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

THE REACTION OF π-CYCLOPENTADIENYLDICARBONYLCOBALT WITH SILYL-SUBSTITUTED ACETYLENES

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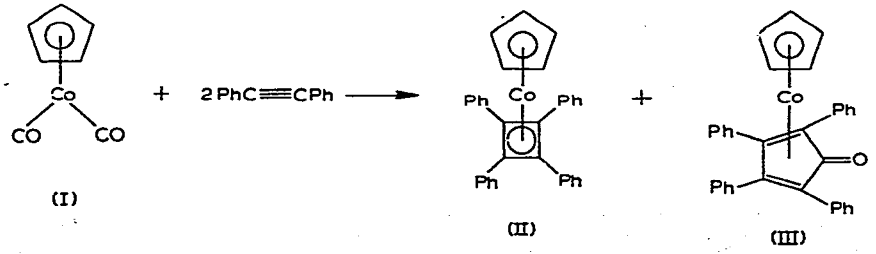
(Received January 4th, 1972)

SUMMARY

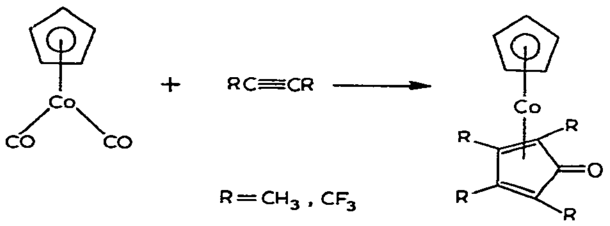
The reaction of $(\pi\text{-}C_5H_5)Co(CO)_2$ with $PhC{\equiv}CSiMe_2R$ ($R = Me, SiMe_3$) gave two isomeric cyclobutadiene complexes, *cis*- and *trans*-$(\pi\text{-}C_5H_5)Co[Ph_2C_4(SiMe_2R)_2]$, in almost quantitative yields. However, the reaction with $RMe_2SiC{\equiv}CSiMe_2R$ ($R = Me, Ph$) led to the formation of new dinuclear cobalt complexes. For example, with bis(trimethylsilyl)acetylene, $(\pi\text{-}C_5H_5)_2Co(CO)[(Me_3Si)_2C_2]$ was obtained quantitatively. The latter was further converted to $(\pi\text{-}C_5H_5)Co(Ph_4C_4)$ and $(\pi\text{-}C_5H_5)Co[\textit{cis}\text{-}Ph_2C_4(Me_3Si)_2]$ by treatment with $PhC{\equiv}CPh$. The physical properties and spectroscopic characteristics of these new compounds are described.

INTRODUCTION

Derivatives of π-cyclopentadienylcyclobutadienecobalt have been prepared by several routes[1-6]. The "direct" synthesis of π-cyclopentadienylcyclobutadiene complexes from π-cyclopentadienyldicarbonylcobalt (I) and acetylenes appeared to be the most simple and convenient, but the method has only been applied successfully to diphenylacetylene[6]. Thus, Rausch and Genetti prepared π-cyclopentadienyl(tetraphenylcyclobutadiene)cobalt (II) in 44–61% yield together with a small amount of π-cyclopentadienyl(tetraphenylcyclopentadienone)cobalt (III, ca. 10%) from (I) and diphenylacetylene:



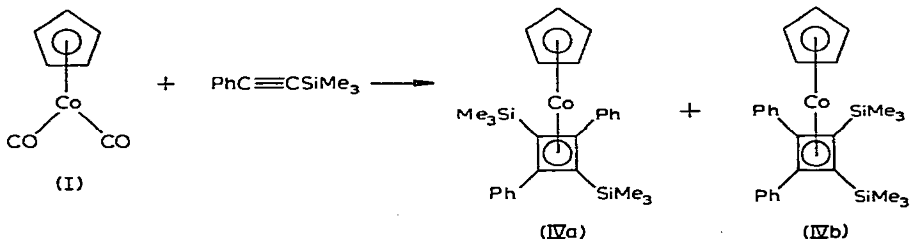
Application of this method failed, however, with other acetylenes such as 2-butyne[7] and hexafluoro-2-butyne[8,9], leading only to cyclopentadienone complexes:



In the course of studies on the properties and reactivities of organosilyl-substituted π-electron systems, we began an investigation of the reaction of (I) with silylacetylenes. We describe below a facile formation of cyclobutadiene complexes and new dinuclear cobalt complexes from silylacetylenes and (I).

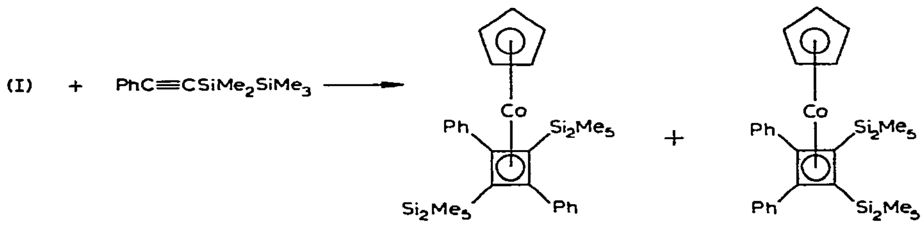
RESULTS AND DISCUSSION

π-Cyclopentadienyldicarbonylcobalt and (trimethylsilyl)phenylacetylene in a two-fold excess were refluxed together in xylene for 24 h under nitrogen at a bath temperature of 150–160°. After evaporation of volatile materials, an almost equimolar mixture of two isomeric cyclobutadiene complexes was obtained in nearly quantitative yield. These isomers, (IVa) and (IVb), were separated by preparative TLC and purified by recrystallization.



The structures of (IVa) and (IVb) were determined by mass spectra and X-ray crystallographic analysis. The mass spectrum (70 eV) of (IVa) showed the following major peaks at *m/e* 472 (M^+, 26%), 399 ($M^+ - \text{SiMe}_3$, 2%), 298 ($M^+ - \text{PhC}{\equiv}\text{CSiMe}_3$, 100%) and 124 ($\text{C}_5\text{H}_5\text{Co}^+$, 34%). The mass spectrum of (IVb) showed peaks at *m/e* 472 (M^+, 63%), 399 ($M^+ - \text{SiMe}_3$, 3%), 302 ($M^+ - \text{Me}_3\text{SiC}{\equiv}\text{CSiMe}_3$, 17%), 298 ($M^+ - \text{PhC}{\equiv}\text{CSiMe}_3$, 100%), 294 ($M^+ - \text{PhC}{\equiv}\text{CPh}$, 64%), and 124 ($\text{C}_5\text{H}_5\text{Co}^+$, 60%). Three kinds of acetylenes were released from the molecular ion of (IVb), whereas only a single acetylene was released from (IVa). Thus the *trans* structure for (IVa) and the *cis* structure for (IVb) can be assigned unequivocally. X-ray crystallography data confirmed these assignments and the results will be published separately[10]. NMR and IR spectra and elemental analyses were in agreement with the assigned structures.

(Pentamethyldisilanyl)phenylacetylene also gave two similar isomeric cyclobutadiene complexes on treatment with (I):



(Va) (Vb)

The mass spectra of (Va) and (Vb) were very complicated because of extensive fragmentations of the pentamethyldisilanyl entities, and so the structures could not be assigned unequivocally. However, the IR spectra of (IVa) and (IVb) in the fingerprint region were almost identical with those of (Va) and (Vb), respectively. Similarities in the NMR spectra as well as in behavior in TLC and GLC between (IVa) and (Va), and between (IVb) and (Vb) indicated *trans* and *cis* structures for (Va) and (Vb), respectively.

Physical properties, analyses, and spectroscopic data for (IVa), (IVb), (Va) and (Vb) are listed in Table 1.

TABLE 1

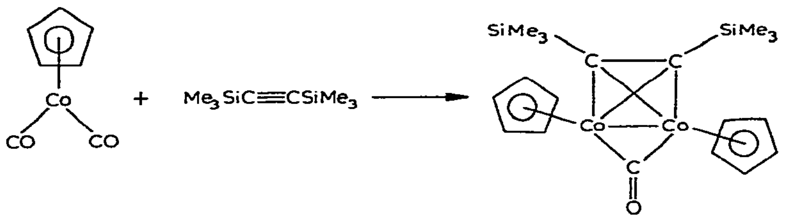
PROPERTIES OF NEW π-CYCLOPENTADIENYLCYCLOBUTADIENE COMPLEXES

Compound	*M.p.* (°C)[a]	*Analysis found (calcd.)* (%)		*NMR*[b]				*IR*[c] (*cm*$^{-1}$)
		C	*H*	*SiMe*$_3$	*SiMe*$_2$	π-C_5H_5	C_6H_5	
(IVa) *trans*	161–163	68.94 (68.61)	7.20 (7.04)	0.095 (s)		4.73 (s)	7.01 (m)	1595, 1489, 1442, 1245, 1108, 1070, 1022, 998
(IVb) *cis*	133–134	68.93 (68.61)	6.75 (7.04)	0.17 (s)		4.69 (s)	7.08 (m)	1598, 1513, 1496, 1443, 1245, 1105, 1070, 1000
(Va) *trans*	112–113	63.55 (63.22)	7.82 (7.70)	−0.12 (s)	0.11 (s)	4.82 (s)	7.10 (m)	1595, 1490, 1442, 1246, 1110, 1070, 1023, 1000
(Vb) *cis*	85–86	63.51 (63.22)	7.87 (7.70)	−0.06 (s)	0.02 (s)	4.77 (s)	7.07 (m)	1598, 1515, 1496, 1443, 1245, 1110, 1070, 1000

[a] Not corrected. [b] In CS_2; δ ppm [c] Only 1600–1000 cm^{-1} region was listed.

The very high yields of cyclobutadienecobalt complexes formed from (silyl)-phenylacetylenes encouraged us to examine the reaction of (I) with bis(trimethylsilyl)-acetylene. However, the reaction did not give the corresponding cyclobutadiene complex, but led to a new dinuclear cobalt complex (VI) in almost quantitative yield. The structure of (VI) was determined by C and H analyses and NMR, IR and mass spectra, (see the Experimental section). A carbonyl vibration at 1780 cm^{-1} was assigned to a bridged carbonyl. The complex (VI) is the first example of a dinuclear cobalt complex having both π-cyclopentadienyl and acetylene ligands. The complex (VI) is thermally stable up to 207°, but it decomposes slowly on exposure to air.

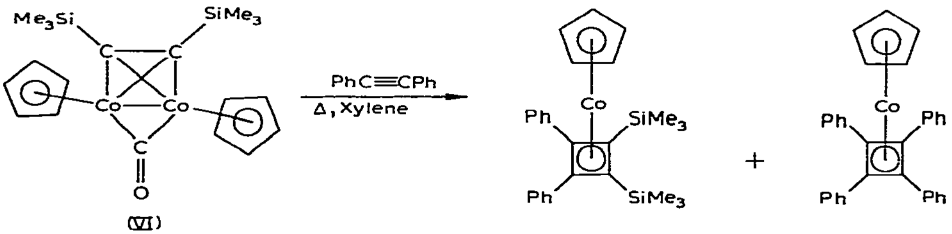
A similar dinuclear cobalt complex (VII) was obtained from bis(phenyldi-



(VI)

methylsilyl)acetylene, but it was very sensitive to air and has not been characterized further.

It is interesting to consider the possibility that dinuclear complexes such as (VI) may be intermediates in the reaction of (I) with acetylenes. Accordingly, we examined the reaction of (VI) with diphenylacetylene. A xylene solution of (VI) and a three equimolar quantity of diphenylacetylene was refluxed under argon for 19 h at a bath temperature of 150–160°. TLC examination of the reaction mixture indicated that two new complexes were present along with unchanged (VI). These were separated and were identified, respectively, as (IVb) and π-cyclopentadienyl(tetraphenylcyclobutadiene)cobalt (VIII). No *trans* isomer, (IVa), was obtained.



(VI) (IVb) (VIII)

EXPERIMENTAL

Related work is in progress, and will be described in a forthcoming paper.

All preparations were carried out under nitrogen or argon. B.p.'s and m.p.'s are uncorrected. NMR spectra were recorded by Mr. K. Sasaki with a Varian Associates HA-100 spectrometer.

(Trimethylsilyl)phenylacetylene

Trimethylchlorosilane (11 g, 0.1 mole) was added to a THF solution of phenylethynyllithium prepared from phenylacetylene (10.2 g, 0.1 mole) and lithium (765 mg, 0.11 mole). After work-up, 11.3 g (67% yield) of (trimethylsilylphenyl)acetylene was fractionated, b.p. 85°/6 mmHg (lit.[11] 87.5°/9 mmHg).

(Pentamethyldisilanyl)phenylacetylene

(Pentamethyldisilanyl)phenylacetylene was obtained analogously in 69% yield, b.p. 88–89°/1 mmHg; IR (neat); ν (cm^{-1}) 2150 (C≡C) and 1248 (Me–Si); NMR*

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* Recorded on a Varian Associates T-60 spectrometer.

(CS_2, cyclohexane, δ): 0.15 (9H, s, Me_3Si), 0.24 (6H, s, Me_2Si) and 9.37 ppm (5H, m, C_6H_5).

Bis(trimethylsilyl)acetylene

This was prepared from the acetylene di-Grignard reagent and trimethylchlorosilane in THF. Fractional distillation gave a pure liquid in 78% yield, b.p. 133–134° (lit.[12] 133–134°).

Bis(phenyldimethylsilyl)acetylene

This was prepared analogously in 72% yield, b.p. 142–143°/2 mmHg: IR (CS_2, solution); ν (cm^{-1}) 1250 (Me–Si); NMR* (CS_2, cyclohexane, δ), 0.36 (12H, s, Me_2Si) and 7.21–7.66 ppm (10H, m, C_6H_5).

π-Cyclopentadienyldicarbonylcobalt (I)

This was prepared by a published method[6] in 81–91% yield as a dark red liquid.

Reaction of (I) with (trimethylsilyl)phenylacetylene

A mixture of 4 g (23 mmoles) of (trimethylsilyl)phenylacetylene, 1.5 ml (ca. 10 mmoles) of (I), and 10 ml of xylene was placed in a 30 ml flask fitted with a reflux condenser and a nitrogen inlet tube. The mixture was flushed with nitrogen and refluxed for 24 h with a bath temperature of 150–160°. The solvent and unchanged (trimethylsilyl)phenylacetylene were evaporated off as completely as possible and the solid residue was chromatographed on a silica gel column (SiO_2, 40 g) with petroleum ether (b.p. 35–40°) as eluent. A mixture of (IVa) and (IVb) was obtained as red-orange crystals (4.35 g, 94.5% yield). Preparative TLC gave pure (IVa) and (IVb). These were recrystallized from ethanol or acetone. Physical properties are listed in Table 1**.

Reaction of (I) with (pentamethyldisilanyl)phenylacetylene

Similarly, a mixture of (Va) and (Vb) was obtained from (I) and (pentamethyldisilanyl)phenylacetylene in 76% yield. Pure (Va) and (Vb) were separated by preparative TLC and purified by recrystallization, (See Table 1).

Reaction of (I) with bis(trimethylsilyl)acetylene

Bis(trimethylsilyl)acetylene (2.4 g, 14 mmoles) and (I) (1 ml, ca. 7 mmoles) were refluxed in 10 ml of xylene for 26½ h as described above. The mixture was evaporated to dryness under reduced pressure, and the residual solid dissolved in petroleum ether. The solution was filtered under nitrogen using a Schlenk type apparatus. Subsequent cooling of the filtrate in a Dry Ice/methanol bath at −50° yielded (VI) as a black solid (1.5 g, 93% yield). (VI) decomposed at 207° without melting. The structure of (VI) was assigned from physical properties as follows: IR (CS_2 solution); (ν cm^{-1}) 1780 (C=O, bridging) and 1249 (Me_3Si); NMR (CS_2, cyclohexane, δ): 0.28 (18H, s, Me_3Si) and 4.56 ppm (10H, s, π-C_5H_5); mass (70 eV): M^+ at m/e 446. (Found: C, 51.18; H, 6.51. $C_{19}H_{28}OSi_2Co_2$ calcd.: C, 51.11; H, 6.32%.)

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* Note: see previous page.

** The formation of (IVa) and (IVb) from cobaltocene or π-cyclopentadienyl-1,5-cyclooctadienecobalt has been reported without any detail[13].

Reaction of (I) with bis(phenyldimethylsilyl)acetylene

By the same manner as above, 1.03 g (3.5 mmoles) of bis(phenyldimethylsilyl)-acetylene and 1 ml (ca. 7 mmoles) of (I) gave 0.448 g (22.5% yield) of $(\pi\text{-}C_5H_5)_2Co(CO)[(PhMe_2Si)_2C_2]$ (VII) as a black solid. (VII) was far more sensitive to air than (VI). The following spectral data indicate the structure: IR (CS_2 solution); (ν cm^{-1}) 1780 (C=O, bridging); NMR (CS_2, cyclohexane, δ): 0.51 (12H, s, Me_2Si), 4.37 (10H, s, $\pi\text{-}C_5H_5$) and 7.44 ppm (10H, m, Ph).

Reaction of (VI) with diphenylacetylene

Diphenylacetylene (270 mg, 1.5 mmoles) and the complex (VI) (225 mg, 0.5 mmole) were dissolved in 10 ml of xylene and the solution was refluxed for 19 h. After evaporation of the solvent, the residual solid was extracted with ether. After work-up, the resulting yellowish solid mixture was subjected to preparative TLC with petroleum ether as an eluent. The first eluted band was collected and the compound was identified as (IVb) (45 mg, 19% yield). GLC examination revealed that no (IVa) was present as contaminant. The second eluted band was then identified as π-cyclopentadienyl(tetraphenylcyclobutadiene)cobalt (VIII) (140 mg, 56% yield), m.p. 258–260° (lit.[1] 256°; lit.[2] 264°; lit.[6] 262–264°).

ACKNOWLEDGEMENT

We are indebted to the Toshiba Silicone Co., Ltd. for a gift of chlorosilanes.

REFERENCES

1 A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, 31 (1961) 452; *Nippon Kagaku Zasshi*, 84 (1963) 339.
2 J. L. Boston, D. W. Sharpe and G. Wilkinson, *J. Chem. Soc.*, (1962) 3488.
3 P. M. Maitlis and M. L. Games, *J. Amer. Chem. Soc.*, 85 (1963) 1887; P. M. Maitlis, A. Efraty and M. L. Games, *J. Organometal. Chem.*, 2 (1964) 284; *J. Amer. Chem. Soc.*, 87 (1965) 719; A. Efraty and P. M. Maitlis, *J. Amer. Chem. Soc.*, 89 (1967) 3744; R. Bruce and P. M. Maitlis, *Can. J. Chem.*, 45 (1967) 2017.
4 R. G. Amiet and R. Pettit, *J. Amer. Chem. Soc.*, 90 (1968) 1059.
5 M. Rosenblum and B. North, *J. Amer. Chem. Soc.*, 90 (1968) 1060.
6 M. D. Rausch and R. A. Genetti, *J. Amer. Chem. Soc.*, 89 (1967) 5502; *J. Org. Chem.*, 35 (1970) 3888.
7 R. Markby, H. W. Sternberg and I. Wender, *Chem. Ind. (London)*, (1959) 1381.
8 R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, (1964) 2699.
9 M. Gerlock and R. Mason, *Proc. Chem. Soc.*, (1963) 107; *Proc. Roy. Soc., Ser. A*, 279 (1964) 170.
10 C. Kabuto, Y. Kitahara, J. Hayashi and H. Sakurai, to be published.
11 A. D. Petrov, L. L. Schukovskaya and Yu. P. Egorrov, *Dokl. Akad. Nauk SSSR*, 93 (1953) 293; *Chem. Abstr.*, 48 (1954) 13616.
12 K. C. Frisch and R. B. Young, *J. Amer. Chem. Soc.*, 74 (1952) 4853.
13 J. F. Helling, S. C. Rennison and A. Merijan, *J. Amer. Chem. Soc.*, 89 (1967) 7140.