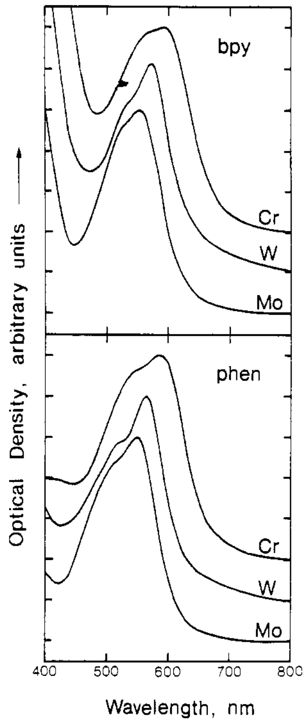

Figure 2. Lowest energy features in the electronic absorption spectra of $M(CO)_4L$ complexes (M = Cr, Mo, W; L = bpy, phen) in isooctane at 298 K.

emission data obtained from all the complexes studied are summarized in Table I. The emission intensities of $M(CO)_4L$ in methanol were very weak, and we were unable to observe maxima at wavelengths longer than 700 nm. These results imply that the emission efficiency of the diimine complexes is strongly dependent on solvent. Both emission bands are assigned as MLCT transitions; the higher energy one shows solvent shifts comparable to that observed in absorption, and the other band is too low in energy to be LF. Attempts to record emission data in isooctane were unsuccessful; this is attributed to either the sparing solubilities of these complexes in isooctane or, in view of the absorption solvent dependence, the possibility that emission in isooctane would likely be so red-shifted it would be difficult to detect experimentally. Further evidence for the MLCT assignment was obtained following a comparison with $M(CO)_4en$ complexes, where M = Cr, Mo, or W and en = ethylenediamine. The $M(CO)_4en$ complexes exhibit LF states at approximately the same energies as our diimine series but do not possess low-lying MLCT excited states.[7] Importantly, we did not observe emission from these complexes in room-temperature solution following excitation directly into the LF state at 400 nm. The observance of multiple emission indicates that interconversion between the emitting states is relatively slow compared to the radiative deactivation routes of the molecule and implies that the characters of these excited states are somewhat different. In this connection Staal et al. have recently reported evidence for both d → $\pi^*(a_2)$ and d → $\pi^*(b_2)$ charge-transfer absorptions in a series of $M(CO)_4$ diazabutadiene (M = Cr, Mo, W) complexes.[10e] Multiple emissions involving intraligand (IL) and MLCT states have been observed from several *fac*-$[XRe(CO)_3phen]$ complexes.[13] However, our $M(CO)_4L$ complexes appear to emit at too low energy to be associated with an unperturbed IL transition. We intend to learn more about the character of the excited states of $M(CO)_4L$ through temperature dependence studies of the emission spectra and lifetimes. Emission has previously been observed for $M(CO)_4L$ complexes (M = Mo, W; L = bpy, phen) in rigid glasses at 77 K.[2b] The low-temperature maxima (640-660-nm region) most likely correspond to the lowest energy maxima reported here, as recent observations of emission from related carbonyl complexes have been at lower energies in fluid solution than in rigid media.[2,6]

A particularly novel aspect of the emission data is that the chromium complexes constitute the only examples of a first-row transition metal carbonyl complex known to emit under fluid conditions. The absence of emission data from first-row metal carbonyl complexes has been attributed to the low spin–orbit coupling values of the central metal atom. In view of these results we prefer to associate the emission properties of the molecule with the presence of a low-lying MLCT excited state.

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Registry No. $Cr(CO)_4bpy$, 15668-63-0; $Mo(CO)_4bpy$, 15668-64-1; $W(CO)_4bpy$, 15668-66-3; $Cr(CO)_4phen$, 14168-63-9; $Mo(CO)_4phen$, 15740-78-0; $W(CO)_4phen$, 14729-20-5.

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Room-Temperature Isolation and Characterization of Group 6 Pentacarbonyls in Porous Vycor Glass

Sir:

In this paper, we describe the use of Corning's code 7930 porous Vycor glass, PVG, as a convenient alternative to low-temperature matrices[1-5] for isolation and characterization of group 6 pentacarbonyls. The adsorbed pentacarbonyls, designated $M(CO)_5(ads)$ and generated by photolysis of the adsorbed hexacarbonyl, have spectroscopically quantitated lifetimes of ≥48 h in vacuo at room temperature.

Code 7930 PVG is a surface-hydroxylated, transparent,[6] porous glass containing $(1.2 \pm 0.3) \times 10^{18}$ pores/g,[7] with a pore diameter of 70 ± 21 Å.[8-14] Pieces of PVG (25 mm ×

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Table I. UV-Visible and Infrared Absorptions of $M(CO)_6$ and $M(CO)_5$ Adsorbed onto PVG at Room Temperature

	$M(CO)_6$[a]		$M(CO)_5$[b]
metal	nm	cm^{-1}	nm
Cr	280 (280)	1999 (1980)	450 (489)
Mo	286 (289)	2005 (1980)	409 (411), 245 (247)
W	287 (290)	1986 (1980)	410 (413), 248 (244)

[a] Values in parentheses are band maxima from spectra of *n*-hexane solutions of the complexes. [b] Values in parentheses are the band maxima reported by Perutz and Turner for the $M(CO)_5$ complex in a 20 K CH_4 matrix.[3]

25 mm × 4 mm) are extracted with acetone and distilled water and then heated at 550 °C in air for 72 h to remove carbonaceous impurities. Cleaned pieces are exposed to a 10^{-3} M hexane solution of the hexacarbonyl and the moles of complex adsorbed is determined from the difference in absorbances of the initial solution and the solution after impregnation. After adsorption, the pieces are rinsed with the solvent and spectra of the rinse liquid show no desorption of the complex. The solvent incorporated during impregnation is removed under vacuum at room temperature, and the dried impregnated samples used in these experiments contain between 3×10^{-7} and 10^{-6} mol of complex/g of PVG.

The similarity of the $M(CO)_6$(ads) electronic and infrared spectra with fluid-solution spectra (Table I), particularly the absence of shifts in the ligand field transitions, which usually accompanies ligand substitution,[15] establishes that adsorption of these hexacarbonyls onto PVG does not disrupt the primary coordination sphere. The complexes appear to be physisorbed, although the infrared spectra are not sufficiently resolved to determine whether adsorption onto PVG induces a distortion from O_h symmetry similar to that observed with $Cr(CO)_6$ in an Ar matrix.[3]

The adsorbed complexes retain a photoactivity similar to that found in fluid solution.[16] A 312-nm photolysis of $W(CO)_6$(ads) in vacuo causes a decline in absorbance at 290 nm, characteristic of $W(CO)_6$(ads), and a concurrent increase in absorbance at 410 nm. An isosbestic point is maintained at 350 nm through ≤45% consumption of $W(CO)_6$(ads), and GC analysis of the vapor phase surrounding the sample yields 1.0 ± 0.1 mol of gaseous CO/mol of $W(CO)_6$(ads) reacted as measured from the decrease in absorbance at 290 nm. The photoinduced reaction is reversible and exposure to 1 atm of CO regenerates ≥99% of the original $W(CO)_6$(ads). The thermal reaction is slow and requires ca. 12 h for quantitative regeneration of $W(CO)_6$(ads).

The similarity of these spectral data with those obtained in low-temperature matrices (Table I) and the stoichiometry of the photoreaction, particularly the maintainance of isosbestic points, establish the photoreaction to be

$$M(CO)_6(ads) \xrightleftharpoons[\text{1-atm CO}]{\text{312 nm}} M(CO)_5(ads) + CO \qquad (1)$$

EPR spectra of $M(CO)_5$(ads), which give no indication of unpaired electrons, are consistant with a singlet ground state of C_{4v} symmetry rather than a triplet ground state of D_{3h} symmetry. This leads us to suggest that $M(CO)_5$(ads) has a square-pyramidal structure and the slight differences in the absorption maxima of the $^1A \rightarrow {}^1E$ transition of $M(CO)_5$(ads) relative to those observed in low-temperature matrices[3,4] indicate that the vacated coordination site is occupied by a silanol group or adsorbed water. Whether this represents formal coordination to the support, which might explain the unusually long lifetime of $M(CO)_5$(ads), is not presently clear, but stability does not occur at the expense of subsequent thermal reactivity.

Exposing $M(CO)_5$(ads) to various ligands, either as gases or dissolved in degassed, noncoordinating solvents, causes rapid quantitative formation of $M(CO)_5L$(ads). For example, absorption and emission spectra recorded after exposing $W(CO)_5$(ads) to 0.1 atm of 1-pentene or degassed 10^{-3} M *n*-hexane solutions of 2,2′-bipyridine (bpy) establish quantitative formation of $W(CO)_5$(1-pentene)(ads)[17] and $W(CO)_4$(bpy)-ads,[18] respectively. Resonance Raman spectra also show that the 992- and 1035-cm^{-1} vibrations of pyridine (py) adsorbed onto PVG shift to 1012 and 1042 cm^{-1} upon reaction with $W(CO)_5$(ads).[19]

Although spectra of species adsorbed onto PVG are not as well resolved as those obtained with low-temperature matrices, PVG is a convenient medium in which to isolate these pentacarbonyls and, being porous, to explore their chemistry.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 1404-11-0; $Cr(CO)_5$, 26319-33-5; $Mo(CO)_5$, 53109-70-9; $W(CO)_5$, 53109-57-2.

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