPT)(DPT)(PPh$_3$)]$^-$ anion in solution. The peak separations (ΔE_p) are of the order 70 mV, again indicative of a diffusion controlled Nernstian process.

A solution of the η^6-arene complex was bubbled with a CO gas for 15 min until the solution turned yellow, and the CV of the resulting solution was recorded (Fig. 4(b)). Only an irreversible oxidation process at $E_p = +0.8$ V was observed. The irreversibility of this process is due to decomposition by loss of CO of the cationic carbonyl Ru(III) complex formed by oxidation.

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