

N), where i_d is the limiting convective-diffusion current for reduction of Cu(II) to Cu at the disk electrode, N is the collection efficiency of the ring electrode, and $\beta^{2/3}$ is a geometric parameter of the rrde. When the ring electrode is completely unshielded, $i_r = \beta^{2/3}i_d$. For surface coverages between 0 and 1, i_r lies between $(\beta^{2/3} - N)i_d$ and Ni_d . Oxygen reduction is completely inhibited (within 99.9%) after 25 sec when one monolayer of zerovalent copper has deposited at underpotential on the disk electrode. The reciprocal of time required to reduce the oxygen reduction current to 50% of the convective-diffusion limiting current, $1/t_{50\%}$, is directly proportional to the square root of the rotation speed at constant concentration. For reasons which are not yet clear, $1/t_{50\%}$ is not quite a linear function of concentration at constant rotation speed.

Table I. Dependence of $t_{50\%}$ on Concentration and Rotation Speed

$C \times 10^6 M$	Rpm	$1/t_{50\%}, \text{sec}^{-1}$
2	2,500	0.0082
6	2,500	0.0223
10	2,500	0.0345
20	2,500	0.0626
40	2,500	0.108
60	2,500	0.144
80	2,500	0.188
6	400	0.0092
6	1,600	0.0188
6	2,500	0.0224
6	3,600	0.0300
6	6,400	0.0384
6	10,000	0.0510
80	400	0.0782
80	1,600	0.164
80	2,500	0.189
80	3,600	0.227
80	6,400	0.294
80	10,000	0.352

The data in Table I and Figure 1 support the view that both oxygen and copper are reduced at the same sites on the electrode surface. For example, the oxygen reduction current is one-half its maximum value at the same time that $i_r = (\beta^{2/3} - N/2)i_d$.

We have obtained, qualitatively, similar results for the inhibition of O_2 reduction by silver deposited at underpotential.

Lead and bismuth have no detectable effects upon the oxygen reduction current.

The level of trace Cu(II) in common reagent grade laboratory reagents is sufficiently high to implicate it as a potential culprit in the inhibition of oxygen reduction at platinum. It seems appropriate to recommend that the level of copper and silver be below $10^{-8} M$ in experiments involving oxygen reduction studies to avoid the effects of copper and silver deposition at underpotential in experiments of less than an hour's duration.

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Photolysis of Diene-Iron Tricarbonyls. Evidence for Norbornadien-7-one

Sir:

Most attempts to prepare the norbornadien-7-one system have failed.¹ Two syntheses, however, were successful, and these resulted in the formation of dibenzonorbornadien-7-one² and (norbornadien-7-one)-iron tricarbonyl (1).³ The latter compound represents the simplest, stabilized derivative of the parent compound, norbornadien-7-one (2), and the precursor to the elusive 2. Little evidence has been forwarded for the intermediacy of a norbornadien-7-one in a reaction system, but the presence of such a system has been inferred from decomposition products.^{1a-c,4} We wish to report here evidence for the existence of free norbornadien-7-one, a highly unstable, short-lived intermediate.

Ultraviolet irradiation of dilute solutions of 1 with a 450-W Hanovia lamp and quartz glassware resulted in a rapid depletion of starting material. The irradiations generally were carried out until all starting material had disappeared (in a representative case, a 0.3% ether solution at -78° took 3 hr). The results of these experiments are summarized in Scheme I.

When 1 was irradiated at room temperature, 0° , or -78° , benzene was detected in the reaction mixtures.⁵ The amount of benzene found varied between 50 and 90% and depended upon the initial concentration of complex and length of irradiation. The reaction was accompanied by insoluble material, a mixture of iron residues, and highly colored organic polymer. When the photolysis was carried out at -78° in the presence of 1,3-diphenylisobenzofuran as trapping agent, 9,10-diphenylanthracene was isolated in 6% yield;⁷ in addition, benzene was formed in 55% yield.⁵

Carrying out the irradiation at liquid nitrogen temperature in an ether-pentane-alcohol (EPA; 3:3:5) glass resulted in the formation of small quantities of quadricyclanone (3) (0.5–5%). The appearance of a band at 1746 cm^{-1} in the crude reaction product⁸ on infrared analysis indicated formation of 9. Its presence was confirmed by the comparison of retention times on vapor phase chromatography (vpc)⁶ with

(1) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (c) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (d) S. Yankelevitch and B. Fuchs, *ibid.*, 4945 (1967).

(2) J. Meinwald and E. G. Miller, *ibid.*, 253 (1961).

(3) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **90**, 1655 (1968).

(4) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4406 (1968); this paper is a recent one that infers a substituted norbornadien-7-one as an intermediate which gives rise to aromatic products.

(5) The presence of benzene was determined by using vapor phase chromatography (vpc)⁶ and comparing the retention time with authentic material. Percentage compositions were estimated with a known quantity of toluene as an internal standard and comparing the results to mixtures of known composition.

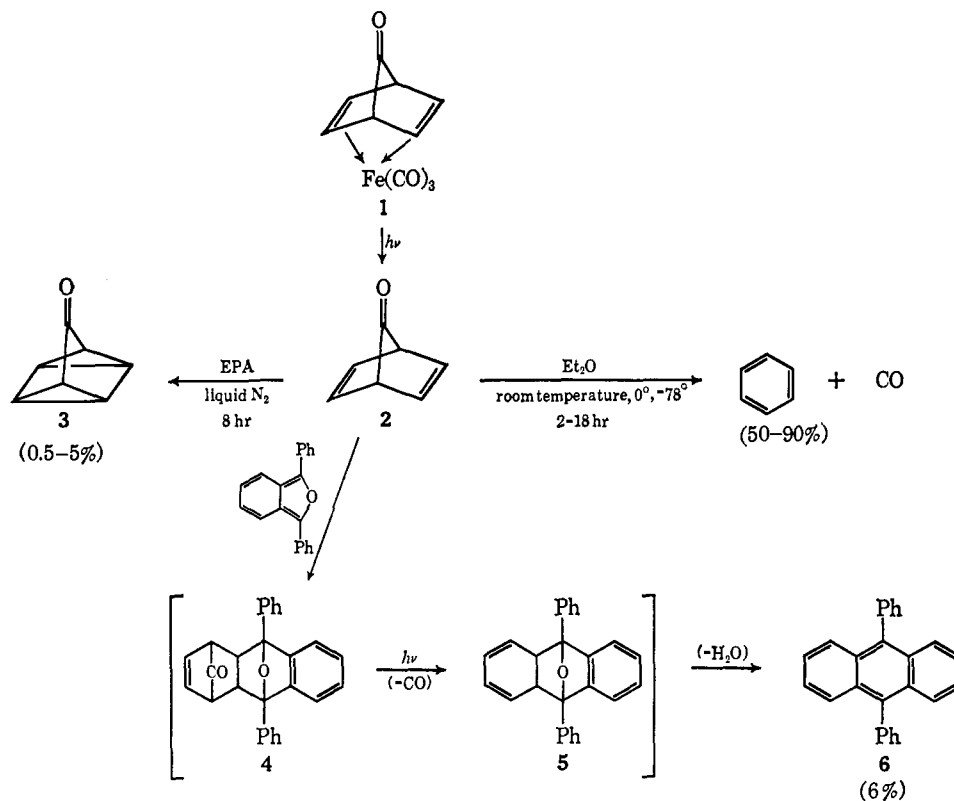
(6) F & M Model 810 with flame ionization detector using a column 6 ft \times 0.25 in. packed with 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb P.

(7) 9,10-Diphenylanthracene was isolated by column chromatography on Florisil and shown to be identical in all respects with commercially available material (K & K Laboratories); yield based on 1,3-diphenylisobenzofuran.

(8) Percentage compositions were estimated on vpc⁶ by adding a known quantity of acetophenone to the solution following irradiation; results were compared to mixtures of known composition; the variable nature in yield was not looked into.

(9) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **86**, 1270 (1964).

Scheme I



authentic material.⁹ In addition, enough material for an infrared spectrum was obtained through preparative vpc¹⁰ of the crude residues, and the spectrum was superimposable on one of authentic 3.

The above results are consistent with the view that a photoinduced decomplexation of 1 occurs to yield 2 (*cf.* cyclobutadieneiron tricarbonyl¹¹ and tris(methylene)methyliron tricarbonyl¹²). A fast thermally allowed disrotatory ring scission¹³ extrudes carbon monoxide and results in the formation of benzene, two thermodynamically stable molecules. In an EPA glass at liquid nitrogen temperature, an intramolecular photodimerization¹⁴ is a competing process and, thus, 3 may be looked upon as an internally "trapped" product. When an external trapping agent is present, *i.e.*, 1,3-diphenylisobenzofuran, 2 undergoes a Diels-Alder reaction yielding the adduct 4.¹⁵ This adduct is capable of undergoing a photoinduced decarbonylation¹⁶ to 5; aromatization by loss of water (either in solution or upon work-up¹⁷) then leads to the observed 9,10-diphenylanthracene.

Furthermore, photoinduced decomplexation of dieneiron tricarbonyls occurred in related systems. Ir-

(10) F & M Model 720 with a thermal conductivity detector using a column 4 ft \times 0.25 in. packed with 20% TCEP on Chromosorb P.

(11) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(12) A. C. Day and J. T. Powell, *ibid.*, 1241 (1968).

(13) J. E. Baldwin, *Can. J. Chem.*, 44, 2051 (1966).

(14) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 57.

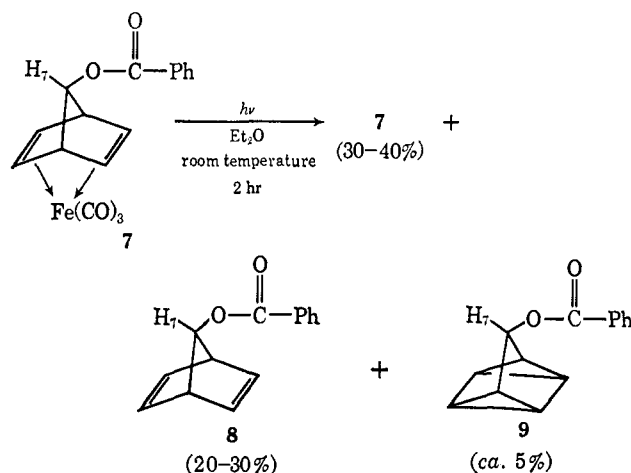
(15) *Cf.* J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, 81, 4273 (1959); S. B. Soloway, *ibid.*, 74, 1027 (1952).

(16) D. I. Schuster, F. T. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, 30, 2262 (1965); B. Fuchs, *Israel J. Chem.*, 6, 517 (1968), and references therein.

(17) Thin layer chromatography (Eastman chromatogram sheets: 6061 silica gel or 6062 alumina) of the crude reaction mixture shows the presence of the 9,10-diphenylanthracene by its characteristic fluorescence under an ultraviolet lamp. The chromatogram support or the Florisil may catalyze the dehydration.

radiation of 7-benzyloxynorbornadieneiron tricarbonyl (7)¹⁸ for 2 hr at room temperature decomposed only part of the starting material. Mixtures of unreacted 7, 7-benzyloxynorbornadiene (8), and 7-benzyloxyquadricyclane (9)¹⁹ were separated from tar and inorganic residues (Scheme II). Unfortunately, the percentage

Scheme II



composition of components in the mixture could not be accurately ascertained since column chromatography gave mixtures of 7 with 8 and 9 and mixtures of 9 with 8 and tarry material. However, the proton magnetic resonance (pmr) spectrum of material from an eluted fraction clearly indicated the presence of all three compounds since the cyclopropyl protons of 9 (δ 1.4-2.2) are cleanly separated from the complexed

(18) D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, 90, 2561 (1968).

(19) A new compound which was characterized by analysis, spectral characteristics, and thermal isomerization to 8.

vinyl protons of **7** (δ 2.7–3.2) and the vinyl protons of **8** (δ 6.4–6.8). One can also see the C_7 proton of each compound clearly: H_7 of **7** at δ 4.45; H_7 of **8** at δ 4.8; H_7 of **9** at δ 5.9. In addition, authentic **9** was prepared by the photoisomerization¹⁴ of **8** and its pmr spectrum corresponded to the signals assigned in the mixture.

While the nature of the photochemical process is not known, it is clear that the appearance of quadricyclic material in both reactions probably arises from the corresponding diene,¹⁴ the diene having been formed through photodecomplexation. The low yields of quadricyclanes may be due, in part, to valence isomerization to the norbornadiene derivative catalyzed by the transition metal complex remaining in solution.²⁰ Work is continuing on the photoinduced decomplexation of vinyl-substituted norbornadiene-7-one iron tricarbonyls as well as related diene-iron tricarbonyls. A more detailed report on further chemistry of **1** is forthcoming.

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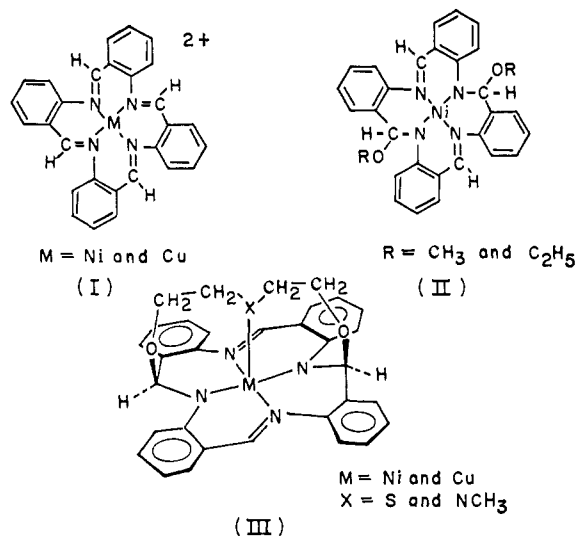
Application of the Coordination Template Effect to Prepare Five-Coordinate Nickel(II) and Copper(II) Complexes Containing a "Basket-Like" Polycyclic Ligand

Sir:

Extensive applications of the coordination template effects¹ have led to the synthesis of tridentate, many tetradentate, pentadentate, and sexadentate macrocyclic ligands. More complicated polycyclic structures should be accessible by related routes, and a novel illustration of this fact is provided by the synthesis of the compounds reported herein.

As was previously reported,^{1,2} neutral compounds II containing α -amino ether linkages can be formed by the interaction of solutions of sodium alkoxide with the cyclotetrameric Schiff base metal(II) complexes derived from *o*-aminobenzaldehyde (I), hereafter abbreviated as $M(\text{TAAB})^{2+}$.

The reactions of the $Ni(\text{TAAB})^{2+}$ and $Cu(\text{TAAB})^{2+}$ complexes with nucleophiles have been extended to bis(2-hydroxyethyl)methylamine and bis(2-hydroxyethyl) sulfide whose two potentially nucleophilic alkoxide ions can add to two *trans*-azomethine positions of the macrocyclic ligand. In such a product, the central nitrogen or sulfur atom is strategically positioned where it may coordinate to the metal ion in an axial position, thereby forming a square-pyramidal five-coordinate complex III. Using the reported procedure



for the preparation of the simple alkoxy adducts,² reaction of $Ni(\text{TAAB})(\text{BF}_4)_2$ and $Cu(\text{TAAB})(\text{NO}_3)_2$ with the above-mentioned nucleophiles gives the following compounds, $M(\text{TAAB})\text{LN}$ and $M(\text{TAAB})\text{LS}$, where $M = \text{Cu}^{2+}$ and Ni^{2+} , $\text{LN} = \text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{O})_2$, and $\text{LS} = \text{S}(\text{CH}_2\text{CH}_2\text{O})_2$. A complete elemental analysis, excluding oxygen determination, supports these assignments. $Ni(\text{TAAB})\text{LN}$ and $Ni(\text{TAAB})\text{LS}$ are microcrystalline dark red solids which are insoluble in water but soluble in most organic solvents giving relatively stable solutions. In acid media, the alkoxide group is eliminated, leading to regeneration of $Ni(\text{TAAB})^{2+}$. The new $Ni(\text{II})$ compounds are low spin at room temperature. The corresponding $Cu(\text{II})$ compounds, $Cu(\text{TAAB})\text{LN}$ and $Cu(\text{TAAB})\text{LS}$, are olive green solids with similar properties. They have magnetic moments of 2.10 and 2.26 BM, respectively.

Infrared spectra of these compounds are very similar with the following significant features: (a) the absence of peaks due to NO_3^- and BF_4^- ; (b) the absence of absorptions due to N–H and O–H vibrational modes, confirming that both hydroxyl groups have reacted; (c) the disappearance of the band at 1650 cm^{-1} originally present in $Ni(\text{TAAB})^{2+}$ and $Cu(\text{TAAB})^{2+}$ (previously assigned as the C=N stretching vibrational mode³) and the appearance of a new band at 1529 cm^{-1} which has been assigned as a stretching vibration of the two remaining azomethine linkages; and (d) the presence of bands in the 2950-cm^{-1} region, at 1465 and 1350 cm^{-1} , which can be attributed to aliphatic C–H stretching and bending vibrations.⁴ Molecular weight determinations (osmometric in 1,2-dichloroethane) confirm that $Ni(\text{TAAB})\text{LN}$ (calcd 588; found 584, 600), $Cu(\text{TAAB})\text{LN}$ (calcd 593; found 610), and $Cu(\text{TAAB})\text{LS}$ (calcd 596; found 580) are monomeric in solution. The electronic spectra of $Ni(\text{TAAB})\text{LN}$ and $Ni(\text{TAAB})\text{LS}$ are similar to the spectra of the simple alkoxy adducts except for the presence of an additional band in the visible region. Bands at 18,200, 19,200, 27,000, and $38,500\text{ cm}^{-1}$ are found in all solvolyzed products of $Ni(\text{TAAB})^{2+}$ and have been attributed to charge-transfer transitions. The spectra of $Ni(\text{TAAB})\text{LN}$ and $Ni(\text{TAAB})\text{LS}$ display a new band in the $16,000\text{-cm}^{-1}$

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(4) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966.