

# Coordination chemistry of dinucleating P<sub>2</sub>N<sub>2</sub>S ligands: preparation and characterization of cationic palladium complexes

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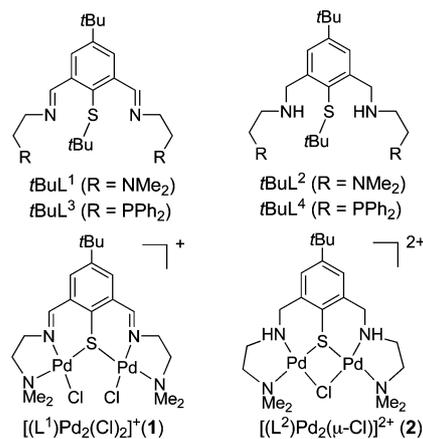
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The thioethers (4-*tert*-butyl-2,6-bis((2-(diphenylphosphino)ethylimino)methyl)phenyl)(*tert*-butyl)sulfane (*t*BuL<sup>3</sup>) and (4-*tert*-butyl-2,6-bis((2-(diphenylphosphino)ethylamino)methyl)phenyl)(*tert*-butyl)sulfane (*t*BuL<sup>4</sup>) react readily with [Pd(NCMe)<sub>2</sub>Cl<sub>2</sub>] to give the dinuclear palladium thiophenolate complexes [(L<sup>3</sup>)Pd<sub>2</sub>(Cl)<sub>2</sub>]<sup>+</sup> (**4**) and [(L<sup>4</sup>)Pd<sub>2</sub>(μ-Cl)]<sup>2+</sup> (**5**) (HL<sup>3</sup> = 2,6-bis((2-(diphenylphosphino)ethylimino)methyl)-4-*tert*-butylbenzenethiol, HL<sup>4</sup> = 2,6-bis((2-(diphenylphosphino)ethylamino)methyl)-4-*tert*-butylbenzenethiol). The chlorides in **4** could be replaced by neutral (MeCN) and anionic ligands (NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>) to give the dinuclear Pd<sup>II</sup> complexes [(L<sup>3</sup>)Pd<sub>2</sub>(NCMe)<sub>2</sub>]<sup>3+</sup> (**6**), [(L<sup>3</sup>)Pd<sub>2</sub>(SCN)<sub>2</sub>]<sup>+</sup> (**7**), [(L<sup>3</sup>)Pd<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (**8**), [(L<sup>3</sup>)Pd<sub>2</sub>(I)<sub>2</sub>]<sup>+</sup> (**9**), and [(L<sup>3</sup>)Pd<sub>2</sub>(CN)<sub>2</sub>]<sup>+</sup> (**10**). The acetonitrile ligands in **6** are readily hydrated to give the corresponding amidato complex [(L<sup>3</sup>)Pd<sub>2</sub>(NHCOMe)]<sup>2+</sup> (**11**). All complexes were isolated as perchlorate salts and studied by infrared, <sup>1</sup>H, and <sup>31</sup>P NMR spectroscopy. In addition, complexes **4**[ClO<sub>4</sub>]·EtOH, **5**[ClO<sub>4</sub>]<sub>2</sub>, **9**[ClO<sub>4</sub>], **10**[ClO<sub>4</sub>]·EtOH, and **11**[ClO<sub>4</sub>]<sub>2</sub>·MeCN·MeOH have been characterized by X-ray crystallography. The dipalladium complex **4** was found to catalyse the vinyl-addition polymerization of norbornene in the presence of MAO (methylalumoxane) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>.

## Introduction

A large number of dinucleating ligands<sup>1</sup> containing thiophenolate subunits have been reported in the past several years.<sup>2–6</sup> These ligands represent “soft” analogues of the more familiar phenolate systems,<sup>7</sup> and offer the potential of forming dinuclear complexes of catalytically active soft late transition metal ions such as Rh, Ir, Pd and Pt.<sup>8,9</sup> In order to enhance their affinity for these metal ions further soft donor centres may be introduced into the ligand backbone. Among these, phosphane functions, R<sub>2</sub>P–, are immediately evident, because these bind very strongly to the late 4d and 5d elements. Unfortunately, multidentate ligands with mixed N/P/S donor sets are not readily available and often require multistep reactions.<sup>10–13</sup> This is true in particular for dinucleating thiophenolate ligands. To the best of our knowledge, there are no previous examples of dinucleating thiophenolate-based systems containing mixed N/P/S donor sets.<sup>9</sup>

In a previous paper we described that the open-chain aromatic thioethers *t*BuL<sup>1</sup> and *t*BuL<sup>2</sup> can be readily deprotected with [Pd(NCMe)<sub>2</sub>Cl<sub>2</sub>] to afford the corresponding dinuclear palladium thiophenolate complexes [(L<sup>1</sup>)Pd<sub>2</sub>(Cl)<sub>2</sub>]<sup>+</sup> and [(L<sup>2</sup>)Pd<sub>2</sub>(μ-Cl)]<sup>2+</sup> (Scheme 1).<sup>14</sup> As part of this program, we sought to explore the scope of this Pd-mediated S-deprotection reaction for the synthesis of the phosphanyl-substituted ligands HL<sup>3</sup> and HL<sup>4</sup>. Herein we report the successful synthesis of these two novel N<sub>2</sub>P<sub>2</sub>S ligands and the X-ray structures of a series of their dinuclear palladium complexes. The structures of the present



**Scheme 1** Structures of the thioethers *t*BuL<sup>1</sup>–*t*BuL<sup>4</sup> and the palladium complexes [(L<sup>1</sup>)Pd<sub>2</sub>(Cl)<sub>2</sub>]<sup>+</sup> (**1**) and [(L<sup>2</sup>)Pd<sub>2</sub>(μ-Cl)]<sup>2+</sup> (**2**).

N<sub>2</sub>P<sub>2</sub>S complexes are compared with those of the related N<sub>4</sub>S complexes that we have reported previously. Results concerning the catalytic activity of [(L<sup>3</sup>)Pd<sub>2</sub>(Cl)<sub>2</sub>]<sup>+</sup> (**4**) in the vinyl-addition polymerisation of norbornene are described.

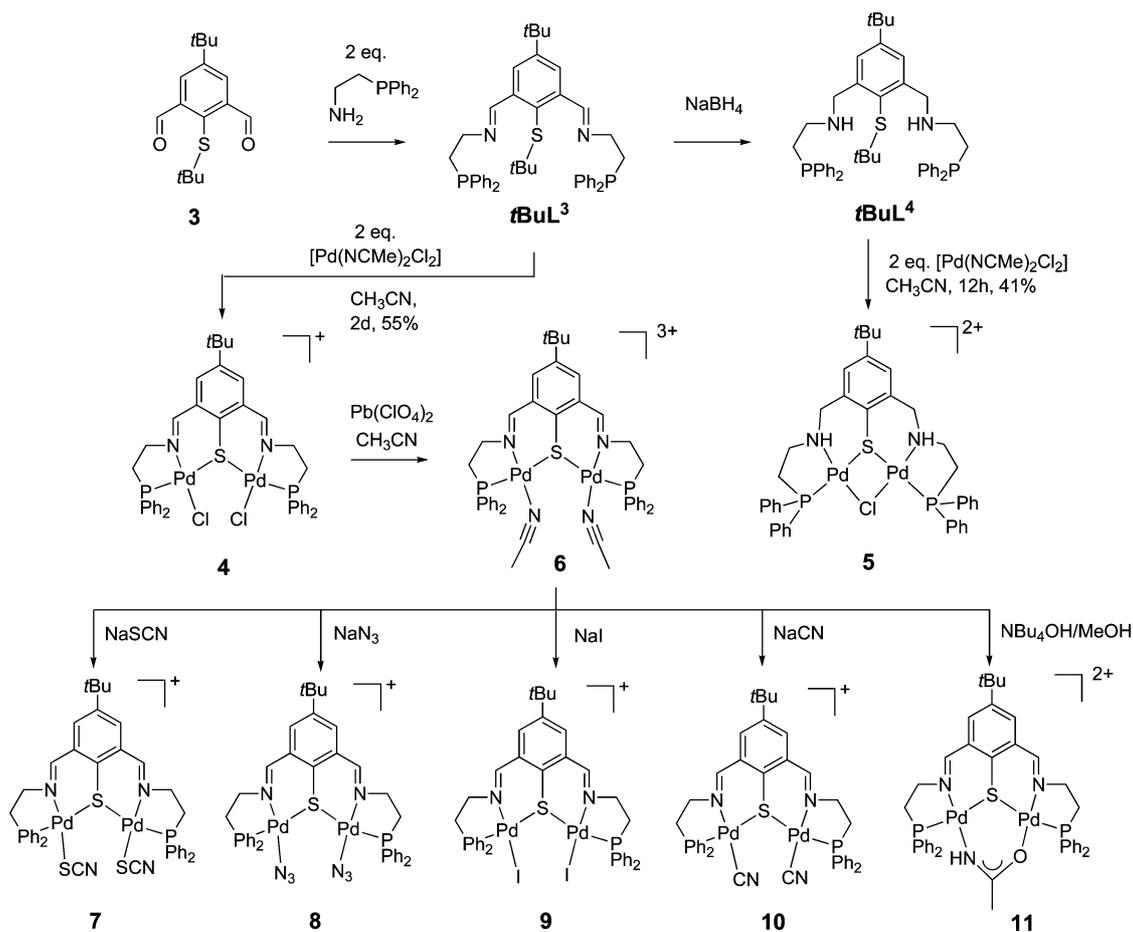
## Results and discussion

### Synthesis and characterization of proligands and complexes

Scheme 2 shows the preparation of the aromatic thioethers *t*BuL<sup>3</sup> and *t*BuL<sup>4</sup> and the palladium thiophenolate complexes **4**–**11**. Following the method of preparing *t*BuL<sup>1</sup>,<sup>14</sup> dialdehyde **3**<sup>15</sup> was condensed with two equivalents of 2-(diphenylphosphino)ethyleneamine to yield the Schiff base *t*BuL<sup>3</sup> as a colourless oil in nearly quantitative yield. Reduction of the imine

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Scheme 2 Synthesis of proligands  $t\text{BuL}^3$  and  $t\text{BuL}^4$  and complexes 4–11.

functions of  $t\text{BuL}^3$  was accomplished with sodium borohydride and produced the phosphanyl-substituted amine-thioether  $t\text{BuL}^4$ . Although the *tert*-butyl protected  $\text{N}_2\text{P}_2\text{S}$  proligands could not be obtained in analytically pure form, they were of sufficient purity for metal complex syntheses. Thus, the reaction of  $t\text{BuL}^3$  with two equivalents of  $[\text{Pd}(\text{NCMe})_2\text{Cl}_2]$  in acetonitrile solution at ambient temperature for 2 days gave a yellow solution, from which, upon addition of an excess of  $\text{LiClO}_4$ , yellow crystals of  $[(\text{L}^3)\text{Pd}_2(\text{Cl})_2][\text{ClO}_4]_4$  (**4**) precipitated in *ca.* 55% yield. Likewise, the reaction of *tert*-butyl protected proligand  $t\text{BuL}^4$  with two equivalents of  $[\text{Pd}(\text{NCMe})_2\text{Cl}_2]$  in acetonitrile at ambient temperature for 12 h gave a yellow solution, from which, upon addition of an excess of  $\text{LiClO}_4$ , a compound of composition  $[(\text{L}^4)\text{Pd}_2(\text{Cl})][\text{ClO}_4]_2$  (**5**) was reproducibly obtained in ~40% yield. Thus the thiolate functions of  $t\text{BuL}^3$  and  $t\text{BuL}^4$  can be selectively deprotected with  $[\text{Pd}(\text{NCMe})_2\text{Cl}_2]$  without affecting the phosphane groups. The selective cleavage of phosphanyl-substituted aromatic thioethers is without precedence in the literature. This reaction can now be further exploited for the design and synthesis of other thiophenolate ligands with mixed P/N/S donor sets.

In the course of this work it was found that the dinuclear palladium complex  $[(\text{L}^3)\text{Pd}_2(\text{Cl})_2]^+$  (**4**) exhibits a rich coordination chemistry. Thus, reaction of **4** with  $\text{Pb}(\text{ClO}_4)_2$  in dry acetonitrile gave the labile acetonitrile complex  $[(\text{L}^3)\text{Pd}_2(\text{NCMe})_2]^{3+}$  (**6**). This compound reacted readily with various anions such as  $\text{SCN}^-$ ,

$\text{N}_3^-$ ,  $\text{I}^-$  and  $\text{CN}^-$  to give the complexes  $[(\text{L}^3)\text{Pd}_2(\text{SCN})_2]^+$  (**7**),  $[(\text{L}^3)\text{Pd}_2(\text{N}_3)_2]^+$  (**8**),  $[(\text{L}^3)\text{Pd}_2(\text{I})_2]^+$  (**9**) and  $[(\text{L}^3)\text{Pd}_2(\text{CN})_2]^+$  (**10**), respectively, in good yields (Scheme 2). As was observed previously for  $[(\text{L}^1)\text{Pd}_2(\text{NCMe})_2]^{3+}$ ,<sup>14</sup> the Pd-bound acetonitrile ligands in **6** are readily transformed into acetamide. Thus, the reaction of **6** with  $\text{NBu}_4\text{OH}$  proceeded smoothly to give the acetamidato complex  $[(\text{L}^3)\text{Pd}_2(\text{NHCOMe})_2]^{2+}$  (**11**). The perchlorate salts of complexes **7**, **9**, **10** and **11** were obtained as analytically pure, yellow to red, microcrystalline solids by crystallization from saturated ethanol or acetonitrile–ethanol solutions. The perchlorate salts of bis(acetonitrile) complex **6** and azido complex **8** could not be obtained in analytically pure form. However, the spectroscopic similarities with  $[(\text{L}^1)\text{Pd}_2(\text{NCMe})_2]^{3+}$  and  $[(\text{L}^1)\text{Pd}_2(\text{N}_3)_2]^+$  reported previously<sup>14</sup> are in good agreement with their formulation (*vide infra*).

Infrared spectra of the perchlorate salts of the complexes **4**–**11** were recorded as KBr pellets. The spectra display the bands expected for the  $\text{P}_2\text{N}_2\text{S}$  ligands, counter ions and coligands. Each compound reveals a strong band around  $1100\text{ cm}^{-1}$ , attributable to the  $\nu_3(\text{F}_2)$  stretching vibration of the  $\text{ClO}_4^-$  ion.<sup>16</sup> The sharp band at  $\sim 1436\text{ cm}^{-1}$  is seen in all complexes and is typical for  $\text{PPh}_2$  groups.<sup>17</sup> The most significant feature in the IR spectrum of **4** is the band at  $1627\text{ cm}^{-1}$ , which can be readily assigned to the  $\text{C}=\text{N}$  stretching frequency of the coordinated imines. As expected, this band is absent in the IR spectrum of the dipalladium complex **5** of the reduced phosphan-amine-thiophenolate ligand

(L<sup>4</sup>)<sup>-</sup>. The IR spectrum of **6**[ClO<sub>4</sub>]<sub>3</sub> shows two bands at 2326 and 2298 cm<sup>-1</sup> attributable to the C≡N stretching frequencies of the Pd-bound acetonitrile ligands. Similar values ( $\nu = 2330$  and 2303 cm<sup>-1</sup>) were observed for [(L<sup>1</sup>)Pd<sub>2</sub>(NCMe)<sub>2</sub>]<sup>3+</sup>.<sup>14</sup> Complex **7**[ClO<sub>4</sub>]<sub>4</sub> exhibits a strong IR band at 2110 cm<sup>-1</sup>, indicative of S-bound thiocyanates.<sup>14</sup> In agreement with the formulation of **8**[ClO<sub>4</sub>]<sub>4</sub> the IR spectrum displays strong bands for the azide groups at 2034 and 2017 cm<sup>-1</sup> ( $\nu(\text{N}_3^-)$ ). The terminal CN<sup>-</sup> groups in **10**[ClO<sub>4</sub>]<sub>4</sub> give rise to a band at 2139 cm<sup>-1</sup> typical of monodentate cyanides.<sup>18</sup> In the tetranuclear complex [(L<sup>1</sup>)Pd<sub>2</sub>(μ-CN)<sub>2</sub>]<sub>2</sub>[ClO<sub>4</sub>]<sub>4</sub>,<sup>14</sup> the band for the bridging cyanides is centred at 2184 cm<sup>-1</sup>. The IR spectrum of **11** exhibits a band at 3363 cm<sup>-1</sup> attributable to the N–H stretching vibration of the carboxamide unit. The bands expected for the asymmetric and symmetric RCONH stretching vibrations are observed at 1571 and 1364 cm<sup>-1</sup>, respectively. Similar values were observed for [(L<sup>1</sup>)Pd<sub>2</sub>(NHCOMe)]<sup>+</sup>,<sup>14</sup> and other acetamidato compounds.<sup>19</sup> Overall, the infrared data for the present P<sub>2</sub>N<sub>2</sub>S complexes are

very similar to those of the corresponding N<sub>4</sub>S compounds that we have described in our earlier paper.<sup>14</sup> The IR data show that the electronic structures of the coligands are not significantly altered when changing the donor set of the supporting ligand from N<sub>4</sub>S to P<sub>2</sub>N<sub>2</sub>S. The similarities between the IR data sets imply that the coligands are in a *trans*-orientation to the imine donors as found in the [(L<sup>1</sup>)Pd<sub>2</sub>(L)]<sup>+</sup> species. These findings are confirmed by the crystal structures described below.

The complexes were further characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. <sup>13</sup>C NMR spectroscopic data were recorded only for *t*BuL<sup>3</sup> and **4**[ClO<sub>4</sub>]. Selected data for the compounds are presented in Table 1.

The most diagnostic signals in the <sup>1</sup>H NMR spectrum of *t*BuL<sup>3</sup> in CDCl<sub>3</sub> solution are the singlets for the *tert*-butyl groups (C<sup>1</sup>H<sub>3</sub>,  $\delta = 1.27$  and C<sup>4</sup>H<sub>3</sub>,  $\delta = 1.08$ , respectively), the aromatic protons (C<sup>8</sup>H,  $\delta = 8.07$ ), and the imine protons (C<sup>11</sup>H,  $\delta = 9.05$ , for atom labels see inset Table 1). These <sup>1</sup>H chemical shifts are very similar to those of the amine-imine-thioether *t*BuL<sup>1</sup>, reported previously.<sup>14</sup>

**Table 1** Selected <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR data for the thioethers *t*BuL<sup>3</sup>, *t*BuL<sup>4</sup> and the palladium complexes **4**–**11**

$\delta(^1\text{H})$	C <sup>1</sup> H <sub>3</sub>	C <sup>4</sup> H <sub>3</sub>	C <sup>5</sup> H <sub>2</sub>	C <sup>6</sup> H <sub>2</sub>	C <sup>8</sup> H	C <sup>11</sup> H(C <sup>11</sup> H <sub>2</sub> )	P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	<sup>31</sup> P			
<i>t</i> BuL <sup>3,a</sup>	1.27 s	1.08 s	3.70 m	2.40 m	8.07 s	9.05 s	7.25–7.43 m	–18.30 <sup>e</sup>			
<i>t</i> BuL <sup>4,a</sup>	1.21 s	1.15 s	2.66 m	2.21 m	obsc. <sup>e</sup>	4.00 br. s	7.29–7.44 m	–20.50 <sup>e</sup>			
<b>4</b> [ClO <sub>4</sub> ] <sup>b</sup>	1.35 s	—	4.05 m	2.59 m	obsc. <sup>e</sup>	8.68 s	7.51–7.68 m	48.95 <sup>e</sup>			
<b>5</b> [ClO <sub>4</sub> ] <sub>2</sub> <sup>b</sup>	1.34 s	—	4.21 m	2.64 m	obsc. <sup>e</sup>	3.30 m	7.91–7.97 m	49.90 <sup>e</sup>			
			3.98 m	2.67 m			7.35–7.89 m				
<b>6</b> [ClO <sub>4</sub> ] <sub>3</sub> <sup>b</sup>	1.40 s	—	4.32 m	3.07 m	8.05 s	8.68 s	7.52–7.71 m	59.40 <sup>e</sup>			
			4.10 m	2.64 m			7.72–7.89 m				
<b>7</b> [ClO <sub>4</sub> ] <sub>4</sub> <sup>b</sup>	1.40 s	—	Coligand: 1.97 (CH <sub>3</sub> CN)		8.02 s	8.77 s	7.54–7.70 m	51.80 <sup>b</sup>			
			4.06 m	2.69 m			7.82–7.95 m				
<b>8</b> [ClO <sub>4</sub> ] <sub>4</sub> <sup>d</sup>	1.39 s	—	4.20 m	2.75 m	8.18 s	9.04 s	7.57–7.70 m	48.70 <sup>d</sup>			
			4.05 m	2.81 m			7.94–8.04 m				
<b>9</b> [ClO <sub>4</sub> ] <sub>4</sub> <sup>b</sup>	1.39 s	—	4.20 m	2.85 m	7.85 s	8.54 s	7.50–7.70 m	49.30 <sup>d</sup>			
			3.88 m	2.62 m			8.00–8.20 m				
<b>10</b> [ClO <sub>4</sub> ] <sub>4</sub> <sup>b</sup>	1.37 s	—	4.13 m	2.62 m	obsc. <sup>e</sup>	8.77 s	7.52–7.67 m	51.70 <sup>b</sup>			
			4.06 m	2.73 m			7.92–8.03 m				
<b>11</b> [ClO <sub>4</sub> ] <sub>4</sub> <sup>c</sup>	1.42 s	—	4.21 m	2.79 m	8.16 s	8.65 s	7.62–7.73 m	49.42 <sup>e</sup>			
			4.43 m	2.72 m			7.85–7.96 m				
Coligand: 2.08 (CH <sub>3</sub> CONH), 6.02 (CH <sub>3</sub> CONH)											
$\delta(^{13}\text{C})$	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>	C <sup>7</sup>	C <sup>8</sup>	C <sup>9</sup>	C <sup>10</sup>	C <sup>11</sup>
<i>t</i> BuL <sup>3,a</sup>	31.6	35.5	49.7	31.7	59.0 (25 Hz) <sup>f</sup>	30.4 (15 Hz) <sup>g</sup>	153.0	141.5	131.7	127.2	162.7
<b>4</b> [ClO <sub>4</sub> ] <sup>c</sup>	30.8	35.2	—	—	64.5 (27 Hz) <sup>f</sup>	27.7 (49 Hz) <sup>g</sup>	150.0	140.8	129.0	127.9	167.8
	PPh <sub>2</sub> : 128.8, 129.0, 133.2, 138.9										
PPh <sub>2</sub> : 130.2, 133.6, 134.3, 134.6											

<sup>a</sup> Recorded in CDCl<sub>3</sub> solution. <sup>b</sup> Recorded in CD<sub>3</sub>CN solution. <sup>c</sup> Recorded in CD<sub>3</sub>NO<sub>2</sub> solution. <sup>d</sup> Recorded in DMSO-*d*<sub>6</sub> solution. <sup>e</sup> Signal obscured by resonances due to the PPh<sub>2</sub> groups. <sup>f</sup> <sup>2</sup>J<sub>CP</sub>. <sup>g</sup> <sup>1</sup>J<sub>CP</sub>.

The same is true for the  $^{13}\text{C}$  NMR data. As expected, however, the signals for the methylene carbon atoms denoted  $\text{C}^5$  and  $\text{C}^6$  appear as doublets. The doublets are caused by one and two bond phosphorus–carbon couplings ( $^2J(^{31}\text{P}-^{13}\text{C}) = 15\text{ Hz}$ ,  $^1J(^{31}\text{P}-^{13}\text{C}) = 25\text{ Hz}$ ). The  $^{31}\text{P}$  NMR spectrum of  $t\text{BuL}^3$  reveals only one signal at  $\delta = -18.3$ .

The conversion of  $t\text{BuL}^3$  to  $t\text{BuL}^4$  was confirmed by  $^1\text{H}$  NMR spectroscopy by the absence of the signal for the imine protons ( $\text{CH}=\text{N}$ ) and the presence of a new signal at  $\delta = 4.00$  for the benzylic methylene protons. The formulation of  $t\text{BuL}^4$  was further confirmed by  $^{31}\text{P}$  NMR spectroscopy (singlet at  $\delta = -20.5$ ) and by a crystal structure determination of one of its metal complexes (see structure of compound **5** described below). Like its parent  $t\text{BuL}^3$ , the diphosphane-diamine-thioether  $t\text{BuL}^4$  could not be obtained in analytically pure form. Nonetheless it was of sufficient purity for metal complex syntheses.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data for the dipalladium complex **4** lack the signals of one  $t\text{Bu}$  group, which confirms the presence of the thiophenolate unit. The coordination of the phosphane functions is supported by the  $^{31}\text{P}$  NMR spectrum by the down field shift of the  $^{31}\text{P}$  NMR resonance from  $\delta = -18.3$  in  $t\text{BuL}^3$  to  $\delta = 48.95$  in **4**. From the  $^1\text{H}$  and  $^{31}\text{P}$  NMR data it can also be seen that the two halves of  $(\text{L}^3)^-$  in **4** are equivalent. For example, single resonances are observed for the imine protons ( $\text{C}^{11}\text{H}$ ) and the pairs of carbon atoms labelled  $\text{C}^{8,8'}$  and  $\text{C}^{9,9'}$ , respectively. It indicates that **4** exhibits  $C_{2v}$  symmetry on the NMR time scale. A similar NMR equivalence of the ligand side arms has been noted for **1** and the dinuclear  $[(\text{L}^5)\text{Pd}_2(\text{Cl})_2]^+$  complex, where  $(\text{L}^5)^{3-}$  is the trianion derived from the condensation product of cyclohexanecarbohydrazide and 2-mercapto-5-methylbenzene-1,3-dialdehyde.<sup>20</sup> It should be noted that complex **4** gives rise to only one  $^{31}\text{P}$  NMR resonance. This is not in agreement with the complex's  $C_1$  point group symmetry found in the solid state. Such a structure would give rise to two  $^{31}\text{P}$  NMR signals. The observed higher symmetry in the solution state is believed to

be a consequence of dynamic behaviour. It is assumed that the two ligand side arms twist about the  $\text{Ar}-\text{CH}(\text{imine})$  bonds. This would result in the coalescence of the  $^{31}\text{P}$  NMR signals and the complex's time-averaged  $C_{2v}$  symmetry. Thus, the conformations found in the solid state are not locked in the solution state. The  $^1\text{H}$  NMR data for  $5[\text{ClO}_4]_2$  were also indicative of the presence of a dinuclear palladium thiophenolate complex, showing only one *tert*-butyl resonance at  $\delta = 1.34$ . The  $^{31}\text{P}$  NMR resonance is shifted down field from  $\delta = -20.5$  in  $t\text{BuL}^4$  to  $\delta = 49.90$  in **5**. The  $^1\text{H}$  NMR data of the complexes **7–11** closely resemble those of **4**. In all cases, singlets are observed for the *tert*-butyl groups labelled  $\text{C}^1\text{H}_3$ , the aromatic  $\text{C}^8\text{H}$  protons ( $\delta = 8.02\text{--}8.18$ ), and the imine  $\text{C}^{11}\text{H}$  protons ( $\delta = 8.68\text{--}9.14$ ), indicative of  $C_{2v}$  or  $C_s$  symmetric structures. Likewise, the  $^{31}\text{P}$  NMR spectra reveal only one  $^{31}\text{P}$  NMR signal for the two equivalent phosphanyl groups, with the  $^{31}\text{P}$  NMR resonances in the 48–60 range. The attachment of a bridging N,O-bound acetamidato unit to the  $[(\text{L}^3)\text{Pd}_2]^{3+}$  fragment in **11** is expected to cause an NMR inequivalence of the two ligand side arms. Indeed, the  $^1\text{H}$  NMR spectrum of  $11[\text{ClO}_4]_2$  in  $\text{CD}_3\text{NO}_2$  solution reveals two equally intense  $^1\text{H}$  signals at  $\delta = 8.65$  and  $8.87$  for the imine CH protons. In addition, two  $^{31}\text{P}$  NMR resonances are clearly discernible in the  $^{31}\text{P}$  NMR spectrum. In summary, the spectroscopic data have clearly established that  $(\text{L}^3)^-$  and  $(\text{L}^4)^-$  are effective dinucleating  $\text{N}_2\text{P}_2\text{S}$  ligands that support the formation of dinuclear palladium complexes with one exchangeable coordination site on each metal ion.

### Description of crystal structures

The formulation of the complexes  $4[\text{ClO}_4]\cdot\text{EtOH}$ ,  $5[\text{ClO}_4]_2$ ,  $9[\text{ClO}_4]$ ,  $10[\text{ClO}_4]\cdot\text{EtOH}$  and  $11[\text{ClO}_4]_2\cdot\text{MeCN}\cdot\text{MeOH}$  was further confirmed by X-ray crystallography. Experimental crystallographic data are summarized in Table 2.

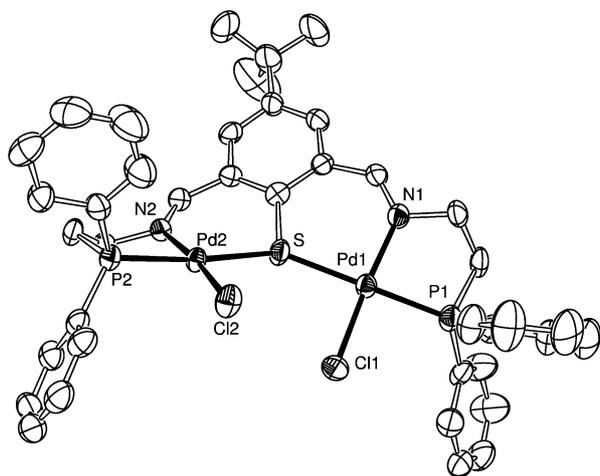
Crystals of  $4[\text{ClO}_4]\cdot\text{EtOH}$  were grown by recrystallization from a mixed acetonitrile–ethanol solvent system. A perspective view

**Table 2** Crystallographic data for  $4[\text{ClO}_4]\cdot\text{EtOH}$ ,  $5[\text{ClO}_4]_2$ ,  $9[\text{ClO}_4]$ ,  $10[\text{ClO}_4]\cdot\text{EtOH}$ , and  $11[\text{ClO}_4]_2\cdot\text{MeCN}\cdot\text{MeOH}$

Compound	$4[\text{ClO}_4]\cdot\text{EtOH}$	$5[\text{ClO}_4]_2$	$9[\text{ClO}_4]$	$10[\text{ClO}_4]\cdot\text{EtOH}$	$11[\text{ClO}_4]_2\cdot\text{MeCN}\cdot\text{MeOH}$
Formula	$\text{C}_{42}\text{H}_{47}\text{Cl}_3\text{N}_2\text{O}_5\text{P}_2\text{Pd}_2\text{S}$	$\text{C}_{40}\text{H}_{45}\text{Cl}_3\text{N}_2\text{O}_8\text{P}_2\text{Pd}_2\text{S}$	$\text{C}_{40}\text{H}_{41}\text{ClI}_2\text{N}_2\text{O}_4\text{P}_2\text{Pd}_2\text{S}$	$\text{C}_{44}\text{H}_{47}\text{ClN}_4\text{O}_5\text{P}_2\text{Pd}_2\text{S}$	$\text{C}_{45}\text{H}_{52}\text{Cl}_2\text{N}_4\text{O}_{10}\text{P}_2\text{Pd}_2\text{S}$
$M_r/\text{g mol}^{-1}$	1072.97	1094.93	1209.80	1054.11	1186.61
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
$a/\text{\AA}$	18.566(4)	12.666(3)	15.572(3)	19.193(4)	12.694(3)
$b/\text{\AA}$	15.313(3)	14.142(3)	13.029(3)	14.913(3)	14.676(3)
$c/\text{\AA}$	16.854(3)	14.318(3)	26.549(5)	17.329(4)	15.751(3)
$\alpha/^\circ$	90.00	60.85(3)	90.00	90.00	65.73(3)
$\beta/^\circ$	116.03(3)	72.15(3)	94.43(3)	115.18(3)	69.65(3)
$\gamma/^\circ$	90.00	81.52(3)	90.00	90.00	89.49(3)
$V/\text{\AA}^3$	4305(2)	2132.0(7)	5370(2)	4489(2)	2477.0(9)
$Z$	4	2	4	4	2
$d_{\text{calcd}}/\text{g cm}^{-3}$	1.655	1.706	1.496	1.560	1.591
Cryst. size/mm	$0.30 \times 0.30 \times 0.20$	$0.45 \times 0.30 \times 0.30$	$0.18 \times 0.15 \times 0.10$	$0.25 \times 0.25 \times 0.25$	$0.35 \times 0.20 \times 0.20$
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.191	1.209	2.001	1.027	1.000
$\theta$ limits/ $^\circ$	1.22–28.32	1.65–28.29	1.31–29.08	1.17–29.01	1.53–28.34
Measured refl.	27042	19048	33663	40331	22308
Independent refl.	10380	9825	13045	11031	11487
Observed refl. <sup>a</sup>	4945	7836	5705	5931	7651
No. parameters	514	523	440	532	595
$R1^b$ ( $R1$ all data)	0.0403 (0.1173)	0.0288 (0.0410)	0.0817 (0.1864)	0.0478 (0.1080)	0.0396 (0.0706)
$wR2^c$ ( $wR2$ all data)	0.0859 (0.1248)	0.0667 (0.0718)	0.2340 (0.2935)	0.1076 (0.1370)	0.0852 (0.0962)
Max., min. peaks/e $\text{\AA}^{-3}$	0.790, $-0.773$	0.665, $-0.573$	1.420, $-1.499$	0.901, $-0.660$	0.994, $-0.747$

<sup>a</sup> Observation criterion:  $I > 2\sigma(I)$ . <sup>b</sup>  $R1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ . <sup>c</sup>  $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

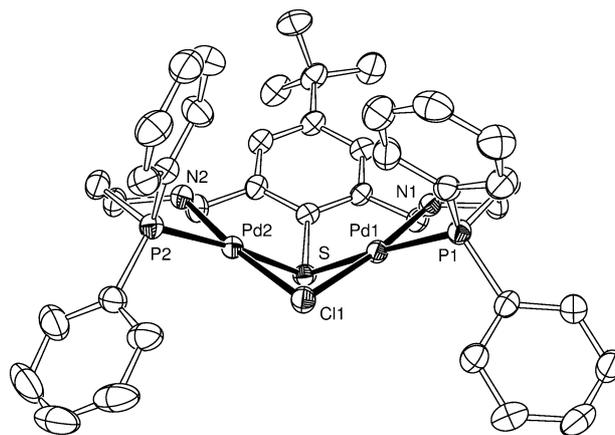
of the structure of the cation **4** is shown in Fig. 1. Selected bond lengths and angles are listed in the caption.



**Fig. 1** Structure of the cation **4** in crystals of  $[\mathbf{4}][\text{ClO}_4] \cdot \text{EtOH}$  with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Pd(1)–N(1) 2.017(5), Pd(1)–P(1) 2.268(2), Pd(1)–S 2.341(2), Pd(1)–Cl(1) 2.294(2), Pd(2)–N(2) 2.018(4), Pd(2)–P(2) 2.246(2), Pd(2)–S 2.378(2), Pd(2)–Cl(2) 2.284(2); Pd(1)  $\cdots$  Pd(2) 4.389(1), Cl(1)  $\cdots$  Cl(2) 3.817(2); Pd(1)–S–Pd(2) 136.87(7).

Each palladium atom is surrounded by a N, S and P atom of  $(\text{L}^3)^-$ , and a terminal chloro ligand in a distorted square planar manner. The maximum deviations from the least-squares planes defined by the atoms Pd(1), N(1), P(1), S, Cl(1) and Pd(2), N(2), P(2), S, Cl(1) are 0.0961 and 0.0527  $\text{\AA}$ , respectively. The overall conformation of the dinucleating  $\text{P}_2\text{N}_2\text{S}$  ligand in **4** is very similar to that of the  $\text{N}_4\text{S}$  ligand  $(\text{L}^1)^-$  in  $[(\text{L}^1)\text{Pd}_2(\text{Cl})_2]^+$  (**1**).<sup>14</sup> Thus, 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. This side arm twisting is presumably enforced by repulsive interactions between the two chloro ligands (Cl(1)  $\cdots$  Cl(2) = 3.817(2)  $\text{\AA}$ ). The coordination plane at Pd(1) is at a dihedral angle of 22.2 $^\circ$  to the central aromatic ring, whereas the corresponding angle for the coordination plane of Pd(2) is at 41.5 $^\circ$ . Similar values were observed for **1** (18.6, 48.3 $^\circ$ ).<sup>14</sup> In contrast to **1**, there seems to be no strain around the bridging thiophenolate sulfur atom in **4**. Thus, the displacement of the S atom from the average plane of the benzene ring to which it is attached has decreased from 0.304  $\text{\AA}$  in **1** to 0.047  $\text{\AA}$  in **4**. Another difference concerns the Pd–S bond distances. These are significantly longer in **4** (2.360(2)  $\text{\AA}$  vs 2.266(2)  $\text{\AA}$  in **1**), presumably due to a *trans* influence of the  $\text{Ph}_2\text{P}$  groups. The Pd  $\cdots$  Pd distance and the Pd–S–Pd angle in **4** (4.389  $\text{\AA}$  and 136.9 $^\circ$ , respectively) are also markedly different from those in **1** (3.922  $\text{\AA}$  and 119.9 $^\circ$ , respectively). Thus, replacement of the  $\text{NMe}_2$  functions in  $(\text{L}^1)^-$  by  $\text{PPh}_2$  groups in  $(\text{L}^3)^-$  does not change the overall ligating properties of the supporting ligand but releases some strain in the ligand backbone due to a lengthening of the Pd–S bonds.

The crystal structure of  $[\mathbf{5}][\text{ClO}_4]_2$  consists of dinuclear  $[(\text{L}^4)\text{Pd}_2(\mu\text{-Cl})]^{2+}$  complexes and perchlorate anions (Fig. 2). One of the two perchlorate ions is hydrogen bonded to the hydrogen atoms of the secondary amine functions; the O(1)  $\cdots$  H(2)N(2) and

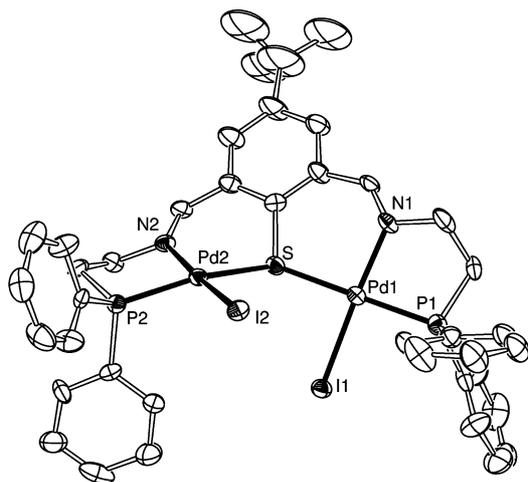


**Fig. 2** Structure of the dication **5** in crystals of  $[(\text{L}^4)\text{Pd}_2(\mu\text{-Cl})][\text{ClO}_4]_2$  ( $[\mathbf{5}][\text{ClO}_4]_2$ ) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Pd(1)–N(1) 2.062(2), Pd(1)–P(1) 2.266(1), Pd(1)–S 2.362(1), Pd(1)–Cl(1) 2.3462(8), Pd(2)–N(2) 2.061(2), Pd(2)–P(2) 2.258(1), Pd(2)–S 2.367(1), Pd(2)–Cl(1) 2.358(1); Pd(1)  $\cdots$  Pd(2) 3.0975(7); Pd(1)–S–Pd(2) 81.84(3), Pd(1)–Cl(1)–Pd(2) 82.36(4).

O(4)  $\cdots$  H(1)N(1) distances being 2.126 and 2.349  $\text{\AA}$ , respectively. This arrangement places the  $\text{ClO}_4^-$  in the vicinity of Pd(1), but the rather long Pd(1)  $\cdots$  O(4) $\text{ClO}_4^-$  distance of 3.135  $\text{\AA}$  seems to rule against any substantial bonding interactions.

The conformation adopted by  $(\text{L}^4)^-$  is very similar to that of  $(\text{L}^2)^-$  in  $[(\text{L}^2)\text{Pd}_2(\mu\text{-Cl})]^{2+}$  (**2**).<sup>14</sup> Thus the side arms associated with Pd(1) and Pd(2) are equally twisted out of the plane of the central aromatic unit; with the coordination planes of Pd(1) and Pd(2) at similar dihedral angles of 49.1 and 45.1 $^\circ$  to the central aromatic ring. Similar angles are observed in **2** (34.1, 43.1 $^\circ$ ). As was observed for the pair of complexes above, the average Pd–S bonds in **5** at 2.365  $\text{\AA}$  are significantly longer than in **2** (by  $\approx 0.10$   $\text{\AA}$ ), again indicative of a *trans* influence of the phosphane groups. The average Pd–N (2.062  $\text{\AA}$ ) and Pd–Cl bond lengths (2.352  $\text{\AA}$ ) compare well with those in **2** and other four-coordinate Pd complexes.<sup>21,22</sup> Thus, as was observed for  $(\text{L}^3)^-$ , the ligating properties of  $(\text{L}^4)^-$  are not markedly affected by conversion of the  $\text{NMe}_2$  into  $\text{PPh}_2$  groups.

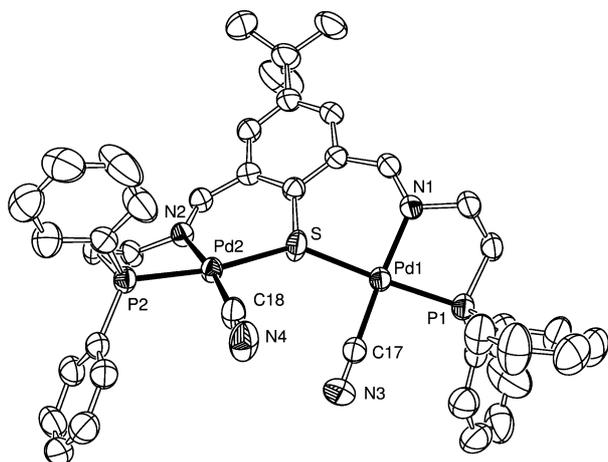
The crystal structure determination of  $[\mathbf{9}][\text{ClO}_4]$  confirmed the formulation of the diiodo complex  $[(\text{L}_3)\text{Pd}_2(\text{I})_2][\text{ClO}_4]$ . Fig. 3 presents a perspective view of the structure of the cation **9** along with the atom labelling scheme. The palladium atoms are four-coordinate; being surrounded by the N, P, and S atoms of  $(\text{L}^3)^-$  and the iodide ligands. The coordination geometry for Pd(1) is almost perfectly planar; as manifested by a maximum deviation of only 0.014  $\text{\AA}$  from the least-squares plane defined by the atoms Pd(1), N(1), P(1), S, and I(1). The coordination geometry for Pd(2), on the other hand, is significantly distorted from square planar towards tetrahedral, as indicated by a P(2)–Pd(2)–I(2)/N(2)–Pd(2)–S dihedral angle of 17.1 $^\circ$  (mean deviation from plane = 0.189  $\text{\AA}$ ). This value is a rather large distortion from planarity. The other palladium complexes described in this study are more rigorously square planar, the tetrahedral twists from the  $\text{PPdL}'/\text{NPdS}$  planes ( $\text{L}' = \text{coligand}$ ) not exceeding 5 $^\circ$ . As in **4**, the two coordination planes are markedly twisted around the hinging sulfur atom so that they are at an angle of 60.8 $^\circ$  to each other



**Fig. 3** Structure of the cation **9** in crystals of  $9[\text{ClO}_4]$  with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for reasons of clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–N(1) 2.069(11), Pd(1)–P(1) 2.245(4), Pd(1)–S 2.313(4), Pd(1)–I(1) 2.5891(15), Pd(2)–N(2) 2.056(11), Pd(2)–P(2) 2.237(4), Pd(2)–S 2.336(4), Pd(2)–I(2) 2.5650(14); Pd(1)⋯Pd(2) 4.154(1), I(1)⋯I(2) 4.112(2); Pd(1)–S–Pd(2) 126.6(2).

(52.6° in **4**). 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(2) is at a dihedral angle of 44.6° to the central aromatic ring whereas the corresponding angle for the coordination plane of Pd(1) is at 16.7°. These values are nearly identical with those in **4**.

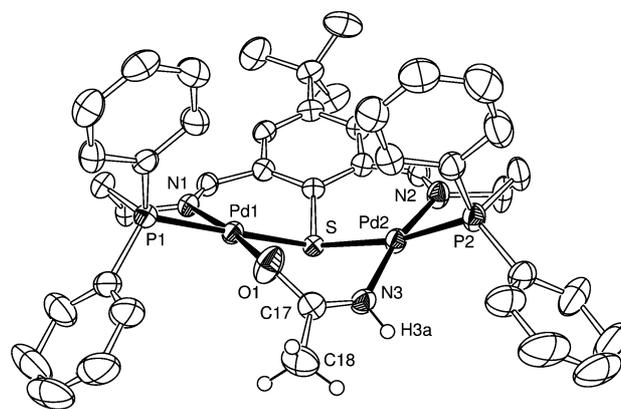
The single-crystal X-ray diffraction study of  $10[\text{ClO}_4] \cdot \text{EtOH}$  unambiguously confirmed the formulation of the dicyano complex  $[(\text{L}^3)\text{Pd}_2(\text{CN})_2]^+$  (Fig. 4). Both cyanides act as monodentate ligands, generating distorted square-planar NSPC environments



**Fig. 4** Structure of the cyanide complex **10** in crystals of  $10[\text{ClO}_4] \cdot \text{EtOH}$  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) 2.043(4), Pd(1)–P(1) 2.263(1), Pd(1)–S 2.320(1), Pd(1)–C(17) 1.956(6), Pd(2)–N(2) 2.024(4), Pd(2)–P(2) 2.255(1), Pd(2)–S 2.342(2), Pd(2)–C(18) 1.957(6), C(17)–N(3) 1.150(6), C(18)–N(4) 1.128(6); Pd(1)⋯Pd(2) 4.357(1); Pd(1)–S–Pd(2) 138.30(7), Pd(1)–C(17)–N(3) 179.2(6), Pd(2)–C(18)–N(4) 176.0(5).

for both palladium atoms. The N(4) atom of the cyanide bonded to Pd(2) seems to be hydrogen bonded to the CH(imine) group of an adjacent complex, as indicated by the relatively short N(4)⋯H(10')C(10') distance (2.437 Å) and the slight deviation of the Pd–C(18)–N(4) angle from 180°. No such interactions are observed for the other CN<sup>−</sup> function. In this case, the Pd–C–N arrangement is almost perfectly linear. The average Pd–N, Pd–P and Pd–S bond lengths of **10** show no unusual features and compare well with those in the dihalogeno complexes **4** and **9** described above. The average Pd–C bond length at 1.958(6) Å is normal for four-coordinate Pd(II) cyanide complexes.<sup>18</sup> The conformation of (L<sup>3</sup>)<sup>−</sup> adopted in **10** is slightly different from that seen in **4** and **9**. In **10**, the side arms associated with Pd(1) and Pd(2) are located above and below the plane of the central aromatic unit. The coordination planes of Pd(1) and Pd(2) are at similar dihedral angles of 32.3° and −32.9° to the central aromatic ring, generating an idealized C<sub>2</sub>-axis of symmetry that contains the sulfur atom and the quaternary carbon atom of the *tert*-butyl group.

Crystals of  $11[\text{ClO}_4]_2 \cdot \text{MeCN} \cdot \text{MeOH}$  grown by slow evaporation from a mixed acetonitrile–methanol solvent system are triclinic space group  $P\bar{1}$ . Fig. 5 displays the structure of the dication **11**. Selected bond lengths and angles are given in the figure caption. The acetamidato unit bridges the two palladium atoms in a  $\mu_{1,3}$ -bridging mode at a Pd⋯Pd distance of 3.711 Å. The NH hydrogen atom H(3a) could be located unambiguously from difference Fourier maps providing strong support that the present orientation of the acetamidato ligand with the N atom bonded to Pd(2) and the O atom attached to Pd(1), respectively, has been assigned correctly. This assignment is further supported by the *R*1 values which converged at *R*1 = 0.0397 for the present structure and at a slightly higher value (*R*1 = 0.0410) for the alternate orientation. The Pd–O and Pd–N bond lengths at 2.023(2) and 2.014(3) Å show no unusual features and compare well with those in  $[(\text{L}^1)\text{Pd}_2(\text{NHCOCH}_2\text{Cl})]^{2+}$ .<sup>14</sup>



**Fig. 5** Structure of the acetamido complex **11** in crystals of  $11[\text{ClO}_4]_2 \cdot \text{MeCN} \cdot \text{MeOH}$  with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, except those of the MeCONH<sup>−</sup> coligand, are omitted for reasons of clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–N(1) 2.013(3), Pd(1)–P(1) 2.271(1), Pd(1)–S 2.364(1), Pd(1)–O(1) 2.032(3), Pd(2)–N(2) 2.021(3), Pd(2)–P(2) 2.257(1), Pd(2)–S 2.313(1), Pd(2)–N(3) 2.014(3), N(3)–C(17) 1.294(5), O(1)–C(17) 1.301(5), Pd(1)⋯Pd(2) 3.711(1); C(17)–N(3)–Pd(2) 133.0(3), C(17)–O(1)–Pd(1) 127.4(3), N(3)–C(17)–O(1) 123.6(4), N(3)–C(17)–C(18) 119.5(4), O(1)–C(17)–C(18) 116.8(4), Pd(1)–S–Pd(2) 104.98(5).

**Table 3** Norbornene polymerization activity of dinuclear complex **4**

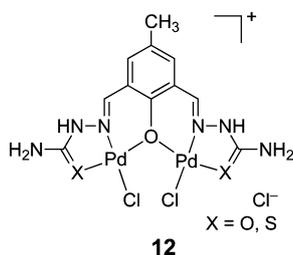
Run <sup>a</sup>	Complex <b>4</b> /mmol	MAO/mmol	Time/min	Polymer yield/g	Activity/g <sub>polymer</sub> mol <sub>Pd</sub> <sup>-1</sup> h <sup>-1</sup>	
1	0.0053	1.056	1	0.1433	8.1 × 10 <sup>5</sup>	
2	0.0053	1.056	1	0.1533	8.7 × 10 <sup>5</sup>	
3	0.0053	—	60	—	0	
4	0.0053	1.056	1	0.1046	5.9 × 10 <sup>5</sup>	
5	0.0053	1.056	1	0.1521	8.6 × 10 <sup>5</sup>	
6	0.0053	1.056	1	0.1307	7.4 × 10 <sup>5</sup>	
Run <sup>b</sup>	Complex <b>4</b> /mmol	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /mmol	AlEt <sub>3</sub> /mmol	Time/min	Polymer yield/g	Activity/g <sub>polymer</sub> mol <sub>Pd</sub> <sup>-1</sup> h <sup>-1</sup>
7	0.015	0.27	0.3	1	0.3812	7.6 × 10 <sup>5</sup>
8	0.015	0.27	0.3	1	0.4180	8.4 × 10 <sup>5</sup>
9	0.015	0.27	—	60	0.0398	1.3 × 10 <sup>3</sup>

<sup>a</sup> General conditions: 1.00 g (10.6 mmol) norbornene; molar ratios: Al(MAO) : Pd = 100 : 1, norbornene : Pd = 1000 : 1; total reaction volume 10 ml (6 ml toluene + 4 ml CH<sub>2</sub>Cl<sub>2</sub>).

<sup>b</sup> General conditions: 2.834 g (30.1 mmol) norbornene; molar ratios: Al(AlEt<sub>3</sub>) : B : Pd = 10 : 9 : 1, norbornene : Pd = 1000 : 1; total reaction volume 40 ml (30 ml toluene + 10 ml CH<sub>2</sub>Cl<sub>2</sub>).

### Activity of **4** in the vinyl-addition polymerization of norbornene

The catalytic behaviour of complex **4** in the vinyl-addition polymerization of norbornene<sup>23–26</sup> was tested in view of literature reports that di- and polynuclear nickel and palladium complexes exhibit high activities.<sup>24,27,28</sup> The polymerization results are summarized in Table 3. The dinuclear complex **4** shows norbornene vinyl-polymerization activities between 10<sup>5</sup> and 10<sup>6</sup> g<sub>polymer</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup> when activated with methylalumoxane (MAO) or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>. The polymerization activities are easily reproducible (run 1–2 and 4–6 with MAO, run 7 and 8 with borane/AlEt<sub>3</sub>). Without a cocatalyst no activity is observed (run 3) and with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone only a very low activity can be obtained (run 9). The polynorbornenes were found to be insoluble in 1,2,4-trichlorobenzene even at elevated temperature as is often the case for palladium-derived vinyl-polynorbornenes, whereby precluding a polymer analysis by gel permeation chromatography.<sup>25,27</sup> In comparison, the activity of **4** is lower than that of the related (2,6-bis-(thio)semicarbazide-4-methylphenolato-*N,O,O'(S)*)-dichloro-dipalladium(II) compounds **12**. Complexes **12** can also be activated with MAO and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> to give activities between 1.3 × 10<sup>6</sup> and 1.0 × 10<sup>7</sup> g<sub>polymer</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>.<sup>27</sup> We trace this observation to the presence of the Ph<sub>2</sub>P-ligating group in **4** which can shield the active centre with its bulkiness and because the Pd–P bond is less likely to open even in the presence of the cocatalysts to create a necessary open coordination site.<sup>26</sup>



### Conclusions

The proligands *t*BuL<sup>3</sup> and *t*BuL<sup>4</sup> can be selectively S-deprotected with [Pd(NCMe)<sub>2</sub>Cl<sub>2</sub>] to afford the phosphan-imine and phosphan-amine substituted thiophenolate ligands (L<sup>3</sup>)<sup>-</sup> and

(L<sup>4</sup>)<sup>-</sup>, respectively. The phosphane groups are not affected under these conditions. The P<sub>2</sub>N<sub>2</sub>S ligands support the formation of dinuclear complexes of the type [(L<sup>3</sup>)Pd(L<sup>4</sup>)<sub>2</sub>]<sup>n+</sup> and [(L<sup>4</sup>)Pd(μ-L)]<sup>n+</sup>, demonstrating that the conversion of the two imine-functions in the lateral side arms of (L<sup>3</sup>)<sup>-</sup> to amine functions in (L<sup>4</sup>)<sup>-</sup> can be used to adjust the type and number of their active coordination sites. The dichloro-complex [(L<sup>3</sup>)Pd<sub>2</sub>(Cl)<sub>2</sub>]<sup>+</sup> exhibits a rich coordination chemistry as illustrated by the synthesis and structural characterization of the corresponding acetonitrile, isothiocyanato, azido, iodo, cyanide, and acetamido complexes. Finally, it has been demonstrated that the dinuclear palladium complex **4** catalyzes the vinyl-addition polymerisation of norbornene when activated with methylalumoxane (MAO) or B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>. Work in progress is now directed towards the elucidation of this polymerization mechanism. We think that such studies can aid in an understanding of cooperative effects in binuclear catalysis.

### Experimental

All manipulations were carried out using standard Schlenk techniques under a protective atmosphere of argon. Compound **3** was prepared as described in the literature.<sup>29</sup> All other reagents were purchased from commercial vendors and used without further purification. 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. <sup>1</sup>H and <sup>13</sup>C chemical shifts refer to solvent signals. <sup>31</sup>P NMR chemical shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> at δ = 0. 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 *t*BuL<sup>3</sup>

To a solution of 2-(diphenylphosphino)ethanamine (1.38 g, 6.02 mmol) in EtOH (20 mL) was added a solution of 5-*tert*-butyl-2-(*tert*-butylthio)benzene-1,3-dialdehyde (835 mg, 3.00 mmol) in

CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The reaction mixture was stirred for 24 h and evaporated to dryness to give a colorless oil. Yield: 2.10 g (>98%). This compound was used without further purification for the preparation of the metal complexes. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.08 (s, 9 H, C<sup>4</sup>H<sub>3</sub>), 1.27 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.40 (m, 4 H, C<sup>6</sup>H<sub>2</sub>), 3.70 (m, 4 H, C<sup>5</sup>H<sub>2</sub>), 7.25–7.43 (m, 20 H, PhH), 8.07 (s, 2 H, C<sup>8</sup>H), 9.05 (s, 2 H, C<sup>11</sup>H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ = 30.4 (d, <sup>1</sup>J<sub>CP</sub> = 15 Hz, C<sup>6</sup>), 31.6 (C<sup>1</sup>), 31.7(C<sup>4</sup>), 35.5 (C<sup>2</sup>), 49.7 (C<sup>3</sup>), 59.0 (d, <sup>2</sup>J<sub>CP</sub> = 25 Hz, C<sup>5</sup>), 127.2 (C<sup>10</sup>), 131.7 (C<sup>9</sup>), 141.5 (C<sup>8</sup>), 153.0 (C<sup>7</sup>), 162.7 (C<sup>11</sup>), 129.0 (PPh), 128.8 (d, J<sub>CP</sub> = 5 Hz, PPh), 133.2 (d, J<sub>CP</sub> = 20 Hz, PPh), 138.9 (d, J<sub>CP</sub> = 10 Hz, PPh). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>): δ = -18.3.

#### Preparation of *t*BuL<sup>4</sup>

To a solution of 2-(diphenylphosphino)ethanamine (211 mg, 0.92 mmol) in EtOH (30 mL) was added a solution of 5-*tert*-butyl-2-(*tert*-butylthio)benzene-1,3-dialdehyde (128 mg, 0.46 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). After stirring for 12 h, sodium borohydride (34 mg, 0.90 mmol) was added and the mixture was stirred for a further 2 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 8 by addition of 3 M KOH. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The organic fractions were combined, dried with K<sub>2</sub>CO<sub>3</sub> and evaporated to dryness to give a colourless oil. Yield: 200 mg (65%). This compound was used without further purification for the preparation of the metal complexes. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 1.15 (s, 9 H, C<sup>4</sup>H<sub>3</sub>), 1.21 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.21 (t, <sup>3</sup>J = 7.7 Hz, 4 H, C<sup>6</sup>H<sub>2</sub>), 2.66 (dt, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, <sup>2</sup>J<sub>H,P</sub> = 7.7 Hz, 4 H, C<sup>5</sup>H<sub>2</sub>), 4.00 (bs, 4 H, C<sup>11</sup>H<sub>2</sub>), 7.29–7.44 (m, 22 H, PhH + C<sup>8</sup>H). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>): δ = -20.5.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>(Cl)<sub>2</sub>][ClO<sub>4</sub>] (4[ClO<sub>4</sub>])

To a solution of *t*BuL<sup>3</sup> (2.10 g, 3.00 mmol) in MeCN (200 mL) was added a solution of [Pd(NCMe)<sub>2</sub>Cl] (1.56 g, 6.00 mmol) in MeCN (50 mL). The reaction mixture was stirred for 2 days, evaporated to dryness, and the residue redissolved in DMF (5 mL). To this solution was added a solution of LiClO<sub>4</sub>·3H<sub>2</sub>O (7.00 g, 43.6 mmol) in MeOH (100 mL). The resulting yellow solid was filtered off, air-dried and recrystallized from MeCN. Yellow crystals. Yield: 1.70 g (1.66 mmol, 55%); mp 294 °C (decomp.). IR (KBr pellet): ν/cm<sup>-1</sup> 3436(br s), 3053(m), 2959(s), 2866(m), 1627(s) ν(C=N), 1540(m), 1478(m) ν(C=C), 1436(s) ν(P-C), 1400(m), 1365(w), 1337(w), 1312(w), 1275(w), 1232(m), 1193(w), 1100(vs) ν(ClO<sub>4</sub><sup>-</sup>), 997(w), 974(w), 946(w), 835(w), 749(m), 721(m), 689(m), 623(m), 548(m), 514(m), 476(m). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ = 1.35 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.59 (m, 2 H, C<sup>6</sup>HH), 2.64 (m, 2 H, C<sup>6</sup>HH), 4.05 (m, 2 H, C<sup>5</sup>HH), 4.21 (m, 2 H, C<sup>5</sup>HH), 7.51–7.68 (m, 12 H, PhH), 7.91–7.97 (m, 8 + 2 H, PhH + C<sup>8</sup>H), 8.68 (s, 2 H, C<sup>11</sup>H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>NO<sub>2</sub>): δ = 27.7 (d, <sup>1</sup>J<sub>CP</sub> = 49 Hz, C<sup>6</sup>), 30.8 (C<sup>1</sup>), 35.2 (C<sup>2</sup>), 64.5 (d, <sup>2</sup>J<sub>CP</sub> = 28 Hz, C<sup>5</sup>), 127.9 (C<sup>10</sup>), 129.0 (C<sup>9</sup>), 140.8 (C<sup>8</sup>), 150.0 (C<sup>7</sup>), 167.8 (C<sup>11</sup>); 130.2 (m, PPh), 133.6 (PPh), 134.3 (m, PPh), 134.6 (m, PPh). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, CD<sub>3</sub>NO<sub>2</sub>): δ = 48.95. Elemental analysis: calc. (%) for C<sub>40</sub>H<sub>41</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>S (1026.98): C 46.78, H 4.02, N 2.73, S 3.12; found C 47.00, H 4.12, N 2.84, S 2.59. This compound was additionally characterized by an X-ray crystal structure determination.

#### Preparation of [(L<sup>4</sup>)Pd<sub>2</sub>(μ-Cl)][ClO<sub>4</sub>]<sub>2</sub> (5[ClO<sub>4</sub>])

To a solution of *t*BuL<sup>4</sup> (200 mg, 0.284 mmol) in MeCN (30 mL) was added a solution of [Pd(NCMe)<sub>2</sub>Cl<sub>2</sub>] (147 mg, 0.568 mmol) in MeCN (10 mL). After stirring for 12 h at ambient temperature the solution was concentrated *in vacuo* and combined with a solution of LiClO<sub>4</sub>·3H<sub>2</sub>O (1.00 g, 6.23 mmol) in MeOH (50 mL). The resulting solid was filtered off, washed with MeOH and dried in air. Yield: 128 mg (41%); mp 210 °C (decomp). IR (KBr pellet): ν/cm<sup>-1</sup> 3425(br s), 3156(m) ν(N-H), 3056(m), 2960(s), 2931(m), 2903(w), 2867(w), 1658(m), 1470(m) ν(C=C), 1457(m), 1436(s) ν(P-C), 1407(m), 1152(w), 1137(m), 1088(vs) ν(ClO<sub>4</sub><sup>-</sup>), 998(w), 976(w), 928(w), 748(m), 723(m), 715(m), 692(s), 622(s). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ = 1.34 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.67 (m, 2 H, C<sup>6</sup>HH), 3.07 (m, 2 H, C<sup>6</sup>HH), 3.30 (m, 2 H, C<sup>11</sup>HH), 3.60 (m, 2 H, C<sup>11</sup>HH), 3.98 (m, 2 H, C<sup>5</sup>HH), 4.32 (m, 2 H, C<sup>5</sup>HH), 5.43 (bs, 2 H, NH), 7.34–7.89 (m, 22 H, PhH + C<sup>8</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, CDCl<sub>3</sub>): δ = 49.90. Elemental analysis: calc. (%) for C<sub>40</sub>H<sub>45</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>S (1095.01): C 43.87, H 4.14, N 2.56, S 2.93; found C 43.52, H 4.20, N 2.44, S 2.47. This compound was additionally characterized by an X-ray crystal structure determination.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>(MeCN)<sub>2</sub>][ClO<sub>4</sub>]<sub>3</sub> (6[ClO<sub>4</sub>])

To a solution of 4[ClO<sub>4</sub>] (513 mg, 0.500 mmol) in acetonitrile (100 mL) was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> (203 mg, 0.500 mmol) in acetonitrile (10 mL). The reaction mixture was stirred for 4 h and the resulting precipitate of PbCl<sub>2</sub> was removed by filtration. The yellow solution was evaporated to dryness and dried in vacuum to give an orange-red powder. The crude material could not be obtained in analytically pure form. IR (KBr pellet): ν/cm<sup>-1</sup> 3444(br s), 3058(m), 2964(s), 2929(s), 2869(w), 2326(m) ν(C≡N), 2298 ν(C≡N), 1685(w), 1624(s) ν(C=N), 1586(w), 1574(m), 1543(m), 1507(w), 1483(m) ν(C=C), 1436(s) ν(P-C), 1397(w), 1366(w), 1338(w), 1312(w), 1278(w), 1233(m), 1191(w), 1091(vs) ν(ClO<sub>4</sub><sup>-</sup>), 997(w), 948(w), 929(w), 910(w), 835(w), 814(w), 747(m), 728(m), 691(s), 625(s). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN): δ = 1.40 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 1.97 (s, 6 H, CH<sub>3</sub>CN), 2.64 (m, 2 H, C<sup>6</sup>HH), 2.73 (m, 2 H, C<sup>6</sup>HH), 4.10 (m, 2 H, C<sup>5</sup>HH), 4.24 (m, 2 H, C<sup>5</sup>HH), 7.52–7.71 (m, 12 H, PhH), 7.72–7.89 (m, 8 H, PhH), 8.05 (s, 2 H, C<sup>8</sup>H), 8.68 (s, 2 H, C<sup>11</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, CD<sub>3</sub>NO<sub>2</sub>): δ = 59.4.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>(SCN)<sub>2</sub>][ClO<sub>4</sub>] (7[ClO<sub>4</sub>])

To a solution of 4[ClO<sub>4</sub>] (103 mg, 0.100 mmol) in MeCN (20 mL) was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> (20.3 mg, 50.0 μmol) in MeCN (2 mL). The reaction mixture was stirred for 4 h before PbCl<sub>2</sub> was removed by filtration. To the yellow filtrate was added a solution of NaSCN (16.2 mg, 0.200 mmol) in 1% aqueous MeOH (20 mL). The solution was concentrated *in vacuo* to ca 10 mL, diluted with EtOH (10 mL), and concentrated again to a final volume of ≈5 mL. The resulting yellow solid was filtered off, washed with EtOH and dried in air. Yield: 66 mg (55%). IR (KBr pellet): ν/cm<sup>-1</sup> = 3443(br s), 3052(w), 2960(s), 2865(m), 2110(vs) ν(SCN<sup>-</sup>), 1628(s) ν(C=N), 1572(w), 1542(m), 1483(m) ν(C=C), 1435(s) ν(P-C), 1395(m), 1363(m), 1336(m), 1311(m), 1234(m), 1188(w), 1166(m), 1101(vs) ν(ClO<sub>4</sub><sup>-</sup>), 997(w), 978(w), 947(m), 833(m), 743(m), 726(m), 712(w), 689(s), 623(s). <sup>1</sup>H NMR

(200 MHz, CD<sub>3</sub>CN):  $\delta$  = 1.40 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.69 (m, 2 H, C<sup>6</sup>HH), 2.75 (m, 2 H, C<sup>6</sup>HH), 4.06 (m, 2 H, C<sup>5</sup>HH), 4.20 (m, 2 H, C<sup>5</sup>HH), 7.54–7.70 (m, 12 H, PhH), 7.82–7.95 (m, 8 H, PhH), 8.02 (s, 2 H, C<sup>8</sup>H), 8.77 (s, 2 H, C<sup>11</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, CD<sub>3</sub>CN):  $\delta$  = 51.8. Elemental analysis calcd (%) for C<sub>42</sub>H<sub>41</sub>ClN<sub>4</sub>O<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub>S<sub>3</sub>·2MeCN·3H<sub>2</sub>O (M = 1072.24 + 136.15): C 45.72, H 4.42, N 6.95; found C 45.16, H 4.35, N 7.57.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> (8[ClO<sub>4</sub>])

To a solution of 4[ClO<sub>4</sub>] (103 mg, 0.100 mmol) in MeCN (20 mL) was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> (20.3 mg, 50.0  $\mu$ mol) in MeCN (2 mL). The reaction mixture was stirred for 4 h before PbCl<sub>2</sub> was removed by filtration. To the yellow filtrate was added a solution of NaN<sub>3</sub> (13.0 mg, 0.200 mmol) in 1% aqueous MeOH (20 mL). The solution was concentrated *in vacuo* to *ca* 10 mL, diluted with EtOH (10 mL), and concentrated again to *ca* 5 mL. The resulting yellow solid was filtered off, washed with EtOH and dried in air. This material could not be obtained in analytically pure form. Yield: 78 mg (75%). IR (KBr pellet):  $\nu/\text{cm}^{-1}$  = 3429(br s), 3051(w), 2957(s), 2864(m), 2034(vs)  $\nu(\text{N}_3^-)$ , 2017(sh)  $\nu(\text{N}_3^-)$ , 1620(s)  $\nu(\text{C}=\text{N})$ , 1541(w), 1483(w)  $\nu(\text{C}=\text{C})$ , 1435(s)  $\nu(\text{P}-\text{C})$ , 1396(m), 1364(m), 1337(m), 1277(m), 1229(m), 1189(m), 1165(m), 1096(vs)  $\nu(\text{ClO}_4^-)$ , 997(w), 974(w), 833(m), 745(m), 726(m), 690(s), 623(s). <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 1.39 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.81 (m, 2 H, C<sup>6</sup>HH), 2.85 (m, 2 H, C<sup>6</sup>HH), 4.05 (m, 2 H, C<sup>5</sup>HH), 4.20 (m, 2 H, C<sup>5</sup>HH), 7.57–7.70 (m, 12 H, PhH), 7.94–8.04 (m, 8 H, PhH), 8.18 (s, 2 H, C<sup>8</sup>H), 9.04 (s, 2 H, C<sup>11</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 48.70.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>(I<sub>2</sub>)][ClO<sub>4</sub>]<sub>2</sub> (9[ClO<sub>4</sub>])

To a solution of 4[ClO<sub>4</sub>] (103 mg, 0.100 mmol) in MeCN (20 mL) was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> (20.3 mg, 50.0  $\mu$ mol) in MeCN (2 mL). The reaction mixture was stirred for 4 h before PbCl<sub>2</sub> was removed by filtration. To the yellow filtrate was added a solution of NBu<sub>4</sub>I (73.9 mg, 0.200 mmol) in 1% aqueous MeOH (20 mL). The solution was concentrated *in vacuo* to *ca* 10 mL, diluted with EtOH (10 mL), and concentrated again to *ca* 5 mL. The resulting yellow solid was filtered off, washed with EtOH and dried in air. Yield: 66 mg (63%). IR (KBr pellet):  $\nu/\text{cm}^{-1}$  = 3421(br s), 3049(w), 2961(m), 2920(m), 2864(m), 1614(s)  $\nu(\text{C}=\text{N})$ , 1536(m), 1481(w)  $\nu(\text{C}=\text{C})$ , 1434(s)  $\nu(\text{P}-\text{C})$ , 1393(m), 1363(w), 1333(m), 1310(w), 1272(m), 1189(m), 1152(m), 1095(vs)  $\nu(\text{ClO}_4^-)$ , 997(w), 972(w), 829(m), 745(m), 714(m), 689(s), 622(s). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN):  $\delta$  = 1.39 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.62 (m, 2 H, C<sup>6</sup>HH), 2.62 (m, 2 H, C<sup>6</sup>HH), 3.88 (m, 2 H, C<sup>5</sup>HH), 4.13 (m, 2 H, C<sup>5</sup>HH), 7.50–7.70 (m, 12 H, PhH), 7.85 (s, 2 H, C<sup>8</sup>H), 8.00–8.20 (m, 8 H, PhH), 7.85 (s, 2 H, C<sup>8</sup>H), 8.54 (s, 2 H, C<sup>11</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 49.30. Elemental analysis: calcd (%) for C<sub>40</sub>H<sub>41</sub>ClI<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub>S (1209.88): C 39.71, H 3.42, N 2.32, S 2.65; found C 40.29, H 3.41, N 2.52, S 1.82.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>(CN)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> (10[ClO<sub>4</sub>])

To a solution of 4[ClO<sub>4</sub>] (103 mg, 0.100 mmol) in MeCN (30 mL) was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> (20.6 mg, 50.0  $\mu$ mol) in MeCN (2 mL). The reaction mixture was stirred for 4 h before PbCl<sub>2</sub> was removed by filtration. To the yellow filtrate was added a solution of NaCN (12.3 mg, 0.250 mmol) in 1% aqueous MeOH (20 mL). The

reaction mixture was allowed to stir for 1 h at 60 °C and was then evaporated to dryness. The resulting yellow solid was recrystallized from a mixed MeCN–EtOH solvent system. Yield: 63 mg (62%); mp 280 °C (decomp.). IR (KBr pellet):  $\nu/\text{cm}^{-1}$  = 3421(bs), 3055(m), 2961(s), 2924(w), 2864(m), 2139(m)  $\nu(\text{C}\equiv\text{N}^-)$ , 1629(s)  $\nu(\text{C}=\text{N})$ , 1540(m), 1474(w)  $\nu(\text{C}=\text{C})$ , 1436(s)  $\nu(\text{P}-\text{C})$ , 1396(w), 1365(w), 1339(w), 1312(w), 1231(w), 1194(w), 1103(vs)  $\nu(\text{ClO}_4^-)$ , 998(w), 947(w), 831(w), 749(m), 725(m), 691(s), 624(s). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN):  $\delta$  = 1.37 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.73 (m, 2 H, C<sup>6</sup>HH), 2.79 (m, 2 H, C<sup>6</sup>HH), 4.06 (m, 2 H, C<sup>5</sup>HH), 4.21 (m, 2 H, C<sup>5</sup>HH), 7.52–7.67 (m, 12 H, PhH), 7.92–8.03 (m, 10 H, PhH + C<sup>8</sup>H), 8.77 (s, 2 H, C<sup>11</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, CD<sub>3</sub>CN):  $\delta$  = 51.70. Elemental analysis: calcd (%) for C<sub>42</sub>H<sub>41</sub>ClN<sub>4</sub>O<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub>S (1008.11): C 50.04, H 4.10, N 5.56, S 3.18; found C 50.03, H 4.42, N 5.28, S 2.76. This compound was additionally characterized by an X-ray crystal structure determination.

#### Preparation of [(L<sup>3</sup>)Pd<sub>2</sub>( $\mu_{1,3}$ -NHCOMe)][ClO<sub>4</sub>]<sub>2</sub> (11[ClO<sub>4</sub>])

To a solution of 4[ClO<sub>4</sub>] (103 mg, 0.100 mmol) in MeCN (50 mL) was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> (20.3 mg, 0.050 mmol) in MeCN (2 mL). The reaction mixture was stirred for 4 h before PbCl<sub>2</sub> was removed by filtration. To the yellow filtrate was added N<sup>n</sup>Bu<sub>4</sub>OH (260 mg of a 40% methanolic solution, 0.400 mmol). The resulting red solution was concentrated *in vacuo* to *ca* 2 mL, diluted with MeOH (10 mL), and kept for 5 days at room temperature. The resulting red crystals were filtered off, washed with MeOH and dried in air. Yield: 34.5 mg (30%). IR (KBr pellet):  $\nu/\text{cm}^{-1}$  = 3435(bs), 3363(s)  $\nu(\text{N}-\text{H})$ , 3056(m), 2961(s), 2932(m), 2863(w), 1632(s)  $\nu(\text{C}=\text{N})$ , 1571(s)  $\nu_{\text{asym}}(\text{MeCONH}^-)$ , 1512(w), 1481(s)  $\nu(\text{C}=\text{C})$ , 1436(s)  $\nu(\text{P}-\text{C})$ , 1397(w), 1364(m)  $\nu_{\text{symm}}(\text{MeCONH}^-)$ , 1311(w), 1278(w), 1233(m), 1189(w), 1169(w), 1093(vs)  $\nu(\text{ClO}_4^-)$ , 997(w), 952(w), 832(w), 746(m), 729(m), 692(s), 622(s). <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  = 1.42 (s, 9 H, C<sup>1</sup>H<sub>3</sub>), 2.08 (s, 3 H, CH<sub>3</sub>CONH), 2.72 (m, 2 H, C<sup>6</sup>HH), 2.83 (m, 2 H, C<sup>6</sup>HH), 4.43 (m, 2 H, C<sup>5</sup>HH), 4.52 (m, 2 H, C<sup>5</sup>HH), 6.02 (m, 1 H, CH<sub>3</sub>CONH), 7.62–7.73 (m, 12 H, ArH), 7.85–7.96 (m, 8 H, Ph), 8.16 (s, 2 H, C<sup>8</sup>H), 8.65 (s, 1 H, C<sup>11</sup>H), 8.87 (s, 1 H, C<sup>11</sup>H). <sup>31</sup>P{<sup>1</sup>H} NMR (81.014 MHz, CD<sub>3</sub>NO<sub>2</sub>):  $\delta$  = 49.42, 48.14. Elemental analysis: calcd (%) for C<sub>42</sub>H<sub>45</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>9</sub>P<sub>2</sub>Pd<sub>2</sub>S·2H<sub>2</sub>O (1113.58 + 36.03): C 43.88, H 4.30, N 3.66; found C 43.51, H 4.37, N 3.97.

#### Polymerization experiments

Norbornene (Aldrich) was purified by distillation and used as a solution in toluene. Toluene was dried over sodium metal, distilled and stored under nitrogen. The pre-catalyst **4** was applied as a solution in methylene chloride (dried over CaH<sub>2</sub>, distilled under argon). A Schlenk-flask was charged with the norbornene solution in toluene. For MAO (10% solution in toluene, Witco) the cocatalyst solution and after 1 min the solution of the pre-catalyst was added *via* syringe. For B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> the solution of the pre-catalyst followed by the separate co-catalyst components [B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Aldrich) and AlEt<sub>3</sub> (1 mol l<sup>-1</sup> solution in hexane, Merck–Schuchardt)] were quickly added *via* syringe. The reaction mixture was stirred with a magnetic stirrer. The polymerization was stopped through the addition of 30–40 mL of a 10 : 1 methanol–conc. HCl mixture. The precipitated polymer was filtered off, washed with methanol and dried *in vacuo* for 5 h.

Polymerizations were conducted at room temperature in a water bath to ensure a constant temperature during the reaction. The IR spectra of the poly(norbornene)s obtained showed the absence of a double bond at 1620 cm<sup>-1</sup> to 1680 cm<sup>-1</sup>. This absence assured that a vinyl/addition polymerization instead of a ring-opening metathesis polymerization (ROMP) had occurred. The conversion was calculated by gravimetric analysis of the polymer.

### X-Ray crystallography

Crystals of **4**[ClO<sub>4</sub>].EtOH, **9**[ClO<sub>4</sub>] and **10**[ClO<sub>4</sub>].EtOH suitable for X-ray crystallography were grown by slow evaporation of a mixed acetonitrile–ethanol solvent system. Crystals of **5**[ClO<sub>4</sub>]<sub>2</sub> were obtained by slow evaporation of a methanolic solution. Crystals of **11**[ClO<sub>4</sub>]<sub>2</sub>.MeCN.MeOH were obtained from a mixed acetonitrile–methanol solvent system. The diffraction experiments were carried out at 180(2) K on a BRUKER CCD X-ray diffractometer using Mo-K $\alpha$  radiation. The data were processed with SAINT<sup>30</sup> and corrected for absorption using SADABS.<sup>31</sup> Structures were solved by direct methods and refined by full-matrix least-squares on the basis of all data against  $F^2$  using SHELXL-97.<sup>32</sup> H atoms were placed in calculated positions and treated isotropically using the 1.2-fold  $U_{\text{iso}}$  value of the parent atom except for the methyl protons, which were assigned the 1.5-fold  $U_{\text{iso}}$  value of the parent C atoms. All non-hydrogen atoms were refined anisotropically.

In the crystal structure of **9**[ClO<sub>4</sub>] the ClO<sub>4</sub><sup>-</sup> anion was found to be severely disordered over two positions. It has not been possible to refine the two orientations. Therefore, the O atoms were placed in calculated positions (equal Cl–O and O...O distances, respectively) and treated isotropically (AFIX 3 instruction implemented in SHELXL) using the 1.2-fold  $U_{\text{iso}}$  value of the parent chlorine atom. The site occupancies were calculated to be 0.35(1) (for Cl(a)O(1a)–O(4a)) and 0.65(1) (for Cl(b)O(1b)–O(4b)).

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613789j

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