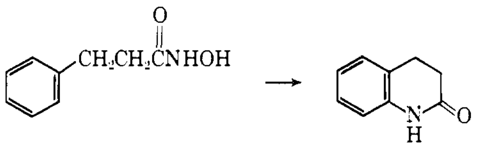
heated in polyphosphoric acid (165–170°, 40 min), hydrocarbostyril was produced in 79% yield.



Intermolecular amidations can be successfully carried out if a large excess of the hydroxamic acid is employed. For example, anisole can be converted to *p*-acetanisidide in 57% yield by the gradual addition of 10 equiv of acetohydroxamic acid[2] to a hot mixture of anisole in polyphosphoric acid. Sharply reduced yields resulted when equimolar amounts of acetohydroxamic acid and anisole were used. Significantly, the crude products from the direct amidation of such monosubstituted benzene derivatives as toluene and anisole were nearly free of *ortho*- and *meta*-substituted isomers.

The mechanism of the direct amidation transformation is uncertain. One possibility which presently appears attractive is a rationalization in terms of an intermediate ketoxime or its conjugate acid. An aromatic compound and a carboxylic acid react in polyphosphoric acid to furnish a ketone;[3,4] in a parallel fashion, an aromatic compound and a hydroxamic acid may be expected to react in the same medium to furnish a ketoxime. A ketoxime, however, can have only a fleeting existence, for it is rapidly and efficiently transformed in the hot acid medium to an amide by a Beckmann rearrangement.[3,4]

$$\mathrm{R\overset{O}{\overset{\|}{C}}NHOH \longrightarrow R\overset{HON}{\overset{\|}{C}}Ar \longrightarrow R\overset{O}{\overset{\|}{C}}NHAr}$$

It is apparent that direct amidation is a promising synthetic method. We are continuing our investigations of the scope and versatility of the reaction.

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(5) University of Connecticut Predoctoral Fellow, 1966–1967.

Frederick W. Wassmundt, Stanley J. Padegimas[5]

Department of Chemistry, University of Connecticut
Storrs, Connecticut 06268

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Phenylrhodium Tetraphenylporphine. A Novel Synthesis of a Rhodium–Carbon σ Bond

Sir:

Compounds containing alkyl- and aryl-metal bonds are usually synthesized by use of Grignard reagents or aryllithium compounds, or by a reaction of a low oxidation state of the metal with alkyl halides.[1–8] We report the synthesis and characterization of a compound containing a rhodium–phenyl σ bond.

Tetraphenylporphine (TPP) and $[Rh(CO)_2Cl]_2$ are refluxed for 10 hr in benzene, and the compounds in the resulting solution are separated by chromatography on an alumina column. The RhTPP fraction[9] gives purple crystals on standing. This new compound contains a σ-bonded phenyl group and can best be represented as $C_6H_5Rh^{IV}TPPCl$.[10] The compound is paramagnetic with a room-temperature susceptibility, $\mu_{eff} = 1.95$ BM.

The characterization of this new metalloporphyrin was accomplished by a three-dimensional X-ray structure determination. The crystal is monoclinic with cell constants $a = 17.33$, $b = 13.09$, $c = 23.28$ Å, $\gamma = 124.8°$. The space group of the crystal is $P2_1/a$ with four molecules per unit cell. The X-ray data were obtained by use of the automatic diffractometer PAILRED with Mo Kα radiation. There were 2382 observed intensities[11] used in the structure analysis. The structure was solved by the symbolic addition method[12–14] employing the computer program MAGIC.[15]

The structure was refined by Fourier and least-squares techniques. The final *R* factor[16] including all reflections with isotopic temperature factors for the 56 atoms (hydrogen atoms not included) is 10.9%. The tetraphenylporphine part of the molecule is similar to other porphyrin structures that have been recently determined.[17–20]

The porphyrin has the usual local planarity of the pyrrole rings and the phenyl rings, but the over-all porphyrin skeleton is nonplanar with respect to the best plane defined by the four pyrrole nitrogen atoms. It is of particular interest that the rhodium atom lies in the plane of the four nitrogen atoms. This observation may help in the interpretation of the iron position in hemoglobin and myoglobin, as these compounds undergo the transformation from the deoxy high-spin to the oxygenated low-spin complexes.[21,22]

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(10) *Anal.* Calcd for $C_{50}H_{33}N_4RhCl \cdot H_2O$: C, 71.0; H, 4.3; N, 6.6; Rh, 12.2. Found: C, 71.9; H, 4.7; N, 5.9; Rh, 12.8. The representation of the rhodium as a +4 oxidation state is only a formalism. The details of the electronic structure of this compound are being studied.
(11) The yield of 25% of the intensities within the copper sphere is due to several reasons. The diffraction of the small crystal used in obtaining the data made it inadvantageous to collect outside a sphere with $2\theta > 50°$. A region containing 3700 peaks was investigated yielding the 2382 "observed" intensities, or a 65% yield. The structure showed no evidence of large thermal motion (isotropic temperature factors *B* were in the range of 2–4 Å^2) nor of general disorder (there is a H_2O solvent that either is disordered or has a large thermal motion).
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(16) $R = \Sigma||F|_o - |F|_c|\Sigma|F|_o$; the average standard deviation in the C–C bond distances is 0.03 Å. The average C–C bond distance for all phenyls is 1.39 Å.
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The Rh is octahedrally coordinated. Four positions are taken up by the porphyrin pyrrole nitrogen atoms (Rh–N average distance 2.04 Å); a chloride ion (Rh–Cl distance of 2.35 Å) and a phenyl group that is σ-bonded to the Rh (Rh–C distance 2.05 Å); complete the coordination. The phenyl group is approximately perpendicular to the mean porphyrin plane.

The mechanism of formation and chemistry of this interesting species is presently under investigation.[23]

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[24] Alfred P. Sloan Fellow.

Everly B. Fleischer,[24] David Lavallee
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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Thermolysis of *exo*- and *endo*-5-Methoxy-2,3-diazabicyclo[2.2.1]-2-heptene[1]

Sir:

Currently there is great interest concerning the mechanistic details of thermal[2-4] and photolytic[3-8] decomposition of azo compounds. We wish to report our investigation of gas-phase thermal decomposition of the stereomeric bicyclic azo compounds Ix and In.

The necessary syntheses were accomplished by methylation of 2,3-dicarbomethoxy-2,3-diazabicyclo-[2.2.1]-5-heptanols of established 5-*exo* and 5-*endo* configuration[9] with sodium hydride and iodomethane in tetrahydrofuran. These methoxyl derivatives were converted by known procedures[10,11] to Ix, bp 61.5° (4.5 mm), and In, bp 73.5° (2.2 mm). Spectral data and elemental analyses were in complete agreement with the structures.

Thermal decomposition of Ix and In gave the 2-methoxybicyclo[2.1.0]pentanes *cis*-III and *trans*-III as the only products (>95%) under our reaction conditions. Identification is based on nmr spectra. Carbon-13 magnetic resonance spectra allowed for conclusive assignment of configuration. The C-5 carbon of *cis*-III was shifted upfield 5 ppm from the corresponding carbon of *trans*-III and bicyclo[2.1.0]pentane.[12]

For gas-phase decomposition, 5–6-μl samples of azo compound were degassed and sealed in 25-ml Pyrex tubes under nitrogen at *ca.* 0.6 mm. Upon completion of reaction the pressure was <100 mm. Product interconversion was examined under decomposition conditions and at higher temperature with the aid of a 47.9% *cis*-III and 52.1% *trans*-III mixture obtained from photolysis of Ix. Some results are summarized in Table I.

Table I. Thermal Decomposition of Ix and In and Isomerization of Products *cis*-III and *trans*-III

Compd	Temp, °C	% composition[a] *cis*-III	 *trans*-III
Ix	135[b]	63.0 ± 0.6	37.0 ± 0.6
Ix	198.9[c]	85.6 ± 0.4	14.4 ± 0.4
Ix	220[d]	85.5 ± 0.4	14.5 ± 0.4
In	135[e]	93.6 ± 0.5	6.4 ± 0.5
In	198.9[c]	85.9 ± 0.5	14.1 ± 0.5
In	220[d]	85.2 ± 0.5	14.8 ± 0.4
47.9% *cis*-III + 52.1% *trans*-III	135[f]	48.9 ± 0.3[g]	51.1 ± 0.3[g]
47.9% *cis*-III + 52.1% *trans*-III	198.9[c]	85.4 ± 0.5	14.6 ± 0.5

[a] Determined with a 20 ft × 0.125 in. 15% tetraethylene glycol on Chromosorb P, gas chromatography column. [b] For five half-lives. [c] For 16 hr. [d] For 5.5 hr. [e] For 2.5 half-lives (100 hr). [f] For 100 hr. [g] Equilibrium composition at 135° is 87.1% *cis*-III and 12.9% *trans*-III as extrapolated from the equilibrium constant data at 198.9 and 220°.

Kinetics of decomposition were followed by gas chromatography by measuring the appearance of combined III against 1,2-dimethoxyethane as an internal standard. A comparison of Ix and In with 2,3-diazabicyclo[2.2.1]-2-heptene (IV) is shown in Table II. Decomposition of *exo*-6-*d*-Ix did not lead to scrambling of the label. This rules out any neighboring group participation by the 5-methoxyl group.

Table II. Kinetics of Ix and In Decomposition at 160.1°

Compd	10^4k, sec^{-1}	Rel rate
IV	0.895[a]	1.0
Ix	5.4[b]	6.0
In	0.80[b]	0.9

[a] Calculated from other reported data.[11] [b] Determined with a 5-ft 15% Carbowax 20M gas chromatography column.

Greatly different product ratios from thermolysis of Ix and In show that a single planar 1,3-diradical intermediate, II, cannot explain the decomposition mechanism. Comparison of decomposition and equilibrium product ratios clearly indicate that net inversion of structure results from each isomer.

Recently Roth and Martin[3] reported an analogous inversion observation. Thermolysis of *exo*-5,6-d_2-IV gave a 75:25 mixture of Va and Vb. These authors attribute inversion to concerted elimination of nitrogen with accompanying back-side p-orbital overlap *via* transition-state VI. However, examination of models casts considerable doubt on this proposal. The geometry required for transition-state VI has diverging orbitals unfavorably oriented for back-side overlap (end view). Furthermore, extended Hückel calculations[2a-c,13] suggest that the developing orbitals will be antisymmetric and "nonbonding." It seems unlikely that such a path will favor inversion.

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