$(C_5H_5)_2Sn\!:\rightarrow BF_3$. The First Example of a Tin→Group III Complex

Sir:

We have recently reported the Sn^{119m} Mössbauer, nmr, and mass spectra of dicyclopentadienyltin(II)[1] (I). From the QS (0.86 ± 0.06 mm/sec)[1] and known structural parameters[2] of I, a point charge calculation was carried out which located the lone-pair electrons of tin in this valence state along the bisecting axis of the angular sandwich structure at *ca.* 1.2 Å from the tin nucleus.[3] On this basis the lone-pair electrons, which are seen to be stereochemically active from the bent structure, reside in an orbital with pronounced directional character and may be available for bonding. This communication reports the isolation of dicyclopentadienyltin(II) boron trifluoride (II), the first complex utilizing the tin(II) lone pair in donation.[4]

Addition of freshly distilled boron trifluoride etherate to a THF solution of freshly sublimed I (not exothermic) in a nitrogen atmosphere followed by removal of most of the THF and addition of petroleum ether and cooling gave a precipitate of II as white needles [mp (sealed tube) 58–60°]. *Anal.* Calcd for $C_{10}H_{10}SnBF_3$: C, 37.9; H, 3.18; Sn, 37.5; B, 3.42; F, 18.0. Found: C, 40.38; H, 4.19; Sn, 38.3; B, 2.87; F, 17.20. II is unchanged after 1 week at room temperature under nitrogen, while I is polymerized *ca.* 90% in 5 days as followed by Mössbauer spectroscopy.[1] II is soluble in THF and methylene dichloride and sparingly soluble in carbon tetrachloride and petrol, while I is generally soluble in organic solvents. In air II turns black in 5–10 min while I turns yellow-red-brown in a longer period.[1] From the mode of formation we conclude that I is a stronger Lewis base toward boron trifluoride than either THF or ether.

The mass spectral data for both I and II are shown in Table I. The most prominent peaks in each pattern are the monotin fragments at 184 ($C_5H_5Sn^+$ = 100%), followed by 119 (Sn^+ = 13 and 20.5%, respectively). This behavior is also shown by vanadium and nickel dicyclopentadienes, but differs from that of ferrocene or from the σ-cyclopentadienyls.[5] Like both ferrocene and nickelocene, I and II give rise to fragments at 158 ($SnC_3H_3^+$ = 3.7 and 4.5%, respectively) and 144 (SnC_2H^+ = 3.0 and 4.0%, respectively).

All the bands assigned in the ir of I[6,7] can be identified in II run either as a KBr pellet or in CH_2Cl_2 (5%). The characteristic features of the spectrum of free BF_3[8] are missing in II, but bands at 1200 vs br and 1160 vs br cm^{-1}, absent in the spectrum of I, have been assigned in the analogous dimethylsulfur and -selenium complexes to $\nu_d(BF_3)$; likewise we assign the bands at 810 vs br and 633 s cm^{-1} as $\nu_s(BF_3)$ and $\delta_s(BF_3)$, respectively.[9] Infrared evidence can be used to rule out a diene-type cyclopentadienyl ring in either I or II in either phase.[10]

Table I. Tin-Containing Fragments in the Mass Spectra (70 eV)

Mass	Intensity $(C_5H_5)_2Sn$	Intensity $(C_5H_5)_2Sn\!:\!BF_3$	Assignment
315		0.073	$[(C_5H_5)_2Sn\!:\!BF_3\text{-}2H]^+$
285		0.073	$[(C_5H_5)_2SnF_2\text{-}2H]^+$
249	4.6	2.5	$(C_5H_5)_2Sn^+$
203		0.183	$C_5H_5SnF^+$
184	100	100	$C_5H_5Sn^+$
168		0.235	$SnBF_2^+$
158	4.52	3.7	$SnC_3H_3^+$
144	4.0	3.0	SnC_2H^+
119	13.0	20.55	Sn^+

The addition of boron trifluoride etherate to a solution of I in THF [sharp singlet at τ 4.19; $J(\mathrm{Sn}^{117,119}\text{–C–H}^1)$ = 15.3 Hz] causes a shift to τ 4.16 and the disappearance of the tin satellites. A solution of II in THF exhibits a sharp singlet at τ 4.16 with no satellites or broadening to −70°. The sharp singlet resonances of the C_5H_5 protons in I and II are interpretable in terms of stereochemically nonrigid systems. The observation of spin–spin coupling in I shows that the processes occurring there are *intra*molecular. The F^{19} spectrum of II in THF at 94.1 MHz is a singlet (half-height width 54 Hz) 256.0 ± 0.2 Hz upfield from the singlet resonance of boron trifluoride etherate (half-height with 1.5 Hz; 12368.7 Hz upfield from $CFCl_3$). No tin satellites are observed. While the absence of tin satellites in the F^{19} spectrum can be explained by a rapid exchange of II and BF_3 molecules, their absence in the proton spectrum may arise from a rapidly established equilibrium involving $(C_5H_5)_2Sn + BF_3 \rightleftharpoons (C_5H_5)_2Sn\!:\!BF_3 \rightleftharpoons C_5H_5SnF + C_5H_5BF_2$. The addition of tin(II) chloride or trimethyltin(IV) chloride gives rise to dissociative processes in I.[1]

The Sn^{119m} Mössbauer resonances of both I (IS = 3.74 ± 0.06; QS = 0.86 ± 0.06)[1] and II (IS = 3.79 ± 0.06; QS = 0.90 ± 0.06) run at 77°K *vs.* a $BaSn^{119m}O_3$ source (New England Nuclear Corp.) fall on the tin(II) side of β-tin.[11] The similarities in the QS values indicate that the relative distances of the two rings and the lone pair from the tin nucleus in I are preserved in II. Similarities in the IS values differ from the situation where tin acts as a Lewis acid. Increase in coordination number there is accompanied by population of 5d orbitals, changing hybridization, and shielding the nucleus from s-electron density. In II,

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(1) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **91**, 6885 (1969). More accurate values reported here result from better curve fitting.

(2) A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometal. Chem.*, 7, 97 (1967).

(3) N. W. G. Debye and J. J. Zuckerman, unpublished results.

(4) (a) We have recently shown from Sn^{116m} Mössbauer studies that the tin–transition metal complexes, sometimes formulated with tin(II) ligands [see, *e.g.*, J. D. Donaldson, *Progr. Inorg. Chem.*, **8**, 287 (1967); J. F. Young, *Advan. Inorg. Chem. Radiochem.*, **11**, 91 (1968)], are actually derivatives of tin(IV) [D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, **8**, 1771 (1969)]; and we have reached the same conclusions concerning $[(C_6H_5)_3SnMgBr]_2$ [P. G. Harrison, J. G. Noltes, and J. J. Zuckerman, unpublished results] formulated as a diphenyltin–phenylmagnesium bromide complex [H. M. J. C. Creemers, J. G. Noltes, and G. J. M. van der Kerk, *J. Organometal. Chem.*, **14**, 217 (1968)]. The reported isolation of $Cl_3Sn\!:\!BF_3^-$ [M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Amer. Chem. Soc.*, **88**, 1588 (1966)] has been retracted [D. F. Shriver, private communication, 1967]. (b) NOTE ADDED IN PROOF. We have recently isolated and characterized the product of I with iron(III) chloride in THF, a true tin(II) transition metal complex.

(5) M. I. Bruice, *Advan. Organometal. Chem.*, **6**, 273 (1968).

(6) L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).

(7) H. P. Fritz, *Chem. Ber.*, **92**, 780 (1959).

(8) D. A. Dows, *J. Chem. Phys.*, **31**, 1637 (1959).

(9) J. LeCalve and J. Lascombe, *Spectrochim. Acta*, **24A**, 737 (1968).

(10) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(11) The IS of β-tin, commonly quoted as 2.65 mm/sec from SnO_2 or $BaSnO_3$, is taken as the dividing line between the two valences of tin, all tin(II) compounds falling above [J. J. Zuckerman, "Mössbauer Effect Methodology," Vol. III, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, p 15; *Advan. Organometal. Chem.*, in press].

by contrast, there is apparently no change in hybridization.

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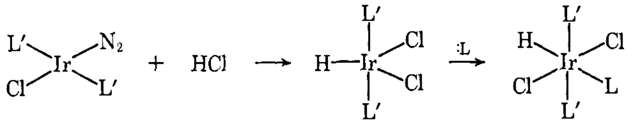
Stereodirection of Nucleophilic Addition to Five-Coordinated Complexes of Iridium

Sir:

The stereochemistry of substitution reactions on octahedral complexes which proceed by the SN1 dissociative path is determined by the stereochemical course of nucleophilic addition to five-coordinated intermediates.[1] Is the addition of the nucleophile stereospecific and, if so, what factors can be used to predict the stereochemical course of addition? If one of the ligands on the five-coordinated complex is strongly *trans*-directing, the results reported herein provide a useful solution to the problem.

Addition of anhydrous hydrogen chloride to *trans*-$[(C_6H_5)_3P]_2ClIrN_2$ in benzene solution gives orange-brown solutions of the five-coordinated iridium(III) complex **1** (d^6 configuration) which was previously isolated by Chatt and coworkers[2–5] (L′ = $(C_6H_5)_3P$). Addition of nucleophiles, :L, to solutions of **1** gives


1 2

high yields of the complexes (**2**) shown in Table I. The configuration shown for **2** is established by four pieces of evidence. (1) When L is dimethyphenylphosphine, the methyl proton resonance appears as a doublet (τ 8.53, J_{P-H} = 8.2 cps) clearly establishing L as *cis* to the two triphenylphosphine ligands.[7] (2) The observation of a single absorption band at 317 ± 8 cm^{-1} in the 250–340-cm^{-1} region for all the complexes is diagnostic of mutually *trans* chloro ligands. Complexes with chlorine *trans* to a hydride absorb in the

Table I. Infrared Data (cm^{-1}, Nujol) for $IrHCl_2[(C_6H_5)_3P]_2L^h$

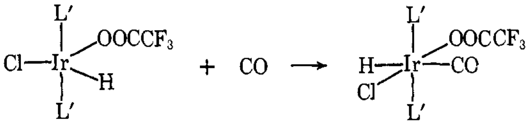
L	ν_{Ir-H}	ν_{Ir-Cl}
CH_3OH^a	2271	318
$As(C_6H_5)_3$	2232	314
As(*p*-tolyl)$_3$	2218	313
m-NH_2-$C_6H_4NO_2$	2223	312
$NC-C_6H_5^b$	2213	317
$P(C_6H_5)_3$	2203	315
p-$NC-C_6H_4-Cl^c$	2194	320
p-$NC-C_6H_4-NO_2^d$	2193	322
p-$NC-C_6H_4-CH_3^e$	2191	315
P(*p*-tolyl)$_3$	2190	312
C_5H_5N	2183	314
$Sb(C_6H_5)_3$	2180	319
$S(C_2H_5)_2$	2178	313
$NH_2CH_2-C_6H_5$	2156	309
CO^f	2154	320
$NC-C_5H_5N^g$	2150	320
$P(CH_3)(C_6H_5)_2$	2125	323
$P(OC_6H_5)_3$	2120	325
$P(CH_3)_2C_6H_5$	2102	312

[a] ν_{OH} at 3410. [b] ν_{CN} at 2083. [c] ν_{CN} at 2082. [d] ν_{CN} at 2087. [e] ν_{CN} at 2083. [f] ν_{CO} at 2003. [g] ν_{CN} at 2230. [h] Nine of these complexes were analyzed and gave satisfactory results.

265-cm^{-1} region, and those with chlorine *trans* to triphenylphosphine absorb in the 275-cm^{-1} region.[8] (3) The observed dependence of ν_{Ir-H} on L is indicative of a *trans* H–Ir–L relationship. (4) When L is carbon monoxide, deuteration reveals vibrational interaction.[9]

The addition of L is thus directed *trans* to the hydrido ligand. Nucleophilic attack is at the most electropositive site on **1**, which is opposite the ligand which is most strongly σ bonded to iridium. This result is also in consonance with the principle of microscopic reversibility, that nucleophilic attack should occur *trans* to the ligand having the strongest labilizing influence.

Addition of CO to the five-coordinated compound obtained from the reaction of trifluoroacetic acid and the Ir–N_2 complex gave compound **3** with *trans* H–Ir–L geometry (ν_{Ir-H} 2145, ν_{CO} 2036, ν_{Ir-Cl} 324 cm^{-1}).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Since the Ir–H bond is entirely σ in character, and because the same metal orbitals are used for Ir–L and Ir–H σ bonding, the Ir–H ir frequencies reflect the σ-*trans* effect[10] of L. A plot of ν_{Ir-H} *vs.* pK_a for complexes derived from donor molecules L such as methanol, *m*-nitroaniline, benzylamine, and pyridine indicates a linear correlation. The strong σ-*trans* effect, for the strong π acceptor triphenylphosphite, indicated by the relatively low Ir–H frequency, is apparently the result of synergic effects.

Particularly significant are the complexes formed by nitriles in which the CN stretching frequencies are considerably decreased (to 2080 cm^{-1}) compared to the CN frequencies in the free nitriles (2230 cm^{-1}). Since the hydride does not use the metal π orbitals

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(1) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 4; (b) F. R. Nordmeyer, *Inorg. Chem.*, **8**, 2780 (1969).

(2) J. Chatt, R. L. Richards, J. R. Sanders, and J. E. Ferguson, *Nature*, **221**, 551 (1969).

(3) Reactions of nucleophiles with a mixture of $[(C_6H_5)_3P]_3IrHCl_2$ and $[(C_6H_5)_3P]_2IrHCl_2$ have been previously reported.[4] The reaction of HCl with $[(C_6H_5)_3P]_2IrH_3$ was reported[4] to give $[(C_6H_5)_3P]_2IrHCl_2$, but the reaction of this compound with CO gave a product unlike that reported herein.

(4) A. Araneo and S. Martinengo, *Gazz. Chim. Ital.*, **95**, 61 (1965).

(5) While the structure of **1** is shown as trigonal bipyramidal, slight increase of the L′–Ir–H angles and decrease of the H–Ir–Cl angles will generate a square-pyramidal structure, such as demonstrated in an analogous five-coordinated d^6 complex.[6]

(6) P. G. H. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).

(7) P. R. Brookes and B. L. Shaw, *J. Chem. Soc., A*, 1079 (1967).

(8) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).

(9) L. Vaska, *J. Amer. Chem. Soc.*, **88**, 4100 (1966).

(10) See ref 1a, Chapter 5.