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Synthesis and Reactivity of New κ^2-[*P,N*]Pt(II) Complexes of Diisopropylphosphino-Substituted 2-Dimethylaminoindene

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Treatment of 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1a**[H]) with either *cis/trans*-(SMe$_2$)$_2$PtCl$_2$ or PtCl$_2$ provided (κ^2-*P,N*-2-NMe$_2$-3-P^{i}Pr$_2$-indene)PtCl$_2$ (**2**) in 84% and 55% yield, respectively, while the reaction of **1a**[H] with (η^4-COD)PtClMe afforded (κ^2-*P,N*-2-NMe$_2$-3-P^{i}Pr$_2$-indene)PtClMe (**3**) in 91% yield. Whereas in the formation of **2** and **3** the ligand precursor **1a**[H] undergoes a rearrangement to give a coordinated 2-NMe$_2$-3-P^{i}Pr$_2$-indene (**1b**[H]) ligand, **1a**[H] reacted cleanly with 0.5 equiv of [(μ-SMe$_2$)PtMe$_2$]$_2$ to give (κ^2-*P,N*-**1a**[H])PtMe$_2$ (**4a**) in 97% yield. The isomerization of **4a** to (κ^2-*P,N*-**1b**[H])PtMe$_2$ (**4b**) in a THF/^{i}PrOH mixture is rapid and allowed for the isolation of **4b** in 99% yield. Heating of **4a** in CH$_2$Cl$_2$ resulted in the quantitative formation of **3**, while the thermolysis of **4a** in toluene in the presence of SMe$_2$ afforded **5**, the apparent product of intramolecular C−H activation of an NMe group. The reactivity of **4a** with a variety of other two-electron donors, as well as E−H-containing substrates (E = main group fragment), is reported. Although NMR spectroscopic evidence indicated the formation of an intermediate of the type (κ^2-*P,N*-**1**[H])Pt(SnPh$_3$)(Me), as well as Ph$_6$Sn$_2$, in the reaction of **4a** with 10 equiv of Ph$_3$SnH, negligible conversion of Ph$_3$SnH to Ph$_6$Sn$_2$ was obtained when employing 1 mol % **4a** as a catalyst. Single-crystal X-ray diffraction data for **2** and **5** are reported.

Introduction

With the goal of developing new and synthetically useful stoichiometric and/or catalytic reaction chemistry based on the metal-mediated activation of E−H bonds (E = main group element),[1] we have recently initiated a research program focused in part on developing charge-neutral alternatives to traditional cationic late metal complexes.[2] Although such cationic species often possess desirable reactivity properties, the inherently polar nature of discrete salts can necessitate the use of high-polarity reaction media. Under such conditions, unfavorable competition between substrate molecules and the counteranion or coordinating solvent molecules for the metal active site can result in diminished reactivity. In the context of Rh(I) we have demonstrated that 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1a**[H]) and 2-NMe$_2$-3-P^{i}Pr$_2$-indene (**1b**[H]) serve as precursors to (κ^2-*P,N*-**1**)-Rh(η^4-COD), the first formally zwitterionic analogue of ubiquitous [κ^2-*P,N*-Rh(η^4-COD)]$^+$X$^-$ cationic catalysts, which is effective in mediating the dehydrogenative cross-coupling of C−H and Si−H units.[2a] Notably, the 10π indenide backbone in (κ^2-*P,N*-**1**)Rh(η^4-COD) functions as a sequestered anionic charge reservoir, rather than as a site for metal binding.[2a]

In expanding our exploration of the coordination chemistry and reactivity behavior of metal complexes supported by **1**[H] and related ligands, we naturally became interested in the study of platinum complexes, owing to their well-established propensity for E−H bond activation under homogeneous reaction conditions.[3] A survey of the literature reveals that most of the Pt(II) complexes that are able to effect intermolecular C−H bond activation are cationic and feature a bidentate N,N ancillary support.[4] However, the viability of intermolecular C−H activation by neutral Pt(II) complexes[5,6] and those featuring P,P ligands[6,7] has been demonstrated.[3b] As such, it has been suggested that the ability of the aforementioned 16-electron, four-coordinate [κ^2-*N,N*-Pt(R)(L)]$^+$X$^-$ complexes to activate C−H bonds may

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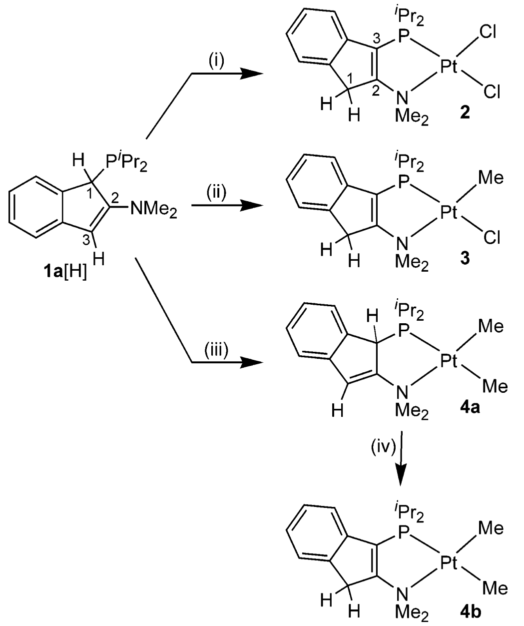
be attributed more to their capacity to generate unsaturated, 14-electron three-coordinate $[\kappa^2\text{-}N,N\text{-Pt(R)}]^+X^-$ intermediates upon loss of a neutral, two-electron donor (L) rather than to the formally cationic nature of the Pt(II) center.[3b] Given that $[L_2Pt(R)]^+X^-$ species are prone to attack by polar solvent molecules and/or the counteranion, we set out to develop alternative classes of reactive Pt(II) complexes that would provide access to *neutral*, unsaturated $LPtR_2$ reactive intermediates in low-polarity solvents (e.g., hydrocarbons). Chelating, mixed-donor P,N-ligands are poised to exhibit hemilabile behavior when coordinated to Pt(II),[8] with the softer P-donor serving to anchor the ligand to the metal and the harder N-donor temporarily occupying a metal coordination site in the absence of substrate molecules.[9] For (κ^2-*P*,*N*-**1**[H])PtX_2 systems in particular, the formation of unsaturated (κ^1-*P*,N-**1**[H])PtX_2 intermediates becomes increasingly favorable since the uncoordinated dimethylamino group is stabilized by entering into conjugation with the π-system of the indene backbone.[2] Bidentate P,N-ligands such as **1**[H] are also advantageous in that they should stabilize both low- and high-oxidation state platinum species formed in the course of E−H bond activation processes. Despite the well-established ability of P,N-ligands to confer desirable reactivity properties to a variety of platinum-group metal fragments,[10] the application of such a ligation strategy to the development of Pt(II) complexes for E−H and E−C bond activation has received relatively little attention.[11−13] Herein we report on the synthesis and characterization of new Pt(II) complexes featuring **1**[H], including a preliminary survey of the E−H bond activation capabilities and other reactivity properties of (κ^2-*P*,*N*-**1a**[H])$PtMe_2$.

Scheme 1[a]



[a] Reagents and conditions: (i) *cis/trans*-$(SMe_2)_2PtCl_2$ or $PtCl_2$; (ii) (η^4-COD)PtClMe; (iii) 0.5 [(μ-SMe_2)$PtMe_2$]$_2$; (iv) (a) 22 °C, 15 days; (b) 50 °C, 45 h; (c) Et_3N, 22 °C, 7 days; or (d) ^{i}PrOH, 22 °C, 10 min.

Results and Discussion

Synthesis and Characterization of (κ^2-*P*,*N*)PtX_2 Complexes. Target complexes of the type (κ^2-*P*,*N*-**1**[H])-PtX_2 were prepared as outlined in Scheme 1. Treatment of **1a**[H] with either *cis/trans*-$(SMe_2)_2PtCl_2$ or $PtCl_2$ affords (κ^2-*P*,*N*-**1b**[H])$PtCl_2$ (**2**) in 84% and 55% yield, respectively. Similarly, the reaction of **1a**[H] with (η^4-COD)PtClMe provides (κ^2-*P*,*N*-**1b**[H])PtClMe (**3**) in 91% isolated yield. In the formation of both **2** and **3**, the ligand precursor **1a**[H] undergoes a structural rearrangement that places the P^{i}Pr$_2$ fragment at the vinylic (C3) position on the indene backbone, resulting in the exclusive formation of (κ^2-*P*,*N*-**1b**[H])PtX_2 species. In contrast, **1a**[H] reacts cleanly with 0.5 equiv of [(μ-SMe_2)$PtMe_2$]$_2$ at 22 °C over 3 h to give pure (κ^2-*P*,*N*-**1a**[H])$PtMe_2$ (**4a**), which was isolated in 97% yield. The isomerization of the allylic isomer **4a** to (κ^2-*P*,*N*-**1b**[H])-$PtMe_2$ (**4b**) does proceed slowly in the solid and in solution; after 15 days at 22 °C in toluene, over 95% conversion to **4b** is observed (based on ^1H and ^{31}P NMR data). Similar results are obtained either by heating toluene solutions of **4a** (50 °C, 45 h) or by the addition of 10 equiv of NEt_3 (22 °C, 7 days). Interestingly, the clean rearrangement of **4a** to **4b** in a THF/^{i}PrOH mixture is rapid (22 °C, 10 min), allowing for the isolation of pure **4b** in nearly quantitative yield. The solvent-dependent interconversion of allylic and vinylic

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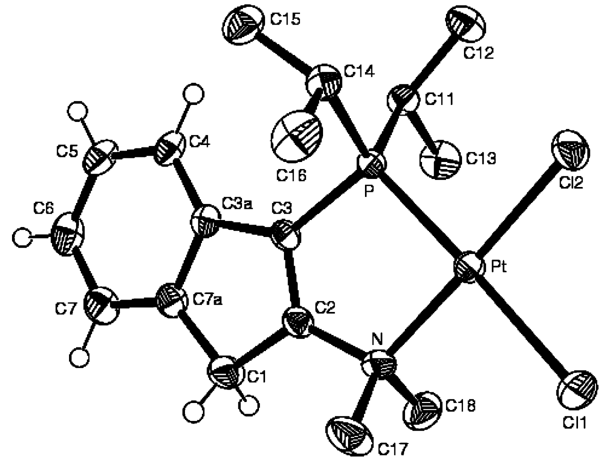

Figure 1. ORTEP diagram for **2**, shown with 50% displacement ellipsoids and with the atomic numbering scheme indicated. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **2**: Pt−Cl1 2.3753(8); Pt−Cl2 2.2978(8); Pt−P 2.2006(7); Pt−N 2.091(2); N−C2 1.472(4); P−C3 1.809(3); C1−C2 1.505(4); C2−C3 1.332(4).

indenylphosphine isomers is an established phenomenon.[2d]

Table 1. Crystallographic Data for 2 and 5

	2	**5**
empirical formula	$C_{17}H_{26}Cl_2NPPt$	$C_{20}H_{34}NPPtS$
fw	541.35	546.60
cryst dimens	0.43 × 0.16 × 0.12	0.36 × 0.20 × 0.09
temp (K)	193(2)	193 (2)
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
a (Å)	7.6580 (3)	10.388 (1)
b (Å)	15.2323 (6)	21.813 (2)
c (Å)	16.8331 (7)	10.570 (1)
β (deg)	90	114.546 (2)
V (Å^3)	1963.6(1)	2178.6 (4)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.831	1.666
μ (mm^{-1})	7.496	6.612
2θ limit (deg)	52.72	52.82
	$-9 \le h \le 9$	$-12 \le h \le 12$
	$-19 \le k \le 18$	$-27 \le k \le 27$
	$-21 \le l \le 20$	$-13 \le l \le 13$
total no. of data collected	12 801	16 628
no. of indep reflns	4011	4466
no. of obsd reflns	3968	3792
R_{int}	0.0202	0.0347
abs corr	Multiscan (SADABS)	Multiscan (SADABS)
range of transmn	0.4666−0.1409	0.5876−0.1994
no. of data/restraints/ params	4011/0/200	4466/0/219
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0155	0.0275
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0381	0.0672
goodness-of-fit	1.085	1.076
largest peak, hole (e Å^{-3})	1.433, −0.459	1.923, −0.331

The structures of **2**, **3**, **4a**, and **4b** depicted in Scheme 1 are supported by 1D- and 2D-NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum for each complex is comprised of a singlet with accompanying platinum satellites. In the case of **3**, the magnitude of this coupling constant ($^1J_{PtP}$ = 4487 Hz) confirms the *cis*-disposition of the phosphine and methyl fragments. The alternative isomer featuring a methyl group *trans* to phosphorus would be expected to give rise to a much lower $^1J_{PtP}$ value, given the stronger *trans*-influence of the methyl substituent, relative to chloride;[12b] indeed, the $^1J_{PtP}$ in **4b** (2039 Hz) is diminished relative to **3**. The C_s symmetry of **2**, **3**, and **4b** is evident in the ^{1}H and ^{13}C NMR data for these complexes. Conversely, the ^{1}H and ^{13}C NMR spectra of **4a** clearly indicate a lack of mirror-plane symmetry, with both vinylic and allylic C−H units on the indene backbone, as well as pairs of nonequivalent ^{i}Pr and Me fragments, being clearly discernible. The structure of **2** was also confirmed on the basis of data obtained from a single-crystal X-ray diffraction study. The crystal structure of **2** is presented in Figure 1, and relevant crystallographic parameters are collected in Table 1. The platinum center in **2** deviates only modestly from ideal square-planar geometry ($\Sigma_{\text{angles at Pt}} \approx 360°$), with the Pt−Cl1 distance *trans* to the P-donor (2.3753(8) Å) being significantly longer than the corresponding Pt−Cl2 distance *trans* to N (2.2978(8) Å), in keeping with the greater *trans*-influence of the P-donor fragment. Although we were unable to identify a crystallographically characterized (κ²-*P*,*N*)PtCl$_2$ from the literature, the interatomic distances in **2** can be compared with those found in other Pt(II) complexes.[11e,12e,13,14] Having established viable synthetic routes to (κ²-*P*,*N*-**1**[H])PtX$_2$ complexes, a preliminary reactivity survey involving **4a** (containing <5% **4b**) was undertaken. The (κ²-*P*,*N*-**1a**[H])PtMe$_2$ complex (**4a**) was selected for these initial studies in light of the established propensity of Pt−CH$_3$ linkages to react with E−H bonds to yield Pt−E and CH$_4$.[3b,4−7,11,12]

Thermolysis of 4a. Complex **4a** is stable in benzene, toluene, or THF at 22 °C, with the exception of the aforementioned slow conversion to **4b**. However, thermolysis (70 °C) of **4a** in each of these solvents generated a complex mixture of phosphorus-containing complexes, including **4a** (δ ^{31}P = 27.6), **4b** (δ ^{31}P = 39.2), and a new platinum-containing species (δ ^{31}P = 19.0, $^1J_{PtP} \approx$ 3000 Hz); this new complex represents the major product after 48 h. We have thus far been unsuccessful in isolating this thermolysis product. However, the observation that the same thermolysis product appears to form in benzene, toluene, and THF suggests that this product might arise due to an intramolecular bond activation process (vide infra), rather than as a result of an intermolecular reaction involving the solvent. Although **4a** is stable in CH$_2$Cl$_2$ at 22 °C, heating in this solvent at 50 °C for 18 h cleanly produces (κ²-*P*,*N*-**1b**[H])PtClMe, **3** (Scheme 2). In keeping with established reactivity trends observed for (κ²-*P*,*N*)PtMe$_2$ species,[15] CHCl$_3$ proved more reactive than CH$_2$Cl$_2$ toward **4a**, producing a complex mixture of products including **3**. Similarly, dissolution of **4a** in CH$_3$CN (or treatment of this complex with 1 equiv of CH$_3$CN in toluene) either at 22 °C or with heating (75 °C for 72 h) resulted in the slow consumption of **4a** (based on ^{31}P NMR data) without the formation of detectable phosphorus-containing product(s) or precipitated solids. Given the complexity of the ^{1}H NMR spectrum of the crude reaction mixture, and the fact that we have not been able to isolate pure materials from this mixture, we are unable to conclusively identify the platinum-containing product(s) of this reaction.

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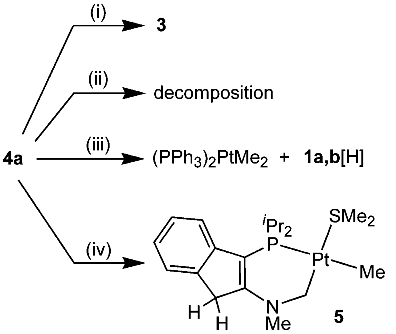
Scheme 2[a]



[a] Reagents and conditions: (i) CH_2Cl_2, 50 °C, 18 h; (ii) (a) $CHCl_3$; (b) 4-(dimethylamino)pyridine, 75 °C, 72 h; or (c) CH_3CN, 75 °C, 72 h; (iii) 10 equiv of PPh_3; (iv) SMe_2, 70 °C, 20 h.

Reactivity of 4a with L-Donors. In an attempt to assess the binding strength of the P,N-chelate in **4a**, this complex was exposed to a variety of two-electron donors (L) in toluene, and the progress of the reaction was monitored by use of ^{31}P NMR spectroscopic techniques. While no reaction was observed between **4a** and 1 equiv of 4-(dimethylamino)pyridine (DMAP) at 22 °C over 24 h, heating of this mixture at 75 °C resulted in the generation of multiple phosphorus-containing products. Conversely, treatment of **4a** with 1 equiv of PPh_3 at 22 °C generated a mixture containing only $(PPh_3)_2PtMe_2$,[16] **1a,b**[H], and unreacted **4a**; upon addition of 10 equiv of PPh_3, only $(PPh_3)_2PtMe_2$, **1a**,**b**[H], and PPh_3 were detected. These observations suggest that putative (κ^1-*P*,N-**1**[H])Pt$(PPh_3)Me_2$ intermediates are more reactive than **4a** toward ligand substitution by PPh_3, a situation that may be attributed to steric crowding in such intermediates. Alternatively, a toluene solution of **4a** was treated with 2.5 equiv of SMe_2 at 22 °C. The usual slow transformation of **4a** into **4b** was observed after several days, accompanied by the appearance of a single new platinum-containing product (δ ^{31}P = 16.8 ppm, $^1J_{PtP}$ = 2006 Hz); after 15 days, this new complex (**5**) represented the major species present in solution. When the reaction was instead conducted at 70 °C, complete conversion was achieved after 20 h, allowing for the isolation of pure **5** as a brown solid in 61% yield. Although ^{1}H and ^{13}C NMR spectroscopic data confirmed the presence of a SMe_2 ligand in **5**, the other spectral features observed clearly indicated that this complex was not a simple adduct of the type (κ^1-*P*,N-**1**[H])Pt$(SMe_2)Me_2$. The connectivity in **5** was ultimately elucidated on the basis of data obtained from a single-crystal X-ray diffraction experiment; the structure of **5** is presented in Figure 2, and relevant crystallographic parameters are collected in Table 1. The platinum center in **5** exhibits typical square-planar geometry ($\Sigma_{\text{angles at Pt}} \approx 360°$) and is ligated by N-$CH_2$ and CH_3 fragments, as well as *cis*-disposed P- and S-donors. The planarity at nitrogen ($\Sigma_{\text{angles at N}} \approx 360°$) and the contracted N−C2 distance (1.326(5) Å) relative to both the other N−C distances in **5** (1.461(5), 1.453(5) Å) and the N−C2 distance in **2** (1.472(4) Å) indicate that the nitrogen fragment in **5** is in conjugation with the indenyl framework. Although details of the mechanistic pathway leading to **5** are unknown, this complex can be viewed as arising from an intramolecular C−H activation process involving one of the NMe groups in a three-coordinate intermediate of the type (κ^1-*P*,N-**1**[H])$PtMe_2$, with the loss of CH_4 and coordination of SMe_2 yielding the observed product. The activation of NMe C−H bonds has been observed for a range of transition metal fragments;[17] the structural features found in **5** are comparable to those observed in a related cyclometalated platinum complex.[17a]

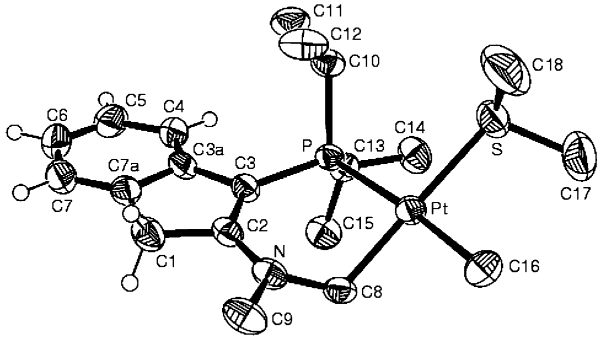


Figure 2. ORTEP diagram for **5**, shown with 50% displacement ellipsoids and with the atomic numbering scheme indicated. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **5**: Pt−S 2.365(1); Pt−C8 2.039(4); Pt−C16 2.094(4); Pt−P 2.303(1); N−C2 1.326(5); N−C8 1.461(5); N−C9 1.453(5); P−C3 1.786(4); C1−C2 1.516(6); C2−C3 1.395(5).

Reactivity of 4a with E−H Bonds. In an attempt to survey the intermolecular E−H bond activation capabilities of **4a**, the reactivity of this complex with a variety of main group substrates (in C_6D_6 or toluene) was examined. Treatment of **4a** with either dihydrogen (1 atm) or pinacolborane (1 equiv) resulted in no observable reaction (^{1}H and ^{31}P NMR), even after heating for 3 days at 50 °C. In contrast, PhC≡CH, Ph_3SiH, Ph_2SiH_2, $PhSiH_3$, and Et_3SiH were each observed to react with **4a** to some extent at 22 °C. However, multiple phosphorus-containing products were generated in each case, regardless of the subtrate:**4a** ratio (1:1, 2:1, or 10:1) or the reaction temperature (22−75 °C) employed, and we have thus far been unable to unequivocally characterize any of the products from these reaction mixtures. In monitoring the reaction of **4a** with the aforementioned silanes by use of ^{1}H NMR techniques, no Pt−H species were detected, and Pt−Me resonances persisted throughout the course of each reaction. Complex reactivity between (κ^2-*P,N*)$PtMe_2$ complexes and organosilanes has been observed previously.[12e]

Braunstein,[18] Schubert,[12f] and others[18c] have demonstrated that complexes of the heavier group 10 metals are capable of mediating the dehydrogenative dimer-

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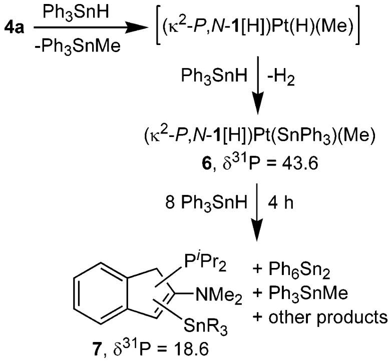
[16] Goodfellow, R. J.; Hardy, M. J.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2450.

[17] For the crystallographic characterization of NMe C−H activation products, see: (a) Fantasia, S.; Manaserro, M.; Pasini, A. *Inorg. Chem. Commun.* **2004**, *7*, 97. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720. (c) Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956. (d) Liu, G.; Beetstra, D. J.; Meetsma, A.; Hessen, B. *Organometallics* **2004**, *23*, 3914. (e) Clot, E.; Chen, J.; Lee, D.-H.; Sung, S. Y.; Appelhans, L. N.; Faller, J. W.; Crabtree, R. H.; Eisenstein, O. *J. Am. Chem. Soc.* **2004**, *126*, 8795.

[18] (a) Braunstein, P.; Morise, X.; Blin, J. *Chem. Commun.* **1995**, 1455. (b) Braunstein, P.; Morise, X. *Organometallics* **1998**, *17*, 540. (c) Braunstein, P.; Morise, X. *Chem. Rev.* **2000**, *100*, 3541, and references therein.

ization of Ph_3SnH to yield Ph_6Sn_2. In this context, the reaction of **4a** with Ph_3SnH (C_6D_6, 22 °C) was examined. Given the known light-sensitivity of Sn−H bonds,[19] the photostability of C_6D_6 solutions of Ph_3SnH in the absence of **4a** was evaluated (^1H and ^{119}Sn NMR). Solutions stored in the dark for 20 days exhibited NMR signals attributable only to Ph_3SnH with no observable H/D exchange involving the Sn−H fragment, and upon exposure to ambient light for 3.5 h, only a trace of Ph_6Sn_2 was detected (^{119}Sn NMR).[12f] The reaction of **4a** with Ph_3SnH (1:1 ratio) generated a mixture of phosphorus-containing products that gave rise to ^{31}P NMR resonances at 43.6 (∼5%), 41.0 (∼5%), and 27.6 (**4a**, ∼90%) ppm; the intensity ratio of these signals did not change significantly over 24 h. In contrast, reactions employing 10 equiv of Ph_3SnH resulted in the consumption of **4a** after 2 min, accompanied by the clean formation of a single phosphorus-containing product (**6**) at 43.6 ppm (singlet with Pt satellites, $^1J_{PtP} = 2601$ Hz). While the presence of unreacted Ph_3SnH and dihydrogen (4.46 ppm) was evident in the ^1H NMR spectrum of the reaction mixture after 5 min, neither well-resolved Pt−Me signals nor low-frequency resonances associated with Pt−H fragments were observed. Analysis of the reaction mixture after 20 min by use of ^{119}Sn NMR techniques indicated the presence of Ph_3SnH (−163.2 ppm, ∼45%), Ph_3SnMe (−90.2 ppm, ∼20%), Ph_6Sn_2 (−141.6 ppm, ∼20%), and an unidentified complex (−125.9 ppm, ∼15%, possibly Ph_4Sn);[12f,20] the Ph_3SnH was ultimately consumed after 4 h, with the product mixture exhibiting ^{119}Sn NMR signals at −228.9 (∼15%),[21] −141.6 (Ph_6Sn_2, ∼40%), −125.8 (∼30%), and −90.2 (Ph_3SnMe, ∼15%) ppm. Notably, no platinum-coupled ^{119}Sn NMR resonances were observed throughout the course of this reaction. The ^{31}P NMR spectrum of the product mixture after 4 h revealed the presence of one dominant phosphorus-containing species at 18.9 ppm (singlet with satellites, $J = 133$ Hz), accompanied by low-intensity resonances at 60.2 and 43.6 ppm. Collectively, these spectroscopic observations are consistent with the reaction pathway tentatively proposed in Scheme 3, in which **4a** initially reacts with Ph_3SnH to give an unobserved (κ^2-*P*,*N*-**1**[H])Pt(H)(Me) intermediate and Ph_3SnMe. Rapid Sn−H oxidative addition of a second molecule of Ph_3SnH, followed by reductive elimination of dihydrogen, yields **6**; this complex can also be generated directly from the Sn−H oxidative addition of Ph_3SnH to **4a**, followed by reductive elimination of methane. Complex **6** could then react with the remaining Ph_3SnH over 4 h to yield a mixture of tin products, possibly including **7**. While the tentative assignment of **7** as a stannylated derivative of **1**[H] is based on the lack of discernible Pt−P coupling and the relative magnitude of the observed J_{PSn} coupling,[22] we were unable to unambiguously identify an accompanying ^{31}P-coupled signal in the ^{119}Sn NMR spectrum that could be assigned to **7**. We have thus far been unable to obtain purified samples of **7** for further characterization. The generation of **7** underscores the possibility that the observed conversion of Ph_3SnH is mediated by ill-defined Pt species (possibly metallic or colloidal), rather than a discrete complex featuring **1**[H].

Scheme 3. Proposed Pathway for the Reaction of 4a with 10 Equiv of Ph_3SnH in C_6D_6



Subsequently, the ability of either **4a** or **4b** to catalyze the dehydrogenative dimerization of Ph_3SnH to Ph_6Sn_2 (1 mol % in C_6D_6) was examined. Unfortunately, under these conditions the consumption of Ph_3SnH was negligible (^{119}Sn NMR) for reactions conducted in either the presence or absence of ambient light after 3.5 h. Braunstein and co-workers[18b] have reported that the palladium-catalyzed dehydrogenative dimerization of Ph_3SnH can be conducted in a variety of solvents (including CH_2Cl_2) without the exclusion of ambient light and that no modification of the kinetic parameters or TON values for various catalysts is observed when reactions are carried out in the presence of radical scavengers and/or in the dark. On the basis of this report, and in preparing to survey the catalytic abilities of **4a** in CH_2Cl_2, control experiments were carried out in which CD_2Cl_2 solutions of Ph_3SnH were monitored (^1H and ^{119}Sn NMR). In the absence of light, no reaction was noted after 4 days; in contrast, upon exposure to ambient light for 1 h, greater than 50% conversion to Ph_3SnCl ($\delta^{119}Sn = -48$)[20] was observed, along with a small amount of Ph_6Sn_2.[23] While no reaction was observed for Ph_3SnH in CD_2Cl_2 in the presence of 1 mol % **4a** in the dark after 3.5 h, exposure to ambient light under analogous conditions resulted in the conversion of Ph_3SnH to a mixture of Ph_3SnCl (∼80%) and Ph_6Sn_2 (∼20%).

Summary and Conclusions

In summary, we have demonstrated that the P,N-substituted indene **1a**[H] can be utilized in the preparation of (κ^2-*P*,*N*-**1**[H])PtX_2 complexes, the design of which is intended to promote the formation of unsaturated

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[19] (a) Davies, A. G. In *Chemistry of Tin*; Harrison, P. G., Ed.; Chapman and Hall: New York, 1989; Chapter 9. (b) Photolytic cleavage of Sn−H in Ph_3SnH: Schmidt, U.; Kabitzke, K.; Markau, K.; Neumann, W. P. *Chem. Ber.* **1965**, *98*, 3827. (c) Photosensitivity of polymers containing Sn−H groups: Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931.

[20] (a) Davies, A. G.; Harrison, P. G.; Kennedy, J. D.; Mitchell, T. N.; Puddephatt, R. J.; McFarlane, W. *J. Chem. Soc. (C)* **1969**, 1136. (b) McFarlane, W.; Wood, R. J. *J. Organomet. Chem.* **1972**, *40*, C17.

[21] Although we are unable to identify the complex that gives rise to the ^{119}Sn NMR resonance at −228.9 ppm, we have observed this species (along with Ph_6Sn_2) as an impurity (up to 20%) in samples of Ph_3SnH obtained from commercial sources.

[22] (a) Almeida, J. F.; Azizian, H.; Earborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *210*, 121. (b) Yoder, C. H.; Margolis, L. A.; Horne, J. M. *J. Organomet. Chem.* **2001**, *633*, 33.

[23] The reduction of alkyl chlorides by R_3SnH promoted by exposure to UV light is well-established: Wardell, J. L. In *Chemistry of Tin*; Harrison, P. G., Ed.; Chapman and Hall: New York, 1989; Chapter 10.

reactive intermediates of the type (κ^1-*P*,N-**1**[H])PtX$_2$. Although reactions involving **4a** and two-electron donors did not result in the trapping of such intermediates, a three-coordinate species may be involved in the formation of the cyclometalated complex, **5**, which can be viewed as arising from an intramolecular C−H activation process involving (κ^1-*P*,N-**1**[H])PtMe$_2$ in the presence of SMe$_2$. However, the role of Lewis bases in mediating such reactivity remains unclear, as divergent reaction pathways are observed when alternative donor molecules are employed (e.g., PPh$_3$, THF, CH$_3$CN, DMAP). Although **4a** also reacts in an intermolecular fashion with various substrates containing E−H bonds, complex reactivity is often observed and we have thus far been unable to isolate any of the products formed in these reactions. We suspect that cyclometalation processes analogous to those leading to **5** may contribute to the complex intermolecular reactivity observed between **4a** and E−H-containing substrates. As such, we are currently developing variations of **1a**[H] that feature more metalation-resistant donor fragments. The coordination chemistry and reactivity properties of complexes supported by these new ancillary ligands will be the subject of future reports.

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven-dried (130 °C) for 5 days and then evacuated for 24 h prior to use. The nondeuterated solvents tetrahydrofuran, dichloromethane, diethyl ether, toluene, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system provided by mBraun Inc. Tetrahydrofuran, dichloromethane, and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Purification of CH$_3$CN was achieved by refluxing over CaH$_2$ for 4 days under dinitrogen, followed by distillation. Purification of NEt$_3$ was achieved by stirring over KOH for 7 days, followed by distillation; the distilled NEt$_3$ was then refluxed over CaH$_2$ for 3 days under dinitrogen, followed by distillation. CHCl$_3$ was degassed by using three repeated freeze−pump−thaw cycles, dried over CaH$_2$ for 7 days, and distilled in vacuo. Technical grade 2-propanol was not purified prior to use. The solvents used within the glovebox were stored over activated 3 Å molecular sieves. C$_6$D$_6$ (Aldrich) was degassed by using three repeated freeze−pump−thaw cycles and then dried over 3 Å molecular sieves for 24 h prior to use. Compounds **1a**[H],[2a] (η^4-COD)PtClMe,[24a] *cis*/*trans*-[(SMe$_2$)$_2$PtCl$_2$],[24b] and [(μ-SMe$_2$)PtMe$_2$]$_2$,[24b] were prepared employing reported methods. With the exception of dihydrogen (99.999%, Air Liquide-UHP Grade), PtCl$_2$ (Fisher), and Ph$_3$SiH (Strem), all reagents were obtained from Aldrich and were used as received (unless otherwise stated); the purification of Ph$_3$SnH is detailed in the experimental description below. All ^{1}H, ^{13}C, ^{31}P, ^{119}Sn, and ^{195}Pt NMR characterization data were collected in C$_6$D$_6$ at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 202.5, 186.5, and 107.1 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe$_4$ (for ^{1}H and ^{13}C), 85% H$_3$PO$_4$ in D$_2$O (for ^{31}P), SnMe$_4$ (for ^{119}Sn), or K$_2$PtCl$_4$ in D$_2$O (for ^{195}Pt). In some cases, slightly fewer than expected independent ^{1}H or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC NMR experiments. Melting points were obtained on an electrothermal apparatus using samples sealed in capillaries under dinitrogen. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. All X-ray data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer, using samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Crystal structure diagrams were generated by use of the ORTEP-3 program.[25] For complete experimental details and tabulated crystallographic data, see the Supporting Information.

Preparation of 2. Method A. To a Schlenk flask containing a magnetic stir bar were added **1a**[H] (0.017 g, 0.63 mmol) and a mixture of *cis*- and *trans*-[(SMe$_2$)$_2$PtCl$_2$] (0.025 g, 0.63 mmol). The flask was then sealed with a septum, and toluene (30 mL) was added via cannula to generate a light yellow solution. Magnetic stirring was initiated, and the solution was stirred for 16 h. The toluene and other volatile materials were then removed in vacuo, and the residue was washed with pentane (2 × 6 mL) and diethyl ether (6 mL). Then residual solvent was evaporated in vacuo, leaving a light yellow powder, **2** (0.29 g, 0.53 mmol, 84%).

Method B. To a vial containing a magnetically stirred suspension of platinum dichloride (0.049 g, 0.18 mmol) in toluene (2 mL) was added a solution of **1a**[H] (0.050 g, 0.18 mmol) in toluene (2 mL). The resulting mixture was stirred at room temperature for 16 h, after which toluene was evaporated in vacuo to yield a light brown solid residue. This solid was dissolved in a minimal amount of dichloromethane (5 mL) and filtered through Celite to yield a clear, orange solution. Dichloromethane was removed in vacuo, and the residue was washed with pentane (2 × 6 mL) to yield a light yellow powder, **2** (0.054 g, 0.10 mmol, 55%). Pale yellow crystals suitable for X-ray diffraction were obtained by diffusing diethyl ether into a dichloromethane solution of **2** and placing the resulting mixture in a freezer at −35 °C. Melting point: 218−221 °C. Anal. Calcd for C$_{17}$H$_{26}$N$_1$P$_1$Cl$_2$Pt$_1$: C 37.72, H 4.84, N 2.59. Found: C 37.43, H 4.72, N 2.47. ^{1}H NMR: δ 7.07−7.04 (m, 2H, aryl-CH's), 7.01−6.99 (m, 2H, aryl-CH's), 3.06 (s, 6H, N(CH$_3$)$_2$), 2.64 (s, 2H, CH$_2$), 2.46 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 1.32 (dd, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 0.89 (dd, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, P(CHCH$_3$C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR: δ 178.5 (s, C2), 143.1 (s, C3a or C7a), 134.7 (s, C3), 130.0 (s, C7a or C3a), 125.8 (s, aryl-CH), 125.2 (s, aryl-CH), 124.6 (s, aryl-CH), 121.2 (s, aryl-CH), 52.7 (s, N(CH$_3$)$_2$), 29.4 (d, $^3J_{PC}$ = 10 Hz, CH$_2$), 22.7 (d, $^1J_{PC}$ = 36 Hz, P(*C*HCH$_3$CH$_3$)$_2$), 17.3 (s, P(CHCH$_3$*C*H$_3$)$_2$), 17.0 (s, P(CH*C*H$_3$CH$_3$)$_2$). ^{31}P{^{1}H} NMR: δ 31.2 (s, with Pt satellites $^1J_{PtP}$ = 3788 Hz).

Preparation of 3. To a Schlenk flask containing a magnetic stir bar were added **1a**[H] (0.13 g, 0.49 mmol) and (η^4-COD)PtClMe (0.16 g, 0.45 mmol). The flask was then sealed with a septum, and toluene (7 mL) was added via cannula to generate a yellow-brown solution. Magnetic stirring was initiated, and the solution was stirred for 16 h. Toluene and other volatile materials were then removed in vacuo, and the residue was washed with pentane (2 × 6 mL) and diethyl ether (2 × 6 mL). Then residual solvent was evaporated in vacuo to leave a finely divided, off-white powder, **3** (0.21 g, 0.41 mmol, 91%). Melting point: 177−180 °C. Anal. Calcd for C$_{18}$H$_{29}$N$_1$P$_1$Cl$_1$Pt$_1$: C 41.50, H 5.61, N 2.69. Found: C 41.12, H 5.53, N 2.68. ^{1}H NMR: δ 7.10−7.06 (m, 3H, aryl-CH's), 6.99 (m, 1H, aryl-CH), 2.79 (s,

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(24) (a) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411. (b) Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J. *Inorg. Synth.* **1998**, *32*, 149.

(25) ORTEP-3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

6H, $\mathrm{N(CH_3)_2}$), 2.48 (s, 2H, $\mathrm{CH_2}$), 2.21 (m, 2H, $\mathrm{P(C\mathit{H}CH_3CH_3)_2}$), 1.42 (d, $^{3}J_{\mathrm{PH}} = 2.2$ Hz, with Pt satellites, $^{2}J_{\mathrm{PtH}} = 72$ Hz, 3H, Pt−$\mathrm{CH_3}$ *trans* to N), 1.05 (dd, $^{3}J_{\mathrm{PH}} = 17.1$ Hz, $^{3}J_{\mathrm{HH}} = 6.6$ Hz, 6H, $\mathrm{P(CHC\mathit{H}_3CH_3)_2}$), 0.85 (dd, $^{3}J_{\mathrm{PH}} = 16.5$ Hz, $^{3}J_{\mathrm{HH}} = 7.1$ Hz, 6H, $\mathrm{P(CHCH_3C\mathit{H}_3)_2}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR: δ 177.1 (d, $^{2}J_{\mathrm{PC}} = 13$ Hz, C2), 143.8 (d, $J_{\mathrm{PC}} = 6$ Hz, C3a or C7a), 138.4 (s, C7a or C3a), 131.9 (d, $^{1}J_{\mathrm{PC}} = 41$ Hz, C3), 126.9 (s, aryl-CH), 125.8 (s, aryl-CH), 125.4 (s, aryl-CH), 122.2 (s, aryl-CH), 49.8 (s, $\mathrm{N(CH_3)_2}$), 30.2 (d, $^{3}J_{\mathrm{PC}} = 10$ Hz, $\mathrm{CH_2}$), 24.2 (d, $^{1}J_{\mathrm{PC}} = 37$ Hz, $\mathrm{P(\mathit{C}HCH_3CH_3)_2}$), 19.1 (s, $\mathrm{P(CHCH_3\mathit{C}H_3)_2}$), 18.6 (s, $\mathrm{P(CH\mathit{C}H_3CH_3)_2}$), −27.2 (d, $^{2}J_{\mathrm{PC}} = 7$ Hz, Pt satellites not resolved, Pt−$\mathrm{CH_3}$ *trans* to N). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR: δ 31.4 (s, with Pt satellites $^{1}J_{\mathrm{PtP}} = 4487$ Hz). ^{195}Pt NMR: δ −2558 (d, $^{1}J_{\mathrm{PtP}} = 4497$ Hz).

Preparation of 4a. In a vial containing a magnetic stir bar, $[(\mu\text{-SMe}_2)\mathrm{PtMe_2}]_2$ (0.031 g, 0.054 mmol) was suspended in toluene (3 mL), and stirring was initiated. A light brown solution of **1a**[H] (0.027 g, 0.098 mmol) in toluene (3 mL) was then added rapidly to the platinum-containing solution. The resulting mixture was stirred for 3 h, after which time $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR indicated quantitative formation of the allylic isomer, **4a**. The solution was filtered through Celite to remove unreacted $[(\mu\text{-SMe}_2)\mathrm{PtMe_2}]_2$, and toluene and other volatiles were removed in vacuo, yielding a light brown solid, **4a** (0.047 g, 0.095 mmol, 97%). Since **4a** isomerizes to **4b**, elemental analysis data are provided only for **4b** (vide infra). Additionally, ^{13}C NMR chemical shift assignments are made on the basis of projections of the cross-peaks from ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC NMR experiments. ^{1}H NMR: δ 7.14−7.01 (m, 4H, aryl-CH's), 5.70 (s, 1H, vinyl-H), 3.82 (d, $^{2}J_{\mathrm{PH}} = 10.5$ Hz, 1H, allylic-H), 2.72 (s with Pt satellites, $^{3}J_{\mathrm{PtH}} = 14.5$ Hz, 3H, $\mathrm{NC\mathit{H}_3aCH_3b}$), 2.68 (s with Pt satellites, $^{3}J_{\mathrm{PtH}} = 16.3$ Hz, 3H, $\mathrm{NCH_3aC\mathit{H}_3b}$), 2.14 (m, 1H, $\mathrm{P(C\mathit{H}CH_3aCH_3b)}$), 2.08 (s with Pt satellites, $^{2}J_{\mathrm{PtH}} = 20.0$ Hz, 3H, Pt−$\mathrm{CH_3}$ *trans* to N), 1.85 (m, 1H, $\mathrm{P(C\mathit{H}CH_3cCH_3d)}$), 1.39 (dd, $^{3}J_{\mathrm{PH}} = 16.8$ Hz, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 3H, $\mathrm{P(CHC\mathit{H}_3cCH_3d)}$), 1.04 (dd, $^{3}J_{\mathrm{PH}} = 18.0$ Hz, $^{3}J_{\mathrm{HH}} = 7.5$ Hz, 3H, $\mathrm{P(CHCH_3cC\mathit{H}_3d)}$), 0.99 (s, Pt satellites not resolved, 3H, Pt−$\mathrm{CH_3}$ *trans* to P), 0.83 (dd, $^{3}J_{\mathrm{PH}} = 14.7$ Hz, $^{3}J_{\mathrm{HH}} = 7.3$ Hz, 3H, $\mathrm{P(CHC\mathit{H}_3aCH_3b)}$), 0.62 (dd, $^{3}J_{\mathrm{PH}} = 16.5$ Hz, $^{3}J_{\mathrm{HH}} = 6.7$ Hz, 3H, $\mathrm{P(CHC\mathit{H}_3aCH_3b)}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR: δ 170.0 (C2), 144.2 (C3a), 137.0 (C7a), 127.0 (aryl-CH), 124.4 (aryl-CH's), 121.3 (aryl-CH), 113.6 (vinyl-CH), 50.8 ($\mathrm{NCH_3a\mathit{C}H_3b}$), 46.7 ($\mathrm{N\mathit{C}H_3aCH_3b}$), 45.8 (allylic-CH), 23.3 ($\mathrm{P(\mathit{C}HCH_3aCH_3b)}$), 21.4 ($\mathrm{P(\mathit{C}HCH_3cCH_3d)}$), 20.1 (Pt−$\mathrm{CH_3}$ *trans* to N), 19.3 ($\mathrm{P(CH\mathit{C}H_3cCH_3d)}$), 18.5 ($\mathrm{P(CHCH_3c\mathit{C}H_3d)}$), 18.1 ($\mathrm{P(CHCH_3a\mathit{C}H_3b)}$), 17.4 ($\mathrm{P(CH\mathit{C}H_3aCH_3b)}$), −7.1 (Pt−$\mathrm{CH_3}$ *trans* to P). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR: δ 27.6 (s, with Pt satellites $^{1}J_{\mathrm{PtP}} = 2063$ Hz).

Preparation of 4b. To a magnetically stirred solution of **4a** (0.103 g, 0.206 mmol) in THF (10 mL) was added ^{i}PrOH (2.5 mL). After 1 h, clean conversion to **4b** (^{31}P NMR) was achieved. The solvents and other volatiles were removed in vacuo to yield **4b** (0.102 g, 0.204 mmol, 99%) as an analytically pure light brown solid. Decomposition point: 109−114 °C (charring, effervescence). Anal. Calcd for $\mathrm{C_{19}H_{32}N_1P_1Pt_1}$: C 45.59, H 6.44, N 2.80. Found: C 45.22, H 6.38, N 2.67. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 7.28−7.10 (m, 4H, aryl-CH's), 2.62 (s, 6H, $\mathrm{N(CH_3)_2}$), 2.60 (s, 2H, $\mathrm{CH_2}$), 2.44 (m, 2H, $\mathrm{P(C\mathit{H}CH_3CH_3)_2}$), 1.49 (d, $^{3}J_{\mathrm{PH}} = 6.5$ Hz, with Pt satellites, $^{2}J_{\mathrm{PtH}} = 90.5$ Hz, 3H, Pt−$\mathrm{CH_3}$ *trans* to N), 1.29 (dd, $^{3}J_{\mathrm{PH}} = 16.0$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{P(CHC\mathit{H}_3CH_3)_2}$), 1.09 (d, $^{3}J_{\mathrm{PH}} = 7.0$ Hz, with Pt satellites, $^{2}J_{\mathrm{PtH}} = 63.5$ Hz, 3H, Pt−$\mathrm{CH_3}$ *trans* to P), 1.00 (dd, $^{3}J_{\mathrm{PH}} = 14.8$ Hz, $^{3}J_{\mathrm{HH}} = 6.9$ Hz, 6H, $\mathrm{P(CHCH_3C\mathit{H}_3)_2}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR: δ 176.7 (d, $^{2}J_{\mathrm{PC}} = 20$ Hz, C2), 144.0 (d, $^{1}J_{\mathrm{PC}} = 4$ Hz, C3), 139.9 (s, C7a), 136.1 (s, C3a), 126.8 (s, C6 or C7), 125.5 (s, C4), 125.2 (s, C5), 122.3 (s, C7 or C6), 49.8 (s, $\mathrm{N(CH_3)_2}$), 29.5 (d, $^{3}J_{\mathrm{PC}} = 9$ Hz, C1), 24.7 (d, $^{1}J_{\mathrm{PC}} = 23$ Hz, $\mathrm{P(\mathit{C}HCH_3CH_3)_2}$), 19.7 (s, $\mathrm{P(CHCH_3\mathit{C}H_3)_2}$), 19.3 (d, $^{2}J_{\mathrm{PC}} = 7$ Hz, $\mathrm{P(CH\mathit{C}H_3CH_3)_2}$), 17.4 (d, $^{2}J_{\mathrm{PC}} = 111$ Hz, Pt satellites not resolved, Pt−$\mathrm{CH_3}$ *trans* to P), −27.2 (d, $^{2}J_{\mathrm{PC}} = 4$ Hz, Pt satellites not resolved, Pt−$\mathrm{CH_3}$ *trans* to N). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR: δ 39.2 (s, with Pt satellites $^{1}J_{\mathrm{PtP}} = 2039$ Hz).

Preparation of 5. In a Schlenk tube containing a magnetic stir bar, **4a** (0.047 g, 0.095 mmol) was dissolved in toluene (3 mL) to form a light brown solution. Dimethyl sulfide (0.018 mL, 0.25 mmol, 2.5 equiv) was added, and the tube was sealed with a rubber septum and placed in a 70 °C oil bath. Stirring was initiated, and after 20 min the solution was noted to be dark brown (nearly black) in color. The solution was stirred for 20 h, at which time toluene and other volatiles were removed in vacuo. The product was dissolved in benzene (6 mL) and filtered through Celite to remove small quantities of insoluble materials. Removal of benzene in vacuo left a dark brown solid, **5** (0.031 g, 0.057 mmol, 61%). Slow evaporation of a pentane solution under an atmosphere of dinitrogen yielded brown crystals suitable for X-ray diffraction. Decomposition point: 135−137 °C (charring, effervescence). Anal. Calcd for $\mathrm{C_{20}H_{34}N_1P_1S_1Pt_1}$: C 43.95, H 6.27, N 2.56. Found: C 44.24, H 6.20, N 2.51. ^{1}H NMR: δ 7.30−7.23 (m, 2H, aryl-CH's), 7.21−7.13 (m, 1H, aryl-CH). 6.99 (td, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, $^{4}J_{\mathrm{HH}} = 1.5$ Hz, 1H, C5 or C6), 4.08 (d, $^{3}J_{\mathrm{PH}} = 8.5$ Hz, with Pt satellites, $^{2}J_{\mathrm{PtH}} = 93.5$ Hz, 2H, N−$\mathrm{CH_2}$), 3.01 (s, 2H, $\mathrm{C(1)H_2}$), 2.98 (m, 2H, $\mathrm{P(C\mathit{H}CH_3CH_3)_2}$), 2.60 (s, 3H, N−$\mathrm{CH_3}$), 1.93 (s with Pt satellites, $^{3}J_{\mathrm{PtH}} = 25.0$ Hz, 6H, $\mathrm{S(CH_3)_2}$), 1.28 (dd, $^{3}J_{\mathrm{PH}} = 15.5$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{P(CHC\mathit{H}_3CH_3)_2}$), 1.24 (dd, $^{3}J_{\mathrm{PH}} = 14.5$ Hz, $^{3}J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{P(CHCH_3C\mathit{H}_3)_2}$), 1.10 (d, $^{3}J_{\mathrm{PH}} = 6.5$ Hz, with Pt satellites, $^{2}J_{\mathrm{PtH}} = 64.3$ Hz, 3H, Pt−$\mathrm{CH_3}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR: δ 169.2 (d, $^{2}J_{\mathrm{PC}} = 13$ Hz, C2), 149.3 (s, C3a or C7a), 135.5 (d, $J = 7$ Hz, C7a or C3a), 126.5 (s, aryl-CH), 122.9 (s, aryl-CH), 119.6 (s, aryl-CH), 118.3 (s, aryl-CH), 88.8 (d, $^{1}J_{\mathrm{PC}} = 51$ Hz, C3), 41.7 (s with Pt satellites, $^{3}J_{\mathrm{PtC}} = 31$ Hz, N−$\mathrm{CH_3}$), 39.8 (d, $^{3}J_{\mathrm{PC}} = 6$ Hz, C1), 38.0 (d, $^{2}J_{\mathrm{PC}} = 8$ Hz, N−$\mathrm{CH_2}$), 25.3 (d, $^{1}J_{\mathrm{PC}} = 27$ Hz, $\mathrm{P(\mathit{C}HCH_3CH_3)_2}$), 20.6 (s, $\mathrm{P(CHCH_3\mathit{C}H_3)_2}$), 20.1 (d, $^{2}J_{\mathrm{PC}} = 6$ Hz, $\mathrm{P(CH\mathit{C}H_3CH_3)_2}$), 19.1 (s, $\mathrm{S(CH_3)_2}$), 9.6 (d, $^{2}J_{\mathrm{PC}} = 99$ Hz, with Pt satellites, $^{1}J_{\mathrm{PtC}} = 667$ Hz, Pt−$\mathrm{CH_3}$). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR: δ 16.8 (s, with Pt satellites $^{1}J_{\mathrm{PtP}} = 2006$ Hz).

Reactions Involving $\mathrm{Ph_3SnH}$. All experiments were conducted in duplicate using $\mathrm{Ph_3SnH}$ that was purified by extraction into diethyl ether, followed by filtration through Celite to remove insoluble impurities and removal of the solvent to yield purified $\mathrm{Ph_3SnH}$ (based on ^{1}H and ^{119}Sn NMR data). Unless otherwise stated, each reaction was carried out without exclusion of ambient light by adding a solution of an appropriate amount of either **4a** or **4b** in 0.75 mL of either $\mathrm{C_6D_6}$ or $\mathrm{CD_2Cl_2}$ to a glass vial containing $\mathrm{Ph_3SnH}$ (30 mg, 0.086 mmol). A homogeneous mixture formed instantly, and this mixture was then transferred immediately to an NMR tube, which was subsequently capped and sealed with PTFE tape. The resulting light brown solutions were observed to darken to orange-brown over 1 min and then to dark orange after 10 min. Clear, homogeneous mixtures were maintained throughout, and for reactions employing a $\mathrm{Ph_3Sn}$:**4a** ratio of 10:1, gas evolution was also observed. The progress of each reaction was monitored periodically by use of NMR techniques, with the relative product distribution estimated from the ratio of the peak heights in the spectrum (for ^{31}P and ^{119}Sn NMR). Details of specific experiments are provided in the text.

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Supporting Information Available: Tabulated single-crystal X-ray diffraction data for **2** and **5** are available free of charge via the Internet at http://pubs.acs.org.

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