and that predicted by the mechanism of eq 13-17 strongly supports the proposed mechanism.

In an alternative scheme the organonickel(III) complex reacts directly with the radical R·′ (eq 19). Not only is it very unlikely

$$RNi(tmc)^{2+} + R^{\cdot\prime} \rightarrow \{RR' + RH + R(-H) + R'H + R'(-H)\} + Ni(tmc)^{2+} \quad (19)$$

that a reaction between a radical and an organometallic intermediate gives the same product distribution as the self reaction of free radicals, but this scheme also requires that R and R′ be equally distributed among the products. The only radical/alkyl halide exchange reaction allowed would be a nonproductive self-exchange reaction of R·′ and R′X (eq 16), since the alkyl group R never passes through a free radical stage.

Similarly, a mechanism that would account for the facile formation of R′Ni(tmc)$^+$ by the involvement of Ni(tmc)$^+$, eq 20-21, cannot account for the stoichiometry of reaction 7 or the distribution of organic products.

$$R^{\cdot\prime} + RNi(tmc)^+ \rightarrow RR' + Ni(tmc)^+ \quad (20)$$

$$Ni(tmc)^+ + 0.5\ R'X \rightarrow 0.5\ Ni(tmc)^{2+} + 0.5\ R'Ni(tmc)^+ + 0.5\ X^- \quad (21)$$

An implication of the mechanism in eq 13-17 is that $k_{obsd} = 2k_{13}$ for reactions with CH_3I, but $k_{obsd} = k_{13}$ in all other cases, since the loss of a second mol of RNi(tmc)$^+$ in the rapid step 15 takes place only with CH_3I. Reaction 15 is kinetically unimportant for R = R′ (self-exchange reaction) and presumably also when R′ = 2-C_3H_7 (no 2-C_3H_7Ni(tmc)$^+$ formation takes place).[25]

Mechanistic differences between the present work and related biaryl formation from $ArNiBr(PEt_3)_2$ and ArBr[21b] can most likely be traced to the coordination properties of macrocycles. In the radical chain mechanism proposed by Tsou and Kochi,[21b] biaryl is formed by reductive elimination from a metastable organonickel(III) species, eq 22. Effective blocking of all four cis

$$(Ar)_2Ni^{III}X \rightarrow ArAr + Ni^IX \quad (22)$$

positions by the macrocyclic ligand rules out the formation of the cis-dialkylnickel complex, *cis*-$(R)_2$Ni(tmc)$^+$. A trans isomer, on the other hand, could be formed (and is probably an intermediate in the exchange reaction 15), but its stereochemistry rules out successful dialkyl and/or alkane/alkene elimination.

Organonickel(III) complexes were proposed as reaction intermediates in an earlier study of the electrochemical reduction of alkyl halides catalyzed by macrocyclic nickel complexes in acetonitrile.[13] The mechanism of the organonickel(III) formation by a one-step oxidative addition of alkyl halides to nickel(I) as well as the proposed product forming steps are, however, inconsistent with our observations.

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Kinetics and Mechanism of Nitrile Hydration Catalyzed by Unhindered Hydridobis(phosphine)platinum(II) Complexes. Regioselective Hydration of Acrylonitrile

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Abstract: The reaction between *trans*-$PtHCl(PR_3)_2$ (R = Me and Et) and 1 equiv of NaOH in 50-50 water/acetonitrile solutions yields a species that catalyzes the hydrolysis of acetonitrile to acetamide at rates of 178 and 70 mol/(mol of catalyst h) for the R = Me and Et derivatives, respectively, at 80 °C. These catalysts remain active for days and give as many as 6000 turnovers. The PMe_3 derivative catalyzes hydrolysis of acrylonitrile but exhibits low regioselectivity between the olefin and nitrile functionalities at 80 °C; at 25 °C, it hydrates 21 mol of acetonitrile/(mol of catalyst h) and regioselectively (97%) hydrates 6.1 mol of acrylonitrile/(mol of catalyst h) to acrylamide. The catalytic intermediates, $[PtH(H_2O)(PEt_3)_2]^+$, $[PtH(N{\equiv}CCH_3)(PEt_3)_2]^+$, and $PtH(NHC(O)Me)(PEt_3)_2$, have been intercepted and spectroscopically characterized and their interconversions demonstrated. Except at low hydroxide concentrations, the rates of catalysis were independent of hydroxide concentration, and proton transfer from solvating water to coordinated *N*-carboxamido, rather than nucleophilic attack of hydroxide on coordinated nitrile, limits the rate. Rate constants of ~8 and ~20 s^{-1} were determined for the proton-transfer process for the PEt_3 and PMe_3 systems, respectively. A kinetic isotope effect of 3.4 was observed in reactions using D_2O. Adjusting the catalytic solutions to pH 8.5 resulted in a linear hydroxide dependence, and rate constants of $4.9 \pm 0.3 \times 10^3$ and $7.0 \pm 0.4 \times 10^3$ M^{-1} s^{-1} were measured for nucleophilic attack of hydroxide on coordinated acetonitrile for the PEt_3 and PMe_3 systems, respectively. Deuterium labeling experiments using *trans*-$PtDCl(PMe_3)_2$ to catalyze acrylonitrile hydration showed that olefin hydration proceeds through a coordinated olefin intermediate and, unlike nitrile hydration, involves a reductive elimination step in the catalytic cycle.

Carboxamides ($RC(O)NH_2$) are generally prepared by hydration of the corresponding nitriles with strong acid or base catalysts[1] (eq 1). These reactions are slow and appreciable hydrolysis of the product carboxamide to the carboxylic acid,[1] as

$$R{-}C{\equiv}N + H_2O \xrightarrow{\text{catalyst}} R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \quad (1)$$

well as the hydrolysis of other functional groups present, occurs faster than nitrile hydration. Increasing use of acrylamide polymers in paper and surfactant production, wastewater treatment, and oil recovery has resulted in acrylamide becoming a major industrial chemical.[2] Difficulties[2] in the conventional

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Table I. Comparison of Catalytic Activities for Hydrolysis of Acetonitrile to Acetamide

catalyst	temp, °C	mol/(mol of catalyst h)	ref
trans-$[PtH(H_2O)(PMe_3)_2][OH]$	78	178.4	this work
trans-$[PtH(H_2O)(PEt_3)_2][OH]$	78	69.9	this work
trans-$Rh(OH)(CO)(Ph_3)_2$	80	50.0	7a
$PdCl(OH)(bipy)(H_2O)$	76	29.4	5h
$Pt[P(c\text{-}C_6H_{11})_3]_2$	80	26.7	9
trans-$[PtH(H_2O)(PMe_3)_2][OH]$	25	21.5	this work
K_2PdCl_4, 2,2′-bipyridine, NaOH	76	8.8	5b, 5h
$Pt(PEt_3)_3$	80	2.7	9
NaOH	78	0.4	this work

sulfuric acid promoted hydration of acrylonitrile have lead to an intensive research[3-9] effort to develop metal catalysts for regioselective hydration of nitriles to amides. Heterogeneous-reduced copper[3] and metal oxide[4] catalysts have been discovered, and higher turnover homogeneous systems have been reported.[5-9] The catalytic mechanism of homogeneous systems, particularly for α-unsaturated nitriles, has been a subject of speculation[6-9] and some controversy.[8,9] Catalytic activities of alkyl,[6,8,9] aryl,[8] and hydrido[9] derivatives of hydroxybis(phosphino) complexes of platinum(II) increase with decreased steric bulk of the phosphine ligands and increased electron-donating ability of the group trans to hydroxide.[8] Complexes containing sterically unhindered phosphines and a trans hydride, *trans*-$[PtH(H_2O)(PR_3)_2][OH]$ (R = Me and Et), have been prepared in our laboratories. These complexes exhibit enhanced rates of catalysis, thereby allowing a detailed kinetic investigation of catalytic hydration mechanisms.

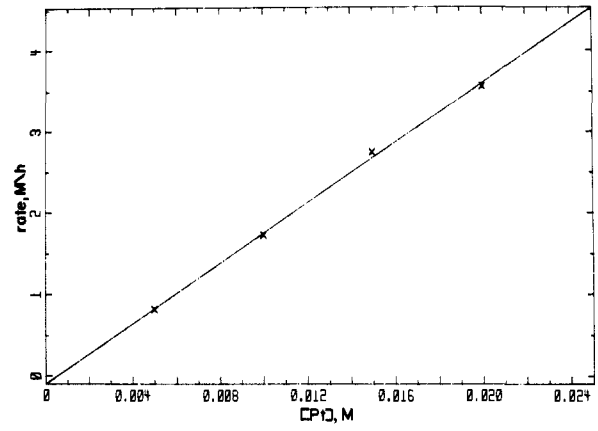

Figure 1. Dependence of the rate of acetonitrile hydration on $[PtH(H_2O)(PMe_3)_2][OH]$ concentration at 80 °C.

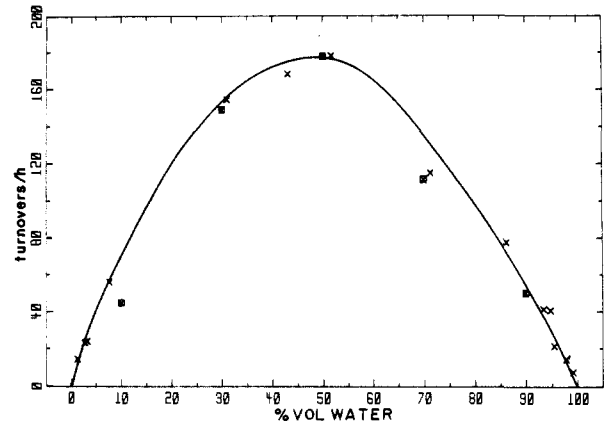

Figure 2. Dependence of the rate of $[PtH(H_2O)(PMe_3)_2][OH]$-catalyzed acetonitrile hydration on % volume water at 80 °C; x = experimental points; □ = calculated by using eq 7.

Results and Discussion

Nitrile Hydration Catalysts. Metathesis of *trans*-$PtHCl(PMe_3)_2$, **1a**, with 1 equiv of NaOH in 50–50 CH_3CN/H_2O solutions yields a catalyst for hydration of acetonitrile with a rate >400 times that of the NaOH-catalyzed reaction and 3.5 times that of the fastest known catalytic system (Table I) at 80 °C. The catalyst is the first reported to exhibit appreciable reactivity (21.5 turnovers/h) at 25 °C.

Formation of the analogous PEt_3 catalyst from *trans*-$PtHCl(PEt_3)_2$, **1b**, requires heating to 75 °C after adding NaOH or prior removal of the chloride ligand with $AgPF_6$. This catalyst produces acetamide at rates of ~70 turnovers/h at 80 °C. The sterically unhindered catalysts studied here retain their activity for days and complete 5000–6000 turnovers before product amides reach

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(3) Representative examples are: (a) Matsuda, F.; Takahashi, T. Ger. Offen. 2036126; *Chem. Abstr.* **1971**, *75*, 35176. (b) Yoshimura, K.; Asano, S.; Honda, T. Ger. Offen. 2162093; *Chem. Abstr.* **1972**, *77*, 113834. (c) Mitsui Toatsu Chemicals Co. Ltd., Ger. Offen. 2240783; *Chem. Abstr.* **1973**, *79*, 32384. (d) Barber, W. A.; Fetchin, J. A. Ger. Offen. 2303648; *Chem. Abstr.* **1973**, *79*, 136549. (e) Habermann, C. E.; Tefertiller, B. A. US Patent 3758578; *Chem. Abstr.* **1973**, *79*, 146992. (f) Kurata, T.; Okano, T.; Tamura, O.; Ohfuchi, K.; Nagashima, S. Ger. Offen. 2256238; *Chem. Abstr.* **1973**, *79*, 67032. (g) Takagi, K.; Matsuda, T. Jpn. Kokai Tokkyo Koho 7472609; *Chem. Abstr.* **1975**, *82*, 17451. (h) Kurata, T.; Okano, T.; Obuchi, K.; Tamaru, A.; Nagashima, S.; Yamada, K. Jpn. Kokai Tokkyo Koho 7493313; *Chem. Abstr.* **1975**, *82*, 58484. (i) Matsuda, F.; Takahashi, T.; Horiuchi, M. Jpn. Kokai Tokkyo Koho 74108015; *Chem. Abstr.* **1975**, *82*, 98747. (j) Wegres, D. L. Belg. Patent 817648; *Chem. Abstr.* **1975**, *83*, 28819. (k) Svarz, J. J.; Goretta, L. A.; Seale, V. L. Ger. Offen 2401142; *Chem. Abstr.* **1975**, *83*, 44014. (m) Watanabe, Y.; Yamahara, T.; Inokuma, S.; Takumara, T. Jpn. Kokai Tokkyo Koho 7514619; *Chem. Abstr.* **1975**, *83*, 79937. (n) Matsuda, F.; Horiuchi, M. Jpn. Kokai Tokkyo Koho 7593919; *Chem. Abstr.* **1976**, *84*, 18027. (o) Svarz, J. J.; Goretta, L. A.; Seale, V. L. US Patent 3920740; *Chem. Abstr.* **1976**, *84*, 60184. (p) Alain, R. J.; Seale, V. L. US Patent 3928443; *Chem. Abstr.* **1976**, *84*, 112297. (q) Tefertiller, B. A.; Habermann, C. E. Ger. Offen. 2065753; *Chem. Abstr.* **1976**, *85*, 32460. (r) Yamahara, T.; Dequchi, T.; Nakamura, S. Jpn. Kokai Tokkyo Koho 76115412; *Chem. Abstr.* **1977**, *86*, 30288. (s) Nakamura, T.; Ogawa, Y. Jpn. Kokai Tokkyo Koho 7719616; *Chem. Abstr.* **1977**, *87*, 38936. (t) Kageyama, Y.; Tamaru, A.; Hisama, S. Jpn. Kokai Tokkyo Koho 7783414; *Chem. Abstr.* **1977**, *87*, 184021. (u) Fetchin, J. A.; Marzluff, W. F. Ger. Offen. 2832641; *Chem. Abstr.* **1979**, *90*, 151620. (v) Platz, R.; Dockner, T.; Heners, J.; Krue, H. US Patent 4176137; *Chem. Abstr.* **1980**, *92*, 75889. (w) Goretta, L. A.; Sibert, F. J. US Patent 4363752; *Chem. Abstr.* **1983**, *98*, 90076. (x) Ravindranathan, M.; Kalyanam, N.; Sivaran, S. *J. Org. Chem.* **1982**, *47*, 4812–4813. (y) Hirui, H.; Wakabayashi, H.; Komiyama, M. *Chem. Lett.* **1983**, *7*, 1047–1050. (z) Wainwright, M. S.; Onuoha, N. I. *Chem. Eng. Commun.* **1984**, *29*, 1–12. (aa) Mikhailishon, I. O.; Yauna, I. M.; Tolopko, D. K.; Mokrivskii, T. M. *Khim. Tekhrol.* (Kiev) **1983**, *3*, 23–24.
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(5) (a) Rauch, F. C.; Nachtigall, G. W. US Patent 3673250; *Chem. Abstr.* **1972**, *77*, 100855. (b) Goetz, R. W.; Mador, I. L. US Patent 3670021; *Chem. Abstr.* **1972**, *77*, 100857. (c) Fanelli, A. J.; Blank, G. M.; Rauch, F. C. US Patent 3801639; *Chem. Abstr.* **1974**, *80*, 145478. (d) Rauch, F. C.; Nachtigall, G. W. US Patent 3821300; *Chem. Abstr.* **1974**, *81*, 170207. (e) Fanelli, A. J.; Rauch, F. C. US Patent 3884975; *Chem. Abstr.* **1975**, *83*, 115331. (f) Feldman, J.; Smith, D. W. US Patent 4096149; *Chem. Abstr.* **1978**, *89*, 179552. (g) Gaset, A.; Constant, G.; Klack, P.; Villain, G. Fr. Demande 2419929; *Chem. Abstr.* **1980**, *93*, 45991. (h) Gaset, A.; Constant, G.; Klack, P.; Villain, G. *J. Mol. Catal.* **1980**, *7*, 355–364. (i) Villain, G.; Klack, P.; Gaset, A. *Tetrahedron Lett.* **1980**, *21*, 2901–2904.
(6) Villain, G.; Gaset, A.; Klack, P. *J. Mol. Catal.* **1981**, *12*, 103–111.
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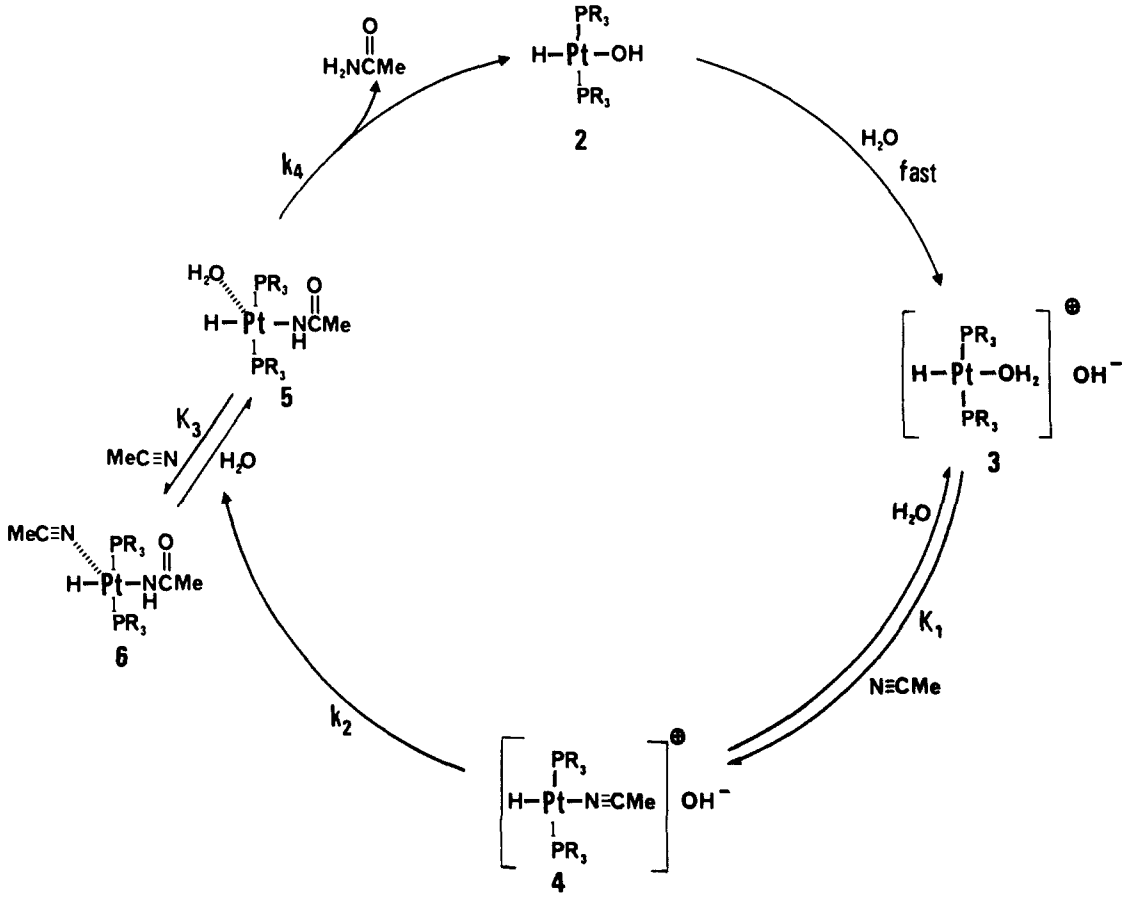
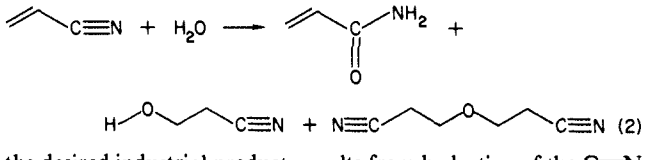
(9) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027–2038.

Scheme I



inhibiting concentrations (see below). Catalyst lifetimes were not reported for other platinum-based catalysts; the maximum turnover reported[9] was 500.

Previous homogeneous platinum catalyst systems[8,9] gave mixtures of acrylamide, β-cyanoethanol, and β-dicyanoethyl ether when acrylonitrile was the substrate (eq 2, Table II). Acrylamide,



(2)

the desired industrial product, results from hydration of the C≡N bond. Hydration of the olefinic bond yields β-cyanoethanol, and β-dicyanoethyl ether results from addition of the O–H bond of β-cyanoethanol to the olefinic moiety of acrylonitrile. Although extremely slow, the NaOH-catalyzed hydration of acrylonitrile was reported[9] to be 98% selective for acrylamide production. We concur with Bennett and co-workers[8] that purification of acrylonitrile increases the proportion of β-cyanoethanol product. The method of analysis employed by Yoshida et al.[9] may also produce erroneously low values of β-cyanoethanol (see Experimental Section). Our studies show that acrylamide constitutes only 17% of the NaOH-catalyzed hydration products at 80 °C when the acrylonitrile is pure and when care is taken so the analytical procedure does not influence product ratios.

At 80 °C, the rate of nitrile hydration with $PtHCl(PMe_3)_2$/NaOH catalyst was 25 times greater than that of the most active platinum catalyst[9] and 4 times greater for the hydration of the olefinic group (Table II) to yield 41% acrylamide. At 25 °C, a remarkable selectivity of 97% for acrylamide production was obtained by using this catalyst.

Mechanistic Studies of Acetonitrile Hydrolysis. The rate of formation of acetamide exhibited a first-order dependence (Figure 1) on the platinum complex, **1a**, added. At hydroxide concentrations greater than the catalytic amount necessary to displace Cl^- from platinum, the rate was independent of hydroxide concentration. The rate of acetamide production exhibited a nonlinear dependence on the water/acetonitrile concentration ratio (Figure 2); however, linear dependencies were found at the two extreme water/acetonitrile ratios. The kinetic behavior of the catalyst generated from **1b** was similar to that of the PMe_3 analogue except that catalytic rates were lower. The **1b**/NaOH catalyst exhibited rates 26 times those reported[9] for $Pt(PEt_3)_3$. Perhaps the catalyst precursor in the latter system is $Pt(PEt_3)_2$ generated by phosphine dissociation. Binding of the excess phosphine ligand to the labile coordination position trans to hydride in the *trans*-$PtH(OH)(PEt_3)_2$, **2b**, catalyst might suppress catalytic rates. To test this hypothesis, the effect of $[PEt_3]$ on the catalytic activity of the **1b**/NaOH catalyst was explored. The linear plot of 1/rate vs. equivalents of added PEt_3 (Figure 3) fits that expected for the inhibiting equilibrium of eq 3, where S = substrate or solvent.

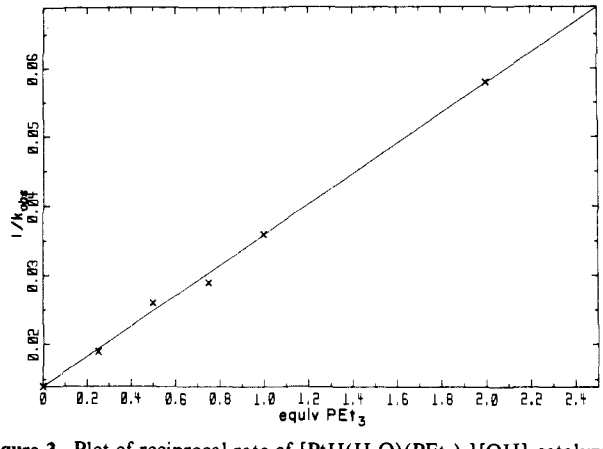


Figure 3. Plot of reciprocal rate of $[PtH(H_2O)(PEt_3)_2][OH]$-catalyzed hydration of acetonitrile on the equivalents of PEt_3 added at 80 °C. The $[Pt]_{Tot}$ = 0.02 M.

$$PEt_3 + PtH(S)(PEt_3)_2^+ \overset{K}{\rightleftharpoons} PtH(PEt_3)_3^+ + S \qquad (3)$$

Table II. Comparison of Catalytic Activities and Product Distributions for Hydrolysis of Acrylonitrile

catalyst	temp, °C	Moles/mole catalyst h			hydrolysis C≡N/C=C	ref
		CH_2=CHC(O)NH_2	$HOCH_2$-CH_2-C≡N	(N≡CCH_2CH_2)$_2O$		
[PtH(H_2O)(PMe_3)$_2$][OH]	25	6.20	0.02	0.19	29.5	this work
[PtH(H_2O)(PMe_3)$_2$][OH]	80	65.0	84.5	10.5	0.41	this work
Pt(PPh_3)$_2$(OH)(CCl=CCl_2)	80	0.50	trace	0.06	8.33	9
Pt[P(*i*-Pr)$_3$]$_3$	80	1.8	2.5	20.9	0.08	9
Pt(C_6H_8)(DPPE)	80	0.68	trace	0.14	4.76	8
Pt(PPh_3)$_2$(Ph)(NHCOMe)	80	2.6	0.4	1.0	1.85	8
NaOH	80	0.43	1.16	0.94	0.20	this work

The value of K obtained from the kinetic data (assuming unit activity of S) is 74.7. A mechanism consistent with these observations is given in Scheme I.

Generation of the catalyst is thought to involve an initial substitution of chloride by hydroxide on treatment of **1a** with NaOH. Preparation of a hydridohydroxy complex by this method is precedented by the formation of RuH(OH)(PPh_3)$_2$(H_2O) on treatment of RuHCl(PPh_3)$_3$ with NaOH.[10] The role of $[OH]^-$ is catalytic since rapid proton transfer from water to coordinated hydroxide regenerates free hydroxide and [*trans*-PtH(H_2O)(PMe_3)$_2$]$^+$, **3a**. Only 0.25 equiv of NaOH is required to transform a D_2O solution of **1a** ($^{31}P\{^1H\}$ NMR δ −12.9 (J_{Pt-P} = 2580 Hz)) to [*trans*-PtH(D_2O)(PMe_3)$_2$][Cl] ($^{31}P\{^1H\}$ NMR δ −18.7 (J_{Pt-P} = 2811 Hz)). The equilibrium for the net reaction under catalytic conditions must also lie far in favor of the aquo complex since the rates of catalysis were independent of $[Cl^-]$. Indeed, when *trans*-[PtH(H_2O)(PEt_3)$_2$]$^+$, prepared from the acetone complex,[11] was used as a substitute for *trans*-PtHCl(PEt_3)$_2$, identical catalytic rates were obtained.

The first step of the catalytic cycle (Scheme I) involves rapid proton transfer from the solvent to produce an aquo cation. Abstraction of a proton from water by coordinated hydroxide was demonstrated previously by Yoshida et al.,[9] who found both Pt(P-*i*-Pr_3)$_3$/H_2O and Pt(Ph)(OH)(PPh_3)$_2$ to be more basic than NaOH.[9] The pH of a 5 × 10^{-3} M aqueous solution of **1a** treated with 1 equiv of NaOH was observed to be 11.7, demonstrating that most hydroxide is not bound to platinum. The proposed protonation of PtH(OH)(PEt_3)$_2$ under catalytic conditions (pH ~12.3) is supported by the pK_a values of 12.9 and 13.5 determined for [PtH(H_2O)(PEt_3)$_2$][PF_6] by ^1H NMR spectroscopy and by a pH titration, respectively.

The second step of the mechanism is substitution of platinum-bound water by acetonitrile. This occurs through a rapid equilibrium that lies in favor of the nitrile complex. This equilibrium was observed spectroscopically by addition of 0.1 mL of acetonitrile-d_3 to a solution of [PtH(D_2O)(PEt_3)$_2$][PF_6], [**3b**][PF_6], in 0.2 mL of 50–50 D_2O–acetone-d_6. The ^1H NMR spectrum of the solution immediately following this treatment revealed a 9.8:1 equilibrium mixture of nitrile and aquo complexes. To verify that equilibrium was reached, 0.1 mL of D_2O was added to a solution of [PtH($NCCD_3$)(PEt_3)$_2$][PF_6], [**4b**][PF_6], in 0.2 mL of 50–50 acetonitrile-d_6/acetone-d_6, and an identical equilibrium ^1H NMR spectrum was obtained. The aquo and acetonitrile complexes used in these spectroscopic experiments were prepared by addition of an equal volume of D_2O or acetonitrile-d_3 to an acetone-d_6 solution of [PtH(acetone-d_6)(PEt_3)$_2$][PF_6],[11] [**7b**][PF_6]. Clark and Manzer[12] have prepared arylnitrile complexes by a similar displacement of coordinated alcohol from [Pt(CH_3)(ROH)(PMe_2Ph)$_2$][BF_4].

The ^1H NMR spectra of the aquo and nitrile complexes show hydride resonances at −25.4 and −17.8 ppm, respectively, suggesting the presence of a group of weak trans influence. The presence of coordinated nitrile was verified by preparation of protio[**4b**][PF_6] by addition of 4 equiv of acetonitrile to an acetone-d_6 solution of [**7b**][PF_6]. The ^1H NMR spectrum of this derivative contained a resonance at δ 2.67 with platinum satellites (J_{Pt-H} = 7.6 Hz). We could not observe a Pt–H stretch in the IR spectrum of a similarly treated H_2O solution of [**3b**][PF_6] because of overlap with the free nitrile C≡N stretch.

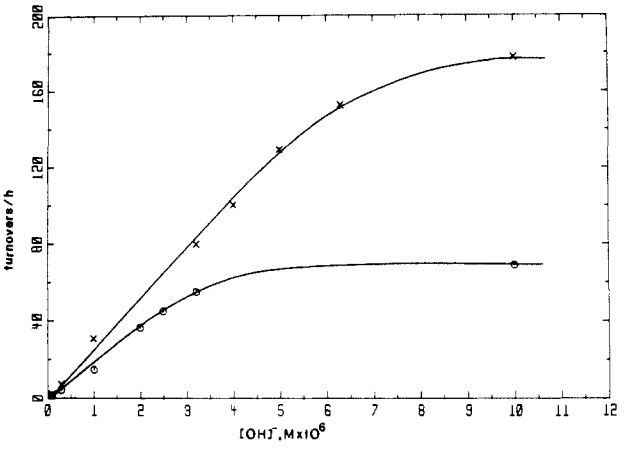


Figure 4. Dependence of the rate of [PtH(H_2O)(PEt_3)$_2$][OH] (○) and [PtH(H_2O)(PMe_3)$_2$][OH] (×) catalyzed acetonitrile hydration on hydroxide concentration at 80 °C.

The third step of the catalytic mechanism is nucleophilic attack of hydroxide on the coordinated nitrile. Rates of catalysis were independent of the base concentration at a pH greater than 10. When the pH of aqueous solutions of **3a** were adjusted before adding acetonitrile, the $[OH]^-$ was lowered to a range where it became rate limiting. A linear dependence of the catalytic rates on $[OH]^-$ was found between pH 8.5 and 8.9 for PMe_3 and between pH 8.1 and 8.5 for PEt_3 derivatives. From plots of $[OH]^-$ vs. the rate of catalysis (Figure 4), rate constants of 4.9 ± 0.3 × 10^3 and 7.0 ± 0.4 × 10^3 M^{-1} s^{-1} were determined for nucleophilic attack of hydroxide on the coordinated nitrile for the PEt_3 and PMe_3 and derivatives, respectively. A similar rate constant, 5.2 ± 0.3 × 10^3 M^{-1} s^{-1} for the nucleophilic attack by hydroxide was determined by monitoring directly the rate of [PtH(N≡CMe)(PEt_3)$_2$][PF_6] decomposition at low OH^- concentration. These rates are 11–7000 times greater than those found in studies of the rate of stoichiometric base hydrolysis of Ru-, Rh-, and Co-coordinated nitriles.[13,14] The enhanced rates observed here may be attributed to higher temperatures (80 vs. 25 °C) as well as to decreased steric barriers in the unhindered platinum(II) complexes. To prove k_2 was rate-limiting under these conditions, catalysis solution of **3a** and **3b** were prepared, and their pH was adjusted to the region where the hydroxide dependence was observed. Examination of these solutions by ^{31}P NMR showed only the presence of **4**.

Nucleophilic attack of OH^- on coordinated acetonitrile can be performed stoichiometrically by addition of 1 equiv of NaOH to an acetonitrile solution of [PtH(N≡CMe)(PEt_3)$_2$]$^+$. A similar synthetic strategy has been employed to prepare bulkier N-bonded carboxamido complexes of platinum(II).[15] Clean conversion to

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(12) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1971**, *10*, 2699–2704.
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(15) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *202*, 107–114.

a single product was evident in the ^{31}P NMR spectrum (δ 31.1, $^1J_{Pt-P}$ = 2626 Hz). The ^1H NMR spectrum contained a hydride resonance at −16.5 ppm ($^1J_{Pt-H}$ = 1140, $^2J_{P-H}$ = 12 Hz) as well as a resonance corresponding to the amide proton at 4.09 ppm. The platinum-bound nature of the *N*-carboxamido group was suggested by the appearance of this resonance as a unresolved multiplet because of platinum coupling. Appearance of the amide proton at a high chemical shift is consistent with the syn conformation found[15] for bulkier analogues. Further evidence for the *N*-carboxamido formulation was obtained in the IR spectrum: N–H stretch at 3380 cm^{-1}; Pt–H stretch at 2205 cm^{-1}; C=O stretch at 1570 cm^{-1}.

The catalytic cycle reaches completion with net substitution of the *N*-carboxamido group by hydroxide. As mentioned above, except at low hydroxide concentrations, $k_2 \gg k_4$ and the rate of acetamide production, k_{obsd}, is given by eq 4. The ^{31}P NMR

$$k_{obsd} = k_4[\mathbf{5}] \tag{4}$$

spectra of solutions of **1a** and **2a** in 50/50 water/acetonitrile-d_3, which were treated with 1 equiv of NaOH and heated at 80 °C for 0.5 h, contained the resonances of **3** and **5** ⇌ **6**. Therefore,

$$[Pt_{total}] = [\mathbf{3}] + [\mathbf{5}] + [\mathbf{6}] \tag{5}$$

Inserting the expression from eq 5 into the equilibrium constant

$$K_3 = \frac{[\mathbf{6}][H_2O]}{[\mathbf{5}][NCMe]} \tag{6}$$

and substituting into eq 4 give

$$k_{obsd} = \frac{k_4([Pt_{total}] - [\mathbf{3}])[H_2O]}{K_3[NCMe] + [H_2O]} \tag{7}$$

Assuming $K_3 = K_1$, substitution of the observed rates at 50/50 water/acetonitrile gives approximate values of 8 and 20 s^{-1} for k_4 in the PEt_3 and PMe_3 systems, respectively.

To test the rate law and rate constants derived from limiting conditions, the concentration of [**3a**] in catalytic solutions of varying water/acetonitrile ratios was determined directly by ^{31}P NMR following 0.5 h of catalytic activity at 80 °C. Inserting these values for [**3a**] into eq 7 predicted values of k_{obsd} that, as seen in Figure 2, were in excellent agreement with those observed experimentally. At water/acetonitrile ratios less than 30/70, no **3a** was detected by ^{31}P NMR, and the rate law simplifies to eq 8. The observed kinetic isotope effect of $k_4(H_2O)/k_4(D_2O)$ =

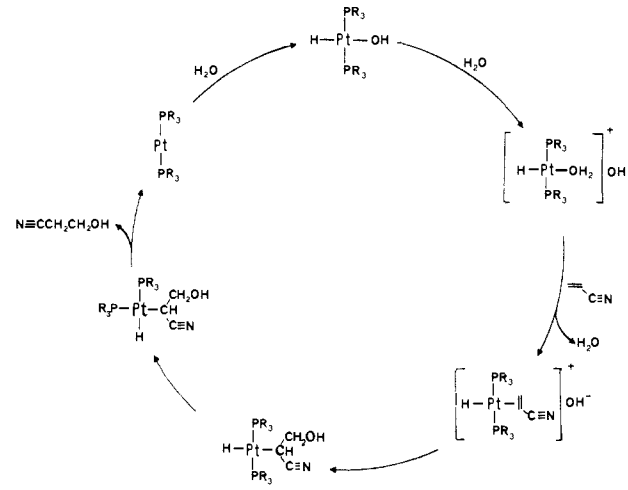
$$k_{obsd} = \frac{k_4[Pt_{total}][H_2O]}{K_3[NCMe] + [H_2O]} \tag{8}$$

3.4 is consistent with the proposed proton transfer from coordinated water to the *N*-carboxamido group. Nitrile or product amide may also compete with water for the proposed fifth coordination or solvation (i.e., weak) site and reduce rates at low water/nitrile ratios or after more than 1000 turnovers (see discussion of product inhibition for acrylonitrile hydrolysis).

Alkyl- and arylbis(phosphine) complexes[8] produce catalytic systems of markedly lower activities than those found for our hydrido complexes or those generated from the tris(phosphine) complexes.[9] The latter system is also believed[9] to contain an *N*-carboxamidohydrido species such as seen in Scheme I. Since elimination of the *N*-carboxamido group is a slow step, substitution of a group with greater trans influence results in weakening of the Pt–N bond and hence faster rates of catalysis. The trans influence of hydride, being greater than that of aryl and alkyl groups,[16,17] may account for the 8-fold increase in hydration rates observed for the hydrido PEt_3 derivative compared to the system where the hydride is replaced by C_6H_5.[8] The smaller size of the hydride compared to alkyl groups would also be expected to enhance the rate of associative attack (k_4) by water.

Otsuka et al. proposed[9] that the final step of the catalytic cycle proceeds by reductive elimination of acetamide from **3** to give

Scheme II



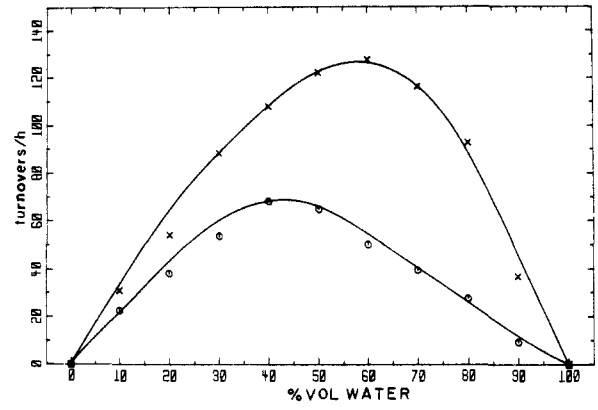


Figure 5. Dependence of the rate of [$PtH(H_2O)(PMe_3)_2$][OH]-catalyzed acrylonitrile hydration on % volume water: (○) rate of acrylamide production; (×) rate of total C=C hydration at 80 °C.

$Pt(PR_3)_2$ which then oxidatively adds water to generate **1**. This is difficult to reconcile with the deuterium isotope effect noted previously. A deuterium-labeling experiment verifies that proton transfer from the solvent, rather than reductive elimination, occurs. One equivalent of NaOH was added to a solution of *trans*-$PtDCl(PMe_3)_2$ in 10/90 water/acetonitrile, and the resulting solution was heated in a sealed tube at 80 °C for 1 h (~180 turnovers). Under these conditions, k_4 limits the catalytic rate and **3** is the dominant species in solution. The $^2H\{^1H\}$ NMR of the reaction mixture contained only a platinum deuteride resonance for **3** at δ −17.4 (J_{Pt-D} = 200 Hz), thereby excluding N–H reductive elimination as a mechanistic possibility in the catalytic cycle.

Mechanism of Acrylonitrile Hydration. A mechanism for catalytic hydration of the olefinic group of acrylonitrile is presented in Scheme II. Hydration of the nitrile group should proceed by the same mechanism (Scheme I) as for acetonitrile. Similar to the results for acetonitrile, the rate of nitrile hydration is independent of [OH$^-$] above 0.25 equiv/Pt. The maximum rate (Figure 5) was also observed at the 40/60 water/nitrile mixture. Rates of nitrile hydration were again observed to diminish at higher turnovers. To verify product inhibition at high amide concentrations, the rate of hydration of acrylonitrile to acrylamide was examined at high acetamide concentrations.[18] These reactions were performed at 25 °C to minimize (to <3%) the competing olefin hydration pathway. As seen in Figure 6, the rate of catalysis decreases with added amide. Amide inhibition has been reported for the PdCl(OH)(bipy)(H_2O)-catalyzed hydration of nitriles.[6]

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(17) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc.* **1965**, 6789.

(18) Acrylamide inhibition occurs only at high concentration, corresponding to >1000 turnovers. Quantification of its production in the presence of such large initial concentrations proved unreliable. To circumvent this problem, the catalytic production of acrylamide was monitored in the presence of inhibiting concentrations of acetamide.

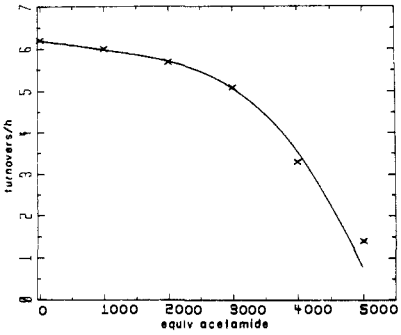
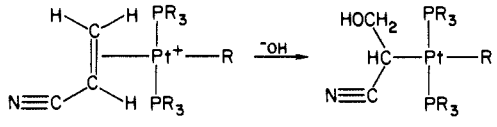
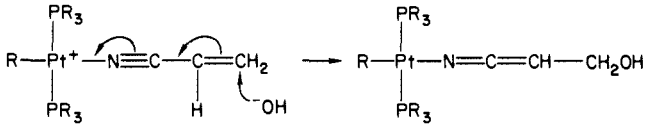


Figure 6. Dependence of the rate of $[PtH(H_2O)(PMe_3)_2][OH]$-catalyzed acrylonitrile hydration on the equivalents of added acetamide per Pt at 25 °C.

The mechanism for hydration of the olefinic group in acrylonitrile has been a matter of debate in the literature.[8,9] Two proposals have emerged. The first[9] requires attack of OH^- on η^2-(C=C)-coordinated acrylonitrile:



The second proposal[8] involves conjugate addition of OH^- to the remote β carbon of N-bonded acrylonitrile:



To distinguish between these possibilities, we performed a deuterium-labeling experiment. One equivalent of NaOH was added to a solution of *trans*-$PtDCl(PMe_3)_2$ in 50/50 water/acrylonitrile that was heated in a sealed tube at 80 °C for 1 h (~65 turnovers of acrylamide and 95 of C=C hydration products). The $^2H\{^1H\}$ NMR of the reaction mixture contained only a singlet at δ 2.43 with no platinum satellites. From the chemical shift of this resonance, we see that the label is incorporated exclusively into the α position of β-cyanoethanol and dicyanoethyl ether. This result is consistent with a mechanism (Scheme II) involving a sequential OH^- nucleophilic attack on coordinated olefin, trans–cis isomerization, and reductive elimination of the hydride and $-CH(CN)(CH_2OH)$ groups. Conjugate addition of OH^- is precluded since this mechanism requires retention of the hydride label just as found for acetonitrile hydration. An important aspect of the sterically unhindered catalysts may be their ability to undergo facile cis–trans isomerization as has been observed[19,20] for corresponding dihydride complexes.

An alternative mechanism consistent with the labeling study involves migration of hydride to the olefin forming an *n*-alkyl species, followed by nucleophilic attack at the platinum center by hydroxide and finally reductive elimination of the alkyl and hydroxide groups. This possibility seems unlikely because of the reported stability of alkyl hydroxide complexes prepared by Arnold and Bennett.[8]

A maximum rate of olefin hydration occurs at a 58/42 water/nitrile mixture (see Figure 5), a higher percent water than that found for the nitrile functionality. This suggests that olefin coordination becomes preferred at high water concentrations. This may be explained by more favorable solvation of the uncomplexed nitrile group with increasing mole fractions of water.

In contrast to nitrile hydration, rate studies show (see Figure 7) that nucleophilic attack of hydroxide on the coordinated olefin

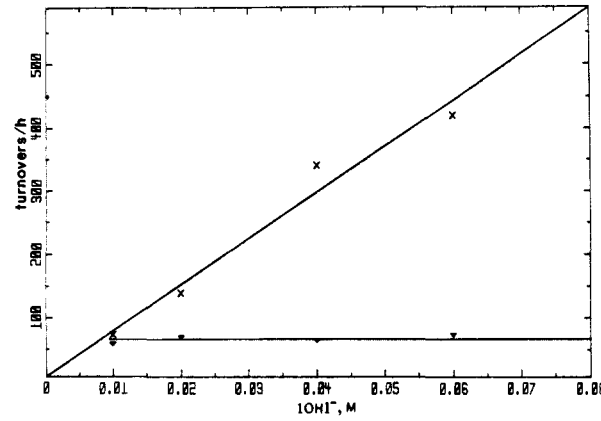


Figure 7. Dependence of the rate of $[PtH(H_2O)(PMe_3)_2][OH]$-catalyzed acrylonitrile hydration on hydroxide concentration at 80 °C; (▼) rate of acrylamide production; (×) rate of total C=C hydration.

is a slow step in the catalytic cycle. This implies that the rates of nucleophilic attack on coordinated olefins is at least 10^2–10^3 slower than those observed for nitriles. This suggests a means of controlling the proportion of nitrile and olefin hydration products with platinum bis(phosphine) catalysts.

Experimental Section

Materials. The following were used without purification: silver hexafluorophosphate; acetamide (Aldrich); trimethylphosphine; triethylphosphine (Strem); sodium hydroxide (Mallinckrodt, 99.1%). The following chemicals were distilled under nitrogen immediately before use with the drying agents given: acetone (Mallinckrodt); acetone-d_6 (Aldrich, Gold Label) from calcium carbonate; acetonitrile (Fischer, HPLC grade); acetonitrile-d_3 (Aldrich, Gold Label); acrylonitrile (Aldrich) from calcium hydride. Water and D_2O (Aldrich) were degassed by three freeze–thaw cycles and distilled under nitrogen immediately before use.

The following compounds were prepared by literature methods: *trans*-$PtHCl(PMe_3)_2$,[19] *trans*-$PtDCl(PMe_3)_2$,[19] *trans*-$PtHCl(PEt_3)_2$,[19] and $[trans\text{-}PtH(acetone)(PEt_3)_2][PF_6]$.[11]

Physical Measurements. Gas chromatographic (GC) measurements were performed with a Hewlett-Packard 5890A instrument using a thermal conductivity detector and a 6-ft Porapak-Q column. Infrared spectra were obtained with a Perkin-Elmer 1320 IR spectrometer in 0.1-mm CaF_2 cells that were flushed with nitrogen before use. The pH measurements were performed with an Orion Research digital ion analyzer/501 using an Orion 91-04 electrode. The ^{31}P and ^2H NMR spectra were obtained with a Nicolet 200 spectrometer at 80.99 and 30.71 MHz, respectively, and ^1H NMR were obtained at 360.247 MHz with a spectrometer fabricated[21] at the UCSD Chemistry Department's NMR Facility. All chemical shifts are positive in the direction of increasing frequency. Proton chemical shifts were referenced to TMS at 0.0 ppm. Deuterium chemical shifts were referenced to a benzene-d_6 internal standard at 7.14 ppm. Phosphorus chemical shifts were referenced to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer such that the resonance of a capillary of 85% H_3PO_4, centered in a 10-mm NMR tube containing the deuterated solvent, appeared at 0 ppm at 20 °C. All samples for the NMR spectroscopic analysis were prepared in 5-mm NMR tubes that were sealed under vacuum.

Rate Studies. Reaction mixtures typically consisted of 0.50 mL of nitrile, 0.50 mL of water and sodium hydroxide (17 μL of a 1.2 M aqueous solution), and 0.02 mmol of complex ($PtHCl(PMe_3)_2$, $PtHCl(PEt_3)_2$, or $[PtH(H_2O)(PEt_3)_2][PF_6]$). Catalysis solutions at 80 °C were contained in ampules that were charged under nitrogen and sealed under vacuum. Experiments performed at 25 °C used solutions contained in test tubes that were charged under nitrogen, capped with rubber septa, and wire-sealed. Concentration dependence studies used varying concentrations of reaction components as well as acetamide and triethylphosphine in the case of inhibition studies. After loading, the reaction vessels were placed in a Brinkmann RM7 constant-temperature (±0.05 °C) bath. At the end of the prescribed time, the vessels were opened and analyzed with the GC. For acrylonitrile, 1.0 mL of acetone was added to homogenate the two-phase solutions before analysis. This method of sample preparation leads to accurate quantification of products. The method of Yoshida et al.,[9] in which catalytic mixtures were concentrated

(19) Packett, D. L.; Jensen, C. M.; Cowan, R. L.; Strouse, C. E.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3578–3583.
(20) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138–1140.
(21) Wright, J. M.; Feigon, J.; Denny, W.; Leupin, W.; Kearns, D. R. *J. Magn. Reson.* **1981**, *45*, 514–519.

under reduced pressure prior to analysis, results in significant loss of β-cyanoethanol. A column pressure of 60 psi was used in the analysis of the acetonitrile reactions, and a time–temperature program was employed in which an initial temperature of 120 °C was maintained for 4 min after which the temperature was increased 15 °C/min to a final temperature of 220 °C. Analysis of the acrylonitrile reactions used an initial column pressure of 40 psi and an initial temperature of 195 °C. After 14 min, the temperature was raised 15 °C/min to 270 °C.

An additional rate study utilizing ^{1}H NMR was conducted. A solution of $[PtH(N{\equiv}CCD_3)(PEt_3)_2][PF_6]$ was prepared by addition of $AgPF_6$ (0.027 g, 0.11 mmol) to an acetonitrile-d_3 solution of $PtHCl(PEt_3)_2$ (0.050 g, 0.11 mmol in 0.6 mL). Following removal of the AgCl by filtration, the solution was divided into two 0.3-mL portions which were adjusted to pH 7.0 and 7.3, respectively. The solutions were transferred to 5-mm NMR tubes, which were sealed under vacuum. After intervals of heating in a 78 °C constant-temperature bath, ^{1}H NMR spectra of the solutions were obtained. The rate of disappearance of $[PtH(N{\equiv}CCD_3)(PEt_3)_2][PF_6]$ was determined by comparison of the integrated intensity of the acetonitrile complex's central hydride signal to that of a TMS internal standard.

pH Measurements. A three-neck, round-bottom flask was charged with 19 mg (0.05 mmole) of *trans*-$PtHCl(PMe_3)_2$, fit with a gas inlet adapter and placed under nitrogen. The complex was dissolved in 10 mL of water, the electrode of the pH meter was introduced under nitrogen purge, and a pH of 6.8 was recorded. Under nitrogen purge, the electrode was removed, 0.10 mL of a 0.5 M aqueous solution of NaOH added, and a pH of 11.0 was registered.

Solutions for the rate studies at low $[OH]^-$ were prepared in similar fashion. Thus, a solution of 0.077 g (0.22 mmol) of *trans*-$PtHCl(PMe_3)_2$ in 10 mL of water was treated with 0.263 mL of 0.76 M aqueous NaOH solution. The pH meter probe was then introduced under N_2 purge, and the pH of the solution was adjusted by using an 0.1 M aqueous HCl solution. Aliquots (0.5 mL) were removed at a series of pH values, combined with 0.55 mL of acetonitrile, and allowed to react at 78 °C for 1 h. For the PEt_3 derivative, the stock solution was prepared by heating a slurry of 0.094 g (0.2 mM) of *trans*-$PtHCl(PEt_3)_2$ and 0.263 mL of 0.76 M aqueous NaOH in 10 mL of water at 75 °C for 5 min. After the solution was cooled to 25 °C, the pH was adjusted as described for the PMe_3 derivative.

$[PtH(H_2O)(PEt_3)_2]^+$ pK_a Determination. Method 1. A 25-mL three-neck, round-bottom flask was charged with $[PtH(H_2O)(PEt_3)_2][PF_6]$ (0.467 g, 1 mM) and a stir bar and placed under nitrogen. The complex was dissolved in 1.8 mL of water, and the electrode of the pH meter was fitted with a Teflon sleeve and inserted into one joint of the flask. The solution was then titrated with 5 M aqueous NaOH. The inflection point of the titration curve was observed at pH 12.9.

Method 2. A 5-mm NMR tube was charged with $[PtH(H_2O)(PEt_3)_2][PF_6]$ (0.117 g, 0.25 mM) and 0.25 mL of D_2O. Under a N_2 flush, the tube was capped with a rubber septum, which was wired on. The resulting solution was then treated sequentially with 5-μL portions of 2.5 M NaOH, and ^{1}H NMR spectra were obtained. After addition of 9 μL (pH 13.5) of base solution, the concentration of $[PtH(H_2O)(PEt_3)_2][PF_6]$ and $PtH(OH)(PEt_3)_2$ was seen to be nearly equal.

Spectroscopic Characterization of Catalytic Intermediates. A. [*trans*-PtH(H$_2$O)(PEt$_3$)$_2$][PF$_6$]. The sample for IR characterization was prepared by treating 5 mL of a 15.7 mM acetone solution of [*trans*-PtH(acetone)$(PEt_3)_2][PF_6]$ with 14.0 μL (0.778 mMol) of water (ν_{Pt-H} = 2295 cm^{-1}). The sample for NMR characterization was prepared by treating 0.30 mL of a 0.26 M acetone-d_6 solution of [*trans*-PtH(acetone-d_6)$(PEt_3)_2][PF_6]$ in a 5-mm NMR tube with 15.7 μL (0.78 mmol) of D_2O: $^{31}P\{^1H\}$ NMR δ 31.0 (J_{Pt-P} = 2705 Hz); ^{1}H NMR δ −25.4 (J_{Pt-H} = 1428, J_{P-H} = 14 Hz (Pt–H)), 1.14 (J_{P-H} = 15 Hz (Pt–P–CH_2CH_3)), 1.89 (br) (Pt–P–CH_2CH_3).

B. [*trans*-PtH(D$_2$O)(PMe$_3$)$_2$][Cl]. A solution of 0.020 g (0.05 mM) of $PtHCl(PMe_3)_2$ in 0.5 mL of D_2O in a 10-mm NMR tube was treated with 69 μL of 0.76 M aqueous NaOH. The ^{31}P NMR spectrum of the resulting solution showed that clean conversion to [*trans*-PtH$(D_2O)(PMe_3)_2][Cl]$ had occurred: $^{31}P\{^1H\}$ NMR δ −18.7 (J_{Pt-P} = 2811 Hz).

C. [*trans*-PtH(NCCH$_3$)(PEt$_3$)$_2$][PF$_6$]. A 5-mm NMR tube was charged with 0.3 mL of a 0.26 M acetone-d_6 solution of [*trans*-PtH-(acetone-d_6)$(PEt_3)_2][PF_6]$ and treated with 16 μL (0.31 mmol) of acetonitrile: $^{31}P\{^1H\}$ NMR δ 25.3 (J_{Pt-P} = 2260 Hz); ^{1}H NMR δ −17.9 (J_{Pt-H} = 1233, J_{P-H} = 14 Hz (Pt–H)), 1.15 (J_{P-H} = 15 Hz (Pt–P–CH_2–CH_3)), 2.00 (br) (Pt–P–CH_2–CH_3), 2.64 (J_{Pt-H} = 7.3 Hz (Pt–NCCH_3)).

D. *trans*-PtH(NHC(O)CH$_3$)(PEt$_3$)$_2$. The sample for NMR analysis was prepared by adding 20 μL of 4 M NaOH to a solution of [*trans*-$PtH(NCCH_3)(PEt_3)_2]^+$, prepared above, following removal of the AgCl by centrifugation: $^{31}P\{^1H\}$ NMR δ 31.2 (J_{Pt-P} = 2826 Hz); ^{1}H NMR δ −16.5 (J_{Pt-H} = 1140, J_{P-H} = 12 Hz (Pt–H)), 1.16 (J_{P-H} = 17 Hz (Pt–P–CH_2CH_3))', 1.99 (br) (Pt–P–CH_2CH_3), 4.09 (m) (Pt–N*H*–C(O)Me), 1.72 (s) (Pt–NHC(O)CH_3). Samples for IR analyses were prepared by first adding 16 μL (0.31 mmol) of acetonitrile to 5 mL of a 15.7 mM acetone solution of $[$*trans*-PtH(acetone)$(PEt_3)_2]^+$ and, following removal of the AgCl by centrifugation, adding 20 μL of a 4 M aqueous solution of NaOH. (ν_{Pt-H} = 2205 cm^{-1}; ν_{N-H} = 3363 cm^{-1}; $\nu_{C=O}$ = 1570 cm^{-1}).

E. *trans*-PtH(OH)(PEt$_3$)$_2$. The sample for NMR characterization was prepared by addition of 60 μL of 5 M NaOH to a D_2O solution of $[$*trans*-$PtH(H_2O)(PEt_3)_2][PF_6]$ (0.053 mmol in 0.3 mL), prepared as described above: $^{31}P\{^1H\}$ NMR δ 24.4 (J_{Pt-P} = 2991 Hz); ^{1}H NMR δ −10.0 (J_{Pt-H} = 896, J_{P-H} = 17 Hz (Pt–H)), 2.45 (m) (Pt–P–CH_2CH_3), 1.69 (m) (Pt–PCH_2CH_3).

F. Catalytic Mixtures. In the glovebox, 10-mm NMR tubes were charged with 10 mg of *trans*-$PtHCl(PMe_3)_2$ (0.026 mmol) or *trans*-$PtHCl(PEt_3)_2$ (0.021 mmol), capped with a rubber septum, and wire-sealed. Acetonitrile-d_3 and water, in varying ratios (D_2O and protio-acetonitrile were used in 10/90 D_2O/$NCCH_3$ experiments), totaling 1.00 mL and 0.76 M aqueous NaOH (34 μL for $PtHCl(PMe_3)_2$ and 28 μL for $PtHCl(PEt_3)_2$) were then added through syringe needles under nitrogen. The tubes were then heated in a constant-temperature bath at 80 °C for 0.5 h, and the ^{31}P NMR spectra of the resulting solutions were obtained. The 10/90 D_2O/$NCCH_3$ mixture contained only PtH(NDC(O)CH_3)$(PR_3)_2$: $^{31}P\{^1H\}$ NMR (R = Me, **5a**) δ 2.52 (J_{Pt-P} = 2582 Hz), (R = Et, **5b**) 18.3 (J_{Pt-P} = 2596 Hz). The 30/70 H_2O/$NCCD_3$ mixtures contained chiefly the same species but a small (~5%) amount of $[PtH(H_2O)(PR_3)_2][OH]$ was also observed: $^{31}P\{^1H\}$ NMR (R = Me, **3a**) δ −18.0 (J_{Pt-P} = 2776 Hz), (R = Et, **3b**) 27.6 (J_{Pt-P} = 2741 Hz). The amount of the aquo complex increased steadily with increased % H_2O (2.5, 30.0, 80.2, 95.0%) and (3.6, 37.5, na, 96.2%) (for 30/70, 50/50, 70/30, 90/10 H_2O/$NCCH_3$) for PMe_3 and PEt_3, respectively.

Samples at pH 8.5 and 9.5 were prepared as described above and heated for 0.5 h at 80 °C. Both pH 8 samples were seen to contain only $[PtH(N{\equiv}CCD_3)(PR_3)_2][OH]$. $^{31}P\{^1H\}$ NMR (R = Me, **4a**) δ 28.0 (J_{Pt-P} = 2681 Hz), (R = Et, **4b**) −17.7 (J_{Pt-P} = 2713 Hz). A sample of the PEt_3 catalyst at pH 8.8 contained a mixture of **3b**, **4b**, and **5b**.

[*trans*-PtH(D$_2$O)(PEt$_3$)$_2$]/[*trans*-PtH(NCCH$_3$)(PEt$_3$)$_2$] Equilibrium Studies. A. Equilibrium Approached through [PtH(D$_2$O)(PEt$_3$)$_2$]. A 5-mm NMR tube was charged with 0.1 mL of an 0.26 M acetone-d_6 solution of [**1**][PF_6] and treated with 0.1 mL of D_2O. A ^{1}H NMR of the resulting solution showed that quantitative formation of $[PtH(D_2O)(PMe_3)_2][OD]$ occurred. Introduction of 0.15 mL of acetonitrile-d_3 resulted in a 9.8:1 mixture $[PtH(NCCD_3)(PMe_3)_2]^+$/$[PtH(H_2O)(PMe_3)_2]^+$.

B. Equilibrium Approached through [*trans*-PtH(D$_2$O)(PMe$_3$)$_2$]. A 5-mm NMR was charged with 0.1 mL of a 0.26 M acetone-d_6 solution of $[PtH(acetone\text{-}d_6)(PMe_3)_2][PF_6]$ and treated with 0.1 mL of acetonitrile-d_3. A ^{1}H NMR showed that complete conversion to $[PtH(NCCD_3)(PMe_3)_2][PF_6]$ occurred. Addition of 0.1 mL of D_2O resulted in a 9.8:1 mixture of $[PtH(NCCD_3)(PMe_3)_2]^+$/$[PtH(D_2O)(PMe_3)_2]^+$.

Hydrolysis of Acetonitrile with *trans*-PtDCl(PMe$_3$)$_2$. A 5-mm NMR tube was charged with 0.020 g (0.052 mmol) of *trans*-$PtDCl(PMe_3)_2$, 0.10 mL (5.56 mmol) of water, 0.29 mL (5.56 mmol) of acetonitrile, and 52 μL of 1 M aqueous NaOH. The tube was sealed and maintained at 80 °C for 1 h. The $^2H\{^1H\}$ NMR spectrum of the resulting mixture contained only a singlet at −17.8 ppm with platinum satellites (J_{Pt-D} = 203 Hz).

Hydrolysis of Acrylonitrile with *trans*-PtDCl(PMe$_3$)$_2$. A 5-mm NMR tube was charged with 0.20 g (0.052 mmol) of *trans*-$PtDCl(PMe_3)_2$, 0.1 mL (5.56 mmol) of water, 0.37 mL (5.56 mmol) of acrylonitrile, and 52 μL of 1 M NaOH. The tube was sealed and maintained at 80 °C for 1 h. The $^2H\{^1H\}$ NMR spectrum of the resulting mixture contained only a singlet at 2.49 ppm.

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Supplementary Material Available: Tables of kinetic data for catalytic hydration of acetamide and acrylonitrile and figures of the turnovers of acetamide produced vs. time and the effect of [NaCl] on catalytic hydration rates for acetamide and acrylonitrile substrates (14 pages). Ordering information is given on any current masthead page.