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The Direct Chlorination of Pentaborane(9)

Sir:

The previously unreported 1-chloropentaborane(9)[1] can be prepared in greater than 90% yields by the direct chlorination of pentaborane in the presence of aluminum chloride. In the absence of this catalyst 2-chloropentaborane[2] is by far the most predominant isomer, but so far the yields have not exceeded 30%.

In a typical experiment 6.5 mmoles of chlorine, 11.6 mmoles of pentaborane, about 1 g of aluminum chloride, and 13 ml of boron trichloride were condensed into a reaction flask on the vacuum line.[3] The flask was then sealed from the vacuum line and warmed from −108 to 0° over a 2-hr period and maintained at 0° for 18 hr. Separation of the reaction mixture by fractional condensation resulted in the isolation of 6.0 mmoles (92% based on chlorine) of 1-chloropentaborane. The mass spectrum of 1-chloropentaborane is almost identical with that of 2-chloropentaborane (some relative intensities are different). The ^{11}B nmr spectrum (32.1 Mc) is similar to that of other 1-halopentaboranes, consisting of a doublet at $\delta = 11.9$ ppm ($BF_3 \cdot O(C_2H_5)_2 = 0.0$), $J = 170 \pm 5$ cps, corresponding to B^{2-5}–H, and a singlet at $\delta = 29.3$ ppm corresponding to B^1–Cl with an area ratio of 4.0:1.0, respectively. The ^{1}H nmr spectrum (100 Mc) consists of a quartet of equally intense lines at τ 7.07, $J = 165 \pm 5$ cps, corresponding to the four identical terminal hydrogens bonded to ^{11}B, and a broad resonance at τ 11.27, corresponding to an equal number (area ratio 1.00 ± 0.03) of bridging hydrogens. The melting range of 1-chloropentaborane is 26–27° and its vapor pressure at 28° is 4.2 mm. The gas-phase infrared spectrum contains bands at: 2610 (s), 1840 (w), 1785 (w), 1610 (vw), 1435 (m), 1380 (m), 1200 (m), 1160 (m), 1065 (w), 905 (m), 855 (w), 765 (w), and 635 (m) cm^{-1}.

A similar reaction was attempted in the absence of aluminum chloride. In this case only traces of 1-chloropentaborane were observed, but a 15% yield of 2-chloropentaborane (based on chlorine) was obtained. Low-temperature liquid-phase reactions and low-pressure gas-phase reactions were carried out in an attempt to improve the yield of 2-chloropentaborane, but in all cases the yields have been between 10 and 30%.

A previous attempt to chlorinate pentaborane in the presence of aluminum chloride in carbon disulfide solution was reported[4] to yield "microquantities" of a chloropentaborane contaminated with carbon tetrachloride, and attempts to duplicate the reaction on a larger scale resulted in explosions.[5]

It appears that in the absence of a strong Lewis acid the chlorination of pentaborane is a radical reaction. By contrast, halogenations with bromine and iodine produce 1-halopentaboranes almost exclusively and in high yields. These reactions can be envisioned as occurring *via* heterolytic cleavage of the halogen followed by electrophilic displacement of a proton from the 1 position in pentaborane by the positive halogen. This is similar in concept to the chlorination in the presence of aluminum chloride, a strong heterolytic catalyst.

The assumption that the uncatalyzed chlorination of pentaborane is a radical reaction is supported by the following observations. First, when the bromination of pentaborane is carried out in the presence of strong ultraviolet irradiation, the reaction proceeds about 100 times faster than usual,[6] and the ratio of 2-bromo- to 1-bromopentaborane increases from the value 0.049 reported by Burg and Sandhu[7] to 1.2 (although the total yield of bromopentaboranes decreases to about 45%, based on bromine). Second, attempts to chlorinate pentaborane with ICl and ICl_3 resulted in the formation of 1-iodopentaborane, in both cases in greater than 90% yields. Further studies of the halogenation of pentaborane are in progress and will be reported shortly.

Acknowledgment. We wish to thank the National Science Foundation and the Wisconsin Alumni Research Foundation for support of this research.

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$S = 1$ Ground State in Six-Coordinated Iron(II)

Sir:

We wish to report here on some results which demonstrate that $S = 1$ ground states may be stabilized in *six-coordinated* d^6 complex compounds. So far, triplet ground states have been assumed in d^6 configuration for square-planar iron(II) systems only, and even there not more than two examples were found.[1,2]

In what follows, the compounds $[Fe(phen)_2ox]\cdot 5H_2O$ (I) and $[Fe(phen)_2mal]\cdot 7H_2O$ (II), where phen = 1,10-phenanthroline, ox = oxalate, and mal = malonate, will be used as examples. Analogous results were obtained for the corresponding compounds where phenanthroline has been replaced by 4,7-dimethyl-1,10-phenanthroline or 2,2′-bipyridyl[3] as well as for $[Fe(phen)_2F_2]\cdot 4H_2O$.

Magnetic susceptibilities were measured repeatedly in an atmosphere of 400 μ pressure of nitrogen on 20- to

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[1] A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

[2] J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).

[3] The formulas of these compounds differ from those of the phenanthroline series in the amount of water of crystallization.

30-mg samples by the Faraday method. Between 77 and 300°K, the susceptibility follows closely the Curie–Weiss law, $\chi_m = C_m/(T - \Theta)$, with $\Theta = -20°$ for I and $\Theta = -12°$ for II. At 292°K, the magnetic moments found are 3.98 ± 0.05 BM for I and 3.80 ± 0.05 BM for II. In 0.05 *M* methanolic solution, moments of 3.80 ± 0.15 BM for I[4] and 3.82 ± 0.15 BM for II were measured by the Gouy method. The agreement between the measurements on solid samples and in solution as well as the rather small Θ values rule out the possibility of a spin-exchange interaction between different iron(II) ions at ambient temperature. The magnetic moments thus indicate an $S = 1$ electronic ground state. As in square-planar compounds,[1,2] an orbital contribution of $\sim$1.0 BM has to be assumed, the source of which is not obvious on the basis of simple ligand field theory.[5]

Studies of the ^{57}Fe Mössbauer effect at 293°K using the coupled-loudspeaker technique result in isomeric shifts[6] $\delta = 0.31 \pm 0.05$ mm/sec for I and $\delta = 0.32 \pm 0.04$ mm/sec for II. Quadrupole splittings were determined as $\Delta E_Q = 0.21 \pm 0.03$ mm/sec for I and $\Delta E_Q = 0.18 \pm 0.02$ mm/sec for II. The same values within experimental uncertainties were obtained at 77°K.[7] These values differ considerably from those measured on [Fe(phen)$_2$X$_2$] compounds having $S = 2$ ground states ($^5T_2$ in strict O_h symmetry[8]). In this case, ΔE_Q values between 2.68 and 3.00 mm/sec are found, whereas δ varies between 0.96 and 1.13 mm/sec.[7] Also, the Mössbauer spectra of I and II do not conform with spectra of those compounds within the same series which exist in thermal equilibria between almost equienergetic $^5T_2$ and $^1A_1$ ground states.[9,10] The possibility that the increased magnetic moments might arise by analogous quintet–triplet equilibria is ruled out simultaneously. The spectra of I and II are rather similar to the Mössbauer spectra of compounds in $^1A_1$ ground states like [Fe(phen)$_2$(CN)$_2$]·H$_2$O, where, at 293°K, $\Delta E_Q = 0.59$ mm/sec and $\delta = 0.22$ mm/sec,[11] although there is a significant difference in that the ΔE_Q values are definitely smaller. Thus, it seems justified to assume that the Mössbauer parameters presented here are characteristic for six-coordinated iron(II) in an $S = 1$ ground state.

The infrared spectra of I and II, which were studied between 4000 and 400 cm^{-1}, show the frequencies ν_1, ν_2, ν_3, ν_4, ν_7, ν_8, ν_9 of the coordinated oxalate and malonate ion.[12] As far as the frequencies of the phenanthroline ligand are concerned, it has been shown[13] that there are significant differences in the infrared between compounds in the $^5T_2$ and $^1A_1$ ground states, these differences being related to metal–ligand distances and bonding. In this regard, the spectra of I and II compare well with those of compounds in $^1A_1$ states. This is demonstrated, *e.g.*, by the C=C and C=N stretching vibrations (very weak bands at 1518, 1514, and 1493 cm^{-1}; strong bands at 1429 and 1413 cm^{-1}) and the α(CCC) mode (561 and 532 cm^{-1}). The bands at 1103 and 867 cm^{-1}, which are characteristic of the $^5T_2$ state, are not observed. Thus, in compounds having $S = 1$ ground states, distances and bonding between the metal ion and the phenanthroline ligands seem to have definite similarities to compounds in $^1A_1$ rather than to those in $^5T_2$ ground states. This inference which is supported by the Mössbauer data is also consistent with results from electronic spectra.

Compound I was precipitated by acetone from an aqueous solution of [Fe(phen)$_3$]C$_2$O$_4$ which was obtained from FeC$_2$O$_4$ and 1,10-phenanthroline (*Anal.* Calcd: C, 52.54; H, 4.41; N, 9.43; Fe, 9.40; H$_2$O, 15.13. Found: C, 52.68; H, 4.28; N, 9.42; Fe, 9.55; H$_2$O, 15.29). Compound II was prepared analogously from [Fe(phen)$_3$]CH$_2$C$_2$O$_4$ which was obtained starting from FeCH$_2$C$_2$O$_4$·py·H$_2$O (*Anal.* Calcd: C, 50.32; H, 5.01; N, 8.70; O, 27.32; Fe, 8.65; H$_2$O, 19.57. Found: C, 50.25; H, 5.04; N, 8.65; O, 27.58; Fe, 8.84; H$_2$O, 19.33). All operations were performed under nitrogen. The compounds are of *cis* configuration, monomeric, and nonelectrolytes (molar conductivity 15.2 and 21.6 mho cm^2/mole in 0.01 *M* methanolic solution at 298°K for I and II, respectively). The detailed preparation procedure and chemical characterization will be reported in a forthcoming publication.[14]

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Oxidative Preparation of 9-Hydroxytetracyclines

Sir:

Methods for hydroxylation of certain tetracyclines at positions 5, 6, and 12a have been disclosed by Holmlund, *et al.*,[1,2] and Miller, *et al.*[3,4] Hlavka, *et al.*,[5] were also able to prepare biologically active 7-hydroxy-6-demethyl-6-deoxytetracycline using a procedure which is limited to modification of 6-demethyl-6-deoxytetracycline.

While exploring alternative hydroxylation methods, we have examined the Udenfriend reagent which has been shown to oxidize a large number of biological compounds. In particular, the hydroxylation of aro-

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