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Electrophilic Cationic Palladium(II) Complexes Containing a Diimine Ligand with Pendant Thienyl Groups. X-ray Structure of {Pd^{II}Me[1,4-bis(2′-(2-thienyl)ethyl)2,3-dimethyl-1,4-diazabutadiene]}$^+$

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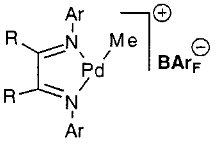
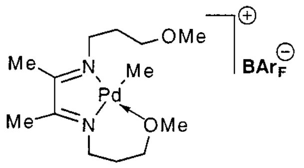
*Summary: Cationic Pd(II) complexes [(N_2S_2)Pd(II)Me][BAr_F] (**3**) and [(N_2S_2)Pd(II)][SO_3CF_3]$_2$ (**7**) have been synthesized by using a new diimine ligand 1,4-bis(2′-(2-thienyl)ethyl)-2,3-dimethyl-1,4-diazabutadiene (N_2S_2) that contains semilabile pendant thienyl groups. Both complexes activated the Et_3Si-H bond and catalyzed the isomerization of 1-hexene to internal hexenes.*

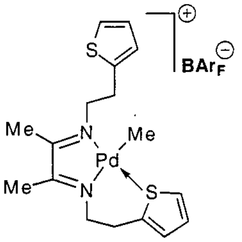
Since the first report from Brookhart's group on aryl diimine cationic Pd(II) complexes with bulky substituents, e.g., **1**, as highly active catalysts for copolymerization of α-olefins with functional vinyl monomers, this area has attracted great attention.[1] Bulky aryls are used to disfavor associative displacement and chain transfer to afford high molecular weight polymers. An alkyl-substituted diimine ligand with sidearms containing labile functional groups might hinder the β-elimination process by temporarily occupying a vacant site and serve the same purpose. Yet we are not aware of any report on such labile-group substituted alkyl−diimine Pd(II) complexes except for our recent study on a methoxypropyl-substituted Pd(II) complex [($MeOCH_2CH_2CH_2N$=C(Me)C(Me)=$NCH_2CH_2CH_2OMe$)PdMe][BAr_F] (BAr_F = B(3,5-$(CF_3)_2C_6H_3)_4$) (**2**).[2] In addition, the semilabile methoxy group was found to stabilize a cationic Pt(IV) complex, [PtH(Me)(Et_3Si)($MeOCH_2CH_2CH_2N$=C(Me)C=N(Me)CH_2-CH_2CH_2OMe)]$^+$, formed by the oxidative addition of Et_3Si-H to the respective Pt(II) cation. The stabilization of Pt(IV) hydride is presumably due to the coordination of a MeO group to the vacant sixth site. We feel it is of interest to further explore diimine complexes with other semilabile sidearms. We report here such a cationic Pd(II) species, **3**, containing the ligand 1,4-bis(2′-(2-thienyl)ethyl)-2,3-dimethyl-1,4-diazabutadiene (N_2S_2).



1



2



3

In an attempt to prepare the thio analogue of **2**, a methylthiopropyl-substituted diimine Pd(II) complex, PdClMe($MeSCH_2CH_2CH_2N$=C(Me)C(Me)=NCH_2CH_2-CH_2SMe), was synthesized using the same method for the preparation of **2**. However, reaction of this complex with $NaBAr_F$ did not afford an isolable cation, i.e., [PdMe($MeSCH_2CH_2CH_2N$=C(Me)C(Me)=$NCH_2CH_2CH_2$-SMe)]$^+$. Considering the easy intramolecular C−H activation of the *CH_2*OMe group in complex **2** that led to a cationic tricyclic Pd(II) complex,[2] it is reasonable to expect the above desired cation might decompose through a similar initial C−H activation process of *CH_2*-SMe. Hindrance of this C−H activation process presumably should stabilize the resulting Pd(II) cation; therefore ligand **4** with a (2-thienyl)ethyl group is chosen because of its lack of a readily accessible C−H group adjacent to sulfur. Furthermore, because thiophene is a notoriously weak ligand to transition metals,[3] it would be of interest to see if this functionality would coordinate to Pd(II) aided by the favorable entropy for intramolecular interaction. Most reports on thiophene-containing Pd(II) complexes describe only nonparticipating thiophene groups except for the complex Pd(SDPDTP), where a thienyl is incorporated in a porphyrin macrocycle (SDPDTP = 5,10-di(*p*-toluenyl)-15,20-diphenyl-21-thiaporphyrinide).[4] In the latter complex, one thienyl group replaces a pyrrole in the porphyin molecule.

Compound **4** (N_2S_2) was readily synthesized by reaction of 2,3-butadione with (2-thienyl)ethylamine (Scheme

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(1) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

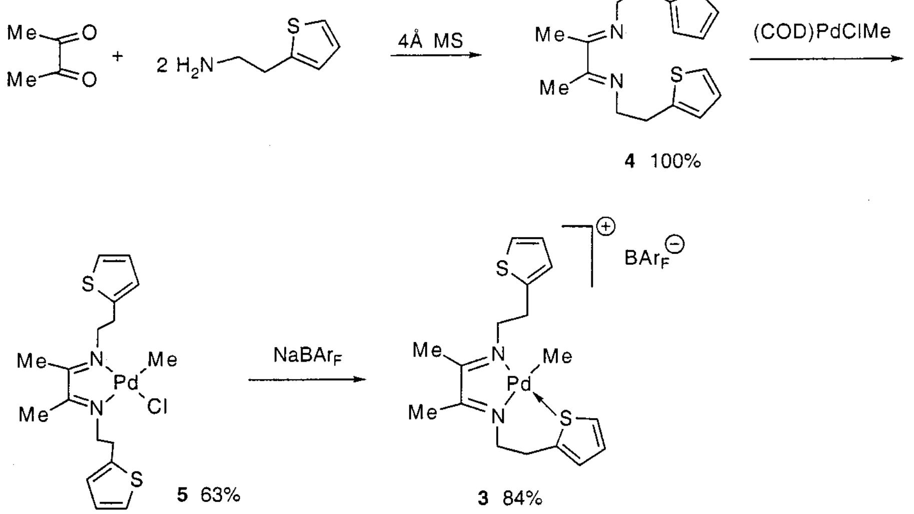
(2) Fang, X.-G.; Scott, B. L.; Watkin, J. G.; Kubas, G. J. *Organometallics* **2000**, *19*, 4193.

(3) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073.

(4) (a) Lato-Grazynski, L.; Lisowski, J.; Chmielewski, P.; Grzeszczuk, M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1994**, *33*, 192. For selected recent examples of a Pd/Pt complex containing nonparticipating thiophene groups: (b) Du Toit, A.; Landman, M.; Lotz, S. *J. Chem. Soc., Dalton Trans.* **1997**, 2955. (c) Xie, Y.; Wu, B.-M.; Xue, F.; Ng. S.-C.; Mak, T. C. W.; Hor, T. S. A. *Organometallics* **1998**, *17*, 3988. (d) Anderson, C.; Crespo, M.; Font-Bardia, M.; Klein, A.; Solans, X. *J. Organomet. Chem.* **2000**, *601*, 22. (e) Riera, X.; Caubet, A.; Lopez, C.; Moreno, V.; Solans, X.; Font Bardia, M. *Organometallics* **2000**, *19*, 1384.

10.1021/om001071+ CCC: $20.00

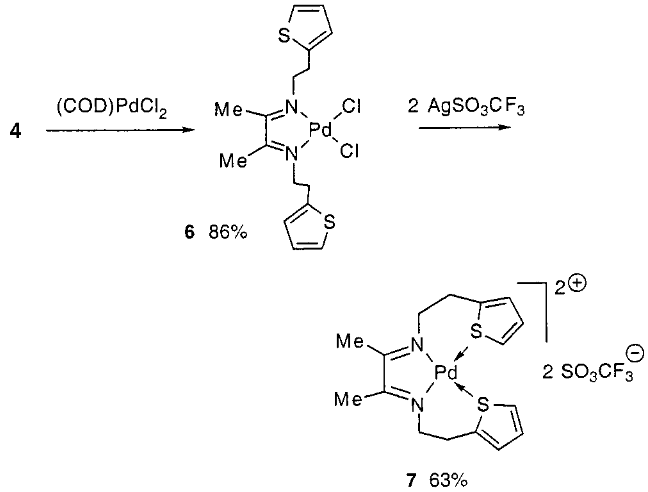
Scheme 1



1; MS = molecular sieve). Treatment of **4** with PdClMe(COD) gave the neutral complex **5** in 63% yield. Metathesis of **5** with NaBAr$_F$ led to the desired cationic species **3** as yellow crystals in 84% yield. In contrast to the easy C−H activation of **2** and the hypothetical cation, [PdMe(MeSCH$_2$CH$_2$CH$_2$N=C(Me)C(Me)=NCH$_2$CH$_2$CH$_2$SMe)]$^+$, complex **3** is indeed very stable. The NMR spectra of a solution of **3** in CDCl$_3$ did not show any change after several days at room temperature.

The ^{1}H NMR spectrum of **3** showed two distinctive sets of signals for the two (2-thienyl)ethyl groups, indicating one arm is bound to the Pd(II) while the other is free. For example, the methylene groups attached to the thienyl have chemical shifts at δ 3.81 and 3.95, respectively. When **3** was treated with excess 1-hexene, a black precipitate (Pd) formed, 1-hexene was transformed into a mixture of 2- and 3-hexenes, and no poly(hexene) was produced (GC−MS evidence). It seems that the semilabile sulfur atom could not prevent the competing β-hydride elimination process by occupying the vacant site (the elimination hinders polymerization). When Et$_3$SiH was added to a solution of **3** in CD$_2$Cl$_2$ at −78 °C, its ^{1}H NMR spectrum became very complicated. Unexpectedly, there was no high-field signal corresponding to a silane σ complex as was observed for the analogous complex **2**. The solution immediately turned black when warmed to room temperature, indicating decomposition to Pd metal. GC−MS analysis of the volatiles showed mostly Et$_3$SiCl and some (Et$_3$Si)$_2$O. Apparently Et$_3$SiH initially coordinated to the Pd center by displacing a bound thienyl pendant group, and subsequently the coordinated η^2-H-SiEt$_3$ ligand underwent heterolytic cleavage to produce the highly reactive silyl cation, SiEt$_3$$^+$, and an unstable methyl hydride species that decomposed to Pd black. The (Et$_3$Si)$_2$O was presumably formed by the reaction of SiEt$_3$$^+$ with adventitious H$_2$O, and Et$_3$SiCl was formed by attack of SiEt$_3$$^+$ on CD$_2$Cl$_2$ solvent. Alternately, the coordinated Si in a transient σ-silane complex underwent concerted attack by solvent/water to give the same products. The result is similar to what was observed for **2**, but differs from the result of the reaction of Et$_3$SiH with [Pt^{II}Me(MeOCH$_2$CH$_2$CH$_2$N=C(Me)C(Me)=NCH$_2$CH$_2$CH$_2$OMe)]$^+$, where a Pt(IV) hydrido-silyl was produced on oxidative addition of the Si−H bond.[2] When Et$_3$SiH was added to a solution of **3** in toluene-d_8, a blackish mixture still formed. GC−MS analysis of the volatiles showed the major component to be (Et$_3$Si)$_2$O, and no Et$_3$SiCl was detected.

Scheme 2



Complex **3** did not activate the C−D bonds in C$_6$D$_6$ or C$_6$D$_5$CD$_3$, and thus it is stable in these two solvents. It is reasonable to expect that removal of the remaining methyl group on the Pd(II) center in **3** should make the metal center more electrophilic, which in turn might induce it to activate C−H bonds. Unexpectedly, in an attempt to remove the Me, neither Ph$_3$CBAr$_F$ nor H(OEt$_2$)$_2$BAr$_F$ even reacted with complex **3**. Eventually a dicationic species **7** was prepared by another route as shown in Scheme 2. Reaction of **4** with PdCl$_2$(COD) afforded PdCl$_2$(N$_2$S$_2$), **6**, in 86% yield. Treatment of **6** with excess NaBAr$_F$ gave a clean product that has a ^{1}H NMR spectrum consistent with only one chloride being metathesized.[5] Reaction of **6** with 2 equiv of AgOSO$_2$CF$_3$ led to the desired dicationic complex **7**, which was characterized by ^{1}H, ^{13}C NMR spectroscopy and elemen-

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(5) ^{1}H NMR (CD$_2$Cl$_2$): δ 2.02 (s, 3H), 2.22 (s, 3H), 2.80 (t, 2H, J = 7.2 Hz), 3.31 (t, 2H, J = 5.8 Hz), 3.50 (t, 2H, J = 7.2 Hz), 3.93 (br, 2H), 6.52 (d, 1H, J = 5.4 Hz), 6.57 (d, 1H, J = 3.7 Hz), 6.89 (m, 1H), 7.12−7.21(m, 3H), 7.73 (s, 4H), 8.03 (s, 8H).

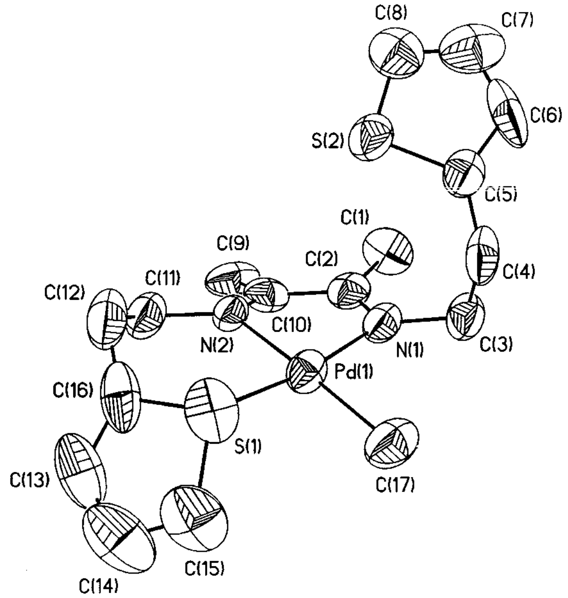

Figure 1. Drawing of the cation {Pd^{II}Me[1,4-bis(2-(2-thienyl)ethyl)-2,3-dimethyl-1,4-diazabutadiene]}$^+$, **3** (thermal ellipsoids are drawn at the 50% level). Selected bond distances (Å) and angles (deg): Pd−N(1), 2.059(6); Pd−N(2), 2.145(5); Pd−C(17), 2.014(7); Pd−S(1), 2.257(2); S(1)−C(15), 1.712(11); S(1)−C(16), 1.750(9); S(2)−C(8), 1.697(14); S(2)−C(5), 1.704(12). N(1)−Pd−N(2), 77.7(2); N(2)−Pd−S(1), 98.98(18); S(1)−Pd−C(17), 88.3(3); C(17)−Pd−N(1), 96.3(s); N(1)−Pd−S(1), 171.40(18).

Table 1. Crystallographic Data of Compound 3[a]

empirical formula	$C_{49}H_{35}BF_{24}N_2PdS_2$
fw	1289.12
space group	$P\bar{1}$
λ, Å	0.71073
temp (K)	203(2)
a (Å)	12.478(1)
b (Å)	12.6904(9)
c (Å)	18.4723(15)
α (deg)	95.783(1)
β (deg)	104.743(1)
γ (deg)	108.212(2)
volume (Å^3)	2634.7(4)
Z	2
ρ_{calc} (g cm^{-1})	1.625
μ (mm^{-1})	0.553
final R indices	R1 = 0.0540, wR2 = 0.1274

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0752P)^2]$.

tal analysis. Unfortunately crystals suitable for X-ray structural analysis could not be obtained. The ^{1}H NMR spectrum of **7** shows one set of signals for the two (2-thienyl)ethyl groups, indicating that two identical pendant groups are likely to be coordinated to the Pd(II) atom. Reaction of **7** with excess 1-hexene again transformed 1-hexene to a mixture of 2- and 3-hexenes. Similar to that found for complex **3**, treatment of **7** in CD_2Cl_2 with Et_3SiH led to precipitation of Pd black, and the volatiles of the reaction mixture are mostly Et_3SiCl and $(Et_3Si)_2O$. Last, complex **7** does not react with C_6D_6.

To determine how the thienyl group in complex **3** coordinates to Pd(II), a single-crystal X-ray structural analysis was performed. The molecular structure of the cationic part is shown in Figure 1, and the crystallographic data are listed in Table 1. The structure shows one thienyl group coordinated to the Pd(II) center through the sulfur atom, while the other group orients away from the metal center, consistent with NMR results. The overall geometry around the Pd(II) atom is square planar. A search of the Cambridge Structural Data Base found no report on sulfur−palladium complexes containing an additional one carbon and two nitrogen atoms.[6] The Pd−S(1) distance of 2.257(2) Å is longer than the value 2.208(5) Å found for the closest analogue, Pd(SDPDTP),[4a] but is within the normal range found for other Pd−S complexes.[7] The Pd−C(17) distance of 2.014(7) Å is within normal values of Pd−C distances.[8]

In summary, novel cationic Pd(II) complexes **3** and **7** containing a (2-thienyl)ethyl-substituted diimine ligand have been synthesized. These complexes are more stable than the analogous methoxypropyl-subsituted diimine Pd(II) complex **2**. Both complexes catalyze the isomerization of 1-hexene to internal hexenes and activate the Si−H bond of Et_3SiH. An analogous complex with a dimethylaminopropyl-substituted diimine has been prepared,[9] but the Me_2N group coordinates to the Pd(II) very tightly and could not be displaced by Et_3SiH or 1-hexene under similar conditions. The influence of the semilabile groups needs to be further explored and further reactions carried out in order to define the mechanistic aspects of the olefin isomerization process (e.g., that for **3** versus **7**) and other chemistry of these complexes.

Experimental Section

All manipulations were performed either under a helium atmosphere in a Vacuum Atmospheres drybox or under an argon atmosphere using standard Schlenk techniques unless otherwise specified. Hexane, toluene, ether, and THF were purified by passing through columns of activated alumina and activated Cu-0226 S copper catalyst (Engelhard). CH_2Cl_2 and $CDCl_3$ were purchased from Aldrich and dried under 4 Å molecular sieves. PdClMe(COD),[10] NaBAr$_F$,[11] H(OEt$_2$)$_2$BAr$_F$,[11] and Ph$_3$CBAr$_F$[12] were prepared as reported. PdCl$_2$(COD) and AgSO$_3$CF$_3$ were purchased from Strem Chemicals and used as received. Other reagents were purchased from Aldrich and Acros Chemicals and used as received. ^{1}H and ^{13}C spectra were recorded on a Varian Unity 300 spectrometer with field strengths of 300 and 75 MHz, respectively. ^{1}H and ^{13}C chemical shifts were referenced to the residual solvent resonance relative to TMS. Elemental analyses were performed in house on a Perkin-Elmer Series II CHNS/O model 2400 analyzer.

1,4-Bis(2′-(2-thienyl)ethyl)-2,3-dimethyl-1,4-diazabutadiene (N$_2$S$_2$, 4). 2′-(2-Thienyl)ethylamine (2.06 mL, 17.06 mmol) was added to a flask containing 4 Å molecular sieves (10 g) and toluene (20 mL) followed by 2,3-butadione (0.70 mL,

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[6] *CSD*, version 5.20, October 2000.

[7] (a) Riera, X. Moerno, V.; Font-Bardia, M. Solans, X. *Polyhedron* **1998**, *17*, 1. (b) Hueso-Urena, F.; Illan-Cabza, N. A.; Moreno-Carretero, N. N. M.; Penas-Chamorro, A. L.; Faure, R. *Inorg. Chem. Comm.* **1999**, *2*, 323. (c) Ghassemzadeh, M.; Bolourtchian, M.; Chitsaz, S.; Neumuller, B.; Heravi, M. M. *Eur. J. Inorg. Chem.* **2000**, 1877.

[8] (a) Rix, R. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436. (b) Alsters, P. L.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1639.

[9] [PdMe(Me$_2$NCH$_2$CH$_2$CH$_2$N=C(Me)C=N(Me)CH$_2$CH$_2$CH$_2$NMe$_2$)][BAr$_F$]: ^{1}H NMR (CD$_2$Cl$_2$) δ 0.70 (s, 3H), 1.70 (qint, 2H, J = 7.6 Hz), 1.97 (br, 2H), 2.14 (s, 3H), 2.20 (s, 6H), 2.29 (s, 3H), 2.30 (m, 2H), 2.57 (s, 6H), 2.66 (m, 2H), 3.47 (br, 2H), 3.64 (t, 2H, J = 7.7 Hz), 7.56 (s, 4H), 7.74 (s, 8H); ^{13}C NMR (CD$_2$Cl$_2$) δ 9.6, 19.7, 20.0, 27.4, 29.2, 47.0, 53.3, 53.6, 54.4, 58.2, 66.4, 174.4, 178.4.

[10] Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

[11] Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

[12] Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545.

8.0 mmol). The mixture was stirred overnight at RT and then filtered through Celite. Volatiles were removed under reduced pressure to give product (2.71 g, 100%) as a yellowish liquid. ^{1}H NMR (CDCl$_3$): δ 2.08 (s, 6H), 3.26 (t, 4H, $J = 6.8$ Hz), 3.69 (t, 4H, $J = 6.8$ Hz), 6.89 (br s, 2H), 6.95 (t, 2H, $J = 4.2$ Hz), 7.15 (d, 2H, $J = 4.2$ Hz). ^{13}C NMR (CDCl$_3$): δ 13.1, 31.7, 54.1, 123.8, 125.1, 126.7, 143.4, 168.8. MS (EI): 302, 192, 97.

PdClMe(N$_2$S$_2$), 5. PdClMe(COD) (0.100 g, 0.38 mmol) was added to a solution of **4** (0.129 g, 0.42 mmol) in CH$_2$Cl$_2$ (2 mL) at −30 °C. The resulting solution was warmed to RT and stirred for 15 min. Volatiles were removed, and the residue was washed with hexane to give a yellow solid. Crystallization from CH$_2$Cl$_2$/hexane at −30 °C afforded product (0.110 g, 63%) as a yellow solid. ^{1}H NMR (CDCl$_3$): δ 0.95 (s, 3H), 1.61 (s, 3H), 1.70 (s, 3H), 3.25 (t, 2H, $J = 6.7$ Hz), 3.43 (t, 2H, $J = 6.8$ Hz), 3.97 (t, 2H, $J = 6.7$ Hz), 4.16 (t, 2H, $J = 6.8$ Hz), 6.84−6.95 (m, 4H), 7.14−7.20 (m, 2H). ^{13}C NMR (CDCl$_3$): δ −0.1, 18.1, 19.3, 31.2, 31.3, 55.3, 56.3, 126.0, 126.4, 127.9, 128.1, 128.7, 128.9, 141.3, 142.6, 171.6, 177.2. Anal. Calcd for $C_{17}H_{23}ClN_2S_2Pd$: C, 44.25; H, 4.99; N, 6.07. Found: C, 43.84; H, 5.29; N, 5.85.

[PdMe(N$_2$S$_2$)][BAr$_F$], 3. CH$_2$Cl$_2$ (3 mL) was added to a mixture of **5** (0.056 g, 0.12 mmol) and NaBAr$_F$ (0.108 g, 0.12 mmol) at RT. The resulting mixture was stirred for 20 min at RT and then filtered through Celite. Volatiles were removed under reduced pressure and residue was crystallized from Et$_2$O/hexane at −30 °C to give product (0.120 g, 84%) as yellow crystals. ^{1}H NMR (CD$_2$Cl$_2$) δ 0.98 (s, 3H), 1.94 (s, 3H), 2.09 (s, 3H), 3.17−3.24 (m, 4H), 3.81 (br t, 2H, $J = 5.0$ Hz), 3.95 (t, 2H, $J = 6.8$ Hz), 6.86 (dd, 1H, $J = 3.4$, 0.7 Hz), 6.96 (dd, 1H, $J = 5.1$, 3.4 Hz), 7.07 (d, 1H, $J = 2.4$ Hz), 7.20−7.29 (m, 3H), 7.59 (s, 4H), 7.75 (s, 8H). ^{13}C NMR (CD$_2$Cl$_2$): δ 1.3, 18.7, 18.8, 28.4, 29.6, 54.4, 57.5, 117.9−138.7 (BAr$_F$ and thienyl), 138.7 (SC), 144.5 (SC), 162.2 (q, $J_{CF} = 49.7$, CF3), 174.7 (NC), 179.0 (NC). Anal. Calcd for $C_{45}H_{35}B F_{24}N_2S_2Pd$: C, 45.65; H, 2.72; N, 2.17. Found: C, 45.39; H, 2.81; N, 2.08.

PdCl$_2$(N$_2$S$_2$), 6. A mixture of PdCl$_2$(COD) (0.349 g, 1.22 mmol) and **4** (0.445 g, 1.46 mmol) was suspended in CHCl$_3$ (8 mL) at RT. The mixture was stirred overnight at RT to give a yellow suspension. The suspension was filtered through a frit and washed with hexane to give product (0.505 g, 86%) as a yellow solid. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.76 (s, 6H), 3.38 (t, 4H), $J = 7.2$ Hz), 4.13 (t, 4H, $J = 7.2$ Hz), 6.92−6.97 (m, 4H), 7.22 (dd, 2H, $J = 6.0$, 1.3 Hz). ^{13}C NMR (CD$_2$Cl$_2$): δ 18.6, 30.2, 56.4, 125.3, 127.2, 127.7.

[Pd(N$_2$S$_2$)][CF$_3$SO$_3$]$_2$, 7. A mixture of **6** (0.082 g, 0.17 mmol) and AgSO$_3$CF$_3$ (0.096 g, 0.36 mmol) in CH$_2$Cl$_2$ (7 mL) was stirred at RT for 3 days to give a yellow suspension. The suspension was filtered through Celite, and volatiles were then removed under reduced pressure to give a yellow solid. The solid was washed with hexane and dried to give product (0.060 g, 63%) as a yellow solid. ^{1}H NMR (CDCl$_3$): δ 2.28 (s, 6H), 3.28 (t, 4H, $J = 6.8$ Hz), 3.86 (t, 4H, $J = 6.8$ Hz), 7.18−7.23 (m, 4H), 7.38 (d, 2H, $J = 4.4$ Hz). ^{13}C NMR (CDCl$_3$): δ 19.5, 29.0, 56.5, 125.9, 128.6, 131.8, 139.8, 185.8. Anal. Calcd for $C_{18}H_{20}F_6N_2O_6S_4Pd$: C, 30.72; H, 2.84; N, 3.98. Found: C, 30.84; H, 2.99; N, 3.80.

Typical Procedures for the Reactions of 3 or 7 with 1-Hexene or Et$_3$SiH. To a solution of **3** in CD$_2$Cl$_2$ at −78 °C was added 1−1.3 equiv of Et$_3$SiH. NMR spectra were recorded immediately from −78 °C to RT, but no signals for bound silane were observed. The solution turned black, and GC−MS analysis of the volatiles showed mostly Et$_3$SiCl and some (Et$_3$Si)$_2$O. Similar experiments were carried out using 1-hexene.

X-ray Structure Determination of 3. An orange, irregular crystal was attached to a glass fiber using a spot of silicone grease. The air-sensitive crystal was mounted from a matrix of mineral oil under an argon flow. The crystal was immediately placed on a Bruker P4/CCD/PC diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected using a sealed, graphite-monochromatized Mo Kα X-ray source. A hemisphere of data was collected using a combination of φ and ω scans, with 20 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART[13] software. Frame integration and final cell parameter calculation were carried out using SAINT[14] software. The data were corrected for absorption using the SADABS[15] program. Decay of reflection intensity was not observed.

The structure was solved in space group $P\bar{1}$ using direct methods and difference Fourier techniques. The initial solution revealed the platinum and the majority of all non-hydrogen atom positions. The remaining atomic positions were determined from subsequent Fourier synthesis. Hydrogen atom positions were fixed (C−H = 0.93 Å for aromatic, 0.97 Å for methylene, and 0.96 Å for methyl). The hydrogen atoms were refined using the riding model, with isotropic temperature factors fixed to 1.5 (methyl) or 1.2 (methylene and aromatic) times the equivalent isotropic U of the carbon atom they were bound to. The unbound thienyl portion of the ligand was disordered over two sites; the C6 and S2 atom positions were modeled as partial occupancy sulfur and carbon, S2′ and C6′, respectively. The site occupancies of the carbon and sulfur atoms on these sites were allowed to vary, with the total occupancy tied to one. The occupancies converged to 0.68(2) for S2 and C6. The final refinement included anisotropic temperature factors on all non-hydrogen atoms except C6′ and converged with final residuals of $R1(I > 2\sigma) = 0.0540$ and $R2_w(I > 2\sigma) = 0.1274$. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.[16] Additional details of data collection and structure refinement are listed in Table 1.

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Supporting Information Available: Detailed X-ray crystallographic data of the structure of compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] *SMART*, Version 4.210; Bruker Analytical X-ray Systems, Inc.: 6300 Enterprise Lane, Madison, WI 53719, 1996.

[14] *SAINT*, Version 4.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI 53719, 1996.

[15] Sheldrick, G. *SADABS*; University of Göttingen: Germany, 1996.

[16] *SHELXTL NT*, Version 5.10; Bruker Analytical X-ray Instruments, Inc.: Madison, WI 53719, 1997.