which rhodium is substituted at the position α to the nitrogen atom, are involved as common intermediates in the present catalytic reactions. An intermediate of type **10** may also be present in the Rh-catalyzed reaction of enamines with $HSiR_3$ and CO.[1] The interaction of a complex having a silicon–rhodium bond with *N,N*- or *N,O*-acetals would be responsible for the formation of **10**, while that of a complex having a hydrogen–rhodium bond with an olefinic moiety might be important in the case of enamines.[1]

Further study on the mechanism and substrate–product structure relationship of the new catalytic reactions is now in progress.

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Supplementary Material Available: Text giving typical experimental procedures and spectral and analytical data for the products obtained (3 pages). Ordering information is given on any current masthead page.

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(4) For reviews on carbonylation, see: (a) Falbe, J. *New Synthesis with Carbon Monoxide*; Springer-Verlag: New York, 1980. (b) Sneeden, R. P. A.; Villeurbanne, N. R. S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1982; Vol. 8. (c) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. For examples of the transition-metal-catalyzed carbonylation with cleavage of a carbon–nitrogen bond in strained molecules, see: (d) Alper, H.; Perera, C. P.; Ahmed, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 1289. (e) Alper, H.; Mahatantila, C. P. *Organometallics* **1982**, *1*, 70. (f) Alper, H.; Urso, F.; Smith, D. J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6737. (g) Roberto, D.; Alper, H. *Organometallics* **1984**, *3*, 1767. (h) Alper, H.; Hamel, N. *Tetrahedron Lett.* **1987**, *28*, 3237. (i) Calet, S.; Urso, F.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 931. (j) Roberto, D.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 7539. (k) Alper, H.; Delledonne, D.; Kameyama, M.; Roberto, D. *Organometallics* **1990**, *9*, 762. (l) Spears, G. W.; Nakanishi, K.; Ohfune, Y. *Synlett* **1991**, 91. For examples of the insertion of CO into a carbon–nitrogen bond of substrates other than strained heterocycles, see: (m) Merger, F.; Kummer, R.; Hutmacher, H. M. German Patent 3401503, 1985; *Chem. Abstr.* **1986**, *104*, 129650g. (n) Murahashi, S.-I.; Imada, Y.; Nishimura, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1578.

Stable Bis(silyl)palladium Complexes: Synthesis, Structure, and Bis-Silylation of Acetylenes

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Summary: A class of unusually stable bis(silyl)palladium complexes is prepared by the reaction of a dinuclear Pd(I) hydride with either simple hydrosilanes or disilanes. The first structure of a palladium bis(silyl) compound and preliminary reaction chemistry with acetylenes are reported.

Silyl complexes of palladium have been implicated as important intermediates in a number of palladium-catalyzed transformations of organosilanes, including the hydrosilylation[1] and bis-silylation[2-4] of organic substrates. In contrast to analogous platinum complexes, palladium silyls are generally considered to be unstable. The few isolated complexes that have been reported to date possess special stabilization from either strongly electron-withdrawing silyl groups (e.g. $SiCl_3$)[5] or by inclusion of the silyl group in a chelate ring.[5,6] Since a fundamental knowledge of the reactivity of palladium silyl compounds is essential to understanding their role as catalytic intermediates, the preparation of simple silyl derivatives of palladium was sought. We now report the general synthesis of a new class of thermally stable (silyl)palladium complexes, the first crystal structure of a palladium–silicon compound, and some preliminary reaction chemistry with acetylenes.

Stable *cis*-bis(silyl)palladium complexes were prepared from the direct reaction of either hydrosilanes or 1,2-dihydrodisilanes with the novel dinuclear palladium hydride $[(dcpe)Pd]_2(\mu\text{-}H)_2$ (**1**; dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[7,8] Reaction of **1** with the hydrosilanes **2a–c** as either neat liquids or toluene solutions, afforded the *cis*-bis(silyl) complexes **3a–c** in 50–70% yields (eq 1)[9].

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(2) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27–C30. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *91*, 931–932. (c) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891–894. (d) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19–C21. (e) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51–62. (f) Matsumato, H.; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43–47. (g) Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149–157. (h) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467–470. (i) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948–1951.

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(7) A similar Pd(I) hydride has been recently reported: Fryzuk, M. D.; Lloyd, R. B.; Clentsmith, G. K. B.; Rettig, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 4332–4334.

(8) Preparation of **1**: A solution consisting of 62 mg (0.1 mmol) of (dcpe)Pd(oxalate) in 35 mL of CH_3CN was placed in a quartz Schlenk tube. While a constant flow of H_2 was maintained through the solution, the tube was irradiated at 350 nm in a Rayonet photochemical reactor for 45 min. Cooling of the photolysate to 0 °C resulted in the formation of an air-sensitive green precipitate. The precipitate was separated from the supernatant, washed in hexane, and dried in vacuo to yield 45 mg (85%) of **1**. Characterization for **1**: ^1H NMR (δ, THF-d_8) −2.28 (quintet, $^1J_{P\text{-}H}$ = 39.8 Hz), 1.2–2.0 (br m, dcpe); $^{31}P\{^1H\}$ NMR (δ, THF-d_8) 50.4 (s); IR (KBr, cm^{-1}) 1620 (s, Pd–H–Pd); MS (EI, 70 eV) *m/z* 1058 (M^+, 5%), 528 ($(dcpe)Pd^+$, 10%), 422 ($dcpe^+$, 20%), 340 ($Cy_2PCH_2CH_2Cy^+$, 100%). Anal. Calcd for $C_{52}H_{98}P_4Pd_2$: C, 58.92; H, 9.32. Found: C, 58.03; H, 9.13.

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The bis(silyl) compounds **3d**,**e** were also prepared in comparable yields from the reaction of **1** with toluene solutions of the disilanes $MeSiH_2SiH_2Me$ and $HMe_2SiSiMe_2H$, respectively (eq 2).[10]

$$\underset{\mathbf{1}}{[(dcpe)Pd]_2(\mu\text{-}H)_2} + \underset{\mathbf{2a{-}c}}{H_2SiPhR} \xrightarrow{25\text{–}60\ °C} \underset{\mathbf{3a{-}c}}{(dcpe)Pd(SiHRPh)_2} \quad (1)$$

a, R = Ph; **b**, R = Me; **c**, R = H

$$\underset{\mathbf{1}}{[(dcpe)Pd]_2(\mu\text{-}H)_2} + HRMeSiSiMeRH \xrightarrow{25\ °C} \underset{\mathbf{3d,e}}{(dcpe)Pd(SiHRMe)_2} \quad (2)$$

d, R = H; **e**, R = Me

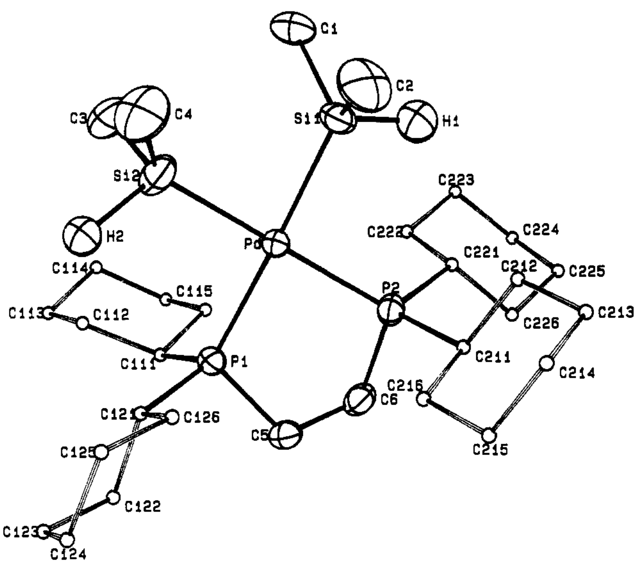
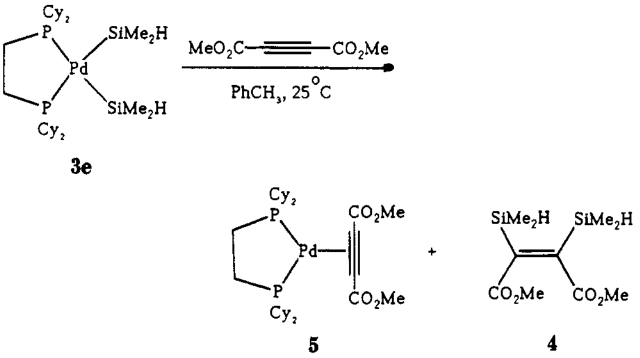


Figure 1. Molecular structure of the major conformer of **3e**. Heavy atoms are shown at the 30% probability level; cyclohexyl carbons are represented by spheres of arbitrary dimension for clarity. Significant bond lengths (Å) and angles (deg): Pd–Si(1), 2.3563 (9); Pd–Si(2), 2.359 (1); Pd–P(1), 2.3518 (7); Pd–P(2), 2.3614 (8); P(1)–Pd–P(2), 85.70 (3); P(1)–Pd–Si(2), 94.91 (4); P(2)–Pd–Si(1), 95.75 (3), Si(1)–Pd–Si(2), 83.77 (4).

Scheme I



Compounds **3a–e** represent the first isolated examples of *cis*-bis(silyl)palladium complexes possessing only simple organic groups and hydrogens on silicon.[11] Schubert and co-workers have previously reported the spectroscopic identification of the complexes *cis*-$(MePh_2P)_2Pd(SiHRPh)_2$, where R = Me or Ph, from the reaction of *cis*-$(MePh_2P)_2PdMe_2$ with H_2SiRPh; however, these complexes could not be isolated due to rapid reductive elimination of disilanes. In contrast, bis(silyl) complexes **3a–e** are crystalline solids stable to air and brief heating to 120 °C. In hydrocarbon solutions, however, these complexes slowly decompose over a period of days to give colloidal palladium and a complicated mixture of phosphine and silane products. Interestingly, no significant amounts of disilanes were formed, as would be expected from simple reductive elimination. The unusually high thermal stability of this family of palladium bis(silyl) compounds is attributed to advantageous properties of the ancillary dcpe ligand, including kinetic protection of the complexes by the sterically large cyclohexyl groups and strengthening of the Pd–Si bond due to the high basicity of the phosphine. An additional stabilization of the complexes to reductive elimination of disilanes may also be imparted by phosphine chelation.[12]

Since no compounds possessing a Pd–Si bond have been structurally characterized, an X-ray crystal structure of

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(9) Procedure of **3a–e**: In a typical preparation, 0.5 mmol of the hydrosilane **2a–e** was dissolved in 10 mL of toluene and added to 50 mg of solid **1** in an argon-filled flask. The resulting suspension was heated until **1** disappeared and a homogeneous solution was formed. The solvent was removed in vacuo and the resulting colorless to pale yellow solid recrystallized from hexane. Compound characterizations are as follows. **3a**: mp 146 °C dec; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 53.4 (s); ^1H NMR (δ, C_6D_6) 0.99–1.90 (48 H, featureless resonance), 5.86 (2 H, dd, $^3J_{H-P(trans)} = {}^3J_{H-P(cis)}$ = 14 Hz), 7.12 (4 H, m), 7.17 (8 H, m), 7.86 (8 H, d); $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2) 22.14 (t, J = 18.11 Hz, $-CH_2CH_2-$), 26.17 (s, Cy), 27.17 (m, Cy), 29.07 (s, Cy), 30.45 (s, Cy), 35.16 (t, J = 6.04 Hz, Cy), 126.93 (s, Ph), 127.06 (s, Ph), 137.14 (s, Ph), 144.17 (broad, Ph); IR (KBr, cm^{-1}) 2052 (s, ν(Si–H)); MS (EI, 70 eV) m/z 896 (M^+ – 2 H, 4%), 528 (M^+ – $2Ph_2SiH$, 20), 366 ($Ph_2HSiSiHPh_2^+$, 100). Anal. Calcd for $C_{50}H_{70}P_2PdSi_2$: C, 67.06; H, 7.88. Found: C, 66.14; H, 7.72. **3b**: mp 128 °C; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 52.50 (s), 53.13 (s); ^1H NMR (δ, C_6D_6) 0.94–1.99 (54 H, featureless resonance), 5.22 (2 H, m), 7.16 (2 H, m), 7.23 (4 H, m), 7.90 (4 H, m); $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2) –0.47 (s, CH_3), 1.34 (s, CH_3), 22.65 (m, $-CH_2CH_2-$), 26.33 (s, Cy), 26.49 (s, Cy), 27.30 (s, Cy), 27.44 (s, Cy), 29.04 (s, Cy), 29.11 (s, Cy), 30.00 (s, Cy), 30.37 (s, Cy), 34.87 (m, Cy), 35.46 (m, Cy), 127.04 (s, Ph), 127.13 (s, Ph), 127.23 (s, Ph), 127.32 (s, Ph), 136.04 (s, Ph), 136.32 (s, Ph), 147.24 (broad, Ph), 147.40 (broad, Ph); IR (KBr, cm^{-1}) 2033 (s, ν(Si–H)); MS (EI, 70 eV) m/z 769 (M^+ – H, 4%), 528 (M^+ – 2PhMeSiH, 80), 242 ($PhMeHSiSiHMePh^+$, 100). Anal. Calcd for $C_{40}H_{66}P_2PdSi_2$: C, 62.23; H, 8.62. Found: C, 62.35; H, 8.62. **3c**: mp 142 °C; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 56.5 (s); ^1H NMR (δ, C_6D_6) 0.85–2.04 (48 H, featureless resonance), 5.34 (4 H, dd, $^3J_{H-P(trans)} = {}^3J_{H-P(cis)}$ = 14 Hz), 7.12 (2 H, m), 7.23 (4 H, t), 7.99 (4 H, d); $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2) 23.20 (t, 17.90 Hz $-CH_2CH_2-$), 26.29 (s, Cy), 27.23–27.44 (m, Cy), 29.00 (s, Cy), 29.79 (s, Cy), 35.23 (t, J = 8.05 Hz, Cy), 127.23 (s, Ph), 127.27 (s, Ph), 137.18 (s, Ph), 142.08 (broad, Ph); IR (KBr, cm^{-1}) 2070 (vs, ν(Si–H)), 2008 (vs, ν(Si–H)); MS (EI, 70 eV) m/z 740 (M^+ – 2H, 8), 528 (M^+ – $2PhH_2Si$, 100). Anal. Calcd for $C_{38}H_{62}P_2PdSi_2$: C, 61.39; H, 8.41. Found: C, 61.09; H, 8.58. **3d**: mp 126 °C; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 55.4 (s); ^1H NMR (δ, C_6D_6) 0.96 (6 H, broad), 1.05–1.66 (48 H, featureless resonance), 4.65 (4 H, m); $^{13}C\{^1H\}$ NMR (δ, C_6D_6) 1.36 (s, CH_3), 22.85 (t, J = 20.12 Hz, $-CH_2CH_2-$), 26.50 (s, Cy), 27.31 (m, Cy), 27.57 (m, Cy), 29.22 (s, Cy), 30.35 (m, Cy), 35.37 (t, J = 8.15 Hz, Cy); IR (KBr, cm^{-1}) 2056 (s, ν(Si–H)); MS (EI, 70 eV) m/z 617 (M^+ – H, 5%), 528 (M^+ – $2MeSiH_2$, 100). Anal. Calcd for $C_{28}H_{58}P_2PdSi_2$: C, 54.33; H, 9.44. Found: C, 54.30; H, 9.31. **3e**: mp 124 °C; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 52.4 (s); ^1H NMR (δ, C_6D_6) 0.92 (12 H, d), 1.09–2.06 (48 H, featureless resonance), 4.84 (2 H, m); $^{13}C\{^1H\}$ NMR (δ, C_6D_6) 1.34 (s, CH_3), 23.27 (t, J = 27.67 Hz, $-CH_2CH_2-$), 26.37 (s, Cy), 27.18 (m, Cy), 27.41 (m, Cy), 29.04 (s, Cy), 29.85 (s, Cy), 35.16 (t, J = 8.05 Hz, Cy); IR (KBr, cm^{-1}) 2006 (s, ν(Si–H)); MS (EI, 70 eV) m/z 645 (M^+ – H, 5%), 528 (M^+ – $2Me_2HSi$, 100). Anal. Calcd for $C_{30}H_{62}P_2PdSi_2$: C, 55.66; H, 9.65. Found: C, 55.66; H, 9.43.

(10) The reaction of these disilanes toward the closely related platinum complex $(dcpe)PtH_2$ also gives bis(silyl) compounds: Michalczyk, M.; Recatto, C.; Calabrese, J.; Fink, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 7995–7997.

(11) Simple platinum *cis*-bis(silyl) species, on the other hand, are well-known: (a) Chatt, J.; Eaborn, C.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 881–884. (b) Chatt, J.; Eaborn, C.; Kapoor, P. N. *J. Chem. Soc. A* **1970**, 1343–1351. (c) Eaborn, C.; Pidcock, A.; Ratcliff, B. *J. Organomet. Chem.* **1974**, *66*, 23–28. (d) Eaborn, C.; Ratcliff, B.; Pidcock, A. *J. Organomet. Chem.* **1974**, *65*, 181–186. (e) Eaborn, C.; Metham, T. M.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1975**, 2212–2214. (f) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411–1444. (g) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1989**, 467–470. (h) Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447–1450. (i) Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917–1919.

(12) Reductive elimination of disilanes leads to a nonlinear high-energy L_2Pd^0 intermediate. For an excellent discussion of related platinum systems see: Hofmann, P. In *Organometallics in Organic Synthesis*; de Meijere, A., Tom Dieck, H., Eds.; Springer-Verlag: Berlin, 1987; pp 1–35.

Organometallics **1992**, *11*, 3497-3499

3e was obtained. Colorless crystals of **3e** suitable for X-ray diffraction were grown by slow cooling in hexane at −15 °C.[13] The resulting structure shows slight rotational disorder about one of the Pd–Si bonds, which was successfully modeled by refining two conformeric structures in an approximately 3:1 ratio. The ORTEP diagram of the major conformer is shown in Figure 1 along with significant bond lengths and angles. The coordination of the palladium is nearly square planar with a slight twist of 2°. The two methyl groups on each silicon atom lie above and below the central square plane and are directed away from the phosphine ligand by the bulky cyclohexyl groups. The Si–Pd bond lengths of 2.3563 (9) and 2.359 (1) Å are within known values of Si–Pt bond lengths in analogous complexes (2.354–2.423 Å)[14,15] but significantly shorter than Sn–Pd bond lengths (2.563–2.585 Å).[16]

Bis(silyl)palladium complexes have been implicated as important intermediates in the palladium-catalyzed bissilylation of acetylenes,[2] dienes,[3] and isonitriles[4] by disilanes; however, little is directly known about the reactivity of these species. A four-step catalytic cycle for the bis-silylation of acetylenes has been proposed in which (1) the disilane adds to the metal center to afford a bis(silyl)metal complex, (2) the bis(silyl) complex coordinates with the acetylene, (3) the coordinated acetylene inserts into a silicon–metal bond to give a vinylmetal complex, and (4) reductive elimination occurs to release the *cis*-olefin and regenerate the catalytic species.[2e] Since we have already demonstrated that disilanes may react with an appropriate palladium precursor to give stable bis(silyl) species (step 1), it was of interest to examine the subsequent reactivity of these palladium bis(silyl) compounds toward acetylenes and their role in catalytic bis-silylation. The palladium bis(silyl) species **3e** was thus found to react stereospecifically with 2.5 equiv of $MeO_2CC{\equiv}CCO_2Me$ at 25 °C to cleanly afford dimethyl *cis*-bis(dimethylsilyl)maleate (**4**) and the palladium π-complex of the alkyne (**5**; Scheme I). These results provide the first experimental verification of the reaction of a palladium bis(silyl) compound with an acetylene to produce a bis-silylated olefin and thereby lend strong support for steps 2–4 in the proposed mechanism.[17] The Pd(0) species which is produced after the reductive elimination (step 4) is apparently scavenged by excess acetylene to afford the π-complex **5**.[18] The complex **3e** also participates in the catalytic bis-silylation of the alkyne: reaction of $HMe_2SiSiMe_2H$ with $MeO_2CC{\equiv}CCO_2Me$ in the presence of catalytic **3e** (2 mol %, 80 °C, 2 h) affords the *cis* olefin **4** in 45% yield. The reactivities of palladium bis(silyl) species toward other organic substrates are currently being investigated.

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Supplementary Material Available: Tables of experimental crystallographic data, positional and thermal parameters, bond lengths and angles, root-mean-square amplitudes, and least-squares planes for **3e** (13 pages). Ordering information is given on any current masthead page.

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(13) Crystal data: dimensions 0.23 × 0.43 × 0.53 mm; crystal system monoclinic; space group $P2_1/n$; a = 12.327 (1) Å; b = 17.557 (2) Å; c = 16.634 (3) Å; β = 102.39 (1)°; Z = 4; absorption coefficient 6.9 cm^{-1}; Mo Kα radiation with graphite monochromator; 2θ range 1.0–48.0°, 5502 unique reflections with 4282 $\geq 3\sigma(I)$. The structure was solved by Patterson methods and refined to convergence with R = 0.027 and R_w = 0.040.

(14) (a) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989**, *8*, 1369–1371. (b) Chang, L. S.; Johnson, M. P.; Fink, M. J. *Organometallics* **1991**, *10*, 1219–1221. The related complex (dcpe)Pt($SiH_2Me)_2$ shows a Pt–Si bond length of 2.354 (2) Å (results to be submitted for publication).

(15) Mullica, D. F.; Sappenfield, E. L.; Hampden-Smith, M. J. *Polyhedron* **1991**, *10*, 867–872.

(16) (a) Mason, R.; Whimp, P. O. *J. Chem. Soc. A* **1969**, 2709–2717. (b) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193–198.

(17) A similar reaction has been recently observed for a platinum bis(silyl) complex with phenylacetylene: Tanaka, M.; Uchimaro, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16–18.

(18) Characterization for **5**: mp 142 °C dec; $^{31}P\{^1H\}$ NMR (δ, C_6D_6) 65.9 (s); ^1H NMR (δ, C_6D_6) 1.09–1.98 (48 H, featureless resonance), 3.50 (6 H, s); $^{13}C\{^1H\}$ NMR (δ, C_6D_6) 22.29 (dd, dcpe), 26.33 (s, dcpe), 27.30 (d, dcpe), 29.34 (s, dcpe), 29.87 (d, dcpe), 34.99 (d, dcpe), 51.92 (s, CH_3), 111.94 (AA′X, $^2J_{C-P(cis)} + {}^2J_{C-P(trans)}$ = 73.8 Hz, $-C{\equiv}$), 168.00 (AA′X, $^3J_{C-P(cis)} + {}^3J_{C-P(trans)}$ = 32.6 Hz, C=O); IR (KBr, cm^{-1}) 1797 (w, $\nu(C{\equiv}C)$), 1696 (vs, $\nu(C{=}O)$); MS (EI, 70 eV) m/z 670 (M^+, 5%), 611 (M^+ − COOMe, 5), 528 (M^+ − $MeOOCC{\equiv}CCOOMe$, 100). Anal. Calcd for $C_{32}H_{54}O_4P_2Pd$: C, 57.27; H, 8.11. Found: C, 56.81; H, 7.99.

Bis(tetramethylthiophene)ruthenium(0) and Its Fe(CO)$_4$ Adduct

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Summary: Reduction of $[Ru(\eta^5\text{-}C_4Me_4S)_2](OTf)_2$ (C_4Me_4S is 2,3,4,5-tetramethylthiophene, OTf is $CF_3SO_3^-$) at −78 °C with 2 equiv of Cp_2Co gives $Ru(C_4Me_4S)_2$ (**1**), which is stable at <−20 °C. DNMR studies suggest that **1** is fluxional as a result of the facile interconversion of η^5-C_4Me_4S and η^4-C_4Me_4S ligands. In contrast, $(\eta^5\text{-}C_4Me_4S)Ru\{(\eta^4{:}\eta^1\text{-}C_4Me_4S)Fe(CO)_4\}$, prepared from **1**, $Fe(CO)_5$, and Me_3NO, is thermally stable and adopts a static structure. In the solid state, **1**·$Fe(CO)_4$ adopts a symmetric structure such that the two pairs of C=C groups are eclipsed.

As an extension of our recent work on ruthenium(0) derivatives of thiophenes,[1] we have prepared the first homoleptic M(0) thiophene complex.[2] This new compound is of interest from a number of perspectives, not the least of which is its possible relationship to the interaction of thiophenes with metal surfaces.[3] The present report is concerned with proof of structure and physical

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