

N-Heterocyclic Carbene-Like Catalysis by a Metal-Organic Framework (MOF) Material

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General Information

All reactions were carried out under a nitrogen atmosphere using traditional Schlenk line techniques in septa-sealed, oven-dried, 2-dram vials without any magnetic stirring. THF, toluene, and methanol were purified by passage through a bed of activated alumina.¹ All other reagents were purchased from Sigma Aldrich. NMR spectra were recorded on a Bruker AVANCE III 500 (500 MHz) spectrometer with direct CH cryo-probe and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Reactions were monitored using an Agilent Systems 6890 Gas Chromatograph with nonpolar Agilent 19091J-413 column, ramping from 30 °C to 280 °C at 10 °C per minute followed by a 10-minute hold at 280 °C. Percent conversion was calculated using HP CORE Chemstation software.

Experimental Details: TIF-1

Synthesis of TIF-1

TIF-1 was prepared according to Willans et al.² with structure confirmation by PXRD (Rigaku XDS 2000 diffractometer using CuK α radiation ($\lambda=1.5418$ Å). Solvent was evacuated by first heating under vacuum for 12 hours at 150 °C followed by heating at 225 °C in an oven at atmospheric pressure. The structure of **TIF-1** was not compromised after the solvent was evacuated, as confirmed by single crystal X-ray diffraction (Bruker, AXS APEX2 diffractometer equipped with CCD detector and CuK α microsource.)

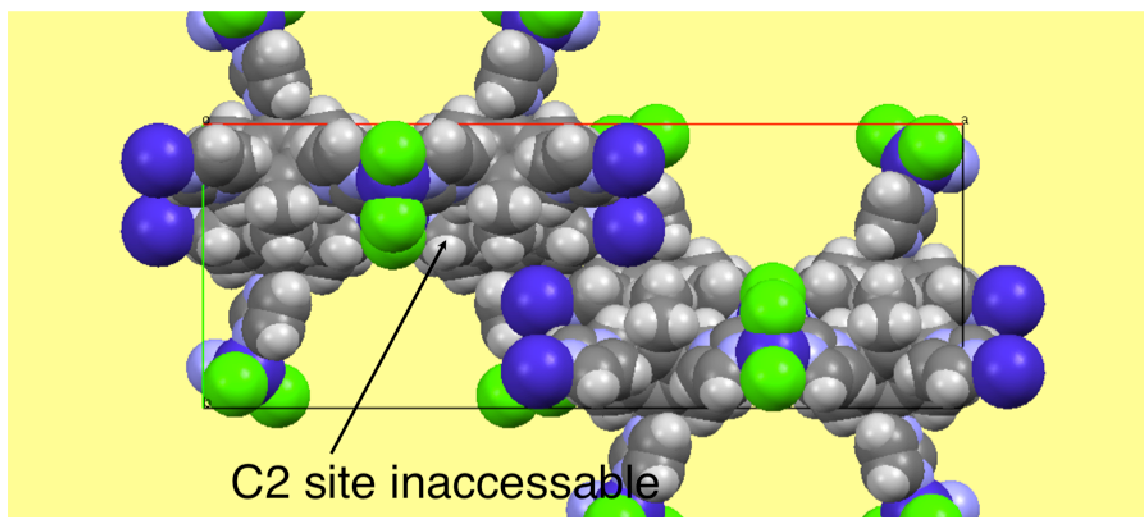


Figure S1: TIF-1 Space-filling model

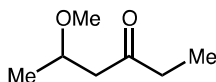
Purple = Co, Green = Cl, Blue = N, Grey = C, White = H

This space-filling model demonstrates the C2 sites of the metal imidazoles in **TIF-1** are blocked sterically by other parts of the rigid framework. The C4/C5 backbone of the imidazole faces the interior of the pore and is exposed.

Experimental Details: Catalysis

General Procedure

This procedure was modified from Phillips et al.³ Catalyst (0.8-5 mol %) was added to a 2-dram oven-dried vial. The vial was sealed with a screw cap equipped with a Teflon septum, and purged with N₂. Under N₂, THF (0.80 mL) was added. The reaction was cooled to -78 °C in a CO₂/acetone bath, and *n*-BuLi (16 μL, 0.02 mmol, 2.50 M in hexanes) was added through a syringe. The reaction was allowed to warm to 20 °C by removing the vial from the dry ice/acetone bath. After 10 minutes, the solvent was removed under vacuum and the vial was backfilled with N₂. A pre-made mixture of (*E*)-hex-4-ene-3-one (92 μL, 0.8 mmol), alcohol, and toluene (0.80 mL) was added to the vial via syringe. The reaction was monitored by gas chromatography at 20 °C under N₂ atmosphere.



As we had not previously used this compound, a pure sample was synthesized according to a literature method⁴ in order to facilitate reaction monitoring by GC.

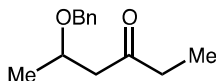
Using TIF-1

The general procedure was followed using 8 mg (0.8 mol %) **TIF-1** and 162 μL (4 mmol) dry methanol. The reaction progress was followed by gas chromatography. After 24 hours the reaction mixture was passed through a plug of silica in 100% dichloromethane and product observed by crude ¹H and ¹³C NMR. The highest observed percent conversion to product was 65%.

Using IMes·HCl

The general procedure was followed using 16 mg (5 mol %) IMes·HCl and 162 μL (4 mmol) dry methanol. The reaction progress was monitored by gas chromatography over 24 hours. The

highest observed percent conversion to product was 77%. Analytical data are consistent with those provided in the literature.⁴



Using TIF-1

The general procedure was followed using 8 mg (0.8 mol %) **TIF-1** and 248 μ L (2.4 mmol) benzyl alcohol. The reaction progress was monitored by gas chromatography over 24 hours. The highest observed percent conversion to product was 83%. Analytical data for the product are consistent with Phillips et al.³

Using IMes·HCl

The general procedure was followed using 16 mg (5 mol %) IMes·HCl and 248 μ L (2.4 mmol) benzyl alcohol. The reaction progress was monitored by gas chromatography over 24 hours. The highest observed percent conversion to product was 72%. Analytical data for the product are consistent with Phillips et al.³

Competition Reactions

The general procedure was followed using 8 mg (0.8 mol %) **TIF-1** and a solution containing equal parts benzyl alcohol (248 μ L, 2.4 mmol) and methanol (97 μ L, 2.4 mmol.) Over the course of 12 hours, no significant preference for either product was observed (products were formed at approximately the same rate.) The reaction was repeated using 16 mg (5 mol %) IMes·HCl to ensure there was no chemical preference for the formation of one product over the other, and again both the benzyl alcohol and methanol products were formed at approximately the same rate.

Surface vs. In-Pore Catalysis Experiments

In order to further test if catalysis was occurring on the surface of the MOF, the addition of MeOH to 4-hex-ene-3-one was repeated with ground **TIF-1** powder and a magnetic stir bar according to the general procedure. The vial stirred vigorously for 3 minutes on a magnetic stir plate before the addition of THF and *n*BuLi, grinding **TIF-1** to a very fine powder. The reaction was monitored by removal of 10 μ L aliquots at various time intervals. The aliquots were passed through a pipette containing 0.5 cm³ of silica gel over a glass wool plug. The pipette columns were flushed with CDCl₃ directly into NMR tubes. Percent conversion was calculated using the methyl ether peak from the product (singlet, 3.33 ppm, 3H), and comparing it to the C4 alkene proton of the starting material (doublet, 6.08 ppm, 1H). The results are plotted in Figure S2, below, and compared to large particles of TIF-1 catalysis of the same reaction. In both cases, the reaction fits logarithmic pattern for reaction progress, i.e. we assumed first-order kinetics. Logarithmic fits were calculated using Microsoft Excel.

For **TIF-1** (large particles): $y = 10.99\ln(x) + 25.73$; $R^2 = 0.92$

For **TIF-1** (ground): $y = 2.91\ln(x) + 85.09$; $R^2 = 0.74$

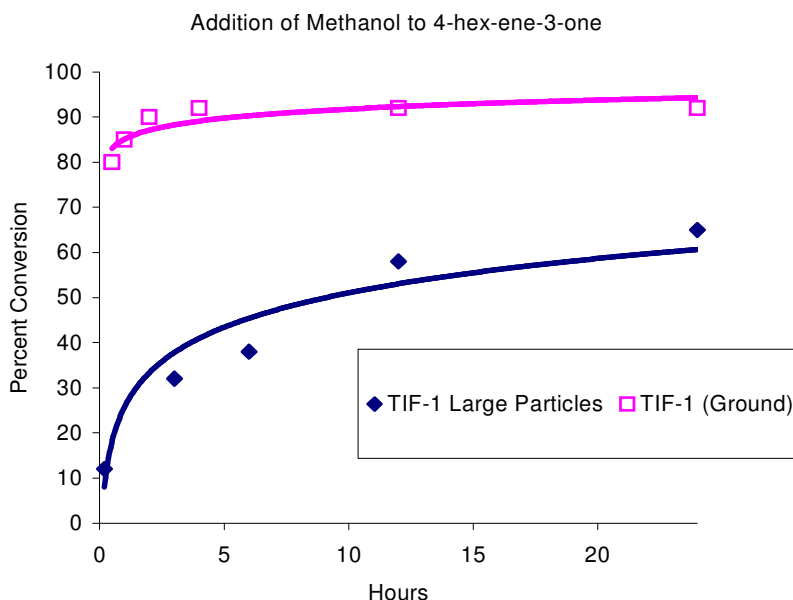


Figure S2: Addition of methanol to 4-hex-ene-3-one by large particles of **TIF-1**, and **TIF-1** that had been mechanically ground. Mechanically ground **TIF-1** was monitored by ¹H NMR, large particles by GC.

Calculation of Ratio of Surface-exposed Imidazole Linkers to Total Imidazole Linkers

Because **TIF-1** has 6 imidazoles (2 struts) per asymmetric unit, we loaded **TIF-1** at 0.8 mol % as opposed to 5 mol % for IMes·HCl (based on the molecular weight of the asymmetric unit) in order to maintain the same number of potential catalytic sites per reaction. However, since we subsequently established through competition reactions that catalysis likely occurs only on the MOF exterior, only a fraction of the imidazole sites are candidate catalysts. As shown in Figure S1, crystals of **TIF-1** vary dramatically in size and shape. In order to choose a representative crystal size, we referenced the original crystal selected to produce **TIF-1** crystal structure data.² (Dimensions = 0.15 x 0.04 x 0.05 mm.) For a unit cell of **TIF-1**, (*Z* = 4), there are 24 imidazoles, and the dimensions are 40.12 x 15.01 x 11.20 Å. The ratio of the surface area for the crystal to

the unit cell, multiplied by 24 imidazoles per unit cell, is 3.09×10^{10} . The ratio of the volume for the crystal to the unit cell, multiplied by 24 imidazoles per unit cell, is 1.07×10^{15} . Taking the 2 previously calculated ratios into account, the ratio of surface-exposed imidazoles to total imidazoles for this crystal is 3×10^{-5} . Therefore, the corrected loading of **TIF-1**, based on available sites for catalysis, appears to be more than four orders of magnitude lower, at $\sim 2 \times 10^{-5}$ mol%.

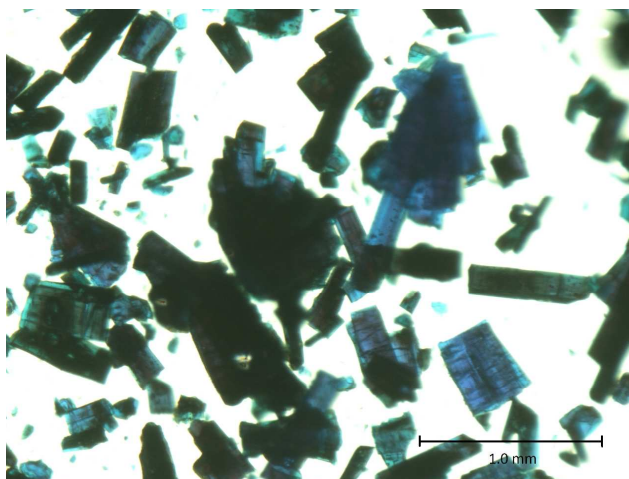


Figure S3: Optical microscope image of TIF-1 crystals

Attempted Trapping of Carbene using D₂O

In an attempt to determine where the deprotonation of **TIF-1** was occurring, 5 mg of **TIF-1** was placed in 0.1 mL 2.5 M *n*BuLi in hexanes in an inert atmosphere for 10 minutes. After 10 minutes, 0.2 mL D₂O was added in order to trap the formed carbene, and the entire reaction vial was quenched with 0.3 mL D₂SO₄ in order to dissolve the MOF structure. The resulting NMR, as compared to an NMR of as synthesized TIF-1 dissolved in D₂SO₄, showed no appreciable differences in integration of the imidazole proton peaks (Figure S4 below.) This finding supports our claim that only a very small portion of the imidazoles in TIF-1 are being converted

to carbenes, (as previously mentioned, we estimated the ratio of surface imidazoles to total imidazoles at 3×10^{-5}) as the amount is indistinguishable by NMR.

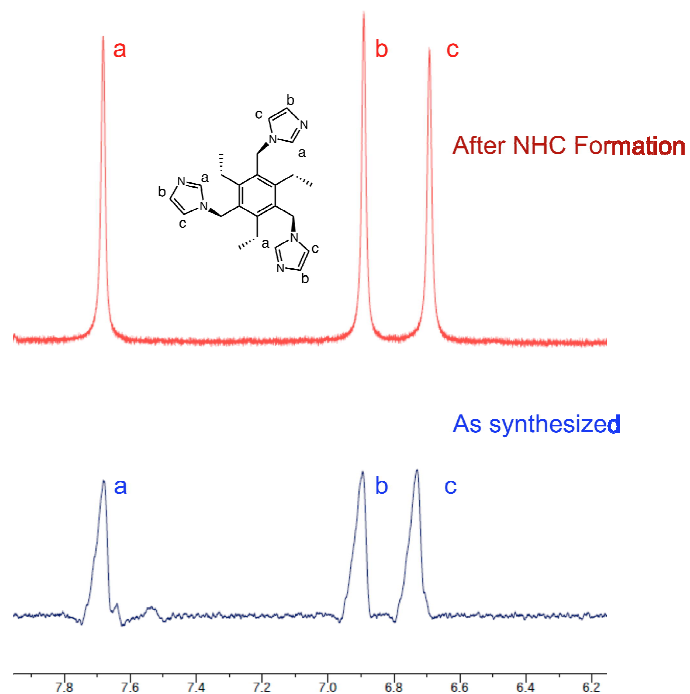


Figure S4: NMR of **TIF-1** as synthesized, (bottom), and after NHC formation and subsequent quenching with D₂O (top.)

Logarithmic Fitting of Percent Conversion Data

Percent conversions were calculated using HP CORE Chemstation software. The percent conversions were plotted versus the time the aliquot was removed from the reaction vessel for GC analysis. Both **TIF-1** and IMes fit a logarithmic pattern for reaction progress, i.e. we assumed first-order kinetics. Logarithmic fits were calculated using Microsoft Excel.

$$\text{For } \mathbf{TIF-1}: y = 6.84\ln(x) + 65.55; R^2 = 0.84$$

$$\text{For IMes: } y = 15.83\ln(x) + 23.82; R^2 = 0.97$$

Retention of Crystallinity After Catalysis

In order to ensure retention of crystallinity after catalysis, a PXRD was taken of activated **TIF-1**, and **TIF-1** that had been used in the addition of MeOH to 4-hex-ene-3-one (Figure S5). Powder X-ray diffraction patterns for nylon-loop mounted samples were obtained at room temperature with a Bruker MX I μ S microsource (CuK α radiation) and ApexII CCD detector. Samples were mounted in paratone oil. The PXRD data were collected with an area detector as rotation frames over 180° in ϕ at 2θ values of 12°, 24°, 36° 48 and 60 and exposed for 10 minutes for each frame. At a distance of 150 mm, the detector area covers 24° in 2θ . Overlapping sections of data were matched and the resulting pattern integrated using the Bruker APEX2 Phase ID program. Powder-pattern data were treated for amorphous background scatter.

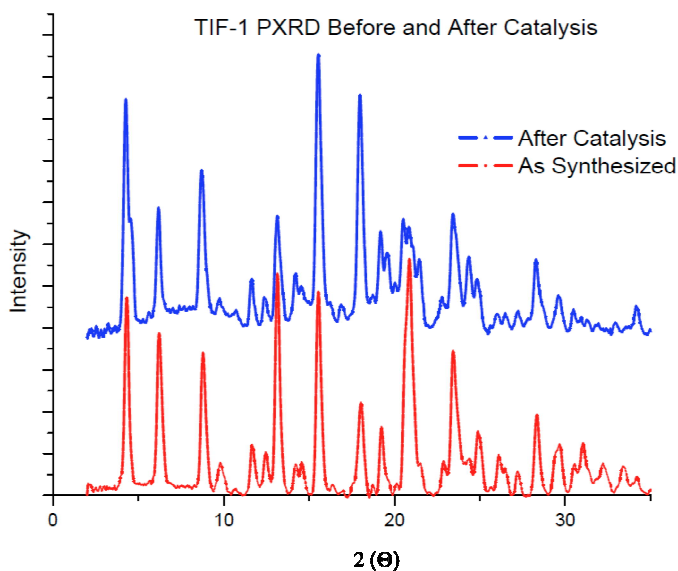


Figure S5: NMR of **TIF-1** as synthesized, (bottom), and after NHC formation and subsequent quenching with D₂O (top.)

References:

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- (2) Willans, C. E.; French, S.; Barbour, L. J.; Gertenbach, J.-A.; Junk, P. C.; Lloyd, G. O.; Steed, J. W. *Dalton Trans.* **2009**, 6480.
- (3) Phillips, E. M.; Riedrich, M.; Scheidt, K. A. *J. Am. Chem. Soc.* **2010**, *132*, 13179.
- (4) Murtagh, J. E.; McCooey, S., H.; Connon, S. J. *Chem. Commun.* **2005**, *2*, 227.