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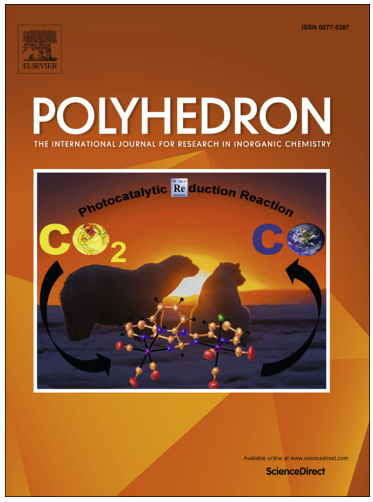

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(*revised to polyhedron*)

Reactivities of organic isothiocyanates and thiocyanates toward dialkyl bis(phosphine) complexes of palladium(II) and platinum(II)

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Abstract

Room-temperature reactions of *trans*-[$PdEt_2L_2$] (L = PMe_3, PEt_3, PMe_2Ph) with organic isothiocyanates [R–NCS; R = benzyl; $CH(CH_3)Ph$, *R*-(−) and *S*-(+); indanyl, *S*-(+)] afforded the *S,S*-coordinated Pd(II) complexes [$Pd(S_2C{=}N{-}R)L_2$] containing a dithiocarbonimidato ($S_2C{=}N{-}R$) group. Similar reactions involving allyl isothiocyanates produced the cationic η^3-allyl Pd complex [$Pd(\eta^3$-allyl)$(PMe_3)_2]^+(NCS)^-$. When [$Pd(S_2C{=}N{-}R)(PMe_3)_2$] was treated with 1 equiv of a chelating phosphine [L~L = depe (1,2-bis(diethylphosphino)ethane) and dmpe (1,2-bis(dimethylphosphino)ethane)], the corresponding complexes [$Pd(S_2C{=}N{-}R)$(L~L)] were produced. Reactions of *trans*-[$PdEt_2L_2$] (L = PMe_3, PMe_2Ph) with organic thiocyanates (R–SCN; R = benzyl, Et) resulted in the formation of [$Pd(CN)_2L_2$] and an organic disulfide by S–C bond cleavage of R–SCN. However, similar reactions of the dimethyl analogs, *trans*-[$PdMe_2L_2$] (L = PMe_3, PEt_3), with benzyl thiocyanate afforded different products, [$Pd(NCS)_2L_2$] or [$PdMe(NCS)L_2$]. Treating [Pt(styrene)$(PMe_3)_2$] with benzyl isothiocyanate gave the *S*-coordinated dithiocarbonimidato Pt(II) complex, [$Pt(S_2C{=}N{-}R)(Me_3P)_2$] (R = benzyl). In contrast, *cis*-[$PtEt_2(PMe_3)_2$] reacted with the isothiocyanate to afford the trialkyl Pt(IV) complex [$PtEt_2(SCN)(CH_2Ph)(PMe_3)_2$].

Key words: Organic Isothiocyanate, Organic Thiocyanate, Oxidative Addition, Palladium, Platinum

Introduction

Organic isothiocyanates (R–NCS), a family of pseudohalides, are widely used for the synthesis of heterocyclic compounds via cycloaddition with organic unsaturated compounds or main-group metal complexes containing unsaturated ligands [1–7]. These species also react with transition-metal complexes bearing pseudohalo [8–16], halo [17–19], unsaturated [20], hydrido [21], silyl [22], and sulfido ligands [23] to form N or S-coordinated heterocycles or metallacycles. Organolanthanide complexes also undergo analogous reactions with organic isothiocyanates [24]. In particular, certain organic isothiocyanates react with zero-valent Co, Rh, Ru, Pd, and Pt complexes to afford S-coordinated metallacycles or cycloaddition products [25–29]. Our group also observed

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the same reactivity in reactions involving group 10 metal azide [13] or silyl complexes [22].

In this study, we attempted to extend the scope of the above-mentioned reactions by investigating the reactions of organic pseudohalides with dialkyl Pd(II) and Pt(II) complexes. To the best of our knowledge, the oxidative addition and cycloaddition of pseudohalides to transition-metal–alkyl complexes have been little studied to date. Here, we report Pd–S, Pd–N, and Pt–N bond formation observed in reactions between dialkyl Pd(II) or Pt(II) complexes and organic isothiocyanates or thiocyanates.

Results and Discussion

Reactions of organic isothiocyanates (R–NCS) with dialkyl Pd(II) complexes

We previously demonstrated that disilyl bis(phosphine) complexes of Pd(II) and Pt(II), $[M(SiHPh_2)_2L_2]$, react with aryl isothiocyanates (Ar–NCS) to afford the S-coordinated dithiocarbonimidato complexes, $[M(S_2C{=}N{-}Ar)L_2]$ [22]. As an extension of that study, the reactions of *trans*-$[PdEt_2L_2]$ (L = PMe_3, PMe_2Ph), a dialkyl analog, with alkyl isothiocyanates were examined. As expected, these dialkyl species react with 2 equiv of isothiocyanates to afford S-coordinated dithiocarbonimidato Pd(II) complexes, $[Pd(S_2C{=}N{-}R)L_2]$ (complexes **1**–**6**), in moderate to good yields (Eq. 1 in Scheme 1). However, the absolute configurations of the products obtained from chiral isothiocyanates could not be unambiguously assigned on the basis of spectroscopic data. Several attempts were therefore made to obtain crystals for X-ray diffraction, but these were unsuccessful. To overcome this problem, we synthesized complexes containing a single chelating phosphine from the corresponding bis(monodentate) phosphine complexes by ligand replacement, and then confirmed their absolute configurations by X-ray diffraction. The bis(trimethylphosphine) Pd(II) complexes $[Pd(S_2C{=}N{-}R)(PMe_3)_2]$ reacts slowly with 1 equiv of a chelating phosphine ligand (L~L = depe or dmpe) to give Pd complexes with one chelating phosphine, $[Pd(S_2C{=}N{-}R)(L\sim L)]$ (complexes **7**–**9**, Eq. 2 in Scheme 1).

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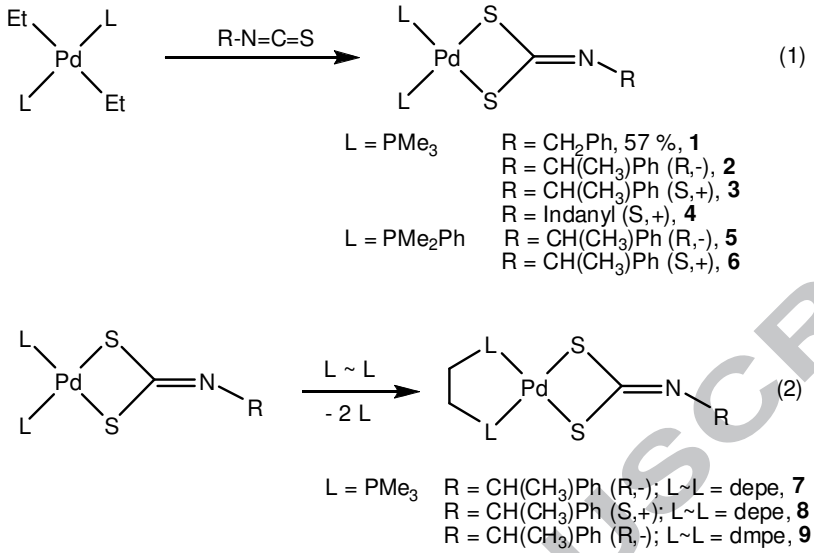

Scheme 1

The IR spectra of complexes **1**–**9** display a strong N=C bond stretching vibration at 1550–1570 cm^{-1}. The PMe_3 and PR_2 regions in the $^{13}C\{^1H\}$ NMR spectra show doublets of two doublets. The $^{31}P\{^1H\}$ NMR spectra also display two doublets, indicating asymmetric *S*,*S*'-coordination of the dithiocarbonimidato ligand to the Pd center. The molecular structures of [Pd{(*R*)-(−)-S_2C=NC(H)(Me)(Ph)}(depe)] (**7**) (Figure 1) and [Pd{(*S*)-(+)-S_2C=NC(H)(Me)(Ph)}(depe)] (**8**) (Figure 2) clearly show the formation of Pd(II) complexes containing a dithiocarbonimidato ligand with an chiral moiety (R,− or S,+), whose absolute configuration remained unchanged during the reaction, as expected. In complexes **7** and **8**, the Pd metal has a slightly distorted square-planar geometry and coordinates to two sulphur atoms (the dithiocarbonimidato ligand) and two phosphorus atoms (depe).

In earlier work on several reactions of Pd(0) complexes with R–NCS (R = Me, Ph) and EtOCONCS), S-coordinated dithiocarbonimidato Pd(II) complexes were obtained [26,27]. In addition, low-oxidation-state Pt [25,28], Ru [29], and Rh [17] species reacted with isothiocyanates (R–NCS; R = Me, Ph, C(O)OEt) to afford the dithiocarbonimidato complexes. As mentioned above, we also reported that bis(silyl) Pd(II) and Pt(II) complexes react with aryl isothiocyanates to afford the corresponding dithiocarbonimidato Pd(II) and Pt(II) complexes depending on the isothiocyanates used [22]. These observations suggest that Pt(0) and Pd(0) species are key intermediates or

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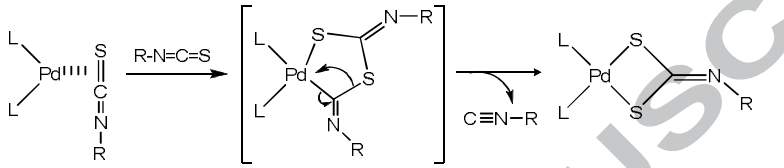
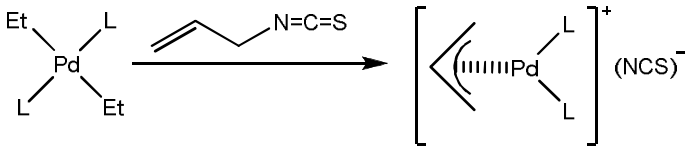
starting materials for cycloaddition of isothiocyanates. The formation of complexes **1–6** can be explained on the basis of the known mechanism of dithiocarbonimidato Pd(II) complexes formation, i.e., a combination of coordination of two R–NCS ligands to a Pd(0) center to form a metallacyclic intermediate, and subsequent elimination of an organic isocyanide (Scheme 2).



Scheme 2

Interestingly, the reaction with allyl isothiocyanate afforded a cationic η^3-allyl Pd complex, $[Pd(\eta^3\text{-allyl})(PMe_3)_2]^+(NCS)^-$ (**10**), which was characterized by NMR spectroscopy and elemental analysis (Scheme 3). The moisture-sensitive complex **10** was obtained as a white solid. The originally expected dithiocarbonimidato Pd(II) complex, $[Pd(S_2C{=}N\text{–allyl})(\eta^3\text{-allyl})(PMe_3)_2]$, was not observed. It is worth noting that allyl halides and pseudohalides have been used for the preparation of η^3-allyl complexes; for example, Boersma and co-workers [30] showed that the reaction of $[PdMe_2(tmeda)]$ (tmeda = tetramethylethylenediamine) with allyl bromide at room temperature affords a cationic complex, $[Pd(\eta^3\text{-allyl})(tmeda)]Br$. In addition, Wilkinson et al. [25] proposed the presence of $[Pt(\eta^3\text{-allyl})(PPh_3)_2](SCN)$ in solution during the reaction of $[Pt(PPh_3)_3]$ with allyl isothiocyanate.



L = PMe_3 **10**

Scheme 3

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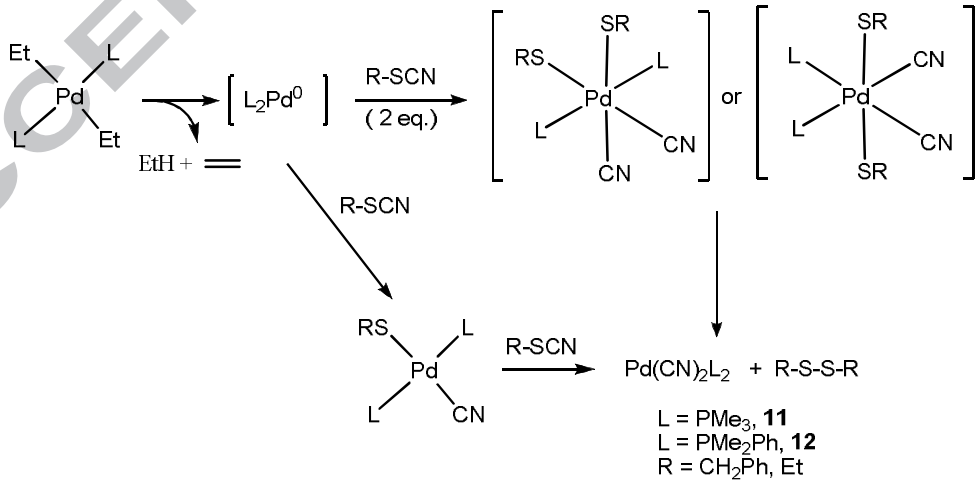
Reactions of organic thiocyanates (R–SCN) with dialkyl Pd(II) complexes

In order to compare the chemical reactivities between R–NCS and R–SCN toward dialkyl bis(phosphine) Pd(II) complexes, we examined reactions involving organic thiocyanates (R–SCN). The addition of 2 equiv of R–SCN (R = benzyl or ethyl) to *trans*-[$PdEt_2L_2$] (L = PMe_3, PMe_2Ph) gave an unexpected product, [$Pd(CN)_2L_2$], as well as an organic dithiolato compound (R–S–S–R) (Scheme 4). However, pseudohalogen products, the thiocyanato complex [$Pd(SCN)_2L_2$] and the isothiocyanato complex [$Pd(NCS)_2L_2$], were not observed. Complexes **11** and **12** are formed by either of two three-step reactions (Scheme 4), both of which involve a Pd(0) intermediate formed by R–R reductive elimination (β-H elimination). The first possible pathway involves *trans* or *cis* S–C oxidative addition of R–SCN to the Pd(0) intermediate to afford the Pd(IV) intermediate; *trans* addition is more plausible because of the C–S bond polarity. In the subsequent step, the intermediate reductively eliminates R–S–S–R, with the formation of [$Pd(CN)_2L_2$]. The second possible pathway involves oxidative addition of R–SCN to the Pd(0) intermediate (L_2Pd), followed by electrophilic attack of another R–SCN at the SR ligand. The second pathway also explains the formation of the final products. Ogawa and co-workers [31] showed that Ph–SCN oxidatively adds to [$Pd(PPh_3)_4$] to afford [$Pd(CN)(SPh)(PPh_3)_2$]. It is worth mentioning that the oxidative addition or reductive elimination of organic halides to zero-valent transition-metal complexes has been extensively studied, but those involving organic pseudohalides are relatively rare.



Scheme 4

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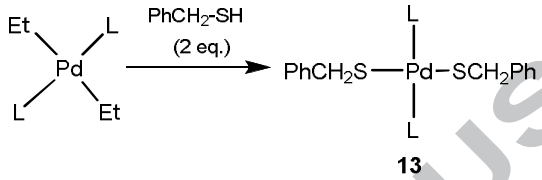
The IR spectra of $[Pd(CN)_2(PR_3)_2]$ display a sharp absorption band at 2123–2126 cm^{-1} from the CN group, which agrees well with those in known bis(cyanato) Pd(II) complexes [13d]. To gain an insight into the possible intermediate in Scheme 4, *trans*-$[PdEt_2L_2]$ was treated with 2 equiv of benzyl mercaptan to give the bis(thiolato) Pd(II) complex *trans*-$[Pd(SCH_2Ph)_2(PMe_3)_2]$ (**13**) (Scheme 5). This product was characterized using spectroscopy and X-ray diffraction (Figure 3).



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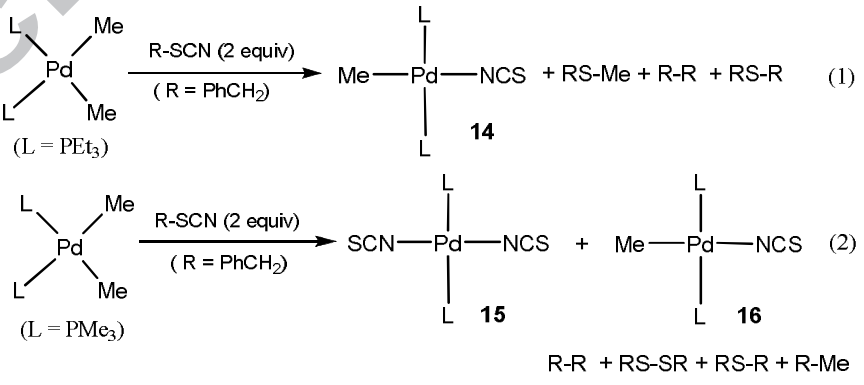
Scheme 5

For comparison, we investigated similar reactions involving *cis*-$[PdMe_2L_2]$ (L = PEt_3, PMe_3; Scheme 6). In the case of *cis*-$[PdMe_2(PEt_3)_2]$, the reaction smoothly proceeded to afford *trans*-$[PdMe(NCS)(PEt_3)_2]$ (**14**) in 50% yield and a mixture of organic products ($PhCH_2SMe$, 12%; $PhCH_2CH_2Ph$, 10%; $PhCH_2SCH_2Ph$, 10%) (Eq.1 in Scheme 6). In contrast, the reaction involving *cis*-$[PdMe_2(PMe_3)_2]$, a PMe_3 analog, produced a mixture of a bis(isothiocyanato) Pd(II) complex, *trans*-$[Pd(NCS)_2(PMe_3)_2]$ (**15**, 33% yield), as the major product, and *trans*-$[PdMe(NCS)(PMe_3)_2]$ (**16**, less than 1% yield) as a minor product, as well as organic products ($PhCH_2Me$, 4%; $PhCH_2CH_2Ph$, 16%; $PhCH_2SCH_2Ph$, 18%; $PhCH_2SSCH_2Ph$, 17%; Eq. 2 in Scheme 6).



Scheme 6

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In the IR and NMR spectra of the crude product in Eq. 1, we observed the CN band of NCS at 2095 cm^{-1} for the major product and the CN band at 2149 cm^{-1} for an unidentified minor product. The GLC and GC–MS data confirmed R–R, RS–R, and RS–Me as organic products. After recrystallization, pure *trans*-[$PdMe(NCS)(PEt_3)_2$] (**14**) was obtained. The IR spectra of the final products in Eq. 2 showed a strong NCS band at 2091 cm^{-1} for the major product (**15**). Unfortunately, the IR bands of the NCS ligands of complexes **15** and **16** in Eq. 2 overlapped. However, the ^1H NMR spectra of the products clearly displayed a triplet at δ −0.19 ppm (J_{PH} = 6.9 Hz) from the Pd–Me bond and a triplet at δ 1.49 ppm (J_{PH} = 3.6 Hz) from the Pd–PMe_3 bond, confirming the stereochemistry of complex **16.**

These results (Scheme 6) indicate that the reactivity of R–SCN toward *cis*-[$PdMe_2(PMe_3)_2$] is more complicated than that toward *cis*-[$PdMe_2(PEt_3)_2$]; i.e., the reactivity appears to depend on the identity of the phosphine ligand. At present, however, we are unable to provide a clear mechanism for these reactions..

Reactions of organic thiocyanates (R–SCN) with dialkyl Pt(II) complexes

In order to examine the difference between the reactivites of Pd(II)- and Pt(II) dialkyl complexes, we performed reactions of *cis*-[$PtR_2(PR_3)_2$] (R = Me, Et; PR_3 = PMe_3, PEt_3) with organic isothiocyanates and thiocyanates. Several attempts to isolate the products from the reactions of *cis*-[$PtMe_2(PR_3)_2$] with 2 equiv of benzyl isothiocyanate ($PhCH_2$–NCS) and thiocyanate ($PhCH_2$–SCN) were unsuccessful. In the case of benzyl thiocyanate, we only observed a Pt intermediate with an IR absorption band at 2100 cm^{-1} assignable to the NCS group, which indicates coordination of the thiocyanate. Furthermore, even under vigorous reaction conditions (heating to 80 °C or prolonged reaction time), only the starting material was recovered after recrystallization. However, as shown in Eq. 1 in Scheme 7, treatment of [$Pt(styrene)(PMe_3)_2$], which was generated from *cis*-[$PtEt_2(PMe_3)_2$] and styrene at 80 °C in toluene, with benzyl isothiocyanate in a 1:2 molar ratio afforded the S-coordinated dithiocarbonimidato Pt(II) complex [$Pt(S_2C{=}N{-}CH_2Ph)(PMe_3)_2$] (**17**), in 28% yield.

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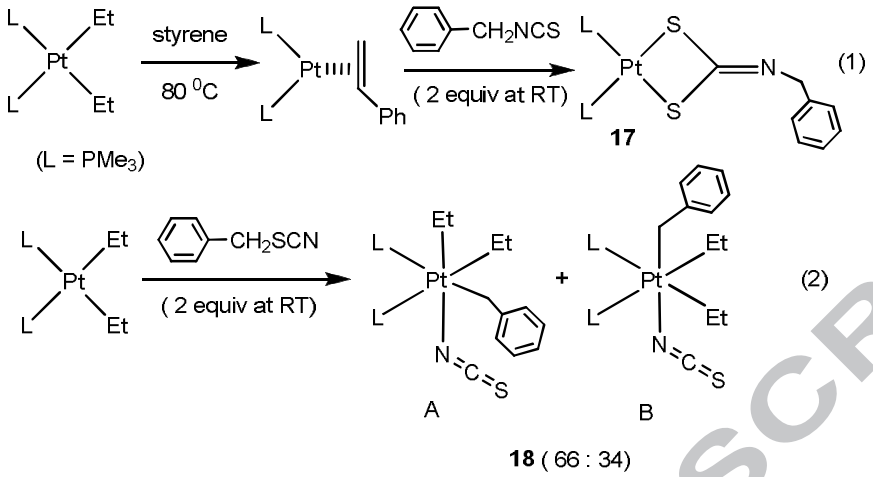

Scheme 7

The pathway of the above-mentioned reaction (Eq. 1) is quite similar to that observed in the reactions of diethyl Pd(II) complexes: π-coordination of R–NCS to the Pt(0) center and subsequent sulfur abstraction. Interestingly, *cis*-[$PtEt_2(PMe_3)$] reacts with $PhCH_2$–SCN (benzyl thiocyanate) to give a C–S oxidative addition product, a six-coordinated Pt(IV) complex (**18**), as white crystals (Eq. 2). The IR spectrum of complex **18** displays a characteristic NCS stretching band at 2107 cm^{-1}. The solution NMR spectrum of **18** indicates that the complex exists as a mixture of *cis*-[$Pt(Et)_2(CH_2Ph)(NCS)(PMe_3)_2$] (A) and *trans*-[$Pt(Et)_2(CH_2Ph)(NCS)(PMe_3)_2$] (B) in a 64:34 ratio. The ^{1}H NMR signals for the benzylic (CH_2Ph) protons exhibit a doublet of doublets (J_{PH} = 10, 20 Hz) with a satellite (J_{PtH} = 91 Hz) at δ 3.06 ppm and δ 2.59 ppm due to the *cis* form (A) and a triplet (J_{PH} =7.7 Hz) with a satellite (J_{PtH} = 103 Hz) at δ 2.55 ppm from the *trans* form (B). In addition, the ^{31}P NMR signals show two doublets (J = 13 Hz) at δ −35.6 and −38.4 ppm with a satellite (J_{PtP} = 1309, 1053 Hz, respectively) from the *cis* form (A) and a singlet at δ −39.4 ppm with a satellite (J_{PtP} = 1118 Hz) from the *trans* form (B). The structure of complex B, one of isomeric pair, was determined using X-ray diffraction (Figure 4). Its molecular structure clearly shows formation of a six-coordinated Pt(IV) complex (B) by oxidative addition of benzyl thiocyanate. In this reaction, we did not observe reductive elimination to give organic compounds by C–C homocoupling or C–N or C–S heterocoupling. The results shown in

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Schemes 4 and 7 can be explained on the basis of the well-known fact that a Pt complex is more thermally stable than the corresponding Pd complex.

As shown in Schemes 4 and 6, direct reactions of R–SCN with dialkyl Pd(II) complexes exhibit S–C or R–S bond cleavage depending on the starting materials. In contrast, similar reactions involving the diethyl Pt(II) complex proceed via *trans* or *cis* oxidative addition of R–SCN to afford the six-coordinated Pt(IV) complexes. The structures of these Pt(IV) complexes were confirmed by comparing them with those reported in the literature, which were prepared by *trans* or *cis* oxidative addition of alkyl halides to dialkyl Pt(II) complexes [32–35].

Conclusion

We investigated the reactivity of organic pseudohalides (R–NCS and R–SCN) toward dialkyl bis(phosphine) complexes of Pd(II) and Pt(II). As expected, the chiral R–NCS reagents reacted with the Pd(II) complexes to afford S,S-coordinated Pd(II) complexes containing a dithiocarbonimidato (S_2C=N–R) moiety, with retention of the absolute configuration at the R group. When allyl isothiocyanate used, the cationic η^3-allyl Pd complex $[Pd(\eta^3\text{-allyl})(PMe_3)_2]^+(NCS)^-$ was obtained. Treatment of a diethyl Pd(II) complex with 2 equiv of R–SCN afforded a Pd(II) cyanide complex and an organic disulfide by selective S–C bond cleavage of R–SCN. In contrast, similar reactions involving a dimethyl analog afforded different products, $[PdMe(NCS)L_2]$ or $[Pd(NCS)_2L_2]$ as the major product, depending on the supporting ligand. Treatment of $[Pt(styrene)(PMe_3)_2]$ with benzyl isothiocyanate afforded the S-coordinated dithiocarbonimidato Pt(II) complex, $[Pt(S_2C{=}N{-}CH_2Ph)(PMe_3)_2]$. In contrast, the reaction of *cis*-$[PtEt_2(PMe_3)_2]$ with benzyl thiocyanate proceeded via *trans* or *cis* oxidative addition of R–SCN to afford a Pt(IV) complex. In conclusion, Pd(II) and Pt(II) diethyl complexes are more reactive toward organic isothiocyanates or thiocyanates than the dimethyl analogs are. Furthermore, the reactivites of the Pd(II) dialkyl complexes toward R–NCS are higher than the Pt(II) analogs. In contrast, similar reactions involving R–SCN produced different products, depending on the metal center and the PR_3 ligands.

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Experimental

All manipulations of air-sensitive compounds were performed under N_2 or Ar using Schlenk-line techniques. Solvents were distilled from Na–benzophenone. Elemental analyses were performed at the analytical laboratories at the Basic Science Institute of Korea and at Kangnung-Wonju National University. IR spectra were recorded using a Perkin Elmer BX spectrophotometer. NMR (^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}) spectra were obtained in $CDCl_3$ using a JEOL Lamda 300 MHz spectrometer. Chemical shifts were referenced to internal Me_4Si and to external 85% H_3PO_4. X-ray reflection data were obtained at either the Korea Basic Science Institute (Jeonju Center) and the Cooperative Center for Research Facilities at Sungkyunkwan University. The complexes *trans*-[PdR_2L_2] (L = PMe_3, PEt_3, and PMe_2Ph) [36] and *cis*-[PtR_2L_2] (PMe_3 and PEt_3) [37] were prepared using the literature method.

Reactions of *trans*-[$PdEt_2L_2$] (L = PMe_3, PMe_2Ph) with R–NCS (R = benzyl; $CH(CH_3)Ph$, R-(−); $CH(CH_3)Ph$, S-(+); 1-Indanyl, S-(+))

Benzyl isothiocyanate (258 μl, 1.94 mmol) and THF (3 cm^3) were sequentially added at 0 ºC to a Schlenk flask containing *trans*-[$PdEt_2(PMe_3)_2$] (0.308 g, 0.97 mmol). The reaction mixture was stirred at room temperature for 5 h; the initial yellow solution turned to a pale-orange solution. The solvent was completely removed under vacuum. The resulting residue was solidified with hexane. The solids were filtered and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were recrystallized from CH_2Cl_2/hexane to give *cis*-[$Pd(S_2C{=}N{-}CH_2Ph)(PMe_3)_2$] (**1,** 0.171 g, 70%) as a pale yellow solids. IR (KBr/cm^{-1}): 1568 (C=N). ^{1}H NMR: δ 1.52 (d, J = 8.4 Hz, 18H, PCH_3), 4.86 (s, 2H, CH_2), 7.12–7.18 (m, 1H, Ph), 7.23–7.28 (m, 2H, Ph), 7.39–7.41 (m, 2H, Ph). ^{131}C{^{1}H} NMR: δ 16.2 (ddd, J = 5.0, 14, 25Hz, PCH$_3$), 51.5(s, CH$_2$), 125.9, 127.9, 128.2, 141.1, 172.8 (s, C=N). ^{31}P{^{1}H}NMR: δ 16.9 (dd, J = 53, 87Hz). *Anal.* Calc. for $C_{14}H_{25}NP_2S_2Pd$: C, 38.23; H, 5.73; N, 3.18. Found: C, 37.75; H, 5.78; N, 3.03.

Complexes *cis*-[$Pd(S_2C{=}N{-}R)(PMe_3)_2$] (R = $CH(CH_3)Ph$, R-(−), **2**), *cis*-[$Pd(S_2C{=}N{-}R)(PMe_3)_2$] (R = $CH(CH_3)Ph$, S-(+), **3**), *cis*-[$Pd(S_2C{=}N{-}R)(PMe_2Ph)_2$] (R = $CH(CH_3)Ph$, R-(-), **4**), *cis*-[$Pd(S_2C{=}N{-}R)(PMe_2Ph)_2$] (R = $CH(CH_3)Ph$, S-(+), **5**), *cis*-[$Pd(S_2C{=}N{-}R)(PMe_3)_2$] (R = 1-indanyl, S-(+), **6**) were prepared analogously.

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Complex **2** (71%). IR (KBr/cm^{-1}): 1556 (C=N). ^{1}H NMR: δ 1.49 (br, 9H, PCH_3), 1.52 (br, 9H, P(CH_3)$_3$), 5.46 (q, J = 6.6 Hz, 1H, CH), 7.11–7.16 (m, 1 H, Ph), 7.22–7.27(m, 2H, Ph), 7.45–7.48(m, 2H, Ph). ^{13}C{^{1}H} NMR: δ 16.2 (ddd, J = 5.6, 17, 25 Hz, PCH$_3$), 23.9 (s, Me), 55.4 (s, CH), 125.8, 127.0, 127.9, 146.4, 172.0 (s, C=N). ^{31}P{^{1}H}NMR: δ –17.1 (dd, J = 51, 77 Hz). *Anal.* Calc. for $C_{15}H_{27}NP_2S_2Pd$: C, 39.69; H, 5.99; N, 3.08. Found: C, 39.78; H, 5.83; N, 2.91.

Complex **3** (65%). IR (KBr/cm^{-1}): 1567 (C=N). ^{1}H NMR: δ 1.50 (d, 18 H, J = 3.6 Hz, PCH_3), 5.46 (q, J = 6.6 Hz, 1H, CH), 7.11–7.16 (m, 1H), 7.23–7.28 (m, 2 H), 7.45–7.48 (m, 2 H). ^{13}C{^{1}H} NMR: δ 16.4 (ddd, J = 5.6, 18, 25 Hz, PCH$_3$), 24.2 (s, Me), 55.5 (s, CH), 126.0, 127.3, 127.6, 146.6, 167.6 (s, C=N). ^{31}P{^{1}H}NMR: δ –16.5 (dd, J = 51, 76 Hz). *Anal.* Calc. for $C_{15}H_{27}NP_2S_2Pd$: C, 39.69; H, 5.99; N, 3.08. Found: C, 39.88; H, 6.01; N, 2.87.

Complex **4** (72%). IR (KBr/cm^{-1}): 1560 (C=N). ^{1}H NM: δ 1.52 (dd, J = 1.1, 9.5 Hz , 18H, PCH_3), 2.11 (m, 1H, CH_2), 2.45 (m, 1H, CH_2), 2.86 (m, 1H, CH_2), 3.04 (m, 1H, CH_2), 5.78 (t, J = 7.3 Hz, 1H, CH), 7.08–7.18 (m, 3H, Ar), 7.28–7.34 (m, 1H, Ar). ^{13}C{^{1}H} NMR: δ 16.2 (ddd, J_{PC} = 5.6, 17, 24 Hz, PCH$_3$), 30.9 (CH$_2$), 34.1 (CH$_2$), 61.4 (d, J_{PC} = 1.2 Hz, CH$_2$), 124.0, 125.1, 126.0, 126.4, 143.5, 146.2, 172.0 (s, C=N) ^{31}P{^{1}H}NMR: δ –16.2 (dd, J = 26, 57 Hz). *Anal.* Calc. for $C_{16}H_{27}NP_2S_2Pd$: C, 41.25; H, 5.84; N, 3.01. Found: C, 41.65; H, 5.87; N, 3.06.

Complex **5** (73%). IR (KBr/cm^{-1}): 1569 (C=N). ^{1}H NMR: δ 1.43–1.48 (m, 12H, PCH_3), 1.55 (d, J = 6.6 Hz, 3H, CH_3), 5.52 (q, J = 6.6 Hz, 1H, CH) 7.13–7.18 (m, 2 H), 7.25–7.40 (m, 9 H), 7.49–7.52 (m, 4H). ^{13}C{^{1}H} NMR: δ 14.0 (ddd, J = 1.9, 5.6, 25 Hz, PCH$_3$), 24.1 (s, CH$_3$), 55.4 (s, CH), 125.8, 127.1, 127.9, 128.7 (t, J_{PC} = 1.9 Hz), 128.9 (t, J_{PC} = 1.9 Hz), 130.6 (ddd, J = 1.9, 5.5, 25 Hz), 148.4, 170.6 (s, C=N). ^{31}P{^{1}H}NMR: δ –7.70 (dd, J = 48, 64 Hz). *Anal.* Calc. for $C_{25}H_{31}NP_2S_2Pd$: C, 51.95; H, 5.40; N, 2.42. Found: C, 51.98; H, 5.57; N, 2.12.

Complex **6** (76%). IR (KBr/cm^{-1}): 1570 (C=N). ^{1}H NMR: δ 1.43–1.48 (m, 12H, PCH_3), 1.55 (d, J = 6.6 Hz, 3H, CH_3), 5.52 (q, J = 6.6 Hz, 1H, CH) 7.13–7.18 (m), 7.25–7.40 (m), 7.49–7.52 (m). ^{13}C{^{1}H} NMR: δ 14.0 (ddd, J_{PC} = 1.9, 5.6, 25 Hz, PCH$_3$), 24.1 (s, CH$_3$), 55.4 (s, CH), 125.8, 127.1, 127.9, 128.8 (dd, J = 1.9, 8.0 Hz), 130.6 (ddd, J = 2.5, 7.5, 9.6 Hz), 146.4, 170.5 (s, C=N). ^{31}P{^{1}H}NMR: δ –7.70 (dd, J = 48, 64 Hz).

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Anal. Calc. for $C_{25}H_{31}NP_2S_2Pd$: C, 51.95; H, 5.40; N, 2.42. Found: C, 52.30; H, 5.54; N, 2.14.

Reactions of *cis*-[Pd(S_2C=N–R)(PMe_3)$_2$] (R = $CH(CH_3)Ph$, R-(−) or S-(+)) with depe or dmpe

THF (7 cm^3) and depe (60 μl, 0.26 mmol) were added at room temperature to a Schlenk flask containing **2** (0.117 g, 0.26 mmol). The reaction mixture was stirred for 1 h, and then the solvent was completely removed under vacuum. The resulting residue was solidified with hexane, filtered, and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were recrystallized from THF/hexane to give white crystals of [Pd{(*R*)-(−)-S_2C=NC(H)(Me)(Ph)}(depe)] (**7**, 0.126 g, 96%). IR (KBr/cm^{-1}): 1566 (C=N). ^{1}H NMR: δ 1.12–1.27 (m, 12H, PCH_2CH_3), 1.49 (d, *J* = 6.6 Hz, 3H, PCH_2CH_3), 1.81–1.88 (m, 12H, P(Et)+P(CH_2), 5.46 (q, *J* = 6.6 Hz, 1H, C*H*), 7.13–7.15 (m, 1H), 7.22–7.27 (m, 2H), 7.48–7.50 (m, 2H). ^{131}C{^{1}H} NMR: δ 8.65 (dd, *J* = 1.9, 5.6 Hz, PCH_2CH_3), 19.3 (m, PCH_2), 24.1 (s, CH_3), 24.4 (ddd, *J* = 4.3, 16, 25 Hz), 55.5 (s, *C*H), 125.4, 127.1, 127.7, 146.7, 172.6 (s, C=N). ^{31}P{^{1}H}NMR: δ 61.9 (s). *Anal.* Calc. for $C_{19}H_{33}NP_2S_2Pd$: C, 44.92; H, 6.55; N, 2.56. Found: C, 45.33; H, 6.59; N, 2.49.

[Pd{(*S*)-(+)-S_2C=NC(H)(Me)(Ph)}(depe)], **8** and [Pd{(*R*)-(−)-S_2C=NC(H)(Me)(Ph)}(depe)], **9** were prepared analogously.

Complex **8** (89%). IR (KBr/cm^{-1}): 1557 (C=N). ^{1}H NMR: δ 1.16–1.28 (m, 12H, PCH_2CH_3), 1.50 (d, *J* = 6.6 Hz, 3H, PCH_2CH_3), 1.86–1.93 (m, 12H, P(Et)+P(CH_2), 5.46 (q, *J* = 6.6 Hz, 1H, C*H*), 7.10–7.15 (m, 1H), 7.22–7.27 (m, 2H), 7.48–7.50 (m, 2H). ^{131}C{^{1}H} NMR: δ 8.69 (dd, *J* = 3.1, 3.4 Hz, PCH_2CH_3), 19.3 (m, PCH_2CH_3), 24.1 (ddd, *J* = 5.0, 19, 25 Hz), 24.2 (s, CH_3), 55.5 (s, *C*H), 125.7, 127.2, 127.9, 127.8, 146.7, 172.5 (s, C=N). ^{31}P{^{1}H}NMR: δ 61.8 (s). *Anal.* Calc. for $C_{19}H_{33}NP_2S_2Pd$: C, 44.92; H, 6.55; N, 2.56. Found: C, 45.08; H, 6.65; N, 2.54.

Complex **9** (87%). IR (KBr/cm^{-1}): 1550 (C=N). ^{1}H NMR: δ 1.48 (d, *J* = 6.6 Hz, 3H, CH_3), 1.56 (ddd, *J* = 4.8, 11 Hz, 12H, PCH_3), 1.81 (m, 4H, PCH_2), 5.44 (q, *J* = 6.6 Hz, 1H, C*H*), 7.11–7.16 (m, 1H), 7.23–7.28 (m, 2H), 7.44–7.47 (m, 2H). ^{13}C{^{1}H} NMR: δ 14.08 (ddd, *J* = 1.9, 15, 25 Hz, PCH_3), 24.0 (s, CH_3), 28.2 (ddd, *J* = 2.5, 30, 57 Hz), 125.8, 127.2, 1273.8, 146.6, 172.4 (s, *C*=N). ^{31}P{^{1}H}NMR: δ 36.4 (dd, *J* = 37, 79

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Hz). *Anal.* Calc. for $C_{15}H_{25}NP_2S_2Pd$: C, 39.87; H, 5.58; N, 3.09. Found: C, 39.62; H, 5.54; N, 3.05.

Reaction of *trans*-[$PdEt_2(PMe_3)_2$] with R–NCS (R = allyl)

Allyl isothiocyanate (267 µl, 2.75 mmol) and THF (5 cm^3) were added at 0 °C to a Schlenk flask containing *trans*-[$PdEt_2(PMe_3)_2$] (0.436 g, 1.38 mmol). The reaction mixture was stirred for 18 h at room temperature, and then the solvent was removed under vacuum. The resulting residue was solidified with diethyl ether/hexane. The solids were filtered and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were recrystallized from CH_2Cl_2/ether to give $[Pd(\eta^3\text{-allyl})(PMe_3)_2]^+(NCS)^-$ (**10**, 0.439 g, 85%) as a white solid. IR (KBr/cm^{-1}): 2051 (NCS). ^{1}H NMR: δ 1.64 (d, J = 8.1 Hz, 18H, PCH_3), 3.80 (br, 4H, CH_2), 5.55 (q, J = 10 Hz, 1H, CH). ^{13}C{^{1}H} NMR: δ 18.2 (d, J_{PC} = 26 Hz, PCH$_3$), 30.3 (s, CH$_2$), 69.7 (s, CH), 120.8 (s, NCS). ^{31}P{^{1}H}NMR: δ –19.2 (s). *Anal.* Calc. for $C_{10}H_{23}NP_2SPd$: C, 33.57; H, 6.48; N, 3.92. Found: C, 33.73; H, 6.65; N, 3.68.

Reactions of *trans*-[$PdEt_2L_2$] (L = PMe_3, PMe_2Ph) with R–SCN (R = benzyl or Et)

Benzyl thiocyanate (0.353 g, 2.36 mmol) and THF (4 cm^3) were added at 0 °C to a Schlenk flask containing *trans*-[$PdEt_2(PMe_3)_2$] (0.375 g, 1.18 mmol). The reaction mixture was stirred for 18 h at room temperature, and then the solvent was completely removed under vacuum. The resulting oily residue was solidified with diethyl ether. The solids were filtered and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were recrystallized from CH_2Cl_2/ether to give $[Pd(CN)_2(PMe_3)_2]$ (**11,** 0.169 g, 67%) as a white solid. IR (KBr/cm^{-1}): 2123 (CN). ^{1}H NMR: δ 1.70 (t, J = 3.8 Hz, 18H, PCH_3). ^{13}C{^{1}H} NMR: δ 16.4 (t, J_{PC} = 17 Hz, PCH$_3$), 131.3 (t, J_{PC} = 17 Hz, CN). ^{31}P{^{1}H}NMR: δ –12.3 (s). Complex **11** was identified with the literature data [12d]. The collected solution was purified by silica gel column (diethyl ether/hexane : 10:1) to yield a pure $PhCH_2SSCH_2Ph$ (64%) which was identified by IR, NMR (^{1}H and ^{13}C) spectroscopy and GC-MS on the basis of literature data [38].

Analogous reactions of *trans*-[PdR_2L_2] (L = PMe_3, PMe_2Ph)$_2$ with benzyl or ethyl isothiocyanate yielded [$Pd(CN)_2L_2$] and ethyl or benzyl disulfide; EtS–SEt (64%) or

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$PhCH_2S–SCH_2Ph$ (67%). The final products were characterized using IR and NMR (^1H and ^{13}C) spectroscopies and GC–MS. $PhCH_2S–SCH_2Ph$: ^1H NMR ($CDCl_3$): δ 3.58 (s, 4H, CH_2), 7.20–7.33 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR: δ 43.2 (s, CH_2), 127.3, 128.4, 129.3, 137.24. MS (M^+): 246.1.

Complex **12** (94%): IR (KBr/cm^{-1}): 2126 (CN). ^1H NMR: δ 1.94 (s, 12H, PCH_3), 7.39–7.41 (m, 6H, Ph), 7.66 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR: δ 16.1 (t, J = 17.1 Hz, PCH_3), 128.1 (dd, J_{PC} = 5.0 Hz, Ph), 129.9, 130.0, 130.1. $^{31}P\{^1H\}$ NMR: δ −5.11 (s).

Reaction of *trans*-[$PdEt_2(PMe_3)_2$] with benzyl mercaptan

Benzyl mercaptan (298 µl, 2.52 mmol) and THF (4 cm^3) were added at 0 °C to a Schlenk flask containing *trans*-[$PdEt_2(PMe_3)_2$] (0.400 g, 1.26 mmol). The reaction mixture was stirred for 5 h at room temperature, and then the solvent was completely removed under vacuum. The resulting residue was solidified with diethyl ether/hexane. The solids were filtered and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were recrystallized from CH_2Cl_2/hexane to give yellow crystals of **13** (0.119 g, 19%). ^1H NMR: δ 1.42 (br, 18H, PCH_3), 3.54 (s, 4H, $S–CH_2$), 7.12–7.18 (m, 2H, Ph), 7.23–7.28 (m, 4H, Ph), 7.35–7.38 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR: δ 13.8 (t, J = 16 Hz, PCH_3), 35.8 (s, $S–CH_2–CH_3$), 125.8, 128.3, 128.4, 145.1. $^{31}P\{^1H\}$ NMR: δ −15.5 (s). *Anal.* Calc. for $C_{20}H_{33}P_2S_2Pd$: C, 47.57; H, 6.39. Found: C, 47.53; H, 6.68.

Reactions of *trans*-[$PdMe_2L_2$] (L = PEt_3, PMe_3) with R–SCN (R = benzyl)

Benzyl thiocyanate (0.278 g, 1.86 mmol) and THF (3 cm^3) were added at 0 °C to a Schlenk flask containing *trans*-[$PdMe_2(PEt_3)_2$] (0.347 g, 0.93 mmol). The reaction mixture was stirred for 18 h at room temperature, and then the solvent was removed. The resulting oily residue was solidified with diethyl ether/hexane. The solids were filtered and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were crystallized from excess diethyl ether to give white crystals of **14** (0.193 g, 50%). IR (KBr/cm^{-1}): 2095 (NCS). ^1H NMR: δ −0.05 (br, 3H, $PdCH_3$), 1.14 (q, J = 8.4 Hz, 18 H, PCH_2CH_3), 1.73 (br, 12H, PCH_2CH_3). $^{13}C\{^1H\}$ NMR: δ −12.0 (br, $PdCH_3$), 8.26 (s, PCH_2CH_3), 14.5 (t, J = 13 Hz, PCH_2CH_3), 135.0 (br, N=C=S).$^{31}P\{^1H\}$ NMR: δ 18.0 (s). *Anal.* Calc. for $C_{14}H_{33}NP_2SPd$: C, 40.44; H, 8.00; N, 3.37. Found: C, 40.47; H, 8.35; N, 3.21. The organic products were identified using GLC and GC-MS.

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The analogous reaction of *trans*-[$PdMe_2(PMe_3)_2$] with benzyl thiocyanate produced a mixture of *trans*-[$Pd(NCS)_2(PMe_3)_2$] (**15**, 33%) as the major product and *trans*-[$PdMe(NCS)(PMe_3)_2$] (**16**, below 1%) as minor product. The organic products were analyzed using GC–MS. Complex **15**: IR (KBr/cm^{-1}): 2091 (NCS). ^{1}H NMR: δ 1.41 (t, J = 3.3 Hz, 18 H, PCH_3). ^{13}C{^{1}H} NMR: δ 13.8 (t, J_{PC} = 15 Hz, PCH$_3$), 134.5 (br, N=C=S). ^{31}P{^{1}H} NMR: δ −14.0 (s).

Complex **16**: ^{1}H NMR: δ −0.19 (t, J_{PH} = 6.9 Hz, 3H, PdCH_3), 1.49 (t, J = 3.3 Hz, 18 H, PCH_3). ^{13}C{^{1}H} NMR: δ −9.85(br, PdCH$_3$), 15.4 (t, J_{PC} = 15 Hz, PCH$_3$), 133.1 (br, N=C=S). ^{31}P{^{1}H} NMR: δ −12.4.0 (s).

Reaction of *cis*-[$PtEt_2(PMe_3)_2$] with R–NCS (R = benzyl)

Styrene (89 μL, 0.78 mmol) and toluene (3 mL) were added at room temperature to a Schlenk flask containing *cis*-[$PtEt_2(PMe_3)_2$] (0.157 g, 0.39 mmol). The mixture was heated at 80 °C for 5 h to give a pale-yellow solution. On addition of benzyl isothiocyanate (103 μL, 0.78 mmol) to the mixture at room temperature, the yellow solution was transformed to a yellow suspension. The mixture was stirred for 3 h, the solvent was removed under vacuum, and the resulting residue was solidified with hexane and CH_2Cl_2 and stored at −35 °C. The precipitates were filtered and washed with hexane (2 mL × 2) to obtain the crude solids. Recrystallization from THF/diethyl ether afforded white crystals of *cis*-[$Pt(S_2C{=}N{-}CH_2Ph)(PMe_3)_2$] (**17**, 0.058 g, 28%). IR (KBr/cm^{-1}): 1573 (C=N). ^{1}H NMR: δ 1.64 (dd, J = 2.4, 4.8 Hz, J_{PtH} = 16 Hz, 18H, PCH_3), 4.84 (s, 2H, CH_2), 7.15–7.17 (m, 1H, Ph), 7.25–7.28 (m, 2H, Ph), 7.38–7.39 (m, 2H, Ph). ^{131}C{^{1}H} NMR: δ 16.6 (m, PCH$_3$), 51.9(s, CH$_2$), 128.0, 128.5, 128.6, 141.0, 170.6 (d, J_{PC} = 3.5 Hz, C=N). ^{31}P{^{1}H}NMR: δ −29.2 (dd, J = 6.5, 13 Hz, J_{PtP} = 1441 Hz). *Anal.* Calc. for $C_{14}H_{25}NP_2S_2Pt$: C, 31.82; H, 4.77; N, 2.65. Found: C, 31.77; H, 4.97; N, 2.11.

Reaction of *cis*-[$PtEt_2(PMe_3)_2$] with R–SCN (R = benzyl)

Benzyl thiocyanate (0.334 g, 2.24 mmol) was added at room temperature to a THF (3 cm^3) solution containing *cis*-[$PtEt_2(PMe_3)_2$] (0.454 g, 1.12 mmol). The reaction mixture was stirred for 18 h at room temperature, and then the solvent was removed under vacuum. The resulting oily residue was solidified with diethyl ether/hexane. The

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solids were filtered and washed with *n*-hexane (2 cm^3 × 2) to give crude solids, which were recrystallized from CH_2Cl_2/hexane to give white crystals of **18** (0.298 g, 48%). *cis*-[$Pt(Et)_2(CH_2Ph)(NCS)(PMe_3)_2$] (**18A**): ^1H NMR: δ 0.80 (dd, J = 5.1 Hz, overlap, $PtCH_2CH_3$), 0.97–1.22 (m, $PtCH_2$), 1.51 (dd, J_{PH} = 5.0, 8.9 Hz, J_{PtH} = overlap, 18H, PCH_3), 2.59 (dd, J = 10, 20 Hz, J_{PtH} = 91 Hz, CH_2), 7.14–7.18 (m, 5 H). $^{13}C\{^1H\}$ NMR: δ −0.94 (s, J_{PC} = 653 Hz, PCH_2CH_3), 7.6 (s, J_{PtC} = 651 Hz, $PtCH_2CH_3$), 20.3 (ddd, J_{PC} = 6.9, 73, 108 Hz, J_{PtC} = 1985 Hz, PCH_3). $^{31}P\{^1H\}$ NMR: δ −35.6 (d, J = 13 Hz, J_{PtP} = 1315 Hz), 38.4(d, J = 13 Hz, J_{PtP} = 1065 Hz)

trans-[$Pt(Et)_2(CH_2Ph)(NCS)(PMe_3)_2$] (**18B**): IR (KBr/$cm^{-1}$): 2107 (NCS). ^1H NMR: δ 0.71 (t, J_{PH} = 75, J_{PtH} = 61 Hz, 6H, $PtCH_2CH_3$), 0.97–1.22 (m, overlap, $PtCH_2$), 1.41 (d, J_{PH} = 8.5 Hz, J_{PtH} = 8.5 Hz, PCH_3), 2.55 (t, J = 7.8 Hz, J_{PtH} = 103 Hz, CH_2), 7.14–7.18 (m, 5 H). $^{13}C\{^1H\}$ NMR: δ −0.94 (s, J_{PC} = 653 Hz, PCH_2CH_3), 7.6 (s, J_{PtC} = 651 Hz, $PtCH_2CH_3$), 23.9 (dd, J_{PC} = 3.5, 40 Hz, PCH_3). $^{31}P\{^1H\}$ NMR: δ −39.4 (s, J_{PtP} = 1122 Hz). *Anal.* Calc. for $C_{18}H_{35}NP_2SPt$: C, 38.98; H, 6.36; N, 2.53. Found: C, 38.99; H, 6.53; N, 2.24.

X-ray structure determination. Single crystals of **7**, **8**, **13** and **18B** for X-ray crystallography were grown from THF/n-hexane or CH_2Cl_2/ *n*-hexane at −35 °C. X-ray data were collected using a Siemens P4 or a Bruker Smart APEX diffractometer equipped with a Mo X-ray tube. All calculations were carried out using SHELXTL programs [39]. All structures were solved by direct methods. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

Details of crystal data, intensity collection, and refinement details are given in Table 1.

Appendix A. Supplementary material

CCDC Nos. 1004233, 1004234, 1004236, and 1004237 contain the supplementary crystallographic data for compounds **7**, **8**, **13**, and **18B.** These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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Table 1. X-ray data collection and structure refinements.

complex	**7**	**8**	**13**	**18B**
formula	$C_{19}H_{33}NP_2PdS_2$	$C_{19}H_{33}NP_2PdS_2$	$C_{20}H_{32}P_2PdS_2$	$C_{18}H_{35}NP_2PtS$
fw	507.92	507.92	504.92	554.56
temperature, K	200(2)	200(2)	293(2)	296(2)
crystal size (mm)	0.12×0.11×0.08	0.25×0.19×0.07	0.80×0.22×0.18	0.40×0.38×0.34
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_1$	$Pca2_1$	$Pbca$
a, Å	10.9697(4)	10.939(4)	17.9262(5)	15.8972(2)
b, Å	13.1747(5)	13.168(5)	5.9010(1)	15.2317(2)
c, Å	15.8585(6)	15.830(5)	22.4934(6)	18.7656(3)
α, deg	90	90	90	90
β, deg	95.422(1)	95.203(7)	90	90
γ, deg	90	90	90	90
V, Å^3	2281.66(15)	2270.7(13)	2379.4(1)	4543.9(1)
Z	4	4	4	8
d_{cal}, g cm^{-3}	1.479	1.486	1.409	1.621
μ, mm^{-1}	1.140	1.145	1.092	6.409
F(000)	1048	1048	1040	2192
T_{min}	0.8753	0.7627	0.4755	0.1186
T_{max}	0.9143	0.9241	0.8277	0.2670
θ range (°)	2.01–28.30	1.29–26.21	1.81–28.33	2.15–28.45
No. of reflns Measured	16617	13495	28249	66050
No. of reflns Unique	9060	7900	5255	5702
No. of reflns with $I > 2\sigma(I)$	6861	6694	3793	4396
No. of params Refined	451	451	227	208
Max., in Δρ (e Å^{-3})	0.925	0.851	0.520	1.472
Min., in Δρ (e Å^{-3})	–0.688	–0.557	–0.266	–0.629
Absolute structure parameter	–0.01(2)	0.00(3)	0.53(4)	
GOF on F^2	0.947	0.985	0.993	1.059
$R1$[a]	0.0336	0.0412	0.0321	0.0249
$wR2$[b]	0.0538	0.0838	0.0595	0.0582

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$, [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

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Figure 1. *ORTEP* drawing [40] of **7** showing the atom-labelling scheme and 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Pd1–P1 2.246(1), Pd1–P2 2.247(1), Pd1–S2 2.320(1), Pd–S1 2.337(1), N1-C11 1.246(5); P1–Pd1–P2 86.40(5), P1–Pd1)–S2 96.81(4), P2–Pd1–S1 100.47(5), S2–Pd1–S1 76.66(4).

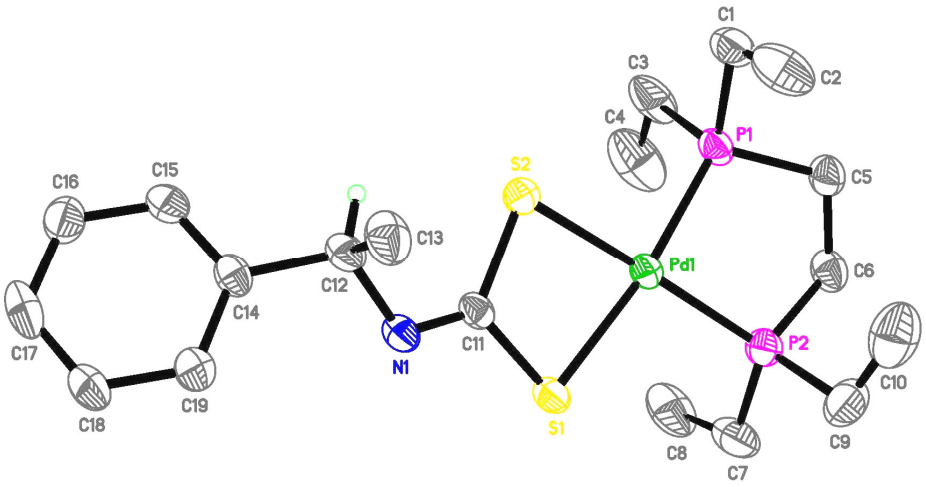

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Figure 2. *ORTEP* drawing of **8**. Selected bond lengths (Å) and angles (°): Pd1–P1 2.244(2), Pd1–P2 2.249(2), Pd1–S2 2.321(2), Pd1–S1 2.330(2), N1–C11 1.263(7); P1–Pd1–P2 86.36(6), P1–Pd1–S2 96.78(6), P2–Pd1–S2 174.76(7), S2–Pd1–S1 76.69(6).

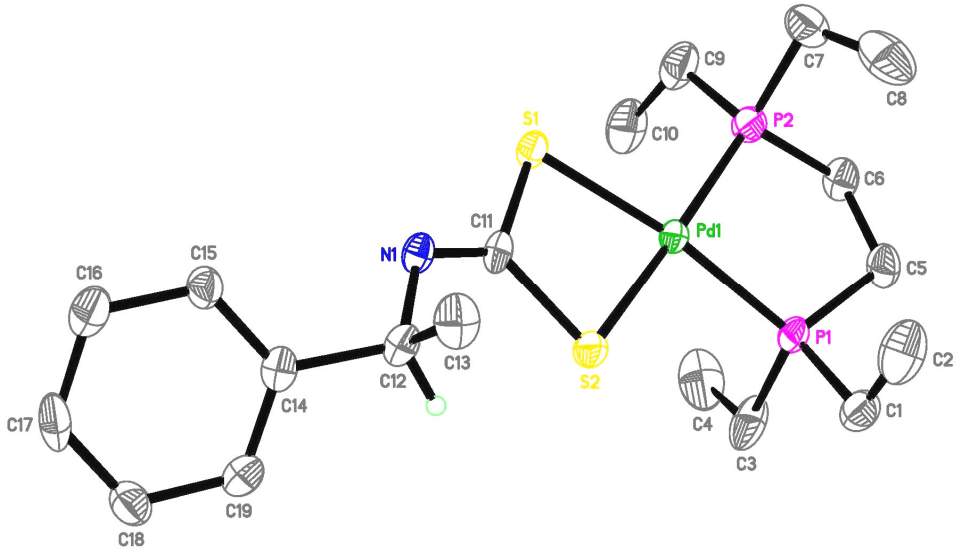

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Figure 3. *ORTEP* drawing of **13**. Selected bond lengths (Å) and angles (°): Pd1–P2 2.314(1), Pd1–P1 2.315(1), Pd1–S2 2.347(1), Pd1–S1 2.347(1), S1–C1 1.827(5), S2–C8 1.836(4); P2–Pd1–P1 179.73(7), P2–Pd1–S2 86.64(5), P1–Pd1–S2 93.43(4), S2–Pd1–S1,179.15(5), C1–S1–Pd1 99.84(16), C8–S2–Pd1 100.4(2).

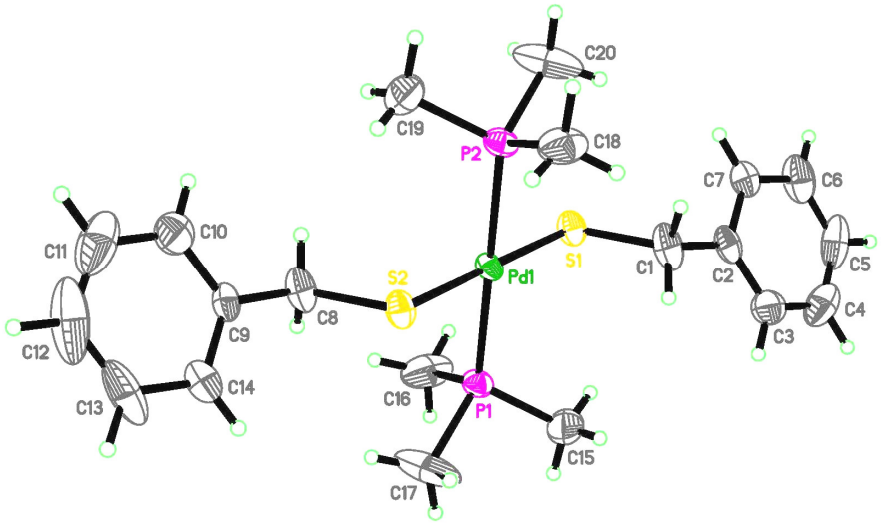

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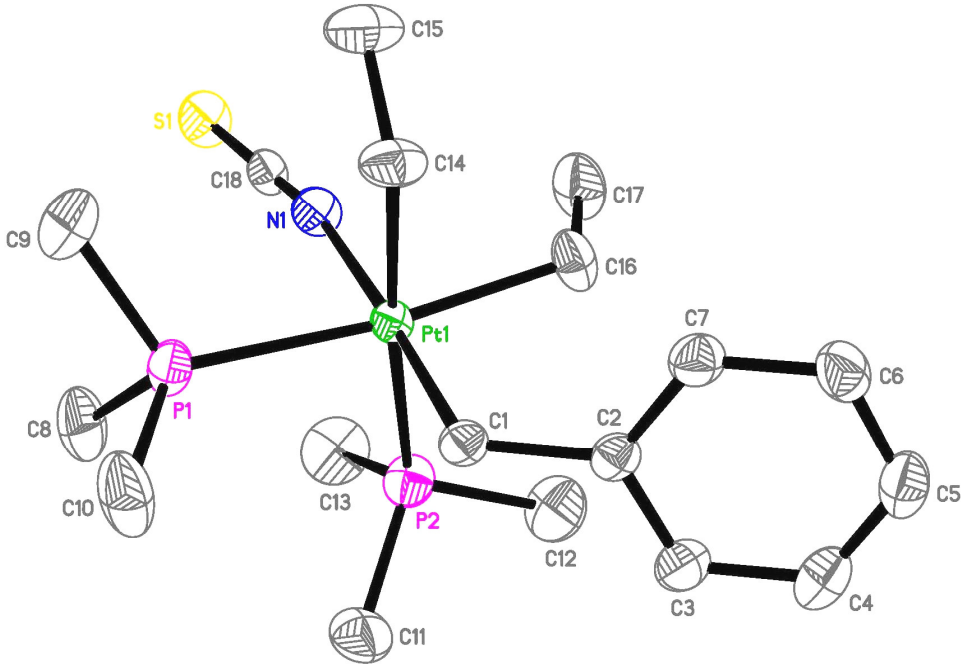
Figure 4. *ORTEP* drawing of **18B**. Selected bond lengths (Å) and angles (°): Pt1–C1 2.100(4), Pt1–C16 2.112(4), Pt1–N1 2.113(4), Pt1–C14 2.125(4), Pt1–P2 2.392(1), Pt1–P1 2.393(1), S1–C18 1.624(4), N1–C18 1.146(5); C1–Pt1–C16 91.7(2), C1–Pt1–N1 176.0(1), C16–Pt1–C14 85.1(2), N1–Pt1–P2 89.3(1), C16–Pt1–P1 173.2(2), P2–Pt1–P1 95.44(4), C18–N1–Pt1 169.2(4), N1–C18–S1 179.0(4).



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Graphical Abstract

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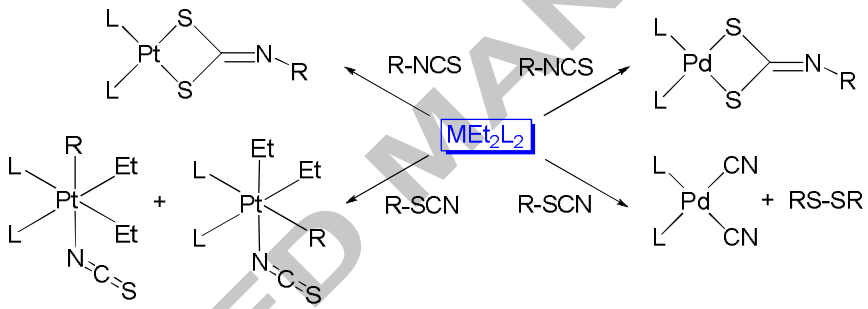
Seon Gye Lee, Keun-Young Choi, Yong-Joo Kim*, SuJin Park, Soon W. Lee



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Reactivities of organic isothiocyanates and thiocyanates toward dialkyl bis(phosphine) complexes of palladium(II) and platinum(II)

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Organic isothiocyanates (R–NCS) reacted with *trans*-[$PdEt_2(PR_3)_2$] to afford *S*,*S*-coordinated dithiocarbonimidato complexes [$Pd(S_2C{=}N{-}R)L_2$]. When allyl isothiocyanates was used, the cationic η^3-allyl Pd complex [Pd(η^3-allyl)$(PMe_3)_2$]$^+$(NCS)$^-$ was formed. In contrast, organic thiocyanates (R–SCN) underwent selective S–C oxidative addition to *trans*-[$PdEt_2L_2$] to afford [$Pd(CN)_2L_2$] and RS–SR. Interestingly, benzyl thiocyanate was oxidatively added to *cis*-[$PtEt_2(PMe_3)_2$] to afford a mixture of two octahedral Pt(IV) complexes.

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