molecules. The compounds studied here apparently do not meet this criterion.

(19) See for example J. D. Roberts, "An Introduction to Spin-Spin Splitting in High Resolution NMR Spectra", W. A. Benjamin, New York, N.Y., 1961; K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra", W. A. Benjamin, New York, N.Y., 1962.

(20) No geminal bis- or geminal tetrakis(trifluoroethoxy) derivatives were present, and, as mentioned in the text, a noticeable reaction rate decrease occurred after the introduction of the first three trifluoroethoxy groups.

(21) R. Keat and R. A. Shaw, *J. Chem. Soc. A*, 908 (1966).

(22) S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 2215 (1965).

(23) R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 7193 (1965).

(24) E. T. McBee, K. Okuhara, and C. J. Morton, *Inorg. Chem.*, **5**, 450 (1966).

(25) S. H. Rose, *J. Polym. Sci., Polym. Lett. Ed.*, **6**, 837 (1968).

(26) G. L. Hagnauer, N. S. Schneider, and R. E. Singler, *Polym. Prepr., Am. Chem. Soc., Div. Polymn. Chem.*, **12**, 525 (1971); *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 699 (1972).

(27) G. S. Kyker and T. A. Antkowiak, *Rubber Chem. Technol.*, **47**, 32 (1974).

(28) Unpublished conformational potential energy calculations and X-ray diffraction data (H. R. Allcock, E. G. Stroh, J. Meister, and J. E. Lehnsen) suggest that the cis,trans planar chain conformation predominates in the solid polymer. See also ref 29.

(29) H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, **11**, 1120 (1972).

(30) F. Oehme and H. Wirth, "The Determination of the Molecular Electrical Dipole Moment", Kahl Scientific Instrument Company, El Cajon, Calif., p 9.

(31) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

(32) J. W. Smith, *Trans. Faraday Soc.*, **46**, 1394 (1950).

Contribution from the Department of Chemistry,
Texas Tech University, Lubbock, Texas 79409

Reactions of the Phosphorus Cage Molecule Tetraphosphorus Hexaoxide with Some Iron Carbonyls

MICHAEL L. WALKER and JERRY L. MILLS*

Received April 4, 1975 AIC50250I

The phosphorus cage molecule P_4O_6 reacts with $Fe(CO)_5$ in diglyme solvent at 140° to produce $(CO)_4Fe(P_4O_6)$, *trans*-$(CO)_3Fe(P_4O_6)_2$, and P_4O_7, whereas the photochemical reaction in benzene or THF solvent yields the same two iron-containing compounds and another phosphorus oxide, presumably P_4O_9. The relative yield of $(CO)_4Fe(P_4O_6)$ to *trans*-$(CO)_3Fe(P_4O_6)_2$ during photochemical reactions is markedly solvent dependent. Under a carbon monoxide atmosphere, $Fe_2(CO)_9$ in THF reacts with P_4O_6 to produce the series of compounds $[(CO)_4Fe]_n(P_4O_6)$, where n = 1–4, where the products are essentially controlled by reaction stoichiometry. The reaction of P_4O_6 with $Fe_3(CO)_{12}$ parallels the reaction with $Fe_2(CO)_9$. Trends in ^{31}P chemical shifts and coupling constants are noted and discussed.

Introduction

Tetraphosphorus hexaoxide, P_4O_6, consists of tetrahedrally arranged phosphorus atoms with bridging oxygen atoms.[1] As such, the phosphorus atoms in one P_4O_6 molecule constitute, at least potentially, a nonchelating, tetrahedral, tetradentate ligand. Previous studies have shown that P_4O_6 does indeed behave as a tetradentate base toward $Ni(CO)_4$;[2] however toward B_2H_6, the phosphorus cage molecule exhibits only moderate basicity.[3] This indication of preferred basicity toward metal carbonyls has prompted the close investigation of P_4O_6 with the iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$. The results of this study are reported herein. A brief reference to the reaction of P_4O_6 with neat $Fe(CO)_5$ and $Fe_2(CO)_9$ has been reported previously.[2]

Experimental Section

All compound transfers and manipulations were carried out in a drybox, in a glove bag, or by use of Schlenk-type glassware using standard inert-atmosphere techniques.[4] All solvents were distilled from CaH_2 and collected and stored over Linde 4A molecular sieves. Solvents were degassed with a nitrogen purge for at least 5 min prior to use. The iron compounds iron pentacarbonyl, $Fe(CO)_5$, diiron enneacarbonyl, $Fe_2(CO)_9$, and triiron dodecacarbonyl, $Fe_3(CO)_{12}$, were purchased from Pressure Chemical Co. The compounds $Fe(CO)_5$ and $Fe_3(CO)_{12}$ were used as received, and $Fe_2(CO)_9$ was dried in vacuo at 50° for 1 hr.[5] The compound P_4O_6 was prepared by controlled oxidation of white phosphorus with air, as previously described.[6] A Varian Associates NMR spectrometer Model XL-100-15 operating at 40.55 MHz was used to obtain ^{31}P spectra, employing either external or internal P_4O_6 as a reference. Ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer with sealed liquid cells equipped with KBr windows. Mass spectra were recorded on a Varian Matt Model 311 spectrometer. Photochemical reactions were carried out using a 100-W medium-pressure Hanovia lamp in Pyrex reaction vessels.

Reactions. (a) Thermal Reaction of P_4O_6 with $Fe(CO)_5$. One milliliter (9.7 mmol) of P_4O_6 was added to 15 ml of degassed diglyme in a 25-ml three-necked round-bottom flask under N_2 atmosphere. To this was added 1.4 ml (10.0 mmol) of $Fe(CO)_5$. With the flask connected to an Hg bubbler, the reaction mixture was heated to 140° in an oil bath for 9 hr. The reaction mixture remained light yellow until a temperature of 110–120° was reached and then gradually darkened and became viscous. The reaction mixture was allowed to cool to room temperature and was filtered. The diglyme was removed from the filtrate at ambient temperature under dynamic vacuum. The residue was fractionally sublimed at 80°.[7] The sublimate consisted of about 3.0 mmol of P_4O_7[6] and 3.0 mmol of the less volatile, clear yellow crystals of $(CO)_4Fe(P_4O_6)$. The residue from the initial sublimation was transferred to a conventional sublimator and heated to 120° for 3 hr yielding crystals (ca. 1.5 mmol) of *trans*-$(CO)_3Fe(P_4O_6)_2$.

(b) Photochemical Reaction of P_4O_6 with $Fe(CO)_5$. One milliliter (9.7 mmol) of P_4O_6 and 1.3 ml (9.3 mmol) of $Fe(CO)_5$ were added to 50 ml of degassed benzene or tetrahydrofuran (THF) and irradiated under N_2 atmosphere for 10–16 hr. Some evidence of reaction was noted after ca. 1 hr of irradiation. The reaction mixture was filtered and the solvent was removed from the filtrate via vapor transfer. The remaining oil was washed five times with 10-ml portions of pentane. The residue showed no ^{31}P resonances. The pentane was removed by vapor transfer and the residue was sublimed under a dynamic vacuum at 80°. The sublimed material was identified as $(CO)_4Fe(P_4O_6)$. The unsublimed residue contained $(CO)_3Fe(P_4O_6)_2$ in addition to an unidentified contaminate (possibly P_4O_9, see Results). A separation of these compounds has not been achieved.

(c) Reaction of P_4O_6 with $Fe_2(CO)_9$. One milliliter (9.7 mmol) of P_4O_6 was added to 20 ml of THF which had been purged with CO. While under CO atmosphere, 12.8 g (36.0 mmol) of $Fe_2(CO)_9$ was added with vigorous stirring to the solution at 35°.[5] The reaction was then heated to 50° for 30 min. After cooling, the THF was removed to give $[(CO)_4Fe]_4(P_4O_6)$ with some $Fe_3(CO)_{12}$. By progressively lowering the mole ratio of $Fe_2(CO)_9$:P_4O_6 in the initial reaction stoichiometry from ca. 4:1 to 1:1, the entire series of compounds $[(CO)_4Fe]_n(P_4O_6)$, where n = 1–4, was observed (see Results).

(d) Reaction of P_4O_6 with $Fe_3(CO)_{12}$. One milliliter (9.7 mmol) of P_4O_6 was added to 30 ml of glyme or THF containing 2.0 g (4.0 mmol) of $Fe_3(CO)_{12}$. The mixture was heated to 70° for 1 hr, during which time the green color of $Fe_3(CO)_{12}$ disappeared. The solution

Table I. ^{31}P NMR Data

Compd	Solvent	Ppm[a]			J, Hz
		Coordinated P	Uncoordinated P	Coordinated P – Uncoordinated P	
$(CO)_4Fe(P_4O_6)$	THF	−44.0	−4.8	39.2	34
$(CO)_4Fe(P_4O_6)$	Benzene	−48.5	−5.6	42.9	34
$[(CO)_4Fe]_2(P_4O_6)$	THF	−54.9	−2.7	52.2	30
$[(CO)_4Fe]_3(P_4O_6)$	THF	−56.1	+8.2	64.3	26
$[(CO)_4Fe]_4(P_4O_6)$	THF	−51.6			
$(CO)_3Fe(P_4O_6)_2$	THF	−53.0	−6.6	46.4	32
P_4O_7	Benzene	−19.9	+173.0	192.9	2.0
P_4O_9	Benzene	−6.6	b		2.5

[a] Relative to internal P_4O_6. [b] Not observed (see text).

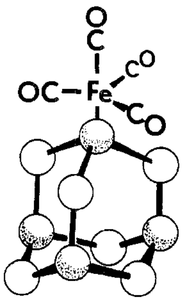

Figure 1. Proposed structure for $(CO)_4Fe(P_4O_6)$. The phosphorus atoms are shaded.

was cooled and filtered, and the solvent removed under dynamic vacuum at ambient temperature. The residue was heated to 48° to remove P_4O_6 and $Fe(CO)_5$. A nearly quantitative yield (based on P_4O_6) of $(CO)_4Fe(P_4O_6)$ was isolated by sublimation at 80°.

Results

The thermal reaction of iron pentacarbonyl with P_4O_6 invariably produced a mixture of three compounds which were separable by fractional sublimation. The most volatile of the three was isolated as clear, colorless crystals indicating the absence of iron and was identified as an intermediate oxidation product of P_4O_6 to P_4O_{10}, viz., P_4O_7. The compound P_4O_7 has been independently synthesized in high yield by the thermal decomposition of P_4O_6 in diglyme.[6] The ^{31}P NMR spectral data for P_4O_7 are summarized in Table I. The more volatile of the two remaining products was isolated as light yellow, clear crystals. The ir data in the carbonyl region (2075 (m), 1995 (m), 1965 (s) cm^{-1}) indicated local C_{3v} symmetry about the iron atom, as in $(CO)_4FePPh_3$.[8] The ^{31}P NMR spectrum (Table I) consisted of a doublet (relative area 3) coupled to a quartet (relative area 1), which leads to the assignment of this compound as $(CO)_4Fe(P_4O_6)$ (Figure 1). Mass spectral data which showed a parent peak (m/e 388, 24% relative intensity) in addition to major peaks for $(CO)_nFe(P_4O_6)$, where n = 3 (360, 42%), 2 (332, 37%), 1 (304, 92%), and 0 (276, 95%), further confirmed the assignment. The remaining, less volatile iron compound is *trans*-$(CO)_3Fe(P_4O_6)_2$. This assignment was made on the basis of ir data in the carbonyl region (1955 (s) cm^{-1}) which indicated local D_{3h} symmetry, as in $(CO)_3Fe(PPh_3)_2$;[8] ^{31}P NMR data which showed a coupled doublet and quartet (Table I); and mass spectral data which showed a parent peak (m/e 580, 16%) in addition to peaks for the progressive loss of CO groups of one (552, 21%), two (524, 24%), and three (496, 90%).

The photochemical reaction of P_4O_6 with $Fe(CO)_5$ produced the same iron-containing products $(CO)_4Fe(P_4O_6)$ and *trans*-$(CO)_3Fe(P_4O_6)_2$, but no P_4O_7 was produced. Rather a new compound exhibiting a ^{31}P NMR quartet (−6.63 ppm, J = 2.5 Hz) was produced. The remaining coupled portion of the spectrum has not been found, and we have been unable to separate the compound from *trans*-$(CO)_3Fe(P_4O_6)_2$. On the basis of the chemical shift and coupling constant (see Discussion), we tentatively assign the compound to P_4O_9. Additionally, the photochemical reaction of P_4O_6 with $Fe(CO)_5$ was found to be solvent dependent. Based on ^{31}P NMR integrated peak intensities, the ratio of $(CO)_4Fe(P_4O_6)$ to *trans*-$(CO)_3Fe(P_4O_6)_2$ in THF solvent was approximately 15:1, whereas in benzene solvent the ratio was 2:1. These product ratios were not appreciably affected by increasing the P_4O_6 concentration over a fourfold range in an effort to increase production of *trans*-$(CO)_3Fe(P_4O_6)_2$.

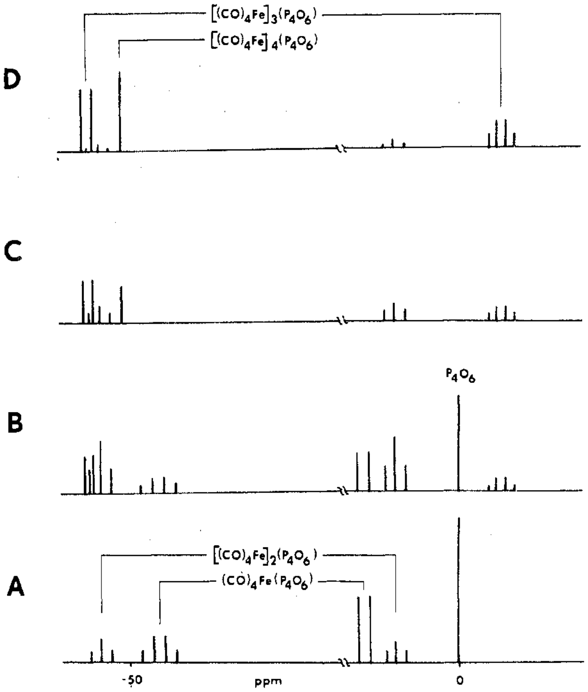

Figure 2. ^{31}P NMR spectra for the reaction mixtures of $Fe_2(CO)_9$ with P_4O_6 of varying stoichiometry. The mole ratio of $Fe_2(CO)_9$ to P_4O_6 is (A) 1:1, (B) 2:1, (C) 3:1, and (D) 4:1. Exact chemical shift and coupling constant data are in Table I.

It has recently been postulated that $Fe_2(CO)_9$ in THF under a CO atmosphere produces the reactive intermediate $(CO)_4Fe{\cdot}THF$.[5] At room temperature the reaction of $Fe_2(CO)_9$ with P_4O_6 in THF under CO atmosphere produced a mixture of products of the general formula $[(CO)_4Fe]_n(P_4O_6)$, which were essentially controlled by the reaction stoichiometry. When a 1:1 mole ratio of $Fe_2(CO)_9$ to P_4O_6 was employed, mono- and disubstitution on the phosphorus cage occurred, i.e., n = 1 or 2. At a mole ratio of approximately 4:1, a ^{31}P NMR spectrum indicated that the reaction mixture contained the following (Figure 2): no $(CO)_4Fe(P_4O_6)$, a barely observable quantity of $[(CO)_4Fe]_2(P_4O_6)$, a small quantity of $[(CO)_4Fe]_3(P_4O_6)$, and approximately 50% (based on the amount of P_4O_6) of $[(CO)_4Fe]_4(P_4O_6)$. Because of the high molecular weights and extreme air sensitivity, the di-, tri-, and tetrasubstituted products have not been isolated.

They were characterized only by ^{31}P NMR (Table I).

An extensive study of the reaction $Fe_3(CO)_{12}$ with P_4O_6 was not pursued; however, in general the behavior of the system appeared to parallel the $Fe_2(CO)_9$–P_4O_6 system. For example, when excess P_4O_6 was allowed to react with $Fe_3(CO)_{12}$ in glyme or THF, an essentially quantitive yield of $(CO)_4Fe(P_4O_6)$ was produced.

Discussion

The thermal reaction of P_4O_6 with $Fe(CO)_5$ can be summarized by the unbalanced equation

$$P_4O_6 + Fe(CO)_5 \xrightarrow[140°]{\text{diglyme}} (CO)_4Fe(P_4O_6) + \textit{trans}\text{-}(CO)_3Fe(P_4O_6)_2 + P_4O_7$$

Presumably P_4O_7 is produced by the autoxidation of P_4O_6, independent of any iron-containing compounds, inasmuch as P_4O_7 can be synthesized in high yield by heating a diglyme solution of P_4O_6.[6] The photochemical reaction of P_4O_6 with $Fe(CO)_5$ produced no observable amounts of P_4O_7 but rather yielded a new compound in addition to the expected mono- and disubstituted iron compounds. This compound is assigned to P_4O_9,[9] the structure being the P_4O_6 cage with three exocyclic oxygen atoms. This assignment is based on (a) the coupling constant of the quartet, $J = 2.5$ Hz, (b) the chemical shift, −6.63 ppm, and (c) the peak multiplicity. The quartet indicates coupling by three equivalent phosphorus atoms, and the coupling constant is in excellent accord with the small P–O–P coupling observed only in P_4O_6-cage-based derivatives.[6] The chemical shift is appropriate for the nonquaternized phosphorus atoms on a P_4O_6 cage. Unfortunately, we have been unable to find the coupled doublet, which we would expect to occur at ca. +185 ppm. This compound is not produced by photolysis of P_4O_6 solutions without $Fe(CO)_5$ present, which, coupled with low volatility and solubility, has thus far resulted in our inability to isolate and characterize the compound.

The reaction of $Fe_2(CO)_9$ with P_4O_6 can be summarized by the equations

$$Fe_2(CO)_9\ \text{THF} \xrightarrow[\text{atmosphere}]{\text{CO}} Fe(CO)_5 + (CO)_4Fe\cdot THF$$

$$n(CO)_4Fe\cdot THF + P_4O_6 \rightarrow [(CO)_4Fe]_nP_4O_6 \quad (n = 1\text{–}4)$$

The degree of substitution was controlled by reaction stoichiometry, with a mixture of products always being present (Figure 2).

The study of the ^{31}P chemical shifts for the $[(CO)_4Fe]_n(P_4O_6)$ system provides some insight into the inductive effects of metal coordination onto the P_4O_6 cage. While ^{31}P chemical shifts are dominated by anisotropic contributions,[10] Grim et al.[11] have shown that upon coordination of a metal carbonyl to phosphorus(III), invariably a downfield shift of the phosphorus resonance occurred. They used with considerable success the coordination chemical shift δ', where $\delta' = \delta$(coordinated P) − δ(free ligand), to help rationalize trends occurring in the complexes of a homologous series of metal carbonyls with various phosphine Lewis bases. We have found that in this study of the $[(CO)_4Fe]_n(P_4O_6)$ system an internal coordination chemical shift δ^*, where $\delta^* = \delta$(coordinated P atoms) − δ(uncoordinated P atoms on the same P_4O_6 cage), is useful. A linear relationship was observed when plotting δ^* vs. the number of $(CO)_4Fe$ units coordinated to the P_4O_6 moiety. With increasing coordination number, a progressive downfield shift occurred for the coordinated phosphorus atoms, while a progressive upfield chemical shift obtained for the uncoordinated phosphorus atoms. In $[(CO)_4Fe]_3(P_4O_6)$, the uncoordinated phosphorus atom resonated upfield of even free P_4O_6. The use of δ^* implies that each $(CO)_4Fe$ unit affects the cage in an equivalent manner and that this effect is additive. This is also observed if the data for the $Ni(CO)_4$–P_4O_6 system[2] are treated in the same way.

Not only did the δ^* value show a linear relationship with increasing numbers of $(CO)_4Fe$ coordination, but J_{P-O-P} coupling also exhibited a linear decrease with increasing coordination of the cage. It is tempting to relate this to the manner of orbital overlap of the coordinated phosphorus dπ through oxygen π^* to uncoordinated phosphorus dπ orbitals. Molecular orbital calculations have predicted considerable π-bond character in the P–O linkage.[12] When coordination of a $(CO)_4Fe$ occurs and the iron back-bonds to the phosphorus atom, less s character of the Fe–P–O linkage should ensue.[6] This argument can be extended by observing P_4O_7 with $J = 2.0$ Hz[6] and $P_4O_6\cdot NC_6H_5$ with $J = 4.5$ Hz,[13] in which the unique phosphorus atoms are formally oxidized or quaternized and undergo appreciable change in hybridization and bond angles, as evidenced by the unusually high chemical shifts which arise from bond angle strain.[10] This argument is somewhat taxed when $(CO)_4Fe(P_4O_7)$ is investigated. This molecule has $J_{P(O)-O-PFe} = 26.0$ Hz and $J_{P(O)-O-P} = 3.0$ Hz.[14] If the coupling mechanism is dependent on oxygen overlap, then a value of near 2.0 Hz would be expected for both J values. Indeed, the $(CO)_4Fe(P_4O_7)$ data suggest that sign changes of the coupling constant may dominate, since $J_{P(O)-O-PFe}$ involves coupling between two quaternized phosphorus atoms, whereas $J_{P(O)-O-P}$ is coupling between three- and four-coordinate atoms.[15] A determination of the signs of the coupling constants is being undertaken to aid in the interpretation of these data.

Acknowledgment. The support of the Robert A. Welch Foundation is gratefully acknowledged. We also thank Mr. Jordan Hodge for help in obtaining mass spectral and NMR data.

Registry No. $(CO)_4Fe(P_4O_6)$, 56083-08-0; $[(CO)_4Fe]_2(P_4O_6)$, 55937-79-6; $[(CO)_4Fe]_3(P_4O_6)$, 55975-90-1; $[(CO)_4Fe]_4(P_4O_6)$, 55937-80-9; *trans*-$(CO)_3Fe(P_4O_6)_2$, 55937-81-0; P_4O_7, 12065-80-4; P_4O_9, 55913-45-6; P_4O_6, 10248-58-5; $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 20982-74-5; $Fe_3(CO)_{12}$, 17685-52-8.

References and Notes

(1) B. Beagley, B. Briaun, D. W. J. Cruickshank, T. G. Hewitt, and K. H. Jost, *Trans. Faraday Soc.*, **65**, 1219 (1969).
(2) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **88**, 2166 (1966).
(3) J. G. Riess and J. R. Van Wazer, *J. Am. Chem. Soc.*, **89**, 851 (1967).
(4) D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(5) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 3438 (1974).
(6) M. L. Walker and J. L. Mills, *Synth. React. Inorg. Met.-Org. Chem.*, **5**, 29 (1975).
(7) K. Gosling and R. E. Bowen, *Anal. Chem.*, **45**, 1574 (1973).
(8) A. F. Clifford and A. K. Mukherjee, *Inorg. Chem.*, **2**, 151 (1963).
(9) B. Beagley, D. W. J. Cruickshank, and T. G. Hewitt, *Trans. Faraday Soc.*, **63**, 836 (1967).
(10) M. M. Crutchfield, C. H. Duncan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 75 (1967).
(11) S. O. Grim and D. A. Wheatland, *Inorg. Chem.*, **8**, 1716 (1969); S. O. Grim, D. A. Wheatland, and P. R. McAllister, *ibid.*, **7**, 161 (1968).
(12) B. J. McAloon and P. G. Perkins, *Theor. Chim. Acta*, **24**, 102 (1972).
(13) M. Berman and J. R. Van Wazer, *Inorg. Chem.*, **12**, 2186 (1973).
(14) M. L. Walker and J. L. Mills, unpublished results.
(15) J. R. Schweiger, A. H. Cowley, E. A. Cohen, D. A. Kroon, and S. L. Manatt, *J. Am. Chem. Soc.*, **96**, 7122 (1974), and references therein.