Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario N6A 5B7, Canada

Preparation and Variable-Temperature Nuclear Magnetic Resonance Studies of Tris(diphenyltrifluoromethylphosphine)platinum(0)

T. G. ATTIG, M. A. A. BEG, and H. C. CLARK*

Received April 27, 1975 AIC50283Y

The preparation of tris(diphenyltrifluoromethylphosphine)platinum(0) is described. Variable-temperature ^{19}F NMR studies show that the rapid phosphine exchange occurring at room temperature is frozen out at ca. −50° and that at lower temperatures a further dynamic process, possibly associated with rotation of phosphine about the Pt–P bond, is reduced in rate. Similar studies of dichloromethane solutions of the title compound in the presence of different excesses of free phosphine show the formation of the tetrakis complex and of a new previously unobserved species. The possible nature of this new species is discussed.

Introduction

A large number of zerovalent platinum compounds are now known, many of which contain a tertiary phosphine as the stabilizing ligand. Aryl-,[1-3] alkyl-,[4] arylalkyl-,[5,6] alkylperfluoroaryl-,[5,6] and fluorophosphines[7] have been used for this purpose. Tri- and tetracoordinate species have long been known as stable solids, although in certain cases[5,8] dissociation of the tetrakis complex occurs in solution to the tris complex and free phosphine. Moreover, rapid phosphine-exchange processes have been observed in solution for a number of the complexes. Dissociation of the tetrakis to the tris complexes has been observed only for the triaryl- and alkyldiarylphosphine complexes, whereas there is no evidence[5] for dissociation in solution of the corresponding tetrakis(trialkyl-, dialkylaryl-, or dialkylperfluoroarylphosphine) complexes. On the other hand, the PtL_3 complexes show no evidence of dissociation to PtL_2 and free ligand, even though kinetic data have been interpreted[9] in terms of such a process. The tendency to stabilize the tris complex has been attributed[10] to the large cone angles of the triaryl- and alkyldiarylphosphines. This is also consistent with the recently reported[11] isolation of the two-coordinate bis(tricyclohexylphosphine)platinum(0) in which the cone angle of the phosphine is particularly large (179 ± 10°).[10]

It has been suggested that the stability of the perfluoroaryldimethylphosphine and fluoro- and perfluoromethylfluorophosphine complexes is due to the delocalization of electron density from the metal onto the ligands which, because of their electronegative substituents, are good π acceptors.[5,7] Kruck and Bauer[12] have suggested that the optimization of electron density at the metal is important in stabilizing a variety of complexes with ligands of different basicity.

We have found[13,14] that diphenyltrifluoromethylphosphine, containing three bulky substituents, gives interesting Pt(II) complexes, the study of which suggests that this phosphine is a weak σ donor and a good π acceptor. It is thus an excellent candidate for the stabilization of Pt(0) complexes. Here we report the preparation of $Pt[P(CF_3)(C_6H_5)_2]_3$ and the results of a detailed study of its ^1H and ^{19}F NMR spectra under a variety of conditions, including that in which excess free phosphine is added.

Experimental Section

The preparation of diphenyltrifluoromethylphosphine has been described previously.[13] The complex $Pt[P(CH_3)(C_6H_5)_2]_4$ was prepared according to the method of Clark and Itoh.[5]

All reactions were carried out under dry nitrogen but the subsequent manipulations of reaction mixtures were performed in air.

Proton and ^{19}F NMR spectral measurements were made on a Varian HA-100 spectrometer with variable-temperature accessories. Dichloromethane was the usual solvent and also the internal standard for proton spectra; $CFCl_3$ was the internal standard for ^{19}F spectra. The mixture of $CFCl_3$ and dichloromethane allowed NMR spectra to be observed at temperatures down to −110°.

Preparation of $Pt[P(CF_3)(C_6H_5)_2]_3$. *cis*-Bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II)[13] (0.621 g, 0.8 mmol) was suspended in 15 ml of ethanol, and the phosphine (0.401 g, 1.6 mmol) was added with stirring. After 1 hr, sodium borohydride (1.6 mmol) was added gradually with vigorous stirring. After 5 min, a yellow solid began depositing; this was filtered off, washed with small portions of 50% aqueous ethanol, and then dissolved in benzene. Excess pentane was added, and yellow, cubic crystals formed; mp 125–126°. *Anal.* Calcd for $C_{39}H_{30}F_9P_3Pt$: C, 48.89; H, 3.13; F, 17.87. Found: C, 48.62; H, 3.01; F, 17.68.

The alcoholic solution on evaporation gave unreacted phosphine (0.25 g, 1 mmol), the yield of pure tris complex being 0.56 g, 68%. The residual material contained diphenylphosphonic acid possibly formed by hydrolysis of the phosphine.

Results

Tris(diphenyltrifluoromethylphosphine)platinum(0) was prepared by reducing *cis*-$PtCl_2[PCF_3(C_6H_5)_2]_2$ in the presence of 2 equiv of phosphine with sodium borohydride. One equivalent of phosphine was always recovered. The complex is isolated as yellow cubic crystals and is stable to aerial oxidation in the solid state at room temperature.

The ^{19}F NMR spectrum of the complex in benzene or dichloromethane solution at probe temperature consisted of a broad band, δ −61.61 ppm. On lowering the temperature stepwise to −110°, the spectrum first is resolved to some extent, probably into an $X_3AX'_3A'_3X''_3A''$ pattern. However, below −50°, coalescence to a broad band begins, and below −90° only a symmetrical broad resonance is observed [Figure 1]. A coalescence of this type does not appear to have been observed for similar compounds previously. Since a similar broadening was not observed in the proton spectrum below −90°, it is unlikely to be due to viscosity effects. In this case, also, over the temperature range +37 to −110°, the change in chemical shift from 61.61 to 62.01 ppm is very small.

The proton NMR spectrum of the tris complex consisted at 37° of an unresolved broad band due to the ortho protons, with well-resolved resonances for the meta and para protons. On lowering the temperature to −10°, the ortho resonance sharpens somewhat and is shifted slightly upfield. At the same time, the other resonances are much less well resolved. At −30°, the resonances begin to merge, until at −104° only a single but unsymmetrical broad band is seen. The center of this band corresponds to the originally observed shift for the meta and para protons, and it is the ortho proton resonance which coalesces.

When 0.5 molar equiv of the phosphine is added to a dichloromethane solution of the tris complex, reaction 1 may

$$2PtL_3 + L \rightarrow PtL_4 + PtL_3 \qquad (1)$$

occur. At room temperature, the ^{19}F NMR spectrum [Figure 2] consists of a sharp, well-resolved doublet centered at 60.70 ppm with $J(P–C–F)$ = 73 Hz. The latter value is essentially

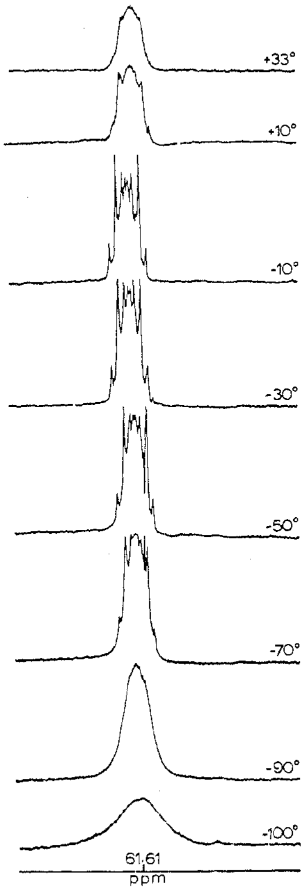

Figure 1. Variable-temperature ^{19}F NMR spectra of $Pt[P(CF_3)(C_6H_5)_2]_3$ in dichloromethane solution.

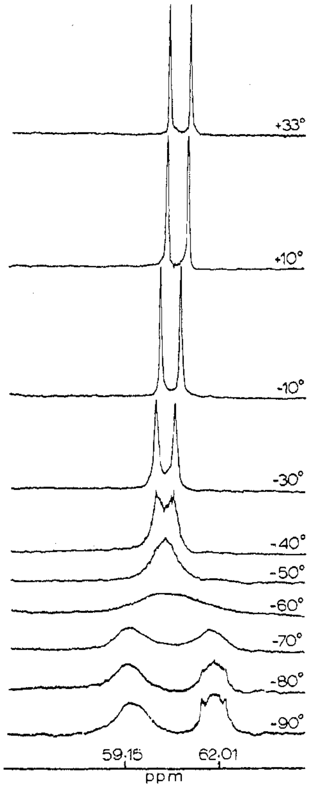

Figure 2. Variable-temperature ^{19}F NMR spectra of $Pt[P(CF_3)(C_6H_5)_2]_3$ in a dichloromethane solution containing 0.5 molar equiv of $P(CF_3)(C_6H_5)_2$.

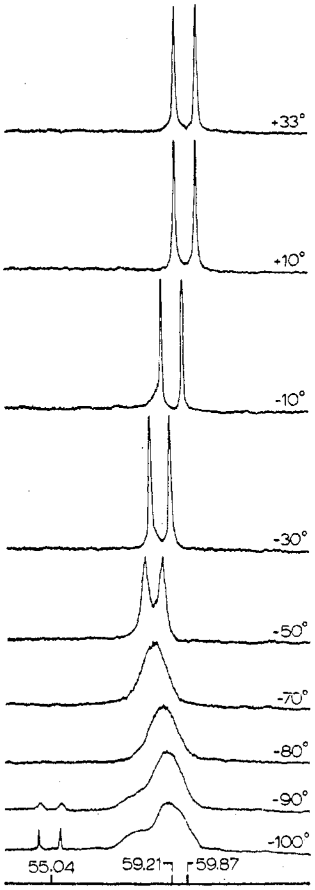

Figure 3. Variable-temperature ^{19}F NMR spectra of $Pt[P(CF_3)(C_6H_5)_2]_3$ in a dichloromethane solution containing 1.0 molar equiv of excess $P(CF_3)(C_6H_5)_2$.

the same as that of the free phosphine (73.2 Hz), presumably by an accidental coincidence, and the chemical shift is in good agreement with the expected weighted average for a 1:2 concentration of free phosphine and PtL_3. On lowering the temperature, the doublet is shifted slightly to low field as the components of the doublet gradually broaden. At −40°, there remains a broad band centered at 60.03 ppm, but at −60 to −70° separation into two resonances is observed. At −65°, the chemical shift of one is slightly less than that of PtL_3 and of the other is 59.15 ppm. At −90°, the resonance at 62.01 ppm shows some fine structure probably due to Pt–F and P–F coupling; from the more prominent components a value of 78 Hz can be estimated for J(P–C–F). From −65 to −100°, the chemical shift of the other band varies only slightly within the range 58.94–59.15 ppm, and in view of the stoichiometry of the mixture, this resonance must arise from a new species, presumably PtL_4.

For a dichloromethane solution 1 M in each of the tris complex and phosphine, the ^{19}F NMR spectrum [Figure 3] at room temperature was again a doublet with J(P–C–F) = 73 Hz and a chemical shift of 59.87 ppm. As the solution is cooled, there is a gradual downfield shift and at −50° a broad doublet at 58.71 ppm with a separation of 60 Hz is observed. This coalesces at −70° into a broad band at 58.0 ppm, with a half-height width of approximately 84 Hz. On further cooling the resonance becomes unsymmetrical due to the emergence of a component on the low-field side, and simultaneously, a doublet attributable to free phosphine appears at 55.15 ppm with J(P–C–F) = 73 Hz. At −100°, the three resonances are clearly distinguishable with the free phosphine showing a doublet at 55.04 ppm [J(P–C–F) = 73 Hz], the main broad resonance at 59.29 ppm, and a weaker, broad

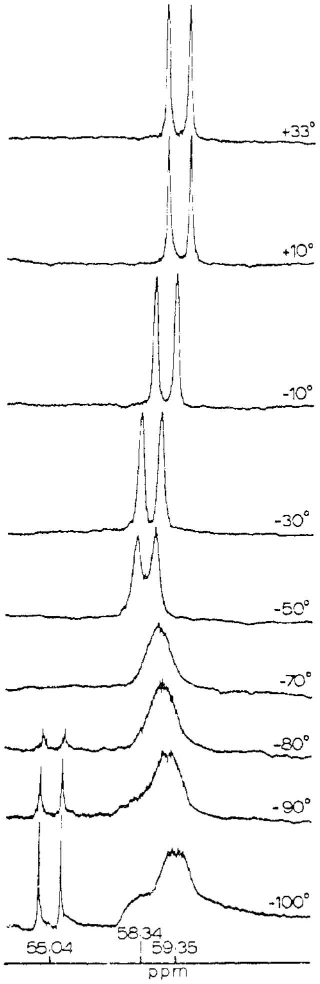

Figure 4. Variable-temperature ^{19}F NMR spectra of Pt[P(CF$_3$)(C$_6$H$_5$)$_2$]$_3$ in a dichloromethane solution containing 2.0 molar equiv of excess P(CF$_3$)(C$_6$H$_5$)$_2$.

resonance at about 58.4 ppm. It should be noted that even at −100°, there is no signal arising from PtL$_3$ and also that the main resonance at 59.29 ppm is very close to the resonance at 59.15 ppm observed in the previous solution containing half the amount of added phosphine and attributed to PtL$_4$. Clearly, however, an additional new species is responsible for the resonance at 58.4 ppm.

When 2 molar equiv of phosphine is added to 1 equiv of PtL$_3$, the ^{19}F NMR spectrum at probe temperature again consists of a doublet at 59.53 ppm with J(P–C–F) = 72 Hz. As the temperature is lowered, the chemical shift decreases slightly to a value of 58.37 ppm at −50°, at which temperature the doublet components are broadened with a separation of 62 Hz. Coalescence into a single broad resonance of half-height width of 84 Hz is observed at −70°, the chemical shift being 58.8 ppm. At −80°, in addition to this broad resonance (half-width 94 Hz) now centered at 58.95 Hz, a doublet at 55.05 ppm with J(P–C–F) = 73 Hz is observed which is obviously attributable to free phosphine. At −90° the phosphine resonances are further sharpened and again an additional broad resonance is observed on the low-field side of the broad resonance centered at 59.13 ppm. At −100°, the excess phosphine resonance, a doublet at 55.04 ppm, is very sharp and it is clear that there are also two broad resonances, one more intense at 59.35 ppm and a less intense peak at 58.34 ppm [Figure 4]. These are the same as the peaks observed in the solution containing 1 molar equiv of excess phosphine.

The ^{19}F spectrum of a dichloromethane solution containing 5 equiv of phosphine and 1 equiv of PtL$_3$ at probe temperature consists of a doublet at 58.11 ppm with J(P–C–F) = 75 Hz. As the temperature is lowered to −35°, the chemical shift of the doublet decreases slightly to 56.54 ppm with some broadening. At −50°, a broad signal at 56.20 ppm with a half-height width of 210 Hz is observed. At −70°, in addition to a broad signal at 58.69 ppm (half-height width of 100 Hz), a doublet appears at 55.4 ppm with J(P–C–F) = 73 Hz. At −100°, three resonances are again observed, a sharp doublet at 55.04 ppm, with J(P–C–F) = 73 Hz, and two broad resonances, the more intense at 59.22 ppm and the less intense at 58.16 ppm. These signals are in approximately the same intensity ratio as those unobserved with solutions containing 1 and 2 equiv of phosphine. [See Figure 5 for chemical shift data.]

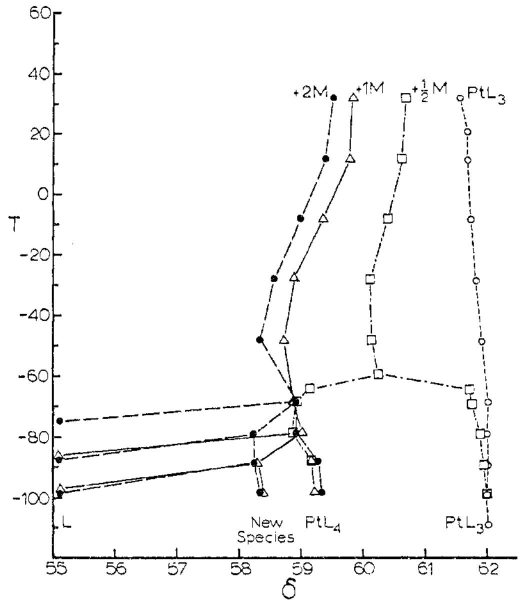

Figure 5. ^{19}F chemical shift data for dichloromethane solutions of Pt[P(CF$_3$)(C$_6$H$_5$)$_2$]$_3$ and P(CF$_3$)(C$_6$H$_5$)$_3$ over the temperature range +37 to −110°C.

Discussion

From the data described above and presented in Figures 1 and 2, the following points can be made about the spectra of the PtL$_3$ solution. First, the ^{19}F spectrum clearly indicates that only one species, PtL$_3$, is present over the temperature range, the observed small change in chemical shift to high field being of no great significance. That a single broad resonance is observed at room temperature is due to a phosphine exchange which is rapid on the NMR time scale; such exchange has been observed for other platinum(0)–phosphine complexes.[5,8] Although partial resolution occurs as the temperature is lowered to −50°, a completely resolved spectrum is not obtained. Clearly the rate of the exchange process is decreased, as the appearance of fine structure, which can only be attributed to ^{19}F–^{31}P and ^{19}F–^{195}Pt couplings, indicates. Not surprisingly, the spectrum at −50° is extremely complex, in part because the exchange process is still significant producing incomplete resolution. However, in any event, complete analysis has not been attempted since there is still a very limited understanding of spin–spin coupling phenomena in trigonal species such as this; presumably, if better resolution were possible, the spectrum could be considered in terms of Harris' general expressions.[16] The loss of resolution below −50° leading to just one broad resonance at −90°, with a virtually constant chemical shift, must indicate the freezing out of some further molecular motion. Such a phenomenon has not been observed in the NMR spectra of any other Pt(0) complexes, and there appear to be only two possibilities: (a) a slowing of the rotation of the phenyl groups about the P–C axis as the temperature is lowered or (b) a slowing of the phosphine rotation about the Pt–P axis. The large steric requirements of the CF_3 group suggest restriction of the former motion as a possibility; however, because of the bulky CF_3 group the cone angle[10] of the phosphine is quite large, approximately 150–152° compared with 145° for triphenylphosphine, so that the second type of rotational restriction is also possible.

An examination of the proton NMR spectrum of the free phosphine over the temperature range +32 to −100° shows little change; the resonances for the ortho protons are as well resolved as those of the meta and para protons, and as the temperature is lowered, the only change is a uniform slight broadening of all resonances. Thus, the broadness of the ortho resonance observed in the room-temperature spectrum of PtL_3 is a consequence of complex formation and presumably indicates an interaction between CF_3 and the ortho protons arising from the steric crowding of the ligands around platinum. Since this interaction may hinder rotation of the phenyl ring about the P–C axis and is observable at room temperature, it seems unlikely that the new phenomenon which causes broadening and loss of resolution of the ^{19}F resonance of PtL_3 below −50° can be attributed to a motion within the phosphine itself. On the other hand, restricted internal rotation about the P–C bond has been invoked[17] to interpret NMR line broadening effects in other phosphine complexes. The observed low-temperature effect may well arise from a slowing of the phosphine rotation about the Pt–P bond, a phenomenon which has been reported[18] for some platinum(II)–phosphine complexes. It should be noted, however, that the NMR spectra show no evidence, in spite of any possible steric crowding created by the bulkiness of the phosphine, of dissociation even at high temperatures to free phosphine and species such as PtL_2. This contrasts with the observation that tricyclohexylphosphine, with one of the largest cone angles, apparently forms only the bis(phosphine)platinum(0) complex.

Addition of Phosphine to PtL_3. The principal features of the ^{19}F NMR spectra of solutions containing PtL_3 and 0.5, 1, 2, or 5 molar equiv of phosphine can be summarized as follows.

1. For all concentrations, the spectrum at room temperature consists of a sharp doublet whose chemical shift is a weighted average of the shifts of PtL_3 and free phosphine. Moreover, the separation of the doublet components is 73 Hz, the same as for the free phosphine.

2. The solution containing 0.5 molar equiv of free phosphine at temperatures below −65° shows clearly the presence of equal concentrations of PtL_3 and another species. The broadness of the two resonances shows that both species are undergoing a rapid exchange process even at these temperatures. From the stoichiometry of the solution, the other species can only be PtL_4.

3. The solutions containing 1, 2, and 5 molar equiv of excess phosphine gave spectra which show, at low temperatures, the presence of PtL_4, free phosphine, and a new species. A comparison of the spectra containing 1 and 2 mol equivalents of phosphine at −100° gives some suggestion that the concentration of this new species is slightly greater in the solution richer in phosphine; however only a very small increase in concentration of the new species is observed with 5 molar equiv of phosphine. Thus the concentration of the new species is not directly dependent on phosphine concentration.

The formation of tetracoordinate platinum(0)–tertiary phosphine complexes in solution at low temperatures has been observed[8] in other similar systems and has been attributed to the slower rate of dissociation of the tetrakis species at low temperatures. Moreover, the fact that for PtL_3 *alone* in solution at room temperature, a broad resonance is seen, while solutions containing PtL_3 and free phosphine show a sharp doublet at room temperature in the ^{19}F NMR spectra indicates a decrease in the lifetime of the ligand in PtL_3 as a consequence of the added ligand. These facts are all consistent with an associative exchange process

$$PtL_3 + L \rightleftarrows PtL_4$$

and the existence, in the presence of low phosphine concentrations (less than 1 molar equiv), of only PtL_3 and PtL_4.

The formation of an additional species other than PtL_3 and PtL_4 has not been previously observed in similar systems, and from the present data the nature of this new species cannot be unambiguously determined. At least two possibilities come to mind. First, the possibility that this new species could be five-coordinate PtL_5 must be considered; certainly the observed chemical shift sequence might be consistent with this. However, two factors argue against it: (a) if the steric requirements of the phosphine are such as to make PtL_3, rather than the more usually expected PtL_4, the stable species under ambient conditions, the existence of the very much more crowded PtL_5 would seem unlikely; (b) the stoichiometry of the solution which contains 1 molar equiv each of PtL_3 and free phosphine cannot possibly allow for the existence of PtL_4, PtL_5, and L as the only species. Moreover, if PtL_5 were formed, increasing phosphine concentration should favor its formation; this is not observed. Second, the spectra reported here may well indicate that PtL_4 can exist in two distinct forms which rapidly interconvert down to ca. −80°. Below this temperature, interconversion is sufficiently slow on the NMR time scale as to allow observation of the two discrete species. Moreover, it may also be suggested that the interconversion involves the dissociation–association of L, with the consequence that the interconversion is retarded by increases in the concentration of free L. Although one may speculate that two such forms of PtL_4 could arise from different geometries (square planar vs. tetrahedral?), the present data do not allow identification of the new species.

We have sought to observe this phenomenon in low-temperature NMR studies of other platinum(0)–phosphine complexes. The proton NMR spectra from probe temperature to −100° of toluene-d_8 solutions of $Pt[P(CH_3)(C_6H_5)_2]_4$ containing 0.5, 1.5, 2.5, and 3.5 molar equiv of $P(CH_3)(C_6H_5)_2$ did not show the presence of any species other than PtL_4, PtL_3, and free phosphine. The only difference in the spectra at various temperatures from these reported by Clark and Itoh[5] was the increase in the temperature at which free phosphine was observed upon increasing the concentration of phosphine. Additionally, the temperature at which the broad signal due to free phosphine sharpened into a doublet also increased with an increase in phosphine concentration. Each of these observations is expected since addition of phosphine causes a shift in the equilibrium

$$PtL_4 + xL \rightleftarrows PtL_3 + (x + 1)L$$

As the equilibrium is shifted toward PtL_4, the temperature at which free phosphine is first observed is expected to increase.

The fact that this type of new species has only been observed in this present case may be associated with the fact that we have been able to use ^{19}F rather than ^1H NMR spectra. In the former, the chemical shifts are greater and hence the chemical shift difference between PtL_4 and the new species is observable. Observation of such new species using ^1H NMR spectra may not be possible because of chemical shift differences that are observationally too small. Further studies would therefore require the use of another fluorine-containing phosphine which is as similar as possible to $P(CF_3)(C_6H_5)_2$ in electronic and steric properties; so far we have been unable to design one, and in this respect $P(CF_3)(C_6H_5)_2$ may thus be unique.

Acknowledgment. The financial support of the National Research Council of Canada and the award of an NRC-CIDA Research Associateship to M.A.A.B. is gratefully acknowledged.

Registry No. $Pt[P(CF_3)(C_6H_5)_2]_3$, 56783-57-4; *cis*-bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II), 21557-77-7; $Pt[P(CF_3)(C_6H_5)_2]_4$, 56783-58-5.

References and Notes

(1) L. Malatesta and C. Carello, *J. Chem. Soc.*, 2323 (1958).
(2) J. Chatt and G. A. Rowe, *Nature (London)*, **191**, 1191 (1951).
(3) L. Malatesta and R. Ugo, *J. Chem. Soc.*, 2080 (1963).
(4) D. H. Gerlach, A. R. Kare, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 3544 (1971).
(5) H. C. Clark and K. Itoh, *Inorg. Chem.*, **10**, 1707 (1971).
(6) A. J. Auktedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3023 (1969).
(7) J. F. Nixon and M. D. Sexton, *J. Chem. Soc. A*, 321 (1967).
(8) C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Am. Chem. Soc.*, **94**, 2669 (1972).
(9) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968).
(10) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(11) S. Otsuka and T. Yoshida, Abstracts, XVIIth International Conference on Coordination Chemistry, Dublin, Aug 1974.
(12) T. H. Kruck and K. Bauer, *Chem. Ber.*, **98**, 3070 (1965).
(13) M. A. A. Beg and H. C. Clark, *Can. J. Chem.*, **38**, 119 (1960).
(14) M. A. A. Beg and H. C. Clark, to be submitted for publication.
(15) A. J. Rest, *J. Chem. Soc. A*, 2212 (1968).
(16) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(17) C. H. Bushweller and M. Z. Lourandos, *Inorg. Chem.*, **13**, 2514 (1974).
(18) B. E. Mann, C. Masters, B. L. Shaw, and R. E. Steinbank, *Chem. Commun.*, 1103 (1971).

Contribution from the Department of Chemistry,
Drexel University, Philadelphia, Pennsylvania 19104

Reactions in Microemulsions. I. Metal Ion Incorporation by Tetraphenylporphine

K. LETTS and R. A. MACKAY*

Received May 19, 1975　AIC50346C

We have investigated the incorporation of divalent metal ions of Cu, Mg, Mn, Zn, and Co by tetraphenylporphine in benzene–water microemulsions stabilized by cyclohexanol and both cationic and anionic surfactants. Only Cu(II) was found to react at the oil–water microdroplet interface in the anionic systems. The addition of various cofactors was found to exhibit positive or negative effects on the reaction rate. A more detailed kinetic study of the effect of quinoline on the rate of metalloporphyrin formation was performed. The results are interpreted in terms of the formation of a copper–cofactor complex.

Introduction

There have been numerous studies of chemical reactions at microscopic "oil-water" interfaces. These studies have been conducted to gain additional understanding of the factors which influence the courses and rates of chemical reactions and to provide insight into the nature of enzymatic catalysis. A variety of systems in which microscopic oil–water interfaces exist have been employed, including normal micelles in aqueous solution,[1,2] reversed micelles,[3] lyotropic liquid crystalline phases,[4] and monolayers and polyelectrolyte solutions. However, there have been no investigations of chemical reactions in microemulsions, liquid media possessing a number of unique properties which may be utilized for the study of "heterogeneous" reactions.

A microemulsion[5] differs from a classical emulsion in several significant respects. As the name implies, the droplet size is smaller, in the range 5–150 nm and more often 10–60 nm. In this range, the microemulsion is monodisperse.[6,7] Due to the small droplet size, microemulsions are transparent but do exhibit the Tyndall effect with visible light. A microemulsion generally consists of four components, water, oil, ionic surfactant, and an alcohol,[5–7] although a suitable nonionic surfactant may be effective.[8,9] The formation of the microemulsion is spontaneous, suggesting that it is thermodynamically stable.[10,11] In any event, it is mechanically stable. For oil in water (O–W) systems of the type examined here, the internal structure may thus be described as a stable collection of "oil" microdroplets in an aqueous continuous phase. Each droplet consists of a 60–600-Å diameter "bulk" oil drop surrounded by a 20–30 Å thick surface phase (interphase) consisting mainly of alcohol molecules and cationic or anionic detergent ions.

The volume fraction of the disperse phase can generally be varied over a fairly wide range (e.g., 20–80%). The molecular weight of the disperse phase is greater than that of most micelles containing solubilized materials, and high ratios of solubilized to solubilizing substances can be obtained.[12]

Table I

Component	Proportions, wt %		
	SCS	CPB	PO
Water	54.54	54.45	54.70
Benzene	6.12	5.73	8.21
Cyclohexanol	23.49	21.62	24.61
Surfactant	15.85	18.20	12.48

The reaction examined was the incorporation of divalent metal ion by tetraphenylporphine. This system was chosen because of both its suitability and its importance. Tetraphenylporphine is soluble only in the oil droplet, while the Cu(II) ion is soluble only in the aqueous phase. This ensures that reaction can take place only in the interphase region of the microdroplet. Due to the biological importance of metalloporphyrins, many studies of the kinetics of metal ion incorporation by porphyrins in various solvent media have been performed.[13–16]

Experimental Section

Preparation of the Microemulsions. The oil in water micellar emulsions used in this study were prepared by mixing water, benzene, cyclohexanol, and sodium cetyl sulfate (SCS), cetylpyridinium bromide (CPB) or potassium oleate (PO) in the proportions given in Table I. Agitation was not required, but the mixture was normally stirred to speed the formation of the transparent microemulsion.

Kinetic Measurements. The incorporation of Cu(II) by tetraphenylporphine was followed spectrophotometerically with a Cary 14 spectrophotometer using 1-cm quartz cells with the solvent as reference. The cell was placed in a hollow metal cell holder through which water was circulated from a constant-temperature bath. All reactants were equilibrated in the bath before mixing. Benzene containing the prophyrin was added to the (equilibrated) mixture of