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A Cyclic Carbamoyl Complex Is a Resting State in Allylic Aminations Catalyzed by $[Cp^*Fe(CO)_2]_2$

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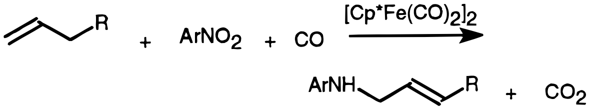
Summary: The major iron-containing species present during and after the $[Cp^*Fe(CO)_2]_2$-catalyzed allylic amination of olefins by nitrobenzene is a novel cyclic carbamoyl complex **2**. *Complex* **2** *is found to be a resting state in the catalytic reaction.*

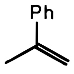
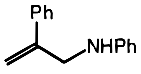
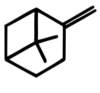
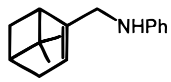
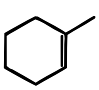
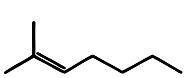
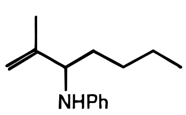
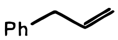
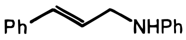
As part of our ongoing efforts to develop metal-catalyzed processes for the direct nitrogenation of hydrocarbons,[1,2] we recently reported that $[CpFe(CO)_2]_2$ (Fp_2) catalyzes the regioselective allylic amination of olefins via the reductive carbonylation of nitroarenes.[3] In this initial study the active involvement of a metal-bound organonitrogen species as the ArN-transfer agent was suggested by the results of trapping experiments. The practical importance of several metal-catalyzed reductive carbonylation reactions[4] and the limited understanding of their mechanisms[5] prompted us to probe further the scope and mechanistic features of these novel Fp-catalyzed reactions. We report herein the isolation, structural elucidation, and preliminary reactivity studies of a novel complex produced during allylic aminations by $PhNO_2$/CO promoted by $[Cp^*Fe(CO)_2]_2$ (Fp^*_2).

Seeking catalyst structure/activity relationships and the identification of iron-containing intermediates or products of the Fp-catalyzed $PhNO_2$/CO/olefin reactions, we turned our attention to $[Cp^*Fe(CO)_2]_2$ (**1**).[6] Indeed, **1** was found to effectively catalyze the reaction of nitrobenzene with several olefins (dioxane, 160 °C, 50 atm CO, 24 h), affording the corresponding allylamines in moderate to excellent yield (eq 1, Table).[7] These reactions, like those catalyzed by Fp_2,[3] proceed with high regioselectivity wherein the −NPh unit adds to the less substituted carbon of the original vinyl unit.



(1)

Table 1. Allylic Amination Catalyzed by $[Cp^*Fe(CO)_2]_2$[a]

Alkene	Allyl Amine	Yield, %[b]
		85
		60
		16
		80
		12 (32)[c]

[a] Conditions; olefin:$phNO_2$:Fp^*_2 = 2:1:0.05; dioxane, 160 °C, 750 psi CO. [b] GC, with naphthalene as internal reference. [c] Yield with 4 Å molecular sieves present.

To probe whether established reactive organonitrogen species are intermediates in the aminations catalyzed by **1**, a Diels−Alder trapping test for the intermediacy of free PhNO was found to be negative,[8] with only allylic amines detected as products (eq 2). Likewise, the intervention of free aryl nitrene was excluded based on the absence of carbazole[9] in the amination of AMS by *o*-nitrobiphenyl (eq 3).

The results of the above trapping experiments suggest that aminations catalyzed by **1** (and by Fp_2) involve the transfer of a coordinated nitrogen species. IR analysis of aliquots taken during the catalytic reaction or after

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[1] Johannsen, M.; Jorgenson, K. A. *Chem. Rev.* **1998**, *98*, 1689.

[2] Mo catalysts: Srivastava, A.; Ma, Y.; Pankayatselvan, R.; Dinges, W.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 853. Srivastava, R. S.; Nicholas, K. M. *J. Org. Chem.* **1994**, *59*, 5365. Srivastava, R. S.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2335. Fe salt catalysts: Srivastava, R. S.; Nicholas, K. M. *Tetrahedron Lett.* **1994**, 8739. Srivastava, R. S.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1996**, *118*, 3311. Srivastava, R. S.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 9, 3302. Fe-complex catalysts: Johannsen, M.; Jorgensen, K. A. *J. Org. Chem.* **1994**, *59*, 214. Johannsen, M.; Jorgensen, K. A. *J. Org. Chem.* **1995**, *60*, 5979.

[3] Srivastava, R. S.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1998**, 2705.

[4] Review: Tafesh, A. M.; Weiguny, J. *Chem. Rev.* **1996**, *96*, 2035.

[5] Review: Cenini, S.; Ragaini, F. *Catalytic Reductive Carbonylation of Organic Nitro Compounds*; Kluwer Publ.: Dordrecht, Netherlands, 1997; Chapter 6.

[6] Both transient and long-lived iron−carbonyl compounds were detected by IR analysis of samples taken during and after amination reactions catalyzed by Fp_2. Although some of these survived flash chromatography (silica gel, 1:9 → 1:1 ethyl acetate/petroleum ether), contamination by organic byproducts precluded their identification.

[7] Organic products were identified by comparison of their NMR and mass spectra with those of authentic samples.

[8] Taylor, E. C.; Tseng, C.-P.; Rampal, J. B. *J. Org. Chem.* **1982**, *47*, 552.

[9] Sundberg, R. J.; Brenner, M.; Suter, S. R.; Das, B. P. *Tetrahedron Lett.* **1970**, 2715. Sundberg, R. J.; Heintzelmen, R. W. *J. Org. Chem.* **1974**, *39*, 2546.

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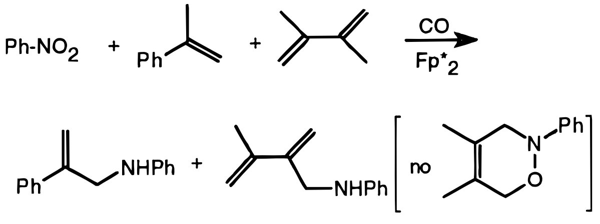
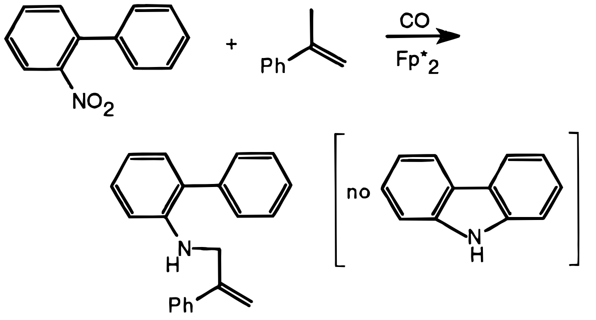


(2)



(3)

its completion revealed the absence of dimer **1** (ν_{CO} 1923, 1748 cm^{-1}) and the predominant formation of a new metal carbonyl species, **2**, with terminal Fe−CO absorptions at 2016 and 1961 cm^{-1}. The same compound is produced in the reaction of **1** with nitrobenzene/CO *in the absence of olefin*. Careful flash chromatography (silica gel, 1:1 petroleum ether/ethyl acetate) provided reasonably pure **2** as a dark red solid. The NMR data for **2**[10] clearly indicate the incorporation of a −NPh unit and the presence of two different Cp−Me groups. Since the MS data for **2** were inconclusive,[10] its structure was finally established by X-ray diffraction.[11]

The structure of **2** (Figure 1, Scheme 1) was thus found to be a monometallic cyclic carbamoyl complex which has incorporated a Cp*-derived methylene group, a carbon monoxide molecule, and a PhN− unit from nitrobenzene. The molecule has approximate C_s symmetry with the Fe−C(O)−NPh−CH_2− chain included in the symmetry plane, indicating sp^2 hybridization at both N(1) and C(13). The Fe−C(13), C(13)−O(3), and C(13)−N(1) distances and the position of the C=O IR absorption (1580 cm^{-1}) indicate significantly delocalized, multiple-bond character in these linkages.[12]

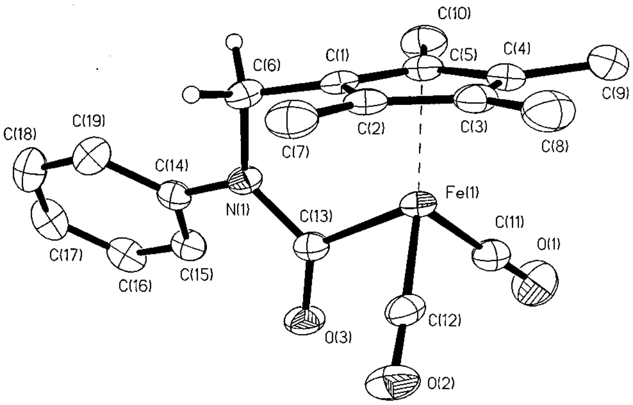
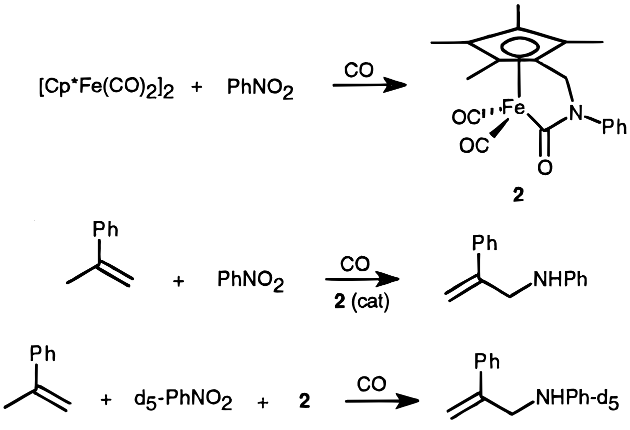


Figure 1. ORTEP diagram for **2** showing thermal ellipsoids at the 40% level; hydrogen atoms except H6a and H6b are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−C(11) 1.762(2), Fe(1)−C(12) 1.757(2), Fe(1)−C(13) 1.971(2), C(13)−O(3) 1.220(3), C(13)−N(1) 1.406(3), N(1)−C(14) 1.424(3), N(1)−C(6) 1.467(3), C(11)−O(1) 1.141(3), C(12)−O(2) 1.151(3); O(1)−C(11)−Fe(1) 178.0(2), O(2)−C(12)−Fe(1) 177.5(2), C(11)−Fe(1)−C(12) 96.6(1), Fe(1)−C(13)−O(3) 125.2(2), N(1)−C(13)−O(3) 119.7(2), C(13)−N(1)−C(14) 123.6(2), C(13)−N(1)−C(6) 117.2(2), C(14)−N(1)−C(6) 118.6(2), N(1)−C(6)−C(1) 108.4(2).

Scheme 1



While the pathway leading to the formation of **2** remains to be established, the intervention of coordinated phenyl imido and phenyl isocyanate precursors appears likely. Homologous Re−carbamoyl derivatives have been reported via carbonylation of *cyclic* imido precursors.[13] Other examples of the activation of coordinated Cp−methyl C−H bonds without the assistance of strong external reagents are rare, especially among the later transition metals.[14] Furthermore, although a number of four- and five-membered metallacycles which incorporate partially deoxygenated $ArNO_2$ and CO or CO_2 fragments have been implicated as intermediates in metal-catalyzed reductive carbonylations of nitroorganics,[15] the cyclic carbamoyl function of **2** is the first of its type to be identified from such a reaction.

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(10) Data for **2**: IR (CH_2Cl_2, cm^{-1}) 2016, 1961, 1602, 1580, 1048; ^1H NMR ($CDCl_3$, δ) 7.37 (m, 4H), 7.15 (m, 1H), 4.04 (s, 2H), 2.13 (s, 6H), 1.88 (s, 6H); ^{13}C NMR ($CDCl_3$, δ) 215.4, 202.8, 141.8, 128.8, 124.8, 124.5, 107.9, 99.4, 92.5, 42.9, 10.2, 9.8; MS (ES^+) 366 ($M + H^+$, 100), 338 ($M + H^+ - CO$, 9), 310 ($M + H^+ - 2CO$, 5), 282 ($M + H^+ - 3CO$).

(11) Crystal data for **2** ($C_{19}H_{19}FeNO_3$): crystal size 0.46 × 0.36 × 0.26 mm; triclinic, space group $P1$; $Z = 2$; $a = 8.3108(7)$ Å, $\alpha = 109.230(5)°$, $b = 10.2541(7)$ Å, $\beta = 98.049(5)°$, $c = 11.6127(8)$ Å, $\gamma = 108.273(5)°$; $V = 854.00(11)$ Å^3; $\rho_{calcd} = 1.420$ Mg/m^3; θ 1.93−24.99°, Mo Kα ($\lambda = 0.71073$ Å), T 173(2) K; 2873 independent reflections, 2662 "observed reflections"; the data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied; the structure was solved by the direct atom method and refined by full-matrix least-squares on F^2 using all reflections. All the non-hydrogen atoms were refined anisotropically, and all the hydrogens were included in the refinement with idealized parameters; final R1 = 0.032, wR2 = 0.079.

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(13) Wang, T.-F.; Hwu, C.-C.; Wen, Y.-S. *Organometallics* **1998**, *17*, 131.

(14) Weber, L.; Kirchhoff, R.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1182. Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665. Riley, P. N.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1999**, *18*, 3579. Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649.

(15) Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. *Organometallics* **1998**, *17*, 2199. Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1638. Skoog, S. J.; Campbell, J. P.; Gladfelter, W. L. *Organometallics* **1994**, *13*, 4137. Gargulak, J. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1994**, *116*, 3792.

An important question is whether **2** plays a role in the catalytic amination mechanism or rather is an unreactive, "dead-end" product. The following observations bear on this question. When **2** was heated with excess α-methylstyrene under typical catalytic conditions (160 °C, 50 atm CO, dioxane), none of the corresponding allylamine was detected and **2** was largely recovered. However, allylamine was slowly produced when nitrobenzene and AMS were heated under the same conditions with **2** as catalyst (5 mol %, turnover = 6 in 5 days); the AMS amination activity of **1**:**2** is approximately 15:1 (Scheme 1). Finally, when **2** and $C_6D_5NO_2$ (1:6) were allowed to react with excess AMS (30 equiv) under CO (50 atm, 160 ° C, 36 h), the resulting allylamine was exclusively that derived from $C_6D_5NO_2$, i.e., $C_6D_5NHCH_2CPh{=}CH_2$ (>97%), and the recovered **2** was undeuterated (>97%), as established by EI GC−MS. Thus, although **2** can serve as a catalyst for amination, it does not transfer its own −NPh unit. The lesser catalytic activity of **2** relative to that of Fp^*_2 indicates that the former is a minor, but significant contributor to the overall catalysis. Experiments that probe further the mechanism of formation of **2** and that of the catalytic amination of olefins by this and other Fp-derived catalysts are in progress.

Acknowledgment. We thank the National Science Foundation (CHE9610277) for support of this project.

Supporting Information Available: Tables of the positional parameters and temperature factors, H atom coordinates, anisotropic displacement parameters, complete list of bond lengths and angles, and least-squares planes for **2**. This material is free of charge via the Internet at http://pubs.acs.org.

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