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Procedure for the degradation of 1,2-$(PR_2)_2$-1,2-dicarba-*closo*-dodecaborane(12) and 1-(PR_2)-2-R′-1,2-dicarba-*closo*-dodecaborane(12)

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Abstract

Monophosphines and bisphosphines bearing anionic groups derived from the 7,8-dicarba-*nido*-undecaborate unit, such as $[7\text{-}PR_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = phenyl, ethyl, isopropyl or ethoxy), were synthesized from *closo*-carborane precursors $1\text{-}PR_2\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}$ and $1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, respectively. In general, the C_c–P bond in the *closo* species is very susceptible degradation reactions, producing C_c–P cleavage and yielding the $[7,8\text{-}C_2B_9H_{10}]_2^-$ anion. Good degradation conditions which retain the C_c–P found are toluene with a carborane-to-piperidine ratio of 1 : 50 and ethanol with carborane-to-piperidine ratio of 1 : 10. The aryl phosphines keep the C_c–P bond best and produce the highest yields. Phosphites also retain the C_c–P bond, but the phosphorus becomes positive and produces a zwitterionic species. Alkylphosphines are intermediate, depending on the bulk and nature of the R group in the $-PR_2$ unit. The crystal structure of $[NMe_4]\,[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]\cdot CH_3CH_2OH$ is described.

Keywords: Carborane; Diphosphine; Phosphine

1. Introduction

The effects of electron-rich elements connected to carbon in 7,8-dicarba-*nido*-undecaborates (1 −) have been the object of several studies [1]. C_c–S compounds are readily prepared but the equivalent C_c–P compounds were unknown until recently [2], when it was shown that the $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ may be generated from $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ upon coordination. The synthesis of the free undecaborate(1 −) was not achieved. Bisphosphines with a two-atom spacer have been widely used in coordination and organometallic chemistry [3–6] and some, such as $Ph_2PCH(Me)\text{-}CH(Me)PPh_2$ [7] and $Ph_2PCH_2CH(Me)PPh_2$ [8], have been used to impose optical chirality on various complexes. However, anionic bisphosphines and monophosphines are still rare. The incorporation of the 7,8-dicarba-*nido*-undecaborate(1 −) moiety into a phosphine is one strategy to obtain such anionic phosphines, some of which may be chiral.

In icosahedral carborane chemistry, part degradation is understood to be the removal of one B vertex from the *closo* species to produce a *nido* system that incorporates a negative charge. General procedures have been known for several years, but no examples of 7,8-dicarba-*nido*-undecaborate(1 −) species with the C_c–PR_2 moiety have been reported. In this paper, we report on the synthesis of 7,8-dicarba-*nido*-undecaborate(1 −) with one and two phosphino substituents, optimization of the reaction conditions, modification of the phosphorus environment and the crystal structure of $[NMe_4]\,[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]\cdot CH_3CH_2OH$ as one example. The starting *closo*-carboranylphosphines employed were $1,2\text{-}(PR_2)_2$-1,2-dicarba-*closo*-dodecaborane(12) and 1-(PR_2)-2-R′-1,2-dicarba-*closo*-dodecaborane(12) (R = Et, ^{i}Pr, Ph or OEt; R′ = Me or H)

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2. Experimental section

2.1. Instrumentation

Elemental analyses were performed using a Perkin-Elmer Model 240-B microanalyzer. IR spectra were obtained in KBr pellets with a Nicolet 710-FT spectrophotometer. ^{1}H, ^{11}B and ^{31}P NMR spectra were obtained on Bruker AM 400WB and AC 400 instruments.

2.2. Materials

Commercial 1,2-dicarba-*closo*-dodecaborane and 1-methyl-1,2-dicarba-*closo*-dodecaborane were sublimed under high vacuum prior to use. Chlorodiethylphosphine, chlorodiisopropylphosphine, chlorodiphenylphosphine, dichlorophenylphosphine and diethoxychlorophosphine from Aldrich were used as purchased. 1,2-Bis(diphenylphospino)-1,2-dicarba-*closo*-dodecaborane [9], 1,2-bis(diethylphosphino)-1,2-dicarba-*closo*-dodecaborane [10] and 1-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane [11] were prepared from *o*-carborane according to the literature. 1-Diethoxyphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane [12], 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane [10,13] and bis(1-methyl-1,2-dicarba-*closo*-dodecaborane) phenylphosphine [14] were prepared from 1-methyl-1,2-dicarba-*closo*-dodecaborane. A 1.6 M solution of *n*-butyllithium in hexane from Fluka was used as purchased. Piperidine, toluene, ethanol and diethyl ether were of reagent quality. All the solvents were deoxygenated and distilled from sodium of an appropriate drying agent. All reactions were carried out under a dinitrogen atmosphere.

2.3. Synthesis of 1,2-Bis(diethoxyphosphino)-1,2-dicarba-closo-dodecaborane(12)

To a three-necked round-bottomed flask (100 ml) fitted with a dinitrogen inlet/outlet and a dropping funnel was added a solution of 1,2-dicarba-*closo*-dodecaborane (1.000 g, 6.933 mmol) in a mixture of diethyl ether and toluene (50 ml, 1 : 1). The flask was cooled in an ice-bath during the addition (10 min) of *n*-butyllithium (dropwise, 8.7 ml, 13.87 mmol). After stirring for 30 min at this temperature, the slurry was kept at room temperature for an additional 30 min, then cooled to −23°C (CCl_4–dry-ice slush) before adding a solution of diethoxychlorophosphine (2.29 g, 13.87 mmol) in diethyl ether–toluene (1 : 1) (10 ml) during 30 min. The resulting dark-orange mixture was stirred overnight at room temperature, during which it turned white. It was then filtered and the filtrate was evaporated under vacuum. A yellow oil, which became crystalline on cooling to −10°C, was isolated (2.07 g, 78%). Anal. Calc. for $C_{10}H_{30}B_{10}O_2P_2$: C, 31.25; H, 7.87. Found: C, 31.71; H, 7.93%. IR (KBr): ν (cm^{-1}) = 2981, 2962, 2929 (C–H); 2613, 2570 (B–H); 1476, 1442, 1388, 1161, 930 (C–H); 1097, 1046, 1023 (P–O). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 4.01–3.93 (m, 2, CH_2), 1.31–1.27 (m, 3, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, 25°C, $BF_3 \cdot Et_2O$): δ = −0.5 (d, ^{1}J(B,H) = 139 Hz, 2B), −7.9 (d, ^{1}J(B,H) = 148 Hz, 2B), −11.0 (4B), −12.3 (2B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 146.70 (s, $P(OCH_2CH_3)_2$).

2.4. Synthesis of 1,2-Bis(diisopropylphosphino)-1,2-dicarba-closo-dodecaborane(12)

The procedure was similar to that described above. From 1,2-dicarba-*closo*-dodecaborane (3.000 g, 20.80 mmol) and diisopropylchlorophosphine (6.62 ml, 41.60 mmol), a crystalline solid (5.01 g, 64%) was isolated at −10°C. Anal. Calc. for $C_{14}H_{38}B_{10}P_2$: C, 44.66; H, 10.17. Found: C, 44.79; H, 10.33%. IR (KBr): ν (cm^{-1}) = 2976, 2951, 2921, 2868 (C–H); 2660, 2651, 2602, 2567, 2556 (B–H); 1464, 1383, 1362, 1222, 1146, 1066, 874, 730, 655, 477 (C–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 2.35–2.30 (m, 1, $-CH=$), 1.42–1.30 (m, 6, CH_3). ^{11}B NMR (128 MHz, $CDCl_3$, 25°C, $BF_3 \cdot Et_2O$): δ = −0.03 (d, ^{1}J(B,H) = 146 Hz, 2B), −7.0 (d, ^{1}J(B,H) = 148 Hz, 2B), −9.9 (d, ^{1}J(B,H) = 156 Hz, 6B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 32.79 (s, $P(CH(CH_3)_2)$).

2.5. Synthesis of 1,1';2,2'-Bis-μ-phenylphosphino-bis-[1,2-dicarba-closo-dodecaborane(12)]

The procedure was similar to that described above. From 1,2-dicarba-*closo*-dodecaborane (1.50 g, 10.40 mmol) and dichlorophenylphosphine (1.40 ml, 10.40 mmol), a white microcrystalline solid (1.48 g, 53%) was isolated. Anal. Calc. for $C_{16}H_{30}B_{20}P_2$: C, 38.38; H, 5.79. Found: C, 38.15; H, 5.77%. IR (KBr): ν (cm^{-1}) = 2627, 2610, 2601, 2594, 2589, 2583, 2571 (B–H); 3079 (C_{aryl}–H); 1483, 1436, 1074, 742, 687, 480, 435 (P–C_6H_5). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ = 7.94, 7.71–7.60, 7.46 (m, C_{aryl}–H). ^{11}B NMR (128 MHz, CH_2Cl_2, 25°C, $BF_3 \cdot Et_2O$): δ = −2.1 (d, ^{1}J(B,H) = 148 Hz, 4B), −4.5 (d, ^{1}J(B,H) = 148 Hz, 4B), −7.6 (d, ^{1}J(B,H) = 163 Hz, 4B), −10.5 (4B), −11.8 (8B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 24.16 (s, $P(C_6H_5)$).

2.6. Synthesis of tetramethylammonium 7,8-bis(diphenylphosphino)-7,8-dicarba-nido-undecaborate (1 −)

An excess of piperidine (848 mg, 9.90 mmol) was added to a solution of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*- dodecaborane (500 mg, 0.99 mmol) in ethanol (75 ml) and heated under reflux overnight. The

mixture was reduced to ca. 25 ml and an excess of tetramethylammonium chloride in water was added to obtain a white solid. This was filtered off, washed with water and cold ethanol and diethyl ether and dried under vacuum. On recrystallization from ethanol, a microcrystalline solid was obtained (490 mg, 86%). Anal. Calc. for $C_{30}H_{42}B_9NP_2 \cdot \frac{1}{2}CH_3CH_2OH$: C, 62.17; H, 7.57; N, 2.34. Found: C, 60.85; H, 7.66; N, 2.14%. IR (KBr): ν (cm^{-1}) = 3051 (C_{aryl}–H); 2973, 2924 (C–H); 2521 (B–H); 1483, 947 (N–C). ^1H NMR (400 MHz, CD_3COCD_3, 25°C, TMS): δ = −2.2 (s, br, 1, B–*H*–B); 7.59, 7.44–7.43, 7.21–7.09 (m, 20, C_{aryl}–*H*); 3.58 (d, ^1J(H,H) = 7 Hz, 2, CH_3CH_2OH); 3.41 (s, 12, $N(CH_3)_4$); 1.19 (t, ^1J(H,H) = 7 Hz, 3, CH_3CH_2OH). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$): δ = −6.8 (d, ^1J(B,H) = 135 Hz, 2B), −13.1 (d, ^1J(B,H) = 138 Hz, 3B), −17.4 (d, ^1J(B,H) = 141 Hz, 2B), −31.2 (d, ^1J(B,H) = 87 Hz, 1B), −33.8 (d, ^1J(B,H) = 138 Hz, 1B). ^{31}P NMR (161 MHz, CD_3COCD_3, 25°C, H_3PO_4): δ = 7.13 (s, $P(C_6H_5)_2$).

2.7. Synthesis of 7-diisopropylphosphino-8-diisopropylphosphoniumyl-7,8-dicarba-nido-undecaborate (1 −)

The procedure was similar to that in the preceding preparation. From 1,2-diisopropylphosphino-1,2-dicarba-*closo*-dodecaborane (500 mg, 0.99 mmol) and piperidine (2.262 g, 26.56 mmol) a white solid (60 mg, 62%) was isolated. Anal. Calc. for $C_{10}H_{39}B_9P_2$: C, 45.86; H, 10.72. Found: C, 45.65; H, 10.50%. IR (KBr): ν (cm^{-1}) = 2968, 2969, 2954, 2928, 2869 (C–H); 2591, 2532 (B–H); 1462, 1453, 1389, 1368, 1094, 1079, 1066, 663 (P–$CH(CH_3)_2$). ^1H NMR (250 MHz, CD_3COCD_3, 25°C, TMS): δ = −2.9 (s, br, 1, B–*H*–B); 1.36–1.42 (m, 24, CH_3); 2.57 (m, 4, –C*H* =); 6.19 (d, ^1J(H,P) = 470 Hz, 1, P–*H*). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$): δ = −6.8 (d, ^1J(B,H) = 140 Hz, 2B), −14.1 (d, ^1J(B,H) = 158 Hz, 3B), −19.6 (2B), −30.8 (d, ^1J(B,H) = 114 Hz, 1B), −33.4 (d, ^1J(B,H) = 130 Hz, 1B).

2.8. Synthesis of tetramethylammonium 7,7';8,8'-Bis-μ-phenylphosphino-bis[7,8-dicarba-nido-undecaborate (1 −)]

The procedure was similar to that in the preceding preparation. From 1,1';2,2'-bis-μ-phenylphosphino-bis [1,2-dicarba-*closo*-dodecaborane (12)] (125 mg, 0.250 mmol) and piperidine (213 mg, 2.50 mmol), a white solid (130 mg, 83%) was isolated. Anal. Calc. for $C_{24}H_{54}B_{18}N_2P_2$: C, 45.99; H, 8.68; N, 4.47. Found: C, 42.66; H, 8.92; N, 4.96%. IR (KBr): ν (cm^{-1}) = 3033 (C_{aryl}–H); 2998, 2954 (C–H); 2508 (B–H); 1433, 1087, 1070, 748, 699 (C–H); 1482, 947 (N–C). ^1H NMR (250 MHz, CD_3COCD_3, 25°C, TMS): δ = −2.1 (s, br, 2, B–*H*–B); 3.35 (s, 24, $N(CH_3)_4$); 7.17 (m, 5, C_{aryl}–*H*); 7.81 (m, 5, C_{aryl}–*H*). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$): δ = −6.9 (d, ^1J(B,H) = 96 Hz, 2B), −13.2 (d, ^1J(B,H) = 176 Hz,), −14.7 (d, ^1J(B,H) = 144 Hz, 3B), −18.0 (d, ^1J(B,H) = 145 Hz, 2B), −33.0 (d, ^1J(B,H) = 141 Hz, 1B), −34.9 (d, ^{1}J(B,H) = 138 Hz, 1B). ^{31}P NMR (101 MHz, CD_3COCD_3, 25°C, H_3PO_4): δ = 26.40 (s, $P(C_6H_5)$).

2.9. Synthesis of 7-Diethylphosphino-8-Diethylphosphoniumyl-7,8-dicarba-nido-undecaborate (1 −)

The procedure was as described in the preceding preparation. From 1,2-bis(ethylphosphino)-1,2-dicarba-*closo*-dodecaborane (100 mg, 0.312 mmol) and piperidine (266 mg, 3.120 mmol), a white solid (40 mg, 41%) was isolated. Anal. Calc. for $C_{10}H_{31}B_9P_2$: C, 38.67; H, 8.58. Found: C, 38.32; H, 10.50%. IR (KBr): ν (cm^{-1}) = 2902, 2929, 2905, 2872 (C–H); 2563, 2540, 2534, 2519, 2515 (B–H); 1462, 1453, 1389, 1368, 1094, 1079, 1066, 663 (C–H). ^1H NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ = −2.5 (s, br, 1, B–*H*–B); 1.20–1.33 (m, 12, CH_3); 1.98–2.20 (m, 8, CH_2); 5.94 (d, ^1J(H,P) = 468 Hz, 1, P–*H*). ^{11}B NMR (128 MHz, $CDCl_3$, 25°C, $BF_3 \cdot Et_2O$): δ = −7.0, −11.5 (4B), −13.9 (d, ^1J(B,H) = 151 Hz, 1B), −17.5, −19.6, −22.5 (2B), −30.0 (d, ^1J(B,H) = 129 Hz, 1B), −33.9 (d, ^1J(B,H) = 144 Hz, 1B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 30.56 (d, $PH(CH_2CH_3)_2$) and −0.66 (s, $P(CH_2CH_3)_2$).

2.10. Synthesis of piperidinium 7,8-diphosphino-7,8-dicarba-nido-undecaborate(1 −) piperidine (1/2)

The procedure was as described in the preceding preparation. From 1,2-bis(ethoxychlorophosphino)-1,2-dicarba-*closo*-dodecaborane (50 mg, 0.130 mmol) and piperidine (553 mg, 6.50 mmol), a white solid (42 mg, 69%) was isolated. Anal. Calc. for $C_{17}H_{46}B_9N_3O_3P_2$: C, 40.85; H, 9.28; N, 8.40. Found: C, 42.00; H, 9.81; N, 8.47%. IR (KBr): ν (cm^{-1}) = 2957, 2861, 2730, 2666, 2623, 2437, 2364, 2341, 2290 (C–H); 2524 (B–H); 1452, 588, 562 (C–H); 1083, 1024 (P–O). ^1H NMR (250 MHz, CD_3OD, 25°C, TMS): δ = −3.0 (s, br, 1, B–*H*–B); 1.69–1.80 (m, 18, CH_2); 3.13 (m, 12, CH_2); 6.99 (d, ^1J(H,P) = 584 Hz, 1, P–*H*). ^{11}B NMR (128 MHz, CD_3OD, 25°C, $BF_3 \cdot Et_2O$): δ = −7.8 (d, ^1J(B,H) = 134 Hz, 2B), −13.7 (d, ^1J(B,H) = 110 Hz, 3B), −18.6 (d, ^1J(B,H) = 148 Hz, 2B), −29.6 (d, ^1J(B,H) = 132 Hz, 1B), −34.5 (d, ^1J(B,H) = 136 Hz, 1B). ^{31}P NMR (161 MHz, CD_3OD, 25°C, H_3PO_4): δ = 7.84 (d, ^1J(P,H) = 590 Hz, *P*H).

2.11. Synthesis of 1-diethylphosphino-2-methyl-1,2-dicarba-closo-dodecaborane (12)

A solution containing diethyl ether (50 ml) and 1-methyl-1,2-dicarba-*closo*-dodecaborane (1.5 g, 9.5

mmol) was cooled to 0°C during the addition (10 min, dropwise) of *n*-butyllithium (6 ml, 9.5 mmol). After stirring for 30 min at 0°C, the mixture was left to stand at room temperature for 30 min, then cooled again to 0°C before adding chlorodiethylphosphine (1.18 g, 1.15 ml, 9.5 mmol) over 30 min. The ice-bath was removed and the mixture stirred for 16 h at room temperature, followed by heating under reflux for 2 h. Once cooled, the solution was concentrated to 15 ml under vacuum and water (20 ml) was then added. Stirring was continued for 10 min before the two layers were separated. The diethyl ether layer was separated and dried with magnesium sulphate and evaporated under vacuum, yielding a yellow oil which solidified at −20°C (1.8 g, 77%). Anal. Calc. for $C_7H_{23}B_{10}P$: C, 34.13; H, 9.41. Found C, 35.79; H, 9.50%. IR (KBr): ν (cm^{-1}) = 2966, 2938, 2875 (C–H), 2579 (B–H). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ = 1.10–1.18 (d, t, ^3J(P,H) = 18.3 Hz, ^{J}(H,H) = 7.3 Hz, 6, CH_3), 1.68 (m, 4, CH_2) 2.09 (s, 3, C_c–CH_3). ^{11}B NMR (128 MHz, $CHCl_3$, 25°C, $BF_3 \cdot Et_2O$): δ = −0.66 (d, ^1J(B,H) = 146.7 Hz, 1B), −5.65 (d, ^{J}(B,H) = 148.2 Hz, 1B), −8.49 (d, ^1J(B,H) = 131.6 Hz, 2B), −9.39 (d, ^1J(B,H) = 139.3 Hz, 2B), −10.66 (d, ^1J(B,H) = 129.8 Hz, 4B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C,H_3PO_4): δ = 5.37 (s, $P(CH_2CH_3)_2$).

2.12. Synthesis of 1-diisopropylphosphino-2-methyl-1,2-dicarba-closo-dodecaborane (12)

The procedure was as described the preceding preparation. From 1-methyl-1,2-dicarba-*closo*-dodecaborane (1.5 g, 9.5 mmol) and chlorodiisopropylphosphine (1.5 ml, 9.5 mmol), a colourless oil that solidified at −20°C was obtained (1.7 g, 64%). Anal. Calc. for $C_9H_{27}B_{10}P$: C, 39.40; H, 9.92. Found: C, 39.66; H, 9.89%. IR (KBr): ν (cm^{-1}) = 2959, 2931, 2868 (C–H); 2586 (B–H). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ = 1.27 (m, 12, CH_3), 2.09 (s, 3, CH_3), 2.20 (m, 2, CH). ^{11}B NMR (128 MHz, $CDCl_3$, 25°C, $BF_3 \cdot Et_2O$): δ = −0.17 (d, ^1J(B,H) = 148.6 Hz, 1B), −5.37 (d, ^1J(B,H) = 152.6 Hz, 1B), −8.49 (d, ^1J(B,H) = 173.8 Hz, 2B), −9.37 (d, ^1J(B,H) = 165.1 Hz, 2B), −10.06 (d, ^{J}(B,H) = 127.7 Hz, 4B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 33.87 (s, $P(CH(CH_3)_2)$.

2.13. Synthesis of Bis-2-μ-[1-methyl-1,2-dicarba-closo-dodecaborane(12)]phenylphosphine

The procedure was described in the preceding preparation. From 1-methyl-1,2-dicarba-*closo*-dodecaborane (1 g, 6.3 mmol) and dichlorophenylphosphine (0.43 ml, 3.16 mmol), a white solid was obtained (1.8 g, 77%) after recrystallization from diethyl ether–light petroleum (1 : 1). Anal. Calc. for $C_{12}H_{31}B_{20}P$: C, 34.11; H, 7.39. Found C, 35.12; H, 6.83%. IR (KBr): ν (cm^{-1}) = 2628, 2579 (B–H), 1426, 1089 (C–H), 751, 688, 489 (P–C). ^{1}H NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ = 2.18 (s, 6, C_c–CH_3), 7.62 (m, 5, P–C_6H_5). ^{11}B NMR (128 MHz, $CDCl_3$, 25°C, $BF_3 \cdot Et_2O$): δ = −1.46 (d, ^1J(B,H) = 139.8 Hz, 2B), −8.16 (d, ^1J(B,H) = 151.3 Hz, 2B), −12.29 (d, 16B). ^{31}P NMR (161 MHz, $CDCl_3$, 25°C, H_3PO_4): δ = 29.53 (s, $P(C_6H_5)$).

2.14. Synthesis of tetramethylammonium [2'-μ-(1'-methyl-1',2'-dicarba-closo-dodecaborane)] (7'-methyl-8'-phenylphosphino-7',8'-dicarba-nido-undecaborate) (1 −)

To a three-necked round-bottomed flask (250 ml) fitted with a dinitrogen inlet/outlet, piperidine (404 mg, 4.74 mmol) and bis2-μ-[1-methyl-1,2-dicarba-*closo*-dodecaborane]phenylphosphine (100 mg, 0.236 mmol) were added, followed by deoxygenated ethanol (15 ml). After heating under reflux for 16 h, the volatiles were evaporated under vacuum and deoxygenated ethanol (5 ml) was added to the solid residue. An aqueous solution of tetramethylammonium chloride was then added to precipitate a white solid, which was filtered, washed several times with water (10 ml) and dried in vacuo. After recrystallization from diethyl ether–hexane (1 : 1), colourless crystals (25 mg) were obtained; yield 25%. Anal. Calc. for $C_{16}H_{43}B_{19}NP$: C, 39.55; H, 8.92; N, 2.8. Found C, 41.5; H, 8.0; N, 2.8%. IR (KBr): ν (cm^{-1}) = 2966, 2931, 2858 (C–H), 2530 (B–H); 1454, 1384, 1096 (C–H), 744, 695, 484 (P–C), 1482, 948 (C–N). ^{1}H NMR (250 MHz, CD_3COCD_3, 25°C TMS): δ = −2.24 (s, br, 1, B–*H*–B), 2.04 (s, 3, C_c–CH_3), 2.11 (s, 3, C_c–CH_3), 3.47 (s, 12, N(CH_3)$_4$), 7.47 (m, 5, P(C_6H_5)). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$): δ = −1.68 (1B), −5.14 (1B), −7.33 (1B), −8.44 (1B), −9.67 (8B), −11.30 (1B), −12.53 (1B), −16.23 (1B), −17.34 (1B), −18.52 (1B), −32.49 (1B), −35.46 (1B). ^{31}P NMR (161 MHz, CD_3COCD_3, 25°C, H_3PO_4): δ = 36.95 (s, $P(C_6H_5)$).

2.15. Synthesis of tetramethylammonium 7-diphenylphosphino-8-methyl-7,8-dicarba-nido-undecaborate (1 −)

Deoxygenated piperidine (12.432 g, 146 mmol) and 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane (1 g, 2.92 mmol) were stirred and heated under reflux for 30 min and the stirring was continued for an additional 30 min at room temperature. Toluene (40 ml) was added, the mixture was heated under reflux for 28 h and then concentrated to ca. 15 ml. An excess of aqueous tetramethylammonium chloride was added and a white solid separated at the interface. This was filtered and washed twice with water (10 ml) and diethyl ether (10 ml); yield 0.9 g (85%). Anal. Calc. for $C_{19}H_{35}B_9P$: C, 56.2; H, 8.7; N, 3.4. Found C, 58.4; H,

8.5; N, 3.2%. IR (KBr): ν (cm^{-1}) = 3045 (arC–H); 2926 (C–H), 2526 (B–H); 1435, 1093, 1038 (C–H), 744, 698 (P–Ph); 1491, 948 (C–N). ^1H NMR (250 MHz, CD_3COCD_3, 25°C, TMS): δ = −2.29 (s, br, 1, B–*H*–B), 1.61 (s, 3, CH_3), 3.45 (s, 12, N(CH_3)$_4$), 7.33 (m, 10, arC–*H*). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$): δ = −6.61 (d, ^{J}(B,H) = 145.3 Hz, 1B), −7.98 (d, ^1J(B,H) = 172.6 Hz, 1B), −9.47 (d, ^1J(B,H) = 189.8 Hz, 1B), −13.46 (d, ^1J(B,H) = 133.9 Hz, 1B), −15.74 (d, ^1J(B,H) = 145.9 Hz, 1B), −16.62 (d, ^1J(B,H) = 132.2 Hz, 1B), −17.85 (d, ^1J(B,H) = 148.5 Hz, 1B), −32.29 (d, ^1J(B,H) = 140.3 Hz, 1B), −34.65 (d, ^1J(B,H) = 138.7 Hz, 1B). ^{31}P NMR (161 MHz, $(CD_3)_2CO$, 25°C, H_3PO_4): δ = 13.68 (s, $P(C_6H_5)_2$).

2.16. Synthesis of tetramethylammonium 7-diphenylphosphino-7,8-dicarba-nido-undecaborate (1 −)

Piperidine (12.963 g, 152 mmol) and 1-diphenylphosphino-1,2-dicarba-*closo*-dodecaborane (1 g, 3.04 mmol) were heated under reflux for 30 min and stirring was continued for additional 30 min at room temperature. Toluene (40 ml) was added. After 28 h of refluxing, the solvent was evaporated and ethanol (15 ml) was added. An excess of aqueous tetramethylammonium chloride was added to precipitate a white solid, which was filtered off and washed with water (2 × 10 ml) and diethyl ether (10 ml); yield 0.7 g (60%). Anal. Calc. for $C_{18}H_{33}B_9PN$: C, 55.2; H, 8.5; N, 3.6. Found C, 54.23; H, 7.75; N, 3.53%. IR (KBr): ν (cm^{-1}) = 3045 (arC–H); 2926 (C–H), 2526 (B–H); 1435, 1093, 1038 (C–H), 744, 698 (P–Ph), 1491, 948 (C–N). ^1H NMR (250 MHz, CD_3COCD_3, 25°C,): δ = −2.24 (s, br, 1, B–*H*–B), 3.45 (s, 12, N(CH_3)$_4$), 7.58 (m, 10, ArC–*H*). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$): δ = −8.97 (d, ^1J(B,H) = 132.3 Hz, 1B), −9.47 (d, ^1J(B,H) = 134.0 Hz, 1B), −14.73 (d, ^1J(B,H) = 199.8 Hz, 1B), −15.38 (d, ^1J(B,H) = 167.5 Hz, 2B), −17.85 (d, ^1J(B,H) = 132.2 Hz, 1B), −20.82 (d, ^1J(B,H) = 142.3 Hz, 1B), −32.39 (d, ^1J(B,H) = 124.2 Hz, 1B), −36.19 (d, ^1J(B,H) = 136.8 Hz, 1B). ^{31}P NMR (161 MHz, CD_3COCD_3, 25°C, H_3PO_4): δ = 19.53 (s, $P(C_6H_5)_2$).

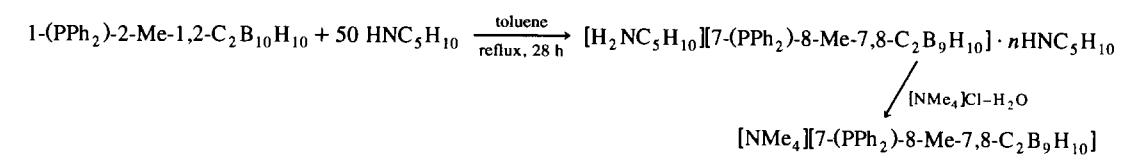
2.17. Synthesis of tetrabutylammonium 7-diisopropylphosphino-8-methyl-7,8-dicarba-nido-undecaborate (1 −)

(a) Piperidine (16.3 g, 190 mmol) and 1-diisopropylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane (1 g, 3.80 mmol) were heated under reflux for 30 min and stirring was continued for an additional 30 min at room temperature. Dry, deoxygenated toluene (40 ml) was added and the mixture was heated under reflux for 24 h. The solvent was then removed under vacuum, ethanol (15 ml) was added and a solution of tetrabutylammonium tetrafluorophosphate was added dropwise to the ethanol solution while dinitrogen was bubbled into the solution, to obtain a white solid. This was filtered off and washed twice with water (10 ml) and diethyl ether (10 ml); yield 0.327 g (16%).

(b) Piperidine (388 mg, 3.63 mmol) and 1-diisopropylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane (50 mg, 0.182 mmol) in deoxygenated ethanol (50 ml) were heated under reflux for 16 h. The solvent was then removed under vacuum and ethanol (15 ml) was added, followed dropwise by an ethanolic solution of tetrabutylammonium tetrafluorophosphate while dinitrogen was bubbled into the solution, giving a white solid. This was filtered off and washed several times with water (10 ml) and diethyl ether (10 ml); yield 64.35 mg (70%). Anal. Calc. for $C_{25}H_{63}B_9NP$: C, 59.3; H, 12.6; N, 2.8. Found C, 59.1; H, 12.4; N, 2.8%. IR (KBr): ν (cm^{-1}) = 2966, 2875 (C–H), 2509 (B–H); 1468, 1384, 1039 (C–H), 885, 737 (P–C). ^1H NMR (250 MHz, $CDCl_3$, 25°C, TMS): δ = −2.24 (s, br, 1, B–*H*–B), 1.02 (t, ^1J(H,H) = 7.2 Hz, 12, CH_3), 1.17 (m, 12, CH_3), 1.44 (hex, ^1J(H,H) = 7.2 Hz, 8, CH_2), 1.60 (q, ^1J(H,H) = 8.2 Hz, 8, CH_2), 1.66 (s, 3, CH_3), 2.2 (m, 2, C*H*), 3.17 (t, ^1J(H,H) = 8.2 Hz, 8, CH_2). ^{11}B NMR (128 MHz, CD_3Cl, 25°C, $BF_3 \cdot Et_2O$): δ = −8.51 (d, ^1J(B,H) = 141.3 Hz, 1B), −9.77 (d, ^{J}(B,H) = 141.0 Hz, 1B), −11.76(d, ^1J(B,H) = 157.8 Hz, 1B), −13.60 (d, ^1J(B,H) = 129.9 Hz, 1B), −17.80 (d, ^1J(B,H) = 146.9 Hz, 2B), −19.95 (d, ^1J(B,H) = 136.0 Hz, 1B), −33.21 (d, ^1J(B,H) = 120.3 Hz, 1B), −35.41 (d, ^1J(B,H) = 137.7 Hz, 1B). ^{31}P NMR (161 MHz, CD_3COCD_3, 25°C, H_3PO_4): δ = 15.73 (s, $P(CH(CH_3)_2)_2$).

2.18. Synthesis of tetrabutylammonium 7-diethylphosphino-8-methyl-7,8-dicarba-nido-undecaborate (1 −)

Piperidine (432 mg, 5.07 mmol), 1-diethylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane (50 mg, 0.203 mmol and deoxygenated ethanol (15 ml) were heated under reflux for 16 h. Once cooled, the solvent was removed in vacuo and deoxygenated ethanol (5 ml) was added to the solution. An aqueous solution of tetrabutylammonium hexafluorophosphate while dinitrogen was bubbled into the solution was added dropwise to precipitate a white solid. This was filtered off, washed several times with water (10 ml) and hexane (20 ml) and dried under vacuum; yield 23 mg (25%). Anal. Calc. for $C_{23}H_{59}B_9NP$: C, 57.8; H, 12.4; N, 2.9. Found C, 55.7; H, 11.6; N, 2.8%. IR (KBr): ν (cm^{-1}) = 2931 (C–H), 2516 (B–H); 1166, 1025 (C–H), 878, 667 (P–C). ^1H NMR (250 MHz, CD_3COCD_3, 25°C,): δ = −2.55 (s, br, B–*H*–B), 0.99 (t, ^1J(H,H) = 7.3 Hz, 12, CH_3), 1.14 (dt, 6, CH_3), 1.41 (hex, ^1J(H,H) = 7.2 Hz, 8, CH_2), 1.63 (m, 4, CH_2), 1.66 (s, 3, CH_3), 1.83 (q, ^1J(H,H) = 8.3 Hz, 8, CH_2), 3.45 (t, ^1J(H,H) = 8.2 Hz, 8, CH_2). ^{11}B NMR (128 MHz, CD_3COCD_3, 25°C, $BF_3 \cdot Et_2O$):



Scheme 1.

$\delta = -8.36$ (d, ^1J(B,H) = 131.3 Hz, 1B), −11.26 (d, ^1J(B,H) = 129.9 Hz, 2B), −14.48 (d, ^1J(B,H) = 121.5 Hz, 1B), −17.44 (d, ^1J(B,H) = 150.0 Hz, 2B), −19.95 (2B), −33.62 (d, ^1J(B,H) = 128.0 Hz, 1B), −35.99 (d, ^1J(B,H) = 126.0 Hz, 1B). ^{31}P NMR (161 MHz, CD_3COCD_3, 25°C, H_3PO_4): $\delta = -8.29$ (s, $P(CH_2CH_3)$).

2.19. Synthesis of 7-methyl-8-P(O)H-7,8-dicarba-nido-undecaborate (1 −)

Piperidine (18.140 g, 213 mmol) and 1-diethoxyphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane (1.185 g, 4.3 mmol) were heated under reflux for 30 min and stirring was continued at room temperature for an additional 30 min. Toluene (50 ml) was added and the mixture was heated under reflux for 28 h. The volatile components were then evaporated to obtain a gummy material, which was treated with $CHCl_3$ (20 ml) to precipitate a white solid. This was filtered off and washed several times with chloroform (10 ml) and diethyl ether (10 ml); yield 0.93 g (78%). Anal. Calc. for $C_8H_{25}B_9NOP$: C, 34.5; H, 8.6; N, 5.0. Found C, 32, 7; H, 8.3; N, 5.6%. IR (KBr): ν (cm^{-1}) = 2959, 2968 (C–H), 2530 (B–H); 2400 (P–H), 1623, 1468, 1454, (C–H); 1131 (P = O). ^{1}H NMR (400 MHz, CD_3OD, 25°C TMS): $\delta = -2.24$ (s, br, 1, B–*H*–B), 1.41 (s, 3, CH_3), 1.53 (d, ^1J(H,H) = 3.5 Hz, 2, CH_2), 1.63 (qt, ^1J(H,H) = 3.5 Hz, 4, CH_2), 2.93 (t, ^1J(H,H) = 3.5 Hz, 4, CH_2), 6.65 (d, ^1J(H,P) = 525 Hz, 1, P–*H*). ^{11}B NMR (128 MHz, CD_3OD, 25°C, $BF_3 \cdot Et_2O$): $\delta = -9.10$ (d, ^{J}(B,H) = 122.9 Hz, 1B), −11.91 (d, ^1J(B,H) = 121.4 Hz, 1B), −12.94 (d, 1B), −16.23 (d, ^1J(B,H) = 134.1 Hz, 1B), −19.18 (d, ^1J(B,H) = 118.7 Hz, 2B), −21.83 (d, $1J$(B,H) = 127.4 Hz, 1B), −35.13 (d, $1J$(B,H) = 128 Hz, 1B), −37.78 (d, ^1J(B,H) = 162.2 Hz, 1B). ^{31}P NMR (161 MHz, CD_3OD, 25°C, H_3PO_4): $\delta = 26.76$ (d, ^1J(P,H) = 525 Hz, 1, O = *P*–H).

2.20. X-ray structure determination of [NMe4][7,8-(PPh2)2-7,8-C2B9H10]-CH3CH2OH

Single-crystal data collection was performed at ambient temperature on a Rigaku AFC7S diffractometer using graphite monochromatized Mo K α radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. Crystallographic data are presented in Table 5.

The structure was solved by direct methods [15] and successive Fourier map calculations. The phosphorus atoms and the oxygen atom were refined anisotropically and the rest of the non-hydrogen atoms isotropically. The phenyl groups were refined as rigid groups (C–C = 1.38 and C–H = 0.96 Å), as were the methyl groups (C–H = 0.96 Å). Only four of the hydrogen atoms of the carbaborane cage could be located from the ΔF

Table 1
Degradation conditions: *closo*-carboranyl–piperidine (1 : 50) in toluene, 24 h

Substance	Non-reacted (%)	Degraded, no C–P (%)	Degraded, with C–P (%)	Cluster decomp. (%)
1-Me-$C_2B_{10}H_{11}$	0	100	–	–
2-Me-1-PEt_2-$C_2B_{10}H_{10}$	38	2	60	–
2-Me-1-P^iPr_2-$C_2B_{10}H_{10}$	73	0	27	–
2-Me-1-$P(OEt)_2$-$C_2B_{10}H_{10}$	0	20	80 [a]	–
2-Me-1-PPh_2-$C_2B_{10}H_{10}$	0	1	99	–
1-PPh_2-$C_2B_{10}H_{11}$	0	7	93	–
2,2′-PPh(1-Me-$C_2B_{10}H_{10}$)$_2$	50	0	50	–
1,2-$C_2B_{10}H_{11}$	0	100	–	–
1,2-$(PEt_2)_2$-$C_2B_{10}H_{10}$	0	66	33 [b]	–
1,2-$(P^iPr)_2$-$C_2B_{10}H_{10}$	8	3	70 [c]	19
1,2-$[P(OEt)_2]_2$-$C_2B_{10}H_{10}$	23	7	64 [d]	6
1,2-$(PPh_2)_2$-$C_2B_{10}H_{10}$	0	1	99	–
$(PPh$-$C_2B_{10}H_{10})_2$	0	0	100	–

[a] 7-Methyl-8-P(O)H-7,8-dicarba-*nido*-undecaborate(1-).
[b] 7-Diethylphosphino-8-diethylphosphoniumyl-7,8-dicarba-*nido*-undecaborate(1-).
[c] 7-Diisopropylphosphino-8-diisopropylphosphoniumyl-7,8-*nido*-undecaborate(1-).
[d] 7,8-Diphosphino-7,8-dicarba-*nido*-undecaborate.

$$1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10} + HNC_5H_{10} \xrightarrow{\text{ethanol, reflux}} [H_2NC_5H_{10}][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}] \cdot n HNC_5H_{10}$$

$$\xrightarrow{[NMe_4]Cl-H_2O} [NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$$

Scheme 2.

map, and the hydrogen atoms were not refined. The O–H hydrogen could not be found. The final R value was 0.103 ($R_w = 0.045$). The high R value is a consequence of weak reflections at high reflection angles and poor statistics of weak reflections. Refinements were performed using the XTAL3.0 program system [15], which minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$. All calculations were carried out on a Convex C3840 computer.

Tables of experimental details, anisotropic thermal parameters, positional parameters, thermal parameters geometric parameters and distances and angles involving the hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

An attempt at direct degradation of the *closo*-compound 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ to [7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]^-$, using the well stablished procedure [17] with KOH in ethanol, was unsuccessful because of C_c–P bond cleavage. In contrast, the degradation process with the piperidine–toluene method [18] with a 1:4 ratio of *closo*-carboranylphosphine to piperidine at 20°C did not attack the *closo* molecule.

Table 2
Degradation conditions: *closo*-carboranyl–piperidine (1 : 10) in ethanol, 16 h

Substance	Non-reacted (%)	Degraded, no C–P (%)	Degraded, with C–P (%)
1-Me-$C_2B_{10}H_{11}$	0	100	–
2-Me-1-PEt_2-$C_2B_{10}H_{10}$	28	2	72
2-Me-1-P^iPr_2-$C_2B_{10}H_{10}$	50	0	50
2-Me-1-$P(OEt)_2$-$C_2B_{10}H_{10}$	0	40	60 [a]
2-Me-1-PPh_2-$C_2B_{10}H_{10}$	0	10	90
1-PPh_2-$C_2B_{10}H_{11}$	0	27	73
2,2′-PPh(1-Me-$C_2B_{10}H_{10})_2$	50	0	50
1,2-$C_2B_{10}H_{11}$	0	100	–
1,2-$(PEt_2)_2$-$C_2B_{10}H_{10}$	0	66	34 [b]
1,2-$(P^iPr)_2$-$C_2B_{10}H_{10}$	90	2	8 [c]
1,2-$[P(OEt)_2]_2$-$C_2B_{10}H_{10}$	0	80	20 [d]
1,2-$(PPh_2)_2$-$C_2B_{10}H_{10}$	0	1	99
$(PPh\text{-}C_2B_{10}H_{10})_2$	0	1	99

[a] 7-Methyl-8-P(O)H-7,8-dicarba-*nido*-undecaborate(1-).
[b] 7-Diethylphosphino-8-diethylphosphoniumyl-7,8-dicarba-*nido*-undecaborate(1-).
[c] 7-Diisopropylphosphino-8-diisopropylphosphoniumyl-7,8-dicarba-*nido*-undecaborate(1-).
[d] 7,8-Diphosphino-7,8-dicarba-*nido*-undecaborate.

These results reflect on the successful synthesis of the C_c–PR_2 derivatives of 7,8-dicarba-*nido*-undecaborate (1 −) and explain why these phosphines had

Table 3
Final positional parameters and isotropic thermal parameters (with e.s.d.s in parentheses) for $[NMe_4]$ [7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]\cdot CH_3CH_2OH$

Atom	x	y	z	U_{eq} [a] (Å^2)
P(1)	0.2565(2)	−0.1083(2)	0.0622(4)	0.037(2)
P(2)	0.1570(2)	0.0377(2)	0.1003(4)	0.037(2)
O	0.2292(6)	−0.0195(7)	0.793(1)	0.080(6)
N	0.3825(8)	0.3671(8)	0.260(1)	0.054(4)
B(1)	0.396(1)	0.093(1)	0.207(2)	0.054(6)
B(2)	0.393(1)	−0.007(1)	0.167(2)	0.041(6)
B(3)	0.318(1)	0.054(1)	0.111(2)	0.040(5)
B(4)	0.305(1)	0.125(1)	0.215(2)	0.053(6)
B(5)	0.370(1)	0.102(1)	0.347(2)	0.054(6)
B(6)	0.425(1)	0.021(1)	0.320(2)	0.048(6)
C(7)	0.3027(7)	−0.0376(9)	0.171(1)	0.035(4)
C(8)	0.2536(7)	0.0358(8)	0.196(1)	0.034(4)
B(9)	0.277(1)	0.066(1)	0.330(2)	0.046(6)
B(10)	0.357(1)	0.005(1)	0.403(2)	0.047(6)
B(11)	0.365(1)	−0.061(1)	0.284(2)	0.040(5)
C(12)	0.3298(5)	−0.1820(7)	0.058(1)	0.067(2)
C(13)	0.3433(6)	−0.2470(8)	0.1280(8)	0.067(2)
C(14)	0.3961(7)	−0.3005(5)	0.1110(8)	0.067(2)
C(15)	0.4355(5)	−0.2890(7)	0.024(1)	0.067(2)
C(16)	0.4220(6)	−0.2242(8)	−0.0462(8)	0.067(2)
C(17)	0.3692(7)	−0.1706(5)	−0.0293(8)	0.067(2)
C(18)	0.1918(6)	−0.1589(5)	0.142(1)	0.060(2)
C(19)	0.2094(4)	−0.1808(6)	0.2572(9)	0.060(2)
C(20)	0.1571(6)	−0.2181(6)	0.3072(7)	0.060(2)
C(21)	0.0871(6)	−0.2336(5)	0.242(1)	0.060(2)
C(22)	0.0696(4)	−0.2117(6)	0.1264(9)	0.060(2)
C(23)	0.1219(7)	−0.1743(6)	0.0764(7)	0.060(2)
C(24)	0.0901(6)	0.0183(7)	0.1954(9)	0.060(2)
C(25)	0.0168(7)	0.0341(6)	0.1455(7)	0.060(2)
C(26)	−0.0393(4)	0.0137(7)	0.2024(9)	0.060(2)
C(27)	−0.0220(5)	−0.0225(6)	0.3094(9)	0.060(2)
C(28)	0.0513(7)	−0.0384(6)	0.3593(7)	0.060(2)
C(29)	0.1073(4)	−0.0179(7)	0.3024(9)	0.060(2)
C(30)	0.1410(6)	0.1434(5)	0.0707(9)	0.061(2)
C(31)	0.1632(5)	0.1714(7)	−0.0271(8)	0.061(2)
C(32)	0.1571(5)	0.2497(7)	−0.0530(7)	0.061(2)
C(33)	0.1289(6)	0.2999(5)	0.0188(9)	0.061(2)
C(34)	0.1067(5)	0.2719(7)	0.1166(8)	0.061(2)
C(35)	0.1128(5)	0.1936(7)	0.1426(7)	0.061(2)
C(36)	0.399(1)	0.447(1)	0.294(2)	0.096(7)
C(37)	0.314(1)	0.366(1)	0.170(2)	0.118(8)
C(38)	0.367(1)	0.325(1)	0.360(2)	0.117(8)
C(39)	0.442(1)	0.329(1)	0.222(2)	0.124(9)
C(40)	0.214(1)	−0.087(2)	0.721(2)	0.14(1)
C(41)	0.216(1)	−0.073(1)	0.606(2)	0.14(1)

[a] U is defined as $U = \frac{1}{3}\Sigma_i\Sigma_j(U_{ij}a_i * a_j * a_i) * a_j$.

not been reported earlier whereas the *closo* species were well known.

Allcock et al. [19] reported in 1983 the successful and quantitative degradation of the C_c–P-bonded carboranylphosphazenes on reaction of the *closo* species with piperidine. The molar ratio of *closo*-carboranylphosphine to piperidine was 1 : 100 in benzene under reflux. When this procedure was employed for 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ a 50% cluster loss due to total degradation was observed. *closo*-Caroboranylmonophosphines with a single phosphorus atom represented an alternative means to investigate the degradation conditions leading to the *nido* species. The reaction of 1-(PPh_2)-2-Me-1,2-$C_2B_{10}H_{10}$ with piperidine in toluene with the ratio 1 : 100 produced 80% degradation with C_c–P retention and 20% with C_c–P cleavage. This was improved when a 1 : 50 molar ratio of carboranylmonophosphine to piperidine in refluxing toluene was used, when no C_c–P cleavage occurred. The work-up and counteraction substitution are critical, as is indicated in the Experimental section in (Scheme 1)

The procedure has been extended to the known monophosphines 1-PPh_2-1,2-$C_2B_{10}H_{11}$, 1-$P(OEt)_2$-2-Me-1,2-$C_2B_{10}H_{10}$ and (1-Me-1,2-$C_2B_{10}H_{11})_2P(C_6H_5)$ and to the new compounds 1-(PEt_2)-2-Me-1,2-$C_2B_{10}H_{10}$ and 1-$(P(^iPr)_2)$-2-Me-1,2-$C_2B_{10}H_{10}$. These compounds include derivatives of aromatic phosphines, alkylphosphines and phosphites. The piperidine-toluene method with a *closo*-carboranylphosphine-to-piperidine ratio of 1 : 50 is of fairly general applicability, but the specific conditions, including reaction time and ratio, have to be tested individually. Furthermore, the conditions, for the replacement of the piperidinium cation depend on each of the individual compounds. The best

Table 4
Selected interatomic distances (Å) and angles (°) (with e.s.d.s in parentheses) for $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}] \cdot CH_3CH_2OH$

P(1)–C(7)	1.84(1)	N–C(39)	1.43(3)
P(1)–C(12)	1.86(1)	C(7)–B(3)	1.77(2)
P(1)–C(18)	1.87(1)	C(7)–C(8)	1.61(2)
P(2)–C(8)	1.90(1)	C(7)–B(11)	1.62(2)
P(2)–C(24)	1.85(1)	C(8)–B(3)	1.72(3)
P(2)–C(30)	1.86(1)	C(8)–B(9)	1.64(2)
O–C(40)	1.43(3)	B(9)–B(10)	1.86(3)
N–C(36)	1.45(2)	B(10)–B(11)	1.83(3)
N–C(37)	1.47(2)	C(40)–C(41)	1.38(4)
N–C(38)	1.46(3)		
C(7)–P(1)–C(12)	103.6(6)	C(8)–B(9)–B(10)	107(1)
C(7)–P(1)–C(18)	102.1(6)	B(9)–B(10)–B(11)	100(1)
C(12)–P(1)–C(18)	103.4(5)	C(7)–B(11)–B(10)	108(1)
C(8)–P(2)–C(24)	107.1(6)	P(1)–C(12)–C(13)	125.5(9)
C(8)–P(2)–C(30)	102.7(6)	P(1)–C(12)–C(17)	114.4(8)
C(24)–P(2)–C(30)	101.0(6)	C(13)–C(12)–C(17)	120(1)
C(7)–B(3)–C(8)	55.0(9)	P(1)–C(18)–C(19)	124.9(7)
P(1)–C(7)–B(3)	113(1)	P(1)–C(18)–C(23)	115.0(8)
P(1)–C(7)–C(8)	116.5(9)	C(19)–C(18)–C(23)	120(1)
P(1)–C(7)–B(11)	124(1)	P(2)–C(24)–C(25)	114.5(8)
C(8)–C(7)–B(11)	112(1)	P(2)–C(24)–C(29)	125.0(7)
P(2)–C(8)–B(3)	109.0(9)	C(25)–C(24)–C(29)	120(1)
P(2)–C(8)–C(7)	113.4(9)	P(2)–C(30)–C(31)	115.7(8)
P(2)–C(8)–B(9)	127(1)	P(2)–C(30)–C(35)	124.1(9)
C(7)–C(8)–B(9)	112(1)	C(31)–C(30)–C(35)	120.1(9)
P(1)–C(7)–C(8)–P(2)	−3(1)		
C(12)–P(1)–C(7)–C(8)	180(1)		
C(24)–P(2)–C(8)–C(7)	111(1)		
C(12)–P(1)–C(7)–B(11)	−33(1)		
C(24)–P(2)–C(8)–B(9)	−36(1)		
C(18)–P(1)–C(7)–C(8)	−73(1)		
C(30)–P(2)–C(8)–C(7)	−143(1)		
C(18)–P(1)–C(7)–B(11)	74(1)		
C(30)–P(2)–C(8)–B(9)	70(1)		
C(7)–P(1)–C(12)–C(13)	89(1)		
C(8)–P(2)–C(24)–C(25)	166.6(9)		
C(7)–P(1)–C(12)–C(17)	−95.6(9)		
C(8)–P(2)–C(24)–C(29)	−21(1)		
C(7)–P(1)–C(18)–C(19)	−41(1)		
C(8)–P(2)–C(30)–C(31)	90.3(9)		
C(7)–P(1)–C(18)–C(23)	139.1(9)		
C(8)–P(2)–C(30)–C(35)	−86(1)		

Table 5
Crystallographic data for $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]\cdot CH_3CH_2OH$

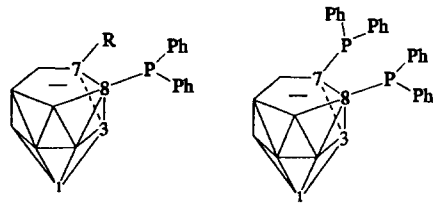
Formula	$C_{32}H_{48}B_9NOP_2$
Formula weight	621.98
a	18.334(3) Å
b	17.199(7) Å
c	11.742(7) Å
β	101.63(2)°
V	3627(2) Å^3
Z	4
Space group	Monoclinic, $P2_1/c$
T	23°C
λ	0.71069 Å
ρ	1.140 g ml^{-1}
μ	1.4 cm^{-1}
Transmission coeff.	0.989–1.000
$R(F_o)$	0.103
$R_w(F_o)$	0.045
Measured reflections	6959
Unique reflections	5440
Reflections with $\|F\| > 4\sigma(F)$	1585

reaction conditions are specified in the Experimental section, but to compare reactions we studied all the degradation process under common conditions. (Table 1). Individual headings correspond to non-reactive species, degraded species retaining the C_c–P bond, degraded species with C_c–P bond cleavage and cluster decomposition. The data are expressed as molar percentages and were obtained by measuring the ^{11}B NMR spectrum of a crude reaction mixture after evaporation of toluene. The reaction conditions were molar ratio of *closo*-carboranylphosphine-to-piperidine = 1 : 50, 50 mg of carboranylphosphine, 15 ml of toluene, reflux conditions and a 24 h reaction.

Although the results in Table 1 are very promising, the high proportion of piperidine is cumbersome. This prompted us to carry out studies with an ethanol–piperidine mixture. This procedure was considered less efficient [5] than that with benzene. However, in our case we have found, with some exceptions, that the *closo*-carboranyldiphosphine-to-piperidine ratio of 1 : 10 is adequate for the degradation. Scheme 2 shows the procedure for $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$.

A comparative study similar to that summarized in Table 1 was undertaken (Table 2). The reaction conditions were molar ratio of *closo*-carboranylphosphine to piperidine = 1 : 10, 50 mg of *closo*-carboranylphosphine, 20 ml of ethanol, reflux conditions and a 16 h reaction.

Both methods are suitable for the degradation, and the choice of one or the other is dependent on each individual compound. *closo*-Carboranylmonophosphines and *closo*-carboranylbisphosphines do not react in the same way in the degradation reaction. The studies indicate that the behaviour of the compounds under the

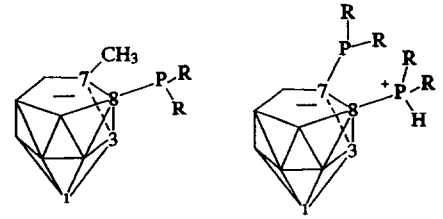


R = H or CH_3

Fig. 1. Proposed structures for *nido*-carboranylmono- and -bis(arylphosphines).

two sets of reaction conditions may be similar when P substituents are aromatic but different when they are alkyl or alkoxyl. This difference seems to be in the variety of reaction pathways that mono- or bisphosphines can adopt. We conclude that the degradation of carboranylaryl, mono- and bisphosphine occurs in good yields owing to the favourable negative-charge delocalization on to the aromatic rings. Fig. 1 shows the proposed structures for the *nido*-carboranylarylphosphines. In these cases the degraded end-products retain the original P substituents with C_c–P bond retention.

When there is no delocalization of the negative charge on to the phosphorus substituents, the formation of a positive charge at phosphorus is more likely, producing a zwitterionic species. The C_c–$P(OR)_2$ compounds may represent an extreme case of this type. Both the mono- and bis(alkoyphosphines) degrade with C_c–P bond retention, but the phosphorus environment changes dramatically to C_c–P(O)H. Carboranylalkylphosphines are intermediate. The carboranylmono(alkylphosphines) retain their initial environment and the behaviour is comparable to that of the carboranylarylphosphines. In the case of carboranylbis(alkylphosphines), one of the phosphorus atoms becomes positive upon degradation, yielding a neutral molecule. Unlike the alkoyphosphines, modification is minor, and only a new P–H bond forms resulting from the initial C_c–PR_2 in C_c–PR_2H^+. Fig. 2 shows the structures proposed. The ^1H NMR spectra of $7\text{-}(PR_2)\text{-}8\text{-}(PHR_2)\text{-}7,8\text{-}C_2B_9H_{10}$ display a resonance at 5.9 ppm (^1J (P,H) = 468 Hz) when R = ethyl. The ^{31}P-NMR spectra show two different phosphorus environments, with δ values at 30.56 ppm (^1J(P,H) = 468 Hz) for R = ethyl. The high ^1J(P,H) value suggests a



R=CH_2CH_3, $CH(CH_3)_2$

Fig. 2. Proposed structures for *nido*-carboranylmono- and -bis(alkylphosphines).

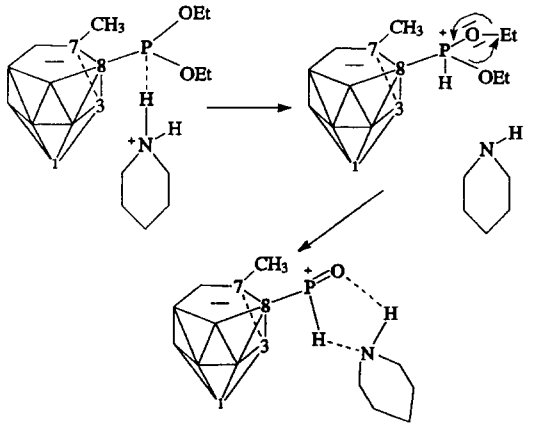


Fig. 3. Suggested mechanism for the conversion of C_c–$P(OR)_2$ into C_c–P(O)H.

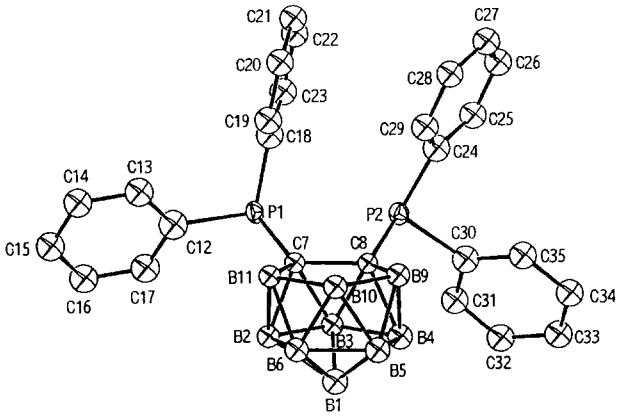


Fig. 5. Perspective view of the substituted anion in $[NME_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]\cdot CH_3CH_2OH$. Hydrogen atoms are omitted for clarity.

P–H bond [20]. Fig. 2 shows the proposed *nido* structure. The tendency for these *nido* species to become zwitterionic has been shown earlier [21]. These molecules tend to compensate the negative charge originating from degradation intramolecularly. This internal charge compensation will take place whenever the molecule finds a suitable reaction pathway.

In the degradation of $1\text{-}(P(OEt)_2)_2\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}$, the C_c–P bond is retained, but the ethoxy group is eliminated and a P=O bond is generated. The ^1H NMR spectrum displays a signal at 6.6 ppm ($^1J(P,H) = 525$ Hz), which is also observed in the ^{31}P NMR spectrum at 26.76 ppm ($^1J(P,H) = 525$ Hz). The high $^1J(P,H)$ value suggests a direct P–H bond. The O–CH_2CH_3 resonances are missing in the ^1H NMR spectra, but there are resonances for the piperidine molecule. However, the ^{31}P NMR resonance at 26.75 ppm is within the range 23–42 ppm, as expected for $OPHR_2$ [7]. We propose a structure (Fig. 3) where a mechanism similar to the Michaelis–Arbusov reaction [22], is also suggested. Fig. 4 shows the proposed structures for carboranylethoxyphosphines.

To prove unambigously that the degradation of *closo*-carboranylphosphines had taken place, an X-ray diffraction analysis of $[NMe_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]\cdot CH_3CH_2OH$ was undertaken. Fig. 5 shows its molecular structure. Table 3 lists positional parameters and Table 4 lists selected interatomic distances and angles in the crystal structure of the bulky anion adopts C_1 symmetry owing to the orientations of the phenyl groups with respect to the *nido*-cage. Two carbon atoms of two phenyl groups and one carbon atom of the cage are bonded to each phosphorus atom in a pyramidal arrangement. The P–C bond lengths of 1.84(1)–1.90(1) Å and C–P–C angles of 101.0(6)–107.1(6)° are similar to those in $1\text{-}PPh_2\text{-}2\text{-}Me\text{-}C_2B_{10}H_{10}$ [23]. Owing to the lower accuracy of the present data, no clear difference between the P–C(aryl) and P–C(cage) separation can be obtained.

The observed conformation of the $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion in the solid state is nearly ideal for a bidentate P_2, or possibly tridentate $P_2H(B_3)$, coordination to the metal. In each of the phenyl rings, the P–C(aryl)–C(aryl) angles show a trend, with one angle being about 10° greater than the other. For example, the P(1)–C(12)–C(13) angle is 125.5(9)°, whereas the P(1)–C(12)–C(17) angle is 114.4(8)°. These differences are assumed to result from the need to avoid repulsion between the phenyl groups and between the phenyl groups and the *nido*-cage. However, the angles around C(7) and C(8) indicate the absence of repulsion between the phosphorus atoms.

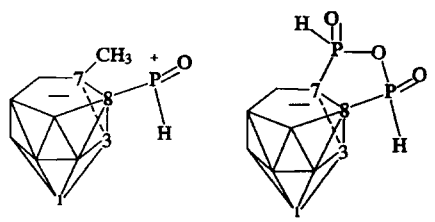


Fig. 4. Proposed structures of *nido*-carboranylmono- and -bis(ethoxyphosphines).

4. Conclusions

It has been proved that C_c–P bond retention is possible in the degradation process of *closo*-carboranylphosphines, and that the optimum reaction conditions are different, depending on the phosphorus substituents. For carboranylmono(arylphosphines) and carboranylbis(arylphosphines), the degradation method with C_c–P bond retention and an unchanged environment provides good yields. Refluxing toluene with a ratio of *closo*-carboranylarylphosphine to piperidine close to 1 : 50 or refluxing ethanol with a 1 : 10 ratio of *closo*-carboranylarylphosphine to piperidine are both suitable. For carboranylmono(alkylphosphines) the best method for degradation with C_c–P bond retention and an unchange phosphorus environment is refluxing ethanol

with a ratio of reactants of 1 : 10. For carboranylbis(alkylphosphines), carboranylmono(ethoxyphospine) and carboranylbis(ethoxyphosphine) no good degradation method has been found. Even though the degradation with C_c–P bond retention occurs using both methods, the phosphorus atom environment is always modified.

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