# **ORGANOMETALLICS**

## Synthesis and Structure of Gold and Platinum Menthyl Complexes

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Supporting Information

**ABSTRACT:** A Grignard reagent derived from (-)-menthyl chloride has been reported to be a 1:1 mixture of menthyl magnesium chloride and neomenthyl magnesium chloride, which do not interconvert. Addition of an excess of this reagent to Au(PPh<sub>3</sub>)(Cl) or Pt(dppe)Cl<sub>2</sub> gave Au(PPh<sub>3</sub>)(Men) (1) and Pt(dppe)(Men)(Br) (2), respectively. Crystallographic studies of these first well-characterized transition metal menthyl complexes showed that the menthyl group adopts a conformation with all three substituents in equatorial positions. NMR spectroscopic data for 2 showed that menthyl has a large *trans* influence, comparable to other alkyl groups. Decomposition of 1 in CDCl<sub>3</sub> gave



 $Au(PPh_3)(Cl)$  and a mixture of menthyl chloride and neomenthyl chloride, while 2 formed the halide complexes  $Pt(dppe)Cl_2$ ,  $Pt(dppe)Br_2$ , and Pt(dppe)(Br)(Cl) and a mixture of 2-menthene and 3-menthene.

#### INTRODUCTION

The properties of metal—carbon bonds have been studied in detail during the continuing development of organometallic chemistry.<sup>1</sup> However, surprisingly little is known about *chiral* alkyl ligands, especially those with a stereogenic sp<sup>3</sup> carbon bound to a transition metal.<sup>2</sup> Such complexes may be useful in studies of the stereochemistry of fundamental reactions of the metal—carbon bond<sup>3</sup> and as chiral reagents or catalysts for asymmetric synthesis.<sup>4</sup>

The simplest syntheses of chiral nonracemic metal alkyls start with enantiomerically pure organic precursors, which are transferred to the metal with control of stereochemistry. Such processes have been reported recently in main group chemistry using (-)-menthyl magnesium chloride ((-)-menthyl = (1*R*,*SS*,2*R*-menthyl)), especially for the preparation of menthyl-tin complexes.<sup>5</sup> Related menthyl-germanium<sup>6</sup> and -aluminum<sup>7</sup> complexes have also been prepared.

This chemistry is particularly attractive since menthyl chloride is commercially available; it may also be prepared on a large scale from menthol,<sup>8</sup> one of the cheapest available chiral materials.<sup>9</sup> However, it is complicated by the formation of a 1:1 mixture of menthyl magnesium chloride and the C1-epimer neomenthyl magnesium chloride on treatment of (-)-menthyl chloride with magnesium (Scheme 1).<sup>10,11</sup> Beckmann and co-workers studied the reactivity of this mixture in detail, including quenching experiments with D<sub>2</sub>O and a variety of other electrophiles, and concluded that the menthyl and neomenthyl Grignard reagents did not interconvert. They proposed that selective menthyl transfer to an electrophile, observed when an excess of the Grignard mixture was used, occurred because MenMgCl was more reactive than NeomMgCl (Scheme 1).<sup>10,12</sup>

We planned to use this chemistry to prepare enantiomerically pure *transition metal* menthyl complexes. Previously, the group 12 complexes dimenthylmercury<sup>13,14</sup> and dimenthylzinc,<sup>15</sup> as well as MenHgX (X = carboxylate),<sup>13</sup> were reported, but very little or no characterizing data were included, and the stereochemistry of these compounds was not elucidated (Chart 1). More recently, the catalytic cross-coupling of MenZnCl and bromoindenes, which was used to prepare chiral indenyl ligands, presumably proceeded via menthyl-palladium and -nickel intermediates.<sup>16a</sup> Similar intermediates in stereoselective catalytic cross-couplings, formed by Zn-to-Pd transmetalation, were recently proposed, and NMR evidence for a Pd-cyclohexyl species was reported.<sup>17</sup> Finally, menthyl-nickel, -palladium, and -copper intermediates were likely involved in the synthesis of menthylpyridine via cross-coupling.<sup>16b,c</sup> Here we describe the synthesis and structural characterization of gold and platinum menthyl complexes.

### RESULTS AND DISCUSSION

Synthesis and Structure of Gold and Platinum Menthyl Complexes. The thermally stable Au(I) complexes Au(PPh<sub>3</sub>)(R) have been prepared for a range of primary, secondary, and tertiary alkyl groups R<sup>18</sup> We extended this series to the chiral (-)-menthyl group. Treatment of Au(PPh<sub>3</sub>)(Cl) with an excess (10 equiv) of Grignard reagent prepared from MenCl gave Au(PPh<sub>3</sub>)(Men) (1) as fine white crystals in 67% yield (Scheme 2). The menthyl group gave rise to characteristic <sup>1</sup>H and <sup>13</sup>C NMR resonances, <sup>19</sup> including that due to the Au-bound carbon ( $\delta$  55.2,  $J_{PC}$  = 97 Hz, THF- $d_8$ ; see the Experimental Section for complete NMR spectral assignments). Complex 1 decomposed quickly in CDCl<sub>3</sub> or acetone- $d_6$  solution (see below) but was more robust in  $C_6D_6$  or THF- $d_8$ .

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# Scheme 1. Formation of a Mixture of Grignard Reagents from (-)-Menthyl Chloride<sup>10</sup>



# Chart 1. Transition Metal Menthyl Complexes and Intermediates



Scheme 2. Synthesis of Gold-Menthyl Complex 1



**Figure 1.** ORTEP diagram of  $Au(PPh_3)((-)-Men)(1)$ .

The crystal structure of 1 (Figure 1; see Table 1 and the Supporting Information for crystallographic details) confirmed

Table 1. Crystallographic Data for 1 and 2

	$Au(PPh_3)(Men)(1)$	$Pt(dppe)(Men)(Br) \cdot 2CHCl_3(2)$
formula	C <sub>28</sub> H <sub>34</sub> AuP	C38H45BrCl6P2Pt
fw	598.49	1051.38
space group	P2(1)2(1)2(1)	P2(1)
a, Å	7.395(3)	11.423(2)
b, Å	16.525(6)	15.391(3)
<i>c,</i> Å	20.417(7)	11.902(2)
α, deg	90	90
$\beta$ , deg	90	94.632(3)
γ, deg	90	90
<i>V</i> , Å <sup>3</sup>	2495.0(15)	2085.6(6)
Ζ	4	2
$D(\text{calcd}), \text{g/cm}^3$	1.593	1.674
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	5.973	4.809
temp, K	293(2)	100(2)
R(F), % <sup><i>a</i></sup>	2.02	2.21
$R_{\rm w}(F^2)$ , % <sup>a</sup>	4.09	5.25

<sup>*a*</sup> Quantity minimized:  $R_w(F^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [(wF_o^2)^2]^{1/2}$ ;  $R = \sum \Delta / \sum (F_o), \Delta = |(F_o - F_c)|, w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP], P = [2F_c^2 + Max(F_o^2, 0)]/3$ . A Bruker CCD diffractometer was used in all cases.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1 and Related  $Au(PPh_3)(R)$  Complexes

R	Au-P	Au-C	P-Au-C	ref
Men (1)	2.299(11)	2.087(4)	177.8(11)	this work
Ph	2.296(2)	2.045(6)	175.5(2)	22
Me	2.290(3)	2.065(10)	178.5(4)	23
CH(SiMe <sub>3</sub> ) <sub>2</sub>	2.271(2)	2.041(6)	177.8(2)	24

Scheme 3. Synthesis of Pt-Menthyl Complex 2



that it contained the (-)-menthyl ligand. The unchanged stereochemistry at the other chiral centers of this group served as an internal check on the assignment of absolute configuration. The isopropyl, methyl, and gold substituents all occupied the expected equatorial positions.

Comparison of the structure to that of related linear twocoordinate gold alkyls showed that the menthyl group formed a Au–C bond of normal length. Its *trans* influence, as judged by the Au–PPh<sub>3</sub> bond length, was similar to that of other gold hydrocarbyls (Table 2). This observation is consistent with earlier reports that increased *trans* influence of the anion X in Au(PPh<sub>3</sub>)(X) had little effect on the Au–P bond length.<sup>20</sup> Instead, increased *trans* influence of X led to significant deshielding of the <sup>31</sup>P NMR resonance.<sup>20</sup> The <sup>31</sup>P NMR chemical shift of 1 ( $\delta$  44.2, THF- $d_8$ ) was similar to that of other Au(PPh<sub>3</sub>) hydrocarbyls, consistent with the structural results.<sup>21</sup>

In contrast to the mild reaction conditions required for the synthesis of **1**, reaction of an excess (10 or 20 equiv) of MenMgCl/ NeomMgCl with Pt(dppe)Cl<sub>2</sub> in THF required heating to 50 °C for 1 h (Scheme 3). Even with an excess of the Grignard reagent, these conditions did not appear to result in disubstitution. According to <sup>31</sup>P NMR spectroscopy in CDCl<sub>3</sub>, the crude reaction mixtures contained mostly a Pt(dppe) complex (**2**) containing phosphorus atoms *trans* to an alkyl group ( $\delta$  40.9,  $J_{Pt-P}$  = 1416 Hz) and to a halide ( $\delta$  45.1,  $J_{Pt-P}$  = 4666 Hz). Unfortunately, we were not able to



Figure 2. ORTEP diagram of  $Pt(dppe)(Men)(Br) \cdot 2CHCl_3$  (2). The solvent molecules are not shown. Selected bond lengths (Å) and angles (deg): Pt(1)-C(1) 2.139(3), Pt(1)-P(1) 2.1978 (10), Pt(1)-P(2) 2.3058(9), Pt(1)-Br(1) 2.4945(5), C(1)-Pt(1)-P(1) 89.80(10), P(1)-Pt(1)-P(2) 86.28(3), C(1)-Pt(1)-Br(1) 93.20(10), P(2)-Pt(1)-Br(1) 90.44(2).

obtain bulk samples of 2 in pure form by recrystallization. It decomposed readily in solution, especially in chloroform (see below).<sup>25</sup>

However, recrystallization from  $CHCl_3$ /petroleum ether gave yellow crystals of 2, which the X-ray crystal structure (Figure 2) showed was Pt(dppe)(Men)(Br), with three equatorial menthyl substituents, as observed for 1.

The bromide presumably came from the dibromoethane used to prepare the Grignard reagent;<sup>12</sup> this type of halide exchange has been reported previously in related reactions, such as the formation of Pt(COD)(Mes)(Br) from Pt(COD)Cl<sub>2</sub> and mesi-tyl magnesium bromide.<sup>26</sup> The crystallographically characterized material, with a bromide ligand, appears to be representative of the bulk, on the basis of several observations: (1) elemental analyses on crude **2** showed close to the expected amount of bromide and only traces of chloride (calcd for C<sub>36</sub>H<sub>43</sub>BrP<sub>2</sub>Pt: Br, 9.83; Cl, 0.00; found: Br, 7.47; Cl, 0.40). (2) Complex **2** decomposed on standing in CDCl<sub>3</sub> to yield a mixture of Pt-(dppe)Br<sub>2</sub>, Pt(dppe)Cl<sub>2</sub>, and Pt(dppe)(Br)(Cl), as observed by <sup>31</sup>P NMR spectroscopy (see also Scheme 4 and discussion below).<sup>27</sup> (3) The Br-containing parent ion was observed in the mass spectrum of **2**.

Crude 2 (ca. 90% purity) was also characterized by NMR spectroscopy. The most distinctive feature was the  ${}^{13}C{}^{1}H{}$  NMR signal of the Pt-CH(menthyl) group ( $\delta$  43.3 (d, J = 98,  $C_6D_6$ )), which was similar to that observed for 1. Unfortunately, we could not observe Pt satellites on this signal or, because of spectral overlap, on the accompanying  ${}^{1}H$  NMR resonance.

Because no other Pt(dppe)(R)(Br) complexes have been crystallographically characterized, the *trans* influence of the menthyl group in 2 could not be assessed by comparison to related structures. However, the established correlation with  $J_{Pt-P}$  coupling constants showed that the menthyl group has a large *trans* influence, with the smallest  $J_{Pt-P}$  for the dppe phosphorus *trans* to the hydrocarbyl group (Table 3).<sup>28</sup>

**Decomposition of 1 and 2 in CDCl<sub>3</sub>.** As mentioned above, menthyl complexes **1** and **2** decomposed readily in CDCl<sub>3</sub> solutions at room temperature. These reactions were not affected by light or by passing the solvent through an alumina column to remove traces of HCl.<sup>32</sup> Gold complex **1** formed Au(PPh<sub>3</sub>)(Cl) and an approximately 1:1 mixture of menthyl chloride and Scheme 4. Decomposition of Menthyl Complexes 1 and 2 in CDCl<sub>3</sub>



Table 3.  $J_{Pt-P}$  Coupling Constants (Hz) in Pt(dppe)(R)(X) Complexes

Pt(dppe)(R)(X)	$J_{\rm Pt-P}$ ( <i>trans</i> to R)	$J_{\rm Pt-P}$ ( <i>trans</i> to X)	solvent (ref)
$Pt(dppe)(Men)(Br)$ $Pt(dppe)(Et)(Cl)$ $Pt(dppe)(Me)(Br)$ $Pt(dppe)(CF_3)(Br)$ $Pt(dppe)(Ph)(Br)$ $Pt(dppe)(Ph)(Cl)$	1416 1561 1744 1821 1615	4666 4386 4242 3930 4083	CDCl <sub>3</sub> (this work) CH <sub>2</sub> Cl <sub>2</sub> (28) CDCl <sub>3</sub> (29) CD <sub>2</sub> Cl <sub>2</sub> (30) C <sub>6</sub> D <sub>6</sub> (27a, 31) C <sub>4</sub> Cl <sub>4</sub> (29)

neomenthyl chloride, which were identified by GC, by NMR spectroscopy, and by spiking the mixture with authentic samples of these alkyl halides (Scheme 4).<sup>33</sup> Similarly, decomposition of **2** gave a mixture of Pt(dppe) dihalides plus a 1:1 mixture of the isomers 2-menthene and 3-menthene, which were characterized by NMR spectra and by spiking with authentic samples (Scheme 4).<sup>34</sup> These observations are consistent with  $\beta$ -hydride elimination in Pt complex **2**, perhaps followed by reaction of the unobserved hydride complex Pt(dppe)(H)(Br) with CDCl<sub>3</sub> to yield Pt(dppe)(Br)(Cl), which disproportionates to yield the other dihalide complexes.<sup>35</sup> In contrast, the formation of menthyl and neomenthyl chlorides from **1** might occur via Au–C bond homolysis, followed by reaction of the resulting radicals with CDCl<sub>3</sub>.<sup>36</sup>

### CONCLUSION

As reported for main group metal complexes, treatment of Au and Pt precursors with an excess of the Grignard reagent obtained from (-)-menthyl chloride selectively gave transition metal menthyl complexes. We assume that the preferred stereochemistry arises from transmetalation with retention of configuration at carbon from the more reactive Grignard reagent MenMgCl. However, as suggested by a reviewer, it is possible that Au- or Pt-neomenthyl groups are formed but isomerize to Chart 2. Atom Numbering for the Menthyl Group in Complexes 1 and 2



the thermodynamically favored menthyl complexes. Although metal—carbon bonds in Au(I) and Pt(II) alkyls are usually robust, the new menthyl complexes decomposed readily in solution. In future work, we hope to use knowledge of these decomposition pathways in order to prepare more durable transition metal menthyl complexes for potential applications in asymmetric synthesis and in stereochemical studies of the reactions of metal—carbon bonds.

### EXPERIMENTAL SECTION

Syntheses were performed, unless otherwise noted, in oven-dried glassware under a N<sub>2</sub> atmosphere in a drybox or using standard Schlenk techniques. THF, toluene, methylene chloride, and petroleum ether (bp 38–53 °C) were dried over alumina columns similar to those described by Grubbs.<sup>37</sup> NMR spectra were recorded utilizing Varian 300 and/or 500 MHz spectrometers. <sup>1</sup>H NMR chemical shifts are reported vs Me<sub>4</sub>Si and were determined by referencing to residual <sup>1</sup>H solvent peaks; <sup>31</sup>P NMR chemical shifts are reported vs H<sub>3</sub>PO<sub>4</sub> (85%) used as an external reference. Coupling constants are reported in Hz. Magnesium metal (50-mesh powder (99+%)), (-)-MenCl (98%), and 1,2-dibromoethane (99%), all from Aldrich, were used as received. The complex Au(PPh<sub>3</sub>)(Cl) was prepared by a literature procedure.<sup>38</sup> Pt(dppe)Cl<sub>2</sub> and Pt(dppen)Cl<sub>2</sub> (dppen = *cis*-Ph<sub>2</sub>PCH=CH-PPh<sub>2</sub>, 1,2-bis(diphenylphosphino)ethylene) were prepared by treatment of Pt(COD)Cl<sub>2</sub> with the diphosphine in CH<sub>2</sub>Cl<sub>2</sub>.<sup>39</sup> Neomenthyl chloride and 3-menthene were prepared by literature methods.<sup>33,34</sup>

Au(Men)(PPh<sub>3</sub>) (1). A Grignard reagent was prepared by activating a stirring mixture of magnesium powder (245 mg, 10 mmol) in 10 mL of THF at 50 °C with 1,2-dibromoethane (85  $\mu$ L, 1 mmol). After 20 min, menthyl chloride (0.94 mL, 5 mmol) was added, a condenser was attached to the flask, and the mixture was refluxed for 5 h at 65 °C. After allowing the excess Mg to settle, the dark gray solution was transferred via cannula to a stirring solution of Au(PPh<sub>3</sub>)(Cl) (124 mg, 0.25 mmol) in 20 mL of THF. After stirring for 2 h, the reaction was quenched with dilute H<sub>2</sub>SO<sub>4</sub> (1 drop of 18 M acid in 20 mL of H<sub>2</sub>O) and opened to air. The aqueous layer was extracted with methylene chloride (3 × 20 mL), and the organic layers were combined, dried over MgSO<sub>4</sub>, treated with activated charcoal, and filtered through Celite. The solvent was removed *in vacuo* to give a white, crystalline solid. The crude product was washed with petroleum ether and dried *in vacuo* to give 100 mg (67%) of an eggshell white, crystalline solid. Recrystallization from ether gave X-ray quality crystals.

Anal. Calcd for  $C_{28}H_{34}PAu$ : C, 56.19; H, 5.73. Found: C, 56.10; H, 5.85. HRMS (ESI): m/z calcd for  $C_{28}H_{34}PAuNa$  (MNa)<sup>+</sup> 621.1961; found 621.1965. <sup>31</sup>P{<sup>1</sup>H} MRR (THF- $d_8$ ):  $\delta$  44.2. <sup>1</sup>H NMR (THF- $d_8$ ):  $\delta$  7.56–7.47 (m, 15H, Ph), 2.39 (apparent d quint, J = 3, 7, 1H, i-Pr CH 7), 2.22 (apparent dt,  $J = 3, 13, 1H, CH_2 2$ ), 1.74–1.66 (m, 3H, Au-CH 1 plus 2H CH<sub>2</sub> 4/5), 1.57–1.53 (m, 1H, CH 6), 1.45 (apparent qd,  $J = 2, 12, 1H, CH_2 2$ ), 1.18–1.16 (m, 1H, CH 3), 0.96 (d, J = 7, 3H, i-Pr Me 8/9), 0.91 (d, J = 7, 3H, i-Pr Me 8/9), 0.97–0.88 (m, 2H, CH<sub>2</sub> 4/5, overlapping Me signals), 0.83 (d, J = 7, 3H, Me 10). <sup>13</sup>C{<sup>1</sup>H} NMR (THF- $d_8$ ):  $\delta$  134.4 (d, J = 14, Ph), 132.4 (d, J = 44, quat Ph), 130.9 (d, J = 2, Ph), 129.0 (d, J = 10, Ph), 55.2 (d, J = 97, Au-CH 1), 51.6 (d, J = 3, CH 6), 46.4 (d, J = 5, CH<sub>2</sub> 2), 37.1 (d, J = 7, CH 3), 36.6 (CH<sub>2</sub> 4), 36.0 (*i*-Pr CH 7), 29.7 (d, J = 9, CH<sub>2</sub> 5), 22.8 (Me 10), 21.5 (*i*-Pr Me 8/9), 16.6 (*i*-Pr Me 8/9).

Note: NMR assignments for the menthyl group in 1 and 2 use the atomnumbering shown in the crystal structures (Figures 1 and 2) and in Chart 2. Assignments were made using DEPT, COSY, HMQC, and NOESY experiments.

Pt(dppe)(Men)(Br) (2). A Grignard reagent was prepared by activating a stirring mixture of magnesium powder (245 mg, 10 mmol) in 10 mL of THF at 50 °C with 1,2-dibromoethane (85  $\mu$ L, 1 mmol). After 10 min, menthyl chloride (0.94 mL, 5 mmol) was added, a condenser was attached to the flask, and the mixture was refluxed for 5 h at 65 °C. After the excess magnesium was allowed to settle, the dark gray solution was transferred via cannula to a stirring solution of Pt(dppe)Cl<sub>2</sub> (166 mg, 0.25 mmol) in 10 mL of THF. After stirring for 1 h at 50 °C, the mixture was allowed to cool to room temperature, quenched with saturated aqueous NH<sub>4</sub>Cl (5 mL), and opened to air. The aqueous layer was extracted with methylene chloride  $(3 \times 15 \text{ mL})$ , and the organic layers were combined, dried over MgSO4, and filtered through Celite. The solvent was removed in vacuo to give a yelloworange solid. The crude product was washed with petroleum ether and dried *in vacuo* to give 166 mg (82%) of a yellow solid that was 90% pure, according to integration of the <sup>31</sup>P NMR spectrum. Although the complex decomposed rapidly in chloroform, recrystallization from CHCl<sub>3</sub>/petroleum ether at -20 °C gave yellow crystals suitable for X-ray crystallography. Solutions of 2 in  $C_6D_6$  or THF- $d_8$  were more robust, enabling NMR studies. A similar procedure using the ligand cis-1,2-bis(diphenylphosphino)ethylene (dppen) gave crude Pt(dppen)-(Men)(Br), which was also not obtained in pure form.  ${}^{31}P{}^{1}H{}$  NMR  $(C_6D_6)$ :  $\delta$  53.5 (d, J = 12,  $J_{Pt-P} = 1443$ ), 49.7 (d, J = 12,  $J_{Pt-P} = 4564$ ).

Anal. Calcd for C<sub>36</sub>H<sub>43</sub>BrP<sub>2</sub>Pt: Br, 9.83; Cl, 0.00. Found: Br, 7.47; Cl, 0.40. ES-MS: m/z 812.6 (MH)<sup>+</sup>, 733.3 (MH - Br)<sup>+</sup>, 673.0 (MH -Men)<sup>+</sup>, 635.1, 594.1 (MH – Br – Men)<sup>+</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ ):  $\delta$ 45.4 ( $J_{Pt-P}$  = 4534), 39.3 ( $J_{Pt-P}$  = 1405). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  8.00-7.97 (m, 2H, P2 o-Ph), 7.87-7.84 (m, 2H, P2 o-Ph), 7.70-7.66 (m, 2H, P1 o-Ph, H12/H16), 7.33-7.30 (m, 2H, P1 o-Ph, H18/H22), 7.04-6.92 (m, 12H, Ph), 3.23–3.14 (m, 1H, CH 6), 2.88–2.79 (m, 1H, *i*-Pr CH 7), 2.02–1.94 (m, 2H, CH<sub>2</sub> 2/5), 1.82–1.69 (m, 5H, 3H dppe CH<sub>2</sub>/1H CH<sub>2</sub> 4/1H Pt-CH 1), 1.33-1.18 (m, 3H, overlapping *i*-Pr Me signal, 1H dppe CH<sub>2</sub>/1H CH<sub>2</sub> 4/1H CH<sub>2</sub> 2), 1.30 (d, *J* = 7, 3H, *i*-Pr Me 8/9), 1.04–0.97  $(m, 1H, CH_2 5), 0.80 (d, J = 7, 3H, Me 10), 0.69-0.60 (m, 1H, overlapping)$ *i*-Pr Me signal, CHMe 3), 0.67 (d, J = 7, 3H, *i*-Pr Me 8/9). <sup>13</sup>C{<sup>1</sup>H} NMR  $(C_6D_6)$ :  $\delta$  135.1 (d, J = 12, P1 o-Ph, C12/C16), 134.5 (d, J = 12, P2 o-Ph), 133.5 (d, J = 11, P2 o-Ph), 132.9 (d, J = 10, P1 o-Ph, C18/C22), 131.7 (Ph), 130.7 (Ph), 130.5 (Ph), 130.2 (Ph), 129.0–127.5 (m, Ph, overlapping C<sub>6</sub>D<sub>6</sub> signals), 47.6 (CH 6), 44.0 (m, CH<sub>2</sub> 2), 43.3 (d, J = 98, Pt-CH 1), 38.0 (d, *J* = 9, CHMe 3), 36.2 (CH<sub>2</sub> 4), 33.6 (*i*-Pr CH 7), 30.7 (dd, *J* = 40, 20, dppe CH<sub>2</sub>), 29.6 (d, J = 10, CH<sub>2</sub> 5), 24.0 (dd, J = 30, 8, dppe CH<sub>2</sub>), 23.3 (Me 10), 22.6 (*i*-Pr Me 8/9), 17.8 (*i*-Pr Me 8/9). Note: <sup>13</sup>C NMR assignments for the aryl groups use the atom numbering from Chart 2 and Figure 2 (see also Figure S1 in the Supporting Information).

**Decomposition of 1 and 2.** An NMR tube containing a solution of Au(Men)(PPh<sub>3</sub>) (1, 15 mg) in 1 mL of CDCl<sub>3</sub> was sealed with Parafilm and kept at room temperature in the light. <sup>31</sup>P NMR after 24 h revealed complete degradation of the sample to Au(PPh<sub>3</sub>)(Cl). The <sup>1</sup>H NMR spectrum showed a 1:1 ratio of two major menthyl species, (–)-menthyl chloride<sup>40</sup> and (+)-neomenthyl chloride,<sup>33</sup> with diagnostic peaks at 3.79 ppm (dt, J = 4, 11) and 4.51 ppm (br m), respectively. To determine whether trace acid in CDCl<sub>3</sub> was responsible for degradation, an NMR sample was prepared with CDCl<sub>3</sub> that had been passed over basic alumina. A sample was also prepared in untreated CDCl<sub>3</sub> and kept in the dark to determine the effect of light on the decomposition. Both samples degraded in the same way as the original sample.

The NMR samples were combined, and the solvent was removed *in vacuo* to give a white solid and traces of an oily film. The menthyl species were extracted with pentane (3 mL). The solvent was removed *in vacuo*, the sample was redissolved in CDCl<sub>3</sub>, and <sup>1</sup>H NMR confirmed the

presence of both menthyl species. The sample was then divided into two aliquots, which were treated with an authentic sample of (-)-menthyl chloride (Aldrich) or (+)-neomenthyl chloride; the <sup>1</sup>H NMR spectra confirmed the identification of the decomposition products.<sup>33</sup> GC analysis was also carried out on a Shimadzu QP2010 Plus GC-MS with a SHRX1-5MS column; the injection temperature was 280 °C, and the initial column temperature was 50 °C. After a 2 min lag time, the column was heated from 50 to 280 °C at a rate of 20 °C/min. The end temperature was then held for 3 min. The retention times for pure samples of (-)-menthyl chloride, (+)-neomenthyl chloride, and the experimental sample were identical (8.25 min).

Similarly, an NMR tube containing a solution of Pt(dppe)(Men)(Br)(2, 10 mg) in 1 mL of  $CDCl_3$  was sealed with Parafilm and kept at room temperature in the light. <sup>31</sup>P NMR after 7 days revealed complete degradation of the sample to a mixture of  $Pt(dppe)Cl_2$ , Pt(dppe)(Cl)-(Br), and  $Pt(dppe)Br_2$ .<sup>27</sup> The <sup>1</sup>H NMR spectrum showed two major menthene species, *trans*-2-menthene and 3-menthene, with diagnostic peaks at 5.53 ppm (br s, 2H) and 5.36 ppm (br s, 1H), respectively.<sup>34</sup> This decomposition was unaffected when the sample was kept in the dark, or when  $CDCl_3$  that had been passed over basic alumina was used. To confirm the identities of the menthenes, the NMR sample containing the degradation products was divided into two aliquots, which were then treated with authentic samples of either *trans*-2-menthene (Aldrich) or 3-menthene.<sup>41</sup>

### ASSOCIATED CONTENT

**Supporting Information.** Crystallographic details, including CIF files, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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