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Note

Synthesis of *fac*-$[Os(CO)_3(L)Me_2]$ (L = THF or MeCN) and some reactions with PPh_3 and trityl salts

Matthew J. Overett [1], John R. Moss *

Department of Chemistry, University of Cape Town, Private Bag, Rondebosch 7701, South Africa

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Dedicated to Professor Gordon Stone in recognition of his many pioneering contributions to organometallic chemistry

Abstract

The reaction of *cis*-$[Os(CO)_4Me_2]$ with Me_3NO in the THF or MeCN yields the complexes *fac*-$[Os(CO)_3(L)Me_2]$ (where L = THF or MeCN). Whereas the THF complex is unstable and only characterised spectroscopically, *fac*-$[Os(CO)_3(MeCN)Me_2]$ has been isolated as a white solid and fully characterized by both analytical and spectroscopic methods. These complexes *fac*-$[Os(CO)_3(L)Me_2]$ are shown to be useful intermediates. Thus, reaction with PPh_3 gives *fac*-$[Os(CO)_3(PPh_3)Me_2]$ in good yield.

Reactions of *fac*-$[Os(CO)_3(L)Me_2]$ (L = CO or MeCN) with CPh_3PF_6 or $B(C_6F_5)_3$ have been investigated. Whereas *cis*-$[Os(CO)_4Me_2]$ showed no reaction with either CPh_3PF_6 or $B(C_6F_5)_3$, the reaction of *fac*-$[Os(CO)_3(MeCN)Me_2]$ with CPh_3PF_6 in CH_2Cl_2 occurred over 16 h at room temperature to give an unstable cationic product and CPh_3Me. The reaction was monitored by both IR and NMR spectroscopies. When this reaction of *fac*-$[Os(CO)_3(MeCN)Me_2]$ was carried out in the presence of a trapping ligand such as MeCN, the stable cationic product $[Os(CO)_3(MeCN)_2Me]^+$ could be isolated and identified spectroscopically.

Keywords: Osmium; Carbonyl; Methyl; Alkyl

1. Introduction

Although the reactions of the metal carbonyl alkyls of the type $[M(CO)_5R]$ (M = Mn and Re) have been extensively studied [1,2], relatively few reactions of metal carbonyl dialkyls have been reported. An example of such a dialkyl compound is *cis*-$[Os(CO)_4Me_2]$. This compound was first reported independently by L'Eplattenier and his coworker [3,4] and Stone and coworkers [5] in the early 1970s. Few reactions of *cis*-$[Os(CO)_4Me_2]$ have, however, been described. Thermal decomposition of *cis*-$[Os(CO)_4Me_2]$ gives methane as the primary organic product; which is believed to form via a radical pathway [6]. Reactions with Br_2, HF and CO have also been described and these reactions yield *cis*-$[Os(CO)_4MeBr]$ [4], *cis*-$[Os(CO)_4F_2]$ [7] and $[Os(CO)_5]$ [4,8], respectively. Binuclear compounds may be formed by reaction of *cis*-$[Os(CO)_4Me_2]$ with hydrido-osmium complexes. For example, reaction with $[Os(CO)_4H_2]$ gives $[HOs_2(CO)_4Me]$ [9]. Thermal [3] and oxidative [9] decarbonylations of $[Os(CO)_4Me_2]$ have been used to prepare *fac*-$[Os(CO)_3(PPh_3)Me_2]$. In the latter case, the oxidative decarbonylation was accomplished by treatment of *cis*-$[Os(CO)_4Me_2]$ with Me_3NO in the presence of PPh_3. However, no attempt was made to isolate *fac*-$[Os(CO)_3(L)Me_2]$, where L is a labile ligand such as a nitrile or ether, and to investigate the coordination chemistry of the resulting activated complex.

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* Corresponding author. Tel.: +27 21 6502535; fax: +27 21 6897499.
E-mail addresses: matthew.overett@sasol.com (M.J. Overett), jrm@science.uct.ac.za (J.R. Moss).

[1] Present address: Sastech R&D, SASOL, P.O. Box 1, Sasolburg 1947.

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In this note, we describe a slightly modified and more convenient synthesis of *cis*-[Os(CO)$_4$Me$_2$] and the conversion of this complex to the useful intermediate *fac*-[Os(CO)$_3$(L)Me$_2$] (L = MeCN, THF). Reactions of these labile intermediates with PPh$_3$ and CPh$_3$PF$_6$ are described. In a subsequent full paper, we will report on the reactions of *fac*-[Os(CO)$_3$(MeCN)Me$_2$] with mono- and bidentate neutral donor ligands to give a range of novel mononuclear and binuclear products [11].

2. Experimental

2.1. General

All reactions were carried out under nitrogen or argon using standard Schlenk-tube techniques. Solvents were purified by distillation under argon from an appropriate drying agent (CaH$_2$ for acetonitrile and dichloromethane; sodium/benzophenone for THF and toluene). Me$_3$NO · 2H$_2$O was purified by sublimation at 60 °C, 0.1 mm Hg onto a cold finger and stored in a glovebox. MeI was distilled under argon from CaH$_2$. Melting points were recorded on Kofler hotstage microscope (Reichert Thermovar) and are uncorrected. Microanalysis data were obtained from the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin–Elmer 983 spectrometer in solution with NaCl windows. NMR spectra were recorded on a Varian Mercury-300 spectrometer. Mass spectrometry was carried out using fast atom bombardment (FAB) ionization at the Cape Technikon.

2.2. Synthesis of *cis*-[Os(CO)$_4$Me$_2$] (1)

cis-[Os(CO)$_4$Me$_2$] (**1**) was prepared by a modification of the method of Stone [5]. Sodium metal (152 mg, 6.6 mmol) was added in small pieces to a suspension of [Os$_3$(CO)$_{12}$] (2.95 g, 3.25 mmol) in liquid ammonia (50 ml) at −78 °C. Completion of the reaction was indicated by the persistence of a blue colour. MeI (1.0 ml, 16 mmol) was added and the mixture was stirred for 1 h. The ammonia was then allowed to evaporate off, and residual MeI and ammonia were removed in vacuo for 2 min. Complex **1** was then recovered from the residues as a white powder by sublimation under passive vacuum (<1 mm) at 60 °C onto a dry ice cooled cold finger. (2.35 g, 73%); m.p. 63–64 °C, lit. 65–66 °C [5]; ν_{max}(CO)/cm^{-1} (hexane) 2130m, 2044vs, 2011s, 1979w; δ_H(400 MHz; CDCl$_3$) 0.05 (6H, s, Os-*Me*). Spectroscopic data are in agreement with the literature [5].

2.3. Synthesis of *fac*-[Os(CO)$_3$(MeCN)Me$_2$] (2)

A stirred solution of **1** (316 mg, 0.951 mmol) in acetonitrile (5 ml) was treated with a slight excess of Me$_3$NO · 2H$_2$O (116 mg, 1.04 mmol) in acetonitrile (6 ml). The mixture was stirred at room temperature for 24 h, after which time the reaction was judged to be complete by IR spectroscopy and TLC (silica, 25% dichloromethane in hexane, R_f = 0.19). The solvents were removed in vacuo and the crude residue was purified by column chromatography (silica gel, 25% dichloromethane in hexane). Upon removal of solvents in vacuo, a white solid was obtained, which was recrystallised from dichloromethane/hexane to give **2** as white microcrystals (231 mg, 70%), m.p. 104–107 °C; *Anal.* Calc. for C$_7$H$_9$NO$_3$Os requires C, 24.3; H, 2.6; N, 4.1. Found: C, 24.6; H, 2.5; N, 4.0%. ν_{max}(CO)/cm^{-1} (dichloromethane) 2072s, 1980vs; δ_H (400 MHz; CDCl$_3$) 2.45 (3H, s, –NC*Me*), 0.062 (6H, s, Os-*Me*); $\delta_{C\{H\}}$(100 MHz; CDCl$_3$) 180.4 (*C*O), 175.9 (*C*O), 117.9 (Me*C*N)3.5 (*Me*CN), −16.3 (Os-*Me*); *m/z* (FAB) 347 (M$^+$, 26%), 332 (M$^+$ – Me, 61%), 319 (M$^+$ – CO, 43%), 304 (M$^+$ – CO–Me, 100%), 291 (M$^+$ – 2CO, 35%), 276 (M$^+$ – 2CO–Me, 30%).

2.4. Synthesis of *fac*-[Os(CO)$_3$(THF)Me$_2$] (3)

To a stirred solution of **1** (65 mg, 0.20 mmol) in THF (5 ml) was added a solution of Me$_3$NO · 2H$_2$O (30 mg, 0.27 mmol) in THF (20 ml). The reaction was monitored by IR spectroscopy. After stirring for 16 h, the reaction was complete and the reaction mixture was filtered through silica. Upon removal of the volatiles in vacuo, a clear oil was recovered, which decomposed after a short time under vacuum. ν_{max}(CO)/cm^{-1} (THF) 2068s, 1969vs.

2.5. Synthesis of *fac*-[Os(CO)$_3$(PPh$_3$)Me$_2$] (4)

2.5.1. From 2

A mixture of **2** (152 mg, 0.440 mmol) and PPh$_3$ (118 mg, 0.45 0mmol) in toluene (10ml) was stirred at 75 °C. The reaction was monitored by infrared spectroscopy and judged to be complete after 48 h. The volatiles were removed in vacuo and after column chromatography (silica, 20% dichloromethane in hexane, R_f = 0.28), **4** was recovered as a white crystalline solid. (192 mg, 77%); m.p. 119–122 °C. *Anal.* Calc. for C$_{23}$H$_{21}$O$_3$POs requires C, 48.8; H, 3.7. Found: C, 48.8; H, 3.7%. ν_{max}(CO)/cm^{-1} (toluene) 2068vs, 1994s, 1960s; δ_H (300 MHz; CDCl$_3$) 7.44–7.42 (15H, m, H_{aryl}), −0.22 (6H, d, ^3J(PH) 8 Hz, Os-*Me*); $\delta_{C\{H\}}$(75 MHz; CDCl$_3$) 178.8 (*C*O), 177.1 (d, ^2J(PC) 9Hz, *C*O), 133.9 (d, ^3J(PC) 10 Hz, $C_{3,5}$ [PPh$_3$]), 131.0 (d, ^1J(PC) 50 Hz, C_1 [PPh$_3$]), 130.6 (d, ^4J(PC) 2 Hz, C_4 [PPh$_3$]), 128.3 (d, ^3J(PC) 10 Hz, $C_{2,6}$ [PPh$_3$]), −22.4 (d, ^2J(PC) 8 Hz, Os-*Me*); $\delta_{P\{H\}}$(120 MHz; CDCl$_3$) 0.89; *m/z* (FAB) 553 (M$^+$ – Me, 7%), 537 (M$^+$ – 2Me–H, 100%), 509 (M$^+$ – 2Me–H–CO, 60%). Spectroscopic data are in agreement with the literature [9].

2.5.2. From **3**

A solution of **3** was prepared by treatment of **2** (50 mg, 0.15 mmol) with an excess of $Me_3NO \cdot 2H_2O$ in THF. The solution was filtered through silica, PPh_3 (40 mg, 0.15 mmol) was added, and the mixture was refluxed for 48 h. The reaction was monitored by IR spectroscopy. After removal of the volatiles in vacuo and column chromatography (silica, 20% dichloromethane in hexane), a white crystalline solid was recovered and identified as **4** by IR and NMR spectroscopies (59 mg, 69%).

2.6. Synthesis of *fac*-$[Os(CO)_3(MeCN)_2Me]PF_6$ (**5**)

A solution of CPh_3PF_6 (46 mg, 0.12 mmol) in acetonitrile (5.5 ml) was added dropwise over 4 h to a stirred solution of **2** (41 mg, 0.12 mmol) in acetonitrile (5 ml). The progress of the reaction was monitored by IR spectroscopy. After stirring for 24 h, the volatiles were removed in vacuo and the white residue was washed with pentane (3 × 10 ml). Recrystallisation from dichloromethane/hexane gave **5** as a white crystalline solid. (48 mg, 78%); m.p. 131–133 °C. *Anal.* Calc. $C_8H_9F_6N_2O_3POs$ requires C, 18.6; H, 1.8; N, 5.4. Found: C, 18.9; H, 1.6; N, 5.3%. $\nu_{max}(CO)/cm^{-1}$ (dichloromethane) 2123s, 2051vs, 2039vs; δ_H (400 MHz; CD_2Cl_2) 2.59 (6H, s, Os-NC*Me*), 0.52 (3H, s, Os-*Me*); $\delta_{C\{H\}}$(100 MHz; CD_2Cl_2) 170.9 (*C*O), 168.4 (*C*O), 123.4 (N*C*Me), 3.6 (NC*Me*), −15.9 (Os-*Me*); *m*/*z* (FAB) 373 ($Os(CO)_3(NCMe)_2Me^+$, 100%), 345 ($Os(CO)_3(NCMe)_2Me^+$ – CO, 66%), 304 ($Os(CO)_3(NCMe)_2Me^+$ – CO–MeCN, 12%).

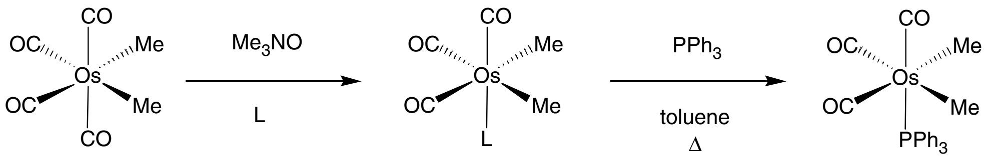
3. Results and discussion

fac-$[Os(CO)_3(L)Me_2]$ (L = MeCN, **2**; L = THF, **3**) may be prepared by treatment of **1** with Me_3NO in acetonitrile and tetrahydrofuran, respectively (Scheme 1). An excess of Me_3NO may be used without evidence of a second decarbonylation and the reactions give exclusively the *fac* isomer. Compound **2** may be isolated as a white involatile powder after flash chromatography. Compound **3** decomposes upon removal of the tetrahydrofuran in vacuo; however, it may be identified by its infrared spectrum and its similar reactivity to **2**. Treatment of **2** or **3** with PPh_3 gives the previously reported [9] *fac*-$[Os(CO)_3(PPh_3)Me_2]$ (**4**) as expected, by displacement of the labile ligand with PPh_3 (Scheme 1). Full characterisation of **4** is reported for the first time.

An interesting feature of **2** is the effect of solvent on its ^1H NMR spectrum (Fig. 1). Substantial differences in chemical shifts are apparent when **2** is dissolved in $CDCl_3$ and C_6D_6. The fine structure in the signals when dissolved in C_6D_6 is due to non-equivalence of the methyl protons on the NMR timescale. The restricted rotation about the Os–CH_3 and NC–CH_3 bonds may be attributed to the π-stacking present in the benzene solvent.

We are interested in alkyl abstraction reactions from neutral dialkyl complexes to form cationic, coordinatively unsaturated alkyl species. Such reactions take place during the activation of many alkene oligomerisation and polymerisation catalysts. To this end, we investigated the reaction of **1** and **2** with alkyl abstraction reagents such as CPh_3PF_6 and $B(C_6F_5)_3$. Both **1** and **2** were unreactive towards methyl abstraction with $B(C_6F_5)_3$, and no reaction was again observed between **1** and CPh_3PF_6. However, treatment of **2** with one equivalent of CPh_3PF_6 in dichloromethane resulted in the clean abstraction of a methyl group to yield a cationic species. The formation of the by-product CPh_3Me could be observed by NMR ($\delta_H = 2.19$ ppm, CPh_3*Me*) [10] and the shift in the infrared absorption bands to higher wave number ($\nu_{CO} = 2114$, 2040, 2013 cm^{-1}) is consistent with this result. However, the postulated 16-electron product $[Os(CO)_3(MeCN)Me]PF_6$ was found to be unstable and could not be isolated or observed in situ by ^1H NMR. However, by performing the reaction in the presence of a donor ligand such as acetonitrile, the cationic species could be 'trapped' as a stable 18-electron salt, and thus *fac*-$[Os(CO)_3(MeCN)_2Me]PF_6$ (**5**) was successfully isolated and characterised (Scheme 2).

The rich coordination chemistry of **2** with monodentate and bidentate ligands will be described in a full paper [11].



1

2 (L= MeCN)
3 (L= THF)

4

Scheme 1.

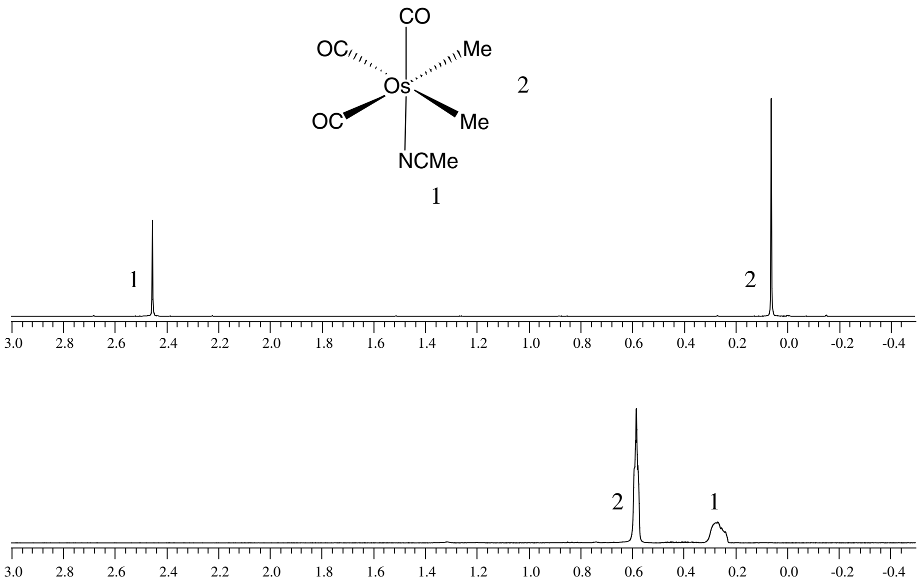
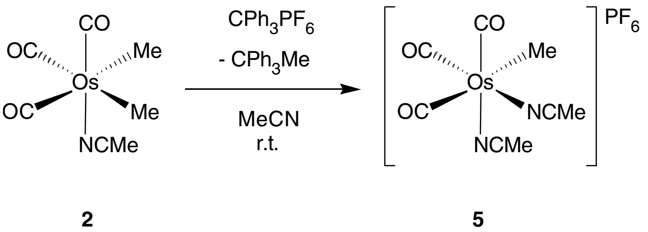


Fig. 1. ^{1}H NMR spectra of **2** in $CDCl_3$ (top) and C_6D_6 (bottom).



Scheme 2.

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