

electronegativity should decrease k_2 by stabilizing the enolate form relative to the carbanion, thus decreasing the availability of the reactive species.

By virtue of a reduction from a second-order reaction to first order, the inner-sphere path presents an entropy advantage over the outer-sphere path. An inner-sphere path is plausible because complexing of pyruvate to the enolate complex, giving the mixed complex, $M(E)(P)$, is rapid, and molecular models show that in the mixed complex the carbonyl carbon of monodentately bound pyruvate can be brought almost into contact with the methylene group of the carbanion. For such an arrangement of ligands to be possible, the metal ion must not impose stringent steric requirements on the complexed pyruvate (the promnastic effect).²² In this re-

spect, an inner-sphere reaction possesses features in common with Schiff base formation where Zn(II) shows kinetic activity but Ni(II) is kinetically inactive.²² Qualitatively, the same order is indicated for k_2 in pyruvate dimerization. The reactivity of Ni(II) in the present system would be a consequence of its relatively small tendency to bind pyruvate compared to the glycinate of the previous work.²²

Because electronegativity and the promnastic effect should both cause k_2 for Zn(II) to be higher than that for Ni(II), the present qualitative data do not distinguish between the two possibilities. The entropy gain, however, would make the inner-sphere reaction more likely, other factors being constant.

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Unusual Metalloporphyrins. IV. Novel Methods for Metal Insertion into Porphyrins^{1a,b}

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Abstract: Several metalloporphyrins including the new chromium and titanium porphyrins have been synthesized by two novel metal insertion methods which use metal carbonyls and the σ -bonded organo-transition metal compound, diphenyltitanium. The compounds were characterized by infrared, ultraviolet, and visible spectra, magnetic susceptibilities, and elemental analyses. The chromium ion is in the dipositive oxidation state and the titanium ion is in the tetrapositive oxidation state as the titanyl species. Evidence for molecular aggregation of the chromium and titanyl porphyrins in the solid and in solution is presented. The applicability of the preparative methods and loss of carbonyl ligands are discussed.

Although metalloporphyrins are widely dispersed in nature²⁻⁴ and many have been synthesized, only those of chromium and titanium of the first-row transition metals have not been prepared,⁵ nor have they been identified in nature. It is proposed, however, that titanium porphyrins are present in crude petroleum.^{2,6} Vanadium porphyrins have been found in crude petroleum and have been synthesized under relatively severe conditions.^{2,3,7}

A series of metalloporphyrins including the chromium and vanadyl mesoporphyrins has been prepared by the facile metal insertion reaction using metal carbonyls. This method, however, was not applicable for the preparation of a titanium porphyrin since titanium carbonyls are unknown and attempts to prepare them are unsuccessful.⁸ Instead, a novel method of metal insertion into the porphyrin was developed using the σ -bonded organo-transition metal compound, diphenyltitanium. This paper presents these novel preparative methods and the characterizations of the prepared metalloporphyrins.

Experimental Section

Reagents, Solvents, and Instrumentation. Solvents used in the metalloporphyrin preparations by metal carbonyls were distilled under purified ^{9a} nitrogen while the solvents used in the titanium porphyrin preparation were distilled under purified argon from typical drying agents:^{9b} mesitylene, *n*-pentane, and *n*-hexane from sodium; benzene, toluene, and ether from lithium aluminum hydride. Decane and decalin were shaken with sulfuric acid,

(1) (a) Supported by National Science Foundation Grant GB-5732.

(b) This work was reported in part in the preliminary communication: M. Tsutsui, M. Ichikawa, F. Vohwinkel, and K. Suzuki, *J. Amer. Chem. Soc.*, **88**, 854 (1966); M. Tsutsui, R. A. Velapoldi, K. Suzuki, and T. Koyano, *Angew. Chem.*, **7**, 891 (1968).

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(5) The phthalocyanines of chromium and titanium have been prepared: (a) F. H. Moser and A. L. Thomas, "Phthalocyanine Compounds," Reinhold Publishing Co., New York, N. Y., 1963; (b) J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, 1257 (1961); A. B. P. Lever, Ph.D. Thesis, London, 1961.

(6) T. Muniyappan, *J. Chem. Educ.*, **32**, 277 (1955).

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(9) (a) Purified indicates bubbled through a Na-K alloy; (b) L. F. Fieser and M. Fieser, "Reagents for Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., 1967; L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957.

sodium hydroxide, and water in that order and were distilled from sodium sulfate. The preparations of the metalloporphyrins were carried out under inert atmospheres: argon for the titanium and nitrogen for the others.

Vanadium hexacarbonyl, $V(CO)_6$, was obtained from a solution of sodium diglyme vanadate.¹⁰ $Cr(CO)_6$ (Pressure Chemical Co.), $Co_2(CO)_8$, $Ni(CO)_4$, $Fe(CO)_5$, and $Fe_3(CO)_{12}$ (all from Alpha Inorganics) were purified by distillation or sublimation.

Spectra. Infrared spectra were taken using Perkin-Elmer 621, 337, and Infracord spectrophotometers, as Nujol mulls and KBr disks, and in solution. Ultraviolet and visible spectra were obtained on a Cary Model 15 recording spectrophotometer using matched quartz 1-cm cells. ESR spectra were obtained on a Varian Model V-FR-4503 spectrometer with an X-band microwave bridge. Samples were run as magnetically diluted and neat solids, as well as chloroform and toluene solutions, and glasses at room and liquid nitrogen temperatures, respectively.

Magnetic Susceptibilities. A Varian Model A-60 nmr spectrometer was used to measure susceptibilities by the nmr method¹¹ and an α -regulated power supply, magnet, and Mettler microanalytical balance were used for the determination of susceptibilities in the solid state by the Guoy method.

Redox Procedures. Hydrogen peroxide (0.5 ml, 3%) was added to a 1×10^{-5} M solution of $Cr^{II}MPIXDME$ in $CHCl_3$ and spectral changes in the visible region were noted. To this oxidized solution, excess solid sodium dithionite was added, the solid filtered off, and the spectrum of the reduced species in solution recorded. In addition, olefin-induced oxidations of the $Cr(II)$ porphyrin were carried out according to procedures reported previously.¹² Oxidative titrations as per the method of Elvidge and Lever^{6b, 13} were also carried out.

Analyses. Compounds were analyzed and molecular weights were determined by Schwarzkopf and Tiedcke Analytical Laboratories. The Signer method was also used for the determination of molecular weights.¹⁴

Preparations. Mesoporphyrin IX dimethyl ester, $MPIXDME$,^{3, 15} and protoporphyrin IX dimethyl ester,^{3, 16} $PPIXDME$, were prepared by literature procedures. Diphenyltitanium, Ph_2Ti , was obtained by thermally decomposing tetraphenyltitanium at -20° ; the latter was prepared from the reaction of phenyllithium and titanium tetrachloride in ether at -78° .¹⁷

Chromium Mesoporphyrin IX Dimethyl Ester, $Cr^{II}MPIXDME$. $MPIXDME$ (0.200 g, 0.34 mmol) and chromium hexacarbonyl (1.00 g, 4.54 mmol) were stirred and heated at 170° in 45 ml of *n*-decane under nitrogen for 1.5 hr. Decalin was also used with excellent results at a bath temperature of 205° . The solution was cooled, and spectroscopic evidence indicated that a metalloporphyrin had formed. Solvent and unreacted $Cr(CO)_6$ were removed under reduced pressure. The residue was dissolved in toluene, the solution concentrated, and the product precipitated by the addition of *n*-pentane. This purification procedure was repeated until no enhancement of the visible absorption spectrum was observed. *Anal.* Calcd for $C_{38}H_{40}O_4N_4Cr$: C, 67.06; H, 6.25; Cr, 8.08; N, 8.69. Found: C, 67.20; H, 6.11; Cr, 7.88; N, 8.61.

Cobalt(II) mesoporphyrin IX dimethyl ester, $Co^{II}MPIXDME$, was prepared in a similar manner to the nickel and chromium porphyrins using $Co_2(CO)_8$ (0.050 g, 0.15 mmol) and $MPIXDME$ (0.007 g, 0.01 mmol). Identification of the product was accomplished by comparing the visible spectrum with that of the known compound. (See Table I in the Results and Discussion section.)

Nickel(II) Protoporphyrin IX Dimethyl Ester, $Ni^{II}PPIXDME$. A solution of nickel tetracarbonyl (8 ml, 6.18 mmol) and 25 ml of toluene was added to $PPIXDME$ (0.125 g, 0.21 mmol) in 25 ml of toluene at -25° . The reaction mixture was gently heated to 95° and kept at this temperature for 15 hr. The reaction mixture was filtered and the filtrate concentrated under reduced pressure and stored in a Dry Ice-acetone bath overnight in order to precipitate the

product. The spectrum of the precipitated metalloporphyrin was identical with that of $Ni^{II}PPIXDME$. The nickel porphyrin was also prepared in a similar manner using pyridine as the reaction solvent and 7-hr heating at 140° .

Iron(III) Protoporphyrin IX Dimethyl Ester Iodide, $Fe^{III}IPPIXDME$. $PPIXDME$ (0.590 g, 1 mmol), iron pentacarbonyl (0.390 g, 2 mmol), iodine (0.507 g, 4 mmol), and mesitylene (30 ml) were mixed and heated for 4 hr at 80° . The solvent was removed under reduced pressure leaving a black residue. The residue was dissolved in a minimum of acetic acid (~ 20 ml) containing a small amount of KI and filtered, and methanol was added to the filtrate to force precipitation. The visible spectrum of the compound in chloroform was identical with that of the known compound. *Anal.* Calcd for $C_{38}H_{36}O_4N_4FeI$: Fe, 7.2. Found: Fe, 7.0.

Iron(III) Protoporphyrin IX Dimethyl Ester Chloride, $Fe^{III}CIPPIXDME$. Triiron dodecacarbonyl (0.300 g, 0.60 mmol), $PPIXDME$ (0.020 g, 0.03 mmol), NaCl (0.500 g, 8.56 mmol), and 25 ml of acetic acid were heated and stirred at 80° for 40 min. Hemin, as identified by its visible spectrum, was obtained.

Vanadyl Mesoporphyrin IX Dimethyl Ester, $VOMPIXDME$. Vanadium hexacarbonyl (0.035 g, 0.16 mmol) and $MPIXDME$ (0.007 g, 0.001 mmol) were stirred and heated at 170° for 1.5 hr in 20 ml of *n*-decane. The solvent and excess $V(CO)_6$ were removed under vacuum. Purification by column chromatography (Al_2O_3 , Merck, chloroform-*n*-heptane eluent) yielded a deep purple-black compound which had the same absorption spectrum as the previously prepared vanadyl compound.⁷

Titanyl Mesoporphyrin IX Dimethyl Ester, $TiOMPIXDME$. $MPIXDME$ (0.692 g, 0.116 mmol) and diphenyltitanium (0.3512 g, 1.75 mmol) were ground in the solid state for 0.5 hr. Mesitylene (75 ml) was added and the mixture put into an oil bath at 240° (mesitylene boils at 164.7° and care must be used in this step; the bath temperature fell to 203°) for 1.5 hr with stirring. Triethylbenzene (bp 216° , bath at 205 – 210°) was also used as a solvent. The mixture was cooled to room temperature and filtered in air. A chloroform extract of the precipitate was passed through a chromatographic column using chloroform as the eluent (basic alumina, Calbiochem) from which a deep purple solid was isolated. Tlc using chloroform as the solvent showed the presence of only one component and the visible spectrum showed little, if any, $MPIXDME$ present as impurity. *Anal.* Calcd for $TiC_{38}H_{40}N_4O_4$: C, 65.85; H, 6.14; N, 8.53; O, 12.2; Ti, 7.29; mol wt, 65.67. Found: C, 65.59; H, 5.89; N, 8.40; O, 13.3; Ti, 7.82; mol wt in 2.7×10^{-4} M chloroform, 685.2; in 5.0×10^{-3} M chloroform and trichloroethylene, 1702; trimeric structure, theoretical, 1970.

Results and Discussion

The preparation of a series of metalloporphyrins by the metal carbonyl insertion method shows wide preparative applicability in addition to ease of preparation. The reactions used in the preparations of the metalloporphyrins are classified as ligand-exchange reactions with metal carbonyls.¹⁸ Behrens, *et al.*,¹⁹ have succeeded in totally replacing the carbonyl ligands in $Cr(CO)_6$ with the neutral ligands, dipyrindyl and tripyridyl. In the preparation of the chromium porphyrin (and the other metalloporphyrins), oxidation of the metal is probably accomplished by the weakly acidic hydrogen on the nitrogen in the free porphyrin.²⁰

A more detailed discussion of the properties and spectra of the new chromium(II) porphyrin follows since the other metalloporphyrins prepared are well known and characterized.

The magnetic susceptibility of solid $Cr^{II}MPIXDME$ was measured by the Guoy method and found to be 2.84 BM. $Cr(II)$ as a true square-planar complex with dsp^2 hybridization would be expected to have four un-

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paired electrons^{5b,21} and thus have a susceptibility of 4.95 BM. Intermolecular interactions between chromium and nitrogen atoms could force an approach to octahedral symmetry resulting in electron pairing and the low magnetic susceptibility observed in the solid state.²²

Susceptibilities determined by nmr for a solution of Cr^{II}MPIXDME in chloroform gave a magnetic susceptibility of 5.19 BM, showing four unpaired electrons. Thus, intermolecular or solvent interactions along the Z axis are reduced (weakened) and electron pairing does not occur, resulting in the high-spin state and the observed magnetic susceptibility of 5.19 BM.

A summary of the visible absorptions of the metalloporphyrins prepared is given in Table I. The Cr^{II}-

Table I. Visible Absorptions^a of the Metalloporphyrins Prepared by the Metal Carbonyl Insertion Method

Compound	Soret band, m μ	β band, m μ	α band, m μ
Cr ^{II} MPIXDME	416	536	572
Co ^{II} MPIXDME	393	518	553
VOMPIXDME	401, 502 ^b	533	570
NiMPIXDME	403	525	562
Fe ^{III} ClMPIXDME	405	535	585

^a In chloroform. ^b Shoulder.

MPIXDME has the usual metalloporphyrin electronic spectrum:²³ an intense band in the near-ultraviolet region due to $a_{1u}(\pi) \rightarrow e_g^*(\pi)$ transitions and two weaker bands in the 500–600 m μ region due to $a_{2u}(\pi) \rightarrow e_g^*(\pi)$ transitions.

The chromium(II) porphyrin is slowly oxidized to the chromium(III) porphyrin in solution by air as shown by absorption shifts given in Table II. These observations

Table II. Spectral Shifts Due to the Air Oxidation of Cr^{II}MPIXDME to [Cr^{III}MPIXDME]⁺ in CHCl₃

Time in CHCl ₃ , hr	Soret, m μ	β band, m μ	α band, m μ	α/β^c
0	415 (4.67) ^a	536 (3.13)	572 (3.64)	3.1
12	418	537	573	1.5
36	419	537	574	1.1
72	423	541	574	0.6
∞^b	438 (4.95)	545 (3.68)	575 (3.40)	0.5

^a Log ϵ . ^b ∞ = no further spectral change, ~ 7 days. ^c Ratio, optical densities.

are in agreement with those found for the chromium(II) phthalocyanines.^{5b}

It is interesting to note that the α/β absorbance ratios decrease as the Cr(II) is oxidized to the Cr(III) species.

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Originally³ an α/β ratio > 1 was proposed to be indicative of metalloporphyrin stability, but recent papers suggest that this is not the case and that the α/β ratios are dependent on solvent and metal oxidation state.²⁴ The latter definitely appears to be substantiated with the chromium(II) and chromium(III) porphyrins. Further evidence for the absorption and α/β solvent dependency (although small) is given in Table III.

Table III. Visible Absorptions and α/β Ratios for Cr^{II}MPIXDME in Several Solvents

Solvent	Soret, m μ	β band, m μ	α band, m μ	α/β
Ether	412	534	570	3.5
Decalin	415	535	572	3.0
Toluene	415	536	573	3.6
Chloroform	416	536	572	3.1

Oxidation of the Cr^{II}MPIXDME with hydrogen peroxide resulted in the formation of [Cr^{III}MPIXDME]⁺ which had the same spectrum as that observed for the Cr(III) species obtained by air oxidation. Addition of sodium dithionite reduced the Cr(III) to Cr(II) supporting the reported oxidation states of the Cr(II) and Cr(III) and their respective electronic spectra.

Addition of unsaturated hydrocarbons induced oxidation of the Cr(II) to Cr(III), but not as rapidly as the originally reported phenomenon using cobalt(II) porphyrins.¹² These redox reactions were followed spectrophotometrically.

Oxidative titrimetry used for evidence supporting the oxidation states of chromium phthalocyanine^{5b,13} was unsuccessful for the Cr(II) porphyrin since oxidation of the porphyrin ring occurs³ resulting in the use of a 20-fold excess of oxidizing agent.

The N-H stretching (~ 3300 cm⁻¹), deformation (~ 1630 cm⁻¹), and rocking (~ 1100 cm⁻¹) vibrations, present in the free porphyrin,²⁵ were not present in the spectrum of the Cr^{II}MPIXDME. No metal-ester carbonyl absorptions were noted in the infrared spectra as shown by the usual uncomplexed ester carbonyl absorption at 1740 cm⁻¹. Other ir absorptions are similar to those assigned for usual MPIXDME or metalloporphyrin spectra.³

No metal-carbonyl absorptions were found in the ir spectra of the metalloporphyrins prepared by the metal carbonyl method. As observed previously,^{18,26} carbonyl groups on transition metals are labilized by strong σ -bonding ligands (such as porphyrins) and are lost upon heating. In the metalloporphyrin, loss of the carbonyl may also be explained by increased hardness of the metal upon going from a 0 to a 2+ oxidation state. Recently, however, the iridium porphyrin has been prepared from the iridium carbonyl chloride,²⁷ and a metal-carbonyl absorption has been observed in the ir suggesting stabilization of the metal-carbonyl bond

(24) D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, **28**, 2363 (1963); A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, **90**, 6577 (1968); A. H. Corwin, D. G. Whitten, E. W. Baker, and G. C. Kleinspehn, *ibid.*, **85**, 3621 (1963).

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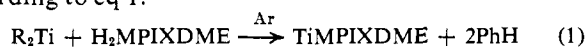
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(27) N. Sadasivan and E. B. Fleischer, *J. Inorg. Nucl. Chem.*, **30**, 591 (1968).

through increased ion size. It is probable, however, that electronic effects are much more important in explaining the loss of carbonyl ligands during the preparation of the chromium porphyrin than size limitations.

VOMPIXDME was prepared under relatively mild reaction conditions as compared to the rather severe methods reported earlier which included the heating of vanadium tetrachloride with the porphyrin in sealed silver or glass tubes.^{3,7}

Preparation of the titanium porphyrin was accomplished by using the σ -bonded diphenyltitanium since titanium carbonyls are unknown²⁸ and the usual metal-porphyrin preparations were not successful. The use of organotitanium compounds in the desired formal oxidation state of 2+ and argon as the inert gas eliminates unwanted side reactions²⁹ and produces inert solvents according to eq 1.



The titanium porphyrin was diamagnetic indicating a 4+ oxidation state for the titanium. This insertion method should result in a titanium(II) porphyrin; however, it is reasonable that the Ti(II) is oxidized to the more stable titanyl species during isolation of the compound in air.

The esr of the solid titanium porphyrin also supports an oxidation state of 4+. No broad absorptions (500–700 G wide) typical of transition metal complexes were observed. However, a spectrum indicative of magnetically diluted Ti(III) was noted which proved that the major portion of the titanium species was present in the 4+ state and that, at most, less than 10% and quite probably less than 1% of the titanium present was in the Ti(III) state. Further work is in progress which will present the esr data obtained for the Cr, Ti, and other metalloporphyrins.

The infrared spectrum of solid titanyl porphyrin showed metal insertion by absence of N–H absorptions. The spectrum also showed metal–ester carbonyl interactions. The carbonyl absorption in the 1700–1735-cm⁻¹ region, normally indicative of the ester functional group in the metalloporphyrin,^{3,16} was a medium weak absorption rather than the strongest observable absorption. A strong absorption at 1600 cm⁻¹, one of several usually weak stretching frequencies assigned to C=C, C=N, and C=O, was observed. Two medium absorptions at 930 and 955 cm⁻¹ were present in the solid and solution spectra.

Spectra were taken in chloroform solutions with various TiOMPIXDME concentrations (5×10^{-2} to 1×10^{-4} M). As solutions became more dilute, the carbonyl absorption at 1710 cm⁻¹ became stronger and sharper, shifting slightly to 1715–1720 cm⁻¹ while the absorption at 1600 cm⁻¹ decreased in intensity. The absorption at 930 cm⁻¹ and a weak absorption at 1038 cm⁻¹ increased in intensity upon dilution while the band at 955 cm⁻¹ decreased (Figure 1). Although 1038 cm⁻¹ is slightly higher than the band assigned at 978 cm⁻¹ for

(28) Since iridium and rhodium porphyrins have been prepared by the use of carbonyl chlorides,²⁵ it is probable that use of Ti(C₂H₅)₂(CO)₂ as a reactant (prepared by J. G. Murray, *J. Amer. Chem. Soc.*, **81**, 752 (1959)) would result in the formation of a titanium porphyrin.

(29) Nitrogen is known to react with titanium compounds in the presence of Grignard reagents: M. E. Volpin and V. E. Shur, *Dokl. Akad. Nauk SSSR*, **156**, 1102 (1964). Diphenyltitanium also reacts with nitrogen at elevated temperatures which, in this case, undoubtedly inhibits titanium insertion: G. Razuvaev, private communication, Moscow, Oct 1967.

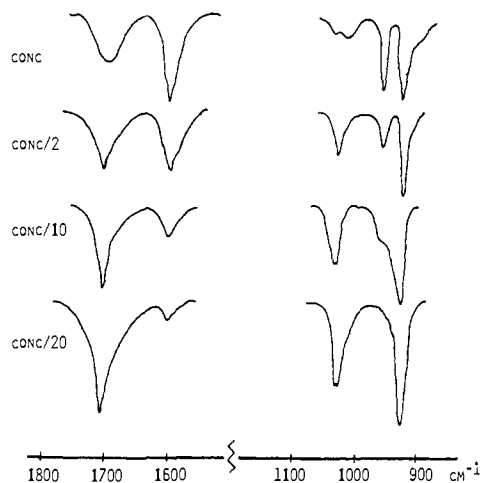


Figure 1. Ester carbonyl and titanyl absorption band changes with concentration; TiOMPIXDME = 5×10^{-2} M.

the Ti–O absorption in titanyl phthalocyanine,³⁰ it is still within the limits imposed for the titanyl absorption of various titanyl species³¹ such as TiO(acac)₂.

The increase in the 1600-cm⁻¹ absorption in the solid or concentrated chloroform solutions undoubtedly resulted from additional contributions due to the carbonyl stretching frequency which has been either split¹⁶ or lowered³² by the titanium interaction. A band at 1640 cm⁻¹ has been assigned as the ester carbonyl absorption in [TiO(OCOCF₃)₂]_n³³ which indicates that titanium–ester interactions lower the carbonyl absorptions. Absorptions in the 970–910-cm⁻¹ region have been assigned to a metal-dependent in-plane porphyrin deformation.²⁵ A nonassociated species would also account for a “freer” complex, and it is probable that the in-plane deformation is of high symmetry explaining the increased intensity of the 933-cm⁻¹ band. The increased wave number for the TiO absorption at 1038 cm⁻¹ suggests a higher double-bond order in going from the associated (TiO absorption at 955 cm⁻¹) to the nonassociated species. Spectra of the TiOMPIXDME in trichloroethylene showed the same spectral dependence on concentration.

The molecular weight of TiOMPIXDME in chloroform or trichloroethylene (5×10^{-3} M) was found to be approximately 1700 supporting metalloporphyrin association (a trimer gives a molecular weight of 1970). The molecular weight in chloroform (1×10^{-4} M) was found to be 685.2 (theoretical 656.7). Thus, the degree of association is concentration dependent as shown by infrared spectra and molecular weight determinations.

The oxygen analysis (13.3% found), although by itself does not differentiate between a Ti–O–Ti or a titanyl species, taken in conjunction with the molecular weight data suggests the presence of the titanyl struc-

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(33) P. Sartori and M. Weidenbruch, *Chem. Ber.*, **100**, 2049 (1967).

ture. In addition, it shows that there are five oxygen/molecule and four oxygen/molecule, which would have a theoretical oxygen analysis of 9.9% rather than the 12.2%, and thus gives further support to the Ti(IV) assignment rather than to a Ti(II) oxidation state.

TiOMPIXDME in chloroform has a typical metalloporphyrin visible spectrum: 407 (5.60), 500 (small shoulder), 536 (2.35), and 574 m μ (2.46) (log ϵ values are given in parentheses). The Ti(IV) species is stable in solution. The shoulder at 500 m μ is also present in the vanadyl mesoporphyrin and thus may be due to a perturbation on the porphyrin system by the doubly bound oxygen.

The organo-transition metal method of metal insertion would probably be applicable for the preparation of the molybdenum, tungsten, and other metalloporphyrins which cannot be prepared easily by any existing methods.

The successful preparation of the chromium and titani-

um porphyrins may be explained by the concept of hard and soft acids and bases.³⁴ Porphyrins are soft bases due to their ability to π bond with the metal. The acid softness of the metals increases with decreasing oxidation state and Cr(II) and Ti(II) are considered to be soft acids. Metal insertion is thereby favorable since soft acids are reacting with a soft base. The low 2+ oxidation state of the chromium would be stabilized by synergistic π bonding with the porphyrin. The titanium is not stabilized in the 2+ oxidation state, probably due to unfilled electronic orbitals of the metal atom¹⁵ which facilitate oxidation by a strong base such as oxygen. Electron density is supplied by the doubly bound oxygen, and the stable effective atomic number of 36 is approached.

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The Reaction of Rhodium Halides with Tri-*o*-tolylphosphine and Related Ligands. Complexes of Divalent Rhodium and Chelate Complexes Containing Rhodium-Carbon σ and μ Bonds¹

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Abstract: Reaction of tri-*o*-tolylphosphine, (*o*-CH₃C₆H₄)₃P, with ethanolic rhodium(III) chloride at 25° gives blue-green RhCl₂{(*o*-tol)₃P}₂ ($\mu_{\text{eff}} = 2.27 \pm 0.03$ BM at 25°), which is one of the few examples of a divalent rhodium complex having one unpaired electron. A purple modification ($\mu_{\text{eff}} = 2.0 \pm 0.05$ BM) can also be made. The blue-green form has a *trans*-planar configuration, as shown by comparison of far-infrared spectra with the isomorphous palladium(II) and platinum(II) complexes. In high-boiling alcohols, tri-*o*-tolylphosphine reacts with rhodium(III) chloride to give initially a trimeric complex of apparent formula [RhCl₂{(*o*-tol)₃P}]₃ and finally a monomeric complex of apparent formula RhCl{(*o*-tol)₃P}₂. In some solvents the carbonyl complex RhCl(CO){(*o*-tol)₃P}₂ is also formed. The trimer reacts with a number of monodentate and bidentate ligands (*e.g.*, CO, tertiary phosphines, tertiary arsines, pyridine) to give octahedral chelate complexes of rhodium(III) which are shown by nmr spectroscopy to contain a metal-carbon σ bond, *e.g.*, RhCl₂(py)₂{(*o*-C₆H₄CH₂-)(*o*-tol)₂P}. The trimeric complex also contains the chelate group (*o*-C₆H₄CH₂-)(*o*-tol)₂P formed by deprotonation of the ligand, and possible structures are discussed. The far-infrared spectra of the complexes are reported; bands due to Rh-Cl stretching are identified and used where possible to derive the stereochemistry of the complexes. The second complex, "RhCl{(*o*-tol)₃P}₂," is shown by infrared and nmr spectroscopy to contain the new ligand, *trans*-2,2'-(di-*o*-tolylphosphino)stilbene, (*o*-tol)₂PC₆H₄CH=CHC₆H₄P(*o*-tol)₂, which is coordinated as a tridentate ligand *via* the double bond and two *trans*-phosphorus atoms. The free ligand, which can be isolated by heating the rhodium complex with sodium cyanide, is derived by coupling two molecules of tri-*o*-tolylphosphine through adjacent methyl groups with the loss of four hydrogen atoms. It is suggested that this proceeds *via* a three-coordinate rhodium(I) complex, RhCl{(*o*-tol)₃P}₂, formed by disproportionation of the rhodium(II) complex. The reactions of phenyldi-*o*-tolylphosphine, (C₆H₅)(*o*-CH₃C₆H₄)₂P, and diphenyl-*o*-tolylphosphine, (C₆H₅)₂(*o*-CH₃C₆H₄)P, with alcoholic rhodium(III) chloride have also been studied. The first gives a red divalent rhodium complex ($\mu_{\text{eff}} \sim 1.0$ BM) which may contain Rh-Rh bonds; the second gives an ill-defined rhodium(I) complex, possibly containing some Rh(II) impurity. At higher temperatures, deprotonation of the ligands, decarbonylation of the solvent, and oxidative coupling of the ligand methyl groups all occur as with tri-*o*-tolylphosphine, the last reaction being favored as the number of *o*-tolyl groups increases.

An outstanding feature of the complex RhCl(Ph₃P)₃³ is the ease with which one molecule of triphenylphosphine is lost.^{4,5} Oxidative additions to the com-

(1) Preliminary communication: M. A. Bennett, R. Bramley, and P. A. Longstaff, *Chem. Commun.*, 806 (1966); presented in part at the

plex often yield complexes containing formally five-co-

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