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LETTERS

# Insertion of Carbenes into O-H Bonds of Alcohols Catalysed by Platinum Complexes

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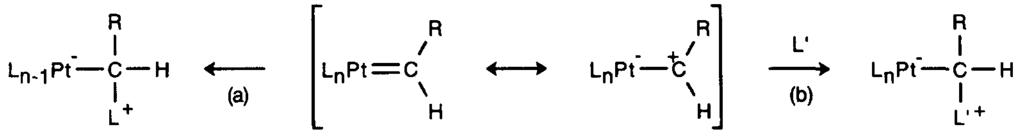
## Abstract

The addition of diazoesters to alcohols in the presence of a catalytic amount of platinum complexes provides the corresponding O-H insertion products in good to excellent yields.

*Keywords: Insertion reactions; Alcohols; Diazo compounds; Platinum and compounds.*

The advent of dirhodium(II) tetracarboxylates as effective catalysts for carbenoid transformations [1] resulted in extensive uses of this methodology for carbenoid insertion into polar X-H (X = N, O, and S) and aliphatic C-H bonds [2, 3]. Our report of their use for insertion into the hydroxyl bond of alcohols [4, 5] initiated the widespread use of these catalysts for O-H [6-9] and N-H insertion reactions [10, 11]. However, despite their high activity, rhodium carboxylates often lack selectivity. For instance, with unsaturated alcohols, the regioselectivity for carbene insertion into the O-H bond is high, although still insufficient as far as synthetic applications are concerned [5]. Depending on the rhodium counter-ions and the carbene substituents, addition to the unsaturated centre can be promoted to some extent, but is scarcely predominant. Finally, copper [5] and ruthenium catalysts [12, 13] have also been used in these reactions, but without any significant improvement of the chemoselectivity.

Platinum derivatives are also known to decompose diazo compounds to yield highly unstable electrophilic platinum-carbene complexes. In an inert solvent, these carbene complexes are stabilized via ligand transfer from the platinum [route (a)], or trapped by a nucleophile [L' = $PR_3$, $NR_3$, or RSR'; route (b)] to give betaines [14]. We therefore reasoned that compounds of type R-X-H (X = N, O, S) should also stabilize the transient platinum-carbene species and then, after hydrogen shift and



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regeneration of the catalyst, insertion of the carbene moiety into the X-H bond should be observed. Herein we wish to present a preliminary account on the use of platinum complexes for promoting insertion of carbenes into the hydroxyl bond of alcohols. For catalytic screening, allyl alcohol was chosen as the starting substrate because it provides an interesting model for chemocontrol : upon addition of ethyl diazoacetate both O-H insertion and olefin cyclopropanation may occur.

We were pleased to find that several platinum complexes were particularly suited to the aforementioned model reaction. Furthermore, with all platinum complexes tested in this study,

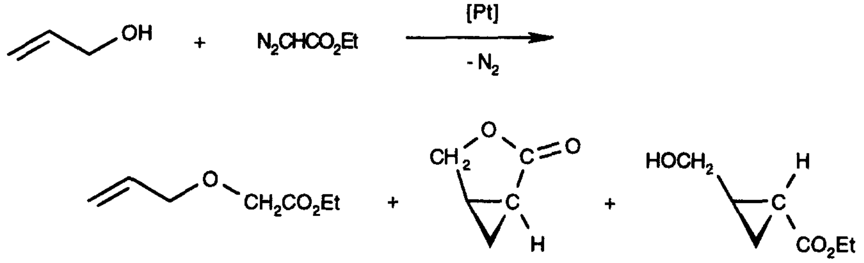

Table 1
Addition of ethyl diazoacetate to allyl alcohol in the presence of representative platinum complexes[a]

| Complex | O-H Insertion yield, %[b] | Complex | O-H Insertion yield, %[b] |
|---|---|---|---|
| $Pt(PPh_3)_4$ | 44 | $PtBr_2$ | 90 |
| $PtCl_2$ | 97 | $PtBr_2$(1,5-cyclooctadiene) | 93 |
| [$PtCl_2$(ethylene)]$_2$ | 96 | $PtI_2$ | 84 |
| [$PtCl_2$(cyclohexene)]$_2$ | 93 | $PtI_2$(1,5-cyclooctadiene) | 90 |
| $PtCl_2$(1,5-cyclooctadiene) | 93 | $PtI_2(NH_3)_2$ | 19 |
| *cis*-$PtCl_2$(benzonitrile)$_2$ | 79 | Pt(acac)$_2$ | 13 |
| *cis*-$PtCl_2$(pyridine)$_2$ | 46 | Pt(hfac)$_2$ | 95 |
| *cis*-$PtCl_2(PPh_3)_2$ | 32 | $PtCl_4$ | 91 |
| *trans*-$PtCl_2(PPh_3)_2$ | 46 | $PtBr_4$ | 85 |

[a] Reaction conditions : catalyst, 0.0075 mmol; allyl alcohol, 20 mmol; ethyl diazoacetate, 1 mmol diluted by the substrate up to 1 mL; addition time, 4 h; temperature, 45°C.

[b] Based on *added* ethyl diazoacetate, and determined by GLC analysis using di-*n*-butyl fumarate as internal standard.

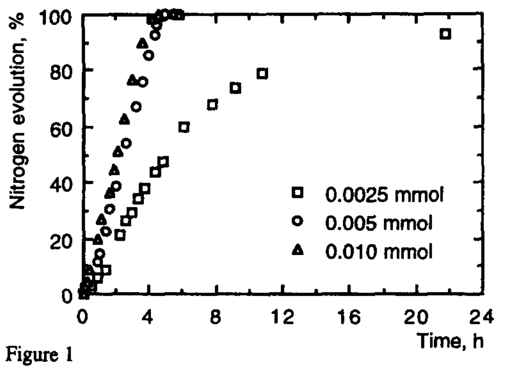

Figure 1
Influence of the amount of $PtCl_2$ on the decomposition rate of ethyl diazoacetate in allyl alcohol. Insertion yield : 80% (□), 96% (○), and 97% (▲).
Reaction conditions same as in Table 1.

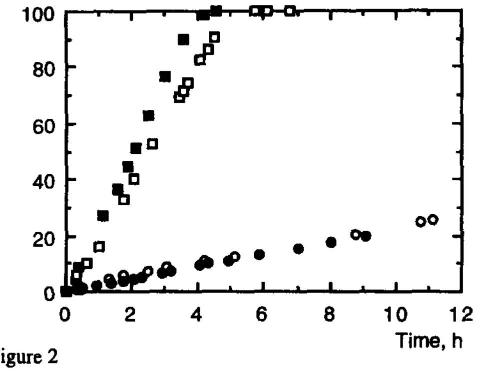

Figure 2
Influence of the ligands on the decomposition rate of ethyl diazoacetate in allyl alcohol in the presence of $PtCl_2$ (■), $PtCl_2$(1,5-cyclooctadiene) (□), *cis*-$PtCl_2$(pyridine)$_2$ (●), and *cis*-$PtCl_2(PPh_3)_2$ (○). Reaction conditions same as in Table 1.

O-H insertion proceeded chemospecifically : olefin cyclopropanation did not occur with allyl alcohol (Table 1), nor with 3-buten-1-ol and 9-decen-1-ol. In this sense, platinum complexes provide a tremendous breakthrough compared to rhodium carboxylates and other catalysts recently introduced in carbene chemistry.

We observed the highest catalytic activity (80-97% O-H insertion yield) with platinum(II) and platinum(IV) halides, including those coordinated to weak ligands such as ethylene, cyclohexene, 1,5-cyclooctadiene, or benzonitrile (Table 1), provided that the diazo compound:catalyst ratio remained lower than 200:1 (Figure 1). Unlike the aforementioned complexes, platinum halides possessing triphenylphosphine, pyridine or ammonia ligands displayed a low catalytic activity as illustrated by the slow decomposition rate of the diazo compound (Figure 2). With the latter complexes, some ethyl diazoacetate was still present in the reaction mixtures after two-three days ($\nu_{diazo} = 2115\ cm^{-1}$), and carbene dimers (diethyl maleate and diethyl fumarate) were the major by-products.

The reactivity profile of platinum hexafluoroacetylacetonate ($Pt(hfac)_2$) was very different to that of platinum acetylacetonate ($Pt(acac)_2$) : the former was highly efficient for promoting O-H insertion whereas the latter very slowly decomposed ethyl diazoacetate at 45°C. This striking difference in reactivity is almost certainly indicative of the higher electrophilicity of the intermediate platinum-carbene complex generated from $Pt(hfac)_2$ compared to that generated from $Pt(acac)_2$.

Addition of ethyl diazoacetate to several representative alcohols and phenol led to the corresponding O-H insertion product in good to excellent yields (80-98%), in the presence of the most active catalytic systems. Primary alcohols were more reactive than tertiary ones as confirmed by competitions between alcohols (Table 2).

$$RO{-}H \ + \ N_2CHCO_2Et \ \xrightarrow[45\ ^{\circ}C]{[Pt]} \ RO{-}CH_2CO_2Et \ + \ N_2$$

R = H, Me, Et, Pr, *i*-Pr, *n*-Bu, *sec*-Bu, *t*-Bu, Ph, Bn, and Ac.

The reasons for the observed reactivity order are best understood on the base of steric hindrance. The effect of alkyl substitution on alcohol reactivity likely results from the accessibility of the oxygen lone pair to the electrophilic platinum-carbene species. Hindered alcohols such as *t*-butyl alcohol prevent electrophilic attack by their bulk, and are therefore less reactive (Table 2).

Table 2

Relative reactivities of representative alcohols and styrene[a,b,c]

| | Catalyst | | | |
|---|---|---|---|---|
| Substrate | $PtCl_2$ | $PtBr_2$ | $Pt(acac)_2$ | $Pt(hfac)_2$ |
| Methanol | 1.05 | 1.20 | 0.99 | 1.00 |
| Ethanol | 1.00 | 1.00 | 1.00 | 1.00 |
| Propanol[d] | 1.00 | 0.97 | 0.96 | 0.99 |
| Isopropanol | 0.72 | 0.72 | 0.41 | 0.70 |
| *t*-Butanol | 0.37 | 0.37 | 0.21 | 0.38 |
| Allyl alcohol | 0.89 | 0.90 | 0.79 | 0.92 |
| Styrene | 0.27 | 0.33 | 0.14 | 0.2 |

[a,b] Reaction conditions same as in Table 1 (45°C).

[c] The ratio of the reaction rates is calculated from the expression $k_a/k_b = P_aO_b/P_bO_a$ where $P$ is the mole per cent. of the product and $O$ is the initial mole per cent. of the olefin [18].

[d] $PtI_2$ : 1.03.

We then became interested in the remarkable chemoselectivity of platinum complexes in favour of O-H insertion. This was confirmed by intermolecular competitions between ethanol and styrene (Table 2) [15]. Ethanol was found to be 3-6 times more reactive than styrene, which is an activated olefin we have previously shown to be in turn 15-30 times more reactive than non activated olefins such as 1-octene and cyclooctene [16]. Following these observations, propargyl alcohol has been tested and found to afford the corresponding O-H insertion product in only 50-70% yield based on ethyl diazoacetate and determined by GLC analysis ($PtCl_2$, 69%; $PtCl_2$(1,5-cyclooctadiene), 54%; $PtBr_2$, 52%; $Pt(hfac)_2$, 71% (reaction conditions same as in Table 1)), presumably due to competitive side reactions of the C-C triple bond [17]. Cyclopropenation of the C≡C bond did not take place either under these conditions.

In summary, platinum complexes have been shown to be outstanding catalysts for the chemospecific insertion of carbenes into the O-H bond to the detriment of the addition to the olefinic or acetylenic centre of unsaturated alcohols. Because of their high efficiency and tremendous chemospecificity, the best platinum complexes should find utility in a variety of applications. In addition, we have begun investigating addition of diazo compounds to N-H bonds of amines and amides. The results of this effort will be reported in due course.

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