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REACTIONS OF (TRIMETHYLSILYL)CYCLOPENTADIENE WITH METAL CARBONYLS

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SUMMARY

The reactions of (trimethylsilyl)cyclopentadiene with a range of metal carbonyls afforded π-[(trimethylsilyl)cyclopentadienyl]metal carbonyls. The only evidence for the cleavage of the silicon–cyclopentadiene bond occurs in the reaction with manganese decacarbonyl. The compounds $[(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$ (I), $[(\pi\text{-}Me_3SiC_5H_4)W(CO)_3]_2$ (II), $(\pi\text{-}Me_3SiC_5H_4)Mn(CO)_3$ (III), $(\pi\text{-}Me_3SiC_5H_4)Re(CO)_3$ (IV), $[(\pi\text{-}Me_3SiC_5H_4)Fe(CO)_2]_2$ (V), $(\pi\text{-}Me_3SiC_5H_4)Fe(\pi\text{-}C_5H_5)$ (VI) and $(\pi\text{-}Me_3SiC_5H_4)Co(CO)_2$ (VII) are described.

INTRODUCTION

The reaction of (trimethylstannyl)cyclopentadiene with metal carbonyls has been reported recently[1]. In such reactions the tin–cyclopentadiene bond invariably undergoes cleavage. Recently the complexes $[(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$ and $[(\pi\text{-}Me_3SiC_5H_4)Fe(CO)_2]_2$ were described[2], and prompt us to report our own findings. Apart from minor changes in colour and other physical properties, the products appear to be exactly analogous in structural characteristics to the unsubstituted π-cyclopentadienyl carbonyl complexes of each metal.

RESULTS AND DISCUSSION

The thermal reactions between (trimethylsilyl)cyclopentadiene and the neutral binary metal carbonyls result in products where the silicon–ring bond remains intact, except in the case of manganese carbonyl, where some product of a silicon–ring cleavage is isolated.

Cobalt carbonyl and (trimethylsilyl)cyclopentadiene undergo reaction at ~40° to produce a good yield of π-[(trimethylsilyl)cyclopentadienyl]cobalt dicarbonyl.

$$2\,Me_3SiC_5H_5 + Co_2(CO)_8 \xrightarrow{40°} 2(\pi\text{-}Me_3SiC_5H_4)Co(CO)_2 + 4\,CO + H_2(?) \quad (1)$$

$$\mathrm{2\,Me_3SiC_5H_5 + Co_2(CO)_8 \xrightarrow{175^\circ} (\pi\text{-}Me_3SiC_5H_4)Co(CO)_2 + (\pi\text{-}Me_3SiC_5H_6)Co(CO)_3 + 3\,CO} \tag{2}$$

$$\mathrm{Me_3SiC_5H_5 + Co(CO)_4H \rightarrow (\pi\text{-}Me_3SiC_5H_6)Co(CO)_3 + CO} \tag{3}$$

When this reaction was repeated at 175°, the yield of $(\pi\text{-}Me_3SiC_5H_4)Co(CO)_2$ was somewhat reduced, but no product of silicon–ring fission was detectable. An additional product, however, was formed and appears to be π-[(trimethylsilyl)-cyclopentenyl]cobalt tricarbonyl [eqn. (2)]. This product was also synthesised from cobalt tetracarbonyl hydride and (trimethylsilyl)cyclopentadiene, using the known[3] hydride 1,3-diene synthesis for comparison [eqn. (3)].

Reactions (1) and (2) may also involve cobalt tetracarbonyl hydride in their actual mechanisms.

Iron pentacarbonyl and (trimethylsilyl)cyclopentadiene form bis{π-[trimethylsilyl)cyclopentadienyl]iron dicarbonyl} in excellent yield

$$\mathrm{2\,Me_3SiC_5H_5 + 2\,Fe(CO)_5 \rightarrow [(\pi\text{-}Me_3SiC_5H_4)Fe(CO)_2]_2 + 6\,CO + H_2(?)} \tag{4}$$

This compound has previously[2] been reported (m.p. 97–99°) to be sensitive to air and light. In our hands (m.p. 107°) it appears stable to air and normal room lighting for over two years.

The analogous dimeric products are formed from similar reactions with molybdenum and tungsten hexacarbonyls.

$$\mathrm{2\,M(CO)_6 + 2\,Me_3SiC_5H_5 \rightarrow [(\pi\text{-}Me_3SiC_5H_4M(CO)_3]_2 + 6\,CO + H_2(?)} \tag{5}$$

$M = Mo, W$

Whilst rhenium decacarbonyl and (trimethylsilyl)cyclopentadiene form only the π-[(trimethylsilyl)cyclopentadienyl]rhenium tricarbonyl, the corresponding reaction with manganese decacarbonyl takes two paths, one (7) in which the silicon–ring bond remains intact, and the other (8) in which silicon–ring fission takes place.

$$\mathrm{Re_2(CO)_{10} + 2\,Me_3SiC_5H_5 \rightarrow 2\,(\pi\text{-}Me_3SiC_5H_4)Re(CO)_3 + 4\,CO + H_2(?)} \tag{6}$$

$$\mathrm{Mn_2(CO)_{10} + 2\,Me_3SiC_5H_5 \rightarrow 2\,(\pi\text{-}Me_3SiC_5H_4)Mn(CO)_3 + 4\,CO + H_2(?)} \tag{7}$$

$$\mathrm{Mn_2(CO)_{10} + Me_3SiC_5H_5 \rightarrow Me_3SiMn(CO)_5 + (\pi\text{-}C_5H_5)Mn(CO)_3 + 2\,CO} \tag{8}$$

Why manganese carbonyl should be unique in causing such a fission reaction under these conditions is not clear at this time.

The predominant product from the reaction of bis(π-cyclopentadienyliron dicarbonyl) and (trimethylsilyl)cyclopentadiene is (trimethylsilyl)ferrocene, but the isolation of small quantities of ferrocene and bis(trimethylsilyl)ferrocene reflects the complexity of the reaction at the high temperature used.

$$\mathrm{[(\pi\text{-}C_5H_5Fe(CO)_2]_2 + 2\,Me_3SiC_5H_5 \rightarrow 2\,Me_3SiC_5H_4FeC_5H_5 + 4\,CO + H_2(?) + (C_5H_5)_2Fe + (Me_3SiC_5H_4)_2Fe} \tag{9}$$

In contrast to the metal carbonyls, the metal carbonyl halides cause fission of the silicon–ring bond to afford the π-cyclopentadienylmetal carbonyls, as for example in the case of manganese and rhenium.

$$Me_3SiC_5H_5 + M(CO)_5X \rightarrow (\pi\text{-}C_5H_5)M(CO)_3 + Me_3SiX + 2\,CO \qquad (10)$$
$$M = Mn, Re$$

EXPERIMENTAL

Reaction of cobalt octacarbonyl and (trimethylsilyl)cyclopentadiene

Dicobalt octacarbonyl (3.42 g) and (trimethylsilyl)cyclopentadiene (10 ml) were heated under reflux in diethyl ether (20 ml) for 1 h. After filtration, ether and excess (trimethylsilyl)cyclopentadiene were removed under reduced pressure. The red liquid residue was sublimed in a small molecular still to yield π-[(trimethylsilyl)-cyclopentadienyl]cobalt dicarbonyl [2.80 g, 56%]. No other carbonyl containing products were isolated under these conditions.

In a further experiment, to (trimethylsilyl)cyclopentadiene (2.0 g) in diglyme under reflux was added dropwise dicobalt octacarbonyl (0.70 g) in diglyme (20 ml) over a period of 3 h. Diglyme was removed from the clear red solution by water washing, and the residue taken up in ether. After drying and removal of solvent, the residue was chromatographed on silica with pentane. The first yellow band (0.26 g) was followed by pure red π-[(trimethylsilyl)cyclopentadienyl]cobalt dicarbonyl (0.46 g, 46%).

The yellow product was characterised as π-[(trimethylsilyl)cyclopentenyl]-cobalt tricarbonyl, and was also synthesised directly from (trimethylsilyl)cyclopentadiene and cobalt tetracarbonyl hydride.

TABLE 1

CHARACTERISATION OF π-[(TRIMETHYLSILYL)CYCLOPENTADIENYL]METAL CARBONYLS

Compound	Yield (%)	M.p. (°C)	Analytical data, found (calcd.)			
			C (%)	H (%)	Metal (%)	Mol.wt.
$[(\pi\text{-}Me_3SiC_5H_4)Mo(CO)_3]_2$	46	177–182	41.2 (41.5)	4.11 (4.10)		644 (634)
$[(\pi\text{-}Me_3SiC_5H_4)W(CO)_3]_2$	51	198–200	32.7 (32.6)	3.21 (3.20)		783 (810)
$(\pi\text{-}Me_3SiC_5H_4)Mn(CO)_3$[a]		Liq.	48.0 (47.8)	4.80 (4.71)	20.3 (19.9)	286 (276)
$(\pi\text{-}Me_3SiC_5H_4)Re(CO)_3$	87	58.5	32.5 (32.4)	3.22 (3.18)	45.8 (45.9)	415 (408)
$[(\pi\text{-}Me_3SiC_5H_4)Fe(CO)_2]_2$	75	106–107	48.3 (48.2)	5.35 (5.23)	22.5 (22.5)	500 (498)
$(\pi\text{-}Me_3SiC_5H_4)Co(CO)_2$	56	Liq.	47.2 (47.6)	4.98 (5.15)		263 (252)

[a] Cleavage of the silicon–cyclopentadiene bond is also observed, to afford $Me_3SiMn(CO)_5 + C_5H_5Mn(CO)_3$.

Reaction of iron carbonyl and (trimethylsilyl)cyclopentadiene

Iron pentacarbonyl (1.96 g) and (trimethylsilyl)cyclopentadiene (10 ml) were heated together at 110°/12 h. Subsequently all volatile materials were removed at 40°/0.1 mm, and the purple residue recrystallized from hexane to produce dark red needles of bis{π-[(trimethylsilyl)cyclopentadienyl]iron dicarbonyl} (1.88 g, 75%), m.p. 107° (under nitrogen).

Reaction of molybdenum carbonyl and (trimethylsilyl)cyclopentadiene

Molybdenum hexacarbonyl (2.60 g) and (trimethylsilyl)cyclopentadiene (8 ml) were heated together under reflux for 4 h. Excess of (trimethylsilyl)cyclopentadiene and unreacted molybdenum hexacarbonyl were removed at 40°/0.1 mm leaving a dark red oil. This was transferred to a Soxhlet extractor and extracted with cyclohexane until the extract was no longer red. From the cooled cyclohexane crystallized red needles of bis{[(trimethylsilyl)cyclopentadienyl]molybdenum tricarbonyl}. (1.44 g, 46%), m.p. 177–182°.

Reaction of tungsten carbonyl and (trimethylsilyl)cyclopentadiene.

Tungsten hexacarbonyl (3.52 g) and (trimethylsilyl)cyclopentadiene (10 ml) were heated under reflux until no further white tungsten carbonyl sublimed out of the reaction mixture. Excess of (trimethylsilyl)cyclopentadiene and unreacted tungsten hexacarbonyl were removed at 40°/0.1 mm over several hours. The sticky semi-solid residue was transferred to a Soxhlet extractor and extracted with cyclohexane until the extract was no longer coloured. Red crystalline needles of bis{π-[(trimethylsilyl)-cyclopentadienyl]tungsten tricarbonyl} (2.07 g, 51%), m.p. 198–200°, were deposited from the cooled solvent.

TABLE 2

INFRARED AND NUCLEAR MAGNETIC RESONANCE DATA ON THE π-[(TRIMETHYLSILYL)CYCLOPENTADIENYL] METAL CARBONYLS

Compound	τ(SiMe$_3$)[a] (ppm)	τ(C$_5$H$_4$)[a] (ppm)	ν(CO)[b] (cm^{-1})
$[(\pi\text{-Me}_3\text{SiC}_5\text{H}_4)\text{Mo(CO)}_3]_2$	9.83	4.82 (triplet)	2016 (0.3), 1958 (10)
		4.92 (triplet)	1919 (8.1), 1908 (4.6)
$[(\pi\text{-Me}_3\text{SiC}_5\text{H}_4)\text{W(CO)}_3]_2$	9.82	4.70 (triplet)	2013 (0.1), 1954 (10)
		4.88 (triplet)	1900 (8.4), 1895 (4.9)
$(\pi\text{-Me}_3\text{SiC}_5\text{H}_4)\text{Mn(CO)}_3$	9.82	5.33 (sharp singlet)	2024 (8.0), 1943 (10)
$(\pi\text{-Me}_3\text{SiC}_5\text{H}_4)\text{Re(CO)}_3$	9.85	4.78 (sharp singlet)	2027 (6.5), 1937 (10)
$[(\pi\text{-Me}_3\text{SiC}_5\text{H}_4)\text{Fe(CO)}_2]_2$	9.73	5.28 (triplet)	2000 (7.6), 1958 (8.7)
		5.69 (triplet)	1786 (10)
$(\pi\text{-Me}_3\text{SiC}_5\text{H}_4)\text{Co(CO)}_2$	9.83	4.96 (triplet)	2025 (10), 1966 (9.1)
		5.26 (triplet)	

[a] Measured on Varian HA 100 in CS$_2$ with signal locked on benzene. [b] Solvent cyclohexane.

Reaction of rhenium carbonyl and (trimethylsilyl)cyclopentadiene

Rhenium decacarbonyl (1.31 g) and (trimethylsilyl)cyclopentadiene (8 ml) were heated together under reflux for 30 h, On cooling, excess of (trimethylsilyl)-cyclopentadiene was removed at 20°/0.01 mm and the semisolid residue was shown to be free of rhenium decacarbonyl by infrared spectroscopy. Sublimation onto a probe maintained at −80° yielded π-[(trimethylsilyl)cyclopentadienyl]rhenium tricarbonyl (1.42 g, 87%), m.p. 58–59°. The product could be recrystallised from hexane to provide a sample of slightly sharper melting point (58.5°).

Reaction of manganese carbonyl and (trimethylsilyl)cyclopentadiene

Manganese decacarbonyl (1.95 g) and (trimethylsilyl)cyclopentadiene (5 ml) in diglyme (10 ml) were heated under reflux in a bath at 160° for 8 h. The diglyme was removed by water washing and then (trimethylsilyl)manganese pentacarbonyl was removed by distillation and characterized by infrared, nuclear magnetic and mass spectrometries. The resulting mixture of π-cyclopentadienylmanganese tricarbonyl and π-[(trimethylsilyl)cyclopentadienyl]manganese tricarbonyl were separated by chromatography in hexane on silica; π-[(trimethylsilyl)cyclopentadienyl]manganese tricarbonyl was only isolated in about 10% yield for this experiment.

The experiment was repeated at a number of higher temperatures up to 260° and in all cases both substitution and cleavage type reactions occurred. It is estimated that at all temperatures the overall reaction comprised cleavage ~60% and substitution ~40%.

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