Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SYNTHESES OF $[(\pi\text{-}Me_3SiC_5H_4)Fe(CO)_2]_2$ AND $[(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$ REACTIONS OF 5-(TRIMETHYLSILYL)CYCLOPENTADIENE WITH $Fe(CO)_5$ AND $Mo(CO)_6$

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(Received January 2nd, 1970)

SUMMARY

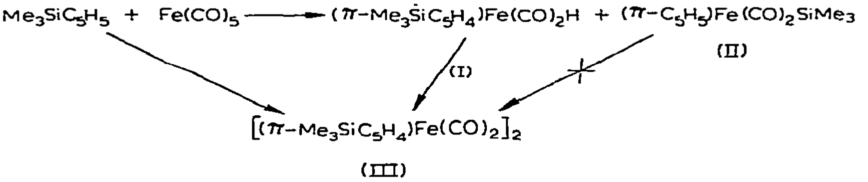
5-(Trimethylsilyl)cyclopentadiene has been observed to react with $Fe(CO)_5$ and $Mo(CO)_6$ at slightly elevated temperatures (110–130°) to yield $[(\pi\text{-}Me_3SiC_5H_4)\text{-}Fe(CO)_2]_2$ and $[(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$, respectively. No evidence of products which might have arisen from cleavage of or insertion into the silicon–ring bond was found.

INTRODUCTION

Quite recently, the compounds $Me_3M'C_5H_5$ (where M' = Ge or Sn) have been reported to react with $(CH_3CN)_3M(CO)_3$ (where M = Cr, Mo or W) to yield $(\pi\text{-}C_5H_5)\text{-}M(CO)_3M'Me_3$[1]. This apparent insertion of $M(CO)_3$ between a ring carbon atom and the $M'Me_3$ group would seem to be related to the reported temperature dependent migration of $M'Me_3$ about the C_5H_5 ring [2]. Although 5-(trimethylsilyl)cyclopentadiene is reported to exhibit the latter property[2], this same compound apparently reacts very slowly, and in an undefined manner, with $(CH_3CN)_3M(CO)_3$[1]. In an earlier paper, one of us has suggested that 5-(trimethylsilyl)cyclopentadiene undergoes isomerization involving hydrogen migration about the cyclopentadiene ring to yield 1- and 2-(trimethylsilyl)cyclopentadienes[3]. This process is equivalent to the shifting of the endocyclic double bonds proposed to account for thermodynamically controlled isomerizations of organo-substituted cyclopentadiene systems[4]. Thus, in considering reactions of compounds such as 5-(trimethylsilyl)cyclopentadiene with metal carbonyls to form π complexes at elevated temperatures, due consideration must be given to the presence of 1- and/or 2-(trimethylsilyl)cyclopentadienes. Either of the two last structures ought to form π-complexes quite readily by loss of a methylene proton. However, we cannot rule out the possibility that 5-(trimethylsilyl)cyclopentadiene might also react by two distinctly different paths to form π-cyclopentadienyl complexes: (1) by separation of the $SiMe_3$ group from the ring; (2) by loss of the methylene H.

RESULTS AND DISCUSSION

We have now carried out thermal reactions of 5-(trimethylsilyl)cyclopentadiene with $Fe(CO)_5$ and $Mo(CO)_6$. In each reaction the structure of the observed product can be explained only if the reaction involves cleavage of H and not $SiMe_3$ from the ring. For example, the only product obtained after refluxing a mixture of 5-(trimethylsilyl)cyclopentadiene and $Fe(CO)_5$ in xylene was (III). While no evidence is available to support either direct formation of (III) or formation of (I) as an intermediate, we feel that the second path is a realistic one since analogs of (I), such as $(C_5H_5)Fe(CO)_2H$, are readily dimerized upon heating. However, the likelihood of (II) as an intermediate is not a distinct possibility inasmuch as (II) has been reported to be thermally stable to 200° [5].



In any event, no trace of any other conceivable products such as $(\pi\text{-}C_5H_5)_2Fe$, $(\pi\text{-}Me_3SiC_5H_4)Fe(\pi\text{-}C_5H_5)$, $(\pi\text{-}Me_3SiC_5H_4)_2Fe$, $(\pi\text{-}Me_3SiC_5H_4)[Fe(CO)_2]_2(\pi\text{-}C_5H_5)$ or $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ was detected. Anyone of these materials if present would have sublimed prior to (III) under the purification procedure employed.

The compound $[(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$ (IV) was obtained by heating a mixture of 5-(trimethylsilyl)cyclopentadiene and $Mo(CO)_6$ under nitrogen without a solvent for 30 h at 110°.

No other sublimable or identifiable products were obtained from the reaction. The failure to isolate an intermediate hydride, in this case $(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3H$, does not preclude its formation and conversion to (IV) under the experimental conditions. The product which might have arisen by cleavage of the silicon–ring bond, that is $(\pi\text{-}C_5H_5)Mo(CO)_3SiMe_3$, has been previously prepared and is known to be difficult to isolate[5]. In all of our attempts to prepare the last substance, we always obtained $[C_5H_5Mo(CO)_3]_2$, a material which was definitely not a product in the reaction between 5-(trimethylsilyl)cyclopentadiene and $Mo(CO)_6$.

Thus, the present results indicate that in thermal reactions of 5-(trimethylsilyl)-cyclopentadiene with metal carbonyls to form π complexes loss of a ring proton is the exclusive cleavage reaction. No evidence was seen to suggest occurrence of either cleavage of a silicon to ring bond or insertion of a metal into the carbon–silicon bond. However, the importance of this particular mode of cleavage in the lower temperature reactions of $Me_3SiC_5H_5$ with $(CH_3CN)_3M(CO)_3$ remains to be proven.

EXPERIMENTAL

Bis-{π-[(trimethylsilyl)cyclopentadienyl]iron dicarbonyl} (*III*)

A mixture of 0.98 ml (7.2 mmole) of iron pentacarbonyl and 1.0 g (7.2 mmole) of 5-(trimethylsilyl)cyclopentadiene in 15 ml of dry xylene was heated at reflux under nitrogen for 16 h. After filtration of the cool dark mixture and removal of the volatile liquids from the filtrate, a dark residue was obtained which yielded upon sublimation

(65–70°/10^{-3} mm) 0.5 g (36%) of (III) as a red solid, m.p. 97–99°. (Found: C, 48.08; H, 5.19; mol. wt. mass spectrometric, 498. $C_{20}H_{26}Fe_2O_4Si_2$ calcd.: C, 48.21; H, 5.26%; mol. wt., 498.)

PMR. 60 MHz, benzene solvent, TMS as internal standard at τ 10. $-SiMe_3$, singlet at 9.67 (rel. area 9); $-C_5H_4$, two apparent triplets (each has rel. area 2) between τ 5.85 and τ 5.35.

This new compound is slowly attacked by chlorinated solvents and is somewhat sensitive to light and air.

Bis-{[π-(trimethylsilyl)cyclopentadienyl]molybdenum tricarbonyl)} (*IV*)

A mixture of 3.75 g (14.4 mmole) of molybdenum hexacarbonyl and 2.0 g (14.4 mmole) of 5-(trimethylsilyl)cyclopentadiene was heated at 110° for 30 hours. After removal of the unreacted starting materials under high vacuum, 0.7 g (15%) of (IV) was obtained as an air and water stable, red solid, m.p. 156–158°, by vacuum sublimation (110°/10^{-3} mm). (Found: C, 41.87; H, 4.23; mol. wt. mass spectrometric, predicted isotope pattern over the range 626–642. $C_{22}H_{26}Mo_2O_6Si_2$ calcd.: C, 41.64; H, 4.13%; mol. wt., 634.)

PMR. 60 MHz, benzene solvent, TMS at τ 10). $-SiMe_3$, singlet at τ 9.84 (rel. area 9); $-C_5H_4$, two apparent triplets (each of relative area 2) between τ 5.10 and τ 4.80.

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