

which are fused at a common iron vertex such that the unique BH caps a triangular Co-Fe-B face on one polyhedron and interacts weakly with the other. There are also several bis(dicarbollyl) transition-metal complexes in which the two  $C_2B_9H_{10}$  ligands are bridged by  $HCS_2$ ,  $CH_3CO_2$ ,<sup>26</sup> or other<sup>21,27</sup> groups.

A fundamental question is whether the observed stereochemical behavior of III is a general phenomenon that is likely to be encountered in other *commo*-metallaboron complexes (either as isolable species or as reaction intermediates) or is, rather, a

consequence of special circumstances associated with the peculiar electronic and steric properties of the  $C_5(CH_3)_5^-$  ligand. Continuing studies in this area may help to resolve this issue.

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**Supplementary Material Available:** Listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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## Synthesis, Structure, and Reactions of $[Mo(SnCl_3)(CN-t-Bu)_6][(Ph_3B)_2CN]$ , Containing a Potentially Useful New Anion for Crystallizations<sup>1</sup>

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**Abstract:** Stannous chloride reacts with yellow chlorohexakis(*tert*-butyl isocyanide)molybdenum(II) chloride to give the maroon complex  $[Mo(SnCl_3)(CN-t-Bu)_6]^+$ , in which insertion of tin into the Mo-Cl bond has formally occurred. Crystals suitable for X-ray analysis were obtained by using the "BBCN" anion,  $[(Ph_3B)_2CN]^-$ , which may be viewed as an analogue of the PPN cation,  $[(Ph_3P)_2N]^+$ . The seven-coordinate complex has crystallographically required  $C_2$  symmetry. Its geometry may be described as that of a  $C_2$  4:3 piano stool or as that of a distorted capped octahedron with  $SnCl_3^-$  as the capping ligand. The Mo-Sn bond length is 2.663 (1) Å, and the Mo-C distances vary from 2.071 (18) to 2.138 (8) Å. The C≡N group in the anion is disordered across a center of symmetry in the crystal lattice and has a bond length of 1.147 (12) Å. The sodium and tetramethylammonium salts of the BBCN anion have been synthesized. The compound  $[Mo(SnCl_3)(CN-t-Bu)_6][(Ph_3B)_2CN]$  crystallizes in the orthorhombic system, space group  $Pbcm$ , with  $a = 11.968$  (7) Å,  $b = 23.012$  (6) Å,  $c = 26.905$  (4) Å, and  $Z = 4$ . Reaction of  $[Mo(SnCl_3)(CN-t-Bu)_6]^+$  with zinc in aqueous ethanol does not lead to reductive coupling of adjacent *tert*-butyl isocyanide ligands to form a coordinated *N,N'*-dialkyldiaminoacetylene, as in the reaction of zinc with other  $[MoX(CN-t-Bu)_6]^+$  complexes. Instead, the  $[Mo(CN-t-Bu)_7]^{2+}$  cation has been isolated from the reaction mixture as the tetraphenylborate salt.

### Introduction

Seven-coordinate alkyl isocyanide (L) complexes of molybdenum(II),  $MoL_5X_2$ ,<sup>3</sup>  $MoL_6X^+$ ,<sup>4,5</sup>  $MoL_7^{2+}$ ,<sup>5,6</sup> (X = halide), have been known for several years. These stable compounds can be prepared by a variety of methods and most recently have been shown<sup>7,8</sup> to form in the reaction of quadruply bonded dimolybdenum(II) complexes with alkyl isocyanides (Figure 1). X-ray structural studies have revealed that the  $MoL_7^{2+}$  cations adopt various heptacoordinate geometries depending upon the

anion and nature of the alkyl substituent.<sup>6,7,9</sup> In the isomorphous series of compounds  $[MoL_6X]Y$ , X = Y = Cl, Br, or I or X = CN and Y =  $PF_6^-$ , the cations all have capped trigonal prismatic structures.<sup>4,5,9</sup>

The reactions of the  $MoL_7^{2+}$  and  $MoL_6X^+$  cations have been the subject of several investigations. Molecular orbital calculations<sup>10</sup> of seven-coordinate molecules suggested that  $d^4$ -capped trigonal prismatic complexes might experience ligand-ligand bonding interactions on the unique edge of the coordination polyhedron at the time that just such a reaction, the reductive coupling of adjacent isocyanides in  $[MoI(CN-t-Bu)_6]I$  to form the novel acetylene complex  $[MoI(CN-t-Bu)_4(t-Bu)HNCCNH-t-Bu]I$ , was reported.<sup>11</sup> Chemical<sup>5</sup> and kinetic<sup>12</sup> studies of the interconversion of the  $MoL_7^{2+}$  and  $MoL_6X^+$  cations have also been carried out. Mixed phosphine-isocyanide complexes can be

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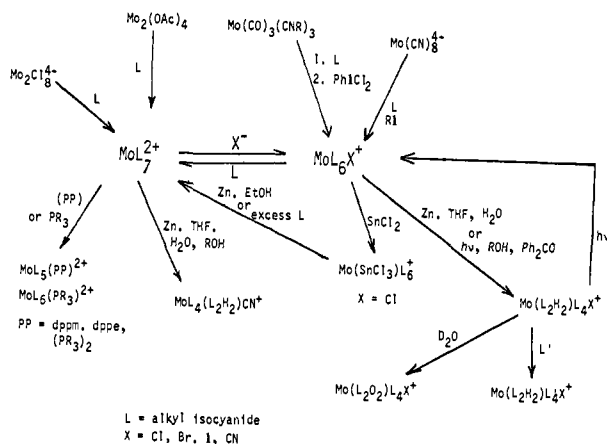
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**Figure 1.** Scheme depicting the synthesis and reactions of  $[\text{MoL}_7]^{2+}$  and  $[\text{MoL}_6\text{X}]^+$  cations (see ref 5–8 and 11–14).

prepared by refluxing the  $\text{MoL}_7^{2+}$  cations with mono- and bidentate phosphine ligands in methanol.<sup>13</sup> From this and other unpublished chemistry,<sup>14</sup> summarized in Figure 1, it is apparent that the molybdenum(II) isocyanide system is rapidly becoming one of the better developed areas of seven-coordination chemistry.<sup>15</sup>

In this paper we report the reaction of  $\text{SnCl}_2$  with  $[\text{MoCl}(\text{CN}-t\text{-Bu})_6]^+$  to form  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6]^+$ , a reaction that has precedence in molybdenum(II) coordination chemistry.<sup>16</sup> As will be shown, the trichlorostannate ligand has an important influence on the reactivity of the “ $\text{MoL}_6$ ” fragment in this cation compared with other  $\text{MoL}_6\text{X}^+$  species. We also describe the previously unreported (to our knowledge) “BBCN” anion,  $[(\text{Ph}_3\text{B})_2\text{CN}]^-$ , which, being analogous to the “PPN” cation,  $[(\text{Ph}_3\text{P})_2\text{N}]^+$ ,<sup>17</sup> should be useful for precipitating counterions in crystalline form suitable for X-ray diffraction work, as was the case here.

### Experimental Section

All reactions were carried out by using the highest purity reagents available. Sodium cyanotriphenylborate was obtained from ICN. The compound  $[\text{MoCl}(\text{CN}-t\text{-Bu})_6]\text{Cl}$ , reported previously,<sup>5b</sup> was obtained from  $\text{Mo}(\text{CO})_3(\text{CN}-t\text{-Bu})_3$  and  $t\text{-BuNC}$  by using  $\text{PhICl}_2$  as the oxidant in a new, high-yield procedure.<sup>14</sup> Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Proton nuclear magnetic resonance spectra were taken with either a Bruker WP 80 or a Perkin-Elmer R 32 spectrometer. A Perkin-Elmer 621 spectrometer was used to record the infrared spectra.

(Trichlorostannyl)hexakis(*tert*-butyl isocyanide)molybdenum(II) hexafluorophosphate,  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6](\text{PF}_6)$ . A 225-mg (1-mmol) portion of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was added to 5 mL of a methanol solution containing 210 mg (0.3 mmol) of  $[\text{MoCl}(\text{CN}-t\text{-Bu})_6]\text{Cl}$ . After 5 min the initially yellow solution turned deep red. When 170 mg (1 mmol) of  $\text{NaPF}_6$  dissolved in 5 mL of methanol was added to the filtered solution, 165 mg (55% yield) of maroon crystals was deposited over a 12-h period at room temperature: NMR ( $\text{CDCl}_3$ )  $\delta$  1.58; IR (KBr pellet) 2978 (m), 2933 (w), 2200 (s), 2170 (s), 2109 (vs), 1472 (w), 1457 (w), 1400 (w), 1371 (m), 1233 (w), 1206 (m), 975 (w), 943 (vs), 550 (m), 530 (m), 460 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{54}\text{N}_6\text{SnCl}_3\text{MoPF}_6$ : C, 37.4; H, 5.64; N, 8.71; Sn, 12.30; Mo, 9.94; P, 3.21. Found: C, 37.0; H, 5.56; N, 8.65; Sn, 12.40; Mo, 10.50; P, 3.21.

(Trichlorostannyl)hexakis(*tert*-butyl isocyanide)molybdenum(II)  $\mu$ -Cyano-bis(triphenylboron),  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6][(\text{Ph}_3\text{B})_2\text{CN}]$ . X-ray quality crystals of this compound were obtained when the red solution in the previous synthesis was treated with sodium cyanotriphenylborate. The  $[(\text{Ph}_3\text{B})_2\text{CN}]^-$  anion, detected during the crystal structure determination, presumably arose through eq 1, which might be driven by the



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reaction of cyanide ion with excess stannous chloride present in the red solution. In subsequent work the compound was obtained as follows. A deep red solution containing 153 mg (0.23 mmol) of  $[\text{MoCl}(\text{CN}-t\text{-Bu})_6]\text{Cl}$  and 656 mg (2.92 mmol) of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 25 mL of ethanol was prepared and filtered. To this solution was added 5 mL of ethanol containing dissolved triphenylboron (67 mg, 0.28 mmol) and sodium cyanotriphenylborate (79 mg, 0.27 mmol). After the solution was left standing for 4 h, 170 mg (56%) of red product was collected by filtration. IR (KBr pellet): 3065 (w), 3040 (w), 2985 (m), 2935 (w), 2255 (w), 2195 (m), 2170 (m), 2115 (s), 1590 (vw), 1490 (w), 1475 (w), 1460 (w), 1432 (m), 1402 (w), 1375 (m), 1235 (w), 1199 (m), 1039 (w), 865 (w), 747 (m), 708 (m), 610 (m), 535 (m), 460 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{67}\text{H}_{84}\text{N}_7\text{SnCl}_3\text{B}_2\text{Mo}$ : C, 60.5; H, 6.37; N, 7.37; Mo, 7.21. Found: C, 60.3; H, 6.38; N, 7.42; Mo, 6.58.

If in the above procedure the solution was allowed to stand for longer than a day there appeared a yellow side product having an infrared spectrum and chemical analysis consistent with the formulation  $[\text{Mo}(\text{NCBPh}_3)(\text{CN}-t\text{-Bu})_6][(\text{Ph}_3\text{B})_2\text{CN}]$ . Metal complexes of the cyanotriphenylborate anion have been reported previously and have a  $\text{C}\equiv\text{N}$  stretching frequency approximately equal to 2205  $\text{cm}^{-1}$ .<sup>18</sup> IR (KBr pellet): 3065 (m), 3045 (m), 2985 (m), 2250 (w), 2208 (w), 2138 (s), 1590 (w), 1488 (w), 1455 (w), 1435 (m), 1375 (m), 1235 (w), 1200 (m), 1160 (w, sh), 1035 (w), 863 (w), 743 (m), 705 (s), 610 (m), 535 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{86}\text{H}_{99}\text{N}_8\text{B}_3\text{Mo}$ : C, 75.2; H, 7.27; N, 8.16; B, 2.36; Mo, 6.99. Found: C, 74.6; H, 7.43; N, 8.23; B, 1.47 and Mo, 6.35.

Tetramethylammonium and Sodium Salts of the  $\mu$ -Cyano-bis(triphenylboron) Anion. The  $[(\text{Ph}_3\text{B})_2\text{CN}]^-$  anion is readily prepared in situ from  $\text{Ph}_3\text{B}$  and  $\text{Na}(\text{Ph}_3\text{BCN})$  as described above, and such a procedure is recommended for its use in precipitating large cations. The tetramethylammonium salt was obtained by dissolving 250 mg (0.86 mmol) of  $\text{Na}(\text{Ph}_3\text{BCN})$  and 100 mg (0.91 mmol) of  $(\text{Me}_4\text{N})\text{Cl}$  in 20 mL of methanol and immediately adding this solution to one of 250 mg (1 mmol) of  $\text{Ph}_3\text{B}$  dissolved in 10 mL of methanol. The white crystalline precipitate was filtered to yield 275 mg (54% yield) of  $(\text{Me}_4\text{N})[(\text{Ph}_3\text{B})_2\text{CN}]$ : IR (KBr pellet)  $\nu_{\text{CN}}$  2248 (s)  $\text{cm}^{-1}$ ; Proton NMR ( $\text{Me}_2\text{SO}-d_6$  solution)  $\delta$  3.06 (s), 6.9–7.3 (m), integrated ratio 12:31 (theoretical 12:30). The sodium salt was prepared by dissolving 0.97 g (4 mmol) of  $\text{Ph}_3\text{B}$  and 1.14 g (3.9 mmol) of  $\text{Na}(\text{Ph}_3\text{BCN})$  in 5 mL of boiling 95% ethanol. Water was added to the cloud point (approximately 5 mL). After several hours of standing at room temperature, a first crop of white crystals (0.96 g, 41% yield) was collected and washed with cold 60:40 water–ethanol. The mother liquor deposited another crop of 250 mg of tan crystals over a 2-day period which was collected and washed with hexanes. Each crop was recrystallized from 60:40 water–ethanol to obtain a total of 720 mg (31% yield) of white crystals. The product analyzed as a trihydrate,  $\text{Na}[(\text{Ph}_3\text{B})_2\text{CN}]\cdot 3\text{H}_2\text{O}$ . IR: (KBr pellet) 2238 (s)  $\text{cm}^{-1}$ ; (MeOH) 2240 (s), 2167 (w)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{37}\text{H}_{36}\text{NNaB}_2\text{O}_3$ : C, 75.67; H, 6.18; N, 2.38; B, 3.68;  $\text{H}_2\text{O}$ , 9.20. Found: C, 75.69; H, 6.27; N, 2.40; B, 3.63;  $\text{H}_2\text{O}$  (Karl Fischer), 9.32.

Reaction of  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6](\text{PF}_6)$  with Zinc. A suspension of 900 mg (0.9 mmol) of  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6](\text{PF}_6)$  and 650 mg (9.9 mmol) of zinc in 95% ethanol was stirred for 18 h at ambient temperature during which time a yellow solution formed. After filtration the solvent was removed in vacuo. The resultant yellow-green powder was redissolved in a small amount of ethanol and 0.675 mg (2 mmol) of  $\text{Na}(\text{BPh}_4)$  was added. The bright yellow precipitate that formed was filtered and recrystallized from ethanol to yield 155 mg (13%) of  $[\text{Mo}(\text{CN}-t\text{-Bu})_7](\text{BPh}_4)_2$ . The product was identified by its proton NMR spectrum ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.54 (s), 7.04 (m), 7.38 (m), intensity ration 64:24:16 vs. the theoretical ratio of 63:24:16 and by chemical analysis. Anal. Calcd for  $\text{C}_{83}\text{H}_{103}\text{N}_7\text{B}_2\text{Mo}$ : C, 75.73; H, 7.89; N, 7.45; Mo, 7.29. Found: C, 75.83; H, 8.13; N, 7.47; Mo, 7.14.

A 70% combined yield of  $[\text{Mo}(\text{CN}-t\text{-Bu})_7]^{2+}$  and  $[\text{Mo}(\text{CN}-t\text{-Bu})_6\text{Cl}]^+$  in a 7:3 ratio, identified by  $^1\text{H}$  NMR spectroscopy, results when a concentrated methanolic solution of  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6]^+$  is treated with zinc and precipitated as hexafluorophosphate salts.

Collection and Reduction of X-ray Data for  $[\text{Mo}(\text{SnCl}_3)(\text{CN}-t\text{-Bu})_6][(\text{Ph}_3\text{B})_2\text{CN}]$ . The crystal used for the diffraction study was a dark orange needle bounded by six faces: (001) and (00 $\bar{1}$ ), 0.60 mm apart, and the two pairs (1 $\bar{1}$ 0), ( $\bar{1}$ 10) and (120), ( $\bar{1}$ 20), both 0.23 mm apart. Study on the diffractometer suggested that the crystal belonged to the orthorhombic crystal system and the *mmm* Laue symmetry was later confirmed by using Weissenberg photographs. The quality of the data crystal was checked by taking open-counter  $\omega$  scans of several low-angle reflections and judged to be acceptable ( $\Delta\omega_{1/2} \approx 0.14^\circ$ ). Further details of the data collection and reduction are given in Table I.

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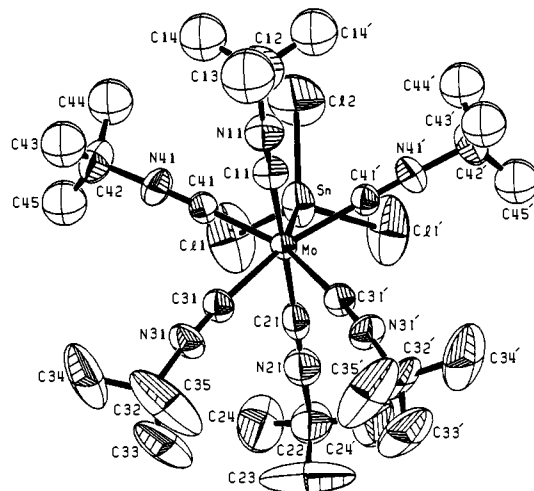
Table I. Experimental Details of the X-ray Diffraction Study of [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]/[(Ph<sub>3</sub>B)<sub>2</sub>CN]

(A) Crystal Parameters <sup>a</sup> at 26 °C	
$a = 11.968 (4) \text{ \AA}$	space group = <i>Pbcm</i>
$b = 23.012 (7) \text{ \AA}$	$Z = 4$
$c = 26.905 (6) \text{ \AA}$	$\rho(\text{calcd}) = 1.192 \text{ g cm}^{-3}$
$V = 7409.8 \text{ \AA}^3$	$\rho(\text{obsd})^b = 1.19 (2) \text{ g cm}^{-3}$
mol wt 1330.1	
(B) Measurement of Intensity Data	
instrument: Enraf-Nonius CAD-4F $\kappa$ geometry diffractometer	
radiation: Mo K $\alpha$ ( $\lambda_{\alpha_1} = 0.70930 \text{ \AA}$ , $\lambda_{\alpha_2} = 0.71073 \text{ \AA}$ ) graphite monochromatized	
takeoff angle: 2.0°	
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan $\theta$ ) mm	
crystal-detector distance: 173 mm	
scan technique: coupled $\omega$ (crystal)- $2\theta$ (counter)	
scan width: variable, $\Delta\omega = (0.8 + 0.35 \tan \theta)^\circ$	
scan rate: variable from 1.26 to 20.12 deg min <sup>-1</sup> in $\omega$	
scan range: $3^\circ \leq 2\theta \leq 55^\circ$	
prescan rejection limit: 1 $\sigma$	
prescan acceptance limit: 100 $\sigma$	
maximum counting time: 60 s	
background measurements: moving crystal-moving detector, 25% added to scan width at both ends of each scan	
standards: three reflections ( $\bar{1}65$ ), (10, $\bar{3}$ ,0) and (16 $\bar{5}$ ), measured every 3600 s of X-ray exposure time, showed only random, statistical fluctuations	
no. of reflections collected: [ $3^\circ \leq 2\theta \leq 25^\circ$ ( $-h, -k, +l$ ), $3^\circ \leq 2\theta \leq 55^\circ$ ( $+h, +k, +l$ )]; 9581 reflections, nonspace group extinguished	
(C) Treatment of Intensity Data	
reduction to $F_o$ and $\sigma(F_o)$ : correction for background, attenuator, and Lorentz-polarization of monochromatized X-radiation as described previously <sup>c</sup>	
absorption correction: <sup>d</sup> $\mu = 6.50 \text{ cm}^{-1}$ ; transmission factors ranged from 0.856 to 0.880	
averaging: 457 equivalent pairs in the inner sphere ( $2\theta \leq 25^\circ$ ); agreement factor $R_{av} = 0.010$	
observed data: 8667 unique reflections of which the 2900 with $F_o > 4\sigma(F_o)$ were used in the structure solution and refinement	

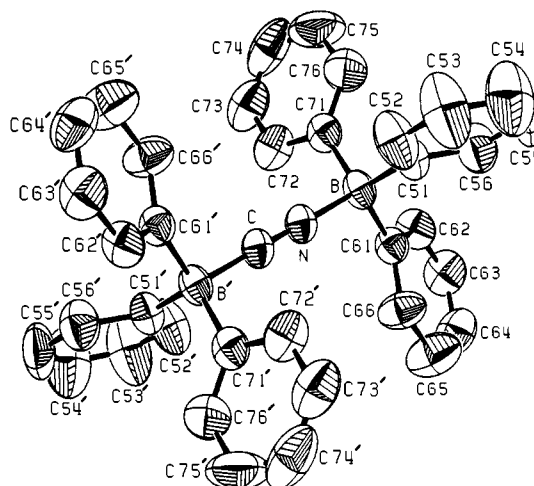
<sup>a</sup> From a least-squares fit to the setting angles of 25 reflections with  $2\theta > 30^\circ$ . Reported here is the unit cell used in final refinement. The unit cell used for the data collection, reduction, and structure solution is described in the text. <sup>b</sup> By suspension in aqueous NaI. <sup>c</sup> Silverman, L. D.; Dewan, J. C.; Glandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* 1980, 19, 3379. <sup>d</sup> Performed with the Wehe-Busing-Levy ORABS program.

**Determination and Refinement of the Structure.** The diffractometer output revealed the extinctions  $0kl$  when  $k \neq 2n$  and  $hk0$  when  $h \neq 2n$ , indicating space group *Pbma* ( $D_{2h}^8$ , No. 57, in a nonstandard setting) or its noncentrosymmetric equivalent *Pb2<sub>1</sub>a* ( $C_{2v}^5$ , No. 29, in a nonstandard setting).<sup>19</sup> The positions of the Mo and Sn atoms, in space group *Pbma*, were obtained by using the direct methods program MULTAN-78. Subsequent difference Fourier maps revealed the positions of the remaining nonhydrogen atoms. With use of the transformation matrix (001, 100, 010), the space group was converted to the standard setting, *Pbcm*, which was used for all subsequent refinement with the SHELX-76 system of programs. Full-matrix least-squares refinement was carried out in two blocks. In the first block (214 parameters) the scale factor and parameters for the atoms of the cation were refined while the second block (198 parameters) contained the scale factor and parameters for the atoms of the anion.

Within the cation, the methyl carbon atoms of two *tert*-butyl groups were found to be disordered about their N-C bond axes, a common occurrence.<sup>4</sup> Accordingly, these methyl carbon atoms were refined with partial occupancy factors and isotropic thermal parameters. The other two *tert*-butyl groups appeared to be ordered and their methyl carbon atoms were assigned anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (C-H = 0.95 Å) and not refined, but a common isotropic temperature factor assigned to them was refined and converged at  $U = 0.133 (10) \text{ \AA}^2$ . Refinement of the anion was



**Figure 2.** Structure of the [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> cation showing the atom-labeling scheme and 40% probability thermal ellipsoids. For clarity, only one set of disordered *tert*-butyl carbon atoms is shown for ligands 1 and 4. Primed and unprimed atoms are related by a crystallographic mirror plane.



**Figure 3.** Structure of the [(Ph<sub>3</sub>B)<sub>2</sub>CN]<sup>-</sup> anion showing the atom-labeling scheme and 50% probability thermal ellipsoids. Primed and unprimed atoms are related by a center of symmetry across which the cyanide group is disordered.

straightforward, apart from the cyanide moiety. The anion is disordered across a center of symmetry, and, since individual positions of the carbon and nitrogen atoms of the cyanide group could not be resolved, a composite half carbon-half nitrogen atom was used in the refinement. Hydrogen atoms of the phenyl rings were placed in calculated positions (C-H = 0.95 Å) and were constrained to "ride" on the carbon atom to which they are attached. A common isotropic temperature factor for the phenyl ring hydrogen atoms converged at  $U = 0.117 (10) \text{ \AA}^2$ .

All nonhydrogen atoms of the structure were refined anisotropically except for some methyl carbon atoms (vide supra). The residual indices<sup>20</sup> converged at  $R_1 = 0.059$  and  $R_2 = 0.065$ . The function minimized in the least squares was  $\sum w(|F_o| - |F_d|)^2$ , where  $w = 2.5188/[\sigma^2(F_o) + 0.000460F_o^2]$ . Neutral atom scattering factors and anomalous dispersion corrections were taken from reference 21. In the final cycle of refinement no variable shifted by more than 0.09 $\sigma$  and most were less than 0.03 $\sigma$ .

The largest three peaks on a final difference-Fourier map were  $\sim 0.8 \text{ e \AA}^{-3}$  located 0.3–1.15 Å from the Sn atom. All remaining peaks were  $< 0.58 \text{ e \AA}^{-3}$ . The average  $w\Delta^2$  for groups of data sectioned according to parity group,  $|F_d|$ ,  $(\sin \theta)/\lambda$ ,  $|h|$ ,  $|k|$ , or  $|l|$  showed reasonable consistency, and the weighting scheme was considered satisfactory.

An attempt at refining the structure in the noncentrosymmetric space group *Pbc2<sub>1</sub>* was abandoned when the internal geometry of the *tert*-butyl

(20)  $R_1 = \sum |F_d| - |F_o| / \sum |F_d|$ ;  $R_2 = [\sum w(|F_d| - |F_o|)^2 / \sum w|F_d|^2]^{1/2}$ .

(19) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. I, pp 145, 115.

(21) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

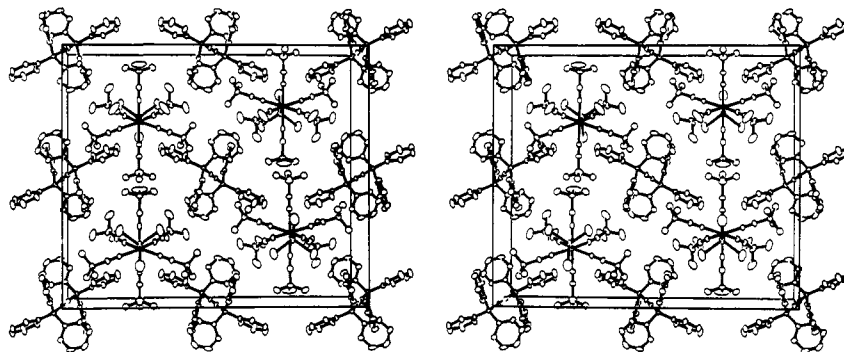


Figure 4. Stereoscopic packing diagram of the  $[\text{Mo}(\text{SnCl}_3)(\text{CN-}t\text{-Bu})_6][(\text{Ph}_3\text{B})_2\text{CN}]$  structure in the [100] projection;  $b$  is vertical and  $c$  is horizontal on the page.

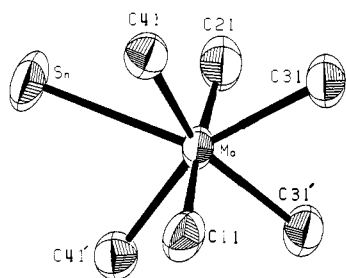


Figure 5. Inner coordination geometry of the  $[\text{Mo}(\text{SnCl}_3)(\text{CN-}t\text{-Bu})_6]^+$  cation showing the 40% probability thermal ellipsoids. The Mo, Sn, C11, and C21 atoms lie on a crystallographic mirror plane that relates the primed and unprimed atoms to one another.

ligands became substantially worse.

## Results and Discussion

Final nonhydrogen atomic positional parameters, with estimated standard deviations, appear in Table II. Interatomic distances and angles, with estimated standard deviations, are reported in Table III. Final observed and calculated structure factors are listed in Table S1, final thermal parameters in Table S2, and hydrogen atom parameters in Table S3.<sup>22</sup> Figure 2 shows the molecular geometry and atom-labeling scheme for the cation while Figure 3 displays similar information for the anion. A unit-cell packing diagram appears in Figure 4.

**Structure of the  $[\text{Mo}(\text{SnCl}_3)(\text{CN-}t\text{-Bu})_6]^+$  Cation.** This seven-coordinate complex sits on a crystallographically required mirror plane passing through atoms C12, Sn, Mo, C11, N11, C12, C13, C21, N21, C22, and C23 (Figure 2). The inner coordination sphere is illustrated in Figure 5.

The choice of an idealized coordination geometry in a seven-coordinate complex is often not simple and has been the subject of several recent articles.<sup>7,9,15,23-25</sup> One simple procedure is to compare the interbond angles at the metal center with the values computed for various idealized coordination polyhedra.<sup>9,15a</sup> Table IV compares the internal (L-M-L) angles of each of the idealized<sup>10</sup> geometries with those of the  $[\text{Mo}(\text{SnCl}_3)(\text{CN-}t\text{-Bu})_6]^+$  cation. Because the cation has rigorous  $C_2$  symmetry, the pattern of internal angles closely resembles that of the 4:3 ( $C_2$ ) piano stool structure.<sup>25</sup> A significant deviation occurs at angle 7, however. In order to evaluate this deviation, we carried out dihedral angle calculations on the coordination geometry normalized to a unit sphere.<sup>23,24</sup> The results are included in Table IV. Although two dihedral angles, equivalent because of the mirror symmetry, of

Table II. Final Positional Parameters for  $[\text{Mo}(\text{SnCl}_3)(\text{CN-}t\text{-Bu})_6][(\text{Ph}_3\text{B})_2\text{CN}]^a$

atom	$x$	$y$	$z$
Mo	0.73820 (7)	0.28048 (5)	0.25
Sn	0.51930 (7)	0.25980 (5)	0.25
C11	0.4437 (3)	0.20440 (19)	0.18471 (14)
C12	0.3947 (4)	0.3363 (3)	0.25
C11	0.7729 (10)	0.3716 (7)	0.25
N11	0.7841 (9)	0.4188 (6)	0.25
C12	0.7753 (15)	0.4842 (9)	0.25
C13	0.880 (4)	0.5095 (16)	0.25
C14	0.7060 (19)	0.5024 (9)	0.2038 (8)
C13A	0.663 (7)	0.497 (3)	0.25
C14A	0.838 (3)	0.5060 (15)	0.2030 (14)
C21	0.7157 (11)	0.1913 (8)	0.25
N21	0.7147 (10)	0.1404 (7)	0.25
C22	0.7000 (18)	0.0744 (8)	0.25
C23	0.8239 (18)	0.0514 (9)	0.25
C24	0.6418 (15)	0.0590 (6)	0.2031 (5)
C31	0.8692 (7)	0.2579 (4)	0.1995 (3)
N31	0.9403 (6)	0.2422 (3)	0.1750 (3)
C32	1.0316 (9)	0.2168 (7)	0.1460 (5)
C33	1.0159 (11)	0.1529 (8)	0.1492 (6)
C34	1.0114 (12)	0.2307 (8)	0.0928 (6)
C35	1.1403 (8)	0.2352 (8)	0.1658 (7)
C41	0.6708 (7)	0.3065 (4)	0.1827 (3)
N41	0.6426 (6)	0.3234 (3)	0.1442 (3)
C42	0.6050 (10)	0.3430 (5)	0.0943 (4)
C43	0.6866 (20)	0.3878 (11)	0.0754 (8)
C44	0.4916 (19)	0.3733 (10)	0.1040 (8)
C45	0.5862 (20)	0.2938 (9)	0.0620 (9)
C43A	0.705 (3)	0.3194 (14)	0.0589 (12)
C44A	0.493 (3)	0.3203 (14)	0.0844 (12)
C45A	0.608 (3)	0.4056 (16)	0.0920 (12)
B	0.1516 (7)	0.4688 (4)	0.0358 (4)
C/N	0.0402 (5)	0.4920 (3)	0.0094 (3)
C51	0.1098 (7)	0.4397 (4)	0.0875 (3)
C52	0.0039 (8)	0.4189 (4)	0.0952 (4)
C53	0.0287 (9)	0.3934 (6)	0.1399 (5)
C54	0.0422 (11)	0.3873 (6)	0.1764 (4)
C55	0.1493 (10)	0.4072 (5)	0.1718 (4)
C56	0.1822 (8)	0.4343 (4)	0.1265 (4)
C61	0.2331 (6)	0.5232 (4)	0.0450 (3)
C62	0.3489 (6)	0.5160 (4)	0.0437 (3)
C63	0.4196 (7)	0.5611 (5)	0.0544 (4)
C64	0.3811 (9)	0.6127 (5)	0.0688 (4)
C65	0.2677 (9)	0.6232 (5)	0.0698 (4)
C66	0.1966 (8)	0.5777 (4)	0.0582 (4)
C71	0.2046 (6)	0.4218 (4)	-0.0022 (4)
C72	0.2289 (7)	0.4358 (4)	-0.0512 (4)
C73	0.2810 (9)	0.3997 (6)	-0.0834 (5)
C74	0.3122 (10)	0.3480 (8)	-0.0693 (6)
C75	0.2933 (11)	0.3321 (5)	-0.0233 (7)
C76	0.2365 (8)	0.3677 (5)	0.0114 (4)

<sup>a</sup> Numbers in parentheses are errors in the last significant digit(s). Atoms are labeled as shown in Figures 2, 3, and 5. Occupancy factors are C13 = C14 = 0.625 (12), C13A = C14A = 0.375 (12), C43 = C44 = C45 = 0.595 (8), and C43A = C44A = C45A = 0.405 (8).

(22) Supplementary material.

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Table III. Interatomic Distances (Å) and Angles (Deg)<sup>a,b</sup>

Coordination Sphere			
Mo-Sn	2.663 (1)	Mo-C31	2.138 (8)
Mo-C11	2.137 (15)	Mo-C41	2.071 (9)
Mo-C21	2.071 (18)		
Sn-Mo-C11	111.5 (3)	C21-Mo-C31	81.6 (4)
Sn-Mo-C21	72.2 (4)	C21-Mo-C41	103.6 (3)
Sn-Mo-C31	132.7 (2)	C31-Mo-C31'	78.8 (4)
Sn-Mo-C41	70.6 (2)	C31-Mo-C41	78.5 (3)
C11-Mo-C21	176.3 (5)	C31-Mo-C41'	155.7 (3)
C11-Mo-C31	95.5 (3)	C41-Mo-C41'	122.0 (5)
C11-Mo-C41	78.0 (3)		
Ligand Geometry			
Sn-Cl1	2.351 (4)	Sn-Cl2	2.306 (6)
Mo-Sn-Cl1	118.4	Cl1-Sn-Cl2	99.5 (1)
Mo-Sn-Cl2	120.0 (2)	Cl1-Sn-Cl1'	96.7 (2)
C11-N11	1.10 (2)	N21-C22	1.53 (2)
C21-N21	1.17 (2)	N31-C32	1.465 (14)
C31-N31	1.136 (11)	N41-C42	1.488 (13)
C41-N41	1.155 (11)	mean C-C(methyl)	1.49 (3) <sup>b</sup>
N11-C12	1.51 (3)	range C-C(methyl)	1.37-1.62
C11-N11-C12	169.0 (14)	mean N-C-C(methyl)	107.4 (12) <sup>b</sup>
C21-N21-C22	174.0 (15)	range N-C-C(methyl)	103-111
C31-N31-C32	174.5 (10)	mean C(methyl)-C-C(methyl)	111.2 (17) <sup>b</sup>
C41-N41-C42	177.9 (9)	range C(methyl)-C-C(methyl)	104.3-116.7
Anion Geometry			
C-N	1.147 (12)	C62-C63	1.369 (13)
C-B	1.603 (11)	C63-C64	1.332 (16)
B-C51	1.622 (12)	C64-C65	1.380 (16)
B-C61	1.606 (12)	C65-C66	1.384 (15)
B-C71	1.619 (13)	C66-C61	1.375 (13)
C51-C52	1.371 (13)	C71-C72	1.388 (13)
C52-C53	1.394 (16)	C72-C73	1.352 (16)
C53-C54	1.306 (17)	C73-C74	1.30 (2)
C54-C55	1.367 (18)	C74-C75	1.31 (2)
C55-C56	1.424 (14)	C75-C76	1.414 (19)
C56-C51	1.367 (13)	C76-C71	1.352 (14)
C61-C62	1.397 (10)		
C-N-B	179.1 (10)	C54-C55-C56	118.9 (10)
N-B-C51	105.1 (6)	C55-C56-C51	121.5 (9)
N-B-C61	108.2 (7)	C56-C51-C52	116.0 (8)
N-B-C71	105.6 (6)	C61-C62-C63	121.3 (8)
C51-B-C61	112.2 (7)	C62-C63-C64	121.5 (9)
C51-B-C71	112.7 (7)	C63-C64-C65	120.2 (10)
C61-B-C71	112.4 (6)	C64-C65-C66	117.8 (10)
B-C51-C52	124.0 (7)	C65-C66-C61	123.6 (9)
B-C51-C56	120.1 (7)	C66-C61-C62	115.4 (8)
B-C61-C62	120.4 (7)	C71-C72-C73	124.1 (10)
B-C61-C66	124.0 (7)	C72-C73-C74	120.5 (12)
B-C71-C72	121.8 (8)	C73-C74-C75	118.6 (14)
B-C71-C76	123.7 (9)	C74-C75-C76	122.9 (13)
C51-C52-C53	122.4 (9)	C75-C76-C71	119.4 (11)
C52-C53-C54	120.8 (11)	C76-C71-C72	114.3 (9)
C53-C54-C55	120.4 (11)		

<sup>a</sup> See footnote *a*, Table II. <sup>b</sup> Standard deviations quoted are the average standard deviations of the individual bond lengths. Values reported have not been corrected for thermal motion. With the assumption of a riding model, the Mo-Sn interatomic distance averaged over thermal motion increases to 2.688 Å. A similar calculation revealed the Sn-Cl bonds to become more equivalent and yielded distances of 2.409 and 2.391 Å for Sn-Cl1 and Sn-Cl2, respectively.

26.3° are reasonably close to the predicted value of 20.5°, the dihedral angle across the quadrilateral face defined by atoms Sn, C41, C41', and C11 deviates from ideality by 11.7°. Moreover, the planes defined by the triangular and quadrilateral faces intersect at an angle of 3.9° compared with the theoretical value of 0° in a 4:3 piano stool.

Since the C<sub>3v</sub> geometry has low symmetry and the present complex is highly distorted, an attempt was made to fit the

Table IV. Summary of Interbond Angles (Deg) for Seven-Coordinate Structures<sup>a</sup>

angle no.	PB (D <sub>5h</sub> )	CO (C <sub>3v</sub> ) <sup>b</sup>	CTP (C <sub>2v</sub> ) <sup>c</sup>	4:3 (C <sub>s</sub> ) <sup>b</sup>	[Mo(SnCl <sub>3</sub> )(CN- <i>t</i> -Bu) <sub>6</sub> ]/[(Ph <sub>3</sub> B) <sub>2</sub> CN]
1	180.0	160.0	164.0	170.0	176.3
2	144.0	160.0	164.0	153.6	155.7
3	144.0	160.0	144.2	153.6	155.7
4	144.0	130.0	144.2	130.8	132.7
5	144.0	130.0	119.0	130.8	132.7
6	144.0	130.0	119.0	120.0	122.0
7	90.0	108.9	118.8	120.0	111.5
8	90.0	108.9	118.8	108.8	103.6
9	90.0	108.9	99.0	108.8	103.6
10	90.0	83.1	99.0	89.4	95.5
11	90.0	83.1	83.7	89.4	95.5
12	90.0	83.1	83.7	83.1	81.6
13	90.0	82.0	80.3	83.1	81.6
14	90.0	82.0	80.3	83.1	78.8
15	90.0	82.0	78.8	75.5	78.5
16	90.0	82.0	78.6	75.5	78.5
17	72.0	82.0	75.2	75.5	78.0
18	72.0	82.0	75.2	75.5	78.0
19	72.0	70.0	75.0	73.3	72.2
20	72.0	70.0	75.0	73.3	70.6
21	72.0	70.0	71.5	70.0	70.6
δ <sub>1</sub> <sup>d</sup>	54.4 <sup>e</sup>	18.8 16.2 <sup>f</sup>	39.4 41.5 <sup>f</sup>	20.5	26.3
δ <sub>2</sub>	54.4	18.8 16.2	0 0	20.5	26.3
δ <sub>3</sub>		18.8 16.2	0 0	0	11.7

<sup>a</sup> Angles are listed by decreasing size. Abbreviations used are PB, pentagonal bipyramid; CO, capped octahedron; CTP, capped trigonal prism; 4:3, the 4:3 "piano stool" structure. <sup>b</sup> The internal and dihedral angles of these reference geometries are calculated from the corresponding optimized geometries for d<sup>4</sup> complexes.<sup>10</sup> <sup>c</sup> The structure of [Mo(CN-*t*-Bu)<sub>6</sub>](PF<sub>6</sub>)<sub>2</sub><sup>6</sup> is used for the reference geometry. <sup>d</sup> The set of three dihedral angles were originally defined in ref 23. As used here they relate the geometries along the reaction coordinate converting PB → 4:3 (C<sub>s</sub>) → CO → CTP. A description of this coordinate and the assignment (except for the J:3(C<sub>s</sub>) geometry) of the dihedral angles are found in ref 24. <sup>e</sup> We have followed the convention<sup>23,24</sup> that leaves δ<sub>3</sub> undefined since in the pentagonal bipyramid it is not formed by exterior faces. <sup>f</sup> These dihedral angles are those of ref 23 and 24.

structure to a geometry of higher symmetry. As evident from Table IV, the C<sub>3v</sub> capped octahedron with tin as the capping atom is the best candidate. Here it may be seen that the internal angles of [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> can be grouped into sets of three approximating the 3:3:3 (1-3, 4-6, 7-9) pattern required in a rigorous capped octahedral structure. The dihedral angles (Table IV) also form a rough group of three with an average value close to that required for C<sub>3v</sub> symmetry. The deviation from ideality originates in a tilt of the capped face by 12.3° with respect to the uncapped face. This distortion is coupled with a slight lengthening of the edge on the capped face closest to the plane defined by the uncapped face. The Mo-Sn bond is nearly perpendicular (88.8°) to the capped face.

The distortions from either ideal geometry are similar in magnitude and lie along the reaction pathway interconverting the C<sub>3v</sub>-capped octahedron and C<sub>s</sub> 4:3 geometry. This result is not surprising since the energy barrier isolating one geometry from another is calculated to be extremely small with none of the possible geometries particularly favored over the others.<sup>10,27</sup> Under these conditions, crystal-packing forces are likely to play a dominant role in determining the solid-state geometry. Nevertheless, the average interbond angles in [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> correspond rather precisely to the deepest minimum in the potential energy surface calculated for a [M(unidentate A)<sub>6</sub>(unidentate B)] structure with a single long bond.<sup>27</sup> In solution, like all other MoL<sub>6</sub>X<sup>+</sup> and MoL<sub>7</sub>2<sup>+</sup> cations, this molecule is fluxional at room temperature and has only a singlet *tert*-butyl resonance in its proton NMR spectrum.

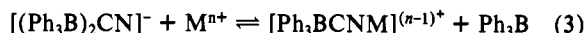
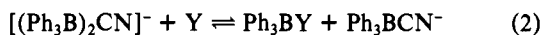
The complexity of assigning coordination geometry to a seven-coordinate structure is amply illustrated by this case. The internal and dihedral angle methods are quite helpful if used sensibly. An accurate scale model was indispensable, however, to sorting out the distortions from ideality.

The Mo–Sn bond length of 2.663 (1) Å is slightly shorter, even when corrected for thermal motion (Table III), than in most other compounds having a trichlorostannate ligand coordinated to Mo(II). For comparison, the uncorrected Mo–Sn distances are 2.688 Å in Mo(SnCl<sub>3</sub>)Cl(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)(CO)<sub>3</sub>,<sup>28</sup> 2.715 Å in Mo(SnCl<sub>3</sub>)Cl(η-C<sub>5</sub>H<sub>5</sub>)(Ph<sub>3</sub>P)(NO),<sup>29</sup> 2.729 Å in [Mo(SnCl<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)(CO)<sub>4</sub>]<sup>+</sup>,<sup>30</sup> and 2.733 Å in [Mo(SnCl<sub>3</sub>)(η-C<sub>5</sub>H<sub>5</sub>)(Ph<sub>3</sub>P)(CO)(NO)](SnCl<sub>3</sub>).<sup>29</sup> It is interesting that both Mo(SnCl<sub>3</sub>)Cl(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)(CO)<sub>3</sub> and Mo(SnCl<sub>3</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)(CO)<sub>4</sub> have capped octahedral structures with the trichlorostannate ion as the capping ligand, analogous to the capped octahedral reference geometry for the [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> cation.

The Mo–C bond lengths on the capped face (2.071 (18), 2.071 (9), and 2.071 (9) Å) are systematically and significantly shorter than the corresponding values on the uncapped face (2.138 (8), 2.138 (8), and 2.137 (15) Å). This result is strikingly parallel to that previously reported for [Mo(CNCH<sub>3</sub>)<sub>7</sub>](BF<sub>4</sub>)<sub>2</sub>, a distorted capped octahedral structure with a 1:3:3 grouping of Mo–C bond distances (2.04 Å; 2.08, 2.09, 2.09 Å; 2.14, 2.14, 2.16 Å).<sup>7</sup> The Mo–C bond length values and the internal ligand geometry all fall within the range observed for many other seven-coordinate molybdenum(II) isocyanide complexes.<sup>4–7,9</sup>

**The [(Ph<sub>3</sub>B)<sub>2</sub>CN]<sup>-</sup> (BBCN) Anion.** The previously unreported BBCN anion lies on a crystallographically required center of inversion. The phenyl rings are therefore in a staggered conformation which is the anticipated lowest energy form (Figure 3). The inversion center also requires the –C≡N– atoms linking the boron atoms to be disordered. Because of this disorder, it was impossible to obtain *crystallographic* evidence for the [(Ph<sub>3</sub>B)<sub>2</sub>CN]<sup>-</sup> formulation. The elemental analyses, charge considerations, the observation of a C≡N stretching band at 2255 cm<sup>-1</sup> in the infrared spectrum (cf ν<sub>CN</sub> at 2260 cm<sup>-1</sup> for the related H<sub>3</sub>BCNBH<sub>3</sub><sup>-</sup> anion<sup>31</sup>), and the independent syntheses of the sodium and tetramethylammonium salts of the BBCN anion, however, leave no doubt as to its chemical nature. The B–C(N) and C–N distances of 1.603 (11) and 1.147 (12) Å, respectively, are in good accord with comparable values found for other cyanoborate anions.<sup>32</sup> The internal geometry of the Ph<sub>3</sub>B portion of the anion is reasonable.

The [(Ph<sub>3</sub>B)<sub>2</sub>CN]<sup>-</sup> anion should prove to be useful as a precipitating reagent, possibly comparable in value to its cationic analogue [(Ph<sub>3</sub>P)<sub>2</sub>N]<sup>+</sup>. The P=N=P angles in the latter are usually bent (but occasionally linear)<sup>33</sup> whereas the BC≡NB unit should be linear and is nearly so (B–C–N = C–N–B = 179.1°) in the present structure. The BBCN anion is easily prepared by addition of a stoichiometric or excess amount of triphenylboron to a solution of sodium cyanotriphenylborate. It is highly soluble in polar organic solvents. The only limitations in its use will be the presence of bases (Y) that coordinate strongly to the Ph<sub>3</sub>B moiety or of metal ions (M<sup>n+</sup>) that complex the Ph<sub>3</sub>BCN<sup>-</sup> anion, eq 2 and 3, respectively. Infrared spectra in the



C≡N stretching region show that Na[(Ph<sub>3</sub>B)<sub>2</sub>CN] is slightly dissociated in methanol, having a strong band at 2240 cm<sup>-1</sup> due to [(Ph<sub>3</sub>B)<sub>2</sub>CN]<sup>-</sup> and a much weaker band at 2167 cm<sup>-1</sup> resulting from Ph<sub>3</sub>BCN<sup>-</sup>.

**Synthesis and Reactivity of the [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> Cation.** The formal insertion of stannous chloride into the Mo–Cl bond of [MoCl(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> is analogous to the reaction of [η-C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Cl with SnCl<sub>2</sub>.<sup>16</sup> Molybdenum(II) complexes of the SnCl<sub>3</sub><sup>-</sup> ion have also been prepared by oxidation of the molybdenum(0) compound (bpy)Mo(CO)<sub>4</sub> with stannic chloride<sup>34</sup> and by cleavage of the [(η-C<sub>5</sub>H<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> dimer with SnCl<sub>2</sub>·2H<sub>2</sub>O.<sup>35</sup> The chemical reactivity of complexes containing the Mo–SnCl<sub>3</sub> bond has not been extensively investigated, however. In the present case, reaction of [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> with zinc in a protic solvent such as ethanol produces an immediate color change. Instead of reductive coupling to form [MoX(CN-*t*-Bu)<sub>4</sub>(*t*-BuNHCCNH-*t*-Bu)]<sup>+</sup>, a reaction known to occur for X = halide and cyanide (Figure 1),<sup>11,14</sup> the reaction yields [Mo(CN-*t*-Bu)<sub>7</sub>]<sup>2+</sup> and [MoX(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> as the major products. The heptakis(*tert*-butyl isocyanide)molybdenum(II) cation may arise from the displacement of the trichlorostannate ligand of the starting material by free isocyanide liberated by decomposition of the initial reduction products. In support of this suggestion it was found that addition of an excess of isocyanide to a methanolic solution of [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> led to quantitative formation of [Mo(CN-*t*-Bu)<sub>7</sub>]<sup>2+</sup>. The latter complex was identified by its proton NMR spectrum and isolated as the tetraphenylborate salt.<sup>14</sup>

The failure to produce a coupled ligand product in the reaction of zinc with [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> may be due to the greater electron-withdrawing ability of the SnCl<sub>3</sub><sup>-</sup> ion compared with that of halide ions. Electrochemical studies<sup>36</sup> have shown that the potentials for the quasi-reversible one-electron oxidations of [MoX(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> complexes vary as X = halide < cyanide < isocyanide < trichlorostannate. This trend is inversely related to the yield of reductively coupled product (Figure 1). Further discussions of the reductive coupling reaction will be reported elsewhere.<sup>14</sup>

### Summary and Conclusions

The seven-coordinate molybdenum(II) alkyl isocyanide complexes have a rich and varied chemistry. Study of the stable [MoL<sub>6</sub>X]<sup>+</sup> compounds has proved especially fruitful since it is possible to modify selectively the unique ligand X providing a range of compounds with a variety of properties. In this case the trichlorostannate ligand is shown to inhibit completely the previously observed reductive coupling of adjacent isocyanide ligands. The geometric analysis of the [Mo(SnCl<sub>3</sub>)(CN-*t*-Bu)<sub>6</sub>]<sup>+</sup> cation, which contains a ligand with substantially different steric requirements than any of the others previously studied, demonstrates once again that crystal-packing forces play a significant role in determining the solid-state geometry of seven-coordinate compounds containing unidentate ligands. An added bonus is the discovery of the BBCN anion which should prove useful in the crystallization of large cations.

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**Supplementary Material Available:** Tables S1–S3 reporting, respectively, the observed and calculated structure factor amplitudes, atomic thermal parameters, and hydrogen atom positional parameters (15 pages). Ordering information is given on any current masthead page.

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