

Infrared Studies of the Solvation of the Sodium Ion. II. Concentration Effects¹⁻³

J. A. Olander and M. C. Day*⁴

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received July 28, 1970

Abstract: The solvation of the sodium ion by tetrahydrofuran (THF) in the system THF–NaAlBu₄–cyclohexane has been investigated using infrared spectra in the 900–1150-cm⁻¹ region. The ν_{COC} of THF normally occurring at 1071 cm⁻¹ is shifted to ca. 1053 cm⁻¹ upon solvation of NaAlBu₄ by THF. The quantitative information obtained from the infrared spectra has been used to construct average-value plots from which the limiting average value ($\lim \bar{n}$) gives the apparent solvation number. For NaAlBu₄ concentrations ranging from ca. 0.004 to 0.269 M, the $\lim \bar{n}$ is seen to increase with increasing concentration of NaAlBu₄. These results are explained in terms of the tight ion pairs present in the more dilute solutions giving way to ion pairs or aggregates at higher concentrations which are destabilized due to increased ion–ion and ion–dipole interactions.

The utility of sodium tetrabutylaluminum (NaAlBu₄) as a novel and unique electrolyte for the study of ion–ion and ion–solvent interactions has been demonstrated.^{1,4-8} This electrolyte is soluble in saturated hydrocarbon solvents which serve essentially as a dispersing medium for the salt,⁴ and yet it shows appreciable conductance in ethers such as THF.⁵

For solutions of NaAlBu₄ dissolved in cyclohexane to which THF is added as a solvating agent, nmr, conductance, and infrared techniques have been used to study the specific solvation of the sodium ion, or ion aggregates, by the THF molecules.^{1,4,5} In addition, by means of infrared measurements it is possible to construct average-value plots which give indications as to the solvation number of the sodium ion in this system.¹

The results from the infrared study of the solvation of NaAlBu₄ in cyclohexane by THF indicate the possibility that the anion, AlBu₄⁻, is involved in the solvating process.¹ Far-infrared studies of this⁸ and other systems^{7,9-14} give some indication as to the extent of anion participation in the cation solvation. In order to clarify the role of the anion in the solvation of the sodium ion by THF in the system THF–NaAlBu₄–cyclohexane, this study of the concentration dependence of ionic solvation was undertaken.

Experimental Section

Procedure. The methods of obtaining spectra, preparation and purification of reagents, and preparation of solutions have been described.¹

(1) Part I: E. G. Höhn, J. A. Olander, and M. C. Day, *J. Phys. Chem.*, **73**, 3880 (1969).

(2) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., Dec 1969.

(3) Abstracted in part from the Ph.D. Dissertation of J. A. Olander, Louisiana State University, 1970.

(4) E. Schaschel and M. C. Day, *J. Amer. Chem. Soc.*, **90**, 503 (1968).

(5) C. N. Hammonds and M. C. Day, *J. Phys. Chem.*, **73**, 1151 (1969).

(6) C. N. Hammonds, T. D. Westmoreland, and M. C. Day, *ibid.*, **73**, 4374 (1969).

(7) J. L. Wuepper and A. I. Popov, *J. Amer. Chem. Soc.*, **92**, 1493 (1970).

(8) A. T. Tsatsas and W. M. Risen, Jr., *ibid.*, **92**, 1789 (1970).

(9) J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **69**, 3223 (1965).

(10) W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

(11) W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, and A. Watts, *ibid.*, **92**, 2240 (1970).

(12) (a) B. W. Maxey and A. I. Popov, *ibid.*, **89**, 2230 (1967); (b) *ibid.*, **91**, 20 (1969).

(13) (a) J. L. Wuepper and A. I. Popov, *ibid.*, **91**, 4352 (1969); (b) W. J. McKinney and A. I. Popov, *J. Phys. Chem.*, **74**, 535 (1970).

(14) M. J. French and J. L. Wood, *J. Chem. Phys.*, **49**, 2358 (1968).

Treatment of Data. A description of the method of quantitative determinations has been reported.¹ Basically, it consists of comparing the net absorbance of the 1071-cm⁻¹ band of THF in THF–NaAlBu₄–cyclohexane solutions to standard plots consisting of the net absorbance of the 1071-cm⁻¹ band *vs.* the concentration of THF in cyclohexane solutions. From this comparison, the concentration of free THF in the THF–NaAlBu₄–cyclohexane solutions can be determined. Since the total amount of THF added to the system is known, the concentration of complexed THF can be determined by difference. The average number of THF molecules per NaAlBu₄ is obtained by dividing the concentration of complexed THF by the concentration of NaAlBu₄ to give the ratio [THF bound]:[NaAlBu₄]. This ratio is plotted *vs.* the ratio of the total concentration of THF to concentration of NaAlBu₄, [THF total]:[NaAlBu₄], to give average-value plots (\bar{n} plots) from which values for the solvation number may be obtained.

Limitations. The range of concentrations of NaAlBu₄ studied was restricted at the upper limit (ca. 0.27 M) by overlap of the 1071- and 1053-cm⁻¹ bands, and at the lower limit (ca. 0.004 M) by the problem of accurately measuring the absorbances of very low concentrations of THF. Another difficulty at low concentrations was that of accurately preparing solutions of NaAlBu₄, owing to its sensitive nature.

The ratios [THF total]:[NaAlBu₄] were not extended past approximately 10:1 since beyond this ratio band overlap becomes an important factor. Although the overlap is less for corresponding ratios of [THF total]:[NaAlBu₄] in solutions of lower NaAlBu₄ concentration, the relative error due to band overlap is believed to be comparable for the different concentrations.

Results

Typical infrared spectra for the system THF–NaAlBu₄–cyclohexane in the region between 900 and 1150 cm⁻¹ have been shown previously.¹ The pertinent details consist of a band at ca. 1053 cm⁻¹ which is assigned to perturbed THF molecules that are solvating the sodium ion (or ion aggregates) in solution, and a band at 1071 cm⁻¹ due to free or nonsolvating THF molecules. At ratios of [THF total]:[NaAlBu₄] below 1:1, the 1071-cm⁻¹ band is not evident, but the 1053-cm⁻¹ band is present. As the concentration of THF is increased, and the [THF total]:[NaAlBu₄] ratio becomes greater than 1:1, the band at 1071 cm⁻¹ appears, and both the 1071- and 1053-cm⁻¹ bands increase in intensity. The spectra obtained for the different concentrations of NaAlBu₄ all behaved in a similar manner and exhibited the same positions for the bands of interest.

Utilizing the quantitative data obtained from the infrared measurements, \bar{n} plots were constructed for a series of different concentrations of NaAlBu₄ from ca. 0.004 to 0.269 M. Typical examples of such plots are shown in Figure 1. Figure 2 shows the effect of varying

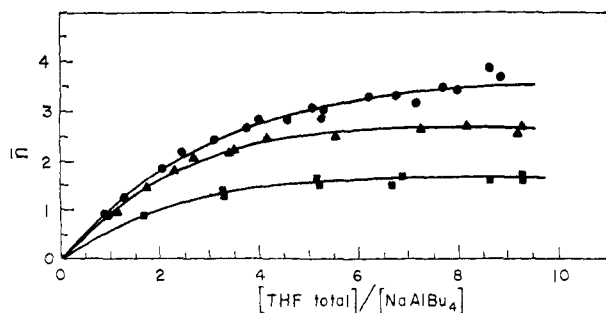


Figure 1. Average-value plots (\bar{n} plots) of the ratio [THF bound]:[NaAlBu₄] vs. the ratio [THF total]:[NaAlBu₄] for NaAlBu₄ concentrations of 0.010 (■), 0.078 (▲), and 0.245 M (●).

the concentration of NaAlBu₄ upon the value obtained for $\lim \bar{n}$. Owing to experimental difficulties, the $\lim \bar{n}$ obtained for the lowest concentration of NaAlBu₄ is of somewhat greater uncertainty, but the smoothness and fit of the curve indicate that the trends are correct. Other than this point, it is estimated that $\lim \bar{n}$ is correct to within *ca.* ± 0.1 unit.

Discussion

The slope of the \bar{n} plot is given by the ratio [THF bound]:[THF total], and so indicates the fraction of all THF present in the system which is solvating the sodium ions. A slope of unity implies that each THF molecule added to the solution is complexed, and a decrease in the slope indicates that an equilibrium exists between free and bound molecules. At the greater ratios of [THF total]:[NaAlBu₄] where the slope tends toward zero, THF molecules are present in solution primarily as free THF molecules.

The dependence of $\lim \bar{n}$ on salt concentration as shown in Figure 2 suggests the possibility of competition between the anion and the solvent molecules for coordination sites on the cation. It would seem that competition of the anions for coordination sites on the cation would be greatest at the higher concentrations of NaAlBu₄. Thus a decrease in the value of $\lim \bar{n}$ with an increase of salt concentration would be expected. As can be seen from Figure 2, the opposite result is obtained. Factors other than the usual anion-solvent competition must be considered to explain such behavior.

The presence of any appreciable cation-anion association in solutions of NaAlBu₄ should be evident from the results of molecular weight determinations. Utilizing a differential vapor pressure technique that allows all measurements to be made in an inert atmosphere, preliminary results¹⁵ indicate that NaAlBu₄ is associated in cyclohexane solution with a tendency to form higher aggregates at higher concentrations of NaAlBu₄. These vary from ion pairs (monomers) at *ca.* 0.01 M to aggregates of the order of hexamers at *ca.* 2 M. The degree of aggregation is seen to increase with salt concentration in cyclohexane solutions of NaAlBu₄, yet it is in the more concentrated solutions that the value of $\lim \bar{n}$ is greatest. This implies that, although the fraction of NaAlBu₄ present as aggregates increases with salt concentration, the strength of the ion-ion interactions must be less. That is, the aggregates must be less stable to-

(15) J. H. Muller and M. C. Day, manuscript in preparation.

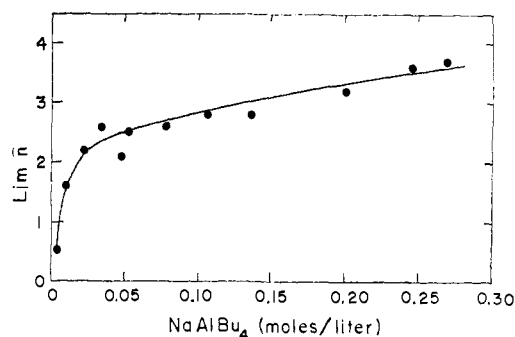


Figure 2. Dependence of apparent solvation number obtained from the \bar{n} plots ($\lim \bar{n}$) upon the concentration of NaAlBu₄.

wards attack by solvating THF molecules than the species present at lower concentrations.

The communication published by Tsatsas and Risen⁸ on the far-infrared studies of NaAlBu₄ in cyclohexane, THF, and THF-cyclohexane mixtures seems to support this view. For solutions of NaAlBu₄ in cyclohexane, two bands are found in the far-infrared region. At low concentrations of NaAlBu₄ (0.03 M) a band at $195 \pm 5 \text{ cm}^{-1}$ is predominant, with another band present at $160 \pm 5 \text{ cm}^{-1}$. With an increase in NaAlBu₄ concentration both bands increase in intensity, but at higher concentrations of salt (0.25 M) the 160-cm^{-1} band is the predominant one. Tsatsas and Risen interpret their spectral results to mean that in NaAlBu₄-cyclohexane solutions there are two different environments for the sodium ion with significantly differing force fields, but they do not identify these species.

They further note that as THF is added to a solution of NaAlBu₄ in cyclohexane (0.02 M), bands at both 160 and 195 cm^{-1} are present at a [THF total]:[NaAlBu₄] ratio of 0.3. As the ratio is increased, the band at 195 cm^{-1} becomes the only one evident, and its intensity continues to increase until the ratio is 4. Increasing the ratio from 4 to 5 produces only a trivial increase in intensity. Their spectra of NaAlBu₄ solutions in THF show a band at 195 cm^{-1} , but no band is observed at 160 cm^{-1} .

From extensive far-infrared studies of THF solutions of sodium salts, Edgell and coworkers^{10,11} have shown that there is a band in the 200-cm^{-1} region which they attribute to the vibration of the solvated contact ion pair. By analogy, it may be concluded that the band at 195 cm^{-1} observed in the spectra of solutions of NaAlBu₄ in THF is due to such an ion-pair vibration. The presence of a band in the same position with cyclohexane as solvent would logically be assigned to the same vibration, although the ion pair is presumably unsolvated in cyclohexane.

In view of the material presented thus far, it is proposed that the band at 160 cm^{-1} is due to the vibrations of aggregates, triple ions or larger. This band predominates over the 195-cm^{-1} band in the spectra of cyclohexane solutions of NaAlBu₄ at higher concentrations, and such behavior would be consistent for the vibrations of aggregates. Since the 160-cm^{-1} band is not observed in the spectra of THF solutions of NaAlBu₄, it is evidently not due to cation-solvent vibrations.

The relative positions of the two bands which are tentatively assigned to the ion pair and aggregate vibrations are what might be expected. Evans and Lo⁹

have reported their results for the far-infrared spectra of benzene solutions of tetraalkylammonium halides and hydrogen dihalides. Bands in the solution spectra which they assign to a quadrupole vibration are near to but somewhat higher in energy than the lattice modes of the solid salts. An analogous situation would be expected for ion pairs and ion aggregates, respectively.

The behavior of the 160-cm^{-1} band when THF is added to cyclohexane solutions of NaAlBu_4 is noteworthy.⁸ If the band assignments presented thus far are correct, THF has the ability to disrupt the NaAlBu_4 aggregates found in cyclohexane solutions but is unable to effectively disrupt the ion pairs. This is consistent with the solvation studies presented here in which $\lim \bar{n}$ is seen to increase with increasing concentration of NaAlBu_4 .

The results obtained in the solvation study reported here, and the spectral results of Tsatsas and Risen⁸ for the same system, enable a model to be proposed which qualitatively accounts for the observations. From the increase in the value of $\lim \bar{n}$ and in the degree of aggregation with increasing concentration of NaAlBu_4 , as well as the spectral studies of Tsatsas and Risen, we conclude that the larger aggregates are less stable than smaller aggregates or ion pairs with respect to disruption and solvation by THF molecules. For the larger aggregates, the average attraction of any one cation for a nearest-neighbor anion will be less than that for a cation and anion in a contact or intimate ion pair. In the aggregates, the cation-anion attractions are averaged over all of the nearest neighbors. A less intense cation-anion attraction would also be expected for any ion pairs present in concentrated solutions of NaAlBu_4 . Owing to the interactions of adjacent dipoles, the proximity of other ionic species in these more concentrated solutions will tend to weaken the attraction between a given cation and anion in an ion pair. This is similar to the "internal Wein effect" proposed by Kraus and coworkers¹⁶ to explain increases in equivalent conductances at higher concentrations. With decreasing salt concentration, this effect correspondingly decreases in importance.

It has been suggested that there is a tendency to form "tighter" ion pairs in solution as the dielectric constant of the solvent is increased.¹⁷ Both increasing the dielectric constant and decreasing the concentration of electrolyte will then tend to reduce the interaction between adjacent ions, pairs, and aggregates in solution. Consequently, this should result in less interaction between the different ionic entities and a resultant stabilization of the cation-anion interaction in a given ion pair. A stronger cation-anion attraction at lower concentrations of NaAlBu_4 is manifest in the lower $\lim \bar{n}$ values obtained in this work and in the predominance of the 195-cm^{-1} band in the far-infrared spectra as observed by Tsatsas and Risen.⁸ This "tighter" ion pair would decrease the tendency of the dipole of the THF molecule to interact with the positive charge of the sodium ion and, in addition, the alkyl groups of the anion would be expected to sterically hinder the addition of THF molecules to the sodium ion in such an ion pair.

As pointed out by Edgell, *et al.*,¹¹ species other than those thus far discussed are not precluded. Conductivity data for the system $\text{THF-NaAlBu}_4\text{-cyclohexane}$ ⁵ and for NaCo(CO)_4 in THF ¹⁸ indicate the presence of conducting species. Charged aggregates analogous to triple ions are one possible source of charge-carrying species, but the concentration of such species would presumably be comparatively low since no band attributable to ion aggregates is observed in the far-infrared spectra of THF solutions of NaAlBu_4 . Solutions of NaAlMe_4 in THF have been shown to contain both contact and solvent-separated ion pairs.¹⁹ By analogy, some solvent-separated ion pairs in $\text{THF-NaAlBu}_4\text{-cyclohexane}$ solutions might be expected. The disruption of a solvent-separated ion pair would yield a totally solvated sodium ion as a possible conducting entity. The absence of any band in the spectra of these solutions attributable to a totally solvated ion may be due to the low concentration of such species, as inferred from the low values of the conductances.^{5,18} Also, vibrations involving only solvent molecules and the sodium ion are found in the same general spectral region, $175\text{--}200\text{ cm}^{-1}$, as those vibrations involving contact ion pairs of sodium salts.¹⁰⁻¹³ Therefore, if any band due to a low concentration of totally solvated sodium ions were present, it would probably be obscured by the more intense ion-ion band at 195 cm^{-1} .

An additional conducting species in the $\text{THF-NaAlBu}_4\text{-cyclohexane}$ system has been postulated by Hammonds and Day.⁵ The equivalent conductance for this system is seen to increase as the $[\text{THF total}]:[\text{NaAlBu}_4]$ ratio is increased to 1. This behavior is attributed to the formation of a singly solvated sodium ion which is the charge carrier. It is interesting to note that Hogen-Esch and Smid²⁰ found that one DMSO molecule per molecule of fluorenyllithium in dioxane solution was sufficient to convert all of the contact ion pairs to solvent-separated ion pairs. Similar results were obtained for the sodium compound.

Summary of Model

Based upon the material and discussions presented, it is proposed that cyclohexane solutions of NaAlBu_4 in the concentration range studied here contain ion pairs and higher aggregates, the degree of aggregation increasing with an increase in concentration. When THF is added to $\text{NaAlBu}_4\text{-cyclohexane}$ solutions, it tends to solvate the sodium ions and competes with the anions of the aggregates for coordination sites. At lower NaAlBu_4 concentrations, the ion pairs are more stable, or "tighter," and therefore are less readily solvated by the THF molecules. At higher concentrations of NaAlBu_4 , the aggregates and ion pairs in solution are not as stable due to increasing dipole-dipole or ion-dipole interaction as the proximity of the ions, ion pairs, and aggregates increases. The anions are, therefore, more easily displaced by the solvent molecules. The very "tight ion pairs" are poorly solvated because their dipole moment is diminished, and there is

(16) L. C. Kepausis, E. C. Evers, and C. A. Kraus, *Proc. Nat. Acad. Sci. U. S.*, **48**, 121 (1962).

(17) R. P. Taylor and I. D. Kuptz, Jr., *J. Amer. Chem. Soc.*, **91**, 4006 (1969).

(18) W. F. Edgell, M. T. Yang, and N. Koizumi, *ibid.*, **87**, 2563 (1965).

(19) E. S. Gore and H. S. Gutowsky, *J. Phys. Chem.*, **73**, 2515 (1969).

(20) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

presumably steric hindrance toward the addition of THF molecules. Weakening of the ion interactions with increasing salt concentration results in a reversal of these trends and increased solvation.

Acknowledgment. Support of this work by National Science Foundation Grants GP-6421 and GP-11427, and a NASA Traineeship for J. A. Olander, is gratefully acknowledged.

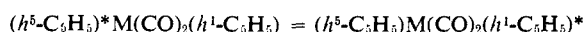
Stereochemically Nonrigid Organometallic Molecules. XXVII. The Fluxional Behavior of Tetra(cyclopentadienyl)titanium^{1,2}

J. L. Calderon,³ F. A. Cotton,* and J. Takats

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received October 12, 1970

Abstract: The temperature dependence of the nmr spectrum of tetra(cyclopentadienyl)titanium from +80° to -140° has been studied. The observations can be explained by assuming that the molecule is $(h^1-C_5H_5)_2(h^5-C_5H_5)_2$ -Ti and that it executes two types of intramolecular rearrangement. At the lowest temperatures of observation the $h^1-C_5H_5$ rings rotate relatively slowly but by about -25° averaging is rapid enough to give a single line as narrow as that for the protons of the $h^5-C_5H_5$ rings. Between about -20° and +35° the separate $h^1-C_5H_5$ and $h^5-C_5H_5$ lines broaden and coalesce to a single line which continues to become narrower as the temperature is raised further. These changes are attributable to interchange of the $h^1-C_5H_5$ and $h^5-C_5H_5$ types of rings and this is the first known observation of such an interchange. The activation parameters are: $E_a = 16.1 \pm 0.3$ kcal/mol and $\log A = 13.5 \pm 0.5$. The relatively ready occurrence of this heretofore unknown process is attributable to the presence of an empty valence-shell orbital on the titanium atom of $(h^1-C_5H_5)_2(h^5-C_5H_5)_2$ Ti which makes a reasonably low-lying transition state accessible. The $(C_5H_5)_3$ TiCl molecule has been observed by pmr in solution. It shows a single sharp line down to at least -100°.

Many molecules containing *monohapto*-cyclopentadienylmetal groups, $(h^1-C_5H_5)M$, which are fluxional are known, and several have been studied in detail.^{1,4,5} The homologous group $(h^5-C_5H_5)Fe(CO)_2$ - $(h^1-C_5H_5)$, $(h^5-C_5H_5)Ru(CO)_2(h^1-C_5H_5)$, $(h^5-C_5H_5)Cr(NO)_2(h^1-C_5H_5)$, has been especially well characterized;^{1,4-7} the rearrangements have been shown to occur through 1,2 shifts^{1,4-6} involving relatively nonpolar transition states,⁷ with activation energies of ~10 kcal/mol.¹ No indication whatever of the ring interchange reaction



has been seen. It may, of course, take place slowly, but the fact that the isomers $(h^5-C_5H_5)Fe(CO)_2(h^1-C_5H_5R)$ and $(h^1-C_5H_5)Fe(CO)_2(h^5-C_5H_5R)$, $R = C_6H_5CH_2$, have been isolated and can be dissolved and recovered unchanged⁸ suggests that the interchange in this case must be exceedingly slow.

The observations reported⁹ for $C_5H_5CuP(C_2H_5)_3$ in liquid SO_2 clearly show the presence of a fluxional

$(h^1-C_5H_5)Cu$ group under the experimental conditions; the most recent work⁵ shows that, contrary to the original suggestion, this also proceeds by a sequence of 1,2 shifts. However, the fact that $C_5H_5CuPR_3$ molecules in the solid state^{10,11} and in more normal solvents¹² contain pentahapto rings beclouds the issue here. Perhaps an SO_2 adduct¹³ in which the ring is peeled back, *e.g.*, $(h^1-C_5H_5)CuP(C_2H_5)_3(SO_2)_x$, $x = 1$ or 2, is the species actually observed in liquid SO_2 .

For $(h^1-C_5H_5)_2Hg$ the structure and fluxional character have been established,¹⁴ but not the rearrangement pathway. For $(h^1-C_5H_5)M(CH_3)_3$ ($M = Si, Ge, Sn$) the pathway has been shown to be 1,2 shifts.^{15,16}

The compound $(C_5H_5)_3MoNO$ is the first one in which interconversion of differently bonded C_5H_5 rings is observed.¹⁷ The possibility that the compound might contain $h^1-C_5H_5$, $h^3-C_5H_5$, and $h^5-C_5H_5$ rings, which was considered plausible at first, has been invalidated for the crystalline material,¹⁸ and is thus considered unlikely in solution as well. As seen in the crystal, the molecule contains an $h^1-C_5H_5$ ring, but each of the other two rings is bound in essentially the same severely tilted poly-

(1) Previous paper in this series, part XXVI: F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7523 (1969).

(2) Supported, in part, by the National Science Foundation, under Grant No. GP 7034X, and The Petroleum Research Fund, administered by the American Chemical Society, to whom grateful acknowledgment is made.

(3) Fellow of the Council for Scientific and Humanistic Development, Central University of Venezuela, Caracas, Venezuela.

(4) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(5) C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, 1318 (1970).

(6) F. A. Cotton, A. Musco, and G. Yagupsky, *J. Amer. Chem. Soc.*, **89**, 6136 (1967).

(7) B. Fuchs, M. Ishaq, and M. Rosenblum, *ibid.*, **90**, 5293 (1968).

(8) B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

(9) G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967).

(10) F. A. Cotton and J. Takats, *ibid.*, **92**, 2353 (1970).

(11) L. T. J. Delbaere, D. W. McBride, and R. B. Ferguson, *Acta Crystallogr., Sect. B*, **26**, 518 (1970).

(12) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 7281 (1969).

(13) Proposed for $C_5H_5Ti(CH_3)_2$ by A. G. Lee and G. M. Sheldrick, *Chem. Commun.*, 441 (1969).

(14) P. West, M. C. Woodville, and M. D. Rausch, *J. Amer. Chem. Soc.*, **91**, 5649 (1969).

(15) A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970).

(16) F. A. Cotton and T. J. Marks, *ibid.*, **9**, 2802 (1970).

(17) F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, **90**, 6232 (1968).

(18) J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, **91**, 2528 (1969).