Inorganica Chimica Acta
LETTER

A powerful organometallic nucleophile: the 2-pyridyl group in (dimethyldithiocarbamate)(2-pyridyl)(triphenylphosphine)platinum(II)

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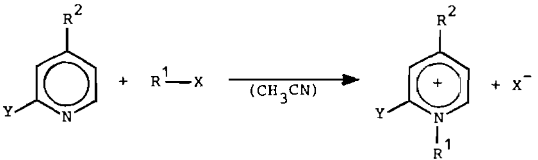
(Received June 6, 1990)

4-Dimethylaminopyridine (DMAP) is widely used as a catalyst in a wealth of organic reactions (e.g. in the acylation of alcohols and amines) thanks to its strong nucleophilic properties [1]. We have recently found that the 2-pyridyl nitrogen in complexes $[PtCl(2\text{-}C_5H_4N)(L)_2]$ (L = tertiary phosphine) displays a marked nucleophilic character, being able even to displace Cl^- ions from chlorinated solvents[2]. In order to compare quantitatively the nucleophilic power, we have carried out a kinetic study of the reactions of DMAP and $[Pt(dmtc)(2\text{-}C_5H_4N)(PPh_3)]$ (**1**, dmtc = dimethyldithiocarbamate) with chloroacetonitrile or 3-bromopropene in acetonitrile.



(1)

$R^1-X = ClCH_2CN, BrCH_2CH=CH_2$
DMAP: $Y = H$, $R^2 = NMe_2$
1: $Y = Pt(dmtc)(PPh_3)$, $R^2 = H$

The course of reaction (1) was followed by monitoring UV–Vis absorbance or electric conductivity changes, either under pseudo-first-order (excess of R^1-X) or second-order conditions. In any case, the reaction goes to completion through a strictly S_N2 mechanism, without any appreciable contribution from an S_N1 solvolytic step. The values of second-order rate constants are listed in Table 1.

TABLE 1. Second-order rate constants (k_2) for reaction (1) at 25 °C

Nucleophile	R^1-X	$10^4 \times k_2$ (s^{-1} mol^{-1} dm^3)
DMAP	$ClCH_2CN$	1.7 ± 0.3
DMAP	$BrCH_2CH=CH_2$	56.39 ± 0.03
1	$ClCH_2CN$	52.63 ± 0.02
1	$BrCH_2CH=CH_2$	1776.7 ± 8

Kinetic measurements in the temperature range 15–40 °C gave the following activation parameters for the reaction of **1** with $ClCH_2CN$ and $BrCH_2CH=CH_2$: $\Delta H^{\ddagger} = 43.3 \pm 0.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -142 \pm 4$ J K^{-1} mol^{-1} and $\Delta H^{\ddagger} = 29.7 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -160 \pm 4$ J K^{-1} mol^{-1}, respectively. These values are in line with those reported for classical S_N2 substitution reactions at saturated carbon, in which substantial charge separation occurs in the transition state with attending solvent organisation [3, 4]. Consistently, the higher reaction rates observed for $BrCH_2CH=CH_2$ relative to $ClCH_2CN$ with each nucleophile reflect a typical leaving group effect. Data in Table 1 also show the nucleophilic power of the 2-pyridyl group in complex **1** to be far superior (*c*. 30-fold) than that of the 'hypernucleophile' DMAP, despite the higher steric crowding around the nucleophilic center of **1**. Accordingly, in CH_2Cl_2 solution at 30 °C, complex **1** (δ_P 17.0 ppm, ^1J(PtP) 4125 Hz) is quantitatively converted into $[Pt(dmtc)\{2\text{-}C_5H_4N(1\text{-}CH_2Cl)\}(PPh_3)]^+$ (δ_P 14.2 ppm, ^1J(PtP) 3487 Hz) in *c*. one day, whereas the corresponding reaction with DMAP proceeds only to a negligible extent in the same period of time.

The enhanced nucleophilicity of **1** is essentially related to the good electron-donating ability of the metal-containing substituent $Pt(dmtc)(PPh_3)$, σ-bonded to the C(2) pyridine carbon. An increased electron density at nitrogen was observed in other imino derivatives with a *trans*-$PdX(L)_2$ unit σ-bonded to the imino carbon [5].

On the other hand, the greater electronic charge at the pyridine nitrogen of **1** is also reflected by its higher basicity. In fact, titration of **1** and DMAP with perchloric acid in water/dioxane (1:1 vol./vol.; ionic strength 0.1 mol dm^{-3} $LiClO_4$) yields pK_a values of 9.6 and 8.5, respectively. The 2-pyridyl group in **1** also appears to be much more basic than pyridine and *trans*-$[PdBr(2\text{-}C_5H_4N)(PPh_3)_2]$ for which pK_a values of 4.47 and 8.04 have been determined, respectively, under comparable conditions [5a].

Details of the preparation of **1** and its derivatives $[Pt(dmtc)\{2\text{-}C_5H_4N(1\text{-}R^1)\}(PPh_3)]X$ ($R^1 = H$, CH_2CN, $CH_2CH=CH_2$, CH_2Cl; $X^- = ClO_4^-$) will be reported in a forthcoming paper. Work is now in

0020-1693/90/$3.50

progress to study the nucleophilic properties of a variety of 2-pyridylplatinum(II) and -palladium(II) complexes and their catalytic activity in typical base-catalysed organic reactions [1].

Acknowledgement

Financial support from the Italian Ministero della Pubblica Istruzione (Research Fund 60%) is gratefully acknowledged.

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