

Matrix Isolation Chemistry in a Porous Metal–Organic Framework: Photochemical Substitutions of N₂ and H₂ in Zn₄O[(η⁶-1,4-Benzenedicarboxylate)Cr(CO)₃]₃

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Reactive metal sites embedded within microporous metal–organic frameworks have garnered considerable recent attention, primarily owing to potential applications in hydrogen storage¹ and catalysis.² Such sites have usually arisen during framework formation as a consequence of structure, but have occasionally been generated through subsequent cation exchange,^{l,j,k} bridge reduction,^{l,i} or metal insertion reactions.^{2b} In the course of studying the hydrogen storage properties of Zn₄O(BDC)₃ (BDC²⁻ = 1,4-benzenedicarboxylate),³ we considered the possibility that transition metal centers might be attached in an η⁶ fashion to the benzene rings constituting most of the internal surface of the material. In particular, piano stool complexes of the type (η⁶-arene)M(CO)₃ (M = Cr, Mo, W) have enjoyed a rich chemistry⁴ and can be generated under mild conditions compatible with the framework stability.⁵ In frozen gas matrices and supercritical fluid solutions, such species have been found to undergo light-activated substitution chemistry in which a CO ligand is replaced by N₂ or H₂.⁶ Here, we show that the benzene rings within Zn₄O(BDC)₃ can be fully loaded with Cr(CO)₃ groups and that the product undergoes analogous photochemical reactions. Moreover, because the metal centers are pinned to the rigid scaffolding of the metal–organic framework, the stability of the resulting N₂ and H₂ complexes is greatly enhanced.

The synthesis of Zn₄O[(η⁶-1,4-benzenedicarboxylate)Cr(CO)₃]₃ (**1**) was accomplished using a route similar to one previously employed in generating a variety of substituted (η⁶-arene)Cr(CO)₃ complexes (see Figure 1).⁵ Recognizing, however, that the solid product could not readily be separated from any insoluble side products formed during the reaction, extra care was taken to purify all reagents and solvents and to exclude oxygen rigorously. Under a nitrogen atmosphere, Zn₄O(BDC)₃ (50 mg, 0.065 mmol), Cr(CO)₆ (140 mg, 0.65 mmol), dibutylether (6 mL), and THF (1 mL) were loaded into a borosilicate ampule. The reaction mixture was cooled to –78 °C and degassed under reduced pressure; the ampule was then flame sealed. The sealed tube was heated at 140 °C for 5 days, during which time the colorless solid turned dark red, indicating the attachment of Cr(CO)₃ units. Upon cooling, the product was removed from the ampule under nitrogen and washed with THF and CH₂Cl₂ to extract any unreacted Cr(CO)₆. The guest solvent was then evacuated to afford 71 mg (92%) of **1** as a red powder. As detailed in the Supporting Information, a similar reaction employing Mo(CO)₆ yielded the partially functionalized compound Zn₄O[(BDC)(Mo(CO)₃)_{0.63}]₃. Both compounds are insoluble in common organic solvents but decompose upon exposure to water, acid, or base.

The powder X-ray diffraction pattern of **1** indexes to a face-centered cubic unit cell nearly identical to that of Zn₄O(BDC)₃, demonstrating that it possesses the same network structure of [Zn₄O]⁶⁺ tetrahedra bridged by linear benzenedicarboxylate units. The infrared spectrum shows two new peaks in the CO stretching region, a sharp peak at 1990 cm⁻¹ and a broader peak at 1929 cm⁻¹. This matches almost perfectly with the CO stretching bands

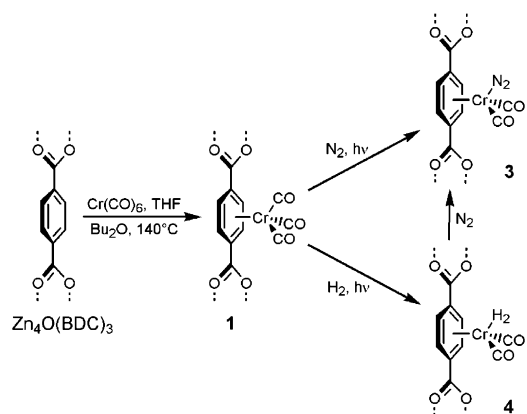


Figure 1. Reaction of Zn₄O(BDC)₃ with Cr(CO)₆ to generate Zn₄O[(BDC)Cr(CO)₃]₃ (**1**), followed by photolysis under N₂ or H₂ to afford Zn₄O[(BDC)Cr(CO)₂(N₂)]₃ (**3**) and Zn₄O[(BDC)Cr(CO)₂(H₂)]₃ (**4**).

observed for (H₂BDC)Cr(CO)₃ (see Figure S1), indicating that **1** indeed contains Cr(CO)₃ groups attached in an η⁶ fashion to the benzene rings of the framework. To determine the extent of their incorporation, a sample was digested using dilute HCl and the insoluble material dissolved in (CD₃)₂CO. The ¹H NMR spectrum of the solution showed the presence of (H₂BDC)Cr(CO)₃ (δ = 6.3 ppm) and no H₂BDC (δ = 8.1 ppm), establishing that ca. 100% of the benzene rings in the framework are coordinated to Cr(CO)₃. Elemental analysis confirmed this result, with chromium accounting for 13 wt % of the material. Consistent with retention of a microporous structure, an N₂ gas adsorption measurement performed on **1** at 77 K revealed a Type I isotherm indicating a BET surface area of 2130 m²/g (see Figure S2).

Attempts were made to generate open chromium coordination sites by simply heating **1** to evolve CO gas. As shown in Figure 2, a thermogravimetric analysis revealed a weight loss of 20.7 wt % between 150 and 210 °C, corresponding to removal of all nine CO ligands per formula unit. Further heating exposed a plateau of compositional stability up to ca. 360 °C. Measurements performed on a solid sample of the molecular complex (H₂BDC)Cr(CO)₃ produced analogous results, with loss of all CO ligands between 150 and 250 °C. To better characterize the decarbonylated framework, a bulk sample was prepared by heating **1** at 200 °C under a flow of nitrogen for 5 h. The infrared spectrum of the resulting gray powder (**2**) displayed no peaks in the range 1800–2300 cm⁻¹, confirming the absence of CO or N₂ ligands. The powder X-ray diffraction pattern indexed to the same unit cell as Zn₄O(BDC)₃, indicating that the framework skeleton is still intact in **2**. Unfortunately, low-pressure N₂ and H₂ adsorption measurements performed at 298 K showed uptake of fewer than 0.2 molecules per formula unit at 298 K (see Figure S3). Thus, far fewer than three open coordination sites per metal are available in **2**, suggesting that the chromium atoms may become mobile and aggregate at 200 °C. Removal of the CO ligands by heating **1** under

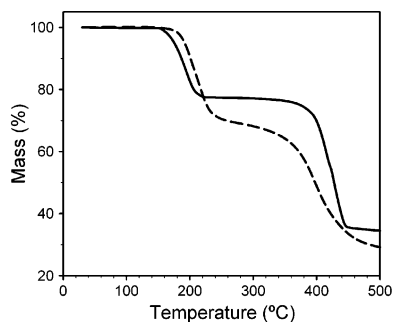


Figure 2. Thermogravimetric analyses of **1** (solid line) and $(\text{H}_2\text{BDC})\text{Cr}(\text{CO})_3$ (dashed line) heated under N_2 at a ramp rate of $0.5\text{ }^\circ\text{C}/\text{min}$.

a flow of He, H_2 , or Ar also produced gray solids exhibiting similar low N_2 and H_2 uptake capacities.

Gentler photolysis conditions enabled substitution of a single CO ligand per metal by N_2 . The UV–vis diffuse reflectance spectrum of **1** displays a peak centered at 430 nm. Accordingly, a sample of **1** was mixed intimately with KBr and irradiated using 450-nm (fwhm = 70 nm) light under a flow of N_2 . During irradiation, the two infrared bands at 1929 and 1990 cm^{-1} gradually disappeared, and, after 5 h, were replaced by two new CO stretching bands at 1921 and 1953 cm^{-1} , along with an N_2 stretching band at 2177 cm^{-1} (see Figure 3). The resulting spectrum is very similar to that of $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{N}_2)$,⁷ as well as numerous other $(\eta^6\text{-arene})\text{-Cr}(\text{CO})_2(\text{N}_2)$ complexes,⁸ indicating that the photolysis product is $\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_2(\text{N}_2)]_3$ (**3**). Here again, powder X-ray diffraction data confirmed that the framework skeleton is intact. While the mechanism of such photosubstitution reactions is not certain, it is thought to involve dissociation of CO to create an open coordination site on the metal, followed by N_2 binding.⁹ Importantly, compound **3** displays remarkable stability under a nitrogen atmosphere. While molecular $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\text{N}_2)$ complexes generated in supercritical Xe gradually decompose at $25\text{ }^\circ\text{C}$ in the dark,^{6c} **3** showed no signs of decomposition even after two weeks in ambient light. This enhanced stability is likely due to the chromium centers being pinned to the walls of the framework, which prevents reactions involving two or more chromium atoms and enables the irreversible evacuation of CO.

Photolysis of **1** under a flow of H_2 afforded a new product, **4**, with an infrared spectrum featuring two CO stretching bands at 1904 and 1947 cm^{-1} (see Figure 3d). The positions and relative intensities of these bands are consistent with an $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2\text{-}(\text{L})$ species.^{7,8} Since **4** was not generated by irradiating **1** under dynamic vacuum, it most likely corresponds to the compound $\text{Zn}_4\text{O}[(\text{BDC})\text{Cr}(\text{CO})_2(\text{H}_2)]_3$, containing a nonclassical H_2 complex. However, as with analogous $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\text{H}_2)$ species, a direct signature of the bound H_2 ligand was not apparent in the infrared spectrum. Compound **4** also exhibits improved stability relative to its molecular analogues. Sealed under 1 Torr of H_2 , **4** showed no signs of decomposition after two weeks at $25\text{ }^\circ\text{C}$ under ambient light. This is a tremendous increase in stability when compared with $(\text{C}_6\text{H}_5\text{Me})\text{Cr}(\text{CO})_2(\text{H}_2)$, which has a half-life of just 3 min at $25\text{ }^\circ\text{C}$ in supercritical Xe.^{6c} Under a nitrogen atmosphere, the infrared spectrum of **4** gradually changes until, after 12 h, the compound has completely converted into **3** (see Figure 3). This substitution of N_2 for H_2 is consistent with the established lability of the $\text{Cr}^0\text{-H}_2$ bond.¹⁰

The foregoing results demonstrate a straightforward method for functionalizing the benzene rings in $\text{Zn}_4\text{O}(\text{BDC})_3$ with photoactive $\text{Cr}(\text{CO})_3$ groups. Most importantly, the work shows how a metal–organic framework can serve as a rigid matrix for isolating metal complexes and carrying out reaction chemistry previously restricted

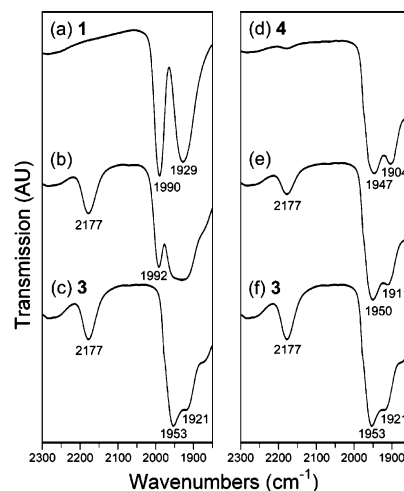


Figure 3. Infrared spectra observed upon irradiating ($\lambda = 450\text{ nm}$, fwhm = 70 nm) a sample of **1** for 0 (a), 2 (b), and 5 (c) h under a flow of N_2 , and for 10 h under a flow of H_2 to give **4** (d). Spectra (e) and (f) were obtained upon exposure of **4** to N_2 for 2 and 12 h, respectively.

to the gas phase, frozen gas matrices, or supercritical fluids. Future efforts will attempt to take advantage of the remarkable stabilizing influence of the framework, focusing, for example, on performing substitutions of the second and third CO ligands, as well as on producing sufficient quantities of the materials to investigate gas sorption properties.

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Supporting Information Available: Details of all experimental procedures, additional spectra, and H_2 and N_2 adsorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506. (b) Chen, B. L.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745. (c) Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvag, H. *Chem. Commun.* **2006**, 959. (d) Ma, S.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 11734. (e) Peterson, V. K.; Liu, Y.; Brown, C. M.; Kepert, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 15578. (f) Forster, P. M.; Eckert, J.; Heiken, B. D.; Parise, J. B.; Yoon, J. W.; Jung, S. H.; Chang, J.-S.; Cheetham, A. K. *J. Am. Chem. Soc.* **2006**, *128*, 16846. (g) Dinca, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876. (h) Dinca, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419. (i) Mulfort, K. L.; Hupp, J. T. *J. Am. Chem. Soc.* **2007**, *129*, 9604. (j) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 11172. (k) Kaye, S. S.; Long, J. R. *Chem. Commun.* **2007**, 4486.
- (2) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (c) Cho, S.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563. (d) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607. (e) Horcajada, P.; Surlbe, S.; Serre, C.; Hong, D.; Seo, Y.; Chang, J.; Greneche, J.; Margiolaki, L.; Ferey, G. *Chem. Commun.* **2007**, 2820.
- (3) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176.
- (4) Kuendig, E. P.; Pache, S. H. *Science of Synthesis*; Thieme: New York, 2003; Vol. 2; p 153 and references therein.
- (5) Hunter, A. D.; Mozoi, V.; Tsai, S. T. *Organometallics* **1992**, *11*, 2251.
- (6) (a) Sellman, D.; Maisel, G. *Z. Naturforsch.* **1972**, *B27*, 718. (b) Denholme, S.; Hunter, G. Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1987**, 2789. (c) Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804.
- (7) (a) Lokshin, B. V.; Greenwald, I. I. *J. Mol. Struct.* **1990**, *222*, 11. (b) Zheng, Y.; Wang, W.; Lin, J.; She, Y.; Fu, K. *J. Phys. Chem.* **1992**, *96*, 9821.
- (8) Goff, S. E. J.; Nolan, T. F.; George, M. W.; Poliakoff, M. *Organometallics* **1998**, *17*, 2730.
- (9) (a) Rest, A. J.; Sodeau, J. R.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1978**, 651. (b) Wang, W.; Jin, P.; Liu, Y.; She, Y.; Fu, K. *J. Phys. Chem.* **1992**, *96*, 1278.
- (10) Walsh, E. F.; George, M. W.; Goff, S.; Nikiforov, S. M.; Popov, V. K.; Sun, X.; Poliakoff, M. *J. Phys. Chem.* **1996**, *100*, 19425.

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