Synthesis and Reactivities of Neutral and Cationic Indenyl−Palladium Complexes

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Received September 24, 2005

The complexes [(1-R-Ind)Pd(PPh_3)Me] (R = H (**3**), Me (**4**)), [(1-R-Ind)Pd(PPh_3)$_2$]BF_4 (R = H (**5**[BF_4]), Me (**6**)), and [(1-R-Ind)Pd(PPh_3)(OSO_2CF_3)] (R = H (**7**), Me (**8**)) have been prepared by reacting their corresponding Pd−Cl derivatives with MeMgCl, $AgBF_4$/PPh_3, and AgOTf, respectively. These complexes have been characterized by NMR spectroscopy and, in the case of **3**, **5**[BF_4], **6** and **7**, by X-ray crystallography. The triflate moiety in complexes **7** and **8** is displaced readily by various ligands to give [(1-R-Ind)Pd(PPh_3)L][OTf] (L = PPh_3 (**5**[OTf]), PMe_3 (**9**), CH_3CN (**10**), PhCN (**11**), *t*-BuNC (**12**)). Reactions of **7** or **8** with various olefins result in isomerization (1-hexene), dimerization and/or trimerization (ethylene, styrene, and *p*-fluorostyrene), oligomerization (*p*-amino- and *p*-methylstyrene), or polymerization (*p*-methoxystyrene). Compounds **1**−**8** promote the addition of $HSiCl_3$ to styrene and phenylacetylene.

Introduction

A number of advantages have favored the use of Ind complexes (Ind = indenyl and its substituted derivatives) in comparison to their Cp analogues in catalytic applications.[1] This is especially true for the Ind complexes of metals from groups 4−9, whereas the catalytic reactivities of group 10 metal−Ind complexes have not been investigated until very recently.[2] Thus, studies on the chemistry of Ni−Ind complexes have led to the discovery of interesting structural and bonding motifs,[3] as well as catalytic reactivities in the oligo- and polymerization of alkenes,[4] alkynes,[5] and $PhSiH_3$[6] and in the hydrosilylation of alkenes and ketones.[7]

Our interest in the structures and catalytic activities of Ni−Ind complexes prompted us to explore the chemistry of analogous Pd compounds in order to elucidate the influence of the metal center on the chemistry of these compounds. Although a number of Ind−Pd complexes had been reported prior to our studies,[8] there were no general synthetic routes to these compounds. Our initial studies were, therefore, aimed primarily at identifying reliable synthetic protocols to Ind−Pd complexes. In a previous report,[9] we described a high-yield preparation of [(η^3-Ind)Pd(μ-Cl)]$_2$ from the reaction of Me_3Si−Ind with $Na_2[PdCl_4]$ in ethanol and showed that reacting this dimeric species with PR_3 or *t*-BuNC gives the complexes [IndPd(PR_3)-Cl] (R = Ph, Me, OMe, Cy) and [(η^1-Ind)(*t*-BuNC)Pd(μ-Cl)]$_2$, respectively. Curiously, however, this protocol proved very sensitive to the presence of substituents on the Ind ligand, thus limiting this approach to the synthesis of the parent (unsubstituted) indenyl complexes.

Since the reactivities of Ind complexes are often influenced significantly by the nature of the substituents on the Ind ligand, we sought an alternative synthetic route to variously substituted Pd−Ind complexes. We have explored, with limited success, the metathetic reaction of Li[R-Ind] with suitable Pd precursors,

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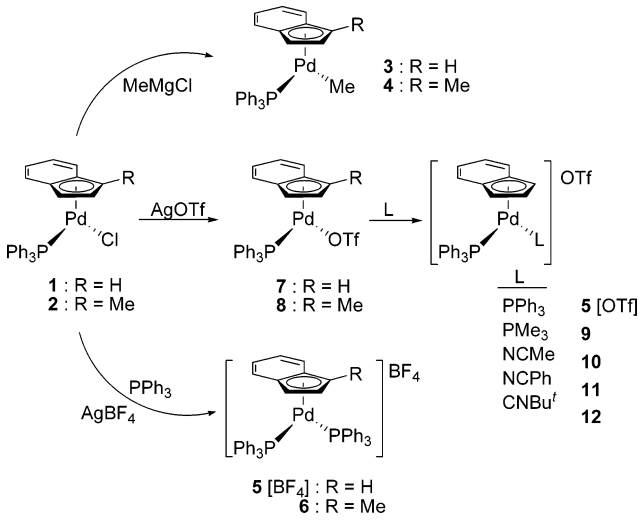
10.1021/om050826f CCC: $33.50
Publication on Web 12/21/2005

Scheme 1

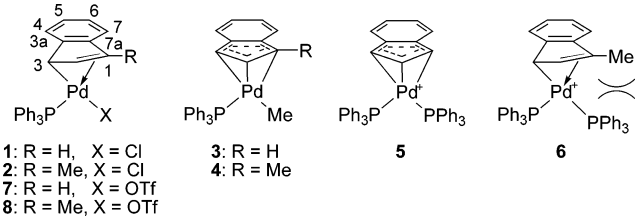


thus preparing a series of 1-Me-Ind derivatives in low yields.[10] Nevertheless, access to the compounds (1-Me-Ind)Pd(PPh_3)X has allowed us to study their structures and reactivities as a function of Ind substituent and X ligand. The present report describes the preparation and characterization of the complexes [(1-R-Ind)Pd(PPh_3)Me] (R = H (**3**) Me (**4**)), [(1-R-Ind)Pd(PPh_3)$_2$][BF_4] (R = H (**5**[BF_4]), Me (**6**)), and [(1-R-Ind)Pd(PPh_3)(OTf)] (R = H (**7**), Me (**8**); OTf = OSO_2CF_3) and discusses the reactivities of some of these complexes with $PhSiH_3$, ethylene, 1-hexene, and *p*-X-styrene (X = H, F, Me, NH_2, OMe). The facile substitution of the OTf moiety in complex **7** has given access to the new cationic complexes $[(Ind)Pd(PPh_3)(L)]^+$ (L = PPh_3 (**5**[OTf]), PMe_3 (**9**), CH_3CN (**10**), PhCN (**11**), *t*-BuNC (**12**)), which are also described briefly. The effectiveness of our Ind−Pd^{II} complexes in catalyzing the addition of $HSiCl_3$ to styrene and phenylacetylene were also examined.

Results and Discussion

Synthesis and Spectroscopic Characterization. The chloro complexes (1-R-Ind)Pd(PPh_3)Cl (R = H (**1**), Me (**2**)) have been prepared by addition of PPh_3 to the dimer [(η^3-Ind)Pd(μ-Cl)]$_2$ (for **1**) or to the mixture of Li[1-Me-Ind] and [$(PhCN)_2PdCl_2$] (for **2**).[9] Complexes **1** and **2** were then used to prepare the analogous Pd−Me, Pd−PPh_3, and Pd−OTf derivatives, as follows (Scheme 1): reaction with MeMgCl gave (1-R-Ind)Pd(PPh_3)Me (R = H (**3**), Me (**4**)) in ca. 25% yield; reaction with $AgBF_4$ in the presence of 1 equiv of PPh_3 gave the cationic complexes [(1-R-Ind)Pd(PPh_3)$_2$][BF_4] (R = H (**5**[BF_4]), Me (**6**)) in ca. 90% yield; reaction with AgOTf gave (1-R-Ind)Pd(PPh_3)(OTf) (R = H (**7**), Me (**8**)) in ca. 80% yield. Complexes **3**−**8** are thermally stable in the solid state and can be stored at room temperature; in solution, however, decomposition takes place after a few days with concomitant deposition of Pd metal. Complexes **3**, **5**[BF_4], **6**, and **7** were isolated in pure form, but the purifications of **4** and **8** were not successful.[11] The NMR spectra of these complexes support their proposed structures, as described below.

Chart 1



The $^{31}P\{^1H\}$ NMR spectra showed one singlet resonance for the PPh_3 ligand in these complexes (at ca. 40 ppm for **3** and **4**, 29−31 ppm for **7** and **8**, and 28 ppm for **5**[BF_4]). On the other hand, the $^{31}P\{^1H\}$ NMR spectrum of complex **6** showed AB doublets at ca. 29 and 30 ppm ($^2J_{P-P} \approx 59$ Hz), reflecting the inequivalence of the two PPh_3 ligands. This is caused by the presence of the Me substituent, which eliminates the mirror plane normally present in (indenyl)ML_2 complexes, such that the C_s symmetry of **5**[BF_4] is reduced to C_1 for **6** in the absence of a rapid rotation of the Ind ligand.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of these compounds were fairly similar to those of their Ni counterparts and proved particularly informative on the coordination mode of the Ind ligands. For instance, **3** and **5**[BF_4] showed only one resonance for the symmetry-related pairs of protons (H1/H3, H4/H7, and H5/H6) or carbons (C1/C3, C4/C7 and C5/C6); the chemical shifts of these resonances were very similar to the corresponding signals in the high-temperature spectrum of complex **1**.[9] In contrast, the ^1H and $^{13}C\{^1H\}$ NMR spectra of the OTf derivative **7** display distinct signals for these nuclei, much like the ambient-temperature spectra of complex **1**.[9] These observations indicate that the rotation of the Ind ligand is similarly hindered in **7** and **1** but is much more facile in **3**.

This conclusion is in accord with the results of variable-temperature NMR studies that have allowed us to calculate an energy barrier of ca. 10.6 kcal/mol for the rotation of the Ind ring in **3**, in contrast to a much higher barrier in **1** (ca. 16.5 kcal/mol).[9] On the basis of previously established correlations between Ind hapticity and rotational barriers,[12] we conclude that, in solution, the Ind ligand in **3** is coordinated to Pd in a more symmetrical fashion and with a greater degree of hapticity than in **1** (Chart 1). The stronger Ind−Pd interactions in this Pd−Me complex can be attributed to the more effective bonding between Ind and the softer Pd center in the alkyl derivative, while the more symmetrical coordination is due to the smaller difference between the trans influence of the ancillary ligands PPh_3 and Me in complex **3**.

The ^1H NMR spectral patterns displayed by **4** and **8** were similar to those observed in the ambient-temperature spectra of (Ind)Pd(PR_3)Cl (R = Ph, Me, OMe, Cy).[9] For example, the ^1H NMR spectrum of **4** contained two doublets (H4/H7) and two triplets (H5/H6) between ca. 6.8 and 7.2 ppm, a doublet of doublets at ca. 6.4 ppm (H2), a singlet at ca. 5.3 ppm (H3), and a doublet at ca. 2.1 ppm (CH_3−Ind); in addition, a doublet was detected at −0.12 ppm ($^3J_{P-H} \approx 4$ Hz) for the Pd−Me moiety. The complete absence of symmetry in **4** and **8** means that the proton and carbon nuclei of the 1-Me-Ind ligand cannot be exchanged by Ind rotation, which is in contrast with the situation in **3** and **6**, wherein the C_1 symmetry becomes C_s as a result of rapid Ind rotation.

(10) The Pd-promoted coupling of Li[R-Ind] is a major side reaction that leads to very low yields of the desired complexes.[9]

(11) Isolating pure samples of complexes **3** and **7** was less complicated than that of their 1-Me-Ind analogues **4** and **8** because of the greater solubility of the latter in common solvents. In addition, the Pd−OTf complex **8** slowly decomposes to [(1-Me-Ind)Pd(PPh_3)$_2$]$^+$ during recrystallization.

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Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters of 3 and 7

	3	**7**
formula	$C_{28}H_{25}PPd$	$C_{28}H_{22}PF_3O_3SPd$
mol wt	498.85	632.89
cryst color, habit	yellow-orange, block	red, block
cryst dimens, mm	0.15× 0.19 × 0.60	0.07× 0.10 × 0.27
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	7.5169(1)	10.3261(1)
b, Å	11.5414(1)	11.2327(2)
c, Å	13.8896(1)	23.9756(3)
α, deg	93.358(1)	80.607(1)
β, deg	96.272(1)	87.530(1)
γ, deg	107.103(1)	74.077(1)
V, Å^3	1139.53(2)	2638.37(6)
Z	2	4
D(calcd), g cm^{-3}	1.454	1.593
diffractometer	Bruker AXS SMART 2K	
temp, K	223	223
λ, Å	1.541 78	1.541 78
μ, mm^{-1}	7.304	7.427
scan type	*ω* scan	*ω* scan
F(000)	508	1272
θ_{max} (deg)	72.83	72.65
h, *k*, *l* range	$-7 \le h \le 8$	$-12 \le h \le 12$
	$-14 \le k \le 14$	$-13 \le k \le 10$
	$-17 \le l \le 16$	$-29 \le l \le 29$
no. of rflns collected/ unique	13 683/4319	32 097/10 061
abs cor	multiscan	multiscan
T(min, max)	0.23, 0.33	0.44, 0.70
$R(F^2 > 2\sigma(F^2))$, $R_w(F^2)$	0.0287, 0.0747	0.0421, 0.1046
GOF	1.053	0.955

Table 2. Crystal Data, Data Collection, and Structure Refinement Parameters of 5[BF$_4$] and 6

	5[BF_4]	**6**
formula	$C_{45}H_{37}P_2PdBF_4$	$C_{46}H_{39}P_2PdBF_4 \cdot 1.5CH_2Cl_2$
mol wt	832.90	974.31
cryst color, habit	red-orange, needle	red-orange, block
cryst dimens, mm	0.08 × 0.14 × 0.27	0.08 × 0.15 × 0.19
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	11.685(5)	11.8930(1)
b, Å	20.765(11)	14.2475(1)
c, Å	15.709(6)	14.2624(3)
α, deg	90	75.970(1)
β, deg	95.89(3)	84.247(1)
γ, deg	90	68.763(1)
V, Å^3	3791(3)	2185.18(3)
Z	4	2
D(calcd), g cm^{-3}	1.459	1.481
diffractometer	Nonius CAD-4	Bruker AXS SMART 2K
temp, K	293	223
λ, Å	1.541 78	1.541 78
μ, mm^{-1}	5.176	6.225
scan type	*ω* scan	*ω* scan
F(000)	992	990
θ_{max} (deg)	69.97	72.84
h, *k*, *l* range	$-14 \le h \le 14$	$-14 \le h \le 14$
	$-25 \le k \le 25$	$-17 \le k \le 17$
	$-19 \le l \le 19$	$-17 \le l \le 17$
no. of rflns collected/ unique	15 548/7177	26 475/8353
abs cor	Ψ scan	multiscan
T(min, max)	0.34, 0.69	0.40, 0.73
$R(F^2 > 2\sigma(F^2))$, $R_w(F^2)$	0.0475, 0.0873	0.0435, 0.1186
GOF	0.643	1.003

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1,[a] 3, and 7[b]

	1 (X = Cl)		**3** (X = C8)	**7** (X = O)
Pd−P	2.2785(6)	2.2673(6)	2.2260(5)	2.283(1)
Pd−X	2.3474(6)	2.3560(7)	2.061(3)	2.157(15)
Pd−C1	2.244(2)	2.282(3)	2.273(2)	2.290(4)
Pd−C2	2.186(2)	2.209(3)	2.273(2)	2.196(4)
Pd−C3	2.192(2)	2.165(3)	2.321(2)	2.135(4)
Pd−C3a	2.607(2)	2.544(3)	2.562(2)	2.554(4)
Pd−C7a	2.610(2)	2.580(2)	2.533(2)	2.615(4)
C1−C2	1.404(4)	1.393(4)	1.410(4)	1.390(7)
C2−C3	1.410(4)	1.413(4)	1.403(4)	1.421(7)
C3−C3a	1.474(4)	1.468(4)	1.449(3)	1.478(6)
C3a−C7a	1.415(4)	1.422(4)	1.425(3)	1.419(6)
C7a−C1	1.464(4)	1.465(4)	1.460(4)	1.478(6)
S−O1				1.415(9)
S−O2				1.418(10)
S−O3				1.377(11)
S−C8				1.817(10)
C8−F1				1.294(12)
P−Pd−X	96.23(2)	97.04(2)	89.85(9)	92.3(4)
C3−Pd−X	158.71(7)	160.78(8)	160.60(11)	165.0(5)
C3−Pd−P	104.91(7)	101.75(8)	109.45(6)	101.35(13)
C1−Pd−X	97.29(7)	99.48(8)	100.86(11)	104.3(5)
C1−Pd−P	164.25(7)	161.72(8)	168.20(7)	160.95(13)
C1−Pd−C3	61.4(1)	61.3(1)	59.74(9)	61.51(17)
Δ(M−C) (Å)	0.39	0.39	0.25	0.37
HA (deg)	15.49	14.58	10.17	15.22
FA (deg)	14.84	14.40	9.29	13.61

[a] See ref 9. [b] The structural parameters for the two independent molecules in the unit cell of **7** were quite similar and have been averaged.

Finally, analysis of the Pd−OTf complexes by IR and $^{19}F\{^1H\}$ NMR spectroscopy showed typical resonances for an η^1-coordinated triflate group:[13] asymmetric sulfonyl stretching modes at ca. 1312 cm^{-1} in the IR spectra and singlet resonances at ca. −80 ppm in the $^{19}F\{^1H\}$ NMR spectra.

Solid-State Structural Studies. The solid-state structures of complexes **3**, **5**[BF_4], **6**, and **7** have been studied by X-ray crystallography. The crystal data are presented in Tables 1 and 2, selected structural parameters are presented in Tables 3 (for **3** and **7**) and 4 (for **5**[BF_4] and **6**), and the ORTEP diagrams for these complexes are shown in Figures 1−4. The overall geometry around Pd in all four complexes is approximately square planar, with the largest distortion arising from the small C1−Pd−C3 angle (ca. 60°). Close inspection of the main structural parameters obtained for these complexes and comparison of their values to those of previously reported Ind−Pd allows an evaluation of the influence of Ind substituents and the Cl, Me, and OTf ligands on the Ind hapticity and overall structures of these complexes, as described below.

The Pd center in each of these complexes is within reasonable bonding distance from the P, C1, C2, C3, and X atoms (X = C8 in **3**, P2 in **5**[BF_4] and **6**, and O in **7**) but considerably farther away from C3a and C7a. This difference in the Pd distances to the allylic and benzo carbons is a reflection of the so-called "slippage" of the Ind ligand. The degree of such slippage away from the idealized η^5 coordination is often measured by calculating parameters such as the slip value (Δ(M−C)) and the hinge and fold angles (HA and FA).[14] Inspection of these parameters (Tables 3 and 4) shows that the degree of slippage in the Pd−OTf complex **7** is similar to those found for the analogous Pd−Cl compounds (1-R-Ind)Pd(PR'_3)Cl (R = H, Me; R′ = Ph, Cy, Me, OMe)[9] but significantly larger than those found for the Pd−Me derivative **3**; evidently, Ind hapticity in IndPd(PPh_3)X is greatly influenced by the nature of the X ligand (Me > Cl ≈ OTf). These results also show that the Ind hapticities are much greater (smaller Δ(M−C), HA, and FA parameters) in the corresponding Ni complexes; this structural

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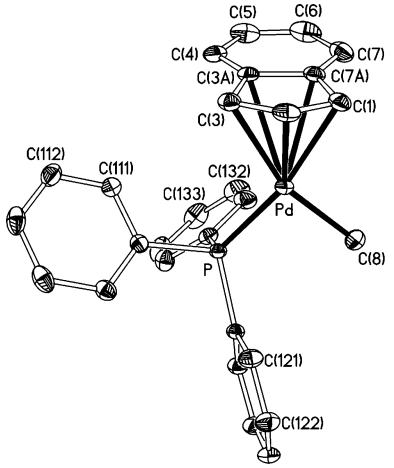


Figure 1. ORTEP view of complex **3**. Thermal ellipsoids are shown at the 30% probability level, and hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for 5[BF_4] and 6

	5[BF_4]	6
Pd−P1	2.301(2)	2.3095(7)
Pd−P2	2.309(2)	2.3227(7)
Pd−C1	2.270(6)	2.336(3)
Pd−C2	2.230(6)	2.233(3)
Pd−C3	2.223(6)	2.209(3)
Pd−C3a	2.570(9)	2.577(3)
Pd−C7a	2.585(9)	2.645(3)
C1−C2	1.418(9)	1.405(5)
C2−C3	1.434(9)	1.425(5)
C3−C3a	1.443(9)	1.459(5)
C3a−C7a	1.422(10)	1.427(5)
C7a−C1	1.445(10)	1.477(5)
C1−C8		1.500(5)
P1−Pd−P2	104.31(7)	103.72(3)
C3−Pd−C1	60.1(3)	60.59(13)
C3−Pd−P2	156.2(2)	158.82(10)
C3−Pd−P1	99.5(2)	97.34(10)
C1−Pd−P1	159.5(2)	156.14(9)
C1−Pd−P2	96.1(2)	98.92(9)
Δ(M−C) (Å)	0.33	0.34
HA (deg)	11.86	13.71
FA (deg)	12.18	15.99

difference is reflected in subtle but important differences in the reactivities of the analogous Ni and Pd complexes (vide infra).

A comparison of the structural parameters found in the cationic complexes 5[BF_4] and **6** on one hand, and the neutral species **1**,[9] **2**,[9] **3**, and **7** on the other, shows again that the most important factor affecting the Pd−Ind interactions is the nature of the X moiety, followed by the overall charge of the complex. Thus, Ind hapticity is reinforced on going from the neutral species **1**, **2**, and **7** (X = Cl, OTf; Δ(M−C) = 0.32−0.39 Å) to the cationic complexes 5[BF_4] and **6** (X = PPh_3; Δ(M−C) = 0.33 and 0.34 Å) to the neutral Pd−Me compound **3** (Δ(M−C) = 0.25 Å). The Ind substituent also appears to play a role, especially in the case of the bis(phosphine) complexes, wherein the Me substituent prevents closer approach of the Ind ligand (in **6**) to the Pd center and results in the less symmetrical coordination of the Ind ligand (Chart 1): Pd−C1 > Pd−C3 by more than 0.12 Å (40 esd) in **6** compared to less than 0.05 Å (8 esd) in 5[BF_4].

(14) Δ(M−C) = 0.5(M−C3a + M−C7a) − 0.5(M−C1 + M−C3). HA is the angle between the planes encompassing the atoms C1, C2, C3 and C1, C3, C3a, C7a. FA is the angle between the planes encompassing the atoms C1, C2, C3 and C3a, C4, C5, C6, C7, C7a. The Δ(M−C), HA, and FA values for a range of Ind complexes are given in ref 12a and the following report: Wetscott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777. The corresponding data for group 10 complexes are given in ref 2.

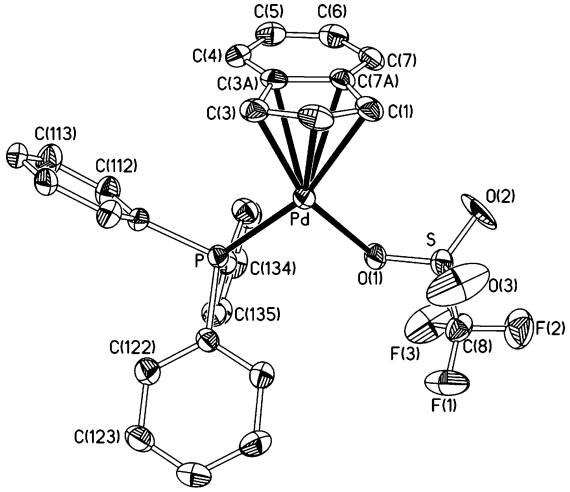


Figure 2. ORTEP view of complex **7**. Only one of the two independent molecules is shown. The OTf anion is disordered over two positions; the view shown in this figure represents the major model. Thermal ellipsoids are shown at the 30% probability level, and hydrogen atoms are omitted for clarity.

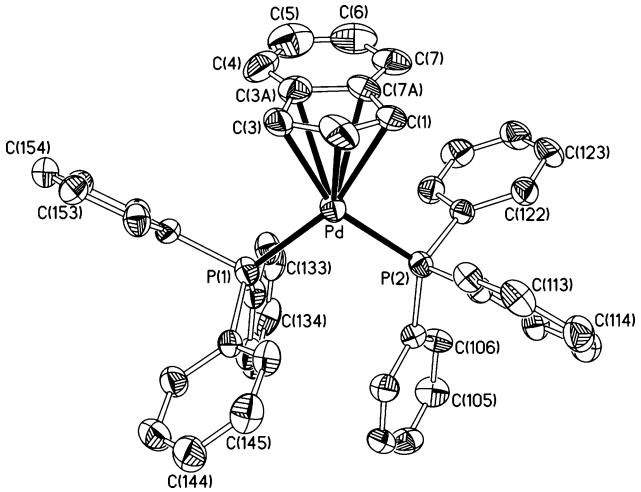


Figure 3. ORTEP view of complex 5[BF_4]. Thermal ellipsoids are shown at the 30% probability level. The BF_4 anion and the hydrogen atoms are omitted for clarity.

Reactivities of the Pd−Triflate Species 7 and 8. We have studied the substitution of the triflate moiety in complex **7** by different nucleophiles L as a route for the preparation of new cationic complexes (Scheme 1). These ligand substitution reactions were carried out by treating **7** with 1 equiv of L in $CDCl_3$. NMR spectroscopy showed rapid and clean displacement of the OTf moiety to give the adducts [IndPd(PPh_3)(L)][OTf] (L = PPh_3 (5[OTf]), PMe_3 (**9**), CH_3CN (**10**), PhCN (**11**), and *t*-BuNC (**12**)). The spectroscopic characterization of these complexes was quite straightforward. For example, the $^{31}P\{^1H\}$ NMR spectra of 5[OTf] and **10**−**12** each showed a new singlet resonance in a narrow chemical shift range (27−31 ppm), attributed to the PPh_3 ligand, whereas the PMe_3 adduct **9** gave rise to an AX set of doublets at 30.0 and −16.6 ppm ($^2J_{P-P}$ = 60 Hz), as expected. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the new species also displayed the expected signals for Ind and PPh_3 ligands. In addition, the presence of the CH_3CN and $CNC(CH_3)_3$ ligands in complexes **10** and **12**, respectively, was signaled by ^1H NMR resonances at 2.07 and 1.15 ppm, respectively.

The IR spectra of **10**−**12** proved valuable, because the

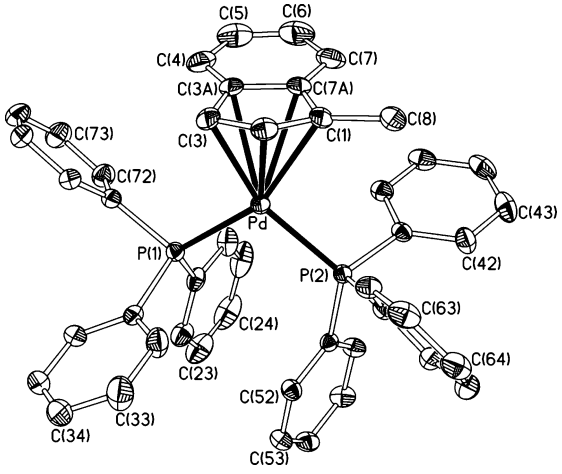
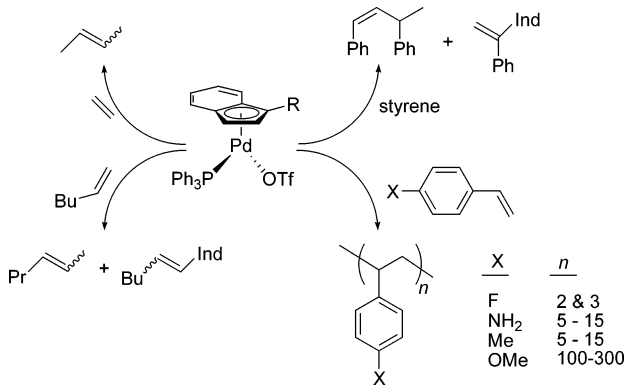


Figure 4. ORTEP view of complex **6**·1.5CH_2Cl_2. Thermal ellipsoids are shown at the 30% probability level. The BF_4 anion, the solvent, and the hydrogen atoms are omitted for clarity.

Scheme 2



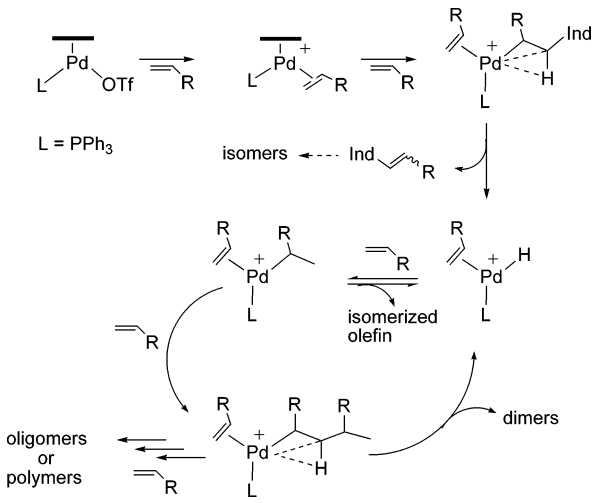
frequencies of the ν(CN) bands reflect the nature of Pd−L interactions. Thus, the ν(CN) frequencies of free and coordinated CH_3CN (2254 vs 2247 cm^{-1})[15] and PhCN (2230 vs 2227 cm^{-1}) indicate a negligible degree of π-back-bonding between these weakly π-acidic ligands and the cationic Pd center. On the other hand, the corresponding ν(CN) frequencies for the *t*-BuNC ligand (2136 cm^{-1} in the free ligand vs 2206 cm^{-1} in complex **12**) signal a greater C−N bond order resulting from significant σ donation from the HOMO of the ligand, which has antibonding character with respect to the C−N bond. Similar IR data have been reported for other Pd(II)−isocyanide complexes.[9,16]

The lability of the triflate moiety also allowed us to explore the reactivities of complexes **7** and **8** with olefins. The reactions with ethylene were performed by bubbling $CDCl_3$ solutions of complexes **7** and **8** with ethylene for ca. 5 min. Careful analysis of the reaction mixtures by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy indicated the formation of (*E*)- and (*Z*)-2-butenes (Scheme 2). In contrast, methyl methacrylate did not react at all with **7** or **8**, whereas 1-hexene was isomerized to (*E*)- and (*Z*)-2-hexene (ca. 3:1). GC/MS analysis of the isomerization reaction catalyzed by complex **7** showed the presence of trace quantities of (1-hexenyl)indene in the reaction mixture: $M^{\bullet+}$ at *m*/*z* 198, $M^{\bullet+}$ − 15 (Me), $M^{\bullet+}$ − 29 (Et), $M^{\bullet+}$ − 43 (Pr), $M^{\bullet+}$ − 57 (Bu), etc.

(15) The assignment of the band at 2247 cm^{-1} to ν(CN) should be considered tentative, because the IR spectrum of complex **10** also showed two equally weak bands at 2291 and 2186 cm^{-1}.

(16) (a) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196. (b) Crociani, B.; Boschi, T.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 2021. (c) Cherwinski, W. J.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1511. (d) De Munno, G.; Bruno, G.; Grazia Arena, C.; Drommi, D.; Faraone, F. *J. Organomet. Chem.* **1993**, *450*, 263.

Scheme 3



The reactions of variously substituted styrenes with **7** or **8** gave interesting results. Thus, 50−70 equiv of styrene reacted with either complex over 15 h at room temperature to give nearly quantitative conversion of the substrate to the head-to-tail dimer (*Z*)-1,3-diphenyl-1-butene. GC/MS analyses of the reaction mixtures confirmed that the main product was a single isomer of the dimer ($M^{\bullet+}$ at *m*/*z* 208) but also revealed the presence of trace quantities (<2%) of a trimer ($M^{\bullet+}$ at *m*/*z* 312) and Ind═C(Ph)CH_3 ($M^{\bullet+}$ at *m*/*z* 218). Analogous reactions with *p*-fluorostyrene gave a 65:35 mixture of the linear dimer ($M^{\bullet+}$ at *m*/*z* 244) and trimer ($M^{\bullet+}$ at *m*/*z* 366); GC/MS analyses showed that the dimer consists of two isomers (ca. 98:2), but structural details could not be established firmly from the ^1H NMR spectra. On the other hand, reactions of complex **7** with electron-rich *p*-X-styrenes (X = NH_2, Me, OMe) gave higher oligomers and polymers, as follows: *p*-aminostyrene was converted quantitatively to an oligomer ($M_w \approx 1050$, $M_w/M_n \approx 1.3$, 100 turnovers) as was *p*-methylstyrene ($M_w \approx 1250$, $M_w/M_n \approx 1.4$, 885 turnovers), whereas *p*-methoxystyrene was polymerized ($M_w \approx 29\,000$, $M_w/M_n \approx 3.2$, 970 turnovers).

The greater reactivities of styrenes encouraged us to explore their co-oligomerization between themselves and with 1-hexene. Unfortunately, however, all reactions with mixtures of olefins failed to induce hetero-oligomerization reactions. For instance, reacting a 1:1 mixture of styrene and 1-hexene with complex **7** led to the formation of (*Z*)-1,3-diphenyl-1-butene and (*E*)- and (*Z*)-2-hexene only.

Taken together, these results indicate that the reactivities of **7** and **8** with olefins are quite sensitive to the nature of the substrates, ranging from no reaction with methyl methacrylate to isomerization with 1-hexene and oligo- and polymerization with ethylene and *p*-X-styrenes. Comparison of these reactivities to those observed with analogous Ni−Ind complexes demonstrates subtle differences. For example, styrene is converted to mostly poly(styrenes) ($M_w \approx 10^4-10^5$) by in situ generated cations $[IndNi(PPh_3)]^+$,[4c,e,f,l] whereas the analogous Pd complexes promote a regioselective dimerization. On the other hand, both Ni− and Pd−Ind precursors show the same reactivities with ethylene and 1-hexene. It is worth noting that reaction of ethylene with the complex **1**, $\{(Ind)Pd(\mu\text{-}Cl)\}_2$, or $IndNi(PR_3)$-Cl in the presence of excess MAO gives polyethylene.[4b,9] We propose that the reactions of the Pd−OTf derivatives with olefins proceed through the common hydrido−Pd species $[L_nPdH]^+$ (Scheme 3), but it is not clear how the specific nature of each olefin can steer the reaction pathway from isomerization to the formation of dimers, oligomers, or polymers.

Table 5. Pd-Catalyzed Hydrosilylation Reactions with $HSiCl_3$[a]

entry	cat.	substrate	products (conversn, %)
1	**1**	styrene	$Ph(SiCl_3)CHCH_3$ (92)
2	**2**	styrene	$Ph(SiCl_3)CHCH_3$ (90)
3[b]	**2**	styrene	$Ph(SiCl_3)CHCH_3$ (100)
4	**3**	styrene	$Ph(SiCl_3)CHCH_3$ (84)
5	**5**[BF_4]	styrene	$Ph(SiCl_3)CHCH_3$ (86)
6	**6**	styrene	$Ph(SiCl_3)CHCH_3$ (93)
7	**7**	styrene	$Ph(SiCl_3)CHCH_3$ (100)
8	**8**	styrene	$Ph(SiCl_3)CHCH_3$ (95)
9[c]	**1**	PhC≡CH	(*E*)-PhCH=$CHSiCl_3$ (50) $Ph(SiCl_3)C=CH_2$ (50)
10[c]	**5**[BF_4]	PhC≡CH	(*E*)-PhCH=$CHSiCl_3$ (52) $Ph(SiCl_3)C=CH_2$ (48)
11[c]	**7**	PhC≡CH	(*E*)-PhCH=$CHSiCl_3$ (58) $Ph(SiCl_3)C=CH_2$ (42)

[a] Unless otherwise specified, all reactions were run in C_6D_6 at room temperature for 24 h using a Pd:(olefin/alkyne):$HSiCl_3$ ratio of 1:100:100. [b] 150 equiv of $HSiCl_3$ was used in this run. [c] In $CDCl_3$ at room temperature for 24 h.

Reactivities of Pd−Ind Complexes with Silanes. Previous studies have shown that Ni−Ind complexes can promote the dehydrogenative oligomerization of hydrosilanes and their additions to olefins and ketones.[6,7,4f,l,17] Our initial explorations on the reactivities of analogous Pd−Ind complexes indicated that the complexes **1** and **2** promote partial conversion of $PhSiH_3$ to products of a redistribution process (Ph_nSiH_{4-n}) and small amounts of Si−Si bond-containing products. These findings motivated us to investigate the reactivities of the Pd−Me and Pd−OTf complexes **3**, **4**, **7**, and **8** with $PhSiH_3$, as follows.

Addition of 100 equiv of $PhSiH_3$ to C_6D_6 solutions of the Pd complexes at room temperature caused an immediate darkening of the reaction mixture and led to a concomitant evolution of gas. Monitoring the reaction mixtures by ^1H NMR spectroscopy indicated that ca. 20% of $PhSiH_3$ was consumed over 20 min, after which the reaction subsided almost completely and an insoluble solid accumulated in the bottom of the NMR tube. The reactions promoted by the Pd−OTf complexes showed new signals characteristic of the dimer $(PhH_2Si)_2$ (<5%), leading us to conclude that these complexes do activate the Si−H bonds in $PhSiH_3$ and promote the formation of H−H[18] and Si−Si bonds, albeit fairly inefficiently. On the other hand, no new signal was detected in the reactions of the Pd−Me precursors. We speculate that these complexes promote the redistribution of Si−Ph and Si−H bonds in the initially formed $(PhSiH)_n$ to give SiH_4 (gas) and insoluble, cross-linked oligomers.

The low degree of substrate conversion and the difficulties in identification of the products of the above reactions prompted us to shift the focus of our studies away from silane oligomerization and onto hydrosilylation reactions. Initial tests with a range of different olefins and silanes showed that all complexes **1**−**8** can promote the addition of $HSiCl_3$ to styrene with the exclusive formation of 1-phenyl-1-(trichlorosilyl)ethane[19] in good yields (Table 5). Addition of $HSiCl_3$ to phenylacetylene was also examined briefly and found to give a mixture of the α-and *β*-addition products $Ph(SiCl_3)C=CH_2$ and (*E*)-PhCH=CH-$SiCl_3$ (Table 5, runs 9−11).[20] That these reactions likely proceed by the initial elimination of IndH was indicated by the reaction of the Pd−Me and Pd−Cl precursors with $HSiCl_3$ in the absence of olefin or alkyne substrates: an instantaneous darkening of the mixture was observed and the formation of IndH was confirmed from the ^1H NMR spectra, and the ^{31}P NMR spectrum of the mixture contained peaks at 36, 32, and 23 ppm, which remain unidentified.

Finally, addition of $HSiCl_3$ to ketones and esters and the more difficult hydrosilylation reactions with $PhSiH_3$, $HSiEt_3$, $HSi(OEt)_3$, and $HSiMe_2Cl$ were not catalyzed by our Pd complexes.

Conclusion

We have prepared and characterized the new Ind−Pd complexes [(1-R-Ind)Pd(PPh_3)Me] (R = H (**3**), Me (**4**)), [(1-R-Ind)Pd$(PPh_3)_2$]BF_4 (R = H (**5**[BF_4]), Me (**6**)), and [(1-R-Ind)Pd(PPh_3)(OTf)] (R = H (**7**), Me (**8**)) by reaction of their chloro analogues [(1-R-Ind)Pd(PPh_3)Cl] (R = H (**1**), Me (**2**)) with MeMgCl, $AgBF_4/PPh_3$ and AgOTf, respectively. Single-crystal X-ray diffraction studies on complexes **3**, **5**[BF_4], **6**, and **7** have shown that Pd−Ind interactions are influenced by the nature of the X ligands, the overall charge, and, to a lesser extent, the Ind substituents. The lability of the OTf moiety in triflate complex **7** has allowed us to generate the new cationic species $[IndPd(PPh_3)(L)]^+$ (L = PPh_3, PMe_3, CH_3CN, PhCN, *t*-BuNC). Exploring the reactivites of complexes **7** and **8** with olefins has shown that these complexes isomerize 1-hexene, dimerize ethylene and styrene, dimerize and trimerize *p*-fluorostyrene, oligomerize *p*-X-styrenes (X = NH_2, Me), and polymerize *p*-methoxystyrene. A brief examination of the reactivities of these complexes with hydrosilanes has shown that they are inefficient promoters of the dehydrogenative oligomerization of $PhSiH_3$ but catalyze the addition of $HSiCl_3$ to styrene and phenylacetylene.

The results of this study indicate that, contrary to our expectations, the preparations of (R-Ind)M(L)(X) complexes are more difficult for Pd relative to those for Ni, especially those derivatives bearing Ind substituents other than Me. Moreover, although the catalytic properties of the Pd complexes complement those of their Ni counterparts, the reactivities of the Ind−Pd compounds appear to be less easy to control and modulate. On the other hand, recent investigations have pointed out that another difference between these analogous complexes is the fairly easy access to aminopalladium derivatives of η^3- and η^1-Ind and dimeric (μ-Ind)Pd^I−Pd^I species. Studies are currently underway on the preparation, characterization, and reactivities of new Ind−Pd complexes and will be communicated in due course.

Experimental Section

General Comments. All manipulations and experiments were performed under an inert atmosphere using standard Schlenk techniques and/or a nitrogen-filled glovebox. Dry, oxygen-free solvents were prepared by distillation from appropriate drying agents and employed throughout. The syntheses of (Ind)Pd(PPh_3)Cl (**1**) and (1-Me-Ind)Pd(PPh_3)Cl (**2**) have been reported previously;[9] all other reagents used in the experiments were obtained from

(17) Chen, Y.; Sui-Seng, C.; Zargarian, D. *Organometallics* **2005**, *24*, 149.

(18) It is worth noting that the evolution of H_2 from the reactions of $PhSiH_3$ with Ind−Ni complexes has been observed previously.[6b]

(19) (a) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozomi, Y. *J. Org. Chem.* **2001**, *66*, 1441. (b) Bringmann, G.; Wuzik, A.; Breuning, M.; Henschel, P.; Peters, K.; Peters, E.-M. *Tetrahedron: Asymmetry* **1999**, *10*, 3025. (c) Uozomi, Y.; Tsuji, H.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 6137. (d) Ricard, L.; Marinetti, A. *Organometallics* **1994**, *13*, 3956. (e) Marinetti, A. *Tetrahedron Lett.* **1994**, *35*, 5861. (f) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143.

(20) (a) Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609. (b) Tamao, K.; Yoshida, J.-I.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355. (c) Auner, N.; Wagner, C.; Ziche, W. *Z. Naturforsch., B* **1994**, *49b*, 831.

commercial sources and used as received. The elemental analyses were performed by the Laboratoire d'Analyse Elémentaire (Université de Montréal). Bruker ARX400, AV400, AMX300, and AV300 spectrometers were employed for recording ^{1}H (400 and 300 MHz), ^{13}C{^{1}H} (100.56 and 75.42 MHz), ^{31}P{^{1}H} (161.92 and 121.49 MHz), and ^{19}F{^{1}H} NMR spectra (376.31 and 282.23 MHz) at ambient temperature. The ^{1}H and ^{13}C NMR spectra were referenced to solvent resonances, as follows: 7.26 and 77.16 ppm for C*H*Cl$_3$ and *C*DCl$_3$, respectively, and 7.16 and 128.06 ppm for C$_6$D$_5$*H* and *C*$_6$D$_6$, respectively. The ^{31}P and ^{19}F NMR spectra were referenced, respectively, to 85% H$_3$*P*O$_4$ (0 ppm) and C$_6$H$_5$C*F*$_3$ (−63.9 ppm). The IR spectra were recorded on a Perkin-Elmer 1750 FTIR instrument (4000−450 cm^{-1}) with samples prepared as KBr pellets.

Crystal Structure Determinations. The crystal data for complex **5**[BF$_4$] were collected on a Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation at 293 K using the CAD-4 software.[21] Refinement of the cell parameters was done with the CAD-4 software, while the data reduction used NRC-2 and NRC-2A.[22] The crystal data for complexes **3**, **6**, and **7** were collected on a Bruker AXS Smart 2K diffractometer using SMART.[23] Graphite-monochromated Cu Kα radiation was used at 223 K. Cell refinement and data reduction were done using SAINT.[24] All structures were solved by direct methods using SHELXS97[25] and difmap synthesis using SHELXL97;[26] the refinements were done on F^2 by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically, while the hydrogens (isotropic) were constrained to the parent atom using a riding model. The crystal data and experimental details are given in Tables 1 and 2, while selected bond distances and angles are given in Tables 3 and 4. The OTf moiety in the crystal structure of **7** was disordered over two positions, with occupancies of 0.54 and 0.46. Two positions were also found for the counterion BF$_4$ in the structures of **5**[BF$_4$] and **6** with occupancy factors of 0.54/0.46 and 0.50/0.50, respectively. One of the solvent molecules (CH$_2$Cl$_2$) present within the crystal structure of **6** was also disordered over two positions (occupancies of 0.62 and 0.38). Each of the disorders was refined anisotropically using restraints (SAME/SADI/EADP/DFIX) applied in order to improve the model.

Synthesis of (Ind)Pd(PPh$_3$)(Me) (3). A solution of MeMgCl (256 μL of a 3 M solution in THF) was added dropwise to a solution of (Ind)Pd(PPh$_3$)Cl (**1**; 400 mg, 0.77 mmol) in Et$_2$O (80 mL) at room temperature. The resulting orange mixture was stirred for approximately 1.5 h, filtered, and concentrated to give an orange precipitate, which was isolated by filtration (110 mg, 29%). Recrystallization of this solid from a cold Et$_2$O/hexane solution yielded crystals suitable for X-ray diffraction studies and elemental analysis. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 7.32−7.26 (m, PPh$_3$), 7.21 (pseudo dd, $^3J_{H-H}$ = 2.9 Hz, H_4 and H_7), 7.08 (pseudo dd, $^3J_{H-H}$ = 2.9 Hz, H_5 and H_6), 6.99−6.96 (m, PPh$_3$), 6.62 (t, $^3J_{H-H}$ = 3.1 Hz, H_2), 5.26 (pseudo t, $^3J_{H-H}$ = 3.5 Hz, H_1 and H_3), 0.57 (d, $^2J_{H-P}$ = 4.8 Hz, Pd−C*H*$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.56 MHz): δ 134.19 (d, $^2J_{C-P}$ = 13.5 Hz, C_{ortho}), 133.8, 132.45, 131.79, 131.54, 130.22 (s, C_{para}), 128.51 (d, $^3J_{C-P}$ = 11.8 Hz, C_{meta}), 126.62, 124.00, 122.20 (s, C_5 and C_6), 117.21 (s, C_4 and C_7), 108.59 (s, C_2), 83.37 (s, C_1 and C_3), −18.33 (d, $^2J_{C-P}$ = 12.6 Hz, Pd−*Me*). ^{31}P{^{1}H} NMR (CDCl$_3$, 161.92 MHz): δ 39.81 (s). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.49 MHz): δ 40.61 (s). Anal. Calcd for C$_{28}$H$_{25}$PPd·H$_2$O: C, 65.06; H, 5.26. Found: C, 65.63; H, 5.19.

Synthesis of (1-Me-Ind)Pd(PPh$_3$)Me (4). A solution of MeMgCl (93 μL of a 3 M solution in THF) was added dropwise to a solution of (1-Me-Ind)Pd(PPh$_3$)Cl (**2**) (165 mg, 0.309 mmol) in benzene (25 mL) at 10 °C. The resulting brown mixture was stirred for approximately 45 min, filtered, and evaporated to dryness. The residue was precipitated from Et$_2$O/hexane at −22 °C to give an orange powder (35 mg, 22%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.35−7.30 (m, PPh$_3$), 7.15 (m, PPh$_3$ and H_7), 7.00 (t, $^3J_{H-H}$ = 7.3 Hz, H_6), 6.88 (t, $^3J_{H-H}$ = 7.1 Hz, H_5), 6.78 (d, $^3J_{H-H}$ = 6.9 Hz, H_4), 6.41 (d, $^3J_{H-H}$ = 2.7 Hz, H_2), 5.34 (s, H_3), 2.07 (d, $^4J_{H-P}$ = 5.7 Hz, 1-*Me*-Ind), −0.12 (d, $^2J_{H-P}$ = 4.1 Hz, C*H*$_3$−Pd). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.56 MHz): δ 138.19, 134.61 (d, $^2J_{C-P}$ = 14.7 Hz, C_{ortho}), 132.11, 131.43, 129.99 (s, C_{para}), 128.76 (d, $^3J_{C-P}$ = 10.2 Hz, C_{meta}), 126.46, 124.92, 123.91, 122.40 (s, C_6), 121.64 (s, C_5), 119.25 (s, C_1), 116.61 (s, C_7), 115.53 (s, C_4), 109.42 (s, C_2), 81.52 (s, C_3), −9.32 (br, Pd−*Me*). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 161.92 MHz): δ 40.24 (s).

Synthesis of [(Ind)Pd(PPh$_3$)$_2$]BF$_4$ (5[BF$_4$]). A mixture of (Ind)Pd(PPh$_3$)Cl (**1**; 130 mg, 0.25 mmol), AgBF$_4$ (49 mg, 0.25 mmol), and PPh$_3$ (60 mg, 0.25 mmol) was stirred in CH$_2$Cl$_2$ (15 mL) for 1.5 h at room temperature and filtered to remove AgCl. Concentration of the filtrate to ca. 5 mL, followed by addition of 10 mL of Et$_2$O, gave a red-orange precipitate, which was isolated by filtration (180 mg, 87%). Recrystallization of a small portion of this solid from a cold CH$_2$Cl$_2$/Et$_2$O solution yielded crystals suitable for X-ray diffraction studies and elemental analysis. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.74−7.21 (m, PPh$_3$ and protons of Ind), 7.10−7.04 (m, PPh$_3$ and protons of Ind), 6.21 (dd, $^3J_{H-H}$ = 2.8 Hz, H_4 and H_7), 5.48 (q, $^3J_{H-H}$ = 3.9 Hz, H_1 and H_3). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.40 MHz): δ 133.54 (t, $^2J_{C-P}$ = 5.9 Hz, C_{ortho}), 131.43 (s, C_{para}), 130.16 (d, $^1J_{C-P}$ = 46 Hz, C_{ipso}), 130.17(s, C_5 and C_6), 129.06 (pseudo t, $^3J_{C-P}$ = 5.3 Hz, C_{meta}), 127.94 (s, C_4 and C_7), 118.83 (s, C_2), 95.46 (pseudo t, $^2J_{C-P}$ = 11.6 Hz, C_1 and C_3). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.49 MHz): δ 27.66 (s). Anal. Calcd for C$_{45}$H$_{37}$BF$_4$P$_2$Pd: C, 64.89; H, 4.48. Found: C, 64.36; H, 4.29.

Synthesis of [(1-Me-Ind)Pd(PPh$_3$)$_2$]BF$_4$ (6). A mixture of (1-Me-Ind)Pd(PPh$_3$)Cl (**2**; 100 mg, 0.19 mmol), AgBF$_4$ (37 mg, 0.19 mmol), and PPh$_3$ (50 mg, 0.19 mmol) was stirred in CH$_2$Cl$_2$ (15 mL) for 3 h at room temperature and filtered to remove AgCl. Concentration of the filtrate to ca. 5 mL, followed by addition of ca. 15 mL of Et$_2$O, gave an orange precipitate, which was isolated by filtration (144 mg, 90%). Recrystallization of a small portion of this solid from a cold CH$_2$Cl$_2$/hexane solution yielded crystals suitable for X-ray diffraction studies and elemental analysis. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.42−6.92 (m, PPh$_3$ and protons of Ind), 6.53 (d, $^3J_{H-H}$ = 7.3 Hz, H_4 or H_7), 6.23 (d, $^3J_{H-H}$ = 7.7 Hz, H_7 or H_4), 5.08 (dd, $^3J_{H-P}$ = 3 Hz, H_3), 1.29 (dd, $^3J_{H-H}$ = 11.4 and 11.5 Hz, 1-*Me*-Ind). ^{13}C{^{1}H} NMR (CDCl$_3$, 100.56 MHz): δ 133.46 (dd, $^2J_{C-P}$ = 26.7 Hz, $^4J_{C-P}$ = 11.8 Hz, C_{ortho}), 131.45 (dd, $^3J_{C-P}$ = 4.8 Hz, $^4J_{C-P}$ = 2.1 Hz, C_{3a}), 131.11 (dd, $^4J_{C-P}$ = 11.1 Hz, $^6J_{C-P}$ = 2.8 Hz, C_{para}), 130.19 (dd, $^1J_{C-P}$ = 45.4 Hz, $^3J_{C-P}$ = 2.1 Hz, C_{ipso}), 128.70 (dd, $^3J_{C-P}$ = 11.1 Hz, $^5J_{C-P}$ = 2.1 Hz, C_{meta}), 128.38 (dd, $^3J_{C-P}$ = 42.9 Hz, $^3J_{C-P}$ = 1.4 Hz, C_{7a}), 128.07 (s, C_5 or C_6), 126.96 (s, C_6 or C_5), 118.24 (s, C_4 or C_7), 117.38 (s, C_7 or C_4), 114.06 (dd, $^2J_{C-P}$ = 19.4 Hz, $^2J_{C-P}$ = 4.2 Hz, C_1), 112.26 (t, $^2J_{C-P}$ = 6.2 Hz, C_2), 90.15 (dd, $^2J_{C-P}$ = 19.4 Hz, $^2J_{C-P}$ = 4.9 Hz, C_3), 11.67 (d, $^3J_{C-P}$ = 4.8 Hz, *Me*). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.49 MHz): δ 29.94 (d, $^2J_{P-P}$ = 58.5 Hz, PPh$_3$), 28.60 (d, $^2J_{P-P}$ = 58.5 Hz, PPh$_3$). Anal. Calcd for C$_{46}$H$_{39}$P$_2$BF$_4$Pd·1.5CH$_2$Cl$_2$: C, 58.55; H, 4.34. Found: C, 58.16; H, 4.28.

Synthesis of (Ind)Pd(PPh$_3$)(OTf) (7). A mixture of (Ind)Pd(PPh$_3$)Cl (**1**; 250 mg, 0.48 mmol) and AgOTf (186 mg, 0.72 mmol) was stirred in CH$_2$Cl$_2$ (50 mL) for 2 h at room temperature and filtered to remove AgCl. Evaporation of the filtrate to dryness and crystallization of the residue from C$_6$H$_6$/hexane at room temperature

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gave the product as a brown-red precipitate (250 mg, 83%). Recrystallization of a small portion of this solid from a C_6H_6/hexane solution yielded crystals suitable for X-ray diffraction studies and elemental analysis. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42−7.34 (m, PPh_3), 7.32 (d, $^2J_{H-H}$ = 7.3 Hz, H_7), 7.15 (t, $^3J_{H-H}$ = 7.4 Hz, H_6), 7.04 (d, $^3J_{H-H}$ = 8.9 Hz, H_1), 6.87 (t, $^3J_{H-H}$ = 7.4 Hz, H_5), 6.77 (br, H_2), 6.29 (d, $^3J_{H-H}$ = 7.4 Hz, H_4), 4.68 (s, H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.56 MHz): δ 136.74 (s, C_{7a}), 135.57 (s, C_{3a}), 133.72 (d, $^2J_{C-P}$ = 12.3 Hz, C_{ortho}), 131.42 (s, C_{para}), 130.09 (d, $^1J_{C-P}$ = 45.5 Hz, C_{ipso}), 129.06 (d, $^3J_{C-P}$ = 9.9 Hz, C_{meta}), 128.65 (s, C_6), 127.65 (s, C_5), 121.24 (s, C_7), 117.65 (s, C_4), 111.78 (s, C_2), 102.51 (s, C_1), 73.18 (s, C_3). The ^{13}C NMR resonance of the triflate group could not be detected. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.92 MHz): δ 29.12 (s). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −80.06 (s). Anal. Calcd for $C_{28}H_{22}O_3F_3PSPd$: C, 53.13; H, 3.50; S, 5.07. Found: C, 53.06; H, 3.31; S, 4.69.

Synthesis of (1-Me-Ind)Pd(PPh_3)(OTf) (8). A mixture of (1-Me-Ind)Pd(PPh_3)Cl (**2**; 450 mg, 0.84 mmol) and AgOTf (325 mg, 1.27 mmol) was stirred in CH_2Cl_2 (50 mL) for 2 h at room temperature and filtered to remove AgCl. Evaporation of the filtrate to dryness and crystallization of the residue from C_6H_6/hexane at room temperature gave a brown-red powder (430 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43−7.37 (m, PPh_3), 7.32 (d, $^2J_{H-H}$ = 7.7 Hz, H_7), 7.16 (t, $^3J_{H-H}$ = 7.8 Hz, H_6), 6.87 (t, $^3J_{H-H}$ = 7.5 Hz, H_5), 6.55 (br, H_2), 6.13 (d, $^3J_{H-H}$ = 7.3 Hz, H_4), 4.54 (s, H_3), 2.09 (d, $^4J_{H-P}$ = 11.3 Hz, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.92 MHz): δ 31.39 (s). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −80.51 (s).

Ligand Substitution Reactions with 7. Substitution of the OTf ligand in **7** by L was monitored by spectroscopy, without isolating the resulting adducts. These reactions were carried out by adding 1 equiv of L to a 0.5 mL $CDCl_3$ solution of **7** (ca. 0.03 mmol) in an NMR tube. The NMR spectra of these samples were then measured at room temperature. The data are given below.

[(Ind)Pd(PPh_3)$_2$][OTf] (5[OTf]). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43−7.26 (m, PPh_3 and protons of Ind), 7.12−7.02 (m, PPh_3 and protons of Ind), 6.19−6.22 (m, H_4 and H_7), 5.48−5.44 (m, H_1 and H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.40 MHz): δ 133.77 (t, $^2J_{C-P}$ = 5.9 Hz, C_{ortho}), 131.68 (s, C_{para}), 130.04 (d, $^1J_{C-P}$ = 46 Hz, C_{ipso}), 129.38 (pseudo t, $^3J_{C-P}$ = 5.3 Hz, C_{meta}), 128.38 (s, C_5 and C_6), 118.88 (s, C_4 and C_7), 113.11 (s, C_2), 95.35 (pseudo t, $^2J_{C-P}$ = 11.6 Hz, C_1 and C_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.49 MHz): δ 27.73 (s). ^{19}F{^{1}H} NMR ($CDCl_3$, 282.23 MHz): δ −78.19 (s).

[(Ind)Pd(PPh_3)(PMe_3)][OTf] (9). ^{31}P{^{1}H} NMR (C_6D_6, 161.92 MHz): δ 30.05 (d, $^2J_{P-P}$ = 59.7 Hz), −16.66 (d, $^2J_{P-P}$ = 59.7 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −80.9 (s).

[(Ind)Pd(PPh_3)(CH_3CN)][OTf] (10). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55−7.45 (m, PPh_3), 7.36−7.27 (m, PPh_3), 7.16 (t, $^3J_{H-H}$ = 7.6 Hz, H_6), 7.05 (br, H_1 and H_7), 6.92 (t, $^3J_{H-H}$ = 7.6 Hz, H_5), 6.72 (pseudo t, $^3J_{H-H}$ = 3.6 Hz, H_2), 6.24 (d, $^3J_{H-H}$ = 7.6 Hz, H_4), 5.04 (br, H_3), 2.07 (s, *Me*CN). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.56 MHz): δ 135.47 (s, C_{7a}), 134.59 (s, C_{3a}), 133.77 (d, $^2J_{C-P}$ = 12.5 Hz, C_{ortho}), 131.61 (s, C_{para}), 129.28 (d, $^3J_{C-P}$ = 11.09 Hz, C_{meta}), 128.97 (s, C_6), 128.04 (s, C_5), 122.34 (s, C_7), 118.92 (s, C_4), 112.09 (s, C_2), 101.14 (d, $^2J_{C-P}$ = 18.6 Hz, C_1), 77.17 (s, C_3), 3.14 (s, CH_3CN). ^{31}P{^{1}H} NMR (C_6D_6, 121.49 MHz): δ 31.05 (s). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −80.8 (s). IR (KBr, cm^{-1}): 2291 (w), 2247 (w), 2186 (w).

[(Ind)Pd(PPh_3)(PhCN)][OTf] (11). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63−7.34 (m, PPh_3 and protons of Ind), 7.31−7.27 (m, protons of Ind and PhCN), 7.19−7.15 (m, protons of Ind and PhCN), 7.09−7.04 (m, protons of Ind and PhCN), 6.94 (t, $^3J_{H-H}$ = 7.6 Hz, H_5), 6.87 (pseudo t, $^3J_{H-H}$ = 2.7 Hz, H_2), 6.24 (d, $^3J_{H-H}$ = 7.6 Hz, H_4), 5.07 (br, H_3). ^{31}P{^{1}H} NMR (C_6D_6, 121.49 MHz): δ 30.97 (s). ^{19}F{^{1}H} NMR ($CDCl_3$, 376.31 MHz): δ −80.6 (s). IR (KBr, cm^{-1}): 2227 (m).

[(Ind)Pd(PPh_3)(*t*-BuNC)][OTf] (12). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62−7.24 (m, protons of Ind and PPh_3), 7.22−7.12 (m, protons of Ind and PPh_3), 7.10−6.95 (m, protons of Ind), 6.69 (br, H_2), 6.32 (d, $^3J_{H-H}$ = 7.5 Hz, H_4), 5.35 (br, H_3), 1.15 (s, CNC-(CH_3)$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.49 MHz): δ 30.05. ^{19}F{^{1}H} NMR ($CDCl_3$, 282.23 MHz): δ −78.2 (s). IR (KBr, cm^{-1}): 2206 (s).

Dimerization of Ethylene Catalyzed by Complexes 7 and 8. Ethylene was bubbled through $CDCl_3$ solutions of **7** and **8** (20 mg in 1 mL) for ca. 5 min prior to analysis by NMR. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.61 (d, $^3J_{H-H}$ = 5.0, CH_3 of (*Z*)-butene), 1.64 (dd, $^3J_{H-H}$ = 5.0 Hz, $^4J_{H-H}$ = 1.2 Hz, CH_3 of (*E*)-butene), 5.44 (m, vinylic H for both (*Z*)- and (*E*)-butenes).

Dimerization of Styrene Catalyzed by Complexes 7 and 8. Styrene (125 μL, 1 mmol) was added to a $CDCl_3$ solution of **7** or **8** (10 mg in 1 mL), and the sample was placed in an ultrasonic bath for 15 h to ensure mixing. Analysis by ^{1}H NMR showed a near-complete conversion of styrene to the dimer (*Z*)-1,3-diphenyl-1-butene. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18−6.98 (m, protons of Ph), 6.29 (br, PhC*H*═), 6.26 (dd, $^3J_{H-H}$ = 1 and 6.1 Hz), 3.38 (quintuplet, J_{H-H} = 6.74 Hz, C*H*), 1.27 (d, J_{H-H} = 7.1 Hz, C*H*$_3$). The GC/MS analysis of the NMR mixtures showed the presence of the dimer 1,3-diphenyl-1-butene ($M^{\bullet+}$, *m*/*z* 208; $M^{\bullet+} - CH_3^{\bullet}$, *m*/*z* 193; $M^{\bullet+}$ − PhH, *m*/*z* 130; $M^{\bullet+} - (PhH + CH_3^{\bullet})$, *m*/*z* 115; etc.), traces of styrene trimer for which the fragmentation pattern was nearly identical with that of the dimer, with the exception of the parent ion peak ($M^{\bullet+}$, *m*/*z* 312), and traces of IndC(Ph)═CH_2 ($M^{\bullet+}$, *m*/*z* 218; $M^{\bullet+} - CH_3^{\bullet}$, *m*/*z* 203; $M^{\bullet+}$ − C(Ph)═CH_2, *m*/*z* 115).

Reaction of Complex 7 with *p*-Fluorostyrene. This reaction was carried out in $CDCl_3$ at room temperature using 100 equiv of *p*-fluorostyrene. After the sample was agitated in an ultrasonic bath for 24 h, the mixture was subjected to NMR and GC/MS analyses that showed complete conversion of the monomer to dimeric and trimeric species. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39−7.01 (m, protons of Ph), 6.45−6.31 (m, C*H*═), 3.69 (quintuplet, J_{H-H} = 6.9 Hz, C*H*), 1.52, 1.34 (d, J_{H-H} = 7.1 Hz, C*H*$_3$). The GC/MS analysis of the sample showed the presence of the dimer (two isomers, totaling 66%) and a trimer (34%). The fragmentation patterns for the two isomers of the dimer were nearly identical: $M^{\bullet+}$, *m*/*z* 244; $M^{\bullet+} - CH_3^{\bullet}$, *m*/*z* 229; $M^{\bullet+} - (CH_3^{\bullet} + C_6H_5F)$, *m*/*z* 133; $[FC_6H_4CH_2]^{\bullet+}$, *m*/*z* 109. The fragmentation pattern for the trimer was nearly identical with that of the dimers, with the exception of the parent ion peak ($M^{\bullet+}$, *m*/*z* 366).

Reaction of Complex 7 with *p*-X-Styrenes (X = NH_2, Me, OMe). The reaction of *p*-aminostyrene was carried out on an NMR scale using 100 equiv of substrate (148 μL) in $CDCl_3$, at room temperature, for 24 h. The reactions with X = Me, OMe were carried out by stirring a mixture of **7** (ca. 20 mg, 0.0316 mmol) and a large excess of the olefin (4.25 mL, 1000 equiv) in toluene (4 mL) for 24 h at room temperature. Evaporation of the solvent and unreacted styrene gave an off-white solid, which was isolated and subjected to NMR and GPC analyses (in THF, relative to poly-(styrene) standards), as follows. X = NH_2: 150 mg, 100% yield; $M_w \approx 1050$, $M_w/M_n \approx 1.3$, $M_w \approx 1250$; ^{1}H NMR ($CDCl_3$) δ 7.08 (br), 6.72−6.48 (m), 4.49 (br), 3.79 (br) 2.49 (br), 1.87 (br), 1.32 (br). X = Me: 3.7 g, 88% yield; $M_w/M_n \approx 1.4$; ^{1}H NMR ($CDCl_3$) δ 7.33 (br), 6.59 (br), 2.55 (br), 1.46 (br). X = OMe: 4.1 g, 96% yield; $M_w \approx 29\,000$, $M_w/M_n \approx 3.2$; ^{1}H NMR ($CDCl_3$) δ 6.62 (br), 3.79 (br), 1.82 (br), 1.42 (br).

Reactivities of Complexes 7 and 8 with 1-Hexene. Monitoring the reaction of 1-hexene (0.1 mL, 0.80 mmol, 1.6 M in $CDCl_3$) with complexes **7** and **8** (ca. 10 mg, 0.016 mmol, 0.032 M in $CDCl_3$) by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy indicated the slow formation of (*E*)- and (*Z*)-2-hexenes (75:25) over 24 h. ^{13}C{^{1}H} NMR data for (*E*)-2-hexene: δ 13.8, 18.0, 22.7, 34.9, 124.8 and 131.5. ^{13}C{^{1}H} NMR data for (*Z*)-2-hexene: δ 12.8, 14.1, 25.7, 29.1, 123.9,

131.0. The GC/MS analysis of the NMR mixture for the reaction with complex **7** showed the presence of hexenes and traces of 1,3-hexenylindene: $M^{\bullet+}$, *m*/*z* 198; $M^{\bullet+} - 15$ (CH_3); $M^{\bullet+} - 29$ (CH_2-CH_3); $M^{\bullet+} - 43$ (Pr); $M^{\bullet+} - 57$ (Bu); etc.

Hydrosilylation of Styrene. The following general procedure was followed for the NMR-scale hydrosilylation experiments: to a $CDCl_3$ solution of styrene and $HSiCl_3$ (180−230 μL, 100 equiv of each) was added the Ind−Pd complex (ca. 10 mg, 0.02 mmol), and the sample was kept in an ultrasonic bath for 24 h to ensure agitation and homogeneity. Analysis by ^{1}H NMR ($CDCl_3$, 400 MHz) showed the formation of 1-phenyl-1-(trichlorosilyl)ethane: 7.19−7.11 (m, protons of the Ph), 2.56 (q, $^3J_{H-H} = 7.5$ Hz, C*H*), 1.41 (q, $^3J_{H-H} = 7.5$ Hz, C*H*$_3$). These data match literature values.[19a] The GC/MS analysis of the NMR mixtures showed only the hydrosilylation product ($M^{\bullet+}$, *m*/*z* 239). The conversions were determined on the basis of the ^{1}H NMR spectra of the reaction mixture; this was deemed as a reliable measure of the yields because no other products were detected in these reactions.

Hydrosilylation of Phenylacetylene. The following general procedure was followed for the NMR-scale hydrosilylation experiments: to a $CDCl_3$ solution of PhC≡CH and $HSiCl_3$ (190−210 μL, 100 equiv of each) was added the precursor complex (**1**−**8**, ca. 10 mg) and the sample placed in an ultrasonic bath for the duration of the reaction to ensure agitation and homogeneity. Analysis by ^{1}H NMR (C_6D_6, 400 MHz) showed that phenylacetylene had been completely hydrosilylated into a 1:1 mixture of 1-phenyl-2-(trichlorosilyl)ethylene and 1-phenyl-1-(trichlorosilyl)-ethylene. ^{1}H NMR: for 1-phenyl-2-(trichlorosilyl)ethylene, δ 7.85 (d, $^3J_{H-H} = 16$ Hz, PhC*H*═), 7.70−7.50 (m, protons of Ph), 6.93 (d, $^3J_{H-H} = 16$ Hz, ═C*H*$SiCl_3$); for 1-phenyl-1-(trichlorosilyl)-ethylene, δ 7.70−7.50 (m, protons of Ph), 6.28 and 6.04 (s, ═C*H*$_2$). The GC/MS analysis of the NMR mixtures showed the presence of the hydrosilylation product ($M^{\bullet+}$, *m*/*z* 237).

Acknowledgment. This work was made possible thanks to the financial support provided by the Natural Sciences and Engineering Research Council of Canada (operating grants to D.Z.) and Université de Montréal (scholarships to C.S.-S.). We are also indebted to Julie Boivin for help with the GPC analyses, to Johnson Matthey for the generous loan of $PdCl_2$, to Dr. M. Simard and Mme F. Bélanger-Gariépy for their assistance with the X-ray diffraction studies, and to Prof. F. Schaper for helpful discussions.

Supporting Information Available: Complete details of the X-ray analysis of **3** and **5**−**7**, including tables of crystal data, collection and refinement parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited at the Cambridge Crystallographic Data Centre (CCDC 283700−283703). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033.

OM050826F