(9) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w|F_o| - |F_c|^2/\Sigma wF_o^2]^{1/2}$.
(10) W. E. Newton and J. W. McDonald in "Proceedings of the Climax Second International Symposium on Chemistry and Uses of Molybdenum, P. C. H. Mitchell, Ed., Climax Molybdenum Co., London, in press.
(11) Compound **5** has Mo···Mo = 2.822 (2) Å and a dihedral angle between the two SPh–Mo–SPh planes of 182°.

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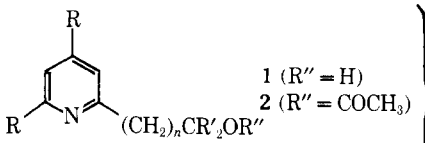
Platinum(II)-Catalyzed Alcohol Acetylations by *N*-Acetylimidazole

Sir:

In our search for template reactions where two reactants are coordinated simultaneously to a metal ion, prior to reaction,[1-5] we have investigated the catalysis by platinum(II) complexes of the acetylation of pyridinic alcohols (**1**) by *N*-acetylimidazole (AcIm) expecting an activation of the coordinated AcIm and an induced proximity between the reactants involved in a ligand exchange on the transition metal.



1 (R'' = H)
2 (R'' = $COCH_3$)

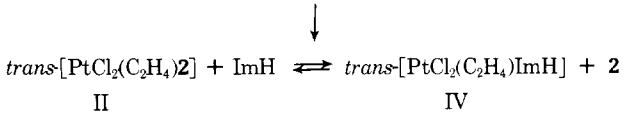
	n	R	R'
a	1	CH_3	H
b	1	H	H
c	2	CH_3	H
d	2	CH_3	CH_3
e	3	CH_3	H
f	6	CH_3	H

trans-[$PtCl_2(C_2H_4)$ **1**] I
trans-[$PtCl_2(C_2H_4)$ **2**] II

trans-[$PtCl_2(C_2H_4)$ (AcIm)] III
trans-[$PtCl_2(nBu_3P)$ (AcIm)] V

We have found that while no acetylation reaction takes place between alcohols **1** and pure AcIm in chloroform at room temperature, this reaction occurs when either one of the two reactants is initially bound in an olefinic complex of platinum(II), according to Scheme I. For instance ^1H NMR monitoring of the reaction starting from Ic + AcIm or III + **1c** ($CDCl_3$) shows that a fast ligand exchange first occurs, within mixing time, between AcIm and the pyridinic group of alcohol **1c**, leading to an equilibrium largely in favor of bound AcIm (ca. 80:20 at 32 °C); then the acetylation reaction gives a new equilibrium in which complex IV and the free acetate **2c** largely predominate (>95%).

Scheme I



The yields, reaction times, and rate constants of the acetylation reactions of several alcohols in the presence of a stoichiometric amount of Pt(II) are compared in Table I.

Pt(II) behaves as a superacid catalyst toward nucleophilic attack of AcIm by the alcohols,[7] but, when AcIm is bound to Pt(II) in complex III, there is no acetylation of a primary alcohol in the absence of base (ligand) (expt 8). In the presence of *s*-collidine the acetylation takes place and is faster the higher the proportion of *s*-collidine (expt 9, 10). (There is no acetylation reaction with **3** + AcIm + P_{246} 1:1:1.) The acetylation reaction is faster with the pyridinic alcohols **1** and depends on the *n* value (expt 1–2, 4, 6, 7). The best result is obtained for $n = 2$ (expt 4): $k_4:k_1 = 4.05$; $k_4:k_6 = 3.2$; $k_4:k_7 = 44$. It is noteworthy that Pt(II) allows a slow but quantitative acetylation of the tertiary alcohol **1d** (expt 5). The influence of the chain length of the pyridinic alcohols **1** could be related to the expected template effect resulting from the observed ligand exchange between alcohols **1** and AcIm or to intramolecular general base catalysis of the reaction by the pyridinic group. The following results support the second proposition. In chloroform a slow reaction can be initiated between alcohols **1** and AcIm by addition of acetic acid;[8] the reactions of various alcohols **1** with AcIm and AcOH, 0.16 M each, give the fol-

Table I. Stoichiometric Acetylation of Alcohols **1a–1f** and Phenyl-3-propanol (**3**) by AcIm in the Presence of Pt(II)[6]

	Reaction	Concn of reactants in $CDCl_3$, M[a]	Acetate yield, %[b]	Reaction time, h (23 °C)[c]	10^3k, M^{-1} s^{-1},[f] 23 °C
(1)	Ia + AcIm (*n* = 1)	0.16	62	0.78	3.± 0.4
(2)	III + **1a** (*n* = 1)	0.16	66	0.80	3.8 ± 0.4
(3)	III + **1b** (*n* = 1)	0.16	52.4	7.5	0.24 ± 0.02
(4)	Ic + AcIm (*n* = 2)	0.16	87.5	0.43	15 ± 1.5
(5)	Id + AcIm (*n* = 2)	0.25	100	312[d]	
(6)	Ie + AcIm (*n* = 3)	0.16	85	1.4	4.7 ± 0.5
(7)	If + AcIm (*n* = 6)	0.16	51	5.5	0.34 ± 0.03
(8)	III + **3** (1:1.2)	0.25	[e][g]	144[d]	
(9)	III + **3** + P_{246}[h] (1:1:0.1)	0.25	32	21[d]	
(10)	III + **3** + P_{246}[h] (1:1:1)	0.26	80	21[d]	
(11)	III + **3** + Et_3N (1:1:1)	0.25	50	0.33[e]	
			70	2.8	
(12)	V + **3** + Et_3N (1:1:1)	0.23	50	0.67[e]	
			70	1.08	
(13)	V + **1c** (*n* = 2)	0.16	74	3.9	0.93 ± 0.1

[a] When the reactions are not stoichiometric for each reactant, Pt complex concentration is given. [b] Results from at least two runs, determined by integration of the ^1H NMR signals of the $-CH_2-$ α to OAc and the ImH 2-H proton in the case of primary acetates, and of the OAc methyl signal in the case of **2d**. [c] The fast reactions are monitored by ^1H NMR, at 23 °C, on a Bruker WH 90 working in FT mode, using tape FID's recording when necessary; the other reactions are run at either [d]23 °C and the NMR spectra recorded on a Varian A60 (insert temp 32 °C), or [e] 33 °C in the insert of a varian EM 390. [f] Second-order rate constants determined by linear regression ($r > 0.992$ with at least six points and up to 50% conversion). [g] Acetate detected by NMR, but <5% yield. [h] P_{246} = 2,4,6-trimethylpyridine (*s*-collidine).

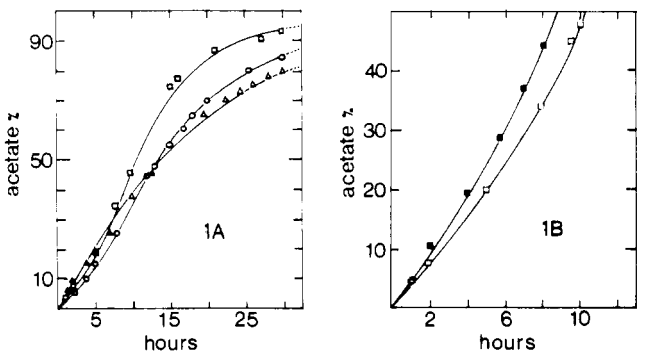


Figure 1. Catalytic acetylations in the presence of complexes III, V, and VI of alcohols **1c** or **3** (5 mmol, 0.5 M in $CDCl_3$) at 33 °C: △ **1c** + AcIm + III, 100:100:1; ○ **1c** AcIm + V, 100:100:1; □ **3** + AcIm + Et_3N + V, 100:100:1:1; ■ **3** + AcIm + Et_3N + VI, 100:100:1:1. For all experiments, controls have been made with the same AcIm in the absence of Pt(II) complex and have shown no acetylation.

lowing yields of acetates **2**, after 21 h at 23 °C: **2a**, 63%, **2c**, 75%; **2e**, 53%, and **2f**, 19.5%. The relative reactivities of the alcohols **1** toward this acetylation are similar to those observed with Pt(II). Acetylation of alcohol **1a** in the presence of complex III is faster than that of alcohol **1b** (expt 2, 3): $k_2:k_3 = 15$, this is in agreement with the relative basicities of the two pyridinic alcohols, but not with their coordination abilities.[9] Furthermore, acetylation of phenyl-3-propanol **3** by complex III is much more efficient in the presence of Et_3N than *s*-collidine (expt 10, 11).[11]

Owing to the trans effect of bound ethylene promoting ligand exchanges between AcIm, ImH, alcohol **1**, and acetate **2** (Scheme I), one could expect the acetylation reactions to be catalytic in Pt. Accordingly the reaction between alcohol **1c**, AcIm (both 0.5 M in $CDCl_3$), and complex III, 100:100:1, gives acetate **2c** in 80% yield (**2c**:Pt = 80:1) after 30 h at 33 °C. The reaction is accompanied by an expected side reaction slowing down the acetylation (Figure 1A) and consuming the Pt complex by substitution of the ethylene ligand[12] to finally give a precipitate of impure $[Pt(ImH)_4]^{2+}\ 2Cl^-$.[14]

The complex *trans*-$[PtCl_2(nBu_3P)(AcIm)]$ (V) can be used to achieve the stoichiometric acetylation of alcohol **3**[15] in the presence of Et_3N without displacement of the activating phosphine ligand (expt 12); however, this acetylation is slower than that with complex III (expt 11). The acetylation of the pyridinic alcohol **1c** is also slower with complex V than with complex III (expt 13, 4). The phosphine complex V can be used for catalytic acetylation of alcohol **3** in the presence of Et_3N, the reaction between **3**, AcIm (both 0.5 M in $CDCl_3$), complex V, and Et_3N, 100:100:1:1, gives a 92% yield of acetate (acetate:Pt = 92:1) after 30 h at 33 °C (Figure 1A). At the end of the catalytic acetylation one can isolate a new complex $[Pt(n\text{-}Bu_3P)(ImH)_3]^{2+}\ 2Cl^-$ (VI).[16] That complex VI could become the actual catalyst of the reaction with complex V is shown by the fact that further addition of the reactants to a solution of isolated VI leads to the acetylation of alcohol **3** and this catalytic acetylation is indeed faster than that initially observed with complex V itself (Figure 1B).

Further work is in progress to find better superacid catalysts[17] and design a bifunctional catalyst[18] complex bearing the general base in a suitable position on the activating ligand.

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(6) A 5-mL $CDCl_3$ stock solution of 0.8 M AcIm (solvent initially passed through an alumina column) is prepared from 440 mg of pure (sublimed) AcIm (4 mmol) and 420 μL of 1,1,2,2-tetrachloroethane as internal standard (4 mmol); a 5-mL $CDCl_3$ stock solution of complex Ic,[5] 0.2 M, is prepared from 459 mg of the Pt complex (1 mmol) and 105 μL of tetrachloroethane (1 mmol). In a typical experiment 125 μL of the AcIm solution are added to 500 μL of the Pt complex solution in an NMR tube, both reactants being 0.16 M.
(7) Very recently the esterification of alcohols with 1-acylimidazoles, assisted by *N*-bromosuccinimide has been reported: T. Katsuki, *Bull. Chem. Soc. Jpn.*, **49**, 2019 (1976).
(8) Catalysis of the reactions between AcIm and nucleophilic reagents is well documented: D. G. Oakenfull, K. Salvesen, and W. P. Jencks, *J. Am. Chem. Soc.*, **93**, 188 (1971).
(9) Ortho methyl groups are known to slow down the exchange of a pyridinic ligand,[10] and at 23 °C the first equilibrium of Scheme I corresponds to 93.5% and ca. 99% of III, respectively, for **1a** and **1b**.
(10) J. C. Chottard, D. Mansuy, and J. F. Bartoli, *J. Organomet. Chem.*, **65**, C19 (1974).
(11) However, Et_3N gives coalescence of the NMR signals of bound ethylene, and ligand substitution[12,13] slowly leads to precipitation of one or several new complexes, therefore one then does not know the exact nature of the Pt active complex (vide infra).
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(14) J. Reedijk and J. K. de Ridder, *Inorg. Nucl. Chem. Lett.*, **12**, 585 (1976). Excess AcIm can also lead to ethylene substitution, giving *trans*-$[PtCl_2(AcIm)_2]$, this reaction is slower and unimportant in our conditions.
(15) ^1H NMR shows that V + ImH, 1:1, gives an equilibrium with 73% ImH bound to Pt(II) at 32 °C.
(16) Mp 188–189 °C, Anal ($C_{21}Cl_2H_{39}N_6PPt$) C, Cl, H, N, P, and correct spectral properties. VI has been independently synthesized from $[Pt_2(n\text{-}Bu_3P)_2Cl_4]$.
(17) For instance, the stoechiometric acetylation of **1c** by *cis*-$[Pt[(n\text{-}Bu)_3P]_2Cl(AcIm)]^+\ ClO_4^-$ is faster than that with III ($10^3k = 20 \pm 2\ M^{-1}\ s^{-1}$ at 23 °C) up to 45% yield, but suffers a side reaction under investigation.
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An Efficient Synthesis of Indole

Sir:

Carbanions, which are stabilized by an isocyano group,[1] have proved to be valuable organic reagents for nucleophilic introduction of masked α-aminoalkyl groups in organic syntheses.[2] Reactions of α-metalated alkyl isocyanides with certain electrophilic reagents have also permitted an efficient synthesis of various heterocycles.[2] Herein, we wish to report a new and versatile synthesis of indole derivatives based on selective ortholithiation of the alkyl group in *o*-alkylphenyl isocyanides and subsequent intramolecular ring closure.

Lithiation[3] at the methyl group of *o*-tolyl isocyanide (**1**) was successfully performed by treatment of **1** with 2 equiv of lithium diisopropylamide (LDA)[4] in diglyme at −78 °C. The red colored carbanion, which was prepared by adding dropwise 176 mg (1.5 mmol) of **1** to LDA (3.0 mmol) in diglyme (4 ml) at −78 °C and then stirring for 30 min at the same temperature, was quenched with D_2O to yield *o*-tolyl isocyanide (>95% yield) with 93% deuterium incorporation at the methyl group. On the other hand, a similar treatment of **1** (1.5 mmol) with LDA (1.5 mmol) was followed by deuterolysis to regenerate