Synthesis and Pseudorotational Barriers of Hypervalent Antimony Compounds Bearing Antimony-Group 6 Transition Metal Bonds

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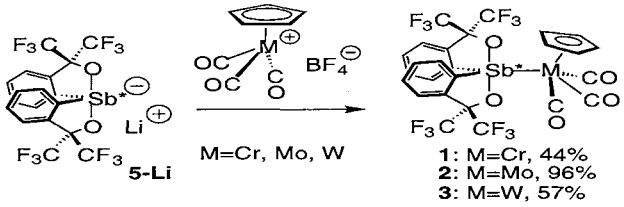
Hypervalent antimony compounds $Rf_2Sb^*M(Cp)(CO)_3$ (Rf=*o*-$C_6H_4C(CF_3)_2O$-, M=Cr **1**, Mo **2**, W **3**) and diastereomeric RfRfm*Sb*Mo(Cp)(CO)$_3$ {**4a** and **4b**, Rfm*=*o*-$C_6H_4C^*(CF_3)(Me)O$-} were synthesized. X-ray analysis of **1** and **4a** and the very high isomerization barrier (31.5 kcal/mol) of **4** showed the strong electron-donating property of the (Cp)M(CO)$_3$ fragments.

The facile pseudorotaion of pentacoordinate species has been well known[1] and the very low barrier has been successfully heightened by introduciton of bidentate ligands such as Martin ligand {Rf=*o*-$C_6H_4C(CF_3)_2O$-}. The chirality of spirocyclic phosphorane Rf_2P^*H with two Martin ligands remains stable even at room temperature.[2] However, the pseudorotaional barrier is strongly dependent on the monodentate ligand and the configuration of the central phosphorus in Rf_2P^*X with an electronegative atom (X) is not stable. In this respect, hypervalent group 15 element compounds bearing a transition metal fragment are quite interesting because of possible electron-donating ability of transition metals. However, systematic investigation of the quantitative effect of the transition metal fragment on the stereochemical rigidity of pentacoordinate compounds has never been carried out mainly because of the instabilty of these compounds.[3] Recently we reported stable diastereomeric hypervalent antimony compounds $Rf_2Sb^*Fe^*(Cp)(CO)(PPh_3)$. The pseudorotational barrier could be estimated to be very high based on the very slow isomerization between the diastereomers but the exact barrier was not obtained due to the partial decomposition at high temperatures.

Here we report preparation of hypervalent antimony compounds, $Rf_2Sb^*MCp(CO)_3$ (M=Cr **1**, Mo **2**, W **3**), directly bonded to a series of group 6 transition metal ligands. In addition, diastereomeric Sb compounds with an antimony-molybdenum bond, RfRfm*Sb*Mo(Cp)(CO)$_3$ **4a** and **4b** {Rfm*=*o*-$C_6H_4C^*(CF_3)(Me)O$-} could also be prepared. After separation into each diastereomer the relative stereochemistry was established by X-ray analysis of **4a**.

Compounds **1** - **3** could be obtained in good yields by the reaction of stiboranide anion **5-Li** ($Rf_2Sb^-{}^*Li^+$)[4] with $[CpM(CO)_3]^+BF_4^-$,[5] which was generated by treatment of $CpMH(CO)_3$ with $Ph_3C^+BF_4^-$.[6] These compounds were stable to atmospheric moisture and could be purified by column chromatography [SiO_2, CH_2Cl_2-*n*-hexane (1 : 1)].[7] RfRfm*Sb*Mo(Cp)(CO)$_3$ (**4a** and **4b**) were prepared by similar procedures using diastereomeric stiboranide anion, $RfRfm^*Sb^-{}^*Et_3HN^+$ (**6-Et$_3$HN**),[8] instead of **5-Li** in good yields (**4a**: 49%, and **4b**: 33% yield).[9] Separation of the diastereomers could be carried out by column chromatography [SiO_2, CH_2Cl_2-*n*-hexane (1 : 1)].

Crystals of **1** and **4a** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2-*n*-hexane. X-ray analysis of **1** is the first example of structurally characterized hypervalent group 15 element compounds bearing a chromium



Scheme 1.

fragmant. Figures 1 and 2 show the ORTEP drawings of **1** and **4a**.[10] The geometry about the antimony atom can be considered as a distorted trigonal bipyramidal (TBP) structure with the $CpM(CO)_3$ fragment at the equatorial site of the TBP. The averaged apical Sb-O lengths in **1** (2.085(1) Å) is almost comparable to that (2.087(3) Å) in $Rf_2Sb^*Fe(Cp)(CO)_2$ (**7**)[4] but are definitely longer than the that of $Rf_2Sb^*(p\text{-}CH_3C_6H_4)$ (**8**) (2.039(3) Å).[8a] X-ray analysis of **4a** unambiguosly established the relative stereochemistry (as shown in Figure 2) and the

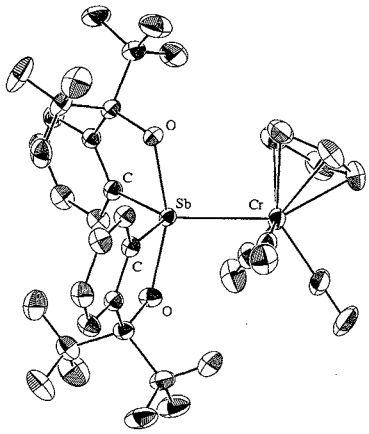


Figure 1. ORTEP drawing of **1** (30% probability ellipsoid).

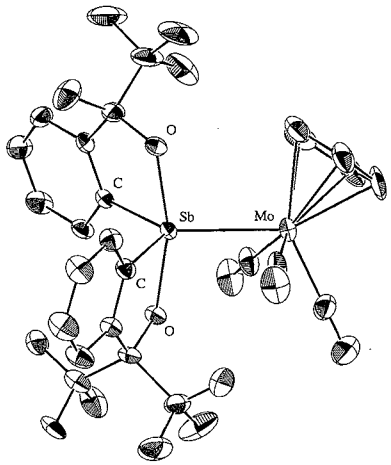
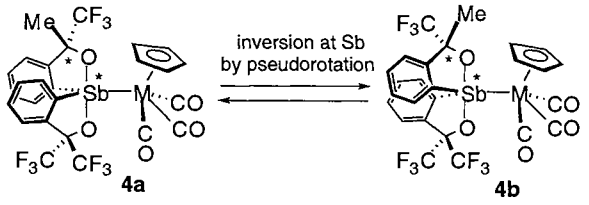


Figure 2. ORTEP drawing of **4a** (30% probability ellipsoid).

averaged apical Sb-O length (2.085(3) Å) is the same as that of **1**. The elongated apical Sb-O lengths in **1** and **4a** indicate the strong electron-donating property of the transition metal fragment (Cp)M(CO)3.

In order to investigate the pseudorotational barrier, each diastereomer of **4** was dissolved in *o*-dichlorobenzene, and was heated to monitor the isomerization by ^{19}F NMR (Scheme 2).



Scheme 2. Isomerization between **4a** and **4b**.

We could observe the isomerization between **4a** and **4b** at 100, 110, 120, 130, and 140 °C to attain the equilibrium (equilibrium ratio: **4a** : **4b** = 1 : 1.7 at 110 °C) without noticeable decomposition. The small values of activation entropy ($\Delta S^{\neq}$ [-2.7 (±5.9) (from **4a** to **4b**) and -0.9 (±4.8) eu (from **4b** to **4a**)]) suggested that the isomerization was a unimolecular process without cleavage of the Sb-Mo bond and was effected by inversion (pseudorotation) at the central antimony atom. At 110 ° C (383 K), the pseudorotational barriers were 31.3 kcal/mol (**4a** to **4b**) and 31.7 kcal/mol (**4b** to **4a**). These are much higher than that of Rf2Sb*Cl (14.6 kcal/mol)[11] and those of RfRfm*Sb*(*p*-CH3C6H4) (28.1 kcal/mol (major to minor), 27.7 kcal/mol (minor to major)) at 110 °C.[8a] Therefore, the equatophilicity of the group 6 transition metal fragment was confirmed to be greater than the tolyl group by three kcal/mol estimated by the pseudorotational barriers.

References and Notes

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6 Preparation of **2**: $[CpMo(CO)_3]^+BF_4^-$ was generated by treatment of $CpMoH(CO)_3$ (1.19 g, 4.82 mmol) with $Ph_3C^+BF_4^-$ (1.59 g, 4.82 mmol) in 20 ml of dichloromethane at room temperature for 15 min and $Rf_2Sb^-Li^+$ (1.50 g, 2.54 mmol) was added to the solution. The mixture was stirred for 3 h at room temperature. Pure **2** (2.00 g, 2.45 mmol) was obtained in 96% yield after chromatography [SiO_2, CH_2Cl_2-*n*-hexane (1 : 1)]. Compounds **1** and **3** were obtained by similar procedures.

7 ^1H NMR ($CDCl_3$): **1**; δ 5.18 (s, 5 H), 7.54 (t, 2H), 7.63 (t, 2 H), 7.71 (d, 2 H), 8.21 (d, 2 H). **2**; ^1H NMR ($CDCl_3$): δ 5.61 (s, 5 H), 7.52 (t, 2H), 7.61 (t, 2 H), 7.70 (d, 2 H), 8.17 (d, 2 H). **3**; ^1H NMR ($CDCl_3$): δ 5.71 (s, 5 H), 7.52 (t, 2H), 7.61 (t, 2 H), 7.70 (d, 2 H), 8.15 (d, 2 H). Elemental analysis of **1** ~ **4** gave correct results.

8 a) S. Kojima, Y. Doi, M. Okuda, and K.-y. Akiba, *Organometallics*, **14**, 1928 (1995). b) K.-y. Akiba, H. Nakata, Y. Yamamoto, and S. Kojima, *Chem. Lett.*, **1992**, 1559.

9 Preparation of **4**: $[CpMo(CO)_3]^+BF_4^-$ was reacted with **6-Et3HN**, which was generated from RfRfm*HSb* (200 mg, 0.36 mmol) and Et3N (51 μL, 0.37 mmol) in 10 mL of THF. The mixture was stirred for 1 h at room temperature. Separation of the diatereomers (**4a** and **4b**) were carried out by column chromatography [SiO_2, CH_2Cl_2-*n*-hexane (1 : 1)]. ^1H NMR ($CDCl_3$): **4a**; δ 1.49 (s, 3H), 5.63 (s, 5 H), 7.4-7.5 (m, 4H), 7.57 (t, 1H), 7.69 (d, 1 H), 8.11 (d, 1 H), 8.21 (d, 1 H). **4b**; δ 1.72 (s, 3H), 5.62 (s, 5 H), 7.5-7.6 (m, 5H), 7.71 (d, 1H), 8.10 (d, 1 H), 8.14 (d, 1 H).

10 Crystal data for **1**: $C_{26}H_{13}O_5F_{12}CrSb$, M = 807.1, monoclinic, space group $P2_1/c$, a = 15.596(6), b = 11.881(4), c = 15.184(5) Å, β = 101.28(3)deg, V = 2759.4(1) Å^3, Z = 4, Dc = 1.94 g cm^{-3}, R = 0.035, Rw = 0.043 for 5773 reflections ($I > 3\ \sigma(I)$). Selected bond distances (Å): Sb-O(ax) 2.072(1), Sb-O(ax) 2.097(1), Sb-C(eq) 2.107(2), Sb-C(eq) 2.111(2), Sb-Cr 2.656(1). Selected bond angles (deg): O(ax)-Sb-O(ax) 159.0(1), C(eq)-Sb-C(eq) 116.9(1), C(eq)-Sb-Cr 122.1(1), C(eq)-Sb-Cr 121.0(1).
Crystal data for **4a**: $C_{26}H_{16}O_5F_9MoSb$, M = 797.1, monoclinic, space group $P2_1/n$, a= 9.681(8), b = 34.14(2), c = 9.029(5) Å, β = 114.28(5)deg, V = 2720.4(1) Å^3, Z = 4, Dc = 1.95 g cm^{-3}, R = 0.067, Rw = 0.081 for 5290 reflections ($I > 3\ \sigma(I)$). Sb-O(Me side) 2.069(3), Sb-O(CF_3 side) 2.100(3), Sb-C(eq) 2.121(4), Sb-C(eq) 2.111(4), Sb-Mo 2.764(1). Selected bond angles (deg): O(ax)-Sb-O(ax) 164.1(2), C(eq)-Sb-C(eq) 109.9(2), C(eq)-Sb-Mo 124.6(1), C(eq)-Sb-Mo 125.3(1).

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