



Fig. 1.—Electron spin resonance spectrum of polycrystalline $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Rh}(\text{MNT})_2]$.

$\text{Pd}(\text{MNT})_2^-$, and $\text{Pt}(\text{MNT})_2^-$ complexes, which have $S = 1/2$.^{7,8} From the e.s.r. and static susceptibility results, we conclude that the square-planar $\text{Rh}(\text{MNT})_2^-$ complex has a spin-doublet ground state. To our knowledge, this is the first well-characterized mononuclear, paramagnetic rhodium(II) complex.¹⁵

The ground state of $\text{Rh}(\text{MNT})_2^-$ is $\dots(4b_{2g})^2(4a_g)^1 = {}^2A_g$, using the molecular orbitals derived² for $\text{Ni}(\text{MNT})_2^-$. The low energy ligand-to- $4a_g$ charge-transfer band is located at $15,800\text{ cm}^{-1}$ ($\epsilon \cong 4000$) in $\text{Rh}(\text{MNT})_2^-$. All the planar complexes mentioned above with a 2A_g ground state show this type of low energy charge-transfer band.

(7) In frozen DMF- CHCl_3 solutions, the following g values have been obtained⁹: $\text{Ni}(\text{MNT})_2^-$, $g_1 = 1.996$, $g_2 = 2.043$, $g_3 = 2.140$; $\text{Pd}(\text{MNT})_2^-$, $g_1 = 1.956$, $g_2 = 2.046$, $g_3 = 2.065$; $\text{Pt}(\text{MNT})_2^-$, $g_1 = 1.825$, $g_2 = 2.067$, $g_3 = 2.221$; these complexes have $S = 1/2$. Solid $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{TDT})_2]$ shows only two lines, with $g_{\perp} = 9.045$ and $g_{\parallel} = 2.193$.¹⁰ However, the in-plane anisotropy is resolved in solid $[(\text{C}_6\text{H}_5)_4\text{As}(\text{CH}_3)][\text{Ni}(\text{TDT})_2]$, with $g_1 = 2.020$, $g_2 = 2.075$, $g_3 = 2.130$.¹¹ In a frozen DMF- CHCl_3 solution $\text{Ni}(\text{TDT})_2^-$ gives $g_1 = 2.011$, $g_2 = 2.043$, $g_3 = 2.181$.¹² The anion $\text{Ni}(\text{TDT})_2^-$ was the first reported example of a nickel complex with a square-planar structure and a spin-doublet ground state.¹⁰

(8) It is interesting to note that $\text{Co}(\text{MNT})_2^-$, for which both spin-quartet¹³ and spin-doublet¹⁴ ground states have been proposed, has a considerably different g_3 from that of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Rh}(\text{MNT})_2]$, which is a spin-doublet; for a single crystal of 5% $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Co}(\text{MNT})_2]$ in $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Ni}(\text{MNT})_2]$, the values $g_1 = 1.977$, $g_2 = 2.025$, and $g_3 = 2.798$ have been reported.¹⁴

(9) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

(10) H. B. Gray and E. Billig, *ibid.*, **85**, 2019 (1963).

(11) I. Bernal, unpublished results.

(12) We thank Dr. N. Edelstein for measuring this spectrum for us.

(13) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(14) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 3049 (1963).

(15) There are very few paramagnetic rhodium compounds of any structural type. Paramagnetic $\text{Rh}(\text{IV})$ fluorides have been reported by R. S. Nyholm and A. G. Sharpe, *J. Chem. Soc.*, 3579 (1952).

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The Triclinic Crystal Form of $\alpha,\beta,\gamma,\delta$ -Tetraphenylporphine¹

Sir:

A recent X-ray structure determination of tetraphenylporphine² does not distinguish between pyrrole rings with and without hydrogen attached to nitrogen, since the tetragonal space group requires 4 molecular symmetry. Since fourfold symmetry is higher than the molecule permits, it may either be inexact or the result of molecular disorder within the crystal. The X-ray analysis of a triclinic tetraphenylporphine³ crystal, space group P1, avoids the above difficulties because of lower, 1, molecular symmetry and thus distinguishes two types of pyrrole rings and the two central hydrogen atoms. Results of this analysis are reported here.

Deviations from a least-squares plane determined by the 24 atoms of the porphine nucleus are given in Fig. 1.

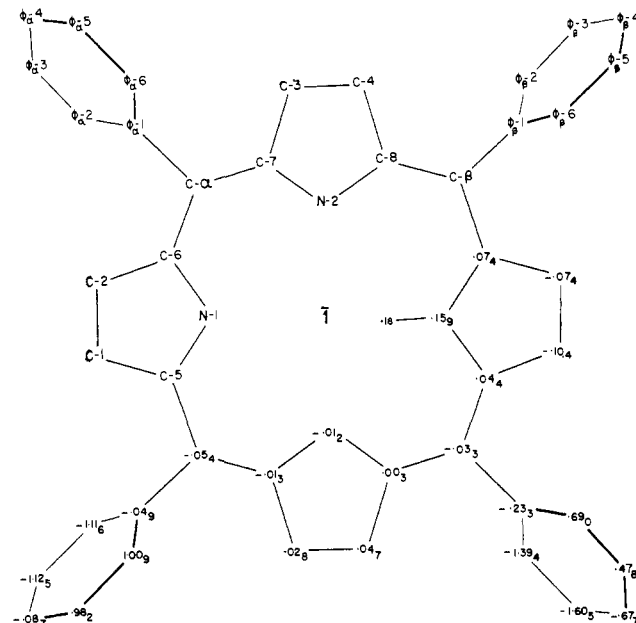


Fig. 1.—Atomic nomenclature and deviations in Å from the nuclear least-squares plane of triclinic tetraphenylporphine.

Of note are (1) the tilt (6.6°) of the N-1 pyrrole ring, which makes the close central hydrogen-hydrogen contact $\sim 0.2\text{ \AA}$. longer than a planar configuration allows; (2) the tilt (9.1°) of the C- α -(C_6H_5) $_{\alpha-4}$ line with respect to the plane, for which a close (3.40 \AA .) intermolecular contact may account; and (3) the rotation of the phenyl groups ($(\text{C}_6\text{H}_5)_\alpha \sim 61.0^\circ$, $(\text{C}_6\text{H}_5)_\beta \sim 63.1^\circ$). The phenyl and pyrrole rings are planar within the error of their determination.

Figure 2 shows the intramolecular bond distances and angles. The standard deviations in bond lengths and angles involving only carbon and nitrogen atoms are of the order of $0.005\text{--}0.010\text{ \AA}$. and $0.5\text{--}0.8^\circ$, respectively. Those for bonds to hydrogen atoms are $\sim 0.05\text{ \AA}$. The accuracy is best for the porphine nucleus and poorest for $(\text{C}_6\text{H}_5)_\beta$. Of significance are (1) single bonds isolating the phenyl rings from the nucleus; (2) approximate double bonds C-1-C-2 and C-3-C-4, which apparently remove these atoms from the interior resonant system; and (3) flat bonding about the interior carbon atoms.

(1) This research has been supported by the National Institutes of Health, U. S. Public Health Service, and Lederle Laboratories Division, American Cyanamid Company.

(2) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *J. Am. Chem. Soc.*, **85**, 2334 (1963).

(3) A highly purified sample was kindly provided by Dr. Henry E. Rosenberg.

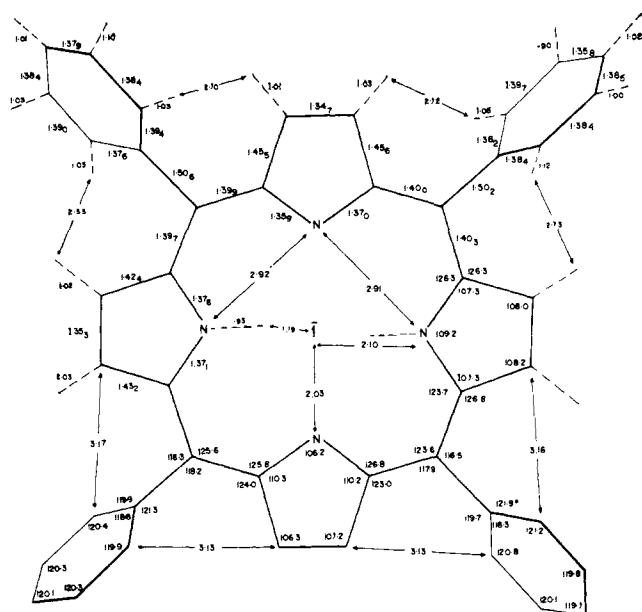


Fig. 2.—Bond angles and distances of triclinic tetraphenylporphine; bonds to hydrogen atoms are broken.

The molecular configuration of triclinic tetraphenylporphine is markedly different from that of the tetragonal form, showing that the porphine system is flexible. Their bond lengths and angles, however, are consistent if the one crystallographically independent pyrrole ring in the tetragonal case is compared to an average of the two independent ones in the triclinic case. Such averaging, however, ignores significant differences between the two types of pyrrole ring. Preliminary results⁴ from this laboratory on silver tetraphenylporphine indicate the possibility of obtaining triclinic crystals of metalloporphines⁵ and thereby observing intramolecular differences among their pyrrole rings also.

The crystallographic details of this structure determination will appear elsewhere.

(4) R. Shapiro and A. Tulinsky, in preparation.

(5) The structures of tetragonal forms of nickel etioporphyrin-II (M. B. Crute, *Acta Cryst.*, **12**, 24 (1959)), nickel etioporphyrin-I (E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963)), and copper tetraphenylporphine (E. B. Fleischer, *ibid.*, **85**, 1353 (1963)), which is isomorphous to tetragonal tetraphenylporphine, have been reported.

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The Influence of Tetrahydrofuran on the Reaction of *n*-Butyllithium with Benzyl Chloride: Halogen-Metal Interconversion *vs.* α -Hydrogen-Metal Interconversion

Sir:

We wish to report an extraordinary influence of tetrahydrofuran upon the mechanism of the reaction of benzyl chloride with *n*-butyllithium. Earlier studies had indicated that this reaction proceeded *via* halogen-metal interconversion (1), leading to the formation of benzyl lithium (I) as a transient intermediate which was rapidly consumed in subsequent coupling reactions to form the observed products, bibenzyl (II) and *n*-amylbenzene (III).^{1,2} When we carried out this reaction at room temperature in tetrahydrofuran, however, there was obtained, in addition to II and III, approximately a 20% yield of *trans*-stilbene. As this

(1) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(2) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

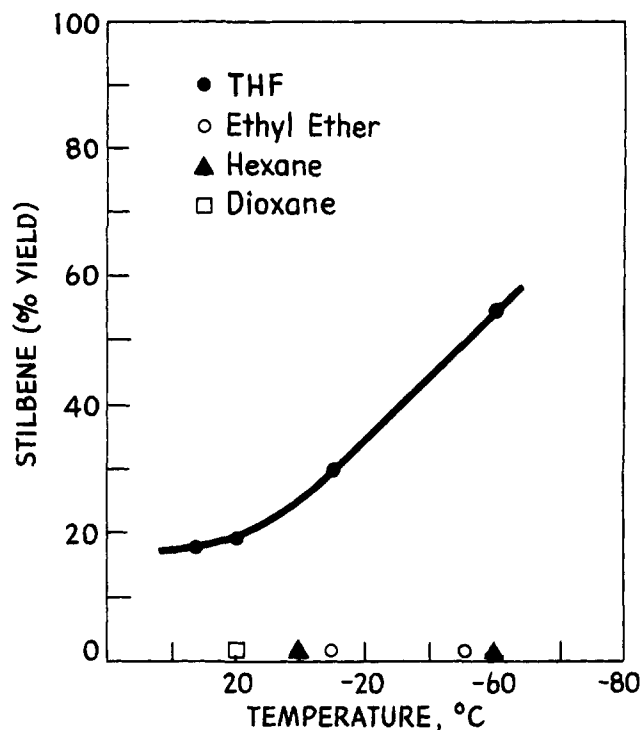
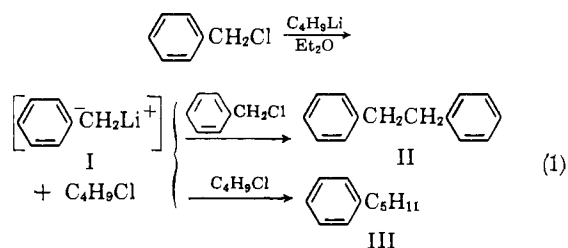


Fig. 1.—The influence of solvent and temperature upon the formation of stilbene from *n*-butyllithium and benzyl chloride.

reaction provides the basis for a widely used analytical method for the quantitative determination of butyllithium, and inasmuch as the presence of stilbene could not be readily accommodated in the proposed mechanism above, we decided to explore how the reaction conditions, such as solvent and temperature, influenced the course of this reaction.³ Figure 1



shows how the yield of *trans*-stilbene was affected by these reaction conditions. The unique influence of tetrahydrofuran as a solvent for this reaction, particularly at low temperatures, is evident from this figure.⁴ Additionally, a small amount of a yellow oil was isolated in the chromatographic separation of the products from the tetrahydrofuran reactions (eluted

(3) The procedure adopted was as follows: At the prescribed temperature, 30 ml. of a solution of *n*-butyllithium in heptane (1 mmole/ml.) was added slowly (5 min.) to a solution of 3.8 g. (30 mmoles) of benzyl chloride in 100 ml. of the appropriate solvent under argon. After 2 hr., the reaction was poured into an equal volume of a 50-50 water-petroleum ether (b.p. 37-54° mixture). The organic phase was separated, dried over Na_2SO_4 , and vacuum stripped. A representative portion of the residue was placed on an alumina column (24 in. \times 1 in.) for chromatographic separation of the products. In a typical separation, the *n*-amylbenzene was the first product eluted with petroleum ether (infrared spectrum identical with authentic sample), followed closely by bibenzyl (m.p. 52°, lit. 52.5°, no depression in mixture melting point, identical infrared spectrum as authentic sample). *trans*-Stilbene (m.p. 124-125°, lit. 124°, identical infrared and ultraviolet spectra with authentic sample). *Anal.* Calcd. for $\text{C}_{11}\text{H}_{12}$: C, 93.3; H, 6.7. Found: C, 93.3; H, 6.9, was eluted with a 25 vol.-% solution of benzene in petroleum ether.

(4) Even very small amounts of tetrahydrofuran exert a discernible effect. Thus, little or no stilbene was detected when the reaction was run in hexane at room temperature. In contrast, when a 1-1 molar ratio of tetrahydrofuran-butyllithium (30 mmoles of each) in hexane (100 ml.) was used, approximately a 10% yield of *trans*-stilbene was isolated after 2 hr. reaction.