al.[26] Support for the mechanism was provided by the fact that, in addition to benzoin, we were able to isolate the diol 1,2-dihydroxy-1,2-diphenylethane, $C_{14}H_{14}O_2$ (15% yield), mp 146–148 °C (lit. mp 149–150 °C), from the reaction of *trans*-stilbene oxide with H_2O_2 in dioxane. The IR spectrum of the diol indicates ν(O—H) at 3300 cm^{-1} and the absence of ν(C=O). The ^{1}H NMR spectrum shows methine absorption at 6.0 ppm. Opening of the epoxide ring has been shown to occur readily in the presence of excess oxidant[26,28] with the subsequent formation of diol and α-hydroxy ketone. In the presence of catalyst, diols may be oxidized further to α-hydroxy ketones.[26]

An alternative mechanism for the formation of the epoxide is suggested by the work of Chong and Sharpless.[27] Those authors concluded that the epoxy oxygen is derived from the peroxy oxygen which is proximal to the metal atom in the transition state, at least in reactions employing alkyl hydroperoxide. With H_2O_2, we are not able to distinguish between the two possibilities.

The epoxide glycidol was obtained by oxidation of allyl alcohol (reaction C). This was evident from the ^{1}H NMR spectrum, which showed three multiplets centered at 2.7, 3.2, and 3.7 ppm. With H_2O_2 and only a catalytic amount of thorium complex (reaction D), the product isolated was glycerol. Its ^{1}H NMR spectrum showed methylene and methine absorptions at 3.61 and 5.15 ppm, respectively, as required by glycerol. The mass spectrum was identical with that of an authentic sample.

Katsuki and Sharpless[7] comment on the low yields of epoxide whenever the product is water soluble. Possibly the hydrolysis involved in the above mechanism is more facile when the epoxide is soluble.

Compounds **9** and **10** failed to oxidize the organic substrates even when refluxing at 120 °C was continued for 24 h. This is presumably due to the enhanced stability afforded by the tridentate ligands.

Acknowledgment. M.T.H.T. is grateful for a Commonwealth Scholarship. Helpful discussions with Professor Howard Alper are greatly appreciated.

Registry No. 1, 81802-63-3; **2**, 81802-64-4; **3**, 81802-65-5; **4**, 69480-50-8; **5**, 81802-66-6; **6**, 81802-67-7; **7**, 81802-68-8; **8**, 81802-69-9; **9**, 81802-70-2; **10**, 81802-62-2; $ThCl_4$, 10026-08-1; *trans*-stilbene, 103-30-0; allyl alcohol, 107-18-6.

(26) Dzhemilev, U. M.; Yur'ev, V. P.; Tolstikov, G. A.; Gersharov, F. B.; Rafikov, S. R. *Dokl. Chem. (Engl. Transl.)* **1971**, *196*, 79. See also: Sheldon, R. A. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 370.

(27) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.

(28) Barusch, M. R.; Payne, J. Q. *J. Am. Chem. Soc.* **1953**, *75*, 1987.

Contribution from the Institute of Physical Chemistry,
University of Perugia, 06100 Perugia, Italy

Hydrido(triphenylsilyl)tetracarbonyliron Derivatives with Phosphine Ligands

G. Bellachioma and G. Cardaci*

Received October 27, 1981

[$Fe(CO)_4(H)SiPh_3$] complexes are intermediates in the hydrosilylation reaction of alkenes, catalyzed photochemically by iron pentacarbonyl.[1] Their formation is not sufficient to account for the catalytic action, since they do not give hydrosilylation of alkenes in the absence of light.[1]

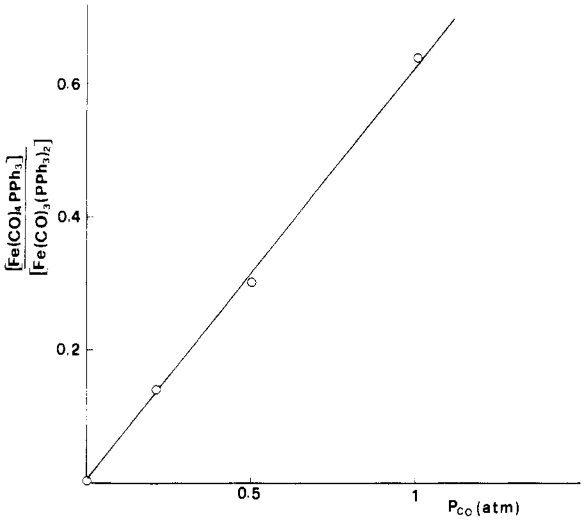


Figure 1. [$Fe(CO)_4PPh_3$]/[$Fe(CO)_3(PPh_3)_2$] vs. P_{CO} plot for the reaction between [$Fe(CO)_4(H)SiPh_3$] and PPh_3 at 25 °C in toluene ([PPh_3] = 5 × 10^{-2} M], [$Fe(CO)_4(H)SiPh_3$] = 6 × 10^{-3} M). The concentration ratio was obtained by measuring the absorbance ratio of the CO stretching bands of the mono- and disubstituted complexes.[3]

So that information about the nature of these catalytic intermediates could be obtained, a study of the thermal reactivity of [$Fe(CO)_4(H)SiPh_3$] with various nucleophiles was started.

Information about the reaction between [$Fe(CO)_4(H)SiPh_3$] and PPh_3 is given in the literature:[2] a reductive elimination of $HSiPh_3$ along with the formation of [$Fe(CO)_4$] and subsequently the reaction with PPh_3 producing [$Fe(CO)_4PPh_3$] was proposed. This mechanism is questionable, because if the intermediate [$Fe(CO)_4$] is formed, the reaction with PPh_3 should give a mixture of [$Fe(CO)_4PPh_3$] and [$Fe(CO)_3(PPh_3)_2$].[3] Therefore the formation of [$Fe(CO)_4PPh_3$] suggests a reaction mechanism that follows a different way.

In this work the results of a study of the reactivity of [$Fe(CO)_4(H)SiPh_3$] and phosphine ligands of different basicities are given.

Experimental Section

[$Fe(CO)_4L$] and [$Fe(CO)_3L_2$] (L = $SbPh_3$, PPh_3, $AsPh_3$) were prepared with the standard methods described in the literature.[3]

[$Fe(CO)_4(H)SiPh_3$] was prepared and purified as described by Graham.[2] Because of the extreme reactivity of [$Fe(CO)_4(H)SiPh_3$] with oxygen, the solvents used were deaerated with nitrogen purified by bubbling in Fieser solutions and appropriately dried. All the IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer; NMR spectra were obtained with a JEOL CHL60 spectrometer, with Me_4Si as reference.

[$Fe(CO)_3(H)(SiPh_3)PPh_3$] (I). The reaction was carried out at −18 °C in ethyl ether dried with $LiAlH_4$, with [$Fe(CO)_4HSiPh_3$) and PPh_3 mixed in the molar ratio 1/2. Two CO stretching bands at 2060 and 2000 cm^{-1} were immediately observed, which were attributed to the complex I. At the same time the formation of small quantities of [$Fe(CO)_3(PPh_3)_2$] was observed. It was not possible to separate these two complexes by fractional crystallization because the complex I reacted quickly, forming [$Fe(CO)_3(PPh_3)_2$]. Therefore only a spectroscopic characterization of the solid obtained after evaporation of the solvent was possible. This reaction occurred in the same way when other solvents (benzene, toluene, etc.) were used. When the reaction was carried out under a controlled CO atmosphere (P_{CO} = 0–1 atm), the formation of a mixture of [$Fe(CO)_4PPh_3$] and [$Fe(CO)_3(PPh_3)_2$] was observed. The plot of the [$Fe(CO)_4PPh_3$]/[Fe-

---

(1) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

(2) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

(3) Cardaci, G.; Narciso, V. *J. Chem. Soc., Dalton Trans.* **1972**, 2289. Cardaci, G. *Int. J. Chem. Kinet.* **1973**, *5*, 805. Cardaci, G. *Inorg. Chem.* **1974**, *13*, 368, 2974.

Table I. IR CO Stretchings and ^{1}H NMR Spectra[a]

complex	ν_{CO}, cm^{-1}	τ_H	J, Hz
[Fe(CO)$_4$(H)SiPh$_3$]	2103 (s), 2045 (s), 2035 (sh), 2025 (vs) E	18.8 (s) ET	
[Fe(CO)$_3$(H)(SiPh$_3$)PPh$_3$] (I)	2065 (s), 2000 (s), 1975 (sh) E	19 (d) ET	47 (P-H)
[Fe(CO)$_2$(H)(SiPh$_3$)PPh$_2$CH$_2$CH$_2$PPh$_2$] (II)	1992 (s), 1947 (s) E	19.3 (t) B 7.63 (d) C (CH$_2$)	32 (P-H) 16.5 (CH$_2$-P)
[Fe(CO)$_4$SiPh$_3$]$^-$[HP(C$_2$H$_5$)$_3$]$^+$ (III)	1996 (m), 1907 (m), 1877 (s) A	8.05 (m) AD (CH$_2$) 8.83 (dt) AD (CH$_3$)	7.5 (CH$_2$-CH$_3$) 19.5 (CH$_3$-P)

[a] Solvent abbreviations: E = hexane; A = acetonitrile; AD = trideuterioacetonitrile; ET = ethyl ether; B = benzene; C = deuteriochloroform. Abbreviations for the IR spectra: s = strong; sh = shoulder; vs = very strong; m = medium. Abbreviations for the NMR spectra: s = singlet; d = doublet; t = triplet; m = multiplet; dt = double triplet.

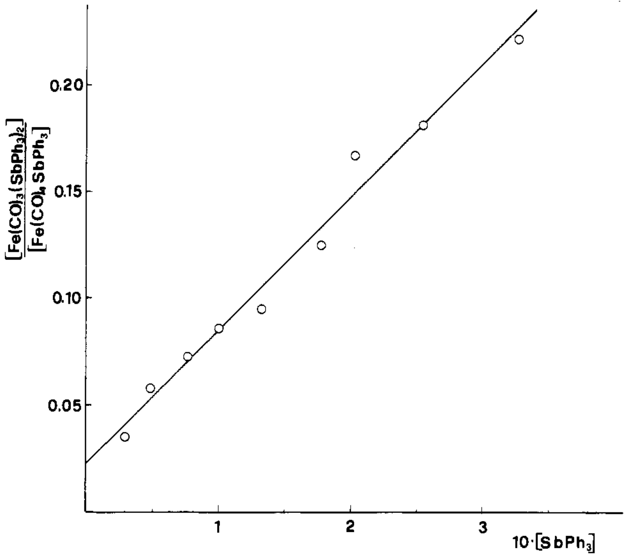


Figure 2. [Fe(CO)$_3$L$_2$]/[Fe(CO)$_4$L] vs. [SbPh$_3$] plot for the reaction between [Fe(CO)$_4$(H)SiPh$_3$] and [SbPh$_3$] at 35 °C in toluene ([Fe(CO)$_4$(H)SiPh$_3$] $\simeq 6 \times 10^{-3}$ M). The concentration ratio was obtained by measuring the absorbance ratio of the CO stretching bands of the di- and monosubstituted complexes.[3]

(CO)$_3$(PPh$_3$)$_2$] ratios vs. P_{CO} is linear as shown in Figure 1.

Reaction of [Fe(CO)$_4$(H)SiPh$_3$] with AsPh$_3$ and SbPh$_3$. These reactions were performed as described with PPh$_3$. In toluene the formation of small amounts of the intermediates [Fe(CO)$_3$(H)(SiPh$_3$)AsPh$_3$) and [Fe(CO)$_3$(H)(SiPh$_3$)SbPh$_3$] were observed spectrophotometrically.

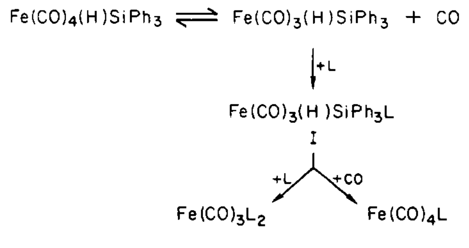
With these ligands the formation of a mixture of Fe(CO)$_4$L and Fe(CO)$_3$L$_2$ was observed also in the absence of carbon monoxide. The [Fe(CO)$_3$L$_2$]/[Fe(CO)$_4$L] ratio increases with the concentration and basicity of the ligand L (Figure 2).

[Fe(CO)$_2$(H)(SiPh$_3$)PPh$_2$CH$_2$CH$_2$PPh$_2$] (II). A 1-g quantity of [Fe(CO)$_4$(H)SiPh$_3$] and 0.930 g of PPh$_2$CH$_2$CH$_2$PPh$_2$ (molar ratio 1/1) reacted at 20 °C in benzene under bubbling nitrogen. The reaction was over after 2 h, and the solution was dried. The solid residue was dissolved in the ethyl ether. A 0.4-g quantity of the yellow solid II was obtained by crystallization of this solution; mp 145–150 °C dec. Anal. Calcd: C, 71.47; H, 5.59. Found: C, 70.60; H, 5.23. Molecular weight: calculated 772.95; found 750 (osmometric method).

[Fe(CO)$_4$SiPh$_3$]$^-$[HPEt$_3$]$^+$ (III). A 0.302-g quantity of PEt$_3$ and 0.880 g of [Fe(CO)$_4$(H)SiPh$_3$] (molar ratio 1/1.2) reacted in benzene rigorously deaerated at room temperature. The formation of III as a white precipitate, very sensitive to oxygen, was immediately observed. The solid was filtered and dried under nitrogen (1.00 g, yield 90%). Anal. Calcd: C, 61.29; H, 6.10. Found: C, 61.00; H, 5.90. III is soluble in CH$_3$CN, where it slowly decomposes. This reaction is very similar to that described in the literature with NEt$_3$.[4]

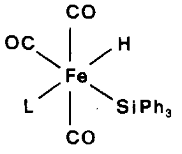
Reaction of II and PPh$_3$. The complex II was reacted with PPh$_3$ (molar ratio 1/1) in toluene at 70–80 °C. The formation in solution of [Fe(CO)$_2$(PPh$_2$CH$_2$CH$_2$PPh$_2$)PPh$_3$][5] was observed after 24 h (ν_{CO} = 1902, 1846 cm^{-1}).

Scheme I

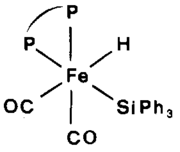


Results and Discussion

The CO stretching frequencies of the characterized complexes and the more significant NMR proton bands are given in Table I. The A structure is attributed to the complexes [Fe(CO)$_3$(H)(SiPh$_3$)L] (L = PPh$_3$, SbPh$_3$, AsPh$_3$) on the basis of the number and relative intensity of the CO stretching.[6] The trans position of L with respect to the hydrido ligand is supported by the J_{H-P} of the hydrido ligand (Table I), which is typical of a trans coupling.[7] The B structure is attributed to the complex II: the cis position of the proton with respect to the phosphorus atoms is supported by the NMR hydrido band, which shows a triplet (relative ratio 1/2/1) with J_{P-H} typical of a cis coupling (Table I).[7] This triplet band points out, moreover, the two phosphorus atoms of PPh$_2$CH$_2$CH$_2$PPh$_2$ are in equivalent positions with respect to the hydrido ligand. The doublet of the CH$_2$ groups of PPh$_2$CH$_2$CH$_2$PPh$_2$ (τ = 7.63, J_{CH_2-P} = 16.5 Hz) also agrees with the B structure.



A



B

The determination of the structure of the complex III (trigonal bipyramidal with SiPh$_3$ in the apical position) is based on the number and relative intensity of the CO stretchings (Table I) which correspond to that given in ref 4 for the anion [Fe(CO)$_4$SiPh$_3$]$^-$ with other cations. The formation of the [PHEt$_3$]$^+$ cation is ascertained on the basis of the NMR spectrum of the phosphonium compound[8] (see in Table I the

---

(4) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1159, 1647.

(5) Bellachioma, G.; Cardaci, G. *J. Organomet. Chem.* **1981**, *205*, 91.

(6) Bratermann, P. S. "Metal Carbonyl Spectra"; Academic Press: London, 1979.

(7) Malatesta, L.; Freni, M.; Valenti, V. *Angew. Chem.* **1961**, *73*, 273. Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, *1407*.

(8) Hendrickson, J. B.; Maddox, M. L.; Sins, J. J.; Kaesz, H. D. *Tetrahedron* **1964**, *20*, 449. Griffin, C. E.; Gordon, M. *J. Organomet. Chem.* **1965**, *3*, 414.

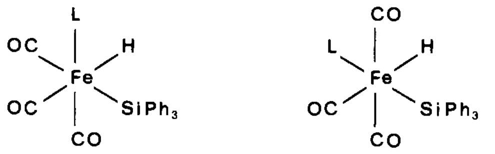
coupling constants). The proton, bonded to the phosphorus atom, was not found in the NMR spectrum; this behavior is common to these phosphonium salts.[9]

The hydrido ligand band in the complexes $[Fe(CO)_4(H)SiPh_3]$, I, and II, shows τ_H shifts to higher field by increasing the number of phosphine ligands (Table I); this is in agreement with the increase of electronic density of the iron atom which shields the proton.

The reactivity of $[Fe(CO)_4(H)SiPh_3]$ with the phosphine ligands shows that the paths of reaction are different according to the ligand basicity. With very basic phosphine ligands (PEt_3 in apolar solvents) $[Fe(CO)_4(H)SiPh_3]$ reacts as an acid and gives the ionic complexes III. The reaction mechanism of the less basic ligands is shown in Scheme I.

The effect of the CO pressure and of the ligand L concentration on the $[Fe(CO)_4L]/[Fe(CO)_3L_2]$ ratio (Figures 1 and 2) is in accord with Scheme I. When L = 1,2-bis(diphenylphosphino)ethane, the intermediate I, formed in the first step of the reaction, gives by chelation the disubstituted complex II without elimination of $HSiPh_3$; in the presence of carbon monoxide the substitution of this ligand is unpaired and the formation of $[Fe(CO)_3PPh_2CH_2CH_2PPh_2]$[10] with elimination of $HSiPh_3$ is observed.

The first step of Scheme I is an equilibrium reaction and indicates that the dissociation of an Fe–CO bond is an easy process at room temperature. Therefore the substitution of a CO with an alkene in the catalytic hydrosilylation does not need photochemical activation. On the other hand the insertion of an alkene in the metal–H bond and the subsequent elimination of the hydrosilylated olefin are very fast reactions[11] and do not need photochemical activation. On the basis of the present results the strong trans effect of the hydrido ligand[12] gives a substituted derivative of A structure. The trans position of the alkene and of the hydrido ligand prevents the insertion reaction. Therefore the photochemical action should isomerize the A structure into the C structures and allow the insertion of an alkene in the Fe–H bond, activating the catalytic process. Photochemical isomerization of octahedral complexes is very common in the literature;[13] in particular photochemical cis ⇌ trans isomerizations are observed for $M(CO)_4X_2$ and $M(CO)_2L_2X_2$ complexes[14] (M = Fe, Ru, Os; L = phosphine ligands; X = halogens).



C

Summary

The reaction between $[Fe(CO)_4(H)SiPh_3]$ and different nucleophiles L (L = CO, PPh_3, $AsPh_3$, $SbPh_3$, $PPh_2CH_2CH_2PPh_2$, or $P(C_2H_5)_3$) has been studied. The structure of the complex $[Fe(CO)_3(H)(SiPh_3)PPh_3]$ (I) is assigned on the basis of spectroscopic evidence; the complexes $[Fe(CO)_2(H)(SiPh_3)PPh_2CH_2CH_2PPh_2]$ (II) and $[Fe(CO)_4SiPh_3]^-[HP(C_2H_5)_3]^+$ (III) are isolated and characterized. A reaction mechanism is proposed on the basis of the reaction product and of the effect of the basicity and concentration of L.

Acknowledgment. Thanks are expressed to Dr. G. Reichenbach for useful discussion. This work was supported in part by the National Research Council of Italy (CNR).

Registry No. I, 81802-57-5; II, 81802-58-6; III, 81845-35-4; $Fe(CO)_4HSiPh_3$, 33361-69-2; $Fe(CO)_3(H)(SiPh_3)AsPh_3$, 81802-59-7; $Fe(CO)_3(H)(SiPh_3)SbPh_3$, 81802-60-0; $Fe(CO)_2(PPh_2CH_2PPh_2)PPh_3$, 81802-61-1; $Fe(CO)_4PPh_3$, 35679-07-3; $Fe(CO)_3(PPh_3)_2$, 21255-52-7; $Fe(CO)_4AsPh_3$, 35644-25-8; $Fe(CO)_4SbPh_3$, 35917-16-9; $Fe(CO)_3(AsPh_3)_2$, 20516-72-7; $Fe(CO)_3(SbPh_3)_2$, 20516-73-8.

---

[9] Khau, M.; Oldham, C.; Taylor, M. J.; Tuck, D. G. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 469.

[10] Manuel, T. A. *Inorg. Chem.* **1963**, *2*, 854. Cullen, W. R.; Harbourne, D. A. *Can. J. Chem.* **1969**, *47*, 3371.

[11] Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1978**, *157*, 359. Lappert, M. F.; Nile, T. A.; Takahashi, S. *Ibid.* **1974**, *72*, 425. Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

[12] Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1966; pp 24–29.

[13] Geoffroy, G. L. *Prog. Inorg. Chem.* **1980**, *27*, 140–141. Scandola, F. *Org. Chem. (N.Y.)* **1980**, *42* (3), 563–567.

[14] Pankowski, M.; Bigorgne, M. *J. Organomet. Chem.* **1969**, *19*, 393; **1975**, *125*, 231. Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1977**, *16*, 744.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Nuclear Magnetic Resonance Studies of the Solution Chemistry of Metal Complexes. 18. Complexation of Palladium(II) by Glycyl-L-histidine and Glycyl-L-histidylglycine

Dallas L. Rabenstein,* Anvarhusein A. Isab,
and Mohamed M. Shoukry

Received December 18, 1981

Metal-induced ionization of hydrogen from amide (peptide) nitrogens with subsequent metal binding to the deprotonated nitrogens is a characteristic feature in the complexation of palladium(II) by small peptides.[1-4] Thus, at neutral pH, dipeptide ligands such as glycylglycine generally react with Pd(II) to form planar complexes with the metal coordinated at the amino and deprotonated peptide nitrogens and the carboxylate oxygen. Tripeptide ligands form planar complexes, with Pd(II) coordinated at the amino group, two deprotonated peptide nitrogens, and the carboxylate group.

The complexation of Pd(II) by the dipeptide glycyl-L-histidine (Gly-His) is thought to deviate from this general pattern.[1] The Gly-His complex of Pd(II) is presumed to have a structure similar to that of the Gly-His complex of Cu(II), which has been shown by X-ray crystallographic analysis to be approximately square planar with the copper coordinated by the amino nitrogen, the deprotonated peptide nitrogen, and the imidazole 1-nitrogen of one dipeptide ligand and the carboxylate group of another.[5,6]

In the present paper, we describe the results of ^1H NMR and potentiometric studies of the complexation of Pd(II) by Gly-His and Gly-His-Gly. In order to elucidate the mode of binding in these complexes, we have included in this study ^1H NMR measurements on the hydrogens of the peptide groups.

Experimental Section

Gly-His and Gly-His-Gly were used as received from Sigma Chemical Co. K_2PdCl_4 was obtained from Alfa Inorganics.

Potentiometric titrations were performed at 25 °C on solutions containing 0.005 M peptide, 0.005 M K_2PdCl_4, and 0.154 M NaCl. The pH was measured with a Fisher Model 620 pH meter equipped with a Fisher microcombination electrode. The pH meter was calibrated with pH 4.00, 7.00, and 10.00 buffers.

---

[1] Wilson, E. W., Jr.; Martin, R. B. *Inorg. Chem.* **1970**, *9*, 528.

[2] Pitner, T. P.; Wilson, E. W., Jr.; Martin, R. B. *Inorg. Chem.* **1972**, *11*, 738.

[3] Martin, R. B. *Met. Ions Biol. Syst.* **1974**, *1*, 129–156.

[4] Vestues, P. I.; Martin, R. B. *J. Am. Chem. Soc.* **1980**, *102*, 7906.

[5] Blount, J. F.; Fraser, K. A.; Freeman, H. C.; Szymanski, M. T.; Wang, C.-H.; Gurd, F. R. N. *J. Chem. Soc., Chem. Commun.* **1966**, 23.

[6] Blount, J. F.; Fraser, K. A.; Freeman, H. C.; Szymanski, J. T.; Wang, C.-H. *Acta Crystallogr.* **1967**, *22*, 396.

0020-1669/82/1321-3234$01.25/0