

# Reactivity of di(azido)bis(phosphine) complexes of Ni(II), Pd(II) and Pt(II) toward organic isothiocyanates: synthesis, structures, and properties of bis(tetrazole-thiolato) and bis(isothiocyanato) complexes

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Di(azido)bis(phosphine) complexes of Group 10 metals  $\{M(N_3)_2(PR_3)_2\}$  underwent substitution with trimethylsilyl isothiocyanate ( $Me_3Si-NCS$ ) to give the corresponding bis(isothiocyanato) complexes,  $M(NCS)_2L_2$  ( $M = Pd$ ,  $L = PMe_3$  (**1**),  $PEt_3$  (**2**),  $PMe_2Ph$  (**3**);  $M = Ni$ ,  $L = PMe_3$  (**4**);  $M = Pt$ ,  $L = PEt_3$  (**5**)), in which the isothiocyanato ligand is N-bound to the metal. By contrast, the bis(azido) complexes of Pd(II) and Pt(II) underwent 1,3-cycloaddition with organic isothiocyanates ( $R-NCS$ ) to give tetrazole-containing thiolato complexes,  $M\{S[CN_4(R)]\}_2L_2$  ( $M = Pd$ ,  $L = PMe_3$ ,  $R = allyl$  (**6**), benzyl (**7**), ethyl (**8**), phenyl (**9**), 2,6-dimethylphenyl (**10**);  $L = PMe_2Ph$ ,  $R = phenyl$  (**11**);  $L = PEt_3$ ,  $R = 2,6$ -dimethylphenyl (**12**);  $M = Pt$ ,  $L = PMe_3$ ,  $R = Ph$  (**13**), Et (**14**);  $L = PEt_3$ ,  $R = Ph$  (**15**)). The chelating phosphine analogues,  $M\{S[CN_4(R)]\}_2L_2$  ( $L-L = depe$  (1,2-bis(diethylphosphino)ethane):  $R = Ph$ ,  $M = Pd$  (**16**),  $Pt$  (**17**);  $R = 2,6$ -dimethylphenyl,  $M = Pt$  (**18**)) could also be obtained. Molecular structures of **6**, **9**, **14** and **18** clearly show the S-coordination of the thiolato ligands in these complexes. Treatments of tetrazole-thiolate complexes with benzoyl halide derivatives afforded various organic sulfides

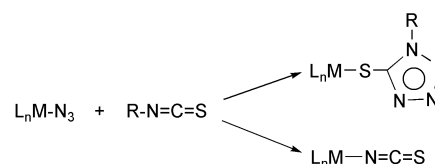
## Introduction

Metal-azido complexes have been an interesting subject for many decades due to their analogous behavior to those of organic azides, including cycloaddition with dipolar nucleophiles or electrophiles and thermal or photo-initiated decomposition to metal nitrides or cluster compounds.<sup>1</sup> Various unsaturated reagents (such as nitriles, alkynes and isocyanides) undergo cycloaddition reactions to the coordinated azido ligand to give a variety of heterocycles.<sup>2-13</sup> In particular, organic isothiocyanates ( $R-NCS$ ) are well known useful reagents for heterocycle formation by dipolar cycloaddition or electrophilic addition.

Recently, we have reported the cycloaddition reaction of azido or di(azido)bis(phosphine) complexes of Ni(II), Pd(II) and Pt(II) with various organic isocyanides.<sup>14</sup> We have also reported that those reactions give complexes containing C-coordinated (five-membered) tetrazolato rings or carbodiimido ( $N=C=N$ ) groups by dipolar cycloaddition, depending upon the nature of the isocyanide. These results prompted us to extend our scope of the dipolar cycloaddition of organic isothiocyanates into the azido ligand, leading to the formation of heterocycles. Although several studies regarding the dipolar cycloaddition of organic isothiocyanates into the azido ligand have been carried out,<sup>3,8,12,15,16</sup> the formation of thiolato complexes containing a tetrazole ring, which has a direct metal-sulfur bond, has not been reported. Even in organic chemistry, the number of cases for the formation of tetrazole-containing thiolato (or tetrazolethiolate) compounds is quite limited.<sup>17</sup>

Beck *et al.* previously prepared anionic Pd(II) and Pt(II) as well as neutral Au(III), Cu(I), Ag(I) and Hg(II) thiolato complexes containing tetrazole rings by the metathesis of metal halides with alkali metal salts of tetrazole mercaptan or by the reactions of metal halides with alkyl mercaptans in the presence of amine.<sup>18</sup> Recently, Nöth *et al.* reported several crystal structures of the above tetrazole-thiolato complexes.<sup>19</sup> In this work, we have found that di(azido)bis(phosphine) complexes of Group 10 metals react with organic isothiocyanates to give

tetrazole-containing thiolato complexes or isothiocyanato complexes, depending upon the nature of organic isothiocyanates (Scheme 1).



Scheme 1

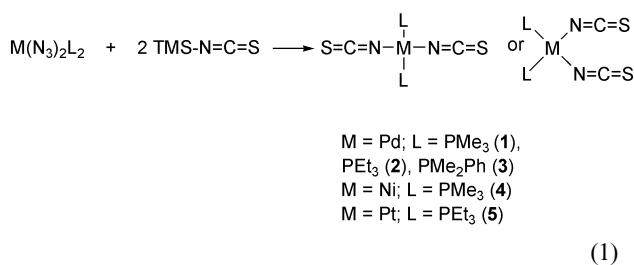
Herein, we report the synthesis and structures of tetrazole-containing thiolato complexes of Pd(II) and Pt(II) as well as isothiocyanato complexes of the Group 10 metal triad. We also report the reactivity of these complexes toward electrophiles, leading to the formation of organic sulfides. Our synthetic strategy for preparing metal-isothiocyanato complexes is expected to apply to the preparation of other metal complexes, and it may be an alternative to the known metathesis reaction that requires relatively vigorous conditions.

## Results and discussion

### Reactions of di(azido)bis(phosphine) complexes of Ni(II), Pd(II) and Pt(II) with organic isothiocyanates

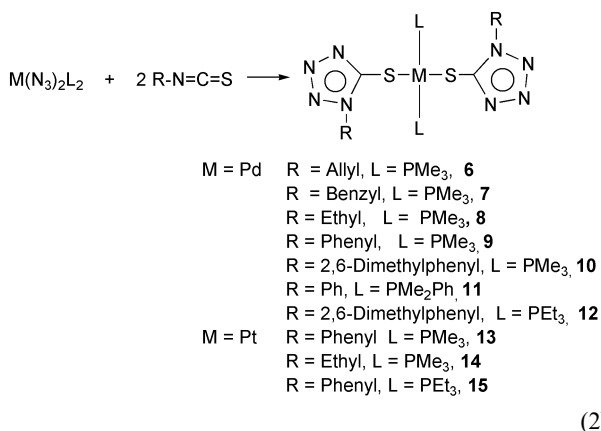
Treating di(azido)-Pd(II), -Ni(II) and -Pt(II) complexes with two equivalents of trimethylsilyl isothiocyanate ( $Me_3Si-NCS$ ) gave the corresponding bis(isothiocyanato) complexes,  $M(NCS)_2L_2$ , in high yields (eqn. (1)).

These reactions proceed smoothly at room temperature. Isolated complexes **1-5** have been characterized by IR, NMR, and elemental analyses. IR spectra of these complexes show strong absorption bands at 2077–2098  $cm^{-1}$  due to the  $N=C=S$  group, which is shifted to a higher wavenumber compared with  $\nu(N_3)$  at ca. 2030  $cm^{-1}$  of the starting material. The values are similar to those reported for other isothiocyanato complexes.<sup>20</sup>



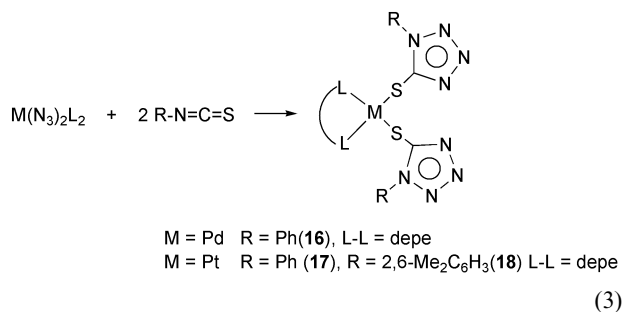
(1)

<sup>13</sup>C{<sup>1</sup>H} NMR spectra display a signal at *ca.* 130 ppm corresponding to the carbon atom of the NCS group. <sup>31</sup>P NMR spectra exhibit the presence of geometric isomers of *trans*- and *cis*-M(NCS)<sub>2</sub>L<sub>2</sub>, depending upon the metal or ligand. Also, the amount of Me<sub>3</sub>SiN<sub>3</sub> formed was identified by GC and compared with a genuine sample. The isothiocyanato complexes are generally obtained by the metathesis of metal halides with KSCN in alcoholic or aqueous media. However, those metathesis reactions frequently give various linkage isomers such as S-coordinated or S,N-mixed coordinated complexes including geometrical isomers. In contrast, our reactions smoothly proceed in organic solvents and undesirable linkage isomers such as M(NCS)(SCN)L<sub>2</sub> and M(SCN)<sub>2</sub>L<sub>2</sub> are not formed.<sup>21–24</sup> To our best knowledge, there is only one example of introduction of an isothiocyanato group into Rh complexes using trimethylsilyl isothiocyanate in organic solvents.<sup>25</sup> Therefore, our synthetic method seems to be a relatively simple and straightforward tool to introduce the isothiocyanato group into transition-metal complexes without forming undesirable linkage isomers. We have carried out similar reactions of di(azido)-bis(phosphine) complexes of Pd(II) and Pt(II) with organic isothiocyanates possessing allyl, benzyl, ethyl, phenyl or 2,6-dimethylphenyl groups. Interestingly, these reactions gave tetrazole-containing thiolato complexes, cycloaddition products rather than substitution products (eqn. (2)).



(2)

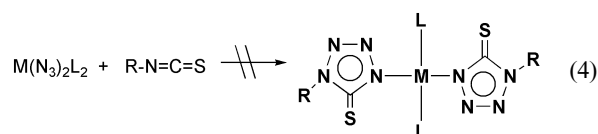
Di(azido)-Pd complexes smoothly react with organic isothiocyanates at room temperature to give the corresponding thiolato complexes. In contrast, the corresponding reaction of di(azido)-Pt(II) complexes at room temperature do not go to completion. However, the reactions at 60 °C for 5 h give a complete conversion to the bis(thiolato) complexes. Unfortunately, the yellow reaction product from Ni(N<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> and two equivalents of 2,6-dimethylphenyl isothiocyanate at room temperature strongly resists characterization because of its extremely poor solubility in organic solvents. In the cases of other organic isothiocyanates, we could identify the presence of the NCS group, presumably arising from the cleavage of the tetrazolato ring or the replacement of N<sub>3</sub> with the NCS group. Similar reactions of di(azido)-Pd(II) and -Pt(II) complexes containing chelating phosphines with organic isothiocyanates also produced the corresponding bis(thiolato) complexes (eqn. (3)), but require longer reaction times or heating conditions (60 °C).



(3)

The formation of bis(tetrazole-thiolato) complexes was easily monitored by the IR spectra. IR spectra of the products do not show any characteristic bands at 2000–2100 cm<sup>-1</sup> due to the ν(N<sub>3</sub>) of starting materials or ν(N=C=S) of possible products, suggesting no replacement of N<sub>3</sub> with NCS. <sup>13</sup>C NMR spectra of all the products display a singlet at 157–161 ppm due to the carbon atom on the tetrazolato ring (CN<sub>4</sub>) bonded to sulfur. In addition, one signal in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the complexes strongly support the absence of geometrical isomers. Of course, the definitive evidence for the connectivity of atoms in products has been obtained from crystallographic studies of some (complexes **6,9,14** and **18**) of these thiolato complexes. Tables 1 and 2 show the analytical and NMR data of the thiolato complexes **6–18**.

Several research groups independently reported that Pd- and Ni-azido complexes reacted with phenyl (or methyl) isothiocyanate to give N-coordinated tetrazolato complexes by 1,3-cycloaddition of the isothiocyanate into the metal-azido bond.<sup>3,8,12,15,16</sup> However, the formation of S-coordinated thiolato compounds from metal-azido complexes and organic isothiocyanates by the dipolar cycloaddition of isothiocyanates to the coordinated azido bond has not been reported yet. In this work, we did not observe the formation of N-coordinated tetrazolato complexes as well as other N-bonded isomers (eqn. (4)). Instead, we have confirmed tetrazole-thiolato complexes to be a sole product in the reactions of di(azido)-Pd(II) and -Pt(II) complexes with organic isothiocyanates.



## Structures

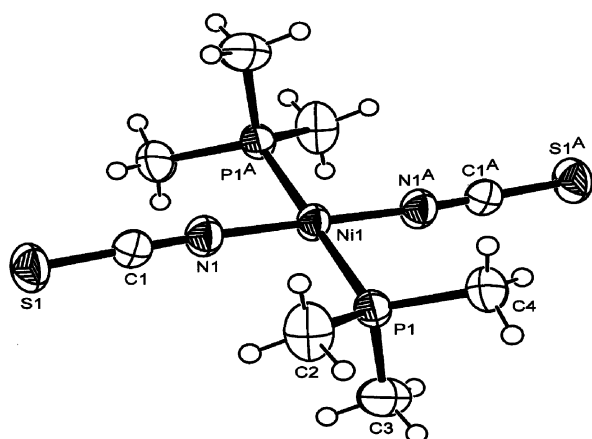
Molecular structures of **4–6, 9, 14** and **18** have been determined by X-ray crystallography. The crystal data and intensity data are given in Table 3. Figs. 1 and 2 show ORTEP drawings of **4** and **5**, which have *trans*- or *cis*-oriented square-planar geometry depending on the coordinated phosphine ligands. These ORTEP drawings clearly show the N-coordination of isothiocyanato ligands (NCS). The bond lengths of Ni–N (1.834(2) Å) in **4** and Pt–N (2.06(1) Å) in **5** are close to those in other terminal isothiocyanato complexes, Ni(NCS)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> (1.802(4) Å),<sup>24</sup> Ni(NCS)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1.819(3) Å),<sup>26</sup> and [Pt(NCS)-(PEt<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>-(C≡C)<sub>2</sub>) (2.024(9) Å).<sup>27</sup> As in the vast majority of other isothiocyanato complexes, complexes **4** and **5** have an essentially linear N=C=S ligand (179.4(2)° in **4** and 178(1)° in **5**). On the basis of the crystallographic data and <sup>31</sup>P NMR spectra of the complexes, we can rule out the possibility of the formation of other linkage isomers such as S-coordinated M(SCN)<sub>2</sub>L<sub>2</sub> or mixed coordinated M(SCN)(NCS)L<sub>2</sub> complexes both in solution and in the solid state.

Figs. 3–6 show the molecular structures of complexes **6, 9, 14** and **18**, respectively. The ORTEP drawings of these complexes clearly show the square-planar coordination, which has two phosphine and two thiolato ligands possessing a five-membered

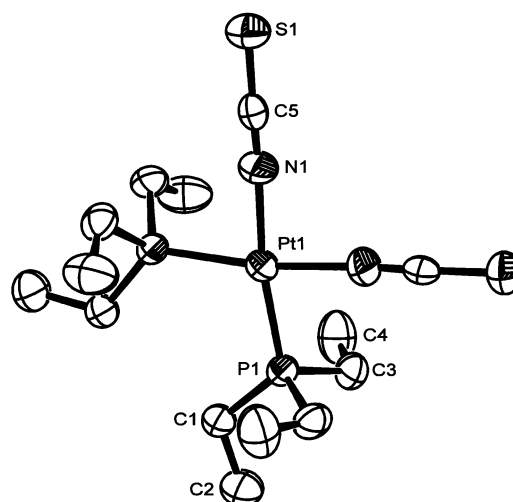
**Table 1** Colors, yields and analytical data for tetrazole-thiolato complexes **6–18**

Complex	Color	Yield (%)	Analyses <sup>a</sup> (%)		
			C	H	N
<b>6</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = allyl)	Yellow	75	31.39 (31.09)	5.31 (5.22)	21.02 (20.72)
<b>7</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = CH <sub>2</sub> Ph)	Yellow	81	41.24 (41.22)	5.05 (5.03)	17.50 (17.48)
<b>8</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = Et)	Yellow	88	27.82 (27.88)	5.46 (5.46)	21.34 (21.68)
<b>9</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = Ph)	Yellow	59	39.25 (39.19)	4.62 (4.60)	18.50 (18.28)
<b>10</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )	Yellow	45	43.27 (43.08)	5.52 (5.42)	16.95 (16.75)
<b>11</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (R = Ph)	Yellow	93	48.35 (48.88)	4.38 (4.38)	15.03 (15.20)
<b>12</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> (R = 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )	Yellow	72	48.01 (47.84)	6.47 (6.42)	14.90 (14.88)
<b>13</b> , Pt(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = Ph)	White	92	33.93 (34.24)	4.02 (4.02)	15.63 (15.97)
<b>14</b> , Pt(SCN <sub>4</sub> R) <sub>2</sub> (PMe <sub>3</sub> ) <sub>2</sub> (R = Et)	White	91	23.82 (23.80)	4.67 (4.66)	18.51 (18.5)
<b>15</b> , Pt(SCN <sub>4</sub> R) <sub>2</sub> (PEt <sub>3</sub> ) <sub>2</sub> (R = Ph)	White	64	39.70 (39.74)	5.21 (5.13)	13.95 (14.26)
<b>16</b> , Pd(SCN <sub>4</sub> R) <sub>2</sub> (depe) (R = Ph)	White	76	43.08 (43.21)	5.29 (5.14)	16.29 (16.80)
<b>17</b> , Pt(SCN <sub>4</sub> R) <sub>2</sub> (depe) (R = Ph)	White	66	38.37 (38.14)	4.65 (4.53)	14.58 (14.83)
<b>18</b> , Pt(SCN <sub>4</sub> R) <sub>2</sub> (depe)·2H <sub>2</sub> O (R = 2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> )	White	92	39.88 (39.66)	5.04 (5.47)	12.39 (13.22)

<sup>a</sup> Calculated values are given in parentheses.



**Fig. 1** ORTEP drawing<sup>34</sup> of **4** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ni1–N1 1.834(2), Ni1–P1 2.2287(6), S1–C1 1.621(2), N1–C1 1.157(3); N1–Ni1–P1 90.98(6), C1–N1–Ni1 176.07(19), N1–C1–S1 179.4(2).



**Fig. 2** ORTEP drawing of **5** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pt1–N(1) 2.06(1), Pt1–P1 2.263(3), S1–C5 1.61(1), N1–C5 1.14(1); N1#1–Pt1–N1 87.1(6), N1–Pt1–P1 171.4(3), N1–Pt1–P1#1 84.3(3), P1–Pt1–P1#1 104.4(2), N1–C5–S1 178(1).

(2-substituted) tetrazole ring. The two tetrazole rings (CN<sub>4</sub>) in Figs. 3–5 are mutually *trans* and oriented perpendicular to the molecular plane, probably to minimize steric repulsion between two phosphines and the two alkyl groups attached to the tetrazole rings. The equatorial plane in Fig. 3, defined by two P, two S, and Pd atoms is almost planar with an average atomic displacement of 0.0063 Å, and the Pd metal lies on the crystallographic center of symmetry.

Recently, Nöth *et al.*<sup>19</sup> reported several crystal structures of neutral and anionic tetrazole-thiolate complexes of transition metals. However, for Group 10 metals, there has been only one anionic tetrazole-thiolate complex, Pd(SCN<sub>4</sub>Me)<sub>4</sub><sup>2-</sup>, and the corresponding neutral complexes have not been reported. The Pd–S bond lengths {2.342(7) Å for **6** and 2.325(8) Å for **9**} and Pt–S bond lengths {2.337(1) Å for **14** and 2.365(3) Å for **18**} are close to those for other tetrazole-thiolato complexes: anionic

Pd(SCN<sub>4</sub>Me)<sub>4</sub><sup>2-</sup> (2.332(1) and 2.339(1) Å), neutral Au(SCN<sub>4</sub>Me)(PPh<sub>3</sub>) (2.325(1) Å) and Au(SCN<sub>4</sub>Ph)(PPh<sub>3</sub>) (2.304(2) Å). However, these bond lengths are much shorter than those in Ag (2.530(1) Å) or Hg (2.566(3) Å)<sup>19</sup> tetrazole-thiolates. The M–S–C bond angle (100.14(9)°) of **6** is smaller than those of **9** (105.3(10)°), **14** (102.2(2)°) and **18** (102.3(4)°), suggesting higher steric hindrance of the 2-allyl group on the tetrazolato ring than those of other 2-substituents, and these M–S–C bond angles fall in the range (97.5–106.9°) as found for other neutral tetrazole-thiolates.<sup>19</sup>

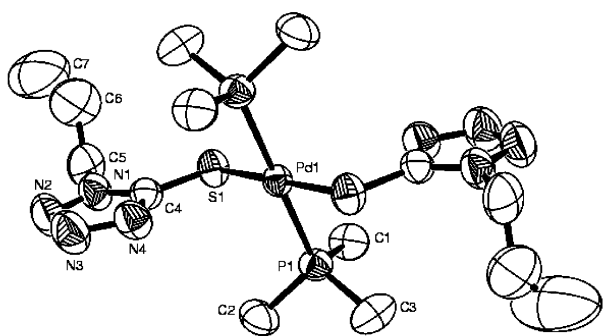
### Chemical properties

We have examined the reactivity of tetrazole-thiolate complexes toward several electrophiles to gain insight into their chemical properties and potential applications to organic synthesis.

**Table 2** NMR data ( $\delta$ ,  $J/\text{Hz}$ ) of tetrazole-thiolato complexes 6–18

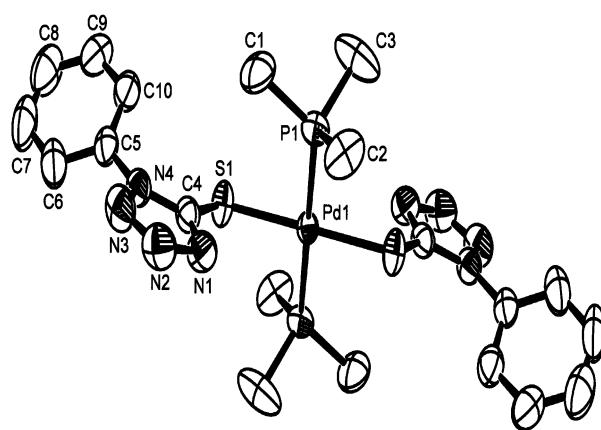
Complex	$^1\text{H NMR}^a$		$^{13}\text{C}\{^1\text{H}\}^b$	$^{31}\text{P}\{^1\text{H}\}^c$
	$\text{PR}_3$ (R = Me, Et)	Others		
6	1.35 (t, 18H, $J = 4$ )	4.93 (dt, 4H, $J = 1.6, 3, \text{CH}_2$ ) 5.25 (dd, 4H, $J = 0.9, 1, \text{CH}_2$ ) 6.00 (m, 2H, CH)	13.3 (t, $J = 16, \text{CH}_3$ ) 49.2, 119.5, 130.5, 159.4 (s, $\text{CN}_4$ )	-11.1
7	1.14 (t, 18H, $J = 4$ )	5.46 (s, 4H, $\text{CH}_2$ ) 7.27 (m, 10H, Ph)	13.2 (t, $J = 16, \text{CH}_3$ ), 50.8, 128.3, 128.5, 128.6, 134.3, 159.5 (br, $\text{CN}_4$ )	-11.5
8	1.36 (t, 18H, $J = 4$ )	1.52 (t, 6H, $J = 7.2, \text{CH}_3$ ) 4.36 (q, 4H, $J = 7.3, \text{CH}_2$ )	13.4 (t, $J = 16, \text{CH}_3$ ) 14.4, 42.4, 158.9 (s, $\text{CN}_4$ )	-11.2
9	1.37 (t, 18H, $J = 4$ )	7.27–7.59 (m, 6H, Ph) 7.85–7.89 (m, 4H, Ph)	13.5 (t, $J = 16, \text{CH}_3$ ), 123.5, 129.0, 129.3, 135.4, 159.4 (s, $\text{CN}_4$ ) 160.9 (s, $\text{CN}_4$ )	-11.0
10	1.41 (t, 18H, $J = 4$ )	2.04 (s, 12H, $\text{CH}_3$ ) 7.20–7.23 (m, 4H, Ph) 7.31–7.38 (m, 2H, Ph)	13.6 (t, $J = 16, \text{CH}_3$ ), 17.8, 128.6, 130.2, 133.1, 135.9, 160.8 (s, $\text{CN}_4$ )	-11.5
11	1.74 (t, 12H, $J = 4$ )	7.20–7.26 (m, 6H, Ph) 7.40–7.54 (m, 14H, Ph)	12.7 (t, $J = 16, \text{CH}_3$ ), 123.3, 127.8 (t, $J = 4$ ), 128.7, 128.9, 129.8, 130.8 (t, $J = 6$ ), 160.9 (s, $\text{CN}_4$ )	-1.37
12	1.10 (q, 18H, $J = 7$ ) 1.79 (m, 12H)	2.05 (s, 12H, $\text{CH}_3$ ) 7.21–7.26 (m, 4H, Ph) 7.33–7.38 (m, 2H, Ph)	8.1, 13.9 (t, $J = 14, \text{CH}_2$ ), 17.7, 128.6, 130.3, 133.2, 135.9, 160.4 (s, $\text{CN}_4$ )	16.4
13	1.44 (t, 18H, $J = 4$ )	7.47–7.59 (m, 6H, Ph) 7.80–7.84 (m, 4H, Ph)	12.6 (t, $J = 19, \text{CH}_3$ ), 123.7, 129.1, 129.3, 135.2, 157.7 (s, $\text{CN}_4$ )	-14.8 ( $J_{\text{Pt-P}} = 2402$ )
14	1.43 (t, 18H, $J = 4$ ) $J_{\text{Pt-P}} = 28$	1.52 (t, 6H, $J = 7, \text{CH}_3$ ) 4.35 (q, 4H, $J = 7, -\text{CH}_2$ )	12.5 (t, $J = 19, J_{\text{Pt-P}} = 30$ ), 14.4 (s, $\text{CH}_3$ ), 42.4 (s, $\text{CH}_2$ ), 157.2 (s, $\text{CN}_4$ )	-14.9 $J_{\text{Pt-P}} = 2386$
15	1.22 (m, 18H) 2.04 (m, 12H)	7.28–7.41 (m, 6H, Ph) 7.56–7.63 (m, 4H, Ph)	8.5 (s, $J_{\text{Pt-C}} = 22, \text{CH}_3$ ), 16.5 (br q, $\text{CH}_3$ ), 123.9, 128.5, 128.9, 135.4, 159.2 (s, $\text{CN}_4$ )	10.5 ( $J_{\text{Pt-P}} = 3054$ )
16	1.21 (t, 6H, $J = 8$ ) 1.27 (t, 6H, $J = 8$ ) 1.92–2.22 (m, 12H)	7.36–7.45 (m, 6H, Ph) 7.72–7.75 (m, 4H, Ph)	8.9 (br d, $J = 1, \text{CH}_3$ ), 19.4 (d, $J = 28, \text{CH}_2$ ), 23.7 (dd, $J = 14, 29, \text{CH}_2$ ), 124.2, 128.5, 128.8, 135.6, 159.8 (s, $\text{CN}_4$ )	72.8
17	1.11 (t, 6H, $J = 8$ ) 1.17 (t, 6H, $J = 8$ ) 1.80–2.15 (m, 12H)	7.35–7.46 (m, 6H, Ph) 7.66–7.69 (m, 4H, Ph)	8.8 (dd, $J = 1, J_{\text{Pt-C}} = 25, \text{CH}_3$ ) 18.7 (d, $J = 36, J_{\text{Pt-C}} = 31, \text{CH}_3$ ) 23.6 (d, $J = 9, 36, \text{CH}_2$ ), 124.7, 128.7, 128.9, 135.4, 158.0 (s, $\text{CN}_4$ )	54.1 ( $J_{\text{Pt-P}} = 3036$ )
18	1.19 (t, 6H, $J = 8$ ) 1.25 (t, 6H, $J = 8$ ) 1.82–2.39 (m, 12H)	1.88 (s, 12H, $\text{CH}_3$ ) 7.08–7.11 (m, 4H, Ph) 7.22–7.27 (m, 2H, Ph)	9.0 (br d, $J = 1, J_{\text{Pt-C}} = 27, \text{CH}_3$ ) 17.9 (s, $\text{CH}_3$ ) 19.0 (d, $J = 36, J_{\text{Pt-C}} = 34, \text{CH}_3$ ) 23.6 (dd, $J = 9, 36, \text{CH}_2$ ), 128.2, 129.9, 133.3, 136.2, 160.3 (s, $\text{CN}_4$ )	53.7 ( $J_{\text{P-P}} = 3076$ )

<sup>a</sup> Obtained in  $\text{CDCl}_3$  at 25 °C. Peak positions were referenced to internal  $\text{SiMe}_4$ . <sup>b</sup> Obtained in  $\text{CDCl}_3$  at 25 °C. Peak positions were referenced to external 85%  $\text{H}_3\text{PO}_4$ . Abbreviation: t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet.



**Fig. 3** ORTEP drawing of 6 showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–P1 2.3237(7), Pd1–S1 2.3415(7), S1–C4 1.717(3), N1–C4 1.343(3), N1–N2 1.352(4), N2–N3 1.276(4), N3–N4 1.359(4), N4–C4 1.326(4); P1–Pd1–S1 87.32(3), C4–S1–Pd1 100.14(9).

Treatment of 9 and 10 with two equivalents of benzoyl chloride ( $\text{PhCOCl}$ ) at room temperature give organic sulfides,  $\text{C}_6\text{H}_5(\text{CO})\text{S}-\text{CN}_4-\text{C}_6\text{H}_5$  (19, 88%) and  $\text{C}_6\text{H}_5(\text{CO})\text{S}-\text{CN}_4-2,6\text{-Me}_2\text{C}_6\text{H}_3$  (20, 85%), respectively (eqn. (5)). In addition, complex 9 reacts with two equivalents of 2-thiophenecarbonyl chloride ( $\text{C}_4\text{H}_3\text{SCOCl}$ ) to give  $\text{C}_4\text{H}_3\text{S}(\text{CO})\text{S}-\text{CN}_4-\text{C}_6\text{H}_5$  (21, 79%). However, the reaction of 9 with iodobenzene does not occur and results only in the recovery of the starting material.



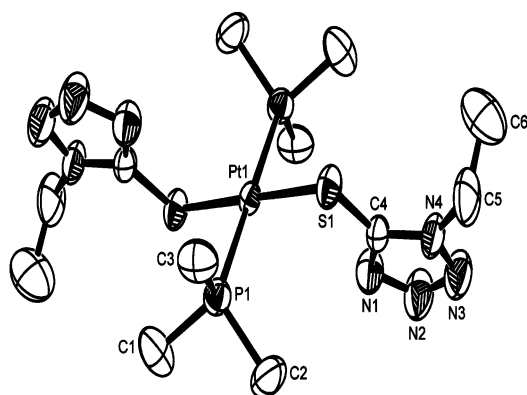
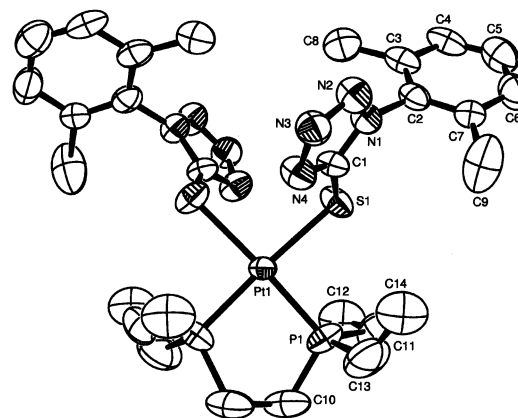
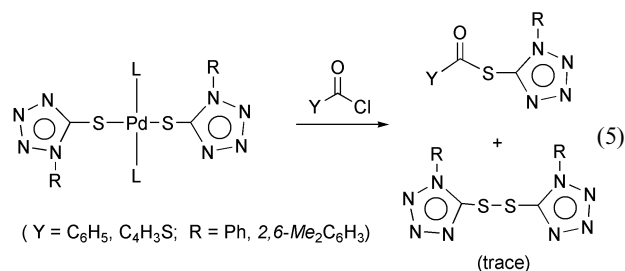
**Fig. 4** ORTEP drawing of 9 showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–S1 2.3248(8), Pd1–P1 2.3341(8), S1–C4 1.719(3), N1–C4 1.328(4), N1–N2 1.362(4), N2–N3 1.288(4), N3–N4 1.361(3), N4–C4 1.357(4), N4–C5 1.439(4); S1–Pd1–P1 93.91(3), C4–S1–Pd1 105.25(10).

These organic sulfides are isolated as white crystals without requiring column chromatography and have been characterized by IR, NMR, and elemental analyses. Compound 20 has been

**Table 3** X-Ray data collection and structure refinement for **4–6, 9, 14** and **18**

	<b>4</b>	<b>5·H<sub>2</sub>O</b>	<b>6</b>	<b>9</b>	<b>14</b>	<b>18·2H<sub>2</sub>O</b>
Formula	C <sub>8</sub> H <sub>18</sub> N <sub>2</sub> P <sub>2</sub> S <sub>2</sub> Ni	C <sub>14</sub> H <sub>32</sub> N <sub>2</sub> OP <sub>2</sub> S <sub>2</sub> Pt	C <sub>14</sub> H <sub>28</sub> N <sub>8</sub> P <sub>2</sub> PdS <sub>2</sub>	C <sub>20</sub> H <sub>28</sub> N <sub>8</sub> P <sub>2</sub> S <sub>2</sub> Pd	C <sub>12</sub> H <sub>28</sub> N <sub>8</sub> P <sub>2</sub> S <sub>2</sub> Pt	C <sub>28</sub> H <sub>46</sub> N <sub>8</sub> O <sub>2</sub> P <sub>2</sub> PtS <sub>2</sub>
<i>M<sub>w</sub></i>	327.01	565.57	540.90	612.96	605.57	847.88
<i>T/K</i>	293(2)	293(2)	293(2)	293(2)	293(2)	2939(2)
Crystal size/mm	0.28 × 0.22 × 0.16	0.08 × 0.08 × 0.08	0.62 × 0.60 × 0.42	0.32 × 0.30 × 0.28	0.16 × 0.14 × 0.12	0.24 × 0.20 × 0.16
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P4<sub>2</sub>/nmc</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>	<i>C222<sub>1</sub></i>
<i>a/Å</i>	6.183(1)	12.207(2)	12.015(2)	6.191(1)	11.367(2)	12.155(3)
<i>b/Å</i>	7.292(1)	12.207(2)	8.3887(4)	17.205(3)	8.531(1)	19.510(5)
<i>c/Å</i>	16.744(3)	16.112(6)	11.8788(9)	12.664(2)	11.587(2)	15.766(3)
$\beta/^\circ$	91.91(2)		96.75(1)	100.53(2)	93.63(1)	
<i>V/Å<sup>3</sup></i>	754.5(2)	2401(1)	1188.9(2)	1326.1(4)	1121.3(3)	3739(1)
<i>Z</i>	2	4	2	2	2	4
<i>D<sub>c</sub>/g cm<sup>-3</sup></i>	1.439	1.565	1.511	1.535	1.794	1.506
$\mu/\text{mm}^{-1}$	1.749	6.154	1.107	1.003	6.599	3.986
<i>F</i> (000)	340	1112	552	624	592	1704
<i>T<sub>min</sub></i>	0.2464	0.2659	0.0319	0.4630	0.5727	0.4370
<i>T<sub>max</sub></i>	0.2892	0.2832	0.0536	0.4770	0.8699	0.8131
No. of reflns. measured	1458	1156	2186	2545	2066	1825
No. of reflns. unique	1329	1155	2075	2320	1963	1825
No. of reflns. with <i>I</i> > 2σ( <i>I</i> )	1235	708	1997	2032	1588	1682
No. of params. refined	71	66	125	151	115	189
Max. in Δρ/e Å <sup>-3</sup>	0.220	0.862	0.487	0.282	0.440	1.604
Min., in Δρ/e Å <sup>-3</sup>	-0.182	-0.529	-0.557	-0.343	-0.464	-0.570
GOF on <i>F</i> <sup>2</sup>	1.086	1.017	1.042	1.041	1.073	1.097
<i>R</i>	0.0237	0.0397	0.0263	0.0264	0.0242	0.0378
<i>wR</i> <sub>2</sub> <sup>a</sup>	0.0629	0.0814	0.0723	0.0638	0.0550	0.0963
<i>R</i> (all data)	0.0262	0.0805	0.0271	0.0325	0.0361	0.0424
<i>wR</i> <sub>2</sub> <sup>a</sup> (all data)	0.0646	0.0962	0.0731	0.0675	0.0600	0.0995

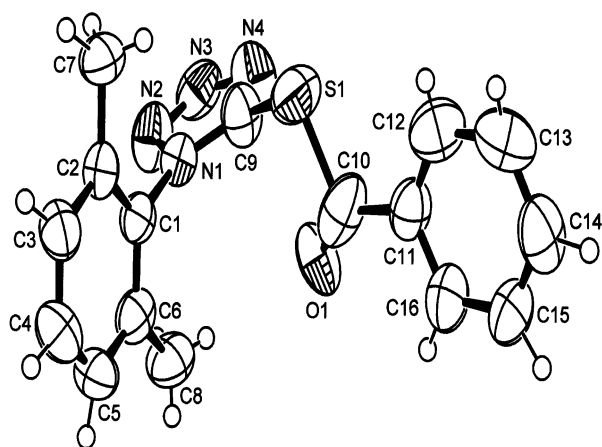
<sup>a</sup>  $wR_2 = \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]^{1/2}$ .


**Fig. 5** ORTEP drawing of **14** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): N4–C17 1.425(11), Pt1–P1 2.313(1), Pt1–S1 2.337(1), S1–C4 1.715(5), N1–C4 1.330(6), N1–N2 1.347(7), N2–N3 1.288(8), N3–N4 1.356(7), N4–C4 1.342(6), N4–C5 1.465(7); P1–Pt1–S1 87.65(5), C4–S1–Pt1 102.2(2).

**Fig. 6** ORTEP drawing of **18** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pt1–P1 2.227(3), Pt1–S1 2.365(3), S1–C1 1.741(12), N1–C1 1.312(13), N1–N2 1.352(13), N1–C2 1.450(15), N2–N3 1.257(15), N3–N4 1.374(14), N4–C1 1.292(17), P1–Pt1–S1 90.93(12), C1–S1–Pt1 102.3(4).


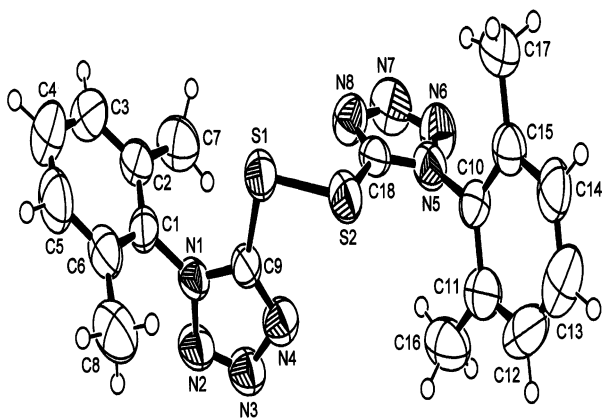
structurally characterized by X-ray diffraction, and its ORTEP drawing in Fig. 7 gives definitive evidence for the proposed structure. Interestingly, treatment of **10** with benzoyl chloride affords a dithio compound, [SCN<sub>4</sub>-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub> (**22**), although in a trace amount (Fig. 8). The present results do not give detailed information about the mechanism, but the electrophilic acyl halide appears to have abstracted the thiolate

group, which might explain the formation of thioacyl compounds **19–21**. On the other hand, the formation of a dimeric compound **22** with an S–S bond, which is apparently a reductive-elimination product of the two thiolato groups, strongly suggests that the reaction proceeds *via* a three-coordinate intermediate ([Pd(PR<sub>3</sub>)(SCN<sub>4</sub>R)<sub>2</sub>]) formed by phosphine dissociation. Otherwise, complex **10** possessing *trans* thiolate ligands cannot fulfill the requirement of the *cis* orientation of the groups to be eliminated unless the reaction proceeds in an intermolecular fashion.

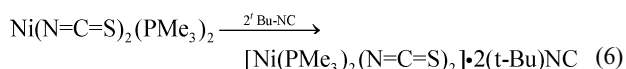
The coordinated isothiocyanato (NCS) ligand is known to react with various electrophiles to give isothiocyanide compounds,<sup>28</sup> but other chemical properties such as dipolar cycloaddition of pseudo-halides such as azide (N<sub>3</sub>) or cyanate (CN) are relatively unexplored. In this regard, we have investigated the cycloaddition reactivity of isothiocyanato complexes toward isocyanides to check whether heterocyclic compounds



**Fig. 7** ORTEP drawing of **20** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): S1–C9 1.779(7), S1–C10 1.807(9), O1–C10 1.090(11), N1–N2 1.329(7), N1–C9 1.345(8), N1–C1 1.467(7), N2–N3 1.297(8), N3–N4 1.301(9), N4–C9 1.293(9); C9–S1–C1 96.9(5).



**Fig. 8** ORTEP drawing of **22** showing the atom-labeling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): S1–S2 2.026(2), S1–C9 1.764(6), S2–C18 1.757(6), N1–C9 1.343(7), N1–N2 1.377(6), N2–N3 1.295(7), N3–N4 1.379(7), N4–C9 1.313(7), N5–C18 1.342(7), N5–N6 1.365(7), N6–N7 1.295(7), N7–N8 1.365(7), N8–C18 1.303(7); C9–S1–S2 100.6(2), C18–S2–S1 100.4(2).



are formed. The reaction of *trans*-Ni(NCS)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**4**) with two equivalents of *tert*-butyl isocyanide smoothly proceeds to give an isocyanide adduct, [Ni(PMe<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>]·2(*t*-Bu)NC (**23**), in 76% yield as shown in eqn. (6).

The IR spectrum of **23** displays two strong bands at 2051 and 2196 cm<sup>-1</sup> assigned to ν(N=C=S) and ν(N≡C). A virtual triplet due to the two PMe<sub>3</sub> ligands both in the <sup>1</sup>H and <sup>13</sup>C NMR indicates the *trans* form of the complex. One singlet in the <sup>31</sup>P NMR spectrum also supports the *trans* symmetry. The integration ratio of the alkyl protons on the <sup>1</sup>H NMR spectrum of **23** is also consistent with that for the proposed structure. One signal corresponding to the NCS carbon is observed at 123 ppm in the <sup>13</sup>C NMR spectrum. Even after several recrystallizations, the *tert*-butyl isocyanide has not been eliminated from the complex (adduct), suggesting its strong association (or interaction) with the coordination sphere of the metal. At present, we do not have any information about the exact mode of interaction between the *tert*-butyl isocyanide and a metal center or between the isothiocyanato group because of the lack of crystallographic information. However, the spectral data clearly indicate that complex **23** is not a cycloaddition product.

In this work we have shown that di(azido)bis(phosphine) complexes of Group 10 metals {M(N<sub>3</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>} react with organic isothiocyanates to give tetrazole-containing thiolato complexes or isothiocyanato complexes, depending upon the nature of the organic isothiocyanates. Treatment of tetrazole-thiolato complexes with benzoyl halide derivatives afford various organic sulfides.

## Experimental

All manipulations of air-sensitive compounds were performed under N<sub>2</sub> or Ar with the use of standard Schlenk techniques. Solvents were distilled from Na–benzophenone. The analytical laboratories at Basic Science Institute of Korea and at Kangnung National University carried out the elemental analyses. IR spectra were recorded on a Perkin Elmer BX spectrophotometer. NMR (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H}) spectra were obtained on JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me<sub>4</sub>Si and to external 85% H<sub>3</sub>PO<sub>4</sub>. Pd(N<sub>3</sub>)<sub>2</sub>L<sub>2</sub> (L = PMe<sub>3</sub>, PET<sub>3</sub>, PMe<sub>2</sub>Ph and L–L = depe) and Pt(N<sub>3</sub>)<sub>2</sub>L<sub>2</sub> (L = PMe<sub>3</sub>, PET<sub>3</sub> and L–L = depe) were prepared by ligand-exchange reactions of Pd(N<sub>3</sub>)<sub>2</sub>(tmeda)<sup>29</sup> (tmeda = *N,N,N',N'*-tetramethylethylenediamine) and Pt(N<sub>3</sub>)<sub>2</sub>(COD)<sup>29</sup> (COD = 1,5-cyclooctadiene) with the appropriate ligands. Ni(N<sub>3</sub>)<sub>2</sub>L<sub>2</sub> (L = PMe<sub>3</sub>) was prepared by the literature method.<sup>30</sup>

### Preparation of M(NCS)<sub>2</sub>L<sub>2</sub> (M = Pd, L = PMe<sub>3</sub> (**1**), PET<sub>3</sub> (**2**), PMe<sub>2</sub>Ph (**3**); M = Ni, L = PMe<sub>3</sub> (**4**); M = Pt, L = PET<sub>3</sub> (**5**))

To a Schlenk flask containing Pd(N<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.312 g, 0.91 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and trimethylsilyl isothiocyanate (0.257 cm<sup>3</sup>, 1.82 mmol) in that order. After stirring the reaction mixture at room temperature for 24 h, the solvent was removed completely and the resulting solids were washed with hexane and dried under vacuum to give pale yellow solids. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane gave pale yellow crystals of *cis*-Pd(NCS)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**1**, 0.371 g, 90%). Data for *cis*-Pd(NCS)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**1**): ν<sub>max</sub>/cm<sup>-1</sup> (NCS): 2089 (vs) (Found: C, 25.42; H, 4.79; N, 6.95. C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>P<sub>2</sub>Pd requires C, 25.64; H, 4.84; N, 7.48%); δ<sub>H</sub> (300 MHz in DMSO-d<sub>6</sub>): 1.62–1.66 (br d, 18H, PMe<sub>3</sub>); δ<sub>C</sub> (75 MHz in DMSO-d<sub>6</sub>) 15.0 (s, P(CH<sub>3</sub>)<sub>3</sub>), 15.2 (br s), 15.5 (s, P(CH<sub>3</sub>)<sub>3</sub>), 132.6 (s, NCS); δ<sub>P</sub> (120 MHz in DMSO-d<sub>6</sub>) 3.3 (s).

Complexes **2–5** were prepared similarly. Data for *trans/cis*-Pd(NCS)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> (**2**, 90%): ν<sub>max</sub>/cm<sup>-1</sup> (NCS): 2098 (vs) (Found: C, 36.94; H, 6.74; N, 6.05. C<sub>14</sub>H<sub>30</sub>N<sub>2</sub>S<sub>2</sub>P<sub>2</sub>Pd requires C, 36.64; H, 6.59; N, 6.10%); δ<sub>H</sub> (300 MHz in CDCl<sub>3</sub>): 1.22 (br q, 18H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.81–2.09 (m, 12H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); δ<sub>C</sub> (75 MHz in CDCl<sub>3</sub>): 7.94 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 8.13 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 14.6 (t, *J* = 14 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 15.1 (t, *J* = 14 Hz, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 131.7 (s, NCS), 135.2 (NCS); δ<sub>P</sub> (120 MHz in CDCl<sub>3</sub>) 22.6 (s), 24.5 (s). Data for *trans/cis*-Pd(NCS)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (**3**, 97%): ν<sub>max</sub>/cm<sup>-1</sup> (NCS): 2099, 2077 (vs) (Found: C, 43.48; H, 4.46; N, 6.00. C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>S<sub>2</sub>P<sub>2</sub>Pd requires C, 43.34; H, 4.44; N, 5.62%); δ<sub>H</sub> (CDCl<sub>3</sub> in 300 MHz): 1.93 (s, 12H, Me), 7.27–7.64 (10H, Ph); δ<sub>C</sub> (75 MHz in CDCl<sub>3</sub>) 12.2 (t, *J* = 16 Hz, PMe<sub>2</sub>Ph), 129.0, 130.8, 131.0, 131.5 (s, Ph); δ<sub>P</sub> (120 MHz in CDCl<sub>3</sub>) 0.67, –6.29. Data for *trans*-Ni(NCS)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**4**, 89%): ν<sub>max</sub>/cm<sup>-1</sup> (NCS): 2105 (vs) (Found: C, 29.69; H, 5.68; N, 8.56. C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>P<sub>2</sub>Ni requires C, 29.38; H, 5.55; N, 8.57%); δ<sub>H</sub> (300 MHz in CDCl<sub>3</sub>) 1.33 (br s, 18H, PMe<sub>3</sub>); δ<sub>C</sub> (75 MHz in CDCl<sub>3</sub>) 12.3 (s, PMe<sub>3</sub>), 145.0 (s, NCS); δ<sub>P</sub> (120 MHz in CDCl<sub>3</sub>) –13.7(s). Data for *cis*-Pt(NCS)<sub>2</sub>(PET<sub>3</sub>)<sub>2</sub> (**5**, 76 %): ν<sub>max</sub>/cm<sup>-1</sup> (NCS): 2096 (vs) (Found: C, 29.66; H, 5.37; N, 4.65. C<sub>14</sub>H<sub>30</sub>N<sub>2</sub>S<sub>2</sub>P<sub>2</sub>Pd requires C, 30.71; H, 5.52; N, 5.12%); δ<sub>H</sub> (DMSO-d<sub>6</sub> in 300 MHz) 1.10 (br q, 18H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.92 (m, 12H, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>); δ<sub>C</sub> (75 MHz in DMSO-d<sub>6</sub>) 7.99 (s, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 15.4 (br d, P(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 134.1 (NCS); δ<sub>P</sub> (120 MHz in DMSO-d<sub>6</sub>) –5.13 (s, *J*<sub>Pt–P</sub> = 3333 Hz). Complex **4** was independently prepared by the reaction of Ni(SCN)<sub>2</sub> with 2 equiv. or excess PMe<sub>3</sub>.<sup>31,32</sup>

**Preparation of Pd{[CN<sub>4</sub>(R)]<sub>2</sub>L<sub>2</sub> (L = PMe<sub>3</sub>, R = allyl (6), benzyl (7), ethyl (8), phenyl (9), 2,6-dimethylphenyl (10); L = PMe<sub>2</sub>Ph, R = phenyl (11); L = PEt<sub>3</sub>, R = 2,6-dimethylphenyl (12)**

To a Schlenk flask containing Pd(N<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.346 g, 1.01 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (7 cm<sup>3</sup>) and allyl isothiocyanate (0.196 cm<sup>3</sup>, 2.02 mmol). After stirring the reaction mixture at room temperature for 18 h, the solvent was removed and the resulting solids were washed with hexane and dried to give yellow solids. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave yellow crystals of *trans*-Pd{[CN<sub>4</sub>(CH<sub>2</sub>CH=CH<sub>2</sub>)]<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**6**, 0.410 g). Analytical and NMR data of the tetrazole-thiolato complexes are summarized in Tables 1 and 2.

Complexes **7–12** were analogously prepared.

**Preparation of Pt{[CN<sub>4</sub>(R)]<sub>2</sub>L<sub>2</sub> (L = PMe<sub>3</sub>, R = Ph (13), Et (14); L = PEt<sub>3</sub>, R = Et (15))**

To a Schlenk flask containing Pt(N<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.266 g, 0.62 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) and phenyl isothiocyanate (0.148 cm<sup>3</sup>, 1.24 mmol). The initial pale yellow solution slowly turned to an orange solution. After stirring the reaction mixture at 60 °C for 5 h, the solvent was removed and the resulting solids were washed with diethyl ether and dried to give white solids. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave white crystals of *trans*-Pt{[CN<sub>4</sub>(Ph)]<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**13**, 0.304 g).

Complexes **14** and **15** were prepared analogously.

**Preparation of M{[CN<sub>4</sub>(R)]<sub>2</sub>L<sub>2</sub> (R = Ph, M = Pd (16), Pt (17); R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, M = Pt (18), L–L = depe)**

To a Schlenk flask containing Pd(N<sub>3</sub>)<sub>2</sub>(depe) (0.250 g, 0.63 mmol) was added CH<sub>2</sub>Cl<sub>2</sub>-THF (4 : 6 cm<sup>3</sup>) and phenyl isothiocyanate (0.151 cm<sup>3</sup>, 1.26 mmol). The initial pale yellow solution slowly turned to an orange solution. After stirring the reaction mixture at 60 °C for 5 h, the solvent was removed and the resulting solids were washed with diethyl ether and dried to give white solids. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane gave white crystals of Pd{[CN<sub>4</sub>(R)]<sub>2</sub>(depe) (**16**, 0.320 g).

Complexes **17** and **18** were prepared analogously.

**Reactions of 9 and 10 with benzoyl chloride (PhCOCl) and 2-thiophenecarbonyl chloride (C<sub>4</sub>H<sub>3</sub>SCOCl)**

To a CH<sub>2</sub>Cl<sub>2</sub> (15 ml) solution containing *trans*-Pd{[CN<sub>4</sub>(Ph)]<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (**9**, 0.520 g, 0.78 mmol) was added benzoyl chloride (0.180 cm<sup>3</sup>, 1.55 mmol) at room temperature. After stirring the reaction mixture for 24 h, the solvent was removed, and the resulting residue was extracted with excess diethyl ether. The collected extracts were again evaporated to give crude solids, which were recrystallized from diethyl ether-hexane to give white crystals of C<sub>6</sub>H<sub>5</sub>(CO)-S-CN<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>) (**19**, 0.549 g, 88%). The remaining residues were identified as PdCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> in quantitative yields, confirmed by IR and NMR spectroscopy. Data for C<sub>6</sub>H<sub>5</sub>(CO)-S-CN<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>):  $\nu_{\max}/\text{cm}^{-1}$ : 1686 (s) (Found: C, 59.45; H, 3.60; N, 19.95. C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>OS requires C, 59.96; H, 3.57; N, 19.85%);  $\delta_{\text{H}}$  (300 MHz in CDCl<sub>3</sub>) 7.46–7.69 (m, 8H, Ph), 7.85–7.90 (m, 2H, Ph);  $\delta_{\text{C}}$  (75 MHz in CDCl<sub>3</sub>) 125.0, 128.1, 129.3, 129.6, 130.7, 133.7, 134.4, 135.2, 146.2, 183.7 (s, C=O). Data for C<sub>6</sub>H<sub>5</sub>(CO)-S-CN<sub>4</sub>-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**20**, 85%):  $\nu_{\max}/\text{cm}^{-1}$ : 1699 (s, CO) (Found: C, 61.99; H, 4.63; N, 18.12. C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>OS requires C, 61.92; H, 4.55; N, 18.05%);  $\delta_{\text{H}}$  (300 MHz in CDCl<sub>3</sub>) 2.03 (s, 6H, Me), 7.18–7.20 (m, 2H, Ph), 7.32–7.37 (m, 1H, Ph), 7.45–7.51 (m, 2H), 7.62–7.68 (m, 1H, Ph), 7.85–7.87 (m, 2H, Ph);  $\delta_{\text{C}}$  (75 MHz in CDCl<sub>3</sub>) 17.5 (s, Me), 128.1, 128.8, 129.1, 129.2, 131.0, 134.5, 135.1, 135.9, 147.6, 183.3 (C=O). Data for C<sub>4</sub>H<sub>3</sub>S(CO)-S-CN<sub>4</sub>-C<sub>6</sub>H<sub>5</sub> (**21**, 79%):  $\nu_{\max}/\text{cm}^{-1}$ : 1677, 1659 (s, CO) (Found: C, 49.72; H, 2.85; N, 19.39. C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>OS requires C, 49.98; H, 2.80; N, 19.43%);  $\delta_{\text{H}}$  (300 MHz in CDCl<sub>3</sub>) 7.19 (dd, 1H, *J* = 4 Hz, thiophenyl C–H), 7.56 (br s, 5H, Ph), 7.79 (dd, 1H, *J* = 1 Hz, thiophenyl C–H), 7.86 (dd, 1H, *J* = 4 Hz, thio-

phenyl C–H);  $\delta_{\text{C}}$  (75 MHz in CDCl<sub>3</sub>) 125.0, 128.6, 129.6, 130.8, 133.7, 133.9, 136.1, 138.5, 145.7, 175.1 (s, C=O).

**Reaction of 4 with *tert*-butyl isocyanide**

To a Schlenk flask containing Ni(NCS)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.294 g, 0.90 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and *tert*-butyl isocyanide (0.203 cm<sup>3</sup>, 1.8 mmol). After stirring the reaction mixture at room temperature for 18 h, the solvent was removed and the resulting solids were washed with diethyl ether and dried to give orange solids. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether gave orange crystals of [Ni(PMe<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>]<sub>2</sub>(*t*-BuNC) (**23**, 0.336 g, 76%);  $\nu_{\max}/\text{cm}^{-1}$  (N≡C): 2196 (vs),  $\nu$ (NCS) 2051 (vs) (Found: C, 43.57; H, 7.48; N, 11.36. C<sub>18</sub>H<sub>36</sub>N<sub>4</sub>S<sub>2</sub>P<sub>2</sub>Ni requires C, 43.83; H, 7.36; N, 11.36%);  $\delta_{\text{H}}$  (300 MHz in CDCl<sub>3</sub>) 1.61 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.69 (t, 18H, *J* = 4 Hz, PMe<sub>3</sub>);  $\delta_{\text{C}}$  (75 MHz in CDCl<sub>3</sub>): 15.4 (t, *J* = 17 Hz, PMe<sub>3</sub>), 30.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 59.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 122.7 (s, NCS);  $\delta_{\text{p}}$  (120 MHz in CDCl<sub>3</sub>) 6.34(s).

**X-Ray structure determination**

All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with  $\psi$ -scan data. All calculations were carried out with the use of SHELXTL<sup>33</sup> programs. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode. Details on crystal data, intensity collection, and refinement details for **4–6**, **9**, **14** and **18** are given in Table 3.

Crystal data for C<sub>6</sub>H<sub>5</sub>(CO)-S-CN<sub>4</sub>-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**20**) are as follows: C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>OS, *M* = 310.37, triclinic, space group *P* $\bar{1}$ , *a* = 7.956(3), *b* = 9.962(3), *c* = 11.165(3) Å,  $\alpha$  = 91.151(18),  $\beta$  = 107.51(2)°,  $\gamma$  = 111.21(2)°, *V* = 778.5(4) Å<sup>3</sup>, *Z* = 2, *T* = 295(2) K,  $\mu$  = 0.215 mm<sup>-1</sup>, 2905 reflections measured, 2697 unique (*R*<sub>int</sub> = 0.284), from which 1440 with *I* > 2σ(*I*) were used in refinements. Final *R*<sub>1</sub> and *wR*<sub>2</sub> values were 0.0995 and 0.2505, respectively.

Crystal data for (SCN<sub>4</sub>-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**22**) are as follows: C<sub>18</sub>H<sub>18</sub>N<sub>8</sub>S<sub>2</sub>, *M* = 410.52, monoclinic, space group *P*<sub>2</sub>/c, *a* = 11.153(3), *b* = 13.732(3), *c* = 13.616(4) Å,  $\beta$  = 93.46(2)°, *V* = 2074.4(10) Å<sup>3</sup>, *Z* = 4, *T* = 295(2) K,  $\mu$  = 0.277 mm<sup>-1</sup>, 3692 reflections measured, 3494 unique (*R*<sub>int</sub> = 0.0494), from which 1504 with *I* > 2σ(*I*) were used in refinements. Final *R*<sub>1</sub> and *wR*<sub>2</sub> values were 0.0750 and 0.1506, respectively.

CCDC reference numbers 210413–210420.

See <http://www.rsc.org/suppdata/dt/b3/b305341p/> for crystallographic data in CIF or other electronic format.

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