Supporting Information

N-Heterocyclic Carbene Stabilized Phosphaalkenyl(chloro)stannylene

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General procedure

All manipulations were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line and glove-box techniques. Glassware was dried at 105 °C overnight and, before using, was oven-dried then by a heat gun at 500 °C for several minutes. Solvents were purified with the MBRAUN SBS-800 purification system. NMR spectra were recorded with a Bruker Avance II 300 apparatus: ^{1}H (300.13 MHz), ^{13}C (75.48 MHz), ^{29}Si (59.63 MHz), ^{31}P (121.50 MHz), ^{119}Sn (111.92 MHz) in C_6D_6 or in toluene-d_8 at 298K. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^{1}H and $^{13}C\{^{1}H\}$) or with an external reference ($SiMe_4$ for ^{29}Si, H_3PO_4 for ^{31}P and $SnMe_4$ for ^{119}Sn). Melting points were measured in a sealed capillary using the Stuart automatic melting point SMP40 apparatus. The compounds NHC–$SnCl_2$[1], Mes*P=CCl_2[2] and Mes*P=C(Cl)$SiMe_3$[3] were prepared according to literature procedures. In the case of compound **3** the assignments of ^{1}H signals together with those in ^{13}C NMR spectra were obtained from 2D heteronuclear experiments (HSQC and HMBC) and for the correct attribution of the signals in the carbone- and silicon NMR spectra, phosphorus-decoupled NMR spectra,$^{13}C\{^{31}P\}$ and $^{29}Si\{^{31}P\}$,were also performed.

Synthesis of Compound 2:

To a solution of Mes*P=C(Cl)$SiMe_3$ (417 mg, 1.05 mmol) in THF (4 mL), *t*-BuLi (0.58 mL, 1.1 mmol) was added dropwise at -85 °C. The reaction mixture was kept at this temperature for 1 h till the solution became orange. The NHC–$SnCl_2$ **1** (388 mg, 1.05 mmol) in THF (4 mL) was added to this mixture at -85 °C. The cooling bath was removed after 30 minutes. After warming up to room temperature and stirring for additional 3h, all the solvents were evaporated under low pressure and the solid phase was washed with pentane (4 mL). The stannylene NHC–Sn(Cl)[C($SiMe_3$)=PMes*] **2** was obtained as an extremely air- and moisture-sensitive yellow powder and was used without elimination of LiCl. A slow crystallization procedure of **2** from a saturated toluene solution at -24 °C gave yellow crystals suitable for X-ray studies. M = 510 mg (0.733 mmol, 70%). Mp.: 135-140 °C (dec.). ^{1}H NMR (C_6D_6): δ (ppm) = 0.19 (s, 9H, $SiMe_3$); 1.32 (m, 12H, $CH\mathit{Me}_2$); 1.37 (s, 9H, C_pCMe_3); 1.56 (s, 6H, =C*Me*); 1.68 (s, 18H, C_oCMe_3); 5.63 (sept, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 2H, $C\mathit{H}Me_2$); 7.68 (s, 2H, C_6H_2). ^{31}P NMR (C_6D_6): δ (ppm) = 344.9 ($^{2}J_{P\text{-}Sn}$ = 298.9 Hz). ^{13}C NMR (tol-d_8): δ (ppm) = 2.10 (d, $^{3}J_{C\text{-}P}$ = 3.6 Hz, $Si\mathit{Me}_3$); 11.08 (=C*Me*); 23.31 ($CH\mathit{Me}_2$); 32.54 ($C_pC\mathit{Me}_3$); 35.16 and 35.27 ($C_oC\mathit{Me}_3$); 35.90 ($C_p\mathit{C}$); 39.60 ($C_o\mathit{C}$); 53.59 ($^{3}J_{C\text{-}Sn}$ = 63.2 Hz, $\mathit{C}HMe_2$); 122.73 (C_m); 127.42 (=*C*Me); 150.24 (C_p); 150.33 (d, $^{1}J_{C\text{-}P}$ = 100.5 Hz, C_iP); 153.46 (C_o); 178.57 (d, $^{3}J_{C\text{-}P}$ = 24.9 Hz, C:); 230.22 (d, $^{1}J_{C\text{-}P}$ = 99.9 Hz, C=P). ^{31}P NMR (tol-d_8): δ (ppm) = 344.5 ($^{2}J_{P\text{-}Sn}$ = 299.5 Hz). ^{29}Si NMR (tol-d_8): δ (ppm) = -9.3 (d, $^{2}J_{Si\text{-}P}$ = 20.9 Hz). ^{119}Sn NMR (tol-d_8): δ (ppm) = 52.2 (d, $^{2}J_{Sn\text{-}P}$ = 304.9 Hz).

Synthesis of Compound 3:

The chloro-stannylene **2** (120 mg, 0.172 mmol) and Me_2SAuCl (51 mg, 0.172 mmol) were mixed and toluene (4 mL) was added at -40 °C. After 5 minutes, the cooling bath was removed and the mixture was allowed to warm up to room temperature. A large quantity of precipitate was formed. The mixture was filtered and the filtrate was evaporated at around half quantity. After several crystallization processes from toluene at 5 °C, air stable yellow crystals were obtained, m = 24 mg (25%). Toluene or benzene could also be used as crystallization solvent. Mp.: 160 °C (dec.). ^{1}H NMR (C_6D_6): δ (ppm) = -0.05 (s, 27H, $SiMe_3$); 1.27 (s, 27H, *p*-CMe_3); 1.81 (s, 54H, *o*-CMe_3); 7.50 (s, 6H, C_6H_2). ^{13}C NMR (C_6D_6): δ (ppm) = 1.32 (d, $^{3}J_{C\text{-}P}$ = 3.8 Hz, $SiMe_3$), 1.38 (d, $^{3}J_{C\text{-}P}$ = 3.9 Hz, $SiMe_3$), 31.35 (*p*-$C\mathit{Me}_3$); 35.15 (*p*-$\mathit{C}Me_3$); 35.29 (*o*-$C\mathit{Me}_3$); 39.03 (*o*-$\mathit{C}Me_3$); 122.94 (*m*-CH); 139.66 (*ipso*-C); 151.92 (*p*-$\mathit{C}Me_3$); 154.30 (*o*-$\mathit{C}Me_3$); 221.73 (dd, $^{1}J_{C\text{-}P}$ = 106.1 Hz, $^{2}J_{C\text{-}P}$ = 9.8 Hz, P=*C*). ^{31}P NMR (C_6D_6): δ (ppm) = 249.5. ^{29}Si NMR (C_6D_6): δ (ppm) = -8.9 (dd, $^{2}J_{Si\text{-}P}$ = 22.8 Hz, $^{3}J_{Si\text{-}P}$ = 8.3 Hz).

X-ray Structure Determinations.

X-ray data for compounds **2** and **3** were collected at low temperature (193 K) on a Bruker-AXS APEX II Quazar diffractometer using a 30 W air-cooled microfocus source with focusing multilayer optics MoKα radiation (wavelength = 0.71073 Å). Phi- and omega-scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[4] The structures were solved by direct methods, using SHELXS-97 and refined using the least–squares method on F^2.[5] All non-H atoms were treated anisotropically and the H atoms were located by difference Fourier maps and refined with a riding model. Crystallographic data are summarized in Table 1.

Table 1. Crystallographic data for compounds 2 and 3

Compound	**2**	**3**
Empirical formula	$C_{33}H_{58}ClN_2PSiSn$	$C_{66}H_{114}Au_3P_3Si_3$, $4(C_6H_6)$
Formula weight (g/mol)	696.01	1988.10
Temperature (K)	193(2)	193(2)
λ(Mo Kα) (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C c
a (Å)	13.9436(13)	20.3176(12)
b (Å)	15.6575(14)	30.5474(16)
c (Å)	19.2277(18)	17.6840(10)
α (deg.)	99.241(4)	90
β (deg.)	105.189(4)	122.067(2)
γ (deg.)	103.438(4)	90
Volume (Å^3)	3829.0(6)	9301.0(9)
Z	4	4
Density calculated (g/cm^3)	1.207	1.420
Absorption coefficient (mm^{-1})	0.832	4.850
F(000)	1464	4008
Crystal size (mm)	0.16 x 0.14 x 0.12	0.18 x 0.16 x 0.08
θ range (deg.)	5.14 - 24.40	5.14 - 26.37
Index range h k l	$-16 \leq h \leq 16$ $-18 \leq k \leq 18$ $-22 \leq l \leq 22$	$-16 \leq h \leq 25$ $-38 \leq k \leq 38$ $-22 \leq l \leq 21$
Reflections collected / Unique	79615 / 12408 R(int) = 0.0411	57843 / 16169 R(int) = 0.0462
Completeness to θ (%)	98.4	98.6
Data/Restraints/Parameters	12408 / 255 / 834	16169 / 669 / 1070
Goodness-of-fit	1.053	0.999
R1, wR2 ($I > 2(\sigma)I$)	0.0706, 0.1632	0.0352, 0.0723
R1, wR2 (all data)	0.0914, 0.1749	0.0484, 0.0764
Largest diff. peak and hole (eÅ^{-3})	2.638, -2.258	1.264, -0.841

References

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