Migration of SnPh$_3$ from metal to Cp in a cobalt cyclopentadienyl complex: preparation of [Co{C$_5$H$_3$(SnPh$_3$)$_2$}(CO)$_2$] under mild conditions

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Abstract

The complex [Co{C$_5$H$_3$(SnPh$_3$)$_2$}(CO)$_2$] is obtained in good yield from [Co(Cp)(CO)$_2$] and SnHPh$_3$ in hexane under carbon monoxide at ambient temperature and pressure: a monosubstituted product can also be isolated. An intermediate, formulated as [Co(Cp){(μ-H)SnPh$_3$}(CO)], is involved in the reaction.

Key words: Cobalt; Tin

1. Introduction

The migration of a group ER$_3$ (E = Si, Ge; R = Me, Ph) from a transition metal to a coordinated cyclopentadienyl (Cp) ligand occurs readily in a number of complexes of Mo, W, Re, Fe and Ru, but requires the participation of an organolithium reagent. Lithiation of the Cp leads to a rapid shift of ER$_3$ from the metal to the Cp and the formation of an anionic metal complex with the ligand C$_5$H$_4$ER$_3$ [1–7]. Mechanistic studies of the migration of the silyl group in the complexes [Fe(Cp)(SiMe$_2$R)(CO)$_2$] have shown the reaction to be intramolecular, the mechanism probably involving deprotonation of the Cp followed by silyl group migration utilising a silicon d orbital [8,9]. To our knowledge this effect has not been reported for complexes containing the ligand SnR$_3$, and was not detected under conditions that favour the migration of GeR$_3$ [2]. Furthermore, such migration is unknown for any group ER$_3$ (E = Si,Ge,Sn) in the absence of a strong base.

We report the derivatisation of a Cp ligand with SnPh$_3$, by an apparently intramolecular reaction that takes place spontaneously in the presence of carbon monoxide.

2. Experimental details

The complex [Co(Cp)(CO)$_2$] was prepared from [Co$_2$(CO)$_8$] by the method described by Rausch and Genetti [10]. [Co$_2$(CO)$_8$] and SnHPh$_3$ were purchased from Merck and Aldrich, respectively. Dichloromethane was distilled from P$_2$O$_5$ and benzene and hexane were dried over CaH$_2$. Petroleum ether (40–60) and *n*-hexane were of the highest available purity and were used as supplied. Silica gel used for chromatographic separations was 70–230 mesh. All operations were performed under carbon monoxide, or, where appropriate, nitrogen. NMR spectra were recorded on a Bruker AC 200 FT spectrometer at 200.13 MHz (^{1}H), 74.63 MHz (^{119}Sn) and 50.32 MHz (^{13}C); IR spectra were recorded on a Jasco FT/IR-5000 spectrometer.

2.1. Preparation of [Co{C$_5$H$_3$(SnPh$_3$)$_2$}(CO)$_2$]

A mixture of [Co(Cp)(CO)$_2$] (0.190 g, 1.06 mmol) and SnHPh$_3$ (0.755 g 2.15 mmol) in hexane (10 ml) under carbon monoxide (atmospheric pressure) was kept at room temperature in the absence of light for 3 days. After approximately 1 day, crystallisation began to occur, with the formation of yellow-orange crystalline lumps. Recrystallisation from CH$_2$Cl$_2$/hexane gave the product as air-stable yellow crystals of the CH$_2$Cl$_2$ solvate (0.714 g, 0.741 mmol, 70%). Anal. Found: C,54.8; H,3.9. C$_{44}$H$_{35}$Cl$_2$CoO$_2$Sn$_2$ calcd: C,54.9; H,3.7%. IR (Nujol mull): ν(CO) 1974, 1928 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 22°C), δ 7.85–7.1 (multiplets, 30H, phenyl); 4.93 (broad, 2H, Cp); 4.33 (t, 1H, J 3.3 Hz, Cp). ^{13}C NMR (C$_6$D$_6$, 22°C): δ 197.3 {J(^{119}Sn–^{13}C) $\simeq J$(^{117}Sn–^{13}C) = 116 Hz (Cp, C–Sn)}; 142.4, 137.3, 129.0, 128.9 (Ph); 88.2 {J(^{119}Sn–^{13}C) $\simeq J$(^{117}Sn–^{13}C) = 8.7 Hz (Cp)}; 74.6 (Cp). ^{119}Sn NMR (C$_6$D$_6$, 22°C); δ

23.4 (SnMe$_4$ ext. standard, positive δ to high frequency).

2.2. Preparation of [Co{C₅H₄(SnPh₃)}(CO)₂]

A mixture of [Co(Cp)(CO)$_2$] (0.15 g, 0.83 mmol) and SnHPh$_3$ (0.29 g, 0.83 mmol) in benzene (7 ml, deoxygenated with CO) in a vessel filled with nitrogen at atmospheric pressure (giving a gas mixture of about 5–10% CO/N$_2$) was kept at room temperature for 24 h. The red-orange solution was concentrated to approximately 0.7 ml and chromatographed on silica gel under CO; elution was first with petroleum ether to remove unchanged [Co(Cp)(CO)$_2$], then with 1:4 benzene:petroleum ether, which gave a yellow fraction. This was concentrated to approximately 2 ml (under CO), hexane was added, and the solution again concentrated and kept at −20°C to give yellow crystals. The solution was centrifuged to remove a light brown powder, concentrated to approximately 0.5 ml, and again kept at −20°C to give a second, larger, crop of yellow crystals. The product was washed with hexane (about 0.5 ml, in which it is moderately soluble). Yield 0.025 g (0.045 mmol 6%). Anal. Found: C,55.9; H,3.9. C$_{25}$H$_{19}$CoO$_2$Sn calcd: C,56.8; H,3.6%. IR (Nujol mull): ν(CO) 2008, 1964 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 22°C): δ 7.9–7.1 (multiplets, 15H, phenyl); 5.15 (mult, 2H, Cp); 3.46 (mult, 2H, Cp).

3. Results and discussion

The compound [Co{C₅H₃(SnPh₃)₂}(CO)₂] (1) is formed by the reaction of [Co(Cp)(CO)₂] and SnHPh₃ in hexane under carbon monoxide at ambient temperature and pressure, crystallising out slowly during 2–3 days. Recrystallisation from CH$_2$Cl$_2$/hexane (under

N$_2$) affords yellow crystals of the CH$_2$Cl$_2$ solvate in 70% yield. The ^{1}H NMR spectrum shows a broadened signal (2H) and a triplet (1H) from the Cp protons, while the ^{13}C{^{1}H} spectrum contains a signal at δ 197.3 from the ring carbons bonded to tin (no signal is observed from the carbonyls).

When a mixture of [Co(Cp)(CO)₂] and SnHPh₃ in benzene is kept under N$_2$, only traces of 1 are detected, the major product containing an unsubstituted Cp ring (^{1}H = 4.45 ppm) and giving a signal in the highfield region of the ^{1}H spectrum. This compound accounts for some 10–20% of the mixture, the remainder being unchanged [Co(Cp)(CO)₂] together with a small amount (increasing during several days) of a monosubstituted compound (see below). The highfield singlet (δ − 13.93) has satellites integrating for approximately 15% of the signal, with $J(^{119}\text{Sn}-^1\text{H}) \approx J(^{117}\text{Sn}-^1\text{H}) = 162$ Hz. The magnitude of the Sn–H coupling constant suggests that the oxidative addition of SnHPh$_3$ to cobalt is incomplete, and that a (weakened) bond still exists between tin and hydrogen: complexes in which SnR$_3$ (R = alkyl, aryl) and hydride are bound as separate ligands show a smaller J(Sn–H) constant coupling, normally in the range of approximately 25–45 Hz [11–15]. The product is therefore assigned the structure 2 (Scheme 1). This formulation is supported by the fact that the analogous chromium and manganese complexes [Cr(C₆H₃Me₃){(μ-H)SnPh₃}(CO)₂] {$J(^{119}\text{Sn}-^1\text{H}) = 327.6$ Hz} [16] and [Mn(C₅H₄Me){(μ-H)SnPh₃}(CO)₂] {$J(^{119}\text{Sn}-^1\text{H}) = 270$ Hz} [17] both exhibit the agostic [18] three-centre bonding interaction proposed for 2, as do the complexes [Mo(Cp)₂{(μ-H)SnMe₃}] {$J(^{119}\text{Sn}-^1\text{H}) = 148$ Hz} [19] and [RhH{(μ-H)SnPh₃}₂(PPh₃)] {$J(^{119}\text{Sn}-^1\text{H}) = 170$ Hz} [14]. Compound 2 can be isolated as an impure yellow-orange oil
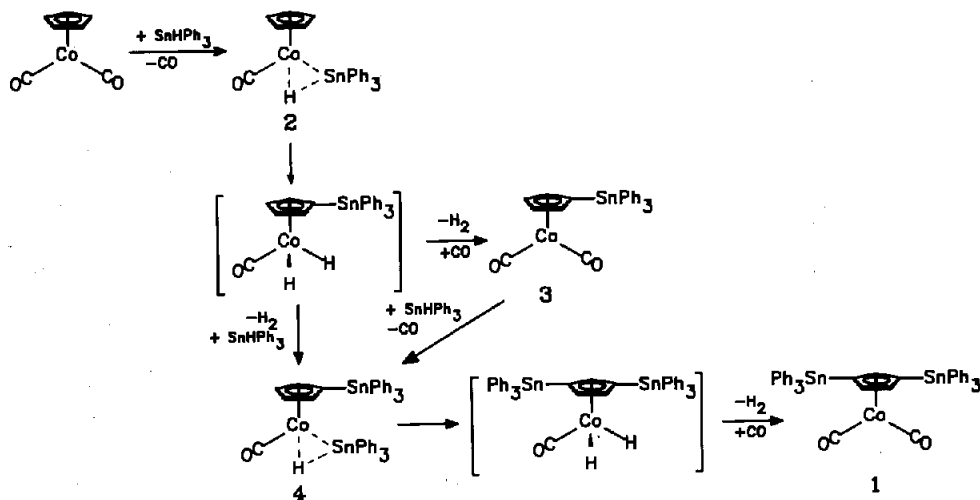
Scheme 1.

by chromatography on silica gel under carbon monoxide, but resists attempts at further purification. In solution under nitrogen it decomposes (probably for the same reason as does [Co(Cp)I₂(Co)] [20], which breaks down readily in the absence of CO), while under carbon monoxide it is converted in a product **3** (Scheme 1) containing a monosubstituted Cp. This product [Co{C₅H₄(SnPh₃)}(CO)₂], (**3**), can be made in low yield (6%) from [Co(Cp)(CO)₂] and SnHPh₃ when the reaction is carried out under nitrogen containing about 5–10% of CO. Chromatography on silica gel under CO yields a fraction from which **3** can be isolated as yellow crystals. The ^{1}H spectrum of **3** contains two multiplets (each 2H) consistent with the AA'BB' pattern expected for an achiral monosubstituted cyclopentadienyl complex.

The conversion of **3** into **1** (Scheme 1) requires an intermediate [Co{C₅H₄(SnPh₃)}{(μ-H)SnPh₃}(CO)] (**4**), formed from **3** by partial oxidative addition of SnHPh₃. Evidence for this compound, present in low concentration in a mixture of **3** and an excess (approximately ten-fold) of SnHPh₃ in C₆D₆, was provided by the ^{1}H NMR spectrum, which showed a hydride resonance at −13.93 ppm. In this reaction **3** is converted steadily into **1** (under nitrogen), the process being complete within 4 h at 22°C.

Carbon monoxide therefore appears to accelerate the conversion of **2** into **3**, but to be of less importance in the conversion of **3** to **1**. The reasons for this are likely to be related to the temporary halting of the rotation of the Cp ring, which is expected to be a requirement of the migration process.

The reaction sequence depicted in Scheme 1 involves a successive (partial) oxidative addition of SnHPh₃ and reductive elimination of H₂ (from the unstable (and undetected) intermediates shown in brackets), with intervening steps in which tin is transferred from cobalt to a Cp carbon in exchange for a hydrogen. This transfer may proceed via a transition state such as that shown in Fig. 1, in which the ability of cyclopentadiene to coordinate to a metal in either an η^5 or an η^4 mode [21,22] allows one carbon to bind
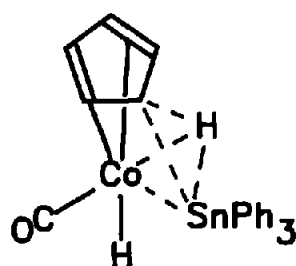

Fig. 1. Transition state.

simultaneously to both hydrogen and tin, thus permitting the migration of tin to the Cp ring. The agostic binding of SnHPh₃ to cobalt may be an important factor in the process; when the tin-transition metal bond order is low the tin may more readily interact with other ligands (in this case Cp), giving rise to effects such as that observed in the case of [RhH{(μ-H)SnPh₃}₂(PPh₃)₂] [14], where rapid relocation of SnPh₃ groups among hydrides bound to rhodium allows one terminal hydride and two bridging hydrides to be seen (by ^{1}H NMR spectroscopy) as equivalent at ambient temperature.

With SnH^{n}Bu₃, SiHPh₃ or CHPh₃ in place of SnHPh₃ there is no reaction with [Co(Cp)(CO)₂].

Acknowledgments

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