carboxylic group.[9,10] The pK_a values of **1e–g** (3.80, 3.94, and 3.93, respectively) seem to reach a limiting value and become independent of the ring size. When the pK_a determinations of **1b**, **1f**, and **1g** were carried out in the presence of a 100-fold excess of urea, we found a small but significant enhancement of the pK_a values of **1f** and **1g** (both 0.10), an effect that hardly exists in the case of **1b** ($\Delta pK_a \leq 0.04$). This increased pK_a value can be attributed to a specific inclusion of urea,[10] a proposed complexation which is supported by the isolation of a crystalline **1f**–urea (1:1) complex.[11] The X-ray analysis of the **1f**–urea complex[12] (Figure 1) shows that the proton of the carboxylic group is coordinated to the urea oxygen atom via a short hydrogen bond (O···O distance 2.54 Å, O–H···O angle 167°). The total encapsulation of urea results in a complex with an apolar exterior, a property that allows for the solubilization of urea in an apolar solvent. A 0.10 M solution of **1f** in $CDCl_3$ solubilized 0.05 M urea (25 °C, 17 h). In the absence of **1f** no urea could be dissolved in $CDCl_3$. These results prove that the electrophilic moiety in crown ethers **1** can assist in the complexation of a neutral molecule, and, therefore, we assumed that other electrophiles should also be able to assist in this type of complexation.[13]

When a dilute solution of 2,6-pyrido-27-crown-9 (**2e**) and an equimolar amount of *lithium perchlorate* was treated with 1–2 equiv of urea in ethanol, a crystalline complex (1:1:2) precipitated.[14] X-ray structure analysis (Figure 1)[15] revealed that one of the urea molecules is encapsulated in the crown ether cavity (N···O distances in hydrogen bonds 2.99–3.17 Å) in a similar way as in the **1f**–urea complex with the Li^+ cation replacing the hydrogen atom of the carboxylic group as a coordinating electrophile (Li···O distance 1.90 Å, Li···N distance 2.20 Å). The tetrahedral coordination of the lithium cation is completed by a crown ether oxygen and the oxygen atom of a second urea molecule. These Li···O distances (1.98 and 1.95 Å) are in agreement with values reported for other 4-fold coordinated Li^+ complexes.[16]

From these results we conclude that electrophiles such as Li^+ or H^+ can be vital bridging species in the cocomplexation of neutral guests by crown ethers.

Acknowledgment. These investigations were supported in part by the Netherlands Technology Foundation (S.T.W.) and by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

Supplementary Material Available: Tables containing listings of positional and thermal parameters of the two structures (12 pages). Ordering information is given on any current masthead page.

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[9] **1d**·H_2O complex (1:1) was obtained from a methanol/water solution (mp 65–67 °C); X-ray analysis shows an encapsulated complex in which three hydrogen bonds are formed between the host and the guest molecule. To be published.

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[11] Yield 88% (mp 75–78 °C); ^1H NMR ($CDCl_3$) δ 3.65 (m, 32 H, CH_2CH_2), 4.70 (s, 4 H, Ar CH_2), 5.6 (br s, 4 H, NH_2), 7.26 (s, 3 H, Ar H).

[12] $C_{25}H_{40}O_{11}\cdot CH_4N_2O$, monoclinic, space group $P2_1/n$, $a = 19.990$ (2) Å, $b = 8.943$ (1) Å, $c = 16.660$ (1) Å, $\beta = 94.54$ (1)°, $V = 2969$ (1) Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, μ(Mo Kα) = 1.0 cm^{-1}. Measured 3887 unique reflections ($3° < \theta < 22.5°$), $T = 159$ K. Structure solved by direct methods. Full-matrix least-squares refinement of 1988 observed reflections ($F_o^2 > 3\sigma(F_o^2)$). Hydrogens from difference Fourier maps; carboxylic and urea hydrogens included in refinement; crown ether hydrogens calculated (C–H distance 0.96 Å). Final $R = 3.6\%$, $R_w = 3.8\%$, $w = 4F_o^2/\sigma^2(F_o^2)$, 382 variables.

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[14] Yield 80% (mp 107–109 °C); ^1H NMR ($CDCl_3$) δ 3.2–3.8 (m, 28 H, CH_2CH_2), 4.73 (s, 4 H, Ar CH_2), 7.2–7.9 (m, 3 H, Ar H). Anal. Calcd for $C_{23}H_{43}ClLiN_5O_{14}$: C, 42.11; H, 6.61; N, 10.68. Found: C, 42.36; H, 6.59; N, 10.63.

[15] $C_{21}H_{35}NO_8\cdot 2(CH_4N_2O)\cdot LiClO_4$, triclinic, space group $P\bar{1}$, $a = 15.687$ (6) Å, $b = 11.797$ (3) Å, $c = 9.280$ (2) Å, $\alpha = 103.64$ (2)°, $\beta = 97.40$ (3)°, $\gamma = 99.90$ (1)°, $V = 1618$ (2) Å^3, $Z = 2$, $D_c = 1.35$ g cm^{-3}, μ(Mo Kα) = 1.8 cm^{-1}. 5660 Unique reflections ($4° < \theta < 25°$), $T = 242$ K. Solution by direct methods. Refinement of 3875 observed reflections, urea hydrogens included, crown ether hydrogens in calculated positions. Final $R = 6.7\%$, $R_w = 9.8\%$, 450 variables.

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Barrier to Reductive Elimination of Hydrogen from Dihydridobis(trimethylphosphine)platinum(II)

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Oxidative addition and reductive elimination of H–H, C–H, and C–C bonds occur in many catalytic and synthetic reactions.[1-4] Mechanistic studies of the reductive elimination of carbon–hydrogen[5-7] and carbon–carbon[8-12] bonds have been reported for several systems. Intermolecular reductive elimination[11] can hamper the study of these reactions on a single metal center.

The intramolecular reductive elimination of molecular hydrogen from a mononuclear platinum, palladium, or nickel complex has not been well characterized, although elimination of hydrogen from metal clusters has been suggested as a model for the behavior of hydrogen on surfaces.[13] Several theoretical studies have considered the oxidative addition and reductive elimination of molecular hydrogen from bis(phosphine)platinum(II) species[14-17] to gain insight into the mechanism of processes that might occur on a platinum surface. These studies suggest reductive elimination proceeds via a "late" transition state that contains an η^2-dihydrogen ligand. Kinetic barriers predicted range between 18 and 42 kcal/mol. We report here the first experimental investigation of intramolecular, rate-determining reductive elimination of H_2 from a mononuclear dihydride complex containing a metal from the nickel triad, a series of metals frequently used as heterogeneous hydrogenation catalysts.

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Table I. Kinetic Data for Reductive Elimination of H_2 from Dihydridobis(trimethylphosphine)platinum(II)

	solvent		
	THF	2,5-Me_2THF	2,2,5,5-Me_4THF
k_1(21 °C), s^{-1}	$(7.3 \pm 0.4) \times 10^{-4}$ [a]	$(1.8 \pm 0.06) \times 10^{-3}$	$(3.0 \pm 0.01) \times 10^{-3}$
$\Delta H^{\ddagger}$,[b] kcal/mol	9.4 ± 1	14.0 ± 0.6	20.0 ± 0.5
$\Delta S^{\ddagger}$,[b] cal/(mol K)	-41 ± 3	-23 ± 2	-2 ± 2
log A[c]	4.3	8.4	12.8

[a] All errors represent the standard deviation obtained from a linear least-squares analysis. [b] From an Eyring plot. [c] Preexponential factor from an Arrhenius plot.

The complex *trans*-dihydridobis(trimethylphosphine)platinum(II), (**1**) was prepared by reduction of *cis*-$PtCl_2(PMe_3)_2$ with sodium naphthalide under a H_2 atmosphere as described previously.[18] In solution, **1** exists as an equilibrium mixture of cis and trans isomers. Solutions of *cis*- and *trans*-**1** are stable under hydrogen, but when exposed to nitrogen they decompose with evolution of H_2 to yield $Pt(PMe_3)_4$ and platinum metal (eq 1)

$$trans\text{-}PtH_2(PMe_3)_2 \underset{K}{\overset{\text{fast}}{\rightleftharpoons}} cis\text{-}PtH_2(PMe_3)_2 \xrightarrow{k_1} Pt(PMe_3)_4 + Pt + H_2 \quad (1)$$

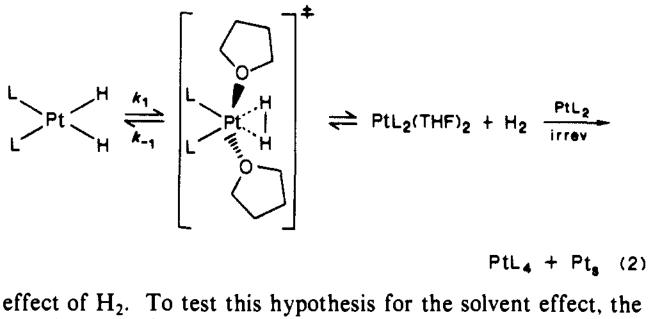
according to a first-order rate law k_{obsd} $[PtH_2(PMe_3)_2]$. It was not possible to trap the intermediate $Pt(PMe_3)_2$ species by reaction with an olefin or acetylene since solutions of **1** react with such substrates (e.g., *tert*-butylethylene) by an associative pathway.[19]

At temperatures above −10 °C, solutions of *cis*- and *trans*-**1** decompose at a rate conveniently measurable by FTIR spectroscopy.[20,21] Since cis–trans isomerization occurs within minutes at −80 °C[18] this process is fast[21,22] compared to reductive elimination. The reaction was followed by monitoring the decrease in absorbance of peaks from *cis*-**1** (ν_{Pt-H} = 1985, 2030 cm^{-1}) or *trans*-**1** (ν_{Pt-H} = 1720 cm^{-1}).[22] These IR data show that *cis*-**1** exists as a dihydride rather than an η^2-dihydrogen complex as found recently for several metal systems.[23,24] Further confirmation of the dihydride structure derives from the absence of $^1J_{H-D} \sim 30$ Hz, expected[24] for η^2-deuterium hydrogen, in the ^1H NMR spectrum of *cis*-$PtHD(PMe_3)_2$.

First-order plots for the disappearance of **1** were linear for several half-lives of the reaction. Rate data and activation parameters are given in Table I. The rate constant k_1 was unaffected by the initial concentration of **1** (0.1–0.3 M) or by the presence of colloidal platinum in the solution. Comparison of the rate of decomposition of $PtD_2(PMe_3)_2$ revealed an inverse kinetic isotope effect of 0.72 ± 0.06 (standard deviation for three determinations). These results are consistent with a mechanism involving unimolecular rate-determining reductive elimination of H_2. An inverse isotope effect is expected for the breaking of a low frequency bond to hydrogen (Pt–H) and formation of a high frequency bond (H–H) in the transition state.[25] Alternatively an η^2-dihydrogen complex could form reversibly in a preequilibrium step as an intermediate. The equilibrium isotope effect would favor η^2-D_2 over η^2-H_2 since the zero point energy of the first species would be significantly less than the second. This could also lead to the observed inverse kinetic isotope effect.[26] It was impossible to investigate the effect of added phosphine ligands on the reaction rate; free phosphines react with **1** to produce the known five-coordinate species $PtH_2(PMe_3)_3$.[27] A mechanism involving phosphine dissociation as the rate-determining step is, however, difficult to reconcile with the inverse kinetic isotope effect. Furthermore, dissociation of phosphine was not observed for reductive elimination in the electronically similar complex *cis*-$PtH(CH_3)(PPh_3)_2$.[5] The inhibiting effect of added H_2 on the reaction suggests that an intermediate forms reversibly en route to $Pt(PMe_3)_4$ and Pt products because addition of H_2 after complete reaction does not reverse the process.

Although PtH_2L_2 species catalyze isotope exchange[27] between H_2 and D_2, crossover experiments at low conversions were possible. Both $PtH_2(PMe_3)_2$ and $PtD_2(PMe_3)_2$ were dissolved in THF solvent at room temperature (under a N_2 atmosphere) and the atmosphere above the solution was analyzed by gas chromatography[28] near the beginning of the reaction. The evolved gas showed H_2 and D_2, but no detectable (<5%) HD. Thus a mechanism that involves dinuclear reductive elimination is excluded.

The reaction rate and activation parameters depend strongly on the coordinating ability of the solvent (see Table I). For these data the reaction is slowest in THF, though the enthalpic barrier to elimination is only 9.4 kcal/mol. The large negative entropy term accounts for the slow rate by destablization (in $\Delta G^{\ddagger}$) of the transition state, which may result from the collection of solvent molecules about a "late" transition state that resembles the reaction products (eq 2). This scheme also accommodates the inhibiting effect of H_2. To test this hypothesis for the solvent effect, the reaction was followed in 2,5-Me_2THF and 2,2,5,5-Me_4THF solvents, which have dielectric constants similar to that of THF but exhibit successively poorer coordinating ability.[29] The activation enthalpy for elimination increased to a maximum value of 20.0 ± 0.5 kcal/mol, while the activation entropy decreased to about zero. The faster reaction rate in less coordinating solvents reflects the reduced entropy term. Rates determined at 21 °C in hexane solvent [(2.63 ± 0.04) × 10^{-3} s^{-1}] were similar to those measured in 2,2,5,5-Me_4THF. In Me_2SO, which has greater



(2)

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[20] Reactions were carried out in Schlenk tubes (under a N_2 atmosphere) placed in a thermostated bath. At timed intervals, aliquots were withdrawn by syringe and transferred into CaF_2 liquid sample cells. It was important to exchange the atmosphere frequently to prevent the buildup of H_2 in the reaction flask, which slows down the reaction. Cells were flushed with nitrogen before use and placed in an IBM 32 FTIR spectrometer. For measurements below 20 °C, the cells were precooled by flushing with nitrogen that was passed through a cooling coil in an N_2/pentane slush bath at −130 °C.

[21] It was not possible to monitor the reaction by NMR spectroscopy, because the dihydride resonances broaden into the base line at temperatures above −30 °C where the reactions occur.

[22] Decay of the IR absorbances attributed to *cis*- and *trans*-**1** proceeds at the same rate, proving that the isomerization *trans*-**1** $\rightleftharpoons$ *cis*-**1** is rapid compared to reductive elimination. The absorbances that were monitored obeyed Beer's Law over the concentration range of interest. According to the scheme of eq 1 $k_{obsd} = k_1(K/K + 1)$. Equilibrium constants were determined in each solvent by NMR spectroscopy at temperatures between −40 and −80 °C and extrapolated to the temperatures of this study. While the accuracy of the multiplicative factor $K/(K + 1)$ effects the absolutes rates it has little influence on the values of activation parameters.

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coordinating ability than THF, k_1 at 40 °C was (7.0 ± 0.4) × 10^{-5} s^{-1}, the rate decreased to 28 times slower than the corresponding rate in THF (k_1 = (2.0 ± 0.1) × 10^{-3} s^{-1} at 40 °C). There is precedent for this solvent dependence in the reductive elimination of ethane from bis(phosphine)dimethylpalladium(II).[9,10] The low activation enthalpy barriers and large negative entropies in polar solvents were also attributed to a late transition state that permits coordination of solvent molecules.

Theoretical studies of H_2 reductive elimination from *cis*-$PtH_2(PH_3)_2$ by the GVB,[15] GVB-CI,[14] RHF,[16] and SD-CI[16] methods have appeared. Calculated activation barriers for H_2 elimination are 18.2, 24.1, 42.1, and 29.7 kcal/mol with endothermicities of +15.9, +6.7, +36.9, and +21.5 kcal/mol, respectively. A SCF calculation for *cis*-$PtH_2(PMe_3)_2$ yielded a kinetic barrier of 18.9 kcal/mol,[14] close to that we observe in the noncoordinating 2,2,5,5-Me_4THF solvent (Table I). The calculated exothermicity of −0.6 kcal/mol agrees with our observation that solutions of the complex decompose readily if H_2 is removed (i.e., $\Delta G \sim 0$). On the other hand the predicted stability of the trans isomer over the cis isomer by 23 kcal/mol does not agree with the experimental difference of 0.3 ± 0.1 kcal/mol.[18] If the ΔH^* of 20.0 ± 0.5 kcal/mol in noncoordinating solvents is taken as the intrinsic barrier to reductive elimination of H_2, this permits the estimation (assuming $T\Delta S° \sim 0$ and that solvation differences are small in Me_4THF) of 62 kcal/mol as an upper limit (with $DH_m{}^{\theta}$(H–H) = 104 kcal/mol) for the Pt–H bond enthalpy. This agrees closely with the theoretical estimate of 60 kcal/mol[15,30] for the Pt–H dissociation energy. Data reported here should provide a benchmark for future theoretical work.

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Synthetic Model Approach to the Manganese(III) Acid Phosphatase and Its Iron(III)-Substituted Form

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Several reports have described the isolation of red-violet acid phosphatases from plants such as soybean,[1] spinach,[2] and sweet potato.[3] The latter enzyme appears to contain a mononuclear Mn(III) site with thiolate (cysteine) and phenoxide (tyrosine) ligation;[3] histidine residues essential for activity possibly indicate imidazole ligation also.[4] The distinctive spectral properties (λ_{max} = 515 nm, ϵ_M = 2460 $L\cdot mol^{-1}\cdot cm^{-1}$) have been attributed to ligand-to-metal charge transfer. However, the precise nature of the coordination sphere, the exact origin of the 515-nm band, and even the identity of the metal have been the objects of recent comment.[5,6] In part this has been stimulated by the spectral similarity of acid phosphatase to known iron tyrosinate enzymes (including iron acid phosphatases[5]), its dissimilarity to known Mn(III) thiolates,[6-8] and the lack of Mn(III) phenoxides for comparison. Substitution of Fe(III) into the native enzyme leads to fairly large (53%) retention of activity and noticeable spectral changes (λ_{max} = 525 nm, ϵ_M = 3000);[9] this suggests the native enzyme indeed contains Mn(III). To help answer other outstanding questions, we have employed a synthetic model approach and have sought, for more valid comparisons, a mixed-O,N,S-ligated Mn(III) complex. We herein report the attainment of the first example of such a species, together with its Fe(III) version.

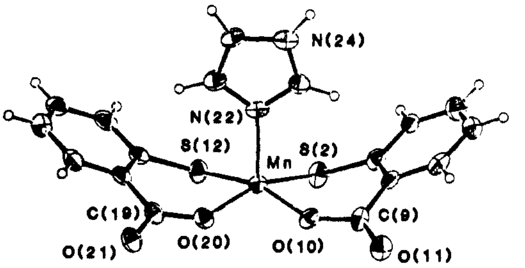

Figure 1. ORTEP projection of the anion of **1**. Pertinent bond distances (A) and angles (deg): Mn–S(2) 2.2913 (24), Mn–S(12) 2.2752 (25), Mn–O(10) 1.948 (5), Mn–O(20) 1.932 (5), Mn–N(22) 2.176 (6), N(22)–Mn–S(2) 106.25 (17), N(22)–Mn–S(12) 103.39, N(22)–Mn–O(10) 96.07 (22), N(22)–Mn–O(20) 96.11 (22), S(2)–Mn–O(20) 157.59 (17), S(12)–Mn–O(10) 160.54 (17).

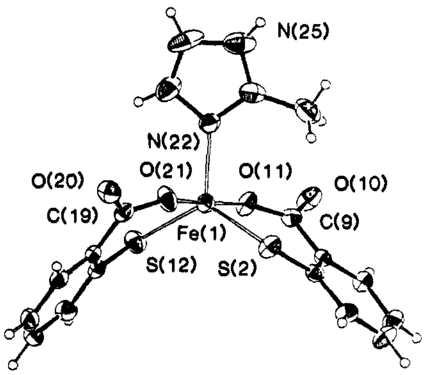

Figure 2. ORTEP projection of the anion of **2**. Pertinent bond distances (Å) and angles (deg): Fe–S(2) 2.2897 (14), Fe–S(12) 2.3010 (14), Fe–O(11) 1.976 (3), Fe–O(21) 1.954 (3), Fe–N(22) 2.065 (4), S(2)–Fe–S(12) 123.36 (6), S(2)–Fe–N(22) 118.07 (11), S(12)–Fe–N(22) 118.53 (11), O(11)–Fe–O(21) 177.02 (13), O(11)–Fe–S(2) 91.01 (9), O(11)–Fe–S(12) 92.32 (10), O(11)–Fe–N(22) 88.50 (14), O(21)–Fe–S(2) 88.46 (11), O(21)–Fe–S(12) 90.42 (10), O(21)–Fe–N(22) 89.16 (14).

$Mn(acac)_3$, NEt_3, thiosalicyclic acid (thiosalH_2), and imidazole (HIm) in a 1:1:2:2 ratio[10] in CH_2Cl_2 at −78 °C yield an intensely red solution. Addition of PPh_4Br and workup yield red-black crystals of $(PPh_4)[Mn(thiosal)_2(HIm)]\cdot 2CH_2Cl_2$ (**1**) in ~25% yield.[11] The Mn is five-coordinate (Figure 1)[12] and square pyramidal with HIm in the apex and *cis* thiolate sulfurs. Complex

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(8) Among the Mn(III) thiolates currently known, $[Mn(edt)_2(HIm)]^-$ (edt = ethane-1,2-dithiolate) is the most similar to **1**. In DMF solution in the presence of excess HIm: λ_{max} (ϵ_M); 596 (815), 392 (8250), 350 (16400), and 288 (6500).

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(10) The acac groups can function as proton acceptors reducing the requirement for added amine.

(11) The crystallographic sample contained two CH_2Cl_2 molecules; the analytical sample dried in vacuo analyzed for one CH_2Cl_2 molecule. Anal. Calcd for $C_{42}H_{34}N_2O_4PS_2Cl_2Mn$: C, 59.23; H, 4.02; N, 3.29. Found: C, 59.71; H, 4.28; N, 3.31%.

(12) Complex **1** crystallizes in space group $P2_1/n$ with (at −155 °C) a = 21.898 (11) Å, b = 13.933 (b) Å, c = 14.065 (6) Å, β = 99.13 (2)°, and Z = 4. 3886 unique reflections with $F > 3\sigma(F)$ were refined to values of discrepancy indices R and R_w of 6.53% and 6.52%, respectively. Anal. Calcd for $C_{24}H_{30}N_3O_4S_2Fe$: C, 52.94; H, 5.55; N, 7.72. Found: C, 52.88; H, 5.69; N, 7.66.

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