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Crystal and molecular structure of benzophenone azine: evidence for an Fe(II) carbene intermediate

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Benzophenone azine crystallizes in the monoclinic space group *A2/a* (No. 15) with a = 16.303(3) Å, b = 5.4864(2) Å, c = 21.973(5) Å, β = 85.52(2)°, V = 1959.4(8) Å^3, and D_{calc} = 1.22 g cm^{-3} for Z = 4. The structure was solved by direct methods and refined against F to a final R value of 0.047. The unit cell contains four molecules of the title compound; the asymmetric unit consists of half a molecule. Despite the high crystallographic symmetry, the two halves of the molecule are *not* related by a center of symmetry; instead, the molecule adopts C_2 symmetry; the molecular C_2 axis is coincident with the crystallographic twofold axis. The formation of benzophenone azine from the reaction of the iron-containing Lewis acid complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+ [BF_4]^-$ and diphenyldiazomethane provides strong evidence for an Fe(II) carbene intermediate.

KEY WORDS: Azine; azitine; iron(II) carbene; catalyst.

Introduction

Diazo compounds are known to undergo catalytic decomposition in the presence of olefins and a suitable transition metal catalyst to form cyclopropanes. For example, rhodium carboxylate, typical of such catalysts, has been shown by Doyle to catalyze the formation of *trans* cyclopropanes in preference to the less thermodynamically stable *cis* cyclopropanes.[1] In contrast to this general trend, an iron-containing Lewis acid, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+ [BF_4]^-$, **1**, has recently been shown to be an effective catalyst for the decomposition of ethyldiazoacetate in the presence of olefins to produce cyclopropanes with predominantly *cis* selectivity.[2] In addition the formation of carbene dimers (diethyl fumerate and diethyl maleate) as the other isolable products in the reaction suggested the participation of an iron(II) carbene intermediate, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CH(COOEt)]^+$, in the catalytic process.[3] Unfortunately, attempts to isolate and characterize such an intermediate have, to date, been unsuccessful.

Diphenyl carbene complexes of chromium and manganese have been isolated and characterized,[4] leading us to attempt the synthesis of the diphenyl iron carbene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(C_6H_5)_2)]^+ [BF_4]^-$ from diphenyldiazomethane and the iron-containing Lewis acid complex, **1**.

Experimental section

General reagents and procedures

All organometallic operations were performed under a nitrogen atmosphere using standard Schlenck techniques. Reagent grade pentane was distilled from sodium under nitrogen immediately prior to use. Reagent grade ether and tetrahydrofuran were freshly distilled under a nitrogen atmosphere over sodium benzophenone ketyl. Dichloromethane was distilled under nitrogen from phosphorus pentoxide. Cyclopen-

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tadienyldicarbonyliron dimer, the tetrafluoroboric acid-diethyl ether complex and benzophenone hydrazone were obtained from Aldrich Chemical Co.; mercuric oxide was purchased from Mallinckrodt Chemical Works; silica gel (40–140 mesh) and potassium fluoride were obtained from J. T. Baker.

Infrared spectra were obtained using a Nicolet MX-1 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 MHz NMR spectrometer.

The synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+$ $[BF_4]^-$ has been described previously.[2] Diphenyldiazomethane was synthesized from benzophenone hydrazone following the procedure described by Miller.[5]

Reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+$ $[BF_4]^-$ with diphenyldiazomethane. The Lewis acid, 1, (0.0341 g, 0.101 mmol) was dissolved in 5 mL of CH_2Cl_2. 0.1968 g (1.014 mmol) of diphenyldiazomethane was added to the solution and the reaction mixture was stirred for 12 h. Following this, pentane was added to precipitate complex 1, followed by filtration through a silica gel plug to remove any residual transition metal complexes. Solvent was removed by rotary evaporation and the residue was eluted on a silica gel column using 20% ethylacetate in pentane as an eluent. Two products were isolated, benzophenone azine, 3, and tetraphenylethylene, 4 (confirmed by NMR[6]).

X-ray structural determination of benzophenone azine. A small crystal 0.1 × 0.1 × 0.15 mm was mounted in a quartz capillary tube and anchored with epoxy. Attempts to grow larger crystals proved unsuccessful. The small size of the crystal resulted in a relatively small number of observed intensities and a low data to parameter ratio. Data were sorted and collected using PCXTL.[7] Orientation and crystal decay were monitored by measuring the intensities of three reference reflections at intervals of 120 minutes. Minimal intensity losses were observed. Data reduction, handling and analysis were performed using NRCVAX.[8] The locations of the heavy atoms were determined by direct methods using SHELXS[9] in combination with tangent expansion and difference Fourier techniques. The structure was originally solved and refined in space group *A*2. Refinement in this space group resulted in large correlation matrix elements and odd shaped thermal ellipsoids. The program MISSYM in NRCVAX[8] indicated the presence of a glide plane and center of symmetry. A suitable origin shift and addition of the glide plane resulted in the correct space group assignment. The structure was refined against F using SHELX.[10] All heavy atoms were refined anisotropically. Hydrogen atoms were allowed to ride on the heavy atom to which they were attached. An average isotropic thermal parameter for the hydrogens was refined to a value of 0.116 Å^2. Neutral atom scattering factors were used for all atoms.[11] Weights based on counting statistics were used in the final stages of refinement. An ORTEP[12] drawing of the molecular structure is shown in Fig. 1. Details of the structural determination are given in Table 1. Table 2 contains the fractional coordinates of all non-hydrogen atoms, and selected bond lengths and angles are listed in Table 3.

Results and discussion

The iron Lewis acid, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\,(THF)]^+$ (1), was synthesized in high yield by protonation of the known iron methyl cyclopentadienyl carbonyl complex, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$.[2] In an attempt to produce the diphenyl iron carbene complex, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C(C_6H_5)_2)]^+$ (7), diphenyldiazomethane (**2**) was treated with 10 mol% of the Lewis acid at room temperature for 12 h. The product mixture was devoid of complex **7**; instead benzophenone azine, **3**, (39% yield) and tetraphenylethylene, **4**, (26% yield) were isolated (Scheme 1).

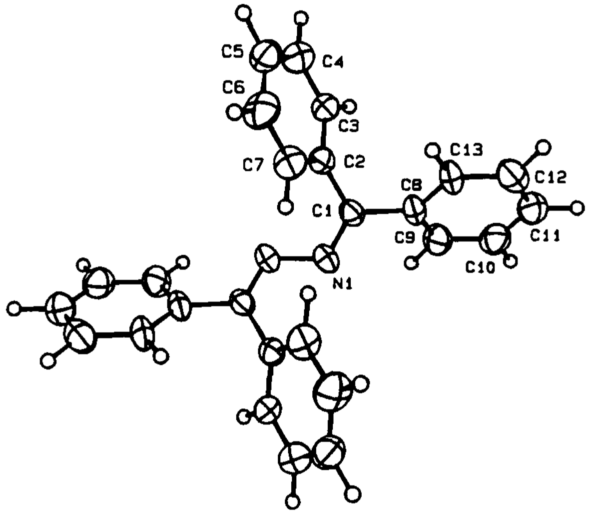
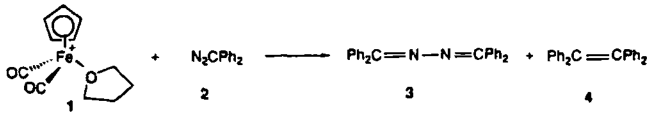


Fig. 1. Structure of benzophenone azine in the solid state. Thermal ellipsoids are plotted at the 35% probability level.

Table 1. Crystallographic data and summary of intensity data collection and structure refinement for benzophenone azine

Compound	$C_{26}H_{20}N_2$
Color/shape	Colorless, rhombus
Molecular mass	360.46
Space group	*A2/a*
Temp., °C	23(1)
Lattice constants[a]	
a, Å	16.303(3)
b, Å	5.4864(2)
c, Å	21.973(5)
β, deg	85.52(2)
Cell volume, Å^3	1959.4(8)
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.22
μ_{calc}, cm^{-1}	0.69
Diffractometer/scan	Picker/θ/2θ
Radiation, Zr Filtered	Mo *K*α, λ = 0.71069 Å
Max. crystal dimensions, mm	0.10 × 0.10 × 0.15
Scan width	0.79 + 0.19 tanθ
Standard reflections	3 1 1, 4 0 2, 2 0 4
Decay of standards	Negligible
Reflections measured	1043
2θ range, deg	$4 \leq 2\theta \leq 40$
Range of *h*, *k*, *l*	±15, +5, +20
Reflections observed $[F_o \geq 5\sigma(F_o)]$[b]	428
Computer programs[c]	SHELX[10], NRCVAX[8], PCXTL[7]
Structure solution	SHELXS[9]
No. of parameters varied	128
Weights	$1/(\sigma(F_o)^2)$
GOF	1.11
$R = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$	0.047
$R_w = \Sigma[w^{1/2} \lvert (F_o - F_c) \rvert] / \Sigma [w^{1/2} \lvert F_o \rvert]$	0.049
Largest feature final diff. map	0.17 e/Å^3

[a] Least squares refinement of diffractometer settings for 15 reflections, each the average of four iteratively centered symmetry equivalent settings.
[b] Corrections: Lorentz polarization.
[c] Neutral scattering factors and anomalous dispersion corrections.[11]



Scheme 1 Iron Lewis acid catalyzed decomposition of diphenyl diazomethane.

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for benzophenone azine

	x	*y*	*z*	U_{iso}[a]
N1	7250(3)	2037(10)	10275(3)	57(4)
C1	7576(4)	2883(15)	10746(3)	54(5)
C2	8386(5)	4194(17)	10724(3)	57(5)
C3	9007(5)	3334(17)	11064(3)	71(6)
C4	9753(6)	4508(21)	11045(4)	87(8)
C5	9890(6)	6618(22)	10710(5)	88(7)
C6	9269(6)	7538(18)	10381(4)	90(7)
C7	8533(5)	6298(16)	10386(4)	71(6)
C8	7105(5)	2653(18)	11339(4)	57(6)
C9	6568(5)	716(18)	11455(4)	74(6)
C10	6090(5)	568(20)	12014(5)	84(7)
C11	6161(6)	2368(23)	12448(4)	87(8)
C12	6705(6)	4284(19)	12345(4)	83(7)
C13	7168(4)	4397(17)	11780(4)	66(6)

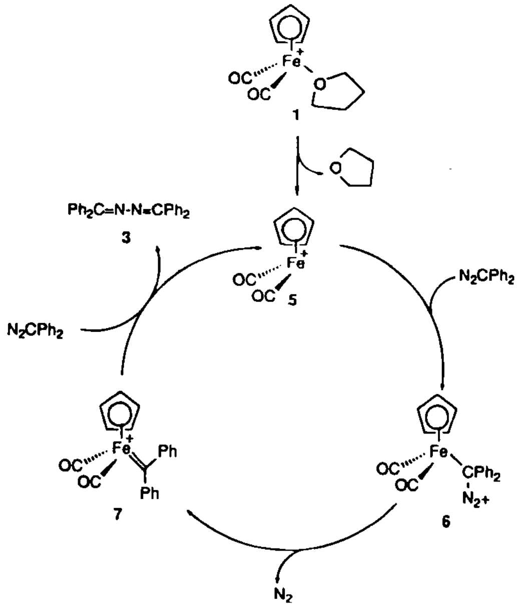
[a] U_{iso} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (Å) and angles (deg) for benzophenone azine

Bond lengths			
N1–N1a	1.402(12)	C5–C6	1.386(15)
N1–C1	1.287(9)	C6–C7	1.379(13)
C1–C2	1.503(11)	C8–C9	1.387(13)
C1–C8	1.463(11)	C8–C13	1.374(13)
C2–C3	1.386(11)	C9–C10	1.403(13)
C2–C7	1.383(12)	C10–C11	1.385(16)
C3–C4	1.374(13)	C11–C12	1.384(15)
C4–C5	1.381(16)	C12–C13	1.401(12)
Bond angles			
N1a–N1–C1	116.6(5)	C5–C6–C7	119.1(9)
N1–C1–C2	124.3(6)	C2–C7–C6	122.1(8)
N1–C1–C8	117.7(6)	C1–C8–C9	120.7(8)
C2–C1–C8	118.0(6)	C1–C8–C13	120.3(8)
C1–C2–C3	119.8(7)	C9–C8–C13	119.0(8)
C1–C2–C7	122.1(7)	C8–C9–C10	120.4(9)
C3–C2–C7	118.0(8)	C9–C10–C11	119.5(9)
C2–C3–C4	120.5(8)	C10–C11–C12	120.9(8)
C3–C4–C5	120.9(9)	C11–C12–C13	118.3(9)
C4–C5–C6	119.4(9)	C8–C13–C12	121.9(8)

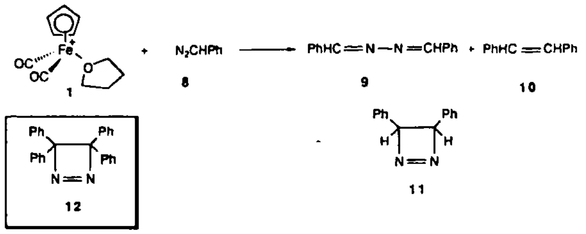
In an attempt to observe the iron carbene complex as a transient species the reaction described above was investigated using variable-temperature ^{13}C NMR spectroscopy. No characteristic resonances for **7** were observed. However, the formation of benzophenone azine, **3**, provides strong indirect proof that an iron(II) carbene intermediate is formed during the reaction between **1** and diphenyl diazomethane, **2**. This is consistent with arguments by Shankar implicating the existence of a rhodium carbene intermediate, based on the formation of benzophenone azine from the decomposition of diphenyldiazomethane by rhodium carboxylate.[3,4]

On the basis of the observations described above we propose a plausible catalytic cycle for the formation of azine **3** from the iron Lewis acid **1** and diphenyl diazomethane (Scheme 2). In this proposed catalytic cycle the relatively weakly coordinated THF ligand dissociates (probably reversibly) from the iron Lewis acid complex, opening a coordination site for attack by diazomethane[13] and the subsequent loss of dinitrogen to form the reactive diphenyl carbene complex, **7**. The carbene complex then immediately (on a scale faster than the NMR time scale) reacts with a second diphenyldiazomethane molecule to produce the azine, **3**, regenerating the chain-carrying active species, **5**.



Scheme 2 A plausible catalytic cycle for the formation of azine.

A similar study in which phenyldiazomethane, **8**, was used in place of diphenyldiazomethane, a mixture of *cis/trans* stilbenes, **10**, a small amount of the azine, **9**, and the azitine, **11**, resulted upon addition of the iron Lewis acid catalyst (Scheme 3).[14] To our knowledge this is the first observed case of azitine being formed catalytically. The formation of an azitine from a diazocompound in this reaction led us to reinvestigate the reaction with diphenyldiazomethane, since standard spectroscopic techniques fail to differentiate unequivocally between the azitine, **12**, and the azine, **3**. The X-ray crystallographic study reported here clearly confirms that the reaction product is benzophenone azine.



Scheme 3 Iron Lewis acid catalyzed decomposition of phenyl diazomethane.

The structure itself exhibits some interesting features. The molecule consists of two identical halves, which, by rotation around the N–N bond (47.5°) would produce a center of symmetry. There appear to be no intramolecular interactions which would preclude such a rotation. In spite of this lack of molecular symmetry, the structure is both centered and centrosymmetric. The molecular symmetry is also crystallographic symmetry, with the two asymmetric units related by a twofold axis, giving the molecule C_2 symmetry. The aromatic rings provide the possibility for resonance structures which would allow for some nitrogen-nitrogen multiple bonding, since each nitrogen contains a lone-pair. However the 1.40 Å bond length is typical of a nitrogen-nitrogen single bond. In contrast the short Cl–N bond length is clear evidence for strong nitrogen-carbon multiple bonding. A recently reported crystal structure of a platinum coordination complex of benzophenone azine further underscores the stability of this bonding scheme.[15] In this complex one nitrogen atom is coordinated to the platinum center, while the other is not. Despite this, the N–N distance of 1.391Å is nearly identical to that of the uncoordinated ligand. The C–N bond distance for the nitrogen not coordinated to the metal center is 1.283Å, virtually identical to that in free benzophenone azine, while the C–N distance for the coordinated nitrogen atom is only slightly longer, at 1.309Å.

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