[from (−)-**6**] provided material in greater than 98% ee on which an accurate optical rotation could be obtained. The benzyl/methyl transfer reaction (excess Pd/C, MeOH, H_2) is noteworthy for it provides a simple procedure with which to convert the N_b-benzyl analogs into the natural N_b-methyl alkaloids (see **17** → **4**) and may be general (**13** → **2**).

Supplementary Material Available: Listing of NMR spectral data for **1**, **3**, **13**, and **17** (4 pages). Ordering information is given on any current masthead page.

Rhodium Geminal Dicarbonyl on $TiO_2(110)$

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Finely dispersed rhodium supported on oxide surfaces catalyzes a series of important industrial processes,[1] including the hydrogenation of carbon monoxide, the reduction of nitrogen monoxide, and the hydroformylation of olefins. The degree of dispersion has economic consequences and influences the activity and selectivity of the catalyst.[2] Consequently, there has been considerable effort in characterizing high area oxide supported rhodium using a variety of structural, spectroscopic, and chemical techniques on alumina,[3-17] silica,[6,16-18] and titania.[16,17,19-21] It appears that rhodium can be present as three-dimensional crystallites, two-dimensional rafts, and in the form of the so-called *gem*-dicarbonyl $[Rh(CO)_2]$ species. Some considerable attention has been given to the generation of highly dispersed rhodium using organometallic precursors, in particular $[Rh(CO)_2Cl]_2$.[22-30] Interconversion of these phases is induced by chemisorbed CO[3,7-11,15,19,21,23,27] and can be accelerated by the presence of surface hydroxyl groups. In an effort to study the fundamental chemistry of the oxide supported *gem*-dicarbonyl, we have for the first time generated, and characterized, the species on a single crystal oxide surface under ultra high vacuum conditions. In order to avoid the more severe pressure conditions likely to be required to produce $Rh(CO)_2$ from the metal, we used the reactive adsorption of $[Rh(CO)_2Cl]_2$ at 300 K on $TiO_2(110)$. Its adsorption and decomposition have been the subjects of an XPS and TPD investigation in the ultra high vacuum environment on amorphous alumina films grown on Al_2O_3.[31-33]

Experiments have been performed in a UHV system incorporating a 1–1000 amu quadrupole mass spectrometer, LEED, XPS,[34] and FT-RAIRS. A more detailed description of the apparatus will appear elsewhere.[35] The $TiO_2(110)$ single crystal surface has been cleaned using cycles of Ar^+ bombardment, annealing at 1000 K, and oxygen treatment at 400 K following procedures described previously.[36] $[Rh(CO)_2Cl]_2$ has been prepared[37] and purified by vacuum sublimation and dosed into the UHV system using a doser situated 10 mm from the sample surface.

Exposure of the $TiO_2(110)$ surface at 300 K to $[Rh(CO_2)Cl]_2$ results in the adsorption of a stable Rh surface species ($E_{BE}[Rh(3d^{5/2})] = 309.1$ eV) which saturates at a Rh coverage of 0.35 ± 0.05 ML.[38] A concomitant adsorption of chlorine is observed with $E_{BE}[Cl(2p^{3/2})] = 198.5$ eV. The Rh and Cl binding energies are shifted from the values associated with the physisorbed parent molecule obtained by adsorption at 200 K ($E_{BE}[Rh(3d^{5/2})] = 309.3$ eV, $E_{BE}[Cl(2p^{3/2})] = 199.1$ eV), in agreement with previous measurements.[1-3] XPS indicates that this surface species is stable to 450–500 K (the physisorbed species desorbs at lower temperature) when CO is desorbed, producing metallic rhodium.[35] The chlorine remains on the surface to 700 K and is associated with chemisorbed chlorine on $TiO_2(100)$; no further change is observed in $E_{BE}[Cl(2p^{3/2})]$ during heating, particularly during the decomposition of the Rh species.

A series of FT-RAIRS spectra obtained while adsorbing $[Rh(CO)_2Cl]_2$ at 300 K is shown in Figure 1. Because of the transparency of titania in the IR, absorption of IR radiation in the adsorbed overlayer can give rise to both an increase (p) or decrease (s) in reflectivity for experiments carried out at angles more grazing than the Brewster angle.[35,39,40] A band is observed

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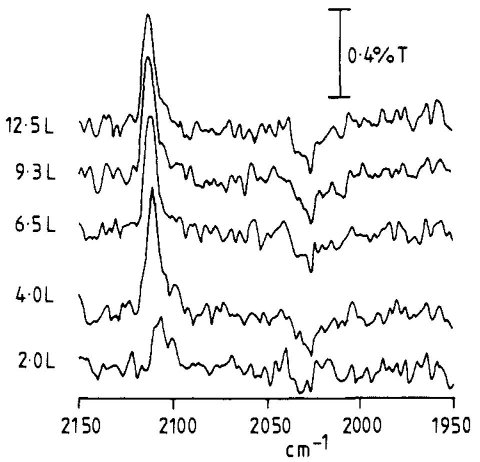

Figure 1. FT-RAIRS spectra of $Rh(CO)_2$ on $TiO_2(110)$ as a function of $[Rh(CO)_2Cl]_2$ exposure.

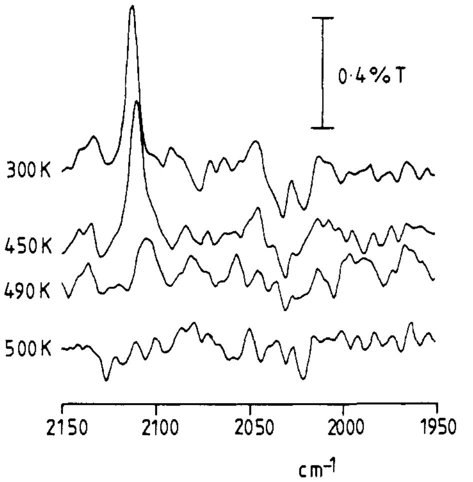

Figure 2. FT-RAIRS spectra of $Rh(CO)_2$ on $TiO_2(110)$ as a function of temperature.

to develop at 2112 cm^{-1} (p) together with a band at 2028 cm^{-1} (s), and they are assigned to the symmetric and antisymmetric ν(CO) vibrations of $Rh(CO)_2$. These values are close to those observed for this species on high area alumina,[3-16] silica,[6,16-18] and titania[6,16,17,19,20] surfaces. The reaction which leads to the *gem*-dicarbonyl involves the dissociation of the dimer and adsorption of chlorine on the TiO_2 surface.

The *gem*-dicarbonyl is stable on the $TiO_2(110)$ surface (in the presence of the chlorine generated by reaction of $[Rh(CO)_2Cl]_2$) to a temperature of 450 K. This is demonstrated in the series of FT-RAIRS spectra shown in Figure 2. These spectra have been obtained by heating the surface to successively higher temperatures, cooling to 300 K, and re-recording the IR spectrum. The peaks associated with the *gem*-dicarbonyl start to reduce in intensity by 450 K and have disappeared at 500 K. We have been able to study, using FT-RAIRS, the reversible CO adsorption on rhodium layers formed following this heat treatment. The $Rh(CO)_2$ species can be regenerated from the small islands or particles of metallic rhodium by the adsorption of CO at 1×10^{-3} Torr at 300 K. This is evidenced by the reappearance of the ν(CO) doublet (Figures 1 and 2) in the FT-RAIRS.

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Solution Conformation of a G·TA Triple in an Intramolecular Pyrimidine·Purine·Pyrimidine DNA Triplex

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The DNA triple helix is a novel structural motif first discovered in homopurine·homopyrimidine polyribonucleotide sequences where the third pyrimidine strand binds in parallel with the purine strand in the major groove.[1,2] The recognition is achieved through sequence-specific hydrogen bonds formed between protonated cytidines and guanines or thymines and adenines leading to isomorphous C^+·GC and T·AT triples. Recently, stimulated by the potential application of triple helices in gene regulation, the scope of the triplex code has been extended to include G·TA[3] and T·CG[4] triples within the pyrimidine·purine·pyrimidine (Y·RY) triplexes. Although a structural model was proposed for the Y·RY motif based on an analysis of X-ray fiber-diffraction data nearly two decades ago,[5] no single-crystal or solution structure of any triplex has been reported.

We have determined the first three-dimensional solution structure of an intramolecular Y·RY triple helix **1**,[6] which contains a central purine·pyrimidine·purine G·TA triple flanked by canonical pyrimidine·purine·pyrimidine T·AT triples. In this report, the conformation of the G·TA triple in **1** will be discussed in detail as it is the only known instance in oligonucleotide-directed DNA recognition where a purine base recognizes a pyrimidine in a parallel orientation.[3] The structure elucidation was based on experimental NMR data[7] which provided torsion angle and proton–proton distance estimates. Our previous work, especially, established the presence of a number of interstrand contacts involving the third strand which were important in defining the

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