SUPPORTING INFORMATION

Real-time monitoring of microwave-promoted organometallic ligand-substitution reactions using *in-situ* Raman spectroscopy

Thomas M. Barnard[a] and Nicholas E. Leadbeater[b,*]

a CEM Microwave Technology, 3100 Smith Farm Road, Matthews, NC 28104 USA

b Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, CT 06269-3060 USA. nicholas.leadbeater@uconn.edu

Description of the apparatus:

Microwave reactions were conducted using a modified monomode microwave unit (CEM Discover®). The machine consists of a continuous Focused™ microwave power delivery system with operator selectable power output from 0-300 W. Reactions were performed in glass vessels (capacity 10 mL) sealed with a septum. The pressure is controlled by a load cell connected to the vessel *via* a non-invasive pressure measurement device above the septum surface. The temperature of the contents of the vessel was monitored using a calibrated infrared temperature control mounted under the reaction vessel. All experiments were performed using a stirring option whereby the contents of the vessel are stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel.

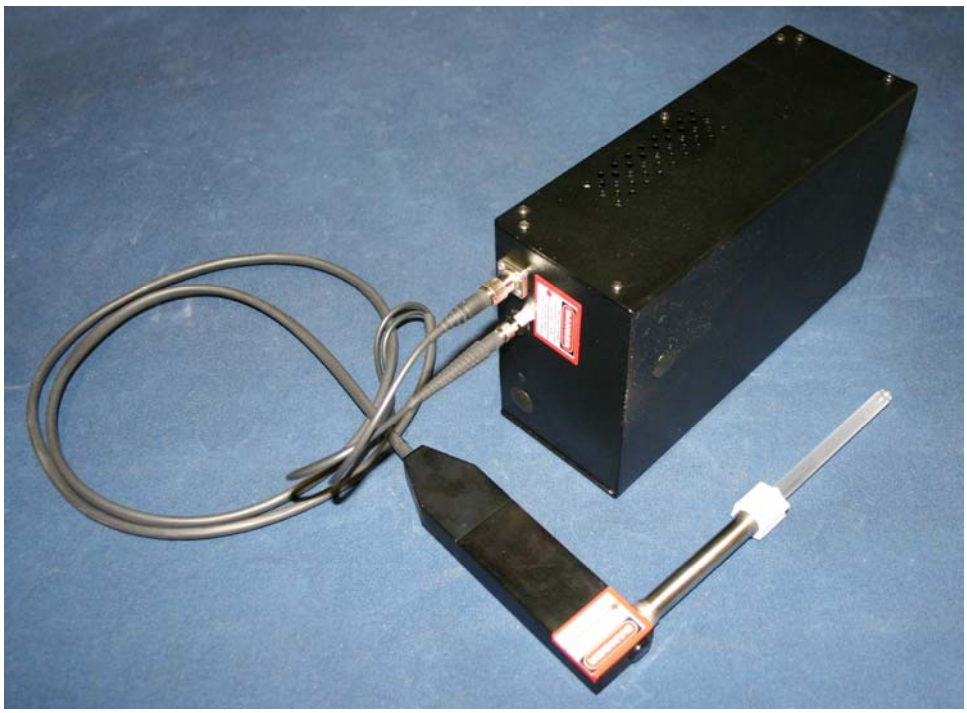
The Raman system was provided by Enwave Optronics (www.enwaveopt.com).

EXCITATION SOURCE:	NIR, frequency stabilized, narrow linewidth diode laser at 785 nm. Laser power at sample ~200 mW. Linewidth < 2 cm^{-1}. Fiber-coupled laser output (100 µm, 0.22 NA).
FIBER-OPTIC PROBE:	Permanently-aligned two single fiber combination 100 µm excitation fiber, 200 µm collection fiber (0.22 NA). Working distance: 8 mm (standard). Rayleigh rejection: O.D. > 7 at laser wavelength.
CCD DETECTOR:	High sensitivity linear CCD array. Temperature regulated (at 13 °C) operation for long integration time and stable dark reference subtraction. Pixel Size:14 µm x 200 µm (2048 Pixels);16 Bit digitization.
SPECTROGRAPH:	Symmetrical crossed Czerny-Turner design. Resolution: ~10 cm^{-1} at 785 nm. Excitation spectral coverage: 200 cm^{-1} to 2400 cm^{-1}. Built-in software calibration.
SYSTEM SOFTWARE:	Data collection software, data files exported into .dat format, converted to .txt and imported into Microsoft Excel.

To interface the microwave unit and Raman spectrometer, a hole (0.8 cm i.d.) was drilled in the microwave cavity and an RF stub attached to the outer cavity wall (to prevent microwave leakage) and an extender (2.16 cm i.d.) attached to this, reaching through to the outer casing of the microwave unit. The fiber-optic probe was placed into the cavity and the laser focused through a quartz light tube. A distance between the reaction vessel and fiber-optic probe tip of 0.5 cm was optimal.

SUPPORTING INFORMATION

Photographs of the apparatus:



SUPPORTING INFORMATION

Experimental procedures:

Reaction of molybdenum hexacarbonyl with pyridine: In a 10 mL glass tube was placed $Mo(CO)_6$ (100 mg 0.38 mmol), pyridine (3 mL, 2.95 g, 37.21 mmol) and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. Microwave irradiation of 150 W was used, the temperature being ramped from r.t. to 180 °C. Once this was reached, the reaction mixture was held at that temperature for 1 min. Raman spectra were recorded every 20 s during the reaction.

Reaction of molybdenum hexacarbonyl with octylamine: In a 10 mL glass tube was placed $Mo(CO)_6$ (100 mg, 0.38 mmol), octylamine (3 mL, 2.34 g, 18.12 mmol) and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. Microwave irradiation of 150 W was used, the temperature being ramped from r.t. to 180 °C. Once this was reached, the reaction mixture was held at that temperature for 1 min. Raman spectra were recorded every 20 s during the reaction.

Reaction of molybdenum hexacarbonyl with triphenylphosphine: In a 10 mL glass tube was placed triphenylphosphine (3 g, 18.12 mmol) and a magnetic stir bar. The triphenylphosphine was melted using a heater before adding $Mo(CO)_6$ (100 mg, 0.38 mmol). The tube was then sealed with a septum and placed into the microwave cavity. Microwave irradiation of 150 W was used, the temperature being ramped from 100 °C to 160 °C. Once this was reached, the reaction mixture was held at that temperature for 1 min. Raman spectra were recorded every 20 s during the reaction.

Spectral data:

$Mo(CO)_5(py)$:[1]	2073 (m), 1989 (w), 1944 (vs), 1924 (sh) cm^{-1}
$Mo(CO)_4(py)_2$:	2008(s), 1873 (m), 1811 (w) cm^{-1}
$Mo(CO)_3(py)_3$:	only band observed is1599 cm^{-1}
	sample IR compared with that in the literature[2] [IR: 1908 (m), 1888 (vs) cm^{-1}]
$Mo(CO)_5$(octylamine):	2062 (m), 1971 (s), 1894 (m), 1851 (m) cm^{-1}
$Mo(CO)_5(PPh_3)$:[3]	2071 (m), 1987 (s), 1943 (m), 1903 (m) cm^{-1}

1. Desseyn, H. O.; van der Veken, B. J.; Moss, J. R.; Smith, B. J.; Verhoeven, P.; Thornton, D. A. *Spectrochim. Acta* **1984**, *40A*, 467

2. Lobo, M. A.; Perpinan, M. F.; Pardo, M. P.; Cano, M. *J. Organomet. Chem.* 1983, 254, 325.

3. Day T. N.; Hendra, P. J.; Rest, A. J.; Rowlands, A. J. *Spectrochim Acta* **1991**, *47A*, 1251.