ET mechanism will be measurement of the dynamic, time-dependent quenching predicting to occur in the solid state by eq 4. These experiments are in progress.

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Hydrogenation and Reduction of Nitrogen-Containing Heteroaromatics. Electron-Transfer and Radical-Induced Dimerization of Phthalazine

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In our continuing investigation of exchange and electron transfer in bis(η^5-cyclopentadienyl)titanium systems, we have studied $Cp_2Ti(bpy)$ (bpy = 2,2-bipyridyl) and have found it to possess a triplet excited state that is thermally accessible from the ground state singlet.[3] Other examples of this intramolecular electron transfer have been observed in various Cp_2Ti complexes of substituted 1,10-phenanthrolines. Recently,[4] we reported an example of intramolecular electron-transfer-inducing methyl group carbon–hydrogen bond dissociation in bis(η^5-cyclopentadienyl)titanium complexes of 4-methyl-substituted 1,10-phenanthrolines. In this communication, we report that the reaction of $Cp_2Ti(CO)_2$ with phthalazine results in electron transfer upon complexation, leading to the formation of a bimolecular complex—bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium] (II).

The complex is prepared[5] by reaction of $Cp_2Ti(CO)_2$ with the ligand in THF under an inert atmosphere. The air-sensitive product was examined by electron-impact mass spectrometry. The mass spectrum showed a weak parent molecular ion at 616, indicating a dimeric product, as well as a major ion peak at 309, one mass unit greater than that expected for the parent peak of monomeric bis(η^5-cyclopentadienyl)(phthalazine)titanium.

The molecular geometry resulting from a single-crystal X-ray structural determination[6] is shown in Figure 1. Important bond distances and angles are given in Table I. The molecule in Figure 1 has two monomeric units related by a C_2 axis. The Ti-Ti distance is 6.17 Å, and the dihedral angle between the two ligands is 78.1°. The two units are bridged by a C(8)–C(8)′ carbon–carbon bond of 1.625 (10) Å, which is considerably longer than usually found for carbon–carbon paraffinic bonds (1.54 Å). A dihedral angle of 11.6° between the ligand and the Ti–N(1)–N(2) plane is observed. This "bent" geometry may be the result of electronic factors as was similarly observed and discussed for $Cp_2Ti(bpy)$.[3]

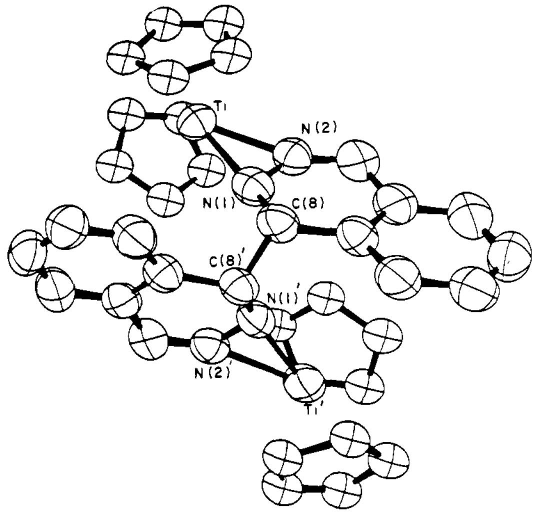

Figure 1. Molecular structure of bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium].

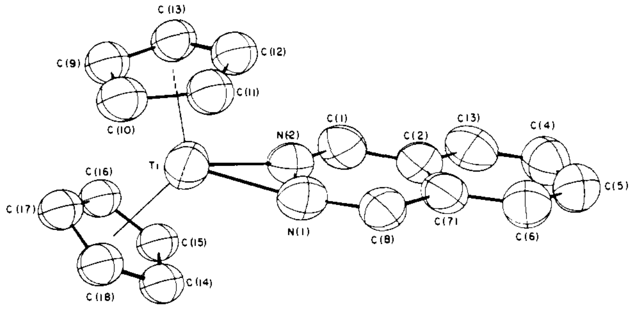

Figure 2. Molecular structure of the monomeric unit of bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium].

Table I. Important Interatomic Bond Distances (Å) and Angles (deg) in Bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium]

Ti-N(1)	2.075 (5)	N(1)-Ti-N(2)	37.2 (2)
Ti-N(2)	2.116 (5)	Ti-N(1)-N(2)	73.0 (3)
N(1)-N(2)	1.338 (6)	Ti-N(2)-N(1)	69.8 (3)
N(1)-C(8)	1.436 (7)	N(2)-N(1)-C(8)	121.9 (4)
C(1)-N(2)	1.284 (7)	C(1)-N(2)-N(1)	124.8 (5)
C(1)-C(2)	1.441 (8)	N(2)-C(1)-C(2)	120.2 (6)
C(2)-C(7)	1.396 (8)	C(1)-C(2)-C(7)	118.9 (5)
C(7)-C(8)	1.525 (7)	C(2)-C(7)-C(8)	119.5 (5)
C(8)-C(8)′	1.625 (10)	C(7)-C(8)-N(1)	112.5 (5)

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(2) (a) E. I. du Pont de Nemours & Company, Central Research and Development, Experimental Station. (b) University of Illinois. (c) Argonne National Laboratory.

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(5) Compound preparation: dicarbonylbis(η^5-cyclopentadienyl)titanium(II) (0.45 g, 2.0 mmol) is added to a solution of phthalazine (0.26 g, 2.0 mmol) in approximately 80 mL of THF under an inert atmosphere. For 12 h, the mixture is stirred with moderate heating. The solvent is then removed under reduced pressure. The product is washed with refluxing hexanes and extracted with refluxing toluene. The filtrate is heated to reflux and allowed to cool slowly. After a short time, crystals form. Anal. Calcd for $C_{36}H_{32}N_4Ti_2$: C, 70.14; H, 5.23; N, 9.09; Ti, 15.54. Found: C, 70.68; H, 5.22; N, 8.89; Ti, 15.60.

(6) Crystal Data: $C_{36}H_{32}N_4Ti_2$, mol wt 616.48; monoclinic; $a = 17.57$ (1), $b = 8.232$ (3), $c = 21.35$ (1) Å; $\beta = 106.41$ (4)°; $Z = 4$; $d_{calcd} = 1.38$ g cm^{-3}; space group C_2/n. Cell and intensity data were collected on a syntex $P2_1$ diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å). Measurements were made to $2\theta = 50°$ for a total of 5761 independent reflections of which 1062 were rejected as being systematically absent. With the criterion $F_o^2 > 3\sigma(F_o)^2$, 1514 reflections were considered observed. A total of 2454 unique reflections were in the refinement of the structure. The structure was solved with direct methods in the SHELX program package[7] with $\omega(|F_o| - |F_c|)^2$ being the function minimized during the least-squares refinement. Intensity statistics strongly suggested the centrosymmetric space group $C2/c$. Fourier and difference Fourier analyses provided all the non-hydrogen-atom positions. Least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms with hydrogen atoms included at calculated positions of 0.95 Å and statistical weights led to R_2 $(=(\sum\omega||F_o| - |F_c||^2/\sum\omega|F_o|^2)^{1/2}) = 0.066$. Due to a large number of correlation coefficients greater than 0.5 between the x and z parameters, a reindexing of the cell was undertaken. The space group $C2/n$ was used for further refinement, with greatly improved correlation coefficients. Refinement led to the final R factors for 190 variables: R_1 $(=\sum||F_o| - |F_c||/\sum|F_o|)$ for $F_o^2 > 3\sigma(F_o)^2 = 0.081$ and $R_2 = 0.087$ for the complete data set. The goodness of fit was 0.84, and the final difference Fourier had a highest peak of 0.56 e/Å^3.

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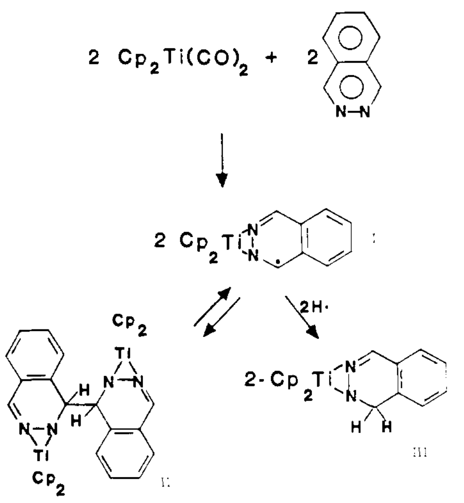

Figure 3. Proposed mechanism for formation of the dimeric and dihydro species formed in the reaction of bis(η^5-cyclopentadienyl)titanium dicarbonyl with phthalazine.

The ring system C(2)–C(3)–C(4)–C(5)–C(6)–C(7) (shown in Figure 2) is clearly aromatic, with an average carbon–carbon bond length of 1.382 (9) Å. The N(1)–N(2) bond length of 1.338 (6) Å is less than that observed for the uncomplexed ligand.[8] The C(7)–C(8) carbon–carbon bond has a length of 1.525 (7) Å and is evidently a carbon–carbon single bond. Additional evidence that C(8) is sp^3 hybridized includes the N(1)–C(8)–C(7) angle of 112.5 (5)° and the C(7)–C(8)–C(8)′ angle of 110.1°. Also, this carbon atom is raised out of the ligand plane by 0.066 Å.[9]

A proposed mechanism for dimerization is given in Figure 3. As in the other heteroaromatic systems we have described,[3,4] an electron is transferred from the electron-rich titanium atom onto the ligand, with the greatest electron density of the unpaired electron at C(8) (I). Fenske–Hall molecular orbital calculations[10] predict a high percent (23%) of carbon p_z character for C(8) in the highest partially occupied molecular orbital. This radical species (I) can subsequently interact with a second monomer to form the dimeric complex (II). Although no direct evidence was found for a bimolecular intermediate in the reaction of $Cp_2Ti(CO)_2$ and 3,4,7,8-tetramethyl-1,10-phenanthroline, which leads to the carbon–hydrogen bond dissociation, a similar bimolecular species was proposed.[4] Similar bimolecular intermediates are also suggested for the flavin one-electron-transfer process in biological systems.[11]

The radical species (I) can also react with the α-hydrogen atoms of the THF solvent or unreacted ligand to give complex III, which accounts for the mass spectral ion peak at 309 *m/e*. Dissociation of II and subsequent reaction with the solvent or unreacted ligand could also give III. Reaction of a similar type of radical species in deuterated THF showed the solvent to be the primary source of the hydrogen.[4]

EPR spectra of toluene/benzene (4:1) glasses of bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium] at liquid-nitrogen temperatures showed a complicated triplet state spectrum. This complex has two titanium(III) ions. Using the relation[12]

$$R = (0.050 g_z^2/D_{dd})^{1/3}$$

where R is the titanium–titanium distance and D_{dd} is the dipolar zero-field splitting parameter, one calculates R = 6.8 Å. This relation assumes the z component of the **g** tensor is colinear with the Ti–Ti vector, which is unlikely in this case. Nonetheless, the calculated value is close to the observed value of 6.14 Å from the crystal structure. It is also possible that the radical species I, formed upon dissociation of the dimer in the solution, could contribute to the complicated triplet-state spectrum.

The intramolecular electron-transfer-induced chemistry observed in this and earlier systems is important in understanding the mechanisms involved in the reduction of heteronuclear aromatics. This type of reduction is important in the radical chemistry associated with coal liquefaction (donor solvent and others) as well as in the hydrotreating and denitrification of crude oil. It now appears that a similar chemistry exists for related complexes of the later transition elements.[13] Additional studies are being conducted in order to further characterize the systems described here and to examine heterogeneous aromatic reduction by other metals.

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Registry No. II, 82080-87-3; $Cp_2Ti(CO)_2$, 12129-51-0; phthalazine, 253-52-1.

Supplementary Material Available: Listings of atomic positional and thermal parameters (Tables II and III, respectively), interatomic bond distances (Table IV), bond angles (Table V), deviation from planarity of rings (Table VI), and observed and calculated structure factors (Table VII) (22 pages). Ordering information is given on any current masthead page.

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2,3-Bis[(trimethylsilyl)methyl]-1,3-butadiene. A Conjunctive Reagent for Tandem Diels–Alder Reactions

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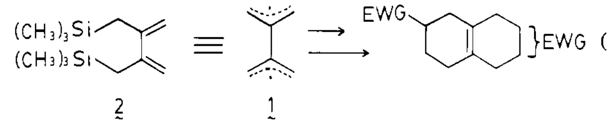
Awareness of the power of the Diels–Alder reaction in organic synthesis stimulates the search for novel dienes and dienophiles. An intriguing possibility is the accessibility of an equivalent of bi-allyl, **1**[1] which would permit simultaneous formation of two



(1)

rings as shown in eq 1. Our interest in generating synthons for reactive intermediates and the limitations posed by the current methods for equivalents of **1**[2,3] induced us to consider the use of 2,3-bis[(trimethylsilyl)methyl]-1,3-butadiene (**2**) as such a synthon.

Diene **2** is available in 70–88% yields from (2-bromoallyl)trimethylsilane[4–6] (eq 2, TMS = trimethylsilane) by oxidative

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