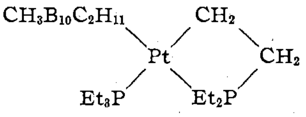
Similar infrared spectra were observed for the entire series of bis[phenyl(methyl)phosphine]bis[methylcarborane(12)]platinum(II) compounds. The peaks characteristic of the carborane cage were observed in each case while the characteristic hydrolysis bands (1630 and 3410 cm^{-1}) increased in intensity as the number of methyl groups on the phosphine was increased.

Magnetic susceptibility data obtained from all the phosphinomethylcarborane(12)–platinum complexes isolated (Guoy) indicate that in every case the complexes are diamagnetic.

General Reaction Procedures for Tri-*n*-butylphosphine Complexes.—The cis and trans isomers of dichlorobis(tri-*n*-butylphosphine)platinum(II) were prepared and characterized according to the method described by Kauffman and Teter.[6] The interaction of methylcarborane(12) with the cis and trans isomers of dichlorobis(tri-*n*-butylphosphine)platinum(II) was accomplished by means of the procedure previously described for the preparation of dichlorobis[methyl(phenyl)phosphine]platinum(II) reactions. Benzene rather than diethyl ether was employed as a solvent for solubility reasons. A small amount [about 5% yield based on the amount of *trans*-dichlorobis(tri-*n*-butylphosphine)platinum(II)] of the trans complex was isolated. This *trans*-bis(tri-*n*-butylphosphine)bis[methylcarborane(12)]platinum(II) complex was susceptible to hydrolysis. Both the OH stretching modes in the infrared and ^{1}H nmr absorptions which are characteristic of the starting methylcarborane(12) [δ 3.5, broad singlet, due to C–H on the carborane(12) cage] grew in intensity when the complex was allowed to remain in air.

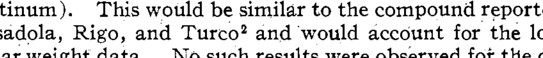
Anal. Calcd for $C_{30}H_{80}B_{20}P_2Pt$: C, 39.42; H, 8.76. Found: C, 39.75; H, 8.30. Molecular weight determined in benzene was 880 (theoretical 913). The melting point was 185 ± 5° dec.

Bresadola, Rigo, and Turco[2] reported that the interaction of methylcarborane(12) with the trans isomer of bis(triethylphosphine)platinum(II) resulted in a product which was formulated as



It is possible that the low yield of *trans*-bis(tri-*n*-butylphosphine)bis[methylcarborane(12)]platinum(II) may be a consequence of the formation of a complex analogous to that reported by Bresadola, Rigo, and Turco,[2] but we were unable to isolate a complex of this composition. The proton nmr spectrum of the complex we did obtain exhibited three resonances, two of which were broad multiplets at δ 1.0 and 1.6 (total intensity 3.1, due to the protons on the *n*-butyl groups). The remaining absorption (δ 2.1, singlet, intensity 1.0) is easily ascribed to the *C*-methyl protons of methylcarborane.

The interaction of *cis*-dichlorobis(tri-*n*-butylphosphine)platinum(II) with methylcarborane(12) was carried out as described for the *trans*-dichlorobis(tri-*n*-butylphosphine)platinum(II) reaction. A pale yellow solid which was very susceptible to hydrolysis was isolated. Attempts to obtain reproducible nmr data from this product were unsuccessful. All attempts to get precise analyses and melting points on this cis compound were unsuccessful. The molecular weight, which was low for the expected methylcarborane(12) complex of dichlorobis(tri-*n*-butylphosphine)platinum(II), is near the theoretical molecular weight for a product formulated as



$$[P(C_4H_9)_3]Pt\left(-C\text{———}C-CH_3 \atop \diagdown\bigcirc\diagup \atop B_{10}H_{10}\right)[P(C_4H_9)_2(C_4H_8)]$$

(where C_4H_8 is a butyl group which is bonded to both phosphorus and platinum). This would be similar to the compound reported by Bresadola, Rigo, and Turco[2] and would account for the low molecular weight data. No such results were observed for the dichlorobis[methyl(phenyl)phosphine]platinum(II) reactions with methylcarborane(12).

Similar reactions involving the use of dichloro salts of palladium and nickel with methylcarborane(12) were attempted. No complexes could be isolated. Studies on these systems are still in progress.

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(6) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, **7**, 245 (1963).

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The Chloramination of Some Heterocyclic Tertiary Phosphines

BY S. E. FRAZIER AND H. H. SISLER*

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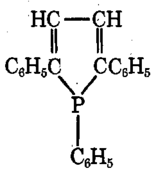
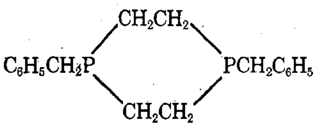
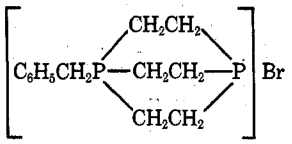
Chloramine has been shown to react with tertiary amines[1] and tertiary phosphines[2] to form the corresponding hydrazinium chlorides and aminophosphonium chlorides, respectively. Since a great number of novel heterocyclic phosphines are now available,[3] we have begun to extend the chloramine reaction to tertiary phosphines of various structural types. This communication reports the results of a study of the reactions of chloramine with 1,2,5-triphenylphosphole (I), with 1,4-dibenzyldiethylenediphosphine (II), and with 1-benzyltriethylenediphosphonium bromide (III).



I



II



III

These heterocyclic derivatives react with the chloramine in a manner similar to other tertiary phosphines and ditertiary phosphines.[4] With I, chloramination occurs at the phosphorus atom yielding 1-amino-1,-2,5-triphenylphospholium chloride. Support for this structure is provided by the occurrence of a strong infrared band at 1120 cm^{-1} in the infrared spectrum. Such a band is usually diagnostic of a phenyl group attached to a tetracoordinate phosphorus atom.

With II, chloramination occurs at both phosphorus atoms as demonstrated by elemental analysis and the nmr spectrum.

In attempting to synthesize triethylene diphosphine by a process which reportedly[5] gives extremely low yields of this product, we obtained the intermediate III. With chloramine, this compound undergoes quaternization and halogen exchange to yield $[C_6H_5CH_2P(C_2H_4)_3PNH_2]Cl_2$.

We were unable to carry out detailed nmr analyses of these products because of their low solubility in suitable solvents. 1-Amino-1,2,5-triphenylphospholium chloride is soluble in $CDCl_3$ and DMSO-d_6 but crystalline adducts precipitate on standing. 1,4-Diamino-1,4-dibenzyldiethylenediphosphonium dichloride and *P*-amino-*P'*-benzyltriethylenediphosphonium dichloride

(1) G. Omietanski and H. H. Sisler, *J. Amer. Chem. Soc.*, **78**, 1211 (1956).

(2) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *ibid.*, **81**, 2982 (1959).

(3) K. D. Berlin and D. M. Hellwege, *Top. Phosphorus Chem.*, **6**, 1 (1969).

(4) S. R. Jain and H. H. Sisler, *Inorg. Chem.*, **8**, 1243 (1969).

(5) R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 2835 (1959).

were examined in D_2O. No peak attributable to the NH_2 group could be assigned with certainty. Since NH_2 signals occur near the phenyl resonances, it is possible that the NH_2 peaks are covered by the phenyl peaks. It is also possible that the NH_2 group is sufficiently quaternized in D_2O solution to facilitate fast intermolecular proton–deuteron exchange. In going from the phosphine to the phosphonium salt the downfield shift in all the proton resonances reflects the lower electron density on the quaternized phosphorus atoms.

Experimental Section

Materials.—Several methods of chloramination were utilized. In some experiments the ammonia–chloramine effluent from a chloramine generator[6] was bubbled through a solution of the phosphine. In other experiments ammonia-free chloramine dissolved in benzene or ether[7] was added to a solution of the phosphine.

1,2,5-Triphenylphospole was synthesized by the method of Campbell, *et al.*;[8] mp 182–184° (lit.[8] mp 187–189°).

The diethylenediphosphine derivative and the triethylenediphosphine derivative were synthesized from tribenzylphosphine by a series of steps reported by Hinton and Mann[5]

$$(C_6H_5CH_2)_3P + Br(CH_2)_2Br \longrightarrow [(C_6H_5CH_2)_3PCH_2CH_2P(CH_2C_6H_5)_3]Br_2$$

$$[(C_6H_5CH_2)_3PCH_2CH_2P(CH_2C_6H_5)_3]Br_2 \xrightarrow{LiAlH_4} (C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2$$

$$(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2 + Br(CH_2)_2Br \longrightarrow [(C_6H_5CH_2)_2P(C_2H_4)_2P(CH_2C_6H_5)_2]Br_2$$

$$[(C_6H_5CH_2)_2P(C_2H_4)_2P(CH_2C_6H_5)_2]Br_2 \xrightarrow{LiAlH_4} C_6H_5CH_2P(C_2H_4)_2PCH_2C_6H_5$$

etc.

The lithium aluminum hydride reduction steps which lead to *sym*-ethylenebis(dibenzylphosphine) and 1,4-dibenzyldiethylenediphosphine yielded results which differ significantly enough from the earlier report to be reported here. This was particularly true of melting points of the compounds (Table I). It was also true of the necessary experimental procedure and condition. For example, 1,4-dibenzyldiethylenediphosphine was prepared by adding 1.21 g (32 mmol) of lithium aluminum hydride to a stirred solution of 9.2 g (14.3 mmol) of 1,1,4,4-tetrabenzyldiethylenediphosphonium dibromide in tetrahydrofuran (50 ml). The mixture was refluxed for 6 hr and cooled, and the solvent was evaporated under vacuum. The solid was hydrolyzed by slowly adding 50 ml of undried ether followed by a 20% aqueous solution of sodium potassium tartrate. When the hydrolysis was complete, fine needlelike crystals were observed in suspension in the ether layer. This layer was siphoned off under nitrogen and filtered; yield 1.5 g (35% of theory); mp 154–156° (see Table I). The ether solution was dried and evaporated to dryness yielding about 3 g of crude product. Recrystallization from ethanol and sublimation at 130–140° *in vacuo* yielded an additional 0.5 g of product (mp 154–158°). The proton magnetic resonance spectrum was recorded on a Varian Model A-60A spectrometer in $CDCl_3$ solution using tetramethylsilane as internal standard. The phenyl protons appear as a multiplet at about τ 2.80, the benzyl methylene protons appearing as a singlet at τ 7.17 and the ethylene protons appearing as a broad multiplet centered at about τ 8. The ratio of average areas under the three groups of peaks was about 10:4:8, consistent with the proposed structure.

TABLE I

MELTING POINTS OF INTERMEDIATES IN THE TRIETHYLENEDIPHOSPHINE SYNTHESIS (°C)

	Lit. data[a]	This work
$(C_6H_5CH_2)_3P$	92–95	90–93
$[(C_6H_5CH_2)_3PCH_2CH_2P(CH_2C_6H_5)_3]Br_2$	275–279	278–279
$(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2$	[b]	108–112
$[(C_6H_5CH_2)_2P(C_2H_4)_2P(CH_2C_6H_5)_2]Br_2$	287–292	295–297
$C_6H_5CH_2P(C_2H_4)_2PCH_2C_6H_5$	128–130	154–156[c]
$[C_6H_5CH_2P(C_2H_4)_3PCH_2C_6H_5]Br_2$	340–344[d]	>360

[a] See ref 5. [b] Sublimed at 180° (0.01 mm). [c] Sublimed at 130–140° (10^{-4} mm). [d] Reported as a hemihydrate.

The Reaction of Chloramine with 1,4-Dibenzyldiethylenediphosphine.—A 1.1-g (3.3-mmol) sample of the diphosphine was dissolved in benzene and exposed to the effluent of the chloramine generator. An excess of chloramine was used. The white solid precipitate (1.90 g) was filtered, dried, and heated at 100° under high vacuum to remove ammonium chloride; yield of crude product 1.31 g (89% of theory). The material was purified by recrystallization from methanol and dried at 50° under high vacuum; mp 277–278° dec, subl. *Anal.* Calcd for $C_{18}H_{26}P_2N_2Cl_2$: C, 53.16; H, 6.50; N, 6.95; P, 15.36; Cl, 17.58. Found: C, 53.7, 53.5; H, 6.4, 6.5; N, 6.8; P, 15.0; Cl, 17.6. Infrared absorption data are included in Table II; nmr data are in Table III.

TABLE II

INFRARED DATA (CM^{-1})[a]

$[C_6H_5CH_2P(NH_2)(C_2H_4)_2P(NH_2)CH_2C_6H_5]Cl_2$

3130 s, 3010 s, 2910 s, 2880 s, 1590 m, 1555 s, 1499 s, 1455 s, 1410 m, 1405 m, 1380 s, 1300 w, 1275 m, 1250 w, 1155 s, 1115 m, 1060 m, 1025 w, 996 w, 960 s, 920 w, 910 w, 850 s, 805 w, 780 m, 765 w, 725 s, 695 s, 655 w, 625 w, b, 595 m, d, 560 m

$[C_6H_5CH_2P(C_2H_4)_3PNH_2]Cl_2$

3130 s, b, 3030 s, b, 2940 s, 3890 s, 1610 m, 1560 m, 1500 s, 1460 s, 1410 s, 1310 s, 1180 s, 1150 s, 1065 m, 1025 m, 970 s, 910 w, 840 s, 750 s, b, 700 s, 650 w, b, 625 w, b, 570 m, 530 m, 478 w

$[C_6H_5P(NH_2)(C_6H_5CCH)_2]Cl$

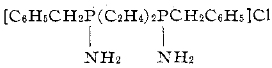
3130 s, 3030 s, 2890 s, b, 1480 w, 1440 m, 1410 s, 1300 w, 1250 w, 1120 s, 990 m, b, 915 w, 865 w, 750 s, 710 w, 675 s, 575 w, 550 w, 490 w, 450 w

[a] Key: s, strong; m, medium; w, weak; d, doublet; b, broad. Samples in KBr pellets.

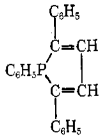
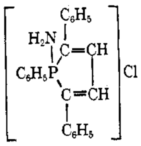
TABLE III

NMR PARAMETERS

Series I

		τ			
Compound	Solvent	A, C_6H_5	B, CH_2 in C_6H_5-CH_2	C, CH_2 in PCH_2-CH_2P	J_{PCH}, cps
$C_6H_5CH_2P(C_2H_4)_2PCH_2C_6H_5$	$CDCl_3$	2.80	7.17	8.08	
		Rel area A:B:C = 5:2:4			
 $[C_6H_5CH_2\underset{NH_2}{P}(C_2H_4)_2\underset{NH_2}{P}CH_2C_6H_5]Cl_2$	D_2O[a]	2.45	6.00 6.23	7.17	14
		Rel area A:B:C = 5:2:4			
$[C_6H_5CH_2P(C_2H_4)_3PNH_2]Cl_2$	D_2O[a]	1.72	5.33 5.55	6.62	13
		Rel area A:B:C = 5:2:12			

Series II

		τ	
Compound	Solvent	A, *C*-C_6H_5	B, *P*-C_6H_5
	$CDCl_3$	2.82[b]	
	$CDCl_3$	2.72	2.40[c]
		Rel area A:B = 10:5	

[a] TMS in CCl_4, external standard. [b] Chemical shift of the strongest peak; *C*-C_6H_5 and *P*-C_6H_5 peaks not separated. [c] A broad unassigned multiplet of relative area 2 also occurs at τ 2.07.

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(6) H. H. Sisler, F. T. Noth, R. S. Drago, and D. Yaney, *J. Amer. Chem. Soc.*, **76**, 3906 (1954).

(7) I. T. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).

(8) I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc.*, 2184 (1965).

Synthesis of *P*-Amino-*P'*-benzyltriethylenediphosphonium Dichloride.—To 7.0 g (14.4 mmol) of dibenzyltriethylenediphosphonium dibromide dissolved in 50 ml of tetrahydrofuran was added an excess of lithium aluminum hydride. The stirred mixture was refluxed for 6 hr until it was uniformly gray. The solvent was removed under vacuum and 50 ml of undried ether was carefully added. Hydrolysis was completed by the addition of 20% aqueous sodium potassium tartrate solution. The ether layer was separated under nitrogen, dried, and evaporated to yield a very small amount of waxy solid.

To a benzene solution of this waxy solid was added about 9 mmol of chloramine dissolved in benzene. A white precipitate formed immediately. This precipitate was filtered, washed repeatedly with hot benzene, and dried under vacuum. About 0.42 g of crude product was obtained. It was heated at 100° under high vacuum to remove traces of ammonium chloride; mp 160–165° dec. *Anal.* Calcd for $C_{13}H_{21}P_2NCl_2$: C, 48.17; H, 6.53; N, 4.32; P, 19.11; Cl, 21.87. Found: C, 46.8; H, 6.7; N, 4.8; P, 19.7; Cl, 22.0. Infrared data (Table II) and nmr data (Table III) are consistent with this formulation.

The Reaction of Chloramine with 1,2,5-Triphenylphosphole.—A 1.01-g (3.2-mmol) sample of 1,2,5-triphenylphosphole was dissolved in a mixture of 75 ml of benzene and 25 ml of ether. An ether solution of chloramine (5 ml, 0.93 *M* NH_2Cl) was added rapidly by pipet to the stirred soluton in the dark. A voluminous yellow precipitate formed immediately. Stirring was continued overnight. The precipitate was filtered, dried under vacuum, and heated for 1.5 days at 80–90° under high vacuum to remove ammonium chloride. It was finally washed with benzene and dried; yield 0.96 g (79% of theory); mp 210–211°. *Anal.* Calcd for $C_{22}H_{19}PNCl$: C, 72.63; H, 5.26; N, 3.85; P, 8.51; Cl, 9.75. Found: C, 72.4; H, 5.2; N, 3.8; P, 8.7; Cl, 9.8.

The material is soluble in water and alcohols, reacts with chloroform and dimethyl sulfoxide, and is slightly soluble in benzene and insoluble in ether. Infrared data and nmr data are listed in Tables II and III, respectively.

Reaction of 1,2,5-triphenylphosphole with the ammonia-chloramine mixture from a chloramine generator and exposure of the mixture to light resulted in an as yet uncharacterized product with a P:N ratio of 1:3.

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Brillouin Spectra of Solutions. II.[1] Molecular Weights of Acetylacetonate Complexes of Magnesium(II) and Nickel(II)

BY FRANK I. SAN FILIPPO, GEORGE A. MILLER,*
AND J. AARON BERTRAND

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Measurement of the intensity of light scattered by a solution relative to the incident beam intensity is a standard procedure for obtaining the weight-average molecular weight of the solute. We have shown previously[1] that one can avoid reference to the incident beam by resolving the scattered light into its Brillouin spectrum of three peaks. If the scattering angle is 90° and the incident light is in the visible region, then the two side peaks are displaced by about 0.1–0.2 cm^{-1} from the unshifted central peak. A highly monochromatic laser is used and the spectrum is resolved with an interferometer. For a dilute, ideal solution, the ratio of intensities of central to side peaks, J, is related to the weight-average molecular weight, M, by the equation $J = J_0 + S(\partial n/\partial c)^2Mc$, where J_0 is the value of J of the pure solvent, n is the refractive index of the solution, and c is the concentration of solute in grams per milliliter. S is a solvent-dependent term given by $S = (J_0 + 1)(\gamma - 1)C_p/\gamma RT^2(\partial n/\partial T)^2$, where γ is the ratio of heat capacities, C_p/C_v, of the solvent, R is the gas constant, T is the absolute temperature, and C_p is the constant-pressure heat capacity of 1 ml of solvent. The quantity S may be determined experimentally using a solute of known molecular weight or calculated using literature values of γ, C_p, and perhaps $\partial n/\partial T$. The molecular weight is calculated from the slope of J *vs.* c. Due to the narrowness of the Brillouin spectrum, adsorption by the solution will attenuate all three peaks equally, and no Beer's law correction is required. We report here the application of this method to the hydrated and anhydrous acetylacetonates of divalent magnesium and nickel.

Experimental Section

The procedure for obtaining the Brillouin spectra with a Ne-He laser (6328 Å) has been described.[1] For colored solutions, a small rectangular fluorimeter cell was used in place of the standard square turbidity cell, and the scattered light was collimated with a spherical lens focused close to one corner of the cell, such that the point from which scattering was observed was about 4 mm from where the incident beam entered and the 90° scattered light left the solution. This represented a balance between minimizing loss of intensity from absorption and minimizing stray scattering from the surfaces of the cell. Extinction coefficients were measured at 6328 Å and the loss in the most concentrated solutions was estimated: NiA_2, 58%; $NiA_2 \cdot 2H_2O$, 40%. Refractive increments were measured on either a Brice-Phoenix differential refractometer or a Bausch and Lomb precision refractometer with the laser as source. The concentration of each solution was determined after the light-scattering measurement by evaporating an aliquot to dryness and weighing. The light-scattering data are given in Table I. A typical spectrum is shown in Figure 1.

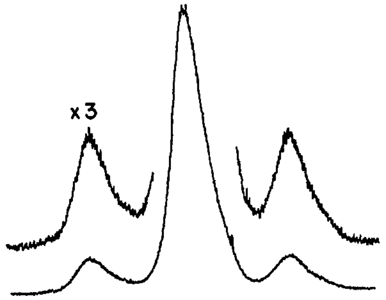

Figure 1.—Spectrum of light scattered by magnesium acetylacetonate in dichloromethane; $c = 2.90 \times 10^{-3}$ g/ml. The central peak is at the incident wavelength, 6328 Å; the side peaks are displaced, 0.05 Å (0.12 cm^{-1}).

Eastman recrystallized naphthalene was used to evaluate S, the solvent parameter, of DMF. Practical 2,4-pentanedione (acetylacetone) was used in the preparations. Otherwise, ACS Certified reagents were used in the preparations and as light-scattering solvents. Nickel(II) acetylacetonate dihydrate ($Ni(C_5H_7O_2)_2 \cdot 2H_2O$) was prepared by a standard procedure.[2] The anhydrous nickel acetylacetonate ($Ni(C_5H_7O_2)_2$) was prepared by heating the dihydrate *in vacuo* at 100° for 12 hr. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Magnesium was analyzed gravimetrically by heating to MgO and volumetrically by EDTA titration. Water of hydration was determined by thermal gravimetric analysis.

Magnesium Acetylacetonate Dihydrate, $Mg(C_5H_7O_2)_2 \cdot 2H_2O$.—A mixture of 6.1 g of magnesium in 100 ml of 2,4-pentanedione was stirred 48 hr at room temperature. Heating to increase the reaction rate also increased the amount of polymeric

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[1] Part I: G. A. Miller, F. I. San Filippo, and D. K. Carpenter, *Macromolecules*, **3**, 125 (1970).

[2] W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957).