

A Cyclometallated (Azobenzene)palladium(II) Complex of 1,4,7-Trithiacyclononane: Synthesis and Reactivity with Thioether-Dithiolate Metalloligands, Single-Crystal X-ray Diffraction Analyses and Electrochemical Studies

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Keywords: Palladium / Heterometallic complexes / S ligands / Ruthenium / Crown compounds

The treatment of $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\mu\text{-Cl})_2]$ (**5**) with $\text{AgPF}_6/\text{NH}_4\text{PF}_6$ in acetone, followed by the addition of two molar equivalents of 1,4,7-trithiacyclononane (9S3), gives the deep red complex $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(9\text{S3})][\text{PF}_6]$ (**6A**) in high yield, whereas the direct reaction of **5** with two molar equivalents of 9S3 gives $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(9\text{S3})][\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)\text{Cl}_2]$ (**6B**) in quantitative yield based on **5**. The subsequent reaction of **5** and **6A** with the metalloligand $[(\text{HMB})\text{Ru}^{\text{II}}(\eta^3\text{-tpdt})]$ [**3**; HMB = $\eta^6\text{-C}_6\text{Me}_6$, tpdt = $\text{S}(\text{CH}_2\text{-CH}_2\text{S}^-)_2$] results in displacement of the chloride and 9S3 ligands, respectively, to give the Ru-Pd heterobimetallic complex $\{[(\text{HMB})\text{Ru}^{\text{II}}(\mu\text{-}\eta^2\text{:}\eta^3\text{-tpdt})][\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)]\}[\text{PF}_6]$ (**7**) in 85 % yield. Similar reactions with the Cp* analogue of **3**, namely $[(\text{Cp}^*)\text{Ru}^{\text{III}}(\eta^3\text{-tpdt})]$ (**4**), give the trinuclear complex

$[(\text{Cp}^*\text{Ru}^{\text{III}}(\mu\text{-}\eta^2\text{:}\eta^3\text{-tpdt}))_2\text{Pd}](\text{PF}_6)_2$ (**8**), in which all the ligands on palladium have been displaced, in a yield of around 80 %. X-ray diffraction analyses of **6A**, **6B** and its solvates (**6B**·H₂O and **6B**·CHCl₃) have shown that short atom–atom interactions between the cation and the counterion and lattice solvent molecules have a significant effect on the bond parameters of the molecules, and ¹H NMR spectroscopy indicates that these interactions persist even in solution. The single-crystal X-ray structure of **7** has also been determined. Cyclic voltammetry experiments have been performed on **6A**, **6B** and **7** in CH₂Cl₂ and CH₃CN at GC and Pt electrodes.

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1. Introduction

The coordination chemistry of crown thioethers such as 1,4,7-trithiacyclononane (9S3) has been extensively studied over the last two decades.^[1] The special interest in their complexes of the group 10 metals lies in the potential catalytic, synthetic and pharmaceutical uses of compounds of these metals. Additionally, early investigations of the homoleptic complexes $[\text{M}(9\text{S3})_2]^{2+}$ (M = Ni, Pd and Pt) revealed interesting structural, spectroscopic and redox features.^[2] Many heteroleptic complexes of Pd and Pt with various types of co-ligands have since been synthesized. These in-

clude the neutral types with halido ligands, such as *cis*- $[\text{MX}_2(9\text{S3})]$ (X = Cl, Br, I),^[3] and with alkyl or aryl ligands, for example *cis*- $[\text{MR}_2(9\text{S3})]$ [M = Pt, R₂ = Me₂, Et₂, Ph₂, (CH₂Me)₂, (CH₂SiMe₃)₂, Me(CH₂SiMe₃) and Cl(CH₂SiMe₃); M = Pd, R₂ = Me₂ and (CH₂SiMe₃)₂].^[4] The cationic examples contain phosphane co-ligands, for example *cis*- $[\text{MClL}(9\text{S3})](\text{PF}_6)$ (L = PPh₃ or PCy₃), *cis*- $[\text{ML}(9\text{S3})](\text{PF}_6)_2$ [L = (PPh₃)₂, Ph₂PCH₂PPh₂ (dppm), Ph₂PCH₂-CH₂PPh₂ (dppe), {(Ph₂PCH₂)₂[Ph₂P(O)CH₂]CMe₃}, 1,1'-bis(diphenylphosphanyl)ferrocene (dppf)]^[5] and diimine co-ligands, for example *cis*- $[\text{ML}(9\text{S3})](\text{PF}_6)_2$ [L = 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen)].^[5a,6] Grant prepared the first monocationic orthometallated 9S3 complexes of Pt^{II}-containing 2-phenylpyridine (ppy),^[7a] and very recently, while this manuscript was in preparation, similar cyclometallated complexes of both Pd^{II} (**1** and **2**, in Figure 1) and Pt^{II} were reported.^[7b]

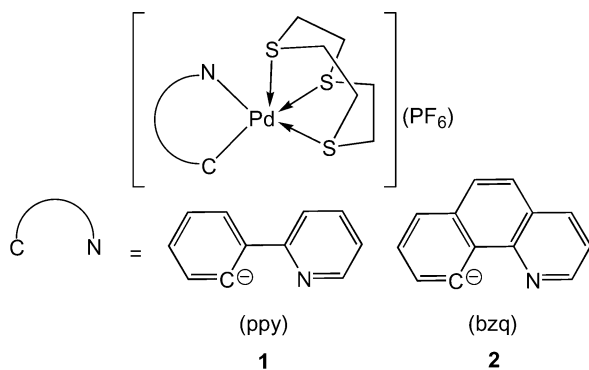
Although 9S3 usually acts as a facial tridentate ligand, it tends to coordinate to Pd or Pt in a bidentate fashion with an additional weak axial M–S interaction, thus generating in a bis(9S3) complex either an elongated square-pyramidal geometry^[2a,2b] or elongated octahedral geometry,^[2c–2e] currently denoted by the respective notations $[\text{S}_4 + \text{S}_1]$ and $[\text{S}_4 + \text{S}_2]$,^[2f,3a,5] as introduced by Schröder.^[5a] A central focus

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Figure 1. Cyclometallated Pd(9S3) complexes.^[7b]

of current interest has been the correlation of this axial interaction with the electronic and electrochemical properties of these complexes.^[7b]

In recent years, we have reported the high efficacy of the Ru^{II} and Ru^{III} metalloligands [(HMB)Ru^{II}(η^3 -tpdt)] (**3**)^[8] and [(Cp*)Ru^{III}(η^3 -tpdt)] (**4**)^[9] [HMB = η^6 -C₆Me₆, Cp* = η^5 -C₅Me₅; tpdt = S(CH₂CH₂S)₂] in the cleavage of metal–X bonds (X = chloride, phosphane, solvent ligand) in a variety of complexes, leading to di- and trinuclear homo- and heterometallic derivatives.^[10] This paper describes the comparative reactivity of species **3** and **4** with a target cyclometallated (azobenzene)Pd^{II}(9S3) complex, the electrochemistry and crystal structure of which are also presented.

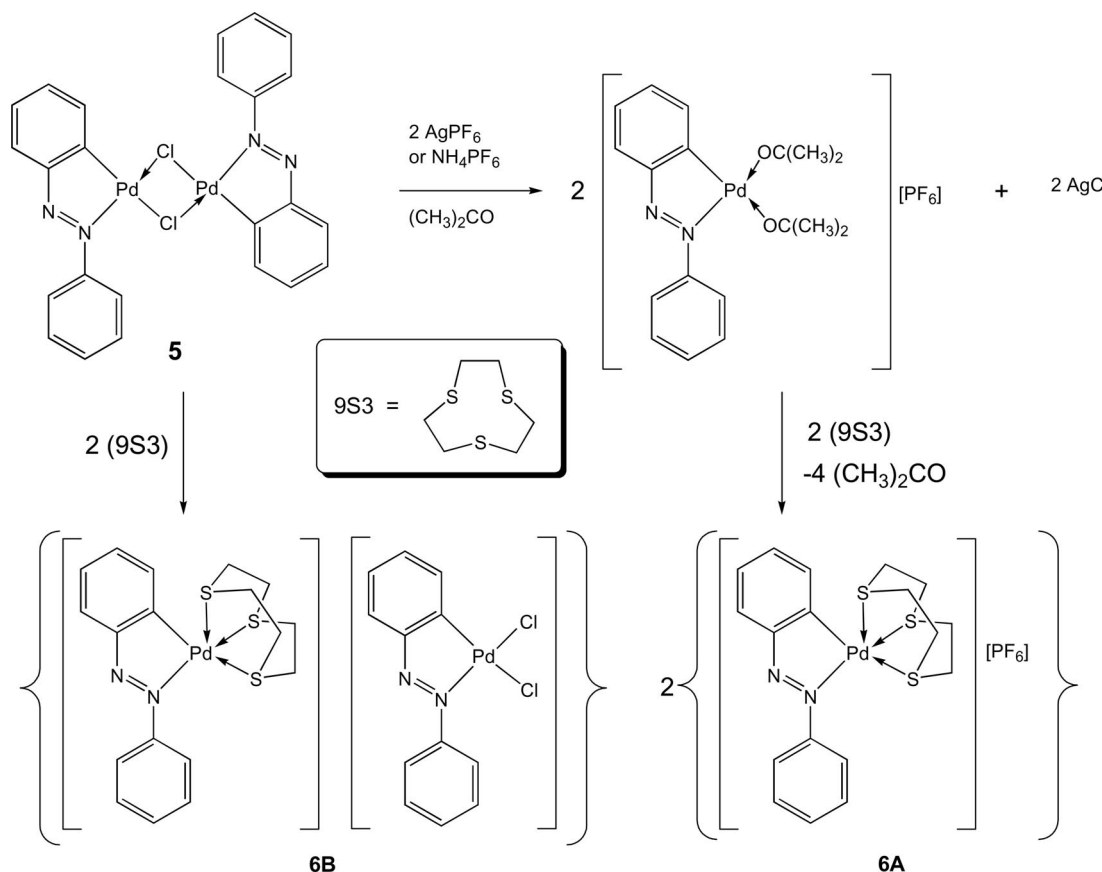
2. Results and Discussion

2.1. Synthesis

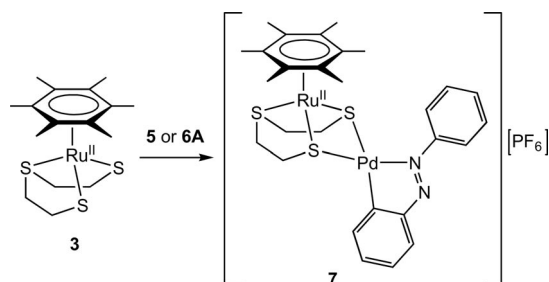
The μ -dichlorido complex [$\{\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\mu\text{-Cl})_2\}_2$] (**5**) was treated with two molar equivalents of 9S3, via its solvato derivative $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\text{OCMe}_2)_2][\text{PF}_6]$, obtained by treatment with AgPF₆ or NH₄PF₆ in acetone. A dark red crystalline complex $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(9\text{S3})][\text{PF}_6]$ (**6A**) was isolated in 80% yield. The direct reaction between **5** and 9S3 led to a quantitative yield of the $[\text{Cl}_2\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)]^-$ salt (**6B**) of the same cationic 9S3 species. Clearly, in this case 9S3 has cleaved two Pd–Cl bonds in **5** and coordinated to the non-chlorido mono-nuclear fragment, but failed to displace the chlorido ligands from the Pd^{II} anion $[\text{Cl}_2\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)]^-$ (Scheme 1).

The reaction of **5** with [(HMB)Ru^{II}(η^3 -tpdt)] (**3**) resulted in cleavage of the Pd–Cl bond to give the thiolate-bridged heterobimetallic complex $\{[(\text{HMB})\text{Ru}^{\text{II}}(\mu\text{-}\eta^2\text{:}\eta^3\text{-tpdt})]\{\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)\}\}\text{PF}_6$ (**7**) in 85% yield after PF₆ metathesis. Complex **3** can also preferentially displace the 9S3 ligand in **6A** to give **7** in 75% yield (Scheme 2).

However, when [(Cp*)Ru^{III}(η^3 -tpdt)] (**4**) was treated with **5** or **6A** the trinuclear complex $[\{\text{Cp}^*\text{Ru}^{\text{III}}(\mu\text{-}\eta^2\text{:}\eta^3\text{-tpdt})\}_2\text{Pd}](\text{PF}_6)_2$ (**8**) was isolated as the only product in 80% and 73% yield, respectively (Scheme 3). In this case, both the azobenzene and 9S3 ligands are displaced by the thiolate sulfur atoms of the tpdt ligand, thus indicating that



Scheme 1.



Scheme 2.

complex **4** is a stronger metalloligand than the HMB analogue **3**. We have previously obtained **8** from the reaction of **4** with PdCl_2 or $[\text{PdCl}_2(\text{MeCN})_2]$.^[11]



Scheme 3.

2.2. Electrochemical Studies

Cyclic voltammograms recorded for 0.5 mM solutions of **6A** show significant differences depending on the electrode surface (GC or Pt), the solvent (CH_2Cl_2 or CH_3CN) and the temperature (Figure 2 and Table 1). CVs performed on solutions of CH_2Cl_2 containing **6A** at 273 K show a reduction process at around -1.2 V vs. Fc/Fc^+ that appears more chemically reversible on Pt than GC (at $\nu = 0.1 \text{ V s}^{-1}$), in the sense that the oxidative (i_p^{ox}) to reductive (i_p^{red}) peak current ratio ($i_p^{\text{ox}}/i_p^{\text{red}}$) is equal to unity on Pt (but not on GC). An oxidation process is evident at around $+1$ V vs. Fc/Fc^+ with an i_p^{red} value at least twice that of the i_p^{ox} value observed for the oxidation process, thereby indicating that the reduction process involves the transfer of a higher number of electrons. The reverse reductive peak observed for the process at around $+1$ V vs. Fc/Fc^+ is very sharp on both GC and Pt, typical of electrochemical processes that involve strong surface interactions, where the oxidized spe-

cies is adsorbed onto the electrode surface on the forward scan and subsequently stripped off when the potential direction is reversed.

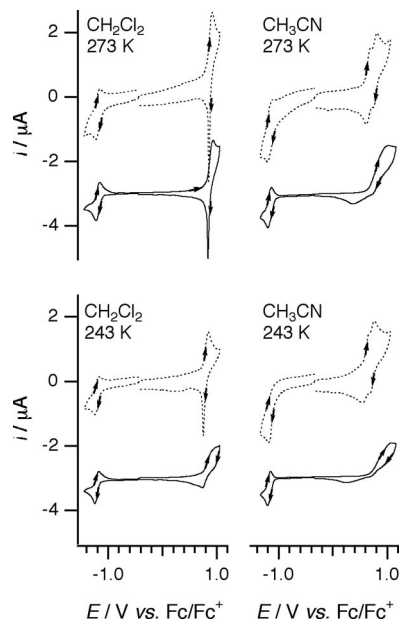


Figure 2. Cyclic voltammograms of 0.5 mM solutions of **6A** performed at 1 mm diameter planar GC (···) and Pt (—) electrodes in CH_2Cl_2 or CH_3CN (containing 0.25 M Bu_4NPF_6) at a scan rate of 100 mV s^{-1} . CV traces at the Pt electrode are offset by $-3 \mu\text{A}$.

The voltammetric processes of **6A** observed in CH_2Cl_2 at 243 K on GC were found to be similar to those observed at 273 K (Figure 2). On Pt, the reduction process appears to be the same as that observed at higher temperature, whereas the oxidation process is substantially different, with smaller i_p^{ox} and i_p^{red} values and with a wide anodic peak potential (E_p^{ox}) to cathodic peak potential (E_p^{red}) separation (ΔE_{pp}) of at least 200 mV (the anodic process was particularly drawn out).

The reduction of **6A** on GC in CH_3CN appears to be chemically irreversible at a scan rate of 0.1 V s^{-1} at high and low temperatures, whilst the oxidation wave split into two chemically reversible processes. It is likely that the oxidation process involves two one-electron steps that are resolved in acetonitrile on GC but appear as one process in CH_2Cl_2 . However, caution is required in reaching this conclusion because the data in CH_3CN may be complicated by coordina-

Table 1. Cyclic voltammetric data for 0.5 mM solutions of **6A** obtained at a scan rate of 0.1 V s^{-1} at 1 mm diameter electrodes at 273 K with 0.25 M Bu_4NPF_6 as the supporting electrolyte.

Electrode	Solvent	Reduction processes ^[a]				Oxidation processes ^[a]			
		E_p^{red} [V] ^[b]	E_p^{ox} [V] ^[c]	$E'_{1/2}$ [V] ^[d]	ΔE [mV] ^[e]	E_p^{red} [V] ^[b]	$E'_{1/2}$ [V] ^[d]	ΔE [mV] ^[e]	
GC	CH_3CN	-1.208							
						+0.698	+0.616	+0.66	82
Pt	CH_2Cl_2	-1.225	-1.157	-1.19	68	+0.814	+0.728	+0.77	86
						+0.931	+0.839		

[a] All potentials are relative to the Fc/Fc^+ redox couple. [b] E_p^{red} = reductive peak potential. [c] E_p^{ox} = oxidative peak potential. [d] $E'_{1/2} = (E_p^{\text{red}} + E_p^{\text{ox}})/2$. [e] $\Delta E = |E_p^{\text{ox}} - E_p^{\text{red}}|$.

tion of the solvent to Pd, either prior to or immediately following the electron-transfer steps. The voltammograms obtained during the reduction of **6A** on Pt in CH₃CN (at high and low temperature) were found to be similar to those observed in CH₂Cl₂, with a chemically reversible process at around -1.2 V vs. Fc/Fc⁺. The oxidation process(es) observed in CH₃CN on Pt (at high and low temperatures) were more drawn out and similar to the voltammograms observed in CH₂Cl₂ at 243 K. Therefore, it is likely that the anodic process on Pt is associated with a slow rate of heterogeneous electron transfer that decreases with lowering temperatures, and increases the ΔE_{pp} values with respect to those observed on GC.

If it is considered that the oxidation process is a two-electron process in CH₂Cl₂, the small peak current observed on Pt at low temperatures might be due to the slow heterogeneous electron-transfer rate increasing the overpotential required to remove a second electron. This would also explain the lack of a stripping peak for the oxidation of **6A** in CH₂Cl₂ at 243 K, if the adsorbed species were associated with the second electron transfer that occurs at a higher potential ($> +1.2$ V vs. Fc/Fc⁺). In CH₃CN, the oxidized species may have improved solubility; hence no stripping peaks are observed.

The voltammograms obtained for solutions of **6B** were found to be similar to those for solutions of **6A**, with oxidation and reduction processes that vary in appearance depending on the temperature and solvent (see Supporting Information). CVs performed on solutions of CH₂Cl₂ containing **7** at 243 K show an oxidation process at $+0.50$ V vs. Fc/Fc⁺ that appears to be chemically reversible at a scan rate of 100 mV s^{-1} (Figure 3). A second chemically irreversible oxidation process is evident at $+0.86$ V vs. Fc/Fc⁺. At temperatures above 243 K, the first (least positive) oxidation process becomes less chemically reversible, thus indicating the instability of the oxidized states. The anodic to cathodic peak-to-peak separation (ΔE_{pp}) for the first oxidation process is similar to that observed for ferrocene under similar conditions, thus suggesting a one-electron process. In CH₃CN solutions the first oxidation process produces a species that is chemically unstable at low and high temperatures, possibly due to irreversible coordination of CH₃CN to the oxidized form of the compound.

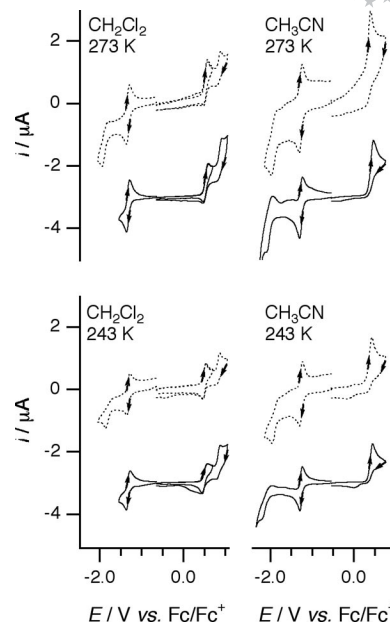


Figure 3. Cyclic voltammograms of 0.5 mM solutions of **7** performed at 1 mm diameter planar GC (···) and Pt (—) electrodes in CH₂Cl₂ or CH₃CN (containing 0.25 M Bu₄NPF₆) at a scan rate of 100 mV s^{-1} . CV traces at the Pt electrode are offset by $-3 \mu\text{A}$.

In CH₂Cl₂ and CH₃CN at high and low temperatures, CV experiments on **7** showed a chemically reversible reduction process at around -1.3 V vs. Fc/Fc⁺ (Figure 3 and Table 2). The ΔE_{pp} value is similar to that observed for the oxidation process, as is the $i_{p, \text{red}}$ value, thus indicating that the reduction is also a one-electron process. On GC electrodes a second diffusion-controlled chemically irreversible reduction process, which was not detected on Pt electrodes, was evident at around -1.9 V vs. Fc/Fc⁺. The second reduction process on Pt electrodes appears as a long drawn-out wave with high currents that are likely due to strong surface-based (adsorption) interactions.

Janzen, Grant et al. have described the electrochemistry of several similar cyclometallated Pt^{II} and Pd^{II} complexes with the 9S3 ligand.^[7b] For several compounds, two closely spaced oxidation processes were detected at approximately $+0.6$ V vs. Fc/Fc⁺, similar to the values obtained in this work. The oxidative electrochemistry was interpreted as se-

Table 2. Cyclic voltammetric data for 0.5 mM solutions of **7** obtained at a scan rate of 0.1 V s^{-1} at a 1 mm diameter GC electrode at 243 K in CH₂Cl₂ or CH₃CN with 0.25 M Bu₄NPF₆ as the supporting electrolyte.

Solvent	Reduction processes ^[a]				Oxidation processes ^[a]			
	$E_{p, \text{red}} [\text{V}]^{\text{[b]}}$	$E_{p, \text{ox}} [\text{V}]^{\text{[c]}}$	$E_{1/2} [\text{V}]^{\text{[d]}}$	$\Delta E [\text{mV}]^{\text{[e]}}$	$E_{p, \text{red}} [\text{V}]^{\text{[b]}}$	$E_{p, \text{ox}} [\text{V}]^{\text{[c]}}$	$E_{1/2} [\text{V}]^{\text{[d]}}$	$\Delta E [\text{mV}]^{\text{[e]}}$
CH ₂ Cl ₂	-1.354 -1.86	-1.279	-1.32	75		$+0.533$ $+0.86$	$+0.465$ $+0.50$	68
CH ₃ CN	-1.303 -1.96	-1.234	-1.27	69		$+0.43$		

[a] All potentials are relative to the Fc/Fc⁺ redox couple. [b] $E_{p, \text{red}}$ = reductive peak potential. [c] $E_{p, \text{ox}}$ = oxidative peak potential. [d] $E_{1/2} = [E_{p, \text{red}} + E_{p, \text{ox}}]/2$. [e] $\Delta E = |E_{p, \text{ox}} - E_{p, \text{red}}|$.

quential one-electron oxidation of the metal ion (i.e. $\text{Pd}^{\text{III/IV}}$ and $\text{Pd}^{\text{III/IV}}$).^[7b] It is therefore possible that the oxidation processes detected in this study are also associated with the sequential one-electron oxidation of Pd ion. However, Ru^{II} complexes can often be oxidized in one- and two-electron processes to Ru^{III} and Ru^{IV} , so there is also a possibility that the Ru ions are involved in the oxidation (and reduction) processes.

2.3 Crystallographic Studies

The molecular structures of complexes **6A**, **6B**, and its solvates **6B**· H_2O and **6B**· CHCl_3 , and **7** have been determined by X-ray diffraction analyses, and are illustrated for **6A**, **6B**· CHCl_3 and **7** in Figures 4, 5 and 8, respectively. The cations adopt a structure that is a compromise between the preference of Pd^{II} to adopt a square-planar geometry and the tendency of the 9S3 ligand to bind to a trigonal face of an octahedron. The distorted square-pyramidal structure is in fact a characteristic feature of 9S3 complexes of Pd^{II} and Pt^{II} . The coordination geometry around the palladium centre in these cations is an elongated square pyramid, with the square plane defined by the C(7) and N(1) atoms of azobenzene and the sulfur atoms S(1) and S(2) of 9S3. The bond parameters for these complexes are listed in Table 3,

which also includes selected data for Grant's cyclometallated complexes **1** and **2**. There are clear variations in the bond parameters of the geometrically identical cations of **6A** and the different solvates of **6B**. Thus, the Pd–S(1) distances range from 2.276(2) to 2.3052(6) Å, similar to those

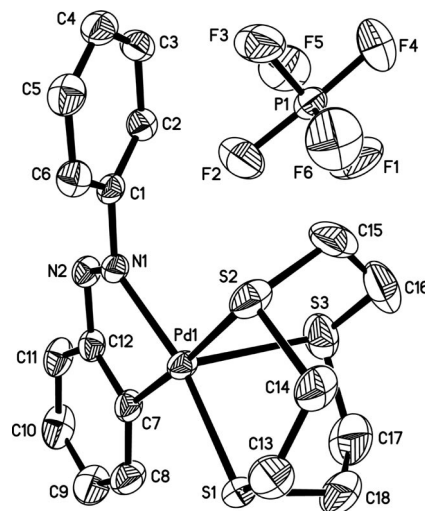


Figure 4. ORTEP diagram for **6A** (50% probability thermal ellipsoids, hydrogen atoms are omitted).

Table 3. Selected bond lengths [Å] and angles [°] in the Ru–Pd complexes.

Compounds	6A	6B	6B · H_2O	6B · CHCl_3	1 ^[a]	2 ^[a]	7
Pd(1)–S(1)	2.3052(6)	2.2773(14)	2.3004(4)	2.276(2)	2.2985(9)	2.2657(10)	Ru(1)–S(1) 2.3537(15)
Pd(1)–S(2)	2.3781(7)	2.4130(13)	2.4035(5)	2.418(2)	2.3842(9)	2.3714(10)	Ru(1)–S(2) 2.3184(18)
Pd(1)–S(3)	2.7113(8)	2.8458(14)	2.7299(5)	2.784(2)	2.8705(10)	3.0066(12)	Ru(1)–S(3) 2.3742(16)
Pd(1)–N(1)	2.0353(19)	2.083(4)	2.0586(15)	2.073(7)	2.0614(18) [2.0289(18)]	2.080(3)	Pd(1)–S(1) 2.2850(15)
Pd(1)–C(7)	1.990(2)	2.002(5)	1.9940(17)	1.994(9)	2.0614(18) [2.0289(18)]	2.023(3)	Pd(1)–S(3) 2.4178(16)
C(1)–N(1)	1.436(3)	1.439(6)	1.428(2)	1.451(11)			Pd(1)–N(1) 2.086(5)
N(1)–N(2)	1.267(3)	1.267(6)	1.273(2)	1.251(11)			Pd(1)–C(7) 1.988(6)
N(2)–C(12)	1.395(3)	1.411(7)	1.397(2)	1.409(12)			C(1)–N(1) 1.403(9)
Pd(2)–Cl(1)	–	2.3059(13)	2.3164(5)	2.305(2)			N(1)–N(2) 1.277(8)
Pd(2)–Cl(2)	–	2.4346(14)	2.4194(5)	2.428(2)			N(2)–C(12) 1.371(9)
Pd(2)–C(19)	–	1.971(5)	1.9711(18)	1.968(8)			
Pd(2)–N(3)	–	2.044(4)	2.0262(14)	2.030(7)			
N(3)–C(25)	–	1.446(6)	1.436(2)	1.442(11)			
N(3)–N(4)	–	1.268(6)	1.269(2)	1.285(10)			
N(4)–C(24)	–	1.390(7)	1.397(2)	1.389(11)			
Pd(2)···S(1)	–	5.046	4.852	4.553			
Pd(2)···S(2)	–	3.646	4.124	3.947			
Pd(2)···S(3)	–	6.948	3.478	3.455			
S(1)–Pd(1)–S(2)	88.70(3)	87.80(5)	88.331(16)	87.68(8)	87.96(3)	88.94(4)	S(1)–Ru(1)–S(2) 85.76(7)
S(1)–Pd(1)–S(3)	87.07(3)	87.44(5)	88.533(16)	89.59(8)	85.95(3)		S(1)–Ru(1)–S(3) 82.82(5)
S(2)–Pd(1)–S(3)	84.80(3)	81.67(4)	84.145(15)	83.42(7)	82.50(3)		S(2)–Ru(1)–S(3) 85.76(9)
S(3)–Pd(1)–N(1)	102.20(6)	91.44(12)	97.16(4)	87.6(2)			S(1)–Pd(1)–S(3) 83.31(5)
S(3)–Pd(1)–C(7)	94.93(8)	107.35(15)	94.80(5)	96.6(3)			S(1)–Pd(1)–C(7) 95.13(19)
S(1)–Pd(1)–C(7)	95.86(8)	90.96(15)	93.45(5)	93.0(3)	93.64(6)	91.75(10)	S(3)–Pd(1)–N(1) 102.56(15)
S(2)–Pd(1)–N(1)	97.26(6)	103.03(12)	100.06(4)	102.3(2)	97.01(5)	97.54(8)	N(1)–Pd(1)–C(7) 78.9(2)
N(1)–Pd(1)–C(7)	78.31(9)	78.77(19)	78.26(7)	77.1(3)	81.14(7) [81.14(7)]	81.91(12)	
Cl(1)–Pd(2)–Cl(2)	–	90.08(5)	91.323(17)	90.28(8)			
Cl(1)–Pd(2)–C(19)	–	92.18(15)	93.03(5)	92.0(3)			
Cl(2)–Pd(2)–N(3)	–	98.79(13)	96.48(4)	99.3(2)			
N(3)–Pd(2)–C(19)	–	78.94(19)	78.80(7)	78.2(3)			
Dihedral angles ^[b] in the cation/anion	58.59/NA	42.63/49.34	44.39/50.26	44.99/50.09			40.38

[a] See Figure 1 and ref. [7b]. [b] Between phenyl rings.

in **1** and **2**^[7b] and in non-cyclometallated complexes;^[5e,6a,6b] the Pd–S(2) distances range from 2.3781(7) to 2.418(2) Å

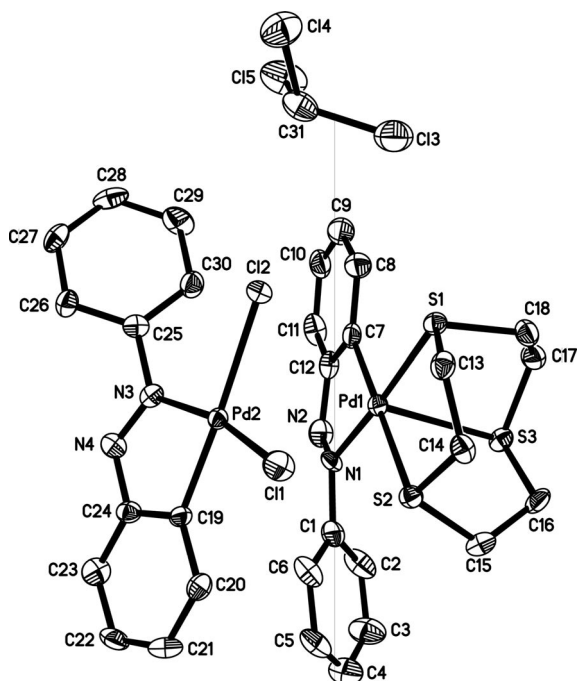


Figure 5. ORTEP diagram for **6B**·CHCl₃ (50% probability thermal ellipsoids, hydrogen atoms are omitted).

(those of **1** and **2** are within this range and slightly lower, respectively). The Pd(1)–S(3) bonds are significantly longer (by 0.32–0.56 Å), more variable (variation of 0.1345 Å), and are slightly shorter than those in Grant's compounds. The Pd–N distances range from 2.0353(19) Å in **6A** to 2.083(4) Å in **6B** (those of **1** and **2** lie within this range). The relative order of magnitude of the bond lengths of Pd(1) to S(1) and S(2) in all these cyclometallated complexes is in agreement with the expected higher *trans* influence of the aryl C(7) vs. the diazo or pyridyl N, since the aryl C is a stronger σ -donor. While the Pd–N distances in the diazo-benzene complexes and in **1** or **2** are very similar, there is a large difference in the Pd–C distances in the two sets of compounds, as expected as they are components of different types of five-membered ring systems (PdC₂N₂ and PdC₃N). The same rationale explains the difference in the N–Pd–C angles of the two sets of complexes. The phenyl rings are planar and the dihedral angles are also listed in Table 3. The ring attached to N(1) is twisted away from the plane of the cyclometallated (chelate) ring, undoubtedly due to steric effects. This “twist” would reduce the conjugation of the phenyl ring with the planar phenylazo moiety and lengthen C(1)–N(1) relative to C(12)–N(2) [1.436(3) and 1.395(3) Å, respectively, in **6A**].

There are only slight variations in the bond parameters of the anion of **6B** and its solvates. As in the cation, the

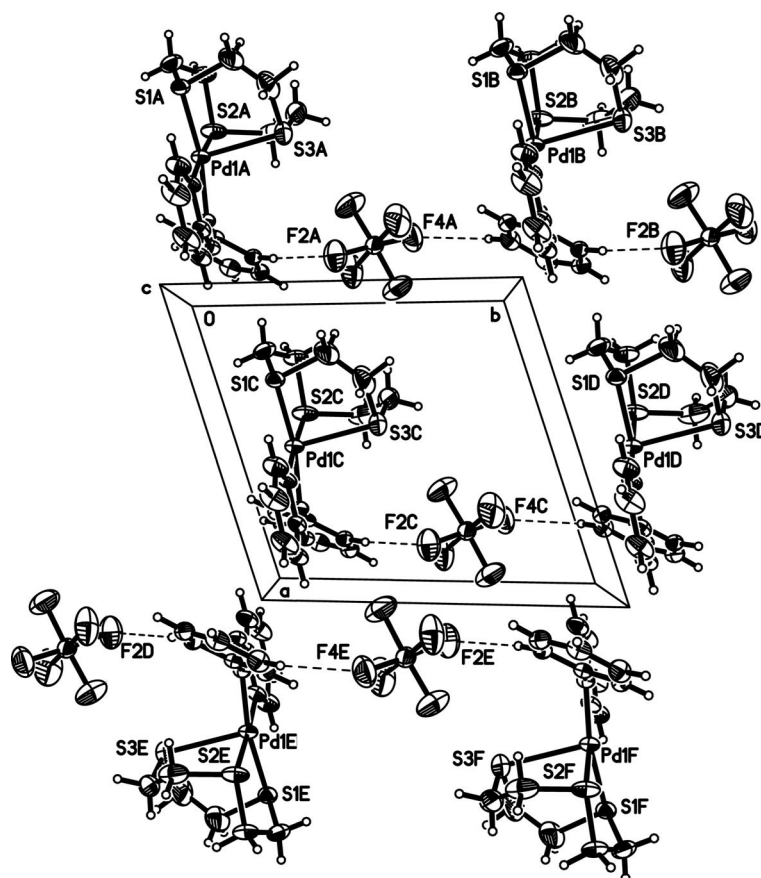


Figure 6. Packing diagram of **6A**, viewed along the *c*-axis. Short contacts between the F atoms of the PF₆ anion and the phenyl ring hydrogen atoms of the cation are shown.

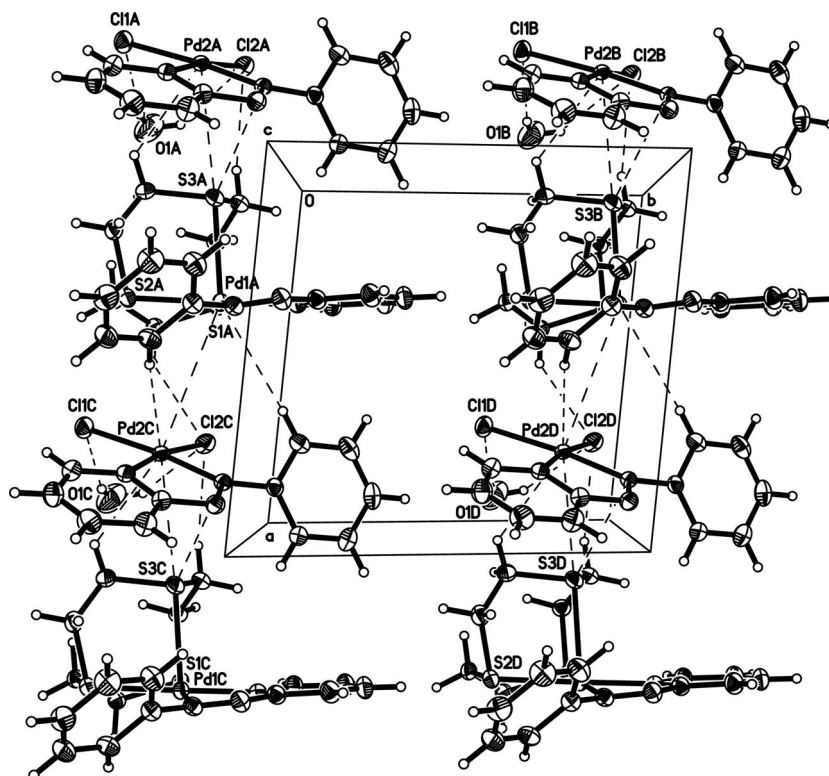


Figure 7. Packing diagram of **6B**·H₂O, viewed along the *c*-axis. Short contacts between the anion and cation are shown.

greater *trans* influence of C(19) vs. N(3) in the anions is reflected in the relative Pd–Cl distances, with the Pd(2)–Cl(2) distances being 0.10–0.13 Å longer than those of Pd(1)–Cl(1). The non-bonding length for Pd(2)··S(*x*) (*x* = 1, 2, 3) is shortest for *x* = 2 in **6B** and for *x* = 3 in the solvato analogues **6B**·H₂O and **6B**·CHCl₃.

Our serendipitous isolation and structure determination of the anionic variants of **6** (**6A** and **6B**) and the solvato variants of **6B** provided us with an opportunity to observe the effect of both anion and lattice solvent molecules on the crystal packing in the structures of these heteroleptic 9S3 complexes of Pd. The variations found in the cation bond parameters in these various species of **6** bring to mind the reports of Schröder^[2c] and Grant^[2f] on the influence of anions on the coordination geometry (S₄+S₁ vs. S₄+S₂) of the thioether ligand in the [Pt(18S6)]²⁺ and [Pt(9S3)]²⁺ cations, as well as those of Grant^[12] and McAuley^[13] on the effect of solvents on “positional linkage” isomerism of [Pd(10S3)]₂(PF₆)₂. Atom–atom contact interactions between the anion and cation in the crystal lattice of **6A** are shown in Figure 6, and Figure 7 also includes interactions between the anion and cation and H₂O in **6B**·H₂O. Colour versions of these and other packing diagrams are depicted in Figures S1–S4 in the Supporting Information. These illustrate interactions between the cation and anion {F atoms of PF₆[−] in **6A** and atoms of [Pd(C₆H₄N=NC₆H₅)Cl₂][−] in the various **6B** species}, and interactions between the cation and anion of the complex and lattice solvent molecules (H₂O or CHCl₃). The MERCURY software provided listings of atom–atom contacts, which are listed in Tables S1–

S4 in the Supporting Information. These contacts (although of comparative qualitative significance, since the hydrogen atoms are not refined in the structure analyses) are shorter than their van der Waal’s distances by 0.037–0.202 (F···H), 0.039–0.223 (C···H), 0.001–0.404 (Cl···H), 0.002–0.193 (N···H), 0.028 (O···H) and 0.023 Å (N···S). Most of these interactions appear to be much stronger than those reported for the [Pt(9S3)]₂²⁺ and [Pt(18S6)]²⁺ complexes,

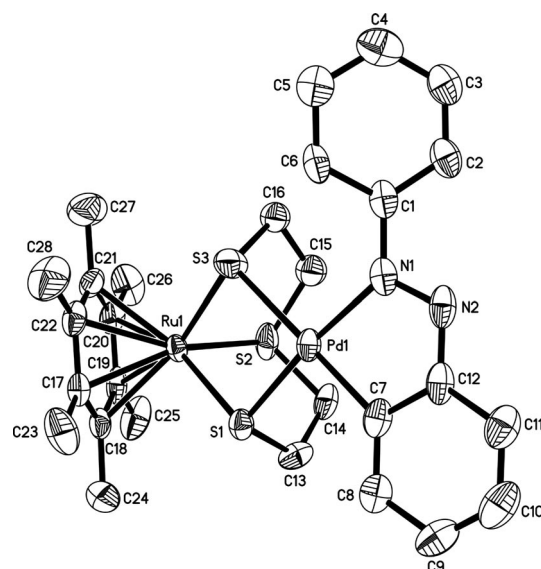


Figure 8. ORTEP diagram for **7** (50% probability thermal ellipsoids, hydrogen atoms are omitted for clarity).

wherein $S \cdots F$ contacts in the PF_6^- or BF_4^- salts, and the $S \cdots O$ contact (of solvent $MeNO_2$), are just above or below the sum of their van der Waal's distances.^[2f]

The molecular structure of **7** shows a $[(HMB)Ru^{II}\{\eta^3\text{-tpdt}\}]$ unit ligated to a $Pd(C_6H_4N=NC_6H_5)$ fragment via the thiolate sulfurs S(1) and S(3), with the Pd atom in a four-coordinate planar environment (Figure 8). As in the structures of the variants of species **6**, a higher *trans* influence of the aryl C(7) vs. N(1) atom results in a substantially longer Pd(1)–S(3) bond [2.4178(16) Å] compared to Pd(1)–S(3) [2.2850(15) Å]. Due to steric repulsion imposed by the phenyl ring attached to N(1), the S(3)–Pd(1)–N(1) angle [102.56(15)°] is much larger than the other three angles at Pd [78.9(2)–95.13(19)°; see Table 3].

2.4 Spectral Characteristics

The NMR characteristics of **6A** and the solvent variants of **6B** are in agreement with their determined solid-state structures. As expected, the proton resonances in the aromatic region for the phenyl ring protons of the cyclometallated azobenzene are very different in **6A** (multiplets in the range $\delta = 7.26$ –8.16 ppm in CD_2Cl_2) and **6B** (unresolved multiplets in the range $\delta = 7.22$ –8.13 ppm in CD_2Cl_2 ; see Figures 9 and 10). The twelve methylene protons of the 9S3 ligand in **6A** and **6B** are observed as two sets of second order AA'BB' multiplets (8-lines) at $\delta = 2.86$ –3.09 and

2.89–3.39 ppm, respectively, with a “dispersion” or separation (Δ) of 0.12 ppm in **6A** and around four times larger in **6B** (0.50 ppm at 298 K and 0.54 ppm at 193 K). The resonances of **6B** in both the aromatic and 9S3 regions are better resolved at low temperature. This characteristic AA'BB' splitting pattern, which arises due to the magnetic inequivalence of the methylene protons caused by their different spatial orientations, has been observed previously for almost all known 9S3 complexes of Pd^{II} and Pt^{II} .^[2b,3,4,5a,5c,7] In **6A**, this multiplet is less resolved in acetone and acetonitrile, probably because of the greater interaction of the 9S3 ligand with these solvent molecules. In $[D_6]$ acetone, the 9S3 proton resonance is a single symmetrical multiplet at $\delta = 3.16$ –3.34 ppm ($\Delta = 0.03$ ppm), centred at $\delta = 3.25$ ppm, while in CD_3CN this resonance is a broad unresolved multiplet at $\delta = 2.87$ –3.03 ppm, with intense “spikes” at $\delta = 2.94$ and 2.95 ppm. Variations in the magnitude of the “dispersion” have ranged from 0–0.84 ppm for $[Pd(9S3)(L_2)]\cdot PF_6$, with Δ in increasing order for L_2 : bipy < phen < dppm < $(PPh_3)_2$ < $Cl[P(C_6H_{11})_3]$.^[5a] In a recent paper, Grant also reported a single multiplet for 9S3 (i.e. $\Delta = 0$ ppm) for cyclometallated Pd and Pt 7,8-benzoquinolate complexes.^[7b] The present observations show the sensitivity of the splitting of the AA'BB' pattern to both the counterion and the solvent.

The ^{13}C NMR spectra of **6A** in CD_3CN and **6B** in $CDCl_3$ show one intense peak at $\delta = 33.9$ and 34.2 ppm, respectively, for the six carbon atoms of the 9S3 ligand, thus

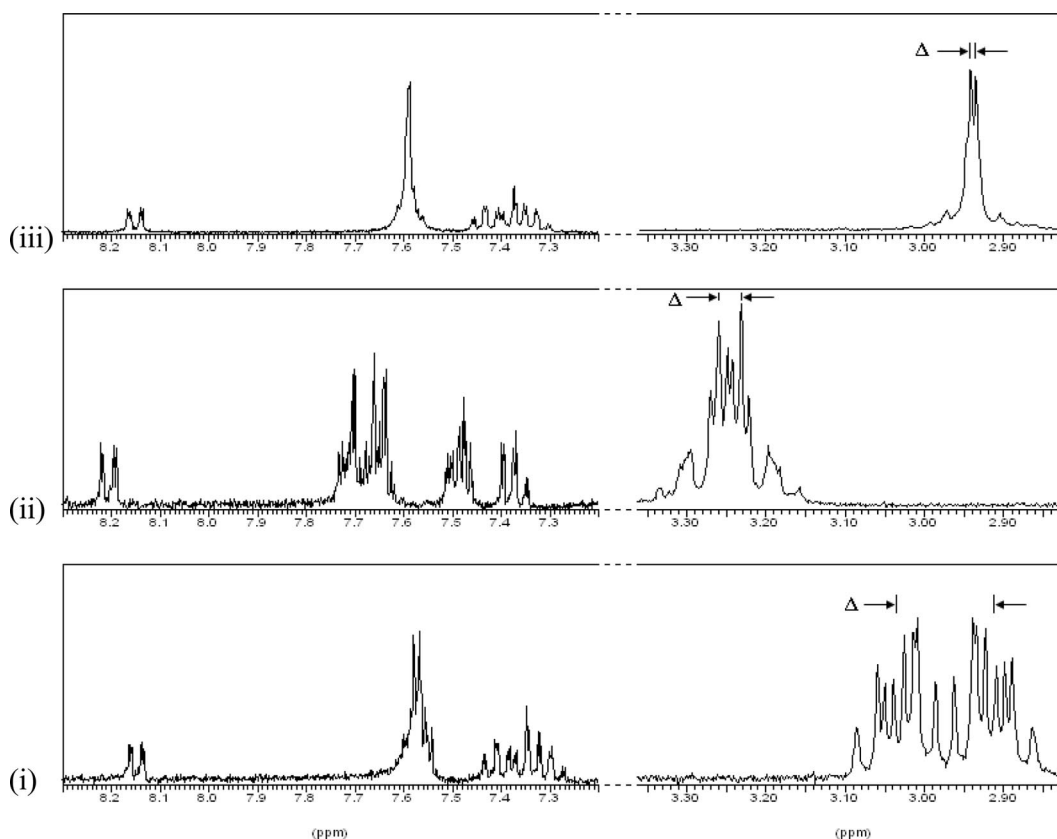


Figure 9. 1H NMR spectra of **6A** in (i) CD_2Cl_2 , (ii) $(CD_3)_2CO$ and (iii) CD_3CN . Δ = “dispersion”.

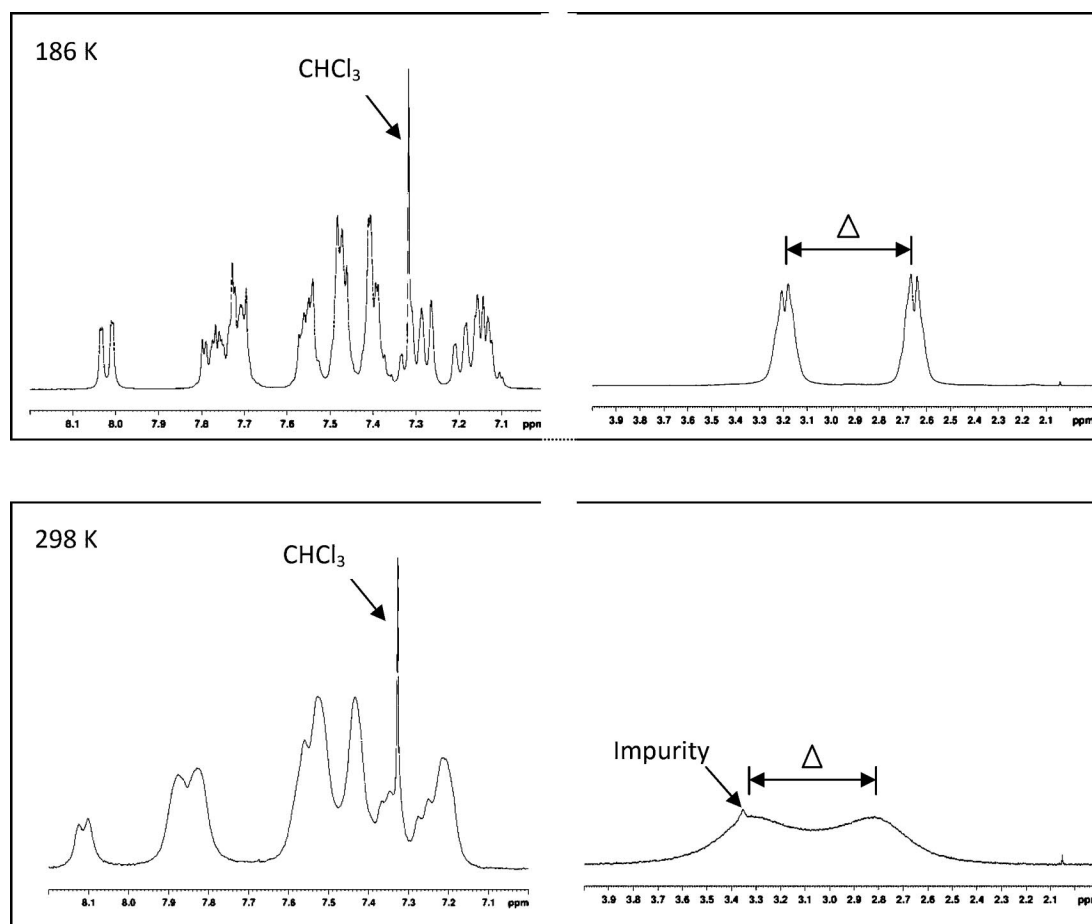


Figure 10. ^1H NMR spectra of $6\text{B}\cdot\text{CHCl}_3$ in CD_2Cl_2 at 298 and 186 K. Δ = “dispersion”.

indicating the rapid intramolecular exchange of the three inequivalent S atoms, presumably via a 1,4-metallotropic shift, as observed in all 9S3 complexes of Pd^{II} and Pt^{II} .^[4,6,14] The phenyl carbon atoms of azobenzene in **6A** are seen as ten resonances (range δ = 165.1–123.2 ppm), in agreement with the pairs of magnetically equivalent *ortho* and *meta* carbons in the non-metallated phenyl ring. Only twelve resonances (range δ = 164.6–122.6) are observed for the two cyclometallated azobenzene moieties in **6B**, presumably due to overlapping of some resonances.

The ^1H NMR spectrum of **7** in CD_3CN shows peaks for the phenyl ring protons of the cyclometallated azobenzene at δ = 7.30–7.99 ppm and seven sets of resolved multiplets at δ = 1.79–3.34 ppm for the methylene protons of the tpd ligand and a singlet at δ = 2.10 ppm for the C_6Me_6 protons. Similar to **6A**, the ^{13}C NMR spectrum of **7** shows 10 peaks at δ = 124.2–166.0 ppm for the azobenzene ligand while resonances at δ = 15.9 and 101.6 ppm belong to the methyl and ring carbons of the C_6Me_6 ligand, respectively. Four signals in the range δ = 27.5–45.5 ppm are also observed for the four SCH_2 carbons.

3. Conclusion

A new cationic heteroleptic complex of palladium containing azobenzene and 9S3 ligands has been isolated, with

counterions PF_6^- (**6A**) and $[\text{Pd}(\text{azobenzene})\text{Cl}_2]^-$ (**6B**). The crystal data for complexes **6A** and **6B**, and the latter's solvate derivatives, show that the molecular structures are influenced by atom–atom contacts between the counterions and/or lattice solvent molecules. These effects are reflected in the variation of the fine structure of the 9S3 proton resonance with both counterion and the NMR solvent. A semi-quantitative estimation of atom–atom contact distances was obtained by calculations using the MERCURY software.

The reactions of **6A** with the metalloligands $[(\text{HMB})\text{-Ru}^{\text{II}}\{\eta^3\text{-tpdt}\}]$ and $[(\text{Cp}^*)\text{Ru}^{\text{III}}\{\eta^3\text{-tpdt}\}]$ show that the tridentate 9S3 ligand is more readily displaced than the bidentate cyclometallated azobenzene ligand.

Compounds **6A**, **6B** and **7** can be electrochemically oxidized and reduced. However, while **6A** and **6B** behave similarly, a significantly different CV was obtained for **7** at the different electrode surfaces (GC and Pt) and in the different solvents (CH_3CN and CH_2Cl_2) as the temperature was varied.

4. Experimental Section

4.1. General Procedures: All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 Inert Gas Sys-

tem. Other procedures were as described previously.^[11] 1,4,7-Trithiacyclononane was obtained from Aldrich and used as supplied. The compounds [(HMB)Ru^{II}{ η^3 -tpdt}] (**3**), [(Cp*)Ru^{III}{ η^3 -tpdt}] (**4**) and [Pd(C₆H₄N=NC₆H₅)(μ -Cl)]₂ (**5**) were prepared as previously reported.^[8,9,15]

4.2. Reaction of [Pd(C₆H₄N=NC₆H₅)(μ -Cl)]₂ (**5**)

(i) With AgPF₆, Followed by 1,4,7-Trithiacyclononane (9S3): Solid AgPF₆ (86 mg, 0.34 mmol) was added, with stirring, to a suspension of **5** (100 mg, 0.15 mmol) in acetone (15 mL). Precipitation of white AgCl occurred almost immediately as the solution gradually changed from red to orange-yellow. After 1 h the solution was filtered and 9S3 (56 mg, 0.31 mmol) was added to the filtrate. An instantaneous colour change to deep red was observed. This mixture was stirred for 1 h and then filtered to remove some insoluble black solids. The dark red filtrate was evaporated to dryness and the residue extracted with MeCN (10 mL) and filtered again. Addition of diethyl ether to the filtrate, followed by cooling at –30 °C for 24 h, led to the formation of red orthorhombic crystals of [(9S3)Pd(C₆H₄N=NC₆H₅)]PF₆ (**6A**; 151 mg, 80%). Concentration of the mother liquor and addition of diethyl ether gave a second crop of **6A** (25 mg, 13%) after 2 days at –30 °C. Diffraction-quality crystals were obtained by the slow diffusion of diethyl ether into a concentrated solution of complex **6A** in acetone at –10 °C after three days.

Data for 6A: ¹H NMR (300 MHz, CD₃CN): δ = 8.18–8.15 (m, 1 H, Ph), 7.60 (unresolved m, 5 H, Ph), 7.47–7.31 (16-line m, 3 H, Ph), 2.95–2.86 (8-line m, 6 H, SCH₂), 3.08–2.98 (8-line m, 6 H, SCH₂) ppm. ¹³C NMR (300 MHz, CD₃CN): δ = 165.1, 163.7, 154.3, 135.1, 133.9, 131.8, 131.7, 130.0, 127.6, 123.2 (all Ph), 33.9 ppm (SCH₂). FAB⁺ MS: m/z 467 [M – PF₆]⁺. FAB[–] MS: m/z 145 [PF₆][–]. IR (KBr): $\tilde{\nu}$ = 2960 (vw), 2936 (vw), 2860 (vw), 1635 (w), 1485 (w), 1447 (w), 1432 (w), 1411 (w), 1394 (m), 1302 (w), 1239 (w), 1130 (vw), 1112 (vw), 1076 (vw), 1040 (vw), 869 (m), 839 [vs. (PF₆)], 776 (s), 762 (m), 712 (m), 700 (m), 668 (vw), 557 [s (PF₆)], 375 (w) 354 cm^{–1}. C₁₈H₂₁F₆N₂PPdS₃ (612.96): calcd. C 35.3, H 3.5, N 4.6, S 15.7; found C 35.0, H 3.4, N 4.3, S 16.0.

(ii) With 1,4,7-Trithiacyclononane (9S3): Dichloromethane (15 mL) was added to a solid mixture of **5** (130 mg, 0.20 mmol) and 9S3 (72 mg, 0.40 mmol). A deep red solution was obtained almost immediately. After stirring for 18 h, the solvent was removed in vacuo and the product was extracted with MeOH (10 mL). The extracts were filtered through a glass sinter (Por. 4) and the deep red filtrate evacuated to dryness. The oily residue obtained was then recrystallised from CHCl₃ and hexane at room temperature to give **6B**·CHCl₃ as black needles (94 mg, 0.10 mmol, 100% based on **5**) after 3 days. Single crystals were obtained by layering a concentrated solution of this complex in non-dried chloroform with hexane at room temperature. After 3 days, diffraction-quality black-red needles of **6B**·H₂O and black needles of **6B**·CHCl₃ were obtained. Another attempt to obtain single crystals from a solution in MeCN/diethyl ether gave red crystals of **6B**.

Data for 6B·CHCl₃: ¹H NMR (400 MHz, CDCl₃ or 300 MHz, CD₂Cl₂): δ = 8.12 (d, J = 7.2 Hz, 1 H, Ph), 7.85 (unresolved m, 4 H, Ph), 7.54 (unresolved m, 5 H, Ph), 7.43 (unresolved m, 3 H, Ph), 7.32 (unresolved m, 2 H, Ph), 7.29–7.22 (unresolved m, 3 H, Ph), 3.43 (br. s, $\nu_{1/2}$ = 70–100 Hz, 6 H, SCH₂), 2.86 ppm (br. s, $\nu_{1/2}$ = 70–100 Hz, 6 H, SCH₂). These broad resonances shifted to δ = 3.64 and 2.80 ppm, respectively, with a slight increase in CHCl₃ content. A resonance at δ = 7.26 ppm (s, CHCl₃) is clearly visible in CD₂Cl₂ solution. ¹³C NMR (400 MHz, CDCl₃): δ = 164.6, 133.9, 133.2, 131.6, 131.1, 130.2, 129.4, 127.9, 126.8, 125.2, 124.6, 122.6 (all Ph), 34.2 ppm (SCH₂). A VT ¹H NMR (298–193 K)

study in CD₂Cl₂ showed that the azobenzene multiplets were most resolved at 263 K, while the SCH₂ resonances sharpened to $\nu_{1/2}$ $\approx$ 30 Hz at δ = 3.41 and 2.78 ppm, respectively, at 263 K. These signals resolved into overlapping doublets at δ = 3.29 and 2.73 ppm, respectively, at 193 K. ESI⁺ MS: m/z 467 [M⁺]. ESI[–] MS: m/z 358 [M[–]], with higher mass “clusters” at m/z 665 and 972. MALDI-TOF MS⁺: m/z 467 [M]⁺. MALDI-TOF MS[–]: m/z 359 [M][–]. IR (KBr): $\tilde{\nu}$ = 3047 (w), 2976 (m), 2959 (w), 2909 (w), 1574 (s), 1551 (w), 1481 (w), 1456 (w), 1445 (m), 1393 (s), 1316 (sh w), 1300 (m), 1258 (m), 1238 (m), 1217 (vw), 1200 (w), 1155 (w), 1109 (w), 1072 (w), 1040 (w), 1020 (w), 1001 (w), 891 (w), 829 (w), 814 (w), 764 (vs), 741 (m), 712 (w), 694 (s), 665 (w), 737 (vw), 611 (vw), 579 (vw), 550 (w), 523 (w), 494 (w), 440 (m) cm^{–1}. C₃₁H₃₁Cl₃N₄PdS₃ (945.92): calcd. C 39.4, H 3.3, N 5.9; found C 39.1, H 3.3, N 5.7.

(iii) With [(HMB)Ru^{II}{ η^3 -tpdt}] (3**):** Complex **5** (12 mg, 0.019 mmol) was added to a stirred solution of **3** (15 mg, 0.036 mmol) in methanol (10 mL). A gradual colour change from red to brown occurred over 30 min. After stirring for 6 h, the solution was filtered to remove unreacted **5**. NH₄PF₆ (20 mg, 0.12 mmol) was added and, after stirring for 15 min, the precipitated brown solids were filtered. The brown product was then dissolved in MeCN (6 mL) and filtered to remove NH₄Cl and the excess NH₄PF₆. Addition of diethyl ether to the filtrate and subsequent cooling to –30 °C for 24 h gave brown needle-shaped crystals of [((HMB)Ru^{II}(μ - η^2 : η^3 -tpdt)) {Pd(C₆H₄N=NC₆H₅)}]PF₆ (**7**; 26 mg, 85%).

Data for 7: ¹H NMR (400 MHz, CD₃CN): δ = 8.00–7.99 (5-line m, 1 H, Ph), 7.76–7.74 (5-line m, 2 H, Ph), 7.63–7.61 (4-line m, 1 H, Ph), 7.58–7.56 (5-line m, 3 H, Ph), 7.37–7.30 (11-line m, 2 H, Ph), 3.34–3.28 (6-line m, 1 H, SCH₂), 3.13–3.06 (7-line m, 1 H, SCH₂), 2.90–2.83 (5-line m, 1 H, SCH₂), 2.71–2.65 (7-line m, 1 H, SCH₂), 2.50–2.42 (8-line m, 1 H, SCH₂), 2.27–2.15 (14-line m, 2 H, SCH₂), 1.88–1.82 (8-line m, 1 H, SCH₂), 2.11 (s, 18 H, C₆Me₆) ppm. ¹³C NMR (400 MHz, CD₃CN): δ = 166.0, 160.5, 152.3, 134.6, 133.6, 131.8, 131.4, 129.7, 127.4, 124.2 (all Ph), 101.6 (C₆Me₆), 45.5, 42.9, 34.0, 27.5 (all SCH₂), 15.9 ppm (C₆Me₆). FAB⁺ MS: m/z 703 [M – PF₆]⁺. FAB[–] MS: m/z 145 [PF₆][–]. IR (KBr): $\tilde{\nu}$ = 3040 (vw), 2956 (vw), 2922 (w), 2853 (vw), 1459 (w), 1389 (m), 1304 (w), 1253 (w), 1236 (w), 1158 (vw), 1109 (w), 1072 (w), 1016 (w), 842 [vs. (PF₆)], 772 (m), 712 (w), 693 (w), 558 [m (PF₆)] cm^{–1}. C₂₈H₃₅F₆N₂PPdRuS₃ (848.25): calcd. C 39.7, H 4.2, N 3.3, S 11.3; found C 40.0, H 4.3, N 3.4, S 11.4.

(iv) With [Cp*Ru^{III}{ η^3 -tpdt}] (4**):** MeOH (10 mL) was added to a mixture of **4** (20 mg, 0.051 mmol) and **5** (17 mg, 0.026 mmol). A colour change from dark purple to dark brown was observed after 5 min. After stirring for 2 h, the solution was filtered through a glass sinter (Por. 4) to remove some unreacted Pd complex **5**. NH₄PF₆ (25 mg, 0.15 mmol) was added to the dark brown filtrate and, after stirring for 15 min, the reaction mixture was evacuated to dryness. The residue was then extracted with MeCN (2 $\times$ 3 mL) and the extracts filtered through a Por. 4 glass sinter. Diethyl ether was added to the filtrate to give a dark brown solid after 24 h at –30 °C. This solid was further purified by recrystallization from MeCN/diethyl ether to give [Cp*Ru^{III}(μ - η^2 : η^3 -tpdt)]₂Pd(PF₆)₂ (**8**; 26 mg, 80%) as a black crystalline solid.

Data for 8: ¹H NMR (300 MHz, CD₃CN): δ = 3.03 (br. s, 8 H, SCH₂), 2.74–2.66 (6-line m, 8 H, SCH₂), 1.77 ppm (s, 30 H, C₅Me₅). FAB⁺ MS: m/z 1028 [M – PF₆ + H]⁺, 883 [M – 2PF₆ + H]⁺, 827 [M – PF₆ – 4CH₂]⁺. FAB[–] MS: m/z 145 [PF₆][–].

4.3. Reaction of [(9S3)Pd(C₆H₄N=NC₆H₅)]PF₆ (**6A**)

(i) With 3: A mixture of **6A** (23 mg, 0.038 mmol) and **3** (16 mg, 0.039 mmol) in MeOH (8 mL) was stirred for 1 h to give a brown

solid. The reaction mixture was then concentrated to half volume and the brown solid was filtered off and washed with MeOH (2 × 3 mL). It was then recrystallised from MeCN/diethyl ether to give brown needle-shaped crystals of **7** (24 mg, 75% yield) after 12 h at –30 °C.

(ii) With 4: A mixture of **6A** (16 mg, 0.026 mmol) and **4** (10 mg, 0.026 mmol) in MeOH (8 mL) was stirred for 2 h. The reaction mixture was then filtered to remove some insoluble blackish solid. The solvent was removed from the filtrate under vacuum and replaced by MeCN. Layering the solution with diethyl ether gave black orthorhombic crystals of **8** (11 mg, 73% yield) after 1 week at –30 °C.

4.4. X-ray Crystal Structure Determinations: The crystals were mounted on glass fibres and X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer (for **6A** and **7**) or Bruker X8 CCD diffractometer (for **6B**, **6B·H₂O**, **6B·CHCl₃**) using Mo-*K_α* radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 223 and 173 K, respectively. SAINT^[16] was used for integration of the intensity of reflections and scaling; SADABS^[17] was used for absorption correction.

The structures were solved by direct methods to locate the heavy atoms, and refined by full-matrix least-squares against F^2 using SHELXL-97.^[18] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The asymmetric unit of the crystal of **7** contains one cation which shows disorder in the ethylene carbons (C3–C4) of the tpdt ligand (60:40 occu-

pancy ratio). There is also one diethyl ether molecule present as space filling solvent in complex **7**.

Crystal and refinement data are summarized in Table 4. The Ortep drawings and packing diagrams were plotted using SHELX/XP. The short atom–atom contact distances were calculated using MERCURY (CCDC, UK).

CCDC-714923 (for **6A**), -714924 (for **6B**), -714925 (for **6B·H₂O**), -714926 (for **6B·CHCl₃**), -714927 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.5. Electrochemistry: Voltammetric experiments were conducted with a computer-controlled Eco Chemie μ Autolab III potentiostat with a 1-mm diameter glassy carbon (GC) and Pt working electrodes. Potentials were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, which was added as an internal standard at the end of the electrochemical experiments. The electrochemical cell was jacketed in a glass sleeve and cooled to between 243–293 K using a Lauda RL6 variable-temperature methanol-circulating bath.

Supporting Information (see footnote on the first page of this article): Tables S1–S4 list selected atom–atom contact distances (obtained by the MERCURY software) in the crystal lattices of **6A**, **6B**, **6B·H₂O** and **6B·CHCl₃**, respectively. Figures S1–S4 show the packing diagrams (in color) of **6A**, **6B**, **6B·H₂O** and **6B·CHCl₃**, respectively, viewed along selected axes. Figure S5 shows the cyclic voltammograms of **6B**.

Table 4. Data collection and processing parameters.

	6A	6B	6B·H₂O	6B·CHCl₃	7
Formula	C ₁₈ H ₂₁ F ₆ N ₂ PPdS ₃	C ₃₀ H ₃₀ Cl ₂ N ₄ Pd ₂ S ₃	C ₃₀ H ₃₂ Cl ₂ N ₄ OPd ₂ S ₃	C ₃₁ H ₃₁ Cl ₅ N ₄ Pd ₂ S ₃	C ₃₂ H ₄₅ F ₆ N ₂ OPPpRuS ₃
<i>M_r</i>	612.92	826.46	844.48	945.83	922.32
Temperature [K]	223(2)	173(2)	173(2)	173(2)	223(2)
Crystal color and habit	red, orthorhombic	red blocks	black red, needle	black needles	brown, cuboid
Crystal size [mm ³]	0.18 × 0.16 × 0.10	0.12 × 0.10 × 0.10	0.30 × 0.10 × 0.05	0.30 × 0.04 × 0.03	0.40 × 0.10 × 0.08
Crystal system	triclinic	triclinic	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pna</i> 2(1)
<i>a</i> [Å]	9.4590(4)	11.5311(5)	10.1248(3)	18.8678(13)	18.4238(11)
<i>b</i> [Å]	10.7392(4)	11.6861(6)	10.6328(3)	10.0045(6)	21.5491(13)
<i>c</i> [Å]	12.1331(5)	13.1943(6)	15.1670(4)	20.5907(15)	9.1320(6)
α [°]	71.8760(10)	80.782(3)	99.796(2)	90	90
β [°]	89.6170(10)	74.533(2)	90.060(2)	115.678(2)	90
γ [°]	72.8130(10)	63.970(2)	95.750(2)	90	90
<i>V</i> [Å ³]	1114.11(8)	1537.86(12)	1600.63(8)	3502.9(4)	3625.6(4)
<i>Z</i>	2	2	2	4	4
Density [g cm ^{–3}]	1.827	1.785	1.752	1.793	1.690
Absorption coeff. [mm ^{–1}]	1.245	1.575	1.518	1.617	1.190
<i>F</i> (000)	612	824	844	1880	1864
θ range for data collection	1.77 to 27.50	1.60 to 27.83	2.46 to 31.19	1.22 to 26.41	1.45 to 27.50
Index ranges	–12 ≤ <i>h</i> ≤ 12 –13 ≤ <i>k</i> ≤ 13 –15 ≤ <i>l</i> ≤ 15	–15 ≤ <i>h</i> ≤ 14 15 ≤ <i>k</i> ≤ 15 –17 ≤ <i>l</i> ≤ 17	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –22 ≤ <i>l</i> ≤ 22	–23 ≤ <i>h</i> ≤ 23 12 ≤ <i>k</i> ≤ 12 –25 ≤ <i>l</i> ≤ 25	–23 ≤ <i>h</i> ≤ 23 –28 ≤ <i>k</i> ≤ 28 –11 ≤ <i>l</i> ≤ 11
Number of reflections collected	14667	27245	63438	36584	46172
Independent reflections	5103	7182	10335	7196	8321
Max. and min. transmission	0.8856 and 0.8070	0.8584 and 0.8335	0.9280 and 0.6588	0.9531 and 0.6426	0.9108 and 0.6476
Number of data/restraints/params.	5103/0/348	7182/0/370	10335/2/387	7196/0/406	8321/7/430
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^[a,b]	<i>R</i> 1 = 0.0317 <i>wR</i> 2 = 0.0753	<i>R</i> 1 = 0.0439 <i>wR</i> 2 = 0.1184	<i>R</i> 1 = 0.0242 <i>wR</i> 2 = 0.0549	<i>R</i> 1 = 0.0617 <i>wR</i> 2 = 0.1661	<i>R</i> 1 = 0.0585 <i>wR</i> 2 = 0.1353
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0339 <i>wR</i> 2 = 0.0765	<i>R</i> 1 = 0.0689 <i>wR</i> 2 = 0.1461	<i>R</i> 1 = 0.0341 <i>wR</i> 2 = 0.0592	<i>R</i> 1 = 0.0884 <i>wR</i> 2 = 0.1897	<i>R</i> 1 = 0.0624 <i>wR</i> 2 = 0.1377
Goodness-of-fit on F^2 ^[c]	1.064	1.123	1.030	1.124	1.173
Largest diff. peak and hole [e Å ^{–3}]	0.820 and –0.486	2.961 and –1.673	1.201 and –0.528	2.237 and –1.447	3.461 and –0.856

[a] $R = (\Sigma|F_o| - |F_c|)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma w|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. [c] $\text{GoF} = [(\Sigma w|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

Acknowledgments

We thank the National University of Singapore for a grant (R143-000-209-112) to L. Y. G., a research graduate scholarship to R. Y. C. S., and support for G. C. L. (Honours Year Project), and Dr. L. L. Koh, Ms. G. K. Tan and Ms. E. L. Goh for technical assistance. Support from the Nanyang Technological University is also gratefully acknowledged (L. Y. G., R. D. W., and Y. X. L.).

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Received: January 15, 2009
Published Online: April 20, 2009