Nucleophilic Addition of N,N-Dimethylaniline to the (Cyclobutadiene)nitrosyldicarbonyliron Cation: A Kinetic and Structural Study[†]

Joseph C. Calabrese and Steven D. Ittel*

Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Hyung Soo Choi, Steven G. Davis, and Dwight A. Sweigart*

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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The electrophilic aromatic substitution reaction between N,N-dimethylaniline and the cyclobutadiene ring in $[(C_4H_4)Fe(CO)_2NO]PF_6$ yields the η^3 -cyclobutenyl complex $[(Me_2NC_6H_4C_4H_4)Fe(CO)_2NO]$ (2). Spectroscopic studies suggest that substitution occurs exclusively at the carbon para to the NMe₂ group and that the product has exo stereochemistry. A kinetic study in acetonitrile showed the reaction to be second order overall with the following activation parameters: $\Delta H^* = 11.2 \pm 1.5$ kcal; $\Delta S^* = -31 \pm 5$ cal deg⁻¹ mol⁻¹. A mechanism is suggested that involves initial π -complex formation followed by rate-determining conversion to a σ complex. A single-crystal X-ray analysis of 2 at -100 °C showed that it crystallizes in the monoclinic space group P_{2_1}/c with a = 16.690 (2) Å, b = 6.310 (1) Å, c = 26.716 (3) Å, $\beta = 96.46$ (1)°, Z = 8, R = 0.036, and $R_w = 0.044$. The structure confirms the exo attack of the N,N-dimethylaniline para carbon on the coordinated cyclobutadiene. The bond distances and angles in the cyclobutenyl group are similar to previously reported structures. The dihedral angle between the enyl plane (C_7, C_4, C_5) and the nonbonded plane (C_5 , C_6 , C_7) is 26.5° (Figure 1).

Introduction

Cyclic π -hydrocarbons can be made electrophilic by coordination to transition metals. Subsequent nucleophilic attack on the activated π -hydrocarbon is a reaction of increasing utility in catalytic and stoichiometric transformations. The most significant synthetic uses involve the direct addition of a carbanion nucleophile to the coordinated ring, thus forming a new carbon-carbon bond.¹ However, with very electrophilic systems, activated aromatic molecules can function as the nucleophile. Thus N,N-dimethylaniline and pyrrole undergo² electrophilic aromatic substitution with the cyclohexadienyl ring in $[(C_6H_7)Fe(CO)_3]^+$ and the tropylium ring in $[(C_7H_7)Cr (CO)_{3}]^{+}$.

Several years ago we reported³ that N,N-dimethylaniline reacts with the cyclobutadiene ring in $[(C_4H_4)Fe(CO)_2NO]^+$ according to reaction 1. In this paper we present the



synthesis and X-ray structure of 2 and a kinetic study of reaction 1. The substitution in reaction 1 occurs quantitatively, with exclusive electrophilic attack at the carbon para to the dimethylamino group. The dimethylanilino substituent in the cyclobutenyl ring in 2 is positioned exo to the metal.

This report appears to be only the fourth full X-ray structure of a transition-metal cyclobutenyl complex.⁴⁻⁶

Experimental Section

General Remarks. Nitromethane and acetonitrile were dried and fractionally distilled under nitrogen prior to use. N,N-dimethylaniline was distilled from KOH pellets. $[(C_4H_4)Fe(C_4H_4$ O_2NO PF₆ was prepared according to a published procedure.⁷

[†]Contribution No. 3096.

Infrared spectra were recorded on a Perkin-Elmer 680 spectrophotometer and ¹H NMR spectra at 250 MHz on a Bruker WM 250 spectrometer.

Synthesis of $(Me_2NC_6H_4C_4H_4)Fe(CO)_2(NO)$ (2). N,N-Dimethylaniline (0.15 g, 1.24 mmol) was added to $[(C_4H_4)Fe(C_5)]$ O_2NO PF₆ (0.30 g, 0.88 mmol) in 10 mL of nitromethane under nitrogen. The reaction mixture was covered with aluminum foil and left for 2.5 h at room temperature. An IR spectrum then showed that the reaction had gone to completion. The solution then was placed on top of an acidic alumina column and eluted with diethyl ether to give a red solution. This solution was washed with water and evaporated. The resulting red solid was dissolved in pentane and slowly cooled to -10 °C to give 0.22 g (79%) of well-formed, deep red crystals: mp 99-100 °C dec; IR (cyclohexane) ν (CO) 2037, 1989 cm⁻¹, ν (NO) 1755 cm⁻¹; NMR (CDCl₃) δ 2.94 (6 H, CH₃), 3.77 (d, J = 5 Hz, 1 H, endo H), 5.20 (s, 2 H, enyl H), 5.40 (d, J = 5 Hz, 1 H, enyl H), 6.70 and 7.18 (d, J =9 Hz, 4 H, phenyl). Anal. Calcd for $C_{14}H_{14}N_2O_3Fe: C, 53.53; H$, 4.49; N, 8.92. Found: C, 53.39; H, 4.48; N, 8.92.

Kinetic Studies. Reaction 1 was followed in nitromethane and acetonitrile solvents under nitrogen. Pseudo-first-order conditions were used with N,N-dimethylaniline in excess (0.05–1.0 M) over the $[(C_4H_4)Fe(CO)_2NO]PF_6$ concentration, which was $(1-5) \times 10^{-3}$ M. The pseudo-first-order rate constant, k_{obsd} , was determined at least twice at each of seven or more nucleophile concentrations. For the nucleophile at 1.0 M, a Durrum stop-

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Table I. Summary of X-ray Diffraction Data

complex	$(Me_NC_H_C_H_)Fe(CO)_(NO)$
formula	FeO.N.C.H.
fw	314.127
a. Å	16,690 (2)
h &	6 310 (1)
c Å	26716(3)
e dog	20.710(3)
	90.40 (1)
V, A ²	2795.70
ρ (calcd), g cm ⁻³	1.4924
space group	$P2_1/c-C_{2h}^5$ (No: 14)
cryst dimens, mm	$0.25 \times 0.22 \times 0.38$
temp, °C	-100
radiatn	Mo Kα 0.710 69 Å from a
	graphite monochrometer
μ, cm^{-1}	10.835
2θ limits, deg	4-55
observns	7137
unique data	4773
$F_{0}^{2} > 3\sigma(F_{0}^{2})$	
final no. of	473
variables	10
R	3 61
P	4.97
nw	4.3(

ped-flow apparatus was used (470 nm). For other concentrations, a Gilford Model 250 spectrophotometer, thermostated at 25 °C, was used. Rate constants also were determined by following the disappearance of the reactant IR $\nu_{\rm CO}$ and $\nu_{\rm NO}$ bands and the appearance of the product IR bands. All three techniques gave consistent results. Plots of $k_{\rm obsd}$ vs. nucleophile concentration were linear with zero intercepts. In acetonitrile solvent the activation parameters for reaction 1 were determined by measuring $k_{\rm obsd}$ at four temperatures in the range 25–47 °C with the nucleophile concentration fixed at 0.05 M. The second-order rate constants, $k_{\rm obsd}/(0.05)$, were used to make a standard Eyring plot.

X-ray Data Collection, Structure Solution, and Refinement. Crystals of $(Me_2NC_6H_4C_4H_4)Fe(CO)_2(NO)$ suitable for diffraction studies were obtained by slow cooling of a pentane solution to -10 °C. The selected crystal of approximate dimensions $0.25 \times 0.22 \times 0.38$ mm was mounted in a glass capillary under nitrogen. Data were collected on a Syntex P3 diffractometer at -100 °C. The crystal was shown to be suitable by ω scans having a peak width at half-height of 0.25°. Cell parameters refined on 50 computer-centered reflections chosen from diverse regions of reciprocal space are presented in Table I together with other crystallographic data.

Intensity data were collected by using the ω -scan technique (scan range 1.0° at 4.0–10.0° min⁻¹); total background time equals scan time. Four standard reflections checked every 200 reflections deviated less than 0.1%. Absorption corrections were not made.

The structure was solved by the Patterson heavy-atom method and the positions of the remaining non-hydrogen atoms were obtained by the usual refinement techniques. In the full-matrix least-squares refinements, the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $w = 1/\sigma^2(F_o)$ and $\sigma(F) = [\sigma(I)^2 + 0.003(I^2)]^{1/2}$. The hydrogen atoms were found in a difference Fourier map. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were refined isotropically. Least square refinement converged to values of R = 0.036 and $R_w = 0.044$. Several peaks of 0.36 e Å⁻³ were located on the midpoints of the aromatic bonds in the final difference Fourier map.

The final positional parameters of the refined atoms appear in Table II. Selected bond distances and angles are presented in Table III.

Results and Discussion

Synthesis and Kinetic Study. The activated aromatic nucleophile N,N-dimethylaniline readily attacks the cyclobutadiene ring in 1. The reaction is very clean with only a single product being formed. The IR ν_{CO} and ν_{NO} bands shift to lower frequencies in 2 as expected. The ¹H NMR spectrum strongly suggests that the substitution occurs

Table II. Fractional Coordinates $(\times 10^4)$ for $(Me_2NC_6H_4C_4H_4)Fe(CO)_2NO$

	molecule 1			molecule 2		
atom	x	У	z	<i>x</i>	у	z
Fe(1)	1088.2 (2)	477.0 (6)	6099.2 (1)	3900.7 (2)	-2986.2 (6)	11337.4 (1)
O(1)	-186 (1)	2227 (4)	5358 (1)	5209 (1)	-779 (4)	11972 (1)
O(2)	2406 (1)	2771 (3)	5686 (1)	2577 (1)	-737 (3)	11756 (1)
O(3)	1182 (1)	-3700 (3)	5738 (1)	3861 (1)	-7051(4)	11776 (1)
N(1)	1130 (1)	-2059 (4)	5940 (1)	3889 (1)	-5462(4)	11547 (1)
N(2)	1465 (1)	23 (4)	9192 (1)	3474 (2)	-5332 (4)	8274 (1)
C(1)	292 (2)	1623 (5)	5656 (1)	4711 (2)	-1597 (5)	11722 (1)
C(2)	1891 (2)	1899 (4)	5842 (1)	3093 (2)	-1557(4)	11595 (1)
C(4)	1045 (2)	2458 (4)	6718 (1)	3883 (2)	-1259 (5)	10676 (1)
C(5)	1664 (2)	933 (4)	6826 (1)	3284 (2)	-2846(5)	10615 (1)
C(6)	1064 (1)	-610(4)	7041 (1)	3888 (2)	-4438(4)	10422 (1)
C(7)	450 (2)	865 (4)	6735 (1)	4496 (2)	-2806(4)	10675 (1)
C(8)	1105 (1)	-500 (4)	7610 (1)	3815 (1)	-4633 (4)	9854 (1)
C(9)	725 (2)	1061 (4)	7862 (1)	4131 (2)	-3157(4)	9538 (1)
C(10)	826 (2)	1224(5)	8383 (1)	4016 (2)	-3366 (4)	9019 (1)
C(11)	1333 (1)	-192(4)	8677 (1)	3579 (2)	-5076 (4)	8790 (1)
C(12)	1699 (2)	-1814(4)	8422 (1)	3257 (2)	-6552(5)	9107 (1)
C(13)	1580 (2)	-1936 (4)	7900 (1)	3384 (2)	-6309 (5)	9626 (1)
C(14)	2008 (2)	-1396 (6)	9491 (1)	2962 (2)	-7005 (6)	8046 (1)
C(15)	1110 (2)	1737 (6)	9444 (1)	3839 (2)	-3893 (6)	7949 (1)
H(4)	976 (20)	3931 (57)	6663 (12)	3901 (18)	254(51)	10695 (11)
H(5)	2253(21)	988 (54)	6904 (12)	2698 (18)	-2816(45)	10556 (10)
H(6)	1057 (18)	-2087(51)	6935 (11)	3886 (17)	-5793 (46)	10573 (10)
H(7)	-123(18)	966 (45)	6718 (10)	5076 (19)	-2785(51)	10700 (11)
H(9)	364 (18)	2101 (48)	7669 (10)	4459 (16)	-1907 (45)	9679(10)
H(10)	568 (20)	2418 (53)	8525 (12)	4217 (18)	-2346 (47)	8809 (10)
H(12)	2025 (19)	-2916 (52)	8609 (11)	2960 (19)	-7776(51)	8980 (11)
H(13)	1869 (17)	-3090 (46)	7747 (10)	3173(20)	-7314(52)	9817 (11)
H(14A)	1859(24)	-2851(69)	9446 (14)	2408 (23)	-6916(58)	8124 (13)
H(14B)	2051(25)	-1069 (69)	9840 (16)	3135(22)	-8383 (63)	8150 (13)
H(14C)	2574(24)	-1217(63)	9403 (14)	2950 (20)	-6994(55)	7687 (13)
H(15A)	545 (25)	1677 (64)	9382 (14)	4391 (23)	-3681(60)	8071 (13)
H(15B)	1245 (20)	1625 (56)	9788 (13)	3579 (27)	-2597 (73)	7892 (16)
H(15C)	1278 (23)	3165 (69)	9302 (14)	3831 (23)	-4499 (63)	7608 (15)

Table III. Selected^{*a*} Bond Distances (Å) and Angles (deg) for $(Me_3NC_4H_4C_4H_4)Fe(CO)_3NO$

Bond Distances								
1.131 (3)								
1.132(3)								
1.412(4)								
1.413(4)								
1.552(4)								
1.547(4)								
1.512(3)								
Bond Angles								
168.0 (2)								
177.8(3)								
177.5 (3)								
70.5(2)								
72.4(2)								
69.8 (1)								
90.5 (2)								
68.3 (1)								
89.1 (2)								
90.8 (2)								
91.1(2)								
80.9 (2)								
113.9 (2)								
117.9 (2)								
91.2 (2)								

^a Additional distances and angles have been deposited in the microfilm edition.

exclusively para, and this is confirmed by X-ray diffraction studies (see below). The lack of any substitution ortho to the NMe₂ group may be due to steric constraints.

The kinetic data for reaction 1 gave a good fit to the equation $k_{obsd} = k[N,N-dimethylaniline]$ with the following results at 25 °C: (CH₃NO₂), $k = 0.014 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$; (CH₃CN), $k = 0.0045 \pm 0.0006$ M⁻¹ s⁻¹. In acetonitrile the activation parameters for k are $\Delta H^* = 11.2 \pm 1.5$ kcal and $\Delta S^* = -31 \pm 5$ cal deg⁻¹ mol⁻¹.

There are many mechanistic possibilities for reaction 1. Initial attack of the amino nitrogen at the metal or coordinated CO followed by migration to the ring seems unlikely because the product 2 has exo stereochemistry and neither visible nor IR spectroscopy gave any evidence of reaction intermediates.

The usual mechanism postulated for electrophilic aromatic substitution reactions is shown below for reaction 1. The initial π complex converts to a Wheland σ complex,

$$\prod_{i=1}^{+} + \bigoplus_{i=1}^{+} NMe_2 \xleftarrow{k_1}{K_{-1}} \Pi - COMPLEX \xleftarrow{k_2}{K_{-2}}$$

Fe(CO) NO



3, and proton loss gives the product. Presumably the proton loss can be assisted by excess nucleophile or the solvent. Since we found the rate law to be strictly first order in nucleophile, it seems likely that proton loss is rapid. A recent report by Kane-Maguire² suggests, however, that dimethylaniline addition to $[(C_7H_7)Cr(CO)_3]^+$ may involve slow proton loss, which gives rise to a term in the rate law that is second order in nucleophile. We tried to test this possibility by following reaction 1 in the presence of a nonnucleophilic proton acceptor. The base-selected 2,6-lutidine reacted with complex 1. Proton sponge rapidly reacted also, most likely by electrophilic aromatic substitution. The formation of a π complex prior to the Wheland intermediate is well-known⁸ to occur in some electrophilic aromatic substitutions and occasionally can be rate determining. Formation of π complexes has recently been shown⁹ to be rapid compared to substitution in the reaction of methoxy benzenes with $[(C_6H_7)Fe (CO)_3$]⁺. We are investigating the reaction of complex 1 with a variety of aromatic nucleophiles so that the mechanistic features such as the importance of π complexes can be better understood.

If the formation of the σ intermediate 3 is rate determining, our results are given by eq 2,

$$k_{\text{obsd}} = (k_1 k_2 / k_{-1}) [\text{nucleophile}]$$
(2)

which also includes the assumption that the preequilibrium formation of the π complex does not saturate to a significant degree. This is supported by the failure to observe any evidence for reaction intermediates. The activation parameters calculated in acetonitrile are clearly consistent with eq 2. In particular the quite negative ΔS^* is reasonable for the composite constant k_1k_2/k_{-1} and would be equal to $\Delta S^{\circ} + \Delta S_2^{*}$ where ΔS° refers to the π -complex equilibrium constant and ΔS_2^{*} to the $\pi \to \sigma$ conversion.

There is evidence suggesting that the mechanism of reaction 1 is not simply rate-determining formation of the σ complex from separated reactants. Studies¹⁰⁻¹³ of phosphine, phosphite, and nitrogen donor nucleophile additions to the rings in $[(C_4H_4)Fe(CO)_2NO]^+$ and $[(C_6H_7)Fe(CO)_3]^+$ consistently show the latter complex to be about a factor of seven less electrophilic than the former. These reactions can not involve the type of π -com-

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Figure 1. Perspective view and atom labeling scheme of $(Me_2NC_6H_4C_4H_4)Fe(CO)_2(NO)$ with thermal ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

plex formation discussed here and probably follow a single bimolecular mechanism. In sharp contrast to this behavior, the reaction of dimethylaniline with $[(C_4H_4)Fe(CO)_2NO]^+$ and $[(C_6H_7)Fe(CO)_3]^+$ occurs at nearly the same rate and with similar activation parameters in acetonitrile. With the assumption that eq 2 hold for both electrophiles, the unexpectedly small reactivity difference with dimethylaniline may merely reflect a smaller π -complex equilibrium constant ($K = k_1/k_{-1}$) for complex 1.

At least two additional mechanisms for reactions such as (1) remains as possibilities. Initial attack on the coordinated ring by the amino nitrogen in dimethylaniline, followed by conversion to a Wheland σ complex cannot be ruled out although at this time there is no evidence for a nitrogen-bonded intermediate. A significant concentration of such an intermediate would be readily detectable by its effect on the IR ν_{CO} and ν_{NO} bands. A mechanism involving rate-determining electron transfer from the nucleophile to the electrophile, followed by collapse of the resulting radicals to products has yet to be suggested for nucleophilic additions to coordinated π -hydrocarbons but is known¹⁴ to occur with some Grignard additions to carbonyl groups. Studies of the reactions of complexes like 1 with other activated aromatic nucleophiles are planned and should help to elucidate the mechanistic pathways followed in these interesting electrophilic substitutions.

Description of the Structure of $(4-Me_2NC_6H_4C_4H_4)Fe(CO)_2(NO)$ (2). The structure of 2 consists of two molecules in the asymmetric unit. The discrete molecules are well separated having no strong intermolecular contacts. The bond distances and angles compiled in Table III indicate the remarkable similarity between the two independent molecules. Figure 1 presents a perspective view of one molecule and gives the atomlabeling scheme.

The observed structure confirms the exo attack of the N_*N -dimethylaniline para carbon on the coordinated cyclobutadiene inferred from spectroscopic results.

The inner coordination sphere is a distorted square pyramid if the η^3 -cyclobutenyl group is considered to occupy two coordination sites. The linear nitrosyl group (\angle Fe-N-O = 167.6 (2)°) occupies the apical site and the central carbon of the η^3 -enyl group is below the basal plane. The complex can be considered to be an 18-electron Fe(0) complex with NO⁺ and enyl⁻ groups.

The bond distances and angles in the cyclobutenyl group are very similar to those reported in previous cyclobutenyl structures.^{4,5} At 26.5° the dihedral angle between the enyl plane (C_7, C_4, C_5) and the nonbonded plane (C_5, C_6, C_7) is also very similar to previous reports (25°, 22°, 27°, and 24°).4-6 These values differ significantly from that observed in a 2-4- η -1-oxo-cyclobutenyl system (11°),⁶ but this variation can be attributed to constraints imposed by the sp^2 hybridization of the carbonyl carbon atom. There is a statistically significant difference in the chemically equivalent Fe- C_5 and Fe- C_7 distances with Fe- C_5 being shorter. This variation is also reflected in the carbonyl Fe-C distances with Fe-C trans to C₅ being the longer of the two. We attribute this variation to the packing forces and orientation of the phenyl ring, whose plane more closely parallels the C_6-C_7 bond.

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Registry No. $[(C_6H_4)Fe(CO)_2NO]PF_6$, 43175-640; (Me₂NC₆H₄C₄H₄)Fe(CO)₂(NO), 84050-91-9; *N*,*N*-dimethylaniline, 121-69-7.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, hydrogen isotopic thermal parameters, interatomic distances, and intramolecular angles (25 pages). Ordering information is given on any current masthead page.

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