

TABLE I

LINE-BROADENING DATA FOR $^{17}\text{O}_2$ IN THE Ni(II)-NH_3 SYSTEM

$10^3/T$, deg $^{-1}$	Δ' , gauss	T'_{2p} , M, sec $\times 10^3$	W_0 , gauss
(A) pH 5.75, ^a total [Ni] = 0.114 M, [NH ₄ NO ₃] = 2.0 M			
3.47	0.31	20.0	0.23
3.46	0.38	16.5	0.23
3.38	0.45	14.0	0.23
3.35	0.44	14.4	0.23
3.23	0.55	10.8	0.20
3.22	0.68	9.24	0.18
3.20	0.78	8.06	0.18
3.13	1.15	5.46	0.19
(B) pH 6.08, ^b total [Ni] = 0.199 M, [NH ₄ NO ₃] = 2.0 M			
3.70	0.20	55.6	0.32
3.62	0.33	33.7	0.22
3.53	0.54	20.6	0.22
3.51	0.45	24.5	0.22
3.37	0.88	12.5	0.22
3.30	1.14	9.62	0.22
3.20	1.48	7.41	0.25
(C) pH 6.37, ^c total [Ni] = 0.116 M, [NH ₄ NO ₃] = 2.1 M			
3.51	0.40	15.9	0.21
3.40	0.62	10.4	0.23
3.30	0.78	8.20	0.20
3.20	0.99	6.43	0.19
3.11	1.21	5.29	0.20
(D) pH 6.39, ^d total [Ni] = 0.201 M, [NH ₄ NO ₃] = 2.0 M			
3.56	0.55	20.0	0.28
3.44	0.79	14.0	0.25
3.34	1.20	9.20	0.22

^a 79.3% $\text{Ni(H}_2\text{O)}_6^{2+}$, 19.4% $\text{Ni(H}_2\text{O)}_5\text{NH}_3^{2+}$, 1.3% $\text{Ni(H}_2\text{O)}_4(\text{NH}_3)_2^{2+}$, and higher species. ^b 62.7% $\text{Ni(H}_2\text{O)}_6^{2+}$, 32.4% $\text{Ni(H}_2\text{O)}_5\text{NH}_3^{2+}$, 4.9% $\text{Ni(H}_2\text{O)}_4(\text{NH}_3)_2^{2+}$, and higher species. ^c 41.7% $\text{Ni(H}_2\text{O)}_6^{2+}$, 44.0% $\text{Ni(H}_2\text{O)}_5\text{NH}_3^{2+}$, 14.3% $\text{Ni(H}_2\text{O)}_4(\text{NH}_3)_2^{2+}$, and higher species. ^d 41.7% $\text{Ni(H}_2\text{O)}_6^{2+}$, 44.0% $\text{Ni(H}_2\text{O)}_5\text{NH}_3^{2+}$, 14.3% $\text{Ni(H}_2\text{O)}_4(\text{NH}_3)_2^{2+}$, and higher species.

the values measured by Swift and Connick at lower pH (ca. 1). At 25° and 1 M $\text{Ni(H}_2\text{O)}_5\text{NH}_3^{2+}$ the rates for exchange of water with the monoammine species

are then calculated to be: at pH 5.75, 1.49×10^6 M sec $^{-1}$; at pH 6.08, 1.13×10^6 ; and at pH 6.38, 1.18×10^6 , with activation energies of 6.7, 7.5, and 7.5 ± 1 kcal/mole, respectively.

Our calculations show that, over the temperature range used, the composition of the solutions with respect to ammine species remains essentially constant so that no large errors are introduced in the activation energies. The activation energy for exchange of water with $\text{Ni(H}_2\text{O)}_6^{2+}$ is 12.2 kcal/mole.

One could attempt to include higher species as contributing to the observed rates. We do not feel that the precision of the data warrants this, and the approximate agreement of the data with the simpler assumptions suggests that contributions from higher species are not large enough to require consideration at this time. It will be of interest as improvement in precision and sensitivity can be made to investigate further the higher ammine species. Perhaps it should be pointed out at this stage that independent exchange paths may exist which are not directly connected with measured substitution rates. Our earlier work² has given some hint that such may be the case. One cannot say from the present results whether 1 or 5 (or some other number) water molecules are labilized so that the statistical factor is unknown.

Comparison of our results with the treatment given by Margerum,⁴ assuming 5 equivalent water molecules per nickel atom to be consistent with his values, suggests that the labilizing effect of ammonia may be similar to that for ethylenediamine which seems not unreasonable.

It would be of interest to have measurements on substitution rates in the monoammine species to see if the results can be compared directly with the water-exchange rate. We plan to continue our studies on water exchange in various complexes of en and EDTA, for example, to provide more direct comparisons.

Correspondence

The Contributions of Ligand Field Stabilization Energies to the Observed Variations with Ligand of Cobalt(II)-Cobalt(III) and Iron(II)-Iron(III) Oxidation Potentials

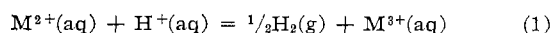
Sir:

The effects of inner orbital splittings on the thermodynamic properties of transition metal compounds has been the subject of several excellent review articles,¹⁻³

- (1) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).
- (2) D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, pp 237-282.
- (3) D. S. McClure in "Some Aspects of Crystal Field Theory," T. M. Dunn, D. S. McClure, and R. G. Pearson, Ed., Harper and Row Publishers, New York, N. Y., 1965, pp 77-95.

and the utility of crystal field theory as an interpretive aid in the explanation of observed variations in thermodynamic properties of transition metal ions is well established.

George and McClure^{1,3} considered the observed variations in the standard oxidation potentials, $\mathcal{E}^{\circ}_{\text{ox}}$, of aqueous M(II)-M(III) couples and found that $\Delta G^{\circ} - \Delta H^{\circ}_{\text{LF}}$ (where $\Delta H^{\circ}_{\text{LF}}$ is the difference in crystal field stabilization energies calculated from spectroscopic data) for the reaction



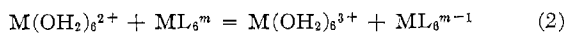
correlated fairly well with the third ionization potential of M(g). In making this correlation George

and McClure assumed that ΔS° for reaction 1 is independent of the nature of M.

George and McClure (and later Buckingham and Sargeson²) also considered the problem of the variation with ligand of $\varepsilon^\circ_{\text{ox}}$ for a given transition metal ion. The approach used involved setting up a thermodynamic cycle involving the ionization of the gaseous M(II) ion, the gaseous complexation reactions of M(II) and M(III), the dissolution of the gaseous complex ions, and lastly, to close the cycle, the oxidation of the M(II) complex to the M(III) complex in solution. This approach, although fundamentally sound, is complicated by the fact that the resulting terms to be evaluated are frequently not available experimentally or are not known with sufficient accuracy to provide a clear-cut test of the importance of ligand field stabilization energies in determining the observed variations in $\varepsilon^\circ_{\text{ox}}$ values.

These difficulties can be largely circumvented by changing somewhat the approach to the problem. In essence we ask the following question: given, say, that the $\text{Fe}(\text{OH}_2)_6^{2+}$ - $\text{Fe}(\text{OH}_2)_6^{3+}$ couple, in water at 25°, has $\varepsilon^\circ_{\text{ox}} = -0.77$ V and the $\text{Fe}(\text{CN})_6^{4-}$ - $\text{Fe}(\text{CN})_6^{3-}$ couple at the same conditions has $\varepsilon^\circ_{\text{ox}} = -0.37$ V, what contribution do ligand field stabilization energies make to this difference?

Consider the reaction



for which

$$\Delta G^\circ = -\mathfrak{F}\varepsilon^\circ = -23.06(\varepsilon^\circ_{\text{aq}} - \varepsilon^\circ_{\text{L}}) \text{ kcal} \quad (3)$$

Further

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

and

$$\Delta S^\circ = [\bar{S}^\circ(3+) - \bar{S}^\circ(2+)] - [\bar{S}^\circ(m) - \bar{S}^\circ(m-1)] \quad (5)$$

and

$$\Delta H^\circ = [\Delta H_f^\circ(3+) - \Delta H_f^\circ(2+)] - [\Delta H_f^\circ(m) - \Delta H_f^\circ(m-1)] \quad (6)$$

In general ΔS° (given by eq 5) can be rather large (as much as 80 gibbs) for a reaction of this type and cannot be assumed to be even approximately constant. This is partly a consequence of the fact that the reaction in question may involve ions of quite different charge type (*e.g.*, 2+, 3+ and 4-, 3-) for which the partial molar entropy differences (eq 5) would be expected to be quite different. In addition, even when dealing with two metal ion couples of the same charge type but involving ions of widely different sizes (*e.g.*, $\text{Fe}(\text{OH}_2)_6^{2+,3+}$ and $\text{Fe}(\text{phen})_3^{2+,3+}$) a large ΔS° for the reaction can result. This effect is due to the fact that for very large complexes in which the transition metal ions are far removed and screened off from the solvent the entropy difference $\bar{S}^\circ(m) - \bar{S}^\circ(m-1)$ tends to be small (0 ± 5 gibbs) presumably because the solvent

in such cases cannot discriminate between a +2 and a +3 charge on the ion.⁴

On the other hand, it is at least a workable hypothesis (subject to direct experimental test using thermochemical data) that the magnitude of ΔH° for a reaction like (2) involving electron transfer from M(II) to M(III) in two different ligand environments⁵ will be governed primarily by differences in ligand field stabilization energies. Our hypothesis then is that for a reaction of type (2)

$$\Delta H^\circ \simeq \Delta H^\circ_{\text{LF}} \simeq \Delta E^\circ_{\text{LF}} \quad (P\Delta V^\circ \ll \Delta E^\circ) \quad (7)$$

The rationalization for this postulate is as follows. The difference between the ground-state energies of M(II) in different ligand environments may well be quite large and difficult to predict accurately, likewise with M(III) in different ligand environments. However, the difference in ground-state energies of M(II) and M(III) in the same ligand environment where the conversion of M(II) to M(III) involves the removal of a 3d electron might be expected to be separable into two terms, the first of these being dependent on the nature of M and the second being dependent on the nature of the metal and ligand. For reactions of the type considered in this paper the term due to M alone will cancel, but the term due to both metal and ligand would not be expected to cancel completely because different ligands will perturb the metal ion orbitals to a different extent. If it is now assumed that the uncanceled part of the metal ligand interaction can be computed from ligand field theory, then eq 7 results. In other words we are assuming that the ionization potentials of $\text{M}^{\text{II}}\text{L}_6(\text{aq})$ and $\text{M}^{\text{III}}\text{L}'_6(\text{aq})$ will differ by an amount that can be calculated from ligand field theory using experimentally determined 3d-orbital splittings; *i.e.*, the magnitudes of the 3d-orbital splitting and of the metal ligand bond strengths are directly related to one another. A consideration of pairing energy terms will presumably account for any changes in the number of spin-paired electrons that occur in the reaction. We shall assume that the electron-pairing energy is independent of L for a given M.

Since $\Delta E^\circ_{\text{LF}}$ can be calculated directly from optical data and considerable progress has been made in the development of various semiempirical equations for the estimation of entropies of complex ions,^{4,6,7} the approach developed above provides a relatively straightforward (admittedly approximate) method for the assessment of the importance of LFSE effects in determining the observed variations in $\varepsilon^\circ_{\text{ox}}$ values with ligand.

In Table I data for Fe(II)-Fe(III) and Co(II)-Co(III) couples have been collected. These systems

(4) G. I. H. Hanania, D. H. Irvine, W. A. Eaton, and P. George, *J. Phys. Chem.*, **71**, 2022 (1967).

(5) This statement is not meant to carry any mechanistic implications. All that is implied is that the reaction can be considered from this viewpoint.

(6) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443, 1446, 1451 (1953).

(7) F. J. C. Rossotti in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Eds., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter I pp 1-77.

TABLE I
THERMODYNAMIC AND OPTICAL DATA FOR
Co(II)-Co(III) AND Fe(II)-Fe(III) SYSTEMS AT 25°

Cobalt						
Co(II): $t_{2g}^5e_g^2(h)$; $t_{2g}^6e_g^1(l)$			Co(III): $t_{2g}^4e_g^2(h)$; $t_{2g}^5(l)$			
LFSE: -0.70Δ ; $\sim -1.80\Delta + P$ LFSE: -0.40Δ ; $-2.40\Delta + 2P$						
Ligand	Charge type	Δ , ^a kK	ϵ° , V	Spin type	ΔH°_{LF} , ^b kcal	ΔS° , ^c gibbs
H ₂ NCH ₂ CH ₂ NH ₂	2+,3+	11.0, 23.2	+0.26	h,l	-41.2	(-39)
NH ₃	2+,3+	10.1, 22.9	-0.10	h,l	-41.0	-39
phen	2+,3+	...	-0.42	h,l	...	+5
C ₂ O ₄ ²⁻	4-,3-	9.1, 18.0	-0.57	h,l	-9.2	(+39)
EDTA ⁴⁻	2-,1-	10.2, 19.7	-0.60	h,l	-18.9	+1
H ₂ O	2+,3+	9.3, 18.2	-1.81	h,l	-10.3	-44

Iron						
Fe(II): $t_{2g}^4e_g^2(h)$; $t_{2g}^5(l)$			Fe(III): $t_{2g}^3e_g^2(h)$; $t_{2g}^5(l)$			
LFSE: -0.40Δ ; $-2.40\Delta + 2P$ LFSE: 0; $-2.00\Delta + 2P$						
Ligand	Charge type	Δ , ^a kK	ϵ° , ^d V	Spin type	ΔH°_{LF} , ^b kcal	S° , ^c gibbs
C ₂ O ₄ ²⁻	4-,3-	10.0, 13.7	+0.01	h,h	11.4	(+39)
EDTA ⁴⁻	2-,1-	9.7, 12.8	-0.12	h,h	11.1	+1
CN ⁻	4-,3-	31.4, 35.0	-0.37	l,l	28.0	+39
H ₂ O	2+,3+	10.4, 14.3	-0.77	h,h	11.9	-43
phen	2+,3+	19.6, 27.4	-1.12	l,l	34.3	+5

^a Optical data taken primarily from: C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, 1962, Chapter 15. Several Δ values given were estimated from data therein. ^b Pairing energies for low-spin Co(II) and Co(III) complexes were taken as 51.5 and 48.0 kcal, respectively. Crystal field stabilization for Co(II) high-spin complexes was taken as -0.70Δ (see ref 1, p 401). Pairing energies for low-spin Fe(II) and Fe(III) complexes were taken as 40.3 and 68.6 kcal, respectively. Pairing energies were obtained by reducing the free ion values by 20%. See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 671. ^c Entropy data taken in part from ref 2 and 6. See also H. C. Ko and L. G. Hepler, *J. Chem. Eng. Data*, **8**, 59 (1963). Values in parentheses were estimated by the author. ^d ϵ°_{ox} data from ref 2, c (above), and A. J. de Bethune and N. A. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C," C. A. Hampel Publishing Co., Skokie, Ill.

constitute those in the first transition series for which a sufficient amount of data is available to make a meaningful analysis. The ΔH°_{LF} entries were calculated from the data using the expressions given in the table under LFSE. For example, consider the Co(NH₃)₆^{2+,3+} couple (2.86 kcal/kK)

$$\Delta H^\circ_{LF} = (-2.40\Delta + 2P) - (-0.70\Delta')$$

$$\Delta H^\circ_{LF} = -2.40(22.9)(2.86) + 2(48.0) + 0.70(10.1) \times (2.86) = -41.0 \text{ kcal}$$

In Table II are presented the results of a comparison of ΔG° values calculated from optical data and experimental (or in some cases estimated) entropy data (i.e., $\Delta G^\circ_{LF} = \Delta H^\circ_{LF} - T\Delta S^\circ$) with $\Delta G^\circ(\text{exptl}) = -\mathfrak{F}(\epsilon^\circ_{aq} - \epsilon^\circ_L)$. Although the agreement is far from perfect, the results are encouraging and it can be seen that differences in partial molar entropies as well as differences in ligand field stabilization energies must be taken into account in any attempt to explain the observed shifts in ϵ° values. In fact for the Fe-(C₂O₄)₃^{4-,3-} and Fe(EDTA)^{2-,1-} couples almost the entire difference (0.78 and 0.65 V, respectively) be-

TABLE II
COMPARISON OF EXPERIMENTAL ΔG° VALUES
WITH THOSE ESTIMATED USING LIGAND FIELD THEORY (25°)

Ligand	$-T$		ΔG° , kcal		ϵ°_{ox} , V	
	ΔH°_{LF} , kcal	ΔS° , kcal	Calcd ^a	Obsd ^b	Calcd	Obsd
Fe(OH ₂) ₆ ²⁺ + Fe ^{III} X _n ^m = Fe(OH ₂) ₆ ³⁺ + Fe ^{II} X _n ^{m-1}						
C ₂ O ₄ ²⁻	0.5	24.4	24.9	18.0	+0.31	+0.01
EDTA ⁴⁻	0.8	13.1	13.9	15.0	-0.17	-0.12
CN ⁻	-16.0	24.4	8.4	9.2	-0.41	-0.37
phen	-22.3	14.3	-8.0	-7.9	-1.11	-1.12
Co(OH ₂) ₆ ²⁺ + Co ^{III} X _n ^m = Co(OH ₂) ₆ ³⁺ + Co ^{II} X _n ^{m-1}						
NH ₃	30.7	1.5	32.2	39.4	-0.42	-0.10
H ₂ NCH ₂ CH ₂ NH ₂	30.9	1.5	32.4	47.7	-0.41	+0.26(?)
EDTA ⁴⁻	8.6	13.4	22.0	27.9	-0.86	-0.60
C ₂ O ₄ ²⁻	-1.1	26.2	25.1	28.6	-0.72	-0.57

^a $\Delta G^\circ_{LF} = \Delta H^\circ_{LF} - T\Delta S^\circ$. ^b $\Delta G^\circ(\text{obsd}) = -23.06(\epsilon^\circ_{aq} - \epsilon^\circ_L)$.

tween the observed ϵ°_{ox} value and that for the Fe-(OH₂)₆^{2+,3+} couple arises from an entropy difference. This is also true of Co(C₂O₄)₃^{4-,3-} relative to Co-(OH₂)₆^{2+,3+}. In general, entropy effects will be most important for couples of different valence type and/or widely different ligand sizes. On the other hand, the difference between the ϵ° values of the Co(NH₃)₆^{2+,3+} and Co(en)₃^{2+,3+} couples⁸ and the Co(OH₂)₆^{2+,3+} couple can be ascribed primarily to a difference in ligand field stabilization energies. For all of the other cases in Table II the entropy and ligand field effects are of comparable importance.

It is also worth noting² that when π bonding is important between the central metal ion, the effect will be maximum for a given ligand when the metal ion has the configuration⁹ t_{2g}^6 . Interestingly enough, since for cobalt this configuration occurs in the Co(III) state whereas for iron it occurs in the Fe(II) state, a π -bonding ligand like phen (1,10-phenanthroline) which shifts the Co(II)-Co(III) oxidation potential to a higher value will shift the Fe(II)-Fe(III) potential to a lower value relative to the aquo couple (see Table I). The reason the Fe(CN)₆^{4-,3-} oxidation potential lies above that for the aquo couple even though cyanide ion is a strong π -bonding ligand is that the entropy change is much larger in this case and acts in the direction opposite to that of the enthalpy change (see Table II).

In summary then, entropy changes as well as ligand field effects must be taken into account in order to understand the observed shifts in ϵ°_{ox} values for Co(II)-Co(III) and Fe(II)-Fe(III) couples. When these two factors are taken into account good agreement is obtained in at least some of the cases considered between observed and calculated ϵ° values. In addition where optical data on both complexes are available and their entropies can be estimated or have been determined, an approximate ϵ°_{ox} can be computed. In those cases where data are available, calculations of this sort could possibly be used as a

(8) Although the agreement is particularly poor for the Co(en)₃^{2+,3+} case it should be noted the experimental evidence has been presented (see ref 2) that indicates that the reported ϵ° value is probably too high. A lower ϵ° would improve the agreement.

(9) L. E. Orgel, "Introduction to Transition Metal Chemistry Ligand Field Theory," Methuen and Co., London, 1960.

rough independent check on the measured value. It may not be fortuitous that the poorest agreement between observed and calculated ϵ° values obtains in just those cases where there is reason to believe the experimental data may not be reliable. In fact, with the exception of the aquo couples and the $\text{Fe}(\text{CN})_6^{4-}$,³⁻ and $\text{Fe}(\text{phen})_3^{2+}$,³⁺ couples, considerable uncertainty is associated with the reported ϵ° values. In many cases appropriate extrapolations that are necessary to anchor the ϵ° value on the conventional hypothetical ideal 1 *m* standard state have not been carried out. In this connection it is the opinion of the author that the results obtained here indicate that a reinvestigation of some of the couples whose ϵ° values have been reported is in order.

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RECEIVED AUGUST 30, 1967

Steric Effects in Organometallic Conformational Equilibria. I. Allylic Complexes of Molybdenum¹

Sir:

The presence of four carbonyl stretching bands in the infrared spectrum of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-}\pi\text{-C}_3\text{H}_4\text{R}$ ($\text{R} = \text{H}$ or CH_3) suggests the existence of two different structures in solution.² Both the infrared and temperature-dependent nmr spectra of this compound have been rationalized by a conformational equilibrium between IA and IB³ (see Figure 1). Although an analogous equilibrium would be expected for the methallyl complex, the novel effect of substitution upon the equilibrium allows one to deduce which of the conformers predominate.

At low temperature the proton nmr of I (see Figure 2) exhibits two π -cyclopentadienyl resonances and two superimposed AM_2X_2 spectra corresponding to the two conformations. As the temperature is raised, the corresponding peaks in the two isomers broaden and coalesce to a limiting high-temperature spectrum of resonances which are approximately weighted averages of those at low temperature. Over the temperature range observed there is no averaging of the *syn* and *anti* protons; this eliminates possible mechanisms for conformer interconversion which require *syn-anti* proton exchange⁴⁻⁶ and suggests a mechanism equivalent

(1) These complexes may be classified as stereochemically nonrigid organometallic compounds. See, for example, W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

(2) R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

(3) A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

(4) F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **6**, 179 (1967).

(5) K. Vrieze, C. Maclean, P. Cossee, and C. W. Hilbers, *Rec. Trav. Chim.*, **85**, 1077 (1966).

(6) J. K. Beccossall, B. E. Job, and S. O'Brien, *J. Chem. Soc., Sect. A*, 423 (1967).

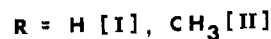
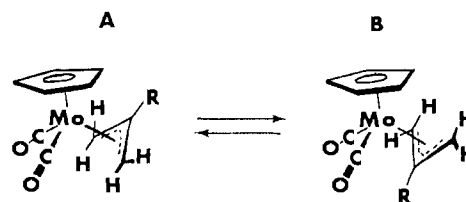


Figure 1.—Probable conformations of $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-}\pi\text{-C}_3\text{H}_4\text{R}$.

to rotation of the planar π -allyl moiety about a molybdenum-allyl axis.⁷

The infrared spectrum in pentane shows two intense carbonyl bands at 1970 and 1902 cm^{-1} , and at low temperature the nmr spectrum apparently indicates that there is only one isomer of the π -methallyl derivative (II). The temperature dependence of the nmr spectrum, however, suggests a configurational equilibrium completely analogous to that of the π -allyl complex. The low concentration of the minor component and the presence of hydrocarbon impurities makes it difficult, but the resonances can be located at high spectrometric gain.^{8,9} A comparison of the low-temperature proton resonances in compounds I and II (see Table I) results in the interesting conclusion that the structure corresponding to the minor constituent in I has become the major constituent in II. This unexpected reversal of concentrations in the equilibrium upon replacement of a hydrogen atom by a methyl group may be rationalized on the basis of steric factors. Examination of molecular models¹⁰ based on the X-ray structural parameters of $(\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3)_2$ ¹¹ and $(\pi\text{-C}_3\text{H}_4\text{RPdCl})_2$ ¹² indicates that the interactions between the ring hydrogen atoms and the two *anti* hydrogen atoms in conformer IB are greater than those with the hydrogen atom on the central carbon in conformer IA. In the methallyl complex the nonbonded interactions between the ring hydrogens and the methyl group in IIA are much greater than with the *anti* hydrogens in IIB, thus destabilizing IIA relative to IIB. Hence, it is concluded that two

(7) The mechanism may perhaps be better described as a pseudo-rotation, such as that found in five-coordinate phosphorus species. The elucidation of this point is being pursued.

(8) Confirmation of the location of the *anti*-proton resonance of the minor component of II was provided by a double irradiation experiment. At 8° the region from 600 to 640 Hz upfield from benzene was irradiated while observing the major-component *anti*-proton resonance at 558 Hz. Assuming configurational interconversion occurs at a faster rate than spin-lattice relaxation of the *anti* protons, irradiation at the resonance position of the *anti* protons of the minor component should result in reduced intensity of the analogous resonance of the other component due to transfer of nuclear-spin polarization.⁹ Irradiation between 620 and 622 Hz resulted in a minimum in the intensity of the resonance at 558 Hz. A similar experiment confirmed the location of the methyl resonance of the minor component of II.

(9) R. A. Hoffman and S. Forsen, *Progr. Nucl. Magnetic Resonance Spectroscopy*, **1**, 15 (1966).

(10) The conformations shown in Figure 1 are distorted for clarity. If there were no steric interactions to distort the bond angles, the model compounds suggest that the C-C-C plane of the allyl in B should be nearly perpendicular ($\sim 77^\circ$) to the plane of the cyclopentadienyl ring; whereas in A the dihedral angle would be about 33° .

(11) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

(12) A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).