Journal of Organometallic Chemistry, 299 (1986) 297–309
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DIRECTED CLEAVAGE OF CARBON–TIN BONDS BY PALLADIUM

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(Received July 19th, 1985)

Summary

The ligands 8-(trimethylstannyl)methylquinoline, n-$Bu_3Sn(CH_2)_3NMe_2$ and $Ph_3Sn(CH_2)_3NMe_2$ react with $(C_6H_5CN)_2PdCl_2$ to give five-membered palladium chelates, in which the nitrogen atom was able to direct palladium insertion into a specific carbon–tin bond. The X-ray crystal structure of the simple chelate $[(Me_2N(CH_2)_3)PdCl]_2$ is presented.

Introduction

One of the most reliable and general methods for the formation of transition metal–carbon bonds is the cyclometallation reaction [1–4]. In this reaction the leaving group is normally a proton, although examples exist of the cleavage of carbon–phosphorous [5], carbon–oxygen [6], carbon–nitrogen [7] and carbon–carbon bonds [8]. A second process for the alkylation of platinum group metals proceeds by cleavage of carbon–tin bonds [9–11]. Recently, the synthetic utility of this latter reaction has been demonstrated by the palladium-catalyzed alkylations of various types of organic substrates with tetraorganotins [12]. If the organotin compound is unsymmetrically substituted, the normal reactivity pattern is for tin–aryl bonds to be more reactive than tin–alkyl bonds and for electron-donating groups to favor the reaction, as would be expected for electrophilic substitution [13]. We wished to discover if directing effects, which play an important role in C–H bond cleavage, could be extended to electrophilic C–Sn bond activation. Additionally, given the difference in lengths between C–H and C–Sn bonds, we wanted to find out if the preference for five-membered ring transition states found in C–H bond activation extended to cleavage of carbon–Group IV element bonds.

Results and discussion

Initially we investigated directed cleavage of benzylic carbon–tin and carbon–silicon bonds in the 8-substituted quinoline ligands **2** and **3** (Scheme 1). These were

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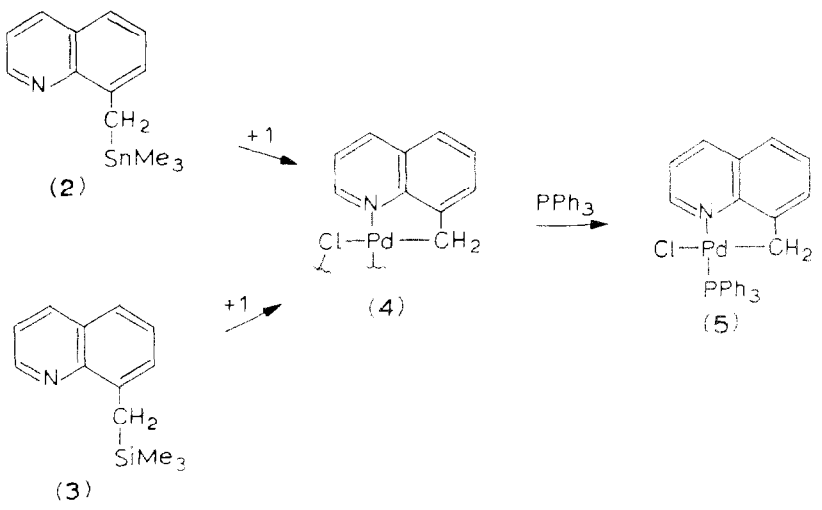
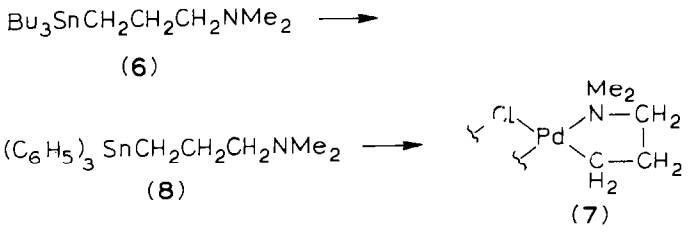


SCHEME 1

made by treating 8-lithiomethyl quinoline with either $ClSnMe_3$ or $ClSiMe_3$ or, in higher yield, from 8-bromomethyl quinoline and either $LiSnMe_3$ or $LiSiMe_3$. In 8-ethyl quinoline, Pd^{2+} complexes rapidly insert into the benzylic carbon–hydrogen bond and no products arising from insertion into the carbon–carbon bond have been reported [14]. In contrast, both **2** and **3** reacted with $Pd(C_6H_5CN)_2Cl_2$ (**1**) in chloroform to give the chlorine-bridged dimer **4** arising from carbon–Group IV bond cleavage. This dimer could be solubilized by PPh_3. There was a significant difference in the reactivity of the carbon–tin vs. the carbon–silicon bond. The benzylic C–Sn bond in **2** reacted upon mixing at 25°C while the C–Si bond in **3** was broken only after extended reflux in chloroform with **1**. Trimethyltin chloride was a byproduct in the metallation of **3** and it reduced **1** to give significant amounts of palladium metal. The cyclometallated complex **4** did not react with Me_3SnCl.

Having shown by these reactions that benzylic carbon–tin bonds could compete effectively with carbon–hydrogen bonds in a cyclometallation reaction, we next synthesized (*N*,*N*-dimethyl-3-aminopropyl)tri-n-butylstannane (**6**). This could be made either by Clark–Eschwiller methylation of (3-aminopropyl)tri-n-butylstannane or by reaction of Bu_3SnLi with *N*,*N*-dimethyl-3-chloropropylamine. In the ligand **6** there are four electronically equivalent carbon–tin bonds, but the dimethylamino group should direct cleavage of only one of them, if one assumes that a preference for forming five-membered rings is retained. Cyclometallation at the CH_2 bonds next to tin was a second possibility, but since the benzylic C–H bonds in **2** did not cyclometallate, the C–H bonds in **6** were not expected to be reactive. Compound **6**, upon reaction with **1** in $CHCl_3$, gave more than a 75% isolated yield of the palladium chelate **7** (Scheme 2). That the yield is greater than the statistical 25% shows that directed carbon–tin bond cleavage had occurred. Metallic palladium was a by-product of this synthesis, arising at least in part from the reaction of **1** with the Bu_3SnCl which ^1H NMR spectroscopy showed was a co-product of the synthesis of **7**. The chelate **7** did not react at room temperature with either Bu_3SnCl or the ligand **6**. In the case of the primary amine ligand $Bu_3Sn(CH_2)_3NH_2$ no stable chelates could be isolated and only reduction to palladium metal took place.



SCHEME 2

The normally higher reactivity of Sn–C(sp^2) bonds relative to Sn–C(sp^3) bonds towards electrophilic metal centers could be reversed with an appropriately placed NMe_2 group. The ligand $Ph_3Sn(CH_2)_3NMe_2$ (**8**), when reacted with **1** in $CHCl_3$ at 25°C gave a 72% isolated yield of the five-membered chelate **7** from insertion into the Sn–C(sp^3) bond (Scheme 2). This clearly shows that the palladium first coordinates to nitrogen and then inserts into the tin–carbon bond which will produce a five-membered chelate ring.

An extension of this directed cleavage strategy to the synthesis of four-and six-membered chelates was attempted. Treatment of $Bu_3Sn(CH_2)_4NMe_2$ (**9**) with **1** at room temperature, however, produced only palladium metal. It is known that the related six-membered platinacycles are at least as stable as five-membered platinacycles [15]. Thus, it is likely that the inability to isolate a six-membered chelate from **9** arose not from the instability of the product, but from the inability of the NMe_2 group to direct formation of a six-membered ring. The only soluble palladium-containing species that could be isolated was the chelated olefin complex $(NMe_2CH_2CH_2CHCH_2PdCl)_2$, which was recovered in quite a low yield. Since stable four-membered chelates have been synthesized by the addition of amines to coordinated olefins [16], we attempted to isolate such compounds by the directed cleavage route using $Bu_3Sn(CH_2)_2NMe_2$ (**10**). At room temperature, only reduction to palladium black took place. To test for the transient formation of a four-membered chelate, **1** was added to a CO-saturated solution of **10** in $CHCl_3$ at 0°C, and CO bubbling was continued for 1 h. Examination of the filtered reaction mixture by IR spectroscopy showed no acylmetal bands. Since CO insertion into the Pd–C bond of the desired four-membered chelate is expected to be facile and since the resulting product should be stable [17], we conclude that in **10** the NMe_2 group was not able to direct formation of a four-membered ring. In all cases in which the starting $Pd(C_6H_5CN)_2Cl_2$ was reduced to palladium metal the organic residue was a complex mixture of products.

The silane $Me_3Si(CH_2)_3NMe_2$ (**11**) was made in order to see if directed cleavage of alkyl carbon–silicon bonds was possible. However, no C–Si cleavage occurred with **1** or with $Pd(O_2CCF_3)_2$ even upon extended reflux in $CHCl_3$. The shift in the ^1H NMR of the NMe_2 resonances in **11** upon addition of **1** from 2.5 to 2.7 indicated that palladium–nitrogen coordination took place, but in this case did not lead to C–Si bond breaking.

Since **7** is one of the simplest palladium chelates reported, it seemed worthwhile to obtain its crystal structure. Such data are useful, among other reasons, as a starting point for molecular mechanics calculations on the conformations of

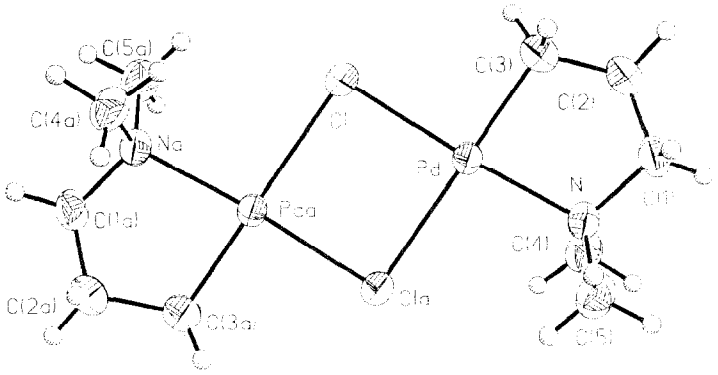


Fig. 1. Computer-generated plot of the molecular structure of 7. Hydrogen atoms are placed at calculated positions.

organometallic compounds. Compound 7 was recrystallized from CH_2Cl_2/pentane as colorless prisms. The crystals were stable for many days at room temperature, while solutions of 7 in $CHCl_3$ slowly darkened over the course of 24 h. A plot of 7's molecular structure resulting from single-crystal X-ray analysis is given in Fig. 1. Tables 1–6 contain the crystallographic parameters, atomic coordinates, bond lengths, bond angles and anisotropic thermal parameters arising from the structure determination.

The palladium–carbon bond length in 7, 1.998(3) Å is slightly compressed as is often seen in chelates and is shorter than the 2.08 Å expected from the sum of covalent radii. The *trans*-influence of carbon is seen in the different Pd–Cl bond lengths of the bridging chlorines, with the Pd–Cl bond *trans* to carbon 0.188 Å longer than the Pd–Cl bond *trans* to nitrogen. The most interesting feature of the structure is the conformation of the five-membered ring (see Fig. 2 for torsion angles). Both half-chair (C_2) and envelope (C_s) conformations have been observed in transition-metal organometallic five-membered rings [18]. The ring in 7 is probably best described as existing in an envelope conformation with C(2) out of the plane of the other ring atoms. For other metallacycles different ring atoms serve as the flap of the envelope. In $(Me_3C_5)Cl_2Ta(CH_2)_4$ the metallacycle is in an envelope conforma-

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($Å \times 10^3$)

Atom	x	y	z	U^a
Pd	4227(1)	1379(1)	4050(1)	29(1)
Cl	6941(1)	927(1)	5582(1)	43(1)
N	1884(3)	1904(2)	2665(2)	33(1)
C(4)	190(4)	2003(3)	3278(3)	44(1)
C(2)	3437(4)	4045(3)	3168(3)	47(1)
C(1)	2326(4)	3216(3)	2130(3)	41(1)
C(3)	5120(4)	3225(3)	3811(3)	45(1)
C(5)	1460(5)	906(4)	1635(3)	49(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 2

BOND LENGTHS (Å)

Pd–Cl	2.337(1)	Pd–N	2.085(2)
Pd–C(3)	1.998(3)	Pd–Cla	2.525(1)
Cl–Pda	2.525(1)	N–C(4)	1.480(4)
N–C(1)	1.498(4)	N–C(5)	1.482(4)
C(2)–C(1)	1.496(4)	C(2)–C(3)	1.513(4)

TABLE 3

BOND ANGLES (deg.)

Cl–Pd–N	176.2(1)	Cl–Pd–C(3)	91.7(1)
N–Pd–C(3)	84.5(1)	Cl–Pd–Cla	88.0
N–Pd–Cla	95.8(1)	C(3)–Pd–Cla	178.0(1)
Pd–Cl–Pda	92.0	Pd–N–C(4)	108.2(2)
Pd–N–C(1)	107.4(2)	C(4)–N–C(1)	110.9(2)
Pd–N–C(5)	112.5(2)	C(4)–N–C(5)	107.8(2)
C(1)–N–C(5)	110.0(2)	C(1)–C(2)–C(3)	107.4(3)
N–C(1)–C(2)	109.2(2)	Pd–C(3)–C(2)	108.9(2)

TABLE 4

ANISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^3$) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	26(1)	30(1)	28(1)	4(1)	2(1)	1(1)
Cl	35(1)	39(1)	47(1)	10(1)	−9(1)	−6(1)
N	31(1)	35(1)	32(1)	5(1)	4(1)	4(1)
C(4)	30(1)	55(2)	48(2)	6(1)	8(1)	6(1)
C(2)	51(2)	34(2)	53(2)	10(1)	6(1)	−3(1)
C(1)	43(2)	39(2)	42(2)	16(1)	6(1)	1(1)
C(3)	44(2)	38(2)	52(2)	9(1)	4(1)	−6(1)
C(5)	56(2)	50(2)	36(2)	−2(1)	−2(1)	6(2)

[a] The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + \ldots + 2hkabU_{12})$.

TABLE 5

HYDROGEN COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($Å^2 \times 10^3$)

Atom	x	y	z	U
H(4a)	392	2707	3891	52
H(4b)	32	1180	3698	52
H(4c)	−937	2184	2657	52
H(2a)	3882	4837	2819	56
H(2b)	2648	4280	3769	56
H(1a)	1155	3660	1776	50
H(1b)	3067	3079	1478	50
H(3a)	6082	3207	3292	53
H(3b)	5643	3606	4622	53
H(5a)	2581	816	1263	57
H(5b)	397	1163	992	57
H(5c)	1185	75	1999	57

TABLE 6

CRYSTALLOGRAPHIC DATA FOR 7

Molecular formula:	$[C_5H_{12}NClPd]_2$
Crystal system:	Monoclinic
Cell dimensions:	a 7.122(1), b 10.079(2), c 10.717(3) Å
	β 100.69(2)°, V 755.9(3) Å^3

Wavelength: 0.71069 Å (Mo-K_α, graphite monochromator)
Range of 2θ: 3.5–50°
Space group: $P2_1/c$
Number of molecules per cell: $Z = 4$
Calculated density: 2.00 g cm^{-3}
Linear absorption coefficient: μ 26.6 cm^{-1}
Number of unique observed reflections 1306
Structure-factor weights $w = 1/[\sigma^2(F) + 0.00007F^2]$
with $\sigma^2(F)$ from counting statistics
Final R factors $R = 0.0183$ $R_w = 0.0302$
Goodness of fit (nominal): 2.481
Goodness of fit (divided by slope of normal probability plot): 1.379
Crystal dimensions: 0.20 × 0.66 × 0.66 mm

tion with the Ta out of the ring plane [19] while in $(PPh_3)_2Pt(CH_2)_4$ it is one of the CH_2 groups bonded to Pt which is out of the ring plane [20]. In **7** there are no obvious crystal packing constraints or close intermolecular contacts that would favor this conformation over another. It is known that in the case of organic five-membered ring heterocycles, the barrier to pseudorotation is very small when all the ring bonds are approximately the same length (for example, tetrahydrofuran). However, when the ring contains a heavy atom, and thus some of the ring bonds are significantly longer than the others, barriers to pseudorotation increase. For example, in thiophane the barrier to pseudorotation is 2.8 kcal mol^{-1} [21] and in selenophane it is 4.8 kcal mol^{-1} [22]. Thus, it is possible that the conformations of

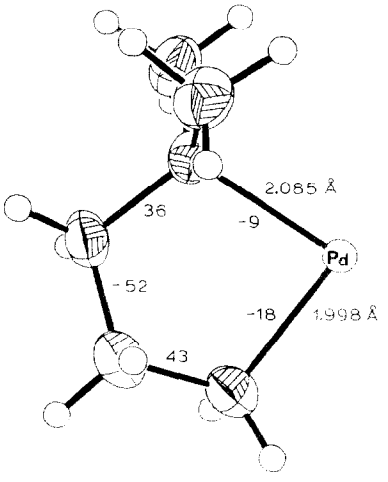


Fig. 2. Torsion angles of the five-membered chelate ring in **7**.

organometallic five-membered rings seen in crystal structures such as **7**'s represent true energy minima and are not dominated by crystal packing effects.

Experimental

Materials and methods

THF and ether were distilled from sodium benzophenone ketyl and hexane from calcium hydride. HMPA was used from a freshly opened bottle and stored over 5 Å molecular sieves. Preparation and handling of air sensitive compounds was carried out under nitrogen. All column chromatography was carried out with either silica gel (70–270 mesh) or Florisil (100–200 mesh). Fractions from column chromatography were monitored by using EM Pre-coated TLC plates (silica gel 60 F-254). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. ^{1}H and ^{13}C NMR spectra were taken on a Varian EM 360A 60 MHz or a Bruker WM-250 MHz NMR spectrometer. IR spectra were taken on a Perkin–Elmer 681 Infrared Spectrophotometer and melting points were measured with a Thomas Hoover capillary melting point apparatus.

Synthesis of 8-[(trimethylstannyl)methyl]quinoline (2)

(A). To 2.2 ml (15.4 mmol, 1.1 equiv.) of diisopropylamine in 10 ml of dry THF in a Schlenk vessel was added 9.5 ml (15.7 mmol) of n-butyllithium (hexane solution), 1.65 *M*) and stirred for 30 min under nitrogen. 2.8 ml (15.8 mmol) of HMPA was added and then the flask cooled to −78°C. To this LDA solution was added 2.0 g of 8-methylquinoline dissolved in 8 ml of dry THF dropwise at −78°C. The mixture grew deep purple and was stirred for another hour at −78°C. 2.8 g (14 mmol) of trimethyltin chloride in 10 ml of dry THF was added to this flask slowly and the solution turned yellowish green. Stirring was continued for 9 h at −78°C then addition of water, evaporation of THF and extraction with CH_2Cl_2 followed. The organic layer was dried over magnesium sulfate and evaporated in vacuo to give a yellow oil. Flash column chromatography over silica gel and preparative TLC eluting with ethyl acetate and hexane (2/5) gave 0.80 g (2.62 mmol) of the organotin compound: yield 18.7%, R_f 0.56.

(B). Lithium clippings (0.49 g, 75 mmol atoms, 10 equiv.) were stirred in 15 ml of dry THF under nitrogen at 5°C and a solution of trimethyltin chloride was added slowly enough to maintain the mixture below 5°C. After the addition had been completed the mixture turned dark green. At that time this solution gave a positive Gilman Test. To the stirred solution of 8-bromomethylquinoline (1.12 g, 5 mmol) was added the above solution of trimethyltin lithium slowly at 5°C. The mixture grew deep purple, but after stirring for 1 h, it turned to dark green again. This dark green solution was stirred for another 2 h and then hydrolysed with saturated ammonium chloride solution. The same purification procedure gave 0.57 g (1.86 mmol) of **2**: yield 37.5%.

IR (neat): 3020, 2970, 2910, 1365, 1310, 1080, 825, 790, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.82 (dd, 1H), 7.98 (dd, 1H), 7.6–7.1 (m, 4H), 2.88 (s, 2H), −0.06 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 148.2, 146.1, 143.3, 136.1, 128.4, 126.4, 126.3, 123.1, 120.7, 17.7, −8.7 ppm. Anal. Found: C, 51.25; H, 5.71; N, 4.53. $C_{13}H_{17}NSn$ calcd.: C, 51.03; H, 5.60; N, 4.58%.

*Synthesis of 8-[(trimethylsilyl)methyl]quinoline (**3**)*

To 1 g (7 mmol) of 8-methylquinoline in 10 ml of dry THF was added a solution of LDA (1.1 equiv.) at −78°C slowly. To this mixture was added 0.76 g (7 mmol) of trimethylsilyl chloride at −78°C. The color of the solution changed to yellowish green from deep purple. After stirring for 3 h at −78°C and for 1 h at room temperature the same work-up and purification procedure as above gave 0.47 g (2.18 mmol) of the product which was a pale yellow oil: yield 31.9%. R_f (ethyl acetate/hexane 2/5 v/v) 0.56.

IR (neat): 3040, 2940, 2890, 1245, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.9 (dd, 1H), 8.1 (dd, 1H), 7.7–7.1 (m, 4H) 2.8 (s, 2H), −0.05 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 148.5, 146.6, 140.6, 136.0, 128.6, 127.8, 126.2, 123.9, 120.6, 22.0, −1.3 ppm. Anal. Found: C, 72.41; H, 8.08; N, 6.62. $C_{13}H_{17}NSi$ calcd.: C, 72.51; H, 7.96; N, 6.50%.

*Synthesis of the palladium chelate **5***

(A). To 0.153 g (0.5 mmol) of 8-[(trimethyltin)methyl]quinoline in 1 ml of $CDCl_3$ was added 0.190 g (0.5 mmol) of $Pd(C_6H_5CN)_2Cl_2$ in 1 ml of $CHCl_3$ at room temperature. As soon as the palladium complex solution was added, which was dark red, the resulting solution turned black and then gave a dark green precipitate. The addition of 0.131 g (0.5 mmol) of triphenylphosphine in 2 ml of $CHCl_3$ followed. The filtration of the organic layer from a black powder which was palladium metal and evaporation of chloroform gave a yellow solid. Recrystallization with methylene chloride/pentane gave 0.028 g of yellowish green crystals, yield 10.3%, m.p. 148°C (dec.).

(B). To 0.108 g (0.5 mmol) of 8-[(trimethylsilyl)methyl]quinoline in 2 ml of $CDCl_3$ was added 0.190 g (0.5 mmol) of $Pd(C_6H_5CN)_2Cl_2$ in 2 ml of $CHCl_3$ at room temperature. The resulting solution was refluxed for 6 d. The dark brown precipitate was separated and dissolved in the solution of triphenylphosphine (0.131 g, 0.5 mmol) in 5 ml of $CHCl_3$. This heterogeneous solution was filtered and the solvent was evaporated in vacuo to give a dark green powder. Recrystallization with methylene chloride/pentane gave a yellowish green solid which showed the same NMR spectrum and m.p. as material prepared from **2**.

IR ($CDCl_3$): 3050, 2880, 1505, 1228, 1100, 1075, 1065, 1055, 1025, 995, 825, 780, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.9 (m, 1H), 8.4 (dd, 1H) 8.1–7.6 (m, 4H) 7.6–7.3 (m, 15H), 2.9 (d, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 150.4, 147.2, 137.9, 135.0, 134.8, 131.8, 131.0, 130.5, 129.1, 128.4, 128.2, 127.7, 123.8, 121.6, 33.4 ppm. Anal. Found: C, 61.56; H, 4.24; N, 2.56. $C_{28}H_{23}ClNPPd$ calcd.: C, 61.52; H, 4.43; N, 2.65%.

*Synthesis of 3-(N,N-dimethylamino)propyltri-n-butyltin (**6**)*

(A) (a) Synthesis of (2-cyanoethyl)tri-n-butyltin. Tri-n-butyltin hydride (1.454 g, 5 mmol) and acrylonitrile (0.398 g, 7.5 mmol) were placed in 25 ml round bottom flask and heated at 80°C for 3 h with a trace of AIBN. This mixture was cooled to room temperature. Flash chromatography over silica gel using methylene chloride and evaporation in vacuo gave a colorless oily liquid which was transferred to the next step directly.

IR (neat): 2950, 2920, 2860, 2840, 2235, 1460, 1425, 1415, 1372, 1068, 995, 957, 870, 690, 660 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.5 (t, 2H), 1.8–0.7 (m, 29H) ppm. ^{13}C NMR ($CDCl_3$): δ 123.7, 26.9, 26.6, 25.2, 12.1, 11.5, 7.7 ppm.

(b) Reduction of (2-cyanoethyl)tri-n-butyltin. In a 100 ml round bottom flask, equipped with a magnetic stirrer, condenser and dropping funnel, were placed 20 ml of dry ether and 0.19 g (5 mmol) of lithium aluminium hydride. A solution of (2-cyanoethyl)tri-n-butyltin in 5 ml of dry ether was added during 30 min with stirring. This resulting solution was heated at reflux temperature for 6 h and cooled in an ice bath and unreacted lithium aluminium hydride was decomposed by the Steinhardt method [23]. The organic layer was dried over magnesium sulfate and evaporated in vacuo to give 1.35 g (3.90 mmol) of a yellow oily liquid: 76.1%.

IR (neat): 3370, 3290, 2950, 2910, 2860, 2840, 1460, 1412, 955, 870, 860, 685, 660 cm^{-1}. ^1H ($CDCl_3$): δ 2.65 (t, 2H), 2.0–1.7 (m, 31H) ppm.

(*c*) To 0.2 g (0.57 mmol) of (3-aminopropyl)tri-n-butyltin in a 25 ml round bottom flask was added 0.105 g (0.23 mmol) of formic acid and 1.45 g (0.17 g) of formaldehyde (37%). This mixture was refluxed at 80°C for 24 h and then cooled to room temperature. A standard ether-aqueous workup for an amine gave 0.20 g of an oil, 93%.

IR (neat): 2950, 2920, 2860, 2840, 1690, 1685, 1590, 1460, 1422, 1290, 1255, 1115, 1068, 1040, 1010, 970, 955, 870, 860, 785, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.2 (m, 8H), 1.7–0.7 (m, 31H) ppm. ^{13}C NMR ($CDCl_3$): δ 64.3, 45.5, 29.3, 27.4, 25.1, 13.6, 9.0, 6.5 ppm. Anal. Found: C, 54.57; H, 10.61; N, 3.79. $C_{17}H_{39}NSn$ calcd.: C, 54.28; H, 10.45; N, 3.72%.

(*B*). To 0.25 g (35 mmol atoms) of lithium clippings which had been washed with methanol and dry hexane quickly in 10 ml of dry THF was added 1.63 g (5 mmol) of tri-n-butyltin chloride at 0°C. The resulting mixture was stirred for 6 h at the same temperature and then turned dark green. 3-Dimethylamino-1-chloropropane was prepared by neutralization of the commercial HCl salt (0.79 g, 5 mmol) with 15% NaOH solution and extraction with ether, and dried over magnesium sulfate. To this dry ether solution of 3-dimethylamino-1-chloropropane was added tributyltin lithium solution at −7°C. As soon as the organolithium compound was added to the flask, the mixture turned white. After stirring for another 2 h, it was followed by reflux for 1 h, addition of water and extracted with methylene chloride. The organic layer was dried over magnesium sulfate and evaporated in vacuo to give 1.89 g of yellow liquid. Bulb to bulb distillation (0.1 mmHg, 120°C) gave 0.34 g (0.90 mmol) of a colorless liquid. This crude product was purified by flash chromatography over Florisil followed by eluting with pentane and addition of a mixture of ethyl acetate/hexane (2/5), 18.1% in the case of 10 mmol scale reaction.

Reaction of 3-N,N-dimethylaminopropyltri-n-butyltin with $Pd(C_6H_5CN)_2Cl_2$ to give **7**

0.188 g (0.50 mmol) of 3-*N*,*N*-dimethylaminopropyltri-n-butyltin in 2 ml of $CHCl_3$ and 0.192 g (0.50 mmol) of **1** in 2 ml of $CHCl_3$ were prepared separately and mixed together at room temperature. The resulting solution gave a dark green precipitate. Recrystallization from methylene chloride and pentane gave 0.09 g (0.197 mmol) of yellowish green powder: yield 78.9%, m.p. 106–109°C.

Also the reaction of 3-*N*,*N*-dimethylaminopropyltriphenyltin with the palladium complex was carried on same manner: yield 72.4%.

IR ($CDCl_3$): 2880, 2230, 1460, 1455, 1225, 1170, 1140, 1100, 1075, 1005, 960, 775 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.72 (s, 6H), 2.43 (m, 2H), 2.16 (m, 2H) 1.08–1.01 (m, 2H) ppm. Anal. Found: C, 26.47; H, 5.50; N, 6.04. $C_{10}H_{24}Cl_2N_2Pd_2$ calcd.: C,

26.34; H, 5.31; N, 6.14%. ^{13}C NMR ($CDCl_3$): δ 67.46, 67.21, 51.06, 50.76, 31.36, 31.11, 26.52, 24.64 (−23°C) ppm.

*Synthesis of 3-N,N-dimethylaminopropyltriphenyltin (**8**)*

Triphenyltin lithium was prepared by adding to a well-stirred suspension of lithium clippings (0.417 g, 60 mmol atoms) in 20 ml of dry THF 1.928 g (5 mmol) of triphenyltin chloride in 20 ml of dry THF at room temperature. After stirring overnight this dark olive solution was transferred to a 100 ml dry round bottom flask by syringe. To this triphenyltin lithium/THF solution was added 3-*N*,*N*-dimethylaminopropyl chloride slowly at −10°C, which was prepared from the hydrochloride salt (0.79 g, 5 mmol) by neutralization, extraction with ether and drying over sodium sulfate. This resulting solution was stirred overnight at room temperature. The addition of 0.1 *M* sulfuric acid gave a white precipitate which was extracted with water. The water layer was neutralized and extracted with 15% NaOH and ether. The ether layer was dried over sodium sulfate and evaporated in vacuo to give colorless oily liquid. Bulb to bulb distillation (0.1 mmHg, 150°C) gave 0.98 g of product: yield 44.9%.

IR (neat): 3050, 3018, 3000, 2960, 2930, 2845, 2805, 2760, 1475, 1457, 1422, 1069, 1018, 992, 722, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7–7.4 (m, 15H), 2.3 (t, 2H), 2.1 (s, 6H), 1.9–1.8 (m, 2H), 1.5 (t, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 139.1, 136.9, 128.3, 63.2, 45.4, 24.8, 8.5 ppm. Anal. Found: C, 63.28; H, 6.43; N, 3.02. $C_{23}H_{25}NSn$ calcd.: C, 63.34; H, 6.24; N, 3.21%.

*Synthesis of 4-N,N-dimethylaminobutyltri-n-butyltin (**9**)*

(a) Synthesis of 3-chloropropyltri-n-butyltin. To 1.57 g (10 mmol) of 1-bromo-3-chloropropane in 20 ml of dry ether was added 1.74 ml (10 mmol) of HMPA and a THF solution of tri-n-butyltin lithium (1.1 equiv.), which was prepared as before, at 0°C dropwise. After stirring for 2 h at the same temperature, work-up was with saturated sodium bicarbonate solution and extraction with methylene chloride. The methylene chloride layer was dried over magnesium sulfate and evaporated under reduced pressure to give a yellow oily liquid: quantitative yield.

IR (neat): 2945, 2915, 2860, 2840 (C–H), 1458, 1370, 1288, 1195, 1065, 980, 870, 740, 662 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.4 (t, 2H), 2.0–1.8 (m, 2H), 1.7–0.7 (m, 29H) ppm. Anal. Found: C, 49.08; H, 9.33. $C_{15}H_{33}ClSn$ calcd.: C, 49.01; H, 9.05%.

(b) Substitution of chlorine with cyanide anion. In a 100 ml round bottom flask were placed 3.93 g (10.7 mmol) of 3-chloropropyltri-n-butyltin, 1.43 g (22 mmol) of potassium cyanide and a catalytic amount of tetra-n-butylammonium chloride and a catalytic amount of 18-crown-6 in 50 ml of a mixture of n-butanol and water (3/1). This mixture was refluxed overnight and then extracted with methylene chloride. Drying and evaporation of the organic layer gave a colorless oily liquid which was transfered to the next step directly.

IR (neat): 2945, 2915, 2860, 2840, 2235, 1450, 1412, 1370, 1335, 1288, 1242, 1175, 1445, 1065, 1040, 1020, 995, 955, 870, 860, 685, 665 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.3 (t, 2H), 1.9–0.7 (m, 31H) ppm.

(c) Reduction and methylation of 3-cyanopropyltri-n-butyltin. In a 100 ml round bottom flask, equipped with a magnetic stirrer, a condenser and a dropping funnel, was placed 0.1 g (2.4 mmol) of lithium aluminum hydride and 20 ml of dry ether. An ether solution of 0.86 g (2.4 mmol) of 3-cyanopropyltri-n-butyltin in a dropping

funnel was added slowly with stirring. This mixture was heated for 6 h at reflux temperature and then cooled in an ice bath. Work-up by the Steinhardt method, drying and evaporation of the ether layer gave yellow liquid which was used in the next methylation step directly.

This 3-aminobutyltri-n-butyltin was methylated by the Clarke–Eschweiler method. In a 25 ml round bottom flask were placed 0.73 g (2 mmol) of 3-aminobutyltri-n-butyltin, 1.456 g (1 mmol) of formic acid and 5.8 g (0.68 mmol) of formaldehyde (36%). After reflux at 80°C for 24 h, the white solid was dissolved in methylene chloride and washed with 1 *N* NaOH solution. Flash chromatography over Florisil eluting with pentane, ethyl acetate-hexane (2 : 5), ethyl acetate and finally methanol, gave **9** as an oil in high yield.

IR (neat): 2950, 2910, 2805, 2770, 1685, 1590, 1415, 765, 745, 685, 660 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.3–2.2 (m, 8H), 1.6–0.7 (m, 33H) ppm. ^{13}C NMR ($CDCl_3$): δ 59.5, 45.3, 32.2, 29.3, 27.4, 25.1, 13.6, 9.2, 9.0 ppm. Anal. Found: C, 54.62; H, 10.34; N, 3.62. $C_{18}H_{41}NSn$ calcd.: C, 55.40; H, 10.34; N, 3.59%.

*Synthesis of 2-N,N-dimethylaminoethyltri-n-butyltin (**10**)*

A THF solution of tri-n-butyltin lithium and an ether solution of 2-dimethylaminoethyl chloride were prepared from tri-n-butyltin chloride and the hydrochloride salt (0.79 g, 5 mmol) by the same manner as above. To the solution of 2-*N*,*N*-dimethylaminoethyl chloride was added tri-n-butyltin lithium solution and 0.87 ml (5 mmol) of HMPA at −7°C. This resulting solution turned beige. After additional stirring for 2 h, it was followed by reflux for another hour, work-up with saturated sodium bicarbonate solution and extraction with methylene chloride. The organic layer was dried over magnesium sulfate and evaporated in vacuo to give a yellow oil. Flash chromatography over Florisil eluting with ethyl acetate gave 0.84 g (2.31 mmol) of an oily liquid: yield 46.2%, R_f 0.25.

IR (neat): 2950, 1439, 1370, 1165, 685, 660 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.5 (m, 2H), 2.2 (s, 6H), 1.7–0.8 (m, 29H) ppm. ^{13}C NMR ($CDCl_3$): δ 57.5, 44.7, 29.3, 27.4, 13.7, 10.1, 9.0 ppm. Anal. Found: C, 53.22; H, 10.05; N, 3.87. $C_{16}H_{37}NSn$ calcd.: C, 53.06; H, 10.30; N, 3.87%.

*Synthesis of 3-N,N-dimethylaminopropyltrimethylsilane (**11**)*

Into a 50 ml flask was placed 5.12 ml (25 mmol) of hexamethyldisilane in 15 ml of dry HMPA and 13.2 ml (20 mmol) of 1.5 *M* methyllithium (ether solution) was added slowly at 0°C. This mixture grew deep red. To 3-*N*,*N*-dimethylaminopropyl chloride in ether, which was isolated from hydrochloride salt (5.74 g, 35 mmol), was added trimethylsilyllithium/HMPA solution at 0°C and it gave a white precipitate. After stirring for 30 min at 0°C and for 2 h at room temperature it was extracted with water. The organic layer was heated with ethylene glycol for 24 h at 90–100°C to remove unreacted chloride and then washed with three portions of water. Drying and evaporation of ether gave a colorless oil in high yield.

^1H NMR ($CDCl_3$): 2.2–2.6 (m, 8H), 1.5–1.3 (m, 2H), 0.4–0.5 (m, 2H), −0.05 (m, 9H) ppm. ^{13}C NMR ($CDCl_3$): δ 64.0, 46.0, 22.7, 14.9, −1.2 ppm.

Structure determination of the chelate 7

Data collection and analysis were carried out on a Nicolet R3m/E diffractometer system at room temperature. The SHELXTL system of programs was used for data

reduction, structure determination, refinement, and graphics and tables. The chief crystallographic data are summarized in Table 6.

Reflection data were collected with 2θ scans, and three standard reflections were measured at the beginning and after every 45 reflections thereafter. Early standard intensity increased to 105% of its initial value during the course of data collection, and the data were scaled to remove this increase.

Absorption corrections were calculated by numerical integration from the positions of the 8 indexed faces that bounded the crystal. The transmission factors ranged from 0.397 to 0.608. Structure factors were then extracted in the usual way.

The structure was determined by multisolution direct methods. The heavy atoms were found readily, and the other nonhydrogen atoms followed from a difference map. Some, but not all, hydrogen atoms appeared as well.

The structure was refined by weighted least squares on F. Temperature factors of all nonhydrogen atoms were taken as anisotropic. All hydrogen atoms were inserted in theoretical positions, each with an isotropic temperature factor parameter 20% larger than the equivalent isotropic parameter for the carbon atom to which it is bonded. A final difference map exhibited no peaks larger than 0.6 electron $Å^{-3}$.

Acknowledgements

This work was supported by the NSF, CHE-8207269. The NSF also contributed to the purchase of the Nicolet diffractometer. J.W.S. is a Research Career Development Awardee of the National Cancer Institute, CA00947. We thank Professors Paul Williard and Gene Carpenter for help and instruction in the solution of the crystal structure.

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