Bis(triphenylphosphine)copper(I) Derivatives of Substituted *arachno* Nine-vertex Borane Anions, $Cu(PPh_3)_2(B_9H_{13}X)$ (X = H, NCS, NCSe, $NCBPh_3$, $NCBH_3$, or $NCBH_2NCBH_3$)

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A series of metallaboranes, $Cu(PPh_3)_2(B_9H_{13}X)$ (**1**)—(**6**), derived from substituted derivatives of the tetradecahydrononaborate(1 −) ions, $[B_9H_{13}X]^-$, in which X is respectively H, NCS, NCSe, $NCBPh_3$, $NCBH_3$, or $NCBH_2NCBH_3$, have been prepared by treating salts of the anions with bis(triphenylphosphine)copper(I) tetrahydroborate. The new bis(triphenylphosphine)copper(I) nonaboranes (**1**)—(**4**) are shown by their ^{11}B, ^1H, and ^{31}P n.m.r. spectra to be fluxional in solution, down to −50 °C. All the neutral complexes are undissociated in dichloromethane but dissociate in acetonitrile solutions. In complexes (**1**)—(**4**), the metal and borane interact through hydrogen bridges on the B_9 cage. In complexes (**5**) and (**6**) the interaction occurs through the BH_3 moiety.

Studies of metallaboranes derived from Cu^IL_n (L = neutral ligand) and borane anions have shown that interaction between the anion and the copper usually occurs in such a way that the copper achieves a four-co-ordinate environment. This occurs through two B–H–Cu bridges in compounds such as $Cu(PPh_3)_2(BH_4)$,[1] $Cu(PPh_3)_2(B_3H_8)$,[2] $[Cu(PPh_3)_2]_2(B_{10}H_{10})$,[3], $Cu(PPh_3)_2[B_3H_7(NCBH_3)]$,[4a] and $Cu(PPh_3)_2(H_3BCO_2R)$ (R = H, Me, or Et).[4b] Other compounds which achieve four co-ordination through single hydrogen bridges include $Cu(PPh_2Me)_3(BH_4)$,[5] $[Cu(PPh_3)_2(NCBH_3)]_2$,[6] or $Cu(PPh_3)_3(H_3BCO_2R)$ (R = H, Me, or Et).[4b,7] Other modes of interaction probably also occur in compounds such as $Cu(PPh_3)(BH_4)$, $Cu(PPh_3)(B_3H_8)$, CuB_3H_8, and $Cu_2B_{10}H_{10}$,[8] for which evidence in solution of some of the compounds suggested co-ordination through three B–H–Cu bridges. Four-co-ordination, and subsequent ion-pair association has been suggested for $Cu(PR_3)_4(B_9H_{14})$ and $Cu(PR_3)_4(B_9H_{12}S)$ (R = Ph or C_6H_4Me-4),[9] and ion pairing has also been indicated for $Cu(PR_3)_3(B_9H_{14})$, $Cu(PR_3)_3(B_9H_{12}S)$, and $Cu(PPh_3)_3(B_{11}H_{14})$.[2c,2e] Compounds in which the co-ordination environment of the copper is not so readily described include $Cu(PPh_3)_2(B_5H_8)$[10] and $Cu(PPh_3)_2(B_{10}H_{13})\cdot CH_2Cl_2$,[2c] in which metal–borane interactions play an important role.

The most frequently used synthetic methods for all of these derivatives have involved metathesis of a Group 1A metal salt of the borane anion with either a preformed copper phosphine halide complex, *e.g.* $Cu(PPh_3)_3Cl$, or with a copper(II) salt in the presence of phosphine ligands. It has further been shown that in many cases the phosphine ligands are labile and this lability resulted in equilibria between complexes containing two, three, or four phosphine ligands; furthermore by removal of a phosphine ligand through complexation, compounds with fewer phosphines were obtained.

We now wish to report a more convenient and versatile route to metallaborane complexes containing the $Cu(PPh_3)_2$ group. This involves a borane-displacement reaction of $Cu(PPh_3)_2(BH_4)$ with a borane salt of a large organic cation {*e.g.* $[N(PPh_3)_2]^+$} in the weakly polar solvent CH_2Cl_2. Using this method we have obtained a new class of metallaboranes from $[B_9H_{14}]^-$ and its monosubstituted derivatives $[B_9H_{13}X]^-$, of general type $Cu(PPh_3)_2(B_9H_{13}X)$ [X = H (**1**), NCS (**2**), NCSe (**3**), or $NCBPh_3$ (**4**)] and a further class in which X is $NCBH_3$ (**5**) or $NCBH_2NCBH_3$ (**6**). The new complexes (**1**)—(**4**) have been shown by their ^{11}B, ^1H, and ^{31}P n.m.r. spectra to be fluxional in solution down to −50 °C, and by conductivity to be undissociated in dichloromethane solution. The data are consistent with structures that involve interaction of the nonaborane anion with the copper through two hydrogen bridges resulting in a time-averaged environment in which there is a plane of symmetry. The ^{11}B, ^1H, and ^{31}P n.m.r. data of (**5**) and (**6**) are consistent with structures derived from interaction of a substituted tetrahydroborate species interacting with the copper through hydrogen bridges.

Experimental

Reagents and Intermediates.—$[B_9H_{14}]^-$, $B_9H_{13}(SMe_2)$, $[N(PPh_3)_2][B_9H_{13}(NCS)]$, and $[N(PPh_3)_2][B_9H_{13}(NCBH_3)]$ were prepared according to established methods.[11,12] $[N(PPh_3)_2][B_9H_{13}(NCSe)]$, $[N(PPh_3)_2][B_9H_{13}(NCBPh_3)]$, and $[N(PPh_3)_2][B_9H_{13}(NCBH_2NCBH_3)]$,[13] were prepared by treating *arachno*-$B_9H_{13}(SMe_2)$ with a slight excess of the $[N(PPh_3)_2]^+$ salt of the anions $[NCSe]^-$, $[NCBPh_3]^-$, or $[NCBH_2NCBH_3]^-$ in refluxing 1,2-dichloroethane. The products were obtained as crystalline white solids, after chromatographic purification on silica using CH_2Cl_2 as eluant, in 40—90% yield and were characterized by their ^1H and ^{11}B n.m.r. spectra.

N.M.R. Spectra.—These were obtained on a Bruker WH 360 spectrometer operating at 360 (^1H), 115.5 (^{11}B), or 145.78 MHz (^{31}P) using the deuterium signal of the solvent as a frequency lock.

Preparation of Bis(triphenylphosphine)copper Nonaborate Derivatives.—Typically, equimolar mixtures of $Cu(PPh_3)_2(BH_4)$ (1 mmol) and the $[N(PPh_3)_2]^+$ salt of the borane anion $[B_9H_{13}X]^-$ (X = H, NCS, NCSe, $NCBPh_3$, $NCBH_3$, or $NCBH_2NCBH_3$) (1 mmol) were placed in a 250-cm^3 round-bottomed flask. Dichloromethane (*ca.* 30 cm^3) was condensed in, under vacuum, and the mixture warmed to room temperature. The solution was stirred for 4 h after which time the solvent was removed under reduced pressure to give a solid (brown for NCS, NCSe, and H substituted borane anions, and white for $NCBPh_3$, $NCBH_3$, and $NCBH_2NCBH_3$ substituted anions). The solid was examined by thin-layer chromatography (t.l.c.) on silica using CH_2Cl_2 as eluant, and in each case a single, major component was observed (R_f 0.80—0.85). The compounds, purified by chromatography on silica gel using CH_2Cl_2 as eluant, gave the *copper complexes* in good yield. Analytical data are presented in Table 1.

Table 1. Analytical data for substituted nine-vertex metallaborane complexes

Compound	T.l.c. (R_f)	Analysis* (%) C	H	N	P
(1) $Cu(PPh_3)_2(B_9H_{14})$	0.81	61.95 (61.80)	6.65 (6.35)	— —	8.10 (8.85)
(3) $Cu(PPh_3)_2[B_9H_{13}(NCSe)]$	0.80	54.80 (55.30)	6.25 (5.40)	1.90 (1.75)	6.35 (7.70)
(2) $Cu(PPh_3)_2[B_9H_{13}(NCS)]$	0.81	55.15 (58.70)	5.85 (5.75)	1.60 (1.85)	8.25 (8.20)
(4) $Cu(PPh_3)_2[B_9H_{13}(NCBPh_3)]$	0.83	67.80 (68.30)	7.80 (6.05)	0.95 (1.45)	5.55 (6.40)
(5) $Cu(PPh_3)_2[B_9H_{13}(NCBH_3)]$	0.82	— —	— —	— —	— —
(6) $Cu(PPh_3)_2[B_9H_{13}(NCBH_2NCBH_3)]$	0.85	58.20 (58.70)	6.55 (6.25)	3.60 (3.60)	6.95 (7.15)

* Required values in parentheses.

Conductivity Measurements.—These were made on solutions in CH_2Cl_2 or CH_3CN (0.002 mol dm^{-3}) using an Electronic Switchgear MC 1 Mark IV conductivity bridge.

Electrochemistry.—Cyclic and a.c. voltammetry were carried out using an EG and G Princeton Applied Research model 363 potentiostat, a Hi-Tek Instruments model PPR1 waveform generator, and a home-constructed unit comprising a.c. amplifier, filter, and phase-sensitive detector. Coulometry was carried out with a Hi-Tek Instruments DT 2101 potentiostat and gated digital integrator. Standard three-electrode cells were used for voltammetry, and a cell divided by Nafion ion-exchange membrane was used for coulometry. Solutions in CH_3CN were referenced to Ag–$AgNO_3$ (0.1 mol dm^{-3}), and solutions in CH_2Cl_2 were referenced to Ag–AgCl $\{[N(PPh_3)_2]Cl, 0.2\ mol\ dm^{-3}\}$.

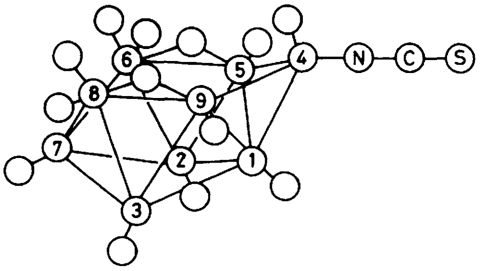
Results and Discussion

Preparations.—Salts of borane anions derived from large organic cations such as $[N(PPh_3)_2]^+$ and $[NBu^n{}_4]^+$ are often easier to isolate in a pure state, and are generally more stable than those of the Group 1A metals. The utility of such derivatives in metathetical synthesis is often limited by the relative solubility of the by-products in non-aqueous media, and hence give incomplete reaction or difficult separation from the desired metallaborane. We have found that by treating the $[N(PPh_3)_2]^+$ salts of the $[B_9H_{14}]^-$ anion and its substituted derivatives $[B_9H_{13}X]^-$ (X = NCS, NCSe, $NCBPh_3$, $NCBH_3$, or $NCBH_2NCBH_3$) with $Cu(PPh_3)_2(BH_4)$ in dichloromethane, the tetrahydroborate ligand is displaced from the copper phosphine complex by the larger borane anion and good yields of the metallaborane complexes $Cu(PPh_3)_2(B_9H_{13}X)$ resulted. Additionally, the product from $[B_9H_{14}]^-$ was different from that described by Muetterties and co-workers[2c] from metathetical reactions.

Structures of the Products.—(*a*) *Conductivity measurements.* The products of the reactions were found by conductivity measurements (Table 2) to be covalent species in solution in CH_2Cl_2, although ready dissociation to the free ions occurred in the co-ordinating solvent, CH_3CN. The conductivity data indicate a specific interaction between the metal and the borane cage.

Table 2. Equivalent conductivities (Λ/S cm^2 mol^{-1})

Compound	Solvent CH_2Cl_2	CH_3CN
(1)	1.3	119
(2)	9.7	96
(3)	2.2	19
(4)	4.2	32
(5)	4.6	31
(6)	4.7	28



(I)

(*b*) *Hydrogen-*1 *and* ^{11}B *n.m.r. spectra.* Details of the ^1H and ^{11}B n.m.r. spectra of the compounds are presented in Table 3 and a typical example, for compound (3), is given in Figure 1. The assignments and numbering of the boron positions are based on earlier work[12] on some of the free ions, which are illustrated in structure (I). In this earlier work, the illustrated static structure, with *exo*- and *endo*-hydrogens at boron positions B(6) and B(8), *endo*-hydrogen at B(4) and with two bridge hydrogens [B(5,6) and B(8,9)] occurred in $[B_9H_{13}(NCS)]^-$ below 233 K; at higher temperatures, the ion was fluxional, and five bridge-like hydrogens at δ –1.40 p.p.m. [derived from the *endo*-hydrogens at B(4), B(6), and B(8); bridge at 5,6 and 8,9 in the static structures] were observed. We have found similar fluxional behaviour in $[B_9H_{13}(NCSe)]^-$ (see Figure 1). In contrast, we have found that the ion $[B_9H_{13}(NCBH_2NCBH_3)]^-$ was static at room temperature, since its ^1H spectrum showed clearly *exo*- and *endo*-hydrogens at B(6,8), a terminal (*endo*-)hydrogen at B(4), and two bridge hydrogens at δ –3.53 p.p.m.

The ^1H and ^{11}B data for compounds (1)—(4) in $CDCl_3$ at ambient temperatures suggest that the plane of symmetry, present in the free anions, is retained in the complexes in the weakly polar solvent, albeit that this may arise as a result of a time-averaged environment. The relative intensity of the bridging hydrogens in the complexes corresponded to three hydrogens, compared with five in the free anions; no signal was detected from the remaining two hydrogens in compounds (2)—(4), strongly indicating Cu–H–B interactions which have been severely broadened by quadrupolar interaction with the Cu, although in (1), a resonance of intensity 2 was observed at δ 0.42 p.p.m. which could be attributed to *endo*-hydrogens interacting with Cu. The ^{11}B resonances of B(7), B(6,8), and B(4) are all broadened to the extent that they are observed as singlets, and this broadening may be attributed to the additional quadrupolar relaxation induced by the presence of the $Cu(PPh_3)_2$ moiety within the complexes. Variable-temperature

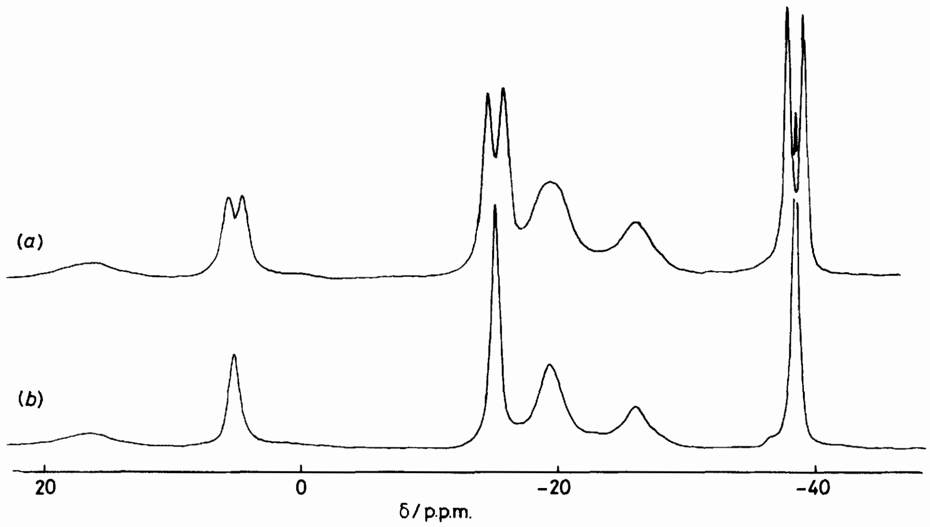


Figure 1. Boron-11 n.m.r. spectra (115 MHz) in $CDCl_3$ of $Cu(PPh_3)_2[B_9H_{13}(NCSe)]$: (*a*) ^{11}B, (*b*) $^{11}B-\{^1H\}$

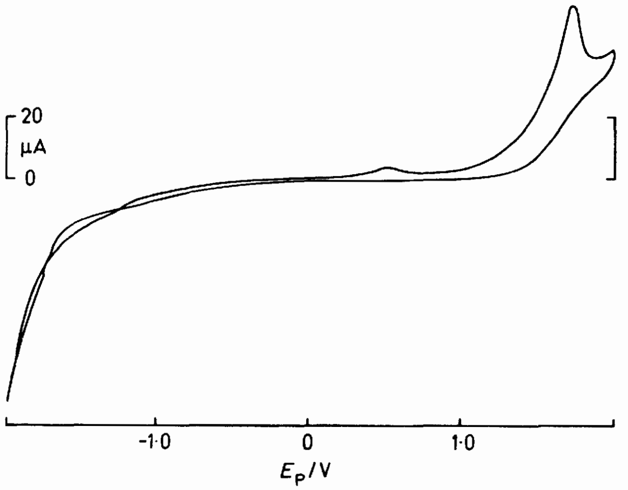
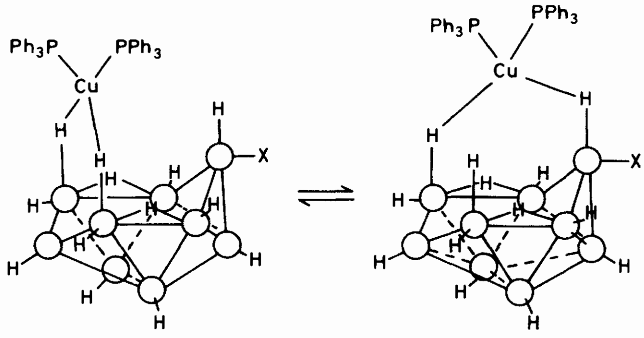
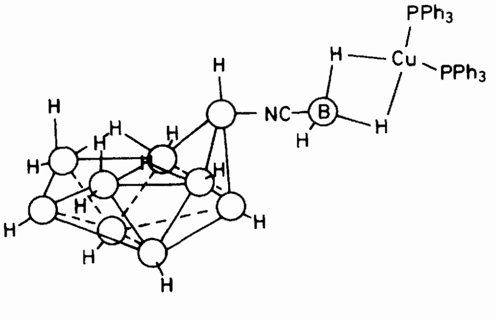


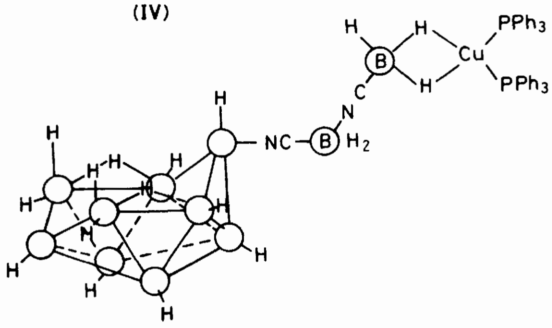
Figure 2. Cyclic voltammogram of $Cu(PPh_3)_2[B_9H_{13}(NCS)]$ at a Pt electrode in CH_2Cl_2–$[NBu^n{}_4][BF_4]$ (0.45 mol dm^{-3}); scan rate 0.05 V s^{-1}



(II) **(III)**



(IV)



(V)

studies of (**2**) and (**4**) in toluene between 290 and 330 K showed that these resonances were broadened almost to the point of being unobservable at low temperatures, although structural resolution was improved at high temperatures.

(*c*) *Phosphorus*-31 *n.m.r. spectra.* The ^{31}P n.m.r. spectra of (**3**) and (**4**) indicated fluxional or exchange behaviour of the phosphine ligands which could be quenched at low temperatures. The spectrum of (**2**) at room temperature comprised a singlet at 0.76 p.p.m. (ref. 85% H_3PO_4) which on cooling to 206 K split into two resonances at 0.95 and 0.11 p.p.m. of relative intensity *ca.* 1:2 respectively, and additional small impurity resonances at 21.5 and 0.5 p.p.m. The spectrum of (**4**) at room temperature comprised a singlet at 0.71 p.p.m. which resolved into two resonances at 0.65 (relative intensity 2) and −1.71 (relative intensity 1) at 206 K, although additional small signals probably due to impurities were observed at 21.6, 3.2, and 2.2 p.p.m. Further cooling (to 171 K) of either compound failed to reveal any further structure, although some broadening of the resonances occurred.

In contrast, the ^{31}P n.m.r. spectrum of (**6**) was a singlet at all temperatures down to 171 K, consistent with a complex whose fluxional behaviour resulted from a much lower energy barrier.

Table 3. Comparison of the correlated ^{11}B and ^{1}H-{^{11}B, continuous wave} spectra of the $[B_9H_{13}X]^-$ anions and the $Cu(PPh_3)_2(B_9H_{13}X)$ complexes in $CDCl_3$

		Free anion		Copper complex	
Compound (anion)	Atom position	$^{11}B^a$/p.p.m.	$^{1}H^b$/p.p.m.	$^{11}B^a$/p.p.m.	$^{1}H^b$/p.p.m.
(**1**) $[B_9H_{14}]^{-c}$	5, 7, 9	−6.8	2.10	−5.3	2.70
	4, 6, 8	−19.2	1.60	−22.5	1.26
	1, 2, 3	−22.4	1.10	−25.4	1.62
	bridge		−1.50 (5)		−1.61 (3)
	PPh_3				7.4 (30)
	CuHB				0.42 (2)
(**2**) $[B_9H_{13}(NCS)]^-$	7	14.8	3.68	15.46	3.91
	1	4.2	2.85	4.49	3.0
	5, 9	−16.4	1.53	−15.6	1.68
	6, 8	−18.0	1.86[d]	−19.1	1.99
			−0.41[d]		
	4	−22.0	0.60[d]	−24	—
	2, 3	−38.3	0.25	−38.4	0.4
	bridge		−1.4 (5)		−1.3 (3)
	PPh_3				7.4 (30)
(**3**) $[B_9H_{13}(NCSe)]^-$	7	15.8	3.73	16.7	3.9
	1	5.2	2.86	5.21	3.05
	5, 9	−15.6	1.58	−15.14	1.73
	6, 8	−17.8	1.89	−19.4	1.91
	4	−22.7	—	−25.7	—
	2, 3	−37.8	0.22	−38.4	0.38
	bridge		−1.42 (5)		−1.3 (3)
	PPh_3				7.4 (30)
(**4**) $[B_9H_{13}(NCBPh_3)]^-$	7	16.6		16.93	4.0
	1	5.2		5.20	3.16
	$NCBPh_3$	−10.7		−10.67	
	5, 9	−14.9		−15.11	1.83
	6, 8	−19.5		−19.40	2.0
	4	−25.7		−26.03	—
	2, 3	−38.4		−38.41	0.5
(**5**) $[B_9H_{13}(NCBH_3)]^-$	7	16.2		17.5	3.97
	1	4.8		4.9	2.97
	5, 9	−15.5		−14.8	1.70
	bridge				−3.55 (2)
	6, 8	−19.4		−20.0	
	exo				1.94
	endo				−0.25
	4	−25.5		−26.6	0.24
	2, 3	−38.6		−38.6	0.41
	BH_3	−43.0		−36.5	1.73
(**6**) $[B_9H_{13}(NCBH_2NCBH_3)]^-$	7	17.1	3.9	17.97	4.08
	1	5.07	3.03	5.3	3.21
	5, 9	−14.7	1.79	−14.4	1.99
	bridge		−3.53 (2)		−3.37 (2)
	6, 8	−20.2		−20.2	
	exo		1.88		2.07
	endo		−0.27		−0.12
	4		0.43		0.55
		−27.3		−26.9	
	BH_2		2.09		2.07
	2, 3	−38.6	0.37	−38.44	0.59
	BH_3	−43.3	0.57	−37	1.83
	PPh_3				7.45 (30)

[a] Reference $Et_2O{\cdot}BF_3$. [b] Reference $SiMe_4$; relative intensities in parentheses. [c] Data from CD_3CN solution. [d] *endo* hydrogens from low-temperature spectra.

(*d*) *Structural conclusions.* The ^{31}P, ^{11}B, and ^{1}H data of compounds (**1**)—(**4**) together indicate a structure which is fluxional at ambient temperature and which results in a time-averaged environment containing a plane of symmetry. The most reasonable structure is therefore one in which two of the three *endo*-hydrogens from boron positions 4, 6, and 8 are involved in Cu–H–B bridges to the $Cu(PPh_3)_2$ moiety, as in structures (**II**) and (**III**). The ^{31}P n.m.r., together with the large shifts of the ^{11}B and ^{1}H resonances in the BH_3 group in compounds (**5**) and (**6**) indicated that interaction with the copper occurred through this group. Hence the structures of (**5**) and (**6**) are proposed to be substituted tetrahydroborate complexes [structures (**IV**) and (**V**) respectively].

In contrast to compounds (**1**)—(**4**), the hydrogens on the B_9 cage in (**5**) and (**6**) are static at ambient temperature.

Electrochemistry.—In contrast to $Cu(PPh_3)_2(BH_4)$ and $Cu(PPh_3)_2(B_3H_8)$, each of which showed irreversible reductions to Cu and irreversible oxidations primarily associated to the borane anion,[14] the derivative $Cu(PPh_3)_2(B_9H_{14})$ failed to show clearly defined oxidation or reduction waves by cyclic voltammetry or cyclic a.c. voltammetry. However, the substituted derivatives showed irreversible oxidations or reductions approaching the electrochemical potential limits of the solvent (CH_2Cl_2). Thus, in $Cu(PPh_3)_2[B_9H_{13}(NCS)]$, an irreversible oxidation was observed at $E_p = 1.75$ V, and is shown in Figure 2. The derivatives $Cu(PPh_3)_2[B_9H_{13}(NCSe)]$ and $Cu(PPh_3)_2[B_9H_{13}(NCBH_2NCBH_3)]$ each showed broad, irreversible oxidations with $E_p > 1.35$ V. In addition, $Cu(PPh_3)_2[B_9H_{13}(NCSe)]$ showed an irreversible reduction with $E_p = -1.4$ V.

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