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# C–S bond activation of thioethers using (dippe)Pt(NBE)<sub>2</sub>

ABSTRACT

several cases.

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This paper is dedicated to the memory and indomitable spirit of Michelle Millar.

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## 1. Introduction

Cleavage of carbon–sulfur bonds plays an important role in the desulfurization of petroleum [1], and homogeneous transition metal complexes have been extensively studied as models for the structures of intermediates involved in the desulfurization [2]. Most of these studies involve C–S cleavage reactions of thiophenes, benzothiophenes, or dibenzothiophenes, which are among the more difficult substrates to be desulfurized [3,4]. Applications of C–S cleavage in organic synthesis have also appeared, but are somewhat rare [5–8].

Reactions in which the C–S bonds of thioethers are cleaved have been less commonly examined with transition metals, with many examples arising from the degradation of macrocyclic or polydentate sulfur-containing ligands [9–15]. For example, reduction of  $[Re(TTCN)_2]^{2+}$  (TTCN = trithiacyclononane) with ascorbic acid leads to a product in which ethylene has been extruded and a dianionic SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>S ligand is now present [16]. Nucleophilic attack on a coordinated thiacycle has also been shown to result in C–S bond cleavage [17–19]. Photochemical cleavage of C–S thioether bonds has been reported using heteropolytungstates [20], and aerobic oxidative cleavage of  $\beta$ -keto-sulfides using a Co(II) complex has been observed [21], the latter via a radical pathway. Methylsulfur C–S cleavage is also believed to be involved in the latter steps of conversion of carbon-dioxide to methane by Me-CoM reductase [22].

A few examples of C–S oxidative addition to metal complexes have been reported as summarized in Scheme 1. In 1998, Komiya observed the addition of allyl phenyl sulfide to Ru(cot)(cod) to give

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a  $\pi$ -allyl complex as product [23]. In 2004, Delgado reported C–S addition of acetylenic thioesters to ruthenium(0), giving bridgedcluster products [24]. C–S cleavage in a sulfoxide via oxidative addition has also been documented by O'Connor et al. [25]. Chirik used zirconium(II) to effect thioether oxidative addition to give Zr(IV) products [26]. More recently, Radius used Ni<sup>0</sup>(NHC)<sub>2</sub> complexes to add to the C–S bond of aryl thioethers [27].

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Recently, we described C–S cleavage in thioesters using (dippe)Pt(NBE)<sub>2</sub> as a source of a reactive platinum fragment [28]. We had shown earlier that this species could react with thiophene to give C–S insertion products [29]. In this paper, we describe C–S bond cleavage of a variety of thioethers including aryl, alkyl, vinyl, and allyl  $sp^2$  and  $sp^3$  hybridized carbon centers.

## 2. Results and discussion

## 2.1. C-S bond activation of diphenyl sulfide

The complex (dippe)Pt(NBE)<sub>2</sub> (NBE = norbornene) reacts with thioethers RSR' upon heating to give C-S

oxidative addition products (RSR' =  $Ph_2S$ , PhSMe, PhSallyl, MeSallyl, PhSvinyl, PhCH<sub>2</sub>SMe, PhSCF<sub>3</sub>, and dithiane). Continued heating leads to disproportionation and formation of  $R'_2$  and (dippe)Pt(SR)<sub>2</sub> in

Treatment of (dippe)Pt(NBE)<sub>2</sub> (**1**) with excess diphenyl sulfide in *p*-xylene at 140 °C for 7 d afforded complex **2** in good yield (76%, Eq. (1)). Complex **2** was isolated as off-white solid and characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and X-ray crystallography Fig 1. The ortho Pt–phenyl hydrogens appear in the <sup>1</sup>H NMR spectrum as a multiplet at  $\delta$  7.57 with platinum satellites ( $J_{Pt-H} = 43$  Hz).







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Scheme 1. Recent examples of thioether C-S cleavage.



Fig. 1. X-ray structure of complex 2. Ellipsoids are shown at the 50% probability level.

## 2.2. C-S bond activation of methyl phenyl sulfide

Similar to diphenyl sulfide, treatment of (dippe)Pt(NBE)<sub>2</sub> (**1**) with excess methyl phenyl sulfide in *p*-xylene at 140 °C for 7 d afforded complex **3a** in good yield (88%, Eq. (2)). Complex **3a** was isolated as off-white solid and characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and X-ray crystallography (Fig. 2). The same reaction at lower temperature (100 °C) did not afford any (dippe)Pt(Me)(SPh) even at earlier reaction time, and only product complex **3a** was identified. The ortho phenyl hydrogens appear in the <sup>1</sup>H NMR spectrum as a triplet at  $\delta$  7.86 with platinum satellites ( $J_{Pt-H} = 46$  Hz). The SMe resonance appears as a doublet ( $J_{P-H} =$ 



Fig. 2. X-ray structure of complex 3a. Ellipsoids are shown at the 50% probability level.

4.9 Hz) also with platinum satellites ( $J_{Pt-H} = 56$  Hz). These data are in agreement with the couplings observed previously for the SMe groups in (dippe)Pt(SMe)<sub>2</sub> ( $\delta$  3.03, d,  $J_{Pt-H} = 44$  Hz,  $J_{P-H} = 5.6$  Hz) [28].



2.3. C-S bond activation of phenyl- and methyl-allyl sulfides

Reaction of (dippe)Pt(NBE)<sub>2</sub> (**1**) with excess allyl methyl sulfide or allyl phenyl sulfide in benzene or *p*-xylene at 100 °C for 20 min afforded the allyl thiolate complex **4a** or **4b** in good yield (70%, Scheme 2), which were isolated and characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. For **4b**, the CH<sub>2</sub> appears at  $\delta$  2.65 as a quartet ( $J_{H-H}$  = 7.4 Hz) with platinum satellites ( $J_{Pt-H}$  = 74 Hz). A single crystal X-ray structure of **4a** is shown in Fig. 3, displaying a  $\sigma$ -allyl moiety. Further reaction occurs upon heating to 140 °C for extended periods. Hexa-1,5-diene was identified as the organic



Scheme 2. Reaction of (dippe)Pt(NBE)<sub>2</sub> with RSallyl.



Fig. 3. X-ray structure of complex  ${\bf 4a}.$  Ellipsoids are shown at the 50% probability level.

product by GC–MS. Complex **5a** was identified by comparison with literature data [28]. Complex **5b** was isolated as off-white solid and characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and X-ray crystallography (Fig. 4).

## 2.4. C-S bond activation in phenyl vinyl sulfide

Treatment of (dippe)Pt(NBE)<sub>2</sub> (**1**) with excess phenyl vinyl sulfide in benzene or *p*-xylene at 100 °C for 20 min afforded  $\pi$ -complex (dippe)Pt( $\eta^2$ -CH<sub>2</sub>CHSPh), **6** '(Scheme 3). Further reaction of **6** occurs upon heating to 140 °C. First, vinyl thiolate complex **7** is observed after 5 d. Next, bis-thiolate **5b** was formed, and butadiene was identified as the organic product by GC–MS. Oxidative addition of a number of aryl vinyl sulfides to [Pt(PPh<sub>3</sub>)<sub>2</sub>] has been reported by Kuniyasu et al., but  $\eta^2$ -vinyl intermediates were not observed [30].

## 2.5. C-S bond activation of benzyl methyl sulfide

The reaction of **1** with excess benzyl methyl sulfide in  $C_6H_6$  at 140 °C yielded a complicated reaction mixture which was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR over the course of several days. The complex (dip-pe)Pt(SMe)(CH<sub>2</sub>Ph) was not identified by <sup>31</sup>P{<sup>1</sup>H} NMR spectros-copy. The major product was instead determined to be (dippe)Pt(SMe)<sub>2</sub> (**5a**) (Eq. (3)). The presence of ~1 mM (sub-stoichi-



Scheme 3. Reaction of (dippe)Pt(NBE)<sub>2</sub> with PhSCH=CH<sub>2</sub>.

ometric) bibenzyl, observed by <sup>1</sup>H NMR spectroscopy and GC–MS in the reaction mixture, provided evidence that  $(dippe)Pt(SMe)(CH_{2-}Ph)$  was an intermediate in the formation of  $(dippe)Pt(SMe)_2$ .



## 2.6. Activation of phenyl trifluoromethyl sulfide

The reaction of **1** with excess phenyl trifluoromethyl sulfide in mesitylene at 160 °C was monitored by <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>H} NMR spectroscopy over the course of 3 d. Partial conversion of the starting material was observed, and the resulting mixture of products was complicated. The <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of the reaction mixture contains a resonance with what appear to be platinum satellites, as well as cis and trans couplings to phosphorus. The <sup>19</sup>F{<sup>1</sup>H} NMR spectra of the known complexes (dppe)Pt(CF<sub>3</sub>)(Br) and (dppe)Pt(CF<sub>3</sub>)(OH) in CDCl<sub>3</sub> show  ${}^{3}J_{Pt-F}$  couplings on the order of 580 Hz, trans- ${}^{3}J_{P-F}$  couplings on the order of 55 Hz, and cis- ${}^{3}J_{P-F}$ couplings on the order of 12 Hz [31]. These couplings are similar to those observed in the <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of the reaction mixture, suggesting that the observed product is (dippe)Pt(SPh)(CF<sub>3</sub>), and not (dippe)Pt(SCF<sub>3</sub>)(Ph) (Eq. (4)). The CF<sub>3</sub> group thus appears to alter the selectivity of C-S activation relative to the analogous non-fluorinated substrate, PhSCH<sub>3</sub>.



#### 2.7. C-S bond activation of dithiane

The reaction of **1** with excess dithiane in mesitylene at 180 °C was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy over the course of 7 d. Complete conversion of the starting material was observed, furnishing (dippe)Pt( $\kappa^2$ -SCH<sub>2</sub>CH<sub>2</sub>S) (**9**) in ~90% yield by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Eq. (5)). This product was characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H COSY, and <sup>1</sup>H-<sup>13</sup>C HSQC NMR. **9** almost certainly forms by the rearrangement of the intermediate (dippe)Pt( $\kappa^2$ -SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>) (**8**). The presence of ethylene in the reaction mixture, observed directly by GC–MS and <sup>1</sup>H NMR spectroscopy ( $\delta$  5.28), provides evidence supporting this claim.



## 2.8. Synthesis of (dippe)Pt(SPh)(Me)

As mentioned above, the activation of methyl phenyl sulfide by **1** furnishes  $(dippe)Pt(SCH_3)(Ph)$ , not  $(dippe)Pt(SPh)(CH_3)$ . It is

possible that the latter complex is a transient kinetic product, which thermally rearranges to yield the observed product under the reaction conditions. To test this hypothesis, (dippe) Pt(SPh)(CH<sub>3</sub>) (**10**) was synthesized from (dippe)Pt(CH<sub>3</sub>)<sub>2</sub> by treatment with PhSH. The mixture containing **10** was held at 140 °C for 1 d, at which point no rearrangement was observed by  $^{31}P{^{1}H}$  NMR. These data indicate that **10** is not a kinetic product, and may also be disfavored thermodynamically.

## 2.9. Activation of allyl methyl sulfide by the complex (dippe)Pt(SPh)(Ph) – evidence for sulfide metathesis

One observed characteristic of the reactivity of thioethers with (dippe)Pt(SR)(R') is the tendency to form the bis-thiolate (dippe)Pt(SR)<sub>2</sub> when heated in the presence of excess substrate. The mechanism for this reaction is proposed to involve an octahedral Pt(IV) species as a likely intermediate. One deviation from this pattern of reactivity is seen in (dippe)Pt(SPh)(Ph) (**2**), the activation product of diphenyl sulfide. Unlike (dippe)Pt(SPh)( $\eta^1$ -CH<sub>2</sub>CHCH<sub>2</sub>) and (dippe)Pt(SPh)(CHCH<sub>2</sub>), **2** does not proceed to the bis-thiolate (dippe)Pt(SPh)<sub>2</sub>. This lack of reactivity may be due to the strength of the Pt-phenyl bond. Alternatively, the bulk of this complex may disallow the addition of a second molecule of substrate. It is also possible that, if a stable intermediate does form, the transition state associated with reductive elimination of biphenyl has a prohibitively high activation barrier due to geometric constraints associated with Csp<sup>2</sup>-Csp<sup>2</sup> bond formation.

To test this hypothesis, a less bulky substrate – allyl methyl sulfide – was reacted with **2** at 160 °C for 2 d. The reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, with the expectation that a mixed bis-thiolate complex (dippe)Pt(SPh)(SMe) and the corresponding cross-linked organic product, allylbenzene, would be formed. Instead, partial conversion (~30% by <sup>31</sup>P{<sup>1</sup>H} NMR) of the starting material to (dippe)Pt(SMe)(Ph) was observed (Scheme 4). The corresponding organic product, allyl phenyl sulfide, was observed by <sup>1</sup>H NMR and GC–MS.

These data are consistent with an octahedral Pt(IV) species (dippe)Pt(SPh)(SMe)(Ph)( $\eta^1$ -CH<sub>2</sub>CHCH<sub>2</sub>) as an intermediate in the formation of **3** (see Fig. 5 for possible geometries). Previous experiments with thioesters have shown reactivity consistent with Scheme 4, in which a hydrocarbon is eliminated from Pt<sup>IV</sup> with the formation of the bis-thiolate [28]. This being the case, it is reasonable to propose the phenolate and allyl ligands are *cis* to each other in the proposed intermediate. The observation of allyl phenyl sulfide suggests the allyl ligand is also *cis* to the phenylthiolate ligand. Two plausible routes for the formation of a species with this geometry are *cis* oxidative addition and an S<sub>N</sub>2-like mechanism seen in the oxidative addition of methyl iodide to square-planar Pt(II) complexes [32].

One question that arises from this experiment is why the observed products are favored over (dippe)Pt(SPh)(SMe) and allylbenzene – the latter pair would appear to be more thermodynam-



Scheme 4. Cleavage of allyl methyl sulfide.



Fig. 4. X-ray structure of complex 5b. Ellipsoids are shown at the 50% probability level.



Fig. 5. Potential classical and pericyclic mechanisms for the reductive elimination of allyl phenyl sulfide from (dippe)Pt(SPh)(SMe)(Ph)( $\eta^1$ -CH<sub>2</sub>CHCH<sub>2</sub>).

ically stable since two platinum–sulfur bonds are formed. It is possible that the allyl ligand affords a kinetic advantage to the former pair: allyl phenyl sulfide could form through a reductive elimination involving a 5-membered transition state (Fig. 5). This transition state could have aromatic character if the plane of the metallacycle is oriented properly with respect to the LUMO of (dippe)Pt(SPh)(SMe)(Ph)( $\eta^1$ -CH<sub>2</sub>CHCH<sub>2</sub>).

## 3. Conclusions

The reactivity of the Pt(0) complex (dippe)Pt(NBE)<sub>2</sub> with a number thioethers has been examined. Physical characterizations of the resulting C–S activation products (dippe)Pt(SR)(R') were carried out by <sup>1</sup>H, <sup>13</sup>C(<sup>1</sup>H}, and <sup>31</sup>P(<sup>1</sup>H} NMR spectroscopy; <sup>1</sup>H COSY and <sup>1</sup>H–<sup>13</sup>C HSQC NMR (as needed); as well as X-ray diffraction and elemental analysis (EA). Both S–Csp<sup>2</sup> and S–Csp<sup>3</sup> bonds can be cleaved. Investigation into the mechanism of methyl phenyl sulfide activation by (dippe)Pt(NBE)<sub>2</sub> indicates (dippe)Pt(SPh)(Me) is not an intermediate in the formation of (dippe)Pt(SMe)(SPh). Instead, the data indicate the former complex is kinetically and possibly thermodynamically disfavored. The investigation into the general mechanism through which bis-thiolates (dippe)Pt(SR)<sub>2</sub> form are

consistent with an octahedral Pt(IV) intermediate. The data also suggest the metathesis of allyl phenyl sulfide seen in the reaction of (dippe)Pt(SPh)(Ph) with allyl methyl sulfide could proceed through an unusual pericyclic mechanism. Further theoretical studies of this pathway are underway.

#### 4. Experimental

## 4.1. General procedures and materials

Unless otherwise stated, all reactions and manipulations were carried out in dry glassware using standard Schlenk and glovebox techniques under an inert atmosphere. Deuterated solvents (Cambridge Isotope Laboratories) for NMR experiments were dried over Na/K and distilled under vacuum. All thioethers were purchased from Aldrich and VWR and used without any further purification. All other reagent grade chemicals were used without any further purification. All NMR spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts ( $\delta$  in ppm) are relative to an external 85% solution of  $H_3PO_4$  in the appropriate solvent. <sup>19</sup>F{<sup>1</sup>H} NMR chemical shifts are relative to internal PhSCF<sub>3</sub>. Elemental analyses were obtained from CENTC Elemental Analysis Facility at the University of Rochester. GC-MS spectra were recorded on SHIMADZU QP2010 using a  $60 \text{ m} \times 0.25 \text{ mm}$  SPB1701 capillary column. (dippe) Pt(NBE)<sub>2</sub> was prepared as previously described [28].

## 4.2. Synthesis of (dippe)Pt(Ph)(SPh) (2)

In a J-Young tube (dippe)Pt(NBE)<sub>2</sub> (20 mg, 0.0309 mmol), diphenyl sulfide (51.6  $\mu$ L, 0.309 mmol), and *p*-xylene- $d_{10}$  (0.5 mL) were combined and heated at 140 °C for 7 d. The reaction was monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The volatiles were removed under vacuum and the remaining light yellow liquid (mostly free diphenyl sulfide) was washed with small quantities of hexane. Complex 2 was obtained as a light brown solid, still containing some diphenyl sulfide. Yield: 76%. Crystals of complex 2 were grown by slow evaporation of the hexane extract. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.56 (m, 2H), 7.30 (m, 3H), 6.93 (m, 5H), 2.24 (m, 2H), 1.91 (m, 2H), 1.37 (m, 6H), 1.04 (m, 4H), 0.89 (m, 6H), 0.74 (m, 12H). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 63.94 (s,  $J_{Pt-P}$  = 1711 Hz), 59.31 (s, J<sub>Pt-P</sub> = 2986 Hz). Anal. Calc. for C<sub>26</sub>H<sub>42</sub>P<sub>2</sub>PtS: C, 48.51; H, 6.58. Found: C, 48.27; H, 6.68%. <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  158.8 (dd,  $J_{P-C}$  = 108, 10 Hz), 143.3 (dd,  $J_{P-C}$  = 8, 3 Hz), 138.9 (s, J<sub>Pt-C</sub> = 22 Hz), 135.8 (s, J<sub>Pt-C</sub> = 29 Hz), 127.3 (d,  $J_{Pt-C} = 114 \text{ Hz}, J_{P-C} = 27 \text{ Hz}$  126.9 (s), 122.9 (s), 122.0 (s), 24.5 (d,  $J_{P-C} = 24$  Hz,  $J_{Pt-C} = 14$  Hz), 24.0 (d,  $J_{P-C} = 31$  Hz,  $J_{Pt-C} = 43$  Hz), 23.7 (dd,  $J_{P-C}$  = 29, 17 Hz), 20.9 (dd,  $J_{P-C}$  = 25, 10 Hz), 19.2 (d,  $J_{P-C}$  = 3 Hz), 18.6 (s), 18.3 (s,  $J_{Pt-C}$  = 12 Hz), 17.5 (s,  $J_{Pt-C}$  = 28 Hz).

### 4.3. Synthesis of (dippe)Pt(Ph)(SCH<sub>3</sub>) (3)

In a J-Young tube (dippe)Pt(NBE)<sub>2</sub> (20 mg, 0.0309 mmol), methyl phenyl sulfide (36.3 µL, 0.309 mmol), and *p*-xylene-*d*<sub>10</sub> (0.5 mL) were combined and heated at 140 °C for 7 d. The reaction was monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The volatiles were removed under vacuum yielding light brown complex **3** (88%). C rystals of complex **3** were grown by slow evaporation from a hexane solution. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.86 (t, *J*<sub>H-H</sub> = 6.8 Hz, *J*<sub>Pt-H</sub> = 46 Hz, 2H), 7.29 (t, *J*<sub>H-H</sub> = 6.8 Hz, 2H), 7.07 (t, *J*<sub>H-H</sub> = 7.2 Hz, 1H), 2.25 (d, *J*<sub>P-H</sub> = 5.2 Hz, *J*<sub>Pt-H</sub> = 56 Hz, 3H), 2.18 (m, 2H), 1.93 (m, 2H), 1.39 (m, 6H), 1.05 (m, 2H), 0.82 (m, 20H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  138.8 (s, *J*<sub>Pt-C</sub> = 24 Hz), 126.8 (s), 125.0 (s), 122.5 (s), 24.4 (d, *J*<sub>P-C</sub> = 25 Hz), 24.0 (d, *J*<sub>P-C</sub> = 30 Hz), 23.7 (dd, *J*<sub>P-C</sub> = 17, 9 Hz), 21.3 (dd, *J*<sub>P-C</sub> = 15, 11 Hz), 19.0 (d, *J*<sub>P-C</sub> = 3 Hz),

18.6 (d,  $J_{P-C} = 1$  Hz), 18.2 (s,  $J_{Pt-C} = 13$  Hz), 17.6 (s,  $J_{Pt-C} = 25$  Hz), 11.4 (dd,  $J_{P-C} = 9$ , 2 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  63.88 (d,  $J_{P-P} = 4$  Hz,  $J_{Pt-P} = 1750$  Hz), 59.74 (d,  $J_{P-P} = 4$  Hz,  $J_{Pt-P} = 2790$  Hz). *Anal.* Calc. for C<sub>21</sub>H<sub>40</sub>P<sub>2</sub>PtS: C, 43.36; H, 6.93. Found: C, 43.32; H, 6.80%.

## 4.4. Synthesis of (dippe)Pt(SMe)( $\eta^1$ -CH<sub>2</sub>CHCH<sub>2</sub>) (**4a**)

In a J. Young tube, allyl methyl sulfide ( $30 \mu$ L, 0.205 mmol) was added to 1 (20 mg, 0.031 mmol) dissolved in 0.7 mL C<sub>6</sub>D<sub>6</sub>. This mixture was heated to 100 °C for 20 min, at which point complete conversion of the starting material was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The reaction mixture was placed under vacuum to remove all volatiles, and the <sup>1</sup>H NMR spectrum was recorded. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.84 (m, 1H), 5.11 (m, 1H), 4.85 (m, 1H), 2.81 (d,  $J_{P-H}$  = 5 Hz,  $J_{Pt-H}$  = 46 Hz, 3H), 2.74 (m, 2H overlapping with SMe), 2.22 (m, 2H), 2.13 (m, 2 H), 1.30 (dd, J<sub>P-H</sub> = 16, 7 Hz, 6H), 1.05 (dd,  $J_{P-H}$  = 15, 7 Hz, 8H), 0.81 (dd,  $J_{P-H}$  = 13, 6 Hz, 7H), 0.77 (dd,  $J_{P-H}$  = 13, 6 Hz, 7H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  148.2 (d,  $J_{Pt-C} = 56$  Hz,  $J_{P-C} = 7$  Hz), 105.7 (d,  $J_{Pt-C} = 54$  Hz,  $J_{P-C} = 8$  Hz), 24.5 (d,  $J_{P-C} = 21 \text{ Hz}$ ), 24.4 (dd,  $J_{P-C} = 30$ , 17 Hz), 24.3 (d,  $J_{P-C} = 16 \text{ Hz}$ ), 23.5 (dd,  $J_{P-C}$  = 30, 17 Hz), 20.8 (dd,  $J_{P-C}$  = 25, 11 Hz), 19.7 (d<sub>P-C</sub>, J = 3 Hz), 19.0 (d<sub>P-C</sub>, J = 3 Hz), 18.2 (d,  $J_{P-C} = 3$  Hz), 18.0 (d,  $J_{P-C} = 3$ 3 Hz), 7.3 (dd,  $J_{P-C} = 8$ , 2 Hz,  $J_{Pt-C} = 20$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  65.32 (s,  $J_{Pt-P}$  = 1836 Hz), 61.82 (s,  $J_{Pt-P}$  = 2954 Hz). Continued heating at 140 °C (2 d) led to the formation of hexa-1,5-diene (δ 5.83, td, J = 17, 7 Hz, 2H; 5.10, dd, J = 19, 13 Hz, 6H; 3.01, d, J = 7 Hz, 4H) and (dippe)Pt(SMe)<sub>2</sub>, **5a**, which has been reported previously [28] (quantitative by <sup>31</sup>P NMR spectroscopy). For **5a**, <sup>1</sup>H (400 MHz,  $C_6D_6$ ):  $\delta$  3.02 (d,  $J_{P-H}$  = 6 Hz,  $J_{Pt-H}$  = 43 Hz, 6H), 2.38 (dquint, J = 9, 7 Hz, 4H), 1.24 (dd, J = 16, 7 Hz, 12H), 0.93 (dd, J = 21, 10 Hz, 4H), 0.77 (dd, J = 14, 7 Hz, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.8 (s,  $J_{Pt-C}$  = 27 Hz), 25.5 (s,  $J_{Pt-C} = 27 \text{ Hz}$ ), 23.0 (dd,  $J_{P-C} = 28$ , 12 Hz;  $J_{Pt-C} = 68 \text{ Hz}$ ), 19.9 (s), 18.8 (s,  $J_{Pt-C} = 21 \text{ Hz}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  68.76 (s,  $J_{\rm Pt-P}$  = 2681 Hz).

### 4.5. Synthesis of (dippe)Pt(SPh)( $\eta^1$ -CH<sub>2</sub>CHCH<sub>2</sub>) (**4b**)

In a J. Young tube, allyl phenyl sulfide (30 µL, 0.205 mmol) was added rapidly to 1 (40.7 mg, 0.0631 mmol) dissolved in 1.3 mL pentane. This mixture was heated to 100 °C for 20 min, at which point complete conversion of the starting material was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The reaction mixture was heated to 40 °C and held under vacuum for 12 h to remove the excess sulfide. Yield: 70%. Assignments in the <sup>1</sup>H NMR spectrum of this complex were facilitated with <sup>1</sup>H COSY data. Assignments in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum were facilitated with <sup>1</sup>H-<sup>13</sup>C HSQC data. For **4b**, <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.97 (d,  $J_{H-H}$  = 7 Hz, 2H), 6.97 (t,  $J_{H-H}$  = 7 Hz, 1H), 6.86 (m, 1H), 4.95 (d,  $J_{H-H}$  = 17 Hz, 1H), 4.77 (d,  $J_{H-H} = 9$  Hz, 1H), 2.64 (quartet,  $J_{Pt-H} = 73$  Hz,  $J_{P-H} = 7$  Hz, 2H), 2.15 (dm,  $J_{P-H} = 64$  Hz,  $J_{H-H} = 8$  Hz, 4H), 1.24 (dd,  $J_{P-H} = 16$  Hz,  $J_{H-H}$  = 7 Hz, 6H), 1.01 (dd,  $J_{P-H}$  = 16 Hz,  $J_{H-H}$  = 7 Hz, 6H), 0.79 (dd,  $J_{P-H}$  = 16 Hz,  $J_{H-H}$  = 7 Hz, 8H),  $\delta$  0.76 (dd,  $J_{P-H}$  = 16 Hz,  $J_{H-H}$  = 7 Hz, 8H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  148.5 (d,  $J_{Pt-C}$  = 53 Hz,  $J_{P-C}$  = 8 Hz), 135.3 (d,  $J_{Pt-C}$  = 34 Hz,  $J_{P-C}$  = 3 Hz), 126.8 (s), 122.9 (s), 104.9 (d,  $J_{Pt-C}$  = 49 Hz,  $J_{P-C}$  = 7 Hz), 24.6 (m), 23.5 (dd,  $J_{P-C}$  = 30, 18 Hz), 20.4 (dd,  $J_{P-C}$  = 24, 10 Hz), 19.7 (d,  $J_{P-C}$  = 2 Hz), 19.2 (d,  $J_{P-C}$  = 4 Hz), 18.2 (s). Note that the Pt–C coupling in the resonance at  $\delta$  23.5 was visible in the <sup>1</sup>H–<sup>13</sup>C HSQC NMR spectrum of **4b**. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  66.4 (s,  $J_{Pt-P}$  = 1787 Hz), 63.0 (s,  $J_{Pt-P}$  = 3170 Hz). Anal. Calc. for C<sub>23</sub>H<sub>42</sub>P<sub>2</sub>PtS: C, 45.46; H, 6.97. Found: C, 45.69; H, 6.79%. Continued heating at 140 °C (2 d) led to the formation of hexa-1,5-diene and (dippe)Pt(SPh)<sub>2</sub>, **5b** (quantitative by <sup>31</sup>P NMR spectroscopy). For **5b**, <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.77 (d,  $J_{H-H}$  = 7 Hz, 4H), 7.02 (t,  $J_{H-H}$  = 7 Hz, 4H), 6.89 (t,

 $\begin{array}{l} J_{\text{H-H}} = 7 \; \text{Hz}, \; 2\text{H}), \; 2.31 \; (\text{sextet}, \; J_{\text{Pt-H}} = 13 \; \text{Hz}, \; J_{\text{P-H}} = 7 \; \text{Hz}, \; 4\text{H}), \; 1.21 \\ (\text{dd}, \; J_{\text{P-H}} = 16 \; \text{Hz}, \; J_{\text{H-H}} = 7 \; \text{Hz}, \; 12\text{H}), \; 0.98 \; (\text{dd}, \; J_{\text{P-H}} = 21 \; \text{Hz}, \; J_{\text{H-H}} = 9.6 \; \text{Hz}, \; 4\text{H}), \; 0.80 \; (\text{dd}, \; J_{\text{P-H}} = 14 \; \text{Hz}, \; J_{\text{H-H}} = 7 \; \text{Hz}, \; 12\text{H}). \; ^{13}\text{C}\{^{1}\text{H}\} \; \text{NMR} \\ (125 \; \text{MHz}, \; C_6\text{D}_6): \; \delta \; 134.4 \; (\text{s}, \; J_{\text{Pt-C}} = 31 \; \text{Hz}), \; 129.2 \; (\text{s}, \; J_{\text{Pt-C}} = 21 \; \text{Hz}), \\ 126.9 \; (\text{s}), \; 122.4 \; (\text{s}), \; 25.10 \; (\text{d}, \; J_{\text{P-C}} = 31 \; \text{Hz}, \; J_{\text{Pt-C}} = 27 \; \text{Hz}), \; 22.20 \; (\text{dd}, \; J_{\text{P-C}} = 29, \; 11 \; \text{Hz}), \; 19.36 \; (\text{s}, \; \; J_{\text{Pt-C}} = 11 \; \text{Hz}), \; 18.18 \\ (\text{s}, \; J_{\text{Pt-C}} = 21 \; \text{Hz}). \; \; ^{31}\text{P}\{^{1}\text{H}\} \; \text{NMR} \; (162 \; \text{MHz}, \; C_6\text{D}_6): \; \delta \; 67.13 \; (\text{s}, \; J_{\text{Pt-P}} = 2765 \; \text{Hz}). \; Anal. \; \text{Calc. for } C_{26}\text{H}_{42}\text{P}_2\text{PtS}_2:\text{C}, \; 46.21; \; \text{H}, \; 6.26. \\ \text{Found: C, \; 47.19; \; \text{H}, \; 6.38. \end{array}$ 

#### 4.6. Synthesis of (dippe)Pt(SPh)(CHCH<sub>2</sub>) (7)

In a J. Young tube, phenyl vinyl sulfide (30 µL, 0.230 mmol) was added rapidly to solution of 1 (40.7 mg, 0.0631 mmol) in 1.3 mL pentane. This mixture was heated to 100 °C for 20 min, at which point complete conversion of the starting material to (dippe)Pt( $\eta^2$ - $CH_2CHSPh$ ) (6) was observed by  ${}^{31}P{}^{1}H$  NMR spectroscopy.  ${}^{1}H$ NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.92 (d,  $J_{H-H}$  = 8 Hz, 2H), 7.20 (t,  $J_{H-H}$  = 7 Hz, 2H), 6.95 (t,  $J_{H-H}$  = 7 Hz, 1H), 3.82 (m,  $J_{Pt-H}$  = 62 Hz, 1H), 2.74 (m,  $J_{Pt-H}$  = 50 Hz, 1H), 2.35 (m,  $J_{Pt-H}$  = 53 Hz, 1H), 1.80 (m, 4H), 1.16 (m, 8H), 0.99 (m, 10H), 0.81 (m, 10H).  $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$  NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  149.1 (dd,  $J_{P-C}$  = 13, 2 Hz,  $J_{Pt-C}$  = 74 Hz), 128.6 (s), 125.6 (s), 123.2 (s), 33.2 (dt,  $J_{P-C} = 41$  Hz,  $J_{P-C} = 5$  Hz,  $J_{Pt-C} = 5$ 242 Hz), 26.6 (dt,  $J_{P-C}$  = 22, 4 Hz), 25.9 (ddd,  $J_{P-C}$  = 30, 14, 4 Hz), 24.4 (dd,  $J_{P-C}$  = 25, 15 Hz), 23.7 (dd,  $J_{P-C}$  = 25, 15 Hz), 18.2–19.6 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  78.20 (d,  $J_{P-P}$  = 58 Hz,  $J_{Pt-P}$  = 3253 Hz), 75.14 (d,  $J_{P-P}$  = 58 Hz,  $J_{Pt-P}$  = 3098 Hz). Anal. Calc. for C<sub>22</sub>H<sub>40</sub>P<sub>2</sub>PtS: C, 44.51; H, 6.79. Found: C, 44.46; H, 6.75%. Volatiles were stripped from the reaction mixture, and the resulting solids were heated to 40 °C and held under vacuum for 12 h to remove excess sulfide. The solids were re-dissolved in C<sub>6</sub>D<sub>6</sub> and the resulting solution was heated to 140 °C for 5 d, yielding 7 in a near quantitative yield by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  7.95 (d,  $J_{H-H}$  = 8 Hz, 2H), 7.73 (m, 1H; obscured by resonance at  $\delta$  7.71), 7.20 (t,  $J_{H-H}$  = 7.3 Hz, 2H), 7.00 (t,  $J_{H-H}$  = 7 Hz, 1H), 6.33 (ddd,  $J_{P-H}$  = 21 Hz,  $J_{H-H}$  = 12, 3 Hz,  $J_{Pt-H}$  = 114 Hz, 1H), 5.55 (ddd,  $J_{P-H}$  = 19, 10, 3 Hz,  $J_{Pt-H}$  = 150 Hz, 1H), 2.13 (dm,  $J_{P-H} = 52 \text{ Hz}, J_{P-H} = 2 \text{ Hz}, J_{H-H} = 7 \text{ Hz}, 4\text{H}), 1.29 \text{ (dd, } J_{P-H} = 16 \text{ Hz},$  $J_{H-H}$  = 7, 6H), 0.99 (dd,  $J_{P-H}$  = 16 Hz,  $J_{H-H}$  = 7, 6H), 0.82 (dd,  $J_{P-H}$  $_{\rm H}$  = 13 Hz,  $J_{\rm H-H}$  = 7, 6H), 0.71 (dd,  $J_{\rm P-H}$  = 14 Hz,  $J_{\rm H-H}$  = 7, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  156.4 (dd,  $J_{P-C}$  = 107 Hz,  $J_{P-C}$  = 10 Hz), 136.1 (d,  $J_{Pt-C}$  = 31 Hz,  $J_{P-C}$  = 3 Hz), 128.6 (s), 127.2 (s), 123.2 (s), 120.0 (s), 24.6 (d,  $J_{Pt-C} = 15$  Hz,  $J_{P-C} = 24$  Hz), 24.0 (d,  $J_{Pt-C} = 41$  Hz,  $J_{P-C} = 32$  Hz), 23.5 (dd,  $J_{P-C} = 25$ , 10 Hz), 20.8 (dd,  $J_{Pt-C}$  = 57 Hz,  $J_{P-C}$  = 25, 10 Hz), 19.2 (m), 18.2 (s,  $J_{Pt-C}$  = 13), 17.9 (s,  $J_{Pt-C} = 28$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  64.9 (s,  $J_{Pt-P} =$ 1706 Hz), 61.4 (s,  $J_{Pt-P}$  = 3005 Hz). Anal. Calc. for  $C_{22}H_{40}P_2PtS \frac{1}{2}C_{6-1}$ H<sub>6</sub>: C, 47.46; H, 6.85. Found: C, 47.40; H, 6.66%.

## 4.7. Activation of benzyl methyl sulfide

In a 20 mL vial, benzyl methyl sulfide (35  $\mu$ L, 0.257 mmol) was added to a stirred solution of **1** (19.7 mg, 0.0305 mmol) in 1.0 mL C<sub>6</sub>D<sub>6</sub>. The reaction was held at 160 °C on a heating block for 3 d, at which point approximately 75% conversion of the starting material was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The major product was (dippe)Pt(SMe)<sub>2</sub> (**5a**), previously characterized [28]. The <sup>1</sup>H NMR spectrum of the reaction mixture shows a characteristic sharp peak at  $\delta$  2.15 due to the aliphatic protons of bibenzyl. The presence of this species was also confirmed by GC–MS. By comparing the chromatogram with a standard, it was determined that the reaction mixture contained ~1 mM bibenzyl.

## 4.8. Activation of phenyl trifluoromethyl sulfide

In a J. Young tube, phenyl trifluoromethyl sulfide (30  $\mu$ L, 0.210 mmol) was added rapidly to a solution of **1** (40.7 mg,

0.0631 mmol) in 1.0 mL mesitylene. The reaction was held at 100 °C for 24 h, and then increased over 3 d, at which point some conversion of the starting material was noted. After 3 d at 160 °C, the reaction mixture was a dark olive green. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture was quite complicated after only minimal conversion of the starting material. The <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of the reaction mixture is similarly complicated, but it shows a characteristic resonance (dd,  $J_{Pt-F} = 240 \text{ Hz}$ ,  $J_{P-F} = 57 \text{ Hz}$ ,  $J_{P-F} = 22 \text{ Hz}$ ) 0.78 ppm upfield of the prominent peak due to PhSCF<sub>3</sub>. The couplings observed in this resonance suggest (dippe)Pt(SPh)(CF<sub>3</sub>) was present in the reaction mixture.

### 4.9. Synthesis of $(dippe)Pt(^2-SCH_2CH_2S)$ (**9**)

In a J. Young tube, dithiane (40 mg, 0.333 mmol) was added to a solution of 1 (40.7 mg, 0.0631 mmol) in 1.0 mL mesitylene. The reaction mixture was held at 180 °C for 1 week, at which point it was dark orange. Total conversion of the starting material was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR data indicated a symmetric structure, and were not consistent with the asymmetric product (dippe)Pt( $\kappa^2$ -SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>) (8). <sup>1</sup>H NMR and GC-MS spectra showed the presence of ethylene in the reaction mixture (s,  $\delta$  5.28). The reaction mixture was then heated to 40 °C and held under vacuum for 2 d to remove solvent. Sublimation of a considerable portion of the excess dithiane was observed, but the product (dippe)Pt( $\kappa^2$ -SCH<sub>2</sub>CH<sub>2</sub>S) (**9**) could not be obtained in pure form. Yield: 48%. For **9**, <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  3.07 (s,  $J_{Pt-H} = 44$  Hz, 4H), 2.15 (m, 4H), 1.25 (dd,  $J_{P-H} = 17$  Hz,  $J_{H-H} = 7$  Hz, 12H), 0.98 (m, 4H), 0.74 (dd,  $J_{P-H} = 14$  Hz,  $J_{H-H} = 7$  Hz, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  39.1 (d,  $J_{Pt-C}$  = 8.3 Hz,  $J_{P-C}$  = 9.6 Hz), 26.1 (d,  $J_{Pt-C}$  = 28.5 Hz,  $J_{P-C}$  = 31.5 Hz), 22.2 (d,  $J_{P-C}$  = 10.6 Hz),18.9 (s,  $J_{Pt-C}$  = 12.2 Hz), 18.2 (s,  $J_{Pt-C}$  = 20.5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $C_6D_6$ ):  $\delta$  72.1 (s,  $J_{Pt-P}$  = 2661 Hz). Anal. Calc. for C<sub>16</sub>H<sub>36</sub>P<sub>2</sub>PtS<sub>2</sub>: C, 34.97; H, 6.60. Found: C, 34.73; H, 6.25%.

## 4.10. Synthesis of (dippe)Pt(Me)<sub>2</sub>

Complex (dippe)Pt(Me)<sub>2</sub> was prepared according to the procedure outlined in Bassan et al. [33]. In a J. Young tube, dippe (17  $\mu$ L, 0.061 mmol) was added to (cod)Pt(Me)<sub>2</sub> (20 mg, 0.060 mmol) in 0.9 mL Et<sub>2</sub>O. The reaction sat at room temperature for 10 min, at which point total conversion of the starting material was observed by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectroscopy.

#### 4.11. Synthesis of (dippe)Pt(SPh)(Me) (10)

In a J. Young tube, thiophenol (7.8 µL, 0.076 mmol) was added to a solution of (dippe)Pt(Me)<sub>2</sub> (30 mg, 0.0631 mmol) in 0.9 mL C<sub>6</sub>H<sub>6</sub>. The reaction mixture was held at 100 °C for 2 d, at which point complete conversion of the starting material was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The volatiles were stripped from the reaction mixture under vacuum, and the remaining off-white solid was dissolved in C<sub>6</sub>D<sub>6</sub>. For **10**, <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 7.96 (d,  $J_{H-H}$  = 7 Hz, 2H), 7.18 (t,  $J_{H-H}$  = 7 Hz, 2H), 6.96 (t,  $J_{H-H}$  = 7 Hz, 1H), 2.21 (dm,  $J_{P-H}$  = 133 Hz,  $J_{H-H}$  = 7 Hz, 4H), 1.45 (dd,  $J_{P-H} = 16$  Hz,  $J_{P-H} = 7$  Hz, 6H), 1.09 (dd,  $J_{P-H} = 16$  Hz,  $J_{P-H} = 7$  Hz, 7H), 0.99 (dd,  $J_{P-H}$  = 13 Hz,  $J_{P-H}$  = 7 Hz, 8H), 0.86 (dd,  $J_{P-H}$  = 14 Hz,  $J_{P-H}$  = 7 Hz, 7H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  144.7 (dd,  $J_{P-C}$  = 7, 3 Hz), 136.0 (d,  $J_{Pt-C}$  = 30 Hz,  $J_{P-C}$  = 3 Hz), 127.4 (s), 123.1 (s), 24.7 (d,  $J_{P-C}$  = 24 Hz), 24.5 (d,  $J_{P-C}$  = 31 Hz), 24.1 (dd,  $J_{P-C}$  = 29, 17 Hz), 20.6 (dd,  $J_{P-C}$  = 24, 10 Hz), 19.1 (d,  $J_{P-C}$  = 4 Hz), 19.0 (d,  $J_{P-C} = 3 \text{ Hz}$ ), 18.2 (s,  $J_{Pt-C} = 14 \text{ Hz}$ ), 18.0 (s,  $J_{Pt-C} = 26 \text{ Hz}$ ), 0.2 (dd,  $J_{P-C} = 89$ , 8 Hz,  $J_{Pt-C} = 860 \text{ Hz}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  71.5 (d,  $J_{P-P}$  = 18 Hz,  $J_{Pt-P}$  = 1779 Hz), 68.1 (s,  $J_{P-P}$  = 18 Hz,  $J_{Pt-P}$  = 3075 Hz).

#### 4.12. Activation of allyl methyl sulfide by (dippe)Pt(SPh)(Ph)

In a vial w/ 180° vacuum adapter, diphenyl sulfide (20  $\mu$ L, 0.120 mmol) was added to a solution of **1** (19.7 mg, 0.0305 mmol) in 1 mL toluene. The reaction mixture was held at 160 °C for 6 d, at which point total conversion of the starting material to (dip-pe)Pt(SPh)(Ph) (**2**) had occurred. Allyl methyl sulfide (30  $\mu$ L, 0.273 mmol) was added, and the reaction was held at 160 °C for an additional 2 d, during which period the color of the mixture lightened noticeably. The presence of allyl phenyl sulfide in the reaction mixture was confirmed by <sup>1</sup>H NMR spectroscopy. Allyl phenyl sulfide was also observed by GC–MS by comparison with an authentic sample. The volatiles were stripped from the reaction mixture, and the remaining solids were dissolved in C<sub>6</sub>D<sub>6</sub>. The presence of (dippe)Pt(SMe)(Ph) (**3**) was confirmed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. One third of the starting material **2** had been consumed, yielding **3** as a single product.

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## Appendix A. Supplementary data

CCDC 889623-889627 contains the supplementary crystallographic data for **2**, **3**, **4a**, **5a**, and **10**. 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. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.07.071.

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