(11) The rate constant k_{cat} is practicably identical with the experimental rate constant k_{exptl} at low to moderate iodide concentrations. At high acidities and iodide concentrations the rate of the uncatalyzed reaction becomes large enough to make it necessary to substract it from the experimental rate: $k_{cal} = k_{exptl} - k_{uncat}$.
(12) F. Hasan and J. Rocek, *J. Am. Chem. Soc.*, **94**, 9073 (1972).
(13) J. Y. Tong and R. L. Johnson, *Inorg. Chem.*, **5**, 1902 (1966).
(14) A. R. Zembrodt, Ph.D. Thesis, Ohio University, 1970.
(15) R. E. DeLury, *J. Phys. Chem.*, **7**, 239 (1903).
(16) R. F. Beard and N. W. Taylor, *J. Am. Chem. Soc.*, **51**, 1973 (1929).
(17) J. O. Edwards, *Chem. Rev.*, **50**, 455 (1952).
(18) K. E. Howlett and S. Sarsfield, *J. Chem. Soc. A*, 683 (1969).
(19) D. C. Gaswick and J. H. Krueger, *J. Am. Chem. Soc.*, **91**, 2240 (1969).
(20) (a) C. Lin and J. K. Beattie, *J. Am. Chem. Soc.*, **94**, 3011 (1972); (b) A. Haim, *Inorg. Chem.*, **11**, 3142 (1972).
(21) A. Granzow, A. Wilson, and F. Ramirez, *J. Am. Chem. Soc.*, **96**, 2454 (1974).
(22) At pH 1.5–3.0 in the presence of 0.5 M ammonium sulfate.
(23) R. E. Hintze and J. Rocek, unpublished results.
(24) In order to test whether ammonium sulfate could in fact change the rate of reaction 14 so drastically, Dr. Hintze in this laboratory measured the rate of oxidation of iodide at pH 2.2 in the presence *of 0.5 M ammonium* sulfate but obtained a rate only 20% lower than that obtained in the nitric acid–sodium nitrate system. Considering the uncertainty in the equilibrium constant for $CrSO_7^{2-}$ and in the dissociation constant of oxalic acid, the rate in sulfate media is in good agreement with the rate in nitrate media.
(25) G. Vandegrift and J. Rocek, to be submitted.
(26) The following values were used in the calculations: $k_{14} = 1.45 \times 10^4$ M^{-1} s^{-1}; $k_{15}/k_{-14} = 39$ M^2; $K_2 = 5.0$ M^2. The value for k_{14} is somewhat higher than the average value of 1.24×10^4 given in Table I. It was used because it gave a better fit and can be well justified in this medium of high acidity and high ionic strength ($\mu = 2.0$ M).
(27) V. Srinivasan and J. Rocek, *J. Am. Chem. Soc.*, **96**, 127 (1974).

Oxidative Coupling of the Phenylethynyl Group in μ-(1–3η:2–4η-*trans,trans*-1,4-Diphenylbutadiene)-bis(bis(η^5-methylcyclopentadienyl)titanium) and the Reaction of 1,4-Diphenyl-1,3-butadiene with Bis(cyclopentadienyl)titanium(II)

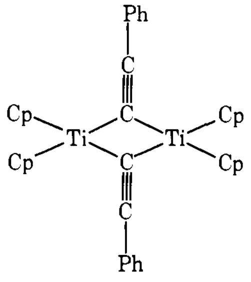
Dennis G. Sekutowski and Galen D. Stucky*

Contribution from the School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

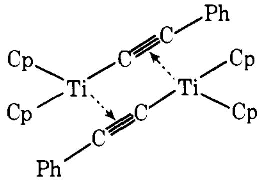
Received April 22, 1975

Abstract: The reaction of phenylethynylsodium, Na(C≡CC_6H_5), with bis(methylcyclopentadienyl)titanium(III) chloride has been shown to result in the oxidative coupling of two phenylethynyl anions with complexation to two $(\eta^5\text{-}CH_3C_5H_4)_2Ti$ groups. The resulting complex, μ-(1-3η:2-4η-*trans,trans*-1,4-diphenylbutadiene)-bis(bis(η^5-methylcyclopentadienyl)titanium), is closely related to the uncoupled dimeric species, $[(\eta^5\text{-}CH_3C_5H_4)_2Ti{\equiv}CC_6H_5]_2$, and it is suggested that the latter is an intermediate in the coupling reaction. In view of the fact that the same molecule can be prepared by the reaction of $(C_5H_5)_2Ti^{II}$ with 1,4-diphenyl-1,3-butadiyne, the compound can be considered as a complex of two molecules of $(\eta^5\text{-}CH_3C_5H_4)_2Ti^{II}$ with 1,4-diphenylbutadiyne. The molecule, $[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2C_4(C_6H_5)_2$, is located in the solid state on a crystallographic center of inversion with all of the atoms of the $(C_6H_5)_2C_4$ group and the two titanium atoms approximately coplanar. The titanium-carbon bond lengths of 2.083 (2) and 2.153 (2) Å are consistent with other titanium σ-bonded species, and the configuration about the titanium atom is the first four-membered metallocyclic geometry observed for an early transition metal organometallic compound. The hydrocarbon bond lengths are close to those expected for 1,4-diphenylbutadiene (or a reduced form of 1,4-diphenylbutadiyne). $[(\eta^5\text{-}CH_3C_5H_4)_2TiC_2C_6H_5]_2$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14, $C_{2h}{}^5$) with $a = 10.133$ (2), $b = 14.838$ (4), $c = 10.530$ (3) Å, $\beta = 106.97$ (1)°, $Z = 2$, $\rho_{calcd} = 1.347$, and $\rho_{exptl} = 1.38$ (3) g cm^{-3}. Full matrix least-squares refinement of 1975 x-ray diffractometer data gave $R_w = 0.037$ and $R = 0.052$.

Bis(cyclopentadienyl)titanium phenylethynyl was first prepared by Teuben and de Liefde Meijer in 1969.[1] They suggested the following two structures to be the most probable for the compound



I



II

but preferred structure II because of the lack of a ν(C≡C) stretching band in the infrared spectrum of the compound. A dimeric structure was assumed from mass spectral evidence, but the possibility of the compound being a polymer was also suggested in view of the compounds' insolubility in both polar and nonpolar solvents.

Our interest in this material developed from earlier studies of magnetic interactions in low valent titanium organometallic systems.[2-4] A remeasurement of the magnetic susceptibility confirmed the fact that the compound is diamagnetic. A superexchange coupling through s or p carbon orbitals in structure I or a direct metal-metal interaction could lead to a large antiferromagnetic exchange interaction and the observed diamagnetism. An example of the geometry shown in configuration I for main group metals is found in $\{[N(CH_3)_3](CH_3)BeC{\equiv}CCH_3\}_2$.[5] A model for structure II has been recently reported, i.e., $[(C_6H_5)_2AlC{\equiv}CC_6H_5]_2$, in which there is a 90° Al-C-Al angle with nonequivalent Al–C(sp) and Al–C(p_π) bond lengths.[6] Metal atoms bonding to both the σ and π orbitals of a single ethynyl group have been found in only a few other cases, these being associated with the electron-rich transition metals[7-10] where the bonding has been described as d back-bonding into the empty p_{π^*} orbitals of the carbon triple bond.[11] This type of configuration (i.e., II above) leads to a relative long Ti–Ti bond length and the prediction of a significant ferromagnetic component to the magnetic exchange. It therefore seemed less consistent with the observed magnetic properties.

Another explanation for the diamagnetism is the possibility that the oxidation state of the titanium atom has been changed. We have recently shown[12] that unsaturated species MR (M = monovalent main group metal, R = unsaturated organic monoanion) undergo oxidative coupling with a d block transition metal halides, $M'X_2$, to give R_2, MX, and a reduced form of the transition metal. Thus, $C_6H_5CH_2Li$ reacts with $CdCl_2$ to give 1,2-diphenylethane and Cd(0). A corresponding reaction with NaC≡CPh and Cp_2TiCl might be envisaged to occur with reduction to Cp_2Ti^{II} along with coupling of Ph—C≡C· and reaction of the coupled product with Cp_2Ti^{II}.

In order to resolve the above and to ascertain the molecular geometry of the compound, a three-dimensional x-ray analysis of the methyl-substituted compound was undertaken. We decided to study the methyl-substituted cyclopentadienyl ring system for a number of reasons. It has been found that methyl substitution of bis(η^5-cyclopentadienyltitanium systems increases their solubility over similar unsubstituted species; thus, the compound should be easier to purify and crystallize. Previous bis(η^5-cyclopentadienyl)titanium(III) structures from our laboratory have shown large thermal motion of the cyclopentadienyl rings;[13] however, methyl substitution "locks" the rings in place.[14,15] We also note that the mass spectrum, infrared spectrum, and magnetic properties of both the substituted and unsubstituted phenyl ethynyl complex are similar, indicating that the bonding is probably the same.

Experimental Section

Synthetic and Spectroscopic Procedures. Solvents were dried and distilled from sodium ketyl and stored under helium in a Vacuum Atm., Inc., drybox. All preparations were performed in the drybox.

Analyses were performed by the Microanalytical Laboratory of the University of Illinois' School of Chemical Sciences. Melting points were determined in sealed capillaries filled with helium and were reported as uncorrected. Nujol and fluorolube ir spectra were run on a Perkin-Elmer 357 using NaCl plates. The cell edges were coated with silicon grease as a precaution against air oxidation. The diamagnetism was measured on a magnetic torsion balance similar to the one described by Evans.[16] An attempt to obtain an NMR spectrum with a Varian A60-A, using a saturated C_6D_5 solution of the compound, was unsuccessful. The mass spectrum was recorded on a CH-5 mass spectrometer.

The complex was prepared by a simplification of the method of Teuben and de Liefde Meijer, through the reaction of $(CH_3C_5H_4)_2TiCl$ with $Na(C{\equiv}CC_6H_5)$ in tetrahydrofuran. An alternative preparation was also used. $(CH_3C_5H_4)_2TiCl$ (2 g, 8.3 mmol) was added to 0.2 g (8.7 mmol) of sodium metal in 40 ml of tetrahydrofuran in the presence of 1.7 g (8.4 mmol) of 1,4-diphenyl-1,3-butadiyne. The mixture was stirred for 48 hr at room temperature. Upon filtering and removal of the solvent at reduced pressure, the solid was extracted with toluene and set aside to crystallize. Dark green crystals (0.6 g; 23.6% yield) were obtained. All the physical properties of this complex were exactly the same as those found for $(\eta^5\text{-}(CH_3C_5H_4)_2Ti)_2C_4(C_6H_5)$, including the x-ray powder pattern.

Spectroscopic Results. Depsite the fact that the magnetic measurement proved the complex to be diamagnetic, an NMR spectrum could not be obtained because of the limited solubility of the complex. The ir spectrum contained all the bands expected with the notable exception of the $\nu(C{\equiv}C)$ stretch around 2000 cm^{-1}. The only unusual feature was that the cyclopentadienyl bands, with the exception of the out-of-plane C–H deformations around 800 cm^{-1}, were of a rather low intensity compared with other bis(cyclopentadienyl)titanium complexes. The mass spectrum had a molecular ion at 614, which agrees with the dimeric formulation for the compound. The largest peak in the spectrum was at 206 and was attributed to $(\eta^5\text{-}CH_3C_5H_4)_2Ti^+$.

X-Ray Data. Preliminary precession photographs of $[(\eta^5\text{-}CH_3C_5H_4)_2TiC_2C_6H_5]_2$ (Mo Kα radiation) revealed that the crystals were monoclinic. The observed systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ are compatible with space group $P2_1/c$ ($C_{2h}{}^5$; No. 14). An eight-sided crystal that had the rough geometry of a polyhedron with sides 0.18 × 0.18 × 0.12 mm was used for data collection.

Lattice parameters were obtained by a least-squares refinement of 18 reflections, which were carefully hand centered on a Picker four-circle diffractometer (T = 23°, λ 0.71069 Å). The final values obtained were: a = 10.133 (2) Å, b = 14.838 (4) Å, c = 10.530 (3) Å, and β = 106.97 (1)°. The density calculated on the basis of two dimers per unit cell is 1.347 g cm^{-3}, while the observed value of 1.38 ± 0.03 g cm^{-3} was obtained by flotation in a m-bromotoluene and cyclohexyl bromide mixture. Several ω scans showed a typical peak width at half-height to be 0.175, indicating that the mosaicity was acceptably low for data collection.

Intensity data were measured on a fully automated Picker four-circle diffractometer using Mo Kα radiation monochromated by a highly oriented graphite crystal. A θ-2θ scan technique was used with a scan width of 1.8°, a scan rate of 2°/min, and a takeoff angle of 1.7°. Background counts, each of 10-sec duration, were taken at both ends of the scan. Copper foil attenuators, whose attenuation factors were known, were automatically inserted in front of the counter whenever the counting rate exceeded 10000 counts/sec. Three standards were measured every 60 reflections in order to check for crystal and counter stability. These standards showed no significant fluctuations throughout data collection. One quadrant of intensity data (hkl and $\bar{h}kl$) was measured to 45° in 2θ. A total of 1975 unique reflections were measured, 1450 of which were considered observed by the criteria $I_{\text{obsd}} > 3\sigma_c(I)$. Here $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$ where T_c is the total counts, t_c/t_b is the ratio of the time counting peak intensity to that spent counting backgrounds, and B_1 and B_2 are the background counts. Initial structure solution was accomplished using just the observed reflections.

Final refinement using all of the data was carried out with weights assigned on the basis of counting statistics. No significant systematic variation of $w(F_o - F_c)^2$ was seen with respect to sin θ/λ or the magnitude of the structure factors. The nonhydrogen scattering factors were taken from the tabulation of Cromer and Waber[17] and the hydrogen scattering factors from Stewart et al.[18] Anomalous dispersion corrections for the titanium atom were those of Cromer and Liberman.[19] Lorentz polarization corrections and calculation of the observed structure factor amplitudes from the raw data were carried out using the program VANDY. As a result of the small value of the linear absorption coefficient (μ = 5.78 cm^{-1}) and the shape of the crystal, errors due to the neglect of absorption corrections were estimated to be less than 6.0% on the intensity and hence no absorption correction was made.

Structure Determination and Refinement. The structure was solved in a straightforward manner by application of direct methods (FAME and MULTAN) and Fourier techniques.

The Vanderbilt System obtained from Dr. P. Galen Lenhart of Vanderbilt University was utilized for automatic operation of the diffractometer. The general plane Fourier mapping program, JIMDAP, modified by Ibers and Ross[20] from the original version FORDAP by H. Zalkin and D. H. Templeton, was used to calculate Fourier maps. The least-squares program used was a local version of ORFLS by Busing, Martin, and Levy.[21] Standard deviations were calculated using ORFFE by Busing, Martin, and Levy.[22] ORTEP by Johnson[23] was used to plot the molecular structures, and theoretical hydrogen atom positions were calculated from known atomic positions and hybridizations using HYGEN by Ross.[24] From the generated E map, the titanium atom and one cyclopentadienyl ring were easily found, yielding R_1 = 0.42. The discrepancy factors used are defined as: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 =$

Table I. Positional Parameters for Nonhydrogen Atoms in $[(\eta^5\text{-}CH_3C_5H_4)_2TiC_2(C_6H_5)]_2$

Atom	*X*	*Y*	*Z*
Ti	0.44656 (4)	0.46230 (3)	0.17222 (4)
C(1)	−0.2292 (3)	−0.0041 (2)	0.2845 (3)
C(2)	−0.3369 (3)	0.0203 (2)	0.1726 (3)
C(3)	−0.4114 (3)	0.0900 (2)	0.2061 (3)
C(4)	−0.3504 (3)	0.1099 (2)	0.3385 (3)
C(5)	−0.2402 (3)	0.0519 (2)	0.3869 (3)
C(6)	0.1162 (3)	0.4304 (2)	0.2099 (4)
C(7)	−0.4304 (4)	0.3535 (2)	0.3327 (3)
C(8)	−0.3880 (3)	0.3366 (2)	0.2195 (3)
C(9)	0.4937 (3)	0.3101 (2)	0.1198 (3)
C(10)	0.3825 (3)	0.3081 (2)	0.1739 (3)
C(11)	0.4317 (3)	0.3336 (2)	0.3060 (3)
C(12)	−0.2453 (3)	0.3378 (2)	0.2100 (3)
C(13)	0.4332 (2)	0.0219 (1)	0.4656 (2)
C(14)	0.3765 (2)	0.0307 (2)	0.3359 (2)
C(15)	0.2468 (2)	0.0759 (2)	0.2659 (2)
C(16)	0.1971 (3)	0.0726 (2)	0.1305 (3)
C(17)	0.0752 (3)	0.1149 (3)	0.0646 (3)
C(18)	0.0014 (3)	0.1605 (2)	0.1311 (4)
C(19)	0.0479 (3)	0.1643 (2)	0.2665 (3)
C(20)	0.1710 (3)	0.1225 (2)	0.3332 (3)

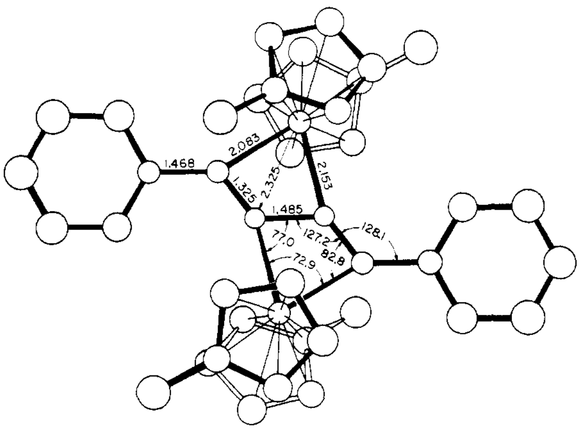


Figure 1. View of the molecular structure of $[(CH_3C_5H_4)_2Ti]_2[C_4(C_6H_5)_2]$ from above the $C_4(C_6H_5)_2$ plane. Isotropic thermal ellipsoids are shown at the 42% probability level.

$(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. All of the subsequent nonhydrogen atoms were easily obtained on the next Fourier mapping.

Isotropic refinement of all nonhydrogen atoms using just the observed reflections gave $R_1 = 0.10$. After several cycles of anisotropic refinement employing the full data set, all of the hydrogen atoms were found on a difference map and their positions agreed fairly well with those calculated from HYGEN using a carbon-hydrogen atom distance of 0.95 Å. All parameters were then refined with the exception of the hydrogen atom temperature factors, which were set equal to the isotropical temperature factor of the carbon to which they were bonded. Final anisotropic refinement gave a final error of fit equal to 1.282 and $R_1 = 0.052$ and $R_2 = 0.037$. The highest peak in the final difference Fourier was 0.31 e/Å^3.

Final positional parameters, anisotropic thermal parameters, interatomic distances, and bond angles are given in Tables I-IV, respectively.

Discussion

Structural Properties. (a) Titanium Atom Coordination. The molecular and crystallographic symmetry of $\{(\eta^5\text{-}CH_3C_5H_4)_2Ti\}_2C_4(C_6H_5)_2$ is rigorously $C_i(\bar{1})$ with a center of inversion located between C(13) and C(13)′. The higher C_{2h} symmetry is eliminated by the staggered configuration of the cyclopentadienyl rings and the trans orientation of the 1,1′-methyl groups with respect to the titanium atoms. The titanium atoms and the diphenylbutadiyne ligand are coplanar to within 0.20 Å so that the titanium atom is σ bonded to C(14) and C(13)′, with titanium-carbon distances of 2.083 (2) and 2.153 (2) Å, respectively. The plane defined by the titanium atom and the centroids of the cyclopentadienyl rings lies 0.06 Å to the π side of C(13). This is accordingly the first example of a four-membered organometallocyclic configuration of an early transition metal. The titanium-carbon bond lengths are in accord with other titanium-carbon bond lengths which have been determined structurally: 2.11 and 2.18 Å in $[(CH_3)_2Ti(C_6H_{12}O_2)]_2$,[25] 2.13, 2.13, 2.15, 2.14 Å in $(C_6H_5CH_2)_2Ti$,[26] 2.27 Å in $(\eta^5Cp)_2Ti(C_6H_5)_2$,[27] and 2.20 Å in $(\eta^5Cp)_2TiO_2CC_6H_4$.[28] The Ti-C distances in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^3\text{-}2\text{-dimethylallyl})$[29] are 2.34, 2.43, and 2.35 Å, and the allyl plane makes an angle of 55.9° with a line from the center of gravity of the allyl molecule to the titanium atom. As noted above, the corresponding angle in $[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2C_4(C_6H_5)_2$ is close to 0°. The observed geometry is also different than that in Cp_3Ti,[30] in which one ring is edge bonded via a Cp π orbital to the titanium atom with Ti-C distances of 2.40 and 2.48 Å. The Cp-Ti-Cp angle of 131.1° is a few degrees less than that observed in most bis(cyclopentadienyl)titanium structures, but on the same order as that observed in $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ and $[(\eta^5\text{-}CH_3C_5H_4)_2TiCl]_2$.[13] The rings on a given titanium atom are staggered with the methyl groups trans to each other with respect to the titanium atom. The titanium atom-ring centroid distances are 2.04 (1) Å.

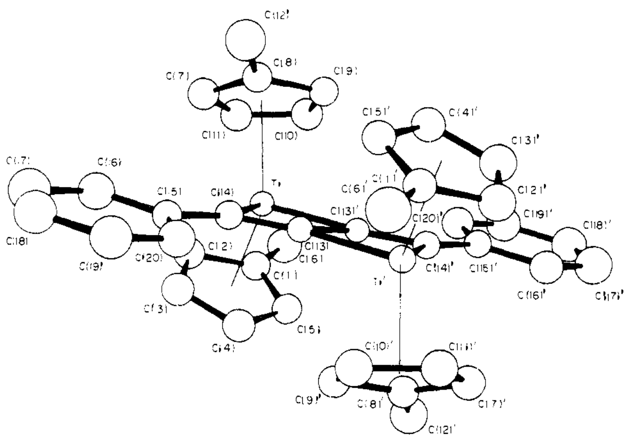


Figure 2. Perspective view of $[(CH_3C_5H_4)_2Ti]_2[C_4(C_6H_5)_2]$ overlooking the edge of the $C_4(C_6H_5)_2$ plane and showing the atomic numbering system. Isotropic thermal ellipsoids are shown at the 42% probability level.

(b) Ph_2C_4 and Cyclopentadienyl Geometries. The configuration of Ph_2C_4 group approaches that observed for butadienes, with a C(14)-C(13)-C(13)′ angle of 128.1 (2) Å. The alternating C-C bond lengths of 1.325 (3) and 1.468 (3) Å are also close to those expected for a diolefin. The largest deviation of a carbon atom from the best plane obtained for the 16 carbon atoms in $(C_2C_6H_5)_2$ is 0.03 Å.

The carbon atoms of the cyclopentadienyl rings have low temperature factors, indicating that the rings are "locked" into place at room temperature. Our ability to easily find the hydrogen atoms, even on the methyl group from a difference Fourier, is added proof of the thermal rigidity. The carbon-carbon distances within the ring vary between 1.383 (4) and 1.403 (4) Å. The methyl carbon atoms C(6) and C(12) are 0.14 and 0.17 Å, respectively, out of the plane defined by the cyclopentadienyl ring carbon atoms and are bent away from the titanium atom.

Electronic Structure. The product formed in the reaction between $NaC{\equiv}CC_6H_5$ and $[(\eta^5\text{-}(C_5H_5)_2TiCl]_2$ has been clearly shown to be a metal complex of the dimer of $C{\equiv}C{-}C_6H_5$ (Figures 1 and 2). The same product is ob-

Table II. Anisotropic Temperature Parameters for the Nonhydrogen Atoms in $[(\eta^5\text{-}CH_3C_5H_4)_2TiC_2(C_6H_5)]_2$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.00770 (6)	0.00231 (2)	0.00652 (5)	0.00003 (3)	0.00252 (4)	0.00031 (3)
C(1)	0.0082 (4)	0.0043 (1)	0.0115 (4)	−0.0004 (2)	0.0048 (3)	−0.0003 (2)
C(2)	0.0133 (4)	0.0047 (2)	0.0090 (3)	−0.0008 (2)	0.0058 (3)	−0.0003 (2)
C(3)	0.0126 (4)	0.0041 (2)	0.0127 (4)	0.0007 (2)	0.0053 (3)	0.0027 (2)
C(4)	0.0137 (4)	0.0028 (2)	0.0158 (5)	−0.0018 (2)	0.0091 (4)	−0.0008 (2)
C(5)	0.0094 (4)	0.0053 (2)	0.0102 (4)	−0.0022 (2)	0.0034 (3)	−0.0007 (2)
C(6)	0.0112 (4)	0.0077 (2)	0.0197 (5)	−0.0006 (3)	0.0070 (4)	0.0010 (3)
C(7)	0.0139 (5)	0.0035 (1)	0.0077 (3)	0.0010 (2)	0.0015 (3)	0.0013 (2)
C(8)	0.0098 (4)	0.0025 (1)	0.0105 (4)	−0.0010 (2)	0.0020 (3)	0.0014 (2)
C(9)	0.0143 (4)	0.0020 (1)	0.0089 (3)	0.0003 (2)	0.0038 (3)	0.0002 (2)
C(10)	0.0113 (4)	0.0026 (1)	0.0127 (4)	−0.0012 (2)	0.0023 (3)	0.0013 (2)
C(11)	0.0146 (5)	0.0039 (2)	0.0121 (4)	0.0010 (2)	0.0069 (4)	0.0025 (2)
C(12)	0.0132 (5)	0.0053 (2)	0.0177 (5)	0.0028 (2)	0.0040 (4)	0.0019 (2)
C(13)	0.0067 (3)	0.0020 (1)	0.0074 (3)	−0.0001 (1)	0.0025 (2)	−0.0001 (1)
C(14)	0.0079 (3)	0.0026 (1)	0.0074 (3)	−0.0002 (2)	0.0022 (2)	0.0001 (2)
C(15)	0.0075 (3)	0.0027 (1)	0.0085 (3)	0.0005 (2)	0.0015 (3)	0.0003 (2)
C(16)	0.0120 (4)	0.0068 (2)	0.0090 (4)	0.0030 (2)	0.0019 (3)	−0.0002 (2)
C(17)	0.0161 (5)	0.0095 (3)	0.0077 (4)	0.0043 (3)	−0.0009 (3)	0.0000 (2)
C(18)	0.0113 (4)	0.0076 (2)	0.0147 (5)	0.0043 (3)	−0.0004 (4)	0.0004 (3)
C(19)	0.0139 (5)	0.0076 (2)	0.0134 (5)	0.0048 (3)	0.0034 (4)	−0.0010 (3)
C(20)	0.0113 (4)	0.0060 (2)	0.0077 (3)	0.0025 (2)	0.0008 (3)	0.0001 (2)

[a] The form of the anisotropic ellipsoids is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Atomic Distances in Å for $[(\eta^5\text{-}CH_3C_5H_4)_2TiC_2(C_6H_5)]_2$

Atoms	Distance[a]	Atoms	Distance
Ti–Ti	4.227 (1)	Cp 1	
Ti–C(1)	2.428 (3)	C(1)–C(2)	1.400 (4)
Ti–C(2)	2.388 (3)	C(2)–C(3)	1.385 (4)
Ti–C(3)	2.372 (3)	C(3)–C(4)	1.383 (4)
Ti–C(4)	2.387 (3)	C(4)–C(5)	1.385 (4)
Ti–C(5)	2.402 (3)	C(5)–C(1)	1.391 (4)
Ti–C(6)	3.516 (3)	C(1)–C(6)	1.491 (4)
Ti–C(7)	2.406 (3)	Cp 2	
Ti–C(8)	2.460 (3)	C(7)–C(8)	1.402 (4)
Ti–C(9)	2.406 (3)	C(8)–C(9)	1.399 (4)
Ti–C(10)	2.379 (3)	C(9)–C(10)	1.403 (4)
Ti–C(11)	2.404 (3)	C(10)–C(11)	1.386 (4)
Ti–C(12)	3.549 (3)	C(11)–C(7)	1.375 (4)
Ti–C(13)	2.153 (2)	C(8)–C(12)	1.479 (4)
Ti–C(13)	2.325 (2)	(C_6H_5) C2	
Ti–C(14)	2.083 (2)	C(13)–C(13)'	1.485 (4)
Ti–C(15)	3.426 (2)	C(13)–C(14)	1.325 (3)
		C(14)–C(15)	1.468 (3)
		C(15)–C(16)	1.367 (3)
		C(16)–C(17)	1.379 (4)
		C(17)–C(18)	1.347 (5)
		C(18)–C(19)	1.365 (4)
		C(19)–C(20)	1.386 (4)
		C(20)–C(15)	1.375 (4)

[a] Errors in the lattice parameters are included in the estimated standard deviation.

Table IV. Bond Angles (deg) for Nonhydrogen Atoms in $[(\eta^5CH_3C_5H_4)_2TiC_2(C_6H_5)]_2$

Atoms	Angle	Atoms	Angle
C(14)–Ti–C(13)'	72.94 (8)	Cp 1	
Ti–C(14)–C(13)	82.8 (1)	C(5)–C(1)–C(2)	106.2 (2)
Ti–C(13)'–C(13)	77.0 (2)	C(1)–C(2)–C(3)	109.2 (3)
C(14)–C(13)–C(13)'	127.2 (3)	C(2)–C(3)–C(4)	107.4 (3)
C(13)–C(14)–C(15)	128.1 (2)	C(3)–C(4)–C(5)	108.2 (3)
Ti–C(13)'–C(14)'	155.8 (2)	C(4)–C(5)–C(1)	109.0 (2)
Ti–C(14)–C(15)	149.0 (2)	Cp 2	
		C(11)–C(7)–C(8)	109.4 (3)
		C(7)–C(8)–C(9)	106.3 (2)
		C(8)–C(9)–C(10)	108.3 (3)
		C(9)–C(10)–C(11)	107.8 (3)
		C(10)–C(11)–C(7)	108.1 (3)
		Phenyl	
		C(20)–C(15)–C(16)	117.7 (2)
		C(15)–C(16)–C(17)	120.8 (3)
		C(16)–C(17)–C(18)	121.2 (3)
		C(17)–C(18)–C(19)	119.3 (3)
		C(18)–C(19)–C(20)	119.7 (3)
		C(19)–C(20)–C(15)	121.3 (3)

tained by the reaction of 2 mol of monomeric $\eta^5\text{-}(C_5H_5)_2Ti^{II}$ with 1,4-diphenyl-1,3-butadiyne, which is consistent with the mechanism proposed below for the coupling reaction. The molecular geometry of the ligand suggests that there is a substantial transfer of charge to the ligand via covalent bond formation, i.e., partial reduction of the dialkyne to an alkene. If the dialkyne is considered to be a 4-electron donor (2 electrons per titanium atom), there are 16 electrons associated with each titanium atom, a common electronic configuration for cyclopentadienyltitanium compounds.

A summary of known Ti-Cp ring centroid distances is given in Table V for Cp_2Ti complexes. The average values are unchanged or perhaps decrease slightly (see footnote *b* of Table V) in the order of d^0 Ti(IV) > d^1 Ti(III) > d^2 Ti(II). These data suggest that the added electrons in going from Cp_2Ti^{IV} to Cp_2Ti^{II} are in a molecular orbital that is nonbonding or slightly bonding with respect to the ring metal bonding. The decrease in the X-Ti-X angle from 94.5° for Cp_2TiCl_2 to 87.9° for $Cp_2Ti(CO)_2$[31] indicates that the added electrons are going into a molecular orbital mainly d_{z^2} in character (see Figures 3 and 4 for orientation), which agrees with the observations made previously for Cp_2M d^0, d^1, and d^2 systems by Green, Green, and Prout[32] and with the molecular orbital calculations of Dahl and Peterson.[15]

There are three in-plane molecular orbitals of relevance to the electronic structure of Cp_2M species. These molecular orbitals are shown in Figure 3 with the correct symmetry combinations of the metal d atomic orbitals and the chlorine p orbitals for Cp_2MCl_2 complexes. The greatest stabilization has been shown by Peterson et al. to be due to the molecular orbital of $6b_2$ symmetry, the next most stable molecular orbital is of $8a_1$ symmetry, and the least of $9a_1$ symmetry. In a d^2 configuration, six chlorine p electrons and two metal d electrons are accommodated in the bonding $6b_2$, $8a_1$, and $9a_1$ orbitals and the $10a_1$ antibonding orbital, respectively.

The symmetry of the lowest unoccupied molecular orbital of $(C_6H_5)_2C_4$ and also the highest occupied orbital of $(C_6H_5)_2C_4^{2-}$ as obtained by INDO calculations for the observed bent configurations is shown in Figure 4. It is of σ

Table V

Compd[a]		L–M–L, deg	d(M–L)$_{av}$, Å	d(M–C$_p$)$_{av}$, Å
$Cp_2Ti(bipy)$[b]	d^2	76.1 (4)	2.140 (12)	2.11
$Cp_2Ti(CO)_2$[c]	d^2	87.9	2.030	2.02
Average:	d^2			2.06[b]
$Cp_2Ti(\eta^2\text{-}Cp)$[d]	d^1		2.45	2.06
$Cp_2Ti(BH_4)$[e]	d^1		1.75 (8)	2.03
$(Cp_2TiCl_2)_2ZnCl_2\cdot 2C_6H_6$[f]	d^1	82.09 (6)	2.580 (2)	2.04
$(Cp_2TiDME)_2(ZnCl_3)_2\cdot C_6H_6$[f]	d^1	76.6 (2)	2.115 (4)	2.04
$(Cp_2TiCl_2)_2MnCl_2\cdot 2THF$[g]	d^1	81.31 (6)	2.575 (2)	2.06
$(Cp_2TiCl)_2$[h]	d^1	77.11 (5) 78.42 (7)$_{av}$	2.546 (2)	2.06
$((CH_3C_5H_4)_2TiCl)_2$[h]	d^1	79.26 (6)$_{av}$	2.537 (2)	2.06
Average:	d^1			2.05 (1)
Cp_2TiCl_2[i]	d^0	94.53 (6)$_{av}$	2.364 (2)	2.06
Cp_2TiS_5[j]	d^0	94.59 (4)	2.435 (1)	2.07
$(CH_2)_3(C_8H_4)_2TiCl_2$[k]	d^0	93.69 (5)	2.368 (2)	2.06
Average:	d^0			2.06 (1)
$((CH_3C_5H_4)_2Ti)_2(C_2C_6H_5)_2$[l]	$d^?$	72.94 (8)	2.153 (2) 2.083 (2)	2.04

[a] Other π-bis(cyclopentadienyl)titanium structural work has been performed, e.g., Cp_4Ti, $(Cp_2TiSiH_2)_2$, $(Cp_2TiAlC_2H_5)_2$, $Cp_2TiCl_2Al(C_2H_5)_2$, and $Cp_2Ti(SME)_2Mo(CO)_4$. They have been left out of the table due to either the inaccuracy of the structural data or lack of the d(M–C$_p$) in publication. [b] Reference 44. Crystallographic problems were encountered in the refinement of this structure and the distance of 2.11 Å has an estimated standard deviation of 0.05 Å. A more accurate estimate of the Cp–Ti distance for the d^2 configuration is probably given by the value obtained for $Cp_2Ti(CO)_2$. [c] Reference 31. [d] Reference 30. [e] K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.*, 12, 232 (1973). [f] Reference 13. [g] D. Sekutowski, R. Jungst, and G. D. Stucky, to be published. [h] Reference 14. [i] A. Clearfield, D. K. Warren, C. H. Saldarriaga-Molina, R. Ropal, and I. Bernal, *Can. J. Chem.*, in press. [j] E. F. Epstein, I. Bernal, and H. Kopf, *J. Organomet. Chem.*, 26, 229 (1971). [k] E. F. Epstein and I. Bernal, *Inorg. Chim. Acta*, 7, 211 (1973). [l] This work.

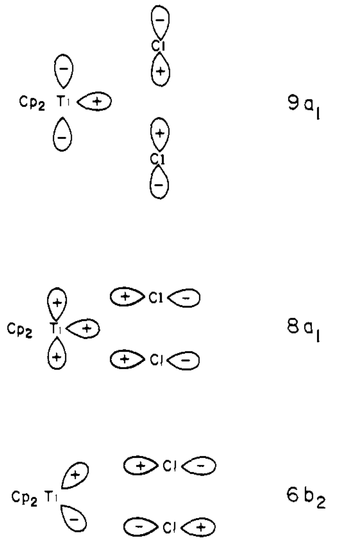


Figure 3. Molecular orbital calculation of Cp_2M species[15] have shown that the cyclopentadienyl rings are bonded by orbitals primarily d_{xy} and d_{yz} in character, while the remaining metal d orbitals form molecular orbitals in a plane bisecting the ring-M-ring angle. In this figure, the three in-plane Cp_2Ti orbitals are shown with the chlorine p orbitals which have the appropriate symmetry for bonding in Cp_2TiCl_2. The a_1 molecular orbitals are mainly $d_{x^2-y^2}$ and d_{z^2} in character while the b_2 molecular orbital is essentially d_{xz} in character. All molecular orbitals are shown in the xz plane, and only part of the d atomic orbitals are shown for clarity.

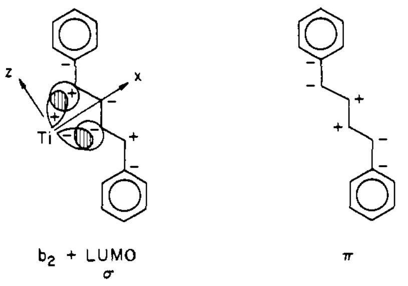
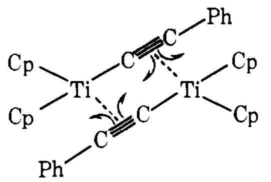


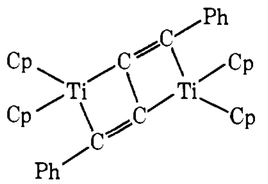
Figure 4. σ interaction of b_2 molecular orbital of Cp_2Ti moiety with the LUMO from an INDO calculation on $(C_6H_5C_2)_2$. Calculations on $(C_6H_5C_2)_2{}^{2-}$ yield the same symmetry for the HOMO. The next lowest unfilled molecular orbital has π symmetry and can interact with the b_1 (d_{xy}) MO of the bis(cyclopentadienyl)titanium system.

rather than π symmetry and can be expected to combine most strongly with the b_2 Cp_2Ti orbital. This appears to be the easiest route of reduction of the butadiyne fragment by a Cp_2Ti^{II} group. The highest occupied molecular orbital of $(C_6H_5)_2C_4{}^{4-}$ is of π symmetry and can interact with the b_1 (d_{xy}) Cp_2Ti orbital to give a bonding π interaction.

Mechanism of the Coupling Reaction. From the standpoint of the overall chemistry of the reaction, the results obtained here are entirely consistent with the oxidation chemistry of monocarbanions which we have reported earlier,[12,43] in which lithium coordinated delocalized carbanions (formed charge = −1) were quantitatively converted to a coupled product by a divalent transition metal halide. In the case of Cp_2TiCl, however, one obtains complexation of the coupled product. A more detailed view of the actual mechanism of coupling is suggested, however, by two experimental observations. As described in the Experimental Section, a purple compound is first formed in the reaction between $(Cp_2TiCl)_2$ and $NaC{\equiv}CC_6H_5$ before the coupled product is obtained. An infrared spectrum of the purple intermediate in benzene shows a band, ν(C≡C), around 2045 cm^{-1}, which is not due to an excess of $NaC{\equiv}CC_6H_5$. If the complex is prepared by treating Cp_2Ti^{II} with $C_6H_5C{\equiv}CC_6H_5$, one does not observe a purple intermediate. A plausible explanation for this, which is currently being investigated, is the initial formation of $[(\eta^5\text{-}CH_3C_5H_4)_2TiC{\equiv}CC_6H_5]_2$. A σ–π bridged geometry for the -C≡CPh species has been suggested by Teuben and Liefde Meijer[1] and has been observed in



III



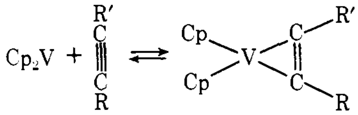
IV

$[(C_6H_5)_2AlC{\equiv}CC_6H_5]_2$.[6] A rearrangement of the electrons in III can give IV, with the inclusion of minor structural changes. The formation of IV by an intramolecular rearrangement of an intermediate such as III appears very feasible considering the chemistry of the Sc and V analogues. Both $(\eta^5\text{-}C_5H_5)_2Sc(C_2C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2V(C_2C_6H_5)$ have been prepared and show $\nu(C{\equiv}C)$ at 2045 and 2060 cm^{-1}, respectively.[1,33] Molecular weight studies in tetrahydrofuran have shown that the scandium compound is a mixture of monomeric and dimeric species. Many scandium organometallics are isostructural with titanium analogs, for instance, $((\eta^5\text{-}C_5H_5)ScCl)_2$[34,35] and $((\eta^5\text{-}C_5H_5)_2TiCl)_2$[14] both crystallize in the space group $P2_1/c$ with lattice parameters a = 13.54 (1), b = 16.00 (1), c = 13.40 (1) Å, β = 93.97 (5)° and a = 13.422 (8), b = 15.666 (1), c = 13.083 (12), β = 94.21 (4), respectively. Scandium does not have any easily attainable oxidation state other than Sc(III). Thus, while the Sc(III) phenylethynyl dimer is stable, the analogous Ti(III) dimeric complex could undergo internal reduction and oxidation to give the species observed.

The V^0 atomic radius is smaller than Ti^0 (1.22 vs. 1.32 Å), and therefore the steric effect of the cyclopentadienyl rings dictates a significant influence upon vanadium chemistry.[36] For instance, in the following reactions only trivalent vanadium complexes are obtained.

$$Cp_2VCl_2 + 2LiR \longrightarrow Cp_2VR + R\cdot + 2LiCl$$
$$2Cp_2V + RCl \longrightarrow Cp_2VR + Cp_2VCl$$
$$Cp_2V + RCl \longrightarrow Cp_2VCl + R\cdot$$
$$R = \text{alkyl, aryl, benzyl}$$

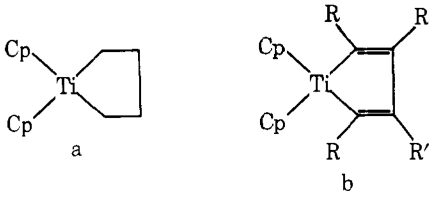
Addition of acetylenes to vanadocene gives products as shown below



while similar titanium products have not been isolated, but are only postulated as reaction intermediates in reactions such as the polymerization of ethylene with Ziegler-Natta catalyst. Even the V(III) allyl complexes are σ bonded instead of π bonded as in the Ti(III) allyls. Assuming bis(cyclopentadienyl)vanadium phenylethynyl to be monomeric, one would have to have association before an intramolecular rearrangement could take place. The activation energy for the association step may be sufficiently large so that the dimeric complex cannot be formed.

Comparison with Other Organotitanium Compounds. A surprising property of the title compound is its stability. The four-membered metallocycle in Figure 1 is very strained, as the C-Ti-C bond angle of 72.94 (8)° is the smallest known to date for a structure with an Cp_2TiL_2 moiety. However, the compound can be stored indefinitely at room temperature in a drybox and even a benzene or THF solution of the compound is air stable in air for 15-30 min before the green color changes to yellow.

Compounds containing titanium-carbon σ bonds generally have low thermal and chemical stability, and such compounds are difficult to isolate and store. Both $(\eta^5\text{-}Cp)_2TiMe_2$ and $(\eta^5\text{-}Cp)_2Ti(C_6H_5)_2$ are air stable but light and thermal sensitive. The stability of the methyl compound has been attributed to its lack of a β hydrogen, and this idea was reinforced by the preparation of $(\eta^5\text{-}(C_5H_5))_2Ti[CH_2Si(CH_3)_3]_2$.[37] The only metallocycles of bis(cyclopentadienyl)titanium that have been prepared are shown below.[38-40]



R = H or C_6H_5
R' = C_6H_5

Attempts at preparing other complexes of b with R or R' ≠ C_6H_5 have led to unstable green oils. Complex a is only stable below −30°C; however, it is more stable than the bis(cyclopentadienyl)titaniumdibutane which decomposes above −50°C.[33] Compound b was argued to be the metallocycle rather than a metal coordinated cyclobutadiene by comparison of the electronic absorption spectra with other metallocycles and the lack of characteristic band of tetrasubstituted cyclobutadiene derivatives in the region of 320 mμ.[40] The actual structure, however, was somewhat in doubt due to the initial unsuccessful attempts to prepare the complex from Cp_2TiCl_2 and the dilithium salt of 1,4-diphenylbutadiene in refluxing ether or tetrahydrofuran. The complex has recently been made by this route in an ether-toluene mixture.[41]

In addition to the infeasibility of hydride elmination, a number of possible reasons can be given for the stability of $[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2C_4(C_6H_5)_2$: (1) steric effects; (2) electron delocalization into the phenyl rings; and (3) π-bond interaction with the metal. The titanium atom is well shielded by the cyclopentadienyl rings and the butadiene and the bulky phenyl groups, from nucleophilic attack. Thus, insertion reactions which are fairly common with bis(cyclopentadienyl)titanium and -zirconium compounds may be prevented. The phenyl rings must play a significant role since the analogous $(Cp_2TiC{\equiv}CH)_n$ is very air sensitive and possibly polymeric. Electron delocalization into the phenyl ring must be important since the diphenylbutadiene ligand lies almost in a perfect plane, which is ideal for a delocalized electronic configuration.[42] Normally, in metallocycles, the phenyl rings are bent out of the metallocyclic plane.[43] Finally, as indicated above, the close proximity of the carbon-carbon double bond to the titanium atom indicates that an interaction with the hydrocarbon π orbitals could be important.

We have shown that it is possible to synthesize $[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2[C_6H_5C{\equiv}C{-}C{\equiv}CC_6H_5]$ by the reductive formation of monomeric titanocene and its subsequent reaction with 1,4-diphenylbutadiyne. Another route to the study of coordinated olefinic compounds of Cp_2Zr^{II} and Cp_2Ti^{III} is also suggested by the results obtained here. Dilithio delocalized anions, such as $[B_2Li]_2$-stilbene (B_2 = tetramethylenediamine), were shown[12] to give the delocalized hydrocarbon, e.g., stilbene, upon reaction with the transition metal halides. The reaction of $[B_2Li]_2$-stilbene (B = tertiary amine base) with Cp_2TiCl or Cp_2MCl_2 (M = Ti or Zi) can be expected to result first in reduction and then possibly subsequent reactions with the stilbene fragment. The above observations are currently being investigated along with related studies of low valent early transition metal organometallic chemistry.

Acknowledgment. The support of the National Science Foundation under Grants NSF-DMR-7203026 and NSF-MPS-74-23000 is gratefully acknowledged.

Supplementary Material Available: listings of structure factors (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. H. Teuben and H. J. de Liefde Meijer, *J. Organomet. Chem.*, **17**, 87 (1969).

(2) R. Jungst, D. Sekutowski, and G. Stucky, *J. Am. Chem. Soc.*, **96**, 8109 (1974).

(3) D. Sekutowski, R. Jungst, and G. Stucky, "Extended Interactions between Metal Ions in Transition Metal Complexes," Vol. 5, L. V. Interrante, Ed., American Chemical Society Symposium Series, Washington, D.C., 1974, Chapter 11.

(4) A. Mootz McPherson, G. L. McPherson, and G. D. Stucky, submitted for publication.

(5) B. Morosin and J. Howatson, *J. Organomet. Chem.*, **29**, 7 (1971).

(6) G. D. Stucky, A. McPherson, W. E. Rhine, J. J. Eisch, and J. Considine, *J. Am. Chem. Soc.*, **96**, 1941 (1974).

(7) P. W. R. Corfield and H. M. M. Shearer, *Acta Crystallogr.*, **20**, 502 (1966); *ibid.*, **21**, 957 (1966).

(8) M. I. Bruce, R. Clark, J. Howard, and P. Woodward, *J. Organomet. Chem.*, **42**, C107 (1972).

(9) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972).

(10) H. A. Patel, R. G. Fischer, A. J. Carty, D. V. Naik, and G. J. Palenik, *J. Organomet. Chem.*, **60**, C49 (1973).

(11) M. L. H. Green, G. E. Coates, and K. Wade, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, p 273.

(12) H. Yasuda, M. Walczak, and G. D. Stucky, *J. Organomet. Chem.*, **90**, 123 (1975).

(13) D. Sekutowski and G. D. Stucky, *Inorg. Chem.*, to be published.

(14) D. Sekutowski, R. Jungst, J. Davis, and G. D. Stucky, to be published.

(15) (a) J. Peterson and L. F. Dahl, *J. Am. Chem. Soc.*, **96**, 2248 (1974); (b) J. L. Peterson, D. L. Lichtenberger, R. F. Fenske, and L. F. Dahl, *ibid.*, in press; (c) L. F. Dahl, private communication.

(16) D. F. Evans, *J. Phys. E:*, **7**, 247 (1974).

(17) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(19) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(20) J. A. Ibers and R. Ross, private communication, 1970.

(21) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program", USAEC Report ORNL--306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(22) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program", USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(23) C. K. Johnson, "ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(24) F. K. Ross, Doctoral Dissertation, University of Illinois, 1969.

(25) A. Yoshino, Y. Shuto, and Y. Iitaka, *Acta Crystallogr., Sect. B*, **26**, 744 (1970).

(26) I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Am. Chem. Soc.*, **93**, 3787 (1971).

(27) V. Kocman, J. C. Rucklidge, R. J. O'Brien, and W. Santo, *Chem. Commun.*, 1340 (1971).

(28) I. S. Kolomnikov, T. S. Lobeeva, V. V. Gorbackevskaya, G. G. Aleksandrov, Yu. T. Struckhov, and M. E. Vol'pin, *Chem. Commun.*, 972 (1971).

(29) R. B. Helmholdt, F. Jellinek, H. A. Martin, and A. Vos, *Recl. Trav. Chim. Pays-Bas*, **86**, 1263 (1967).

(30) C. R. Lucas, M. Green, R. A. Forder, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 97 (1973).

(31) J. L. Atwood, private communication.

(32) (a) J. C. Green, M. L. H. Green, and C. K. Prout, *J. Chem. Soc., Chem. Commun.*, 421 (1972); (b) K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, **30**, 2290 (1974).

(33) R. S. P. Coutts and P. C. Wailes, *J. Organomet. Chem.*, **25**, 117 (1970).

(34) K. D. Smith and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 593 (1972).

(35) J. L. Atwood and K. D. Smith, *J. Chem. Soc., Dalton Trans.*, 2487 (1973).

(36) H. J. de Liefde and F. Jellinek, *Inorg. Chim. Acta*, **4**, 651 (1970).

(37) M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organomet. Chem.*, **25**, C36 (1970).

(38) J. X. McDermott and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 947 (1974).

(39) M. E. Vol'pin, V. A. Dubovitskii, O. V. Nogina, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **151**, 1100 (1963).

(40) K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jpn.*, **39**, 1178 (1966).

(41) F. W. Siegert and H. J. de Liefde Meijer, *Recl. Trav. Chim. Pay-Bas*, **89**, 764 (1970).

(42) As another example of this, the stilbene group has been found to be completely coplanar in bis[(tetramethylethylenediamine)lithium]stilbene: M. Walczak and G. D. Stucky, submitted for publication.

(43) E. A. Jeffery and T. Mole, *J. Organomet. Chem.*, **11**, 393 (1968).

(44) A. McPherson, Ph.D. Dissertation, University of Illinois, 1974.

Solvation of the Tris(1,10-phenanthroline)iron(II) Cation as Measured by Solubility and Nuclear Magnetic Resonance Shifts[1]

F. M. Van Meter and H. M. Neumann*

Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332.

Received August 4, 1975

Abstract: A model for the solvation of the $[Fe(phen)_3]^{2+}$ cation is proposed based on the geometry of the complex. The solvation energy is considered to be the sum of two parts: that due to the ion-dipole interaction with the solvent and that due to the van der Waals interaction between the solvent and the aromatic ligands. The model was tested, and verified, by measuring the solubilities of $Fe(phen)_3(ClO_4)_2$ and naphthalene in ten pure solvents, and in mixtures of water with methanol, acetone, and *N,N*-dimethylformamide. The van der Waals interaction with the ligands was shown to parallel the interaction with naphthalene. The NMR chemical shifts of the 5,6 protons on $Fe(phen)_3{}^{2+}$ were measured in some of the solvent systems.

In attempting to understand the effect of solvent on the rates of racemization and dissociation of the complex $[Fe(phen)_3]^{2+}$ cation,[2] it became apparent that it would be necessary to investigate by independent methods the extent of the solvation of this ion. The large size of the ion, its nonspherical shape, and the aromatic character of the ligands cause this ion to have some unusual features in its interaction with solvents. Although a wide variety of experiments provide some hints about the interaction, there has been no attempt made to measure the solvation energy. This paper reports such an attempt.

We began with the view that the solvation of $[Fe(phen)_3{}^{2+}]$ is governed by two factors; one is the ion-dipole solvation energy, and the other is the solvation of the ligands by solvent molecules via an interaction of the van der Waals type. The solvation of the ligands by the latter interaction would then be similar to the solvation of an aromatic hydrocarbon by the solvent. If this view is correct it should be possible to relate the solubility of $Fe(phen)_3(ClO_4)_2$ to: (1) the solvent dielectric constant, and (2) the solubility of an aromatic compound whose solvent-solute interactions approximate those of the coordinated phenanthroline li-