Journal of Organometallic Chemistry, 202 (1980) 263—267
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PREPARATION AND PROPERTIES OF $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ AND $(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2$; TRIMETHYLSILYL GROUP TRANSFER FROM MERCURY TO ZIRCONIUM

A.J. BLAKENEY and J.A. GLADYSZ *

Department of Chemistry, University of California, Los Angeles, California 90024 (U.S.A.)

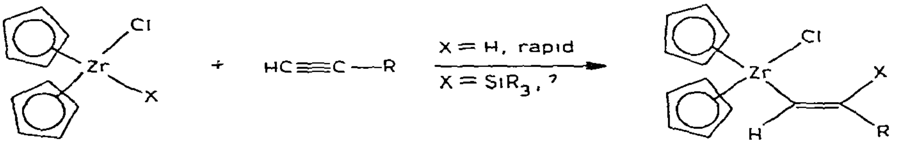
(Received January 28th, 1980)

Summary

Two silyl-zirconium compounds $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ (I) and $(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2$ (II), have been prepared by the reaction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ with $Hg[Si(CH_3)_3]_2$ in refluxing benzene. While I is unreactive toward 1-hexyne (55—60°C) and CO (350 psi), the zirconium—silicon bond is cleaved by electrophiles such as Cl_2, $HgCl_2$, and $AlCl_3$.

Introduction

Our interest in the chemistry [1] and physical properties [2] of transition metal trialkylsilanes prompted us to attempt the preparation of zirconocene trimethylsilanes. The only cyclopentadienylzirconium silane previously prepared, $(\eta\text{-}C_5H_5)_2ZrCl[Si(C_6H_5)_3]$ [3], was obtained in 90% yield by the reaction of $(\eta\text{-}C_5H_5)_2ZrCl_2$ with $Li[Si(C_6H_5)_3]$; however, its chemistry was not explored in detail. We set out to synthesize $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ (I), since transition metal trimethylsilanes are considerably more reactive than other transition metal silanes [4], and the wealth of useful reactions effected by $(\eta\text{-}C_5H_5)_2ZrClH$ [5] might be paralleled with I (eq. 1).



(1)

Since many transition-metal trimethylsilanes have limited stability in oxygen-containing solvents [1], we sought a route to I which would be feasible in hydrocarbons. Unfortunately, $(CH_3)_3Si^-$ is usually generated in HMPA or THF [6]. Therefore we decided to investigate the reaction of $Hg[Si(CH_3)_3]_2$ [7]

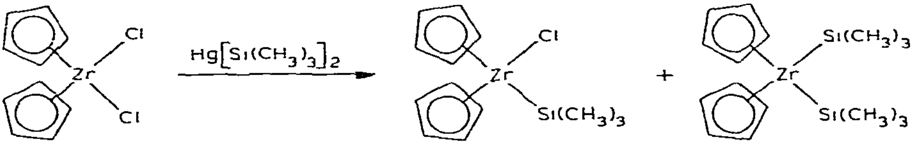
0022—328X/80/0000—0000/$02.25, © 1980, Elsevier Sequoia S.A.

with $(\eta\text{-}C_5H_5)_2ZrCl_2$. Previously, $[(C_2H_5)_3P]_2PtCl_2$ had been converted to $[(C_2H_5)_3P]_2PtCl[Si(CH_3)_3]$ with this reagent; other metal silanes have been prepared by related methods [8].

Results and discussion

A mixture of $Hg[Si(CH_3)_3]_2$ and $(\eta\text{-}C_5H_5)_2ZrCl_2$ in 3 : 1 molar ratio was heated in refluxing benzene for 9 days. After solvent removal, stepwise sublimation of the resulting reaction mixture yielded first yellow unreacted $Hg[Si(CH_3)_3]_2$, and then a white powder. The microanalysis and ^1H and ^{13}C NMR spectra of this material (Experimental Section) clearly indicated it to be $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ (I; 33% yield). While long reaction times are required to prepare I by this route, by-products and unreacted starting materials are easily removed.

When $Hg[Si(CH_3)_3]_2$ and $(\eta\text{-}C_5H_5)_2ZrCl_2$ (3 : 1 molar ratio) were allowed to react for 15 days in refluxing benzene, a second, more volatile, white zirconium compound formed (eq. 2). Fractional sublimation yielded $(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2$ (II, 11%), as well as I (58%). No attempts were made to maximize the yield of II.



(2)

(I) (major) (II) (minor)

Several reactions of I were attempted. Unfortunately, I proved inert to 1-hexyne, both neat (55—60°C, 20 h) and in C_6D_6 (55—60°C, 3 days). With $(\eta\text{-}C_5H_5)_2ZrHCl$, acetylenes are hydrozirconated (eq. 1) within 2 h at 25°C [9]. Olefins and fluoroacetylenes have been previously observed to insert into metal—trimethylsilyl bonds [10]. Hence we believe the lack of reactivity of I is steric in origin. Although alkyls of the formula $(\eta\text{-}C_5H_5)_2ZrRCl$ are readily carbonylated under CO (20 psi, 25°C) [5], I was inert to 350 psi CO.

With electrophilic reagents, I and II underwent cleavage reactions. At —78°C in toluene-d_8, Cl_2 gas converted I to $(\eta\text{-}C_5H_5)_2ZrCl_2$ and $(CH_3)_3SiCl$. The same products were obtained from II and Cl_2. When I and $HgCl_2$ were allowed to react in C_6D_6 at 60°C, $(\eta\text{-}C_5H_5)_2ZrCl_2$, $(CH_3)_3SiCl$, and Hg formed over the course of five days. The initial product of this reaction is likely $(CH_3)_3SiHgCl$, which has been independently demonstrated to rapidly decompose to $(CH_3)_3SiCl$ and Hg [11]. No reaction occurred between I and C_6H_5HgCl at 60°C in C_6D_6.

Rapid reactions also occurred when benzene solutions of I and II were treated with $AlCl_3$. New trimethylsilyl-containing compounds were evident by NMR (Experimental), and $(\eta\text{-}C_5H_5)_2ZrCl_2$ was formed quantitatively. Recently, the high yield transfer of alkyl groups from $(\eta\text{-}C_5H_5)_2ZrRCl$ to $AlCl_3$ has been demonstrated by Schwartz [12]. We suggest that a similar trimethylsilyl group transfer can take place between $AlCl_3$ and I and II. Unfortunately, the trimethylsilyl-containing products were extremely sensitive species. Since product distributions clearly depend upon stoichiometry, and initially formed species are subject to redistribution reactions, detailed characterization of these reactions was not attempted. Important recent work by Rösch [13] indicates $Al[Si(CH_3)_3]_3$ to be a labile compound (dec. ca. 60°C) which is isolable only under exacting conditions.

In summary, trimethylsilyl group transfer from $Hg[Si(CH_3)_3]_2$ to zirconium is believed to be driven by the irreversible decomposition of initially generated $(CH_3)_3SiHgCl$ [11]. In this fashion, zirconium can be substituted for chlorine on a highly electropositive transition metal. The zirconium—silicon bond therefore possesses considerable reactivity towards electrophiles. Hence trimethylsilyl group transfer from I and II to $AlCl_3$ proceeds rapidly. While several initial objectives of this study were not realized, it can be anticipated that heretofore inaccessible metal trimethylsilanes will be available from I and II and appropriate metal halides.

Experimental

General procedures

All reactions were conducted with the rigorous exclusion of air and water. Benzene and toluene were purified by refluxing over CaH_2, distillation, and then freeze-thaw degassing. For petroleum ether (bp 20—40°C) purification, Li powder or $LiAlH_4$ was used instead of CaH_2. $(\eta\text{-}C_5H_5)_2ZrCl_2$ was purchased from Aldrich and Alfa-Ventron. $Hg[Si(CH_3)_3]_2$ was prepared by a published procedure [7b]. ^1H NMR spectra and ^{13}C NMR spectra (50 MHz) were obtained on Varian T-60 and Bruker WP-200 * spectrometers, respectively. All ^1H NMR chemical shifts are relative to $(CH_3)_4Si$, and ^{13}C NMR chemical shifts are referenced to the middle C_6D_6 absorption at 129.02 ppm. Elemental analyses were conducted by Schwartzkopf. Melting points were taken on a Büchi Schmeltzpunktbestimmungsapparat, and are uncorrected.

Preparation of chlorobis(η-cyclopentadienyl)trimethylsilylzirconium (I)

A 25 ml Schlenk flask was charged with $Hg[Si(CH_3)_3]_2$ (1.25 g, 3.6 mmol), $(\eta\text{-}C_5H_5)_2ZrCl_2$ (0.35 g, 1.2 mmol), and 3.5 ml of dry degassed benzene in a N_2 filled glovebox. An airtight assemblage of the Schlenk flask, a reflux condensor, and a curved adapter with stopcock was then removed from the glove box, attached to an argon line, and covered with Al foil. The yellow reaction mixture was refluxed for 9 days and cooled. The flask was returned to the glove box and the benzene removed in vacuo. The residue was taken up in petroleum ether, and filtered to remove $(\eta\text{-}C_5H_5)_2ZrCl_2$ and Hg. The petroleum ether was removed in vacuo and the residue sublimed. At 75°C and 1 mm, 0.35 g of $Hg[Si(CH_3)_3]_2$ was recovered. The product $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ (0.13 g, 33%) was obtained as a white powder upon sublimation at 60—70°C and 2×10^{-4} mm. Some white residue remained in the sublimator. Data on I: mp 98—100°C, sealed capillary. ^1H NMR: (δ, C_6D_6): 0.12 (s, 9H), 6.00 (s, 10H) ppm. ^{13}C NMR (C_6D_6, 10°C): 114.0, 1.8 ppm. Anal. Found: C, 47.60; H, 5.80; Cl,

---

* This instrument was provided by a NSF department instrument grant (CHE76-05926).

10.40; Si, 8.36; Zr, 27.65. $C_{13}H_{19}ClSiZr$ Calcd.: C, 47.31; H, 5.80; Cl, 10.74; Si, 8.51; Zr, 27.64%.

Preparation of bis(η-cyclopentadienyl)bis(trimethylsilyl)zirconium (II)

Using general procedures as described in the above experimental, 3.75 g (10.8 mmol) of $Hg[Si(CH_3)_3]_2$ and 1.05 g (3.6 mmol) of $(\eta\text{-}C_5H_5)_2ZrCl_2$ were refluxed for 15 days in 9 ml of benzene. Workup as above and repeated fractional sublimations yielded 0.141 g (11%) of $(\eta\text{-}C_5H_5)_2Zr[Si(CH_3)_3]_2$ (II) (40—50°C, 4×10^{-4} mm) and 0.689 g (58%) of $(\eta\text{-}C_5H_5)_2ZrCl[Si(CH_3)_3]$ (60—70°C, 4×10^{-4} mm). Data on II: mp 83—87°C (sealed capillary). ^1H NMR (δ, C_6D_6): 0.15 (s, 18H), 5.99 (s, 10H) ppm. ^{13}C NMR (C_6D_6, 10°C): 112.5, 2.3 ppm.

Attempted reactions of I with 1-hexyne and CO

To 0.5 ml of degassed anhydrous C_6D_6 in a ^1H NMR tube were added I (75 mg, 0.227 mmol) and 1-hexyne (25 μl). The solution was heated at 55—60°C for 3 days. No reaction occurred by ^1H NMR; any vinylic protons would have been easily detected.

A ^1H NMR tube containing I (50 mg) and 0.5 ml of degassed 1-hexyne was heated at 55—60°C for 20 h. No reaction occurred.

In 0.5 ml of degassed anhydrous C_6D_6 was dissolved 50 mg of I. This solution was pressurized with 350 psi of CO in a Fischer-Porter bottle and allowed to stir for 17 h, during which time the pressure dropped to 75 psi due to a slow leak. By ^1H NMR, I had not reacted.

Reactions of I and II with Cl_2

Nitrogen was flushed for 18 h through a H_2SO_4 tower and out through a Schlenk flask connected to a bubbler. This system was then purged for 2 h with Cl_2 gas. 30 mg (0.09 mmol) of I was dissolved in 0.4 ml of toluene-d_8 in a ^1H NMR tube, which was then capped with a septum. The solution was cooled to —78°C and treated with 4 ml of Cl_2 gas withdrawn from the Schlenk flask via a gas tight syringe; some $(\eta\text{-}C_5H_5)_2ZrCl_2$ precipitated. Analysis by ^1H and ^{13}C NMR (at room temperature) indicated the reaction to be complete, and $(\eta\text{-}C_5H_5)_2ZrCl_2$ to be the sole zirconium containing product. $(CH_3)_3SiCl$ (accompanied by a small amount of $[(CH_3)_3Si]_2O$) was identified as the other product by GLC, ^1H NMR, and ^{13}C NMR.

Identical results were obtained when 15 mg (0.041 mmol) of II was similarly reacted with Cl_2.

Reaction of I with $HgCl_2$

A ^1H NMR tube was charged with 25 mg (0.075 mmol) of I, 22 mg (0.082 mmol) of freshly sublimed $HgCl_2$, and 0.4 ml of dry degassed C_6D_6. The tube was capped and heated for 5 days at 60°C. ^1H NMR and GLC analysis indicated the clean formation of $(\eta\text{-}C_5H_5)_2ZrCl_2$ and $(CH_3)_3SiCl$.

A similar experiment with I (25 mg, 0.075 mmol) and C_6H_5HgCl (23 mg, 0.073 mmol) did not result in a reaction.

Reactions of I and II with $AlCl_3$

To a ^1H NMR tube was added 22 mg (0.067 mmol) of I, 0.4 ml of dry, degassed C_6D_6, and 3 mg (0.022 mmol) of sublimed $AlCl_3$. The tube was capped and vigorously agitated until the $AlCl_3$ dissolved (2—3 minutes). Within 2—3 minutes, crystals of $(\eta\text{-}C_5H_5)_2ZrCl_2$ (subsequently isolated and identified by ^1H and ^{13}C NMR and melting point) began to precipitate. New trimethylsilyl ^1H NMR (δ 0.23 ppm) and ^{13}C NMR (2.95 ± 0.06 ppm) resonances appeared.

To a ^1H NMR tube was added 25 mg (0.068 mmol) of II, 0.4 ml of C_6D_6, and 6 mg (0.045 mmol) of $AlCl_3$. After capping and shaking the tube, results identical to those described for I above were obtained.

Acknowledgement

We are grateful to the National Science Foundation for financial support and Mr. W.A. Kiel for assistance in obtaining the ^{13}C NMR spectra.

References

1 D.L. Johnson and J.A. Gladysz, J. Amer. Chem. Soc., 101 (1979) 6433.
2 S. Li, D.L. Johnson, J.A. Gladysz and K.L. Servis, J. Organometal. Chem., 166 (1979) 317.
3 B.M. Kingstone and M.F. Lappert, J. Chem. Soc., Dalton Trans., (1972) 69.
4 W. Malisch and M. Kuhn, Chem. Ber., 107 (1974) 979.
5 J. Schwartz and J.A. Labinger, Angew. Chem., Int. Ed. Engl., 15 (1976) 333.
6 (a) P.B. Dervan and M.A. Shippey, J. Amer. Chem. Soc., 98 (1976) 1265. (b) W.C. Still, J. Org. Chem., 41 (1976) 3063. (c) E. Hengge and N. Holtschmidt, J. Organometal. Chem., 12 (1968) P5. (d) H. Sakurai, F. Kondo, J. Organometal. Chem., 92 (1975) C46. (e) O.W. Steward, J.E. Dzeidzic and J.S. Johnson, J. Org. Chem., 36 (1971) 3475.
7 (a) W.P. Neumann and K. Reuter, J. Organometal. Chem. Library, 7 (1979) 229. (b) R. Fields, R.N. Haszeldine and R.E. Hulton, J. Chem. Soc. C, (1967) 2559.
8 (a) F. Glocking and K.A. Hooton, J. Chem. Soc. A, (1967) 1066. (b) F. Höfler, Topics Curr. Chem., 50 (1974) 129; see p. 136.
9 D.W. Hart, T.F. Blackburn and J. Schwartz, J. Amer. Chem. Soc., 97 (1975) 679.
10 (a) E.J. Bichler, M.R. Booth and H.C. Clark, J. Organometal. Chem., 24 (1970) 145. (b) H.C. Clark and T.L. Hauw, J. Organometal. Chem., 42 (1972) 429. (c) M.A. Schroeder and M.S. Wrighton, J. Organometal. Chem., 128 (1977) 345.
11 (a) D. Seyferth, R.J. Cross and B. Prokai, J. Organometal. Chem., 7 (1967) P20. (b) A.G. Lee, J. Organometal. Chem., 16 (1969) 321.
12 D.B. Carr and J. Schwartz, J. Amer. Chem. Soc., 101 (1979) 3521.
13 L. Rösch, Angew. Chem., Int. Ed. Engl., 16 (1977) 480; L. Rösch and G. Altnau, J. Organometal. Chem., 195 (1980) 47.