INORG. NUCL. CHEM. LETTERS Vol. 6, pp. 507-508, 1970. Pergamon Press. Printed in Great Britain

SYNTHESIS OF SILVLCYCLOPENTADIENE

ARNULF P. HAGEN and PETER J. RUSSO Department of Chemistry, University of Oklahoma Norman, Oklahoma 73069 (U.S.A.)

(Received 24 February 1970)

The molecule $H_3CC_5H_5$ has been known for several years and has been used as a ligand in transition metal compounds such as $(H_3CC_5H_4)Mn(CO)_3^1$ and $[(H_3CC_5H_4)Fe(CO)_2]_2^1$. Related group IV compounds where the alkyl group has been replaced by a silicon containing group such as $Si(CH_3)_3^2$ or $SiCl_3^3$ have been reported. Here we report the synthesis of $H_3SiC_5H_5$, the silyl analog of methylcyclopentadiene, and some of its reactions.

Potassium cyclopentadienide (1.089g, 0.0104 mole) is prepared in vacuo from cyclopentadiene and potassium metal using diethylether as a solvent at -78°. The ether and unreacted cyclopentadiene are removed slowly at -30° leaving a white solid residue. Silyl bromide (2.357g, 0.0212 mole) is then added at -196°. The reaction vessel is then permitted to slowly warm to room temperature after being held at -78° for fifteen minutes. In addition to excess silyl bromide a volatile material having an empirical formula corresponding to $C_{5}H_{5}SiH_{3}$ is obtained in 89% yield based on the amount of $KC_{5}H_{5}$ employed. This material melts at -94° to -96° in vacuo without any decomposition, boils at 59-61°, and is stable to air oxidation and moisture. Anal. Calcd. for $C_{5}H_{8}Si:$ C, 62.4; H, 8.4; Si, 29.2%. Found: C, 62.7; H, 8.6; Si, 28.8%. The gas phase infrared spectrum [Beckman IR-10] shows a strong band with a shoulder in the silicon hydrogen stretching region [2138(s), 2158(sh) cm⁻¹].

The synthesis of (silyl)(methyl)cyclopentadiene has been carried out by a similar procedure. In the absence of solvent, when $K[C_5H_4CH_3]$ (17.41g, 0.0147 mole.) is combined with silyl bromide (3.683g, 0.0332 mole) at -78° for fifteen minutes, a volatile species having the empirical formula $C_5H_4(SiH_3)(CH_3)$ is

507

obtained in 99% yield. This compound melts at -146° to -148° in vacuo and is stable to air oxidation and moisture. Anal. Calcd. for $C_6H_{10}Si$, 65.4; H, 9.1; Si, 25.5%. Found: C, 65.2; H, 9.2; Si, 25.5%. The gas phase infrared spectrum of this compound shows a strong band in the silicon hydrogen stretching region [2156 cm⁻¹].

Several reactions of silyl- and (silyl)(methyl)cyclopentadiene have been studied. Both compounds react with gaseous HCl, forming silyl chloride, the appropriate cyclopentadiene derivative and a high molecular weight substance containing silyl groups. Trimethylamine has been found to readily cleave the silicon carbon linkage at room temperature forming H₃SiN(CH₃)₂.

Nuclear magnetic resonance measurements indicate that for both compounds the only isomer which is present at -50° has the silyl- (or the silyl- and methyl-) grouping at the saturated carbon atom, however, at higher temperatures no fine structure is observed⁴.

ACKNOWLEDGEMENTS

This work was initiated by NASA grant No. NGL 37-003-026 and continued with support from the Petroleum Research Fund, administered by the American Chemical Society. Certain reagents were generously supplied by the Union Carbide Corporation and by the Enjay Chemical Company.

REFERENCES

- L. T. Reynolds and G. Wilkinson, J. Inorg. & Nuclear Chem., <u>9</u>, 86 (1958).
 K. C. Frisch, J. Amer. Chem. Soc., <u>75</u>, 6050 (1953).
- V. B. Jex, U. S. 2,974,157, March 7, 1959 (to Union Carbide Corp.); Chem. Abst., <u>55</u>, 17537b (1961).
- 4. A. Davison and P. E. Rakita, J. Amer. Chem. Soc., 90, 4479 (1968).

508