

The heavy-atom positions in all three compounds were obtained from three dimensional Patterson functions, and the structure for **3** was refined to convergence by using anisotropic thermal parameters for all nonhydrogen atoms. The refinement proceeded straightforwardly for this structure.

For compound **2** the structure refinement also proceeded uneventfully with all atoms being found and refined isotropically with $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.099$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.138$.

At this stage it was noted that the thermal parameters for the fluorine atoms in the bidentate trifluoroacetato group were unexpectedly high, suggesting a possible disorder problem. An electron density map at this point revealed three high peaks at distances of 0.45, 0.70, and 0.74 Å from F(4), F(5), and F(6) and the three additional peaks were refined, treating them as fluorine atoms. This produced occupancy factors of approximately 0.75 for the original fluorine atoms and 0.25 for the three additional peaks. The occupancy factors were fixed at these values, and all nonhydrogen atoms except for the three lower-occupancy fluorine atoms were henceforth treated anisotropically. The final agreement factors were $R_1 = 0.042$ and $R_2 = 0.058$. No attempt was made to locate any hydrogen atoms.

Compound **1** crystallized in the space group $P\bar{1}$ with cell constants of $a = 9.083$ (2) Å, $b = 19.897$ (6) Å, $c = 18.828$ (3) Å, $\alpha = 134.62$ (3)°, $\beta = 98.34$ (2)°, $\gamma = 94.12$ (2)°, $V = 2323$ (3) Å³, and $Z = 2$

with one molecule as the asymmetric unit. The two independent molybdenum atoms were located from a three-dimensional Patterson function, and the coordination sphere about the Mo_2^{4+} unit was found in the first electron density map. Alternate refinement and electron density map steps revealed positions for 63 of the 68 atoms, and the discrepancy indices at this point were $R_1 = 0.194$ and $R_2 = 0.285$. The missing atoms belonged to phenyl groups, and further effort, using additional electron density maps, did not provide any clear evidence for them. Moreover, the already complete phenyl groups were found to be badly distorted. In view of the time and cost involved in each stage of computation for such a large structure (253 variables and 6131 observations), together with the fact that qualitative demonstration that the phosphine ligands are axially coordinated fulfilled our main purpose in conducting a crystallographic study of this compound, we decided not to continue the work with this structure.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. **1**, 41772-59-2; **2**, 76036-80-1; **3**, 76036-79-8; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 35489-62-4; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Et}_2\text{O})_2$, 76036-78-7.

Supplementary Material Available: Tables of observed and calculated structure factors for compounds **2** and **3** (20 pages). Ordering information is given on any current masthead page.

Notes

Contribution from Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545

¹⁵N NMR Study of Complexation of 1-Methylimidazole by Zinc(II) and Cadmium(II) in Aqueous Solution¹

M. Alei, Jr.,* L. O. Morgan, and W. E. Wageman

Received July 10, 1980

In prior publications we have reported on ¹⁵N NMR studies of complexation of doubly ¹⁵N-labeled imidazole (Im) by Zn(II)² and Cd(II)³ in aqueous solution. In those systems, rapid N-H proton exchange between imidazole species and rapid Im exchange between all metal ion-imidazole complexes ($\text{M}(\text{Im})_i^{2+}$, $1 \leq i \leq 6$) allows observation of only a single ¹⁵N resonance in any given solution. In treating the experimental data to extract the ¹⁵N shift produced by complexation of Im with Zn²⁺ or Cd²⁺, we were thus limited to determination of the average shift over both imidazole nitrogens (¹⁵N₁ and ¹⁵N₃). To measure the effect of metal ion complexation on each nitrogen, we felt it would be useful to do a similar study with doubly ¹⁵N-labeled 1-methylimidazole (1-MeIm) which displays separate ¹⁵N₁ and ¹⁵N₃ resonances. Since metal ion complexation occurs at ¹⁵N₃, it is expected to produce a large shift at that nitrogen and a much smaller shift at ¹⁵N₁, with the average being comparable to the shift observed for the ¹⁵N resonance of Im when complexed by the same ion. The results of such a study should enable us to predict more accurately the effects of metal ion complexation on imidazole-ring ¹⁵N shifts in biological systems where the two nitrogens are usually distinguishable.

Experimental Section

Doubly ¹⁵N-labeled 1-MeIm was prepared as described in an earlier publication.⁴ Preparation of the metal ion-1-MeIm solutions and

Table I. ¹⁵N Shifts for 1-MeIm in Aqueous Zn(NO₃)₂ or Cd(NO₃)₂ Solutions

sample	[TL], ^a mol/L	[TA], ^b mol/L	[TM], ^c mol/L	pH ^d	δ_{obsd}^e	
					¹⁵ N ₃	¹⁵ N ₁
Zn(II)						
A	0.0787	0.0501	0.0498	5.66	59.0	-6.1
B	0.1121	0.0501	0.0495	5.90	52.1	-5.4
C	0.1334	0.0500	0.0495	6.09	49.8	-5.3
D	0.1649	0.0497	0.0494	6.22	47.9	-5.2
E	0.2188	0.0496	0.0492	6.51	46.0	-5.2
F	0.2489	0.0493	0.0492	6.70	44.6	-5.2
G	0.3220	0.0491	0.0488	7.25	37.0	-4.4
H	0.3544	0.0490	0.0486	7.34	33.8	-4.1
Cd(II)						
A	0.0768	0.0503	0.0493	5.62	58.3	-6.1
B	0.1299	0.0499	0.0492	6.29	44.4	-4.7
C	0.1565	0.0499	0.0490	6.60	38.6	-4.1
D	0.2391	0.0495	0.0486	7.14	28.7	-3.1
E	0.3997	0.0487	0.0481	7.61	18.4	-2.1

^a Total 1-MeIm concentration. ^b Total added HNO₃ concentration. ^c Total Zn(NO₃)₂ or Cd(NO₃)₂ concentration. ^d Uncertainty $\leq \pm 0.05$ pH unit. ^e All ¹⁵N₃ shifts are *upfield* and all ¹⁵N₁ shifts *downfield* relative to their respective positions in aqueous 1-MeIm at pH > 10.

acquisition of ¹⁵N NMR data were also as described earlier² with the exception that in the present work constant ionic strength of 0.2 was maintained for all solutions. The pH of each solution was measured with an Orion combination electrode and Corning Digital 110 pH meter. Samples were thermostated at 25.0 ± 0.1 °C and flushed with argon to exclude atmospheric CO₂ during the pH measurement. Since Avdeef and Bucher⁵ have found a significant difference between true hydrogen ion concentration and measured pH on a Beckman combination electrode, we have used their expressions to correct our measured pH (at ionic strength of 0.2, the true pH is 0.15 unit less than measured pH for all the solutions used in this work). The corrected pH values are listed in Table I.

- (1) This work was performed under the auspices of the U.S. Department of Energy.
 (2) Alei, M., Jr.; Morgan, L. O.; Wageman, W. E. *Inorg. Chem.* **1978**, *17*, 2288.
 (3) Alei, M., Jr.; Wageman, W. E.; Morgan, L. O. *Inorg. Chem.* **1978**, *17*, 3314.

- (4) Alei, M., Jr.; Morgan, L. O.; Wageman, W. E.; Whaley, T. W. *J. Am. Chem. Soc.* **1980**, *102*, 2881.
 (5) Avdeef, A.; Bucher, J. J. *Anal. Chem.* **1978**, *50*, 2137.

The pK_a for 1-MeIm was found by pH titration (with use of an experimental setup similar to that described above) to be 7.15 ± 0.05 at 25.0°C and ionic strength of 0.2.

Results and Discussion

The compositional parameters, measured pH, and observed $^{15}\text{N}_3$ and $^{15}\text{N}_1$ shifts for the solutions used in this study are summarized in Table I. Each solution contains 1-methylimidazole in a number of chemical environments, viz., the uncomplexed, unprotonated ligand, L (1-MeIm), the protonated ligand, LH (1-MeImH⁺ protonated at $^{15}\text{N}_3$), and the ligand in a number of complexes, ML_i^{2+} ($M = \text{Zn}^{2+}$ or Cd^{2+} , $1 < i < 6$). In a given solution, we observe only a single $^{15}\text{N}_3$ and a single $^{15}\text{N}_1$ resonance due to rapid chemical exchange which averages all the aforementioned ^{15}N environments. As discussed in detail in a prior publication,² treatment of the experimental data to extract the ^{15}N shifts for the ligands in each of the ML_i^{2+} species relative to the uncomplexed, unprotonated ligand requires knowledge of the stepwise formation constants for the ML_i^{2+} species. In the absence of such information, one can still use the data in Table I in conjunction with the pK_a value for 1-MeImH⁺ to calculate the average number of ligands complexed per metal ion ($\bar{\nu}$) and the average ^{15}N shift for a complexed ligand ($\bar{\delta}$). Thus

$$\bar{\nu} = ([\text{TL}] - [\text{LH}] - [\text{L}]) / [\text{TM}] \quad (1)$$

With a pK_a of 7.15 for 1-MeImH⁺ (cf. Experimental Section) and with the assumption that the formation constants for the metal ion complexes of 1-MeIm are comparable in magnitude to those for the same complexes of Im, it follows that under the present experimental conditions $[\text{LH}] = [\text{TA}]$ to a degree of approximation that is well within the experimental uncertainty. Thus

$$\bar{\nu} = ([\text{TL}] - [\text{TA}] - [\text{L}]) / [\text{TM}] \quad (2)$$

To evaluate $\bar{\nu}$ we need only to determine $[\text{L}]$, the equilibrium concentration of uncomplexed, unprotonated ligand which is given by

$$[\text{L}] = 10^{\text{pH} - \text{p}K_a} [\text{TA}] \quad (3)$$

Given $\bar{\nu}$ and the data in Table I, we may evaluate $\bar{\delta}$. Thus

$$\bar{\delta} = \frac{\delta_{\text{obsd}} - ([\text{LH}] / [\text{TL}]) \delta_{\text{LH}}^\circ}{([\text{TL}] - [\text{LH}] - [\text{L}]) / [\text{TL}]} \quad (4)$$

and again assuming $[\text{LH}] = [\text{TA}]$, we have

$$\bar{\delta} = ([\text{TL}] \delta_{\text{obsd}} - [\text{TA}] \delta_{\text{LH}}^\circ) / \bar{\nu} [\text{TM}] \quad (5)$$

From prior work,⁴ δ_{LH}° values (the ^{15}N shifts for 1-MeImH⁺ relative to 1-MeIm) are $+73.0$ ppm (upfield) for $^{15}\text{N}_3$ and -8.0 ppm (downfield) for $^{15}\text{N}_1$. We may thus use eq 2-5 to prepare plots of $\bar{\delta}$ vs. $\bar{\nu}$ for the $^{15}\text{N}_3$ and $^{15}\text{N}_1$ resonances of 1-MeIm. The plots are shown in Figure 1 which demonstrates several important points.

(1) Complexation of 1-MeIm by Zn^{2+} or Cd^{2+} leads to a large upfield shift at $^{15}\text{N}_3$ (~ 40 ppm for Zn^{2+} and ~ 15 - 30 ppm for Cd^{2+}) and a much smaller (by about 1 order of magnitude) downfield shift at $^{15}\text{N}_1$. For a given value of $\bar{\nu}$, the average of $\bar{\delta}_{\text{N}_1}$ and $\bar{\delta}_{\text{N}_3}$ is within 2.5 ppm of the observed $\bar{\delta}$ in the corresponding M^{2+} -Im system.^{2,3} This supports earlier observations⁴ that replacement of a proton by a methyl group at N_1 does not greatly alter the ^{15}N NMR properties of the imidazole-ring nitrogens.

(2) The magnitude of the average shift for either $^{15}\text{N}_3$ or $^{15}\text{N}_1$ of 1-MeIm increases slightly with increasing i in the $\text{Zn}(1\text{-MeIm})_i^{2+}$ species (at least out to $\bar{\nu} = 3$) and decreases with increasing i in the $\text{Cd}(1\text{-MeIm})_i^{2+}$ species.

(3) The magnitude of $\bar{\delta}$ and the trend in $\bar{\delta}$ with $\bar{\nu}$ for the $^{15}\text{N}_3$ shift in the two systems correlate well with expected relative magnitudes and trends in the stepwise intrinsic for-

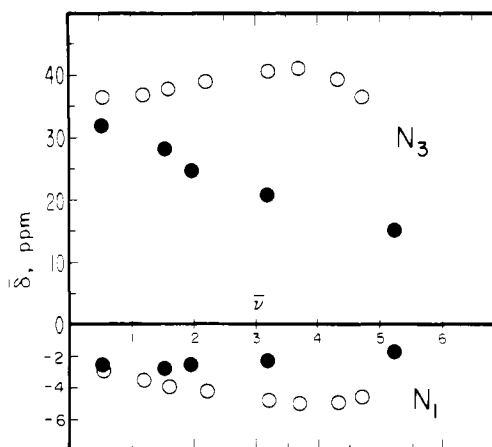


Figure 1. Average ^{15}N shift for a bound 1-methylimidazole ($\bar{\delta}$) vs. average number of 1-methylimidazoles bound by an M^{2+} ion ($\bar{\nu}$) for $\text{Zn}(1\text{-MeIm})_i^{2+}$ and $\text{Cd}(1\text{-MeIm})_i^{2+}$ complexes in aqueous solution at 25°C : O, $\text{Zn}(1\text{-MeIm})_i^{2+}$ complexes; ●, $\text{Cd}(1\text{-MeIm})_i^{2+}$ complexes.

mation constants for the $\text{Zn}(1\text{-MeIm})_i^{2+}$ and $\text{Cd}(1\text{-MeIm})_i^{2+}$ systems. Thus, on the basis of known values for imidazole, we expect (a) generally larger formation constants for $\text{Zn}(1\text{-MeIm})_i^{2+}$ species than for $\text{Cd}(1\text{-MeIm})_i^{2+}$ species and (b) a trend to larger intrinsic formation constants (κ_i) with increasing i (at least up to $i = 3$ or 4) for $\text{Zn}(1\text{-MeIm})_i^{2+}$ and a trend to lower κ_i with increasing i for $\text{Cd}(1\text{-MeIm})_i^{2+}$. Within the experimental uncertainty, it is possible that $\bar{\delta}$ may go through a maximum in the vicinity of $\bar{\nu} = 4$ for the $\text{Zn}(1\text{-MeIm})_i^{2+}$ system. Due to the increasing tendency for complexation of Zn^{2+} by hydroxide at $\text{pH} > 7.5$, it is difficult to extend the data to higher pH with confidence.

Appleton and Sarkar⁶ have studied the complexation of 1-MeIm by Zn^{2+} and report a set of stepwise formation constants which display an interesting alternation in magnitude, viz., $K_1 > K_2 < K_3 > K_4 < K_5 > K_6$. These K_i , when used with our compositional and shift data in a calculation described in detail in ref 2, yield a plot of $\bar{\delta}$ vs. $\bar{\nu}$ which agrees very well with the plot shown in Figure 1 (derived from our pH measurements as outlined earlier in this paper). However, we can also find other sets of K_i , one of these displaying a trend similar to that for the ZnIm_i^{2+} system (i.e., smoothly trending through a maximum around K_4 ; cf. ref 2) which also give excellent fits of the $\bar{\delta}$ vs. $\bar{\nu}$ plot in Figure 1. Clearly the data are not sufficiently precise to establish exact values or trends for the stepwise formation constants.

As implied in the introduction, an underlying motivation for our work has been the expectation that the ^{15}N NMR behavior for 1-methylimidazole might be similar to that for imidazole-ring nitrogens in biological systems. In this regard, it is interesting to note that as early as 1966, Happe and Morales⁷ used ^{15}N shift measurements as a basis for determining the mode of Zn^{2+} binding to the adenine ring of adenosine triphosphate (ATP) in aqueous solution. Their work implies that bidentate Zn^{2+} complexation via the 6-amino nitrogen and N-7 leads to an upfield shift of 3.0 ppm in the ^{15}N -7 resonance and downfield shifts of 1.5 and 3.1 ppm at ^{15}N -9 and the 6-amino- ^{15}N , respectively. These observations were ostensibly made under conditions such that essentially all the ATP was complexed by Zn^{2+} . On the basis of our present results with 1-methylimidazole, we would have properly predicted the *directions* of the ^{15}N shifts reported for N-7 (similar to our N_3) and N-9 (similar to our N_1) but the *magnitudes* and especially the ratio of shift at N-7 to shift at

(6) Appleton, D. W.; Sarkar, B. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 1686.

(7) Happe, J. A.; Morales, M. *J. Am. Chem. Soc.* **1966**, *88*, 2077.

N-9 seem to be significantly different for ATP than the ratio of N_3 to N_1 shifts in 1-methylimidazole. Given the limited available data and the number of possible interpretations, we simply note these discrepancies without speculating as to their origins.

Registry No. 1-MeIm, 616-47-7; Zn, 7440-66-6; Cd, 7440-43-9; ^{15}N , 14390-96-6.

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Synthesis of a Metal Complex of Benzenethiol, [Fe(C₅H₅)(CO)₂(PhSH)]BF₄, and Its Characterization as a Strong Acid

P. M. Treichel* and L. D. Rosenheim

Received August 6, 1980

The acid-base chemistry of metal thiolate complexes has attracted some attention. The recent paper by Gingerich and Angelici¹ described the attempted protonation of PPN[W(CO)₅SH]. This reaction was intended to form the known compound W(CO)₅(SH)₂ by protonation at sulfur but gave instead a thiolato-bridged complex, $\mu\text{-HS[W(CO)}_5\text{]}_2^-$. That W(CO)₅(SH)₂ is a very strong acid is supported by the fact² that loss of a proton occurs even on treatment with [N(C₂H₅)₄]Br; bromide ion is of course a very weak base. Interestingly [W(CO)₅SH]⁻ does not give up its proton even to very strong bases. In contrast $\mu\text{-HS[W(CO)}_5\text{]}_2^-$ can be deprotonated with sodium ethoxide.¹

In addition, the reaction of [Mn(C₅H₄CH₃)(CO)₂SET]⁻ with strong acid to give [Mn₂(C₅H₄CH₃)₂(CO)₄SET]⁺ is noted.³ This dimerization reaction resembles the reaction of [W(CO)₅SH]⁻ with acid in that a thiolato-bridged product is formed.

The only instances of simple protonation at sulfur in thiolato complexes involve non-organometallic species such as [Ru(NH₃)₅SR]⁺ (R = H, C₂H₅). Values of pK_a for the complexes [Ru(NH₃)₅(RSH)]²⁺ were determined to be 4.0 (for the H₂S complex) and 9.2 (for the C₂H₅SH complex). The acidity is increased moderately over the free ligand pK_a values of 7 and 12, respectively.⁴

We describe here an organometallic complex of benzenethiol, having the formula [Fe(C₅H₅)(CO)₂(PhSH)]BF₄ (I). The synthesis of this complex was accomplished with use of the method developed by Reger and Coleman.⁵ Of particular interest in this work was the ability of this complex to function as a strong acid, and experiments were carried out to attempt to further define this property.

Experimental Section

The compound [Fe(C₅H₅)(CO)₂(THF)]BF₄ was prepared by the literature method.⁵ Reactions were routinely carried out under N₂.

Infrared data were recorded on a Beckman Acculab 7 spectrophotometer; NMR spectra were run on a Jeol NM-MH-100 spectrometer. Optical absorbance measurements were made on Cary 14 and 118 instruments using 1.0-cm quartz cells. The analysis of I was done by Galbraith Laboratories, Knoxville, Tenn.

Preparation of [Fe(C₅H₅)(CO)₂(PhSH)]BF₄ (I). A 2.0-g (6.0 mmol) sample of [Fe(C₅H₅)(CO)₂(THF)]BF₄⁵ was dissolved in 50

Table I. Equilibrium Data for the Systems
I + Base \rightleftharpoons II + BH⁺ in CH₂Cl₂

$C_B^b \times 10^3$	C_{II}^- (measd) ^c $\times 10^3$	$[B]^d \times 10^3$	$C_I^e \times 10^3$	K_e^f	K_{assoc}^g
(a) B = THF, $C_T^a = 2.56 \times 10^3$ M					
9.08	0.620	8.46	1.94	2.34	37.8
18.2	0.939	17.2	1.62	3.16	33.6
27.2	1.17	26.1	1.39	3.75	32.2
36.3	1.35	35.0	1.21	4.33	32.0
45.4	1.48	43.9	1.08	4.64	31.3
54.5	1.61	52.9	0.948	5.19	32.2
(b) B = Me ₂ SO, $C_T^a = 4.27 \times 10^3$ M					
0.471	0.378	0.0938	3.89	0.391	1030
0.943	0.719	0.223	3.55	0.652	907
1.41	1.07	0.342	3.20	1.05	980
1.89	1.35	0.539	2.92	1.15	855
2.36	1.70	0.659	2.57	1.70	1000
2.83	2.10	0.726	2.17	2.81	1340
(c) B = Ph ₂ NH, $C_T^a = 4.89 \times 10^3$ M					
0.708	0.530	0.178	4.36	0.362	683
1.42	1.21	0.209	3.68	1.90	1570
2.12	1.90	0.220	2.99	5.52	2900
2.38	2.31	0.522	2.58	3.96	1720
4.25	3.05	1.20	1.84	4.22	1380
5.66	3.65	2.02	1.24	5.32	1460

^a $C_T = C_I + C_{II}$. ^b $C_B = [B] + [BH^+]$. ^c Determined spectrophotometrically; see text. ^d $[B] = C_B - C_{II}$. ^e $C_I = C_T - C_{II}$. ^f Equilibrium constant for the reaction I + B \rightleftharpoons II + [BH]⁺; $K_e = [II][BH^+]/[I][B]$. ^g Equilibrium constant for the reaction I + B \rightleftharpoons [II ··· H-B]⁺; $K_{assoc} = [II]/[I][B]$; see text for discussion.

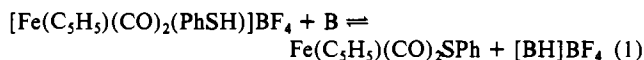
mL of CH₂Cl₂, and 1.30 g (12.0 mmol) of PhSH was added. The solution was stirred at room temperature for 3 h. A brown solid was then precipitated from solution by addition of hexane. Purification by recrystallization from CH₂Cl₂/hexane gave yellow crystals; 0.80 g (40%), mp 133-136 °C.

Anal. Calcd for C₁₃H₁₁BF₄FeS: C, 41.75; H, 2.97; Fe, 14.93. Found: C, 42.05; H, 2.89; Fe, 14.73.

IR: $\nu(\text{CO})$ 2055, 2015 cm⁻¹ in CH₃NO₂. NMR (CD₂Cl₂): δ 7.49 (C₆H₅), 5.39 (C₅H₅). The S-H resonance occurs between δ 5.0 and 6.0, its position dependent upon concentration.

The product could be handled only in CH₂Cl₂ and CH₃NO₂. It was not soluble in nonpolar solvents and was deprotonated in typical polar solvents (acetone, acetonitrile), giving Fe(C₅H₅)(CO)₂SPh (II); $\nu(\text{CO}) = 2030, 1987$ cm⁻¹.⁶

Equilibrium Studies. We hoped to determine more quantitatively the acidity of I by studying its reaction with several weak bases, viz, eq 1. This could be done by taking advantage of the different



absorption spectra of the starting material and product. The product of deprotonation, II, is maroon and shows a maximum at 560 nm having an extinction coefficient ϵ_{II} of 278 cm⁻¹ M⁻¹ (CH₂Cl₂). In contrast, yellow I has a maximum in the ultraviolet region of the spectrum which trails into the visible region. At 560 nm the extinction coefficient for this compound, ϵ_I , is 24 cm⁻¹ M⁻¹. (This measured value, which was presumed to be somewhat uncertain due to its small magnitude, was verified by the method of Rose and Drago.⁷)

The measurements of equilibrium concentrations were carried out as follows. A solution of I in CH₂Cl₂ between 0.01 and 0.03 M was prepared. A measured quantity of the base used was added to 5.00 mL of this solution. The resulting mixture was diluted to 25.0 mL, and C_T (total concentration of I and II) and C_B (total concentration of B and BH⁺) were calculated. The concentration of species II, C_{II} , was related to the absorbance, A , by the relationship $C_{II} = (A - \epsilon_I b C_T) / (\epsilon_{II} - \epsilon_I b)$. Knowing C_{II} , one can determine the value of C_I ($C_I = C_T - C_{II}$). The equilibrium concentration of base is assumed

- Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604-5608.
- Herberhold, M.; Suss, G. *J. Chem. Res. Miniprint* **1977**, 2720-2743.
- Burkett-St. Laurent, J. C. T. R.; Cairn, M. R.; English, R. B.; Haines, R. J.; Nassimbeni, L. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1077-1081.
- Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689-702.
- Reger, D. L.; Coleman, C. J. *Organomet. Chem.* **1977**, *131*, 153-162.

- Ahmad, M.; Bruce, R.; Knox, G. R. *J. Organomet. Chem.* **1966**, *6*, 1-10.
- Rose, N. J.; Drago, R. S. *J. Am. Chem. Soc.* **1959**, *81*, 6138-6145.