of oxyrhodium species **1** to the glycolate less kinetically favorable, enabling 1,2-shift pathways to compete.[19]

The simplicity of the oxidation system described above in terms of catalyst synthesis, resiliency of its ligand environment, and simple oxidation reagent requirement suggests its practicality for partial oxidation of olefins. Optimization studies, as well as those of catalyst recycle and other catalyst analogues, are now under way.

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Supplementary Material Available: A plot of relative rate data for oxidation of several styrenes (1 page). Ordering information is given on any current masthead page.

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[19] Interestingly, for propene oxidation, addition of water enhances the relative yield of non-"Wacker" product, propanal.

Surface Chemistry on Colloidal Metals: A High-Resolution Nuclear Magnetic Resonance Study of Carbon Monoxide Adsorbed on Metallic Palladium Crystallites in Colloidal Suspension

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There is a continuing interest in the spectroscopic characterization of small molecules adsorbed on the surfaces of catalytically interesting metal particles. Several fruitful studies have involved solid-state techniques such as solid-state and magic angle spinning NMR and surface vibrational spectroscopies, applied to supported metal particles. We have adopted an alternative approach to such surface species in an investigation of small molecules adsorbed on *colloidal* transition metals in the liquid phase, using spectroscopic techniques more often applied to molecular species in solution.

We have reported elsewhere the use of high-resolution liquid NMR to characterize carbon monoxide on highly dispersed colloidal palladium and platinum.[1] Those studies revealed ^{13}C chemical shifts near 200 ppm for adsorbed CO, and the absence of a Knight shift for the adsorbed CO, in contrast to the observations for CO on supported metallic crystallites of palladium,[2] was ascribed to pseudomolecular (nonmetallic) character in the colloidal metal particles, which were less than 20 Å in diameter. In this paper we describe the observation, by the same technique, of the adsorbed state of carbon monoxide on a palladium colloid of 70-Å mean diameter, a size range in which *metallic* character should manifest itself.

The palladium colloid was prepared by the reduction of palladium acetate to palladium metal by methanol in the presence of poly(vinylpyrrolidone) (PVP). Palladium acetate (50 mg) was added to a solution of PVP (MW 40 000; 2.5 g) in methanol (150 mL) and the mixture refluxed for 2 h. The resulting brown liquid was filtered (0.2-μm Teflon millipore) and concentrated to 25 mL. This procedure reproducibly yields colloidal palladium particles in the form of well-formed microcrystallites with a mean diameter (by transmission electron microscopy (TEM) and small angle X-ray scattering SAXS) of 70 Å. The colloid shows no tendency to precipitate on standing for at least several weeks. X-ray diffraction shows the presence of fcc palladium, with line widths consistent with the particle size shown by TEM and SAXS. Carbon monoxide adsorbs readily on the colloid in methanol, occupying only bridging sites (ν_{CO} 1944 cm^{-1}), similarly to CO on Pd(111) surfaces,[3] and consistent with the crystalline nature of the colloid particles. (On the smaller pseudomolecular Pd colloid, both bridging and terminal CO are observed.[1])

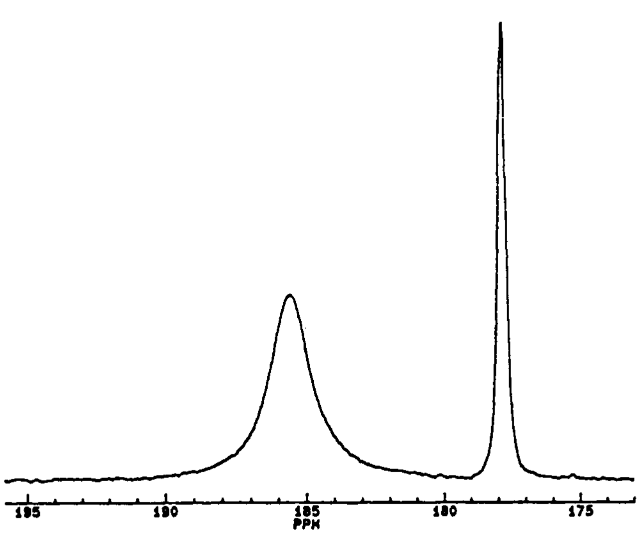

Figure 1. The carbonyl region of the room temperature ^{13}C NMR spectrum of the PVP stabilized Pd colloid under 3 atm of ^{13}CO. The spectrum is the result of 50 acquisitions taken with a 2-s recycle delay. Dissolved CO appears at 185.5 ppm and the PVP carbonyl at 178 ppm.

The carbonyl region of the 75-MHz room temperature ^{13}C NMR spectrum of a concentrated solution of the colloid under 3 atm of 99% ^{13}CO is shown in Figure 1. It consists of a resonance at 178 ppm due to the carbonyl group in PVP and a resonance at 185.5 ppm with a line width of 3 ppm. In variable-temperature studies the latter resonance reversibly narrows down to 233 K and broadens reversibly up to 348 K. The chemical shift is coincident with that observed for CO dissolved in a methanol solution of PVP (a resonance that shows no such variable-temperature behavior) and is thus assigned to dissolved CO, its width at 298 K being caused by chemical change, presumably with CO bound to the colloidal metal (vide infra). So far we have not been able to detect this species directly, which is hardly surprising, given its low concentration and probable line width. Solid-state ^{13}C NMR experiments performed at 198 K for CO adsorbed on Pd/η-alumina[2] (ca. 65 Å average diameter) show a broad, strongly Knight shifted peak[4] centered at 540 ppm with a half-width of 400 ppm (at room temperature this peak moves to 675 ppm and is narrowed to ca. 50 ppm by diffusion processes). Similarly, the room temperature ^{13}C chemical shift of CO adsorbed on Pd/SiO$_2$[5] is 750 ppm.

We have, however, observed the adsorbed CO resonance indirectly, using a variation of the Forsén–Hoffman spin saturation transfer experiment,[6] in which we measure the integrated intensity of the free CO resonance as a function of the frequency of a low-power, long-duration rf pulse, varied in increments of 25 ppm between +1400 and +200 ppm (see Figure 2). In addition, to establish a base line, for each such frequency, we also irradiated at its "mirror image" frequency, i.e., at the frequency displaced symmetrically with respect to the dissolved CO resonance (e.g., 170.5, 145.5, ..., −1214.5 ppm). A maximum (80%) saturation of the free CO resonance was observed at an irradiation frequency

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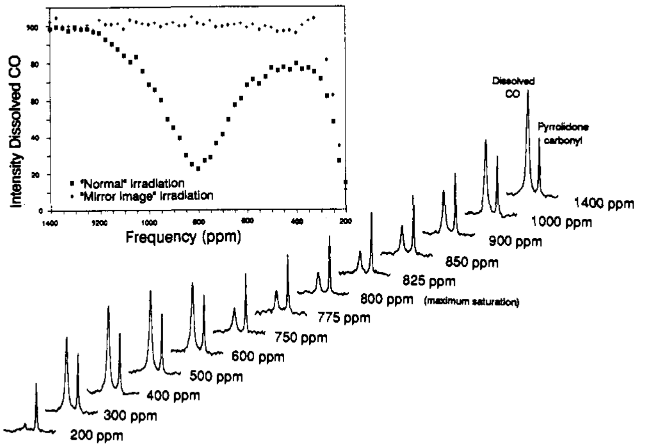

Figure 2. Room temperature ^{13}C spectra of free CO (185.5 ppm) in the presence of Pd colloid under 3 atm of ^{13}CO. Each spectrum shows the region between 215 and 150 ppm, and the frequencies of the respective irradiation pulses are shown at the right. The PVP carbonyl peak at 178 ppm serves as internal reference. Each spectrum is the result of 600 acquisitions with a 1-s recycle delay, obtained by using a 10-mW 100-ms irradiation pulse. T_1 for free CO was not measured, but changes in recycle delay near 1 s caused no variation in intensity. Inset: Plot of integrated intensity of the dissolved CO resonance vs irradiation frequency for "normal" (saturating) irradiation and "mirror image" (base line).

of 800 ppm (Figure 2), and a plot of the intensity of the free CO resonance vs irradiation frequency shows a broad minimum centered at 800 ppm. The shape of this saturation curve must of course depend not only on the line shape of the adsorbed CO resonance but also on the relative T_1's and motional properties of CO molecules on the various sites in the sample (vide infra), but it is clear that the colloid-bound CO is strongly Knight shifted,[4] consistent with the presumed metallic nature of the colloid particles.

We tentatively ascribe the line width, which extends from 1200 to <300 ppm and is greater than that reported for CO on supported palladium at room temperature,[5] to a distribution of Knight shifts which vary with particle size (the colloid contains detectable numbers of particles ranging in size from 30 to 150 Å), and it would be expected that the smaller particles would be less shifted. Variation of pulse length and power produced little variation in the indirectly observed line shape. Clearly the observed line shape also is a function of the exchange rate between the dissolved CO and the adsorbed species and could also be affected by restricted surface diffusion of CO on the colloid particles caused by particle morphology and the presence of the PVP. Of course it is also possible that the width of the resonance reflects in part a slow, restricted tumbling of the colloid particles in the polymer solution. Approximate calculations can be made, using the Stokes–Einstein equation, of correlation times for motion of colloidal particles as a means of estimating the importance of motional effects on NMR line widths.[7] For particles of diameter 75 Å, correlation times of 10^{-8} s are calculated, which would result in relatively narrow (<1 ppm) line widths, but the presence of PVP at the periphery of the palladium particles in our study would presumably result in some restriction of motion. Variable-temperature and "hole-burning" experiments[8] in a related colloidal palladium system[1] ruled out a significant contribution to the ^{13}C line width of adsorbed CO from restricted motion in solution, and similar experiments are planned to investigate these possibilities in the present system. Interpretation of the indirectly observed line shape as a distribution of isotropic shifts of CO on the polydispersed colloid is consistent with the recent observation that magic angle spinning does not narrow the resonance of CO adsorbed on Pd/SiO_2.[5,9]

The relative ease with which these experiments can be carried out with a colloidal metal sample presents the possibility that kinetic ligand exchange investigations can now be performed on the adsorption–desorption phenomena which play an important role in heterogeneous catalysis, using colloidal transition metals as an easily accessible analogue to supported catalyst particles. Colloid metals are active in numerous catalytic processes, and we anticipate NMR studies of working catalysts and of model colloid systems.

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Molecular Laminates. Three Distinct Crystal Packing Modes

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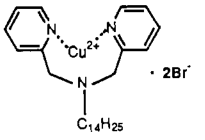
Periodicity in crystalline solids leads to cooperative electronic effects and thus to materials with useful electrical, magnetic, and optical properties.[1] Yet the rational design of periodicity ("crystal engineering") remains a primitive art and an attractive area for further pursuit.[2] With this in mind (and with an ongoing affection for diverse organized assemblies of which crystals are the most perfect),[3] we set out to prepare crystalline solids with alternating layers of metal and hydrocarbon. Such "molecular laminates" were ultimately achieved via the three new long-chain copper complexes **1–3**. As will be seen momentarily, the compounds crystallize into layered arrays, each with its own peculiar packing mode.



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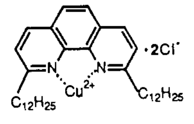

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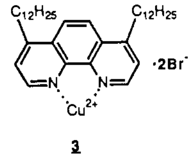

3

The ligand in **1** was synthesized from 2-picolyl chloride hydrochloride and 1-tetradecylamine in basic THF/water. The other two ligands were prepared by treatment of commercially available dimethylphenanthrolines with lithium diisopropylamide followed by 1-iodoundecane. Ligands were characterized by FAB-MS, NMR, and elemental analysis prior to their conversion into the copper chelates using $CuCl_2$ or $CuBr_2$ in absolute ethanol. X-ray quality crystals were obtained from methanol (**1** and **2**) and chloroform/acetonitrile (**3**).

Publications from England,[4] Germany,[5] Japan,[6] and Sweden[7] can be consulted for packing data on various long-chain compounds. Previous X-ray studies of layered compounds involving

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