

Catalytic Hydration of Alkynes with Platinum(II) Complexes

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In a previous report, Zeise's dimer, $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, was shown to catalytically hydrate "unactivated" (electron-rich) alkynes.¹ In comparison to hydration catalysts such as Hg(II), Zeise's dimer shows considerable promise.^{2,3} For example, the crude reaction mixtures for the hydration of 4-methyl-2-pentyne are compared in Figure 1 via NMR spectroscopy. It is clear that the Pt(II)-catalyzed process yields a much cleaner mixture of the two products, 4-methyl-3-pentanone and 4-methyl-2-pentanone. For terminal alkynes, the difference is more dramatic in that Hg(II) yields a variety of oligomers. The one difficulty with Zeise's dimer is that it is expensive and/or it must be prepared via an inconvenient procedure. Since the proposed reaction mechanism (Scheme I) involves an olefin- or alkyne-complexed platinum dichloride, it was obligatory to try other and perhaps less-cumbersome platinum complexes. The results for three alkynes and four catalysts are listed in Table I. It is apparent from these data that indeed hydration occurs with these simple catalytic complexes and they are readily available. Further, steric factors on both the alkyne and the catalyst may be employed to attain modest regioselectivity. The authors believe that this regioselectivity arises when the platinum moiety is forced aside from the alkyne center by steric factors creating a partial cationic center at the distal carbon where water attacks. Unfortunately, the selectivity is not as impressive as we would have liked, but further efforts are continuing.

There are two additional features to be addressed. First, PtBr_2 is very insoluble, and extended times are required initially to get the complex in solution. Second, the case of 4,4-dimethyl-2-pentyne with PtI_2 exhibits a slight reversal of expected regioselectivity. Our rationale for this result is that while the Pt(II) moiety is displaced away from the tertiary butyl moiety, the combined steric factors now inhibit the attack by water. The rate for this reaction has not been measured quantitatively, but it is qualitatively much slower than the chloride and bromide.

Finally, a few kinetic runs were made using 4-methyl-2-pentyne to determine the reaction characteristics and relative rates. The reaction rates are on the order of 10^{-3} s^{-1} and are well behaved except in the initial phase where some acceleration is observed. The half-lifetimes for three catalysts are listed in Table II using 4-methyl-2-pentyne. The insolubility of PtBr_2 reduces the reliability of its kinetic data and thus is not reported. As expected, higher regioselectivity is attained with slower reaction rates.

In summary, new, simple alkyne hydration catalysts have been elaborated using a limited number of unactivated alkynes. These platinum(II) complexes offer some distinct advantages over Hg(II) catalysts in that cleaner reaction

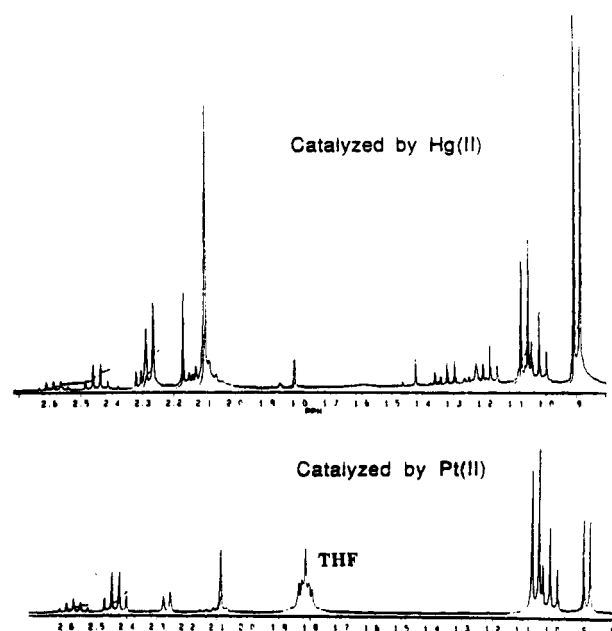
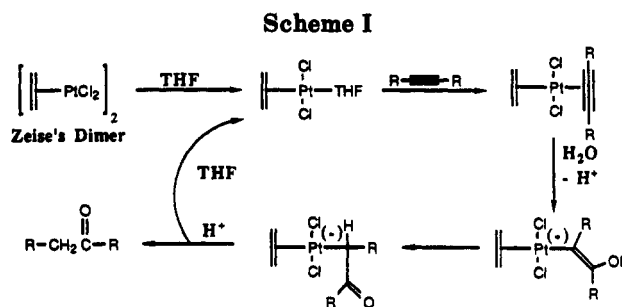


Figure 1. NMR comparison of the crude reaction mixture for the hydration of 4-methyl-2-pentyne.



products are obtained and enhanced regioselectivity is observed with some substrates.

Experimental Section

General. Product ratios were obtained using a Varian 3500 capillary gas chromatograph with an Alltech SE-54 capillary column. Kinetic studies were conducted using a Bruker 250-MHz NMR spectrometer with temperature probe $\pm 3^\circ\text{C}$. Zeise's dimer was prepared from K_2PtCl_4 generously loaned from Johnson Matthey. Platinum(II) chloride and platinum(II) iodide were used as purchased from Strem Chemicals. The alkyne substrates 2-hexyne, 4-methyl-2-pentyne, and 4,4-dimethyl-2-pentyne were used as purchased from Lancaster Synthesis.

Platinum(II) Chloride-, Bromide-, and Iodide-Catalyzed Hydration of Alkyne Substrates. In a 25-mL round-bottom flask were placed THF (10 mL), PtCl_2 (0.095 mmol) (or PtBr_2 for the bromide), alkyne (13.5 mmol), and water (22 mmol). The reaction mixture was stirred at reflux (ca. 60°C) for 12 h. The platinum(II) catalyst was removed from the reaction mixture by Kugelrohr distillation. Product ratios for the resulting distillates were determined by capillary GC and are listed in Table I.

Mercury(II)-Catalyzed Hydration of Alkyne Substrates.^{4,5} In a 5-mL round-bottom flask were placed methanol (1.0 mL),

(1) Hiscox, William; Jennings, P. W. *Organometallics* 1990, 9, 1997.
(2) Bassetti, M.; Floris, B. *J. Chem. Soc. Perkin Trans. 2* 1988, 227.
(3) Janout, V.; Regen, S. L. *J. Org. Chem.* 1982, 47, 3331.

(4) Wilcox, C. F., Jr. *Experimental Organic Chemistry: A Small-Scale Approach*; MacMillan: New York, 1988; pp 279-280.

(5) Thomas, R. J.; Campbell, K. N.; Hennion, G. F. *J. Am. Chem. Soc.* 1938, 60, 718.

Table I. Product Ratios from the Catalytic Hydration of Three Alkynes with Five Catalysts

alkyne	products	
	3-hexanone	2-hexanone
2-hexyne		
ZD*	65	35
PtCl ₂	62	38
PtBr ₂	65	35
PtI ₂	64	36
HgO	50	50
4-methyl-2-pentyne	4-methyl-3-pentanone	4-methyl-2-pentanone
ZD	71**	29**
PtCl ₂	64	36
PtBr ₂	74	26
PtI ₂	78	22
HgO	31	69
HgSO ₄ (70% MeOH)	31	69
HgSO ₄ (70% acetone)	42	58
4,4-dimethyl-2-pentyne	4,4-dimethyl-3-pentanone	4,4-dimethyl-2-pentanone
ZD	76	24
PtCl ₂	65	35
PtBr ₂	78	22
PtI ₂	61	39
HgO	50	50

* Zeise's dimer. **Without special care and using a short-path distillation, the yield was 91% of ketone products.

red HgO (0.046 mmol), alkyne (2.2 mol), water (0.4 mL), and concd H₂SO₄ (0.2 mL). The reaction mixture was stirred at reflux

Table II. Half-Lifetimes for three Catalysts with 4-Methyl-2-pentyne

catalyst	<i>t</i> _{1/2} (h)
ZD	4.0
PtCl ₂	3.0
PtI ₂	14.8

(ca. 60 °C) for 12 h. Water (2 mL) was then added followed by NaCl (0.3 g) to salt out the products. The mixture was subsequently decanted from the undissolved salts and extracted with 1 mL of methylene chloride. These extractions were Kugelrohr distilled and the distillate dried with anhydrous MgSO₄. Product ratios were determined by capillary GC and are listed in Table I.

Kinetic Studies on the Platinum(II)-Catalyzed Hydration of 4-Methyl-2-Pentyne. In a 5-mm NMR tube were placed *d*₈-THF (0.5 mL), 4-methyl-2-pentyne (0.675 mmol), platinum(II) catalyst (0.005 mmol), water (1.1 mmol), and CHCl₃ (0.33 mmol) (internal standard). The sample was then placed in the Bruker 250-MHz NMR spectrometer at a temperature of 50 °C and data collected for more than 12 h. Integration of the spectra, with respect to the peak of 1.65 (s) ppm which corresponds to the C-1 methyl of the alkyne, allowed for monitoring the disappearance of 4-methyl-2-pentyne. First-order kinetic treatment of this data afforded half-lives which are listed in Table II.

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