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Disappearance of the α-Effect: Reaction of p-Nitrophenyl Acetate with Various Aryloxides and Benzohydroxamates in the Presence of Cetyltrimethylammonium Bromide

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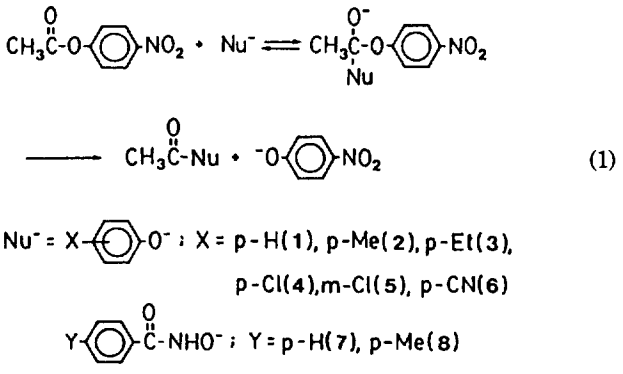
The rate constants for the reactions of *p*-nitrophenyl acetate with 6 different aryloxides and 2 benzohydroxamates have been measured spectrophotometrically in water containing various concentrations of cetyltrimethylammonium bromide (CTAB). The reactivity of the nucleophiles has been demonstrated to be significantly enhanced as the concentration of the surfactant increases up to a certain point. When the basicities of the aryloxides are comparable, the rate enhancement is more prominent for the aryloxide having larger binding constant to the micellar aggregate. Benzohydroxamates exhibitis significantly large α-effect in the absence of the surfactant, although, the α-effect nucleophiles are considered to be more solvated in water than the corresponding normal nucleophile. Thus, the solvation effect does not appear to be solely responsible for the α-effect. Interestingly, the large α-effect disappears in the presence of the surfactant. Therefore, one might attribute the disappearance of the α-effect to solvent effect. However, a structural change of the reactive α-effect nucleophile into unreactive ones would also be considered to be responsible for the absence of the α-effect in the present system.

Introduction

Rationalization of nucleophilicity has intrigued organic chemists for some decades and numerous factors have been suggested to be important for correlation of nucleophilic reactivity.[1-3] Among them, the basicity of nucleophiles has most successfully been used as a measure of nucleophilicity.[3] However, a group of nucleophiles containing a hetero atom in the α-position from the reaction center has exhibited abnormally higher nucleophilicity than would be expected from their respective basicity. Thus, the enhanced reactivity of these nucleophiles has been termed the α-effect.[4] The origin of the α-effect has not been well understood.[5] Particularly, the theory concerning solvent effect has been contradictory, *i.e.*, some studies have claimed solvent effect is unimportant for the α-effect[6] but other studies have suggested that solvation should be an important factor.[7]

Recently a series of systematic studies has revealed that

the α-effect is significantly medium dependent for the reaction of *p*-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate and 4-chlorophenoxide as an α-effect nucleophile and its corresponding normal nucleophile, respectively, in various solvent systems.[8] We now extend our study to a differnt type of α-effect nucleophile, benzohydroxamate, in aqueous medium containing various concentrations of cetyltrimethylammonium bromide (CTAB) as shown in Eq. (1) and wish to report the kinetic results together with the binding constants (K_S) of nucleophiles to the cationic micelles of CTAB.



(1)

Experimental

Materials. The substrate PNPA was easily prepared by literature procedures using acetyl chloride and 4-nitrophenol in the presence of triethylamine as a catalyst in anhydrous ether.[9] Benzohydroxamic and 4-methylbenzohydroxamic acids (**7**, **8**) were also synthesized by the known method using hydroxyl amine and corresponding benzoyl chlorides.[10] The purity was checked by means of their melting point and spectral data such as IR and ^{1}H-NMR characteristics. The phenols and CTAB used in the present study were of the highest quality available (Aldrich) and generally recrystalized before use. Doubly glass distilled water was boiled and cooled under a nitrogen atmosphere. All the solutions were prepared just before use.

Measurement of Binding Constant (K_S). Binding constants (K_S) of the anions were determined by literature methods[11] using Eq. (2),

$$K_S=[S_M]/\{[S_W]([CTAB]-cmc-[S_M])\} \quad (2)$$

where S_W and S_M represent solute in aqueous and micellar pseudophases, *cmc* is the critical micelle concentration, and concentrations are expressed as molarities. The absorbance of the individual anions (2×10^{-4} M) was measured at 305, 310, 310, 314, 305, 296, and 296 nm for the anions of **1**, **2**, **3**, **4**, **5**, **7**, and **8**, respectively, using a Hitachi U-2000 Model UV-VIS spectrophotometer at 25.0+/−0.1℃. Experiments were performed in 0.02 M NaOH solution containing CTAB over a range up to 3×10^{-2} M which is large enough to neglect changes in the *cmc* due to the solute.

Kinetics. The kinetic studies were performed with a Shimazu UV-120-02 Spectrophotometer equipped with a Neslab RTE-110 Model constant temperature circulating bath to keep the reaction temperature at 25.0+/−0.1℃. The reactions were followed by monitoring the appearance of the leaving 4-nitrophenoxide ion at 400 nm. In the case of the reactions run in the presence of CTAB, the concentration of reactants were diluted to 1.0×10^{-5} M and 2.00×10^{-4} M for the substrate and nucleophiles, respectively, in order to minimize perturbation of micellar structures. Other detailed kinetic procedures have been described in the previous reports.[12]

Table 1. Summary of Binding Constants (K_S) of Aryloxides and Benzohydroxamates to Micelle of CTAB at 25℃

Nu^-	K_S, M^{-1}	π^b
$C_6H_5O^-$	1800± 80 (1980)[a]	0.00
4-Me-$C_6H_4O^-$	3200± 150 (3350)[a]	0.56
4-Et-$C_6H_4O^-$	4570± 210 (5320)[a]	1.02
4-Cl-$C_6H_4O^-$	7400± 340	0.71
3-Cl-$C_6H_4O^-$	7490± 310	0.71
$C_6H_5C(O)NHO^-$	650± 30	–
4-Me-$C_6H_4C(O)NHO^-$	870± 40	–

[a]Data from ref. 11. [b]Lipophilicity constant for the substituent on phenyl ring, data from ref. 14.

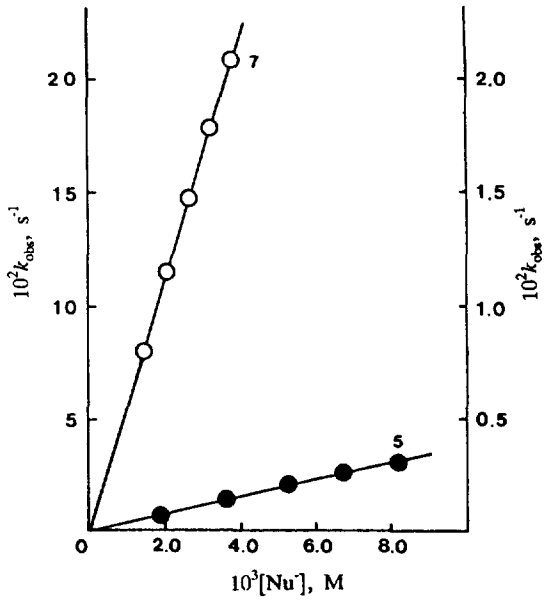


Figure 1. Plots showing dependence of k_{obs} on the nucleophile concentration for the reaction of PNPA with benzohydroxamate (**7**: left hand side scale) and *m*-chlorophenoxide (**5**: right hand side scale) in H_2O at 25℃.

Results

The binding constants (K_S) for the aryloxides (**1-5**) and benzohydroxamates (**7**, **8**) are summarized in Table 1 together with the lipophilicity constant (π) of the substituent on the phenyl ring. The K_S values for $C_6H_5O^-$, 4-Me-$C_6H_4O^-$ and 4-Et-$C_6H_4O^-$ are obtained to be slightly smaller than the ones reported in the literature.[11] However, such small differences in K_S values would not be significant enough to affect our argument.

All the reactions here obeyed pseudo-first-order kinetics

Table 2. Summary of Second-Order Rate Constants (k_2) for the Reactions of *p*-Nitrophenyl Acetate with Aryloxides and Benzohydroxamates in H_2O at 25℃

Nu^-	*pKa* (NuH)[a]	k_2, $M^{-1}s^{-1}$
(1) $C_6H_5O^-$	9.95	1.13[b]
(2) 4-Me-$C_6H_4O^-$	10.19	2.13[b]
(3) 4-Et-$C_6H_4O^-$	10.0	2.05
(4) 4-Cl-$C_6H_4O^-$	9.38	0.685[b]
(5) 3-Cl-$C_6H_4O^-$	9.02	0.362
(6) 4-CN-$C_6H_4O^-$	7.95	0.030[b]
(7) $C_6H_5C(O)NHO^-$	8.88	58.5
(8) 4-Me-$C_6H_4C(O)NHO^-$	8.90	63.8

[a] *pKa* values are taken from ref. 24. [b] Data from ref. 16.

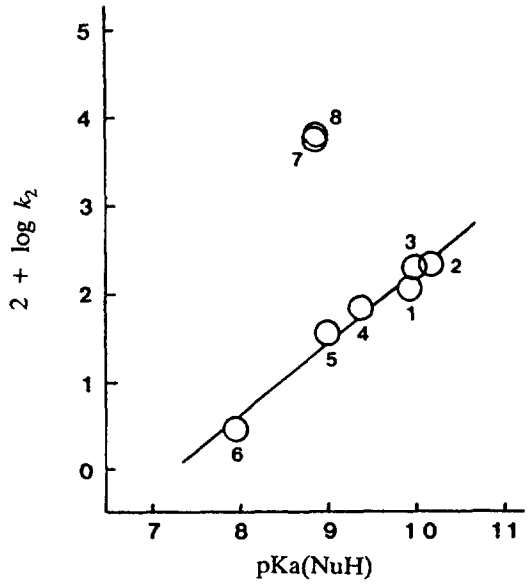


Figure 2. A Brønsted plot showing a manifestation of the α-effect for the reaction of PNPA with aryloxides and hydroxamates in H_2O at 25℃. The numbers refer to nucleophiles in Table 2.

up to over 90% of the total reaction. Pseudo-first-order rate constants (k_{obs}) were obtained from the Guggenheim equation, $\ln (A_\infty - A_t) = -k_{obs}t + C$. Second-order rate constants (k_2) were calculated from the plots of k_{obs} *vs.* the concentration of nucleophile (See Figure 1 for example).

The second-order rate constants for the reactions of PNPA with various aryloxides and benzohydroxamates in the absence of CTAB were summarized in Table 2. In Figure 2 is demonstrated a Brønsted type plot for the reaction of PNPA with the aryloxides (**1-6**) and benzohydroxamates (**7**, **8**) in the absence of CTAB. The kinetic results for the reactions run in the presence of CTAB were summarized in Table 3 and plotted in Figures 3 and 4.

Discussion

Binding Constant (K_S). Two major factors have been suggested to influence the magnitude of the binding constant (K_S), *e.g.*, electrostatic and hydrophobic interactions.[13] The electrostatic interaction between the positively charged micelles and the anionic nucleophiles used in the present study would be considered to be similar each other. Therefore, the difference in the K_S value would be mainly attributed to the difference in hydrophobicity of the anions. This is demonstrated in Table 1 where K_S value increases with increasing hydrophobicity constant (π) for the aryloxides system. However, chlorophenoxides (**4**, **5**) exhibit much larger K_S values than 4-ethylphenoxide (**3**) although Et group is considered to be more hydrophobic than Cl based on the π value. It is not however surprising if one takes into consideration the electron withdrawing nature of chlorine atom. The presence of Cl atom would cause a decrease in charge density of the oxygen atom of the chlorophenoxides. In consequence, such an inductive effect would result in a signifi-cantly decreased hydrogen bonding interaction and give large K_S values.

On the contrary, benzohydroxamate (**7**) exhibits very small K_S value. Besides, an introduction of CH_3 group on the phenyl ring of the hydroxamate causes an increase in K_S value only by 220 M^{-1}, which is significantly small increase com-

Table 3. Summary of Observed Rate Constants (k_{obs}, min^{-1}) for the Reactions of *p*-Nitrophenyl Acetate (PNPA) with Aryloxides and Benzohydroxamates in 0.1 M Borate Buffer (pH=9.27) Containing Various Concentrations of CTAB at 25.0℃[a]

10^4[CTAB], M	k_{obs}, min^{-1}								
	(1)[b]	(2)	(3)	(4)	(5)	(6)	(7)	(8)	buffer
0.0	.029	.029	.030	.034	.028	.026	.037	.038	.024
4.0	.059	.114	.197	.198	.115	.057	.059	.085	.055
6.0	.097	.186	.323	.275	.160	.060	.084	.114	.060
8.0	.131	.248	.401	.340	.192	.068	.097	.139	.069
10.0	.160	.292	.505	.385	.216	.070	.112	.160	.068
14.0	.215	.374	.589	.432	.237	.087	.133	.193	.077
20.0	.265	.440	.672	.458	.264	.103	.164	.218	.092
36.0	.323	.530	.708	.501	.267	.109	.198	.248	.104
48.0	.344	.530	.690	.499	.267	.114	.208	.247	.101
76.0	.352	.520	.612	.479	.265	.125	.213	.246	.106

[a] [PNPA] = 1.0×10^{-5} M, [NuH] = 2.0×10^{-4} M. [b] The numbers refer to nucleophiles in Table 2.

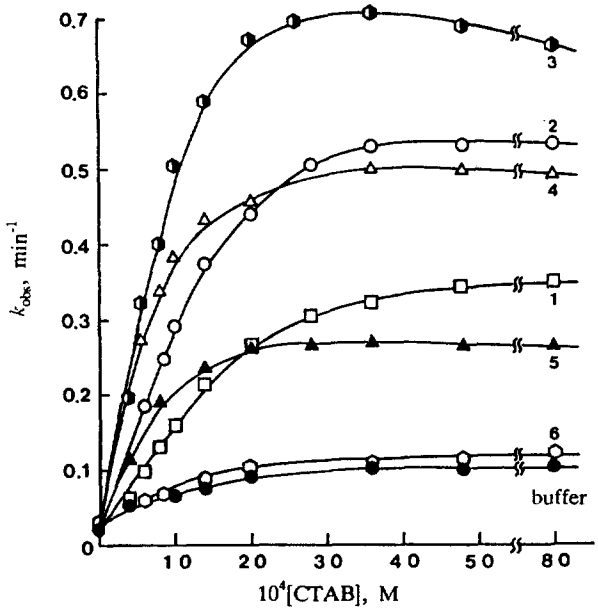


Figure 3. Plots showing micellar effect on rates for reaction of PNPA with various aryloxides (**1-6**) in 0.1 M borate buffer (pH=9.27) at 25℃.

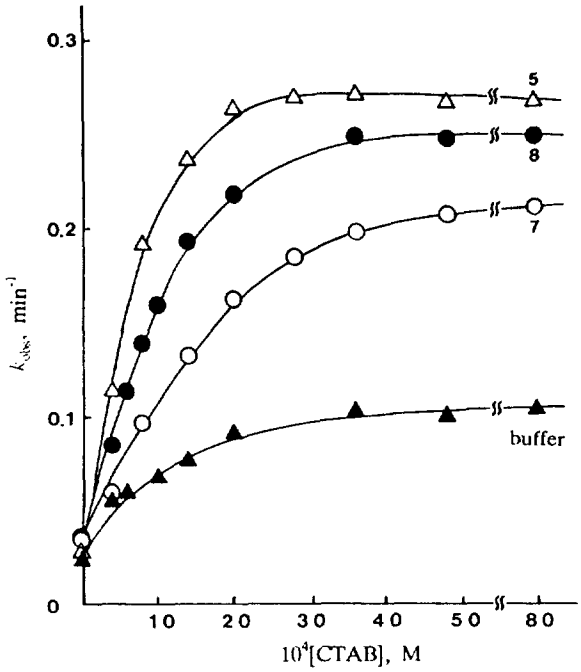


Figure 4. Plots showing micellar effect on rates for reactions of PNPA with *m*-chlorophenoxide (**5**) and benzohydroxamates (**7**, **8**) in 0.1 M borate buffer (pH=9.27) at 25℃.

pared with the phenoxide system. Therefore, the present results clearly indicate that benzohydroxamates (**7**, **8**) are much more strongly solvated than the aryloxides (**1-5**) in H_2O. This is consistent with the report that -C(O)NHOH group is about 3 folds more hydrophilic than -OH group.[14]

The α-Effect in the Absence of CTAB. As shown in Figure 1 both 3-chlorophenoxide (**5**) and benzohydroxamate (**7**) show good linear correlations between k_{obs} and the concentration of nucleophile. The slope of the plot is steeper for the benzohydroxamate than for the 3-chlorophenoxide, indicating that the former is more reactive than the latter although the basicities of the two nucleophiles are similar each other. A comparison of reactivity with basicity has been made more quantitatively in Figure 2. As shown in Figure 2, the aryloxides exhibit a good Brønsted correlation while the two benzohydroxamates (**7**, **8**) deviate significantly from the Brønsted linearity. A break in a Brønsted plot has often been understood as a change in reaction mechanism.[15] However, the present deviations shown by **7** and **8** are not considered due to any mechanistic change. Numerous evidences are available to support that the acyl transfer reaction of the present type proceed *via* a common reaction mechanism, *i.e.*, a rate-determining formation of a tetrahedral intermediate followed by a fast leaving group departure.[3,12,16,17] Therefore, the positive deviations shown by **7** and **8** are considered to be a manifestation of the α-effect in the present system.

However, the enhanced reactivity of the hydroxamates would not be attributed to the solvation effect. If solvation effect is mainly responsible for the α-effect, one would expect that **7** and **8** should not exhibit enhanced reactivity. Because the α-effect nucleophiles **7** and **8** are considered to be more strongly solvated than the corresponding normal nucleophile based on the magnitude of the K_S values, *i.e.*, the K_S values for the α-effect nucleophiles obtained are significantly smaller than the one for the corresponding normal nucleophile as shown in Table 1. The finding of a large α-effect in the present system is clearly an indication that solvation effect is not solely responsible for the α-effect.

The Micellar Effect on Rate. Anionic nucleophilic substitution reactions have often been reported to cause dramatic rate enhancements upon the addition of cationic surfactants in the reaction medium.[13] Such an enhancement in reaction rate has generally been believed due to the result of bringing the two reactants together in a small volume of the surfactant aggregate but not due to an enhancement of the second-order rate constant.[18,19] In fact, Bunton demonstrated that the second-order rate constant in the micellar solution is similar to or smaller than the one in pure H_2O for various S_N2 reactions.[19]

As shown in Table 3 and Figure 3, the reactivity increases significantly with increasing surfactant concentration up to a certain point as expected. However, the rate enhancement for the cyanophenoxide (**6**) is unusually smaller than the one for the other aryloxides as shown in Figure 3. The observed rate constants for **6** in the borate buffer solutions containing CTAB are almost indentical to the one for the buffer solution alone. Such a small contribution of **6** to the observed rate constants would be attributed to its low basicity. This argument is consistent with the result of chlorophenoxide (**4** and **5**) system. Although **4** and **5** are similar in the structure and K_S value, the less basic **5** shows significantly smaller micellar effect than the more basic **4** upon the addition of CTAB.

As shown in Figure 3, the difference in the acidity of the basic aryloxides (**1**, **2** and **3**) is negligible but the rate enhancement upon the addition of CTAB is significantly different each other, *i.e.*, the magnitude of micellar effect increases

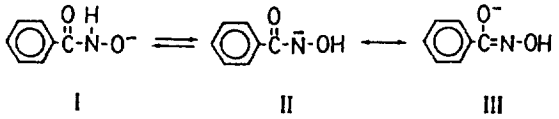
in the same order with increasing the binding constant of them. This clearly indicates that the binding constant K_S is the main factor to influence the reactivity in the micellar solution when the basicity of nucleophiles are comparable each other. This has been more clearly demonstrated in a comparison of the reactivity between **1** and **4**. In the presence of CTAB, **1** exhibits lower reactivity than **4**, although **1** is more basic and reactive than **4** in the absence of the surfactant. One would attribute this unusual reativity of **1** to the low pH of the borate buffer (pH=9.27) in which the basic PhOH would not be completely deprotonated. However, such an unusual reactivity order has also been reported in the previous communication for the same reactions run in carbonate buffer (pH=10.0) in which phenols would be considered to exist mostly as phenoxide ions.[8d] Therefore, the unusual reactivity of **1** would not be attributed to the low pH of the medium but the unusually high interaction of **4** toward the cationic micelle appears to be more responsible for the high reactivity of **4** in the presence of CTAB.

Disappearance of the α-Effect in the Presence of CTAB. As shown in Figure 4, the trend of micellar effect on rate for the α-effect nucleophiles (**7** and **8**) is similar to the one for the aryloxides, *i.e.*, an initial rate enhancement followed by a saturation upon the additions of CTAB to the reaction medium. However, the magnitude of micellar effect for the α-effect nucleophiles is smaller than the one for the normal nucleophile. In consequence, the large α-effect observed in the absence of CTAB has disappeared in the presence of the surfactant. Strikingly, this is an opposite result from the previous one, *i.e.*, an increasing α-effect with increasing CTAB concentration up to a certain point for the reaction of PNPA with butane-2,3-dione monoximate and **4** in borate buffer solution.[8d]

Similarly, no α-effect has been observed for the reactions of substituted phenyl esters in hydroxamic acid surfactants.[20] The absence of the α-effect has been attributed to an improper spacial orientation for the reactants in the stern layer of the micelle.[20] However, the structure of the hydroxamates studied here is quite different from the one used previously and therefore, the argument concerning improper spacial orientation would not be compelling in the present system.

Since the difference in the basicity among **5**, **7** and **8** is considered to be negligible, the effect of micelle on rate would be governed mainly by the difference in the binding constant. As shown in Table 1, the K_S value for the α-effect nucleophiles **7** and **8** are about 10 folds smaller than the one for the corresponding normal nucleophile **5**. Therefore, one might attribute the present disappearance of the α-effect to the solvation effect.

It has been suggested that hydroxamates can have the following structures, namely the oxygen acid and nitrogen acid.[21-23] From extensive IR and UV spectroscopic and acidity measurments Exner has concluded that structure II is more predominent than I in dioxane and aqueous alcohol solvents.[21] A similar conclusion has also been drawn from ^{17}O-NMR study in methanol[22] and from acidity measurment in DMSO.[23] Furthermore, it has not been ruled out the existence of structure III (no longer an α-effect nucleophile) by resonance of II. Thus, one might expect that the reactivity of **7** and **8** is decreased either by steric hindrance of II or by the presence of non α-effect nucleophile (III).



I II III

However, there has been no report that II or III reacted as a nucleophile to give IV or V, as far as our knowledge. Therefore, I would be considered to be the most reactive species among the three structures, and the disappearance of the α-effect in the present system would be the result of the equilibrium of I with II and/or III, since such an equilibrium would decrease the observed rate constant by decreasing the concentration of I.

IV V

However, more systematic studies are required for a better understanding of the unusual α-effect behavior in the present system. Product analysis and investigation of spacial orientation of the reactants in the stern layer are currently underway together with a use of N-substituted benzohydroxamates to avoid the equilibrium of I with II or III in various kinds of buffer solutions.

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Chemistry of Ruthenium Hydridonitrosyl Complexes Containing Chelating Triphosphines I-Structures of $RuH(NO)P_3$ (P_3 : Chelating Triphosphines)

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Chelating triphosphines were applied to freeze the fluxionality and to minimize the number of isomers found in the monophosphine analogues and this technique was proved to be useful. $RuH(NO)P_3(P_3$; Cyttp, ttp and etp) complexes were characterized to have similar trigonal bipyramidal structures with linear NO groups. Cyttp prefers to have a meridional geometry while etp prefers a facial one and ttp complexes are mixture of these two isomers. The crystal structure of RuH(NO)(Cyttp) has been determined to have a distorted trigonal bipyramidal structure with a linear NO in the equatorial plane. The crystals are orthorhombic, space group P_{nma}, with unit cell dimensions $a=16.356(2)$, $b=20.474(2)$, $c=10.915(1)$ Å, $V=3655$ Å^3, $Z=4$, $R=0.035$ and $R_w=0.034$ for the 2900 intensities with $F_o^2>3\sigma(F_o^2)$ and the 208 variables.

Introduction

Although hydridocarbonyl complexes have attracted much attention due to their utility in organic syntheses[1] and catalytic reactions,[2] hydridonitrosyl complexes have been remained unnoticed. Only a few complexes of this category are known ($RuH(NO)L_3$,[3] $[IrH(NO)(PPh_3)_3]^+$,[4] $CpRe(CO)(NO)H$,[5] $CpW(NO)_2H$[6] and $CpW(NO)H(CH_2SiMe_3)$[7] where L is a phosphine or a phosphite) and even fewer examples of chemistry of these complexes are reported.[3,6,8] Considering the flexible nature of NO ligand (formally, $3e^-$ or $1e^-$ donor) and rich chemistry of hydride complexes, it is surprising that the chemistry of these complexes has not been investigated thoroughly up to date. This might be due to some fluxionality[3] and many isomers.[4] Since chelating triphosphine ligands reduce the rate of intramolecular exchange and limit the number of chemically reasonable pathways for the rearrangement,[9,10] it is expected that $MH(NO)P_3$ (P_3; chelating triphosphines) may stop or minimize the fluxional behavior and allowed to be studied easily by spectroscopic method at the room temperature. Also there are several advantages of chelating triphophines over monophosphines such as control of stoichiometry and coordination number due to less tendency toward dissociation.[10] This character appears to be very im-