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PREPARATION OF (π-CYCLOPENTADIENYL)[π-TETRAKIS(TRIMETHYLSILYL)CYCLOBUTADIENE]COBALT

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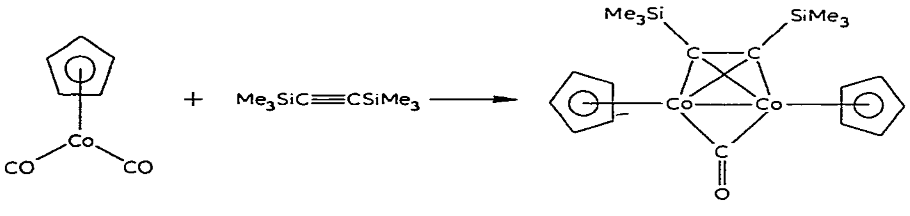
Summary

A (π-cyclopentadienyl)cobalt complex of tetrakis(trimethylsilyl)cyclobutadiene has been prepared by the reaction of bis(trimethylsilyl)acetylene and the dinuclear cobalt complex, di-π-cyclopentadienyl-μ-carbonyl-μ-bis(trimethylsilyl)-acetylenedicobalt.

Introduction

In a previous paper [1], we reported a new dinuclear cobalt complex (I) having both π-cyclopentadienyl and bis(trimethylsilyl)acetylene ligands. The complex (I) was obtained from π-cyclopentadienyldicarbonylcobalt and bis-(trimethylsilyl)acetylene in almost quantitative yield.

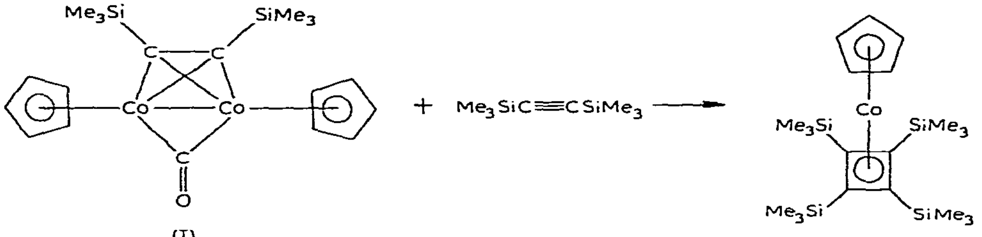


(I)

It is possible that (I) is a kind of intermediate in the formation of π-cyclobutadiene complexes from acetylene, since (I) was converted to $(\pi\text{-}C_5H_5)Co(\pi\text{-}Ph_4C_4)$ and $(\pi\text{-}C_5H_5)Co[\pi\text{-}cis\text{-}Ph_2C_2(Me_3Si)_2]$ by treatment with PhC≡CPh [1]. In this paper we report that under forcing conditions, (I) can be converted into the novel (π-cyclopentadienyl)[π-tetrakis(trimethylsilyl)cyclobutadiene]-cobalt (II) in the presence of an excess of bis(trimethylsilyl)acetylene.

Results and discussion

When a mixture of (I) and bis(trimethylsilyl)acetylene in 1/6 molar ratio dissolved in xylene was heated under nitrogen in an autoclave, (II) was obtained as yellow crystals in low yield.

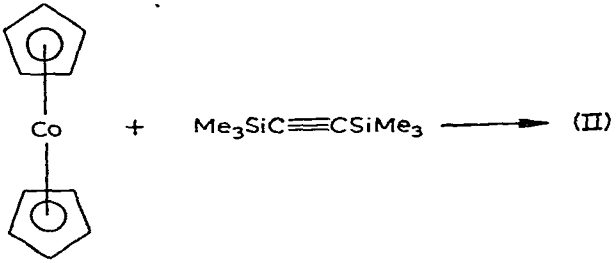


(I)

(II)

The structure of (I) was determined by elemental analysis, and mass and NMR spectra. As we have shown previously [1], the mass spectrum is particularly useful in the structural determination of a π-cyclobutadiene complex. The mass spectrum (75 eV, 80°) of (II) showed the following major peaks at m/e 464 (M^+, 16%), 294 (M^+—$Me_3SiC{\equiv}CSiMe_3$, 100%), 124 ($C_5H_5Co^+$, 9%), and 73 (Me_3Si^+, 32%), being in complete agreement with the assigned structure. The NMR spectrum (CS_2, cyclohexane) is very simple showing two singlets at δ 0.16 ppm (Me_3Si) and 5.17 ppm (C_5H_5).

After the successful isolation of pure (II), we examined the reaction of bis(trimethylsilyl)acetylene with cobaltocene, since the latter is known to react with diphenylacetylene to lead to (π-C_5H_5)Co(π-Ph_4C_4) [2, 3]. Under similar reaction conditions, cobaltocene was also converted to (II), although in extremely low yield.



The new complex (II) would be useful as a starting material to compounds such as hexakis(trimethylsilyl)benzene, although the yield of (II) is too low to permit further study of this possibility at this moment.

Experimental

Reaction of dicyclopentadienyl-μ-carbonyl-μ-bis(trimethylsilyl)acetylenedicobalt(I) with bis(trimethylsilyl)acetylene

A mixture of 1.35 g (3 mmoles) of (I) (ref. 1), 3.25 g (18 mmoles) of bis(trimethylsilyl)acetylene, and 10 ml of nitrogen-saturated *p*-xylene was placed in an autoclave under nitrogen. The mixture was heated by means of an oil bath at 200°C for 26.5 h, and then filtered. The solid obtained inflamed on access of air and was not studied further. The filtrate was evaporated under reduced pressure to give a yellow oil which was chromatographed on silica gel, and then subjected to preparative TLC with petroleum ether as an eluent to give pure (I) as yellow crystals (130 mg, 4.7% yield), m.p. 213 - 214°. (Found: C, 54.71; H, 8.99. $C_{21}H_{41}Si_4Co$ calcd.: C, 54.26; H, 8.89%.

Reaction of cobaltocene with bis(trimethylsilyl)acetylene

In the same manner, 3.19 g (17 mmoles) of freshly sublimed cobaltocene and 5.8 g (34 mmoles) of bis(trimethylsilyl)acetylene dissolved in 20 ml of *p*-xylene were heated at 180° for 43 h. Similar work-up, followed by preparative TLC, gave 96 mg (1.2% yield) of pure (II).

References

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3 J.F. Helling, S.C. Rennison, and A. Merijan, J. Amer. Chem. Soc., 89 (1967) 7140.