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Carbometalation of a Stiba-alkene Resulting in an In(III)/Sb(III) C-Centered *Geminal* Organodimetallic Complex

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Summary: The stiba-alkene nature of the red oil produced from the 2:1 reaction of [2-Pyr(SiMe$_3$)$_2$CLi·tmeda] (Pyr = C_5H_4N) with $SbCl_3$ has been confirmed by mass spectrometry. The low-temperature addition of Et_3In to a hexane solution of the stiba-alkene, [2-Pyr(SiMe$_3$)$_2$-CSb═C(SiMe$_3$)2-Pyr], results in the first structurally authenticated In(III)/Sb(III) carbon-centered geminal organodimetallic complex, via carbometalation at the Sb═C double bond.

Geminal organodimetallic complexes that contain two metals on a single carbon center have been recognized as important synthetic reagents for over two decades now.[1] Their appeal as reactive intermediates lies in the potential they have to react sequentially or simultaneously with similar or differing electrophiles at the dimetalated carbon center. To achieve control over reactivity and a greater degree of selectivity than that shown by 1,1-dilithio or 1,1-dimagnesio complexes, it would be preferable for the complex to contain two different metals of differing reactivity: either two p-block elements or an s- and p-block element. Indeed Kaufmann has demonstrated the facile synthesis of mixed s- and p-block 1,1-dimetalated methane derivatives.[2] However, despite their synthetic utility there have been very few structurally authenticated *geminal* organodimetallic complexes of either type outside of the polymetalated group 14 methane derivatives. The limited examples include $\{[PhO_2S(SiMe_3)C]Li_2\}_6Li_2O\cdot 10thf$,[3] $[(SiMe_3)_2C(MgBr)_2\cdot 4thf]$,[4] $(Ph_2Sb)_2CH_2$,[5] which was characterized as a ligand coordinated to PhPdCl, and $[(Me_3Si)_2CH]_2AlCH_2Al[(Me_3Si)_2CH]_2$.[6]

Recently we reported on the synthesis of a *geminal* Al(III)/Sb(III) C-centered *geminal* dimetallic heterocycle, **1**, which formed on the addition of Me_3Al to an implied stiba-alkene intermediate, **2**.[7] Highlighting a degree of variability, the addition of Et_2Zn to the stiba-alkene, which is a deep red oil, resulted not in carbometalation but transmetalation to give the 1,1-dizinc tetrameric complex, [2-Pyr(SiMe$_3$)CZn]$_4$.[8] Herein we now report the first synthesis and characterization by single-crystal X-ray crystallography of an In(III)/Sb(III) *geminal* organodimetallic complex, **3**, and confirm the stiba-alkene nature of the red oil, **2**.

As previously described,[7] the stiba-alkene, [2-Pyr(SiMe$_3$)$_2$CSb═C(SiMe$_3$)2-Pyr], is isolated as a red oil on the low-temperature β-elimination of Me_3SiCl from [2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl, itself formed from the 2:1 addition of [2-Pyr(SiMe$_3$)$_2$CLi·tmeda] to $SbCl_3$ in thf. It has been found that if tmeda is not present, decomposition to elemental Sb occurs readily and yield of the red oil is significantly reduced. The actual structure of **2** had only been deduced from its reaction with Me_3Al. The structure has now been confirmed by both EI and electrospray mass spectrometry.[9] The electrospray was the gentler of the two techniques, and a dry thf solution of the red oil was introduced into the spectrometer with pneumatic assistance and a source temperature of 60 °C. The spectrum produced shows clearly a dominant peak pattern at 521.0 (M^+/Z) consistent with $[\mathbf{2} + H]^+$ and the calculated isotope pattern for **2**. For EI the source temperature was 200 °C, leading to a significant degree of cleavage at the Sb═C double bond with other major bond cleavages, particularly of $[Me_3Si]^+$, clearly apparent. The major peaks containing Sb and showing the expected isotope pattern are at 356.03 (M^+/Z) for $[2\text{-Pyr}(SiMe_3)_2Sb - H]^+$. The other half of the molecule, $[2\text{-Pyr}(SiMe_3)C]^+$, is located at 162.07, although in a comparatively reduced amount. Surprisingly even at 200 °C a significant amount of the stiba-alkene remains intact and is located, as expected, at 520.12 (M^+/Z). Previous NMR spectra had indicated that the oil was not pure, and this is highlighted by the electrospray, while the higher temperature EI shows a cleaner spectrum, as the more volatile components (e.g., residual tmeda) are removed quickly.

Addition of a slight stoichiometric excess of neat Et_3In to a hexane solution of the red oil at −80 °C with subsequent stirring and warming to ambient temperature, followed by refrigeration at 4 °C, produced a large crop of pale pink crystals.[10,11] Single-crystal X-ray diffraction studies show the crystals to be the In(III)/Sb(III) C-centered *geminal* organodimetallic complex [2-Pyr(SiMe$_3$)$_2$CSb(Et)-C(SiMe$_3$)$_2$2-Pyr-In(Et)$_2$], **3**, aris-

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[9] Mass spectrometry for 2: EI-MS (red oil, calcd for $C_{21}H_{35}N_2Si_3Sb$ = 520.12 = M) *m/z* (%); 520.12 $[M]^+$ (12) 446.08 (8), 433.05 (1.5), 392.00 (10), 372.06 (18), 356.03 $[M - H - (2\text{-Pyr}(SiMe_3)C)]^+$ (89), 341.00 (21), 300.02 (21), 295.13 (21), 283.99 (8), 268.96 (21), 221.11 (36), 206.08 (100), 162.07 $[M - (2\text{-Pyr}(SiMe_3)_2CSb)]^+$ (26), 149.07 (36), 148.06 (37), 132.03 (17); ES-MS (selected peak) 521.1 $[M + H]^+$ (55).

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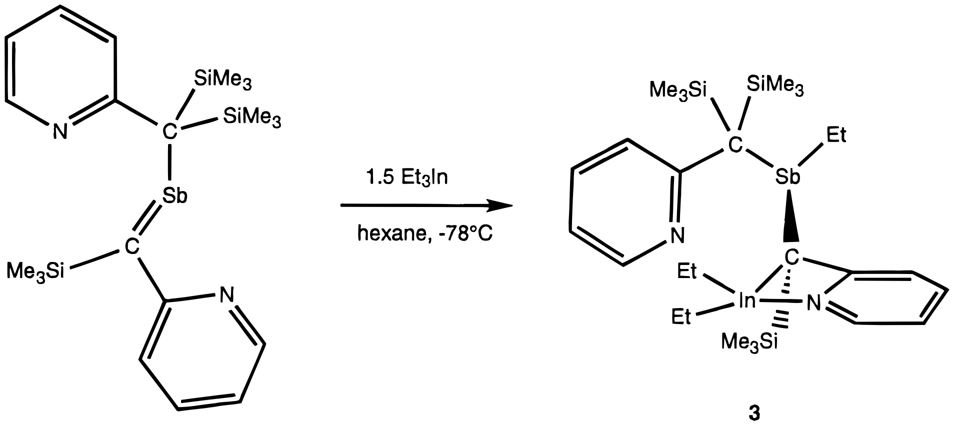
Scheme 1. Synthesis of [2-Pyr(SiMe$_3$)$_2$CSb(Et)C(SiMe$_3$)$_2$2-Pyr-In(Et)$_2$], 3



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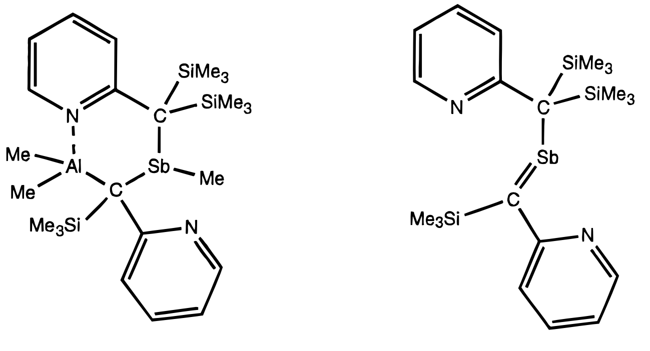

1 **2**

Figure 1. Molecular structure of Al/Sb complex **1**.

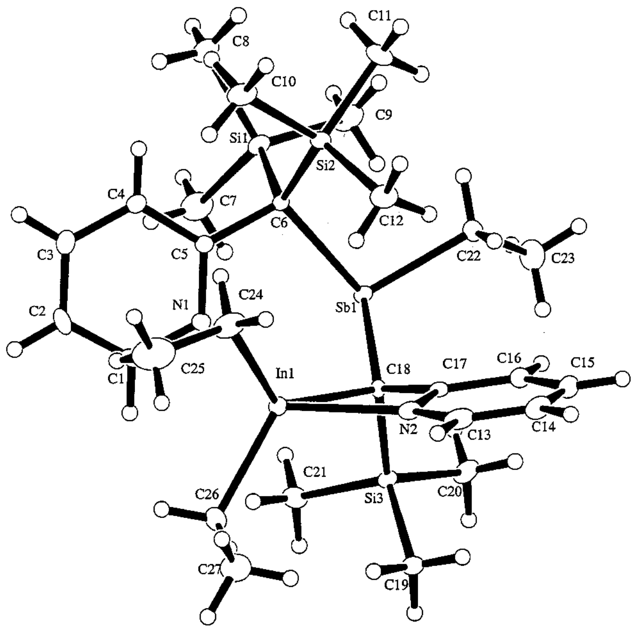

Figure 2. Molecular structure of **3**.

ing from 1,2-addition, or carbometalation, of the stiba-alkene intermediate (Scheme 1).[12]

The structure is shown in Figure 2. The crystals are air and moisture sensitive and become orange on melting at 84−86 °C. Unlike the complex formed by Me$_3$Al, **1**, in which a six-membered dimetallic heterocycle is achieved through bonding of N$_{\text{pyr}}$ to Me$_2$Al−, there is no evidence for any ring closure on this occasion. In fact In forms an unambiguous dative bond with N(2), 2.428(2) Å, giving a planar unit composed of two rings: C(17)−N(2)−In−C(18) and the pyridyl ring to which N(2) and C(17) belong. Probably as a result of ring strain the In−N(2) bond length is slightly longer than those commonly found in systems where Me$_3$In accepts only one Lewis base N donor atom, e.g., [Me$_3$In.MeN(H)CH$_2$-CH$_2$(H)NMe·Me$_3$In][13] 2.369 Å, [Me$_3$In·^{t}BuNH$_2$][14] 2.360 Å, [Me$_2$InPh(2-NEt$_2$)][15] 2.383 Å, the exception being the Me$_3$In complex with sterically demanding 2,2,6,6-tetramethylpiperidine,[9] 2.503 Å. There are only a handful of complexes in which In accepts two or more Lewis base donor atoms, the most relevant being [2-Pyr(SiMe$_3$)$_2$C]$_2$InCl,[16] which has relatively short N$_{\text{pyr}}$−In bonds, 2.440 and 2.411 Å, and the more representative [Me$_3$In·DABCO]$_\infty$, in which the N−In bond is longer at 2.626 Å.[13] The longest In−N dative bond is found in [Me$_3$In·(Pr^{i}NCH$_2$)$_3$][17] at 2.776(13) Å. This would suggest that the second possible In−N bond in **3**, that of In−

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(10) Synthesis of 3: Et$_3$In (7.5 mmol, 1.52 g) was added dropwise to a hexane (13 mL) solution of the stiba-alkene at −78 °C. The cold bath was removed, and the reaction mixture was stirred and allowed to warm slowly to room temperature. The pale orange solution was filtered and placed in the freezer. A large crop of pale pink crystals was grown overnight. On isolation, a small amount of colorless oil was also present. The crystals were washed in cold toluene and shown to be [2-Pyr(SiMe$_3$)$_2$CSb(Et)C(SiMe$_3$)$_2$2-Pyr-In(Et)$_2$].

(11) Analytical data for 3: Yield 2.3 g, 63%, mp 84−86 °C; NMR (proton/carbon numbering as normal for 2-methylpyridine, br = broad) ^{1}H (C$_6$D$_6$, 25 °C, 400 MHz); δ 8.23 (3d, J = 0.9, 2.0, 5.1 Hz, 1H, H^{6a}), δ 7.80 (3d, J = 1.0, 1.9, 5.2 Hz, 1H, H^{6b}), δ 7.13 (3d, J = 1.0, 1.0, 8.3, 1H, H^{3a}), δ 7.06 (3d, J = 1.9, 7.3, 8.0 Hz, 1H, H^{5b}), δ 6.94 (3d, J = 2.0, 7.3, 8.3 Hz, 1H, H^{5a}), δ 6.88 (3d, J = 1.1, 1.1, 8.0 Hz, 1H, H^{3b}), δ 6.49 (3d, J = 1.1, 5.1, 6.1 Hz, 1H, H^{4a}), δ 6.41 (3d, J = 1.1, 5.2, 6.3 Hz, 1H, H^{4b}), δ 1.85 (q, J = 7.9 Hz, 2H, CH$_2$Sb), δ 1.54−145 (m, 9H, CH$_3$), δ 0.62 (br, 2H, CH$_2$In), δ 0.52 (br, 2H, CH$_2$In), δ 0.37 (s, 9H, SiMe$_3$), δ 0.12 (s, 9H, SiMe$_3$), δ 0.11 (s, 9H, SiMe$_3$); ^{13}C (C$_6$D$_6$, 25 °C, 100.6 MHz) 172.7 (C^{2a}), 168.5(C^{2b}), 148.3 (C^{6a}), 147.3 (C^{6b}), 136.9 (C^{3a}), 136.0 (C^{3b}), 126.7 (C^{5a}), 125.7 (C^{5b}), 19.2 (C^{4a}), 118.5 (C^{4b}), 34.0 (C−Si), 33.3 (C−Si), 13.6 (CH$_3$), 12.8 (CH$_3$), 10.3 (br, CH$_2$In), 9.4 (CH$_2$Sb), 5.0 (SiMe$_3$), 2.2 (SiMe$_3$), 1.5 (SiMe$_3$). Anal. Found (calcd for C$_{27}$H$_{47}$N$_2$Si$_3$InSb): C 44.79 (44.82), H 7.03 (6.97), N 3.91 (3.87).

(12) Crystallographic data for 3 (Siemens SMART CCD, T = 123 K, crystals mounted in oil under Ar gas): C$_{27}$H$_{47}$N$_2$Si$_3$InSb, M = 720.51, monoclinic, $P2_1/n$ (No. 14), a = 12.1935(1) Å, b = 14.9966(1) Å, c = 18.6139(2) Å, β = 103.0158(6)°, V = 3316.31(5) Å^3, D_c (Z = 4) = 1.443 g cm^{-3}; F(000) = 1460 $\mu_{\text{MoK}\alpha}$ = 16.33 cm^{-1} (no correction), $2\theta_{\max}$ = 60.1°, Mo Kα radiation, final R, R_w = 0.028, 0.028; GoF 1.70, N_o = 7471 "observed" ($I > 3\sigma(I)$) reflections out of N = 9980 unique. Solved by direct methods. All hydrogen atoms placed in calculated positions.

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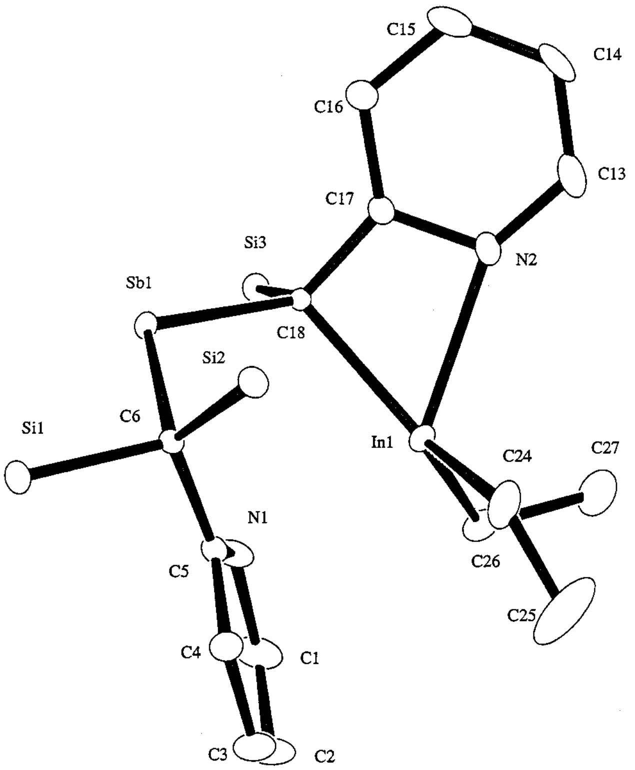

Figure 3. Skeletal backbone of **3** showing the orientation and proximity of In to N1.

N(1), of 2.773 Å is real. However the direction of the N lone pair is not toward the In center but is almost perpendicular to an idealized position for a direct dative bond. Given the position of the two nearby Me_3Si groups, it is most likely that ring closure is prevented by steric factors, despite the increase in metal size from Al to In. The proximity of In and N(1) may simply be a consequence of crystal packing, although as can be seen from the alternative view offered in Figure 3, there is clearly an open coordination site available at the In center which may reflect, or allow for, some degree of bonding to the π system covering C(1)−N.

The *geminal* carbon center is chiral, bearing a pyridyl group, Si, Sb, and In, and it is the *S* form of the molecule that is depicted in Figure 2, although both the *S* and *R* forms are present in the crystal. For $[(SiMe_3)_2C(MgBr)_2 \cdot 4thf]$, Bickelhaupt[4] comments on the reduced M−C bond lengths at the *geminal* carbon occurring as a result of increased negative charge on that C. The In−C(18) bond at 2.236(2) Å (Table 1) is in fact much longer than that normally found for trialkyl, 4-coordinate In, as also indicated by the shorter In−C(24, 26) distances of 2.187(2) and 2.193(2) Å, respectively, which are at the long end of the range of typical bond distances, av 2.167 Å. The equivalent bonds in $[2\text{-Pyr(SiMe3)}_2\text{C}]_2\text{InCl}$ average 2.259 Å, although in this case In is 5-coordinate. Again the longer C_{gem}−In distance in **3** could simply be a result of strain in the four-membered ring. In comparison with **1** the Sb−C(18) bond is slightly longer at 2.180(2) Å as compared to 2.167(7) Å, but, as was also found in **1,** it is much shorter than the bond from Sb to the C in the unmodified ligand, Sb−C(6) 2.262(2) Å. In $[2\text{-Pyr(SiMe}_3)_2\text{SbCl}_2]$ this bond distance is 2.213 Å. If a case can be made for significant bond shortening at the C_{gem}, then the increase in nuclear charge should be apparent in the ^{13}C NMR.

Table 1. Selected Bond Distances [Å] and Angles [deg] for 3

Sb(1)−C(6)	2.262(2)	Sb(1)−C(18)−In(1)	114.80(9)
Sb(1)−C(22)	2.180(2)	C(6)−Sb(1)−C(18)	110.86(7)
Sb(1)−C(18)	2.180(2)	C(18)−Sb(1)−C(22)	101.67(9)
In(1)−C(18)	2.236(2)	C(6)−Sb(1)−C(22)	99.26(8)
In(1)−C(26)	2.193(2)	C(5)−C(6)−Sb(1)	106.4(1)
In(1)−C(24)	2.187(2)	N(2)−In(1)−C(24)	97.55(9)
In(1)−N(2)	2.428(2)	C(24)−In(1)−C(26)	110.3(1)
Si(3)−C(18)	1.883(2)	C(18)−In(1)−C(24)	129.07(9)
C(18)−C(17)	1.400(3)	C(17)−C(18)−In(1)	95.4(1)
C(5)−C(6)	1.511(3)	C(17)−C(18)−Sb(1)	124.0(1)

1D and 2D ^1H and ^{13}C NMR studies were carried out in benzene-d_6. While it has not been possible yet to assign which specific set of signals belong to which ligand (i.e., $2\text{-Pyr(SiMe}_3)_2\text{C}^-$ or $2\text{-Pyr(SiMe}_3)\text{C}^-$), $^1H/^{13}C$ correlations have clearly identified which pyridyl protons are related and which Et groups correspond with which signals. Thus the protons in "CH_2Sb" are found at a higher frequency than the "CH_2In" proton signals, which are very broad, most likely as a result of the quadrupolar In nuclei. In the ^{13}C NMR spectrum the quaternary signals for Sb−*C* and Sb-*C*−In appear at δ 33.9 and δ 33.3, which surprisingly is not that different from the free ligand $[2\text{-Pyr(SiMe}_3)_2\text{CH}]$, δ 33.4. This would suggest that the complex is highly covalent, with more negative charge residing on that carbon than in $[2\text{-Pyr(SiMe}_3)_2\text{C}]\text{SbCl}_2$, δ 51.3,[18] or $[6\text{-Me-2-Pyr(SiMe}_3)_2\text{C}]\text{InCl}_2$, δ 51.9.[19] However, it is consistent with $\{[6\text{-Me-2-Pyr(SiMe}_3)_2\text{C}]_2\text{InCl}\}$, δ 32.5.[19]

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Supporting Information Available: Crystallographic data for **3**. EI-MS and ES-MS for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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