

Cyclopentadienyliron complexes of nitrosobenzene: Preparation, structure and reactivity with olefins

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Abstract

The preparation, characterization and reactivity of (η^5 -cyclopentadienyl)iron complexes of nitrosobenzene are investigated as potential intermediates in the $[\text{CpFe}(\text{CO})_2]_2$ (**1**)-catalyzed allylic amination of olefins by nitroarenes. The oxidation of **1** by $[\text{Cp}_2\text{Fe}]^+$ in the presence of PhNO produces a novel dinuclear complex $\{[\text{CpFe}-\mu-(\eta^2-(N,O)\text{-PhNO})]_2-\mu\text{-NHPh}\}\text{BF}_4$ (**2**) along with $[\text{CpFe}(\text{CO})_3]\text{BF}_4$ and $[\text{CpFe}(\text{CO})_2(\text{NH}_2\text{Ph})]\text{BF}_4$; **2** has been characterized spectroscopically and by X-ray diffraction. Reaction of $\text{CpFe}(\text{CO})_2\text{I}$ with PhNO and AgSbF_6 produces the mononuclear complex $[\text{CpFe}(\text{CO})_2(\eta^2\text{-PhNO})]\text{SbF}_6$ (**3**) which has also been characterized spectroscopically, crystallographically and by PM3 MO calculations. The reaction of **3** with α -methyl styrene affords $[\text{CpFe}(\text{CO})_2(\text{PhNH}_2)\text{SbF}_6]$ and a trace of *N*-phenyl-2-phenylallyl amine **4**, while the reaction of **3** with 2,3-dimethyl-1,3-butadiene affords the aniline complex and a hetero-Diels-Alder adduct **5**, indicative of PhNO dissociation. Together these results preclude the involvement of nitrosoarene complex **3** as an important intermediate in the allylic amination catalyzed by $[\text{CpFe}(\text{CO})_2]_2$.
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Keywords: Nitrosoarene–iron complex; Allylic amination

1. Introduction

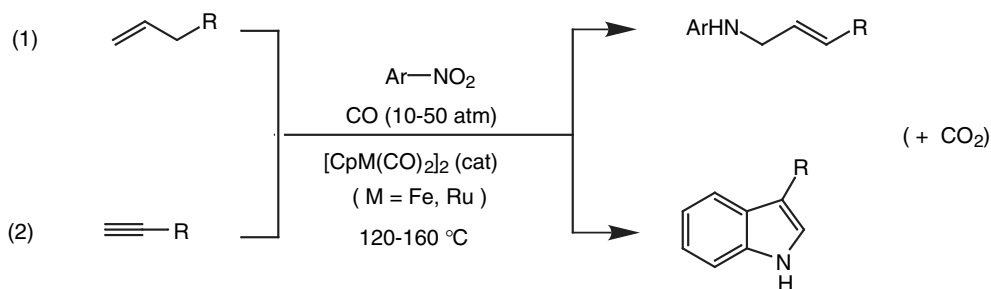
Transition metal-promoted reductions of nitroorganics by carbon monoxide have been widely investigated as a means for the production of a variety of valuable organonitrogen compounds, including amines, isocyanates, carbamates, ureas and heterocycles [1]. We recently discovered that dinuclear complexes $[\text{Cp}^*\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{Cp}^* = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$) catalyze the allylic amination of olefins [2] and the indolization of alkynes [3] by nitroarenes/CO (Scheme 1). These novel transformations feature high regioselectivity with respect to the hydrocarbon component with the ArN-unit being introduced at the less substituted carbon of the substrate. A photo-assisted, low pressure variant of the $[\text{Cp}^*\text{Fe}$

$(\text{CO})_2]_2$ -catalyzed allylic amination was also developed which allows the reactions to be conducted in common laboratory glassware [4]. Cenini and Ragaini have described a $\text{Ru}_3(\text{CO})_{12}$ -diimine catalytic system for allylic amination using nitroarenes as the aminating agent [5].

Mechanistic insight into these nitroarene reductive processes is very limited, especially with respect to the reactive nitrogen species involved. A few studies have demonstrated the involvement of various metallacycles incorporating RNO_2 and CO in the deoxygenation process [6–8]. Nitrenoid species, free or coordinated, have often been presumed to be intermediates in these reactions [1], but direct evidence for their involvement or the intervention of other reactive intermediates in the reactions is scarce. Trapping experiments, product isolation and kinetics studies of the Fp-catalyzed allylic amination in our laboratory [2,9,10] have ruled out the intervention of free nitrosoarenes or nitrenes as reaction

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Scheme 1.

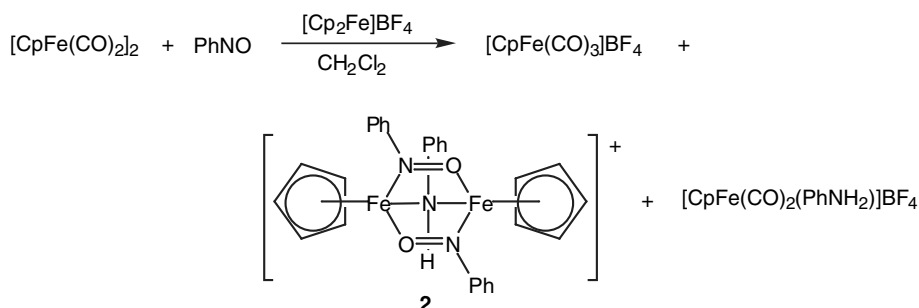
intermediates and have provided evidence for the involvement of mononuclear complex intermediate(s) in which both the olefin and an organonitrogen species are associated.

To further probe the nature of the reactive complexes involved in these reactions we are seeking to prepare and establish the reactivity of CpM-complexes of organonitrogen species which could be prospective intermediates. Since low valent metal complexes can serve as one-electron reductants of nitroarenes (oxidizing the organometallic) [11], we considered that cationic CpM-complexes of organonitrogen species could be possible intermediates. Accordingly, the complex [CpFe(CO)₂(η¹-(O)-PhNO₂)]PF₆ was prepared and structurally characterized, but found to be unreactive towards olefins [12].

Metal carbonyl-assisted deoxygenation of a nitroarene would initially produce a nitrosoarene species. Although metal complexes of C-nitroso compounds are well known and exhibit a diversity of coordination modes, their reactivity has not been significantly developed [13]. We thus sought to obtain corresponding cyclopentadienylmetal nitrosoarene (ArNO) complexes and to investigate their relevant reactivity vis a vis the allylic amination reaction. We describe here the preparation and structural elucidation of the first structurally characterized CpFe-complexes of nitrosoarenes [14] and investigate the reactivity of one of these towards a representative olefin and 1,3-diene, reactions which bear on the possible role of such complexes in the Fp-catalyzed allylic amination reactions.

2. Results and discussion

The capability of producing [CpFe(CO)₂L]⁺ complexes by oxidation of [CpFe(CO)₂]₂ (1) in the presence of appropriate ligands L [15] led us first to carry out the reaction of dimer 1 with ferrocenium salts and nitrosobenzene (CH₂Cl₂, r.t., 14–15 h, Scheme 2). Selective precipitation and trituration of the product mixture allowed the isolation of two metal complexes and detection of a third. A major product proved to be [CpFe(CO)₃]BF₄ based on its spectral data [16]. A dark brown second compound isolated, 2, was devoid of metal carbonyls judging from its IR spectrum, possessed one or more Ar-NO_x and Cp moieties based on its ¹H NMR spectrum, and appeared to be dinuclear based on its ESI-mass spectrum. The detailed structure of 2 was revealed by X-ray diffraction and found to be {[CpFe-μ-(η²-(N,O)-PhNO)]₂-μ-NHPh}BF₄; the cationic portion of 2 is shown in Fig. 1. The cationic unit has two CpFe moieties bridged by two η²-N,O-bonded nitrosobenzene units and one bridging phenyl amido unit. Formulation of the -NHPh fragment is based in part on electron counting considerations (18 electron count on each iron without a M–M bond); it is also supported by IR and ¹H NMR absorptions assigned to the N–H unit and the apparent H-bonding interaction to the BF₄⁻ ions in the crystal structure (see Supporting Information). The bridging PhNO coordination mode in 2 has been observed in some other dinuclear complexes [13]. Although the two PhNO units are environmentally inequivalent



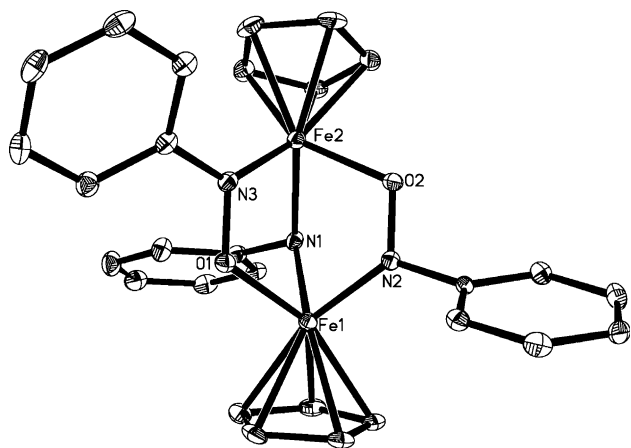
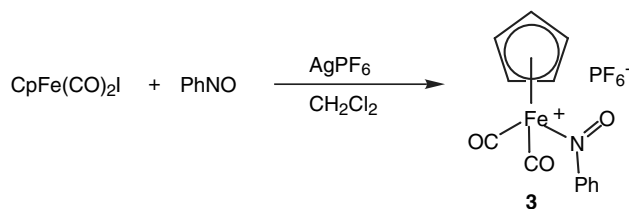


Fig. 1. X-ray ORTEP diagram for the cation of **2**. Thermal ellipsoids are shown at the 50% level.

because of their relationship with the bridging PhNH unit (one *syn*, one *anti*), the N–O bond lengths are the same ($1.318/1.319 \pm 0.002$ Å, partial listing in Fig. 1). These distances are somewhat longer than those of free ArNO monomers (ca. 1.25 Å) [13], suggesting a degree of Fe-to-NO π^* backbonding. The corresponding Fe–N and Fe–O distances at the two iron atoms are also very similar, showing that the PhNH unit is symmetrically bridged between the two irons, the result of a 3-center-4-electron interaction. A minor iron-containing product detected in the ferrocenium-induced reaction of Fp_2 with PhNO was tentatively identified as $[\text{CpFe}(\text{CO})_2(\text{PhNH}_2)]\text{BF}_4$ based on a comparison of its spectral characteristics with an authentic sample [17] prepared from the reaction of $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ with aniline.

The transformations involved in the reaction of Eq. (1) are clearly complex, especially the formation of iron complexes of reduced organonitrogen species, i.e., **2** and $[\text{CpFe}(\text{CO})_2(\text{PhNH}_2)]\text{BF}_4$, under oxidative conditions. The apparent redox imbalance could be accounted for by the formation of N-oxidized organics (e.g. NO, ArNO_2 , etc.), but we have not identified the potentially volatile organic products of the reaction. The source of hydrogen to produce these complexes is similarly unknown but could be derived from the solvent CH_2Cl_2 or adventitious moisture.

Seeking a monoiron-nitrosobenzene complex for reactivity studies, we investigated Ag^+ -induced halide abstraction from $\text{CpFe}(\text{CO})_2\text{I}$ in the presence of potentially ligating PhNO. Treatment of the iodide complex with excess PhNO and one equivalent of AgSbF_6 (CH_2Cl_2 , r.t.) resulted in rapid disappearance of the iodo complex as indicated by a series of color changes and IR monitoring. Addition of ether afforded a maroon compound **3** (83%), identified as $[\text{CpFe}(\text{CO})_2(\text{PhNO})]\text{SbF}_6$ by spectroscopic analysis and X-ray diffraction (Scheme 3). The molecular structure of **3**, shown in Fig. 2, features



Scheme 3.

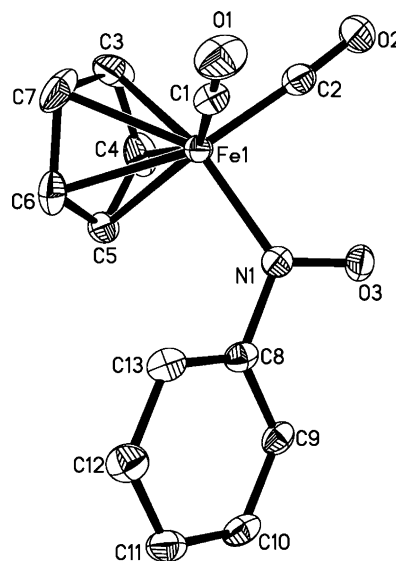


Fig. 2. X-ray ORTEP diagram for cation of **3**. Thermal ellipsoids are shown at the 50% level.

a typical $[\text{CpFe}(\text{CO})_2\text{L}]^+$ piano-stool geometry with the nitrosobenzene ligand coordinated in an η^1 -fashion through N. This coordination mode is common to many M–RNO complexes, including the only other structurally characterized CpFe-derivative, $\text{CpFe}(\text{CO})(\text{PPh}_3)(t\text{-BuNO})$ [14]. As with the latter, the nitroso ligand of **3** is nearly planar and approximately aligned with one of the Fe–CO units (C2-Fe-N-O dihedral, 9°). This could be the result of a stabilizing back-bonding interaction from a filled iron d orbital to π^* of the N–O unit. The importance of such an interaction, however, is not apparent from various probes of the Fe–N(O)Ar unit. The Fe–N and N–O bond lengths are comparable in both complexes (1.88 and 1.92 Å; 1.23 and 1.22 Å) and are typical of Fe–N single and N–O double bonds, suggesting a weak back-bonding interaction at most. A PM3 MO computational analysis [18] of **3** resulted in the energy-minimized geometry shown in Fig. 3, similar to the experimental X-ray structure with a slightly skewed ArNO plane relative to Fe–CO (C2-Fe-N-O dihedral, 17°). The calculated frontier bonding MOs of **3** (HOMO shown in Fig. 4(a)) are largely localized on the Cp–Fe fragment, giving little evidence of an Fe-to-NO π^* bonding interaction. The origin of the observed conformational preference for **3** in the solid state structure thus remains uncertain and could

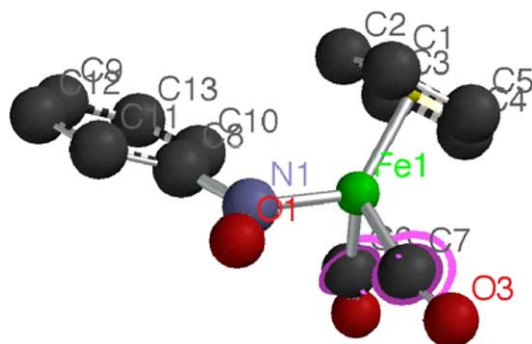


Fig. 3. PM3-calculated structure of **3**.

result from crystal packing forces. The electronic character of **3** is also of interest with respect to its reactivity, especially towards nucleophilic agents such as olefins (*vide infra*). The calculated LUMO (electron acceptor orbital) of **3** is seen to be substantially localized at the N(O)Ph unit (Fig. 4(b)) and the net positive charge is calculated to be greatest at the coordinated nitrogen (+1.0). Complex **3** could thus be anticipated to act as an N-centered electrophile [19].

To assess the viability of **3** as a possible intermediate in allylic amination a sample of **3** was heated with excess α -methyl styrene under typical catalytic conditions (120 °C, 41 atm. CO, Cl(CH₂)₂Cl). Only a trace of the allyl amine **4** was detected (2%), along with [CpFe(CO)₃]SbF₆ and [CpFe(CO)₂(PhNH₂)]SbF₆, which were identified spectroscopically (Scheme 4). To determine if the formation of the allyl amine was the result of PhNO dissociation from **3** (and subsequent ene-reaction/reduction with AMS), **3** was also heated with 2,3-dimethyl-

1,3-butadiene as above, an efficient trapping agent for PhNO via Diels-Alder reaction [20]. In this case the adduct **5** was isolated as the major organic product, strongly suggesting the intervention of free PhNO. Since this result stands in contrast to the formation of allyl amines from diene/alkene mixtures in the Fp₂-catalyzed reaction, complex **3** is excluded as an important intermediate in the catalytic allylic amination reactions.

3. Conclusions

Two nitrosoarene complexes {[CpFe- μ (η^2 -(*N,O*)-PhNO)]₂- μ -NHPH}BF₄ (**2**) and [CpFe(CO)₂(η^1 -PhNO)]Z (**3**) have been prepared and structurally characterized. Although MO calculations on **3** suggest potential electrophilic reactivity of the coordinated nitrosoarene, reactions of **3** with α -methyl styrene and dimethylbutadiene preclude the involvement of this compound as an important intermediate in the allylic amination of olefins by nitrosoarenes catalyzed by [CpFe(CO)₂]₂. Further probes of the pathways of catalytic allylic amination and of the reactivity of coordinated C-nitroso compounds are in progress.

4. Experimental

4.1. General

The following were prepared by literature methods: (η^5 -C₅H₅)Fe(CO)₂I [21], [(η^5 -C₅H₅)Fe(CO)₂(PhNH₂)]-BF₄[17].

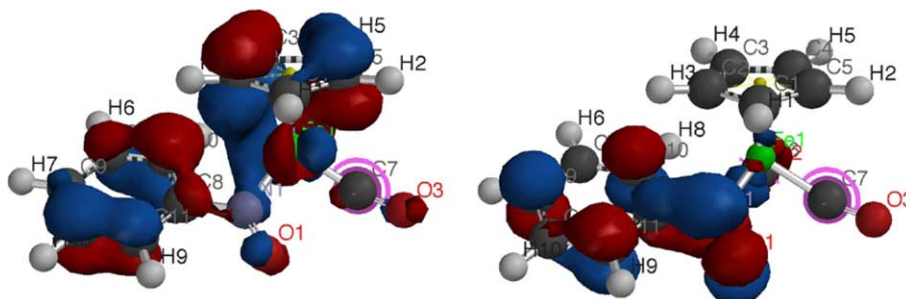
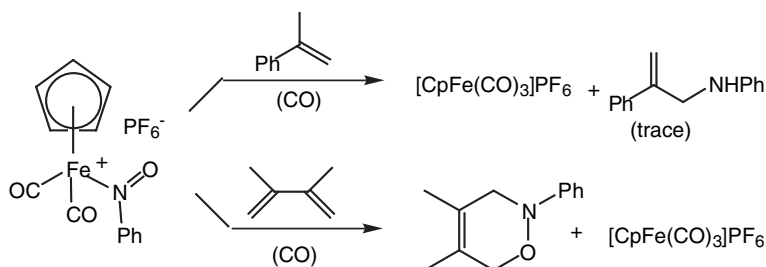


Fig. 4. PM3-calculated HOMO (left) and LUMO (right) of complex **3**.



Scheme 4.

4.2. Synthesis of $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}(\eta^2\text{-}(\text{N},\text{O})\text{-PhNO}))]_2\text{-}\mu\text{-NHPPh}\}\text{BF}_4$ (**2**)

$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (4.8 g, 0.014 mol) and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]\text{BF}_4$ (7.5 g, 0.027 mol) were added to a side-arm reaction flask and dissolved in 400 ml of dichloromethane. Nitrosobenzene (4.4 g, 0.041 mol) was added to the solution, whereupon its color changed from dark blue to dark red-brown. The reaction mixture was stirred for 14–15 h; then the volume was reduced by 80% at reduced pressure. Addition of 150 ml of anhydrous ether produced a dark red-brown precipitate. The precipitate was collected and washed with 300 ml of anhydrous ether. From the initial filtrate and ether washings dark brown crystals of $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PhNO})]_2(\mu_2\text{-NHPPh})\}\text{BF}_4$ (**2**) were isolated (1.2 g, 14%). IR (KBr, cm^{-1}) 3259, 3102, 3063; ^1H NMR (CD_2Cl_2 , δ) 7.8–7.2 (m, 10H), 7–6.6 (m, 5H), 5.4 (s, 5H), 5.3 (s, 5H); MS (ESI) 548 $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PhNO})]_2(\mu_2\text{-NHPPh})\}^+$, 441 $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]_2(\text{PhNO})\text{-}(\mu_2\text{-NHPPh})\}^+$, and 349 $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}]_2(\text{PhNO})\}^+$. Trituration of the aforementioned red-brown precipitate with dichloromethane left insoluble $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]\text{-BF}_4$, which was isolated by filtration (4.3 g, 55%); MS (ESI) 204 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$; IR (KBr, cm^{-1}) 3126, 2125, 2067. The volume of the filtrate was reduced under vacuum and addition of anhydrous ether produced a red-brown precipitate (2.7 g) which was largely (>80%) dinuclear **2** containing <20% of a second inseparable compound, assigned to $[\text{CpFe}(\text{CO})_2(\text{PhNH}_2)]\text{BF}_4$ based on its IR and NMR spectra (see Tables 1 and 2).

4.3. Synthesis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-PhNO})]\text{SbF}_6$ (**3**)

Solid AgSbF_6 (2.5 g, 0.0073 mol) was added to a solution containing $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ (2.2 g, 0.0072 mol) and PhNO (3.9 g, 0.036 mol) in 300 ml of dichloromethane. Upon addition the reaction color instantly changed from blue to orange and subsequently to dark red-brown over the course of stirring for 4–5 h. The mixture was filtered using a double-sided fritted funnel and the volume reduced by 90%. The solution was layered with 3 mL of anhydrous ether and placed in a freezer at -10°C over night, affording dark maroon crystals of **3** (3.1 g, 83%). IR (KBr, cm^{-1}) 3124, 2086, 2044, 1131; ^1H NMR (CD_2Cl_2 , δ) 7.99 (t, $J = 8$ Hz, 1H), 7.84 (d, $J = 8$ Hz, 2H), 7.70 (t, $J = 8$ Hz, 2H), 5.41 (s, 5H). MS (ESI) 162 $[\text{Fe}(\text{PhNO})]^+$, 228 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PhNO})]^+$, 284 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PhNO})]^+$.

5. X-ray structure determinations

The data for **2** were collected at 120(2) K and for **3** at 110(2) K on a Bruker Apex diffractometer [1] using $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Intensity data, which

Table 1
Selected bond lengths (\AA) and bond angles ($^\circ$) for the cation of **2**

Fe(1)–N(2)	1.8027(19)
Fe(1)–O(1)	1.9085(16)
Fe(1)–N(1)	1.986(2)
Fe(2)–N(3)	1.828(2)
Fe(2)–O(2)	1.9362(16)
Fe(2)–N(1)	1.9836(18)
N(2)–C(7)	1.446(3)
N(3)–C(13)	1.441(3)
O(1)–N(3)	1.319(2)
O(2)–N(2)	1.318(2)
N(2)–Fe(1)–O(1)	93.66(8)
N(2)–Fe(1)–N(1)	87.05(8)
O(1)–Fe(1)–N(1)	85.43(8)
N(3)–Fe(2)–O(2)	93.09(8)
N(3)–Fe(2)–N(1)	88.47(8)
O(2)–Fe(2)–N(1)	83.93(7)
Fe(2)–N(1)–Fe(1)	102.64(8)
O(2)–N(2)–C(7)	109.53(17)
O(2)–N(2)–Fe(1)	121.46(14)
O(1)–N(3)–C(13)	107.87(19)
O(1)–N(3)–Fe(2)	119.83(14)

Table 2
Selected bond lengths (\AA) and bond angles ($^\circ$) for cation of **3**

Fe(1)–C(1)	1.808(3)
Fe(1)–N(1)	1.916(2)
N(1)–C(8)	1.450(3)
O(2)–C(2)	1.129(3)
Fe(1)–C(2)	1.810(3)
O(3)–N(1)	1.226(3)
O(1)–C(1)	1.133(3)
O(2)–C(2)	1.129(3)
C(1)–Fe(1)–C(2)	91.02(13)
C(2)–Fe(1)–N(1)	91.93(11)
O(3)–N(1)–C(8)	114.4(2)
C(2)–Fe(1)–N(1)–O(3)	–8.8(2)
C(1)–Fe(1)–N(1)	96.03(10)
O(3)–N(1)–Fe(1)	121.58(17)
C(8)–N(1)–Fe(1)	123.66(17)

approximately covered the full sphere of the reciprocal space, were measured as a series of ω oscillation frames each 0.3° for 21 s/frame. The detector was operated in 512×512 mode and was positioned 6.12 cm from the crystal. Coverage of unique data for **2** was 95.3% complete to 56.6° (2θ) and 99.3% complete to 55° (2θ) for **3**. Cell parameters for **2** were determined from a non-linear least squares fit of 8923 reflections in the range of $3.2^\circ < \theta < 26.4^\circ$; a total of 27,306 reflections were measured. Cell parameters for **3** were determined from a non-linear least squares fit of 8140 reflections in the range of $2.3^\circ < \theta < 28.3^\circ$; a total of 74,589 reflections were measured. Crystal data and structure refinement information for **2** and **3** are provided in Table 3.

Both structures were solved by the direct method using the SHELXTL system [2], and refined by full-matrix least squares on F^2 using all reflections. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms

Table 3
Crystal data and structure refinement for **2** and **3**

Empirical formula	C ₉₂ H ₉₈ B ₃ F ₁₂ Fe ₆ N ₉ O ₈	C ₁₃ H ₁₀ F ₆ FeNO ₃ Sb
Formula weight	2053.32	519.82
Temperature (K)	120(2)	110(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2/ <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	31.829(2)	19.0896(14)
<i>b</i> (Å)	16.2455(12)	7.8838(6)
<i>c</i> (Å)	43.150(3)	
α (°)	90	90
β (°)	103.6880(10)	92.6170(10)
γ (°)	90	90
Volume (Å ³)	8960.0(12)	6487.2(8)
<i>Z</i>	4	16
Density (calculated) (Mg/m ³)	1.522	2.129
Absorption coefficient (mm ⁻¹)	1.033	2.637
<i>F</i> (000)	4224	4000
Crystal size (mm ³)	0.18 × 0.08 × 0.02	0.18 × 0.14 × 0.08
θ Range for data collection (°)	1.74–28.34	2.14–27.50
Index ranges	−42 ≤ <i>h</i> ≤ 42, −21 ≤ <i>k</i> ≤ 21, −23 ≤ <i>l</i> ≤ 22	−23 ≤ <i>h</i> ≤ 24, −10 ≤ <i>k</i> ≤ 10, −56 ≤ <i>l</i> ≤ 55
Reflections collected	74,589	27,306
Independent reflections [<i>R</i> (int)]	21317 [0.0671]	7417 [0.0212]
Completeness to $\theta = 26.50^\circ$	99.5%	99.3%
Absorption correction	Semi-empirical from equivalents	None
Max. and min. transmission	0.9796 and 0.8359	0.8167 and 0.6482
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	21317/0/1175	7417/0/451
Goodness-of-fit on <i>F</i> ²	1.008	1.122
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0482, <i>wR</i> ₂ = 0.0841	<i>R</i> ₁ = 0.0265, <i>wR</i> ₂ = 0.0610
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0973, <i>wR</i> ₂ = 0.0967	<i>R</i> ₁ = 0.0287, <i>wR</i> ₂ = 0.0619
Largest difference in peak and hole (e Å ⁻³)	0.849 and −0.852	1.023 and −0.770

were included with idealized parameters. The asymmetric unit of **2** contains three (C₂₈H₂₆N₃O₂Fe₂) cations, three BF₄[−] ions, and two (C₄H₁₀O) solvent molecules as shown in Fig. S6. The F(9) and F(10) atoms are disordered as evident from the large thermal parameters of these atoms. The C₂₈H₂₆N₃O₂Fe₂ cations form H-bonds with the F atoms of BF₄[−] ions as listed in Table S6. The Final *R*₁ = 0.048 is based on 13,462 “observed reflections” [*I* > 2 σ (*I*)], and *wR*² = 0.097 is based on all reflections (21,317 unique reflections). The asymmetric unit of **3** contains two C₁₃H₁₀FeNO₃ cations and two SbF₆[−] ions, which pack along the crystallographic *a*-axis as shown in the packing diagram (SI). The Final *R*₁ = 0.027 is based on 7001 “observed reflections” [*I* > 2 σ (*I*)], and *wR*² = 0.062 is based on all reflections (7417 reflections).

The following X-ray data tables for **2** and **3** are provided in the Supporting Information:

Atomic coordinates and equivalent isotropic displacement parameters; complete listing of bond lengths and angles; anisotropic displacement parameters; hydrogen coordinates and isotropic displacement parameters; torsion angles; hydrogen bonds.

1. Bruker (2002) SMART (version 5.625), GEMINI (version 1.0) and SAINT-plus (version 6.29), Bruker AXS Inc., Madison, Wisconsin.

2. Bruker (1997) SHELXTL: Version 6.12, Bruker AXS, and Madison, Wisconsin.

Crystallographic data for the structural analyses of **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre and assigned numbers CCD 274509 (for **2**) and 274510 (for **3**).

5.1. Reaction of α -methyl styrene with [(C₅H₅)Fe(CO)₂(PhNO)]SbF₆ (**3**)

α -Methyl styrene (0.50 ml, 3.9 mmol) was added to a solution of [(η^5 -C₅H₅)Fe(CO)₂(PhNO)]SbF₆ (0.41 g, 0.79 mmol) in 40 ml of 1,2-dichloroethane in the glass liner of a stainless steel pressure vessel. The glass liner was placed in a 125-ml stainless steel reactor (Parr) and pressurized with CO (41 atm.). The reaction mixture was stirred for 24 h at 110 °C, cooled, and depressurized (hood!). The volatiles were removed under vacuum, the residue was triturated with Et₂O, and the Et₂O solution was concentrated under vacuum. Preparative TLC of the residue (3:2 dichloromethane/hexane) afforded a trace of *N*-phenyl-2-phenyl-allylamine (0.004 g, 2%); ¹H NMR (CDCl₃, δ) 7.40 (d, *J* = 7 Hz, 2H) 7.33–7.086 (m, 5H), 6.68 (t, *J* = 7 Hz, 1H), 6.57 (d, *J* = 8 Hz, 2H), 5.41 (s, 1H), 5.27 (s, 1H), 4.10 (s, 2H), 3.87 (s, 1H); and several

other unidentified minor organic products (GC–MS). The ether-insoluble material was found to contain $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{NH}_2\text{C}_6\text{H}_5)]\text{SbF}_6$ (0.10 g, 27%); IR (KBr, cm^{-1}) 2062, 2009; ^1H NMR (CD_2Cl_2 , δ) 7.24 (t, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 7.2$ Hz, 2H), 6.93 (d, $J = 7.9$ Hz, 1H), 5.18 (s, 5H), 4.43 (s, 2H); MS (ESI, m/e) 270 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{NH}_2\text{Ph})]^+$, 214 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{NH}_2\text{Ph})]^+$.

5.2. Reaction of 2,3-dimethyl-1,3-butadiene with $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PhNO})]\text{SbF}_6$ (**3**)

2,3-Dimethyl-1,3-butadiene (0.87 ml, 7.7 mmol) was added to a solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PhNO})]\text{SbF}_6$ (0.40 g, 0.78 mmol) in 40 ml of 1,2-dichloroethane in a cylindrical glass liner which was placed in a 125-ml stainless steel reactor and pressurized with CO (41 atm.). The reaction mixture was stirred for 24 h at 110 °C, cooled, and depressurized (hood!). The volatiles were removed under vacuum and the residue was triturated with Et_2O . The Et_2O solution was concentrated under vacuum. Preparative TLC of the residue (4:1 ethyl acetate/hexane) afforded hetero Diels-Alder adduct **5** (0.0016 g, 11%) ^1H NMR (CDCl_3 , δ) 7.23 (t, $J = 8$ Hz, 2H), 7.06 (d, $J = 8$ Hz, 2H), 6.92 (t, $J = 7$ Hz, 1H), 4.26 (s, 2H), 3.59 (s, 2H), 1.67 (s, 3H), 1.57 (s, 3H) and some other inseparable minor organic products. The ether-insoluble residue was $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{NH}_2\text{C}_6\text{H}_5)]\text{SbF}_6$ (0.057 g, 14%). IR (KBr, cm^{-1}) 2062, 2009; ^1H NMR (CD_2Cl_2 , δ) 7.24 (t, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 7$ Hz, 2H), 6.93 (d, $J = 8$ Hz, 1H), 5.18 (s, 5H), 4.43 (s, 2H); MS (ESI, m/e) 270 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{NH}_2\text{Ph})]^+$, 214 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{NH}_2\text{Ph})]^+$.

6. Computational methods

PM3(TM)-level computations were carried out with the MacSpartan Plus program (Wavefunction, inc.) using the Unrestricted Hartree-Fock (UHF) model. The computational output listing of frontier molecular orbitals, energies and spin/charge densities is provided in the Supporting Information.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.06.045.

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