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

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An apparatus has been developed for real-time monitoring of organometallic reactions under microwave irradiation using *in situ* Raman spectroscopy and its application for monitoring ligand substitution reactions of $Mo(CO)_6$ demonstrated.

The use of microwave irradiation as a tool for synthetic chemistry is an area of increasing interest in both academic and industrial laboratories. It can enhance the rate of reactions and, in many cases, improve product yields.[1] Many of the problems associated with using domestic microwave apparatus, such as reproducibility, accurate temperature measurement and safety, have been overcome with the development of dedicated scientific microwave apparatus. With these it is possible to perform reactions either in sealed tubes or open vessels, monitoring reaction temperature and pressure as well as microwave power input.

A major problem with performing reactions using microwave apparatus is that monitoring its progress generally requires stopping it, allowing the reaction mixture to cool and then using standard analysis techniques such as IR and NMR spectroscopy. Therefore, optimization of reaction conditions such as time and temperature is often a matter of trial and error. This can be a particular problem when trying to prepare organometallic complexes. For example, in ligand exchange reactions, stopping a reaction after a desired number of substitutions is difficult if the reaction cannot be continually monitored. With conventional heating the reaction can be slow and aliquots removed and analyzed over time, but with microwave heating the reaction may be complete within a matter of minutes and accessing a sealed vessel during a reaction is not possible. This may be one reason why there have been very few reports of the application of microwave heating to preparative organometallic chemistry.[2]

There have been some attempts to monitor reactions under microwave irradiation. Neutron and X-ray scattering have been used for studying the preparation of inorganic materials.[3–6] Near IR spectroscopy has been used for the study of a C=O band shift during the reaction between 3-pentanone and triethylorthoformate to form 3,3-diethoxypentane and ethylformate.[7] Pivonka and Empfield have reported the use of Raman spectroscopy as a tool for monitoring organic transformations.[8] They studied an imine formation reaction and a Knovenagel condensation. Raman spectroscopy is a particularly useful technique for *in situ* spectroscopy because it relies on light scattering and hence no mechanical interaction with the sample. In addition, glass vessels typically give a low background signal in Raman scattering. Given the extensive use of time-resolved vibrational spectroscopy as a tool for probing reactive organometallic intermediates,[9,10] we wanted to develop an apparatus for the monitoring of organometallic reactions under microwave irradiation using *in situ* Raman spectroscopy.

Construction of the apparatus involved interfacing a scientific monomode microwave apparatus with a commercially available Raman module (excitation source 785 nm; spectral coverage 2400 cm^{-1}–200 cm^{-1}). This was achieved by drilling a hole (0.8 cm id) in the microwave cavity then attachment of an RF stub to the outer cavity wall (to prevent microwave leakage) and an extender (2.16 cm id) through to the outer casing of the microwave unit. A fiber-optic probe attached to the Raman module was introduced into the microwave cavity, the laser being focused *via* a quartz light tube positioned 5 mm from the reaction vessel. To test the applicability of the apparatus, we decided to study ligand substitution reactions of $Mo(CO)_6$. Heating a solution of $Mo(CO)_6$ in pyridine (py) from room temperature to 180 °C over a period of 90 s using a microwave power of 150 W, we monitored the Raman spectrum in the region 2400–1550 cm^{-1}. Scans were taken at 6 s intervals. In pyridine, $Mo(CO)_6$ shows two bands in the CO region of the Raman spectrum at 2119 cm^{-1} (E_g) and 2015 cm^{-1} (A_{1g}) as shown in Fig. 1 (the signal observed at 1580 cm^{-1} is from pyridine).

Upon microwave irradiation, within 20 s these bands were seen to decrease in intensity and four new bands grew in (Fig. 2). By comparison with spectra from authentic samples, the bands at 2071 cm^{-1} and 1981 cm^{-1} were attributed to $Mo(CO)_5(py)$, that at 1892 cm^{-1} to $Mo(CO)_4(py)_2$ and that at 1600 cm^{-1} to

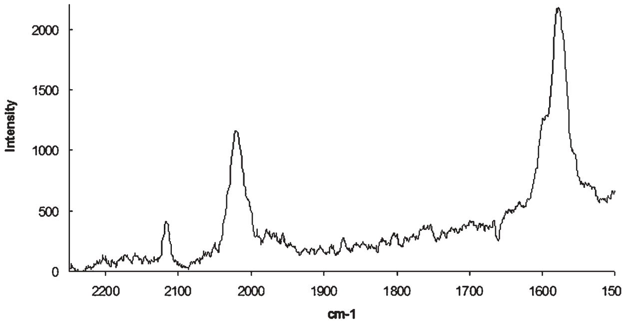

Fig. 1 Raman spectrum of $Mo(CO)_6$ in pyridine (in the region 2400–1500 cm^{-1}).

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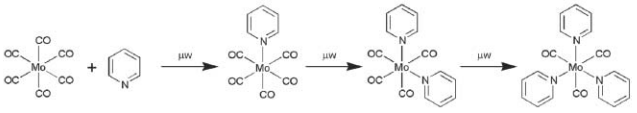

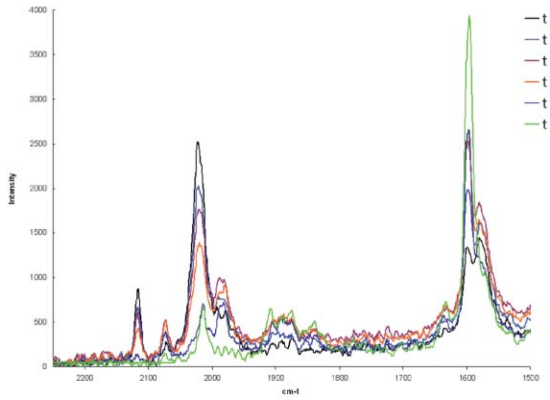

Fig. 2 Raman spectra of $Mo(CO)_6$ in pyridine as a function of time upon microwave irradiation (in the region 2400–1500 cm^{-1}).

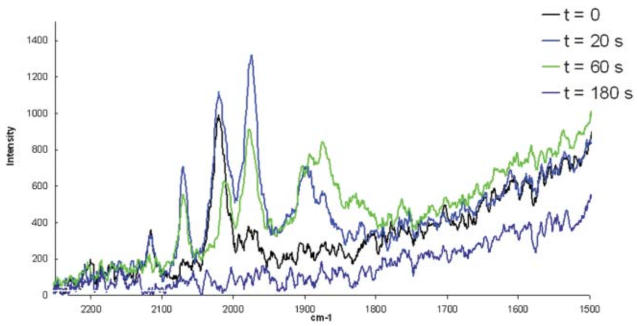

Fig. 3 Raman spectra of $Mo(CO)_6$ in octylamine as a function of time upon microwave irradiation (in the region 2400–1500 cm^{-1}).

$Mo(CO)_3(py)_3$. Holding the reaction mixture at 180 °C for a further 1 min resulted in further conversion to $Mo(CO)_3(py)_3$.

The results of a similar study using octylamine (oct) are shown in Fig. 3. Formation of $Mo(CO)_5(oct)$ (2072 cm^{-1} and 1976 cm^{-1}) and some $Mo(CO)_4(oct)_2$ (1899 cm^{-1}) was observed after 20 s microwave heating. Heating for 1 min leads to the formation of more $Mo(CO)_4(oct)_2$ but prolonging the microwave irradiation to 3 min leads to extensive decomposition.

We also performed the reaction using triphenylphosphine as a ligand. The reaction mixture was heated from 100 °C to 160 °C over a period of 60 s using a microwave power of 150 W and monitoring the Raman spectrum in the region 2400–1500 cm^{-1} (Fig. 4). The bands from the parent hexacarbonyl decreased in intensity and three new bands grew in at 2073 cm^{-1}, 1988 cm^{-1} and 1943 cm^{-1} (the band at 1584 cm^{-1} originates from triphenylphosphine). By comparison with literature data,[11] the three bands can be attributed to the formation of $Mo(CO)_5(PPh_3)$. Holding the reaction mixture at 160 °C for a further 1 min has little effect.

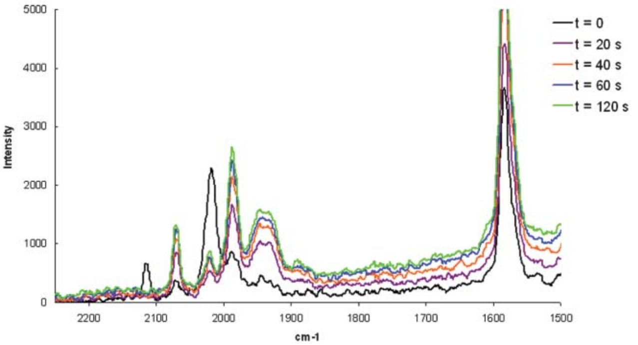

Fig. 4 Raman spectra of $Mo(CO)_6$ in PPh_3 as a function of time upon microwave irradiation (in the region 2400–1500 cm^{-1}).

Our results show the potential for using *in situ* Raman spectroscopy as a tool for monitoring the progress of organometallic reactions performed using microwave heating. Work is now underway to broaden the scope of the method for organometallic reactions as well as expand it to organic and metal-mediated catalytic transformations.

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