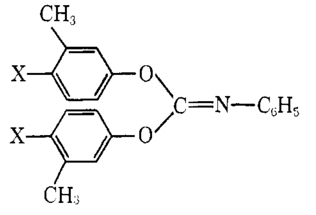
Table I. Data on Isomerization of Iminocarbonates of Structure I[a]

X	Solvent	Concn[b]	Tc, °C	$\Delta\nu$, cps	k^{60}, 10^3 sec^{-1}	E_a, kcal	log A
H	Acetone	25	+0.8	9.13	1.6	13.4 ± 0.3	12.0
H	Acetone	35	+1.2	8.33	1.7	13.2 ± 0.4	11.9
H	Acetone	15	−0.4	9.89	1.7	13.8 ± 0.4	12.4
Cl	Acetone	25	−1.6	7.14	5.1	16.6 ± 0.3	14.6
CH_3	Acetone	25	+2.8	8.03	2.1	15.5 ± 0.3	13.5
H	Chloroform	25	+0.1	11.46	2.8	14.4 ± 0.3	12.9
Cl	Chloroform	25	+3.6	9.22	1.4	13.8 ± 0.3	12.2
CH_3	Chloroform	25	+5.5	10.37	1.1	13.2 ± 0.5	11.7

[a] A Varian A-60 equipped with a Varian variable-temperature probe was used to observe the chemical shift as a function of temperature. Temperatures were measured with an accuracy of ±0.8°. A given temperature could be held constant to ±0.1°. Spectra were calibrated by the side-band method, using a frequency counter to measure the side-band frequency. The method described by J. A. Pople, W. S. Schneider, and H. J. Beinstein ("High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 224) was used to calculate τ values. At each temperature no less than six determinations were made, with 15 determinations being made at the point of maximum separation. All errors are root-mean-square errors. The E_a values represent slopes plotted using no less than seven temperatures. All slopes gave a correlation coefficient of better than 0.99 when treated by the method of least squares. [b] By volume.

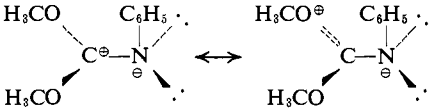
for acetone anil to that for I, X = H, shows that substitution of methoxyl for methyl increases the isomerization rate by a factor of 10,000. This demonstrates the susceptibility of the isomerization rate to the nature of the group bonded to the imino carbon.

Further evidence for this is found in the fact that iminocarbonates II[7] in acetone, chloroform, or diphenyl ether give one temperature-invariant signal for the *m*-methyl protons.



II, X = H, Cl, CH_3, NO_2

The low activation energy for the isomerization of imines relative to olefins and the effect of substituents on the rate, particularly the insensitivity of the isomerization rate to substituents on the aryl group bonded to the imino carbon in compounds such as $Ar_1Ar_2C{=}N{-}CH_3$, have been interpreted in terms of a mechanism which proceeds *via* a linear transition state in which the π bond remains intact and the nonbonded electron pair on nitrogen rehybridizes to a p orbital.[2] The very low activation energy and large isomerization rate found for the iminocarbonates is more easily explained in terms of a mechanism proceeding through a polar transition state in which unsharing of the electrons of the π bond has occurred.



Since oxygen is more electronegative than carbon, substitution of methoxyl for alkyl or aryl groups attached to the imino carbon might be expected to decrease the extent of polarization of the carbon–nitrogen double bond. Resonance effects would operate in an opposite fashion, but can be neglected as making an important contribution to the ground state. The over-all effect should be a stabilization of the ground state. However, resonance effects become important in excited states and, in this case, would be expected to stabilize the transition state by delocalization of the positive charge being generated on the imino carbon. The expected net effect should be a decrease in the required activation energy.

The large isomerization rates found for N-aryliminocarbonates suggest that stereoisomeric compounds of this type cannot be isolated with the possible exception of those bearing an electronegative atom on the imino nitrogen. In order to test this, the N-chloro compound, $(H_3CO)_2C{=}N{-}Cl$,[8] was examined in the solvents chloroform, carbon tetrachloride, methylcyclohexane, acetonitrile, and diphenyl ether. In all cases, a methyl doublet was observed at room temperature and there was no change in the nmr spectrum when heated in methylcyclohexane to 105° or diphenyl ether to 170°.[9] This result demonstrates the extraordinary susceptibility of the isomerization rates of iminocarbonates as well as imines to the group on the imino nitrogen.

Acknowledgment. We wish to thank the Army Research Office, Durham, and donors to the Petroleum Research Fund administered by the American Chemical Society for financial assistance.

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[7] Prepared by heating phenylimido phosgene with the appropriate phenol in collidine. All compounds were solids and purified by recrystallization to constant melting point. Physical properties found were as follows: for X = H, mp 68–69° (*Anal.* Found: C, 79.36; H, 6.24; N, 4.48); for X = Cl, mp 115–116° (*Anal.* Found: C, 65.53; H, 4.60; N, 3.54); for X = CH_3, mp 72–73° (*Anal.* Found: C, 80.19; H, 6.84; N, 4.12); and for X = NO_2, mp 125° (*Anal.* Found: C, 61.77; H, 4.31; N, 10.35). The infrared and integrated nmr spectra were consistent with the assigned structure.

(8) E. Ofstead, Ph.D. Thesis, University of Maryland, College Park, Md., 1963, p 39.

(9) We are grateful to F. Vogtle for communicating to us the result in diphenyl ether.

(10) National Aeronautics and Space Administration Predoctoral Fellow.

N. P. Marullo, E. H. Wagener[10]
Department of Chemistry and Geology, Clemson University
Clemson, South Carolina 29631

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Synthesis of Metal–Metal Bonds *via* Iridium and Rhodium Anions[1]

Sir:

The preparation of compounds containing covalent metal–metal bonds is a subject of extensive current in-

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Table I. Analytical Data

Compound[a]	%C Calcd	%C Found	%H Calcd	%H Found	%P Calcd	%P Found	Mol wt Calcd	Mol wt Found
III	40.98	41.42	3.42	3.66	4.41	4.46	703	718
V	43.04	43.46	2.93	2.99	5.05	5.10	1227	1250
IV	52.66	52.89	3.38	3.52	3.49	3.26	889	896
VI	46.88	46.65	3.01	3.24	6.21	6.13	998	990
VII	39.40	39.62	2.35	2.83	4.85	4.76	....[b]	....
X	58.12	58.59	4.61	4.63	7.32	7.19	847	722
XI	32.00	32.25	2.00	2.24	4.12	4.27	....[b]	....

[a] See Figure 1. [b] Solubility too low to permit measurement.

Table II. Spectral Data

Compound	ν_{CO}, cm^{-1} [a]	Proton nmr signals, τ[b]	$J_{Sn^{119}-H}$, cps
III	1950 (vs) 2010 (m)	2.58 m (17) 9.49 d (9)[c]	49
V	1950 (vs)	2.62 m (5) 8.96 t (1)[c]	40
IV	1965 (vs) 2025 (w)	... ...	....
VI	1930 (vs) 1990 (w)	... ...	....
VII	1945 (vs) 1985 (m)	...[d] ...	....
X	1930 (vs) 1975 (vs)	2.81 m (31.5) 9.86 s (9)	46.5
XI	2060 (vs) 2160 (s)	... ...	....

[a] Approximate intensities indicated by: vs (very strong), s (strong), m (medium), w (weak). Spectra reported for KBr disks, but solution spectra are very similar. [b] Chemical shifts in τ values relative to TMS. Relative integral intensities in parentheses. Coupling pattern indicated by: m (multiplet), s (singlet), d (doublet). [c] $J_{P^{31}-H}$ is 1 cps. [d] Not soluble enough to permit measurement.

vestigation.[2] Our interest in electron transport through chains of metal–metal bonds[3] has prompted us to study syntheses of individual metal–metal bonds. Initially our efforts have focused on the preparation of metal–metal bonds involving group VIII metals.

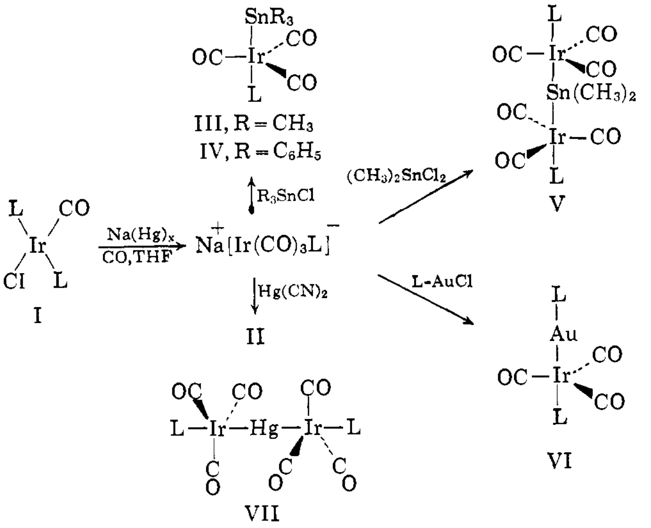

Figure 1. L represents triphenylphosphine.

Two approaches have been taken to this problem: (a) oxidative additions of mercuric and tin halides to complexes having a d^8 configuration and (b) metathetical reactions between a metal anion and a metal halide. The first method has been used to prepare iridium–mercury,[4] iridium–tin,[5] ruthenium–mercury,[6] and osmium–mercury[6] bonds. The second method has not been employed to prepare metal–metal bonds with osmium, rhodium, and iridium because anionic complexes in which these metals possess basic electron pairs were hitherto unknown. Herein are reported syntheses of sodium derivatives of iridium and rhodium and their *in situ* transformation into stable compounds containing previously unknown metal–metal bonds.

Reduction of Vaska's[7] iridium(I) complex (I)[8] with sodium amalgam in tetrahydrofuran under a CO atmosphere of 60 psi yielded an intermediate sodium salt (II) in which one of the triphenylphosphine ligands was replaced by a CO group. Attempts to isolate the anionic complex (II) were frustrated by its strongly basic character. When II was allowed to react with triphenylphosphinegold(I) chloride, triphenyltin chloride, trimethyltin chloride, dimethyltin dichloride, and mercuric cyanide, high yields of crystalline, air-stable compounds ensued (Figure 1). These compounds apparently contain metal–metal bonds. Analytical data are presented in Table I, and selected spectral properties are outlined in Table II.

The provisional structures assigned to these compounds (Figure 1) depict the five ligands bound to the central iridium in a trigonal bipyramidal arrangement in which the two bulky ligands (triphenylphosphine and other metal) are located at the apices. Some support for this supposition stems from the single very intense carbonyl infrared peak centered around 1950 cm^{-1} (Table II) which may be assigned to three equivalent CO groups about the trigonal plane. The weaker peak about 2000 cm^{-1} is thought to arise from a small amount of another stereoisomer. However, it is equally possible that these complexes have some lower symmetry and that all of the expected carbonyl infrared bands have not been fully resolved.

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[2] J. Lewis and R. S. Nyholm, *Sci. Progr.*, **52**, 557 (1964).

[3] C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ülkü, *J. Am. Chem. Soc.*, **88**, 4286 (1966).

[4] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).

[5] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

[6] J. P. Collman and W. R. Roper, *Chem. Commun.*, 244 (1966).

[7] L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

[8] A more convenient preparation of I involves heating $IrCl_3 \cdot 3H_2O$ and $4(C_6H_5)_3P$ in DMF at reflux under N_2 for 12 hr. High (85–95%) yields of pure I result upon cooling and adding excess CH_3OH.

Under the same reducing conditions the analogous rhodium(I) complex (VIII) forms a dicarbonyl anionic complex (IX) in which neither triphenylphosphine is replaced. The origin of this disparity is not clear. This complex combines readily with trimethyltin chloride to form an air-stable crystalline compound, X.

$$\underset{\text{VIII}}{[\mathrm{RhL_2(CO)Cl}]} \xrightarrow[\text{CO, THF}]{\mathrm{Na(Hg)}_x} \underset{\text{IX}}{\mathrm{Na^+[RhL_2(CO)_2]^-}} \xrightarrow{\mathrm{(CH_3)_3SnCl}} \underset{\text{X}}{\mathrm{(CH_3)_3Sn{-}RhL_2(CO)_2}}$$

The Sn^{119}–H coupling constants (Table II) for methyltin derivatives containing iridium and rhodium are similar to those reported[9] for other complexes containing transition metal–tin bonds.

It was anticipated that these five-coordinate complexes containing iridium or rhodium bound to another metal might undergo stepwise oxidative addition reactions in the manner of similar five-coordinate complexes having a d^8 configuration.[10] Unfortunately reaction with mercuric halides, iodine, and bromine occurs with concomitant cleavage of iridium–tin or iridium–gold bonds. Unless an excess of oxidizing agents is used, intractable mixtures result. This type of process is illustrated by the reaction of IV with excess bromine to yield 1 equiv of CO (gas buret analysis), bromobenzene (gas chromatographic analysis), and an iridium(III) complex, XI.

$$\underset{\text{IV}}{\mathrm{Ir(CO)_3LSn(C_6H_5)_3}} + 5\mathrm{Br_2} \longrightarrow \mathrm{CO} + \underset{\text{XI}}{[\mathrm{IrL(CO)_2Br_3}]} + 3\mathrm{C_6H_5Br} + \mathrm{SnBr_4}$$

[9] H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965).

[10] J. P. Collman and W. R. Roper, *ibid.*, **87**, 4008 (1965); **88**, 3504 (1966).

[11] Fellow of the Alfred P. Sloan Foundation.

James P. Collman,[11] Frederick D. Vastine, Warren R. Roper
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514
Received July 11, 1966

Structure of Chlorophyll c[1]

Sir:

Chlorophyll *c*, a widely distributed constituent of marine algae,[2] has been the least investigated of the major photosynthetic pigments. The following evidence now indicates that chlorophyll *c*, isolated from the marine diatom *Nitzschia closterium* by a recently described procedure,[3] is a mixture of magnesium hexadehydropheoporphyrin a_5 monomethyl ester (Figure 1a) and magnesium tetradehydropheoporphyrin a_5 monomethyl ester (Figure 1b).

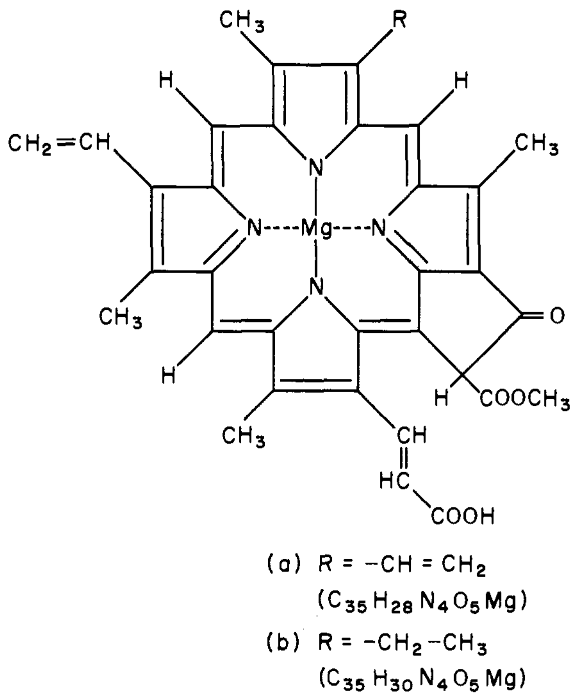

Figure 1. Proposed structures for chlorophylls *c*.

Chlorophyll *c*, crystallized from tetrahydrofuran (THF) and petroleum ether,[3] proved to be the bis-tetrahydrofuranate, as shown by the characteristic high-field THF resonance[4] near 2 ppm (relative area 8) in the nmr and by elemental analysis (*Anal.* Calcd for $C_{35}H_{30}N_4O_5Mg{\cdot}(C_4H_8O)_2$: C, 68.34; H, 6.09. Found: C, 68.60; H, 6.16; one CH_3O group/mole).[5]

Chlorophyll *c* without THF has no resonances above 3 ppm except for a variable intensity triplet at 1.7 ppm; hence this chlorophyll contains no lipophile group and is a free acid.[6] The chemical shift (1.7 ppm) and the relative area (~1.5) of the triplet ($|J| = 7.2$ cps) in the chlorophyll *c* dissolved in trifluoroacetic acid (TFA) indicate the presence of a porphyrin ethyl group in one component of the preparation.

The low-field methyl region[7] of the chlorophyll *c* nmr is very narrow in TFA (3.77–4.09 ppm, relative area 15), indicating the absence of chlorin hydrogen or oxygenated side chains[7] such as $-C{\mathit H}OHCH_3$, $-CH_2COOR$, or $-CH_2CH_2COOR$. The chemical shifts of the ring methine protons also exclude the presence of chlorins and formyl-substituted porphyrins.

Assignment of the resonances below 4.1 ppm in the chlorophyll *c* nmr spectrum (Table I) followed directly from nmr studies of other porphyrins and chlorins.[7]

Crystalline chlorophyll *c* is infusible;[8] consequently more volatile derivatives were required for determination of the mass spectrum. Treatment of solutions of chlorophyll *c* with dilute hydrochloric acid yielded pheoporphyrin c_5 monomethyl ester derivatives (formerly called pheophytin c) in quantitative yield. The nmr and infrared spectra of this material were

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission. Supported in part by a grant to R. C. D. from the Research Corporation.

[2] H. H. Strain and W. M. Manning, *J. Biol. Chem.*, **144**, 625 (1942); H. H. Strain, W. M. Manning, and G. Hardin, *ibid.*, **148**, 655 (1943).

[3] H. H. Strain and W. A. Svec in "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press Inc., New York, N. Y., 1966, p 57 ff.

[4] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 77.

[5] By Crobaugh Laboratories.

[6] The diatoms were treated with rapidly boiling water prior to extraction, thus minimizing the possibility of enzymatic deesterification of native chlorophyll *c*. The extraction conditions were so mild that an acrylate ester would certainly have survived after the death of the cell (*cf.* ref 1 and 2).

[7] J. J. Katz, R. C. Dougherty, and L. J. Boucher in ref 3, p 230.

[8] *Cf.* magnesium pheoporphyrin a_5 monomethyl ester which is also infusible. H. Fischer and A. Stern, "Die Chemie des Pyrrols," Akademische Verlag, Leipzig, 1940, p 170.