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Communications

Triple Bonding to Tin: Synthesis and Characterization of the Square-Pyramidal Stannylyne Complex Cation $[(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$, Mes = C_6H_2-2,4,6-Me_3)

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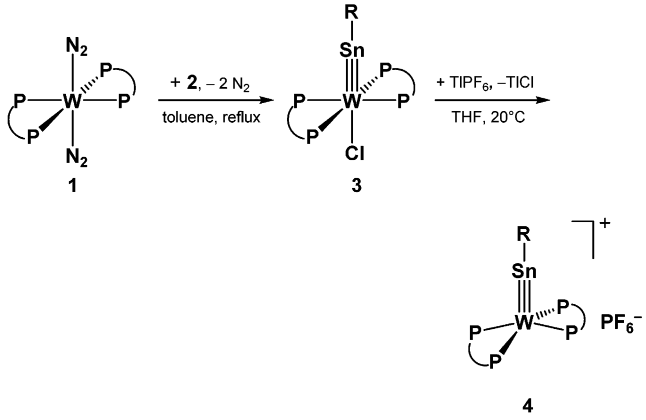
Summary: The reaction of trans-$[W(dppe)_2(N_2)_2]$ *(**1**) with the m-terphenyl tin(II) chloride* $\{Sn(Cl)(C_6H_3\text{-}2,6\text{-}Mes_2)\}_2$ *(**2**) affords by elimination of dinitrogen the 18-electron stannylyne complex trans-*$[Cl(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]$ *(**3**; dppe =* $Ph_2PCH_2CH_2PPh_2$*, Mes =* C_6H_2*-2,4,6-*Me_3*). Chloride abstraction occurs readily from **3** with* $TlPF_6$ *to give the cationic 16-electron stannylyne complex* $[(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]PF_6$ *(**4**), which dissolves in acetonitrile-*d_3 *to give the cationic 18-electron stannylyne complex trans-*$[(CD_3CN)(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]PF_6$ *(**5**). The complexes **3** and **4** reveal by X-ray crystallography a very short W−Sn triple bond (2.504(1) Å (**3**), 2.4641(7) Å (**4**)) and a linear geometry at the tin atom (*$W{-}Sn{-}C_{aryl}$ *= 175.88(8)° (**3**), 178.77(9)° (**4**)). Comparative quantum-chemical analyses of the W−E triple bonds of the model compounds trans-*$[Cl(PH_3)_4W{\equiv}E{-}Me]$ *(E = C, Sn) are presented.*

Carbon forms triple bonds to many elements, and these bonds are the origin of a rich and diverse chemistry of the resulting unsaturated compounds. In comparison, the heavier group 14 elements Si, Ge, Sn, and Pb reluctantly participate in double bonding and even more reluctantly in triple bonding.[1] In this context, the isolation of compounds featuring triple bonding to a group 14 element heavier than carbon is one of the most challenging research areas in main-group chemistry.[1] Remarkable achievements in this field were recently the syntheses of the germylyne complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M{\equiv}Ge{-}R]$ (M = Cr, Mo, W; R = C_6H_3-2,6-Mes_2, C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-$i$$Pr_3$))[2] and *trans*-$[X(L)_4M{\equiv}Ge(\eta^1\text{-}C_5Me_5)]$ (X = Cl, Br, I; M = Mo, W; L_2 = dppe; L = PMe_3),[3] the isolation of the first complex featuring a triple bond to tin, *trans*-$[Cl(PMe_3)_4W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]$,[4] and isolation of the complex $[(\eta^5\text{-}C_5Me_5)(dmpe)Mo(H)SiMes][B(C_6F_5)_4]$ (dmpe = $Me_2PCH_2CH_2PMe_2$), possessing silylyne character.[5] Here we report the synthesis and full characterization of the stannylyne complex cation $[(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]^+$. In addition, the W−E bonds of the model compounds *trans*-$[Cl(PH_3)_4W{\equiv}E\text{-}Me]$ (E = C, Sn) were analyzed by quantum-chemical methods.

Scheme 1. Syntheses of the Stannylyne Complexes 3 and 4[a]



[a] P⌒P = dppe; R = C_6H_3-2,6-Mes_2.

Heating of an equimolar mixture of *trans*-$[W(dppe)_2(N_2)_2]$ (**1**)[6] and $\{Sn(Cl)(C_6H_3\text{-}2,6\text{-}Mes_2)\}_2$ (**2**)[7] in refluxing toluene affords rapidly the stannylyne complex *trans*-$[Cl(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]$ (**3**) (Scheme 1). The reaction is less selective than that of *cis*-$[W(PMe_3)_4(N_2)_2]$ with **2**, as evidenced by the concomitant formation of elementary tin, C_6H_4-1,3-Mes_2, and some *trans*-$[W(dppe)_2Cl_2]$.[8] The stannylyne complex **3** was isolated

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[1] (a) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463−3503. (b) Jutzi, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3797−3800 and references therein. (c) Massey, A. G. *Main Group Chemistry*, 2nd ed.; Wiley: Chichester, U.K., 2000.

[2] (a) Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966−11967. (b) Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 650−656.

[3] (a) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Neumann, D. U. *Angew. Chem., Int. Ed.* **2000**, *39*, 2778−2781. (b) Filippou, A. C.; Portius, P.; Philippopoulos, A. I. *Organometallics* **2002**, *21*, 653−661.

[4] Filippou, A. C.; Portius, P.; Philippopoulos, A. I.; Rohde, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 445−447.

[5] Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357−360.

[6] Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 119−127.

[7] Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920−1925.

[8] Over, D. E.; Critchlow, S. C.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4643−4648.

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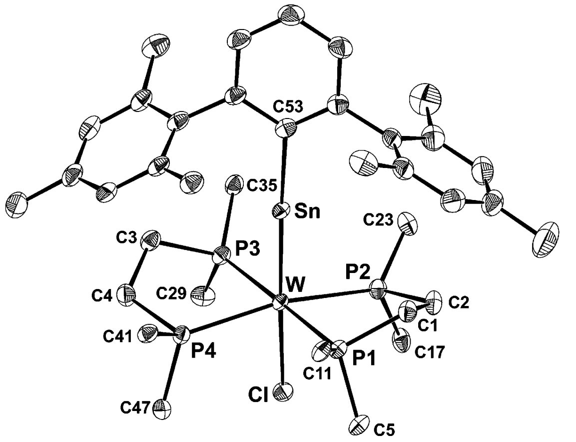

Figure 1. DIAMOND plot of the molecular structure of **3** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted, and only the ipso carbon atoms of the P-bonded phenyl groups are drawn for clarity. Selected bond lengths (Å) and angles (deg): W−Sn = 2.504(1), W−Cl = 2.441(1), W−P1 = 2.468(1), W−P2 = 2.471(1), W−P3 = 2.488(1), W−P4 = 2.504(1), Sn−C53 = 2.183(3); W−Sn−C53 = 175.88(8), Sn−W−Cl = 177.81(2), Sn−W−P1 = 90.21(3), Sn−W−P2 = 94.56(3), Sn−W−P3 = 90.49(3), Sn−W−P4 = 98.29(3), P1−W−P2 = 78.57(4), P3−W−P4 = 77.98(4), P1−W−P3 = 179.25(2), P2−W−P4 = 167.15(3).

after workup as a red-brown solid in 69% yield. Complex **3** is soluble in warm benzene and toluene, less soluble in THF, and insoluble in acetone or acetonitrile. It decomposes upon melting at 165 °C[9] and is extremely air-sensitive, its red-brown solutions turning rapidly yellow upon exposure to air. The most striking spectroscopic feature of **3** is the singlet signal at δ 49.9 ppm in the $^{31}P\{^1H\}$ spectrum (THF-d_8, room temperature), which is flanked by two pairs of satellites arising from coupling with the ^{183}W ($^1J(W,P) = 259.8$ Hz) and $^{117}Sn/^{119}Sn$ nuclei ($^2J(Sn,P) = 125$ Hz). The ^{31}P NMR signal of **3** appears at slightly lower field than that of *trans*-$[Cl(dppe)_2W{\equiv}Ge(\eta^1\text{-}C_5Me_5)]$ (δ 46.3 ppm, $^1J(W,P) = 264.7$ Hz). The molecular structure of **3** shows a distorted-octahedral complex with a trans arrangement of the stannylyne and chloro ligands (Cl−W−Sn = 177.81(2)°) (Figure 1).[10] Complex **3** features a very short W−Sn bond (2.504(1) Å) and a linear coordination geometry at the tin atom (W−Sn−C_{aryl} = 175.88(8)°), as found in *trans*-$[Cl(PMe_3)_4W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]$ (W−Sn = 2.4902(8) Å, W−Sn−C_{aryl} = 178.2(1)°).[4] The W−Cl distance in **3** (2.441(1) Å) is shorter than that in *trans*-$[Cl(dppe)_2W{\equiv}Ge(\eta^1\text{-}C_5Me_5)]$ (2.486(1) Å), suggesting a weaker trans influence of the stannylyne compared with the germylyne ligand.[3]

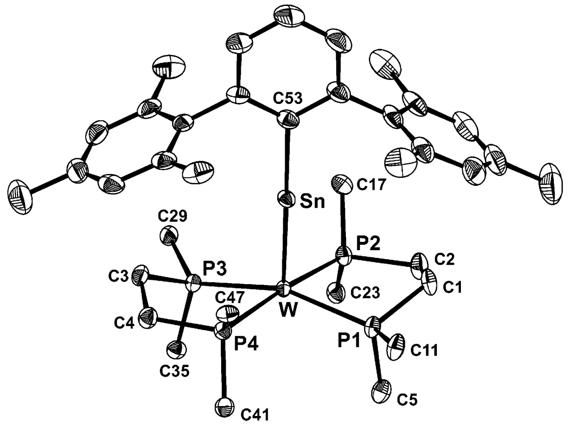

Figure 2. DIAMOND plot of the structure of the complex cation in **4** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted, and only the ipso carbon atoms of the P-bonded phenyl groups are drawn for clarity. Selected bond lengths (Å) and angles (deg): W−Sn = 2.4641(7), W−P1 = 2.424(1), W−P2 = 2.460(1), W−P3 = 2.445(1), W−P4 = 2.465(1), Sn−C53 = 2.146(3); W−Sn−C53 = 178.77(9), Sn−W−P1 = 100.64(3), Sn−W−P2 = 92.26(3), Sn−W−P3 = 101.00(3), Sn−W−P4 = 93.48(3), P1−W−P2 = 78.93(4), P3−W−P4 = 79.28(4), P1−W−P3 = 158.35(3), P2−W−P4 = 174.26(3).

Despite the shortness of the W−Cl bond, chloride abstraction occurs easily from **3** with $TlPF_6$ to afford the green, very air-sensitive stannylyne complex **4** in 51% yield (Scheme 1).[11]

Complex **4** is a remarkably thermostable solid, which does not decompose upon heating to 260 °C, is soluble in THF, and dissolves in acetonitrile-d_3 to give instantaneously the cationic stannylyne complex *trans*-$[(CD_3CN)(dppe)_2W{\equiv}Sn{-}C_6H_3\text{-}2,6\text{-}Mes_2]PF_6$ (**5**). The crystal structure of **4**·5THF reveals the presence of 16-electron stannylyne complex cations, which are well separated from the THF solvent molecules and the PF_6 anions, the shortest W···F and Sn···F contacts between cations and anions being 6.88 and 7.12 Å, respectively.[10] The cations are roughly C_2 symmetric and exhibit as other five-coordinate d^6 metal complexes[12] a square-pyramidal coordination geometry with the stannylyne ligand as the best π-acceptor group occupying the apical position (Figure 2).[13] The tungsten atom lies at a distance of 2.4641(7) Å from the linear-coordinated tin atom (W−Sn−C_{aryl} = 178.77(9)°), which is the shortest length observed so far for a W−Sn bond. The vacant trans coordination site is sterically shielded by two phenyl groups at P1 and P3, which are more strongly inclined to the metal (W−P1−C5/W−P3−C35 = 106.7(1)/109.9(1)° vs W−P2−C23/W−P4−C41 = 115.0(1)/116.4(1)°)[14] and display short contacts via one ortho C−H group with the tungsten atom (W···H10/C10 = 2.93/3.48 Å,

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(9) Complex **3** discolorates upon thermal decomposition from red-brown to brown and liberates dppe, $C_6H_4\text{-}Mes_2$, and *trans*-$[W(dppe)_2Cl_2]$.

(10) Suitable dark red single crystals of **3**·3.5(benzene) were obtained upon slow diffusion of pentane into a benzene-d_6 solution of **3** at 6 °C. Suitable dark green single crystals of **4**·5THF were obtained upon slow diffusion of pentane into a THF solution of **4** at 6 °C. Data were collected on a STOE STADI4 (**3**·3.5(benzene)) or a STOE IPDS diffractometer (**4**·5THF) at 180 K. Crystal data for $C_{97}H_{94}ClP_4SnW$ (**3**·3.5(benzene)): monoclinic, space group $P2_1/n$, $a = 15.304(5)$ Å, $b = 25.377(11)$ Å, $c = 21.585(9)$ Å, $\beta = 105.52(3)°$, $V = 8077(6)$ Å^3 ($Z = 4$); R1 = 0.0328, wR2 = 0.0864 ($I > 2\sigma(I)$); R1 = 0.0355, wR2 = 0.0898 (all data). Crystal data for $C_{96}H_{113}F_6O_5P_5SnW$ (**4**·5THF): triclinic, space group $P\bar{1}$, $a = 13.777(3)$ Å, $b = 13.772(3)$ Å, $c = 25.715(6)$ Å, $\alpha = 103.64(3)°$, $\beta = 100.72(3)°$, $\gamma = 102.12(3)°$, $V = 4490.7(18)$ Å^3 ($Z = 2$); R1 = 0.0296, wR2 = 0.0746 ($I > 2\sigma(I)$); R1 = 0.0371, wR2 = 0.0777 (all data).

(11) It is noteworthy that the reaction of *trans*-$[Cl(dppe)_2W{\equiv}Ge(\eta^1\text{-}C_5Me_5)]$ with $TlPF_6$ in toluene affords only the adduct *trans*-$[Cl(dppe)_2W{\equiv}Ge(\eta^1\text{-}C_5Me_5)]{\cdot}TlPF_6{\cdot}3(toluene)$, featuring a Tl−Cl acceptor−donor interaction (d(Tl−Cl) = 2.906(2) Å).

(12) The tungsten center attains in **3** and **4** a d^6 electron configuration, if the stannylyne ligand is considered to be a positively charged two-electron σ-donor and four-electron π-acceptor like the carbyne and the germylyne ligand in the analogous complexes.[3a] This choice agrees well with the actual charge distribution in these compounds.

(13) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447−4452 and refereneces therein.

(14) The W−P−C_{aryl} bond angles of the phenyl groups pointing to the stannylyne ligand are larger and range from 123.1(1) to 129.8(1)°.

Table 1. Selected Calculated Geometrical Parameters[a] and Results of the Bonding Analyses of *trans*-[Cl(PH$_3$)$_4$W≡E-Me] (6, E = C; 7, E = Sn)[17]

	W−E (Å)	W−P (Å)	E−C (Å)	W−Cl (Å)	W−E−C (deg)	NPA[b] partial charges	NBO[c]						BDE[d] (kJ mol^{-1})	EDA[e] (kJ mol^{-1})			
							occ	W (%)	hyb	E (%)	hyb	WBI		$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{\mathrm{elstat}}$	ΔE_{orb}	ΔE_{int}
6	1.826	2.500	1.475	2.613	179.7	W: −0.68	σ: 1.94	33.2	sd$^{2.86}$	66.8	sp$^{0.7}$	2.16	635.2	+949.3	−907.7	−1480.0 (62.0%);	−1438.4
						C: −0.08	π: 1.92	59.6	d	40.4	p					−845.2 ($\Delta E_{\sigma+\pi}$(a′))	
						CMe: −0.11	π: 1.91	59.3	d	40.7	p					−634.8 (ΔE_{π}(a″))	
7	2.525	2.487	2.191	2.528	179.5	W: −1.42	σ: 1.81	37.8	sd$^{1.59}$	62.2	sp$^{0.6}$	1.62	295.0	+431.8	−674.7	−656.8 (49.3%);	−899.7
						Sn: +1.12	π: 1.79	76.5	d	23.5	p					−390.5 ($\Delta E_{\sigma+\pi}$(a′))	
						SnMe: +0.64	π: 1.77	76.2	d	23.8	p					−266.3 (ΔE_{π}(a″))	

[a] B3LYP/6-311G* (LANL2DZ and LANL2-ECP for W, Sn). [b] Natural population analysis. [c] Natural bond orbital analysis of the W−E bonds: occupation, polarity in % W and % E, hydridization and Wiberg bond index. [d] Homolytic bond dissociation energy of the W−E bond to the fragments in their electronic ground states. [e] Energy decomposition analysis (BP86/TZVPP): Pauli repulsion, electrostatic, orbital interaction, and total interaction energy between the fragments [Cl(PH$_3$)$_4$W]$^-$ and [EMe]$^+$. The values in parentheses are the percentage contribution of ΔE_{orb} to the total attractive interactions ($\Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$), reflecting the covalent character of the W−E bond. $\Delta E_{\mathrm{orb}} = \Delta E_{\sigma+\pi}$(a′, in mirror plane) + ΔE_{π}(a″, out of mirror plane); $\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}}$.

W···H36/C36 = 3.22/3.68 Å). The W···H10 distance lies between the van der Waals contact (3.37 Å)[15] and the W···H separation of [W(CO)$_3$(PCy$_3$)$_2$] (2.27 Å), suggesting a weak W···H−C agostic interaction.[16] Additional evidence for this is provided by the ^{1}H NMR spectrum of **4**, which displays a signal for the ortho hydrogen atoms at field higher (δ 5.61) than that of **3** (δ 6.56) or **5** (δ 6.47). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** display, as do those of **3**, a double set of resonances for the diastereotopic methylene protons and the P-bonded phenyl groups, indicating that the square-pyramidal structure is stereochemically rigid in solution on the NMR time scale. In addition, the ^{31}P{^{1}H} NMR spectrum of **4** (THF-d_8, room temperature) shows one singlet resonance for the dppe ligands at considerably lower field (δ 85.7 ppm, ^1J(W,P) = 282.2 Hz) than that of **3** (δ 49.9). This suggests that the agostic interactions of the ortho C−H groups with the tungsten center are rapidly interchanged in a on−off fashion on the NMR time scale.

DFT calculations of the model compounds *trans*-[Cl(PH$_3$)$_4$W≡E-Me] (**6**, E = C; **7**, E = Sn) were carried out (Table 1).[17] Both compounds have a C_s-symmetric minimum structure and display a linear geometry at the E atom, the calculated bond lengths and angles comparing well with experimental values. The NBO analyses show that both W−E bonds are composed of one σ bond, which is polarized toward the E atom, and two nearly degenerate π bonds, which are polarized toward the tungsten atom. The polarity of the π bonds increases and that of the σ bond decreases from the carbyne complex **6** to the stannylyne complex **7**. A comparison of the NPA partial charges reveals a considerable increase of negative charge at the tungsten atom from **6** to **7**, which provides an explanation for the high air sensitivity of the stannylyne complex **3**. It also shows that the carbyne carbon atom is nearly electroneutral, while the Sn atom and the SnMe ligand are positively charged. Finally, the energy decomposition analysis shows a lower total interaction energy ΔE_{int} in the stannylyne complex **7** than in the carbyne complex **6** and a lower covalent character of the W−Sn triple bond (49.3%) than the W−C triple bond (62.0%), which is also reflected in the Wiberg bond indexes (W−Sn, 1.62; W−C, 2.16). Furthermore, the analysis evinces that the [Cl(PH$_3$)$_4$W]$^-$→[EMe]$^+$ π-back-donation is in both cases the dominant contribution to the covalent bonding energy ΔE_{orb} and provides additional evidence for the high degree of π-character in the W−E bonds of **6** and **7**.[18]

We are currently investigating the reactivity of the electronically unsaturated stannylyne complex **4**.

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Supporting Information Available: An Experimental Section including the syntheses and analytical and spectroscopic data of the stannylyne complexes **3** − **5** and tables giving X-ray crystallographic data for the structure determinations of **3** and **4** and the results of electronic structure calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(16) (a) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294−2301. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124.

(17) The calculations were carried out with Gaussian 98 (A11.3) and ADF-2000.02 (see Supporting Information).

(18) Given the degeneracy of the π-bonds the σ-bonding energy ΔE_{σ} can be estimated as $\Delta E_{\sigma+\pi}$(a′) − ΔE_{π}(a″). This leads in the case of **7** to a total π-bonding energy ΔE_{π} of 532.6 kJ mol^{-1} (81% of ΔE_{orb}).