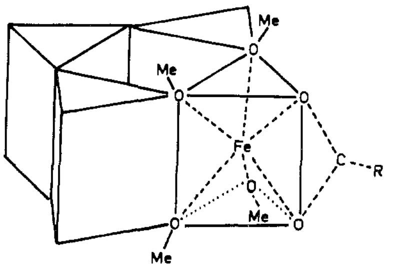
coordinate iron(III) is a cluster of four trigonal-prismatic iron atoms sharing parallel edges (I).



I

Registry No. Fe(*m*-methylbenzoate)(OMe)$_2$, 50803-72-0; Fe(*m*-methoxybenzoate)(OMe)$_2$, 50803-73-1; Fe(*m*-chlorobenzoate)(OMe)$_2$, 50803-70-8; Fe(*m*-nitrobenzoate)(OMe)$_2$, 50803-71-9.

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Bis(trifluoromethyl)phosphino Derivatives of *closo*-2,4-Dicarbaheptaborane(7)

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The derivative chemistry of the lighter carboranes is worthy of considerable further development; for instance, their phosphino derivatives should be interesting either as ligands for transition element complexes or for making new inorganic polymer systems. A major difficulty is the relatively high reactivity of the lighter carboranes, such that they may easily convert to intractable resins under conditions (*e.g.*, presence of a base) tolerated by the larger carboranes. For example, the carbon base $LiC(CH)B_5H_5$ is seriously unstable in solution, and $(LiC)_2B_5H_5$ may be largely destroyed in attempts to make derivatives from it,[1] whereas alkali "salts" of $C_2B_{10}H_{12}$ can be used for high-yield syntheses of many derivatives.[2]

The present study led to the synthesis of three derivatives in which the $(CF_3)_2P$ group is attached to carbon in the $C_2B_5H_7$ cage. Their stability may well be due in part to the lack of effective base action by the $(CF_3)_2P$ group. However, extensive destruction of the Li-C bases during the syntheses led to poor yields of $(CF_3)_2PC(CH)B_5H_5$ or $[(CF_3)_2PC]_2B_5H_5$. The difficulties may have been like those encountered when HCl attacked $(LiC)_2B_5H_5$ to give only 11% recovery of $C_2B_5H_7$, in contrast to better than 70% yields of $(CH_3C)_2B_5H_5$ by action of methyl iodide.[1] The base $LiC(CH_3C)B_5H_5$ was relatively satisfactory, reacting with $(CF_3)_2PCl$ to give a 29% yield of $(CF_3)_2PC(CH_3C)B_5H_5$. In this case, the methyl group was expected to minimize polymerization; and since the initially insoluble $LiC(CH_3C)B_5H_5$ was wholly dissolved during the reaction, occlusion did no harm.

Syntheses and Characterizations

Methods. All volatile substances were managed by means of Stock-type high-vacuum techniques. The carborane $C_2B_5H_7$ was isolated from a mixture of light carboranes kindly given to us by Drs. R. E. Williams and J. F. Ditter, of Chemical Systems, Inc. The method of isolation included removal of B_5H_9 by the action of alcohols or tertiary amines. The final purification of each reaction product was by high-vacuum fractional condensation.

The Monophosphino Derivative. A commercial hexane solution of 2.0 mmol of butyllithium was mixed stepwise into a 1:1 ether-hexane solution of 1.0 mmol of $C_2B_5H_7$, at −23°. The mixture was held at −23° for 3 hr and then stirred for 15 hr at 25°. The solvent was removed from the precipitated $(LiC)_2B_5H_5$ and replaced by 2 ml of fresh ether, followed by 1.0 mmol of $(CF_3)_2PI$. The mixture was stirred first at −95° and then at 25° for 1 hr. Now the second Li-C bond was converted to H-C by action of 1.1 mmol of HCl, added at −196° and allowed to react during slow warming to 25°, with stirring. It now was possible to isolate 0.20 mmol of an equimolar mixture of $C_2H_5OP(CF_3)_2$ and $(CF_3)_2PC(CH)B_5H_5$. The ethoxyphosphine (formed by unavoidable cleavage of the ether and hard to remove by distillation) was absorbed by Al_2Cl_6 (10 min, 25°), with some destruction of the desired product: final yield, 0.05 mmol, or 5%. When $(CF_3)_2PCl$ was used for the action upon $(LiC)_2B_5H_5$ (in 1:1 molar ratio), the ether cleavage did not occur, but both the mono- and diphosphino derivatives were formed, in far inferior yields.

The new compound $(CF_3)_2PC(CH)B_5H_5$ showed an equilibrium vapor pressure of 10 mm at 25°. Its formula was confirmed by a mass spectrographic parent peak pattern having the right mix of boron isotopic effects. Its infrared and nmr spectra proved to be consistent with the assumed structure.

The Bis(phosphino)carborane. The dilithium compound from 1.0 mmol of $C_2B_5H_7$ was treated with 2.0 mmol of $(CF_3)_2PCl$ in diethyl ether, during slow warming from −23 to +25°, with good stirring. The yield of $[(CF_3)_2PC]_2B_5H_5$ (authenticated by its mass, nmr, and infrared spectra) was 0.11 mmol, or 11%. Its volatility as a pure liquid was 0.5 mm at 0° or 2.0 mm at 25°. A trace of $(CF_3)_2PC(CH)B_5H_5$ was found as a by-product.

We next tried a procedure based upon a very successful method for making $[(CH_3)_2SiClC]_2B_5H_5$:[3] stepwise addition of 2.1 mmol of $(LiC)_2B_5H_5$ (slurry in 3 ml of ether-hexane) to 4.6 mmol of $(CF_3)_2PI$ in 1 ml of hexane (2 hr, −23°, stirred; 0.5 hr, 25°, stirred); yield of $[(CF_3)_2PC]_2B_5H_5$, 88.5 mg, or 10%.

The *C*-Methylphosphinocarborane. A 1.07 mmol sample of $CH_3C(CH)B_5H_5$, prepared according to the literature,[1] was treated with 1.32 mmol of LiC_2H_5, in 2 ml of hexane with 1 ml of ether. The mixture was stirred for 15 hr at 25°. After vacuum removal of the solvent, the white residue was suspended in 2 ml of fresh ether at −95°. Treatment with 1.2 mmol of $(CF_3)_2PCl$, during gradual warming (with periods of constancy at −78 and −23°), led to formation of 0.31 mmol (29% yield) of $(CF_3)_2PC(CH_3C)B_5H_5$, which was easily isolated and confirmed by mass, nmr, and infrared spectra. Vapor pressures: 1.0 mm at −10°, 2.0 mm at 0°, and 7.0 mm at 25°.

Acetonitrile as Solvent. The "salt" $(LiC)_2B_5H_5$, precipitated from the ether-hexane mixture, dissolved completely in CH_3CN, and HCl acted upon the fresh solution to restore

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[1] R. R. Olsen and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 5072 (1970).

[2] Bibliography cited by ref 1.

[3] J. F. Ditter and A. J. Gotcher, Technical Report No. 9, to the Office of Naval Research, Nov. 12, 1973. (Issued by Chemical Systems, Inc., Irvine, Calif. 92705.)

38% of the original $C_2B_5H_7$ (*vs.*11% in ether).[1] However, the fresh solution with 2 $(CF_3)_2PI$ per $(LiC)_2B_5H_5$ produced no phosphinocarboranes.

The ^{11}B nmr spectrum (at 32.1 Mc, with methyl borate as reference) of the fresh solution showed partially superposed doublets at 14 ppm ($J = ca.$ 190 Hz) and 17 ppm ($J = ca.$ 152 Hz) with combined relative intensity 31, a doublet at 42.4 ppm (J = 178 Hz; relative intensity 19), and a doublet at 73.5 ppm (J = 158 Hz; relative intensity 12). Ten minutes later, another scan showed collapse of the downfield doublets into one rough doublet at 18 ppm ("J" = 112 Hz; relative intensity 34), while the 42.4-ppm doublet lost intensity to 9 and the 73.5-ppm doublet gained intensity to 17. The initial spectrum showed a close relation to $C_2B_5H_7$, but it disappeared with an increase of foreign material represented in part by the 73.5-ppm doublet; however, a parallel experiment at this stage failed to yield an intelligible product from the solution. After 24 hr, the solution had become more viscous and showed the wide signal indicative of polymerization. However, a doublet at 70.5 ppm (J = 160 Hz) persisted. The irreversibility of the polymerization was indicated by the failure of HCl to liberate any volatile carborane from the solution. Also, the solute, evacuated at 250°, failed to yield anything volatile.

Hydrogen Iodide with the Dilithium Salt. Although it is clear that $Li_2C_2B_5H_5$ is a very uncertain reagent for syntheses, we were able to obtain a 58% recovery of $C_2B_5H_7$ from it by the action of HI in ether, in contrast to 11% reported for HCl action under similar conditions.[1] This result, taken with the high yields of *C*-methylcarboranes from the action of methyl iodide,[1] might suggest some special advantage in the use of iodides, but $(CF_3)_2PI$ proved to be no better than $(CF_3)_2PCl$ for our purposes.

Nmr Spectra. The nmr spectra of the three new derivatives are compared with those of the parent carborane in Table I.

All of these spectra were recorded by the Varian HA-100 instrument, with δ measured upfield from $(CH_3O)_3B$ or Cl_3CF, or downfield (with minus signs) from tetramethylsilane. Our samples were too small to show the diffuse quartets expected for B-H protons. However, the boron and fluorine spectra (mutually consistent among four compounds) leave no doubt that the three new compounds were C-substitution derivatives of $C_2B_5H_7$.

Infrared Spectra. The Beckman IR 20A instrument was used for infrared characterization of the three new phosphinocarboranes, with expanded scale for accurate frequencies and reference to a well-calibrated IR 7 instrument for verification. The readily observable frequencies (cm^{-1}) are listed below, with relative intensities, defined as $k = (100/PL) \log I_0/I$ for path L and pressure P (both in cm), shown in parentheses.

$(CF_3)_2PC(CH)B_5H_5$: 2960 (3.1), 2920 (3.1), 2635 (16), 1181 (17), 1164 (26), 1151 (15), 1127 (21), 900 (2.0), 852 (1.7), 835 (1.3), 815 (1.2), 708 (1.4), 438 (1.5).

$[(CF_3)_2PC]_2B_5H_5$: 2650 (1.4), 1203 sh (8), 1190 (12), 1170 (20), 1156 (14), 1135 (16).

$(CF_3)_2PC(CH_3C)B_5H_5$: 2953 (1.4), 2891 (0.65), 2635 (11), 2621 sh (9), 1305 (1.9), 1195 (31), 1168 (51), 1155 (26), 1134 (34), 903 (1.5), 863 (1.9), 788 (0.9), 737 (2.7), 588 (1.8), 564 (1.2), 459 (3.4).

Table I. Comparison of Nmr Spectra

	^{11}B doublets			^{19}F doublets		
Compd	δ, ppm	J, Hz	Position of B	δ, ppm	J, Hz	C-H singlets δ, ppm
$C_2B_5H_7$	13.2	187	3			−5.30[a]
	16.2	170	5,6			
	41.7	178	1,7			
$(CF_3)_2PC(CH)B_5H_5$	9.8	182	3	53.6	80	−5.7
	12.5	168	5,6			
	36.7	188	1,7			
$(CF_3)_2PC(CH_3C)B_5H_5$	8.8	180	3	52.7	81	−2.22 (CH_3)
	11.6	172	5,6			
	34.4	180	1,7			
$[(CF_3)_2PC]_2B_5H_5$	8.5	188	3	53.1	79	
	11.1	182	5,6			
	34.0	193	1,7			

[a] R. N. Grimes, *J. Amer. Chem. Soc.*, 88, 1897 (1966). The present ^{11}B spectra agree with his, within experimental error.

Isotopic Patterns in the Mass Spectra. As indicated before, the molecular weight of each phosphinocarborane was represented by a main parent peak corresponding to the isotopic mix $^{10}B^{11}B_4$, with smaller peaks corresponding to $^{11}B_5$, $^{10}B_2{}^{11}B_3$, $^{10}B_3{}^{11}B_2$, $^{10}B_4{}^{11}B$, and $^{10}B_5$. Of further interest is a series of similar clusters of peaks for smaller fragments, from which various atoms and groups had been lost. The most intense of these are described by subtraction of the masses of the atoms and groups lost from the molecular weight parent ion, with relative intensities (based on the molecular weight peak as 100) shown in parentheses. Only the molecular weight (major) peak for each cluster is shown in the following listing.

For $[(CF_3)_2PC]_2B_5H_5$: 421 − F = 402 (10); −2F = 383 (5); −CF_3 = 352 (1); −(F + CF_3) = 333 (5); −$(CF_3)_2P$ = 252 (1); − [2F + $(CF_3)_2P$] = 214 (12); − [CF_3 + $(CF_3)_2P$] = 183 (11); − [2$(CF_3)_2P$] = 83 (24) = $C_2B_5H_5$.

For $(CF_3)_2PC(CH_3C)B_5H_5$: 267 − CH_3 = 252 (22); −(CH_3 + 2F) = 214 (26); −(CH_3 + CF_3) = 183 (22); −$(CF_3)_2P$ = 98 (35); −[CH_3 + $(CF_3)_2P$] = 83 (87) = $C_2B_5H_5$.

For $(CF_3)_2PC(CH)B_5H_5$: 253 − 2F = 215 (220); −CF_3 = 184 (10); −$(CF_3)_2P$ = 84 (190) = $C_2B_5H_6$.

These results were obtained by means of the Hitachi Perkin-Elmer RMU-6 instrument, operating at 20 V. It is interesting that the chief fragmentation concerned the $(CF_3)_2P$ ligand (and loss of CH_3 in one case); removal of H from B or C was too infrequent for appreciable disturbance of the statistical pattern of any cluster. At 80 V, it was difficult to find any of the parent ions, and hydrogen removal was extensive.

Comment. It is evident that any extensive study of the new bis-phosphine $[(CF_3)_2PC]_2B_5H_5$ as a bifunctional ligand for transition elements will be severely limited until a more efficient synthesis can be devised. The prospect remains interesting beacuse of the 2,4 positions of the phosphine groups on the pentagonal bipyramid, raising the question whether chelate action ever will be possible. Bonding strength would be gained by the use of $(CH_3)_2P$ groups instead of $(CF_3)_2P$ groups, but our attempts to attack the dilithium precipitate with $(CH_3)_2PCl$ led to no intelligible product.

Acknowledgment. We gratefully acknowledge generous support by the Office of Naval Research for the exploratory stage of this research and by the National Science Foundation (Grant No. GP-17472) for its completion. Thanks are due also to Dr. Thomas J. Reilly, who recorded the mass spectra of our new compounds.

Registry No. $(CF_3)_2PC(CH)B_5H_5$, 51015-20-4; $[(CF_3)_2PC]_2B_5H_5$, 51015-18-0; $(CF_3)_2PC(CH_3C)B_5H_5$, 51015-19-1; $C_2B_5H_7$, 20693-69-0; $(CF_3)_2PI$, 359-64-8; $(CF_3)_2PCl$, 650-52-2; $CH_3C(CH)B_5H_5$, 23704-80-5.

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Partial Nucleophilic Displacement of Chloride in *mer*-Trichlorotris(triphenylstibine)rhodium(III)

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Chatt, *et al.*, have prepared the orange complexes *mer*-$[RhL_3Cl_3]$ by addition of LR_3 to hot alcoholic $RhCl_3$ ($R_3 = Et_3$, n-Pr_3, n-Bu_3, Me_2Ph, Et_2Ph, L = P) (R = Et_3, n-Pr_3, n-Bu_3, L = As).[1] The trans chlorines are more labile than the chlorine trans to the phosphine and, on treatment with MX in hot acetone or ethanol, complexes of the type *mer*-$[RhL_3ClX_2]$ are formed. Under reflux for extended periods the third chlorine is replaced to give *mer*-$[RhL_3X_3]$ (L = PMe_2Ph, $AsMe_2Ph$; X = NCO, Br, I, N_3, NCS).[2] It is also well-established that, as well as producing complexes of type $[RhL_3Cl_3]$, mono(tertiary arsines) react with $RhCl_3{\cdot}3H_2O$ to yield the chloro-bridged $[Rh_2L_4Cl_6]$ or $[Rh_2L_3Cl_6]$, according to the amount of arsine employed.[1]

We wish to report here the reaction of $RhCl_3{\cdot}3H_2O$ with triphenylstibine in ethanol yields only the product *mer*-$[Rh(SbPh_3)_3Cl_3]$. This product is formed regardless of the ratio of reactants and differs significantly from similar complexes of phosphines and arsines, in that substitution by nucleophiles does not proceed to completion but stops at *mer*-$[Rh(SbPh_3)_3Cl_2X]$ (X = Br, I, NCS, $SnCl_3$).

Table I

Compd	Color	Analyses, % C Calcd	C Found	H Calcd	H Found	Cl Calcd	Cl Found	Other Calcd	Other Found
$[Rh(SbPh_3)_3Cl_3]$	Orange	51.0	50.0	3.5	3.6	8.3	8.3		
$[Rh(SbPh_3)_3Cl_2Br]$	Orange-brown	49.4	49.6	3.4	3.7	5.4	5.7	6.1[a]	6.1
$[Rh(SbPh_3)_3Cl_2I]$	Brown	47.6	47.7	3.3	3.4	5.2	5.4	9.3[b]	9.5
$[Rh(SbPh_3)_3Cl_2(NCS)]$	Orange	51.2	51.0	3.5	3.5	5.5	5.5	1.1[c]	1.1
$[Rh(SbPh_3)_3Cl_2(SnCl_3)]$	Orange	44.4	45.0	3.1	3.3	12.2	12.4		

[a] Bromine. [b] Iodine. [c] Nitrogen.

Table II. Electronic Spectra of the Complexes in Dichloromethane (cm^{-1})[a]

$Rh(SbPh_3)_3Cl_3$	$Rh(SbPh_3)_3Cl_2Br$	$Rh(SbPh_3)_3Cl_2I$	$Rh(SbPh_3)_3Cl_2(NCS)$	$Rh(SbPh_3)_3Cl_2(SnCl_3)$
39,200 (20,900)	39,190 (29,500)	38,580 (24,200)		39,100 (34,100)
31,950 (19,650)	31,250 (15,100)	32,400 (15,800) 27,700 (15,650)	33,300 (13,400)	32,900 (11,700)
25,640 (22,500)	25,300 (9530)	25,000 (13,100)	27,800 (23,200)	26,040 (31,000) 20,900 (1960)

[a] Molar extinction coefficients in parentheses.

Experimental Section

mer-**$[Rh(SbPh_3)_3Cl_3]$.** Rhodium trichloride trihydrate (2.6 g, 0.01 mol) and triphenylstibine (10.6 g, 0.03 mol) in ethanol (150 ml) were stirred under reflux for 3 hr, during which time an orange solid formed. This was filtered while hot and washed with hot ethanol (150 ml). The complex was recrystallized from dichloromethane–ethanol and dried *in vacuo*; yield 11.8 g (89%).

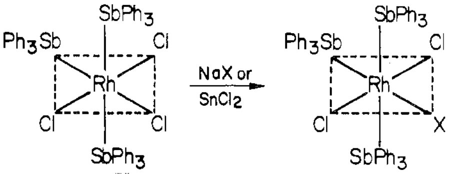
mer-**$[Rh(SbPh_3)_3Cl_2X]$.** To a suspension of *mer*-$[Rh(SbPh_3)_3Cl_3]$ (2.0 g) in ethanol (50 ml) was added a 5 molar equiv of NaX (X = Br, I, SCN) or $SnCl_2$. The mixture was stirred under reflux for 24 hr and filtered while hot. The resulting solids were extracted into dichloromethane, filtered to remove any insoluble material, allowed to crystallize, and dried *in vacuo*; yields ~70–80%.

Physical Measurements. Dipole moments of *mer*-$[Rh(SbPh_3)_3Cl_3]$ (7.4 D) and *mer*-$[Rh(SbPh_3)_3Cl_2Br]$ (7.6 D) were determined in benzene at 25° and calculated as described.[3] Other physical measurements were carried out as previously reported.[4]

Results and Discussion

The reaction of $SbPh_3$ with $RhCl_3{\cdot}3H_2O$ in ethanol was found to yield only one product, the orange *mer*-$[Rh(SbPh_3)_3Cl_3]$. Varying the metal:ligand ratio did not effect the production of any complexes of the type $[Rh_2(SbPh_3)_4Cl_6]$ or $[Rh_2(SbPh_3)_3Cl_6]$ analogous to the arsine complexes.[1] The mer configuration was assigned by a dipole moment measurement in benzene. A value of *ca.* 7 D is expected for a mer complex; fac complexes are associated with moments of *ca.* 11 D.[1]

On refluxing *mer*-$[Rh(SbPh_3)_3Cl_3]$ with NaX (X = Br, I, NCS) or $SnCl_2$ in ethanol we were surprised to find that reaction was complete after only one chlorine, presumably the one trans to antimony, is substituted by the nucleophile to produce complexes of type *mer*-$[Rh(SbPh_3)_3Cl_2X]$ (Table I), *i.e.*



Extended reflux with excess nucleophile did not lead to further substitution. Thus triphenylstibine reverses the substitution trend of analogous phosphine and arsine complexes which at first yield $[RhL_3ClX_2]$ and subsequently $[RhL_3X_3]$. The first and only product of the reactions we carried out yields $[Rh(SbPh_3)_3Cl_2X]$ derivatives.

Table II lists the electronic spectral maxima of the complexes which are characterized by three bands. The highest energy band, *ca.* 39 kK, is probably due to rhodium-antimony charge transfer, and the band *ca.* 32 kK is due to rhodium-halogen charge transfer. The lowest energy absorption is obviously dependent on the nature of X and moves to

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(1) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 2508 (1964).

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

(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959); 4020 (1959).

(4) L. Baracco and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 948 (1972).