SHORT COMMUNICATIONS

π Complexes of Vinyl Alcohol and Propenyl Alcohol with Platinum(II)

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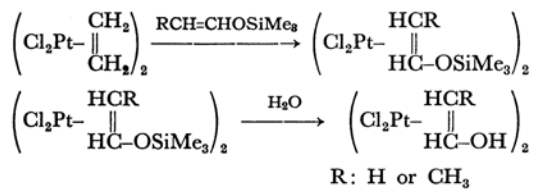
The first description of the vinyl alcohol complex with a transition metal was made by Ariyaratne and Green; it was prepared by the protonation of an oxoalkyl-iron complex.[1]

In the present communication, we wish to report the preparation of vinyl alcohol and propenyl alcohol complexes with Pt(II) in a completely different manner. As is shown below, 1,3-bis-(alkenyl trimethylsilyl ether)-2,4-dichloro-μ-dichlorodiplatinum was synthesized by the replacement of ethylene by alkenyl trimethylsilyl ether, and then the Si–O bond was hydrolyzed to give alkenyl alcohol complexes.



R: H or CH_3

To a suspension of 100 mg of Zeise's dimer, $(Cl_2PtC_2H_4)_2$, in 5 m*l* of toluene, there was added about 0.1 m*l* of vinyl trimethylsilyl ether. The mixture turned orange and became homogeneous shortly after the addition. The toluene and the excess of vinyl trimethylsilyl ether were then evaporated at room temperature to give a yellow powder of $(Cl_2PtCH_2{=}CH{-}OSiMe_3)_2$, which decomposed under nitrogen at 120—122°C. Found: C, 15.77; H, 2.86; Cl, 19.13; Pt, 51.27%. Calcd for $C_5H_{12}Cl_2OSiPt$: C, 15.71; H, 3.16; Cl, 18.55; Pt, 51.04%. This powder was dissolved in 10 m*l* of benzene containing about 200 ppm of water. When the solution was allowed to stand overnight at room temperature, fine yellow crystals of the vinyl alcohol complex precipitated in a 68% yield; these crystals decomposed at 127—131°C. Found: C, 7.91; H, 1.33; Cl, 22.77; Pt, 62.77%. Calcd for $C_2H_4Cl_2OPt$: C, 7.75; H, 1.30; Cl, 22.87; Pt, 62.92%. IR(KBr disk): ν_{O-H} 3200(vs), $\nu_{=C-H}$ 3020(w) and $\nu_{C=C}$ 1548 cm^{-1}(vs).

Since the O–Si bond of the vinyl trimethylsilyl ether complex is extremely sensitive to moisture, the vinyl alcohol complex was also formed when the vinyl trimethylsilyl ether complex was exposed to air (70% humidity) at room temperature for about 10 min.

On the decomposition of the vinyl alcohol complex with pyridine, acetaldehyde was liberated; it was detected by gas chromatography.

A similar reaction of propenyl trimethylsilyl ether gave an orange-yellow powder of $(Cl_2Pt\ CH_3{-}CH{=}CHOSiMe_3)_2$ which decomposed at 118—121°C. Found: C, 18.02; H, 3.42; Cl, 18.68%. Calcd for $C_6H_{14}Cl_2OSiPt$: C, 18.19; H, 3.56; Cl, 17.90%. The hydrolysis was carried out similarly in moist benzene to give brown-yellow crystals of the propenyl alcohol complex after 10 days at room temperature. The yield was 61%. It decomposed at 118—121°C. Found: C, 11.28; H, 1.84; Cl, 22.37; Pt, 60.22%. Calcd for $C_3H_6Cl_2OPt$: C, 11.12; H, 1.87; Cl, 21.88; Pt, 60.20%. IR (Nujol mull): ν_{O-H} 3300(vs), $\nu_{=C-H}$ 3020(w) and $\nu_{C=C}$ 1545 cm^{-1}(s).

These specific absorptions and the absence of carbonyl absorption in the IR spectra are consistent with the proposed structure of the complexes. The NMR spectra were not studied because of the poor solubility of the complexes. The study of the *cis-trans* isomerism of the complexed olefin is now in progress.

1) J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, **1964**, 1.