Manganese−Tin Triple Bonds: A New Synthetic Route to the Manganese Stannylidyne Complex Cation *trans*-[H(dmpe)$_2$Mn≡Sn(C$_6$H$_3$-2,6-Mes$_2$)]$^+$ (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$, Mes = 2,4,6-Trimethylphenyl)

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ⓢ Supporting Information

ABSTRACT: A new approach to the first complex featuring a manganese−tin triple bond that takes advantage of the propensity of dihydrogen complexes to eliminate H$_2$ is reported. Reaction of the 18-valence-electron manganese dihydrogen hydride complex [MnH-(η^2-H$_2$)(dmpe)$_2$] (1) (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) with the organotin(II) chloride SnCl(C$_6$H$_3$-2,6-Mes$_2$) (Mes = 2,4,6-trimethylphenyl) selectively afforded by H$_2$ elimination the chlorostannylidene complex *trans*-[H-(dmpe)$_2$Mn=Sn(Cl)(C$_6$H$_3$-2,6-Mes$_2$)] (2), which upon treatment with Na[B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$] and Li[Al(OC-(CF$_3$)$_3$)$_4$] was transformed quantitatively into the stannylidyne complex salts *trans*-[H(dmpe)$_2$Mn≡Sn-(C$_6$H$_3$-2,6-Mes$_2$)]A [A = B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$ (3a), Al(OC(CF$_3$)$_3$)$_4$ (3b)]. Complexes 2 and 3a/3b were fully characterized, and the structures of 2 and 3a were determined by single-crystal X-ray diffraction. Complex 2 features the shortest Mn−Sn double bond reported to date, a large Mn−Sn−C$_{aryl}$ bond angle, and a long Sn−Cl bond of the trigonal-planar-coordinated tin center. These bonding features can be rationalized in valence-bond terms by a strong contribution of the triply bonded resonance structure [L$_n$Mn≡SnR]Cl and were verified by a natural resonance theory (NRT) analysis of the electron density of the DFT-minimized structure of 2. Complex 3a features the shortest Mn−Sn bond reported to date and a linearly coordinated tin atom. Natural bond order and NRT analyses of the electronic structure of the complex cation in 3a/3b suggested a highly polar Mn−Sn triple bond with a 65% ionic contribution to the NRT Mn−Sn bond order of 2.25. Complex 3a undergoes reversible one-electron reduction, suggesting that open-shell stannylidyne complexes might be accessible using strong reducing agents.

Compounds featuring triple bonds between transition metals and the heavier group 14 congeners of carbon are of fundamental importance for the understanding of chemical bonding and outline a challenging research field with many new perspectives for the molecular chemistry of transition metals and main-group elements stemming from the electronic structure and polarity of the M≡E triple bond (M = transition metal; E = Si−Pb).[1] Following the first report of a molybdenum germylidyne complex in 1996 by Power and co-workers,[2] a series of closed-shell Mo and W complexes containing linearly coordinated, triply bonded Ge−Pb atoms have been isolated by our group using a very efficient N$_2$/PMe$_3$ elimination method.[3] Recent studies in our group showed that this method could also be successfully employed to prepare the rhenium germylidyne complexes *mer*-[X$_2$(PMe$_3$)$_3$Re≡Ge(C$_6$H$_3$-2,6-Trip$_2$)] (X = Cl, I, H; Trip = C$_6$H$_2$-2,4,6-^{i}Pr$_3$)[4] and cationic germylidyne and stannylidyne complexes of group 8 metals, [(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$M≡E(C$_6$H$_3$-2,6-R′$_2$)]A (M = Fe, Ru; E = Ge, Sn; R = Me, Et; R′ = Mes, Trip; A = singly charged anion).[5] Lately we also accomplished the synthesis of the first silylidyne complex, [(η^5-C$_5$H$_5$)(CO)$_2$Mo≡Si(C$_6$H$_3$-2,6-Trip$_2$)].[6] To date, the vast majority of these compounds involve second- and third-row transition metals, whereas examples involving 3d metals are extremely rare.[2b,5a] This is not surprising, since shrinkage of the d orbitals is predicted to reduce the M−E σ- and π-orbital overlap, weakening the M≡E triple bond.[7] In this context, there may be great benefit in pursuing new routes employing transition-metal complexes with labile ligands other than those used so far. In recent years, transition-metal polyhydrides[8] and dihydrogen complexes[9] have attracted ample attention because of their fascinating chemistry toward C−H activation[10] and potential applications in hydrogen storage.[11] Taking advantage of the propensity of these compounds to eliminate dihydrogen, we present here a new stepwise approach to the first manganese complex featuring a Mn−Sn triple bond.

The 18-valence-electron (18VE) manganese dihydrogen hydride complex [MnH(η^2-H$_2$)(dmpe)$_2$] (1) was chosen as a promising starting material for an entry into Mn−Sn multiple-bond chemistry, since 1 has been shown to lose H$_2$ easily to give a 16VE intermediate that can be trapped quantitatively by a variety of ligands.[12] In fact, treatment of 1 with 1 equiv of SnCl(C$_6$H$_3$-2,6-Mes$_2$) in toluene was accompanied by a rapid color change from yellow to dark red-brown with concomitant evolution of H$_2$. Monitoring of the reaction by ^{31}P NMR spectroscopy revealed the selective formation of a new complex that was isolated as an air-sensitive, red-brown solid in 93% yield and shown by elemental analysis, IR and multinuclear NMR spectroscopy, and single-crystal X-ray diffraction (scXRD) to be the chlorostannylidene complex *trans*-[H(dmpe)$_2$Mn=Sn(Cl)(C$_6$H$_3$-2,6-Mes$_2$)] (2) (Scheme 1). Complex 2 shows
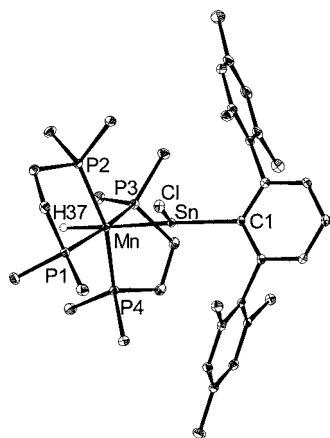
remarkable thermal stability and does not melt or decompose upon heating to 240 °C.

Scheme 1. Synthesis of Manganese Chlorostannylidene and Stannylidyne Complexes
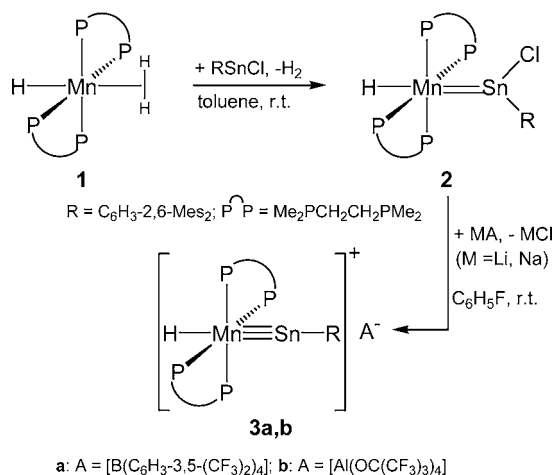

The molecular structure of **2** (Figure 1) shows a distorted octahedral complex with a trans arrangement of the stannylidene

Figure 1. DIAMOND plot of the molecular structure of **2**. Thermal ellipsoids are set at 30% probability. H atoms have been omitted except for H37 bonded to Mn. Selected bond lengths (Å) and angles (deg): Mn–Sn, 2.3997(3); Mn–H37, 1.51(2); Sn–Cl, 2.5566(5); Sn–C1, 2.209(2); Mn–Sn–C1, 158.53(4); Mn–Sn–Cl, 113.66(1); C1–Sn–Cl, 87.69(5); Sn–Mn–H37, 176.6(9); Sn–Mn–P1, 96.24(2); Sn–Mn–P2, 98.50(2); Sn–Mn–P3, 96.02(2); Sn–Mn–P4, 101.50(2).

ligand and the hydrido ligand, which could be located in the difference Fourier map and refined isotropically to a Mn–H distance of 1.51(2) Å. The P atoms are inclined toward the hydrido ligand, as evidenced by the Sn–Mn–P bond angles of 96–102°, to minimize the steric pressure exerted by the bulky chlorostannylidene ligand. Complex **2** reveals some remarkable structural features. The Mn–Sn bond of **2** [2.3997(3) Å] is shorter than all previously reported Mn–Sn double bonds (2.44–2.52 Å)[13] and is also considerably shorter than Mn–Sn single bonds (median value 2.625 Å).[14] This suggests a strong Mn–Sn bonding interaction in **2**. Furthermore, the angles at the trigonal-planar-coordinated tin atom (sum of angles at Sn = 359.9°) differ markedly. Thus, the Mn–Sn–C_{aryl} angle is considerably widened to 158.53(4)°, mainly because of the

large steric demand of the *m*-terphenyl substituent, whereas the C_{aryl}–Sn–Cl angle is lowered to 87.69(5)°, indicating that the tin center uses only p orbitals for σ bonding to its substituents. Finally, the Sn–Cl bond of **2** [2.5566(5) Å] is considerably elongated relative to the Sn–Cl bond lengths of two- or three-coordinate Sn^{II} centers in organotin chlorides [$SnCl(C_6H_3$-2,6-$Trip_2)$, 2.4088(8) Å; $SnCl(C_6H_3$-2,6-$Trip_2)(py)$: 2.448(2) Å].[15] The same features (short M=E bond, large M–E–C_{aryl} angle, long E–Cl bond) are also shown by other chlorotetrelylidene complexes of electron-rich metal centers[16] recently isolated in our group[4,5] and can be rationalized in valence-bond terms by a contribution of the ylidyne resonance form **d** to the bonding (Figure 2).

E = Si - Pb; M= transition metal; R = *m*-terphenyl
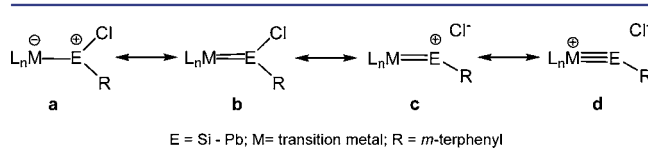
Figure 2. Resonance forms for the metal–tetrel bond in electron-rich metal chlorotetrelylidene complexes.

This was verified by a natural resonance theory (NRT) analysis of the density functional theory (DFT) electron density of **2**,[17a] which showed a major triply bonded resonance structure similar to **d** with a weight of 23% followed by several doubly bonded (overall weight 50%) and singly bonded (overall weight 21%) resonance structures, leading to an NRT bond order of 2.08 (Table 1).[17b] The Mn–Sn double bond of **2** has low covalent character, as evidenced by the low covalent (0.69) and high ionic (1.39) contributions to the natural bond order (NBO) (Table 1).[17b] The high polarity of the Mn–Sn double bond is also reflected in the high opposite natural population analysis (NPA) charges (Mn, −0.87; Sn, +1.46). An NBO analysis of **2** indicated that the σ and π components of the Mn=Sn bond are strongly polarized toward the Sn and Mn atoms, respectively, as in the M=C bonds of Fischer-type carbene complexes.[18]

The IR and NMR spectra corroborate the solid-state structure of **2**. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 79.1 ppm indicating the trans configuration of complex **2**. The singlet signal is accompanied by tin satellites [$^2J(^{119}Sn,P)$ = 210 Hz] and appears at slightly higher field than that of **1** (82.73 ppm).[12] The ^1H and $^{13}C\{^1H\}$ NMR spectra suggest an overall C_s-symmetric complex in solution in which the *m*-terphenyl substituent is fixed in the orthogonal conformation observed in the solid state.[19] In combination with the hindered rotation about the C–mesityl bond, this renders the ortho and meta positions of the enantiotopic mesityl substituents diastereotopic, giving rise to a double set of resonances for the ortho and meta ^1H and ^{13}C nuclei (Figure S1 in the Supporting Information). The ^1H NMR spectrum of **2** also displays a characteristic high-field signal (−13.73 ppm) for the hydrido ligand, which is split into a quintet by coupling to the four equivalent ^{31}P nuclei [$^2J(P,H)$ = 59 Hz]. The presence of a hydrido ligand is also verified by a characteristic IR absorption band at 1760 cm^{-1} originating from the ν(Mn–H) stretching vibration (Figures S5 and S7). Interestingly, the $^{119}Sn\{^1H\}$ NMR spectrum of **2** displays a very broad signal at 540 ppm.[20]

The strong polarization of the Sn–Cl bond of complex **2** (vide supra) led us to assume that the chloride group might be easily removed. In fact, treatment of **2** with a nonoxidizing halide-abstraction agent such as $Na[B(C_6H_3$-3,5-$(CF_3)_2)_4]$ or $Li[Al$-

Table 1. Selected B3LYP-Calculated[a] and Experimental Bond Lengths and Angles and Selected Results of the NBO and NRT Analyses of 2 and 3

	bond lengths (pm)		bond angles (deg)		NPA charges			NBO analysis[b]			NRT analysis[c]
	Mn−Sn	Mn−H	Mn−Sn−C1	H−Mn−Sn	Mn	Sn	H	bond	occ.	pol.	bond: BO (cov./ionic)
2 calc	2.486	1.566	158.2	173.8	−0.87	+1.46	−0.18	σ	1.92	72.6% Sn	Mn−Sn: 2.08 (0.69/1.39)
								π	1.82	83.3% Mn	Mn−H37: 0.35 (0.04/0.31)
2 exp	2.3997(3)	1.51(2)	158.53(4)	176.6(9)							
3 calc	2.373	1.552	180.0	180.0	−0.87	+1.35	−0.14	σ	1.93	73.0% Sn	Mn−Sn: 2.25 (0.80/1.45)
								π	1.44	76.6% Mn	Mn−H75: 0.50 (0.39/0.11)
3 exp	2.3434(5)	1.44(3)	176.85(9)	177.1(14)							

[a]Basis sets: TZVPP for Mn, Sn, P, Cl, $H_{hydride}$; 6-31G* for all other atoms. [b]NBO analysis: bond (Mn−Sn σ or Mn−Sn π), occupancy (occ.), and bond polarization (pol.). [c]NRT analysis: bond: total bond order (covalent bond order/ionic bond order).

$(OC(CF_3)_3)_4]$ in fluorobenzene was accompanied by rapid precipitation of MCl (M = Li, Na), selectively affording the stannylidyne complex salts **3a** and **3b**, respectively (Scheme 1). Complexes **3a** and **3b** were isolated in 90% yield as purple, extremely air-sensitive solids. The thermal stabilities of **3a** and **3b** are remarkable; **3a** melted at 195 °C, whereas **3b** neither melted nor decomposed upon heating to 240 °C.

The solid-state structure determined by scXRD (Figure 3) shows that **3a** is composed of well-separated cations and anions,
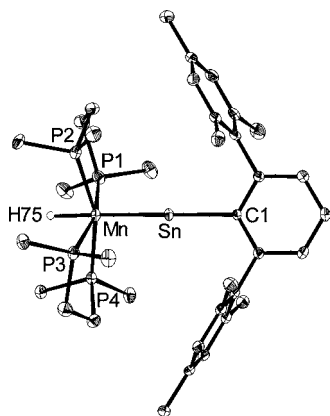

Figure 3. DIAMOND plot of the molecular structure of the complex cation in **3a**. Thermal ellipsoids are set at 30% probability. H atoms have been omitted except for H75 bonded to Mn. Selected bond lengths (Å) and angles (deg): Mn−Sn, 2.3434(5); Sn−C1, 2.159(3); Mn−H75, 1.44(3); Mn−Sn−C1, 176.85(9); Sn−Mn−H75, 177.1(14); Sn−Mn−P1, 97.40(3); Sn−Mn−P2, 100.94(3); Sn−Mn−P3, 98.16(3); Sn−Mn−P4, 99.17(3).

excluding any bonding contact between the electrophilic tin center and the counteranion.[21,22] The trans-configured, distorted-octahedral 18VE stannylidyne complex cation features a nearly linearly coordinated tin atom [Mn−Sn−C1 = 176.85(9)°] and the shortest Mn−Sn bond reported to date [2.3434(5) Å]. Notably, the Mn−Sn bond is 0.3 Å shorter than that found in the manganostannylene *mer,trans*-[Mn-

$(CO)_3(CNR)_2SnCl]$ (R = C_6H_3-2,6-$Dipp_2$; Dipp = 2,6-diisopropylphenyl), which contains a singly bonded, V-shaped SnCl ligand,[23] and compares very well with that predicted for a Mn−Sn triple bond [d(Mn≡Sn) = 2.35 Å] using the theoretically calculated triple-bond radii of Mn (1.03 Å) and tin (1.32 Å).[24]

NRT analysis of the electron density of the DFT-minimized structure of the complex cation of **3a**/**3b** suggests a highly polar Mn≡Sn bond, as evidenced by the low covalent (0.85) and high ionic (1.45) contributions to the total Mn−Sn NBO of 2.25, which is slightly larger than that of **2**, rationalizing the observed shorter Mn−Sn bond in **3a**/**3b** than in **2**. The polarity of the Mn≡Sn bond is also reflected in the high opposite NPA charges of Mn (−0.87) and Sn (+1.35). A look at the frontier Kohn−Sham orbitals of the complex cation of **3a**/**3b** shows that the LUMO+1 and LUMO correspond to the π_{in}* and π_{out}* Mn−Sn bonds and that two π-type molecular orbitals (HOMO, π_{out}; HOMO−2, π_{in}) in combination with the Mn−Sn σ-type orbital (HOMO−8) contribute to the formation of the Mn−Sn triple bond (Figure 4). The composition and structure of **3a** and **3b** were further confirmed by elemental analyses and IR and NMR spectroscopy. Analogous to **2**, the $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** show a singlet flanked by tin satellites [$^2J(^{119}Sn,P) = 200–215$ Hz] at slightly higher field (71.0 ppm) than in **2**, and the ^1H NMR spectra show a distinctive quintet signal [$^2J(P,H) = 66$ Hz] for the hydrido ligand, which appears at slightly higher field (−14.59 ppm) than that of **2**. Notably, the position of the ν(Mn−H) absorption band in the IR spectrum is dependent on the counteranion (**3a**, 1792 cm^{-1}; **3b**, 1778 cm^{-1}). The stannylidyne complex cation has a time-averaged C_{2v}-symmetric structure in solution, which renders the mesityl substituents of the *m*-terphenyl group homotopic. Therefore, only a single set of signals is observed for the ortho and meta ^1H and ^{13}C nuclei of the mesityl groups, respectively (Figure S3). Furthermore, the $^{13}C\{^1H\}$ NMR spectra of **3a** and **3b** display a distinctive low-field signal for the tin-bonded C_{aryl} atom at 188.2 ppm, which is typical for stannylidyne complexes.[3b,7d] Finally, **3a** is distinguished by a broad ^{119}Sn NMR signal appearing at lower field (761 ppm) than that of **2**.
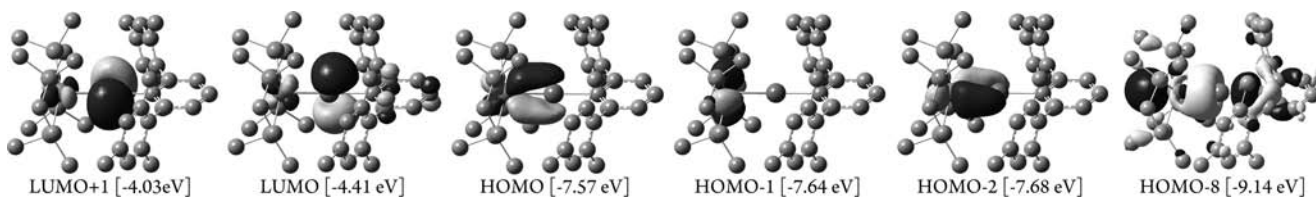
Figure 4. Frontier Kohn−Sham orbitals of the complex cation of **3a**/**3b** (isosurface value, 0.04 e Å^{-3}; energies in eV).

The electrochemical properties of complex **3a** were studied by cyclic voltammetry. Remarkably, **3a** undergoes a reversible one-electron reduction at a half-wave potential of −1.58 V vs $[Fe(C_5Me_5)_2]^{+1/0}$ (−2.03 V vs $[Fe(C_5H_5)_2]^{+1/0}$) (Figure S8). This suggests that open-shell stannylidyne complexes might be accessible using strong reducing agents such as $[Fe(C_5Me_5)-(C_6Me_6)]$.[25] Studies in this direction are currently underway.

The presented mild and selective approach to the first manganese complex featuring a Mn−Sn triple bond illustrates the synthetic potential of dihydrogen complexes in metal−tetrel multiple-bond chemistry. Further investigations to explore this synthetic potential for building up metal complexes with nonclassical π-acceptor ligands of the heavier group 14 elements are currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(19) The orthogonal orientation of the *m*-terphenyl substituent in **2** is best evidenced by the dihedral angle of 87.64(8)° between the stannylidene ligand plane passing through the Mn, Sn, Cl, and C1 atoms and the central aryl ring plane (C1−C6).

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(22) The solid-state structure of **3b** was also determined using scXRD and showed the same structural motif and very similar bonding parameters for the complex cation as in **3a**. However, because of the low quality of two data sets for two different samples, the structure of **3b** was not further considered.

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