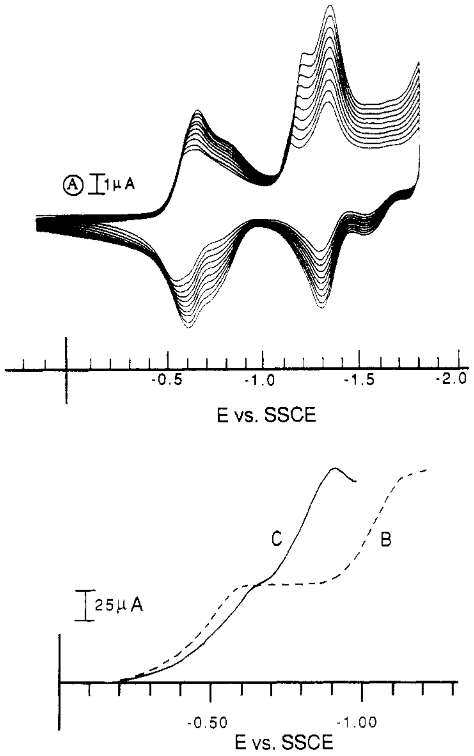

Figure 2. (A) Consecutive cyclic voltammograms at 100 mV/s for a glassy-carbon electrode in contact with an acetonitrile/0.1 M TBAP solution of the cobalt divinylquinquepyridine complex. (B, C) Rotated disk voltammograms (at 500 rpm) at 10 mV/s in oxygen-saturated pH 8.7 aqueous phosphate buffer for bare (B) and surface-modified (C) ($\Gamma = 5 \times 10^{-9}$ mol/cm^2) glassy-carbon electrodes.

the four-electron reduction dominates. A similar coverage dependence has been reported by Murray et al.[16] for the reduction of oxygen at electrodes modified with a cobalt porphyrin.

The close proximity of two cobalt centers for simultaneous electron transfer may be essential, or dimers may be formed so as to achieve a four-electron transfer. The close proximity of the metal centers may arise as a result of changes in the packing density of the electropolymerized material as a function of surface coverage. We have previously shown that this occurs for the $[Co(v\text{-}terpy)_2]^{2+}$ complex, and we assume that a similar process is operative here.

From plots of $1/i_{\lim}$ vs $\omega^{-1/2}$ and the Koutecky-Levich equation, we determined that for electrodes modified with polymeric films of the cobalt complexes (at coverages ranging from 5×10^{-9} to 10×10^{-9} mol/cm^2) the second-order rate constant for the four-electron reduction of oxygen to water in pH 8.7 aqueous buffer was $2\ (\pm 1) \times 10^6$ M^{-1} s^{-1}.

We have also investigated the reduction of carbon dioxide, but the catalytic effects are not as strong as for the $[Co(v\text{-}terpy)_2]^{2+}$ case. We ascribe this to changes in the electronic environment around the cobalt center by the presence of the axial chloride ligands. Thus, there appears to be a delicate interplay between electronic and structural factors in the catalysis.

Conclusions. We have demonstrated that the use of quinquedentate pyridine-based ligands enforces a heptacoordinate helical coordination around Co(II). Such an unusual coordination (to our knowledge, the first reported for a cobalt complex) is a direct result of the steric constraints imposed by the ligand. In addition, the incorporation of vinyl groups allows for the smooth electropolymerization of the monomer complexes to yield adherent and electrochemically active polymer films that exhibit catalytic activity in the four-electron reduction of oxygen to water. We believe that this activity is largely due to the ease of generation of an empty coordination site at the metal where binding and activation of the substrate can readily occur. We believe that this may be a general reactivity pattern, and we are currently characterizing other catalytic processes as well as elaborating on the synthesis of related ligands.

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Supplementary Material Available: Tables of crystal data, positional parameters and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom parameters (6 pages). Ordering information is given on any current masthead page.

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A Convenient Synthesis of Solvated and Unsolvated Anhydrous Metal Chlorides via Dehydration of Metal Chloride Hydrates with Trimethylchlorosilane

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Although there are several methods for preparing anhydrous metal halides,[1] thermal and chemical methods of removing water from hydrated metal halides are the most frequently employed. The pyrolysis of metal halide hydrates has been studied extensively and can lead to anhydrous salts although temperature control is important for many hydrates because water is released stepwise and mixtures of hydrates can be obtained.[2] Dehydrating agents such as 2,2-dimethoxypropane and thionyl chloride are efficient and have been widely used although each has some disadvantages.

2,2-Dimethoxypropane, for example, reacts with metal hydrates producing acetone and methanol, which often complex to the metal halide[3] (eq 1). Both groups are barriers to further reactions with

$$MX_n{\cdot}xH_2O + xCH_3C(OCH_3)_2CH_3 \rightarrow MX_n + x(CH_3)_2CO + 2xCH_3OH \quad (1)$$

active metals and many organometallic reagents. Thionyl chloride reacts with water, evolving hydrogen chloride and sulfur dioxide as gases, thereby reducing the opportunity for contamination of the product halide[4] (eq 2). However, thionyl chloride is a severe

$$[Cr(H_2O)_6]Cl_3 + 6SOCl_2 \rightarrow CrCl_3 + 12HCl + 6SO_2 \quad (2)$$

lachrymator that must be freshly distilled before use. Moreover, it must be used in excess to achieve reasonable rates and removing the last traces of thionyl chloride is sometimes difficult.

We report here our finding that trimethylchlorosilane is a quick and efficient dehydrating agent for metal chloride hydrates that is free of the drawbacks mentioned above (eq 3).

$$MX_n{\cdot}xH_2O + 2x(CH_3)_3SiCl \rightarrow MX_n + [(CH_3)_3Si]_2O + 2xHCl \quad (3)$$

Experimental Section

All reactions were carried out in a hood. Commercially available metal chloride hydrates and trimethylchlorosilane were used without further purification. Tetrahydrofuran (THF) was freshly distilled from

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Table I. Dehydration of Metal Chlorides with Trimethylchlorosilane

$MX_n\cdot xH_2O$	color	product	color	yield, %
$CrCl_3\cdot H_2O$[a,b]	green	$Cr(THF)_3Cl_3$	purple	89
$CuCl_2\cdot 2H_2O$[b]	blue	$Cu(THF)_{0.8}Cl_2$	yellow	95
$BaCl_2\cdot 2H_2O$[b]	white	$BaCl_2$	white	95
$ZnCl_2\cdot nH_2O$[c]	white	$Zn(THF)_2Cl_2$	white	71
$ZnCl_2\cdot nH_2O$[c,d]	white	$ZnCl_2$	white	96
$BaCl_2\cdot 2H_2O$[d]	white	$BaCl_2$	white	95
$CuCl_2\cdot 2H_2O$[d]	blue	$CuCl_2$	yellow	90
$CoCl_2\cdot 6H_2O$[d,e]	red	$CoCl_2$	blue	95
$FeCl_3\cdot 6H_2O$[d,e]	orange	$FeCl_3$	dk green	95

[a] Requires THF for complete dehydration. [b] Approximate composition of reaction mixture: 30 mL of trimethylchlorosilane/20 mL of THF/10 mmol of hydrate. [c] Samples of hydrated $ZnCl_2$ were made by adding water (10% by weight) to anhydrous $ZnCl_2$. [d] Dehydrations were performed in trimethylchlorosilane: 30 mL/10 mmol of hydrate. [e] $FeCl_3$ and $CoCl_2$ react with THF; reactions must be run in neat trimethylchlorosilane.

sodium benzophenone ketyl. IR spectra were obtained as Nujol mulls on a Beckman Model 4240 IR spectrometer.

In a typical experiment, 2.66 g of chromium(III) chloride hexahydrate (10.0 mmol) and 20 mL of THF were placed in a 100-mL three-necked round-bottomed flask equipped with a condenser fitted with a drying tube. At room temperature, 32 mL of trimethylchlorosilane (253 mmol) was added dropwise with stirring to the slurry, causing the evolution of heat. The color of the reaction mixture changed from dark green to deep purple. The purple solid that precipitated was washed with hexane followed by evaporation of residual solvent at reduced pressure to give 3.34 g (8.9 mmol), 89% yield, of chromium(III) chloride tris(tetrahydrofuran). The C–O–C stretches were observed at 850 (symmetric) and 1010 cm^{-1} (asymmetric). No O–H absorptions (3500–3300 cm^{-1}) were detected.

Treatment of iron(III) chloride hexahydrate by the above procedure leads to polymerization of THF. However, the reaction can be conveniently carried out without solvent. Thus, 30 mL of trimethylchlorosilane was added to 10 mmol of powdered iron(III) chloride hexahydrate at room temperature. Stirring for 30 min followed by refluxing for an additional 3 h led to 95% yield of the green anhydrous salt after removal of the liquid under reduced pressure. The IR spectrum showed no O–H absorptions nor Si–C–H peaks (1225–1275 cm^{-1}), indicating all water and organosilicon compounds were removed.

Results and Discussion

Solvated and unsolvated anhydrous metal chlorides can be conveniently prepared in very high yields under mild conditions via dehydration of metal chloride hydrates with trimethylchlorosilane. When THF is used as a solvent, the metal chloride is obtained as a tetrahydrofuranate complex, with the exception of barium chloride which is isolated as the simple salt. The high solubilities of metal chloride hydrates in THF result in homogeneous reactions and shorter reaction times than when neat trimethylchlorosilane is used. With THF, the reactions were complete in less than 1 h, while reactions in neat trimethylchlorosilane were heterogeneous and required 3–4 h of refluxing. Our results are summarized in Table I.

The formation of HCl and of the very strong silicon–oxygen bonds in hexamethyldisiloxane drives the reaction. The reactions are easily monitored by characteristic color changes, and workup is relatively simple because the byproducts have low boiling points (HCl (−84 °C), trimethylchlorosilane (57 °C), hexamethyldisiloxane (101 °C)) and are efficiently removed under reduced pressure. The THF adducts were characterized by IR spectroscopy by comparing the C–O–C symmetric and asymmetric stretches with those reported by Kern.[5a] Excellent agreement was obtained in each case. The reported yields are an average of two trials.

Some salts could not be dehydrated in THF. Iron(III) chloride, for example, polymerizes THF[5a] and must be prepared with neat trimethylchlorosilane. Cobalt(II) chloride dihydrate gave a similar result, requiring neat trimethylchlorosilane. In both cases, nearly quantitative yields of the anhydrous salt were obtained. Hydrated zinc chloride, which we prepared by adding 10 wt % water to the anhydrous chloride because well-defined hydrates are not commercially available, was very efficiently dehydrated in neat trimethylchlorosilane to give 96% zinc chloride. In contrast, the THF/trimethylchlorosilane mixture afforded a comparatively modest 71% yield of the tetrahydrofuranate. Chromium(III) chloride hexahydrate, on the other hand, could not be completely dehydrated in neat trimethylchlorosilane and required THF for an efficient reaction, giving 89% yield of chromium(III) chloride tris(tetrahydrofuran).

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