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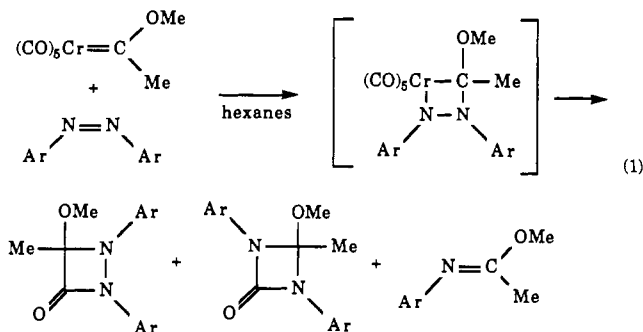
Reactions of $[\text{Cp}(\text{CO})_2\text{Fe}=\text{CHAr}]^+$ ($\text{Ar} = p\text{-C}_6\text{H}_4\text{OMe}$) with $\text{O}=\text{N}-\text{Ar}'$ ($\text{Ar}' = \text{C}_6\text{H}_5$, $p\text{-C}_6\text{H}_4\text{NMe}_2$) and $\text{PhN}=\text{NPh}$

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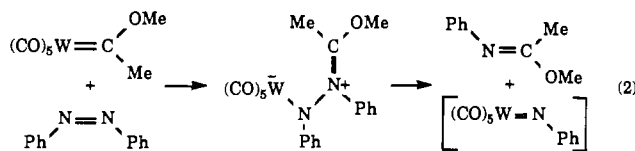
Received May 22, 1989

Organometallic products formed from the reaction of an electrophilic iron carbene complex with nitrosoarenes or azobenzene reflect net insertion of the $\text{ArN}=\text{X}$ moiety into the $\text{Fe}=\text{CHAr}$ bond. $\text{Cp}(\text{CO})_2\text{Fe}-\text{O}-\text{N}(\text{Ar}')=\text{CHAr}^+$ and $\text{Cp}(\text{CO})_2\text{FeN}(\text{Ph})-\text{N}(\text{Ph})=\text{CHAr}^+$ ($\text{Ar} = p\text{-C}_6\text{H}_4\text{OMe}$, $\text{Ar}' = p\text{-C}_6\text{H}_4\text{NMe}_2$) have been isolated and spectroscopically characterized; the crystal structure of $\text{Cp}(\text{CO})_2\text{Fe}-\text{O}-\text{N}(\text{Ph})=\text{CHAr}^+$ is reported. Exposure of acetone solutions of $\text{Cp}(\text{CO})_2\text{Fe}-\text{O}-\text{N}(\text{Ar}')=\text{CHAr}^+$ or $\text{Cp}(\text{CO})_2\text{FeN}(\text{Ph})-\text{N}(\text{Ph})=\text{CHAr}^+$ to light yields imine products $\text{Ar}'\text{N}=\text{CHAr}$ or $\text{PhN}=\text{CHAr}$, respectively. We have no evidence to support the formation of the simple stoichiometric iron-containing products of these reactions, the oxo and nitrene complexes $\text{Cp}(\text{CO})_2\text{Fe}=\text{O}^+$ and $\text{Cp}(\text{CO})_2\text{Fe}=\text{NPh}^+$. Hydrolysis of the nitrene complexes $\text{Cp}(\text{CO})_2\text{Fe}-\text{O}-\text{N}(\text{Ar}')=\text{CHAr}^+$ in aqueous acetone yields aldehyde products $\text{Ar}'\text{CHO}$.

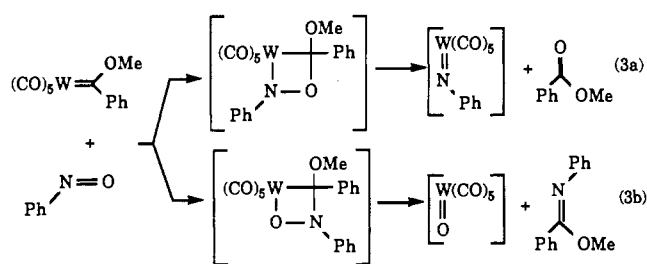
Transition-metal nitrene complexes have potential applications as stable nitrene sources in organic synthesis.¹ Most approaches to the synthesis of low-valent late-transition-metal nitrene complexes have used organic azides and appropriate transition-metal complexes.²⁻⁴ Recent efforts to prepare metal nitrenes have utilized metal carbenes and nitrogen-containing organic reagents, such as azobenzene or aromatic nitroso compounds. Hegedus and Kramer reported that photolysis of azobenzenes and a chromium carbene complex, $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Me}$, produced mixtures of 1,2- and 1,3-diazetidines and methyl *N*-arylacetimides (eq 1).⁵ A diazametallacyclobutane, shown in eq 1, was suggested



as a reasonable intermediate. Sleiman and McElwee-White^{6a} reported that reaction of *cis*-azobenzene with a tungsten carbene complex, $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Me}$, produced a zwitterion, which, upon photolysis, produced an imide and an unstable metal complex speculated to be a tungsten nitrene complex (eq 2).^{6a,b}



Again a metallacycle was proposed as an intermediate. Geoffroy and co-workers reported reactions of organic nitroso reagents with a similar tungsten carbene complex, $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$.⁷ This carbene complex reacts with nitrosobenzene to produce methyl benzoate and methyl *N*-phenylbenzimidate (eq 3). Aniline and

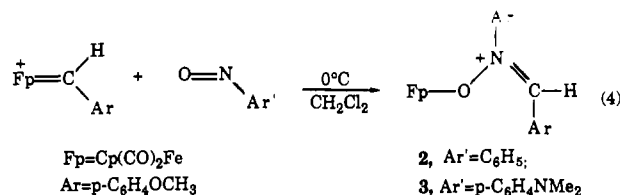


azobenzene were also isolated from this reaction, products expected from generation of transient phenylnitrene.⁸ Two metallacycles, differing by the direction of addition of the nitroso reagent to the metal carbene, were suggested to account for the two different products.

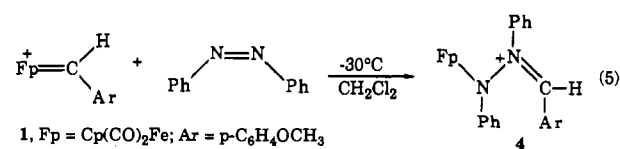
We report here the reaction of a cationic iron carbene complex, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}(p\text{-C}_6\text{H}_4\text{OMe})][\text{X}]^+$ ($\text{X} = \text{SO}_3\text{CF}_3^-$ or BF_4^-) (1), with nitrosobenzene, 4-nitroso-*N,N*-dimethylaniline, and azobenzene. The crystal structure of one of the products, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{O}-\text{N}(\text{C}_6\text{H}_5)=\text{CH}(p\text{-C}_6\text{H}_4\text{OMe})][\text{SO}_3\text{CF}_3]$ (2), has been determined.

Results and Discussion

The iron carbene complex, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}(p\text{-C}_6\text{H}_4\text{OMe})][\text{SO}_3\text{CF}_3]$ (1), reacts with nitrosobenzene and 4-nitroso-*N,N*-dimethylaniline to form oxygen-bound iron nitrene complexes, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{O}-\text{N}(p\text{-C}_6\text{H}_4\text{R})=\text{CH}(p\text{-C}_6\text{H}_4\text{OMe})][\text{SO}_3\text{CF}_3]$ (2, $\text{R} = \text{H}$; 3, $\text{R} = \text{N}(\text{CH}_3)_2$) (eq 4).



Similarly, 1 reacts with the *cis* isomer of azobenzene to form an analogous complex, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeN}(\text{C}_6\text{H}_5)\text{N}(\text{C}_6\text{H}_5)=\text{CH}(p\text{-C}_6\text{H}_4\text{OMe})][\text{X}]$ (4a, $\text{X} = \text{BF}_4^-$; 4b, the $\text{X} = \text{SO}_3\text{CF}_3^-$) (eq 5).

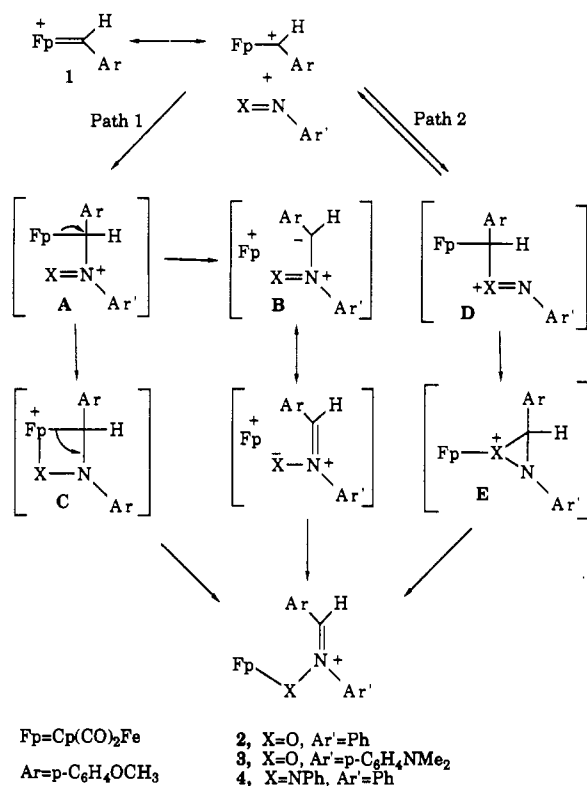


These products reflect net insertion of the $\text{O}=\text{N}$ or $\text{N}=\text{N}$ bond into the iron-carbon double bond of the metal carbene reagent.

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Scheme I



Formation of an N=C bond was confirmed in the case of complex **2** by an X-ray diffraction study (vide infra). In addition, a strong IR stretch near 1600 cm^{-1} and a low-field chemical shift for the carbon-bound proton resonance (8.32 ppm for **2**, 8.09 ppm for **3**, 9.10 for **4a**, and 9.00 for **4b**) are consistent with a N=CHAr unit. Metal carbonyl absorptions in the IR spectra are similar for all four compounds (**2**, 2048, 1998 cm^{-1} ; **3**, 2048, 1999 cm^{-1} ; **4a**, 2049, 2003 cm^{-1} ; **4b**, 2046, 1998 cm^{-1}). The stretches in the region from 1603 to 1550 cm^{-1} , however, differ; stretches at 1603 cm^{-1} for **2** and **3** are about twice as intense as those for **4a** and **4b**, and there are three extra stretches for **4a** and **4b** with intensities similar to those at 1603 cm^{-1} .

The ^1H NMR spectrum of complex **4** indicates that the phenyl groups on the two nitrogen atoms are in substantially different environments. We believe the five protons on the C-bound *N*-phenyl overlap at about 7.7 ppm, by analogy with the *N*-phenyl protons in complex **2**. The five protons on the Fe-bound *N*-phenyl are resolved at higher fields as a doublet and two triplets for meta, ortho, and para protons (7.2, 6.8, and 6.6 ppm, respectively).

Several conceivable pathways exist for the reaction of **1** with nitroso compounds to form nitron complexes. One straightforward and attractive mechanism is described in path 1 of Scheme I. In this mechanism, reaction occurs by attack of the nitroso nitrogen atom on the electrophilic carbene carbon of the iron complex to form A. A then yields the product either via ion pair B or via metallacycle C. An alternative mechanism (path 2 of Scheme I), which is consistent with the fact that electrophiles attack at the oxygen atom of 4-nitroso-*N,N*-dimethylaniline,^{11,12} involves attack of the nitroso oxygen atom on the electrophilic carbene carbon of the iron complex to form D. An oxazirane intermediate, E, could form the product by O-C bond cleavage of the oxazirane ring. The rearrangement of oxazirane rings to give nitrones is well-known.¹⁰ We believe the formation of the strained oxazirane ring (D \rightarrow E) is energetically unattractive. It is possible that formation of D is kinetically favored over A, but

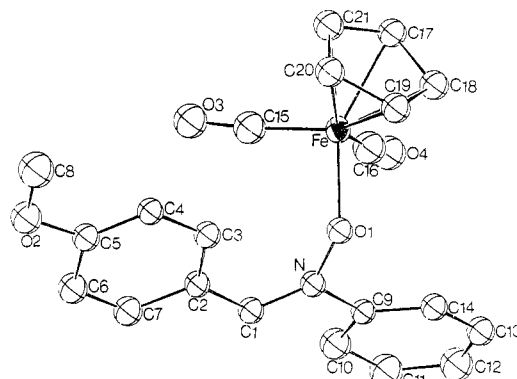
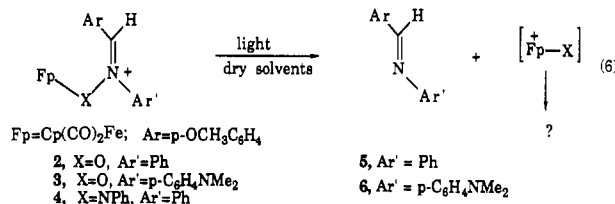


Figure 1. ORTEP drawing of $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}-\text{O}-\text{N}(\text{Ph})=\text{CH}(\text{p-C}_6\text{H}_4\text{OMe})^+$ (cation of **2**).

if formation of D is reversible, then the product could still be produced by pathway 1.

Although complexes **2** and **3** are stable in dry solvents under nitrogen for at least 12 h in the dark, they are light sensitive in solution. Complex **4** is less stable in solution; it decomposes in the dark within 12 h to form unidentified products. On exposure to light in CD_2Cl_2 or acetone- d_6 , complexes **2** and **4** produce imine $(\text{p-C}_6\text{H}_4\text{OMe})\text{C}(\text{H})=\text{NPh}^{13}$ (**5**), and complex **3** also yields imine $(\text{p-C}_6\text{H}_4\text{OMe})\text{C}(\text{H})=\text{N}(\text{p-C}_6\text{H}_4\text{NMe}_2)^{13}$ (**6**) (eq 6). We



have no evidence for the identity of the iron-containing products formed in these reactions. $\text{Cp}(\text{CO})_2\text{Fe}=\text{O}^+$ and $\text{Cp}(\text{CO})_2\text{Fe}=\text{NPh}^+$ are the simple stoichiometric products one would predict, but these are expected to be highly reactive. Attempts were made to trap the hypothetical phenylnitrene complex by adding $\text{P}(\text{OMe})_3$ prior to the photolysis of **4** in acetone- d_6 . The product of nitrene transfer to $\text{P}(\text{OMe})_3$, $\text{PhN}=\text{P}(\text{OMe})_3$,¹⁴ was not observed by $^{31}\text{P}\{\text{H}\}$ NMR spectroscopy. This result does not exclude the production of $\text{Cp}(\text{CO})_2\text{Fe}=\text{NPh}^+$ in the reaction since a nitrene ligand might immediately couple with a CO ligand in the coordination sphere following generation.^{15,16}

Complex **2** can be hydrolyzed in the dark at room temperature in acetone- d_6 . Anisaldehyde (**9**) is the major initial product observed by ^1H NMR spectroscopy of the reaction solution. The other products of this hydrolysis have not yet been identified. The aldehyde is consumed later in a slower secondary reaction. These observations indicate that formation of aldehyde products from reaction of electrophilic metal carbenes with nitroso compounds may be the result of hydrolysis of nitron complexes.

The structure of the nitron complex (**2**) was determined by single-crystal X-ray diffraction. An ORTEP drawing of the cationic complex **2** is shown in Figure 1. Data collection parameters are shown in Table I. Atomic coordinates are listed in Table II, and selected bond distances and angles are listed in Tables III and IV, respectively. The coordination geometry about the iron is approximately octahedral, with the cyclopentadienyl ligand occupying three coordination sites while two carbonyls and the nitron ligand complete the coordination sphere.

The average Fe-C and C-O bond lengths in the metal carbonyl fragment are 1.74 (1) and 1.17 (1) Å, respectively. The bond distances from iron to the cyclopentadienyl ring carbon atoms

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Table I. Crystallographic Data and Collection and Refinement Parameters for **2**

| | |
|--|---|
| molecular formula | FeSF ₃ O ₇ NC ₂₂ H ₁₈ |
| fw | 553.30 |
| crystal dims, mm | 0.30 × 0.30 × 0.20 |
| space group | <i>Pbca</i> |
| cell params | |
| <i>a</i> , Å | 20.41 (1) |
| <i>b</i> , Å | 14.597 (5) |
| <i>c</i> , Å | 15.672 (5) |
| vol Å ³ | 4668.9 |
| <i>Z</i> | 8 |
| density calcd, g/cm ³ | 1.574 |
| radiation (wavelength, Å) | Mo Kα (0.71073) |
| monochromator | Zr filter |
| linear abs coeff, cm ⁻¹ | 8.225 |
| scan type | ω/0.67θ |
| background | 25% of full scan width on both sides |
| θ limits, deg | 2 < θ < 24 |
| quadrant collected | + <i>h</i> , + <i>k</i> , + <i>l</i> |
| total no. of rflns | 3655 |
| no. of data with <i>I</i> ≥ 3σ(<i>I</i>) | 1291 |
| <i>R</i> | 7.2% |
| <i>R</i> _w | 5.5% |
| GOF | 2.48 |
| no. of params | 146 |
| largest param shift | 0.01 |

Table II. Complete Atomic Positions for **2**

| atom | <i>x</i> | <i>y</i> | <i>z</i> |
|------|-------------|-------------|-------------|
| Fe | 0.19531 (8) | 0.0810 (1) | 0.1517 (1) |
| S | 0.3164 (2) | 0.1902 (2) | 0.4076 (2) |
| F1 | 0.2624 (4) | 0.3494 (5) | 0.3800 (5) |
| F2 | 0.3260 (4) | 0.3056 (6) | 0.2823 (5) |
| F3 | 0.3652 (4) | 0.3549 (6) | 0.4007 (6) |
| O1 | 0.1295 (3) | 0.0828 (5) | 0.0581 (5) |
| O2 | -0.0201 (4) | -0.2838 (6) | 0.1820 (5) |
| O3 | 0.1131 (4) | 0.0210 (6) | 0.2921 (6) |
| O4 | 0.1890 (4) | 0.2708 (6) | 0.2056 (5) |
| O5 | 0.3138 (4) | 0.2052 (6) | 0.4976 (5) |
| O6 | 0.3756 (4) | 0.1554 (6) | 0.3746 (6) |
| O7 | 0.2593 (4) | 0.1497 (6) | 0.3709 (5) |
| N | 0.0722 (4) | 0.1258 (6) | 0.0724 (6) |
| C1 | 0.0204 (5) | 0.0815 (8) | 0.0902 (7) |
| C2 | 0.0146 (5) | -0.0158 (8) | 0.1086 (7) |
| C3 | 0.0615 (5) | -0.0840 (8) | 0.0925 (7) |
| C4 | 0.0514 (5) | -0.1747 (8) | 0.1171 (7) |
| C5 | -0.0048 (6) | -0.1977 (8) | 0.1538 (8) |
| C6 | -0.0545 (6) | -0.1323 (8) | 0.1703 (8) |
| C7 | -0.0444 (5) | -0.0444 (8) | 0.1466 (8) |
| C8 | 0.0265 (6) | -0.3535 (9) | 0.164 (1) |
| C9 | 0.0745 (5) | 0.2243 (7) | 0.0578 (7) |
| C10 | 0.0290 (6) | 0.2780 (8) | 0.0996 (8) |
| C11 | 0.0324 (6) | 0.3738 (9) | 0.0838 (9) |
| C12 | 0.0779 (6) | 0.4073 (9) | 0.0307 (8) |
| C13 | 0.1219 (6) | 0.3506 (8) | -0.0080 (8) |
| C14 | 0.1190 (6) | 0.2594 (9) | 0.0037 (8) |
| C15 | 0.1436 (6) | 0.0454 (9) | 0.2329 (9) |
| C16 | 0.1891 (7) | 0.1957 (9) | 0.1799 (8) |
| C17 | 0.2943 (5) | 0.0849 (8) | 0.1783 (7) |
| C18 | 0.2850 (5) | 0.0958 (8) | 0.0884 (7) |
| C19 | 0.2549 (6) | 0.0182 (8) | 0.0578 (8) |
| C20 | 0.2433 (6) | -0.0421 (8) | 0.1254 (7) |
| C21 | 0.2690 (6) | -0.0011 (9) | 0.1991 (8) |
| C22 | 0.3180 (7) | 0.307 (1) | 0.3649 (9) |

Table III. Selected Bond Distances (Å) for **2**

| | | | |
|--------|-----------|--------|-----------|
| Fe–O1 | 1.988 (5) | Fe–C21 | 2.062 (9) |
| Fe–C15 | 1.73 (1) | O1–N | 1.347 (7) |
| Fe–C16 | 1.74 (1) | O3–C15 | 1.17 (1) |
| Fe–C17 | 2.063 (8) | O4–C16 | 1.169 (9) |
| Fe–C18 | 2.093 (8) | N–C1 | 1.270 (8) |
| Fe–C19 | 2.118 (9) | N–C9 | 1.456 (8) |
| Fe–C20 | 2.088 (8) | C1–C2 | 1.45 (1) |

range from 2.062 (9) to 2.118 (8) Å. The five ring carbon atoms are coplanar to within 0.011 Å. These values mimic those of

Table IV. Selected Bond Angles (deg) for **2**

| | | | |
|------------|-----------|---------|-----------|
| O1–Fe–C15 | 97.7 (3) | O1–N–C1 | 121.5 (7) |
| O1–Fe–C16 | 97.2 (4) | O1–N–C9 | 113.9 (7) |
| C15–Fe–C16 | 93.3 (4) | C1–N–C9 | 124.4 (8) |
| Fe–O1–N | 118.1 (4) | N–C1–C2 | 127.5 (8) |

comparable systems.^{17,18} The Fe–O1 bond length of 1.988 (5) Å is a normal value for an iron–oxygen single bond and agrees well with the Fe–O distance of 2.007 (3) Å reported for [η⁵-C₅Me₅](CO)₂FeOSO₂CF₃¹⁹ and the bond length of 1.957 (2) Å observed in (Cp)(CO)₂FeCOH.¹⁷ The N–O bond length of 1.347 (5) Å is longer than those reported for similar free nitrones (1.284 Å in *p*-ClC₆H₄C(H)=N(O)CH₃²⁰ and 1.327 Å in (C₆H₅)₂C=N(O)C₆H₅.²¹ It is shorter than the single N–O bond length of 1.388 (5) Å in (CH₃)₃NO.²² The N=C1 bond distance of 1.270 (8) Å is shorter than the N=C bonds in free nitrones mentioned above (1.309 and 1.327 Å for *p*-ClC₆H₄C(H)=N(O)CH₃ and (C₆H₅)₂C=N(O)C₆H₅, respectively). This distance is appropriate for an isolated carbon–nitrogen double bond (1.29–1.31 Å²³). The lengthened N–O bond and shortened N=C bond relative to free nitrones probably reflect that oxygen coordination reduces the contribution of the following resonance structure on the right:



resonance structures of nitroso compounds

Other structural features discussed below suggest that the N=C1 bond is slightly conjugated with the C-bound *p*-methoxyphenyl group.

The nitrone ligand is relatively flat. The planes defined by the two phenyl rings make a small dihedral angle of 16.1°, and the plane defined by O1NC1 makes dihedral angles of 13.3 and 26.8° with the planes defined by the C1-bound and the N-bound phenyl rings, respectively. The dihedral angle of 13.3° between the O1NC1 plane and the C-bound *p*-methoxyphenyl plane indicates some conjugation between the two fragments. The existence of this conjugation is also demonstrated by the C1–C2 bond length of 1.45 (1) Å, which is close to the average value of a C–C single bond length of 1.53 Å and a C–C double bond length of 1.33 Å. This conjugation is presumably enhanced by the electron-donating methoxy group on the para position of the C-bound phenyl group:



resonance structures of the nitrone ligand

Summary

Reactions of nitrosoarenes and *cis*-azobenzene reagents with an electrophilic iron carbene complex generate iron products that reflect net insertion of the nitroso or azo unit into the iron–carbene bond. Imine products form upon photolysis of the zwitterionic iron complexes in dry solvents, while hydrolysis of these complexes yields aldehyde products. These iron complexes and organic imines and aldehydes are compatible with intermediate metallacycles and

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reactive iron nitrene intermediates, but we have no hard evidence for either of these interesting species. Plausible routes to these products that involve neither metallacycles nor metal nitrenes can be formulated.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere by glovebox or Schlenk techniques. Solvents were dried prior to use. Nitrosobenzene, 4-nitroso-*N,N*-dimethylaniline, and azobenzene were purchased from Aldrich Chemical Co. and used as received. Azobenzene solutions containing about 30% *cis* isomers were generated by photolyzing 0.1 M CH₂Cl₂ solutions of the *trans* isomer for 5 h with a mercury lamp.²⁴ These solutions were used immediately.

Synthesis of [(Cp)(CO)₂Fe—ON(C₆H₅)=CH(*p*-C₆H₄OMe)]SO₃CF₃] (2). To a cold methylene chloride solution (10 mL, -30 °C) of (Cp)(CO)₂Fe—CH(OCH₃)(*p*-C₆H₄OMe)⁹ (0.64 g, 2.0 mmol) was added (CH₃)₃SiOSO₂CF₃ (0.38 mL, 2.0 mmol) with stirring. The color of the solution immediately changed from orange to dark red. After the solution was stirred nitrosobenzene (0.22 g, 2.0 mmol) in methylene chloride (10 mL) was added at -30 °C. The solution was then stirred and allowed to slowly warm to room temperature. Stirring was continued for 30 min at room temperature before the volume of the solvent was reduced under vacuum. The resulting saturated solution was cooled to -20 °C, inducing the formation of dark red crystals. Yield: 0.59 g (58%). ¹H NMR (CD₂Cl₂, 250 MHz), δ: 4.00 (s, 3 H, OCH₃); 5.10 (s, 5 H, C₅H₅); 7.20, 8.26 (d, *J* = 9.0 Hz, 2 H each, ortho and meta H's of -C₆H₄OCH₃); 7.66 (broad m, 5 H, NC₆H₅); 8.32 (s, 1 H, N=CH). ¹³C{¹H} NMR (acetone-*d*₆, 100.6 MHz), δ: 56.4 (s, -OCH₃); 85.8 (s, C₅H₅); 115.5 (s, C's ortho to -OCH₃ of *p*-C₆H₄OMe); 136.0 (s, C's meta to -OCH₃ of *p*-C₆H₄OMe); 123.4, 130.6, 132.2 (s, meta, ortho, and para C's of -NC₆H₅); 120.3, 143.8, 166.2 (s, ipso C's); 152.8 (s, N=C); 211.1 (s, 2 CO). IR (KBr, selected peaks), cm⁻¹: 2048, 1998 (vs, CO stretches); 1603 (vs, N=C stretch). Anal. Calcd for C₂₂H₁₈NO₇FeSF₃: C, 47.76; H, 3.28; N, 2.53. Found: C, 47.81; H, 3.32; N, 2.38.

Synthesis of [(Cp)(CO)₂Fe—ON(*p*-C₆H₄NMe₂)=CH(*p*-C₆H₄OMe)]SO₃CF₃] (3). Complex 3 was synthesized by the same procedure as complex 2, except that *p*-nitroso-*N,N*-dimethylaniline (0.30 g, 2.0 mmol) was used instead of nitrosobenzene. Compound 3 is much more soluble in methylene chloride than 2, and a saturated solution was obtained by adding hexanes to the concentrated methylene chloride solution. A powdery product was obtained. Yield: 0.5 g (50%). ¹H NMR (CD₂Cl₂, 250 MHz), δ: 3.10 (s, 6 H, N(CH₃)₂); 3.98 (s, 3 H, OCH₃); 5.10 (s, 5 H, C₅H₅); 6.71, 7.18, 7.35, 8.12 (doublets, *J* = 9.0 Hz, 2 H each, phenyl H's); 8.09 (s, 1 H, N=CH). IR (KBr, selected peaks), cm⁻¹: 2048, 1999 (vs, CO stretches); 1603 (vs, N=C stretch). Anal. Calcd for C₂₄H₂₃N₂O₇FeSF₃: C, 48.34; H, 3.89; N, 4.70. Found: C, 47.70; H, 3.90; N, 4.64.

Synthesis of [(Cp)(CO)₂Fe—N(C₆H₅)N(C₆H₅)=CH(*p*-C₆H₄OMe)]BF₄] (4a). Freshly prepared carbene complex, [(η⁵-C₅H₅)(CO)₂Fe=CH(*p*-C₆H₄OMe)]BF₄¹⁶ (0.81 g, 2.0 mmol), was dissolved in 20 mL of cold CH₂Cl₂ (0 °C). Azobenzene (1.82 g, 10 mmol, about 30% *cis* isomer) in 100 mL of CH₂Cl₂ was added with stirring at 0 °C. After the solution was stirred for 15 min at 0 °C, its volume was reduced to 20 mL. The concentrated solution was transferred to 150 mL of cold (0 °C) diethyl ether; a green powder precipitated. The solid product was separated, washed with ether (3 × 15 mL), and dried under vacuum. Yield: 0.8 g (71%). ¹H NMR (CD₂Cl₂, 250 MHz), δ: 3.92 (s, 3 H, -OCH₃); 4.91 (s, 5 H, C₅H₅); 6.64 (t, 1 H, *J* = 8.0 Hz, para H of Fe-bound NC₆H₅); 6.82 (d, 2 H, *J* = 8.0 Hz, ortho H of Fe-bound NC₆H₅); 7.02 (d, 2 H, *J* = 9.0 Hz, *p*-C₆H₄OMe); 7.20 (t, 2 H, *J* = 8.0 Hz, meta H of Fe-bound NC₆H₅); 7.70 (m, 5 H, C-bound NC₆H₅); 7.85 (d, 2 H, *J* = 9.0 Hz, *p*-C₆H₄OMe); 9.00 (s, 1 H, N=CH). IR (KBr, selected peaks), cm⁻¹: 2049, 2003 (vs, CO stretches); 1602 (s, N=C stretch); 1600, 1573, 1560 (s). Anal. Calcd for C₂₇H₂₃BF₄N₂O₃Fe: C, 57.28; H, 4.09; N, 4.95. Found: C, 56.81; H, 4.17; N, 4.96.

Synthesis of [(Cp)(CO)₂Fe—N(C₆H₅)N(C₆H₅)=CH(*p*-C₆H₄OMe)]SO₃CF₃] (4b). The carbene complex, **1** (0.88 g, 2.0 mmol), was generated in CH₂Cl₂ as described in the synthesis of complex 2. Azobenzene (1.82 g, 10.0 mmol, about 30% *cis* isomer) in 100 mL of CH₂Cl₂ was added to the carbene solution with stirring at 0 °C, resulting in a red-brown solution. Stirring was contained at 0 °C for 10 min, and then the solution was stored in a -20 °C freezer overnight. The solution became dark green in color. The volume of the solution was reduced to 20 mL at 0 °C, and the concentrated solution was transferred to 200 mL of diethyl ether at 0 °C. The green precipitate that separated was washed with ether (3 × 15 mL) and dried under vacuum. Yield: 0.8 g (64%). ¹H NMR (CD₂Cl₂, 250 MHz), δ: 3.90 (s, 3 H, -OCH₃); 4.90 (s, 5 H,

C₅H₅); 6.65 (t, 1 H, *J* = 8.0 Hz, para H of Fe-bound NC₆H₅); 6.82 (d, 2 H, *J* = 8.0 Hz, ortho H of Fe-bound NC₆H₅); 7.00 (d, 2 H, *J* = 9.0 Hz, *p*-C₆H₄OMe); 7.22 (t, 2 H, *J* = 8.0 Hz, meta H of Fe-bound NC₆H₅); 7.70 (m, 5 H, C-bound NC₆H₅); 7.87 (d, 2 H, *J* = 9.0 Hz, *p*-C₆H₄OMe); 9.10 (s, 1 H, -N=CH). IR (KBr, selected peaks), cm⁻¹: 2046, 1998 (vs, CO stretches); 1602 (s, N=C stretch); 1593, 1573, 1556 (s).

Photolysis of Complex 2. An NMR sample of **2** (0.054 g, 0.10 mmol, in 1 mL of acetone-*d*₆) was exposed to direct sunlight for 2 h. A ¹H NMR spectrum showed that complex **2** had disappeared. The spectrum was dominated by unidentified products, but *N*-phenyl-*p*-methoxyphenylimine (**5**) was evident (about 40%). This compound was identified by comparing the ¹H NMR spectrum of the reaction mixture with that of the independently prepared imine.¹³ ¹H NMR of **5** (acetone-*d*₆, 250 MHz), δ: 3.90 (s, 3 H, OCH₃); 7.07 (d, 2 H, *J* = 8.6 Hz, H's ortho to OMe); 7.23 (t, 1 H, *J* = 8.6, para H of *N*-phenyl); 7.25 (d, 2 H, *J* = 8.6 Hz, ortho H's of *N*-phenyl); 7.40 (t, 2 H, *J* = 8.6 Hz, meta H's of *N*-phenyl); 7.95 (d, 2 H, *J* = 8.6 Hz, H's ortho to OMe); 8.50 (s, 1 H, N=CH).

Photolysis of Complex 3. An NMR sample of **3** (0.060 g, 0.10 mmol, in 1 mL of acetone-*d*₆) was exposed to direct sunlight for 1 h. A ¹H NMR spectrum was then recorded. An imine product, (*p*-C₆H₄NMe₂)N=C(H)(*p*-C₆H₄OMe) (**6**), was observed in over 90% yield. The imine was characterized by comparing the ¹H NMR spectrum of the reaction mixture with that of the separately prepared imine.¹¹ ¹H NMR of **6** (acetone-*d*₆, 250 MHz), δ: 2.91 (s, 6 H, N(CH₃)₂); 3.90 (s, 3 H, OCH₃); 6.80 (d, 2 H, *J* = 8.8 Hz, H's ortho to NMe₂); 7.07 (d, 2 H, *J* = 8.8 Hz, H's ortho to OMe); 7.27 (d, 2 H, *J* = 8.8 Hz, H's meta to NMe₂); 7.91 (d, 2 H, *J* = 8.8 Hz, H's meta to OMe); 8.60 (s, 1 H, N=CH).

Photolysis of Complex 4a. An NMR sample of **4a** (0.063 g, 0.10 mmol, in CD₂Cl₂) was photolyzed with a mercury lamp for 4 h at 0 °C. A yellow precipitate formed on the walls of the NMR tube. The sample was then filtered in a drybox to separate a red solution from the yellow solid. The ¹H NMR spectrum of the red solution showed that it contained more than 50% of imine **5**. The yellow solid has not been identified.

Photolysis of 4a in the Presence of P(OMe)₃. An NMR sample of **4a** (0.063 g, 0.10 mmol, in CD₂Cl₂) was cooled to -78 °C, and 2.5 equiv of P(OMe)₃ was added. The solution remained green upon addition of trimethyl phosphite. When the sample was warmed to 0 °C it was still green. ¹H NMR spectra taken at -78, -25, and 0 °C confirmed that there was no thermal reaction between **4a** and trimethyl phosphite at these temperatures.

The sample was then photolyzed with a mercury lamp at 0 °C for 2.5 h. A red homogeneous solution was obtained. A ¹H NMR spectrum showed that **5** was formed in greater than 90% yield. ³¹P{¹H} NMR of this solution (160 MHz, referenced to P(OMe)₃ at 141 ppm), δ: 141 (s, free P(OMe)₃); 180 (s, iron-bound P(OMe)₃). ³¹P{¹H} NMR of (MeO)₃P=NPh²⁵ (CD₂Cl₂, 160 MHz, referenced to external P(OMe)₃ at 141 ppm), δ: 1.4.

Hydrolysis of 2. Complex **2** (0.055 g, 0.10 mmol) was dissolved in 1 mL of acetone-*d*₆ containing degassed H₂O (50 μL, 2.7 mmol). The sample was sealed in an NMR tube wrapped with aluminum foil and kept at room temperature. ¹H NMR spectra were taken at reaction times of 20 min, and 2, 19, and 24 h. Starting material (**2**), anisaldehyde (**9**), and an additional product were observed in all these spectra.

X-ray Diffraction Data Collection for Complex 2. A ruby octahedron of dimensions 0.30 × 0.30 × 0.20 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.²⁷ Twenty-five centered reflections found in the region 14.0 < θ < 15.0° and refined by least-squares calculations indicated an orthorhombic cell. The cell parameters are listed in Table IV.

Diffraction data were collected in the quadrant +*h*, +*k*, +*l* under the conditions specified in Table IV. Three reflections chosen as intensity standards were monitored every 3 h and showed no significant (<1.5%) decay. The crystal was checked for orientation every 300 reflections and was recentered if necessary. Only data with *I* > 3σ(*I*)²⁸ were used in

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(26) This signal measures one proton in the spectra obtained in benzene-*d*₆ or CD₂Cl₂.

(27) Programs used during solution and refinement were from the Enraf-Nonius structure determination package.

(28) $I = S(C + RB)$ and $s(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where *S* = scan rate, *C* = total integrated peak count, *R* = ratio of scan count time to background count time, *B* = total background count time, and ρ = 0.01 is a correction factor.

structure solution and refinement. The data were corrected for Lorentz-polarization effects during the final stages of data reduction.

Solution and Refinement of the Structure of Complex 2. Solution of the structure was straightforward from application of the heavy-atom method. Space group *Pbca* was confirmed and the position of the iron atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

Least-squares refinement²⁹ of the 35 non-hydrogen atoms, varying the iron atom anisotropically, produced unweighted and weighted residuals of 8.7% and 7.1%,³⁰ respectively. Hydrogen atom positions were calcu-

lated by using a C-H distance of 0.95 Å and an isotropic thermal parameter of 6.0 Å². Further refinement resulted in residuals of *R* = 7.2% and *R_w* = 5.5%. The final difference Fourier map had no peak greater than 0.26 e/Å³.

Acknowledgment is made to the National Institutes of Health (GM 28938) and the Department of Energy, Office of Basic Energy Sciences (85ER 13430), for support of this work.

Supplementary Material Available: Tables of complete anisotropic and isotropic temperature factors, bond distances and angles, calculated hydrogen positions, and defined planes and calculated dihedral angles for **2** (3 pages); a table of calculated and observed structure factors for **2** (10 pages). Ordering information is given on any current masthead page.

(29) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

(30) $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

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Synthesis of Salts of the Hydrogen Dichloride Anion in Aromatic Solvents. 2. Syntheses and Crystal Structures of [K·18-crown-6][Cl-H-Cl], [Mg·18-crown-6][Cl-H-Cl]₂, [H₃O·18-crown-6][Cl-H-Cl], and the Related [H₃O·18-crown-6][Br-H-Br]

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Received March 7, 1989

The reaction of HCl(g), H₂O, and 18-crown-6 in toluene gives [H₃O·18-crown-6][Cl-H-Cl]·3.6tol (tol = toluene), from which crystals of [H₃O·18-crown-6][Cl-H-Cl] are isolated: space group *P2₁/c*; *a* = 10.475 (7), *b* = 20.767 (9), *c* = 8.583 (7) Å; β = 96.23 (3)°; *Z* = 4 for *D_c* = 1.28 g cm⁻³; *R* = 0.042 for 493 independent observed reflections. The liquid clathrate [H₃O·18-crown-6][Cl-H-Cl]·3.6tol dissolves KCl, and upon standing, the solution affords crystals of [K·18-crown-6][Cl-H-Cl]: space group *P2₁/c*; *a* = 8.325 (2), *b* = 14.094 (4), *c* = 7.893 (6) Å; β = 98.56 (4)°; *Z* = 2 for *D_c* = 1.37 g cm⁻³; *R* = 0.055 for 1194 independent observed reflections. In a similar fashion, the liquid clathrate dissolves MgCl₂ and yields [Mg·18-crown-6][Cl-H-Cl]₂: space group *Pbca*; *a* = 18.310 (7), *b* = 7.512 (6), *c* = 29.085 (8) Å; *Z* = 8 for *D_c* = 1.44 g cm⁻³; *R* = 0.066 for 1204 observed reflections. The [Br-H-Br]⁻ anion is produced by the reaction of HBr(g), H₂O, and 18-crown-6 in toluene. [H₃O·18-crown-6][Br-H-Br] is isomorphous with the [Cl-H-Cl]⁻ analogue, and the crystals belong to space group *P2₁/c* with *a* = 10.588 (1) Å, *b* = 21.060 (2) Å, *c* = 8.753 (1) Å, β = 95.25 (4)°, and *D_c* = 1.52 g cm⁻³ for *Z* = 4; *R* = 0.059 for 1697 observed reflections. The Cl...Cl separations range from 3.11 (1) Å in the H₃O⁺ salt to 3.331 (2) Å in the Mg²⁺ analogue. The angle at the hydrogen atom in the hydrogen dichloride ranges from 161° for the [Mg·18-crown-6]²⁺ salt to 180° for the [K·18-crown-6]⁺ salt. The short Cl...Cl separations in the H₃O⁺ and K⁺ salts are attributed to the absence of a strong directional interaction of the anion with the cation. For the long Cl...Cl in the Mg²⁺ case, the magnesium atom is bonded to one of the chlorine atoms at 2.428 (6) and 2.454 (3) Å (two independent anions). The Br...Br distance in [H₃O·18-crown-6][Br-H-Br] is 3.377 (1) Å.

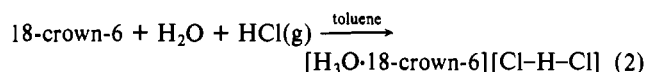
Introduction

The hydrogen dichloride ion, Cl-H-Cl⁻, was first inferred by Kaufler and Kunz¹ in 1909 in the reaction



More recently, salts containing the hydrogen dichloride ion were prepared by the reaction of an alkali-metal chloride with HCl in aqueous media² or by the reaction of phosphonium halides or phosphanes with hydrogen chloride.³

In an effort to convert O- and N-containing bases into salts that might exhibit the liquid clathrate effect,⁴ our group has begun a thorough investigation of the interaction of HCl(g) with these bases in aromatic solvents. The first communication in this series⁵ involved the reaction with 18-crown-6 according to eq 2. Here



we show that a range of hydrogen dichloride salts are available from a similar synthetic approach, and we present the crystal structures of three examples. In addition, a related salt of hydrogen dibromide is reported.

Experimental Section

Materials. Anhydrous HCl(g) and HBr(g) were purchased from Airco and were further dried by passage through two H₂SO₄ traps immediately before use. The H₂O was distilled. KCl, MgCl₂, and KBr were analytical reagent grade and were used without additional purification. 18-crown-6 was purchased from Aldrich and was dried under vacuum at 105 °C. The toluene and benzene were dried in the usual manner and distilled under nitrogen before use.

Solution Studies. The characterization of the liquid clathrates was done by ¹H NMR integration. For the toluene liquid clathrate, the 18-crown-6 resonance is observed at 3.07 ppm and that of H₃O⁺ at 10.36 ppm. Those of the toluene are observed at 7.05 and 2.25 ppm. The resonance due to [Cl-H-Cl]⁻ was not observed.

Synthesis of [H₃O·18-crown-6][Cl-H-Cl]. A 1.32-g amount of 18-crown-6 (0.005 mol) was moistened with 0.09 mL of distilled water (0.005 mol), and ca. 30 mL of toluene was layered over the mixture, which was contained in a Schlenk tube. Anhydrous HCl(g) was bubbled

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