be due to vibrational coupling between adjacent proline residues in polyproline. It is interesting that the proline band in HRG is at 1457 cm^{-1}, the same frequency as in native ribonuclease, although the proline bonds in HRG are suggested on the basis of circular dichroism measurements to be trans.[26] Thus there appears to be some variability for the proline frequency among residues with the same imide isomer. This may also contribute to the breadth of the band in protein spectra. It is evidently not possible to associate proline conformation uniquely with fixed Raman frequencies. Nevertheless the distinct frequency difference observed for ribonuclease A at pH 7 and 1.5 indicates that UVRR spectroscopy may be quite useful in monitoring specific proline isomerization processes.

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Registry No. Proline, 147-85-3; polyproline, 25191-13-3; ribonuclease A, 9001-99-4; polylysine, 25104-18-1.

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Phosphate Ester Hydrolysis Catalyzed by Metallomicelles

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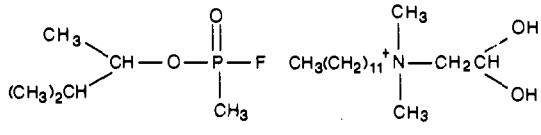
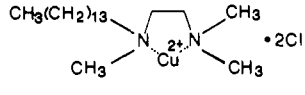
Abstract: Two long-chained cupric ion complexes were synthesized and found to possess remarkable catalytic activity toward phosphate triesters, diesters, and other phosphorus(V) compounds (including some particularly toxic and persistent materials). The complexes form "metallomicelles" which bind substrates with enzyme-like efficiency ($K_{assoc} > 10^5$ M). Rate accelerations approach the 10^5-fold level with turnover behavior. Possible reasons for the huge rate accelerations include enhanced electrophilicity of the micellized metal (demonstrated by polarography) and enhanced acidity of copper-bound water (demonstrated by rate vs. pH studies).

In Reston, VA, 1980, a gathering of American chemists[1] was challenged to devise methods for destroying some of the most noxious compounds known to man, compounds which a saner world would never produce. These are the phosphate esters and related phosphorus(V) materials known as nerve agents (e.g., GD or "Soman") and used in chemical weaponry. Owing to our interest in catalysis,[2] especially in reactions of biologically important systems such as phosphate esters, we undertook the challenge and began developing catalysts that hydrolyze phosphorus(V) substrates. The first of these,[3] dubbed Atlanta-1 or A1, operates by (a) binding noncovalently a phosphate ester, (b) accepting the phosphoryl group on one of its hydroxyls, and (c) dephosphorylating to produce an aldehyde that immediately regenerates the original A1. Thus, true catalysis or "turnover" was



GD A1

achieved, one of our major goals. The overall rate enhancement with 8 mM A1 was substantial (1800-fold), yet we set our sights on attaining even greater reactivity. This led to the synthesis of an entirely different catalyst, A2, whose remarkable properties are described below.



A2

Experimental Section

Synthesis. Preparation of *N,N,N'*-Trimethyl-*N'*-tetradecylethylenediamine. *N,N,N'*-Trimethylethylenediamine (12.0 g, 0.12 mol) and 1-bromotetradecane (14.0 g, 0.05 mol) in 70 mL of absolute ethanol were refluxed for 10 min. A solution of NaOH (2.4 g in 4 mL of water) was added, and the mixture was further refluxed for 5 h, cooled, and shaken with a solvent mixture consisting of 20 mL of 1-butanol, 20 mL of benzene, and 100 mL of water. The organic layer was removed and washed with 120 mL of water (creating an emulsion that required several hours standing to separate). After removing the volatiles from the organic layer with the aid of a rotary evaporator, we distilled under reduced pressure the residue at 150-170 °C and 0.25 mmHg. An initial cut of 4.7 g (containing considerable amounts of alkyl bromide) was dissolved in 100 mL of ether and treated with dry HCl gas to generate a hydrochloride salt that precipitated from solution. The salt was removed by filtration and washed with ether. Free amine was isolated with use of aqueous base and an ether extraction in the usual manner. A second cut from the vacuum distillation (3.7 g) was virtually pure amine. The combined product, 7.7 g, had satisfactory ^1H and ^{13}C NMR spectra. No attempt was made to optimize yields. Anal. Calcd for $C_{19}H_{42}N_2$: C, 76.43; H, 14.18; N, 9.39. Found: C, 76.52; H, 14.11; N, 9.29.

$CuCl_2$ Complex of *N,N,N'*-Trimethyl-*N'*-tetradecylethylenediamine ("A2"). A solution of diamine prepared above (0.99 g, 3.3 mmol) in 10 mL of absolute ethanol was added slowly with magnetic stirring to a filtered solution of anhydrous $CuCl_2$ (0.55 g, 4.1 mmol) in 15 mL of absolute ethanol. The resulting precipitate was washed with four portions of cold absolute ethanol (30 mL each), recrystallized from absolute ethanol or methanol-ether, and dried in a desiccator at 72 °C for 1 h to give material with mp 104-105 °C dec. Anal. Calcd for $C_{19}H_{42}Cl_2CuN_2$: C, 52.70; H, 9.78; N, 6.47. Found: C, 52.66; H, 9.81; N, 6.44.

***N,N'*-Dimethyl-*N,N'*-ditetradecylethylenediamine.** *N,N'*-Dimethylethylenediamine (2.0 g, 0.023 mol) and 1-bromotetradecane (18 g, 0.065 mol) dissolved in 50 mL of absolute ethanol were refluxed for 15 min. A solution of NaOH (2 g in 3 mL of water) was then added dropwise over a period of 5 min after which the solution was further refluxed for 6 h. TLC analysis indicated that after this time period most of the initial diamine had reacted. A mixture composed of 40 mL of benzene, 40 mL of 1-butanol, and 200 mL of water was next added to the filtered reaction mixture. The resulting organic layer was separated, reduced in volume

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to about 50 mL, and added to 500 mL of ether. A fine white powder precipitated when dry HCl gas was bubbled through the ether. Free amine was regenerated by dissolving the salt (4.6 g) in a mixture of 120 mL of water and 15 mL of ethanol, neutralizing the solution with 1 N NaOH, and extracting the mixture with ether (4 × 100 mL). The ether layer was dried over Na_2SO_4 and stripped, leaving material which, upon standing, solidified except for a small amount of oil. The solid was physically separated from the oil and subjected to column chromatography (Mallinkrodt Silicar silica gel, 100–200 mesh, type 60A eluted with a mixture of *n*-hexane, chloroform, and absolute ethanol in a ratio of 20:6:5). Under these chromatographic conditions, single-chain impurities move slowly relative to the desired double-chain material. The final product melted at 38 °C and possessed the expected NMR spectra. Anal. Calcd for $C_{32}H_{68}N_2$: C, 79.92; H, 14.25; N, 5.83. Found: C, 79.94; H, 14.21; N, 5.77.

$CuCl_2$ Complex of *N*,*N*′-Dimethyl-*N*,*N*′-ditetradecylethylenediamine ("A3"). This green solid was prepared in 87% yield as described above. Upon recrystallization from cold methanol and drying under reduced pressure in a desiccator for 3 h, the complex melted at 81–81.5 °C dec. Anal. Calcd for $C_{32}H_{68}Cl_2CuN_2$: C, 62.46; H, 11.14; N, 4.55. Found: C, 62.47; H, 11.18; N, 4.50.

***p*-Nitrophenyl Diphenyl Phosphate (PNPDPP).** This substrate, prepared according to a literature procedure,[4] was was crystallized from absolute ethanol, mp 47.5–48 °C.

Bis(*p*-nitrophenyl) Phosphate. The hydrated material, purchased from Aldrich, was crystallized twice from acetone, mp 171.5–172 °C.

Kinetics. The following kinetic run is typical of that used throughout the study. A 1-cm cuvette was filled with an aqueous solution containing 1.27 mM A2 and 0.01 M *N*-ethylmorpholine buffer that had been adjusted to pH 8.00. Note: *N*-Ethylmorpholine (pK_a 7.70) was an ideal buffer because (a) it was compatible with the catalyst, (b) it functioned in the mildly basic pH range where we wished to secure the rate constants, and (c) it was totally unreactive toward the substrates of interest. The cuvette was then stoppered and placed for 15 min in the sample chamber of a Hewlett Packard 8451 A Diode Array spectrophotometer thermostated at 25 ± 0.1 °C. The reaction was initiated by adding 10 mM PNPDPP solution in purified acetonitrile (4 μL) followed by rapid stirring of the cuvette with a glass rod flattened at one end. Liberation of *p*-nitrophenolate as the reaction proceeded was monitored at 400 nm for greater than 8 half-lives. Linear first-order plots were always obtained for at least 2 half-lives.

Soman ("GD") hydrolysis was followed by measuring the appearance of fluoride ion with an Orion Model 960900 combination fluoride electrode attached to an Orion 901 Microprocessor Ionanalyzer. Immediately prior to the kinetic measurements, the electrode was calibrated with 0.100 and 1.00 mM sodium fluoride. This calibration allowed the ionmeter to read concentration directly from the fluoride electrode potential output (an output that was recorded with an Orion 951 thermal printer at 0.1- or 1.0-min intervals). The ion selective electrode was fitted to a magnetically stirred reaction vessel that was thermostated at 25.0 ± 0.1 °C. Owing to the extreme toxicity of GD, the entire apparatus was housed inside a high-draft hood, and all transfers were made with use of heavy butyl rubber gloves. The reaction cell was first filled with 5 mL of buffer (0.05 M HEPES, pH 7.0) containing a known amount of A2 catalyst. After thermal equilibration, a 1% solution of GD in 2-propanol (50 μL) was added to initiate hydrolysis. Following completion of a run, the entire reaction solution was mixed with excess 2% aqueous NaOH and allowed to stand for 24 h before discarding. Rate constants were calculated from the concentration–time data with the aid of an Apple IIe computer and a weighted least-squares program. Kinetic runs, carried out always in duplicate, gave rate constants with an uncertainty of less than ±5%.

Results and Discussion

In the interest of space and palatability, raw kinetic data on A2 catalysis will be listed only when this is deemed useful; the remaining rate constants will have their properties summarized in sentence form.

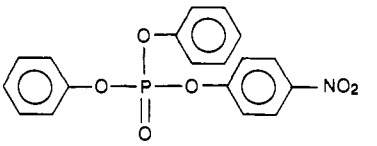
A2 is a long-chain chelate of cupric ion. The amino groups were deliberately made tertiary to preclude possible irreversible reactions between the nitrogens and a substrate. When dissolved in water above its critical micelle concentration of 1.8×10^{-4} M (determined tensiometrically), A2 forms "metallomicelles" having a Stern region filled with cupric ion. Only a few other examples of copper surfactants are known. Moroi et al.[5] prepared poorly soluble copper(II) alkylsulfonates. Gutsche and Mei[6] found that the copper complex of a tetradentate ligand bearing a hydrocarbon chain catalyzes the hydrolysis of acetyl phosphate by a factor of ten. Grätzel et al.[7] studied copper(II)–crown ether surfactants, while the groups of Kunitake[8] and Fuhrhop[9] synthesized copper-bound vesicles. Catalytically active copper bolaforms were reported by Tonellato et al.[10] Several groups, including those of Tagaki,[11] Breslow,[12] and Tonellato,[13] examined micelles containing heavy metals other than copper.

Table I. Pseudo-First-Order Rate Constants for PNPDPP Hydrolysis in Aqueous Buffers at 25.0 °C

10^4[A2], M	pH	10^2k_{obsd}, s^{-1}	10^4[A2], M	pH	10^2k_{obsd}, s^{-1}
0.13	8.00	0.04	19.0	8.00	5.29
0.38	8.00	0.52	25.3	8.00	5.53
0.62	8.00	0.98	38.0	8.00	4.95
1.22	8.00	2.02	15.0	6.03	4.05
2.37	8.00	3.19	15.0	6.63	4.42
3.80	8.00	3.90	15.0	7.22	4.37
6.33	8.00	4.59	15.0	7.62	4.58
7.60	8.00	4.79	15.0	7.79	4.72
8.86	8.00	4.98	15.0	8.14	5.44
10.1	8.00	4.97	15.0	8.28	5.77
12.7	8.00	5.02			

[a] All reactions were carried out in 0.01 M *N*-ethylmorpholine buffers and monitored spectrophotometrically at 400 nm for the production of *p*-nitrophenolate from an initial [PNPDPP] = 0.04 mM.

p-Nitrophenyl diphenyl phosphate (PNPDPP) was selected as the principal substrate for our study because: (a) It is an easily handled "simulant" of more important but also more dangerous phosphorus(V) compounds such as GD. (*b*) Since PNPDPP is less reactive than GD and other toxic substrates, any catalyst that manages to hydrolyze PNPDPP is likely to be generally effective. (c) Considerable work has already been carried out on PNPDPP, so that there exists a large body of data with which to judge the efficiency of our catalysts. (d) The hydrolysis of PNPDPP can be monitored spectrophotometrically.



PNPDPP

A2 is an extremely potent catalyst for the hydrolysis of PNPDPP: $k_{obsd} = 4.1 \times 10^{-2}$ s^{-1} with 1.5 mM A2 (25.0 °C, pH 6.0). The following comparisons testify to the speed of the A2-promoted hydrolysis: (a) The reaction proceeds 8000 times faster at 1.5 mM A2 and pH 6.0 than in the absence of catalyst at pH 8.0. If both reactions could be compared at pH 6.0 (the uncatalyzed hydrolysis being too slow to do this experimentally), the rate difference would be $>10^5$. Stated in another way, 1.5 mM A2 causes the PNPDPP half-life to decrease from about 20 days to 17 s. (b) A2-promoted hydrolyses are >200 times faster than those catalyzed by an equivalent concentration of curpic ion complexed with tetramethylethylenediamine (TMED). Cupric ion, known from past work to catalyze phosphate ester hydrolysis,[14,15] is therefore much more effective when the metal is confined

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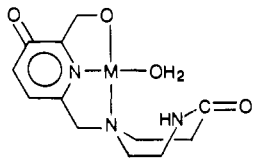
to a micelle surface. In other words, the fast rates associated with A2 stem from a micellization effect superimposed upon a metal catalysis. (c) In order to achieve the rates observed with A2 at pH 6.0, conventional surfactant catalysis with CTAB[16] must be carried out at 0.01 N NaOH—conditions that are far too caustic for most uses outside the laboratory. (d) A2 at pH 6.0 hydrolyzes PNPDPP about 24 times more rapidly than do tetracoordinated zinc complexes solubilized in neutral surfactants (pH 8.0) reported by Breslow et al.[12] (e) Among the "phosphotriesterase" models, only the micellar *o*-iodosobenzoates of Moss et al.[17] surpass A2. From a practical point of view, however, the iodoso compounds possess less than ideal stability especially in the presence of sulfur atoms, enols, etc. Moreover, preliminary work has shown that the Moss compounds, in contrast to A2, are inert toward some particularly toxic and persistent phosphorus(V) compounds, namely the phosphothiolates of which VX is the best known.[18]

Rate constants for PNPDPP hydrolysis at various A2 concentrations and pH values are compiled in Table I. Note that the rates initially increase sharply with increasing [A2] and then level off as the substrate becomes fully bound to the micelles. By applying an equation developed years ago for analyzing micellar kinetics,[19] we calculate the $K_{assoc} = 2.6 \times 10^5$ M^{-1} for PNPDPP–micelle complexation. Substrate hydrophobicity and, very likely, an affinity of the P=O group for cupric ion[20] contribute to the enzyme-like magnitude of the binding constant.

Neither buffer (0.1 M *N*-ethylmorpholine) nor TMED ligand (which was used to "model" the water-insoluble *N,N,N'*-trimethyl-*N'*-tetradecylethylenediamine) reacts by itself with PNPDPP. Thus, PNPDPP hydrolysis in the presence of A2 is ascribable solely to the cupric ion complex. All runs in Table I were carried out at low ionic strength (<0.01). Addition of large amounts of KCl has only a minor effect on the rate: $k_{obsd} = 4.95 \times 10^{-2}$, 3.72×10^{-2}, and 2.25×10^{-2} s^{-1} at 0.00, 0.38, and 0.75 M KCl, respectively, ([A2] = 1.1×10^{-3} M, 25.0 °C, and pH 8.0).

Two species could conceivably function as the catalytically active nucleophile within the A2 micelles: (a) the OH of a hydroxo chelate ($Cu[L][OH]^+$) and (b) hydroxide ion loosely associated with the cationic micelle surface. Since the data in Table I show that the hydrolysis rate is pH insensitive (varying only from 4.1×10^{-2} to 5.8×10^{-2} s^{-1} between pH 6.0–8.3), hydroxide ion cannot be the reactive entity. Instead, phosphate ester must be attacked by an OH formed from a water molecule that has lost a proton after binding to the metal. But the pK_a of copper-bound water, estimated by Allison and Angelici,[21] equals 9. Clearly, the observed pH insensitivity of the rates between 6.0 and 8.3 demands that metal-bound water exists in the deprotonated state 3 units below the "normal" pK_a. Such an environmentally induced decrease in pK_a of copper-bound water is not unprecedented. For example, Groves and Dias[22] found that the tridentate copper complex drawn below possesses an "extraordinarily" low pK_a of



7.6. Water bonded to micellized A2 should have an even lower pK_a owing to the highly cationic Stern region wherein the water resides. Moreover, release of a proton from $Cu-OH_2$ would be promoted by a low dielectric constant (approximately equal to 36) known to exist at micelle surfaces.[23]

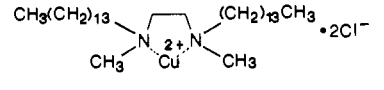
Only one (unsuccessful) attempt was made to further enhance hydrolysis rates via addition of external nucleophiles to the A2 micelles. Thus, 1.4 and 4.6 mM sodium octanoate mixed with 1.5 mM A2 (pH 8.0, 25.0 °C) decreases k_{obsd} to 64% and 16% of that in the absence of additive. A precipitate forms when the octanoate concentration exceeds 6 mM.

A nearly quantitative yield of *p*-nitrophenolate was produced when the initial PNPDPP concentration was in a 2-fold excess over A2 (i.e., 0.60 mM PNPDPP and 0.30 mM A2 in a pH 8.0 buffer containing 0.01 M CTAC).[24] Although substrate insolubility prevented the use of larger PNPDPP/A2 ratios, the results with a 2:1 ratio suffice to prove the existence of turnover behavior. Turnover is, of course, a key component of any truly catalytic system.[3]

The observed 10^5 rate enhancement probably arises from multiple effects: (a) PNPDPP binds to the micelle surface[25] where the nucleophile, the OH of $Cu[L][OH]^+$, is located. Thus, attack on the PNPDPP phosphorus simulates an intramolecular reaction (resembling that observed by Groves and Dias[22] with their tridentate copper complex). Intramolecular reactions can be very fast for reasons discussed elsewhere.[2] (b) As mentioned above, water bound to micellar copper has an unusually low pK_a, thereby freeing the oxygen for reaction at pH values near neutrality. (c) Cupric ion can polarize the P=O group.[20] Electrophilic catalysis should be greater than that found with monomeric copper[15] owing to the cationic nature of the Stern region. Polarographic studies confirmed this expectation. Thus, we found that the half-wave potential $E_{1/2}$ moves from −0.26 V for monomeric Cu^{2+} with TMED as its ligand to roughly +0.04 V for micellar A2 under identical conditions.[26,27] Since micellization facilitates reduction, it should also promote the electrophilicity of the metal toward micelle-bound substrates.

When the nerve agent GD was treated with 5.3 mM A2 at 25.0 °C and pH 7.0, fluoride ion was released and monitored with a fluoride-selective electrode. The half-life of GD under these conditions is only 0.85 min as opposed to 60 h at pH 10 in the absence of A2. A2 also manifests "phosphodiesterase" activity. Thus, 1.5 mM A2 at pH 7.9 and 25.0 °C catalyzes the hydrolysis of bis(*p*-nitrophenyl) phosphate with a $k_{obsd} = 5.4 \times 10^{-5}$ s^{-1}; this is 2.7 times faster than the hydrolysis rate of the same substrate in 1.0 M NaOH (constituting a 10^6 catalysis). A2 obviously displays remarkable catalytic activity toward a variety of phosphorus(V) compounds: phosphotriesters, phosphodiesters, and phosphonofluoridates.

In a final set of experiments, a 2-chained copper complex, A3, was synthesized and examined kinetically (Table II). A3 has



A3

Table II. Pseudo-First-Order Rate Constants for PNPDPP Hydrolysis in pH 8.00 Aqueous Buffers at 25.0 °C

10^5[A3], M	$10^3 k_{obsd}$, s^{-1}	10^5[A3], M	$10^3 k_{obsd}$, s^{-1}
0.54	0.16	2.82	2.43
0.81	0.19	4.51	3.88
1.05	0.37	5.63	5.24
1.69	0.86	8.45	6.82

[a] All reactions were carried out in 0.01 M *N*-ethylmorpholine buffers with 2% methanol (v/v) and monitored spectrophotometrically for the production of *p*-nitrophenolate from an initial [PNPDPP] = 6.8×10^{-6} M.

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a low water solubility (precipitating near 10^{-4} M) and a critical micelle (or vesicle) concentration too small to measure. PNPDPP is hydrolyzed with a $k_{obsd} = 3.9 \times 10^{-3}$ s^{-1} (25.0 °C, pH 8.0) at exceedingly low A3 concentrations: 4.5×10^{-5} M. Binding of PNPDPP to A3 aggregates, estimated kinetically,[19] is also enzyme-like: $K_{assoc} = 4 \times 10^{5}$ M^{-1}. Although A3 has impressive rate and binding parameters, its low water solubility makes A3 less generally useful than its sibling.

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Stereoselective Formation of Rhodium and Iridium Hydrides via Intramolecular Hydrogen Bonding

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Abstract: Dihydrogen addition to $Ir(CH_3)I[N(SiMe_2CH_2PR_2)_2]$ (R = Ph, i-Pr), under ambient conditions, results in protonation of the iridium amide bond to give an iridium amine monohydride complex, $IrH(CH_3)I[NH(SiMe_2CH_2PR_2)_2]$. $IrH(CH_3)I[NH(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.412$ (2) Å, $b = 14.712$ (3) Å, $c = 9.913$ (1) Å, $\alpha = 106.97$ (1)°, $\beta = 112.41$ (1)°, $\gamma = 70.99$ (1)° ($Z = 2$, $R_w = 0.040$). When these derivatives are heated under dihydrogen in toluene at 80 °C, the iridium amine dihydrides, $IrH_2I[NH(SiMe_2CH_2PR_2)_2]$, are produced. The analogous rhodium amides, $Rh(CH_3)I[N(SiMe_2CH_2PR_2)_2]$, yield only dihydride products, $RhH_2I[NH(SiMe_2CH_2PR_2)_2]$, under 1 atm of dihydrogen at room temperature. One of these, $RhH_2I[NH(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$, has been crystallographically characterized; the complex belongs to the monoclinic space group $P2_1/n$ having the following cell dimensions: $a = 10.287$ (1) Å, $b = 21.317$ (1) Å, $c = 13.740$ (2) Å, $\beta = 110.296$ (6)° ($Z = 4$, $R_w = 0.034$). Reaction of $M(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ (M = Rh, Ir) with H_2 in the presence of CH_2X_2 (X = Cl, Br, I) also yields the amine dihydrides, $MH_2X[NH(SiMe_2CH_2PPh_2)_2]$. $IrH_2Cl[NH(SiMe_2CH_2PPh_2)_2]$, prepared by this route, was analyzed by X-ray crystallography and found to be a member of the monoclinic space group $P2_1/a$ with $a = 28.064$ (3) Å, $b = 10.817$ (1) Å, $c = 12.695$ (2) Å, $\beta = 97.27$ (1)° ($Z = 4$, $R_w = 0.039$). As shown by spectroscopic and crystallographic information, all of these M(III) amine hydride species possess a common structural feature: the amine N–H bond is syn to the metal–halide linkage. This orientation, as well as the concomitant stereoselectivity of these reactions, appears to be a direct consequence of intramolecular N–H···X hydrogen bonding.

An important structural feature in many organic compounds, especially those of biological significance, as well as a number of transition-metal complexes is the occurrence of hydrogen bonding;[1-5] such interactions are usually critically linked to stabilization and even reactivity of these species. With regard to hydrogen bonding in transition-metal derivatives, probably the most extensively studied[6-9] are the amine (amine ≡ ethylenediamine or ammonia) complexes of Co(III), Rh(III), Cr(III), and Ru(II), in which the outer-sphere interactions between the N–H moiety and the counterion (Cl^-, Br^-, I^-) are clearly demonstrated by both spectroscopic and X-ray diffraction data. More recently,[10] a series of crown-ether derivatives of W(0), Pt(II), Cu(II), and Co(III) amines have been prepared, in which the "soft" transition-metal center has been linked to the "hard" crown-ether via second sphere N–H···O hydrogen bonds; since crown-ethers do not readily bind to the later transition elements (due to mismatching of hard/soft[11] interactions), this is an indication of the stabilizing influence of hydrogen bonding. Other examples of such interactions in transition-metal systems are known[5] but are apparently fortuitous and have not been examined extensively.

A variety of spectroscopic techniques have been well utilized[3] for the assignment of such interactions. Traditionally, lowering of appropriate infra-red frequencies (ν_{NH} or ν_{OH}) or downfield shifts of ^{1}H NMR chemical shift values has been diagnostic. For transition-metal complexes containing π-acceptor ligands (such as CO or N_2), the decrease in $\nu_{\pi L}$ with increased outer-sphere hydrogen bonding can be a useful correlation.[8] Crystallographic analyses of a wide number of hydrogen-bonded transition-metal complexes[9] have shown significant shortening of the N–H···X distance (vs. sum of the van der Waals radii), the degree of contraction thus giving a useful approximation of the strength of these interactions. Solution spectroscopic information is usually insufficient to provide insight into the significance of these effects[12,13] since solvation sometimes results in breaking of these rather weak bonds.

In the course of our study of the coordination chemistry and reactivity of transition-metal amides, we discovered that a number of these rhodium and iridium species react with dihydrogen to

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