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Sterically Hindered and Robust Pnictogen Ligands Derived from Carboranes: Synthesis and X-ray Structure Determination of Tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))phosphine, Tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))arsine and Chloro(Tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))phosphine)gold(I)

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Sterically hindered phosphine and arsine ligands derived from *ortho*-carborane were synthesized and characterized by X-ray crystallography. Tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))phosphine, **2** (crystal data, hexagonal, space group $P6_3$, $a = b = 12.251(3)$ Å, $c = 11.514(4)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1496.6(7)$ Å^3, $Z = 2$, $R_1 = 0.0568$) and tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))arsine, **3** (crystal data, hexagonal, space group $P6_3$, $a = b = 12.330(3)$ Å, $c = 11.474(4)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1510.7(7)$ Å^3, $Z = 2$, $R_1 = 0.0930$) were prepared in 82% and 68% yield, respectively. The phosphine ligand is resistant to air-oxidation but was converted to corresponding oxide when heated with hydrogen peroxide. The tertiary carboranyl phosphine reacted with (Tht)AuCl to yield chloro(tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))phosphine)gold(I), **4** (crystal data, monoclinic, space group $P2_1/c$, $a = 19.101(4)$ Å, $b = 12.167(2)$ Å, $c = 13.846(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 91.13(3)°$, $V = 3217.2(11)$ Å^3, $Z = 4$, $R_1 = 0.0396$) in 82% yield. From the X-ray structure of the gold complex, the cone angle of the phosphine was determined to be 213(2)°, which is among the largest values reported to date.

Introduction

Sterically hindered tertiary pnictogen ligands continue to play an important role in modern inorganic chemistry.[1] Not only are they employed to prepare unique coordination complexes, they are also being used to promote Pd-mediated cross-coupling reactions that do not occur with less-hindered ligands such as Ph_3P.[2] Unfortunately, the majority of conventional hindered phosphine ligands, such as tBu_3P, have low oxidation potentials. To prevent unwanted conversion to P(V), the ligands must be handled under anoxic conditions or used as their HBF_4 salts.[2d] There is a need for sterically encumbered tertiary phosphine ligands that are resistant to oxidation.

Dicarba-*closo*-dodecaboranes are icosahedral clusters of boron, carbon, and hydrogen atoms ($C_2B_{10}H_{12}$) which occupy a volume similar to that of a rotating phenyl group.[3] In addition to possessing significant steric bulk, carboranes are robust and readily functionalized at both carbon and select boron vertexes. In light of these features, carboranes are attractive synthons from which to construct hindered ligands.

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A variety of different carboranyl−phosphine ligands including [$Ph_2P(1-X-C_2B_{10}H_{10})$] (X = H, Me, Ph, HS, R_2-SiH),[4] [1,2-$(PPh_2)_2C_2B_{10}H_{10}$],[5] and the related *nido*-anion [1,2-$(PPh_2)_2C_2B_{10}H_9$]$^-$,[6] have been reported. The [Ph_2P-$(1-X-C_2B_{10}H_{10})$] type ligands are particularly noteworthy because they have been shown to be resistant to oxidation.[6c] Little work has been reported on the chemistry of related ligands in which all of the substituents around the phosphorus atom are carboranes. Like the monosubstituted analogues, tris(carboranyl)pnictogens could also prove to be stable to oxidation, which, along with their substantial steric bulk, would make these ligands very useful for the preparation of novel metal complexes and as robust reagents in the aforementioned Pd-catalyzed cross-coupling reactions. This class of ligands would be exceptionally versatile because their solubility and electronic properties could be easily tuned by introducing substituents at select boron or carbon vertexes or by converting the cages to the corresponding *nido*-clusters. These types of transformations can be accomplished using well-established synthetic protocols.[7]

The synthesis of tris(carboranyl)phosphine has not yet been achieved, which is likely a consequence of steric hindrance.[8] It has been reported, however, that insertion of a methylene spacer between the carbon atom of the carborane cage and the phosphorus atom makes it possible to incorporate three clusters around the pnictogen.[9] Because there is little known about the chemistry of tris(carboranyl)phosphines, the objective of this study was to investigate the structure and reactivity of the carborane analogue of tris(benzyl)phosphine. Particular emphasis was placed on determining the cone angle of the ligand, evaluating its stability to oxidation, and testing its reactivity toward a selection of different electrophiles. These studies were designed to determine whether tris(carboranyl)phosphines can be used as robust substitutes for conventional bulky phosphine ligands.

Experimental Section

Materials and General Procedures. All commercial reagents were used as supplied. Decaborane was purchased from Katchem Ltd. Et_2O was distilled under nitrogen from sodium and benzophenone, CH_2Cl_2 was distilled from CaH_2, and acetone was distilled from K_2CO_3. Analytical TLC was performed on silica gel 60-F_{254} (Merck). Boron compounds were visualized with 0.1% $PdCl_2$ in hydrochloric acid (3.0 M), which upon heating gave dark brown spots.[10]

NMR spectroscopy was performed on Bruker Avance AV200, AV300, or AV600 spectrometers. BF_3-Et_2O and 85% H_3PO_4 in D_2O were used as reference standards for the ^{11}B and ^{31}P spectra, respectively. Electrospray mass spectrometry experiments were performed on a Micromass Quattro Ultima instrument. Samples were dissolved in 50:50 CH_3CN/H_2O or acetone, and, for compounds run in negative ion detection mode, one drop of 0.10 M NH_4OH was added. High-resolution ESI data were acquired on a Waters QTOF Ultima Global instrument. EI experiments were performed on a Micromass GCT instrument. Microanalyses were performed by Guelph Chemical Laboratories (Guelph, ON). IR spectra were acquired on a Bio-Rad FTS-40 FTIR spectrometer.

Structure Determination by X-ray Crystallography. X-ray crystallographic data were collected from single-crystal samples of compounds **2**, **3**, and **4** mounted on glass fibers. Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), with a P4 Bruker diffractometer equipped with a Bruker SMART 1K CCD area detector and a rotating anode. The program SMART[11] was used for data collection. Data reduction was carried out using the SAINT program,[12] which applied Lorentz and polarization corrections to the three-dimensionally integrated diffraction spots. The program SADABS[13] was used to scale diffraction data and apply decay and empirical absorption corrections based on redundant reflections. Structures were solved using the direct-methods procedure in the Bruker SHELXTL program library,[14] and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.

Compounds **2** and **3** showed multiple orientations for the carborane cages, which complicated the refinement. Two orientations of the aliphatic portion of the carborane cage were observed, with approximately 75% and 25% occupancy. In the case of compound **3**, a rigid carborane cage was used in two orientations for the refinement. The minor component was given one isotropic atomic temperature factor and the major component was allowed a highly restrained anisotropic refinement.

Synthesis of Tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))phosphine, 2. Magnesium turnings (100 mg, 4.11 mmol) were suspended in dry ether (5 mL) in a dry three-necked flask. The flask was purged with argon and 1,2-dibromoethane (10 μL) was added. After 20 min of stirring, 1.00 g (4.21 mmol) of 1′-

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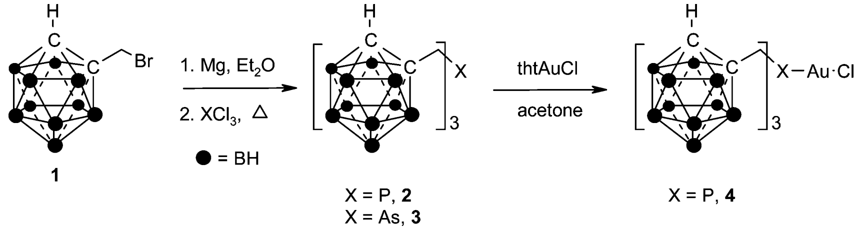
Scheme 1



bromomethyl-1,2-dicarba-*closo*-dodecaboran-1-yl,[15] dissolved in dry diethyl ether (5 mL), was added dropwise to the activated magnesium. The reaction mixture was then heated to reflux until the remaining magnesium disappeared. The reaction mixture was cooled to room temperature, and PCl_3 (125 μL, 1.4 mmol) added dropwise, whereupon formation of a white precipitate was observed. After the addition of PCl_3, the reaction mixture was heated to reflux for 8 h, cooled to room temperature, and then quenched with 0.5 M HCl (10 mL). Ethyl acetate (5 mL) was added to the reaction mixture to solubilize the precipitate, and the solution was extracted with diethyl ether (3 × 10 mL). The organic extracts were combined, dried over Na_2SO_4, and evaporated to dryness. The product, a white solid (577 mg, 82%), was purified by silica gel chromatography (50% hexanes/Et_2O to 100% Et_2O). TLC R_f (Et_2O) = 0.5; mp >260 °C (decomp.). ^{1}H NMR (acetone-d_6, 200 MHz) δ 4.89 (s, CH), 3.80−0.90 (br, BH), 2.84 (d, PCH_2, J ^{31}P−^{1}H = 6.6 Hz). ^{13}C{^{1}H} NMR (acetone-d_6, 50.3 MHz) δ 74.40 (d, J ^{31}P−^{13}C = 24.1 Hz), 65.24, 35.84 (d, J ^{31}P−^{13}C = 19.1 Hz). ^{11}B{^{1}H} NMR (acetone-d_6, 96.3 MHz) δ −1.99, −5.11, −8.73, −10.97, −11.99. ^{31}P{^{1}H} NMR (acetone-d_6, 121.5 MHz) δ −13.6. FTIR (KBr, cm^{-1}): 3060 (m), 2599 (s). HRMS (EI) Calcd for $C_9H_{39}B_{30}P$: 502.5865. Found: 502.5846.

Synthesis of Tris((1′-methyl)-1,2-dicarba-*closo*-dodecaboran-1-yl)arsine, 3. This compound was made following the procedure used to prepare compound **2** except that 120 μL (1.42 mmol) of arsenic trichloride was substituted for phosphorus trichloride. The compound was isolated as a white powder (528 mg, 68%). TLC R_f (Et_2O) = 0.5; mp >260 °C (decomp.). ^{1}H NMR (acetone-d_6, 300 MHz) δ 4.84 (s, CH), 3.3−1.2 (br, BH), 2.73 (s, AsCH_2). ^{13}C{^{1}H} NMR (acetone-d_6, 75.4 MHz) δ 75.30, 65.59, 34.01. ^{11}B{^{1}H} NMR (acetone-d_6, 160.5 MHz) δ −8.84, −12.37, −15.58, −17.68, −18.96;. FTIR (KBr, cm^{-1}): 3061 (s), 2927 (w), 2610 (s, BH). HRMS (ESMS, negative ion) Calcd for $C_9H_{39}B_{30}As$: 546.5172. Found: 546.5170.

Synthesis of Chloro(tris(1′-methyl(1,2-dicarba-*closo*-dodecaboran-1-yl))phosphine)gold(I), 4. Chloro(tetrahydrothiophene)gold (I) (71 mg, 0.22 mmol) was suspended in dry acetone (1 mL), and compound **2** (100 mg, 0.20 mmol) dissolved in dry acetone (1 mL) was added. Once the resulting reaction mixture became homogeneous, CH_2Cl_2 (3 mL) was added and the reaction mixture was stored at −20 °C overnight. The resulting white solid (120 mg, 82%) was collected by filtration. TLC R_f (60% EtOAc/hexanes) = 0.4; mp 206−208 °C (decomp.). ^{1}H NMR (acetone-d_6, 200 MHz) δ 5.03 (s, CH), 4.1−0.9 (br, BH) 3.37 (d, PCH_2, J ^{31}P−^{1}H = 6.0 Hz). ^{13}C{^{1}H} NMR (50.3 MHz, acetone-d_6) δ: 69.67, 65.91, 33.47 (d, J ^{31}P−^{13}C = 35.7 Hz). ^{11}B{^{1}H} (acetone-d_6, 96.3 MHz) δ −1.83, −3.94, −8.40, −10.96. ^{31}P{^{1}H} NMR (acetone-d_6, 81.0 MHz) δ 23.1. FTIR (KBr, cm^{-1}): 3055 (m), 3009 (s), 2965 (m), 2599 (s). FTIR (Nujol on polyethylene plates, cm^{-1}): 337 (m). HRMS (ESMS, negative ion) Calcd for $C_9H_{39}AuB_{30}ClP$: 734.5055. Found: 734.5026.

Synthesis of Tris((1′-methyl)-1,2-dicarba-*closo*-dodecaboran-1-yl)phosphine oxide, 5. To compound **2** (100 mg, 0.20 mmol) dissolved in 25 mL of dry THF, hydrogen peroxide (0.5 mL, 30% aq solution) was added. The reaction was heated to reflux under nitrogen for 16 h, whereupon an additional aliquot of hydrogen peroxide (0.5 mL) was added and the reaction was heated to reflux for a further 24 h. The solvent was then removed by rotary evaporation, and the reaction mixture was dissolved in ethyl acetate (50 mL). The ethyl acetate solution was extracted with a saturated sodium chloride solution (3 × 50 mL), which were subsequently combined and extracted with ethyl acetate (2 × 100 mL). The organic layers were pooled and dried over sodium sulfate. Following filtration, the solvent was removed by rotary evaporation, and the oily residue was dissolved in a small volume of ethyl acetate. The desired product was isolated by preparative TLC (100% ether) as a colorless solid (92 mg, 85%). TLC R_f (Et_2O) = 0.6; mp >260 °C (decomp.). ^{1}H NMR (acetone-d_6, 200 MHz) δ 5.09 (s, 3H, CH), 3.27 (d, 6H, ^2J ^{31}P−^{1}H = 11.2 Hz, PCH_2), 2.1−0.9 (br, BH). ^{13}C{^{1}H} NMR (acetone-d_6, 50.3 MHz) δ 69.08, 63.00, 36.70 (d, J ^{31}P−^{13}C = 64.8 Hz). ^{11}B{^{1}H} NMR (acetone-d_6, 192.5 MHz) δ −1.84, −4.19, −8.70, −10.03, −10.77, −12.01. ^{31}P{^{1}H} NMR (acetone-d_6, 81.0 MHz) δ 37.5. FTIR (KBr, cm^{-1}): 3056 (m), 2999 (m), 2946 (m), 2601 (s), 1182 (s). HRMS (EI) Calcd for $C_9H_{39}B_{30}PO$: 518.5709. Found: 518.5754.

Synthesis of Tri(tetra-*n*-butylammonium) tris((1′-methyl)-7,8-dicarba-*nido*-undecaboran-7-ate)phosphine, 6. Compound **2** (100 mg, 0.20 mmol) was dissolved in THF (10 mL), and tetrabutylammonium fluoride hydrate (784 mg, 3.0 mmol) was added. The reaction mixture turned light yellow and was stirred for 12 h, open to the atmosphere, at room temperature. The solvent was subsequently removed by rotary evaporation and the desired product was isolated via silica gel flash chromatography (1:4 v/v acetonitrile/toluene) as a colorless oil (192 mg, 79%). TLC R_f (25% acetonitrile/75% toluene): 0.4. ^{1}H NMR (CD_3CN, 600 MHz) δ 3.08 (m, NCH_2CH$_2$), 2.1−0.9 (br, BH), 1.89 (s, br, carborane CH), 1.80 (s, 1H, carborane CH), 1.72 (s, 1H, carborane CH), 1.62 (m, CH_2CH$_2$CH$_3$), 1.35 (m, CH_2CH$_3$), 0.98 (t, CH$_3$). ^{13}C{^{1}H} NMR (acetone-d_6, 50.3 MHz) δ 59.15, 53.21, 44.31, 28.50, 24.17, 20.14. ^{11}B{^{1}H} NMR (acetone-d_6, 192.5 MHz) δ −9.34, −11.63, −13.06, −18.77, −19.60, −21.89, −31.59, −35.65. ^{31}P{^{1}H} NMR (acetone-d_6, 81.0 MHz) δ 22.3, 20.4. FTIR (KBr, cm^{-1}): 2962 (m), 2522 (s). HRMS (ESMS, negative ion) Calcd for $C_{25}H_{76}B_{27}NP$: 713.8427. Found: 713.8455.

Results and Discussion

The carborane analogue of tribenzylphosphine was prepared following the method of Zakharkin et al.[9] PCl_3 was added to 1-bromomethyl-*o*-carborane **1**[15] following its conversion to the corresponding Grignard reagent (Scheme 1). After heating to reflux in ether, the trisubstituted phosphine **2** was isolated by column chromatography in 82% yield. As a result of the limited experimental data available for

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Table 1. Crystal and Structure Refinement Data for Compounds **2**, **3**, and **4**

	compound **2**	compound **3**	compound **4**
empirical formula	$C_9H_{39}B_{30}P$	$C_9H_{39}B_{30}As$	$C_9H_{39}AuB_{30}ClP$
fw	502.67	546.62	735.09
T (K)	190(2)	190(2)	293(2)
cryst syst	hexagonal	hexagonal	monoclinic
space group	$P6_3$	$P6_3$	$P2_1/c$
unit cell dimensions			
a (Å)	12.251(3)	12.330(3)	19.101(4)
b (Å)	12.251(3)	12.330(3)	12.167(2)
c (Å)	11.514(4)	11.474(4)	13.846(3)
α (deg)	90	90	90
β (deg)	90	90	91.13(3)
γ (deg)	120	120	90
V (Å^3)	1496.6(7)	1510.7(7)	3217.2(11)
Z	2	2	4
$D_{calcd.}$ (mg/m^3)	1.115	1.202	
abs. coeff. (mm^{-1})	0.098	1.131	4.714
F(000)	516	552	1416
crystal size (mm)	0.20 × 0.08 × 0.06	0.25 × 0.12 × 0.06	0.10 × 0.08 × 0.04
reflns collected	13 601	13 340	35 056
data	2283	2303	7363
restraints	327	25	0
parameters	174	97	380
GOF on F^2	1.090	1.122	1.035
final R indices [$I > 2\sigma(I)$]			
R_1	0.0568	0.0930	0.0396
wR^2	0.1216	0.2450	0.0609
R indices (all data)			
R_1	0.0846	0.0977	0.0702
wR^2	0.1318	0.2481	0.0668
largest diff. peak and hole (e·Å^{-3})	0.256 and −0.206	1.036 and −1.062	0.657 and −1.123

compound **2** (elemental analysis and melting point), detailed characterization of the ligand was undertaken.

The FTIR spectrum of the product exhibits a strong B−H stretch at 2599 cm^{-1}, which is characteristic of a carborane cage. The ^{1}H NMR of **2** (200 MHz, acetone-d_6) shows coupling ($^2J = 6.6$ Hz) between the phosphorus nuclei and the protons on the methylene spacer group. Other features of the ^{1}H spectrum include the broad carborane B−H signals occurring between 3.80 and 0.90 ppm and a singlet at 4.89 ppm, associated with the carborane C−H group. The ^{11}B NMR of **2** contains five peaks ranging from −11.99 to −1.99 ppm, which is consistent with the presence of three equivalent *closo*-carborane cages.[16]

The ^{31}P chemical shift for **2** is found at −13.6 ppm, which is similar to the corresponding value for phenanthryl(diphenyl)phosphine ($\delta = -12.1$ ppm)[17] but shifted to lower frequency than the two chemical shift values reported for tribenzylphosphine ($\delta = 12.9$ ppm[18] and 10.4 ppm[19]). The ^{31}P chemical shift for **2** is also shifted to lower frequency than those of other *closo*-carboranyl phosphines, P(L)Ph$_2$ (L = 1-yl-1,2-dicarba-*closo*-dodecaborane, 1-yl-2-Me-1,2-dicarba-*closo*-dodecaborane, and 1-yl-2-Ph-1,2-dicarba-*closo*-dodecaborane; $\delta = 11.0-25.6$ ppm).[6c] The increased shielding of the phosphorus nuclei in **2** compared to the *closo*-carboranyl phosphines is a good indication that the methylene spacer moderates the strong electron-accepting character of the carborane substituents.[6c]

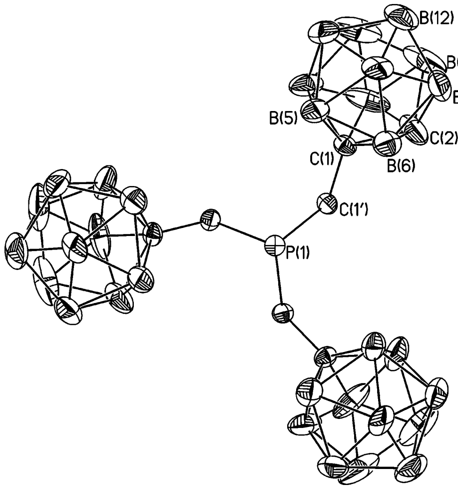

Figure 1. X-ray structure of **2** showing 50% thermal probability ellipsoids. Hydrogen atoms have been omitted for clarity.

For the sake of comparison, and because triarylarsines have been shown to enhance the rate of Stille cross-coupling reactions,[20] the arsenic analogue of **2** was also synthesized. Following the same procedure used to prepare **2**, substituting AsCl$_3$ for PCl$_3$, the arsine **3** (Scheme 1) was isolated by column chromatography in 68% yield. The chemical shift of the carborane CH group in the ^{1}H NMR of **3** is similar to that for **2** (4.84 versus 4.89 ppm). The methylene group appears as a singlet at 2.73 ppm, which is shifted to a slightly lower frequency than that for **2** (2.84 ppm). The ^{13}C NMR shows, as expected, three resonances appearing at 75.30, 65.59, and 34.01 ppm. The ^{11}B NMR has peaks at −8.84, −12.37, −15.58, −17.68, and −18.96 ppm, which is consistent with the proposed structure containing three equivalent *closo*-carborane cages.

Single crystals of **2** and **3** were grown from ether (Table 1). Both compounds crystallized in the $P6_3$ space group and have propeller-like structures with C_{3v} symmetry. The molecules pack in a columnar fashion with the central pnictogen atoms aligned parallel to the 6_3 screw axis. There proved to be two major orientations for the aliphatic portions of the carborane cages in both structures. As a result, two major packing modes were observed, and the crystal structure solution for each molecule contains two sets of superimposed carborane cages. The occupancies of the two major packing modes differ with the dominant mode having 74.81(4)% occupancy in **2** and 64.22(13)% occupancy in **3**. All bond distances and angles are reported from the higher-occupancy positions, although bond distances and angles do not differ appreciably between the two packing modes in **2** and **3**.

In compound **2** (Figure 1) the P(1)−C(1′) bond distance and C(1)−C(1′)−P(1) angle are 1.887(3) Å and 114.95(19)°, respectively (Table 2). These values are larger than the same values for triphenylphosphine (1.828 Å, 103.0°), trimesi-

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Table 2. Selected Bond Lengths [Å] and Angles [°] for **2**

P(1)−C(1′)	1.887(3)	C(1)−C(1′)−P(1)	114.95(19)
C(1′)−C(1)	1.519(4)	C(1′)−C(1)−C(2)	116.4(3)
C(1)−C(2)	1.635(5)	C(1′)−C(1)−B(3)	116.3(3)
C(1)−B(3)	1.703(5)	C(2)−C(1)−B(3)	60.3(3)
C(1)−B(4)	1.709(6)	C(1′)−C(1)−B(4)	123.7(3)
C(1)−B(5)	1.710(6)	C(2)−C(1)−B(4)	109.4(3)
C(1)−B(6)	1.713(6)	C(1′)−C(1)−B(6)	115.9(3)
C(2)−B(11)	1.658(8)	C(2)−C(1)−B(6)	61.5(3)
C(2)−B(3)	1.677(8)	C(1)−C(2)−B(3)	61.9(3)
C(2)−B(7)	1.686(7)	C(1)−C(2)−B(6)	61.5(2)
C(2)−B(6)	1.714(7)		

Table 3. Bond Lengths [Å] and Angles [°] for **3**

As(1)−C(1′)	2.009(10)
C(1′)−C(1)	1.5073
C(1)−C(2)	1.6216
C(1)−B(4)	1.7080
C(1)−B(3)	1.7353
C(1)−B(6)	1.7357
C(2)−B(7)	1.6908
C(2)−B(6)	1.7122
C(2)−B(3)	1.7575
C(1)−C(1′)−As(1)	111.3(4)
C(1′)−C(1)−C(2)	119.1

tylphosphine (1.837 Å, 109.7°) and tris(2,4,6-triisopropylphenyl)phosphine) (1.845 Å, 111.5°),[21] which is a reflection of the steric bulk of **2** (vide infra). The carborane substituents in **2** are distorted icosahedra with no particularly unusual bond distances or angles. The carborane C−C distance is 1.635(5) Å, whereas the average B−C distance is 1.696(20) Å, ranging from 1.658(8) to 1.714(7) Å. The average B−B bond distance for compound **2** is 1.769(16) Å, ranging from 1.731(7) to 1.792(8) Å, whereas the C(1)−C(1′) distance is 1.519(4) Å.

The As−C(1′) bond distance in **3** (Table 3) is long (2.009(10) Å) and comparable to that found in tris(2,4,6-triisopropylphenyl)arsine) (1.986 Å).[21] The C(1)−C(1′)−As angle is 111.3(4)° which is smaller than the C(1)−C(1′)−P(1) angle for **2** (114.95(19)°) but comparable to the value for tris(2,4,6-triisopropylphenyl)arsine) (109.2°). It should be noted that the structure of the arsine **3** (Figure 2) is more disordered than the phosphine analogue, and, as a result, rigid body refinement was needed to adequately model the carborane cages. The absence of standard deviation values for the bond lengths and angles associated with the carborane cages is a direct consequence of the rigid group refinement. The increase in disorder is likely associated with the longer As−C bond which allows for greater variation in the number of packing modes.

It has been reported that *closo*-carboranylphosphine ligands containing a carborane directly bonded to the phosphorus atom do not react with certain transition metal complexes including those containing Pd(II), Cu(I), Au(I), Rh(I), and Ru(II).[6c] This is thought to be a direct consequence of the strong electron-accepting character of *closo-ortho*-carboranes. To determine if the methylene spacer in **2** was sufficient to negate the electronic influence of the carborane substituents on the basicity of the phosphine, we investigated the reactivity of **2** with Au(I).

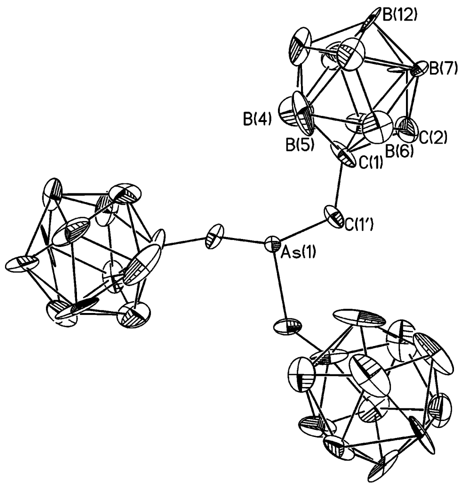

Figure 2. X-ray structure of **3** showing 30% thermal probability ellipsoids. Hydrogen atoms have been omitted for clarity.

The phosphine ligand **2** was added to a suspension containing a slight excess of (tetrahydrothiophene)gold(I) chloride[22,23] in acetone. The reaction became homogeneous after only five minutes, and the desired product was isolated by precipitation following the addition of CH_2Cl_2 and cooling to −20 °C. Compound **4**, which was stable to both air and light, was collected by filtration as a colorless solid in excellent yield (82%).

The IR of **4** shows the characteristic ν_{Au-Cl} stretch at 337 cm^{-1}, which is shifted from that of the starting material. The B−H stretch of the carborane is also clearly visible appearing at 2599 cm^{-1}. The ^{31}P spectrum of **4** exhibits only one resonance, appearing at 23.1 ppm, which is shifted to higher frequency than the resonance observed for the free ligand **2** (−13.6 ppm). The phosphorus resonance observed for **4** is comparable to ^{31}P chemical shifts reported for other chlorogold(I)phosphine complexes including $ClAuPPh_3$ ($\delta = 33.7$ ppm) and $ClAuP(phenanthrene)Ph_2$ ($\delta = 26.7$ ppm).[17]

The X-ray structure of **4** was determined and the ORTEP drawing is shown in Figure 3. Compound **4** demonstrates columnar packing, with the gold centers aligned and running parallel to the unique axis. The molecules pack in an alternating fashion to accommodate the bulk of the phosphine ligand. The P−Au−Cl bond angle is, as expected, nearly linear (178.21(5)°; Table 4) and in agreement with reported values for structural analogues. The Au−P distance of 2.2163(12) Å is shorter than the typical distances found in other chloro−phosphine gold(I) compounds,[24a] while the Au−Cl distance (2.2804(13) Å) is more comparable. The average $C_{carborane}$−C−P bond angle in **4** (118.1(3)°) is larger than the same angle found in the free ligand (114.95(19)°). There is no evidence of aurophilic interactions in **4** as the closest Au−Au distance is 9.409 Å.

The structures of the carborane substituents in **4** are very similar. The average B−C bond distances for each cage are

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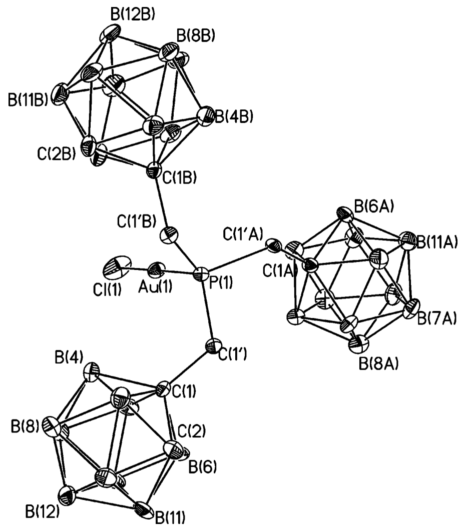

Figure 3. X-ray structure of **4** showing 50% thermal probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengths [Å] and Angles [°] for **4**

Au(1)−P(1)	2.2163(12)	P(1)−Au(1)−Cl(1)	178.21(5)
Au(1)−Cl(1)	2.2804(13)	C(1′)−P(1)−C(1′A)	100.78(19)
P(1)−C(1′)	1.840(4)	C(1′)−P(1)−C(1′B)	100.97(19)
P(1)−C(1′A)	1.842(4)	C(1′A)−P(1)−C(1′B)	101.29(19)
P(1)−C(1′B)	1.843(4)	C(1′)−P(1)−Au(1)	117.25(15)
C(1)−C(1′)	1.533(6)	C(1′A)−P(1)−Au(1)	116.45(14)
C(1)−C(2)	1.664(6)	C(1′B)−P(1)−Au(1)	117.27(14)
C(1A)−C(1′A)	1.540(6)	C(1)−C(1′)−P(1)	118.6(3)
C(1A)−C(2A)	1.681(6)	C(1′A)−C(1A)−C(2A)	114.9(3)
C(1B)−C(1′B)	1.537(6)	C(1A)−C(1′A)−P(1)	117.9(3)
C(1B)−C(2B)	1.663(6)	C(1′B)−C(1B)−C(2B)	115.5(3)
		C(1B)−C(1′B)−P(1)	117.8(3)

1.719(11), 1.714(15), and 1.713(17) Å, with an overall average of 1.715(14) Å. The average B−B distances in each cage are 1.777(12), 1.780(13), and 1.781(8) Å, with an overall average of 1.780(11) Å. The C−C distances in the carboranes range from 1.663(6) to 1.681(6) Å. The average of the C(1′)−C(1), C(1′A)−C(1A), and C(1′B)−C(1B) distances (1.537(6) Å) is similar to the same distance found for the free ligand (1.519(4) Å). The average distance between the phosphine and the methylene spacer group is 1.842(4) Å, which is shorter than the value observed for **2** (1.887(3) Å).

The cone angle for the phosphine ligand was determined from the crystal structure of **4** using the method of Ferguson et al.[25] The calculated value is 213(2)°, which is significantly larger than the cone angles reported for tri(benzyl)phosphine (165°) and tri(*tert*-butyl)phosphine (182°) and comparable to the value reported for trimesitylphosphine (212°), making compound **2** one of the bulkiest phosphine ligands known to date.[24]

The stability of **2** to oxidation was tested by leaving a solution of the phosphine in deuterated acetone open to the atmosphere and then periodically running a ^{31}P NMR spectrum over 168 h. The resulting spectra (Figure 4) clearly demonstrate that compound **2** does not oxidize in solution even over a prolonged period of time. To further demonstrate the stability of compound **2**, after 168 h, air was bubbled into the acetone solution for 2 h. The ^{31}P NMR spectrum, shown at $t = 170$ h, remained unchanged. Comparable experiments with triphenylphosphine showed over 10% conversion to the corresponding oxide, whereas bulky alkyl ligands such as tBu_3P, as was mentioned in the Introduction, are known to be even more sensitive to air-oxidation.

Compound **2** can be converted to the corresponding oxide **5** (Scheme 2) by prolonged treatment with 30% H_2O_2 in THF. To achieve complete conversion to **5**, the reaction had to be heated to reflux for 40 h and an additional aliquot of peroxide was required. The desired product was isolated by preparative TLC in good yield (85%) as a colorless solid.

The ^{31}P NMR of compound **5** showed, as expected, a significant downfield shift from the P(III) ligand (−13.6 to 37.5 ppm). The impact of the oxidation on the chemical shifts of neighboring groups could also be detected in the ^{1}H and ^{13}C NMR. The methylene protons, for example, shifted downfield from 2.84 to 3.27 ppm. The B−H stretches in the IR of **5** were similar to those of the starting material which indicates that the B−H vertexes were not modified during the course of the reaction. The formation of the desired product was further confirmed by high-resolution mass spectrometry.

Attempts to alkylate compound **2** with methyl iodide failed to produce the phosphonium salt. Changing the stoichiometry of the reaction, the temperature, or the nature of the solvent did not improve the yield of the desired product. Treatment of the phosphine with methyl triflate or other reactive alkylating agents such as benzyl bromide and allyl bromide, similarly failed to produce the phosphonium salt. Unlike the reaction with Au(I), which can undergo a more dissociative type mechanism, it is apparent from these results that the steric bulk of the ligand prevents direct alkylation at phosphorus.

Compound **2** can be transformed into a negatively charged phosphine ligand by converting the *closo*-carborane cages to the corresponding *nido*-clusters. Anionic phosphine ligands have garnered attention recently as ligands for catalysis and for preparing charge-compensated and novel metal complexes.[26] The tris(carboranyl)phosphine ligand was converted to the tris-*nido* phosphine **6** by treating compound **2** with an excess of tetra-*n*-butylammonium fluoride (TBAF) for 12 h. The product, which is the first example of a tri-anionic pnictogen ligand, was isolated as a colorless oil in 79% yield following column chromatography. Compound **6** is resistant to oxidation in solution (stable for greater than 170 h) and, unlike compound **2**,[27] is soluble in a wide range of organic solvents, including THF, acetone, acetonitrile, ethyl acetate, and dichloromethane.

The isotope distribution in the high-resolution mass spectrum of **6** was consistent with the presence of three B_9 clusters while the IR shows the presence of a strong B−H stretch at 2522 cm^{-1}. The ^{1}H NMR of **6** showed three distinct

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(27) Compound **2** is soluble only in DMSO, acetone, and THF.

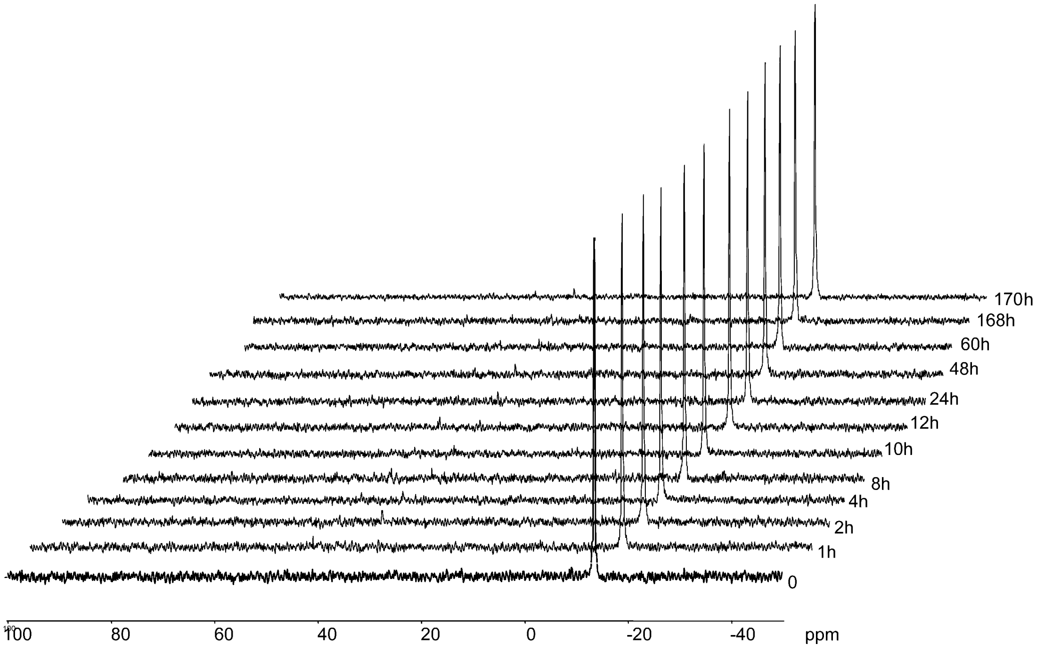
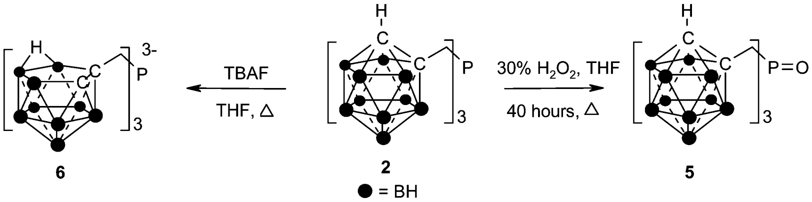


Figure 4. ^{31}P NMR spectra of **2** (acetone-d_6, 121.5 MHz) over time.

Scheme 2



carborane CH signals which were shifted to lower frequency (1.72, 1.80, and 1.88 ppm) than the one signal seen in the starting material (4.89 ppm). The $^{13}C\{^1H\}$ NMR spectrum showed a doublet arising from the carbon atoms of the methylene spacer, which, somewhat surprisingly are also shifted to lower frequency than the corresponding signal in the $^{13}C\{^1H\}$ NMR of **2**. The $^{31}P\{^1H\}$NMR of **6** shows two resonances at 20.3 and 22.3 ppm in approximately a 1:4 ratio, which are shifted to higher frequency than those of the starting material. The two peaks arise because diastereomers are formed during the reaction with fluoride which is a consequence of the fact that the degradation reaction can take place at either the B(3) or B(6) vertex of each carborane cage.[28]

Conclusions

Four unique and sterically hindered pnictogen ligands derived from carboranes were prepared in good to excellent yields. The phosphine ligand **2**, which was remarkably resistant to oxidation, was subsequently used to prepare a complex with Au(I). The cone angle of the carborane–phosphine ligand was determined from the X-ray structure of the Au(I) complex and was found to be 213(2)°, which is among the largest values reported to date. The ease of synthesis, steric bulk, and remarkable resistance to oxidation of compounds **2** and **6** indicates that they can be used as robust substitutes for conventional hindered phosphine ligands. Future work will entail evaluating compounds **2**, **3,** and **6** as ligands for preparing novel coordination complexes and for carrying out Pd-catalyzed cross-coupling reactions.

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Supporting Information Available: Spectra for compounds **2**, **3**, **4**, **5**, and **6**, and crystallographic data (tables of crystallographic details, non-hydrogen coordinates, bond-distances and angles, anisotropic displacement parameters, and hydrogen coordinates) for compounds **2**, **3** and **4** (pdf). Crystallographic information files for the compounds studied (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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