Preparation and characterization of dinuclear Pd(II) complexes of binucleating tetraaza-thiophenolate ligands

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The thioethers 4-*tert*-butyl-2,6-bis((2-(dimethylamino)ethylimino)methyl)phenyl(*tert*-butyl)sulfane (*t*Bu–L³) and 4-*tert*-butyl-2,6-bis((2-(dimethylamino)ethylimino)methyl)phenyl(*tert*-butyl)sulfane (*t*Bu–L⁴) react with PdCl₂(NCMe)₂ to give the dinuclear palladium thiophenolate complexes [(L³)Pd₂Cl₂]⁺ (**2**) and [(L⁴)Pd₂(µ-Cl)]²⁺ (**3**) (HL³ = 2,6-bis((2-(dimethylamino)ethylimino)methyl)-4-*tert*-butylbenzenethiol, HL⁴ = 2,6-bis((2-(dimethylamino)ethylamino)methyl)-4-*tert*-butylbenzenethiol). The chloride ligands in **2** could be replaced by neutral (NCMe) and anionic ligands (NCS⁻, N₃⁻, CN⁻, OAc⁻) to give the diamagnetic Pd^{II} complexes [(L³)Pd₂(NCMe)₂]³⁺ (**4**), [(L³)Pd₂(NCS)₂]⁺ (**5**), [(L³)Pd₂(NCCH₂Cl)₂]³⁺ (**6**), [{(L³)Pd₂(µ-CN)}₂]⁴⁺ (**7**) and [(L³)Pd₂(OAc)]²⁺ (**9**). The nitrile ligands in **4** and in [(L³)Pd₂(NCCH₂Cl)₂]³⁺ are readily hydrated to give the corresponding amidato complexes [(L³)Pd₂(NCMe)₂]³⁺ with NaBPh₄ gave the diphenyl complex [(L³)Pd₂(Ph)₂]⁺ (**11**). All complexes were either isolated as perchlorate or tetraphenylborate salts and studied by IR, ¹H and ¹³C NMR spectroscopy. In addition, complexes **2**[ClO₄], **3**[ClO₄]₂, **5**[BPh₄], **6**[BPh₄], **7**[ClO₄]₄, **9**[ClO₄]₂, **10**[ClO₄]₂ and **11**[BPh₄] have been characterized by X-ray crystallography.

Introduction

The coordination chemistry of binucleating thiophenolate ligands has been actively pursued in the past several years.¹⁻⁴ Motivations in this area are diverse and include the preparation of model compounds for dinuclear metallo enzymes,⁵ the stabilization of unusual metal oxidation states,⁶ and attempts to understand, achieve and control binuclear metal reactivity,⁷⁻⁹ to name a few. Traditional routes to such complexes make use of the free thiophenols, but their synthetic procedures are often time-consuming and tedious, thereby hampering a more rapid exploitation of this research area. With this in mind several groups are currently involved in the development of alternative synthetic strategies which provide more direct access to binucleating thiophenolate ligand systems.^{10,11} Among many procedures in the literature, the metal-ion-promoted S-deprotection of arylthioesters¹² or arylthioethers¹³ has turned out to be a very convenient and efficient one.

Recently we found that the macrobicyclic hexaazadithioether L¹ undergoes a S–C bond cleavage reaction in the presence of PdCl₂(NCMe)₂ to afford the dinuclear complex $[(L^2)Pd_2Cl_2]^+$ of the ring-opened hexaaza-vinylthioether/thiophenolate derivative $(L^2)^-$ (Scheme 1).¹⁴ This led us to investigate the possibility of synthesizing related palladium thiophenolate complexes by using the open-chain thioethers $tBu-L^3$ and $tBu-L^4$ as starting materials. Herein we report on the reactions of these two thioethers with PdCl₂(NCMe)₂ and describe the coordination chemistry of the new dinuclear palladium thiophenolate complexes formed.



Scheme 1 Structures of L^1 and $[(L^2)Pd_2Cl_2]^*$ and of the thioethers $tBu-L^3$ and $tBu-L^4$ used in the synthesis of dinuclear palladium(II) complexes.

Results and discussion

Synthesis of proligands and complexes

Scheme 2 shows the preparation of the proligands $tBu-L^3$ and $tBu-L^4$ and the complexes 2–7. The imine-amine-thioether $tBu-L^3$ was prepared in nearly quantitative yield by a Schiff-base condensation reaction between dialdehyde 1¹⁵ and N', N'-dimethylethane-1,2-diamine. The subsequent sodium-borohydride reduction of $tBu-L^3$ gave the tetraamine-thioether $tBu-L^4$. Unlike its parent $tBu-L^3$, the tetraamine-thioether $tBu-L^4$ could not be obtained in analytically pure form. Nonetheless it was of sufficient purity for metal complex syntheses. Treatment of $tBu-L^3$ with two equivalents of PdCl₂(NCMe)₂ in acetonitrile solution at ambient temperature for 2 days gave a yellow solution, from which upon addition of an excess of LiClO₄ yellow crystals of 2[ClO₄]

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Scheme 2 Synthesis of proligands $tBu-L^3$ and $tBu-L^4$ and complexes 2–7.

precipitated in *ca.* 70% yield. Similarly, reaction of tetraaminethioether $tBu-L^4$ with two equivalents of PdCl₂(MeCN)₂ in a mixed acetonitrile–dichloromethane solvent system at ambient temperature for 12 h gave a yellow solution, from which upon addition of an excess of LiClO₄ a compound of composition [(L⁴)Pd₂(μ -Cl)][ClO₄]₂ (**3**[ClO₄]₂) precipitated in *ca.* 77% yield. Thus, as was observed previously for the macrobicyclic compound L¹,¹⁴ the two thioethers undergo a Pd-promoted S–C bond cleavage reaction to generate dinuclear palladium complexes of the binucleating thiophenolate ligand (L³)⁻ and (L⁴)⁻, respectively.

Dinuclear palladium complexes of binucleating thiolate ligands such as those reported by McKenzie and Robson,^{16,24} are known to exhibit a rich coordination chemistry as the terminal chloride ligands can be readily exchanged for other neutral or anionic species. These observations dictated that complex **2** would display a similar rich coordination chemistry. In the following we will show that this is the case. The bisacetonitrile derivative $[(L^3)Pd_2(NCMe)_2]^{3+}$ (**4**) was selected as the first target compound. This complex was obtained by Cl⁻ abstraction from $[(L^3)Pd_2Cl_2]^+$ (**2**) with anhydrous Pb(ClO₄)₂ and isolated as its triperchlorate salt in 76% yield. Treatment of this material with 2 equivalents of NaSCN at ambient temperature resulted in the formation of a red solution from which an orange-colored product of composition $[(L^3)Pd_2(SCN)_2][ClO_4]$ (5[ClO₄]) could be isolated in 53% yield. The reaction of 4[ClO₄]₃ with two equivalents of sodium azide in a mixed acetone-methanol solvent system produced the azido complex $[(L^3)Pd_2(N_3)_2]^+$ (6), which was isolated as its perchlorate in 81% yield. Complexes 5 and 6 were also isolated as their tetraphenylborate salts. When complex 2 was treated with $Pb(ClO_4)_2$ in propionitrile as the solvent a tetranuclear cyanide complex $[{(L^3)Pd_2(\mu_{1,2}-CN)}_2][ClO_4]_4$ (7[ClO_4]_4) was obtained in high yields. The cyanide ions are presumably generated via a Pb²⁺mediated retro-hydrocyanation of the solvent (CH₃CH₂CN \rightarrow $CH_2 = CH_2 + HCN$). This is supported by the fact that propionitrile solutions of Pb(ClO₄)₂ develop ethylene gas and HCN which can be detected by gas chromatography. It can be ruled out that the cyanide ions stem from an HCN impurity in the solvent, because this was carefully purified (washing with K₂CO₃ and KMnO₄ solution) and freshly distilled from appropriate drying agents. Likewise, the fact that there is no detectable $CH_2 = CH_2$ in the gas phase above a propionitrile solution of the palladium complex $4[ClO_4]_3$ rules out the possibility that the retro-hydrocyanation is catalyzed by the palladium thiolate complexes.

In the course of this work it was found that the Pd-bound acetonitriles in 4 are readily hydrated to acetamide. Thus, the reaction of 4 with water proceeded smoothly to give the MeCONH⁻ complex [(L3)Pd2(NHCOMe)]2+ (8) which could be isolated as its perchlorate salt (8[ClO₄]₂) in ca. 60% yield (Scheme 3). The acetato-bridged compound $[(L^3)Pd_2(OAc)][ClO_4]_2$ (9[ClO₄]₂) was prepared for comparative purposes. Unfortunately, we have not been able to grow single crystals of $8[ClO_4]_2$ suitable for an Xray crystal structure determination. On these grounds we chose to investigate the hydration of 2-chloroacetonitrile. As indicated in Scheme 3, the trication $[(L^3)Pd_2(NCCH_2Cl)_2]^{3+}$ (prepared in situ from $2[ClO_4]_2$ and Pb(ClO_4)_2 in neat 2-chloroacetonitrile) is also readily hydrated by aqueous methanol to give the corresponding 2-chloroacetamido complex [(L³)Pd₂(NHOCCH₂Cl)]²⁺ (10). Note that the chloro-function is not hydrolyzed under these conditions. The dipalladium(II) complex $[(L^3)Pd_2(\eta^1-Ph)_2][BPh_4]$ (11[BPh_4]) bearing two phenyl groups represents the last complex of this study. Complex 11 formed as a side product in the salt metathesis reaction between 4[ClO₄]₃ and NaBPh₄ in a mixed ethanol-acetonitrile (1: 1) solvent system (Scheme 3). The ability of the tetraphenylborate to transfer a $C_6H_5^-$ unit to cationic Pd(II) complexes has been reported previously,¹⁷ but to the best of our knowledge a double $C_6H_5^-$ -transfer to a dinuclear Pd₂ complex is unprecedented. Complex 11[BPh₄] is stable toward heat (mp >140 °C decomp.), moisture and air. This stability is unusual compared to the lower stability of mononuclear Pd-Ph complexes.¹⁸ The presence of the adjacent phenyl rings might be expected to encourage the reductive elimination of biphenyl from the binuclear palladium complex. and yet this compound is stable indefinitely.

[(L³)Pd₂(CH₃CONH)]²⁴ $[(L^{3})Pd_{2}(NCMe)_{2}]^{3+}$ 12h. 61% 8 Pd(OAc)₂ [(L³)Pd₂(CH₃CO₂)]² t-BuL³ 24h, 63% 9 1. Pb(ClO₄)₂/ CH₂ClCN 2. MeOH/H₂O [(L3)Pd2(CI)2] $[(L^3)Pd_2(CH_2CICONH)]^{2+}$ 12h, 91% 2 10 NaBPh₂ [(L³)Pd₂(Ph)₂] [(L³)Pd₂(NCMe)₂]³ CH₃CN/EtOH 4 (7 %) 11 8(R = H)11 10 (R = Cl)

H₂O / acetone

Scheme 3 Synthesis of complexes 8–11.

All compounds gave satisfactory elemental analyses and were characterized by spectroscopic methods (IR, ¹H and ¹³C NMR spectroscopy) and X-ray crystallography.

Table 1 Selected IR spectroscopic data (cm⁻¹) for compounds $tBu-L^3$, **2**[ClO₄] and **8**[ClO₄]₂-**10**[ClO₄]₂

	v(C=N)	$v_{\rm as}, v_{\rm s}({\rm RCO}_2)$	v_{as}, v_s (RCONH)	v(N–H)
<i>t</i> Bu–L ³ 2 [ClO ₄] 8 [ClO ₄] ₂ 9 [ClO ₄] ₂ 10 [ClO ₄] ₂	1632 1637 1648 1628 1643 1649 1630	1555, 1437 1573, 1414	1553, 1436	3316 3308

Spectroscopic characterization of proligands and complexes

The most significant feature in the IR spectrum of crystalline tBu-L³ is the strong band at 1632 cm⁻¹, which can be readily assigned to the C=N stretching frequency of the imine functions due to its absence in the IR of its reduced derivative tBu-L⁴ (Table 1). The IR spectrum of 4[ClO₄]₃ shows intense absorption bands at 2330 and 2303 cm⁻¹ attributable to the C=N stretching frequencies of the Pd-bound acetonitriles. Free acetonitrile absorbs at much lower frequencies ($v(C \equiv N) \sim 2250 \text{ cm}^{-1}$), indicative of a polarisation of the carbon nitrogen triple bond in 4.19 A strong IR band at 2108 cm⁻¹ in the IR spectrum of 5[ClO₄] was indicative of the coordination of thiocyanate ions.20 In agreement with the formulation of 6[ClO₄] the IR spectrum displays strong bands at 2030 and 2017 cm⁻¹ for the azide groups $v_{as}(N_3^-)$ and at 1100 cm⁻¹ for the ClO_4^- anion. The bridging CN^- groups in $7[ClO_4]_4$ are readily identified by the strong v(CN) band at 2184 cm⁻¹. Monodentate cyanides absorb at much lower wavenumbers.²¹ The IR spectrum of 8 contrasts that of 9 in that it exhibits an additional band at 3316 cm⁻¹ for the N-H stretching vibration. Similar values are observed for $10[ClO_4]_2$ and other acetamido complexes.²²

Selected ¹H and ¹³C NMR data for the compounds are presented in Table 2. The ¹H NMR spectrum of $tBu-L^3$ in CDCl₃ solution shows in accordance with its structure singlets for the two *tert*butyl groups (δ 1.06 and 1.26 ppm), the methyl protons of the four NCH₃ groups (δ 2.21 ppm), the aromatic protons (δ 8.07 ppm) and the two imine protons (δ 9.08 ppm). The methylene protons give rise to two triplets centred at δ 2.55 and 3.68 ppm. The ¹³C NMR spectrum of $tBu-L^3$ displays seven aliphatic, one imine and four aromatic ¹³C signals. Conversion of the two imine groups of $tBu-L^3$ to secondary amine functions in $tBu-L^4$ is supported by the absence of the signal for the imine protons (CH=N) and the presence of a new signal at δ 2.62 ppm for the benzylic methylene protons.

The ¹H NMR signal for the *tert*-butyl group of the thioether moiety of *t*Bu–L³ at δ 1.06 ppm is absent in the ¹H NMR spectrum of **2**. Likewise, the ¹³C NMR spectrum revealed only the ¹³C signals (δ 30.6, 35.7) for the *tert*-butyl group bonded to the aromatic carbon atom C10 (for atom labels see inset Table 2). It is also apparent from the ¹H and the ¹³C NMR data that the two halves of (L³)⁻ in **2** are equivalent. For example, single resonances are observed for the aromatic protons (C¹¹H) and the imine protons (C⁹H) and for the pairs of carbon atoms labelled C¹¹, C¹¹' and C¹², C¹²'. Thus, complex **2** is C_{2v} symmetric on the NMR time scale. This is in contrast to the complexes **8** and **10** described below in which the two palladium centres become inequivalent upon coordination of bridging acetamidato units carrying two distinguishable N and O donors. A similar NMR equivalence of the ligand side arms has been noted for the dinuclear [(L⁵)Pd₂(Cl)₂]⁺ complex

				11' 12'	10 10 11 12			10 11 12 12 11 12					
			8	9'	13 S N-	9	7'	9' 13 -N SH N	9				
			5'—	N	₹ ³ 4	N-5	5' <u>N</u>		N 5				
			6	/	<i>t</i> Bu-L ³	<u>`</u> 6	6' /	HL ³	`6				
	C^1H_3	C^4H_3	C^5H_3	C^6H_3	C^7H_2	C^8H_2	$C^{11}H$	$C^9H(C^9H_2)$					
$tBu-L^{3,a}$	1.26	1.06	2.21	2.21	3.68	2.55	8.07	9.08					
$tBu-L^{4,a}$	1.26	1.30	2.14	2.14	2.34	2.57	7.35	2.62					
2[ClO ₄] ^b	1.37		2.76	2.76	4.12	2.76	8.07	8.68					
$3[ClO_4]_2^c$	1.31		2.78	2.85	2.64	3.00	7.46	3.43					
4610.1	1 40				3.73	4.17	0.15	4.98					
$4[ClO_4]_3^c$ Coligand: 1.	1.40 97 (CH₃C	N)	2.87	2.87	4.30	3.00	8.17	8.38					
$4[ClO_4]_3^d$	1.42	. D	3.00	3.00	4.44	3.17	8.23	8.47					
Coligand: 2.	$24(CH_{3}C)$	N)	0.77	0.77	4.17	2.02	0.00	0.70					
6[CIO ₄] [#]	1.43		2.77	2.77	4.1/	2.83	8.22	8.79					
6[BPn ₄] [°]	1.35		2.70	2.70	4.08	2.75	8.14	8./1					
8 [CIO ₄] ₂ ^c	1.40		2.81	2.83	4.07	2.73	8.12	8.30					
Calicond. 2	22 (CII C				4.15	2.87	8.15	8.39					
Conganu: 2.	$52(CH_3C)$	UNH), 0.1	275	2 75	2 0 2	2.62	8.08	8 15					
o[DFII4]2	1.40		2.15	2.15	3.93 4.00	2.03	0.00	8.40					
Coligand: 2	30 (CH.C	'ONH) 6 ()5 (CH.C	ONH	4.00	2.71		0.40					
9[C]Q.]. ^b	1 40	0111), 0.0	2 78	2 78	4 25	2.83	8 32	8 78					
Coligand: 2	36 (CH.C	(O .)	2.70	2.70	ч.25	2.05	0.52	0.70					
10[C]Q.]. ^b	1 37	(U ₂)	2 84	2 84	4 16	2 78	8 28	8 72					
10[0104]2	1.57		2.01	2.01	4 25	2.70	8 30	8.92					
Coligand: 4.	53 (ClCH	CONH).	7.47 (ClC	H ₂ CON <i>H</i>)		0.50	0.92					
11[BPh ₄] ^e	1.39	2 = = =),	2.86	2.86	4.02	2.86	8.19	8.30					
1 43					4.08			8.55					
	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}
$tBu-L^{3,a}$	31.5	35.5	31.6	46.2	49.7	49.7	60.2	60.5	163.3	152.9	141.6	131.6	127.2
$tBu-L^{4,a}$	29.8	33.3	30.2	47.6	44.0	44.0	51.9	57.5	44.8	150.8	144.3	124.4	126.7
$2[ClO_4]^e$	30.6	35.7			48.7	51.8	62.9	64.8	165.2	151.8	139.6	134.2	128.7
$3[ClO_4]_2^c$	30.2	34.5			49.3	51.7	54.2	56.9	63.2	151.6	136.0	128.7	129.9
$4[ClO_4]_3^d$	31.0	36.1			50.6	53.2	62.8	67.3	168.4	153.8	142.7	133.4	127.4
Coligand: 4.	$4(CH_3CN)$	N), 123.3 (O	$CH_3CN)$										
6[ClO ₄] ^b	30.8	34.9			49.3	49.3	61.3	63.6	165.9	150.2	139.5	133.6	121.9
$8[ClO_4]_2^d$	31.0	35.9			49.6	50.7	64.6	66.7	166.8	153.1	142.3	133.6	125.5
									167.7		142.9	135.1	
Coligand: 24	$4.1 (CH_3C)$	ONH), 17	$9.6 (CH_3 C)$	CONH)									
$[BPh_4]_2^c$	30.8	34.5			49.1	50.2	60.3	63.6	166.4	152.0	141.0	134.5	124.7
Caliar 1.24							62.6	65.8	165.4		141.6	132.8	
Coligand: 23	0.4 (CH ₃ C	ONH), 18	$0.7 (CH_3 C$	JONH)	40 1	40.1	50 ((4.0	166.0	150.5	140 5	122.5	122.4
$\mathcal{Y}[ClO_4]_2^{"}$	30.1 1.1.(CU.C	34.4)	48.1	48.1	39.6	04.9	166.0	150.5	140.5	132.5	122.4
Collgand: 24	+.1 (CH ₃ C 20.7	$(U_2), 1/9.6$	(CH_3CO_2)	2)	10 (40.7	60.0	62.1	164.0	150.0	140.0	122.2	122.0
10[CIO ₄] ₂ "	30.7	34.9			48.0	49./	00.0 62 1	03.1	104.8	130.9	140.9	132.3	122.9
Coligand: 43	3.8 (Cl <i>C</i> H	₂ CONH),	174.8 (Cl C	CH ₂ CONH	H)		02.1	03.3	100.9		141.5	133.0	

Table 2 Selected ¹H and ¹³C NMR data for the thioethers $tBu-L^3$, $tBu-L^4$ and the palladium complexes **2–9**

^{*a*} Recorded in CDCl₃ solution. ^{*b*} Recorded in DMSO-d₆ solution. ^{*c*} Recorded in CD₃CN solution. ^{*d*} Recorded in CD₃NO₂ solution. ^{*e*} Recorded in acetone-d₆ solution.

where $(L^5)^{3-}$ is the trianion derived from the condensation product of cyclohexanecarbohydrazide and 2-mercapto-5-methylbenzene-1,3-dialdehyde (Scheme 4).²³

The ¹H and ¹³C NMR spectral data for complex **3** were also indicative of complete removal of the S-bonded *t*Bu group, showing only one singlet at δ 1.31 for the C(10) bound *para t*Bu group. The ¹H NMR spectrum of **4**[ClO₄]₃ in CD₃NO₂ solution revealed a signal at δ 2.24 ppm attributable to the methyl protons

of the acetonitrile molecules. The ¹H NMR spectrum of **5**[ClO₄] showed only complicated multiplets in the aliphatic as well as in the aromatic region and could not be analyzed. The same was true for the ¹³C NMR spectrum. The ¹H NMR of **6**[ClO₄] in DMSO-d₆ solution displays only one set of signals, indicating that **6** exists as a single isomer in solution. The *tert*-butyl, N-methyl, aromatic and the imine protons all appear as singlets indicative of local C_2 or C_s -symmetry. This is also supported by the ¹³C NMR



Scheme 4 Structures of ligands H₃L⁵ and HL⁶.^{24,25}

spectrum which displays only 10 signals (one for the imine, four for the aromatic and five for the aliphatic carbon atoms). It can be readily seen that the spectroscopic data for the acetate-complex **9** and the acetamido species **8** differ significantly from each other. For example, the ¹H NMR spectrum of **8** in CD₃CN solution reveals a signal at δ 6.15 ppm that is not observed for the acetato complex **9**. This signal is readily assigned to the acetamidato NH protons, as it vanishes in the presence of D₂O due to NH/ND exchange. Finally, the ¹³C NMR spectrum of **8**[ClO₄]₂ shows six signals for the aromatic protons whereas only four such signals are observed for **9**[ClO₄]₂. These data provide sufficient evidence for the formulation of **8**[ClO₄]₂ as a dipalladium complex coligated by a deprotonated acetamide. The ¹H and ¹³C NMR data for the perchlorate salt **10**[ClO₄]₂ are very similar to those of **8** and prove the formulation of the acetamidato compounds.

Description of crystal structures

The X-ray crystal structures of complexes $2[ClO_4]$, $3[ClO_4]_2$. MeOH, $4[ClO_4]_3$, $5[BPh_4]$ ·MeCN, $6[BPh_4]$ ·MeCN, $7[ClO_4]_4$. 2EtCN·MeCN, $9[ClO_4]_2$, $10[ClO_4]_2$ and $11[BPh_4]$ were determined to establish the geometries about the metal ions as well as the bonding modes of the coligands. Experimental crystallographic data are summarized in Table 3.

The crystal structure of $2[ClO_4]$ consists of well-separated $[(L^3)Pd_2Cl_2]^+$ complexes and perchlorate anions. Fig. 1 presents a perspective view of the structure of 2 along with the atom labelling scheme used. Selected bond lengths and angles are given in the Figure caption.

The crystal structure determination of $2[ClO_4]$ confirmed the presence of the dichloro complex 2 of the novel imine-aminethiophenolate ligand $(L^3)^-$. Each palladium atoms is coordinated by one bridging thiolate sulfur atom, two nitrogen atoms and a terminal chloro ligand in a distorted square planar fashion. The maximum deviations from the least-squares planes defined by the atoms Pd(1), N(1), N(2), S, Cl(1) and Pd(2), N(3), N(4), S, Cl(2) are 0.043 and 0.048 Å, respectively. The overall conformation of $(L^3)^-$ in 2 is very similar to that of the related diimine-dipyridyl-thiophenolate ligand $(L^6)^-$ in $[(L^6)Pd_2Cl_2]^+$ (HL⁶ = 2,6-bis((2-(pyridin-2-yl)ethylimino)methyl)-4-methylbenzenethiol, Scheme 4).24 For example, in both compounds the two coordination planes are markedly twisted around the hinging sulfur atoms presumably as a consequence of repulsive interactions between the two chloro ligands. Likewise, in both structures the side arm associated with Pd(2) is much more twisted out of the plane of the central aromatic unit than the other. In 2, the coordination plane of Pd(1) is at a dihedral angle of 18.6° to the central aromatic ring whereas the corresponding angle for the

$\begin{array}{ccc} \mbox{rmula} & \mbox{C}_{20}\mbox{H}_3\mbox{C}_3\mbox{N}_4\mbox{O}_4\mbox{P}\\ 744.71 & 744.71 & \\ 744.71 & 274.71 & \\ 27660(3) & 274.71 & \\ 12.660(3) & 12.660(3) & \\ A & 12.313(3) & \\ A & 13.313(3) & \\ A & 16.634(3) & \\ 0.00 & 0.00 & \\ 0.00 & 0.00 & \\ \end{array}$	10011712000	5[BPh4]·McCN	6[BPh4]·MeCN	7[ClO4]4(EtCN)2MeCN	9[CIO ₄] ₂	10[C1O4]2	$11[BPh_4]$
ace group 221/n A 12.660(3) A 13.313(3) A 13.313(3) A 10.034(3) 0.000	$2d_2S = C_{21}H_{41}Cl_3N_4O_9Pd_2S = 844.79$	$C_{48}H_{59}BN_7Pd_2S_3$ 1053.81	C ₄₆ H ₅₆ BN ₁₁ Pd ₂ S 1018.69	$C_{50}H_{79}Cl_4N_{13}O_{16}Pd_4S_2$ 1749.78	$C_{22}H_{36}Cl_2N_4O_{10}Pd_2S$ 832.31	$C_{22}H_{36}Cl_3N_5O_9Pd_2S$ 865.77	$C_{56}H_{63}BN_4Pd_2S$ 1047.77
A 12.660(3) A 13.13(3) A 13.13(3) A 10.024(3) A 10.024(3)	$Pca2_1$	$P\overline{1}$	$P2_1/n$	C2/c	$P2_1/n$	$P\overline{l}$	$P\overline{1}$
Å 13.313(3) Å 16.634(3) مر 00.00	17.285(4)	12.459(3)	11.646(2)	23.689(5)	11.410(3)	11.351(2)	12.375(2)
Å 16.634(3) 20 00 00	14.357(3)	13.980(3)	19.717(3)	11.289(2)	12.245(2)	11.518(2)	13.557(3)
00.00	12.751(3)	15.412(3)	20.203(3	27.918(6)	22.395(4)	12.189(2)	17.310(3)
0000	90.00	103.97(3)	90.00	90.00	90.00	85.70(3)	74.396(3)
,0 98.47(3)	90.00	96.68(3)	94.976(3)	90.71(3)	102.20(3)	84.74(3)	78.886(3)
00.06	90.00	109.90(3)	90.00	00.06	90.00	83.01(3)	62.886(3)
$/\text{Å}^{3}$ 2773(1)	3164(1)	2390.7(8)	4621(1)	7466(3)	3058(1)	1571.8(5)	2481.1(8)
4	4	7	4	4	4	2	2
$c/g cm^{-3}$ 1.784	1.773	1.464	1.464	1.618	1.808	1.829	1.402
rystal size/mm $0.25 \times 0.20 \times 0.21$	$0.0 0.30 \times 0.15 \times 0.15$	$0.35 \times 0.26 \times 0.18$	$0.30 \times 0.25 \times 0.20$	$0.15 \times 0.15 \times 0.15$	$0.20 \times 0.20 \times 0.15$	$0.32 \times 0.15 \times 0.15$	$0.20 \times 0.20 \times 0.20$
$Mo-K\alpha)/mm^{-1}$ 1.694	1.507	0.924	0.869	1.212	1.476	1.521	0.808
Limits/ ^o 1.89–28.79	1.42 - 28.89	1.39 - 28.65	1.45 - 28.96	1.46-28.84	1.86 - 28.77	1.68-28.78	1.23 - 28.89
leasured refl. 17078	19240	20729	41364	32483	26837	13926	21123
idependent refl. 6510	7209	10883	11258	9087	7412	7300	11263
bserved refl.a 3927	4239	6872	6150	5038	4259	5548	6367
o. parameters 341	325	543	554	429	370	442	577
1^{b} (<i>R</i> 1 all data) 0.0420 (0.0894)	0.0540(0.1133)	0.0487 (0.0881)	0.0548 (0.1226)	0.0581 (0.1275)	0.0563 (0.1187)	0.0440 (0.0623)	0.0483 (0.1002)
R2 ^c (wR2 all data) 0.0954 (0.1326)	0.1178(0.1554)	0.1134 (0.1315)	0.0928(0.1188)	0.1493(0.1893)	0.1105(0.1464)	0.1262 (0.1396)	0.0905(0.1174)
lax., min. peaks/e Å ⁻³ 0.897/-1.131	1.035/-1.111	1.423/-0.964	1.187 / -1.355	1.612/-0.673	1.288/-1.158	1.029/-2.115	1.185/-1.217
CDC 286854	286855	286856	286857	286858	286859	286860	286861



Fig. 1 Structure of the cation **2** in crystals of $[(L^3)Pd_2Cl_2][ClO_4]$ (**2**[ClO_4]) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.978(5), Pd(1)–N(2) 2.091(5), Pd(1)–S 2.252(2), Pd(1)–Cl(1) 2.296(2), Pd(2)–N(3) 2.000(5), Pd(2)–N(4) 2.105(5), Pd(2)–S 2.280(2), Pd(2)–Cl(2) 2.299(2); Pd(1) ··· Pd(2) 3.922(1), Cl(1) ··· Cl(2) 3.633(2); Pd(1)–S–Pd(2) 119.87(7).

coordination plane of Pd(2) is at 48.3°. For $[(L^6)Pd_2Cl_2]^+$, these angles are very similar at 13.9 and 62.5°, respectively. It is also worth mentioning that both compounds reveal significant strain around the thiophenolate sulfur atoms. This strain is manifested in the displacement of the sulfur atom from the average plane of the benzene ring to which it is attached (0.223 Å in $[(L^6)Pd_2Cl_2]^+$, 0.304 Å in **2**).

Single crystals of $3[ClO_4]_2$ ·MeOH were grown by recrystallization from methanol. A perspective view of the structure of 3 together with the atomic numbering scheme is shown in Fig. 2.



Fig. 2 Structure of the cation 3 in crystals of $[(L^4)Pd_2(\mu-Cl)][ClO_4]_2$ (3[ClO₄]₂) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.016(9), Pd(1)–N(2) 2.120(8), Pd(1)–S 2.257(2), Pd(1)–Cl(1) 2.359(3), Pd(2)–N(3) 2.026(8), Pd(2)–N(4) 2.075(8), Pd(2)–S 2.275(2), Pd(2)–Cl(1) 2.376(3), Pd(1) ··· Pd(2) 3.087(1); Pd(1)–S–Pd(2) 85.84(8), Pd(1)–Cl(1)–Pd(2) 81.36(8).

Again, each palladium atom is coordinated by one bridging thiolate sulfur atom, two nitrogen atoms and a chloro ligand, but in contrast to **2** the latter is in a bridging mode. As a consequence, the distance between the Pd atoms is much shorter at 3.087 Å and the Pd–S–Pd angle has decreased to 85.84° . The side arms associated with Pd(1) and Pd(2) are now equally twisted out of the plane of the central aromatic unit. Thus, the coordination planes of Pd(1) and Pd(2) are at similar dihedral angles of 34.1 and 43.1° to the central aromatic ring. This in turn results in an idealized $C_{\rm s}$ symmetry for the dication **3**. The average Pd–N, Pd–S and Pd–Cl bond lengths are unexceptional and compare well with those of other four-coordinate N₂S₂Pd or PdN₂SCl complexes.^{25,26}

It should be noted that metal-ion promoted C–S bond cleavage reactions have been reported previously for a large number of aliphatic thioether ligands.²⁷ The related ring opening of cyclic thioethers *via* C–S bond cleavage is also well-documented. For example, macrocyclic 1,4,7-trithiacyclononane is known to reversibly react with Rh^{III} ions to afford vinyl thioether–thiolate complexes in basic solution.²⁸ However, there have been only few reports in the literature concerning sulfur desalkylations of aromatic thioether compounds such as $tBu-L^3$ or $tBu-L^4$. This metal-ion promoted cleavage of thioether ligands is of interest in several respects. It not only represents a convenient method for the deprotection of thiolate sulfur atoms.²⁹⁻³¹ It is also of importance in the design and synthesis of new ligands for more robust thioether complexes.³²

Although, the structure determination of $4[ClO_4]_3$ is of low quality and not as good as desired for publication,³³ it can serve to confirm the formulation and the atom connectivity of the bisacetonitrile complex 4. The structure is depicted in Fig. 3, but not discussed further.



Fig. 3 Structure of the trication **4** in crystals of $[(L^3)Pd_2(NCMe)_2][ClO_4]_3$ (**4**[ClO_4]_3) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Only one orientation of the disordered *t*Bu group and the disordered S atom is displayed. Symmetry code used to generate equivalent atoms: (') -x, +y, 1.5 - z.

The crystal structure determination of $5[BPh_4]MeCN$ revealed the presence of well-separated complexes of the diisothiocyanate complex 5, BPh_4^- anions and acetonitrile molecules of solvation (Fig. 4). The palladium atoms are four-coordinate and bind the



Fig. 4 Structure of the isothiocyanato complex 5 in crystals of $[(L^3)Pd_2(SCN)_2][BPh_4]$ ·MeCN (5[BPh_4]·MeCN). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.994(4), Pd(1)–N(2) 2.114(4), Pd(1)–S(1) 2.256(2), Pd(1)–S(2) 2.313(2), Pd(2)–N(3) 2.019(4), Pd(2)–N(4) 2.112(4), Pd(2)–S(1) 2.274(1), Pd(2)–S(2) 2.316(2), S(2)–C(21) 1.693(8), S(3)–C(22) 1.668(6), N(5)–C(21) 1.159(8), N(6)–C(22) 1.138(6), Pd(1) ··· Pd(2) 3.877(1); C(21)–S(2)–Pd(1) 102.8(2), C(22)–S(3)–Pd(2) 101.16(19), N(5)–C(21)–S(2) 174.5(7), N(6)–C(22)–S(3) 177.6(5), Pd(1)–S(1)–Pd(2) 117.7.

thiocyanates via their S atoms in a monodentate fashion. One of the thiocyanates is coordinated in such a way that its CN function is located above the Pd(1) plane, but the long Pd(1) \cdots C(22) distance at 3.278 Å is too long for a secondary Pd · · · NCS bonding interaction. This is also supported by the CN and CS distances which reveal no significant elongation or contraction from the usual values.³⁴ Interestingly, the Pd–S bond lengths involving the thiocyanate ions (mean 2.315 Å) are longer than those involving the thiophenolate sulfur atom (2.265 Å) despite the fact that the latter is a bridging atom. These values should be compared with the corresponding Pd–Cl and Pd–µ-Cl distances in 2, where the reverse situation is observed. The conformation of $(L^3)^-$ adopted in 5 is very similar to that in 2. Thus, the two coordination planes are again markedly twisted around the hinging sulfur atom so that they are at an angle of 68.1° to each other (66.1° in 2). Likewise, the side arm associated with Pd(2) is much more twisted out of the plane of the central aromatic unit than the other. The coordination plane of Pd(1) is at a dihedral angle of 18.8° to the central aromatic ring whereas the corresponding angle for the coordination plane of Pd(2) is at 50.5°. These values are essentially identical with those in $2(18.6, 48.3^{\circ})$. Finally, significant strain around the thiophenolate sulfur atom is also manifested in 5 in its displacement from the average plane of the benzene ring to which it is attached by 0.315 Å (0.304 Å **2**).

Fig. 5 shows the structure of complex **6** in crystals of **6**[BPh₄]·MeCN. As can be seen, the two azide ions are both coordinated in an end-on fashion. The average Pd–N(azide) bond length at 2.006 Å and the average Pd–N–NN bond angle at 124.9° are normal for four-coordinate palladium azido complexes.³⁵ In [Pd(py)₂(N₃)₂], for example, the mean P–N(azide) bond lengths and Pd–N–NN bond angles are at 2.037 Å and 125.2°, respectively.³⁶ The conformation of (L³)⁻ adopted in **6** is very similar to that in **2** and **5**. The two coordination planes are at



Fig. 5 Structure of the azido complex 6 in crystals of $[(L^3)Pd_2(N_3)_2]$ -[BPh₄]·MeCN (6[BPh₄]·MeCN) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.959(5), Pd(1)–N(2) 2.088(5), Pd(1)–N(5) 2.003(6), Pd(1)–S 2.245(1), Pd(2)–N(3) 1.998(4), Pd(2)–N(4) 2.099(4), Pd(2)–N(8) 2.009(5), Pd(2)–S 2.257(1), N(5)–N(6) 1.175(7), N(6)–N(7) 1.138(7), N(8)–N(9) 1.186(7), N(9)–N(10) 1.141(7), Pd(1)…Pd(2) 3.971(1); Pd(1)–N(5)–N(6) 127.6(5), Pd(2)–N(8)–N(9) 122.2(4), N(5)–N(6)–N(7) 175.2(7), N(8)–N(9)–N(10) 174.4(7).

an angle of 54.8° to each other. Likewise, the side arm associated with Pd(2) is much more twisted out of the plane of the central aromatic unit than the other. The coordination plane of Pd(1) is at a dihedral angle of 17.7° to the central aromatic ring whereas the corresponding angle for the coordination plane of Pd(2) is at 37.7° . Significant strain around the thiophenolate sulfur atom is also manifested in **6** in the displacement of the S atom from the average plane of the benzene ring to which it is attached by 0.210 Å.

Single crystals of 7[ClO₄]₄·2EtCN·MeCN were grown from a mixed propionitrile/acetonitrile solvent system. This salt crystallizes in the space group C2/c. A perspective view of the molecular structure of 7 is shown in Fig. 6. Complex 7 possesses crystallographically imposed C_2 symmetry. Two $[(L^3)Pd_2]^{2+}$ units are linked via two $\mu_{1,2}$ -bridging cyanide ions to give a tetranuclear Pd(II) complex. The separation of the $\mu_{1,2}$ -CN-bridged Pd atoms is at 5.090 Å, which is much longer than the Pd · · · Pd distances in the $[(L^3)Pd_2]^{2+}$ units at 3.981 Å. It should be noted that the orientation of the cyanides could not be determined unambiguously from the present data set. The R values for the two orientations are within experimental error identical. It is also significant that for the present orientation (see Fig. 6) the U_{eq} values for the cyanide carbon $(U_{eq}(C(21)) = 0.026(1))$ and nitrogen atoms $(U_{eq}(N(5)) = 0.44(1))$ are either smaller or larger than the arithmetic average of the U_{eq} values of a selected number of carbon atoms (C(1)–C(6), average $U_{eq} = 0.0368$). The reverse is true for the alternate orientation. This is indicative of a statistical distribution $(\sim 50/50\%)$ of the two possible orientations. Thus, the bond lengths given in the figure caption should be taken as indicative rather than definitive.

Crystals of $10[ClO_4]_2$ grown by recrystallization from acetonitrile are triclinic, space group $P\overline{1}$. Fig. 7 displays the structure of



Fig. 6 Structure of the cyanide complex 7 in crystals of $[{(L^3)Pd_2(\mu-CN)_2}_2][ClO_4]_4 \cdot (EtCN)_2 \cdot MeCN (7[ClO_4]_4 \cdot (EtCN)_2 \cdot MeCN)$ with thermal ellipsoids drawn at the 50% probability level. *tert*-Butyl groups, NMe groups and hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.983(5), Pd(1)–N(2) 2.096(5), Pd(1)–C(21) 1.974(5), Pd(1)–S 2.2685(16), Pd(2)–N(3) 1.998(5), Pd(2)–N(4) 2.094(6), Pd(2)–N(5) 1.989(6), Pd(2)–S 2.2904(18), Pd(1) \cdots Pd(2) 3.981(1), C(21)–N(5)' 1.136(7); Pd(1)–C(21)–N(5)' 177.8(6), C(21)–N(5)–Pd(2) 173.9(5). Symmetry code used to generate equivalent atoms: 2 - x, +y, 0.5 - z.



Fig. 7 Structure of the 2-chloroacetamido complex 10 in crystals of $[(L^3)Pd_2(NHOCCH_2Cl)_2][ClO_4]_2$ (10[ClO_4]_2) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.994(4), Pd(1)–N(2) 2.103(4), Pd(1)–S 2.252(1), Pd(1)–N(5) 2.021(4), Pd(2)–N(3) 1.981(4), Pd(2)–N(4) 2.099(4), Pd(2)–S 2.2700(1), Pd(2)–O(1) 2.023(4), Pd(1)…Pd(2) 3.688, O(1)…N(5) 2.294, N(5)–C(21) 1.285(7), O(1)–C(21) 1.290(6); Pd(2)–O(1)–C(21) 129.1(4), Pd(1)–N(5)–C(21) 129.9(4), O(1)–C(21)–N(5) 125.9(5), C(22)–C(21)–N(5)–Pd(1) 18.9, O(2)–C(21)–N(5)–Pd(1) 14.5, C(22)–C(21)–O(1)–Pd(2) 38.2, C(22)–C(21)–O(1)–Pd(2) 42.6.

10. Selected bond lengths and angles are given in the figure caption. The 2-chloroacetamidato unit bridges the two palladium atoms in a $\mu_{1,3}$ -bridging mode to generate a N₃S coordination environment for Pd(1) and a N₂OS coordination environment for Pd(2). The Pd \cdots Pd distance is at 3.688 Å. The Pd–O and Pd–N bond lengths are identical, indicative of sp²-hybridized N and O atoms and a delocalized electronic structure of the carboxamidato function. This is supported by the fact that the amide NH hydrogen atom is coplanar with the amidato plane. It should be noted in this respect that the NH hydrogen atom H(1) could be located unambiguously from difference Fourier maps providing strong support that the

present orientation of the 2-chloroacetamide with the N atom bonded to Pd(1) and the O atom bonded to Pd(2), respectively, has been assigned correctly. This also follows from the *R*1 values which converged at R1 = 0.0421 for the present structure and at a slightly higher value (R1 = 0.0432) for the alternate orientation.

Fig. 8 shows the structure of the dication **9** along with the atomic labelling scheme. Each palladium features a planar coordination comprised of tertiary amine, imine and thiophenolate sulfur atoms from the supporting ligand and one oxygen atom of a $\mu_{1,3}$ -bridging acetate ion. The metal–ligand bond lengths in the acetato-bridged complex **9** are practically identical with those in the acetamidatobridged compound **10**. The same is true for the Pd \cdots Pd distance at 3.685 Å. The major difference occurs in the C(22)–C(21)–O(2)–Pd(2) and O(1)–C(21)–O(2)–Pd(2) torsional angles which are somewhat larger (by ~10°) in **10**.



Fig. 8 Structure of the cation 9 in crystals of $[(L^3)Pd_2(OAc)][ClO_4]_2$ (9[ClO_4]_2) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.979(5), Pd(1)–N(2) 2.097(5), Pd(1)–S 2.242(2), Pd(1)–O(1) 2.031(5), Pd(2)–N(3) 1.993(5), Pd(2)–N(4) 2.093(5), Pd(2)–S 2.254(2), Pd(2)–O(2) 2.022(5), Pd(1) \cdots Pd(2) 3.685, O(1) \cdots O(2) 2.287(5), O(1)–C(21) 1.292(8), O(2)–C(21) 1.283(8); Pd(1)–O(1)–C(21) 127.6(5), Pd(2)–O(2)–C(21) 127.5(5), O(1)–C(21) -O(2) 125.3(6), C(22)–C(21)–O(1)–Pd(1) 15.1, O(2)–C(21)–O(1)–Pd(1) 13.2, C(22)–C(21)–O(2)–Pd(2) 48.1, O(1)–C(21)–O(2)–Pd(2) 49.9.

The metal-mediated hydration of nitriles has been observed previously for a number of mono- and binuclear complexes.^{37,38} In the binuclear palladium thiophenolate complexes $[(L^5)Pd_2(\mu-L')_2]^+$ and $[(L^6)Pd_2(\mu-L')_2]^+$, the nitrile hydration proceeds by a two-metal ion mechanism in which a nucleophilic hydroxide ion bound to one palladium atom attacks the activated nitrile bound to the adjacent palladium, as outlined in Scheme 5. It is assumed that hydration of nitriles by the $[(L^3)Pd_2]^{3+}$ units proceeds in a similar



Scheme 5 Hydration of nitriles in binuclear palladium complexes.

manner. The reactive hydroxo intermediate A may be generated by substitution of an acetonitrile by a water molecule and subsequent deprotonation of the aqua complex. The nucleophilic attack of the hydroxide on the adjacent nitrile and a final proton shift then yields the amidato-bridges in **8** and **10**.

Fig. 9 shows the structure of **11**. Both phenyl groups are η^1 -coordinated to the planar palladium atoms. The average Pd–C distance of 1.991 Å is normal for four-coordinate palladium(II) complexes with η^1 -phenyl ligation.³⁹ The planes through the phenyl rings are neither coplanar nor perpendicular to the PdN₂SC planes indicative of negligible Pd(d_\pi)-aryl(p_\pi^*) back bonding interactions. However, the Pd–N(imine) bond lengths in **11** are slightly longer than in **2–10** indicative of a small *trans* effect of the phenyl group.



Fig. 9 Structure of the cation 11 in crystals of $[(L^3)Pd_2(\eta^1-Ph)_2][BPh_4]$ (11[BPh_4]) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.049(4), Pd(1)–N(2) 2.128(4), Pd(1)–S 2.241(1), Pd(1)–C(21) 1.998(5), Pd(2)–N(3) 2.066(4), Pd(2)–N(4) 2.133(4), Pd(2)–S 2.265(1), Pd(2)–C(27) 1.983(5), Pd(1) \cdots Pd(2) 3.925.

Conclusion

The aromatic thioethers $tBu-L^3$ and $tBu-L^4$ can be readily deprotected with PdCl₂(NCMe)₂ to afford the binucleating diiminediamine- and tetraamine-thiophenolate ligands $(L^3)^-$ and $(L^4)^-$, respectively. These ligands support the formation of dinuclear complexes of the type $[(L^3)Pd(L')_2]^{n+}$ and $[(L^4)Pd_2(\mu-L')]^{n+}$, demonstrating that the conversion of the two imine-functions in the lateral side arms of $(L^3)^-$ to amine functions in $(L^4)^-$ can be used to adjust the type and number of their active coordination sites. The dichloro-complex $[(L^3)Pd_2(Cl)_2]^+$ exhibits a rich coordination chemistry as illustrated by the synthesis and structural characterization of the corresponding acetonitrile, azido, cyanide, isothiocyanato and phenyl complexes. It has also been established that the $[(L^3)Pd_2]^{3+}$ fragment mediates the hydration of nitrile ligands. Work in progress is now directed towards the catalytic activity of these compounds by taking advantage of the reactive dipalladium site offered by the supporting ligand. Such compounds may also aid in an understanding of cooperative effects in binuclear catalysis.

Experimental

All syntheses were carried out under a protective atmosphere of argon. Melting points were determined in open glass capillaries and are uncorrected. NMR spectra were recorded on a Bruker AVANCE DPX-200 spectrometer at 300 K. Chemical shifts refer to solvent signals. Infrared spectra were recorded on a Bruker VECTOR 22 FT-IR-spectrometer. Elemental analyses were carried out with a VARIO EL-elemental analyzer.

Caution! Perchlorate salts are potentially explosive and should therefore be prepared only in small quantities and handled with appropriate care.

Preparation of tBu-L³

To a solution of *N'*,*N'*-dimethylethane-1,2-diamine (85 mg, 0.96 mmol) in ethanol (20 mL) was added a solution of 5-*tert*-butyl-2-(*tert*-butylthio)benzene-1,3-dialdehyde¹⁵ (134 mg, 0.48 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 24 h. Evaporation to dryness gave a colourless oil which crystallized on standing. Yield: 201 mg (0.48 mmol, 100%). Mp 58 °C. IR (KBr pellet, cm⁻¹): $\tilde{v} = 3419(s)$, 3255(w), 3056(s), 2963(m), 2894(m), 2851(m), 2813(s), 2764(s), 1692(m), 1632(s) v(C=N), 1587(w), 1456(s), 1404(w), 1391(w), 1362(s), 1342(m), 1287(m), 1272(m), 1240(m), 1226(m), 1182(w), 1165(w), 1151(w), 1137(m), 1098(w), 1066(w), 1044(m), 1033(m), 973(w), 953(w), 934(m), 899(w), 881(w), 784(m), 748(w), 669(w), 644(w). Elemental analysis: calc. (%) for C₂₄H₄₂N₄S (418.68): C 68.85, H 10.11, N 13.38, S 7.66; found: C 68.67, H 10.10, N 12.66, S 7.79.

Preparation of tBu-L4

To a solution of N', N'-dimethylethane-1,2-diamine (566 mg, 6.42 mmol) in ethanol (50 mL) was added a solution of 5-*tert*-butyl-2-(*tert*-butylthio)benzene-1,3-dialdehyde (892 mg, 3.20 mmol) in dichloromethane (10 mL). After stirring for 12 h, sodium borohydride (244 mg, 6.44 mmol) was added and the mixture was stirred for further 4 h. The solution was acidified with 12 M HCl and evaporated to dryness. Water (50 mL) was added and the pH of the solution adjusted to 10 by addition of 3 M potassium hydroxide solution. The product was extracted with dichloromethane (3 × 50 mL). The organic fractions were combined, dried with K₂CO₃ and evaporated to dryness to give a colourless oil. Yield: 1.20 g (88%). This compound was used without further purification for the preparation of the metal complexes.

Preparation of [(L³)Pd₂Cl₂][ClO₄] (2[ClO₄])

To a solution of N',N'-dimethylethane-1,2-diamine (1.00 g, 11.3 mmol) in ethanol (50 mL) was added a solution of 5-*tert*-butyl-2-(*tert*-butylthio)benzene-1,3-dialdehyde (1.58 g, 5.67 mmol) in dichloromethane (50 mL). The solution was stirred for 24 h after which it was evaporated to dryness. The residue was redissolved in acetonitrile (100 mL) and combined with a solution of PdCl₂(NCMe)₂ (2.94 g, 11.3 mmol) in acetonitrile (150 mL). The reaction mixture was stirred for 2 days, evaporated to dryness, and the residue was dissolved in dimethylformamide (5 mL). To this solution was added a solution of LiClO₄·3H₂O (3.00 g,

18.7 mmol) in methanol (200 mL). The resulting yellow solid was filtered off, air-dried and recrystallized from an acetonitrile– ethanol mixed solvent system. Yield: 2.93 g (3.93 mmol, 69%). Mp 294 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{\nu} = 3423$ (s), 3060(m), 2962(s), 2931(m), 2871(m), 2840(w), 1637(s) ν (C=N), 1569(w), 1544(m), 1459(s) ν (C=C), 1396(w), 1365(w), 1232(m), 1145(m), 1088(s) ν (CIO₄), 1007(w), 945(w), 943(w), 909(w), 780(m), 731(w), 689(s), 624(m), 503(w). Elemental analysis: calc. (%) for C₂₀H₃₃Cl₃N₄O₄Pd₂S·MeCN (744.76 + 41.05): C 33.63, H 4.62, N 8.91, S 4.08; found: C 33.14, H 4.53, N 8.57, S 3.45.

Preparation of $[(L^4)Pd_2(\mu-Cl)][ClO_4]_2$ (3[ClO₄]₂)

To a solution of $tBu-L^4$ (106 mg, 0.250 mmol) in dichloromethane (10 mL) was added a solution of PdCl₂(MeCN)₂ (129 mg, 0.500 mmol) in acetonitrile (40 mL). The reaction mixture was allowed to stir for further 12 h at ambient temperature and was then evaporated to dryness. The residue was taken up in methanol (50 mL) and filtered. To the clear filtrate was added a solution of $LiClO_4 \cdot 3H_2O$ (1.00 g, 6.24 mmol) in methanol (10 mL) to give the title compound as a yellow solid. The crude product was purified by recrystallization from acetonitrile. Yield: 156 mg (77%). Mp 244 °C. IR (KBr pellet, cm⁻¹): $\tilde{v} = 3430(s), 3202(w) v(NH), 2958(s),$ 2902(s), 1778(m), 1658(w), 1629(m), 1548(m), 1528(w), 1478(m), 1464(s) v(C=C), 1442(m), 1394(w), 1365(w), 1337(w), 1309(w), 1229(m), 1146(m), 1122(vs), 1109(vs) v(ClO₄), 1093(vs), 999(m), 944(w), 907(w), 888(w), 784(m), 745(w), 697(w), 623(s). Elemental analysis: calc. (%) for $C_{20}H_{37}Cl_3N_4O_8Pd_2S \cdot H_2O$ (812.79 + 41.05): C 28.91, H 4.73, N 6.74, S 3.86; found: C 28.84, H 4.79, N 5.58, S 3.35.

Preparation of [(L³)Pd₂(NCMe)₂][ClO₄]₃ (4[ClO₄]₃)

The dichloro complex **2**[ClO₄] (1.00 g, 1.34 mmol) and anhydrous lead perchlorate (1.00 g, 2.46 mmol) were dissolved in acetonitrile (230 mL). The resulting mixture was stirred for 4 h and filtered off from PbCl₂. The title compound crystallized upon evaporation of *ca.* 90% of the solvent. The yellow microcrystalline material was filtered off and dried in air. Yield: 972 mg (1.02 mmol, 76%). IR (KBr pellet, cm⁻¹): $\tilde{v} = 3424$ (br), 3282(w), 3058(w), 2964(s), 2934(s), 2873(w), 2812(w), 2724(w), 2330(m) v(C=N), 2303(m) v(C=N), 2017(w), 1645(s) v(C=N), 1595(w), 1545(m), 1467(s) v(C=C), 1398(w), 1368(w), 1331(w), 1234(m), 1141(vs), 1100(vs) (ClO₄), 1006(w), 954(w), 941(w), 910(w), 780(m), 729(m), 625(s). Elemental analysis: calc. (%) for C₂₄H₃₉Cl₃N₆O₁₂Pd₂S (954.86): C 30.19, H 4.12, N 8.80, S 3.36; found: C 29.78, H 4.27, N 8.60, S 2.85.

Preparation of [(L³)Pd₂(SCN)₂][BPh₄] (5[BPh₄])

To a solution of $4[ClO_4]_3$ (100 mg, 0.105 mmol) in acetone (60 mL) was added a solution of NaSCN (17 mg, 0.21 mmol) in methanol (1 mL). The mixture was allowed to stir for 24 h. Upon concentration of the solution (final volume ~10 ml) a red–yellow solid formed. This material was filtered off, washed with a few millilitres of methanol and dried in air. Yield: 44 mg (0.056 mmol, 53%). Mp 282 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{v} = 3443$ (br s), 2959(s), 2935(s), 2868(m), 2108 (vs) v(NCS), 1637(s) v(C=N), 1541(m), 1461(s) v(C=C), 1408(w), 1394(w), 1366(w), 1340(w), 1229(s), 1165(w), 1087(vs) v(ClO₄), 1006(s), 941(s),

910(m), 815(m), 780(s), 684(m), 623(s). Elemental analysis calc. (%) for C₂₂H₃₃ClN₆O₄Pd₂S₃ (790.02): C 33.45, H 4.21, N 10.64, S 12.18; found: C 33.04, H 4.63, N 10.35, S 11.07. To a solution of the perchlorate salt 5[ClO₄] (100 mg, 0.127 mmol) in acetonitrile (10 mL) was added a solution of NaBPh₄ (500 mg, 1.46 mmol) in methanol (10 mL). The solution was concentrated in vacuum (final volume \sim 5 mL). A few crystals of 5BPh₄ separated on standing overnight. Mp 220 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{\nu}$ = 3432(br s), 3051(w), 3030(w), 2964(s), 2927(m), 2108 (vs) v(NCS), 1636(s) v(C=N), 1579(m), 1508(m), 1465(s) v(C=C), 1427(m), 1365(w), 1229(m), 1182(w), 1146(w), 1082(m), 1007(w), 953(w), 908(w), 845(m), 778(m), 747(s), 738(s) v(BPh₄), 708(s) v(BPh₄), 610(s). Elemental analysis: calc. (%) for $C_{46}H_{57}BN_6O_2Pd_2S_3 \cdot 2H_2O$ (1045.83 + 36.03): C 52.83, H 5.49, N 8.04, S 9.20; found: C 52.38, H 5.08, N 8.30, S 9.03. This compound was additionally characterized by X-ray diffraction.

Preparation of [(L³)Pd₂(N₃)₂][BPh₄] (6[BPh₄])

To a solution of $3[ClO_4]_3$ (300 mg, 0.315 mmol) in acetone (180 mL) was added a solution of NaN₃ (41 mg, 0.63 mmol) in 1% aqueous methanol (50 mL). The mixture was allowed to stir for 24 h. Upon concentration of the solution (final volume ~ 10 ml) a red-yellow solid (6[ClO₄]) formed. This material was filtered off, washed with a few millilitres of methanol and dried in air. Yield: 193 mg (0.255 mmol, 81%). Mp 250 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{v} = 3430$ (br s), 3066(w), 2961(s), 2938(s), 2035 (vs) $v_{as}(N_3)$, 1640(s) v(C=N), 1544(m), 1464(s) v(C=C), 1437(m), 1397(w), 1365(w), $1292(m) v_s(N_3), 1237(m) v_s(N_3), 1086(vs) v(ClO_4), 1008(w), 966(w),$ 956(w), 942(w), 908(w), 817(m), 729(w), 623(s). Elemental analysis: calc. (%) for C₂₀H₃₃ClN₁₀O₄Pd₂S (757.90): C 31.69, H 4.39, N 18.48, S 4.23; found: C 31.80, H 4.62, N 17.83, S 4.00. To a solution of 6[ClO₄] (100 mg, 0.132 mmol) in acetonitrile (10 mL) was added a solution of NaBPh₄ (500 mg, 1.46 mmol) in methanol (10 mL). The solution was concentrated in vacuum (final volume ~ 10 mL). Orange-coloured crystals separated on standing overnight. Mp 180 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{v} = 3430(\text{br s}), 3051(\text{m}), 3035(\text{m}), 2964(\text{s}), 2926(\text{s}), 2029(\text{vs})$ $v_{as}(N_3)$, 2012(vs) $v_{as}(N_3)$, 1636(s) v(C=N), 1578(m), 1542(w), 1457(s) v(C=C), 1427(m), 1395(w), 1288(m) $v_s(N_3)$, 1228(m) *v*_s(N₃), 1178(w), 1032(w), 955(w), 908(w), 941(w), 907(w), 733(s) $v(BPh_4)$, 707(s) $v(BPh_4)$, 612(s). Elemental analysis: calc. (%) for C₄₄H₅₃BN₁₀Pd₂S (977.68): C 54.05, H 5.46, N 14.33, S 3.28; found: C 53.47, H 5.58, N 14.76, S 3.04.

Preparation of $[{(L^3)Pd_2(CN)_2}_2][ClO_4]_4$ (7[ClO_4]_4)

A solution of $2 \cdot \text{ClO}_4$ (100 mg, 134 mmol) and Pb(ClO₄)₂ (100 mg, 246 mmol) in propionitrile (80 mL) was stirred for 12 h. The solution was filtered off from PbCl₂ and concentrated in vacuum to 10 mL. The resulting yellow solid was filtered off, washed with a few millilitres of propionitrile and dried in air. Yield: 60 mg (56%). Mp 260 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{v} = 3419$ (br s), 2965(s), 2872(m), 2183(m) v(C=N), 1638(s) v(C=N), 1545(s), 1460(w) v(C=C), 1405(w), 1378(w), 1233(m), 1144(s), 1088(vs) v(ClO₄), 1008(m), 960(m), 953(m), 941(m), 908(m), 780(s), 729(w), 636(s), 626(s). Elemental analysis: calc. (%) for C₂₁H₃₃Cl₂N₅O₈Pd₂S (799.33): C 31.55, H 4.16, N 8.76, S 4.01; found: C 31.46, H 4.34, N 8.58, S 3.19. This compound

was additionally characterized by an X-ray crystal structure determination

Preparation of [(L³)Pd₂(µ_{1,3}-MeCONH)][ClO₄]₂ (8[ClO₄]₂)

Method A: To a solution of $4[ClO_4]_3$ (100 mg, 0.105 mmol) in acetone (10 mL) was added 5% aqueous methanol (20 mL). The mixture was stirred at room temperature for 12 h. The resulting yellow solid was filtered off, washed with methanol and dried in air. Yield: 53 mg (61%). Mp 220 °C (decomp.). Method B: Compound 3[ClO₄]₃ (100 mg, 0.105 mmol) was dissolved in hot water (60 °C). The title compound crystallized on cooling. This material was filtered and dried over phosphorous pentaoxide. Yield: 60 mg (69%). Method C: A suspension of compound 3[ClO₄]₃ (100 mg, 0.105 mmol) in water was stirred for four days at room temperature. The solid was then filtered off and dried over P₄O₁₀. Yield: 65 mg (74%). IR (KBr pellet, cm⁻¹): $\tilde{v} = 3316(s) v(N-H)$, 3069(w), 2966(m), 2871(m), 2837(vw), 1648(s) v(C=N), 1628(s) v(C=N), 1553(s) $v_{as}(CONH)$, 1477(s) v(C=C), 1458(w), 1436(w) v_{sym}(CONH), 1399(w), 1368(w), 1344(w), 1336(w), 1308(vw), 1241(s), 1234(s), 1236(s), 1099(vs) v(ClO₄), 1002(w), 971(w), 955(w), 941(w), 903(m), 778(m), 730(w), 624(s). Elemental analysis: calc. (%) for $C_{22}H_{37}Cl_2N_5O_9Pd_2S$ (831.37): C 31.78, H 4.49, N 8.42, S 3.86; found: C 31.52, H 4.56, N 8.18, S 3.79.

Preparation of [(L³)Pd₂(µ-MeCONH)][BPh₄]₂ (8[BPh₄]₂)

Method A: To a solution of **4**[ClO₄]₃ (100 mg, 0.105 mmol) in acetonitrile (10 mL) was added a solution of NaBPh₄ (371 mg, 1.08 mmol) in acetonitrile. 5% Aqueous ethanol was added (20 mL). The product precipitated upon concentration. It was filtered off, washed with ethanol and dried in air. Yield: 85 mg (64%). *Method B*: To a hot solution of **3**(ClO₄)₃ (100 mg, 0.105 mmol) in acetonitrile (30 mL) was added a solution of NaBPh₄ (371 mg, 1.08 mmol) in water. The resulting solid was filtered off, washed with water, and dried over P₄O₁₀. Yield: 112 mg (84%). IR (KBr pellet, cm⁻¹): $\tilde{\nu}$ = 3435(br s), 3120(w), 3053(w), 3033(s), 2998(s), 2982(s), 2929(s), 1639(s) ν (C=N), 1578(s) ν (CONH), 1558(s), 1478(s) ν (C=C), 1458(w), 1426(s) ν (CONH), 1396(w), 1365(w), 1337(w), 1230(m), 1182(w), 1148(w), 1101(w), 1077(w), 1032(w), 1000(w), 955(w), 943(w), 908(m), 845(m), 780(s), 733(s) ν (BPh₄), 705(s) ν (BPh₄, 610(s).

Preparation of [(L³)Pd₂(OAc)][ClO₄]₂ (9[ClO₄]₂)

To a solution of N',N'-dimethylethane-1,2-diamine (131 mg, 1.49 mmol) in ethanol (30 mL) was added a solution of 5-*tert*-butyl-2-(*tert*-butylthio)benzene-1,3-dialdehyde (0.20 g, 0.72 mmol) in dichloromethane (15 mL). The solution was stirred for 24 h after which it was evaporated to dryness. The residue was redissolved in dichloromethane (20 mL) and combined with a solution of Pd(OAc)₂ (335 mg, 1.49 mmol) in dichloromethane (20 mL). After the resulting yellow solution was stirred for further 24 h, a solution of LiClO₄·3H₂O (1.00 g, 6.24 mmol) in methanol (50 mL) was added. Evaporation of the solvent gave a yellow solid, which was filtered off, washed with methanol and dried in air. Yield: 387 mg (0.460 mmol, 63%). Mp 263 °C (decomp.). IR (KBr pellet, cm⁻¹): $\tilde{\nu} = 3017(w)$, 2993(s), 2959(s), 2943(m), 2911(w), 1643(s) ν (C=N), 1555(s) ν_{as} (OAc), 1457(m),

1462(s) ν (C=C), 1437(s) ν _s(OAc), 1238(m), 1189(m), 1174(w), 1160(w), 1120(s), 1082(vs) ν (ClO₄), 1027(m), 999(w), 954(w), 907(w), 779(s), 726(w), 680(w), 623(s). Elemental analysis: calc. (%) for C₂₂H₃₇Cl₂N₄O₁₀Pd₂S (833.36): C 31.71, H 4.48, N 6.72, S 3.85; found: C 31.54, H 4.38, N 6.63, S 3.67.

Preparation of [(L³)Pd₂(µ-ClCH₂CONH)][ClO₄]₂ (10[ClO₄]₂)

The dichloro complex **2**[ClO₄] (74 mg, 0.10 mmol) and anhydrous lead perchlorate (100 mg, 0.246 mmol) were dissolved in chloroace-tonitrile (10 mL). The resulting mixture was stirred for 4 h and filtered off from PbCl₂. To this solution was added 5% aqueous methanol (20 mL). The solution was concentrated in vacuum. The resulting yellow solid was filtered off, washed with ethanol, and dried in vacuum. Yield: 85 mg (91%). IR (KBr pellet, cm⁻¹): $\tilde{\nu}$ = 3429(br s), 3309(s) ν (N–H), 3066(w), 3031(w), 2966(s), 2871(w), 1649(s) ν (C=N), 1630(s) ν (C=N), 1573 ν _{as}(CONH), 1545(m), 1459(s) ν (C=C), 1414(w) ν (CONH), 1396(w), 1368(w), 1348(w), 1336(w), 1303(w), 1095(vs) ν (ClO₄), 1001(w), 972(w), 953(w), 910(w), 814(w), 780(s), 730(w), 624(s). Elemental analysis: calc. (%) for C₂₂H₃₆Cl₃N₅O₉Pd₂S (865.81): C 30.52, H 4.19, N 8.09, S 3.70; found: C 30.57, H 4.21, N 8.08, S 3.48.

Preparation of [(L³)Pd₂(Ph₂)][BPh₄] (11[BPh₄])

To a solution of 3[ClO₄]₃ in acetonitrile (10 mL) was added a solution of NaBPh₄ (370 mg, 1.08 mmol) in acetonitrile. Ethanol (20 mL) was added and the resulting mixture was reduced to half of its original volume. The resulting solid was isolated by filtration. Yield: 8 mg (7%). Mp 140 °C. IR (KBr pellet, cm⁻¹): $\tilde{v} = 3530$ (br s), 3120(w), 3052(s), 3034(s), 2996(s), 2963(s), 2925(s), 2839(w), 2791(w), 1664(s) v(C=N), 1472(s) v(C=C), 1438(m), 1425(s), 1405(s), 1392(w), 1364(w), 1338(w), 1327(w), 1224(m), 1179(m), 1161(m), 1121(m), 1105(m), 1075(m), 1065(w), 1032(m), 1021(m), 997(m), 964(w), 951(w), 937(w), 904(w), 891(w), 814(w), 750(m), 732(s) v(BPh₄), 707(s) v(BPh₄), 612(s). ¹H NMR (200 MHz, acetone-d₆): δ 1.39 (s, 9 H, *t*Bu), 2.86 (m, 12 H + 4 H, C⁵H₃, $C^{6}H_{3}$, $C^{7}H_{2}$), 4.02 (t, 2 H, $^{3}J = 5.5$ Hz, $C^{8}H_{2}$), 4.08 (t, 2 H, $^{3}J =$ 5.5 Hz, C⁸'H₂), 6.77 (m, 6 H, BPh₄ + PdPh), 6.92 (m, 12 H, BPh₄ + PdPh), 7.33 (m, 12 H, BPh₄ + PdPh), 8.19 (s, 2 H, $C^{11}H$), 8.30 (s, 1 H, $C^{9'}H$), 8.55 (s, 1 H, $C^{9}H$). Elemental analysis: calc. (%) for C₅₆H₆₃BN₄Pd₂S (1047.84): C 64.19, H 6.06, N 5.35, S 3.06; found: C 61.77, H 5.94, N 5.09, S 2.62.

Collection and reduction of X-ray data

Single crystals of $2[ClO_4]$ and $3[ClO_4]_2$ ·MeOH were grown by slow evaporation of methanolic solutions. Crystals of $5[BPh_4]$ ·MeCN were taken directly from the reaction mixture. Crystals of $6[BPh_4]$ ·MeCN and $11[BPh_4]$ were grown by slow evaporation of a mixed acetonitrile–ethanol solvent system. Crystals of $7[ClO_4]_2$ ·2CH₃CH₂CN·CH₃CN were grown by slow evaporation of a mixed propionitrile/acetonitrile solvent system. Crystals of $9[ClO_4]_2$ were grown by slow evaporation of a mixed acetone– methanol solvent system. Crystals of $10[ClO_4]_2$ were grown by slow evaporation of a mixed chloroacetonitrile–ethanol solvent system. The crystals were mounted on the tips of glass fibers using perfluoropolyether oil. All data were collected at 210(2) K, using a Bruker CCD X-ray diffractometer. Graphite-monochromated Mo-K α radiation (0.71073 Å) was used. The data were processed with SAINT⁴⁰ and corrected for absorption using SADABS.⁴¹ The structures were solved by direct methods or by the heavy atom method (for **3**) using the program SHELXS-86.⁴² Refinements were carried out by full-matrix least-squares techniques against F^2 using SHELXL-97.⁴³ Platon was used to search for higher symmetry.⁴⁴ Drawings were produced with Ortep-3.⁴⁵ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and given isotropic thermal parameters 1.2 times (1.5 times for CH₃ groups) the thermal parameter of the atom to which they were attached. Selected crystallograpic data are summarized in Table 3.

In the crystal structure of $2[ClO_4]$ one of the CH₂CH₂NMe₂ units and the ClO₄⁻ anion were found to be disordered over two positions. The two CH₂CH₂NMe₂ orientations were refined by using the SADI instruction (equal N-C and $C \cdots C$ distances, respectively) implemented in the ShelXL program to give site occupancies of 0.55(2) (for C8a-C11a) and 0.45(2) (for C8b–C11b). The disordered C atoms were refined isotropically. The two ClO₄⁻ orientations were refined without constraints to give site occupancies of 0.65(2) (for O1a–O4a) and 0.35(2) (for O1b-O4b), respectively. The crystal structure of 3[ClO₄]₂MeOH revealed the MeOH solvate disordered over two positions. The site occupancies of the two positions were refined as follows: O(9a)C(21a)/O(9b)C(21b) 0.62(3)/0.38(3). The disordered C and O atoms were refined with isotropic thermal parameters. The Flack parameter (absolute structure parameter) was calculated to be 0.03(6) (0.97(6) for the inverted structure) thus providing strong evidence that the absolute structure has been assigned correctly. In the crystal structure of 5[BPh₄]·MeCN the acetonitrile solvate was found to be disordered over two positions at site occupancies of 0.42(2) and 0.58(2), respectively. No hydrogen atoms were calculated for this solvate molecule and the C and N atoms were refined with isotropic thermal parameters. In the crystal structure of 7[ClO₄]₄(EtCN)₂(MeCN) one *tert*-butyl group was found to be disordered over two positions. A split atom model was used to account for this disorder. The site occupancies of the two positions were refined as follows: C(18a)-C(20A)/C(18b)-C(20b) 0.51(2)/0.49(2). The acetonitrile solvate was also found to be disordered over two positions. The site occupancies were fixed at 0.50. The C and N atoms of this solvate molecule were refined with isotropic thermal parameters. In the crystal structure of 10[ClO₄]₂ both perchlorates and the tert-butyl group were found to be disordered. Two split positions were successfully refined using the SADI instruction (equal Cl-O and $O \cdots O$ or C-C and $C \cdots C$ distances, respectively) implemented in the ShelXL program to give the following site occupancies: Cl(2)O(3a)-O(5a)O(6)/Cl(2)O(3b)-O(5b)O(6) = 0.36(4)/0.64(4);Cl(3)O(7a)-O(10a)/Cl(3)O(7b)-O(10b) = 0.57(2)/0.43(2) and C(17)C(18a)-C(20a)/C(17)C(18b)-C(20b) = 0.56(2)/0.44(2),respectively. The C atoms of the disordered t-Bu group were refined with isotropic thermal parameters.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516071e

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