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Convenient syntheses of [$RuCl(CO)_2(Cp)$] and [$OsCl(CO)_2(Cp)$]

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Abstract

[$RuCl(CO)_2(Cp)$] (1) is obtained in two simple steps from [$RuCl_3(H_2O)_x$]. [$RuCl_2(CO)_3$]$_2$, produced by refluxing [$RuCl_3(H_2O)_x$] in hydrochloric and formic acids, reacts cleanly with [$SiMe_3(C_5H_5)$] to give [$RuCl(CO)_2(Cp)$] (1) in 74% overall yield from [$RuCl_3(H_2O)_x$]. [$OsCl(CO)_2(Cp)$] (2) is similarly obtained in four steps from [OsO_4]. Known conversion of [OsO_4] to [NH_4]$_2$[$OsCl_6$], reduction to [$OsCl_3$] and carbonylation to [$OsCl_2(CO)_3$]$_2$ in a tube furnace, and finally reaction with [$SiMe_3(C_5H_5)$] give [$OsCl(CO)_2(Cp)$] (2) in 26% overall yield from [OsO_4]. These preparations are a significant improvement over previous published methods, avoiding the intermediacy of [$M_3(CO)_{12}$].

Key words: Ruthenium; Osmium; Cyclopentadienyl; Carbonyl; Chloride; Nuclear magnetic resonance

1. Introduction

The [$Fe(CO)_2(Cp)$] (Fp) moiety is one of the most widely utilized transition metal functional groups in organometallic chemistry [1,2]. Many Fp compounds are obtained by reacting nucleophiles with the halides [$FeX(CO)_2(Cp)$] (X = Cl, Br, I). The congeneric ruthenium and osmium systems are much less developed, because the metal precursors are more expensive and the previously reported preparations of the halides [$MX(CO)_2(Cp)$] (M = Ru, Os) are much less convenient than for iron [3]. [$RuCl(CO)_2(Cp)$] has been previously prepared in satisfactory yield by:

a. chlorination of *in situ* prepared [$RuH(CO)_2(Cp)$] with CCl_4 (85%) [4];
b. chlorination of [$Ru_2(CO)_4(Cp)_2$] with CCl_4 (about 90%) [4], $CHCl_3$/ HCl /O_2 (90%) [5] or elemental chlorine (70–85%) [6,7]; or
c. reaction of [$RuCl_2(CO)_3$]$_2$ with [$Tl(Cp)$] (50%) [5,8, 9].

Methods a and b suffer the disadvantage that they require expensive [$Ru_3(CO)_{12}$] as a starting material [10]. Although [$Ru_3(CO)_{12}$] can be prepared in high yield by the high-pressure carbonylation of [$RuCl_3(H_2O)_x$] [11], this procedure requires an autoclave, with the scale of the reaction limited by the size of the autoclave. Drawbacks of method c include the modest yield and the formation of [$Ru_2(CO)_4(Cp)_2$] as a byproduct [9].

Osmium halides [$OsX(CO)_2(Cp)$] are even less accessible. [$OsCl(CO)_2(Cp)$] has been obtained in unspecified yield from chlorination of [$Os_2(CO)_4(Cp)_4$] [12], which is itself obtained in only 1.8% yield from [$OsCl_2(CO)_3$]$_2$ [13]. [$OsBr(CO)_2(Cp)$] is obtained in 41% yield from [$OsBr_2(CO)_4$] and dicyclopentadiene in refluxing decane, and [$OsI(CO)_2(Cp)$] is obtained in 51% yield from the sequential reactions of [$OsBr_2(CO)_4$] with [$Tl(Cp)$] and I_2 [14], or in 17–25% yield from the two-step treatment of [$OsCl_2(CO)_3$]$_2$ with [$Na(Cp)$] and I_2 [15].

Improved preparations of [$RuCl(CO)_2(Cp)$] and [$OsCl(CO)_2(Cp)$] which begin with the most readily available ruthenium and osmium starting materials, [$RuCl_3(H_2O)_x$] and [OsO_4] [10*], without the intermediacy of the binary metal carbonyls are clearly desirable. We report here such procedures.

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* Reference number with asterisk indicates a note in the list of references.

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2. Experimental details

2.1. General procedures

Reactions were carried out under nitrogen, using tetrahydrofuran (THF) distilled from sodium benzophenone ketyl. Chromatography was carried out in air, using reagent-grade solvents on neutral alumina (Activity I, −150 mesh) used as received from Aldrich Chemical. $[RuCl_3(H_2O)_x]$ (Johnson Matthey, Ru = 43.48%) was converted to $[RuCl_2(CO)_3]_2$ in 98% yield by treatment with refluxing hydrochloric and formic acids [7,16]. $[NH_4]_2[OsCl_6]$ was prepared from $[OsO_4]$ by treatment with $[FeCl_2]$ and NH_4Cl in 12 M HCl [17]. $[SiMe_3(C_5H_5)]$ was prepared from [Na(Cp)] and $[SiClMe_3]$ [18–20]. Melting points were measured in sealed capillaries. Infrared spectra were recorded by using a Perkin-Elmer 1710 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 or Varian VXR-400 spectrometers and are referenced to the solvent peak. Mass spectra were obtained by using a VG Micromass ZAB-2F mass spectrometer (EI mode, 70 eV).

2.2. Preparation of $[RuCl(CO)_2(Cp)]$

$[SiMe_3(C_5H_5)]$ (11.04 g, 79.94 mmol) was added to a solution of $[RuCl_2(CO)_3]_2$ (10.05 g, 19.62 mmol) in THF (250 ml). The resulting solution was refluxed, and the progress of the reaction was monitored by using infrared spectroscopy. After 18–20 h, when the absorption at 2128 cm^{-1} due to one of the carbonyl peaks of $[RuCl_2(CO)_3]_2$ had disappeared, the reaction mixture was cooled to room temperature. The resulting bright yellow solution was evaporated to dryness *in vacuo*. The solid, yellow residue was dissolved in CH_2Cl_2 (10 ml) and applied to a 20 mm × 20 cm alumina column. Elution with CH_2Cl_2 gave a single yellow band. The eluate was reduced in volume to about 15 ml by using a rotary evaporator and cooled to −78°C. Addition of cold pentane (about 15 ml) gave yellow crystals of $[RuCl(CO)_2(Cp)]$ (7.67 g, 76%). ^1H NMR ($CDCl_3$): δ 5.42 (Cp) (lit., $CDCl_3$: δ 5.52 (Cp) [6]). ^{13}C-{^1H} NMR ($CDCl_3$): δ_C 195.8 (CO); 87.4 (Cp). IR (THF): ν(CO) 2048s, 1994s cm^{-1}; (CH_2Cl_2): 2056s, 2004s cm^{-1} (lit., (CH_2Cl_2): 2059s, 2008s cm^{-1} [6]). MS for $^{12}C_7{}^1H_5{}^{35}Cl^{16}O_2{}^{102}Ru$: 258 ($M^+$), 230 ($M^+$-CO), 202 ($M^+$-2CO), 167 ($M^+$-2CO-Cl). M.P. 100–100.5°C (lit. 100–101°C [4]).

2.3. Preparation of $[OsCl_2(CO)_3]_2$

$[NH_4]_2[OsCl_6]$ (0.505 g, 1.15 mmol) was charged to a 1 cm × 6 cm porcelain boat, which was placed in the center of a 2 cm × 60 cm quartz tube. The tube was connected to a chlorine cylinder and a mineral oil bubbler. The tube was placed in a tube furnace and heated to 360°C as a slow stream of chlorine gas was passed through it. After about 4 h, when the red color of $[NH_4]_2[OsCl_6]$ had changed to the deep brown of $OsCl_3$, the tube was cooled to room temperature. The direction of the reaction tube was reversed, and it was connected to a CO cylinder and a mineral oil bubbler. The tube was returned to the tube furnace and heated to 270°C as a slow stream of CO, saturated with ice-cold methanol, was passed through it. After about 12 h, the white sublimate of $[OsCl_2(CO)_3]_2$ (0.237 g, 60%) which had collected at the exit end of the reaction tube was scraped out. IR (KBr): ν(CO) 2132s, 2039s cm^{-1} (lit., (KBr): 2130s, 2040s cm^{-1} [15].)

2.4. Preparation of $[OsCl(CO)_2(Cp)]$

$[OsCl_2(CO)_3]_2$ (85 mg, 0.12 mmol), $[SiMe_3(Cp)]$ (0.20 g, 1.45 mmol) and THF (30 ml) were sealed in a Carius tube with a Teflon stopcock. The reaction mixture was heated to about 160°C. (**CAUTION:** This procedure should be carried out behind a safety shield.) Within 30 min, the colorless solution gradually changed to pale yellow. The progress of the reaction was monitored by using infrared spectroscopy. After 30–35 h, when the absorption at 2120 cm^{-1} due to one of the carbonyl peaks of $[OsCl_2(CO)_3]_2$ had disappeared, the reaction mixture was cooled to room temperature. The resulting orange–yellow solution was transferred into a flask and evaporated to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (4 ml) and applied to a 20 mm × 20 cm alumina column. Elution with CH_2Cl_2 gave a single yellow band. The eluate was reduced in volume to about 3 ml by using a rotary evaporator and cooled to −78°C. Addition of cold pentane (4 ml) gave pale yellow $[OsCl(CO)_2(Cp)]$ (37 mg, 44%). ^1H NMR ($CDCl_3$): δ 5.58 (Cp); (acetone-d_6): δ 5.83 (Cp); (lit., (acetone-d_6): δ 5.60 (Cp) [12]); ^{13}C-{^1H} NMR ($CDCl_3$): δ_C 178.9 (CO), 87.0 (Cp). IR (THF): ν(CO) 2031s, 1971s cm^{-1}; (CH_2Cl_2): 2039s, 1979s cm^{-1} (lit., (CH_2Cl_2): 2029, 1975 cm^{-1} [12]). MS for $^{12}C_7{}^1H_5{}^{35}Cl^{16}O_2{}^{192}Os$: 348 ($M^+$), 320 ($M^+$-CO), 292 ($M^+$-2CO), 256 ($M^+$-2CO-HCl). M.P. 102–104°C.

3. Results

$[RuCl(CO)_2(Cp)]$ (1) is obtained in 74% overall yield from $[RuCl_3(H_2O)_x]$ in two steps, eqns. (1) and (2), which are carried out in ordinary laboratory glassware. The first step, conversion of $[RuCl_3(H_2O)_x]$ to $[RuCl_2(CO)_3]_2$, is carried out in refluxing hydrochloric and formic acids [7,16,21]. Refluxing a THF solution of $[RuCl_2(CO)_3]_2$ with $[SiMe_3(C_5H_5)]$ gives pure

[RuCl(CO)$_2$(Cp)] after simple filtration through a column of alumina.

$$2[RuCl_3(H_2O)_x] + 7HCO_2H \rightarrow [RuCl_2(CO)_3]_2 + (2x+6)H_2O + 2HCl + CO_2 \tag{1}$$

$$[RuCl_2(CO)_3]_2 + 2[SiMe_3(C_5H_5)] \longrightarrow 2[RuCl(CO)_2(Cp)] + 2[SiClMe_3] + 2CO \tag{2}$$

(1)

By utilizing the reaction sequence, eqns. (3)–(6), [OsCl(CO)$_2$(Cp)] (**2**) is obtained in 26% overall yield from [OsO$_4$].

$$[OsO_4] + 4[FeCl_2] + 8HCl + 2NH_4Cl \longrightarrow [NH_4]_2[OsCl_6] + 4[FeCl_3] + 4H_2O \tag{3}$$

$$[NH_4]_2[OsCl_6] \xrightarrow[360°C]{Cl_2} [OsCl_3] + 2NH_3 + 2HCl + \tfrac{1}{2}Cl_2 \tag{4}$$

$$2[OsCl_3] + 6CO \xrightarrow[270°C]{CO} [OsCl_2(CO)_3]_2 + Cl_2 \tag{5}$$

$$[OsCl_2(CO)_3]_2 + 2[SiMe_3(C_5H_5)] \longrightarrow 2[OsCl(CO)_2(Cp)] + 2[SiClMe_3] + 2CO \tag{6}$$

(2)

The reaction of eqn. (3) is carried out in an open Erlenmeyer flask, giving red microcrystals of [NH$_4$]$_2$[OsCl$_6$] in 97% yield [17]. The next two steps (eqns. (4) and (5)) are carried out in a single quartz reaction tube heated in a tube furnace. [NH$_4$]$_2$[OsCl$_6$] reacts with flowing chlorine to give [OsCl$_3$] [22] and a small amount of [OsCl$_4$], which sublimes to the cooler end of the tube. The direction of the reaction tube is reversed and connected to a source of CO, which produces a sublimate of [OsCl$_2$(CO)$_3$]$_2$ [15,22–24] in a clean area of the tube in 60% yield based on [NH$_4$]$_2$[OsCl$_6$]. The final reaction of [OsCl$_2$(CO)$_3$]$_2$ with [SiMe$_3$(C$_5$H$_5$)] (eqn. (6)) requires much more severe reaction conditions than the ruthenium reaction. The use of a heavy-walled glass reaction vessel sealed with a Teflon stopcock allows the reaction to be be carried out at about 160°C in tetrahydrofuran. Simple filtration through a column of alumina gives pure [OsCl(CO)$_2$(Cp)] [12] in satisfactory yield.

4. Discussion

The new preparations of [RuCl(CO)$_2$(Cp)] (**1**) and [OsCl(CO)$_2$(Cp)] (**2**) reported here give the compounds in good yields from readily available starting materials, without the use of an autoclave. Modified literature methods are used to prepare the penultimate products [RuCl$_2$(CO)$_3$]$_2$ [7,16,21] and [OsCl$_2$(CO)$_3$]$_2$ [15,22–24]. Alternative syntheses of [RuCl$_2$(CO)$_3$]$_2$ from [Ru$_3$(CO)$_{12}$] [25–28] are reported on scales under 1 g, with yields ranging from about 40% to 70%. Carbonylation of [RuCl$_3$(H$_2$O)$_x$] (methanol, 10 atm, 65°C) [8] or [Ru(η^4-norbornadiene)Cl$_2$]$_x$ [29] is effective, but the formic acid method offers advantages of cost, scale and convenience, having been reported on a 35 g scale [7]. Similarly, [OsCl$_2$(CO)$_3$]$_2$ can be prepared by reacting [Os$_3$(CO)$_{12}$] with HCl [30], Cl$_2$ [31] or CCl$_4$/hν [32], but these methods offer no advantage over the carbonylation of OsCl$_3$ [15,33].

The final steps, reactions of [MCl$_2$(CO)$_3$]$_2$ with [SiMe$_3$(C$_5$H$_5$)], are new reactions. Similar reactions of metal halides with cyclopentadienyl silicon [20,34] and tin [35,36] reagents have been used to synthesize many cyclopentadienyl complexes, especially of the early transition metals. Abel has reported the syntheses of [M(CO)$_3$(Cp)] (M = Mn, Re) from [MX(CO)$_5$] (X = halide) and [EMe$_3$(C$_5$H$_5$)] (E = Si, Sn) [20,36,37]. Whereas [SnMe$_3$(C$_5$H$_5$)] effectively cyclopentadienylates [FeI$_2$(CO)$_4$] to [FeI(CO)$_2$(Cp)] in 85% yield, the tin compound reacts with [RuCl$_2$(CO)$_3$]$_2$ to give mainly [Ru(SnMe$_3$)(CO)$_2$(Cp)], plus some **1** and [Ru$_2$(CO)$_4$(Cp)$_2$] [36]. [SiMe$_3$(C$_5$H$_5$)] reacts with [RuCl$_3$(H$_2$O)$_2$] in ethanol to give [Ru(Cp)$_2$] in 96% yield [38], but we are not aware of previous applications of cyclopentadienylsilanes to synthesize mono(cyclopentadienyl) ruthenium or osmium carbonyl halides.

Reactions of other cyclopentadienyl sources with [RuCl$_2$(CO)$_3$]$_2$ did not give [RuCl(CO)$_2$(Cp)] in good yield. In our hands, the reaction of [RuCl$_2$(CO)$_3$]$_2$ with [Tl(Cp)] [5,9] proceeded in less than 40% yield. [Na(Cp)] gives [Ru$_2$(CO)$_4$(Cp)$_2$] as the principal product [7,39]. The use of THF as a solvent is essential, since attempts to carry out the reaction of eqn. (2) in toluene or dichloromethane were unsuccessful. Possibly cleavage of [RuCl$_2$(CO)$_3$]$_2$ to [RuCl$_2$(thf)(CO)$_3$] [8,28] is a prerequisite for reaction with [SiMe$_3$(C$_5$H$_5$)].

The sluggish reactivity of [OsCl$_2$(CO)$_3$]$_2$ required more severe reaction conditions than for ruthenium. The sealed-tube reaction of [OsCl$_2$(CO)$_3$]$_2$ with [SiMe$_3$(C$_5$H$_5$)] in THF at 160°C was much more effective than reactions in refluxing butyl ether (142–143°C, 36 h, < 10% yield of **2**), 1,4-dioxane, diglyme and isooctane (traces of **2**). Attempts to use [Tl(Cp)] as the cyclopentadienylating agent also failed to give more than traces of **2**. As for ruthenium, cleavage of [OsCl$_2$(CO)$_3$]$_2$ to [OsCl$_2$(thf)(CO)$_3$] [40*] may precede its reaction with [SiMe$_3$(C$_5$H$_5$)].

5. Conclusion

We have developed convenient new syntheses of [RuCl(CO)$_2$(Cp)] (**1**) and [OsCl(CO)$_2$(Cp)] (**2**), which can be carried out without the intermediacy of [M$_3$-

$(CO)_{12}]$. The improved availability of these useful starting materials may expedite progress in $[Ru(CO)_2(Cp)]$ and $[Os(CO)_2(Cp)]$ chemistry.

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