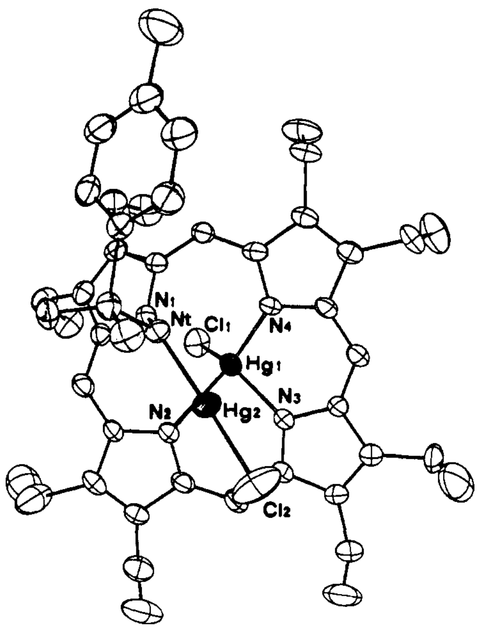

Figure 1. Computer-drawn model of the binuclear complex. The mercury–nitrogen distances are drawn up to 2.50 Å and the tosyl group is artificially darkened for clarity. Selected angles: Cl(2)–Hg(2)–N(t), 162.1 (2); Cl(1)–Hg(1)–N(2), 105.8 (1); Cl(1)–Hg(1)–N(3), 148.0 (2); Cl(1)–Hg(1)–N(4), 125.1 (1); N(2)–Hg(1)–N(3), 75.4 (2); N(2)–Hg(1)–N(4), 115.3 (2); N(3)–Hg(1)–N(4), 79.3 (2)°.

phinato core[13] are for N–C(α), 1.382 (8); C(α)–C(β), 1.443 (9); C(β)–C(β), 1.36 (1); and C(α)–C(m), 1.389 (9) Å. These distances are quite similar to those found in normal metalloporphyrins.[14]

Sitting-atop mercury complexes of porphyrins were formulated as polynuclear with porphyrins acting as bidentate or tridentate ligands with respect to each mercury atom[4] and in N-substituted porphyrin complexes a linear coordination geometry was preferred.[5] Our results demonstrate that tetracoordination (Hg(1)) is more general and also applied in the N-substituted case. On the other hand a linear coordination is a better description for the Hg(2) atom.

Supplementary Material Available: Atomic parameters (Table 1), bond distances and angles (Table 2), and listings of observed and calculated structure factors (Table 3) (34 pages). Ordering information is given on any current masthead page.

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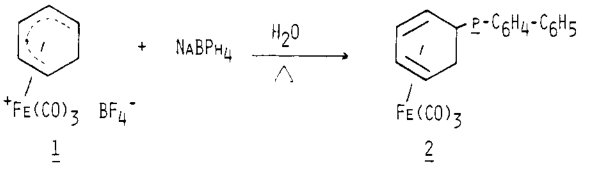
Nucleophilic Biphenylyl Transfer with the Tetraphenylborate Ion. A New Amphophilic Reagent

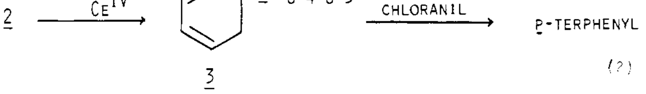
Sir:

Owing to the insolubility and high crystallinity of tetraphenylborate salts, the tetraphenylborate ion (Ph_4B^-) is extensively used in the analysis of various metallic ions, as well as in the characterization of ammonium and other cationic species.[1] Accordingly, this ion is widely regarded as being chemically inert[2] to all but oxidizing agents and strong protonic acids.[3] We now report the facile ability of the tetraphenylborate ion to serve as a biphenylyl anion synthon.

Reaction of an aqueous solution of the electrophilic species η^5-cyclohexadienyltricarbonyliron tetrafluoroborate (**1**)[4] with sodium tetraphenylborate[5] at 90 °C yields 5-*p*-biphenylyl-1,3-cyclohexadienetricarbonyliron (**2**),[6] mp 120.5–121.5 °C, in 35–65% yield[7] (eq 1). Structural elucidation was accomplished by the oxidative liberation of the free ligand, 5-*p*-biphenylyl-1,3-cyclohexadiene (**3**)[8] (1,6-dihydro-*p*-terphenyl), in quantitative yield using ceric ammonium nitrate, followed by dehydrogenation to *p*-terphenyl in ~85% yield using chloranil (eq 2).[9]

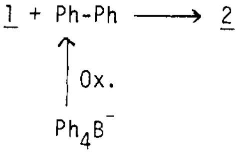


(1)



(2)

With regard to the mechanistic rationalization of the nucleophilic biphenyl transfer, at the onset several mechanisms appeared reasonable. In view of the reports of the facile oxidation of Ph_4B^- by oxygen,[3a,10] as well as by a variety of metallic species,[3b-e] to yield biphenyl, and in view of the reported ability of cation **1** to react by electrophilic substitution with various benzenoid species,[11] mechanism A involving aromatic electrophilic substitution of biphenyl was of immediate concern.



mechanism A

However, such a mechanism can be ruled out by the failure of cation **1** to react with biphenyl under the same reaction conditions used to prepare complex **2**. Although, with the solvents used (water–hexane), the cation and biphenyl were in different phases, even in refluxing acetonitrile, a solvent in which both species are mutually soluble, formation of complex **2** from cation **1** and biphenyl was not observed.[12]

A more tenable mechanistic pathway is indicated in mechanism Ba, in which a phenyl group on boron is attacked by the

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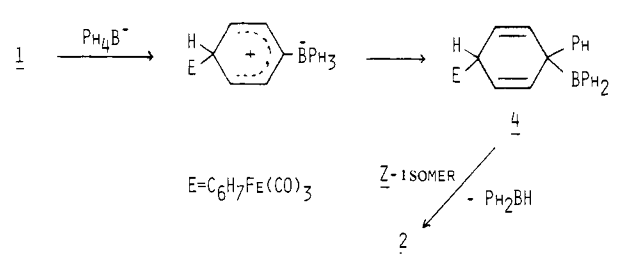
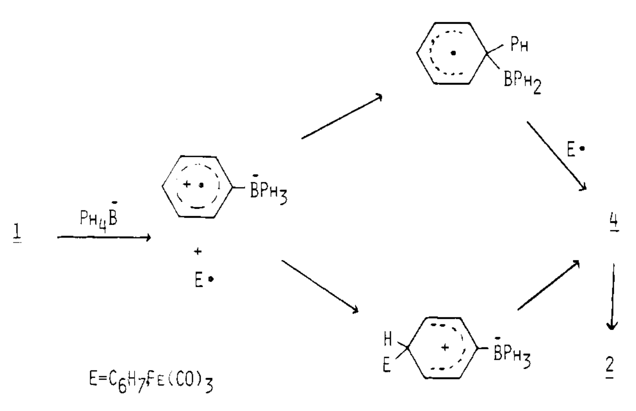


mechanism Ba

electrophilic cation **1** followed by intramolecular nucleophilic attack by another phenyl group ,[13] the net effect being what Negishi[2a,c] refers to as "amphophilic substitution" of a phenyl group attached to boron.

In view of the relatively high yield of **2**, the formation of **2** presumably occurs predominately, if not exclusively, by an "allowed"[14] concerted, syn-1,4-elimination of diphenylborane from the *Z* isomer of the intermediate **4**.[15] Steric considerations would argue for the predominance of the *Z* isomer over the *E* isomer.

An alternative, modified mechanism (mechanism Bb) involving initial electron transfer from the borate ion to the cation is deemed less likely, but cannot be ruled out.[16]



mechanism Bb

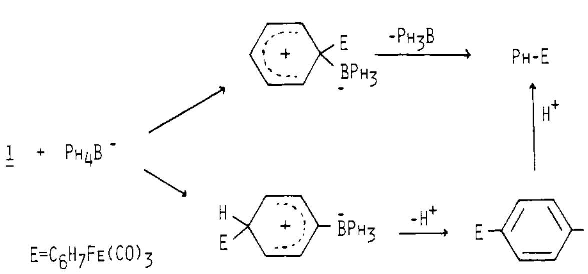
Complex **2** would be formed from the same substituted 1,4-cyclohexadiene derivative **4** (*E* and *Z* isomers) in the manner suggested in the ionic mechanism Ba.

The ability of the tetraphenylborate ion to serve as a biphenylyl anion transfering agent for transition-metal π-complexed cations appears to be general, but with varying degrees of success. For example, η^5-cycloheptadienyltricarbonyliron tetrafluoroborate[17] reacts with Ph$_4$B$^-$ under the previously mentioned reaction conditions to give biphenylyl transfer, but in only 9% yield.

At the present time the biphenylyl transfer reaction appears to be limited to those π-complexed cations which are stable to the aqueous media used, since the use of nonaqueous, aprotic media such as THF or CH$_3$CN has so far afforded only a complex mixture of products, which have not as yet been identified.[18]

The amphophilic nature of the phenyl group of Ph$_4$B$^-$, which results in biphenylyl transfer, is of interest in view of the alternative possibility of observing only electrophilic attack on a phenyl group with subsequent deboronation which would result in phenyl rather than biphenylyl transfer. Either ipso[19] electrophilic attack or possibly para (or ortho) attack followed by rapid aromatization with loss of a proton could in principle give phenyl transfer (eq 3). There was, however, no evidence for the formation of 5-phenyl-1,3-cyclohexadienetricarbonyliron, the expected product of phenyl transfer.

Although ipso attack of electrophiles on the tetraphenylboron anion has been reported,[2c,3] the failure to observe it in the present instance could be due to the bulk of cation **1**. On the other hand, Negishi in his studies[3c] on the methylation of the 1-naphthyltri-*n*-butylborate ion in which the effect of the leaving group was examined observed that ipso attack was dramatically reduced at the expense of ortho attack with the more readily dissociating methylating agents. By extrapolation, a carbon electrophile bearing a full positive charge would be expected to give virtually no ipso attack, which, perhaps fortuitously, is in fact observed in the reaction reported here.



(3)

That para attack by cation **1** leads to biphenylyl rather than phenyl transfer is presumably simply a reflection of the greater rate of intramolecular phenyl migration relative to the rate of aromatization by loss of a proton.

In view of the reactivity of Ph$_4$B$^-$ reported here, the observed instability of the Ph$_4$B$^-$ salts of several organic cations (pyridinium, trityl)[20] is currently being examined.

Acknowledgment. Partial support by the National Science Foundation (Grant CHE 76-05571) in the purchase of the FT NMR accessory is gratefully acknowledged.

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(6) (a) Satisfactory elemental analysis was obtained for complex **2,** as well as compound **3.** (b) Complex **2:** IR (KBr) 2045, 1980, 1475, 835, 770, 735, 700 cm^{-1}; ^{1}H NMR (CS$_2$) σ 1.5–1.7 (dm, 1 H), 2.1–2.5 (m, 1 H), 3.0–3.8 (2 H), 3.2–3.4 (dt, 1 H), 5.2–5.5 (m, 2 H), 7.0–7.4 (m, 9 H); ^{13}C NMR (CDCl$_3$) (coupled data) σ 44.2 (d, J_{CH} = 140 Hz, C$_5$), 33.5 (t, J_{CH} = 130 Hz, C$_6$), 60.6 (d, J_{CH} = 154 Hz, C$_1$(C$_4$)), 66.8 (d, J_{CH} = 160 Hz, C$_4$(C$_1$)), 84.3 (d, J_{CH} = 170 Hz, C$_2$(C$_3$)), 86.0 (d, J_{CH} = 170 Hz, C$_3$(C$_2$)), 126.8 (d, J_{CH} = 160 Hz, C$_2{}'$(C$_2{}''$)), 126.9 (d, J_{CH} = 160 Hz, C$_2{}''$(C$_2{}'$)), 127.0 (d, J_{CH} = 160 Hz, C$_4{}''$), 127.2 (d, J_{CH} = 160 Hz, C$_3{}''$). 128.5 (d, J_{CH} = 160 Hz, C$_3{}'$) , 139.0 (s, C$_4{}'$), 140.6 (s, C$_1{}'$), 145.7 (s, C$_1{}''$); MS *m*/*e* 371 (M$^+$), 343 (M$^+$ – CO), 314 (M$^+$ – 3CO), 231 (M$^+$ – Fe(CO)$_3$). (c) The biphenyl group is probably exo by analogy to the course of other nucleophilic additions to cation **1.** For a review, see Birch, A. J.; Jenkins, I. D. In "Transition Metal Organometallics in Organic Synthesis", Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1, pp 1–82.

(7) The reaction was conducted under N$_2$ with a degassed two-phase solvent system (H$_2$O–hexane, 1:1) with rapid stirring for 10–24 h. Longer reaction times gave greater yields. The neutral reaction products were recovered from the hexane layer and taken up in a minimum amount of pentane. Cooling of the pentane solution afforded crystalline complex **2.** Two recrystallizations from Skelly B afforded analytically pure **2.**

(8) (a) Compound **3:** mp 67–68 °C; IR (KBr) 1480, 830, 765, 700, 675 cm^{-1}: ^{1}H NMR (CS$_2$) σ 2.24–2.52 (m, 2 H), 3.55 (br tt, 1 H), 5.64–6.0 (m, 4 H),

7.14–7.50 (m, 9 H); ^{13}C NMR ($CDCl_3$) σ 31.6, 39.4, 123.8, 124.4, 125.3, 126.8, 126.9, 127.8, 128.5, 129.7, 139.1, 140.8, 144.3. (b) Several dihydro derivatives of *p*-terphenyl, such as as 1,4- and 5,6-dihydro-*p*-terphenyl, have been obtained by dissolved metal reductions of *p*-terphenyl. However, compound **3** (1,6-dihydro-*p*-terphenyl) cannot be prepared in this manner: Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *J. Am. Chem. Soc.* **1972,** *94,* 5412.

(9) *p*-Terphenyl: mp 208–210 °C (lit. mp 213 °C); the IR (KBr) and ^1H NMR spectra of our sample were identical with those reported for authentic *p*-terphenyl.

(10) Geske, D. H. *J. Phys. Chem.* **1959,** *63,* 1062.

(11) See, e.g. Kane-Maguire, L. A. P.; Mansfield, C. A. *J. Chem. Soc., Chem. Commun.* **1973,** 540.

(12) Only a small quantity of a mixture of 1,3-cyclohexadienetricarbonyliron and the dimer, 5,5′-bis(1,3-cyclohexadiene)hexacarbonyldiiron, was isolated.

(13) Similar migration of an aryl group has been observed in the oxidation of tetraarylborate ions.[3] (For a detailed discussion of this and related rearrangements, see Eisch, J. J. *Adv. Organomet. Chem.* **1977,** *16,* 67.) The intramolecular nature of the migration has been demonstrated in the cases of electrochemical and ceric ion oxidation[3c] and appears to obtain with other oxidants as well.[3e]

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(15) (a) Similar mechanistic arguments for ortho attack have been offered in the reaction of CH_3OSO_2F and the tri-*n*-butyl-1-naphthylborate ion (Negishi and Merrill, ref 2a). (b) Facile oxidation of the dihydro derivative obtained from deboronation of the *E* isomer under the reaction conditions (degassed solvents; inert atmosphere) or nonconcerted loss of the elements of Ph_2BH from the *E* isomer of **4** would appear unfavorable.

(16) The initial electron transfer and subsequent phenyl migration in mechanism Bb parallels that suggested for the oxidation of Ph_4B^- by metallic species, as well as by DDQ.[3e]

(17) Burton, R.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961,** 594. Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961,** *83,* 497.

(18) An attempt to oxidatively deboronate the possible intermediate **4** by treatment of the reaction products obtained in THF with $^-OH/H_2O_2$ failed to yield complex **2** or any evidence for the free ligand **3.** In CH_3CN (with or without H_2O) the only characterizable complexes were 1,3-cyclohexadienetricarbonyliron and the dimer 5,5′-bis(cyclohexadiene)hexacarbonyldiiron.

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(20) Unpublished observations, this laboratory.

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Received August 13, 1979

Transfer of CIDNP via Proton Exchange and Nuclear Overhauser Effect

Sir:

It is typically assumed that, if a molecule displays CIDNP,[1] its polarized nuclei experience a hyperfine coupling in an intermediate paramagnetic state. We point out here that CIDNP can become transferred *intermolecularly,*[2] for example,[3] via chemical exchange[4] of spin polarized protons. Furthermore, the well-known nuclear Overhauser effect (NOE)[5] causes a secondary nuclear spin polarization in all those nuclei which are coupled by either scalar ("negative NOE") or dipolar ("positive NOE") interactions to the exchanging protons. Consequently, "*inert*" molecules may display "CIDNP" deceptively, whereas this phenomenon is really a "chemically induced (or 'pumped') NOE" (CINOE). The latter may complicate the analysis of CIDNP spectra, but it may also be exploited for the following applications: (a) selective signal enhancement of protons and of other nuclei (^{15}N), (b) assignment assistance for specific resonances (for example α protons in alcohols), and (c) study of proton exchange and the dynamics thereof.

The concept of CINOE follows readily from the polarization transfer experiments of Hoffman and Forsén[6] together with the known negative or positive NOE associated with chemical exchange of spin polarized protons.[5] Whereas NOE is typically "pumped" electronically, CINOE offers certain advantages: (a) the initial polarization can be orders of magnitude larger (by the enhancement factor of CIDNP[1]) than those generated electronically; (b) the sign of the transferred polarization can conveniently be chosen to be either positive or negative by changing one of the parameters connected by Kaptein's rules of CIDNP[7] or the recent additions thereto;[8] (c) broad resonances can be pumped too. The latter allows pumping of the broad resonances of protons attached to ^{14}N (or any other fast relaxing quadrupole nucleus), since only the T_2 and not the T_1 of these protons is short.[5] Electronically such broad resonances are very difficult if not impossible to pump. Figure 1 illustrates the results for formamide (2×10^{-3} mol/L) and Figure 1b for the ^{15}N enriched (95%) species. In addition to the NMR spectra[9] the CINOE spectra are shown (Figure 1a′ and 1b′), obtained by using equimolar mixtures (8×10^{-3} mol/L) of biphenyl-d_{10} and triethylamine (TEA) in CD_3CN as solvent for a pump. The spectra were recorded on a slightly modified Varian HA 100 spectrometer in an all-quartz probe during UV irradiation with the $NiSO_4$-filtered[10] light of a 1 kW mercury-xenon lamp (Hanovia 977B-1).

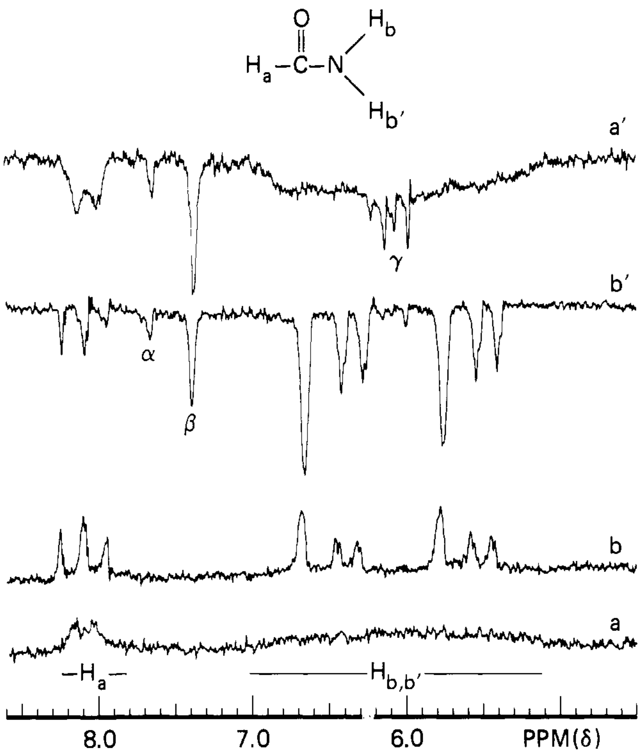

Figure 1. NMR spectra of formamide (a) and of formamide-^{15}N (b) in CD_3CN and CINOE spectra (a′ and b′).

A prerequisite for CINOE studies, namely an efficient pump was found in photoinduced electron-transfer reactions between tertiary aliphatic amines as donors and a variety of acceptors (A) listed in Table I. The α protons namely, i.e., the protons attached to the α carbons of the tertiary amine derived radical

Table I

acceptor	donor	polarized in -*H*	-H*	-H**
biphenyl	TEA	E	E	A
naphthalene	TEA	E	E	A
naphthalene	$CH_3CH_2CH_2N(CH_3)_2$	E	E	A
naphthalene	$CH_3CH_2CD_2N(CD_3)_2$		none	
naphthalene	*N*-alkylpyrrole	A	A	E
CD_3CN	TEA	A	A	E
C_6H_5CN	TEA	A	A	E
benzophenone	TEA	A	A	E
anthraquinone	TEA	A	A	E

[a] E denotes emission, A absorption. For explanation of -*H*, -H*, and -H**, cf. Chart I.

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