Platinum(II) Complexes of *cis* Chelating Phosphines with Electronegative Substituents Containing *o*-Carborane as a Backbone

W. E. HILL, B. G. RACKLEY and L. M. SILVA-TRIVINO

Chemistry Department, Auburn University, Auburn, Ala. 36849, U.S.A.

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The cis *chelating ligands* $(C_6H_5)_2P[B_{10}H_{10}C_2]PRR'$ $(R = R' = C_6H_5, NMe_2, F; R = NMe_2, R' = F)$ *and* $[Me_2N]_2P[B_{10}H_{10}C_2]PRR'$ $(R = R' = C_6F_5; R = NMe_2, R' = F)$ *form chelates with platinum(II) of the type* $[PtCl_2(ligand)]$*. These complexes have been characterized by infrared,* ^1H*,* ^{19}F*, and* ^{31}P *NMR spectroscopy and by elemental analyses. The predicted order of* trans *influence for the various donors is* $P(C_6H_5)_2 > P(C_6F_5)_2 > P(NMe_2)_2 > P(F)NMe_2 > PF_2$ *whereas the* cis *influence is* $P(C_6F_5)_2 > P(F)NMe_2 > P(C_6H_5)_2 > P(NMe_2)_2$.

Introduction

In contrast to the large volume of work reported on chelating symmetrical ditertiary phosphines, only a few chelating unsymmetrical ditertiary phosphines have been studied. These unsymmetrical ditertiary phosphines are of interest since comparative studies can be made of the relative *cis* and *trans* influences of each phosphorus in the unsymmetrical chelate [1, 2]. Most of the studies to date have been carried out with ligands of the type $(C_6H_5)_2P(CH_2)_nPRR'$ (R = alkyl, aryl; R′ = alkyl, cycloalkyl) which behave as bidentate, monodentate and bridging ligands [3,4].

The presence of highly electronegative substituents in unsymmetrical phosphine chelates is even more rare. Morse *et al.*, have prepared an interesting series of potentially chelating unsymmetrical fluorophosphines containing hydrocarbon backbones but these are rather unstable and few complexes have been reported [5]. Sharp, *et al.*, have prepared the stable ligands $(C_6H_5)_2P(CH_2)_2P(C_6F_5)_2$ and $(C_6H_5)_2P(CH_2)_2P(CF_3)_2$ as well as their platinum(II) and palladium(II) complexes [6]. The weak *trans* influence of the $P(CF_3)_2$ group has been unequivocally shown by an X-ray crystallographic study of the palladium(II) complex [7].

We have prepared a series of stable symmetrical and unsymmetrical ditertiary phosphines containing C_6F_5, F and $N(CH_3)_2$ groups utilizing *ortho*-carborane as the backbone [8]. These derivatives are remarkably stable to air and moisture. Stable complexes of the symmetrical derivatives $R_2P(B_{10}H_{10}C_2)PR_2$ (R = Et, Ph) with nickel(II), cobalt(II), palladium(II) and iron(0), have been reported [9–12]. We now report platinum(II) complexes with the unsymmetrical derivatives containing the substi-

TABLE I. Analytical Data and Yields of the Complexes.

	%, yield[a]	%C		%H		%N		%Cl	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}]$	55	25.4	25.2	3.0	3.2			10.7	10.8
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe_2)_2\}]$	73	30.3	30.6	4.5	4.6	3.9	3.9	10.0	9.6
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$	42	27.9	27.3	3.8	3.7	2.0	2.1	10.3	10.0
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2\}]$	65	24.2	24.5	2.5	2.3	3.1	2.9	7.9	7.7
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$	85	15.5	15.9	4.5	4.8	6.8	6.6	11.4	11.0
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PPh_2\}]$	65	40.1	40.3	3.9	4.1			9.1	8.8

[a] Based on $[PtCl_2(NCR)_2]$.

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TABLE II. Infrared Spectra of Analytically Significant Bands of Complexes, cm^{-1}.[a]

Complex	PC_6H_5 Def.	N–C st.	P–C St	P–N St.	P–F St.
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PPh_2\}$]	1438vs		1100s		
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe)_2\}$]	1433vs	1295m 1270m 1196m	1096s	998ms 969ms	
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}$]	1436vs	1305s 1259w 1170s,br	1091s	997s	846ms
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}$]	1439vs		1095s		845s
cis-[$PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}$]		1305m 1295ms 1172s		1000s 992vs 973vs	845m
cis-[$PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2\}$]				982s 970s	

[a] Abbreviations: Def = deformation, st. = stretching, v = very, s = strong, m = medium, w = weak, br = broad.

TABLE III. Pt–P and Pt–Cl Stretching Frequencies (cm^{-1}) of the Complexes.

Complex	Pt–P	Pt–Cl
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PPh_2\}$]	307, 308	330, 297
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe_2)_2\}$]	372, 352	333, 295
cis-[$PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}$]	420, 305	328, 293
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}$]	443, 378	334, 297
cis-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}$]	445, 405	333, 296

tuents C_6F_5, F and NMe_2. The platinum(II) complex of $(C_6H_5)_2P(B_{10}H_{10}C_2)P(C_6H_5)_2$ was also made for comparison.

Results and Discussion

The complexes were prepared by the following displacement reaction:

$$[PtCl_2(NCR)_2] + R_2P[B_{10}H_{10}C_2]PR_2 \longrightarrow$$

$$cis\text{-}[PtCl_2\{R_2P(B_{10}H_{10}C_2)PR_2\}] + 2RCN$$

The complexes prepared, yields, and elemental analyses are listed in Table I. Stoichiometric amounts of the ligand and either [$PtCl_2(NCCH_3)_2$] or [$PtCl_2(NCC_6H_5)_2$] were mixed in benzene or chloroform and stirred at room temperature for several hours. Gentle heating accelerated the reactions but was undesirable with the ligands containing P–F bonds as partial decomposition occurred. The products were precipitated by the addition of a fivefold excess of n-hexane. All of the complexes were soluble in C_6H_6 and $CHCl_3$ with the exception of *cis*-[$PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}$] which would not redissolve once it had been precipitated.

Infrared spectra of the complexes showed typical absorptions of the carborane cage. Thus, strong bands in the 2540–2620 cm^{-1} region (B–H stretching), a medium band in the 720–727 cm^{-1} region (cage deformation) and two or three bands in the 995–1080 cm^{-1} region (B–H deformation modes) were observed for all of the complexes. These bands were essentially the same as those observed for the free ligands indicating that the cage is unaltered upon coordination.

Table II lists the infrared absorptions tentatively assigned to the N–C, P–N and P–F stretching vibrations as well as the P–C_6H_5 planar ring deformation for the complexes. Assignments were made by analogy with similar systems [13, 14]. All of these vibrations occur at higher energy in the complexes compared to the free ligand. The largest increases

TABLE IV. ^{1}H NMR Spectral Data of Complexes.[a]

Complex	δ C_6H_5, ppm	δ Me, ppm	$^{3}J_{PH}$, Hz	$^{4}J_{FH}$, Hz
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PPh_2\}]$	7.90m			
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe_2)_2\}]$	7.65m	2.90d	11.4(9.0)	
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$	7.85m	2.73dd	12.2(9.6)	3.7(4.5)
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}]$	7.80m			
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$		2.60d	11.7	
		2.50d	12.3(9.7)	
		2.53dd	10.2(9.0)	3.1(2.8)
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2\}]$		2.90d	9.9(9.6)	

[a] Solvent $CDCl_3$. Free ligand values given in parentheses. m = multiplet, d = doublet, dd = doublet of doublets.

TABLE V. J/J_L Values for $^{3}J_{PH}$ and $^{1}J_{PF}$ in the Complexes.

Complex	J/J_L	
	$^{3}J_{PH}$	$^{1}J_{PF}$
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe_2)_2\}]$	0.27	
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$	0.27	0.034
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$	0.24[a]	0.027
	0.13[b]	
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2\}]$	0.03	

[a] Mean value for NMe_2 group. [b] For $P(F)NMe_2$ group.

were observed for the P–N stretch (10–25 cm^{-1}) indicating that as electron density is donated from phosphorus to platinum, the phosphorus–nitrogen bond is strengthened.

Frequencies assigned to the Pt–P and Pt–Cl stretching vibrations are listed in Table III. Assignments again were made by analogy with similar systems [15–17]. Two Pt–P and two Pt–Cl stretching vibrations are observed indicative of *cis* geometry. An overall increase in the platinum–phosphorus stretching vibration is observed in the order $Ph_2P(B_{10}H_{10}C_2)PF_2$ > $Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2$ > $(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2$ > $Ph_2P(B_{10}H_{10}C_2)P(NMe_2)_2$ > $Ph_2P(B_{10}H_{10}C_2)PPh_2$ (*i.e.* with increasing electronegativity of the substituents on phosphorus). This apparent strengthening of the Pt–P bond is supported by the NMR results.

Proton NMR data are given in Table IV. While the chemical shifts of both the methyl and phenyl protons were similar to those of the free ligand, the values of $^{3}J_{PH}$ for the $PNMe_2$ groups increase upon coordination of the ligand by increments from 0.3 to 2.6 Hz consistent with earlier results [18–20]. $^{4}J_{HF}$ changes in an irregular fashion upon coordination. No long range Pt–H coupling is observed.

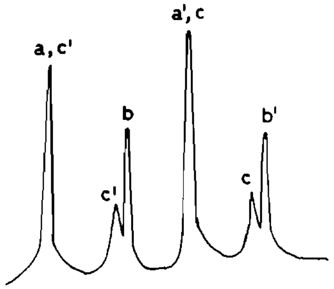

Fig. 1. ^{1}H NMR (methyl region) of *cis*-$[PtCl_2\{(Me_2N)P(B_{10}H_{10}C_2)P(F)NMe_2\}]$.

The ^{1}H NMR spectrum in the methyl region of *cis*-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$ is shown in Fig. 1. Clearly three types of methyl groups are observed. The pairs of lines labeled a–a' and b–b' are the doublets for each NMe_2 group in $P(NMe_2)_2$. The peaks labeled c–c and c'–c' constitute the doublet of doublets for the methyl groups in $P(F)NMe_2$. The magnitudes of $^{3}J_{PH}$ and $^{4}J_{PH}$ are consistent with parameters in analogous systems [21–23].

TABLE VI. $^{31}P\{^1H\}$ Chemical Shifts of the Complexes.[a]

Complex	δPPh_2	$\delta P(NMe_2)_2$	$\delta P(F)NMe_2$	$\delta P(C_6F_5)_2$
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PPh_2\}]$	56.5t(+48.3)			
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe)_2\}]$	57.1t(+39.3)	107.3t(+4.6)		
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2)\}]$	36.9t(+26.5)		115.3dt(−28.6)	
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$		105.2t(−2.0)	118.3dt(−27.6)	
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2\}]$		95.9t(−1.3)		31.5t(+57.6)

[a] In ppm relative to 85% H_3PO_4. Solvent C_6D_6. t = 1:4:1 triplets, d = doublet. Coordination chemical shifts, Δ = Free ligand − complex, given in parentheses.

TABLE VII. Platinum–Phosphorus Coupling Constants in the Complexes (Hz).

Complex	$P(C_6H_5)_2$	$P(NMe_2)_2$	$P(C_6F_5)_2$	$P(CF_3)_2$	$P(F)NMe_2$
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PPh_2\}]$	3757.6				
cis-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(NMe_2)_2\}]$	3988.4	4425.2			
cis-$[PtCl_2\{(Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$	3678.0				5043.5
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$		4376.0			5400.0
cis-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2\}]$		4300.0	4120.0		
cis-$[PtCl_2\{(C_6H_5)_2P(CH_2)_2P(C_6F_5)_2\}]$[a]	3445.0		3845.0		
cis-$[PtCl_2\{(C_6H_5)_2P(CH_2)_2P(CF_3)_2\}]$[a]	3120.0			4013.0	

[a] Reference 6.

The ^{19}F NMR spectrum of *cis*-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$ consists of a doublet centered at −87.7 ppm (upfield from CCl_3F) with $^1J_{PF}$ = 1043 Hz. Further splitting due to ^{195}Pt is observed ($^2J_{PtF}$ = 333 Hz). The ^{19}F NMR spectrum of *cis*-$[PtCl_2\{(Me_2N)_2P(B_{10}H_{10}C_2)P(F)NMe_2\}]$ was not recorded but $^1J_{P-F}$ = 1034 Hz from the ^{31}P NMR spectrum. As expected, the value of $^1J_{PF}$ increases upon coordination (by 34 Hz and 27 Hz respectively). Similar increases in $^1J_{PF}$ for fluorophosphine ligands have been reported for complexes of $EtN(PF_2)_2$ or Cr, Mo and W [24] and for complexes of Me_2NPF_2, Et_2NPF_2 and analogous fluorophosphines coordinated to nickel(0) [21].

Stelzer and Schmutzler have proposed that the value of J/J_L ($J = J_{complex} - J_{ligand}$; $J_L = J_{ligand}$) is a measure of the relative change in s-character of a bond upon coordination [25]. Table IV lists the J/J_L values for $^3J_{PH}$ and $^1J_{PF}$ in the complexes. It should be noted that the increase in s-character along the PNCH bonds is considerably larger than that along the PF bonds.

Tables VI and VII lists the ^{31}P chemical shifts and $^1J_{Pt-P}$ values for the complexes. Coordination chemical shifts are also given for each donor group. The largest coordination chemical shift is observed for the $P(C_6H_5)_2$ group as expected from a significant sigma P → Pt donation [26, 27]. The coordination chemical shifts of the $P(NMe_2)_2$ and $P(F)NMe_2$ groups are much smaller reflecting the increase in electron density at phosphorus due to $p\pi \rightarrow d\pi$ nitrogen to phosphorus interactions of σ-bonding from platinum to phosphorus. The latter interaction is expected to increase in the order $P(C_6H_5)_2 < P(NMe_2)_2 < P(F)NMe_2$ as the electronegativity of the substituents increases.

Interestingly no long range phosphorus–phosphorus coupling is observed in the complexes although values of $^3J_{PP}$ for the free ligands range from 120 to 178 Hz. Decreases in the phosphorus–phosphorus coupling constants of *ca.* 35 Hz occur when the ligands $(C_6H_5)_2PCH_2CH_2PR_2$ (R = CF_3, C_6F_5) are coordinated to platinum [6], in complexes of $RN(PF_2)_2$ [24], and is zero for *cis*-$[PtCl_2\{P(NMe_2)_3\}_2]$ [20]. Grim *et al.* has observed decreases in $^3J_{PP}$ upon coordination of $(C_6H_5)_2PCH_2OP(C_6H_5)_2$ and $Ph_2P(CH_2)_3PPhR$ (R = Me, Et, i-Pr) to Cr, Mo, and W [3]. These workers suggested that this reduction is due to cancellation process where phosphorus–phosphorus coupling is transmitted through the metal center (J_{PP^m}) and through the backbone (J_{PP^b}). Thus, J_{PP}(overall) = $J_{PP^b} + J_{PP^m}$. If this argument is applied to the platinum(II) complexes reported here the magnitudes of $^3J_{PP^b}$ and $^3J_{PP^m}$ must be the same but have opposite signs.

The Pt–P coupling constants for the complexes increase with the electronegativity of the substituents on phosphorus (*i.e.*, $P(C_6H_5)_2 < P(C_6F_5)_2 < P(NMe_2)_2 < P(F)NMe_2$). Since a larger Pt–P coupling has been observed for shorter Pt–P bond distances and the Pt–P stretching frequencies in the infrared also increase in the same order as the ${}^1J_{Pt-P}$ values (see Table III), the suggestion is that the Pt–P bond strength increases in the same order [6, 28, 29]. The increased Pt–P bond strength is expected since the $d\pi \rightarrow d\pi$ interaction between the metal and the phosphorus donor is enhanced by the higher electronegative substituents on the phosphorus atom [30, 31]. Such back donation would also increase the σ-bond character of the Pt–P bond by a synergistic effect [31]. This increase in the sigma-character would account for the observed trend of the ${}^1J_{Pt-P}$ values [32, 33].

In *cis*-$[PtCl_2\{(C_6H_5)_2PCH_2CH_2P(CF_3)_2\}]$ the particularly strong $Pt-P(CF_3)_2$ bond strengthens the *trans* Pt–Cl bond [6]. The donor center $P(CF_3)_2$ therefore has a smaller *trans* influence than the donor center $P(C_6H_5)_2$ and ${}^1J_{PtP(CF_3)_2} > {}^1J_{PtP(C_6H_5)_2}$. Using these observations, we may predict that the *trans* influence increases in the order:

$$PF_2 < P(F)NMe_2 < P(NMe_2)_2 < P(C_6F_5)_2 < P(C_6H_5)_2$$

The placement of PF_2 as a donor center is based on infrared studies only since *cis*-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}]$ has a very low solubility. Of course, only a determination of the bond distances will confirm the predicted trend.

Assuming that the ${}^1J_{Pt-P}$ value reflects the strength of the Pt–P bond, the phosphine donor centers can also be ordered according to their *cis* influence. Thus, as the C_6F_5 group is replaced by the CF_3 group in $(C_6H_5)_2PCH_2CH_2P(C_6F_5)_2$, the $Pt-P(C_6H_5)_2$ coupling is lowered and ${}^1J_{Pt-P(CF_3)_2} > {}^1J_{Pt-P(C_6F_5)_2}$ (see Table VII); this indicates that the donor center $P(CF_3)_2$ has a stronger *cis* influence than the donor center $P(C_6F_5)_2$. Using a similar argument, the increasing order to *cis* influence for the donor centers studied here would be

$$P(NMe_2)_2 < P(C_6H_5)_2 < P(F)NMe_2 < P(C_6F_5)_2$$

Although most of the complexes are remarkably stable, hydrolysis of *cis*-$[PtCl_2\{Ph_2P(B_{10}H_{10}C_2)PF_2\}]$ occurred during attempts to dissolve the complex and grow crystals. The crystal structure of the resulting product which had lost the PF_2 moiety and had undergone a B-cyclometallation reaction has been reported [34]. Other B-cyclometallation reactions occur with other complexes. These results will be reported at a later date.

Experimental

Infrared spectra were recorded on a Perkin Elmer 621 spectrophotometer. Proton and fluorine NMR spectra were obtained on a Varian EM-390 spectrometer at 90.0 and 84.6 MHz respectively. Phosphorus NMR spectra were obtained at 32.1 MHz on a Varian CFT 20 spectrometer. Fluorine chemical shifts are reported relative to CCl_3F as an internal standard. Phosphorus chemical shifts are reported relative to the external reference 85% H_3PO_4. All chemical shifts are reported as positive if they are deshielded relative to H_3PO_4.

The ligands $(C_6H_5)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$, $(C_6H_5)_2P[B_{10}H_{10}C_2]P(NMe_2)_2$, $(Me_2N)_2P[B_{10}H_{10}C_2]\cdot P(NMe_2)_2$ and $(C_6H_5)_2P[B_{10}H_{10}C_2]P(F)NMe_2$ were prepared as described by Hill and Silva-Trivino [8]. The ligand $(C_6H_5)_2P[B_{10}H_{10}C_2]P(C_6H_5)_2$ was prepared according to the method of Alexander and Schroeder [35], K_2PtCl_4 was prepared as indicated by Keller but $N_2H_4\cdot 2HCl$ was used as a reducing agent [36]. The cyanide complexes *cis*-$[PtCl_2(NCR)_2]$ (R = Me, C_6H_5) were prepared as described by Walton [37].

General Synthetic Procedure for the Complexes

To a suspension of 1.1 mmol of $[PtCl_2(NCR)_2]$ (R = C_6H_5, or CH_3) in 50 ml of benzene, 1.1 mmol of the appropriate ligand was added. The mixture was stirred at room temperature for 40 hours. The clear solution was filtered and the solution reduced to about one-third volume. Five times the volume of cold n-hexane was then added and the white solid product precipitated. The solid was washed with hexane and dried *in vacuo.*

Synthesis of $(C_6F_5)_2P[B_{10}H_{10}C_2]H$

Bromobis(pentafluorophenyl)phosphine (150 mmol) in 10 ml of benzene was added slowly, under nitrogen, to an ice-bath cooled slurry of lithium-*o*-carborane (150 mmol) in 20 ml of benzene. After the addition was complete the reaction mixture was allowed to warm to room temperature and then refluxed for 30 h. The solvent was then removed *in vacuo* and the residue extracted with diethyl ether. Evaporation of the solvent gave $(C_6F_5)_2P(B_{10}H_{10}C_2)H$ as a white solid, yield 27%.

Synthesis of $(Me_2N_2)_2P(B_{10}H_{10}C_2)P(C_6F_5)_2$

n-Butylithium (20 mmol) in hexane is added dropwise to $H(B_{10}H_{10}C_2)P(C_6F_5)_2$ (20 mmol) in 20 ml of benzene at 0 °C under nitrogen. After the addition was complete, bis(dimetylamino)chlorophosphine (20 mmol) was added dropwise with vigorous stirring. The reaction mixture was then refluxed for 20 h, cooled to room temperature and the mixture was filtered. The solvent was removed *in vacuo*. The residue was extracted with hot n-hexane. Evaporation of the hexane gave the compound as a white solid, yield 63%.

References

1 D. W. Meek and T. J. Mazanec, *Acc. Chem. Res., 14,* 266 (1981).

2 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev., 10,* 335 (1973).

3 (a) S. O. Grim, P. H. Smith, I. J. Colquhoun and W. MacFarlane, *Inorg. Chem., 19,* 3195 (1980).
(b) S. O. Grim and E. D. Walton, *Ibid., 19,* 1982 (1980).
(c) S. O. Grim and J. D. Mitchell, *Ibid., 16,* 1762 (1977).
(d) *Ibid., 16,* 1770 (1977).
(e) S. O. Grim, R. C. Barth, J. D. Mitchell and J. D. Gaudio, *Ibid., 16,* 1776 (1977).

4 R. B. King and J. C. Cloyd, *Inorg. Chem., 14,* 1550 (1975).

5 (a) J. G. Morse and K. W. Morse, *J. Am. Chem. Soc., 95,* 8469 (1973).
(b) E. R. Falardeau , K. W. Morse and J. G. Morse, *Inorg. Chem., 13,* 1974 (1974).
(c) *Ibid., 14,* 132 (1975).
(d) J. G. Morse and K. W. Morse, *Inorg. Chem., 14,* 565 (1975).
(e) N. R. Zach, K. W. Morse and J. G. Morse, *Inorg. Chem., 14,* 3131 (1975).

6 I. Macleoud, L. Manojlovic-Muir, D. Millington, K. W. Muir, D. W. A. Sharp and R. Walker, *J. Organomet. Chem., 97,* C7 (1975).

7 L. M. Muir, D. Millington, K. W. Muir, D. W. A. Sharp, W. E. Hill, J. V. Quagliano and L. M. Vallarino, *J. Chem. Soc., Chem. Commun.,* 999 (1974).

8 (a) W. E. Hill and L. M. Silva-Trivino, *Inorg. Chem., 17,* 2495 (1978).
(b) *Ibid., 18,* 361 (1974).

9 H. D. Smith, *J. Am. Chem. Soc., 87,* 1817 (1965).

10 W. E. Hill, W. Levason and C. A. McAuliffe, *Inorg. Chem., 13,* 244 (1974).

11 L. Zakharkin and G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 932 (1965).

12 R. H. Holm and F. Rohrschied, *J. Organomet. Chem., 4,* 335 (1975).

13 S. Sandhu, *J. Organomet. Chem., 77,* 45 (1969).

14 R. Mathis, L. Lafaille and R. Burgada, *Spectrochim. Acta, Part A, 30,* 357 (1974).

15 U. Belluco, 'Organometalic and Coordination Chemistry of Platinum', Academic Press: New York, 1974.

16 M. J. Hudson, R. S. Nyholm and M. H. B. Stiddard, *J. Chem. Soc. (A),* 40 (1968).

17 J. M. Jenkins and J. G. Verkade, *Inorg. Chem., 6,* 2250 (1967).

18 R. B. King, *Inorg. Chem., 2,* 936 (1963).

19 C. E. Jones and K. J. Coskran, *Inorg. Chem., 10,* 55 (1971).

20 F. B. Ogilive, J. M. Jenkins and J. G. Verkade, *J. Am. Chem. Soc., 92,* 1916 (1970).

21 G. S. Reddy and R. Schmutzler, *Inorg. Chem., 6,* 823 (1967).

22 A. H. Cowley and R. P. Pinnell, *J. Am. Chem. Soc., 87,* 725 (1965).

23 A. E. Goya, M. D. Rosario and J. W. Gilje, *Inorg. Chem., 8,* 725 (1969).

24 T. R. Johnson and J. F. Nixon, *J. Chem. Soc. (A),* 2518 (1969).

25 O. Stelzer and R. Schmutzler, *J. Chem. Soc. (A),* 2867 (1971).

26 R. Matheiu, M. Lenzi and R. Pioblanc, *Inorg. Chem., 9,* 2030 (1970).

27 J. R. VanWazer and J. H. Letcher, *Topics Phosphorus Chem., 5,* 169 (1967).

28 F. H. Allen and S. N. Sze, *J. Chem. Soc. (A),* 2054 (1971).

29 (a) A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. (A),* 1707 (1966).
(b) G. G. Mather, A. Pidcock and G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.,* 2095 (1973).

30 S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem., 6,* 1133 (1967).

31 S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Am. Chem. Soc., 89,* 5573 (1967).

32 J. A. Pople and D. P. Santry, *Mol. Phys., 8,* 1 (1964).

33 J. F. Nixon and A. Pidcock, *Ann. Rep. NMR Spectrosc., 2,* 345 (1969).

34 L. M. Muir and K. W. Muir, *J. Chem. Soc., Dalton Trans,* 317 (1980).

35 R. P. Alexander and H. Schroeder, *Inorg. Chem., 2,* 247 (1963).

36 R. N. Keller, *Inorg. Syn., 2,* 247 (1946).

37 R. A. Walton, *Spectrochim. Acta, 21,* 1795 (1965).