Journal of Organometallic Chemistry, 57 (1973) C93–C94

Preliminary communication

Vinylmetallics as ligands
III*. Synthesis and characterization of potassium trichloro(trimethylvinylsilane)platinate(II)

ELLIOT M. HASCHKE and JOHN W. FITCH

Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666 (U.S.A.)

(Received June 6th, 1973)

SUMMARY

The preparation and some reactions of the compound potassium trichloro(trimethylvinylsilane)platinate(II) are reported.

Several recent investigations have indicated that vinylsilanes are cleaved at the vinyl–carbon to silicon bond by both platinum(II)[1] and palladium(II)[2] species. We now wish to report that the π complex, potassium trichloro(trimethylvinylsilane)platinate(II) [Compound I], is readily prepared by metathesis of Zeise's salt, $K[PtCl_3(C_2H_4)]$, in acetone as shown below.

$$(CH_3)_3SiCH{=}CH_2 + K[PtCl_3(C_2H_4)] \rightarrow K[PtCl_3(CH_3)_3SiCH{=}CH_2] + C_2H_4 \qquad (1)$$

(I)

In a typical reaction, Zeise's salt (2.6 mmol) was allowed to react with an excess of trimethylvinylsilane (20.7 mmole) in acetone (20 ml). After approximately thirty minutes the solvent and excess ligand were removed at reduced pressure to yield (I) as a pale yellow, crystalline solid (m.p. = 107–120° dec.) in 90–95% yield. (Found: C, 13.62; H, 2.74; Pt, 44.30. $C_5H_{12}Cl_3KPtSi$ calcd.: C, 13.61; H, 2.72; Pt, 44.26%.)

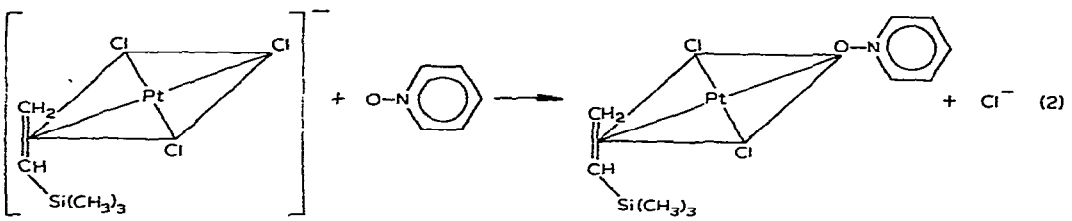
The infrared spectrum of (I) in KBr exhibited bands at 1245, 828 and 745 cm^{-1} which are typically[3] associated with the grouping, $Si(CH_3)_3$, and a weak band at 1470 cm^{-1} which might be tentatively assigned to the complexed vinyl stretching vibration.

The ^1H NMR spectrum of (I) in acetone-d_6 shows a vinyl multiplet at δ 3.96–4.40 (3H) and a single methyl resonance at δ 0.26 (9H). The vinyl multiplet in the free ligand occurs at δ 5.37–6.49.

*For Part II, see ref. 5.

If (I) is allowed to stand in acetone-d_6 which is wet, it slowly decomposes to give Zeise's salt and hexamethyldisiloxane. The Zeise's salt was identified using ^{1}H NMR by comparison to authentic samples. The hexamethyldisiloxane was identified by gas chromatography. That this cleavage reaction is catalytic in (I) has been confirmed by allowing acetone-d_6 solutions containing excess trimethylvinylsilane and (I) to stand for one month (with periodic venting). ^{1}H NMR on these solutions shows Zeise's salt and hexamethyldisiloxane, but no free trimethylvinylsilane.

(I) reacts with pyridine *N*-oxide in ethanol solution, as shown in eqn. (2) to yield the non-ionic yellow compound, *trans*-dichloro(trimethylvinylsilane)(pyridine *N*-oxide)-platinum(II) (m.p. = 87–90 dec). (Found: C, 26.39; H, 3.42; Pt, 42.70. $C_{10}H_{17}Cl_2NOPtSi$ *calcd.*: *C, 26.31; H, 3.73;* Pt, 42.78%.)



(I) (II)

The *trans* configuration is assigned by analogy with previous work on the similar reaction of Zeise's salt[4]. Compound (II) exhibits characteristic $Si(CH_3)_3$ bands at 1248 and 745 cm^{-1}. The other band expected around 840 cm^{-1} is indeed observed at 830 cm^{-1}, but it could be arising from the pyridine *N*-oxide ligand. The ^{1}H NMR spectrum of (II) in $CDCl_3$ shows a vinyl multiplet at δ 5.48–3.98 (3H), a singlet arising from $Si(CH_3)_3$ at δ 0.39 (9H) and pyridine *N*-oxide multiplets at δ 8.60–8.83 and δ 7.58–8.08 (Total of 5H).

We are currently investigating other substitution reactions of $K[PtCl_3(CH_3)_3SiCH{=}CH_2]$ as well as the mechanisms of its decomposition and cleavage reactions. These data will be the subject of a future communication.

ACKNOWLEDGEMENT

The authors are pleased to acknowledge the support of this work by the Robert A. Welch Foundation (Grant No. AI-306).

REFERENCES

1 J.E. Poist and C.S. Kraihanzel, *Chem. Commun.*, (1968) 607.
2 W.P. Weber, R.A. Felix, A.K. Willard and K.E. Koenig, *Tetrahedron Lett.*, (1971) 4701.
3 N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964, pp. 295–296.
4 L. Garcia, S.I. Shupack and M. Orchin, *Inorg. Chem.*, 1 (1962) 893.
5 J.W. Fitch and C.A. Kettner, *Tex. J. Sci.*, 25 (1973) in press.