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Assessing the Activating Effect of the (η^5-C_5Me_5)Ru^+ Group: A Kinetic and NMR Study of the Ionization of the (η^6-Phenylnitromethane)-(η^5-pentamethylcyclopentadienyl)ruthenium Cation in H_2O-Me_2SO Mixtures

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Rates of proton abstraction from the (η^6-phenylnitromethane)(η^5-pentamethylcylopentadienyl)ruthenium cation (**6**) by a variety of bases B (OH^-, carboxylate ions, primary and secondary amines) and of reprotonation of the resulting carbon base **C-6** by the conjugate acids BH have been measured in a 50:50 (v/v) H_2O-Me_2SO mixture at 25 °C. The intrinsic reactivity of **6**, as determined from the Brönsted plots for carboxylate ion or primary amine reactions is rather low: log $k_0^{RCOO^-} = 0.6$; log $k_0^{RNH_2} = 0.1$. These values together with the pK_a value for the ionization of **6** (p$K_a = 5.90$) are typical for the formation of a nitronate-type carbon base, indicating that the $RuCp^{*+}$-complexed phenyl ring is not capable of competing with the exocyclic nitro group in absorbing the negative charge generated by the ionization of **6**. Additional evidence that the cation **6** ionizes to give a zwitterionic carbon base with an exocyclic nitronate functionality comes from the observation that **C-6** undergoes instantaneous protonation at low pH (pH < 3) to give a nitronic acid. ^1H and ^{13}C NMR data collected for the ionization of **6** in 50:50 (v/v) H_2O-Me_2SO and pure Me_2SO agree with the above conclusions. From a comparison of the behavior of **6** with that of (4-nitrophenyl)-nitromethane, the inductive effect of a $RuCp^{*+}$-coordinated phenyl ring is shown to be identical to that of a 4-nitrophenyl ring.

π-Coordination of organotransition metal units is largely used to enhance the electrophilic character of arene or heteroarene rings which would be otherwise unable to react with nucleophilic reagents under reasonably smooth experimental conditions.[1−5] Activation by groups such as $Cr(CO)_3$, $Mn(CO)_3^+$, (η^5-C_5H_5)Fe^+, (η^5-C_5H_5)Ru^+, or (η^5-C_5Me_5)Ru^+ thus allows one to carry out nucleophilic aromatic displacements on unactivated aryl halides and related derivatives.[1−10] These groups are also efficient in promoting breaking of C−H bonds, both in the complexed arene ring or in an alkyl side chain, favoring the generation of carbanionic-type intermediates, which can then react in situ as nucleophiles with various substrates to give a wide range of synthetic applications.[1,3,11−23] Recent works have included the use of the activation provided by organotransition metal units to achieve enantiospecific or diastereospecific deprotonation of the arene or heteroarene ring, leading to challenging developments in asymmetric synthesis.[15−18] With appropriate aromatic substrates, stereoselective benzylic functionalization can also be achieved.[19−21]

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(1) (a) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2979. (b) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Editor-in-Chief; Fleming, I., Deputy Editor-in-Chief; Semmelhack, M. F., Volume Editor; Pergamon: Oxford, U.K., 1991; Vol. 4, p 517.

(2) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

(3) Astruc, D. *Tetrahedron* **1983**, *39*, 4027.

(4) (a) Sutherland, R. G.; Iqbal, M.; Piorko, A. *J. Organomet. Chem.* **1986**, *202*, 307. (b) Lee, C. C.; Abd-El-Aziz, A. J.; Chowdhury, R. L.; Piorko, A.; Sutherland, R. G. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 541. (c) Chowdhury, R. L.; Lee, C.C.; Piorko, A.; Sutherland, R. G. *Ibid.* **1985**, *15*, 2237.

(5) (a) Kündig, E. P.; Jeger, P.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2161. (b) Quattropani, A.; Anderson, G.; Bernardinelli, G.; Kündig, E. P. *J. Am. Chem. Soc.* **1997**, *119*, 4773.

(6) Kamukawa, K.; Uemura, M. *Tetrahedron Lett.* **1996**, *37*, 6359.

(7) Schmalz, H. G.; Schellhaas, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2146.

(8) Semmelhack, M. F.; Schmalz, H. G. *Tetrahedron Lett.* **1996**, *37*, 3089.

(9) (a) Balssa, F.; Gagliardini, V.; Le Corre-Susanne, C.; Rose-Munch, F.; Rose, E.; Vaisserman, *J. Bull. Soc. Chim. Fr.* **1997**, *134*, 537. (b) Rose-Munch, F.; Rose, E. *Trends Organomet. Chem.* **1994**, *1*, 669.

(10) Terrier, F. In *Nucleophilic Aromatic Displacement*; Feuer, H., Ed.; VCH Publishers: New York, 1991; pp 169, 180.

(11) Malas, L.; Jhurry, D.; Latxagne, L.; Grellier, S.; Morel, Y.; Hamdani, M.; Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1990**, 401.

(12) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535, and references therein.

(13) (a) Top, S.; Jaouen, G.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6426. (b) Jaouen, G.; Top, S.; Laconi, A.; Couturier, D.; Brocard, J. *Ibid.* **1984**, *106*, 2207. (c) Top, S.; Vessières, A.; Abjean, J. P.; Jaouen, G. *J. Chem. Soc., Chem. Commun.* **1984**, 428.

(14) (a) Blagg, J.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 492. (b) Blagg, J.; Davies, S. G.; Goodfellow, C. C.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1805.

(15) (a) Kündig, E. P.; Dessboy, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173. (b) Kündig, E. P.; Perret, C.; Rudolph, B. *Helv. Chim. Acta* **1990**, *73*, 1970. (c) Kündig, E. P.; Dessboy, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6962.

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In the past few years, there has been a growing interest in physical organic chemistry studies of σ-complexation or ionization processes involving arenes activated by transition metal−ligand residues.[24−27] The aim of these studies is to provide a better understanding of the electronic mode of action of these moieties by looking at the way they may affect the thermodynamics and kinetics of these processes. Studies of the ionization of diphenylmethane and fluorene carbon acids activated by $Cr(CO)_3$, $(\eta^5\text{-}C_5H_5)Fe^+$, and $Mn(CO)_3^+$ units, e.g. **1**−**3**, as well as of Fischer carbene complexes activated by $Cr(CO)_5$ and $W(CO)_5$ moieties, e.g. **4** and **5**, have recently proved to be very informative on the electronic effect of the corresponding groups.[22a,24,26,27] Interestingly, very comprehensive information on the electronic effect of the $(\eta^5\text{-}C_5H_5)Fe^+$ residue could also be obtained from a determination of metal core electron-binding energies of a number of $(\eta^6$-arene$)(\eta^5$-cyclopentadienyl)iron(II) complexes by X-ray photoelectron spectroscopy.[25]

So far, very little quantitative information is available on the electronic effect of the $(\eta^5\text{-}C_5Me_5)Ru^+$ moiety, i.e., the Cp^*Ru^+ moiety, which has been however used as an activating group in organic synthesis.[28] In this paper, we report a kinetic, thermodynamic and structural study of the ionization of the $(\eta^6$-phenylnitromethane$)(\eta^5$-pentamethylcyclopentadienyl)ruthenium cation **6** according to eq 1 in a 50:50 (v/v) H_2O-Me_2SO mixture and/or pure Me_2SO. As will be seen, the results obtained support the view that the resulting carbon base **C-6** exists mainly as the zwitterion **C-6a**, implying that the −M effect of the exocyclic nitro group overcomes essentially the resonance effect of the Cp^*Ru^+-coordinated phenyl ring. Interestingly, the −I effect of this moiety appears to be the same as that of a (4-nitrophenyl) ring.

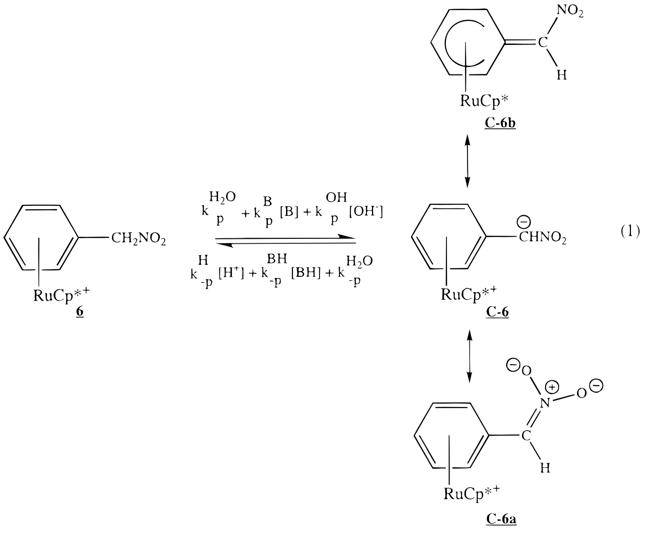
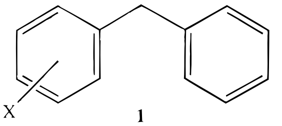


Table 1. Selected Chemical Shift and Coupling Constant Data for the Ionization of 6 in $Me_2SO\text{-}d_6$[a]

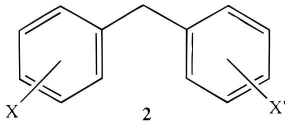
	H_α[b]	C_α[b]	$H_{3,5}$	$C_{3,5}$	$H_{2,6}$	$C_{2,6}$	H_4	C_4
6	5.62	75.8	6.10	87.9	6.10	89.2	6.10	87.6
C-6	6.27	99.9	5.75	86.0	6.35	80.2	5.70	83.9
$\Delta\delta$	0.65	23.9	−0.35	−1.9	0.25	−9.0	−0.40	−3.7

[a] δ in ppm relative to internal reference $SiMe_4$; J in Hz. [b] $^1J(C_\alpha H_\alpha)$ = 150.5 Hz for **6**; $^1J(C_\alpha H_\alpha)$ = 182.1 Hz for **C-6**; ΔJ = 31.6.



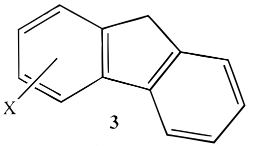
1

X = $Cr(CO)_3$
X = $FeCp^+$



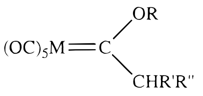
2

X = X' = $Cr(CO)_3$
X = X' = $FeCp^+$



3

X = $Cr(CO)_3$
X = $FeCp^+$
X = $Mn(CO)_3^+$



4 M = Cr
5 M = W

R = CH_3, CH_3CH_2
R' = H,
R" = H, C_6H_5

Results

Structural Studies. Addition of dilute potassium hydroxide to a $\approx 10^{-4}$ mol L^{-1} solution of the cation **6** in 50:50 (v/v) H_2O-Me_2SO resulted in an essentially complete formation of a new species exhibiting an absorption maximum at 324 nm ($\epsilon = 5.7 \times 10^3$ L mol^{-1} cm^{-1}). The idea that the process afforded the carbon base **C-6** as shown in eq 1 was first supported by the finding of a full recovery of **6** upon acidification of the above solution by HCl.

Unambiguous evidence for the formation of **C-6** was obtained by carrying out a ^1H and ^{13}C NMR study of eq 1 in the solvent mixture at hand as well as in $Me_2SO\text{-}d_6$. Only the most pertinent data required for the discussion are given in Table 1. The whole chemical shift and coupling constant data are summarized in Tables S1 and S2. At this stage, two major findings can

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(16) (a) Heppert, J. A.; Thomas-Miller, M. E.; Milligan, M. L.; Van der Velde, D.; Aubé, J. *Organometallics* **1988**, *7*, 2581. (b) Aubé, J.; Heppert, J. A.; Milligan, M. L.; Smith, M. J.; Zeuk, P. *J. Org. Chem.* **1992**, *57*, 3563.

(17) (a) Uemura, J.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859. (b) Uemura, M.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5277.

(18) Schmalz, H. G.; Volk, T.; Bernicke, D.; Haneck, S. *Tetrahedron* **1997**, *53*, 9219.

(19) (a) Gibson (née Thomas), S. E.; Ham, P.; Jefferson, G. R.; Smith, M. H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2161. (b) Gibson (née Thomas), S. E.; Potter, P. C. V.; Smith, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 2757.

(20) (a) Uemura, M.; Isobe, K.; Hayashi, Y. *Tetrahedron Lett.* **1985**, *26*, 767. (b) Uemura, M.; Isobe, K.; Hayashi, Y. *Chem. Lett.* **1985**, 91.

(21) (a) Simpkins, N. S.; Price, D. A.; MacLoed, A. M.; Watat, A. P. *J. Org. Chem.* **1994**, *59*, 1961. (b) Simpkins, N. S.; Price, D. A.; MacLoed, A. M.; Watt, A. P. *Tetrahedron Lett.* **1994**, *35*, 6159.

(22) (a) Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427; (b) *Organometallics* **1982**, *1*, 931.

(23) (a) Cambie, R. C.; Clark, G. R.; Coombe, S. L.; Coulson, S. A.; Rutledge, P. S.; Woodgate, P. D. *J. Organomet. Chem.* **1996**, 507, 1. (b) Janetka, J. W.; Rich, D. H. *J. Am. Chem. Soc.* **1995**, *117*, 7, 10585.

(24) (a) Terrier, F.; Vichard, D.; Chatrousse, A. P.; Top, S.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 690. (b) Terrier, F.; Farrell, P. J.; Lelievre, J.; Top, S.; Jaouen, G. *Ibid.* **1985**, *4*, 1291.

(25) (a) Gassman, P. G.; Deck, P. A. *Organometallics* **1994**, *13*, 1934 and 2890. (b) Deck, P. A.; Jackson, W. F. *Ibid.* **1996**, *15*, 5287.

(26) Zhang, S.; Bordwell, F. G. *Organometallics* **1994**, *13*, 2920.

(27) (a) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526. (b) Bernasconi, C. F.; Flores, F. X.; Sun, W. *Ibid.* **1995**, *117*, 4875. (c) Bernasconi, C. F.; Sun, W. *Organometallics* **1995**, *14*, 5615. (d) Bernasconi, C. F.; Sun, W. *Ibid.* **1997**, *16*, 1926. (e) Bernasconi, C. F.; Leyes, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5169. (f) Bernasconi, C. F.; Sun, W.; Garcia-Rio, L.; Yan, K.; Kittredge, K. *Ibid* **1997**, *119*, 5583. (g) Bernasconi, C. F.; Leyes, A. E. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1641.

(28) Dembek, A. A.; Fagan, P. J. *Organometallics* **1996**, *15*, 1319.

Table 2. pK_a^{CH} and pK_a^{NOH} Values and Related Tautomerization Constants, K_T, for 6, Phenylnitromethane 7, and (4-Nitrophenyl)nitromethane 8 in 50:50 (v/v) H_2O-Me_2SO at 25 °C

	6	**7**[a]	**8**[b]
pK_a^{CH}	5.90	7.93	6.02
pK_a^{NOH}	3	4.75	3.36
K_T	1.2×10^{-4}	6.61×10^{-4}	2.18×10^{-3}

[a] Ref 35 at 20 °C. [b] Ref 36. [c] See eq 12.

be emphasized: (1) the resonances of the exocyclic H_α and C_α atoms of **6** suffer large downfield shifts upon ionization ($\Delta\delta H_\alpha = 1.04$; $\Delta\delta C_\alpha = 30$ ppm in 50% Me_2SO); (2) all recorded ^1H and ^{13}C NMR spectra show the equivalence of the ortho, as well as the meta, protons and carbons of the carbon base **C-6** at probe temperature. A similar situation also prevailed in acetonitrile solution at −45 °C. As will be considered in more detail in the discussion, these results suggest that the C_α carbon of **C-6** is strongly olefinic in nature but that most of the negative charge resulting from the ionization process resides on the exocyclic nitro group in all solvents studied. In other words, the NMR data favor the zwitterionic structure **C-6a** as the main resonance contributor for the carbon base **C-6**.

Kinetic and Equilibrium Measurements. All rate and equilibrium measurements pertaining to the ionization of **6** according to the general eq 1 were carried out in 50:50 (v/v) H_2O-Me_2SO at 25 °C and constant ionic strength I of 0.5 mol L^{-1} maintained with KCl. Pseudo-first-order conditions were used throughout with a large excess of the buffer base or acid reagents over the substrate concentration ($\approx 10^{-4}$ mol L^{-1}). In eq 1, k_p^{OH}, k_p^B and $k_p^{H_2O}$ are the rate constants referring to the deprotonation of **6** by hydroxide ion, the buffer base species ($B = RNH_2$, $RR'NH$, $RCOO^-$), and the solvent, respectively, while k_{-p}^H, k_{-p}^{BH}, and $k_{-p}^{H_2O}$ are the rate constants referring to the reprotonation of **C-6** by hydronium ion, the buffer acid species ($BH = RNH_3^+$, $RR'NH_2^+$, RCOOH), and the solvent, respectively.

Acidity (pK_a^{CH}) of 6. The pK_a^{CH} of **6** was determined from the observed absorbance variations at λ_{max} of **C-6** (324 nm) obtained at equilibrium as a function of pH. Acetic acid buffers of various compositions were used for this purpose. In accordance with eq 2, an excellent straight line with unit slope was obtained on plotting the log values of the ratio of ionized to nonionized **6** as a function of pH. From this plot (not shown), we obtained $pK_a^{CH} = 5.90 \pm 0.04$ (Table 2).

$$\log \frac{[\mathbf{C\text{-}6}]}{[\mathbf{6}]} = pH - pK_a^{CH} \qquad (2)$$

Reaction of 6 in NaOH and Amine Buffer Solutions. In agreement with a direct equilibrium approach according to eq 1, oscilloscope traces of the reaction progress obtained in stopped-flow experiments revealed that only one relaxation time is associated with the interconversion of **6** and **C-6** in all amine buffers as well as in all dilute NaOH solutions employed. Supplementary Table S3 summarizes the observed pseudo-first-order rate constants, k_{obsd}, measured under the different experimental conditions studied.

From the k_{obsd} values obtained in NaOH solutions, an excellent straight line fitting the simple eq 3 was

$$k_{obsd} = k_p^{OH}[OH^-] \qquad (3)$$

obtained (not shown), which afforded $k_p^{OH} = 2.8 \times 10^4$ L mol^{-1} s^{-1}. Since the intercept was negligible, the rate constant $k_{-p}^{H_2O}$ was calculated from $k_{-p}^{H_2O} = k_p^{OH}(K_s/K_a^{CH})$, where K_s is the autoprotolysis constant of the 50:50 (v/v) H_2O-Me_2SO mixture at $I = 0.5$ mol L^{-1} ($pK_s = 15.83$ at 25 °C):[29] $k_{-p}^{H_2O} = 3.5 \times 10^{-6}$ s^{-1}.

Working out the data obtained in the pH range 7.54−9.99 covered by the various amine buffers employed indicated that both the hydroxide ion pathway and the buffer base pathway were important in determining k_{obsd} in these systems; that is, k_{obsd} is given in eq 4. Thus, the various k_p^B rate constants were determined from the slopes of the various linear plots of k_{obsd} vs [B] obtained at constant pH in the different buffer systems studied. The k_p^B values, together with the related k_{-p}^{BH} values which were calculated by means of eq 5, are summarized in Table 3.

$$k_{obsd} = k_p^B[B] + k_p^{OH}[OH^-] \qquad (4)$$

$$k_{-p}^{BH} = k_p^B \frac{K_a^{BH}}{K_a^{CH}} \qquad (5)$$

Reaction of 6 in HCl and Carboxylic Acid Buffer Solutions. The simple equilibrium approach of eq 1 also prevailed in the pH range of 4.45−6.32 covered by buffers made up from acetic acid ($pK_a^{BH} = 5.84$), methoxyacetic acid ($pK_a^{BH} = 4.65$), and formic acid ($pK_a^{BH} = 4.45$). The corresponding k_{obsd} values are collected in supplementary Table S4. In the acetic acid buffers, where eq 1 could be approached from both reactant and product sides ($pK_a^{BH} \approx pK_a^{CH}$), both buffer base and acid pathways contributed to k_{obsd}, with the data fitting eq 6. In accordance with this equation, plots of k_{obsd} vs [CH_3COOH] at constant pH, i.e., at a given p = [$RCOO^-$]/[RCOOH] ratio, were linear with negligible intercepts, but the slopes of these plots decreased with decreasing pH (Figure S1). From a standard treatment of the data, one obtains $k_p^{CH_3COO^-} = 3.90$ L mol^{-1} s^{-1}; $k_{-p}^{CH_3COOH} = 5.65$ L mol^{-1} s^{-1}. For the two other buffer systems with $pK_a^{BH} \le pK_a^{CH} - 1.25$, experimental conditions were chosen so that to have eq 6 reducing to eq 7, making the determination of the k_{-p}^{BH} rate constants straightforward.

$$k_{obsd} = k_p^B[B] + k_{-p}^{BH}[BH] = (pk_p^B + k_{-p}^{BH})[BH] \qquad (6)$$

$$k_{obsd} = k_{-p}^{BH}[BH] \qquad (7)$$

Contrasting with the above situation, oscilloscope pictures revealed that reprotonation of **C-6** no longer occurred according to eq 1 in dilute HCl solutions (7×10^{-4} to 5×10^{-3} mol L^{-1}) as well as in the most acidic chloroacetic acid buffers (pH: 3.23−4.19). Instead, they

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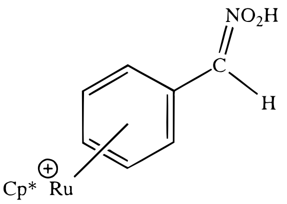
(29) Terrier, F.; Lelièvre, J.; Chatrousse, A. P.; Farrell, P. G. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1479.

Table 3. Second-Order Rate Constants for the Ionization of 6 in 50:50 (v/v) H_2O-Me_2SO[a]

numbering	buffer (BH or B)	pK_a	k_p^B (L mol^{-1} s^{-1})	k_{-p}^{BH} (L mol^{-1} s^{-1})
1	butylamine	9.99	456	0.042[c]
2	2-(*N*-methylamino)ethanol	9.39	434	0.16[c]
3	2-methoxyethylamine	9.11	74.1	0.052[c]
4	allylamine	9.08	62.5	0.047[c]
5	glycinamide	8.01	18.4	0.16[c]
6	glycine ethyl ester	7.24	20.9	1.09[c]
7	acetate ion	5.84	3.93[c]	5.65
8	methoxyacetate ion	4.65	2.81[c]	57.40
9	formate ion	4.45	1.45[c]	46.80
10	chloroacetate ion	3.71	0.65[c]	115.4
11	OH^-	17.34	2.8×10^4	1.19×10^{-7}[b]
12	H_3O^+	−1.44	2.53×10^{-5}[d]	555

[a] $I = 0.5$ mol L^{-1} (KCl); $T = 25$ °C. [b] $k_{-p}^{H_2O}/27.6$ with $k_{-p}^{H_2O}$ calculated from $k_p^{OH}K_s/K_a^{CH}$ with pK_s = 15.83 at 25 °C.[29] [c] Calculated from k_p^B or k_{-p}^{BH} via eq 5. [d] $k_p^{H_2O}/27.6$ with $k_p^{H_2O}$ calculated from $K_a^{CH}k_{-p}^{H}$.

showed two steps with the instantaneous formation of an intermediate species X, which subsequently decomposed to **6**. As will be discussed later, there is little doubt that X arises from protonation of the nitro group of **C-6** and is therefore the nitronic acid **C-6aH**. Figure S$_2$ shows the UV−visible absorption spectrum of **C-6aH** (λ_{max} = 290 nm), recorded for a 5×10^{-3} mol L^{-1} HCl solution.



C-6aH

In view of the fast initial formation of X, the appropriate scheme for the conversion of **C-6** to **6** at low pH is as depicted in eq 8, where K_a^{NOH} is the acidity constant of the nitronic acid functionality of **C-6aH**. Accordingly, the measured k_{obsd} values (Table S2) for this process should fit the general eq 9 in chloroacetic acid buffer solutions and the reduced eq 10 in HCl solutions.

$$\mathbf{C\text{-}6aH} \xrightleftharpoons{K_a^{NOH}} \mathbf{C\text{-}6} \xrightarrow{k_{-p}^{H}[H^+] + k_{-p}^{H_2O} + k_{-p}^{BH}[BH]} \mathbf{6} \tag{8}$$

$$k_{obsd} = (k_{-p}^{H}[H^+] + k_{-p}^{H_2O})\frac{K_a^{NOH}}{K_a^{NOH} + [H^+]} + k_{-p}^{BH}[BH]\frac{K_a^{NOH}}{K_a^{NOH} + [H^+]} \tag{9}$$

$$k_{obsd} = (k_{-p}^{H}[H^+] + k_{-p}^{H_2O})\frac{K_a^{NOH}}{K_a^{NOH} + [H^+]} \tag{10}$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_{-p}^{H}[H^+]} + \frac{1}{k_{-p}^{H}K_a^{NOH}} \tag{11}$$

In accord with eq 10, a curvilinear k_{obsd} vs [H$^+$] plot was obtained from measurements in HCl solutions. Since the solvent contribution to the reprotonation of **C-6** is negligible in the pH range at hand (vide supra), eq 10 may be rewritten in the form of eq 11, which predicts that a plot of 1/k_{obsd} vs 1/[H$^+$] should afford a satisfactory straight line. Figure 1 confirms this expectation, leading to k_{-p}^{H} = 555 L mol^{-1} s^{-1}; $k_{-p}^{H}K_a^{NaOH}$ = 0.42 s^{-1}. Interestingly, the latter value compares well with that of the plateau observed at the highest HCl concentrations (see Table S4): $k_{-p}^{H}K_a^{NOH}$ = 0.46 s^{-1}. Combining the k_{-p}^{H} and $k_{-p}^{H}K_a^{NOH}$ values thus gives a pK_a^{NOH} value of ≈3 for the ionization of the NOH function of **C-6aH**. From the k_{-p}^{H} value, we also calculated the $k_p^{H_2O}$ rate constant for deprotonation of **6** by the solvent: $k_p^{H_2O} = 6.08 \times 10^{-4}$ s^{-1}.

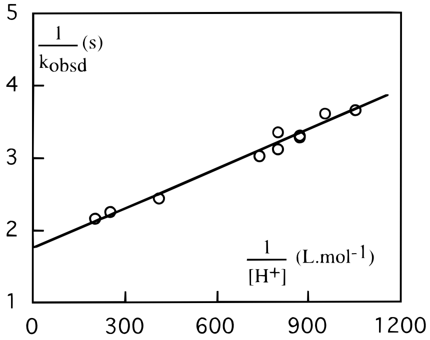


Figure 1. Inversion plot according to eq 11 for protonation of **C-6** in HCl solutions in 50% H_2O/50% Me_2SO (v/v); T = 25 °C; I = 0.5 mol L^{-1}.

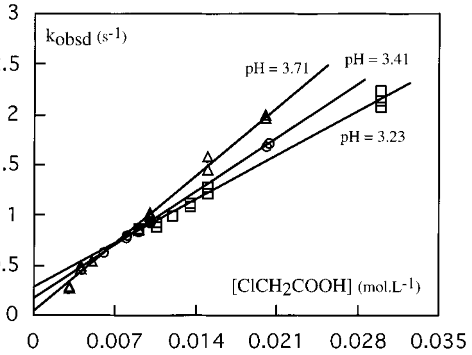


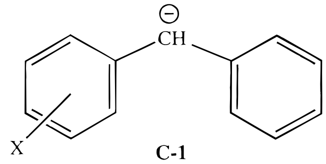
Figure 2. Effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for protonation of **C-6** in chloroacetic acid buffers in 50% H_2O/50% Me_2SO (v/v); T = 25 °C; I = 0.5 mol L^{-1}.

Considering the reprotonation of **C-6** in chloroacetic acid buffers, eq 9 implies that linear plots of k_{obsd} vs [BH] should be obtained at constant pH but that the slopes of these plots should decrease with increasing H$^+$ concentration. As shown in Figure 2, the data obtained at pH 3.23, 3.41, and 3.71 confirmed these expectations. In addition, the values of the intercepts agreed well with estimates made from eq 10. After appropriate correction for the $K_a^{NOH}/K_a^{NOH} + [H^+]$ terms, the slopes of the lines in eq 9 gave three consistent values for $k_{-p}^{ClCH_2COOH}$ (115 L mol^{-1} s^{-1}). The corresponding $k_p^{ClCH_2COO^-}$ rate constant was calculated from eq 5. All second-order rate constants for deprotonation of **6** (k_p^{OH}, k_p^{B}, $k_p^{H_2O}/27.6$) and reprotonation of **C-6** (k_{-p}^{H}, k_{-p}^{BH}, $k_{-p}^{H_2O}/27.6$) in 50:50 (v/v) H_2O-Me_2SO are collected in Table 3.

Discussion

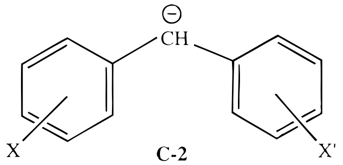
Structure of the Carbon Base C-6 and the Related Nitronic Acid C-6aH. As can be seen in Table 1, the ionization of the cation **6** is associated with large downfield shifts of the resonances of the exocyclic H_α and C_α atoms: $\Delta\delta H_\alpha = 1.04$, $\Delta\delta C_\alpha = 30$ ppm in 50% H_2O−50% Me_2SO (Tables S1 and S2). Although such $\Delta\delta$ values are the results of two opposing effects, namely, a high-field shift caused by increased electron density at C_α in the ionized species **C-6** and a low-field shift caused by the sp_3-sp_2 rehybridization of this carbon, their large positive character suggests that the rehybridization factor is predominant on going from **6** to **C-6**.[24,30−32] Consistent with the idea of a strong olefinic nature of C_α in **C-6** is the concomitant observation that the ionization of **6** induces a large increase in the $^1J_{C\alpha H\alpha}$ coupling constant ($\Delta J = 31.6$ Hz) together with the high value of this coupling constant for the carbon base **C-6**: $^1J_{C\alpha H\alpha} = 182.1$ Hz in Me_2SO-d_6.[30] These features imply that breaking of a $C_\alpha H_\alpha$ bond in **6** goes along with an extensive delocalization of the resulting negative charge either on the exocyclic nitro group (structure **C-6a**) or through the Cp*Ru$^+$-complexed ring (structure **C-6b**) of the conjugate carbon base.

In fact, several observations leave no doubt that it is the nitronate canonical form **C-6a** and not the cyclohexadienyl structure **C-6b** that plays the major role in determining the stability of **C-6**. First it is found that the ionization of **6** does not induce a nonequivalence of the ortho as well as of the meta protons and carbons of the complexed ring of **C-6**. Such a situation is in marked contrast with that found to prevail in the case of carbon bases such as **C-1** (X = $Cr(CO)_3$, $FeCp^+$) and **C-2** (X = X′ = $Cr(CO)_3$, X = X′ = $FeCp^+$). In these instances, the importance of the cyclohexadienyl structures and therefore of the absorption of the negative charge by the complexed ring was also demonstrated by other significant features which are not observed in the case of **C-6**:[22,24,33,34] (1) with the exception of that for the ipso carbon, the resonances of the carbons of the coordinated ring move noticeably to high field upon ionization of the parent carbon acids; for example, $\Delta\delta C$ values on the order of 36, 15, and 9 ppm were observed for the ortho, para, and meta carbons, respectively, upon ionization of the diphenylmethane **1** (X = $FeCp^+$) to give the carbon base **C-1** (X = $FeCp^+$); (2) there was a concomitant upfield shift of the resonances of the protons of this ring as well as of the proton and carbon resonances of the cyclopentadienyl ring; again for the ionization of **1** (X = $FeCp^+$), we have $\Delta\delta(H) = 0.4-2.4$ for the complexed ring; $\Delta\delta(H) = 0.78$, $\Delta\delta(C) = 6.42$ for the cyclopentadienyl ring.[24a] Obviously Table 1 does not reveal similar changes in the absorption patterns upon ionization of the cation **6**. Instead, it is observed in Me_2SO that the resonances of the ortho protons of the Cp*Ru$^+$-complexed ring move slightly to low field ($\Delta\delta = 0.25$) while those of the meta and para protons move to high field ($\Delta\delta H_{3,5} = -0.35$, $\Delta\delta H_4 = -0.4$) to a much lower extent than in the $FeCp^+$ systems. At the same time, the corresponding carbon resonances of this ring suffer very modest upfield shifts, as it is also the case for the resonances due to the ring and methyl groups of the cyclopentadienyl moiety of **C-6** (see Table S2). Clearly, all these results agree with the view that the zwitterionic form **C-6a** provides the best representation for the carbon base **C-6**.



C-1

X = $Cr(CO)_3$
X = $FeCp^+$



C-2

X = X′ = $Cr(CO)_3$
X = X′ = $FeCp^+$

That the NO_2 group overcomes the Cp*Ru$^+$-complexed phenyl ring in accommodating the negative charge accounts very well for the finding that the UV−visible spectrum of **C-6** shows an absorption maximum at a wavelength ($\lambda_{max} = 324$ nm) that is essentially the same as that of the phenylnitromethane anion **C-7a** in 50:50 (v/v) H_2O-Me_2SO.[35,36] In general, benzylic-type carbon acids activated by organometallic residues give rise to strongly colored conjugate carbon bases,[22,24] e.g., $\lambda_{max} = 585$ nm for **C-2** (X = X′ = $FeCp^+$) in 50:50 (v/v) H_2O-Me_2SO. Also it is noteworthy that the changes in the proton and carbon chemical shifts brought about by the ionization of **6** are similar to those observed upon ionization of (4-nitrophenyl)nitromethane **8** to give the carbanion **C-8**, whose stability has been shown to derive mostly from the nitronate resonance structure **C-8a** and only very little from the cyclohexadienyl structure **C-8b**.[36] As far as the nitronate structure **C-6a** is largely predominant in determining the stability of **C-6**, it is reasonable to suggest that the protonation process observed at low pH affords the nitronic acid **C-6aH**.

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(30) Stothers, J. P. In *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 210.

(31) Bradamante, S.; Pagani, G. A. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1035.

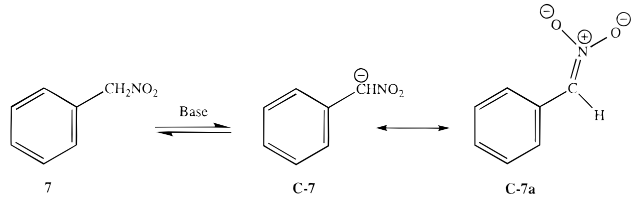
(32) Simonnin, M. P.; Xie, H. Q.; Terrier, F.; Lelièvre, J.; Farrell, P. G. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1553.

(33) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1977**, *141*, 99.

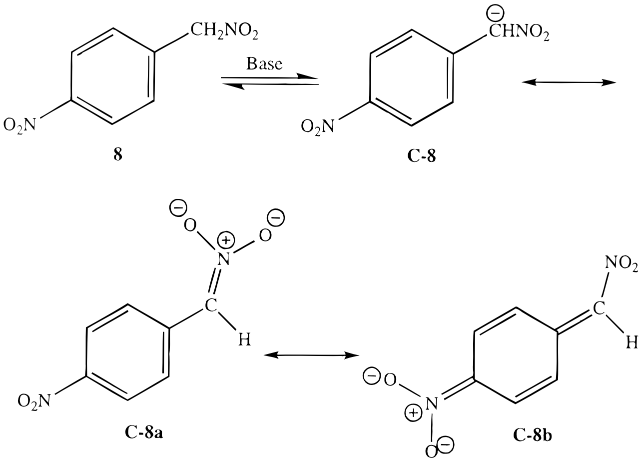
(34) (a) Hamon, J. R.; Astruc, D.; Roman, E. *J. Am. Chem. Soc.* **1981**, *103*, 2431. (b) Astruc, D.; Hamon, J. R.; Roman, E.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 7502.

(35) Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S.; Ni, J. X. *J. Org. Chem.* **1988**, *53*, 3342.

(36) Moutiers, G.; Thuet, V.; Terrier, F. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1479.



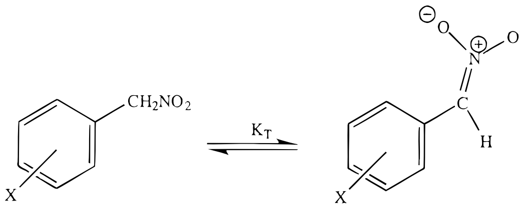
7 C-7 C-7a



8 C-8 C-8a C-8b

CH and NOH Acidities of 6. The pK_a^{CH} value for ionization of the cationic carbon acid **6** is 5.90 as compared with pK_a^{CH} values of 7.93 and 6.02, respectively, for phenylnitromethane **7** and (4-nitro-phenyl)-nitromethane **8** in 50:50 (v/v) H_2O-Me_2SO (Table 3).[35,36] Complexation of the phenyl group of **6** by the Cp*Ru$^+$ moiety has therefore the same acidifying influence ($\Delta pK \approx 2$) as that exerted by the para-NO_2 group in **8**. Taking into account that the role of the resonance cyclohexadienyl structures **C-6b** and **C-8b** is of minor importance in the stabilization of the corresponding carbon bases **C-6** and **C-8**, it is reasonable to consider the above acidifying effects as being for the most part the reflection of the −I effects of a Cp*Ru$^+$-complexed phenyl ring and a para-nitrophenyl ring.

Table 2 also shows that the aci-forms of the Cp*Ru$^+$ and paranitro-derivatives **6** and **8** are similarly acidic, exhibiting pK_a^{NOH} values of 3 and 3.36, respectively, in 50:50 (v/v) H_2O-Me_2SO compared with a pK_a^{NOH} value of 4.75 for the aci-form of phenylnitromethane **7** in the same solvent mixture. Combining the pK_a^{CH} and pK_a^{NOH} values leads to the equilibrium constant K_T measuring the extent of the conversion of these carbon acids into their corresponding aci-forms (eq 12).



(12)

6 X=Cp*Ru$^+$ **C-6aH**
7 X= H **C-7aH**
8 X= NO_2 **C-8aH**

As found previously for the phenylnitromethane systems the K_T value for the conversion **6** ⟺ **C-6aH** is low: $K_T \approx 1.2 \times 10^{-4}$. This accounts for the failure to detect the presence of **C-6aH** in ^1H and ^{13}C NMR spectra recorded under common experimental conditions in 50:50 (v/v) H_2O-Me_2SO or pure Me_2SO.

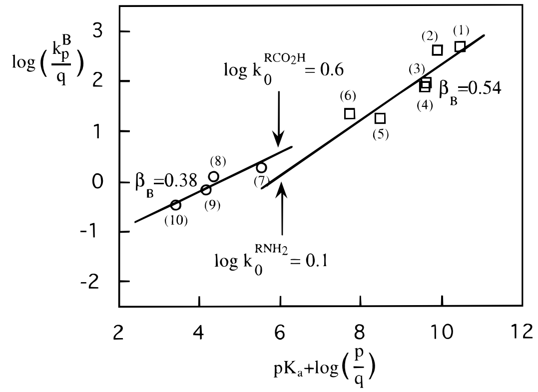


Figure 3. Brönsted plots for deprotonation of **6** by various amine catalysts and carboxylic acid catalysts in 50% H_2O/50% Me_2SO (v/v); $T = 25$ °C; $I = 0.5$ mol L^{-1}. The numbering of the catalysts is given in Table 3.

Intrinsic Reactivity of 6. Brönsted plots pertaining to the deprotonation of **6** by primary amines and carboxylate ions are shown in Figure 3. All related Brönsted β_B and α_{BH} coefficients, e.g., $\beta_{RNH2} = 0.54$; $\beta_{RCOO^-} = 0.38$, fall in the range (0.5 ± 0.1) commonly found for ionization of carbon acids, suggesting that proton transfer is about half-complete at the transition states of reactions 1. To be noted, however, is that β_{RNH2} is somewhat higher than β_{RCOO^-}, in constrast with what is generally observed and in disagreement with the idea that this coefficient should be higher for the less thermodynamically favored carboxylate systems.[37] Failure of the reactivity−selectivity principle in accounting for data pertaining to the ionization of carbon acids has often been noted by various authors.[37−39] Also noteworthy in Figure 3 is that the point for *N*-methylaminoethanol—a secondary amine—does not strongly deviate from the Brönsted line for primary amines. Due to the stronger solvation of the conjugate acids of primary amines compared to that of secondary amines, coupled with late development of this solvation along the reaction coordinate, secondary amines are generally more efficient catalysts than similarly basic primary amines by a factor of 5−10. Steric factors have generally been invoked to account for the reduced reactivity of secondary amines,[37] but such a situation has not been encountered in studies of the ionization of phenylnitromethane **7**. On these grounds it remains difficult at this stage to understand why the reactivity of *N*-methylaminoethanol is apparently reduced in the ionization of **6**.

Extrapolation of the various Brönsted plots in Figure 3 to $pK_a^{BH} + \log p/q = pK_a^{CH}$ afforded the values of the intrinsic rate constants, k_0, for deprotonation of **6** by primary amines and carboxylic acid catalysts.[37,40] These

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[37] (a) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (c) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119. (d) Bernasconi, C. F.; Panda, M.; Stronach, M. W. *J. Am. Chem. Soc.* **1995**, *117*, 9206, and references therein.

[38] (a) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1976**, *16*, 125.

[39] Moutiers, G.; El Fahid, B.; Goumont, R.; Chatrousse, A. P.; Terrier, F. *J. Org. Chem.* **1996**, *61*, 1978.

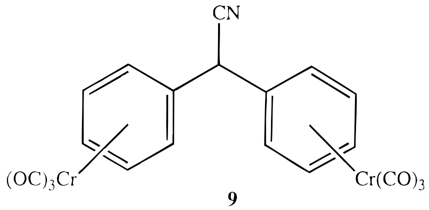
[40] (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249.

Table 4. Intrinsic Reactivities for Ionization of 6 and Some Representative Carbon Acids in 50:50 (v/v) H_2O-Me_2SO

CH acid	base	log k_0
11a	RR′NH	$4.58^{a,d}$
	RNH_2	$3.76^{a,d}$
9	$RCOO^-$	$4.59^{a,c}$
	RR′NH	$3.30^{a,c}$
	RNH_2	$2.94^{a,c}$
11b	RNH_2	$2.84^{a,d}$
10a	RR′NH	$3.70^{a,c}$
	RNH_2	$(3)^{a,f}$
10b	RR′NH	$2.70^{a,e}$
	RNH_2	$(2)^{a,f}$
2 ($X = X' = FeCp^+$)	RNH_2	$\approx 2.30^{b,g}$
6	$RCOO^-$	0.6^{b}
	RNH_2	0.1^{b}
CH_3NO_2	RR′NH	$0.73^{a,h}$
	RNH_2	$\approx(0)^{a,f}$
7	$RCOO^-$	$-0.57^{a,h}$
	RR′NH	$-0.25^{a,h}$
	RNH_2	$(-0.95)^{a,f}$
8	$RCOO^-$	$0.11^{b,i}$
	RNH_2	$-1.08^{b,i}$

[a] $T = 20$ °C. [b] $T = 25$ °C. [c] Ref 42a. [d] Ref 43. [e] Ref 42c. [f] Values in parentheses estimated on the basis that log k_0 values for primary amines are generally lower than those for secondary amines by about 0.7 log k unit.[37] [g] Estimated value in 30:70 (v/v) H_2O-Me_2SO; see ref 24a. [h] Ref 35. [i] Ref 36.

k_0 values are compared in Table 4 with similar data available for some carbon acids known to exhibit either a nitroalkane behavior, i.e., nitromethane, **7** and **8**, or a nitrobenzyl behavior. The key feature in Table 4 is that the intrinsic reactivity of **6** is very low, i.e., log $k_0^{RNH_2} = 0.1$, log $k_0^{RCOO^-} = 0.6$, comparing well with that of nitromethane,[35] phenylnitromethane **7**,[35] and (4-nitrophenyl)nitromethane **8**[36,41] but not at all with that of the $Cr(CO)_3$ and $CpFe^+$-complexed diphenylmethanes **2** and **9**,[24a,42a] the benzylcyanides **10** ($X = H, NO_2$),[42b,c] or the fluorenes **11** ($X = CN, CO_2CH_3$).[43] Interestingly, these six compounds have all been shown to ionize with formation of carbanions whose negative charge is essentially delocalized through the complexed or nitro-substituted phenyl ring or the fluorenyl system. On the basis of intrinsic reactivity data, there is therefore no doubt that **6** behaves largely as a phenylnitromethane compound.



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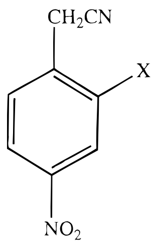
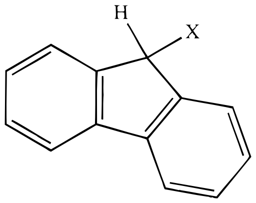


10 X=H
X=NO_2



11 X=CN
X=CO_2CH_3

Experimental Section

Synthesis. Manipulations were carried out on a vacuum line using standard Schlenk techniques under argon; solvents were purified and dried prior to use by conventional distillation techniques under argon. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300-MHz instrument, and chemical shifts are related in Tables 1 and 2. The high-resolution mass spectra were obtained on a conventional EB-geometry mass spectrometer JEOL-AX-500 and DEC data system (JEOL-Europe-sa, Croissy sur Seine, France). Fast-atom bombardment ionization was performed with xenon atoms at 6 keV formed from a beam of 10 mA flux.

[(η^6-Phenylnitromethane)(η^5-pentamethylcyclopentadienyl)ruthenium][CF_3SO_3] (6). A 1.03 mmol amount of [Cp*Ru(CH_3CN)$_3$][CF_3SO_3] (prepared in situ following Fagan's method[44]) in a mixture of CH_3CN/THF (10/10 mL) was refluxed 5 h in the presence of 1.41 mmol (193 mg) of phenylnitromethane (obtained from the reaction of silver nitrite with benzylbromide, following the litterature[45]). The brown solution was concentrated under vacuum, followed by addition of 50 mL of diethyl ether to give a brown precipitate, which was washed several times by diethyl ether (yield: 420 mg; 78%). Mass spectrum (obsd): m/z 374.0665 (reference m-nitrobenzyl alcohol); $C_{17}H_{22}NO_2Ru$ requires 374.0694.

C-6. The ionization of **6** was monitored in an NMR tube in the presence of an excess of potassium *tert*-butoxide in various deuterated solvents.

Kinetic Studies. Materials. Me_2SO was purified by fractional distillation from CaH_2 under reduced pressure and stored under nitrogen and over molecular sieves. Buffers (carboxylic acids and primary amines) were all commercial products which were purified or distilled prior to use. Solutions in 50:50 (v/v) H_2O-Me_2SO were made up as described previously.[36]

Rate and pK_a Measurements. The pK_a^{CH} values of **6** were measured at 25 °C in 50:50 (v/v) H_2O-Me_2SO, using a conventional spectrophotometer and previously calibrated acetic acid buffers. The pK_a^{NOH} value of **C-6aH** was measured by using a Durrum stopped-flow spectrophotometer, following the initial absorbance changes brought about by protonation of the conjugate carbanion **C-6** in dilute HCl and chloroacetic acid buffer solutions. Kinetic measurements were also carried out with a Durrum stopped-flow spectrophotometer equipped with a thermostated cell compartment (25 ± 0.2 °C). Pseudo-first-order rate constants summarized in supplementary Tables S1 and S2 are based upon average values obtained from at least three repetitive runs conducted at a given pH and a given buffer composition. All reactions were found to be kinetically first-order in **6** up to at least 90% of the overall reaction.

Supporting Information Available: ^1H and ^{13}C NMR data for the cation **6** and the related carbon base **C-6** in $(CD_3)_2SO$ and 50:50 (v/v) $H_2O-(CD_3)_2SO$ mixture in Tables S1 and S2; observed first-order rate constants, k_{obsd}, for the ionization of **6** by hydroxide solutions and amine buffers (Table S3) and protonation of carbon base **C-6** by hydrochloric acid

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(41) As suggested by a referee, the somewhat lower log k_0 value for **8** than for **6** tends to indicate that the resonance effect of the p-nitrophenyl group is not completely negligible as compared to its inductive effect in governing the stability of the related carbanion and therefore the pK_a value of **8**.

(42) (a) Bernasconi, C. F.; Bunnell, R. D.; Terrier, F. *J. Am. Chem. Soc.* **1988**, *110*, 6514. (b) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 11446. (c) Bernasconi, C. F.; Hibdon, S. A. *Ibid.* **1983**, *105*, 4343.

(43) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1987**, *109*, 7115.

(44) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *11*, 1698.

(45) (a) Kornblum, N. *Org. React. (N. Y.)* **1962**, *12*, 101. (b) Avery, S.; Butler, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1110.

solutions and carboxylic acid buffers (Table S4); effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for protonation of **C-6** in acetic acid buffers in a 50:50 (v/v) mixture (Figure S1); and the UV–vis absorption spectra of **C-6** and the related nitronic acid **C-6aH** in a 5×10^{-2} mol L^{-1} solution in a 50:50 (v/v) mixture (Figure S2) (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfiche version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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