of this change in hapticity may explain the scarcity of η^1,S-thiophene complexes and is of likely relevance to the dynamics of chemisorbed thiophene.

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters, bond distances and angles, and structure factors (35 pages). Ordering information is given on any current masthead page.

(18) CoHon, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; pp 1167 and 1230 ff.

A New Cyclopalladation Reaction Involving Facile Chelated Transmetalation: Selective Cleavage of C–Sn and C–Si Bonds of Stannyl and Silyl Ketoximes

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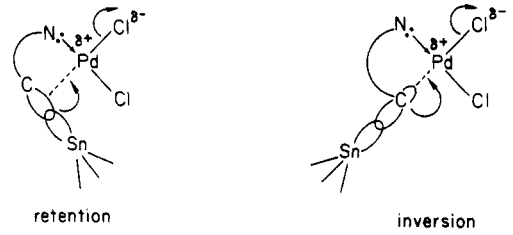
Summary: A new cyclopalladation involving a facile chelated transmetalation with the stannyl ketoximes **1–4** was found to form the five- and six-membered ring oxime complexes of palladium **5–8** in high yields. The silyl ketoxime **18** can react in a similar manner to give the complex of palladium **19** at higher temperature for longer reaction time than that of the stannyl derivatives.

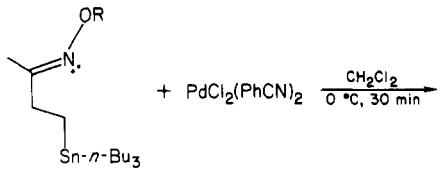
Cyclopalladation has been well documented as a significant reaction in organometallic chemistry and has recently been examined from the view point of C–H bond activation of both aromatic and aliphatic hydrocarbons.[1] Although several cyclopalladation reactions have been reported in which a carbon–hydrogen bond on *alkyl* moiety is cleaved, the reactions are limited to substrates involving intramolecular coordinating compounds with sterically hindered alkyl groups or benzylic ones.[2] In this context, transmetalation by empolying organostannyl or organosilyl functions as a selective electrophilic group may provide a new strategy for formation of a metal–carbon σ-bond in

Chart I

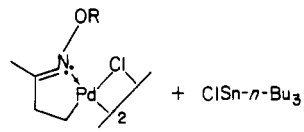


cyclic systems.[3] We report here a new cyclopalladation reaction involving a chelated transmetalation with stannyl or silyl ketoximes.

Reaction of the (*E*)-β-tributylstannyl ketoxime **1**[4] with dichlorobis(benzonitrile)palladium (1 equiv) in dichloromethane at 0 °C for 30 min yielded 78% of the cyclopalladation product **5**. Similarly, the stannyl ketoxime acetate **2** readily gave the corresponding complex **6**. Interestingly, the six-membered ring complexes **7** and **8** were also obtained from the (*E*)-γ-tributylstannyl ketoxime derivatives (Table I).[5]



1, R=H
2, R=Ac



5, R=H
6, R=Ac

It is quite noteworthy that the transmetalation of the stannyl group by the palladium species takes place under such an extremely mild condition for short reaction time and that the C–Sn bond on the side chain of the oxime is cleaved exclusively and not Me or Bu groups. In contrast

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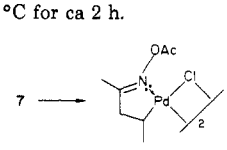
(2) For (oxime)palladium complexes, see: (a) Onoue, H.; Minami, K.; Nakagawa, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480. (b) Grigor, B. A.; Nielson, A. J. *J. Organomet. Chem.* **1977**, *132*, 439. (c) Nielson, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 205. (d) Constable, A. G.; McDonald, W. S.; Sawkins, L. C.; Shaw, B. L. *Ibid.* **1980**, 1992. (e) Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1227. (f) Baldwin, J. E.; Najera, C.; Yust, M. *Ibid.* **1985**, 126. For other cycloalkylpalladium complexes, see: (g) Fuchita, Y.; Hiraki, K.; Uchiyama, T. *J. Chem. Soc., Dalton Trans.* **1983**, 897. (h) Hartwell, G. E.; Lawrence, R. V.; Smas, M. J. *J. Chem. Soc., Chem. Commun.* **1970**, 912. (i) Sokolov, V. I.; Sorokina, T. A.; Troitskaya, L. L.; Solovieva, L. I.; Reutov, O. a. *J. Organomet. Chem.* **1972**, *36*, 389. (j) Mutet, C.; Pfeffer, M. *Ibid.* **1979**, *171*, C34.

(3) For transmetalation with alkenyl silanes and stannanes, see: (a) Kliegman, J. M. *J. Organometa. Chem.* **1971**, *29*, 73. (b) Itoh, K.; Fukui, M.; Kurachi, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 500. (c) Hayashi, T.; Konishi, M.; Kumada, M. *Ibid.* **1983**, 736. (d) Abel, E. W.; Rowley, R. J. *J. Chem. Soc., Daton Trans*, **1975**, 1096. (e) Abel, E. W.; Moorhouse, S. *Ibid.* **1973**, 1706. (f) Cardin, D. J.; Norton, R. J. *J. Chem. Soc., Chem. Commun.* **1979**, 513.

(4) Oximation was carried out with $HONH_2$·HCl and NaOAc in ethanol by using the corresponding ketones. For the ketones, see: (a) Nakatani, K.; Isoe, S. *Tetrahedron Lett.* **1984**, *25*, 5335. (b) Ochiai, M.; Ukita, T.; Nagao, Y.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1984**, 1007 and references cited therein.

(5) Spectroscopic data. **5**: IR (KBr) 3390, 2910, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz), 1.93 (s, 3 H, CH_3), 2.23 (t, 2 H), 2.63 (t, 2 H), 8.13 (s, 1 H, OH) ppm; ^{13}C ($CDCl_3$) 13.96 (t, CPd), 21.30 (q, CH_3), 41.83 (t, CC=N), 172.06 (s, C=N) ppm. **6**: IR (KBr) 2920, 1782, 1628 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) 1.89 (s, 3 H, CH_3CN), 2.15 (s, 3 H, CH_3C=O), 2.40 (m, 4 H), CH_2CH_2) ppm. **7**: IR (KBr) 3390, 1650 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) 0.69 (quintet, 2 H, CH_2CPd), 2.04 (s, 3 H), 2.28 (t, 2 H, CH_2C=N), 2.49 (t, 2 H, CH_2Pd), 8.93 (s, 1 H, OH) ppm; ^{13}C NMR ($CDCl_3$) 19.08 (q, CH_3), 22.01 (t, CH_2Pd), 23.47 (t, CCPd), 38.00 (t, CC=N), 160.40 (s) ppm. **8**: IR (KBr) 1780, 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) 0.93 (quintet, 2 H, CH_2CPd), 2.30 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.38 (t, 2 H, CH_2Pd), 2.70 (t, 2 H, CH_2C=N) ppm. The acetate complex **7** isomerized to the five-membered ring complex **20** in a chloroform solution at 20 °C for ca 2 h.



20

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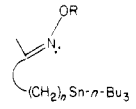
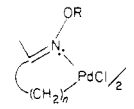
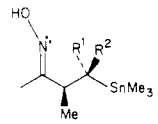
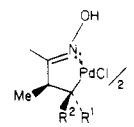
Table I. Cyclopalladation with the Stannyl Ketoximes[a]

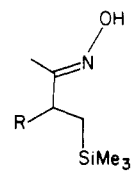
run	substrate (n, R)	product[b] (ratio)[c]	yield,[d] %	mp, °C (dec)	color
					
1	1 (2, H)	5	76	136-139	pale yellow
2	2 (2, Ac)	6	71	143-144	pale orange
3	3 (3, H)	7	74	105-107	pale yellow
4	4 (3, Ac)	8	75	122-125	pale orange
					
	9, R^1=Me, R^2=H 10, R^1=H, R^2=Me 11, R^1=Ph, R^2=H 12, R^1=H, R^2=Ph	13, R^1=Me, R^2=H 14, R^1=H, R^2=Me 15, R^1=Ph, R^2=H 16, R^1=H, R^2=Ph			
5	9	13:14 (56:44)	90[e]		
6	10	13:14 (60:40)	91[e]		
7	11	15:16 (89:11)	95		
8	12	15:16 (100:0)	87		

[a] The substrate (0.5-1.0 mmol), CH_2Cl_2 (2-4 mL), 0 °C, 30 min. [b] After concentration of the mixture under reduced pressure, addition of ether gave the crude product. Filtration, redissolution in CH_2Cl_2 (2 mL), and addition of ether gave the almost pure product. The products are stable in solid state or neat. Microanal. Found for **5** (Calcd): C, 21.08 (21.07); H, 3.55 (3.54); N, 6.04 (6.14). Found for **6** (Calcd): C, 26.61 (26.69); H, 3.60 (3.73); N, 4.91 (5.19). Found for **7** (Calcd): C, 24.73 (24.82); H, 4.04 (4.17); N, 5.75 (5.79). Found for **8** (Calcd): C, 29.60 (29.60); H, 4.18 (4.26); N, 4.83 (4.93). [c] Determined by ^1H NMR. [d] Isolated yields. [e] $PdCl_2(CH_3CN)_2$ was used; room temperature, 30 min.

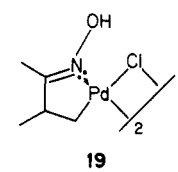
to our observations, Stille's procedure for the palladium-catalyzed coupling reaction with homotetraalkyltins in a polar solvent requires a much higher temperature.[6] Cyclopalladation of a sterically hindered alkyl oximes has been reported to require 2 days or more at room temperature.[2d]

Other examples include the α,β-disubstituted oximes **9**–**12**[7] which afforded the transmetalized complexes **13**–**16** (runs 5–8). The dimethyl oximes **9** and **10** gave the mixture of the cis and trans complexes **13** and **14**.[8] While both isomers **11** and **12** gave the trans disubstituted oxime complex **15**[9] predominantly. These stereochemical outcomes were interpreted as follows: (1) an equilibrium isomerization involving β-hydrogen elimination of the initially forming product followed by hydrogen insertion; (2) the transmetalation could proceed by both retention and inversion process of the C–Sn bond (Chart I).[10]

In place of the tributylstannyl function, a trimethylsilyl group can act as a directing group. Treatment of the (*E*)-β-silyl ketoxime **17** with dichlorobis(benzonitrile)-palladium in dichloromethane *at room temperature for 1 day* gave **5** in 50% yield but contaminated with butanoxime complex derived from protonation of **5**.[11] Introduction of one α-methyl group on the silyl ketoxime as shown in **18** increases the yield of the corresponding cyclometalated product **19**[12] in 88% yield as a pure form,[13] since the **19** is more stable than **5** for prolonged reaction time.



17, R=H
18, R=Me



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Thus we have demonstrated a new cyclopalladation reaction with organostannyl or organosilyl groups as a directing group in chelation systems of oximes.

(6) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (b) Tanaka, M. *Tetrahedron Lett.* **1979**, 2601. (c) Kosugi, M.; Shimizu, Y.; Migita, T. *J. Organomet. Chem.* **1977**, *129*, C36.

(7) For the starting ketones, see: Fleming, I.; Urch, C. J. *Tetrahedron Lett.* **1983**, *24*, 4591.

(8) ^1H NMR (90 MHz, $CDCl_3$): δ 0.71 (d, J = 7.2 Hz, 14, H_3CCPd), 0.90 (d, J = 7.0 Hz, 13, H_3CCPd), 1.21 (d, J = 7.2 Hz, 3 H, 13 and 14 $H_3CCC{=}N$), 1.91 (s, 13, $H_3CC{=}N$), 1.92 (s, 14, $H_3CC{=}N$), 1.97 (m,1 H, HCPd), 3.02 (double q, J = 7.0 × 3 and 3.8 Hz, 13, HCC=N), 3.57 (double q, J = 7.2 × 3 and 5.7 Hz, 14, HCC=N), 8.23 (br, 1 H, HON).

(9) ^1H NMR (90 MHz, $CDCl_3$): δ 0.98 (d, J = 7.4 Hz, 16, H_3CCPd), 1.32 (d, J = 7.0 Hz, 15, H_3CCPd), 2.00 (s, 15 and 16, 3 H, $H_3CC{=}N$), 2.25 (m, 15 and 16, 1 H, HCCC=N), 4.08 (d, J = 2.5 Hz, 15, HCCPd), 4.34 (d, J = 7.0 Hz, 16, HCCPd), 7.18 (m, 5 H, Ph), 8.05 (br, 1 H, HON).

(10) Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177. Olszoy, H. A.; Kitching, W. *Organometallics* **1984**, *3*, 1676. Also see ref 7.

(11) The decomposition could be attributable to formation of hydrogen chloride by reactions of hydroxy moiety of the oxime and generated trimethylchlorosilane for long reaction periods.

(12) ^1H NMR (60 MHz, $CDCl_3$): δ 1.24 (d, J = 7.2 Hz, 3 H, $H_3CCC{=}N$), 1.93 (s, 3 H, $H_3CC{=}N$), 2.20 (m, 2 H), 2.92 (m, 1 H), 7.95 (br, 1 H, HON). Microanal. Found (Calcd): C, 24.79 (24.82); H, 4.19 (4.17); N, 5.66 (5.59).

(13) In place of the stannyl ketoximes **9**–**11**, the corresponding silyl derivatives was treated with dichlorobis(benzonitrile)palladium but gave only dichlorooxime complexes. Expected transmetalation was not observed.

Neutral Bis(perhalophenyl)dicarbonylpalladium(II) and -platinum(II) Complexes

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Summary: Normal pressure carbonylation of *cis*-$[M(C_6X_5)_2(OC_4H_8)_2]$ (M = Pd, Pt; X = F, Cl; OC_4H_8 = tetrahydrofuran) leads to the isolation of *cis*-$[M(C_6X_5)_2(CO)_2]$. High ν(CO) stretching bands (far-IR, 2186 cm^{-1} for M = Pd and X = F) point to negligible metal-to-CO π-back-bonding.

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