Cyclopenta[*b*]thienyl ligand in organometallic chemistry. Studies of the regioselectivity of the synthesis of new σ-element-substituted cyclopenta[*b*]thiophene derivatives

D. A. Kissounko, M. V. Zabalov, Yu. F. Oprunenko, and D. A. Lemenovskii*

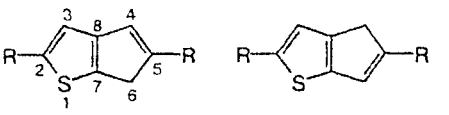
Department of Chemistry, M. V. Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 932 8846. E-mail: kis@org.chem.msu.su

Reactions of 2-ethyl-5-methylcyclopenta[*b*]thienyllithium (thiopentalenyllithium) (**2**) with various electrophilic reagents afford σ-element-substituted thiopentalenes. However, the reaction with Ph_3SnCl yields only one of two possible isomers, *viz.*, triphenyl(4*H*-cyclopenta[*b*]thiophen-4-yl)stannane (**4c**), whereas the reactions with Me_3SiCl, Me_3SnCl, or Ph_2PCl give both possible isomers, *viz.*, trimethyl(6*H*-cyclopenta[*b*]thiophen-6-yl)silane (**3a**) and trimethyl(4*H*-cyclopenta[*b*]thiophen-4-yl)silane (**4a**), trimethyl(6*H*-cyclopenta[*b*]thiophen-6-yl)stannane (**3b**) and trimethyl(4*H*-cyclopenta[*b*]thiophen-4-yl)stannane (**4b**), or diphenyl(6*H*-cyclopenta[*b*]thiophen-6-yl)phosphine (**3d**) and diphenyl(4*H*-cyclopenta[*b*]thiophen-4-yl)phosphine (**4d**) in ratios of 1 : 2, 1 : 2, or 1 : 1, respectively. The structure of compound **4c** was established by X-ray diffraction analysis. The observed regioselectivity of formation of compound **4c** is attributed to the specific precoordination of the tin atom by the sulfur atom of the thiopentalenyl ligand and to the steric overcrowding of the Sn atom in organotin electrophiles.

Key words: thiopentalenyl ligand, regioselective substitution, specific precoordination.

The synthesis, structural studies, and dynamic behavior of σ-heteroelement derivatives of cyclopentadiene and indene are among the high-priority fields of modern organometallic chemistry[1,2] owing to the wide use of these compounds as mild carriers of organic groups in electrophilic substitution applied in organic chemistry[3] and organometallic synthesis of σ- and π-complexes of transition and main-group elements.[4–6] However, only a few examples of heterocyclic π-complexes of transition metals are available due primarily to problems associated with their synthesis as well as to their lower thermodynamic stability compared to the corresponding cyclopentadienyl and indenyl analogs. The most significant results in this field involve the syntheses of various thiophene and benzothiophene complexes of manganese, rhodium, iridium, and chromium,[7] which are of great importance in studies of catalytic processes of hydrodesulfurization,[8] and the syntheses of heterocyclic thio and aza analogs of indenyl and fluorenyl zirconocene π-complexes as catalysts of stereoregular polymerization of propylene.[9] Recently, we have also studied the ability of the thiopentalenyl ligand to undergo reversible $\eta^5 \leftrightarrow \eta^3$-haptotropic shifts using the $Mn(\eta^5\text{-Th})(CO)_3$ complex[10] as an example (Th = 2-ethyl-5-methylcyclopenta[*b*]-thienyl; hereinafter, thiopentalenyl).

In this work, the regioselectivity of the synthesis of heteroorganic thiopentalene derivatives containing organosilicon, -tin, or -phosphorus substituents was studied.



Previously,[11] we have demonstrated that regioselective substitution can occur in reactions of the 4-azapentalenyl anion with different electrophilic reagents. However, the participation of the lone electron pair of the nitrogen atom in the π-electron aromatic system of the 4-azapentalenyl anion virtually excludes precoordination of nitrogen with electrophilic reagents. The sulfur atom in the thiopentalenyl anion of **2** is virtually identical to the carbon atom in electronegativity and, consequently, in σ-acceptor properties and yet possesses both the lone electron pair on the 2*p* orbital, which is not involved in π-conjugation, and unoccupied 3*d*-orbitals. Both these factors can contribute to the control over the regioselectivity of the reaction.

Results and Discussion

2-Ethyl-5-methylcyclopenta[*b*]thiophene was synthesized as a mixture of isomers **1a** and **1b** according to a

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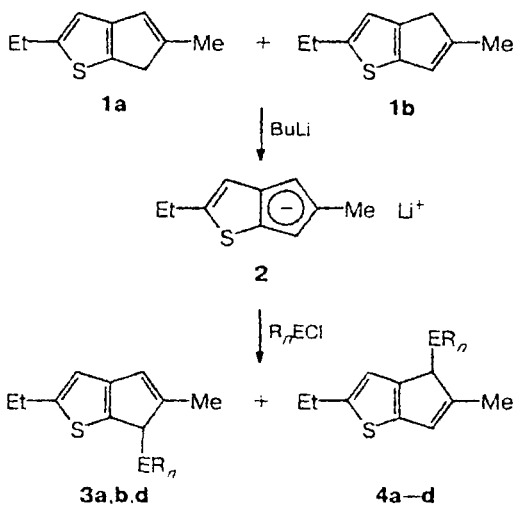
procedure reported previously.[12] The addition of an equimolar amount of Bu^nLi in hexane to an ethereal solution of **1a** and **1b** immediately afforded a precipitate of thiopentalenyllithium (**2**).

Scheme 1



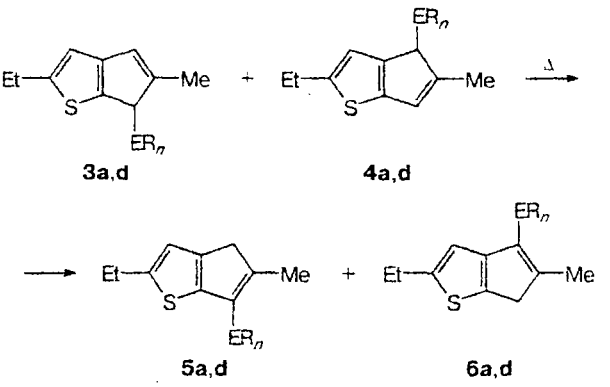
Compound	E	*n*	R
3a, **4a**	Si	3	Me
3b, **4b**	Sn	3	Me
4c	Sn	3	Ph
3d, **4d**	P	2	Ph

The subsequent reactions of salt **2** with electrophilic reagents Me_3SiCl, Me_3SnCl, Ph_3SnCl, and Ph_2PCl gave the corresponding thiopentalenyl derivatives (**3a** and **4a**; **3b** and **4b**; **4c**; and **3d** and **4d**, respectively) in yields of higher than 70%. A 1 : 2 mixture of isomeric organosilicon derivatives **3a** and **4a** was obtained as an air-stable viscous yellow oil readily soluble in organic solvents. The structures of **3a** and **4a** were confirmed by ^1H and $^{13}C\{^1H\}$ spectroscopy, mass spectrometry, and DEPT 135 experiments.

When a mixture of **3a** and **4a** was heated at 60 °C for 16 h, these isomers were completely isomerized to the corresponding vinyl isomers, *viz.*, trimethyl(4*H*-cyclopenta[*b*]thiophen-6-yl)silane (**5a**) and trimethyl(6*H*-cyclopenta[*b*]thiophen-4-yl)silane (**6a**), in a ratio of ~3 : 2 (Scheme 2).

As a result of the rearrangement, the ^1H NMR spectrum of a mixture of **5a** and **6a** has two additional singlets at δ −0.01 and −0.42 corresponding to the $SiMe_3$ groups of vinyl isomers **5a** and **6a**, respectively. Two new signals appear also in the region of methylene protons at δ 3.13 (H(4), **5a**) and 3.28 (H(6), **6a**). The $^{13}C\{^1H\}$ NMR spectrum has signals at δ 1.32 (**5a**) and 1.93 (**6a**) corresponding to the $SiMe_3$ groups and signals of the carbon atoms of the methylene groups at δ 44.6 (C(4), **5a**) and 45.3 (C(6), **6a**). The structures of both isomers were also confirmed by DEPT 135 experiments.

Scheme 2



E = Si, R = Me, *n* = 3 (**a**); E = P, R = Ph, *n* = 2 (**d**)

The $^{119}Sn\{^1H\}$ NMR spectrum of the mixture obtained in the reaction of salt **2** with Me_3SnCl has two peaks at δ_{Sn} 11.1 and 8.8 with an intensity ratio of ~1 : 2, which are assigned to isomers **3b** and **4b**, respectively. Unfortunately, we failed to obtain derivatives **3b** and **4b** in the individual state due to the high lability of the Sn—C bonds. All tin derivatives completely decomposed at a temperature higher than 40 °C.

In contrast to Me_3Sn derivatives, lithium salt **2** reacted with Ph_3SnCl to give only isomer **4c** (Scheme 1). Compound **4c** is a bright-yellow crystalline substance and undergoes slow hydrolysis in air and in protic solvents. At a temperature lower than 40 °C, the migration of the Ph_3Sn group was not observed.

The structure of compound **4c** was determined based on the data of ^1H, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectroscopy, mass spectrometry, and elemental analysis.

X-ray diffraction study of compound **4c** confirmed the structure (Tables 1 and 2; Fig. 1) in which the Ph_3Sn group is bound to the C(4) atom. The tin atom has tetrahedral coordination; the bond angles are in the range of 107°—113° and the Sn—Ph_{ipso} bond lengths (2.127—2.148 Å) have standard values. The Sn—C(4) bond length (2.196(10) Å) is somewhat larger than the average Sn—C(sp^3) bond length,[13] which is apparently associated with steric crowding of both the Ph_3Sn group and the thiopentalenyl ligand.

The substantial downfield shifts of the signals of the H(4) and C(4) atoms in compound **4c** compared to those of the structurally similar indene derivatives are among the most remarkable spectral characteristics of **4c**. Thus, the chemical shift of the signal of the H(4) proton in the ^1H NMR spectrum is 4.78 ppm, and the corresponding chemical shift of the C(4) atom in the $^{13}C\{^1H\}$ NMR spectrum is 76.5 ppm. The chemical shifts of the remaining vinylic, allylic, and quaternary carbon atoms are in the range 117—146 ppm. The

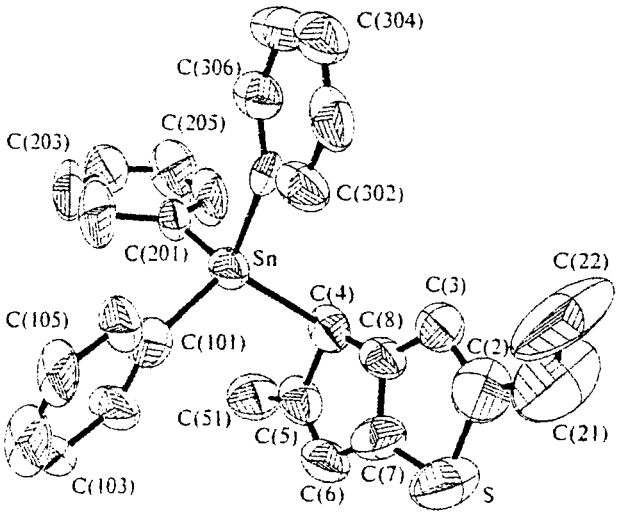


Fig. 1. Molecular structure of compound **4c** (thermal ellipsoids with 50% probability).

$^{119}Sn\{^1H\}$ NMR spectrum has only a peak at δ −123.9, which is close to that observed for α-thienyltriphenyltin derivatives.[14]

To account for the regiospecificity of the reaction of thiopentalenyllithium **2** with Ph_3SnCl compared to that with Me_3SnCl, we suggested that both reactions proceed through precoordination of the tin atom as a Lewis acid by the sulfur atom of the thiopentalenyl ligand. However, the phenyl substituents shielded the adjacent C(6) atom due to the substantial steric crowding of the Ph_3Sn groups, thus preventing the subsequent reaction of the C(6) atom with the electrophilic tin atom. As a result, the Ph_3Sn group regiospecifically reacts at the C(4) atom from the sterically uncrowded side of another intermediate molecule. On the contrary, the small Me_3Sn group shields the C(6) atom to a lesser extent, which leads to electrophilic attack on both positions 4 and 6.

To confirm or refute our suggestion that precoordination of organotin Lewis acids occurs, we studied the reaction of lithium salt **2** with diphenylphosphine chloride. The latter is similar to Ph_3SnCl in steric crowding, but, being a Lewis base, cannot form adducts with the sulfur atom. Under similar conditions, this reaction afforded a mixture of both possible isomers **3d** and **4d** as a yellow crystalline substance in a ratio of approximately 1 : 1 (Scheme 1). In our opinion, the fact that the donor phosphorus atom cannot be involved in precoordination with the sulfur atom results in the formation of 4- and 6-substituted isomers with nearly equal probability.

Compounds **3d** and **4d**, like (1-indenyl)diphenylphosphine,[15] are virtually insoluble in hydrocarbon solvents and are readily soluble in most other organic solvents. These compounds are also very sensitive to oxidation in air.

Table 1. Crystallographic data for compound **4c**

Parameter	Value
Molecular formula	$C_{28}H_{26}SSn$
Molecular weight	513.24
T/K	223(2)
System	Monoclinic
Space group	$P2_1/n$
Unit cell parameters:	
a/Å	10.573(3)
b/Å	9.695(3)
c/Å	23.986(7)
β/deg	93.98(3)
V/Å^3	2452.8(12)
Z	4
d_{calc}/g cm^{-3}	1.390
Absorption coefficient, μ/mm^{-1}	1.138
F(000)	1040
Crystal dimensions/mm	0.3×0.15×0.1
Range, θ/deg	2.06 < θ < 25.00
Range of indices	$-12 \le h \le 1$; $-11 \le k \le 1$; $-28 \le l \le 28$
Number of measured reflections	5685
Number of reflections used in least squares	4289
Number of parameters refined in least squares	273
R	0.0811
R_w	0.1855

Table 2. Selected bond lengths (d) and bond angles (ω) in molecule **4c**

Bond	d/Å	Angle	ω/deg
Sn—C(201)	2.127(11)	C(201)—Sn—C(101)	109.2(4)
Sn—C(101)	2.129(11)	C(201)—Sn—C(301)	108.9(4)
Sn—C(301)	2.148(10)	C(101)—Sn—C(301)	106.9(4)
Sn—C(4)	2.196(10)	C(201)—Sn—C(4)	108.4(5)
S—C(7)	1.707(13)	C(101)—Sn—C(4)	112.9(4)
S—C(2)	1.736(15)	C(301)—Sn—C(4)	110.4(4)
C(2)—C(3)	1.397(19)	C(8)—C(4)—Sn	110.8(7)
C(2)—C(21)	1.46(2)	C(5)—C(4)—Sn	107.7(7)
C(21)—C(22)	1.25(2)	C(7)—C(8)—C(4)	108.3(10)
C(3)—C(8)	1.420(15)	C(3)—C(8)—C(4)	138.1(11)
C(4)—C(8)	1.470(16)	C(106)—C(101)—Sn	120.5(9)
C(4)—C(5)	1.509(14)	C(102)—C(101)—Sn	122.5(9)
C(5)—C(6)	1.339(16)	C(206)—C(201)—Sn	123.1(9)
C(5)—C(51)	1.486(17)	C(202)—C(201)—Sn	120.4(9)
C(6)—C(7)	1.417(16)	C(302)—C(301)—Sn	122.1(8)
C(7)—C(8)	1.359(15)	C(306)—C(301)—Sn	120.9(9)

The ^1H NMR spectrum of a mixture of **3d** and **4d** has two broadened peaks at δ 4.15 and 4.31 belonging to the H(4) (**4d**) and H(6) (**3d**) protons, respectively. In

addition, the spectrum has singlets at δ 5.71 (H(4), **3d**) and 6.49 (H(6), **4d**). In the $^{13}C\{^1H\}$ NMR spectrum, the corresponding signals are observed at δ 50.4 (J_{PC} = 24 Hz, C(4), **4d**), 50.8 (J_{PC} = 22 Hz, C(6), **3d**), 116.8 (C(4), **3d**), and 117.6 (C(6), **4d**). The structures of isomers **3d** and **4d** were also confirmed by NMR spectroscopy using the DEPT 135 procedure.

At −20 °C, allylic isomers **3d** and **4d** undergo slow irreversible rearrangement to form a 5 : 3 mixture of the corresponding vinylic isomers, *viz.*, diphenyl(4*H*-cyclopenta[*b*]thiophen-6-yl)phosphine (**5d**) and diphenyl(6*H*-cyclopenta[*b*]thiophen-4-yl)phosphine (**6d**) (Scheme 2). The resulting ^1H NMR spectrum has signals in the region of methylene protons at δ 3.27 (H(4), **5d**) and 3.39 (H(6), **6d**). The $^{13}C\{^1H\}$ NMR spectrum also has two signals at δ 41.9 (C(4), **5d**) and 42.2 (C(6), **6d**) with J_{PC} ≈ 1.5 Hz and two signals of the vinyl C(3) atom at δ 115.1 (C(3), **6d**) and 118.9 (C(3), **5d**). In the $^{31}P\{^1H\}$ NMR spectrum, signals corresponding to vinyl isomers **5d** and **6d** are observed at δ 0.6 and −0.3, respectively.

Thus, we demonstrated the possibility of regiospecific metallation of the thioindenyl anion of **2** with bulky Lewis acids, such as Ph_3SnCl. Analogous reaction with Ph_2PCl proceeded nonregioselectively. We interpreted the observed regiospecificity of the reaction of compound **2** with Ph_3SnCl from the viewpoint of precoordination of the electrophilic reagents with the sulfur atom of the thiopentalenyl ligand. Studies of the mechanism of the reaction of the anion of **2** are being continued with the aim of extending the range of σ-derivatives of thioindene and their subsequent use in the organometallic synthesis of transition metal π-complexes.

Experimental

All reactions were carried out under an inert atmosphere of argon. All syntheses were performed with the use of anhydrous solvents, *viz.*, ether (Na/benzophenone) and hexane (Na). Trimethylchlorosilane was dried by refluxing over magnesium chips. Trimethylchlorostannane, triphenylchlorostannane, and diphenylchlorophosphine as well as a solution of Bu^nLi (Aldrich) were used without additional purification.

The NMR spectra were recorded in $CDCl_3$ on Bruker AC-300 (300.13 and 75.47 MHz for ^1H and ^{13}C, respectively) and JEOL EX 90 (33 MHz for ^{119}Sn with $SnMe_4$ as the external standard; 36.2 MHz for ^{31}P with $P(OPh)_3$ as the external standard) instruments. The mass spectra (EI, 70 eV) were measured on an MX 1320 spectrometer. Elemental analysis was carried out by the Microanalysis, of the Department of Chemistry of the M. V. Lomonosov Moscow State University.

Synthesis of σ-heteroelement-substituted thiopentalenes E(σ-Th)R_n (E = Si, *n* = 3, R = Me (3a and 4a); E = Sn, *n* = 3, R = Me (3b and 4b); R = Ph (4c); E = P, *n* = 2, R = Ph (3d and 4d)) (general procedure). A 2.5 *M* Bu^nLi solution in hexane (0.8 mL) was added to a stirred solution of a mixture of **1a** and **1b** (0.32 g, 2 mmol) in Et_2O (30 mL) at −20 °C. A pale-yellow precipitate of lithium salt **2** immediately formed. The reaction mixture was stirred at −20 °C for 2 h and then cooled to −78 °C. Then the corresponding electrophilic reagent (2 mmol) was added, and the mixture was allowed to warm to −20 °C and stirred for 1 h. The solution was filtered off from the precipitate and concentrated to ~5 mL. Then hexane (~3 mL) was added to the solution and the mixture was kept at −78 °C for 18 h to obtain crystals (of compounds **4c**, **3d**, and **4d**); compounds **3a** and **3b** were distilled *in vacuo*.

Trimethyl(6*H*-cyclopenta[*b*]thiophen-6-yl)silane (3a) and trimethyl(4*H*-cyclopenta[*b*]thiophen-4-yl)silane (4a). The yield was 0.6 g (77%) (**3a** : **4a** = 1 : 2), a viscous yellow oil, b.p. 74 °C (0.01 Torr). ^1H NMR, δ: −0.87 (s, 9 H, $SiMe_3$, **4a**); 0.62 (s, 9 H, $SiMe_3$, **3a**); 1.29 (t, 6 H, $\underline{CH_3}CH_2$, **3a** + **4a**, ^3J = 7.6 Hz); 2.15 (s, 6 H, Me, **3a** + **4a**); 2.83 (q, 4 H, $\underline{CH_3}CH_2$, **3a** + **4a**, ^3J = 7.6 Hz); 3.16 (s, 2 H, H(4), **4a**); 3.19 (s, 2 H, H(6), **3a**); 6.38 (m, 1 H, H(4), **3a**); 6.39 (m, 1 H, H(6), **4a**); 6.63 (s, 1 H, H(3), **4a**); 6.80 (s, 1 H, H(3), **3a**). $^{13}C\{^1H\}$ NMR, δ: −3.0 ($SiMe_3$, **3a**); −2.4 ($SiMe_3$, **4a**); 16.18 ($\underline{CH_3}CH_2$, **3a**); 16.4 ($\underline{CH_3}CH_2$, **4a**); 16.9 (Me, **3a**); 17.6 (Me, **4a**); 24.1 ($CH_3\underline{CH_2}$, **3a**); 24.5 ($CH_3\underline{CH_2}$, **4a**); 47.6 (C(4), **4a**); 48.1 (C(6), **3a**); 114.9 (C(6), **4a**); 118.1 (C(4), **3a**); 118.3 (C(3), **4a**); 120.8 (C(3), **3a**); 122.0 (C(5), **4a**); 123.1 (C(5), **3a**); 145.4, 145.7, 146.2, 146.4, 147.6, 147.9 (C(2), C(7), C(8), **3a** + **4a**). MS, *m/z* (I_{rel} (%)): 236 $[M]^+$ (96), 221 $[M - Me]^+$ (26), 163 $[C_{10}H_{11}]^+$ (12), 73 $[SiMe_3]^+$ (100). Found (%): C, 65.88; H, 8.30; Si, 11.25. $C_{13}H_{20}SSi$. Calculated (%): C, 66.10; H, 8.47; Si, 11.86.

Triphenyl(4*H*-cyclopenta[*b*]thiophen-4-yl)stannane (4c). The yield was 0.95 g (74%), yellow crystals, m.p. 84 °C. ^1H NMR, δ: 1.87 (t, 3 H, $\underline{CH_3}CH_2$, ^3J = 7.6 Hz); 2.06 (s, 3 H, Me); 2.72 (q, 2 H, $CH_3\underline{CH_2}$, ^3J = 7.5 Hz); 4.78 (br.s, 1 H, H(4)); 6.27 (s, 1 H, H(6)); 7.20—7.40 (m, 15 H, Ph); 7.32 (s, 1 H, H(3)). $^{13}C\{^1H\}$ NMR, δ: 16.3 ($\underline{CH_3}CH_2$); 17.4 (Me); 15.0 ($CH_3\underline{CH_2}$); 76.5 (C(4)); 117.1 (C(6)); 128.5 (t, *m*-Ph, J_{SnC} = 25 Hz); 129.2 (*p*-C_6H_4); 130.5 (C(7)); 136.2 (C(2)); 136.9 (C(3)); 137.1 (t, *o*-Ph, J_{SnC} = 18 Hz); 139.4 (C(5)); 137.3 (t, Ph*ipso*, J_{SnC} = 621.5 Hz); 145.5 (C(8)); 145.8 (C(7)). $^{119}Sn\{^1H\}$ NMR, δ: −123.9. MS, *m/z* (I_{rel} (%)): 514 $[M]^+$ (5), 351 $[^{120}SnPh_3]^+$ (100), 197 $[^{120}SnPh_3]^+$ (38), 163 $[Th]^+$ (29), 148 $[Th - Me]^+$ (31). Found (%): C, 65.38; H, 4.95; Sn, 22.96. $C_{28}H_{26}SSn$. Calculated (%): C, 65.52; H, 5.07; Sn, 23.15.

Diphenyl(6*H*-cyclopenta[*b*]thiophen-6-yl)phosphine (3d) and diphenyl(4*H*-cyclopenta[*b*]thiophen-4-yl)phosphine (4d) (**3d** : **4d** = 1 : 1), 0.56 g (77%), yellow crystals, m.p. 101 °C. ^1H NMR, δ: 1.32 and 1.36 (both t, 6 H, $\underline{CH_3}CH_2$, **3d** + **4d**, ^3J = 7.4 Hz); 2.02 (br.s, 6 H, Me, **3d** + **4d**); 2.66 and 2.68 (both q, 4 H, $CH_3\underline{CH_2}$, **3d** + **4d**, ^3J = 7.4 Hz); 4.15 (br.s, 1 H, H(4), **4d**); 4.31 (br.s, 1 H, H(6), **3d**); 5.71 (s 1 H, H(4), **3d**); 6.22 and 6.26 (both s, 2 H, H(3), **3d** + **4d**); 6.49 (s, 1 H, H(6), **4d**); 7.00—8.00 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR, δ: 16.3 ($\underline{CH_3}CH_2$, **3d** + **4d**); 16.0, 16.9 (Me, **3d** + **4d**); 23.9 ($CH_3\underline{CH_2}$, **3d** + **4d**); 50.4 (d, C(4), **4d**, J_{PC} = 23.9 Hz); 50.9 (d, C(6), **3d**, J_{PC} = 22.4 Hz); 116.8 (C(3), **3d**); 117.6 (C(3), **4d**); 123.0 (C(4), **3d**); 124.0 (C(6), **4d**); 128.0—150.0 (C(2), C(5), C(7), C(8), Ph, **3d** + **4d**). $^{31}P\{^1H\}$ NMR, δ: −27.4, −28.4 (PPh_2, **3d** + **4d**). MS, *m/z* (I_{rel} (%)): 348 $[M]^+$ (18), 201 $[PPh_2MeH]^+$ (100), 164 $[ThH]^+$ (21), 148 $[Th - Me]^+$ (6), 77 $[Ph]^+$ (82). Found (%): C, 75.33; H, 6.51; P, 8.98. $C_{22}H_{21}PS$. Calculated (%): C, 75.86; H, 6.03; P, 8.91.

X-ray diffraction analysis of 4c. Single crystals of **4c** were prepared by slow crystallization from a dilute ethereal solution at −20 °C. The structure of **4c** was solved by the direct method and refined anisotropically by the full-matrix least-squares method using the SHELX-97 program package[16] to R = 0.0811 and R_w = 0.1855 (for reflections with $I > 2\sigma(I)$, a total of 273 parameters were refined by least squares). In each cycle, the positions of the hydrogen atoms were calculated geometrically and only their isotropic thermal factors were refined. The crystallographic data and the selected bond lengths and bond angles for compound **4c** are given in Tables 1 and 2. The

atomic coordinates for the structure of **4c** and the complete tables of bond lengths and bond angles were deposited with the Cambridge Structural Database.

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