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Neutral and Cationic Platinum(II) Complexes Supported by a P,N-Functionalized Indene Ligand: Structural and Reactivity Comparisons with a Related Gold(III) Zwitterion

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The structural and reactivity properties of new Pt(II) and Au(III) complexes featuring κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indene (**1b**) or κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indenide (**1c**) ancillary ligands are examined. Complex [**1c**]AuMe$_2$ (**3**), a formally zwitterionic relative of the neutral complex [**1b**]PtMe$_2$ (**2b**), was prepared in 41% isolated yield from [**1c**]Li and 0.5 [Me$_2$AuCl]$_2$. Whereas **2b** was observed to react with H$_2$O, Ph$_3$SiH, and PhSiH$_3$ over 48 h at 50 °C, complex **3** proved unreactive under these reaction conditions. Similarly, **2b** exhibited modest catalytic activity for the addition of triethylsilane to styrene, while no conversion was achieved by use of **3** as a catalyst. Observations made during the course of examining the catalytic abilities of [**1b**]PtClMe (**7**) and **7**/AgX (X = BF$_4$ or OTf) for this addition reaction prompted the rational preparation of the dinuclear cation [{(**1b**)PtMe}$_2$Cl]$^+$BF$_4^-$ ([**8**]$^+$BF$_4^-$; 61%) as well as the monomeric cations [(**1b**)PtMeL]$^+$BF$_4^-$ (L = SMe$_2$, [**9**]$^+$BF$_4^-$, 77%; L = MeCN, [**10**]$^+$BF$_4^-$, 84%). Single-crystal X-ray diffraction data are provided for **2b**, **3**, [**8**]$^+$BF$_4^-$, and [**9**]$^+$BF$_4^-$.

Introduction

The rational design of new ancillary ligands for use in influencing the stability and reactivity properties of coordinated platinum-group metal fragments is a well-established, yet relevant pursuit in modern organometallic chemistry.[1] Complexes supported by mixed-donor bidentate ligands, including those pairing phosphorus- and nitrogen-based fragments, remain the focus of intense scrutiny; notably, Rh, Ir, and Pd complexes supported by bidentate P,N-ligands often exhibit reactivity properties that are superior to those displayed by analogous P,P, and N,N species.[2] Notwithstanding investigations by Jones,[3] Milstein,[4] Schubert,[5] and others,[6] the utilization of P,N-type ligands in Pt chemistry has received comparatively less attention. As well, the development of new classes of isostructural neutral and anionic bidentate ligands, in which the design of the latter is intended to prohibit delocalization of the negative charge onto the donor atoms by way of classical resonance structures, is also of current interest in platinum-group metal chemistry. Whereas the neutral ligands can be used in the preparation of cationic complexes, the anionic ligands can be employed in the synthesis of structurally analogous, formally zwitterionic species.[7,8] In addition to the practical benefits that can be derived from the implementation of zwitterionic platinum-group metal and related complexes in catalytic applications,[7−10] fundamental studies examining isostructural and isoelectronic cationic and zwitterionic complexes of a given metal have provided a means of assessing how altering the electronic (*and not steric*) characteristics of an ancillary ligand influences the behavior of

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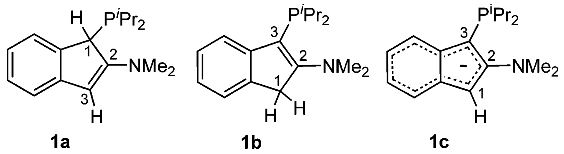
[7] A comparison of formally zwitterionic Rh, Pd, and Pt complexes featuring either κ^2-[Ph$_2$B(CH$_2$*P*R$_2$)$_2$]$^-$ or κ^2-[Ph$_2$B(CH$_2$*N*R$_2$)$_2$]$^-$ ancillary ligands with related cationic complexes has been reported by Peters and co-workers. For example, see: (a) Betley, T. A.; Peters, J. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2385. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870. (c) Lu, C. C.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 15818.

[8] For comparative structural and reactivity studies involving Ru, Rh, and Ir cations supported by κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indene (**1b**) and related zwitterions ligated by κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indenide (**1c**), see: (a) Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618. (b) Cipot, J.; McDonald, R.; Stradiotto, M. *Chem. Commun.* **2005**, 4932. (c) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3603. (d) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 4981.

10.1021/om050910v CCC: $33.50

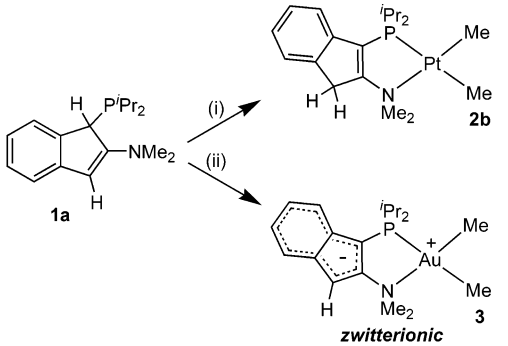
Chart 1



the associated formally cationic metal fragment.[7,8,11,12] Less common are studies in which related neutral and anionic bidentate ligands are employed in the preparation of structurally related neutral (*non-charge-separated*) and zwitterionic (*charge-separated*) complexes of a given platinum-group metal and its right-side neighbor on the periodic table, respectively.[13]

In this context we are examining new coordinatively unsaturated platinum-group metal complexes that feature κ^2-1-P^iPr$_2$-2-NMe$_2$-indene (**1a**), κ^2-2-NMe$_2$-3-P^iPr$_2$-indene (**1b**), κ^2-2-NMe$_2$-3-P^iPr$_2$-indenide (**1c**), and related ligands (Chart 1), with the goal of identifying complexes that exhibit new and/or synthetically useful reactivity involving the activation of E−H bonds (E = main group fragment).[6a,8] In addition to evaluating how geometric differences between **1a** and **1b** influence the properties of the associated complexes, we have carried out comparative structural and reactivity investigations involving Ru, Rh, and Ir cations supported by **1b**, as well as analogous zwitterions supported by **1c**;[8] zwitterions of this type can be viewed as comprising a formally cationic metal fragment counterbalanced by a sequestered, uncoordinated 10 π-electron indenide unit built into the backbone of the P,N-ligand. In the course of studying neutral Pt(II) complexes of **1a** and **1b**,[6a] we became interested in developing cationic Pt(II) species supported by these ligands, as well as related Au(III) zwitterions featuring **1c**. Whereas the relationship between neutral Pt(II) and cationic Au(III) complexes has been recognized for decades,[14] to the best of our knowledge no comparative structural and E−H bond activation study involving neutral Pt(II) and zwitterionic Au(III) species supported by isosteric ancillary ligands has been reported.[15] Herein we present preliminary results of such a comparison involving the neutral complex [**1b**]PtMe$_2$ (**2b**) and the related zwitterion [**1c**]AuMe$_2$ (**3**). Also described are our efforts to assess the catalytic utility of these complexes, as well as newly prepared mono- and dinuclear Pt(II) cations ligated by **1b**, for the addition of triethylsilane to styrene.

Scheme 1. Synthesis of the Pt(II) Complex 2b and the Au(III) Zwitterion 3[a]



[a] Reagents: (i) 0.5 [(μ-SMe$_2$)PtMe$_2$]$_2$, then ^{i}PrOH, 22 °C; (ii) n-BuLi, then 0.5 [Me$_2$AuCl]$_2$.

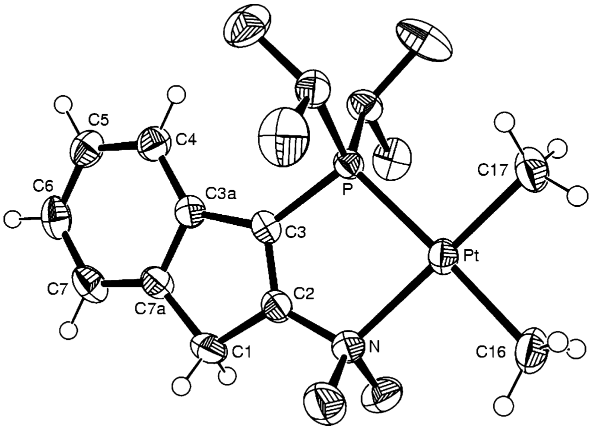


Figure 1. ORTEP diagram for **2b** shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **2b**: Pt−P 2.2474(9); Pt−N 2.228(3); Pt−C16 2.095(4); Pt−C17 2.043(4); P−C3 1.814(4); N−C2 1.450(4); C1−C2 1.510(5); C2−C3 1.341(5); C1−C7A 1.496(5); C3−C3A 1.478(5); C3A−C4 1.397(5); C3A−C7A 1.404(5); C4−C5 1.379(5); C5−C6 1.381(6); C6−C7 1.377(6); C7−C7A 1.383(5).

Results and Discussion

Structural and Reactivity Comparisons of [1b]PtMe$_2$ (2b) and [1c]AuMe$_2$ (3). As described previously,[6a] treatment of **1a** with 0.5 [(μ-SMe$_2$)PtMe$_2$]$_2$ affords [**1a**]PtMe$_2$ (**2a**), which can be cleanly converted to [**1b**]PtMe$_2$ (**2b**) by stirring in a solution of 2-propanol in THF (Scheme 1). In the pursuit of an analogous Au(III) species, **1a** was lithiated followed by the addition of 0.5 [Me$_2$AuCl]$_2$; after workup, [**1c**]AuMe$_2$ (**3**) was isolated as an analytically pure bright yellow solid in 41% yield. We have previously reported the spectroscopic characterization of **2b**,[6a] and herein we report single-crystal X-ray diffraction data for this compound (Figure 1; Table 1). Both spectroscopic and crystallographic data for **3** (Figure 2) support the structural formulation proposed for this formally zwitterionic complex. Collectively, these structural data confirm the geometric relationship between **2b** and **3**, in which the Pt and Au metals each adopt a square-planar geometry and are ligated by a chelating P,N-ligand as well as *cis*-methyl ligands. The overall features

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(9) Selected examples: (a) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674. (b) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863. (c) Bianchini, C.; Burnaby, D. G.; Evans, J.; Frediani, P.; Meli, A.; Oberhauser, W.; Psaro, R.; Sordelli, L.; Vizza, F. *J. Am. Chem. Soc.* **1999**, *121*, 5961. (d) Van den Hoven, B. G.; Alper, H. *J. Am. Chem. Soc.* **2001**, *123*, 10214. (e) Dorta, R.; Shimon, L.; Milstein, D. *J. Organomet. Chem.* **2004**, *689*, 751.

(10) Catalytically active Cu complexes featuring chiral, boron-bridged bisoxazoline ligands have recently been developed: Mazet, C.; Köhler, V.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4888.

(11) For a recent, conceptually related study of tris(pyrazolyl)methane and tris(pyrazolyl)borate complexes of Ir, see: Padilla-Martínez, I. I.; Poveda, M. L.; Carmona, E.; Monge, M. A.; Ruiz-Valero, C. *Organometallics* **2002**, *21*, 93.

(12) For a discussion regarding the way in which net charge on platinum-group metal complexes influences their catalytic behavior, see: Hahn, C. *Chem. Eur. J.* **2004**, *10*, 5888.

(13) The study of neutral group 3 complexes has provided considerable insight into the reactivity properties of structurally related cationic group 4 species. For example, see: Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74.

(14) For early examples and a review, see: (a) Shiotani, A.; Schmidbaur, H. *Chem. Ber.* **1971**, *104*, 2838. (b) Kuch, P. L.; Tobias, R. S. *J. Organomet. Chem.* **1976**, *122*, 429. (c) Puddephatt, R. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Toronto, 1982; Vol. 2, Chapter 15.

(15) Formally zwitterionic Au(I) and Au(III) complexes featuring a positive charge on Au have been reported, for example: (a) Usón, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 839. (b) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Olmos, E. *Organometallics* **1997**, *16*, 1130. (c) McWhannell, M. A.; Rosair, G. M.; Welch, A. J.; Teixidor, F.; Viñas, C. *J. Organomet. Chem.* **1999**, *573*, 165. (d) Ronig, B.; Schulze, H.; Pantenburg, I.; Wesemann, L. *Eur. J. Inorg. Chem.* **2005**, 314.

Table 1. Crystallographic Data for 2b, 3, [8]$^+$BF$_4$$^-$, and [9]$^+BF_4$$^-$

	2b	**3**	[**8**]$^+$BF$_4$$^-$	[**9**]$^+$BF$_4$$^-$
empirical formula	$C_{19}H_{32}NPPt$	$C_{19}H_{31}AuNP$	$C_{36}H_{58}BClF_4N_2P_2Pt_2$	$C_{20}H_{35}BF_4NPPtS$
fw	500.52	501.38	1093.22	634.42
cryst dimens	0.35 × 0.17 × 0.16	0.47 × 0.24 × 0.05	0.36 × 0.22 × 0.10	0.52 × 0.30 × 0.08
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	*Pbca* (No. 61)	*Pbca* (No. 61)	$P2_1/n$
a (Å)	13.3126 (11)	13.2290 (8)	17.2031 (9)	9.4505 (6)
b (Å)	16.7227 (14)	15.9825 (10)	14.2970 (7)	18.1064 (11)
c (Å)	18.1608 (15)	18.6367 (12)	32.2154 (16)	14.4908 (9)
α (deg)	90	90	90	90
β (deg)	90	90	90	92.3590 (10)
γ (deg)	90	90	90	90
V (Å^3)	4043.0 (6)	3940.4 (4)	7923.5 (7)	2477.5 (3)
Z	8	8	8	4
ρ_{calcd} (g cm^{-3})	1.645	1.690	1.833	1.701
μ (mm^{-1})	7.018	7.546	7.249	5.849
2θ limit (deg)	52.82	52.78	52.80	52.82
	$-16 \leq h \leq 16$	$-16 \leq h \leq 16$	$-21 \leq h \leq 21$	$-11 \leq h \leq 11$
	$-20 \leq k \leq 20$	$-19 \leq k \leq 18$	$-17 \leq k \leq 17$	$-22 \leq k \leq 22$
	$-22 \leq l \leq 22$	$-23 \leq l \leq 23$	$-40 \leq l \leq 40$	$-18 \leq l \leq 18$
total data collected	28 838	25 994	50 983	18 843
indep reflns	4144	4030	8107	5075
R_{int}	0.0409	0.0378	0.0511	0.0364
no. of obsd reflns	3349	3313	7032	4572
abs corr	multiscan (SADABS)	multiscan (SADABS)	multiscan (SADABS)	multiscan (SADABS)
range of transmn	0.3997−0.1926	0.7041−0.1256	0.5309−0.1800	0.6519−0.1509
no. of data/restraints/params	4144/0/201	4030/0/201	8107/0/432	5075/0/263
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0257	0.0219	0.0492	0.0211
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0650	0.0585	0.1198	0.0542
goodness-of-fit	1.060	1.016	1.298	1.068
largest peak, hole (e Å^{-3})	1.724, −0.646	1.266, −0.829	2.541, −1.555	0.838, −0.764

in **2b** mirror those observed in other κ^2-[*P*,*N*]PtMe$_2$ complexes,[5b,e] with the Pt−Me distance *trans* to P being significantly longer than the Pt−Me distance *trans* to N; a similar situation exists for the Au−Me distances in **3**.[16] While a trend toward localized C−C and C═C bonds is observed within the indene backbone of **2b**, the carbocyclic framework in **3** exhibits a more delocalized structure consistent with a 10 π-electron indenide fragment, as is found in the related crystallographically characterized zwitterions [**1c**]Rh(COD),[8a] [**1c**]Ir(COD),[8b] and [**1c**]-Ru(MeCN)(η^5-C$_5$Me$_5$) (COD = η^4-1,5-cyclooctadiene).[8d] However, as with these platinum-group metal complexes of **1c**, the contracted P−C3 and C1−C2 distances in the formally zwitterionic **3** (1.749(3) and 1.374(4) Å), when compared with those in **2b** (1.814(4) and 1.510(5) Å), point to the existence of a less-conventional resonance contributor in **3** featuring a P═C3 bond that places the anionic formal charge on phosphorus.[17] As well, the Au−P distance in **3** is comparable to those found in other structurally related Au(III) complexes,[15b] and the observation of identical M−N distances (**2b**, 2.228(3); **3**, 2.195(3) Å) but significantly different M−P distances (**2b**, 2.2474(9); **3**, 2.3523(8) Å) in **2b** and **3** is a trend that has been noted in isostructural cation/zwitterion pairs of Rh or Ir supported by **1b** and **1c**, respectively.[8a,b]

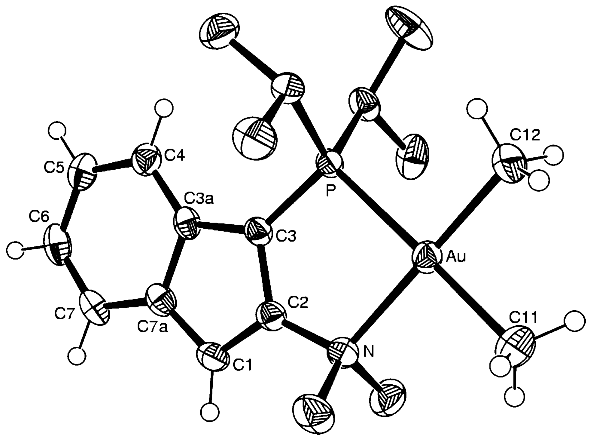

Figure 2. ORTEP diagram for **3** shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for **3**: Au−P 2.3523(8); Au−N 2.195(3); Au−C11 2.071(4); Au−C12 2.045(3); P−C3 1.749(3); N−C2 1.474(4); C1−C2 1.374(4); C2−C3 1.422(4); C1−C7A 1.422(5); C3−C3A 1.441(4); C3A−C4 1.400(5); C3A−C7A 1.437(4); C4−C5 1.383(4); C5−C6 1.396(5); C6−C7 1.368(5); C7−C7A 1.416(4).

We have reported that heating solutions of **2a** (70 °C) results in conversion to **2b** and ultimately generates a mixture of phosphorus-containing products.[6a] In contrast, **3** exhibits remarkable thermal stability; toluene solutions of **3** can be kept at 110 °C for 24 h with negligible decomposition to Au(0) or other phosphorus-containing products (^{31}P NMR). The stability of **3** contrasts with that of [**1c**]Ru(MeCN)(η^5-C$_5$Me$_5$), which upon dissolution in benzene at 22 °C is rapidly transformed by way of double geminal C−H bond activation into a new complex featuring a Cp*Ru(H) fragment supported by a modified form of **1b**, whereby the NMe$_2$ unit has been transformed into a nitrogen-stabilized carbene donor group to give a κ^2-*P*,*C* complex.[8d] Some notable differences in reactivity were also noted upon exposure of either **2b** or **3** to a stoichiometric equivalent (except where noted) of various E−H containing substrates in C$_6$D$_6$ (48 h, 50 °C). No observable reaction (^{1}H and ^{31}P NMR) was noted for either complex upon treatment with H$_2$ (1 atm) or pinacolborane. While **2b** was observed to react to some extent with each of H$_2$O (ca. 350 equiv in THF), Ph$_3$SiH, and PhSiH$_3$ to give a mixture of products including in some cases free **1a** and **1b**, complex **3** proved unreactive under these reaction conditions. The stability

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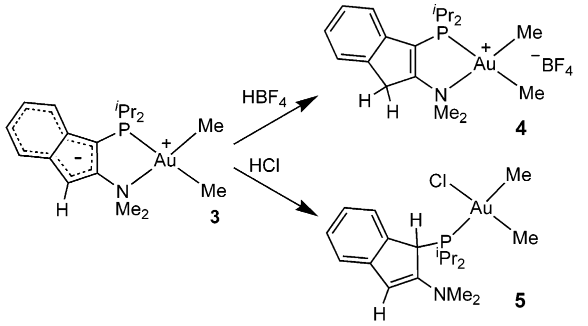
(16) Although a crystallographically characterized [κ^2-(*P*,*N*)AuMe$_2$]$^+$ complex has been reported, the disordered nature of the structure precludes a detailed structural comparison with **3**: Assmann, B.; Angermaier, K.; Paul, M.; Riede, J.; Schmidbaur, H. *Chem. Ber.* **1995**, *128*, 891.

(17) For the stabilization of α-carbanions by phosphorus, see: Izod, K. *Coord. Chem. Rev.* **2002**, *227*, 153.

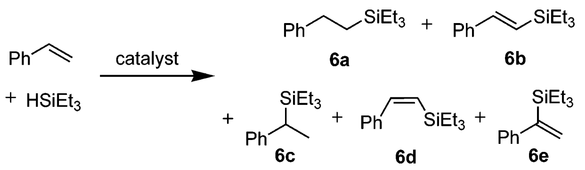
Scheme 2. Reactivity of the Au(III) Zwitterion 3 with Brønsted Acids



to hydrolysis of the indenide unit in **3** is remarkable (>48 h, 110 °C), especially when compared with the highly moisture-sensitive nature of [**1c**]Li.[18]

The reactivity differences observed for the structurally analogous complexes **2b** and **3** warrant further commentary. Complex **2b** can be viewed as reacting either directly with an E−H containing substrate by way of oxidative addition to give a Pt(IV) species or by way of reductive elimination of ethane followed by oxidative addition of E−H to "[**1b**]Pt".[19] In the case of **3** direct oxidative addition would yield an unreasonable Au(V) addition product; as such, reductive elimination of ethane may be seen as a prerequisite for E−H additions to **3**. Given that reductive elimination of ethane from *cis*-$[L_2AuMe_2]^+$ complexes is greatly inhibited upon addition of excess L, it has been suggested that dissociation of L is the initial step in the reductive elimination process.[14c] As such, the lack of reactivity observed for **3** may be attributed to the bidentate and anionic nature of the ancillary ligand **1c**, which coordinates strongly to the $AuMe_2^+$ fragment, thereby preventing access to the three-coordinate $LAuMe_2$ intermediate required for reductive elimination. By comparison, similar dissociation of a ligand arm in **2b** to yield an $LPtMe_2$ species is anticipated to be much easier than in **3**, owing to the diminished electrostatic forces between the neutral ligand (**1b**) and the neutral $PtMe_2$ fragment. Given that dialkylgold(III) complexes are generally inert to protonolysis,[14c] and in an effort to explore further the stability of the indenide unit in **3** to electrophilic attack, this complex was treated separately with HBF_4 and HCl at 22 °C (Scheme 2). In the case of HBF_4, clean conversion to the cationic complex $[(\mathbf{1b})AuMe_2]^+BF_4^-$ (**4**) was observed after 0.5 h,[20] while addition of anhydrous HCl yielded the κ^1-*P*,N species, **5**, which was isolated as an analytically pure white solid in 82% yield.

Metal-Mediated Addition of Triethylsilane to Styrene. The addition of triethylsilane to styrene was examined in a preliminary effort to compare the catalytic abilities of **2b** and **3** in E−H addition reactions; the predominant silicon-containing products of this reaction are given in eq 1.[21] While the activity of Pt-based catalysts in alkene hydrosilylation is well-established, such reactions are rarely regioselective (giving **6a** and **6c**) and are commonly accompanied by side-reactions including dehydrogenative silylation (giving **6b**, **6d**, and **6e**).[21,22] In light of the selectivity that has been observed in stoichiometric reactions of κ^2-[*P*,*N*]Pt(II) complexes with silanes,[5] we became interested in examining if similar selectivity benefits could be derived from employing **2b** and related Pt-complexes as catalysts for alkene hydrosilylation. To the best of our knowledge, the use of P,N-ligands in tuning Pt-mediated hydrosilylation has not been examined thoroughly. The vinylsilanes **6b**, **6d**, and **6e** in eq 1 are presumed to arise by way of the modified Chalk−Harrod mechanism, which involves alkene 1,2-insertion into the M−Si bond in an intermediate of the type $L_nM(H)(SiR_3)(alkene)$, followed by β-hydrogen elimination.[23] Gold complexes do not normally undergo β-hydrogen elimination,[14c] and as such, the use of **3** as a catalyst for this reaction was explored as a means of increasing the selectivity for **6a** and/or **6c** in eq 1. While the utilization of Au-based complexes as homogeneous catalysts for E−H additions to alkenes is gaining attention,[24,25] the ability of such complexes to mediate the addition of Si−H bonds to alkenes has not yet been demonstrated.



(1)

While negligible conversion was achieved by use of 5 mol % **2b** as catalyst at 22 °C over 24 h, at 50 °C modest turnover was noted; 26% conversion was obtained using an equimolar substrate ratio (Table 2; entry 1), whereas 43% conversion was achieved by employing 3 equiv of styrene (entry 2). Evidently, no selectivity advantages are brought about by the incorporation of the P,N-ligand in **2b**, as the observed product distributions mirror those obtained when employing a range of other Pt-based catalyst complexes.[21,22] Catalytic reactions employing 5.0 mol % $CODPtMe_2$ provided further evidence that the ancillary ligand **1b** serves to attenuate rather than enhance the activity of Pt-

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[18] Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185.

[19] While oxidative addition/reductive elimination reaction cycles are likely the most appropriate mechanistic descriptors for reactions involving the addition of E−H bonds to relatively low oxidation state late metal complexes, alternative reaction mechanisms featuring σ-bond metathesis steps and not involving formal oxidation state changes can also be envisaged.

[20] Although **4** is cleanly generated in-situ upon treatment of **3** with HBF_4, we have yet to isolate **4** in analytically pure form; we are currently exploring alternative synthetic routes to **4**. NMR Data for **4**: ^1H NMR ($CDCl_3$): δ 7.56 (m, 1H, aryl-CH), 7.42−7.33 (m, 3H, aryl-CH's), 3.98 (s, 2H, CH_2), 3.18 (s, 6H, $N(CH_3)_2$), 3.09 (m, 2H, $P(CHCH_3CH_3)_2$), 1.52 (d, $^3J_{PH} = 7.0$ Hz, 3H, Au-CH_3 *trans* to P), 1.41 (dd, $^3J_{PH} = 19.0$ Hz, $^3J_{HH} = 7.0$ Hz, 6H, $P(CHCH_3CH_3)_2$), 1.32 (dd, $^3J_{PH} = 17.5$ Hz, $^3J_{HH} = 7.0$ Hz, 6H, $P(CHCH_3CH_3)_2$), 1.08 (d, $^3J_{PH} = 7.5$ Hz, 3H, Au-CH_3 *trans* to N). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 178.0 (d, $^2J_{PC} = 16$ Hz, C2), 143.8 (d, $J_{PC} = 6$ Hz, C7a or C3a), 136.5 (s, C3a or C7a), 127.8 (s, aryl-CH), 127.5 (s, aryl-CH), 126.5 (s, aryl-CH), 122.0 (s, aryl-CH), 50.7 (s, $N(CH_3)_2$), 33.1 (d, $^3J_{PC} = 9$ Hz, CH_2), 27.6 (d, $^2J_{PC} = 100$ Hz, Au-CH_3 *trans* to P), 24.4 (d, $^1J_{PC} = 26$ Hz, $P(CHCH_3CH_3)_2$), 19.6 (s, $P(CHCH_3CH_3)_2$), 18.7 (d, $^2J_{PC} = 3$ Hz, $P(CHCH_3CH_3)_2$), 1.8 (d, $^2J_{PC} = 5$ Hz, Au-CH_3 *trans* to N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.6 (s).

[21] (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds, Part 2*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Toronto, 1989; Chapter 24. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds, Part 2*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Toronto, 1989; Chapter 25. (c) Brook, M. A. In *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley & Sons: Toronto, 2000.

[22] For selected examples of alkene hydrosilylation mediated by neutral Pt complexes, see: (a) Albinati, A.; Caseri, W. R.; Pregosin, P. S. *Organometallics* **1987**, *6*, 788. (b) Markó, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P. *Science* **2002**, *298*, 204. (c) Sprengers, J. W.; de Greef, M.; Duin, M. A.; Elsevier, C. J. *Eur. J. Inorg. Chem.* **2003**, 3811. (d) Sprengers, J. W.; Agerbeek, M. J.; Elsevier, C. J.; Kooijman, H.; Spek, A. L. *Organometallics* **2004**, *23*, 3117, and references therein.

[23] For recent discussions, see: (a) Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510, and references therein. (b) Sakaki, S.; Sumimoto, M.; Fukuhara, M.; Sugimoto, M.; Fujimoto, H.; Matsuzaki, S. *Organometallics* **2002**, *21*, 3788.

[24] (a) Dyker, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4237. (b) Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387.

[25] Selected examples: (a) Ito, H.; Yajima, T.; Tateiwa, J.; Hosomi, A. *Chem. Commun.* **2000**, 981. (b) Yao, X.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 6884. (c) González-Arellano, C.; Corma, A.; Iglesias, M.; Sánchez, F. *Chem. Commun.* **2005**, 3451.

Table 2. Addition of Triethylsilane to Styrene[a]

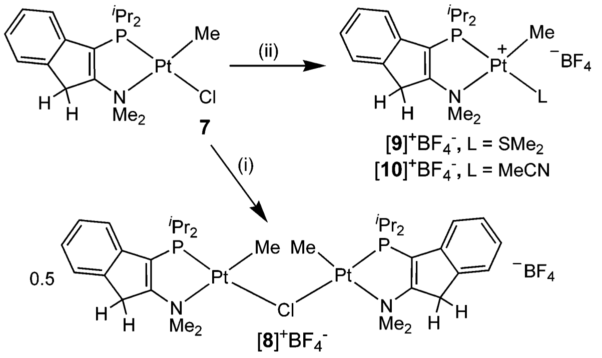
entry	catalyst	styrene: Et_3SiH	yield [%][b]	**6a**[c]	**6b**[c]	**6c**[c]	other[c]
1	**2b**	1:1	26	10	8	5	3
2	**2b**	3:1	43	25	12	3	3
3[d]	$CODPtMe_2$	1:1	88	74	11	1	2
4[d]	$CODPtMe_2$	3:1	>99	66	32	<1	2
5	**7**	1:1	47	37	8	<1	2
6[e]	**7**	1:1	33	20	8	2	3
7	CODPtClMe	1:1	89	66	18	<1	5
8	**7** + 1 $AgBF_4$	1:1	16	9	5	1	<1
9[e]	**7** + 1 $AgBF_4$	1:1	43	15	20	3	5
10	CODPtClMe + 1 $AgBF_4$	1:1	78	59	14	<1	5
11	**7** + 1 AgOTf	1:1	26	14	5	7	<1
12[f]	[**8**]$^+BF_4^-$	1:1	7	3	4	<1	<1

[a] Reactions run for 24 h employing 5 mol % catalyst at 50 °C in C_6H_6, except where noted (COD = η^4-1,5-cyclooctadiene). [b] Based on consumption of triethylsilane. [c] Product distribution based on GC-MS and GC-FID data, rounded to the nearest percent; other silicon-containing products include **6d** and **6e**. [d] Experiment conducted at 22 °C. [e] Experiment conducted in THF. [f] 5 mol % catalyst was used, which effectively provides 10 mol % Pt.

mediated hydrosilylations (entries 3 and 4). As well, in the case of hydrosilylation experiments employing 5 mol % **3** as catalyst and 3 equiv of styrene, no conversion was noted at 22, 50, or 70 °C over a 24 h period.

Encouraged by the work of Widenhoefer and co-workers, who have employed κ^2-[*N*,*N*]$PtMe_2$ complexes activated by $B(C_6F_5)_3$ as catalysts for the cyclization/hydrosilylation of functionalized diynes using triethylsilane,[26] and in light of the observation that hydrosilylation catalysis is enhanced by the opening of a coordination site at Pt,[22] efforts were made to improve the catalytic performance of **2b** and **3** by employing $B(C_6F_5)_3$ as a methide-abstracting agent. A reaction between **2b** and $B(C_6F_5)_3$ in a 1:1 toluene/THF mixture was observed, with the consumption of the starting Pt complex (δ ^{31}P = 39.2, $^1J_{PtP}$ = 2039 Hz) noted after 20 min, along with the formation of two new phosphorus-containing products (δ ^{31}P = 29.8, $^1J_{PtP}$ = 4924 Hz, *major*; δ ^{31}P = 36.3, $^1J_{PtP}$ = 2873 Hz, *minor*); at this stage, two ^{11}B NMR signals were observed at 7.0 and −14.1 ppm. The Au(III) complex **3** (δ ^{31}P = 46.3) was also quantitatively consumed upon addition of an equivalent of borane, exhibiting two ^{31}P NMR resonances (50.2 and 43.0 ppm) as well as two ^{11}B NMR signals (0.0 and −14.3 ppm). The hydrosilylation of styrene with equimolar triethylsilane (22 °C) was subsequently attempted in a 1:1 toluene/THF mixture, employing 10 mol % of **2a** or **3** pretreated with an equivalent of the borane activator. However, after 1 h greater than 80% conversion to *n*-$BuOSiEt_3$ (derived from ring-opening of THF) was observed, in the absence of alkene addition products. In contrast to the aforementioned cyclization/hydrosilylation process examined by Widenhoefer and co-workers, which is not mediated by κ^2-[*N*,*N*]-$PtMe_2$ complexes or $B(C_6F_5)_3$ alone,[26] control experiments revealed that the formation of *n*-$BuOSiEt_3$ described herein can be attributed entirely to the borane.[27] As well, negligible metal-mediated catalysis was observed for analogous reactions conducted in toluene, CH_2Cl_2, or MeCN.

Scheme 3. Synthesis of Cationic Pt(II) Complexes[a]



[a] Reagents: (i) 0.5 $AgBF_4$ in toluene; (ii) $AgBF_4$ in THF, then SMe_2 (for [**9**]$^+BF_4^-$) or MeCN (for [**10**]$^+BF_4^-$).

In an alternative approach to the generation of a potentially reactive [(**1b**)PtMe]$^+$ fragment in situ, the catalytic abilities of [**1b**]PtClMe (**7**), as well as products derived from in situ chloride abstraction, were evaluated. While **7** proved to be a more effective alkene hydrosilylation catalyst than **2b** in benzene (entries 1 and 5), CODPtClMe outperformed both of these catalyst complexes under analogous conditions (entry 7), in keeping with the aforementioned L_2PtMe_2 system (vide supra). Treatment of **7** with an equivalent of either AgOTf (entry 11) or $AgBF_4$ (entry 8) in benzene gave rise to a progressively poorer catalyst system versus **7**, while a less pronounced reduction in activity was noted upon treatment of CODPtClMe with $AgBF_4$ in benzene (entry 10).[28] Conversely, the **7**/$AgBF_4$ catalyst system performed somewhat better than **7** in THF (entries 6 and 9). The decrease in activity observed when AgX was employed as an activator prompted us to investigate the nature of the species formed under these reaction conditions.

Rational Preparation of Mono- and Dinuclear κ^2-[*P*,*N*]-Pt(II) Cations. In an effort to characterize cationic Pt(II) species derived from **7** that may have been generated in the course of the previously described catalytic experiments, the rational synthesis of new cationic Pt(II) complexes ligated by **1b** was undertaken (Scheme 3). Treatment of **7** with either 0.5 or 1.0 equiv of $AgBF_4$ in benzene or toluene produced a precipitate; although **7** was the only phosphorus-containing complex detected in the resulting supernatant, extraction of this precipitate with CH_2Cl_2 afforded [**8**]$^+BF_4^-$ as an analytically pure off-white powder in 61% isolated yield. The formation of [**8**]$^+BF_4^-$ can be viewed as arising from the trapping of [(**1b**)PtMe(solv)]$^+BF_4^-$ species by **7**. To investigate the strength of the chloride bridge, an equivalent of MeCN was added to a solution of [**8**]$^+BF_4^-$ in THF, which resulted in the clean formation of a 1:1 mixture of **7** and the monomeric cation [**10**]$^+BF_4^-$ (vide infra). The crystal structure of [**8**]$^+BF_4^-$ is presented in Figure 3 and features two corner-sharing square-planar Pt(II) moieties that are offset by 73.4(1)°. Whereas the Pt−N and Pt−Me distances in [**8**]$^+BF_4^-$ are indistinguishable from those found in **2b**, the Pt−P distances in the dinuclear complex are shortened significantly, in keeping with the presence of a chloride ligand (in [**8**]$^+BF_4^-$) versus a methyl ligand (in **2b**) *trans* to phosphorus. The interatomic Pt···Pt distance (>4.0 Å) precludes any metal−metal bonding interactions in [**8**]$^+BF_4^-$, and the structural features of this cation mirror those found in a related [{κ^2-(*P*,*N*)PtMe}$_2$Cl]$^+$ complex reported by Braunstein and co-workers.[6c] Notably, dinuclear cations of this type featuring two Pt fragments bridged only by a single chloride are uncommon.[29] Alternatively, treatment of

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[26] (a) Madine, J. W.; Wang, X.; Widenhoefer, R. A. *Org. Lett.* **2001**, *3*, 385. (b) Madine, J. W.; Wang, X.; Widenhoefer, R. A. *Org. Lett.* **2001**, *3*, 1591. (c) Wang, X.; Chakrapani, H.; Madine, J. W.; Keyerleber, M. A.; Widenhoefer, R. A. *J. Org. Chem.* **2002**, *67*, 2778.

[27] Such reactivity mediated by $B(C_6F_5)_3$ has precedent in the literature: (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. (c) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247. (d) Chivers, T.; Shatte, G. *Eur. J. Inorg. Chem.* **2003**, 3314.

[28] $AgBF_4$ and AgOTf are inactive for the hydrosilylation of styrene with triethylsilane under the conditions reported herein.

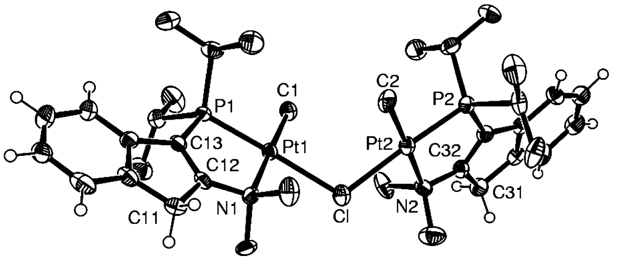

Figure 3. ORTEP diagram for $[\mathbf{8}]^+BF_4^-$ shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms and the tetrafluoroborate counteranion have been omitted for clarity. Selected bond lengths (Å) for $[\mathbf{8}]^+BF_4^-$: Pt1−P1 2.182(2); Pt1−N1 2.192(7); Pt2−P2 2.177(2); Pt2−N2 2.218(8); Pt1−Cl 2.421(2); Pt2−C1 2.399(2); Pt1−C1(Me) 2.049(9); Pt2−C2(Me) 2.043(9); P1−C13 1.807(9); P2−C33 1.811(9); N1−C12 1.47(1); N2−C32 1.44(1); C11−C12 1.51(1); C12−C13 1.33(1); C31−C32 1.51(1); C32−C33 1.35(1).

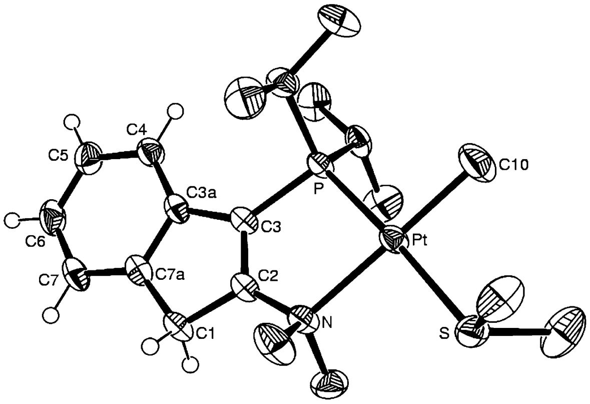

Figure 4. ORTEP diagram for $[\mathbf{9}]^+BF_4^-$ shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms and the tetrafluoroborate counteranion have been omitted for clarity. Selected bond lengths (Å) for $[\mathbf{9}]^+BF_4^-$: Pt−P 2.2283(7); Pt−N 2.213(2); Pt−S 2.3611(8); Pt−C10 2.037(4); P−C3 1.807(3); N−C2 1.444(4); C1−C2 1.513(4); C2−C3 1.342(4).

7 with an equivalent of $AgBF_4$ in THF,[30] followed by the addition of L, yields the corresponding monomeric cation, $[(\mathbf{1b})PtMeL]^+BF_4^-$ (L = SMe_2, $[\mathbf{9}]^+BF_4^-$, 77%; L = MeCN, $[\mathbf{10}]^+BF_4^-$, 84%), as an analytically pure white powder. Spectroscopic and elemental analysis data are consistent with the structural formulations provided for these cations, and in the case of $[\mathbf{9}]^+BF_4^-$ the structure was confirmed by use of X-ray diffraction techniques (Figure 4). While the Pt−P, Pt−N, and Pt−Me distances in $[\mathbf{9}]^+BF_4^-$ are consistent with those observed in **2b** and $[\mathbf{8}]^+BF_4^-$, the Pt−S distance (*trans* to phosphorus) is significantly longer than those found in some structurally related $[\kappa^2\text{-}(N,N)PtMe(SMe_2)]^+$ complexes.[31]

These synthetic studies provided some insight regarding the catalytic behavior of cationic Pt species supported by **1b**. Given the poor catalytic performance exhibited by purified $[\mathbf{8}]^+BF_4^-$, which contains 2 mol of Pt per molecule of catalyst (entry 12), it seems plausible that the modest catalytic conversion observed upon treatment of **7** with $AgBF_4$ in benzene (entry 8) can be attributed to residual **7** (entry 5). The activity of CODPtClMe is only slightly diminished upon exposure to $AgBF_4$ in benzene; it is conceivable that a related $[(CODPtMe)_2Cl]^+$ complex, if formed, is either significantly more active than $[\mathbf{8}]^+BF_4^-$ or more prone to dissociation to give catalytically active CODPtClMe and/or $[CODPtMe(solv)]^+$ species. Conversely, in THF, $[\mathbf{8}]^+BF_4^-$ is not formed upon addition of $AgBF_4$ to **7**. Instead, **7** is quantitatively converted to a new phosphorus-containing complex, which may correspond to $[(\mathbf{1b})PtMe(THF)]^+BF_4^-$.[30] In this context, the modestly increased catalytic conversion observed upon treatment of **7** with $AgBF_4$ in THF (entry 9) may reflect the heightened activity of this proposed cationic intermediate, relative to **7**. As well, **7** and AgOTf react cleanly in benzene to give a single phosphorus-containing product (δ ^{31}P = 28.6, $^1J_{PtP}$ = 5276 Hz) without the formation of $[\mathbf{8}]^+BF_4$. It is viable that salt metathesis in this case produces the inner-sphere $[\mathbf{1b}]$PtMeOTf complex (entry 11), thereby circumventing the formation of the related dimer, $[\mathbf{8}]^+OTf^-$.

Summary and Conclusions

Notwithstanding the structural relationship between $[\mathbf{1b}]PtMe_2$ (**2b**) and $[\mathbf{1c}]AuMe_2$ (**3**), the reactivity properties of these species differ considerably; for example, while **2b** has been shown to react in a stoichiometric and catalytic fashion with silanes, no such reactivity was noted for **3** under similar conditions. It is likely that these observations can be attributed in part to differences both in the metal formal oxidation state (Pt(II) versus Au(III)) and in the charge of the ancillary bidentate ligand (neutral in **2b** versus anionic in **3**). In addition, catalytic studies employing **2b** and related Pt(II) cations supported by **1b** revealed that no selectivity advantages for the Pt-mediated addition of triethylsilane to styrene are brought about by the incorporation of this bidentate ligand, despite the established precedent of P,N-ligands in providing heightened selectivity in myriad transformations mediated by platinum-group metal complexes.[2] In the course of this catalytic survey it was discovered that the identity of the Pt(II) species formed in situ upon treatment of $[\mathbf{1b}]$PtClMe (**7**) with AgX (X = BF_4 or OTf) is dictated by the solvent employed, as well as the nature of X. In benzene, **7** and $AgBF_4$ combine to give $[\mathbf{8}]^+BF_4^-$, while in THF $[(\mathbf{1b})PtMe(THF)]^+BF_4^-$ is presumably formed, which can be converted to $[\mathbf{9}]^+BF_4^-$ or $[\mathbf{10}]^+BF_4^-$ upon treatment with SMe_2 or MeCN. These latter findings underscore the problems that can arise when attempting to develop thorough structure−reactivity relationships based on the investigation of reactive metal species formed in situ. We are currently in the process of comparing the structural and reactivity properties of other related complexes of neighboring metals ligated by **1b** and **1c** and will report on these studies in due course.

Experimental Section

General Considerations. Except where noted, 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. 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

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(29) For related crystallographically characterized Pt_2Cl^+ complexes, see: (a) Dahlenburg, L.; Mertel, S. *J. Organomet. Chem.* **2001**, *630*, 221. (b) Barr, C. R.; Jenkins, H. A.; Jennings, M. C.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 4870. (c) Albano, V. G.; Di Serio, M.; Monari, M.; Orabona, I.; Panunzi, A.; Ruffo, F. *Inorg. Chem.* **2002**, *41*, 2672. (d) Ref 6c.

(30) Although the putative $[(\mathbf{1b})PtMe(THF)]^+BF_4^-$ intermediate is formed quantitatively (^{31}P NMR) upon treatment of **7** with $AgBF_4$ in THF (δ ^{31}P = 29.9, $^1J_{PtP}$ = 4893 Hz in THF), all attempts to isolate this complex were unsuccessful.

(31) Song, D.; Wang, S. *Organometallics* **2003**, *22*, 2187.

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 acetonitrile was achieved by refluxing over CaH_2 for 4 days under dinitrogen, followed by distillation. The solvents used within the glovebox were stored over activated 4 Å molecular sieves. The deuterated solvents C_6D_6 (Aldrich), CD_2Cl_2 (Cambridge Isotope Laboratories), THF-d_8 (CIL), and CD_3CN (CIL), as well as styrene (containing 10−15 ppm 4-*tert*-butylcatechol as inhibitor) and Et_3SiH, were degassed by using three repeated freeze−pump−thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. $AgBF_4$ and AgOTf were dried in vacuo for a minimum of 48 h prior to use. Compounds [**1c**]Li,[8a] **2b**,[6a] **7**,[6a] $(Me_2AuCl)_2$,[32] CODPtClMe,[33] and $CODPtMe_2$[33] were prepared employing reported methods. With the exception of dihydrogen (99.999%, Air Liquide-UHP Grade) and $B(C_6F_5)_3$ (Boulder Scientific), all chemicals were obtained from Aldrich and were used as received. All ^1H, ^{13}C, ^{31}P, and ^{11}B NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 202.5, and 160.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^1H and ^{13}C), 85% H_3PO_4 in D_2O (for ^{31}P), or BF_3 in diethyl ether (for ^{11}B). In some cases, slightly fewer than expected independent ^1H or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^1H and ^{13}C NMR chemical shift assignments are based on data obtained from $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMBC, and DEPT NMR experiments. GC-MS and GC-FID were performed on a Perkin-Elmer AutoSystem XL gas chromatograph equipped with a TurboMass mass spectrometer. GC-MS analyses were performed using a Supelco 30 m × 0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm, temperature programmed: 60 °C, 1 min; 20 °C/min to 200 °C; 200 °C, 7 min. GC-FID analyses were done in a similar way except on a Supelco DB200 column. Melting points were obtained on an electrothermal apparatus using samples sealed in capillaries under dinitrogen. Elemental analyses for all compounds were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada, with the exception of **3**, which was performed by Desert Analytics, Tucson, AZ.

Preparation of 3. To a magnetically stirred suspension of $[Me_2AuCl]_2$ (0.098 g, 0.19 mmol) in 3 mL of toluene was rapidly added a light brown solution of [**1c**]Li (0.11 g, 0.39 mmol) in 3 mL of toluene. The resulting mixture was stirred for 4 h, after which time, toluene and other volatiles were removed in vacuo, yielding a bright yellow solid, interspersed with white powder. To this solid was added pentane (5 mL), and the resulting mixture was filtered through Celite, giving a bright yellow solution. Removal of the pentane in vacuo yielded a bright yellow solid, **3** (0.079 g, 0.16 mmol, 41%). Crystals suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C. Decomposition point: 122 °C (charring; effervescence noted at 143−144 °C). Anal. Calcd for $C_{19}H_{31}N_1P_1Au_1$: C 45.51, H 6.23, N 2.79. Found: C 45.23, H 6.34, N 2.86. ^1H NMR (C_6D_6): δ 7.93 (d, J = 7.5 Hz, 1H, aryl-CH), 7.66 (d, J = 8.0 Hz, 1H, aryl-CH), 7.45−7.25 (m, 2H, aryl-CH's), 6.25 (d, $^4J_{PH}$ = 4.0 Hz, 1H, C1−H), 2.74 (s, 6H, $N(CH_3)_2$), 2.49 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 1.06 (d, $^3J_{PH}$ = 5.5 Hz, 3H, Au−CH$_3$ *trans* to P), 1.01 (dd, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 0.85 (dd, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHCH$_3$C*H*$_3$)$_2$), 0.58 (d, $^3J_{PH}$ = 7.0 Hz, 3H, Au-CH$_3$ *trans* to N). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 162.2 (d, $^2J_{PC}$ = 25 Hz, C2), 139.2 (d, $^2J_{PC}$ = 16 Hz, C3a), 129.3 (s, C7a), 121.8 (s, aryl-CH), 119.5 (s, aryl-CH), 117.7 (s, aryl-CH), 117.5 (s, aryl-CH), 90.7 (d, $^3J_{PC}$ = 12 Hz, C1), 53.7 (s, $N(CH_3)_2$), 26.4 (s, Au-CH$_3$ *trans* to P), 25.4 (d, $^1J_{PC}$ = 33 Hz, P(*C*HCH$_3$CH$_3$)$_2$), 19.5 (s, P(CHCH$_3$*C*H$_3$)$_2$), 18.6 (s, P(CH*C*H$_3$CH$_3$)$_2$), −2.0 (d, $^2J_{PC}$ = 5 Hz, Au-CH$_3$ *trans* to N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 46.3 (s).

Preparation of 5. A solution of **3** (0.050 g, 0.099 mmol) in a mixture of diethyl ether (0.80 mL) and tetrahydrofuran (0.85 mL) was cooled to −35 °C. Magnetic stirring was initiated, and HCl (0.052 mL of a 2.0 M solution in diethyl ether, 0.10 mmol) was added. After 2 h, the solvent and other volatiles were removed in vacuo. The resulting solid was rinsed with pentane (2 × 1.5 mL) to leave a white solid, **5** (0.044 g, 0.082 mmol, 82%). Anal. Calcd for $C_{19}H_{32}N_1P_1Au_1Cl_1$: C 42.43, H 6.00, N 2.60. Found: C 42.67, H 5.92, N 2.41. ^1H NMR (C_6D_6): δ 8.39 (d, J = 7.0 Hz, 1H, aryl-CH), 7.14−7.01 (m, 2H, aryl-CH's), 6.97 (m, 1H, aryl-CH), 5.50 (s, 1H, vinylic-CH), (br s, 1H, allylic-CH), 3.04 (m, 1H, P(C*H*CH$_3$-aCH$_3$b)), 2.22 (s, 6H, $N(CH_3)_2$), 2.16 (m, 1H, P(C*H*CH$_3$cCH$_3$d)), 1.71 (d, $^3J_{PH}$ = 9.0 Hz, 3H, Au-CH$_3$ *trans* to P), 1.38 (dd, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHC*H*$_3$aCH$_3$b)), 0.98 (d, $^3J_{PH}$ = 7.5 Hz, 3H, Au-CH$_3$ *cis* to P), 0.94 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHC*H*$_3$cCH$_3$d), 0.87 (dd, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHCH$_3$aC*H*$_3$b)), 0.41 (dd, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHCH$_3$cC*H*$_3$d)). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.6 (d, $^2J_{PC}$ = 8 Hz, C2), 144.9 (d, J_{PC} = 4 Hz, C7a or C3a), 137.7 (s, C3a or C7a), 125.7 (s, aryl-CH), 122.9 (s, aryl-CH), 119.1 (s, aryl-CH), 109.5 (s, vinylic-CH), 43.0 (s, $N(CH_3)_2$), 41.1 (d, $^1J_{PC}$ = 7 Hz, allylic-CH), 22.1 (d, $^1J_{PC}$ = 18 Hz, P(*C*HCH$_3$cCH$_3$d)), 21.3 (d, $^2J_{PC}$ = 111 Hz, Au-CH$_3$ *trans* to P), 21.2 (d, $^2J_{PC}$ = 4 Hz, P(CH*C*H$_3$aCH$_3$b), 20.7 (d, $^1J_{PC}$ = 17 Hz, P(*C*HCH$_3$aCH$_3$b)), 18.5 (s, P(CH*C*H$_3$cCH$_3$d)), 18.4 (s, P(CHCH$_3$c*C*H$_3$d)), 16.7 (d, $^2J_{PC}$ = 6 Hz, P(CHCH$_3$a*C*H$_3$b), 5.5 (d, $^2J_{PC}$ = 5 Hz, Au-CH$_3$ *cis* to P). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.3 (s).

Preparation of [8]$^+$BF$_4^-$. To a magnetically stirred solution of **7** (0.11 g, 0.21 mmol) in 3 mL of toluene was added a suspension of $AgBF_4$ (0.021 g, 0.11 mmol) in 2 mL of toluene. The reaction was stirred for 5 h, after which time the solution was placed in a −35 °C freezer for 16 h to induce precipitation. The cold solution was filtered through Celite; ^{31}P NMR analysis of the filtrate revealed only the presence of **7**. The filtrate was discarded, and the solid material remaining on the filter was subsequently isolated by passing 3 mL of dichloromethane through the filter and collecting this filtrate. Dichloromethane and other volatiles were removed in vacuo, and the residue was washed with pentane (2 × 3 mL) to yield an off-white powder, [**8**]$^+$BF$_4^-$ (0.070 g, 0.064 mmol, 61%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a solution of [**8**]$^+$BF$_4^-$ in tetrahydrofuran. Decomposition point: 255−257 °C (charring, effervescence). Anal. Calcd for $C_{36}H_{58}N_2P_2Pt_2Cl_1B_1F_4$: C 39.55, H 5.35, N 2.56. Found: C 39.44, H 5.30, N 2.64. ^1H NMR (CD_2Cl_2): δ 7.54 (m, 4H, aryl-CH's), 7.39 (m, 4H, aryl-CH's), 3.68 (s, 4H, CH$_2$), 3.21 (s, 12H, $N(CH_3)_2$), 2.82 (m, 4H, P(C*H*CH$_3$CH$_3$)$_2$), 1.41 (dd, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CHC*H*$_3$CH$_3$)$_2$), 1.32 (dd, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CHCH$_3$C*H*$_3$)$_2$), 1.04 (s, with Pt satellites, $^2J_{PtH}$ = 63.5 Hz, 3H, Pt-CH$_3$ *trans* to N). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 176.9 (d, $^2J_{PC}$ = 11 Hz, C2), 144.1 (d, J_{PC} = 7 Hz, C3a or C7a), 137.3 (s, C7a or C3a), 130.5 (d, $^1J_{PC}$ = 46 Hz, C3), 127.5 (s, aryl-CH), 127.0 (s, aryl-CH), 125.9 (s, aryl-CH), 122.8 (s, aryl-CH), 51.0 (s, $N(CH_3)_2$), 31.3 (d, $^3J_{PC}$ = 9 Hz, CH$_2$), 25.0 (d, $^1J_{PC}$ = 39 Hz, P(*C*HCH$_3$CH$_3$)$_2$), 19.5 (s, with Pt satellites, $^3J_{PtC}$ = 41 Hz, P(CHCH$_3$*C*H$_3$)$_2$), 18.9 (s, P(CH*C*H$_3$CH$_3$)$_2$), −24.5 (d, $^2J_{PC}$ = 7 Hz, Pt satellites not resolved, Pt-CH$_3$ *trans* to N). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.4 (s, with Pt satellites $^1J_{PtP}$ = 4936 Hz).

Preparation of [9]$^+$BF$_4^-$. To a magnetically stirred solution of **7** (0.096 g, 0.18 mmol) in 3 mL of tetrahydrofuran was added solid $AgBF_4$ (0.043 g, 0.22 mmol). The reaction was stirred for 1 h, after which time, dimethyl sulfide (0.14 mL, 1.9 mmol) was added and the solution stirred for an additional 1 h. The solvent and other volatiles were then removed in vacuo, and 5 mL of dichloromethane was added to the solid. Insoluble materials were removed by filtration through a Celite column, from which the filtrate was

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collected, and the dichloromethane and other volatiles were removed in vacuo. This white residue was rinsed with pentane (2 × 3 mL) to yield a white powder, [**9**]$^+\mathrm{BF}_4^-$ (0.090 g, 0.14 mmol, 77%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of pentane into a concentrated solution of [**9**]$^+\mathrm{BF}_4^-$ in dichloromethane. Decomposition point: 137−144 °C (charring). Anal. Calcd for $\mathrm{C_{20}H_{35}N_1P_1S_1Pt_1B_1F_4}$: C 37.86, H 5.56, N 2.21. Found: C 37.90, H 5.57, N 1.93. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.53−7.46 (m, 2H, aryl-CH's), 7.40−7.32 (m, 2H, aryl-CH's), 3.69 (s, 2H, CH$_2$), 3.08 (s, with Pt satellites, $^3J_{\mathrm{PtH}} = 12.0$ Hz, 6H, N(CH$_3$)$_2$), 2.84 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 2.52 (d, $^4J_{\mathrm{PH}} = 3.5$ Hz, with Pt satellites, $^3J_{\mathrm{PtH}} = 36.5$ Hz, 6H, S(CH$_3$)$_2$), 1.37 (dd, $^3J_{\mathrm{PH}} = 18.0$ Hz, $^3J_{\mathrm{HH}} = 7.5$ Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 1.29 (dd, $^3J_{\mathrm{PH}} = 17.5$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, P(CHCH$_3$C*H*$_3$)$_2$), 0.78 (d, $^3J_{\mathrm{PH}} = 2.5$ Hz, with Pt satellites, $^2J_{\mathrm{PtH}} = 71.0$ Hz, 3H, Pt-CH$_3$ *trans* to N). ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 177.6 (d, $^2J_{\mathrm{PC}} = 13$ Hz, C2), 144.4 (d, $J_{\mathrm{PC}} = 7$ Hz, C3a or C7a), 137.2 (s, C7a or C3a), 131.2 (s, C3), 127.9 (s, aryl-CH), 127.6 (s, aryl-CH), 126.4 (s, aryl-CH), 123.1 (s, aryl-CH), 51.3 (s, N(CH$_3$)$_2$), 31.6 (d, $^3J_{\mathrm{PC}} = 9$ Hz, CH$_2$), 25.0 (d, $^1J_{\mathrm{PC}} = 35$ Hz, P(*C*HCH$_3$CH$_3$)$_2$), 20.4 (s, S(CH$_3$)$_2$), 19.9 (s, with Pt satellites, $^3J_{\mathrm{PtC}} = 34$ Hz, P(CHCH$_3$*C*H$_3$)$_2$), 19.3 (s, P(CH*C*H$_3$CH$_3$)$_2$), −24.2 (d, $^2J_{\mathrm{PC}} = 6$ Hz, Pt satellites not resolved, Pt-CH$_3$ *trans* to N). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 39.0 (s, with Pt satellites $^1J_{\mathrm{PtP}} = 3936$ Hz).

Preparation of [10]$^+$BF$_4^-$. To a magnetically stirred solution of **7** (0.10 g, 0.20 mmol) in 3 mL of tetrahydrofuran was added solid AgBF$_4$ (0.044 g, 0.23 mmol). The reaction was stirred for 0.5 h, after which time, acetonitrile (0.10 mL, 1.9 mmol) was added and the solution stirred for an additional 1 h. The solvent and other volatiles were removed in vacuo, and the solid was treated with 5 mL of dichloromethane. Insoluble materials were removed by filtration through a Celite column, from which the filtrate was collected and the dichloromethane and other volatiles were then removed in vacuo. The residual white solid was rinsed with pentane (2 × 3 mL) to leave a white powder, [**10**]$^+\mathrm{BF}_4^-$ (0.098 g, 0.16 mmol, 84%). Melting point: 111−114 °C. Anal. Calcd for $\mathrm{C_{20}H_{32}N_2P_1Pt_1B_1F_4}$: C 39.16, H 5.26, N 4.57. Found: C 39.02, H 4.98, N 4.19. ^{1}H NMR (CD$_3$CN): δ 7.56 (m, 1H, aryl-CH), 7.49 (m, 1H, aryl-CH), 7.38−7.31 (m, 2H, aryl-CH's), 3.68 (s, 2H, CH$_2$), 3.08 (s, 6H, N(CH$_3$)$_2$), 2.79 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 1.31 (dd, $^3J_{\mathrm{PH}} = 18.0$ Hz, $^3J_{\mathrm{HH}} = 7.5$ Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 1.22 (dd, $^3J_{\mathrm{PH}} = 17.5$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, P(CHCH$_3$C*H*$_3$)$_2$), 0.67 (d, $^3J_{\mathrm{PH}} = 2.0$ Hz, with Pt satellites, $^2J_{\mathrm{PtH}} = 70.0$ Hz, 3H, Pt-CH$_3$ *trans* to N). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 178.0 (d, $^2J_{\mathrm{PC}} = 11$ Hz, C2), 145.7 (d, $J_{\mathrm{PC}} = 7$ Hz, C3a or C7a), 138.0 (s, C7a or C3a), 131.0 (d, $^1J_{\mathrm{PC}} = 47$ Hz, C3), 128.1 (s, aryl-CH), 127.7 (s, aryl-CH), 126.7 (s, aryl-CH), 123.7 (s, aryl-CH), 53.5 (s, N(CH$_3$)$_2$), 31.9 (d, $^3J_{\mathrm{PC}} = 9$ Hz, CH$_2$), 24.9 (d, $^1J_{\mathrm{PC}} = 39$ Hz, P(*C*HCH$_3$CH$_3$)$_2$), 19.7 (s, with Pt satellites, $^3J_{\mathrm{PtC}} = 39$ Hz, P(CHCH$_3$*C*H$_3$)$_2$), 19.2 (s, P(CH*C*H$_3$CH$_3$)$_2$), −28.0 (d, $^2J_{\mathrm{PC}} = 8$ Hz, with Pt satellites, $^1J_{\mathrm{PtC}} = 600$ Hz, Pt-CH$_3$ *trans* to N); ^{1}H and ^{13}C resonances attributable to the coordinated MeCN ligand in [**10**]$^+\mathrm{BF}_4^-$ were not observed in CD$_3$CN, presumably due to facile ligand displacement with the deuterated solvent. ^{31}P{^{1}H} NMR (CD$_3$CN): δ 29.5 (s, with Pt satellites $^1J_{\mathrm{PtP}} = 4562$ Hz). ^{1}H NMR (THF-d_8): δ 7.60 (m, 1H, aryl-CH), 7.49 (m, 1H, aryl-CH), 7.33−7.25 (m, 2H, aryl-CH's), 3.79 (s, 2H, CH$_2$), 3.19 (s, 6H, N(CH$_3$)$_2$), 2.83 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 2.58 (s, 3H, NCCH$_3$), 1.34 (dd, $^3J_{\mathrm{PH}} = 17.6$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 1.24 (dd, $^3J_{\mathrm{PH}} = 17.2$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, P(CHCH$_3$C*H*$_3$)$_2$), 0.67 (d, $^3J_{\mathrm{PH}} = 2.0$ Hz, with Pt satellites, $^2J_{\mathrm{PtH}} = 67.0$ Hz, 3H, Pt-CH$_3$ *trans* to N). ^{13}C{^{1}H} NMR (THF-d_8): δ 179.1 (d, $^2J_{\mathrm{PC}} = 11$ Hz, C2), 145.9 (d, $J_{\mathrm{PC}} = 7$ Hz, C3a or C7a), 138.1 (s, C7a or C3a), 130.5 (d, $^1J_{\mathrm{PC}} = 47$ Hz, C3), 127.7 (s, aryl-CH), 127.2 (s, aryl-CH), 126.5 (s, aryl-CH), 123.3 (s, aryl-CH), 120.9 (d, $^3J_{\mathrm{PC}} = 18$ Hz, N*C*CH$_3$), 52.0 (s, N(CH$_3$)$_2$), 31.8 (d, $^3J_{\mathrm{PC}} = 9$ Hz, CH$_2$), 24.8 (d, $^1J_{\mathrm{PC}} = 39$ Hz, P(*C*HCH$_3$CH$_3$)$_2$), 19.7 (s, with Pt satellites, $_3J_{\mathrm{PtC}} = 36$ Hz, P(CHCH$_3$*C*H$_3$)$_2$), 19.2 (s, P(CH*C*H$_3$CH$_3$)$_2$), 2.9 (s, NC*C*H$_3$), −28.1 (d, $^2J_{\mathrm{PC}} = 8$ Hz, with Pt satellites, $^1J_{\mathrm{PtC}} = 594$ Hz, Pt-CH$_3$ *trans* to N). ^{31}P{^{1}H} NMR (THF-d_8): δ 28.0 (s, with Pt satellites $^1J_{\mathrm{PtP}} = 4600$ Hz).

General Protocol for Hydrosilylation Experiments. The protocol used for hydrosilylation reactions employing 5 mol % catalyst loading in C$_6$H$_6$ is provided as a representative procedure. A solution of the catalyst compound in C$_6$H$_6$ (0.05 mmol in 4 mL of solvent) was allowed to equilibrate for 5 min under the influence of magnetic stirring, at which point, styrene (1.0 or 3.0 mmol, as noted) was added by use of an Eppendorf pipet. The resultant solution was stirred for an additional 10 min to ensure equilibration of the styrene with the catalyst, after which triethylsilane (1.0 mmol) was added. Subsequently, 0.7 mL aliquots were placed in NMR tubes and sealed with polypropylene tube caps and PTFE tape. For runs conducted at elevated temperatures, the NMR tubes were immediately transferred to a Schlenk tube filled partially with heavy mineral oil, which in turn was placed within a temperature-controlled mineral oil bath. No precipitates were observed throughout the course of all catalytic reactions, with the exception of reactions employing AgBF$_4$ or AgOTf, in which case AgCl is presumably generated. At the desired sampling time, NMR tubes were opened and filtered through a short Al$_2$O$_3$ column (5 cm long × 0.5 cm diameter), from which clear, colorless solutions eluted. Benzene was passed through the column to increase the total eluted volume to between 1.0 and 1.5 mL. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, and quantitative data were obtained from GC-FID analysis;[34] tabulated data represent the average of two runs.

Crystallographic Solution and Refinement Details. Crystallographic data were obtained at 193 (±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. The structures were solved by use of direct methods (except in the case of [**8**]$^+\mathrm{BF}_4^-$, where a Patterson search/structure expansion was employed) and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Crystals of **2b** suitable for X-ray diffraction analysis were grown by slow evaporation of a pentane solution of **2b** at room temperature.

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Supporting Information Available: Single-crystal X-ray diffraction data in CIF format for **2b**, **3**, [**8**]$^+\mathrm{BF}_4^-$, and [**9**]$^+\mathrm{BF}_4^-$ are available free of charge via the Internet at http://pubs.acs.org.

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