Hz) due to the carbon atoms of the Me_2Si, Me_3Si, and $(Me_3Si)_2N$ groups, respectively, and a triplet centered at δ 68.8 (J_{CH} = 120 Hz) due to the methylene carbon atom. The bright yellow, paramagnetic (μ_B = 2.7 BM at 30 °C by Evans' method) uranium metallocycle,[14] mp 126–129 °C, was further characterized by its ^1H NMR spectrum which consists of four singlets at δ + 2.08, −9.90, −23.3, and −128.6 in an area ratio of 6:9:36:2 due to Me_2Si, Me_3Si, $(Me_3Si)_2N$, and CH_2 groups, respectively. An X-ray analysis is in progress.[15] The only volatile, organic product isolated from pyrolysis of the hydrides is hydrogen and methane from pyrolysis of the methyl derivatives. The transformation is reversible in the case of X = H since exposure of the metallocycles to an atmosphere of molecular hydrogen yields the hydrides. Further, exposure of the metallocycles to deuterium yields the perdeuteriothorium or -uranium amides. The uranium metallocycle can also be prepared by reaction of $[(Me_3Si)_2N]_3UCl$ and ethyllithium or trimethylsilylmethyllithium, the organic product being ethane or tetramethylsilane, respectively.

Observation of the facile hydride-metallocycle interconversion suggests the mechanism shown in Scheme I. The first step in Scheme I proposes that metal hydride-deuterium exchange occurs by way of a four-center interaction similar to that proposed by Schwartz to account for metal H-D exchange in $Cp_2Zr(H)(R)$.[16] The next step is elimination of HD yielding the ylide (A) or its valence tautomer, the fully developed metallocycle (B). This intermediate is the key to the mechanistic proposal since it allows incorporation of the deuterium label into the silylamido ligands. This scrambling mechanism is rather different from that proposed by Bercaw to account for formation of perdeuterio-$(Me_5C_5)_2ZrH_2$ which occurs by conventional oxidative-addition, reductive elimination steps, though these authors isolate a compound which is thought to be $(Me_5C_5)ZrMe_3C_5(CH_2)_2$.[17]

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(4) The melting point of the undeuterated hydride is 97–98 °C.[3]
(5) Anal. Calcd for $C_{18}D_{55}N_3Si_6U$: C, 27.9; D, 14.2; N, 5.43. Found: C, 27.8; D, 13.7; N, 5.34.
(6) The perdeuterioamide was hydrolyzed with NaOD in D_2O and the amine was transferred under vacuum to a vessel which was connected to a mass spectrometer. Analysis of the fragmentation pattern relative to that of undeuterated amine[7,8] showed that the amine was ≥98% deuterated.
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(11) The melting point of the undeuterated hydride is 145–147 °C.[3]
(12) Anal. Calcd for $C_{18}D_{55}N_3Si_6Th$: C, 28.1; D, 14.3; N, 5.49. Found: C, 28.4; D, 13.6; N, 5.54.
(13) The amine is ≥91% deuterated.[6-8]
(14) Anal. Calcd for $C_{18}H_{53}N_3Si_6Th$: C, 30.3; H, 7.45; N, 5.90. Found: C, 30.0; H, 7.14; N, 5.69; M^+ (by mass spectrometry), 711. Calcd for $C_{18}H_{53}N_3Si_6U$: C, 30.1; H, 7.39; N, 5.86. Found: C, 29.8; H, 7.14; N, 5.77; M^+ (by mass spectrometry), 717.
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Sitting-atop Porphyrin Complexes. The Structure of the Bischloromercury(II) Complex of *N*-Tosylaminooctaethylporphyrin

Sir:

Metalloporphyrins in which the metal is bonded to fewer than four nitrogen atoms, sitting-atop complexes, may be considered as models for the initial steps of the metalation of the macrocycle. Such complexes are known for ruthenium and technetium,[1] rhodium,[2] and platinum.[3] Also several examples of mercury complexes have been formulated,[4,5] but no X-ray structural data are available so far. In this communication we describe the molecular structure of a bischloromercury complex of *N*-tosylaminooctaethylporphyrin which represents the first X-ray structural proof for the existence of mercury(II) porphyrin sitting-atop complexes.

The bischloromercury(II) complex of *N*-tosylaminooctaethylporphyrin, $C_{43}H_{51}N_5O_2SCl_2Hg_2$, was prepared from the corresponding base[6] and mercury(II) chloride.[7] Single crystals were grown by slow evaporation from a $CHCl_3$-CH_2Cl_2-CH_3OH solution. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 17.887 (6), b = 17.121 (6), c = 15.301 (4) Å; β = 113.48 (8)°; Z = 4; F_{000} = 2280; D_c = 1.814 g cm^{-3}. Intensity data were collected on a Philips PW1100 diffractometer and corrected for absorption (Mo Kα radiation, μ = 75.01 cm^{-1}, 2θ < 65°, step scan techniques); 7224 reflections with $I > 4\sigma(I)$ were used in structure refinement and resolution. The structure was solved by the heavy-atom method and anisotropically refined by full-matrix least-square techniques (R_1 = 0.040 and R_2 = 0.058).[8] Figure 1 gives a perspective view of the molecular compound which appears as a sitting-atop complex. Atoms Hg(1) and Hg(2) are located on both sides of the macrocycle and separated by 3.39 Å. The most interesting distances from mercury atoms to the ligand are summarized in Table I. It must be noted that the mercury-nitrogen distances are largely diversified from ~2 to >3 Å. As currently observed even in highly distorted metalloporphyrins the four pyrrole nitrogens N(1)-N(4) are here coplanar within ±0.03 Å. The tosyl nitrogen N(t) is considerably removed from the (4N) plane; its displacement of 1.36 Å is in the same direction that the linked Hg(2) atom, itself displaced by 2.05 Å. Hg(1) is 1.28 Å out of plane in the opposite direction. The porphyrin macrocycle is distorted. Indeed the distortion appears as a result of the *N*-tosyl group. Thus, pyrrole N(1) to which is attached the *N*-tosyl is the most deviate from the (4N) plane, making a dihedral angle of 40.8°, whereas small angles of 1.6, 9.1 and 10.2° occur with pyrroles N(2), N(3), and N(4), respectively. Dihedral angles between pyrroles are 39.6 for N(1)-N(2), 7.5 for N(2)-N(3), 1.1 for N(3)-N(4), and 33.3° for N(4)-N(1). Similar influence on the overall structure, causing the N-substituted pyrrole ring to deviate strongly from the mean plane of the remainder of the porphyrin ligand, has been previously reported in N-substituted metalloporphyrin complexes of cobalt,[9] manganese,[10] zinc,[11] and nickel.[7,12] Distortion of the porphinato core has little or no effect on π-electron delocalization and on bond parameters. The average values for both lengths in the por-

Table I. Interatomic Distances around Mercury Atoms

from Hg(1) to	Å	from Hg(2) to	Å
Cl(1)	2.318 (2)	Cl(2)	2.285 (2)
N(3)	2.194 (5)	N(t)	2.075 (5)
N(4)	2.325 (5)	N(2)	2.597 (5)
N(2)	2.496 (5)	N(3)	2.863 (6)
N(1)	2.829 (5)	N(1)	3.090 (5)
		N(4)	3.264 (5)

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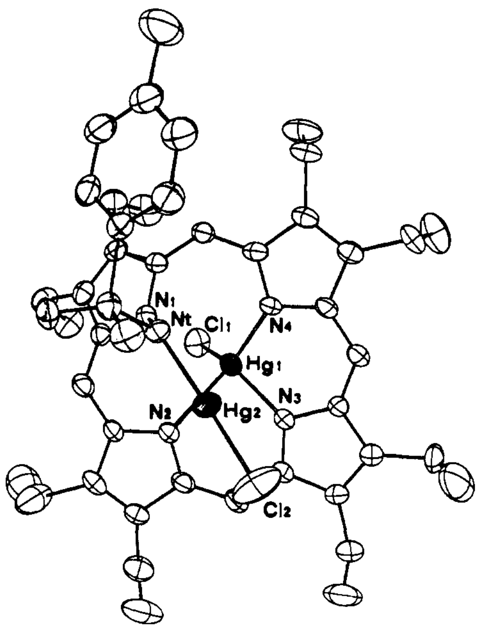

Figure 1. Computer-drawn model of the binuclear complex. The mercury-nitrogen distances are drawn up to 2.50 Å and the tosyl group is artificially darkened for clarity. Selected angles: Cl(2)-Hg(2)-N(t), 162.1 (2); Cl(1)-Hg(1)-N(2), 105.8 (1); Cl(1)-Hg(1)-N(3), 148.0 (2); Cl(1)-Hg(1)-N(4), 125.1 (1); 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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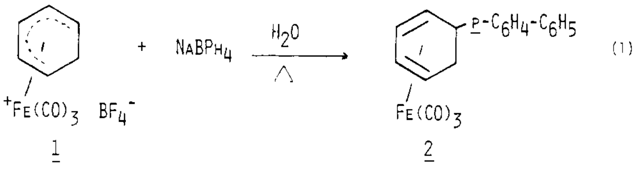
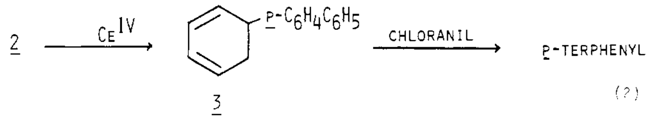
Nucleophilic Biphenylyl Transfer with the Tetraphenylborate Ion. A New Amphophilic Reagent

Sir:

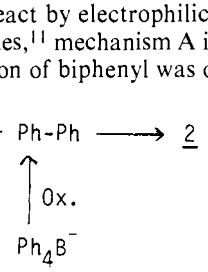
Owing to the insolubility and high crystallinity of tetraphenylborate salts, the tetraphenylborate ion (Ph_4B^-) is extensively used in the analysis of various metallic ions, as well as in the characterization of ammonium and other cationic species.[1] Accordingly, this ion is widely regarded as being 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]





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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