

Recrystallization from cyclohexane afforded 0.93 g of orange needles, mp 99–100°; (lit.<sup>22</sup> mp 102–104°);  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  443 nm ( $\epsilon$  14,000). The same product was obtained from XVIIIId.

When the cupric chloride was omitted from the above reaction with XVIIIId, a 62% yield of XX was isolated. An authentic sample of XX was prepared by coupling phenyldiazonium chloride to 2-naphthylamine. The two samples had the same  $R_f$  value on thin layer chromatography (Silica Gel G, 2:1 benzene-cyclohexane) and had very similar visible and infrared spectra.

**1-(*o*-Bromophenyl)-3,5-diphenylformazan (XXI).**—To a mixture of 12.9 g (0.075 mol) of *o*-bromoaniline and 22 ml of concentrated hydrochloric acid in 75 ml of water at 5° was added by drops a solution of 5.2 g of sodium nitrite in 15 ml of water. The excess nitrous acid was then destroyed by adding a small amount of sulfamic acid. The coupler solution was made by adding a solution of 15 g (0.076 mol) of benzaldehyde phenylhydrazone in 150 ml of pyridine to a solution of 15 g of sodium hydroxide in 375 ml of methanol. The cold diazonium solution was then added by drops to the coupler solution at 5–8°. Stirring was continued at 3–5° for 45 min, after which the crystals of XXI which had formed were filtered off and washed in turn with methanol and water; yield 13.8 g; mp 133–138°. After a recrystallization from isopropyl alcohol the solid melted at 155–156°; yield 8 g (28%);  $\lambda_{\text{max}}^{\text{DMF}}$  486 nm ( $\epsilon$  14,600). *Anal.* Calcd for  $\text{C}_{19}\text{H}_{16}\text{BrN}_4$ : C, 60.2; H, 3.99; N, 14.8; Br, 21.1. Found: C, 60.2; H, 4.0; N, 14.7; Br, 20.5.

**Reaction of XXI with Ethylenediamine and Cupric Chloride.**—To the red solution of 2.5 g (0.0066 mol) of XXI at 60° was added a solution of 1.2 g (0.007 mol) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 3 ml of water and 10 ml of ethylenediamine. The mixture was deep blue after 10 min at 60° and was then cooled to room temperature and stirred overnight at room temperature. The blue diamond-shaped plates of XXIIa which had formed were filtered off and washed with methanol; yield, 1.2 g (42%); mp 220–222° dec;  $\lambda_{\text{max}}^{\text{DMF}}$  620 nm ( $\epsilon$  17,400), 500 (4500). When a similar reaction was carried out entirely at room temperature over a 22-hr period, the yield of complex XXIIa was 62%. *Anal.* Calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_6\text{Cu} \cdot 0.5\text{C}_2\text{H}_6\text{N}_2$ : C, 58.7; H, 5.37; N, 21.8; Cu, 14.1. Found: C, 58.6; H, 5.3; N, 21.6; Cu, 13.7.

To a solution of 0.2 g of XXIIa in 30 ml of pyridine was added

15 ml of water by drops. The crystals of XXIIb which separated were collected and washed with water; yield, 0.09 g; mp 200–204° dec;  $\lambda_{\text{max}}^{\text{DMF}}$  620 nm ( $\epsilon$  21,300), 500 (5600). *Anal.* Calcd for  $\text{C}_{21}\text{H}_{20}\text{N}_6\text{Cu} \cdot \text{C}_2\text{H}_6\text{N}_2 \cdot 0.5\text{H}_2\text{O}$ : C, 61.5; H, 5.16; N, 19.3. Found: C, 61.5; H, 5.2; N, 19.6.

**Coupling of Methyl Anthranilate to *p*-Cresol.**—To a solution of 15.1 g of methyl anthranilate in 200 ml of water plus 20 ml of concentrated hydrochloric acid at 0–5° was added slowly 20 ml of 5 *N* sodium nitrite. After 15 min the excess nitrous acid was destroyed by adding sulfamic acid. This diazonium solution was then added slowly at 0–5° to a mixture of 16 g of *p*-cresol, 5.6 g of sodium hydroxide, and 200 ml of water.

The product turned crystalline near the end of the addition of the diazonium solution. The pH was maintained at 10–11 by adding 30% sodium hydroxide until the test for diazo was negative. The yield of crude XXIII was 23.6 g (87%); after recrystallization from methanol, the yield was 19.9 g (73%); mp 63–64°. The infrared spectrum shows a strong band at 1727  $\text{cm}^{-1}$  (C=O stretch). *Anal.* Calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ : C, 66.6; H, 5.22; N, 10.4. Found: C, 66.7; H, 5.3; N, 10.4.

**Reaction of XXIII with Ethylenediamine and Cupric Chloride.**—A solution of 5.1 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 10 ml of water was added slowly to a solution of 5.4 g of XXIII in 40 ml of ethylenediamine. The mixture was then heated overnight at 70–80°, after which 60 ml of water was added by drops at room temperature. The resulting solid was filtered off, washed with a 2:1 water-ethylenediamine mixture, followed by water; yield, 6.1 g. A 2-g portion of this solid was extracted with 125 ml of hot methanol and the resulting solution was chromatographed on a silicic acid (5% water content) column, using methanol as the eluent. The main orange fraction was collected and concentrated to dryness to give 0.88 g of XXIV. The product gave a single spot on thin layer chromatography and was recrystallized (Soxhlet)<sup>21</sup> from methanol before analysis; yield, 0.59 g. *Anal.* Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2\text{Cu}$ : C, 53.4; H, 4.5; N, 15.6. Found: C, 53.4; H, 4.6; N, 15.4.

**Acknowledgment.**—We thank Dr. Robert K. Miller for his assistance in the interpretation of the infrared spectra, Dr. James F. Weiher for determining and interpreting the magnetic susceptibility data, and Bernard Blinichikoff and Charles R. Haff, Jr., for skillful assistance in the laboratory.

(22) T. A. Lawson, *Ber.*, **18**, 798 (1885).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,  
UNIVERSITY OF SOUTH DAKOTA, VERMILION, SOUTH DAKOTA 57069

## *gem*-Dibasic Ligands with Phosphorus, Sulfur, and Nitrogen Sites, and Some Borane Derivatives<sup>1</sup>

By K. L. LUNDBERG,<sup>2a</sup> R. J. ROWATT,<sup>2a</sup> AND N. E. MILLER<sup>2b</sup>

Received November 11, 1968

Three *gem*-dibasic ligands, dimethylphosphinomethyl dimethylamine [( $\text{CH}_3$ )<sub>2</sub>PCH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>] (pcn), dimethylphosphino-methyl methyl sulfide [( $\text{CH}_3$ )<sub>2</sub>PCH<sub>2</sub>SCH<sub>3</sub>] (pcs), and dimethylaminomethyl methyl sulfide [( $\text{CH}_3$ )<sub>2</sub>NCH<sub>2</sub>SCH<sub>3</sub>] (ncs) were prepared using chloromethyl dimethylamine or chloromethyl methyl sulfide as starting materials. All three are colorless liquids of low vapor pressure (5–10 mm at room temperature), pcn and pcs being very inflammable in air. Monoborane adducts, H<sub>3</sub>Bpcn, H<sub>3</sub>Bpcs, and H<sub>3</sub>Bncs, form readily with diborane. The only stable diadduct was H<sub>3</sub>BpcnBH<sub>3</sub>. A new borane cation type was demonstrated in the preparation of CH<sub>3</sub>pcnBH<sub>3</sub><sup>+</sup>.

The preparation and characterization of some 1,3-dihetero skeletons were conducted as a part of a syn-

(1) Presented at the Midwest Regional Meeting of the American Chemical Society, Manhattan, Kan., Oct 31, 1968.

(2) (a) National Defense and Education Act Fellows. (b) Author to whom correspondence should be directed at the University of South Dakota.

thetic program in small ring chemistry. Of special interest in this program were compounds with two different heteroatom base sites that could be used to incorporate functional chemistry into complexes without the complication of chelate formation or polymerization.

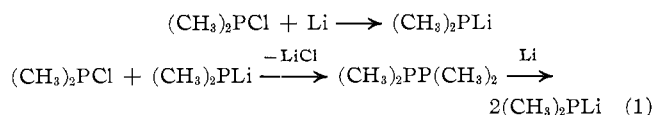
TABLE I  
<sup>1</sup>H NMR SPECTRA<sup>a</sup>

Compound	Solvent	Chemical shift, ppm (downfield from TMSi)			Coupling constants, cps				Peak intensities <sup>b</sup>
		CH <sub>3</sub> P	CH <sub>3</sub> S	CH <sub>3</sub> N	CH <sub>2</sub>	PCH	PCHS	Long range	
pcs	Neat	1.05	2.12	...	2.46	3	4	..	6:2:2.8
H <sub>3</sub> Bpcs	CHCl <sub>3</sub>	1.36	2.26	...	2.71	10	6	1 <sup>c</sup>	6:2.9:1.8
CH <sub>3</sub> pcs + I <sup>-</sup>	CD <sub>3</sub> CN	2.08	2.38	...	3.72	14	9	1 <sup>c</sup>	9:2.7:1.6
CH <sub>3</sub> SCH <sub>2</sub> pcs + PF <sub>6</sub> <sup>-</sup>	CH <sub>2</sub> Cl <sub>2</sub>	1.98	2.34	...	3.31	14	9	1 <sup>c</sup>	5.8:6:4.7
H <sub>3</sub> Bpcn	CHCl <sub>3</sub>	1.32	...	2.38	2.70	10	4	..	6:6:2
H <sub>3</sub> PpcnBH <sub>3</sub>	CHCl <sub>3</sub>	1.50	...	2.88	3.29	10	7	..	6:5.8:2
CH <sub>3</sub> pcn + Cl <sup>-</sup>	CH <sub>2</sub> Cl <sub>2</sub>	2.17	...	2.51	3.86	14	6	..	9:5.8:1.8
CH <sub>3</sub> pcnCH <sub>3</sub> <sup>2+</sup> + (PF <sub>6</sub> <sup>-</sup> ) <sub>2</sub>	CD <sub>3</sub> CN	2.14	...	3.25	4.36	14	10	1 <sup>d</sup>	9:8.6:1.9
CH <sub>3</sub> pcnBH <sub>3</sub> + PF <sub>6</sub> <sup>-</sup>	CD <sub>3</sub> CN	2.04	...	2.83	3.82	14	10	..	9:5.9:2.1
ncs	Neat	...	2.18	2.33	3.93	..	..	..	3.1:6:2.2
H <sub>3</sub> Bncs	CDCl <sub>3</sub>	...	2.30	2.59	3.97	..	..	..	...
CH <sub>3</sub> ncs + PF <sub>6</sub> <sup>-</sup>	CD <sub>3</sub> CN	...	2.36	2.95	4.40	..	..	..	...
CH <sub>3</sub> SCH <sub>2</sub> ncs + PF <sub>6</sub> <sup>-</sup>	CH <sub>2</sub> Cl <sub>2</sub>	...	2.42	3.00	...	..	..	..	...

<sup>a</sup> Run on Varian A-60A spectrometer. <sup>b</sup> The ratio of resonance intensities is given in the order appearing in the table. <sup>c</sup> PCSCH. <sup>d</sup> PCNCH.

Geminal dibasic ligands with one type of base site are becoming a well-established class of ligands. Along with the common examples, [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>CH<sub>2</sub>, (CH<sub>3</sub>O)<sub>2</sub>-CH<sub>2</sub>, and (CH<sub>3</sub>S)<sub>2</sub>CH<sub>2</sub>, there is a growing list of bis phosphines, (CF<sub>3</sub>)<sub>2</sub>POP(CF<sub>3</sub>)<sub>2</sub>,<sup>3</sup> (CF<sub>3</sub>)<sub>2</sub>PSP(CF<sub>3</sub>)<sub>2</sub>,<sup>4</sup> (CF<sub>3</sub>)<sub>2</sub>PNCH<sub>3</sub>P(CF<sub>3</sub>)<sub>2</sub>,<sup>5</sup> and (H<sub>2</sub>P)<sub>2</sub>CH<sub>2</sub>.<sup>6</sup> Rather less is known about geminal mixed bases with two strongly basic sites. Since those with methylene bridges are more suited to our purpose, attention has been directed to exploring the chemistry of ligands with P-C-S, P-C-N, and N-C-S skeletons.

Two dimethylphosphinomethyl bases, (CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>N-(CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>SCH<sub>3</sub>, hereafter referred to as pcn and pcs, were synthesized using lithiodimethylphosphine. The lithium reagent had been prepared by Issleib and Tzschah from dimethylphosphine and phenyllithium.<sup>7</sup> However, as the dimethylphosphine itself must be made from a dimethylhalophosphine, it seemed to us more direct to treat lithium with dimethylchlorophosphine. The procedure that Hewertson and Watson used to prepare LiP(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was adapted to our purposes<sup>8</sup>



The intermediate (CH<sub>3</sub>)<sub>2</sub>PCl was prepared by the method of Burg and Slota.<sup>9</sup>

pcs was prepared by adding CH<sub>3</sub>SCH<sub>2</sub>Cl to (CH<sub>3</sub>)<sub>2</sub>PLi in tetrahydrofuran and separating by fractional condensation. The pure material is a water-clear, very spontaneously flammable liquid, bp 45° (8 mm) (5 mm vapor pressure at 28°) which appears indefinitely stable in glass ampoules. It is soluble in chloroform, methylene chloride, and tetrahydrofuran.

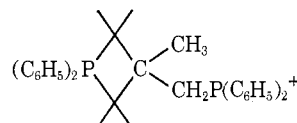
In a similar way pcn was prepared, but it could only

be isolated in tetrahydrofuran solution on distillation, presumably because of azeotrope formation.

ncs, first prepared by a Mannich reaction,<sup>10</sup> was readily synthesized from dimethylamine and chloromethyl methyl sulfide. It is a clear liquid, bp 65° (100 mm).

Toward nucleophiles pcs, pcn, and ncs were very reactive. With methyl iodide pcs and ncs form monomethyl iodides exclusively with the methyl on phosphorus and nitrogen, respectively. The site of methylation was determined from nmr peak intensities and, with pcs, by independent synthesis of CH<sub>3</sub>pcs + Cl<sup>-</sup> from trimethylphosphine and chloromethyl methyl sulfide in acetonitrile. Contrariwise, pcn did not monoalkylate cleanly at one site, for the product had nmr absorption in addition to that of authentic CH<sub>3</sub>pcn<sup>+</sup> prepared independently. It is concluded that methylation produces a mixture of P- and N-monomethylated products.

The methylated cations CH<sub>3</sub>pcs<sup>+</sup>, CH<sub>3</sub>pcn<sup>+</sup>, and CH<sub>3</sub>ncs<sup>+</sup> are potentially useful cationic ligands for synthesis of new metal coordination complexes. Because of their positive charge, ligation would lead to a charge buildup atypical of group 5 and 6 ligands. Berglund and Meek<sup>11</sup> report a diphosphorus ligand of this type



and several cobalt complexes prepared with it. We have also prepared two potentially chelating cationic ligands, (CH<sub>3</sub>SCH<sub>2</sub>)<sub>2</sub>P(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> and (CH<sub>3</sub>SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>, but have not studied their complexing properties.

Only one of the cationic ligands was examined for nucleophilic properties; viz., CH<sub>3</sub>pcn<sup>+</sup> in chloroform at 50° was methylated by methyl iodide to form CH<sub>3</sub>pcn-CH<sub>3</sub><sup>+</sup>.<sup>2</sup>

CH<sub>3</sub>pcs<sup>+</sup>, CH<sub>3</sub>ncs<sup>+</sup>, and CH<sub>3</sub>pcn<sup>+</sup> are basic toward diborane. Adducts of the first two rearrange apparently by 1,3 hydride shifts (*vide infra*). The borane

- (3) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).  
 (4) (a) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964);  
 (b) A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965).  
 (5) A. B. Burg and R. A. Sinclair, *ibid.*, **88**, 5354 (1966).  
 (6) H. R. Hays and T. J. Logan, *J. Org. Chem.*, **31**, 3391 (1966).  
 (7) K. Issleib and A. Tzschah, *Chem. Ber.*, **93**, 1852 (1960).  
 (8) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).  
 (9) A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

(10) W. P. Webb, U. S. Patent 2,283,515 (1958).

(11) D. Berglund and D. W. Meek, *J. Am. Chem. Soc.*, **90**, 518 (1968).

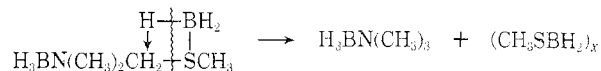
adduct of  $\text{CH}_3\text{pcn}^+$ , however, is "stable" and is the first example of a borane cation with a  $\text{BH}_3$  moiety,  $(\text{CH}_3)_3\text{-PCH}_2\text{N}(\text{CH}_3)_2\text{BH}_3^+$ . The hexafluorophosphate salt is sparingly water soluble so it is possible to purify the cation *via* this salt. Because hydrolysis is noticeable above  $40\text{--}50^\circ$ , it is necessary to recrystallize the salt below  $50^\circ$ , working rapidly. No significant contamination with the starting cation is to be expected since  $\text{CH}_3\text{pcn}^+\text{PF}_6^-$  is much more soluble. The structure assignment is based upon analyses and spectral data. There is a sharp infrared absorption at  $2800\text{ cm}^{-1}$  for  $\text{CH}_3\text{pcn}^+$  that may be assigned to a symmetrical C-H stretching motion of an  $>\dot{\text{N}}\text{CH}_3$  group. Brannholtz, Ebsworth, Mann, and Sheppard<sup>12</sup> have shown experimentally that N-methyl compounds with trivalent nitrogen have a symmetrical stretch in the  $2760\text{--}2820\text{-cm}^{-1}$  spectral region while similar N-methyl compounds with tetravalent nitrogen do not. That the borane adduct  $\text{CH}_3\text{pcnBH}_3^+$  does not have an infrared absorption in this region supports its formulation with tetravalent nitrogen, and this observation completes a rather convincing argument that the spectral assignment and the proposed structures are correct. In the proton magnetic resonance spectra of  $\text{CH}_3\text{pcn}^+$  and  $\text{CH}_3\text{pcnBH}_3^+$  the methylene PCH coupling constant was found to increase by 60% on coordination of the borane, an increase that exactly paralleled the change in going from  $\text{CH}_3\text{pcn}^+$  to  $\text{CH}_3\text{pcnCH}_3^{2+}$ .

Reactions of the new *gem* diligands with diborane were also explored. Stable monoborane adducts of *pcn*, *pcs*, and *ncs* were isolated. Borane bonding to phosphorus in  $\text{H}_3\text{B-pcn}$  and  $\text{H}_3\text{B-pcs}$  was assigned because the phosphorus-methyl proton resonances were shifted more downfield than the other proton resonances on coordination with borane. Further evidence of phosphorus bonding is the observed enhanced PCH coupling constants. (Without exception it was observed that quaternization of phosphorus led to greater PCH coupling.) An absorption at  $2790\text{ cm}^{-1}$  in the infrared spectrum of  $\text{H}_3\text{Bpcn}$  also conclusively demonstrates the presence of trivalent nitrogen in this compound, based upon the argument previously advanced. The linkage of boron to *pcn* neatly illustrates the greater basicity of phosphorus over nitrogen toward borane. Since both sites are in the same molecule, there is no ambiguity arising from solvent factors and experimental technique.

Only *pcn* formed a stable 1:1 diborane adduct. The adduct is a nonvolatile white solid, soluble in tetrahydrofuran and chloroform (with decomposition). The simple bis-borane adduct structure,  $\text{H}_3\text{BpcnBH}_3$ , is favored for this compound as opposed to the symmetrical salt structure,  $\text{H}_2\text{Bpcn}^+\text{BH}_4^-$ , since the ir spectrum does not have the strong bending absorption of  $\text{BH}_4^-$  in the  $1070\text{--}1170\text{-cm}^{-1}$  region.

The reaction of *ncs* and diborane at 1:1 stoichiometry apparently produced the  $\text{ncs}\cdot 2\text{BH}_3$  adduct as a readily hydrolyzable liquid which did not react with methyl

iodide. It was very unstable even at room temperature and formed gross quantities of trimethylamine-borane, possibly by a 1,3 hydride shift with cleavage of the carbon-sulfur bond.



Attempts to methylate *scnBH}\_3 led to interesting results. Methyl iodide reacted to produce a poorly defined, saltlike material which analyzed approximately for  $\text{H}_3\text{BncsCH}_3^+\text{I}^-$ . When this product was treated with pyridine and worked up in water, some  $\text{pyBH}_2\text{N}(\text{CH}_3)_3^+$  cation was isolated (as the hexafluorophosphate salt). Thus the chemical nature of the methylation product was not that expected for  $\text{H}_3\text{BncsCH}_3^+$ . Even more enigmatic was the behavior of the methylation product with water. Hydrogen was released, and upon addition of hexafluorophosphate there precipitated small quantities of the hexafluorophosphate of the bis-borane cation  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{SCH}_3^+$ .<sup>13</sup>*

A tentative rationale of the methylation reaction suggests that the cation  $\text{H}_3\text{BncsCH}_3^+$  is formed, and it then rearranges by means of a 1,3 hydride shift with cleavage of a carbon-sulfur bond to produce  $(\text{CH}_3)_3\text{NBH}_2\text{S}(\text{CH}_3)_2^+\text{I}^-$ . The proton resonance spectrum of the methylated product in chloroform could be completely accounted for by a mixture of unreacted  $\text{H}_3\text{Bncs}$ , with some  $(\text{CH}_3)_3\text{NBH}_2\text{S}(\text{CH}_3)_2^+$ <sup>14</sup> and  $(\text{CH}_3)_3\text{NBH}_2\text{I}$ . Both of the postulated products are known to react with pyridine to form  $(\text{CH}_3)_3\text{NBH}_2\text{py}^+$ . The  $\text{H}_3\text{Bncs}$  impurity might be expected to undergo a 1,3 hydride shift to form  $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_3$  during the hydrolysis, and thus the two components  $(\text{CH}_3)_3\text{NBH}_2\text{SCH}_3$  and  $(\text{CH}_3)_3\text{-NBH}_2\text{I}$  would be present and these are known to form the bis-borane cation.

### Experimental Details

Owing to their flammability, dimethylphosphino compounds were handled under an inert atmosphere or in a high-vacuum line.

**Lithiodimethylphosphine.**—Chlorodimethylphosphine, 4.5 g (0.047 mol), was condensed under vacuum at  $-78^\circ$  into a round-bottomed flask equipped with a reflux condenser and magnetic stirring bar and containing 1 g of lithium foil and 30 ml of tetrahydrofuran. On warming to near  $0^\circ$ , under an atmosphere of argon, an exothermic reaction began. (In larger scale preparations external cooling had to be applied to prevent violence.) After the reaction subsided, the mixture was refluxed for 2 hr to complete the cleavage of the tetramethyldiphosphine. Any diphosphine not removed will contaminate the final product since it has a similar basicity and volatility to the ultimate products sought. The yield was determined by evaporating a 1-ml aliquot to dryness and hydrolyzing in the vacuum line. The evolved dimethylphosphine was measured as a gas and identified from its infrared spectrum. Yields ranged near 70%.

**Dimethylchlorophosphine.**—The intermediate  $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2$  was obtained from dimethylaminodichlorophosphine and methylmagnesium bromide in ether; 59% yield.<sup>9</sup> A typical conversion to the title compound is given.

A 3.85-g portion (36.7 mmol) of  $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2$  in a 50-ml

(12) J. R. Brannholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 2780 (1958).

(13) R. J. Rowatt and N. E. Miller, *J. Am. Chem. Soc.*, **89**, 5509 (1967).

(14) This cation was prepared independently in this laboratory by Mr. Gary King from methyl iodide and trimethylamine-methylthioborane.

round-bottomed flask equipped with a magnetic stirring bar was exposed to dry gaseous hydrogen chloride (73.4 mmol) until absorption ceased. Then the mixture was allowed to stir several hours at room temperature and the product was trapped by passing the volatile material through a  $-78^\circ$  U tube; yield, 3.4 g (95%). This reaction proved more troublesome with increased scale. The critical experimental parameter appears to be stirring, because good yields were obtained only when efficient mechanical stirring was provided. It would seem that in the first stages of the reaction dimethylammonium chloride coats over the  $(\text{CH}_3)_2\text{PN}(\text{CH}_3)_2$  reactant and removes it from further contact with the hydrogen chloride. The stirring would then break the coating and provide contact again.

$(\text{CH}_3)_2\text{PCH}_2\text{N}(\text{CH}_3)_2$ , *pcn*.—To a slurry of 0.53 g (5.55 mmol) of chloromethyl dimethylamine in 20 ml of tetrahydrofuran contained in a 50-ml flask equipped with a stirring bar was added with stirring 8 ml of lithiodimethylphosphine solution in tetrahydrofuran (0.74 mmol/ml). The addition was made dropwise using a syringe while the flask was kept at  $0^\circ$ . The mixture was stirred for 1 hr at  $0^\circ$  and then 15 min at  $30^\circ$ . Volatile contents were fractionated through U traps at  $-30$ ,  $-40$ ,  $-50$ , and  $-78^\circ$ . Separation of *pcn* from solvent was not complete, for the contents of the  $-30$  and  $-50^\circ$  traps were not homogeneous and contained tetrahydrofuran; nevertheless this solution of  $(\text{CH}_3)_2\text{NCH}_2\text{P}(\text{CH}_3)_2$  in tetrahydrofuran was judged satisfactory for the study of its chemistry.

$\text{CH}_3\text{SCH}_2\text{P}(\text{CH}_3)_2$ , *pcs*.—A solution of 9.8 mmol of lithiodimethylphosphine in 20 ml of tetrahydrofuran was placed in a 100-ml round-bottomed flask equipped with a magnetic stirring bar and an addition funnel. Under dry nitrogen a solution of 0.85 g (1.0 mmol) of chloromethyl methyl sulfide in 5 ml of tetrahydrofuran was added dropwise at  $0^\circ$  with stirring. After addition was completed, the mixture was stirred an additional 2 hr at room temperature, and the volatile material was fractionated through a series of U traps at  $-20$ ,  $-30$ ,  $-50$ , and  $-78^\circ$ . Most of the product stopped at the  $-20^\circ$  trap. It had a 28° vapor pressure of 5 mm; yield, 0.61 g (56%). Characterization was based on its nmr spectrum and the chemical analysis of its borane adduct. Because the pure liquid flamed instantly on exposure to air, no attempt was made to analyze the product or take its infrared spectrum.

$(\text{CH}_3)_2\text{NCH}_2\text{SCH}_3$ , *ncs*.—At  $-78^\circ$ , 24 g (0.25 mol) of chloromethyl methyl sulfide was added to 22 g (0.5 mol) of dimethylamine with stirring. Then 150 ml of dry ether was added to the mixture and stirring was continued for 2 hr, allowing the temperature to rise to that of the room. The solid was filtered, and the filtrate was evaporated to a yellow liquid which slowly formed crystals (apparently these were dissolved salts). This liquid was treated with water and the insoluble oil was separated, dried over magnesium sulfate, and distilled; yield, 7.9 g (35%) of colorless liquid, bp  $65^\circ$  (100 mm). *Anal.* Calcd for  $\text{CH}_3\text{SCH}_2\text{N}(\text{CH}_3)_2$ : C, 45.7; H, 10.5; N, 13.3. Found: C, 46.3; H, 10.4; N, 13.5.

Alkylation proceeded readily on addition of an equivalent amount of alkyl halide to a solution of ligand in ether or pentane. The precipitated salts from the reactions with methyl iodide were nearly analytically pure. Conversion to the slightly soluble hexafluorophosphate salts was accomplished by addition of saturated ammonium hexafluorophosphate solution to the chloride or iodide salts. *Anal.* Calcd for  $(\text{CH}_3)_3\text{PCH}_2\text{SCH}_3^+\text{I}^-$  (not recrystallized): C, 22.7; H, 5.5; S, 12.1; P, 11.7. Found: C, 21.3; H, 4.6; S, 11.3; P, 11.0. Calcd for  $(\text{CH}_3)_3\text{NCH}_2\text{SCH}_3^+\text{PF}_6^-$ : C, 22.6; H, 5.3; S, 12.1; N, 5.3. Found: C, 24.0; H, 5.0; S, 13.1; N, 5.7. Calcd for  $(\text{CH}_3\text{SCH}_2)_2\text{N}(\text{CH}_3)_2^+\text{PF}_6^-$ : C, 23.1; H, 5.2; N, 4.5; S, 20.6. Found: C, 24.4; H, 5.4; N, 4.3; S, 23.9. Calcd for  $(\text{CH}_3\text{SCH}_2)_2\text{P}(\text{CH}_3)_2^+\text{PF}_6^-$ : C, 22.0; H, 4.9; S, 19.5. Found: C, 23.1; H, 4.8; S, 18.2.

Independent synthesis of  $(\text{CH}_3)_3\text{PCH}_2\text{SCH}_3^+$  was accomplished by the reaction of trimethylphosphine (53 mmol) with chloromethyl methyl sulfide (83 mmol) at room temperature for 1 week. Volatile material was removed under vacuum and the residue was

crystallized from methylene chloride to give  $(\text{CH}_3)_3\text{PCH}_2\text{SCH}_3^+\text{Cl}^-$  (8 g, 90%) as white crystals. The  $\text{PF}_6^-$  salt prepared by metathesis had an infrared spectrum identical with that of the cation salt obtained initially from *pcs* and methyl iodide.

$(\text{CH}_3)_3\text{PCH}_2\text{N}(\text{CH}_3)_2^+$  was prepared as the chloride by heating trimethylphosphine (10.5 mmol) and "chloromethyl dimethylamine"<sup>15</sup> (1.94 g, 10 mmol) in 30 ml of acetonitrile for 20 hr at  $54^\circ$ . The solvent was removed and the residue was recrystallized twice from methylene chloride-pentane. *Anal.* Calcd for  $(\text{CH}_3)_3\text{PCH}_2\text{N}(\text{CH}_3)_2^+\text{Cl}^-$ : C, 42.4; H, 10.1; N, 8.3. Found: C, 40.5; H, 10.1; N, 8.3.

The dipositive cation  $(\text{CH}_3)_3\text{PCH}_2\text{N}(\text{CH}_3)_2^{2+}$  was prepared from excess methyl iodide and 64 mg (0.32 mmol) of  $\text{CH}_3\text{pcn}^+\text{Cl}^-$  in 4 ml of chloroform by heating 3 days at  $50^\circ$  in a sealed tube. After solvent was removed, the residue was treated with ammonium hexafluorophosphate to give 126 mg of white salt, 77%. *Anal.* Calcd for  $(\text{CH}_3)_3\text{PCH}_2\text{N}(\text{CH}_3)_2^{2+}(\text{PF}_6^-)_2$ : C, 19.1; H, 4.6; N, 3.2; P, 21.2. Found: C, 18.8; H, 4.2; N, 3.5; P, 18.5.

To prepare  $(\text{CH}_3)_3\text{PCH}_2\text{N}(\text{CH}_3)_2\text{BH}_3^+\text{PF}_6^-$ , a slurry of 99 mg (0.58 mmol) of  $\text{CH}_3\text{pcn}^+\text{Cl}^-$  in 20 ml of ether was stirred with 1 mmol of diborane at room temperature for 20 hr. The non-volatile product was dissolved in water and metathesized to the sparingly soluble hexafluorophosphate that was collected and recrystallized from  $50^\circ$  water. *Anal.* Calcd for  $(\text{CH}_3)_3\text{PCH}_2\text{N}(\text{CH}_3)_2\text{BH}_3^+\text{PF}_6^-$ : C, 24.6; H, 6.8; P, 21.2; N, 4.8; B, 3.7. Found: C, 24.6; H, 7.1; P, 20.3; N, 4.8; B, 0.7. The boron analysis is the average of duplicate analyses and for some reason is spurious. A hydrolytic hydrogen value of  $9.8 \times 10^{-4}$  mmol/mg run in dilute sulfuric acid with platinum black compared well with  $10.2 \times 10^{-4}$  mmol/mg expected. Since the hydrogen can only come from B-H bonds, it is certain that the analytical boron is not correct.

Borane adducts were simply obtained by combining stoichiometric amounts of the ligands with diborane in a vacuum line using pentane or ether as solvent. *Anal.* Calcd for  $\text{H}_3\text{BP}(\text{CH}_3)_2\text{CH}_2\text{SCH}_3^{16}$ : C, 35.3; H, 10.4; S, 23.6; P, 22.8; B, 7.6. Found: C, 35.7; H, 9.8; S, 23.6; P, 23.1; B, 7.8. Calcd for  $\text{H}_3\text{BP}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2$ : C, 45.2; H, 12.9. Found: C, 41.9; H, 12.6. Calcd for  $\text{H}_3\text{BP}(\text{CH}_3)_2\text{CH}_2\text{N}(\text{CH}_3)_2\text{BH}_3$ : C, 40.9; H, 13.7; N, 9.5; B, 14.8. Found: C, 40.8; H, 13.7; N, 10.2; B, 13.3. Calcd for  $\text{H}_3\text{BN}(\text{CH}_3)_2\text{CH}_2\text{SCH}_3$ : C, 40.4; H, 11.9; N, 11.8; S, 26.9. Found: C, 40.4; H, 12.1; N, 12.4; S, 21.1.

Methylation of  $\text{H}_3\text{Bncs}$ .—Addition of 0.35 ml (5.6 mmol) of methyl iodide to 670 mg (5.63 mmol) of  $\text{H}_3\text{Bncs}$  resulted in an immediate precipitation of a white solid. Methylene chloride (3 ml) was added and the mixture was stirred for 1 hr. The non-volatile product after solvent evaporation (under vacuum) was 990 mg (66%) of a tacky semisolid. After pumping 12 hr under high vacuum, it was analyzed. *Anal.* Calcd for  $\text{H}_3\text{BN}(\text{CH}_3)_2\text{CH}_2\text{S}(\text{CH}_3)_2^+\text{I}^-$ <sup>17</sup>: C, 23.0; H, 6.6; N, 5.4; S, 12.6; B, 4.1. Found: C, 24.9; H, 6.7; N, 6.7; S, 11.6; B, 2.6.

Addition of water to the tacky material from a 7.5-mmol run effected solution with gas (hydrogen) evolution, and subsequent addition of ammonium hexafluorophosphate precipitated  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{SCH}_3^+\text{PF}_6^-$ ; yield, 244 mg (20%). An analytical sample was obtained by recrystallization from hot water. *Anal.* Calcd for  $[(\text{CH}_3)_3\text{NBH}_2]_2\text{SCH}_3^+\text{PF}_6^-$ : C, 25.0; H, 7.2; N, 8.4. Found: C, 25.1; H, 7.4; N, 9.6.

(15) H. Böhme, W. Lehnert, and G. Keitzer, *Chem. Ber.*, **91**, 340 (1958).

(16) It is a practical observation that borane adducts are much better suited for analytical characterization of ligands than are alkylated salts, especially with phosphorus-containing ligands. Carbon and hydrogen analyses are very unpredictable with salts but uniformly good with adducts. One is led to suspect that the borane provides good combustion at the basic atom sites.

(17) There is no evidence for this compound, see discussion. The residue analyzes approximately for this composition. Present evidence favors a mixture of  $(\text{CH}_3)_3\text{NBH}_2\text{I}$  and  $(\text{CH}_3)_3\text{NBH}_2\text{S}(\text{CH}_3)_2^+\text{I}^-$ .

If pyridine is added to the reaction mixture before the solvent is removed, the nonvolatile residue has much  $\text{pyBH}_2\text{N}(\text{CH}_3)_3^+$  present. For example, addition of  $\text{PF}_6^-$  to a 8.1 mmol size run led to precipitation of 1.3 g (58%) of salt. After recrystallization the salt had an infrared spectrum identical with that of an ana-

lyzed sample of  $(\text{CH}_3)_3\text{NBH}_2\text{py}^+\text{PF}_6^-$ . *Anal.* Calcd: C, 32.5; H, 4.8; N, 9.5. Found: C, 32.2; H, 5.3; N, 9.3.

**Acknowledgment.**—Partial support by a grant from the National Science Foundation is appreciated.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,  
THE UNIVERSITY, SHEFFIELD S3 7HF, ENGLAND

## Transition Metal Dithiolene Complexes. IX.<sup>1</sup> Manganese $\pi$ -Cyclopentadienyl(nitrosyl)dithiolene and Related Metal Complexes

By J. A. McCLEVERTY, T. A. JAMES,<sup>2</sup> AND E. J. WHARTON<sup>2</sup>

Received December 26, 1968

The preparation of new monodithiolene complexes  $\pi\text{-C}_5\text{H}_4\text{RMn}(\text{NO})(\text{S-S})^z$ , where R = H or  $\text{CH}_3$  and  $z = 0$  or  $-1$  and where S-S represents  $\text{S}_2\text{C}_2(\text{CN})_2$ ,  $\text{S}_2\text{C}_6\text{H}_5\text{CH}_3$ , or  $\text{S}_2\text{C}_6\text{Cl}_4$ , is reported. The analogous dithiocarbamates,  $\pi\text{-C}_5\text{H}_4\text{RMn}(\text{NO})\text{S}_2\text{CNR}'_2$ , where R' =  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , and 1,1-dicyanoethylene-2,2-dithiolenes,  $\pi\text{-C}_5\text{H}_4\text{RMn}(\text{NO})\text{S}_2\text{C}=\text{C}(\text{CN})_2^-$ , are also described. These complexes have been investigated by voltammetry and it is shown that the 1,2-dithiolenes exist as part of a three-membered electron-transfer series,  $z = +1, 0$ , or  $-1$ , the 1,1-dithiolene is part of at least a two-membered series,  $z = 0$  or  $-1$ , and the dithiocarbamates can be oxidized to monocations; the complexes have been further characterized by ir and esr spectroscopy. The voltammetric properties of certain  $\pi$ -cyclopentadienyldicyano-1,2-dithiolenes,  $(\pi\text{-C}_5\text{H}_5)_2\text{Ti-S}_2\text{C}_2(\text{CN})_2$ ,  $\pi\text{-C}_5\text{H}_5\text{MS}_4\text{C}_4(\text{CN})_4^-$  (M = Mo, W, or Ti), and  $\pi\text{-C}_5\text{H}_5\text{CoS}_2\text{C}_2(\text{CN})_2$ , are reported, and evidence for  $\pi\text{-C}_5\text{H}_5\text{CoS}_2\text{C}_2(\text{CN})_2^-$  is presented.

In this article, we describe the synthesis and electron-transfer reactions of manganese  $\pi$ -cyclopentadienyl(nitrosyl)-1,2-dithiolenes and related sulfur complexes. The reduction of  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{NO})\text{S}_2\text{C}_2(\text{CF}_3)_2^0$  to  $\text{Mn}(\text{NO})\text{S}_4\text{C}_4(\text{CF}_3)_4^{2-}$  using ethanolic hydrazine<sup>3</sup> first drew our attention to this class of compounds, which we represent generally as  $\pi\text{-C}_5\text{H}_4\text{RMn}(\text{NO})(\text{S-S})^z$ ,<sup>4</sup> as potential intermediates in the syntheses of manganese(nitrosyl)bisdithiolenes,  $\text{Mn}(\text{NO})(\text{S-S})_2^z$ . Because the latter group of compounds were of interest to us in a continuing study of five-coordinate nitrosylbisdithiolene complexes, but were relatively inaccessible synthetically, we initiated a program of research designed to produce and investigate the properties of the intended intermediates  $\pi\text{-C}_5\text{H}_4\text{RMn}(\text{NO})(\text{S-S})^z$ . At the same time, we prepared several similar compounds containing 1,1-dicyanoethylene-2,2-dithiolate and dimethyl- and diethyldithiocarbamates. Some of our results have been reported in a preliminary communication,<sup>5</sup> but the use of these cyclopentadienyl complexes in the preparation of  $\text{Mn}(\text{NO})(\text{S-S})_2^z$  will be described elsewhere.

Bis- and tris-dithiolene complexes readily undergo electron-transfer reactions,<sup>6</sup> but this behavior is not well established in systems containing only one dithiolato ligand. Our voltammetric study of the new cyclopentadienyl complexes shows that these monodithiolenes can readily undergo reversible one-electron-transfer reactions, and we have used the electrochemical results to design synthetic routes to the various oxidized and reduced species which we have detected. In addition, we have investigated the electron-transfer properties of the  $\pi$ -cyclopentadienyldicyano-1,2-dithiolenes described in part I of this series.<sup>7</sup>

### Experimental Section

Disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate,  $\text{Na}_2\text{S}_2\text{C}_2(\text{CN})_2$ ,<sup>8</sup> tetrachlorobenzene-1,2-dithiol,<sup>1</sup> and disodium 1,1-dicyanoethylene-2,2-dithiolate<sup>9</sup> were prepared by published methods, as were  $[\pi\text{-C}_5\text{H}_5\text{Mn}(\text{NO})(\text{CO})_2][\text{PF}_6]$  and  $[\pi\text{-C}_5\text{H}_4\text{CH}_3\text{Mn}(\text{NO})(\text{CO})_2][\text{PF}_6]$ .<sup>10</sup> Toluene-3,4-dithiol was purchased from Eastman Kodak, and sodium dimethyl- and diethyldithiocarbamate hydrates were from BDH.

Conductivity measurements were determined at room temperature (22°) using a Philips conductivity meter. Magnetic measurements were made at room temperature by the Gouy method, nmr spectra were obtained in solution using a Varian A-60 spectrometer, and esr spectra were obtained in solution at room temperature using a Varian V-4500 X-band spectrometer. Electronic and infrared spectra were recorded with Unicam SP700 and SP100 and Infracord 457 spectrophotometers.

Voltammetric data were obtained using a Heathkit Model EUW-401 polarograph with a platinum electrode rotating at 620 rpm. Dichloromethane was employed as the solvent and  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ClO}_4]$  as the base electrolyte. All measurements were standardized against a saturated calomel electrode containing 1 M aqueous LiCl.

All melting points are uncorrected, and yields are calculated

(1) Part VII: E. J. Wharton and J. A. McCleverty, *J. Chem. Soc., A*, in press.

(2) Supported by the Science Research Council of Great Britain.

(3) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

(4) The use of the abbreviation (S-S) is meant to refer to a bidentate sulfur ligand and not to diatomic sulfur.

(5) J. A. McCleverty, T. A. James, E. J. Wharton, and C. J. Winscom, *Chem. Commun.*, 933 (1968).

(6) References in J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); and also in G. N. Schrauzer, *Transition Metal Chem.*, **4**, 229 (1968).

(7) J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).

(8) G. Bähr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955); an improved synthesis is described in ref 7.

(9) R. Gomper and E. Kutler, *Angew. Chem.*, **74**, 251 (1962).

(10) R. B. King, "Organometallic Syntheses," Vol. I, J. J. Eisch and R. B. King, Ed., Academic Press, New York, N. Y., 1965, p 111.