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Reactions of Transition Metal-stannyl Trichloride with Potassium Poly(1-pyrazolyl)borates

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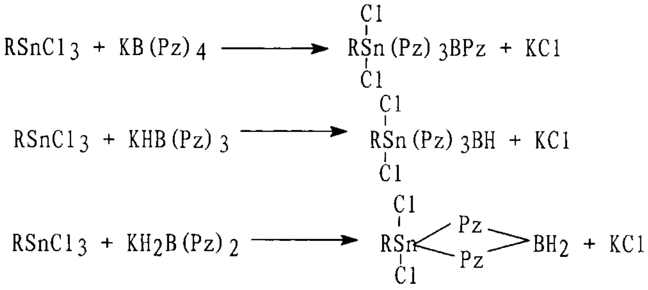
ABSTRACT: *The reactions of transition metal-stannyl trichlorides ($MSnCl_3$) with potassium tetrakis(1-pyrazolyl)borate or hydrokis(1-pyrazolyl)borate give hexacoordinate tin chelates. However, the same trichlorides react with potassium dihydrotris(1-pyrazolyl)borate anomalously to give the unexpected trimetallic complexes Cl_2SnM_2, where $M = W(CO)_3Cp$, $Mo(CO)_3Cp$, $Fe(CO)_2Cp$.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:479–483, 1998

INTRODUCTION

Complex tin chlorides containing two or more heteronuclear metals are interesting because they show different electrophilic properties in comparison with mononuclear tin chlorides. The mononuclear tin chlorides react with ordinary nucleophiles with loss of one or more chloride ions forming the corresponding tin derivatives, the coordination number of tin remaining four. Polynuclear metal-stannyl chlorides may show different patterns of Cl^- displacement, depending upon the nucleophiles; for instance, a bidentate ligand may displace two Cl^-, as we have reported in the preparation of bicycloazastannoxides, in which the tin atom forms pentacoordinate complexes [3]. A poly(1-pyrazolyl)borate anion is a polydentate nucleophile, displacing one Cl^- from the tin trichloride, and giving higher coordinate tin chelates. A simple compound of type $RSnCl_3$ reacts with potassium tetrakis(1-pyrazolyl)borate or with trikis(1-pyrazolyl)borate to form $RSnCl_2[Pz]_4B$ or $RSnCl_2[Pz]_3BH$, respectively, in which tin is hexacoordinated (Scheme 1).

If $RSnCl_3$ reacts with potassium dihydrobis(1-pyrazolyl)borate, $K[B(Pz)_2H_2]$, by displacement of one Cl^-, the resulting chelate is pentacoordinated with respect to the tin, $RSnCl_2[Pz]_2BH_2$. This shows that the nitrogen atoms on the pyrazolyl ligands determine the coordination number of the tin [4]. We are particularly interested in the behavior of transition metal-stannyl trichlorides, $Cp(CO)_nMSnCl_3$ ($M = $ Mo, W or Fe; $n = 3$ for Mo and W, and $n = 2$ for Fe); we wished to determine the extent to which the back π bonding of the metals affects the chelation when the polydentate nucleophiles, poly(1-pyrazolyl)borate anions, react with $RSnCl_3$. It was found



SCHEME 1 $RSnCl_3$ reactions with potassium tetrakis(1-pyrazolyl)borate, tris(1-pyrazoly) borate, and bis(1-pyrazolyl)borate (where R = alkyl or aryl; Pz = pyrazolyl).

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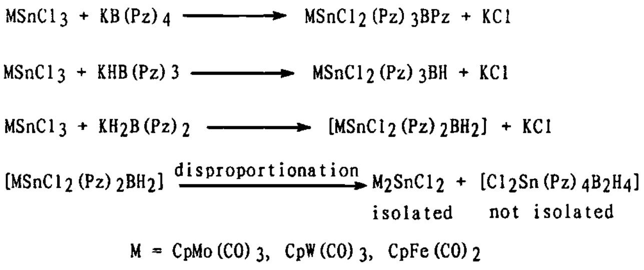
that the tetrakis(1-pyrazolyl) and trikis(1-pyrazolyl)borate anions gave the expected hexacoordinate tin complexes, while the dihydrobis(1-pyrazolyl)borate anion did not give the pentacoordinate tin chelate as the mononuclear substrate; instead, a trimetallic complex was isolated (Scheme 2).

EXPERIMENTAL

All reactions were carried out under an argon atmosphere. Methylene chloride was dried with P_2O_5. Absolute alcohol was distilled from sodium and diethyl phthalate. $CpFe(CO)_2SnCl_3$, $CpMo(CO)_3SnCl_3$, and $CpW(CO)_3SnCl_3$ were prepared as described in the literature [5]. $CH_3C_5H_4Mo(CO)_3SnCl_3$ and $CH_3C_5H_4W(CO)_3SnCl_3$ were prepared in a similar way. Potassium tetrakis(1-pyrazolyl)borate $KB(Pz)_4$, potassium hydrotris(1-pyrazolyl)borate $KHB(Pz)_3$, and potassium dihydrobis(1-pyrazolyl)borate were synthesized by the standard published procedures [6].

Elemental analyses and melting point (uncorrected) determinations were performed with a Perkin–Elmer model 240C analyzer and a Yanako MP-500 apparatus, respectively. IR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer and ^1H NMR spectra on a Jeol Fx 90Q and a Bruker AC200 NMR spectrometer. Mass spectra were collected on an HP5089A spectrometer.



SCHEME 2 $MSnCl_3$ reacting with poly(1-pyrazoly)borates.

TABLE 1 The IR Spectral Data of **1–9** (KBr disc, cm^{-1})

Complex	ν_{CO}	ν_{BH}
1	2007.8, 1942.2, 1925.8	
2	2007.8, 1917.6	
3	2016.0, 1934.0	
4	2016.0, 1934.0	
5	2012.3, 1957.7, 1922.7	2508.3
6	2016.0, 1958.6, 1925.8	2491.8
7	2024.2, 1966.8, 1934.0	2508.2
8	2024.2, 1934.0	2491.8
9	2007.8, 1966.8	2491.8

Reactions with Potassium Tetrakis(1-pyrazolyl)borate

$CpW(CO)_3SnCl_2[B(Pz)_4]$ (1). A mixture of 0.55 g (1 mmol) of $CpW(CO)_3SnCl_3$ and 0.32 g (1 mmol) of $KB(Pz)_4$ in 20 mL of methylene chloride was stirred at room temperature for 3 hours. The mixture was filtered under an argon atmosphere, and 10 mL of ethyl alcohol was added. The solution was evaporated in vacuum at room temperature until nearly dry and then cooled in a refrigerator (−10°C) for a few days to afford 0.7 g of a yellow solid; yield 78%, mp 153–155°C. Anal. calcd for $C_{20}H_{17}BCl_2N_8O_7SnW$ (%): C, 29.93; H, 2.14; N, 13.97. Found (%): C, 29.93; H, 2.06; N, 13.94.

$CH_3C_5H_4W(CO)_3SnCl_2[B(Pz)_4]$ (**2**). This compound was obtained similarly to **1**. Yield 69%, mp 129–130.5°C. Anal. calcd for $C_{21}H_{19}BCl_2N_8O_9SnW$ (%): C, 30.88; H, 2.35; N, 13.73. Found (%): C, 30.93; H, 2.65; N, 13.54.

$CpMo(CO)_3SnCl_2[B(Pz)_4]$ (**3**). This was obtained similarly to **1**. Yield 74%, mp 134° dec. Anal. calcd for $C_{20}H_{17}BCl_2MoN_8O_3Sn$(%): C, 33.52; H, 2.39; N, 15.65. Found (%): C, 33.10; H, 2.24; N, 15.66.

$CpFe(CO)_2SnCl_2[B(Pz)_4)]$ (**4**). This was obtained similarly to **1**. Yield 81%, mp 160° dec. Anal. calcd for $C_{19}H_{17}BCl_2FeN_8O_2Sn$(%), C, 35.30; H, 2.65; N, 17.34. Found (%): C, 35.71; H, 2.79; B, 16.96.

Reactions with Potassium Hydrotris(1-pyrazolyl)borate

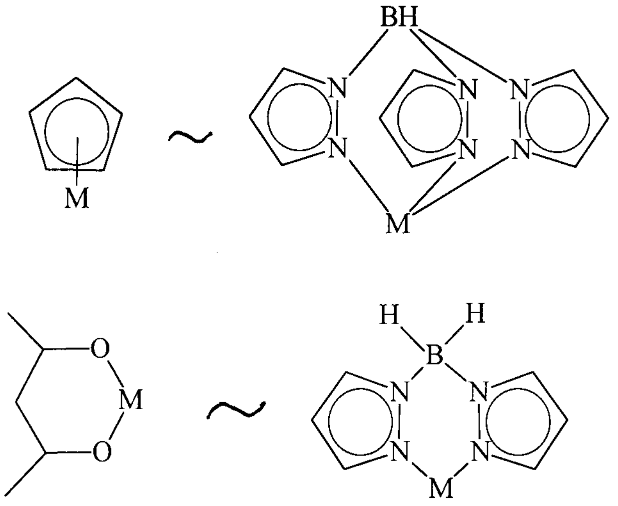
$CpW(CO)_3SnCl_2[BH(Pz)_3]$ (**5**). An amount of 0.26 g (1 mmol) of $KBH(Pz)_3$ was added to a solution of 0.55 g (1 mmol) $CpW(CO)_3SnCl_3$ in 20 mL of methylene chloride and the mixture was stirred for 4 hours. The clear solution became muddy, and the color changed from yellow to red. The mixture was filtered under an argon atmosphere and concentrated in vacuum to ca. 10 mL then cooled in a refrigerator (−10°) to give a yellow product; yield 72%, mp 154° dec. Anal. calcd for $C_{17}H_{15}BCl_2N_6O_3SnW$ (%): C, 27.72; H, 2.05; N, 11.42. Found (%): C, 27.49; H, 2.03; N, 11.38.

$CH_3C5H_4W(CO)_3SnCl_2[BH(Pz)_3]$ (**6**). This was obtained similarly to **5** in a crystalline state. Yield, 70%, mp 144–145°. Anal. calcd for $C_{18}H_{17}BCl_2N_6O_3SnW$ (%): C, 28.80; H, 2.28, N, 11.20. Found (%): C, 28.84; H, 2.36; N, 11.08.

$CpMo(CO)_3SnCl_2[BH(Pz)_3]$ (**7**). This was obtained similarly to **5**. Yield 68%, mp 152° dec. Anal.

TABLE 2 The ^{1}H NMR Spectral Data of **1–9** in $CDCl_3$ (δ)

	1	2	3	4	5	6	7	8	9
CH_3		2.31(s) 3H				2.30(s) 3H		2.18(s) 3H	
CpH	5.70(s) 5.84(s) 5H	5.62(t) 5.76(t) 5.84(t) 5.95(t) 4H	5.60(s) 5.74(s) 5H	5.20(s) 5H	5.79(s) 5.93(s) 5H	5.61(t) 5.76(t) 5.83(t) 5.95(t) 4H	5.69(s) 5.83(s) 5H	5.51(t) 5.68(t) 5.75(t) 5.86(t) 4H	5.27(s) 5H
Pz H-4	6.24(t) 4H	6.35(t) 4H	6.28(t) 4H	6.35(t) 4H	6.25(t) 6.36(t) 3H	6.24(t) 6.38(m) 3H	6.25(t) 6.36(m) 3H	6.25(t) 6.37(m) 3H	6.25(t) 3H
Pz H-3,5	7.08(d) 7.58(d) 4H 7.66(d) 7.98(d) 4H	7.15(d) 7.66(d) 4H 7.75(d) 8.08(d) 4H	7.06(d) 7.60(d) 4H 7.68(d) 8.00(d) 4H	7.66(d) 4H 8.14(d) 4H	7.60(dd) 7.73(m) 3H 7.84(d) 8.00(br) 3H	7.60(dd) 7.73(m) 3H 7.83(d) 8.01(br) 3H	7.60(dd) 7.75(m) 3H 7.85(br) 8.02(br) 3H	7.61(dd) 7.74(br) 3H 7.85(br) 8.02(br)	7.60(br) 3H 8.07(br) 3H



SCHEME 3 The analogy of Cp and acac to poly(Pz)B$^-$ ligands.

calcd for $C_{17}H_{15}BCl_2MoN_6O_3Sn$(%): C, 31.39; H, 2.33; N, 12.03. Found (%): C, 31.61; H, 2.18; N, 12.97.

$CH_3C_5H_4Mo(CO)_3SnCl_2[BH(Pz)_3]$ (8). This compound was obtained similarly to **5** in a crystalline state. Yield 81%, mp 144–145. Anal. calcd for $C_{22}H_{23}BCl_2N_6O_3MoSn$(%): C, 32.54, H, 2.58; N, 12.66. Found (%): C, 32.36; H, 2.50; N, 12.59.

$CpFe(CO)_2SnCl_2[BH(Pz)_3]$ (**9**). This was obtained similarly to **5**. Yield 75%, mp 175° dec. Anal. calcd for $C_{22}H_{12}BCl_2FeN_6O_2Sn$(%): C, 33.11; H, 2.61; N, 14.49. Found (%): C, 32.91; H, 2.52; N, 14.35.

Reactions with Potassum Dihydrobis(1-pyrazolyl)borate

A 0.20 g (1 mmol) amount of $KBH_2(Pz)_2$ was added to 0.40 g (1 mmol) of $Cp(CO)_2FeSnCl_3$ in 20 mL of methylene chloride. An immediate color change from yellow to red was observed upon mixing the reactants. The reaction mixture was stirred at room temperature for 4 hours and filtered. The filtrate was concentrated in vacuum to ca. 10 mL and cooled in a refrigerator to give a yellow solid product, which was proved to be $[Cp(CO)_2Fe]_2SnCl_2$ by means of melting point, elemental analysis, IR, and ^{1}H NMR spectra, all identical to those reported for the known complexes [7].

With $Cp(CO)_3WSnCl_3$, $Cp(CO)_3MoSnCl_3$, the dihydrobis(1-pyrazolyl)borate reacted to give the reported $[Cp(CO)_3W]_2SnCl_2$ and $[Cp(CO)_3Mo]_2SnCl_2$.

RESULTS AND DISCUSSION

The Synthesis and Reactivity

The reactions of equimolecular amounts of each $CpM(CO)_nSnCl_3$ (M = Mo, W, or Fe) with multidentate ligands tetrakis(1-pyrazolyl)borate or tris(1-pyrazolyl)borate anions, smoothly afforded compounds **1–9**, respectively. Each reaction generally proceeded without complication in methylene chloride. All products gave fairly satisfactory yields, elementary analyses, definite melting points (some with decomposition), IR (Table 1), ^{1}H NMR (Table 2), and MS spectra (Table 3) suggesting the respective formulas. Complexes **6** and **9** were obtained easily in a crystalline state; unfortunately, they decomposed on X-ray determination. These complexes are moderately

TABLE 3 The Fragments of the Mass Spectra of **1–9**

Complex	*Fragment*
1	614 [$(Pz)_3BSnCl_2W(CO)$, 6], 469 [$(Pz)_4BSnCl_2$, 8], 399 [$(Pz)_4BSn$, 51], 187 [(Pz)Sn, 42], 284 [CpWCl, 100], 249 [CpW, 30]
2	614 [$(Pz)_3BSnCl_2W(CO)$, 8], 544 [$(Pz)_3BSnW(CO)$, 4], 399 [$(Pz)_4BSn$, 100], 402 [$(Pz)_3BSnCl_2$, 21], 367 [$(Pz)_3BSnCl$, 29], 298 [$CH_3C_5H_4WCl$, 10]
3	458 [$(Pz)_3BSnMo(CO)$, 6], 399 [$(Pz)_4BSn$, 100], 367 [$(Pz)_3BSnCl$, 35], 198 [CpMoCl, 66], 163 [CpMo, 60], 187 [Sn(Pz), 69]
4	402 [$(Pz)_3BSnCl_2$, 97], 156 [CpFeCl, 43], 121 [CpFe, 100]
5	610 [$(Pz)_3HBSnW(CO)Cp$, 2], 582 [$(Pz)_3HBSnWCp$, 1], 333 [$(Pz)_3HBSn$, 100], 284 [CpWCl, 24], 249 [CpW, 21], 187 [SnPz, 31]
6	333 [$(Pz)_3HBSn$, 100], 298 [$CH_3C_5H_4WCl$, 38], 263 [$CH_3C_5H_4W$, 20], 187 [SnPz, 46]
7	650 [$(Pz)_3HBSnCl_2Mo(CO)_3Cp$, 2], 594 [$(Pz)_3HBSnCl_2Mo(CO)Cp$, 2] 566 [$(Pz)_3HBSnCl_2MoCp$, 4], 403 [$(Pz)_3HBSnCl_2$, 8], 333 [$(Pz)_3HBSn$, 100], 198 [CpMoCl, 12], 187 [Sn(Pz), 57]
8	594 [$(Pz)_3HBSnMo(CO)_3C_5H_4CH_3$, 1], 538 [$(Pz)_3HBSnMo(CO)C_5H_4CH_3$, 8], 368 [$(Pz)_3HBSnCl$], 12] 333 [$(Pz)_3HBSn$, 100], 212 [$CH_3C_5H_4MoCl$, 15], 187 [Sn(Pz), 49]
9	482 [$(Pz)_3HBSnFe(CO)Cp$, 100], 367 [$CpFe(CO)_2SnCl_2$, 12], 336 [CpFe(CO)Sn-(Pz), 84], 269 [CpFe(CO)Sn, 62], 156 [CpFeCl, 26], 121 [CpFe, 56]

stable in the solid state and showed some deterioration in solution within several hours when exposed to air. Tetrakis(1-pyrazolyl)borate derivatives are more stable and soluble in a given solvent than the hydrotris(1-pyrazolyl)borate derivatives. The former remains stable in ethyl alcohol in the refrigerator, whereas the hydrotris(1-pyrazolyl)borate derivatives decomposed upon standing in solution or air.

The same substrate when reacted with potassium dihydrobis(1-pyrazolyl)borate, however, gave the unexpected trinuclear metallic derivatives $[CpM(CO)_n]_2SnCl_2$ that were identified by the known physical data for the reported complexes [7,8].

Structural Considerations

The poly(1-pyrazolyl)borate are multidentate ligands, the tetrakis- and tris(1-pyrazolyl)borate, are tridentate ligands acting similarly to the cyclopentadienyl ligand, and the dihydrobis(1-pyrazolyl)borate similarly to the acetylacetonate ligand (Scheme 3).

It is postulated that the tridentate derivatives are more stable than the bidentate ones. In the late 1980s, people investigated the poly(1-pyrazolyl)borate tin complexes, and they found that the pentaco-coordinated tin derivatives were not as stable as the hexaco-coordinated tin derivatives. It is known that a simple tin trichloride $RSnCl_3$ can react with dihydrobis(1-pyrazolyl)borate to give the pentaco-coordinated tin chelate. However, we have found that the transition metal-bonded tin trichloride did not give the pentaco-coordinated tin chelate, $CpM(CO)nSnCl_2[H_2Pz_2]B$; instead, it disproportionated to $CpM(CO)_nSnCl_2$ and $Cl_2Sn[H_2B(Pz)_2]_2$. In the latter compound, the tin would be in the state of a dichelate form, which is undoubtedly impossible to exist. Only in the mixed product of $CpFe(CO)_2SnCl_3$ with $KH_2(Pz)_2$ was the presence of two cluster peaks at 516 (corresponding to $Cp_2(CO)Fe_2SnCl_2$ by loss of one CO from $[CpFe(CO)]_2SnCl_2$) and 484 (corresponding to $[H_2B(Pz)_2]_2SnCl_2$ identified by mass spectroscopy).

Spectral Properties

The IR spectra of **1–9** (Table 1) exhibit ν_{CO} lower than those of the reactants by 20–30 cm^{-1}. This suggests that the coordination of Sn with the pyrazolyl borate weakens the π back bonding. The $\nu_{B\text{-}H}$ are observed at 2491.9 and 2508.2 cm^{-1}.

The ^1H NMR spectral data are shown in Table 2. The presence of only one type of signal of the pyrazolyl ring N–H in the Fe derivative suggests that the chelate ligands are fluxional in solution. Yet the ^1H NMR spectra of W and Mo derivatives exhibit two types of pyrazolyl ring protons and two sets of Cp (or methyl cyclopentadienyl). This may be due to the operation of a configurational equilibrium involving the metal W or Mo, but more adequate evidence is unavailable. Kubacek et al. [15], by means of theoretical analysis, showed that, in $CpML_4$ complexes, M having a 3:3:1 configuration represents a minimum potential energy surface, whereas the global minimum (ground state) always assumes a 3:4 structure. $CpML_4$ complexes in X-ray crystal structures (including the reported four coordinated MSn complexes) adopt a 3:4 configuration with respect to M in most cases. However, in place of Cp, the $HN(Pz)_3$ analog in $[BH(Pz)_3]Mo(CO)_3SnPh_3$ was found to adopt a 3:3:1 configuration around Mo [16]. This indicates that different ligands bonded to Mo probably change the configuration of Mo. When W or Mo is bonded to a bulky poly(1-pyrazolyl)borate stannyl group, a 3:3:1 intermediate is possible. This rationalizes the presence of two sets of Cp proton signals in each $CpM(CO)_3SnR_3$ complex, the chemical shift of the protons on Cp being influenced greatly by the ligand R [17].

The fragmentation ions of **1–9** in the mass spectra are listed in Table 3. The molecular ion peak was observed for $CpM(CO)_3SnCl_2[BH(Pz)_3]$. There is a tendency for loss of an uncoordinated pyrazolyl ring of the tetrakis(1-pyrazolyl)borate derivative to give ions containing the tris(1-pyrazolyl)borate group. It is generally found that ions containing the tris(1-pyrazolyl)borate group were abundant, and the base peak is for $Sn[BH(Pz)_3]$ for most complexes in their mass spectra. The stability of these ions suggests that three pyrazolyl rings firmly combine with tin.

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