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C−H and Si−H Activation on Palladium(II) and Platinum(II) Complexes with a New Methoxyalkyl-Substituted Diimine Ligand

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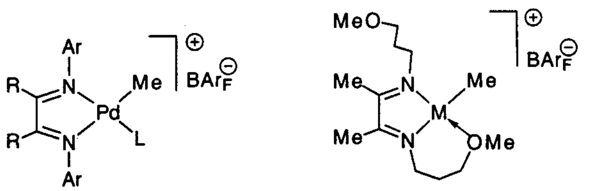
Summary: Electrophilic 1,4-bis(methoxypropyl)-2,3-dimethyl-1,4-diazabutadiene Pd(II) and Pt(II) cations ***2a***,***b*** *with a* BAr_F *counteranion have been prepared. Complex* ***2a*** *undergoes intramolecular C−H activation to form tricyclic* ***5****, and complex* ***2b*** *adds to* Et_3SiH *to form an octahedral diimine Pt(IV) silyl hydride complex,* ***7****.*

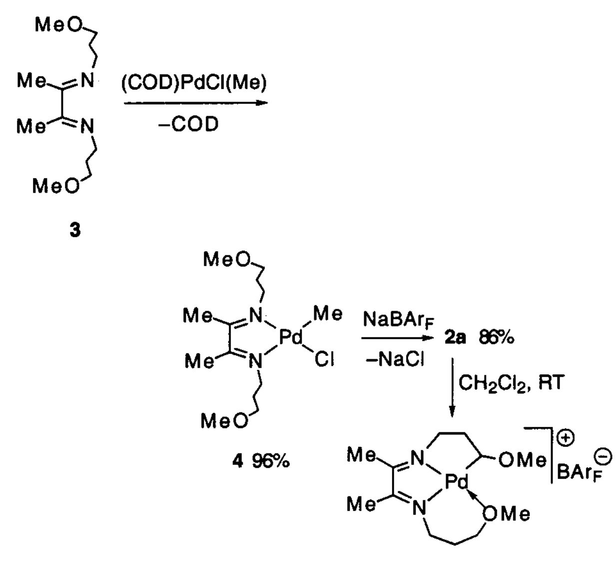
Since the first report from Brookhart's group on aryl diimine cationic Pd(II) complexes with bulky substituents, **1**, as highly active catalysts for copolymerization of α-olefins with functional vinyl monomers, this area has attracted great attention.[1] A significant amount of



1 M = Pd (**2a**), Pt (**2b**)

research has aimed at tuning the electronic and steric environments by changing aryl substituents or replacing one aryl with an alkyl group, which leads to complexes of diverse olefin polymerization properties.[2] Bulky aryls are used to disfavor associative displacement and chain transfer to afford high-molecular-weight polymers. An alkyl-substituted diimine ligand with side arms containing labile functional groups might hinder the β-elimination process by temporarily occupying a vacant site and serve the same purpose. We are not aware of any report on such alkyl-substituted diimine Pd(II) complexes and report here the first examples of such Pd(II) and Pt(II) complexes (**2a**,**b**) with a new methoxyalkyl-substituted diimine ligand. **2a** activates the C−H bond of the CH_2 unit proximal to a pendant methoxy, and we also find that **2b** oxidatively adds $HSiEt_3$ to form an octahedral Pt(IV) silyl hydride complex.

Cationic **2a** with the weakly coordinating BAr_F anion ($B[C_6H_3(3,5\text{-}CF_3)_2]_4$) is readily synthesized (eq 1).[3] Reaction of 3-(methoxypropyl)-substituted diazabutadiene (**3**,



(1)

denoted as NN) with (COD)PdCl(Me)[4] affords the neutral complex (NN)PdCl(Me) (**4**) as yellow crystals, for which a single-crystal X-ray structure has been obtained.[5] The side arms orient away from Pd as shown in eq 1. Metathesis of **4** with $NaBAr_F$[6] leads to the desired complex [(NN)Pd(Me)][BAr_F] (**2a**) as an orange solid. The ^1H and ^{13}C NMR spectra of **2a** show two distinguishable 3-methoxypropyl groups, where presumably one methoxy coordinates to the vacant site to form a six-membered ring and the other is unbound. The bound OMe displays NMR signals at δ 3.57 (OCH_3) and 77.8 (OCH_3), both shifted downfield from the δ 3.30 (OCH_3) and 65.4 (OCH_3) of the free OMe. Solutions of **2a** are stable to air/moisture and are more thermally stable than the aryl diimine complexes **1** (L = diethyl ether).[1a] The ^1H NMR spectrum of **2a** in $CDCl_3$ exhibits no noticeable change at room temperature over 30 min or 1 week if stored at −30 °C. This increased stability is likely due to the intramolecular coordination of OMe. However, prolonged standing of a solution of **2a** at room temperature leads to the formation of the tricyclic complex **5**, which is possibly formed by addition of a C−H of the CH_2 group proximal to the coordinated OMe, followed by CH_4 elimination. While Pd insertion into vinyl or aryl C−H is not unusual,[7] this is the first example of alkyl C−H activation with a cationic diimine Pd(II) complex under such mild conditions. One other closely related C−H activation occurs for cationic

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$[(TMEDA)Pt^{II}(Me)(OEt_2)]^+$, reported recently by Bercaw, which eventually leads to a carbene hydride, $[(TMEDA)Pt^{II}(H)(C(Me)(OEt))]^+$.[8] **5** is thermally stable, and its solution does not decompose at room temperature over days. The structure of **5** has been confirmed by X-ray analysis (Figure 1)[9] and shows distorted-square-planar cooordination around Pd. The Pd−N(1) distance, 2.025(12) Å, is longer than Pd−N(2), 1.960(8) Å, reflecting the stronger trans effects of covalent bound CH than coordinated OMe. The Pd−O(1) distance, 2.085(7) Å, is typical of Pd−O distances,[10a] but Pd−C(11), 2.109(8) Å, is longer than normal Pd−C distances,[10] possibly because of ring strain.

Reaction of **2a** in CD_2Cl_2 with $HSiEt_3$ at −78 °C cleanly gives a product consistent with σ-silane coordination, $[(NN)Pd^{II}(Me)(\eta^2\text{-}HSiEt_3)]^+$.[11] The ^1H NMR spectrum contains a high-field signal at δ −9.87 corresponding to the Si−H proton and one single peak at δ 3.22 consistent with equivalent, noncoordinating OCH_3 groups. Apparently the η^2-$HSiEt_3$ group displaces the

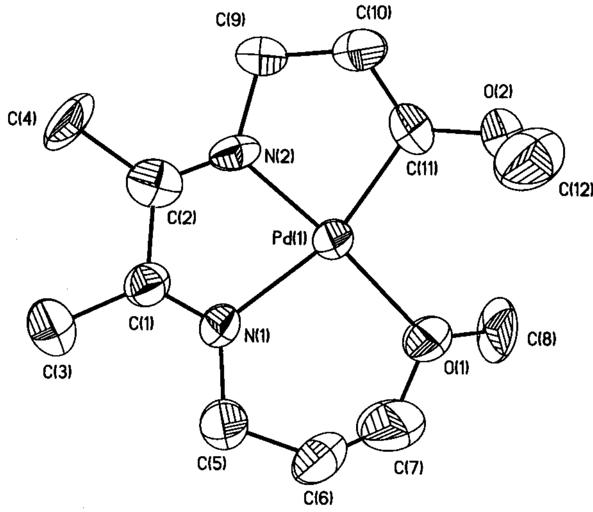

Figure 1. Drawing of **5** showing thermal ellipsoids at the 50% level. Selected bond distances (Å) and angles (deg): Pd(1)−N(1), 2.02(1); Pd(1)−N(2), 1.960(8); Pd(1)−C(11), 2.109(8); Pd(1)−O(1), 2.085(7). N(1)−Pd(1)−N(2), 78.3(3); N(1)−Pd(1)−O(1), 96.2(3); N(2)−Pd(1)−C(11), 84.9(4).

(3) Experimental procedures and characterization of new compounds are as follows. (a) **3 (NN)**: $NH_2(CH_2)_3OMe$ (2.25 mL, 22.0 mmol) was added to a suspension of 4 Å molecular sieves (9.60 g) in toluene (35 mL) at room temperature, followed by 2,3-butanedione (0.88 mL, 10.0 mmol). The resulting mixture was stirred at room temperature for 2 days. The mixture was then filtered through Celite and washed with CH_2Cl_2. Volatiles were removed to give a red oil. The oil was crystallized from hexane at −78 °C to give the product (1.80 g, 79%) as a red oil. ^1H NMR ($CDCl_3$): δ 1.93 (quintet, 4H, J = 7.6 Hz), 2.02 (s, 6H), 3.31 (s, 6H), 3.45 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 12.7, 30.9, 49.1, 58.7, 70.9, 168.4. MS (EI): 228 (M^+), 197, 169, 114, 73. (b) **4**: (COD)PdCl(Me) (0.226 g, 0.853 mmol) was added to a solution of **3** (0.214 g, 0.938 mmol) in Et_2O (10 mL) at −30 °C. The mixture was stirred at room temperature for 30 min. Volatiles were removed and the residue was washed with hexane (3×) to give yellow product (0.315 g, 96%). ^1H NMR ($CDCl_3$): δ 0.71 (s, 3H), 1.83 (quintet, 2H, J = 6.4 Hz), 1.94 (quintet, 2H, J = 6.5 Hz), 2.15 (s, 3H), 2.20 (s, 3H), 3.26 (s, 3H), 3.27 (s, 3H), 3.34 (t, 4H, J = 5.8 Hz), 3.73 (t, 2H, J = 7.6 Hz), 3.88 (t, 2H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ −1.2, 17.0, 18.1, 29.6, 49.4, 50.8, 58.6, 58.8, 69.5, 70.0, 169.0, 174.6. Anal. Calcd for $C_{13}H_{27}N_2O_2Pd$: C, 40.58; H, 7.02; N, 7.28. Found: C, 40.30; H, 7.32; N, 7.09. (c) **2a**: CH_2Cl_2 (4 mL) was added to a mixture of **4** (0.096 g, 0.25 mmol) and $NaBAr_F$ (0.222 g, 0.25 mmol) at room temperature. The resulting mixture was stirred for 20 min at room temperature and then filtered through Celite. Volatiles were removed to give a red syrup, which was washed with hexane (3×) to give a yellow solid (0.260 g, 86%). ^1H NMR ($CDCl_3$): δ 0.79 (s, 3H), 1.81 (quintet, 2H, J = 6.1 Hz), 1.98 (s, br, 5H), 2.21 (s, 3H), 3.30 (s, 3H), 3.35 (t, 2H, J = 5.4 Hz), 3.43 (br, 2H), 3.57 (s, 3H), 3.69 (t, 2H, J = 7.4 Hz), 3.76 (t, 2H, J = 4.5 Hz), 7.55 (s, 4H), 7.70 (s, 8H). ^{13}C NMR ($CDCl_3$): δ 6.4, 17.6, 18.2, 27.8, 29.4, 51.7, 52.7, 58.7, 65.4, 68.8, 77.8, 177.8, 181.7. Anal. Calcd for $C_{45}H_{39}BF_{24}N_2O_2Pd$: C, 44.55; H, 3.22; N, 2.31. Found: C, 44.44; H, 3.60; N, 2.23. (d) **5**: A solution of **2a** (0.140 g, 0.116 mmol) in CH_2Cl_2 (3 mL) was allowed to stand at room temperature in the glovebox for 2 days. A sample was removed, and a ^1H NMR spectrum was recorded after solvent removal. The data showed the coexistence of **2a** and **5** in a ratio of ca. 1/2. Volatiles were removed. Residue was crystallized from Et_2O/hexane at −30 °C to give product (0.015 g, 11%) as red crystals. ^1H NMR (CD_2Cl_2): δ 1.80 (m, 1H), 2.09 (m, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 3.44 (s, 3H), 3.45 (m, 2H), 3.71 (m, 2H), 3.72 (s, 3H), 3.89 (m, 2H), 4.78 (dd, 1H, J = 7.7, 3.8 Hz). ^{13}C NMR (CD_2Cl_2): δ 17.0, 18.5, 29.7, 40.9, 51.8, 53.8, 57.5, 65.8, 78.6, 89.3. Anal. Calcd for $C_{44}H_{35}BF_{24}N_2O_2Pd$: C, 44.15; H, 2.93; N, 2.34. Found: C, 44.28; H, 3.19; N, 2.30. (e) Reaction of **2a** with $HSiEt_3$: To a solution of **2a** (8.6 mg) in CD_2Cl_2 (~0.5 mL) at −78 °C was added Et_3SiH (4 μL) to give a yellow solution. ^1H NMR spectra were then recorded at −78 to 20 °C. ^1H NMR (−78 °C): δ −9.87 (s, 1H, Pd−*H*), 0.90 (m, 15H, $SiCH_2CH_3$ and $PdCH_3$), 1.90 (br, 4H), 2.26 (s, 6H), 3.22 (s, 6H), 3.29 (m, 4H), 3.78 (br, 4H). The signal at −9.87 ppm started to decrease when the temperature was raised to −20 °C and disappeared completely at 20 °C. Meanwhile, the rest of the spectrum at 20 °C became complicated, indicating formation of several products. Volatiles of the reaction mixture were then analyzed by GC-MS analysis, which showed Et_3SiCl and $(Et_3Si)_2O$ as two major components. (f) **6**: $[Pt(SMe_2)Me_2]_2$ (0.178 g, 0.31 mmol) was added to a solution of **3** (0.205 g, 0.90 mmol) in CH_2Cl_2 (4 mL) at −30 °C. The resulting red solution was stirred at room temperature for 2 h. Hexane (~12 mL) was then added, and the mixture was cooled to −30 °C to give the product (0.170 g, 60%) as black crystals. ^1H NMR ($CDCl_3$): δ 1.13 (s, 6H, J_{Pt-H} = 83.5 Hz), 1.70 (s, 6H), 1.99(m, 4H), 3.30 (s, 6H), 3.38 (t, 4H, J = 5.4 Hz), 4.10 (t, 4H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ −14.7 (s, J_{Pt-C} = 777.2 Hz), 18.3, 30.2, 50.5 (s, J_{Pt-C} = 30.8 Hz), 69.9, 76.8, 170.6. Anal. Calcd for $C_{14}H_{30}N_2O_2Pt$: C, 37.09; H, 6.62; N, 6.18. Found: C, 37.19; H, 6.93; N, 6.08. (g) **2b**: $H(OEt_2)_2BAr_F$ (0.0996 g, 0.098 mmol) was added to a deep red solution of **6** (0.0446 g, 0.098 mmol), and the resulting solution was stirred at room temperature for 10 min. Volatiles were removed, and the residue was triturated with hexane to give yellow product (0.1050 g, 82%). ^1H NMR (CD_2Cl_2): δ 1.14 (s, 3H, J_{Pt-H} = 69.6 Hz), 1.95 (s, 3H), 2.05 (s, 3H), 1.90−2.05 (br, 2H), 2.22 (br, 2H), 3.29 (s, 3H), 3.37 (t, 2H, J = 5.4 Hz), 3.72 (m, 2H), 3.76 (s, 3H), 3.94 (t, 2H, J = 7.3 Hz), 4.09 (m, 2H), 7.58 (s, 4H), 7.74 (s, 8H). ^{13}C NMR (CD_2Cl_2): δ −7.0 (J_{Pt-C} = 783 Hz), 18.1, 18.7, 28.2, 30.2, 52.4, 55.0, 58.9, 67.8, 69.0, 80.2, 178.5, 178.6. Anal. Calcd for $C_{45}H_{39}BF_{24}N_2O_2Pt$: C, 41.51; H, 3.00; N, 2.15. Found: C, 41.67; H, 3.27; N, 2.13. (h) **7**: Et_3SiH (0.10 mL) was added to a solution of **2b** (0.030 g, 0.023 mmol) in CH_2Cl_2 (2 mL) at −30 °C. After the mixture was kept at −30 °C for 30 min, hexane (10 mL, −30 °C) was added and the mixture was kept at −30 °C overnight to give the product (0.027 g, 83%) as light yellow crystals. ^1H NMR (−10 °C, CD_2Cl_2): δ −17.31 (s, 1H, J_{Pt-H} = 1297.6 Hz), 0.73 (q, 6H, J = 7.4 Hz), 0.88 (t, 9H, J = 7.5 Hz), 1.01 (s, 3H, J_{Pt-H} = 60.0 Hz), 1.73 (br, 1H), 1.87 (br, 2H), 2.14 (br, 1H), 2.22 (s, 3H), 2.37 (s, 3H), 3.28 (s, 3H), 3.30 (s, 3H), 3.41 (t, 2H, J = 5.4 Hz), 3.55 (br, 1H), 3.85 (t, 1H, J = 9.8 Hz), 3.99−4.09 (m, 3H), 4.44 (m, 1H). ^{13}C NMR (−40 °C, CD_2Cl_2): δ −12.8 (J_{Pt-C} = 810 Hz), 7.7 ($SiCH_2$, J_{Pt-C} = 52.8 Hz), 7.9, 18.6, 19.0, 30.0, 31.2, 50.0, 56.5, 59.2, 60.6, 69.1, 73.6, 175.3, 179.4.

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(5) Crystal data for **4**: monoclinic, $C2/c$, a = 7.6081(7) Å, b = 9.2632(9) Å, c = 23.878(2) Å, β = 92.126(2)°, V = 1681.7(3) Å^3, Z = 4, R1($I > 2\sigma$) = 0.0312 and wR2 = 0.0744.

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(8) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. Very recently Tempel et al. reported C−H activation of the methyl groups of both *tert*-butyl and isopropyl groups of the aryl diimine complexes **1**; see: Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686.

(9) Crystal data for **5**: monoclinic, $P2_1/c$, a = 12.7833(9) Å, b = 20.4625(12) Å, c = 18.2923(13) Å, β = 95.962(1)°, V = 4759.0(6) Å^3, Z = 4, R1($I > 2\sigma$) = 0.1003 and wR2 = 0.1948.

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(11) For examples of similar Fe and Mo silane σ complexes, see: (a) Scharrer, E.; Change, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686. (b) Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312. The complex could also be a diimine Pd(IV) silyl hydride; see: Brookhart, M.; Grant, B. E.; Lenges, C. P.; Prosenc, M. H.; White, P. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1676.

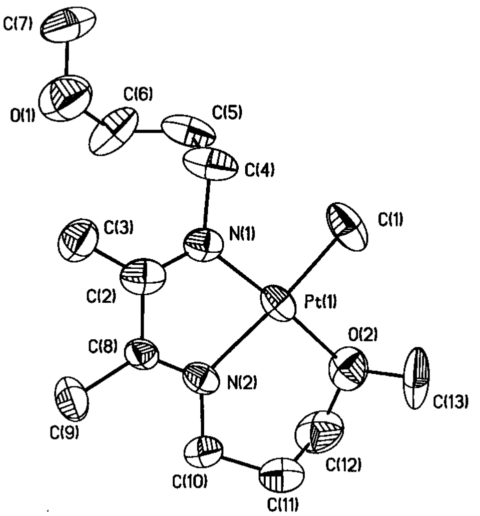
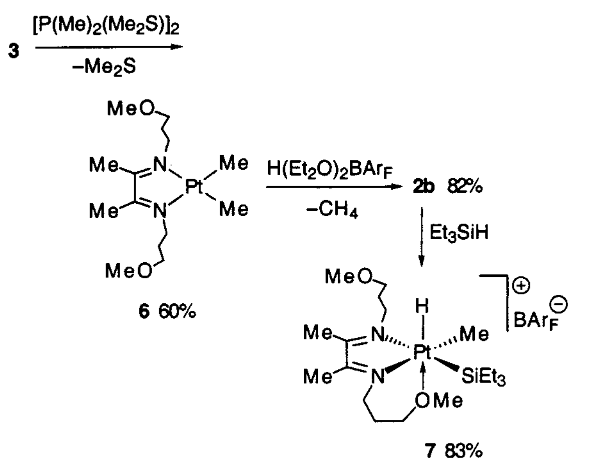


Figure 2. Drawing of **2b** showing thermal ellipsoids at the 50% level. Selected bond distances (Å) and angles (deg): Pt(1)−N(1), 1.956(1); Pt(1)−N(2), 2.056(9); Pt(1)−C(1), 2.03(1); Pt(1)−O(2), 2.070(1); N(1)−C(2), 1.31(1); N(2)−Pt(1)−O(2), 96.6(4); N(2)−Pt(1)−N(1), 78.7(4); O(2)−Pt(1)−C(1), 86.1(6).

bound OMe in **2a**. However, the complex is thermally unstable and rapidly decomposes as its solution is warmed to room temperature. As measured by GC-MS, the volatile products of the reaction contain Et_3SiCl and $(Et_3Si)_2O$ as two major components, characteristic of heterolytic cleavage of the η^2-Si−H bond.[12]

The Pt(II) complex **2b** is prepared in a related manner (eq 2). On analogy to **2a**, one OMe arm in **2b** is bound



(2)

to the vacant site. The bound OMe has a ^{1}H NMR signal at δ 3.76 vs the signal at δ 3.29 of unbound OMe. The structure is confirmed by X-ray analysis (Figure 2).[13] On analogy to **5**, **2b** exhibits a distorted-square-planar geometry around Pt, and the Pt−N(2) distance, 2.0558(9) Å, is longer than the respective Pt−N(1) distance, 1.9555(97) Å, presumably due to the stronger trans effects of the CH_3. The Pt−C(1) distance of 2.0337(123) Å and Pt−O(2) distance of 2.0696(89) Å are within normal ranges.[10b,14]

Unlike those of **2a** and the Bercaw complex, solutions of complex **2b** are stable and the NMR spectra in $CDCl_3$ do not change for weeks at room temperature in air. This high stability is in drastic contrast to the analogous aryl diimine analogue $[(NN)Pt^{II}(Me)(OEt_2)]^+$, where NN = ArNCMeCMeNAr (Ar = *p*-MeC_6H_4), which is not even observable by NMR spectroscopy because of its extremely high instability.[15] It is clear that coordination of the intramolecular OMe confers stability, and accordingly, **2b** does not add to the C−H bonds of alkanes, benzene, or toluene. However, the bound OMe is readily displaced by a Si−H group when the complex is treated with $HSiEt_3$ at −30 °C, eventually affording the octahedral Pt(IV) hydride **7** as colorless crystals (eq 2). While oxidative addition of Si−H bonds to cationic diphosphine Pt(II) complexes to form Pt(IV) silyl hydrides is known,[16] this is the first case of addition to a cationic diimine Pt(II) complex. Previously, diimine Pt(IV) silyl hydrides were suggested to be too unstable to be observable;[17] therefore, it is likely that a pendant OMe stabilizes the complex by coordinating to the vacant sixth site.[18] Still, solutions of **7** are unstable at room temperature and decompose to a unidentifiable mixture within ∼20 min.

In summary, we have prepared the first cationic Pd(II) and Pt(II) complexes of a new methoxyalkyl-substituted diimine ligand. The Pt(II) complex **2a** activates an alkyl C−H bond of the methylene proximal to the coordinated OMe group, and the Pt(II) complex activates a Si−H bond to form a diimine Pt(IV) silyl complex. Determination of other chemical properties of these and related complexes with other functional groups is in progress.[19]

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Supporting Information Available: Detailed X-ray crystallographic data of the structures of compounds **4**, **5**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for **2b**: triclinic, $P\bar{1}$, a = 13.0244(9) Å, b = 13.099(1) Å, c = 16.628(1) Å, α = 87.756(1)°, β = 82.167(1)°. γ = 61.316(1)°, V = 2464.5(3) Å^3, Z = 2, R1($I > 2\sigma$) = 0.0585 and wR2 = 0.1282.

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(19) For example, **2a** is found to catalyze polymerization of *tert*-butylacetylene to give stereoregular polymers.