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Preparation of methyl hydride and dimethyl complexes of osmium and iron: reaction of $M(CO)_2(PMe_3)_2CH_3I$ and $[M(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (M = Os, Fe) with borohydrides and lithium methyl

Gianfranco Bellachioma, Giuseppe Cardaci *, Alceo Macchioni, Cristiano Zuccaccia

Laboratorio di Chimica Fisica, Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, I-06100 Perugia, Italy

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Abstract

cis,trans-$Os(CO)_2(PMe_3)_2CH_3I$ (**1**) and *fac*-$[Os(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**3**) react with borohydrides ($NaBH_4$, NBu_4BH_4, $LiBEt_3H$) in diethyl ether to form the methyl hydride complex $Os(CO)_2(PMe_3)_2(CH_3)H$ (**7**). Similarly the monosubstituted *fac*-$Os(CO)_3(PMe_3)CH_3I$ (**9**) reacts with borohydrides to give *fac*-$Os(CO)_3(PMe_3)(CH_3)H$ (**10**). The isoelectronic complexes of iron *cis,trans*-$Fe(CO)_2(PMe_3)_2CH_3I$ (**2**) and *fac*-$[Fe(CO)_3(PMe_3)_2CH_3]BPh_4$ (**4**) give instead the dihydride complex *cis,trans*-$Fe(CO)_2(PMe_3)_2H_2$ (**8**). Complexes (**1**)–(**4**) react with lithium methyl to form the dimethyl complexes *cis,trans*-$M(CO)_2(PMe_3)_2(CH_3)_2$ [M = Os (**5**), Fe (**6**)]. The structures of the complexes are studied by IR and ^1H-, $^{13}C\{^1H\}$-, $^{31}P\{^1H\}$-NMR spectroscopies. The different results are explained on the basis of a fast reductive elimination reaction in the case of iron and a fast decarbonylation reaction in the case of osmium.

Keywords: Reductive elimination; Methylhydride osmium complexes; Dimethyl osmium complexes; Dimethyl iron complexes; Reduction

1. Introduction

Reductive elimination is a key step in many stoichiometric and catalytic organometallic reactions [1]. In particular, the coupling of C–C and C–H bonds are important steps in organic synthesis and catalysis [2]. While this reaction has already received significant attention, the mechanism is not completely understood and a study of the effect due to the nature of the metal is lacking [3].

In the past few years our research group has studied the oxidative addition of alkyl halides [4] in mono- and di-substituted derivatives of $M(CO)_5$ (M = Fe, Ru, Os) and the insertion of carbon monoxide [5] into the alkyl–metal bond in isostructural organometallic complexes of iron, ruthenium and osmium in order to compare the mechanisms and rates. The results of the kinetic study show that oxidative addition follows the order $Os > Ru \gg Fe$ [6], while carbon monoxide insertion follows the order $Ru > Fe \gg Os$ [7]. These trends explain why osmium and iron are poor catalysts in homogeneous catalysis: the slow rates of insertion (Os) and oxidative addition (Fe) break the catalytic cycle, while all the steps are fast with ruthenium and the catalytic cycle is completed. The same behaviour was observed for the series Co, Rh and Ir [8] and Ni, Pd and Pt [9] for which the rhodium and palladium complexes have a greater aptitude to act as homogeneous catalysts.

In the present work we report the preparation of some dimethyl and methyl hydride complexes of iron and osmium and their reductive elimination in order to obtain information about the effect of the metal within the same group on the last process and to extend the comparison between the metals to all the steps involved in the catalytic cycle [10].

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* Corresponding author. Tel.: +39-075-5855578; fax: +39-075-5855598.

E-mail address: cardchim@unipg.it (G. Cardaci).

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2. Experimental

cis,trans-$M(CO)_2(PMe_3)_2CH_3I$ (M = Os (**1**) [11], Fe (**2**) [12]) and *fac*-$[M(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (M = Os (**3**) [11], Fe (**4**) [13]) were prepared according to the literature methods. *fac*-$Os(CO)_3(PMe_3)CH_3I$ (**9**) was prepared according to Ref. [11]. All the other compounds used ($NaBH_4$, NBu_4BH_4, $LiBEt_3H$, CH_3Li) are commercial. MeCN was purified as described in the literature [14]; Et_2O was purified by refluxing with $LiAlH_4$ and distilled under nitrogen; *n*-hexane, C_6H_6 and THF were purified by refluxing with Na and benzophenone and distilled immediately before using; CH_2Cl_2 was distilled from P_2O_5. All the reactions were carried out under nitrogen.

The infrared spectra were recorded on a Perkin–Elmer 1725X FTIR or 983 Perkin–Elmer spectrophotometers. The NMR spectra were performed on a Bruker Avance DRX 400 spectrometer operating at 400.13 MHz (^1H), 161.98 MHz (^{31}P) and 100.61 MHz (^{13}C); referencing is relative to Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were performed on a Carlo Erba 1106 elemental microanalyzer.

2.1. Preparation of cis,trans-$Os(CO)_2(PMe_3)_2(CH_3)H$ (7)

(a) 100 mg (0.18 mmol) of *cis,trans*-$Os(CO)_2(PMe_3)_2CH_3I$ (**1**) was dissolved in MeCN; an excess of $NaBH_4$ was added and the suspension was stirred at room temperature (r.t.). After 4 days the reaction was completed and the solution was then filtered and dried. The solid residue was dissolved in *n*-hexane and crystallized at -20°C. About 64 mg of white crystals of complex **7** was obtained (yield 87%).

(b) 100 mg (0.18 mmol) of *fac*-$[Os(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$(**3**) was dissolved in MeCN (50 ml) and cooled to 0°C. An excess of $NaBH_4$ was added to the stirred solution. An instantaneous reaction was observed with the formation of complex **7**. No intermediate complex was observed. The solution was filtered and dried. The residue was extracted by *n*-hexane and complex **7** was purified as described in (a). The same reaction was observed using *fac*-$[Os(CO)_3(PMe_3)_2CH_3]^+I^-$ in Et_2O. Anal. Found: C, 24.52; H, 5.50. Calc. for $C_9H_{22}O_2P_2Os$: C, 26.09; H, 5.31%.

^1H-NMR (CD_2Cl_2, 298 K, δ ppm): 1.66 (Harris t, $[|^2J_{HP} + {}^4J_{HP}| = 8.0$ Hz], PMe_3); -0.45 (td, $[^3J_{HP} = 8.8$ Hz, $^3J_{HH} = 2.8$ Hz], Me); -7.8 (tq, $[^2J_{HP} = 24.4$ Hz, $^3J_{HH} = 2.8$ Hz], H). $^{13}C\{H\}$-NMR (CD_2Cl_2, 298 K, δ ppm): 185.7 (t, $[^2J_{CP} = 6.9$ Hz], CO_a);182.7 (t, $[^2J_{CP} = 7.1$ Hz], CO_b); 20.5 (Harris t, $[|^1J_{CP} + {}^3J_{CP}| = 57.1$ Hz], PMe_3); -37.2 (t, $[^2J_{CP} = 9$ Hz], Me). $^{31}P\{H\}$-NMR (CD_2Cl_2, 298 K, δ ppm): -44.7 (s, PMe_3). IR (cm^{-1}, *n*-hexane): $\nu_{CO} = 2003, 1927$.

2.2. Preparation of fac-$Os(CO)_3(PMe_3)(CH_3)H$ (10)

100 mg (0.20 mmol) of *fac*-$Os(CO)_3(PMe_3)CH_3I$ (**9**) was dissolved in MeCN; an excess of $NaBH_4$ was added and the solution was stirred at r.t. After three days the reaction was completed; the solution was filtered and dried. The solution residue was dissolved in *n*-hexane and crystallized at -20°C. About 50 mg of white crystals of complex **10** was obtained (yield 68%). Anal. Found: C, 23.21; H, 3.71. Calc. for $C_7H_{13}O_3POs$: C, 22.95; H, 3.58%.

^1H-NMR (CD_2Cl_2, 298 K,δ ppm): 1.72 (d, $[^2J_{HP} = 9.89$ Hz], PMe_3); -0.20 (dd, $[^3J_{CH_3-H} = 2.6$ Hz, $^3J_{CH_3-P} = 9.12$ Hz], CH_3); -7.78 (dq, $[^2J_{HP} = 26.6$ Hz, $^3J_{H-CH_3} = 2.6$ Hz], H). $^{13}C\{H\}$-NMR (CD_2Cl_2, 298 K, δ ppm): -41.53 (d, $[^2J_{CH_3-P} = 9.35$ Hz], CH_3); 19.08 (d, $^2J_{CP} = 37.53$ Hz, PMe_3); 180.06 (d, $[^2J_{CO-P} = 83.50$ Hz], CO_a); 179.39 (d, $[^2J_{CO-P} = 8.03$ Hz], CO_c); 176.50 (d, $[^2J_{CO-P} = 8.25$ Hz], CO_b). $^{31}P\{H\}$-NMR (CD_2Cl_2, 298 K, δ ppm): 47.03 (s, PMe_3). IR (cm^{-1}, *n*-hexane): $\nu_{CO} = 2072, 2011, 1976$.

2.3. Preparation of cis,trans-$Os(CO)_2(PMe_3)_2(CH_3)_2$ (5)

(a) 100 mg (0.13 mmol) of *fac*-$[Os(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**3**) was suspended in 50 ml of THF and cooled to 0°C; 0.1 ml of a 1.6 M solution of CH_3Li in Et_2O was then added. The reaction was instantaneous. The suspension was dried. The residue was then extracted with *n*-hexane and crystallized at -20°C. About 30 mg of white crystals of complex **5** was obtained (yield 54%). Anal. Found: C, 28.10 H, 5.95; Calc. for $C_8H_{15}O_3POs$: C, 27.97; H, 5.87%.

^1H-NMR (CD_2Cl_2, 298 K, δ ppm): 1.28 (Harris t, $[|^2J_{HP} + {}^4J_{HP}| = 7.3$ Hz], PMe_3); 0.022 (t, $[^3J_{HP} = 8.86$ Hz], Me). $^{13}C\{H\}$-NMR (C_6D_6, 298 K, δ ppm): 183.3(t, $[^2J_{CP} = 7.1$ Hz], CO); 15.35(Harris t, $[|^1J_{CP} + {}^3J_{CP}| = 17.35$ Hz], PMe_3); -22.53 (t, $[^2J_{CP} = 7.95$ Hz], Me). $^{31}P\{H\}$-NMR (C_6D_6, 298 K, δ ppm): -53.68 (s, PMe_3). IR (cm^{-1}, THF), $\nu_{CO} = 1998, 1930$.

(b) 230 mg (0.43 mmol) of *cis,trans*-$Os(CO)_2(PMe_3)_2CH_3I$ (**1**) was dissolved in freshly distilled Et_2O at r.t.; 0.27 ml of a 1.6 M solution of CH_3Li in Et_2O was then added. The reaction was followed by IR; it did not go to completion even after more CH_3Li was added. A mixture of the starting complex **1** and complex **5** was obtained.

2.4. Preparation of cis,trans-$Fe(CO)_2(PMe_3)_2H_2$ (8)

(a) 1.0 g (1.6 mmol) of *fac*-$[Fe(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**4**) was dissolved in 50 ml of MeCN deaerated by fluxing nitrogen and cooled to -20°C. An excess of $NaBH_4$ was added to the stirred solution. After 10 min the $Fe(CO)_2(PMe_3)_2(CH_3CN)$ complex formed and was identified by the IR spectrum ($\nu_{CO} = 1852, 1790\ cm^{-1}$). The solution was warmed to r.t. and left to react for 24 h. The complete transformation of $Fe(CO)_2(PMe_3)_2(CH_3CN)$ into complex **8** was observed. The solution was filtered and dried. The solid residue was sublimated and 200 mg of a yellow solid were obtained (yield 47%). Anal. Found: C, 36.20; H, 7.81. Calc. for $C_8H_{21}O_2P_2Fe$: C, 36.10; H, 7.58%.

^1H-NMR (CD_3CN, 298 K, δ ppm): 1.32 (Harris t, $[|^2J_{HP} + {}^4J_{HP}| = 8.7$ Hz], PMe_3); −9.78 (t, $[^3J_{HP} = 61$ Hz], H). IR (cm^{-1}, CH_3CN): $\nu_{CO} = 1955, 1922$. In Et_2O the CO stretching frequencies are 1970 and 1925 cm^{-1}.

During the first step of the reduction of complex **4** with $NaBH_4$, CH_3CHO formed and was identified by the CO stretching ($\nu_{CO} = 1723\ cm^{-1}$ in CH_3CN). Since CH_3CHO is reduced to CH_3CH_2OH by $NaBH_4$, the quantities of both products were determined by gas chromatographic analysis. In the initial step of the reaction, the formation of CH_3CHO is quantitative; successively, CH_3CHO decreases and CH_3CH_2OH forms. The sum of the CH_3CHO and CH_3CH_2OH concentrations always corresponds to the amount of complex **4** reacted.

(b) 200 mg (0.49 mmol) of *cis,trans*-$Fe(CO)_2(PMe_3)_2CH_3I$ (**2**) was dissolved in CH_3CN (30 ml) and cooled to −15°C. An excess of $NaBH_4$ was added and the solution was stirred for 1 h. The quantitative formation of complex $Fe(CO)_2(PMe_3)_2(CH_3CN)$ was observed. The solution was then warmed to r.t. and complex **8** formed within 2 days. Complex **8** was purified as described previously.

Other borohydrides were used to carry out the reactions ($LiB(C_2H_5)_3H$, NBu_4BH_4). In every case the reduction followed the same trend as that observed with $NaBH_4$ and complex **8** was the final product.

2.5. Preparation of cis,trans-$Fe(CO)_2(PMe_3)_2(CH_3)_2$ (6)

(a) 200 mg (0.49 mmol) of *cis,trans*-$Fe(CO)_2(PMe_3)_2CH_3I$ (**2**) was dissolved in Et_2O (30 ml) and cooled to 0°C. Equimolar quantities of CH_3Li (0.3 ml of a 1.6 M solution of CH_3Li in Et_2O) were added to the stirred solution in two steps. The reaction was instantaneous and complex **6** formed ($\nu_{CO} = 1974, 1909\ cm^{-1}$). The solution was filtered and dried. The solid residue was dissolved in *n*-hexane and crystallized at −20°C. About 80 mg of yellow crystals of complex **6** was obtained (yield 55%). Anal. Found: C, 41.05; H, 8.31. Calc. for $C_{10}H_{24}O_2P_2Fe$: C, 40.84; H, 8.23.

^1H-NMR (C_6D_6, 298 K, δ ppm): −0.16 (t, $[^3J_{HP} = 9.98$ Hz], CH_3); 1.12 (Harris t, $[|^2J_{HP} + {}^4J_{HP}| = 7.32$ Hz], PMe_3). $^{13}C\{H\}$-NMR (C_6D_6, 298 K, δ ppm): 1.43 (t, $[^3J_{CP} = 23.8$ Hz], CH_3); 15.46 (Harris t, $[|^1J_{CP} + {}^3J_{CP}| = 25.2$ Hz], PMe_3); 215.32 (t, $[^2J_{CP} = 16.6$ Hz], CO). $^{31}P\{H\}$-NMR (C_6D_6, 298 K, δ ppm): 25.85 (s, PMe_3).

(b) About 220 mg (0.35 mmol) of *fac*-$[Fe(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**4**) was suspended in 30 ml of THF. The suspension was cooled to −15°C. About 0.25 ml of a 1.6 M solution of CH_3Li in Et_2O was added in three steps to the cooled and stirred solution. IR was used to follow the reaction in the CO stretching region. Initially the formation of *cis,trans*-$Fe(CO)_2(PMe_3)_2(COCH_3)(CH_3)$ (**12**) was observed with two CO stretchings at 1996 and 1932 cm^{-1} and a $COCH_3$ stretching at 1591 cm^{-1}. Successively, this complex gave complex **6** and $Fe(CO)_3(PMe_3)_2$. By fluxing N_2, complex **12** was decarbonylated into complex **6**. Pure complex **6** was never obtained by this method.

2.6. Reaction of complex 6 with carbon monoxide

Complex **6**, dissolved in Et_2O, was left under carbon monoxide flux at r.t. and the reaction was followed by IR. Only $Fe(CO)_3(PMe_3)_2$ formed and no other intermediate complex was observed during the reaction which went to completion in 5 h. Besides $Fe(CO)_3(PMe_3)_2$, diacetyl ($CH_3CO–COCH_3$) also formed and was identified on the basis of the CO stretching bands ($\nu_{CO} = 1719, 1633\ cm^{-1}$ in Et_2O).

3. Results

The structures of all the complexes are given in Chart 1.

3.1. Reaction with borohydrides

The reactions were carried out with various borohydrides such as $NaBH_4$, NBu_4BH_4, $LiBEt_3H$. Since the behaviour of all the borohydrides was similar, we will describe only the reaction with $NaBH_4$.

Complex *fac*-$[Fe(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**4**) reacts very quickly with $NaBH_4$ at −15°C in MeCN. Initially complex $Fe(CO)_2(PMe_3)_2(MeCN)$ and CH_3CHO formed. $Fe(CO)_2(PMe_3)_2(MeCN)$ was characterized previously by us as the reduction product with sodium amalgam of $Fe(CO)_2L_2X_2$ (L = phosphine ligands and X = halide) in MeCN [15]. CH_3CHO was identified by its IR spectrum (CO stretching frequency at 1723 cm^{-1} in MeCN); its concentration increases to a maximum value and then decreases. The chromatographic analysis of the solution shows that CH_3CH_2OH is formed by the reduction of CH_3CHO with $NaBH_4$. The sum of the concentrations of CH_3CHO and CH_3CH_2OH corresponds to the quantity of the reacted complex **4**.

When the solution is warmed to room temperature *cis,trans*-$Fe(CO)_2(PMe_3)_2H_2$ (**8**) forms. The structure of complex **8** was assigned on the basis of its IR CO stretching bands (two CO stretchings of equal intensity at $\nu_{CO} = 1955, 1922\ cm^{-1}$ in MeCN) and ^1H-NMR spectrum (in CD_3CN) which shows a Harris triplet [16] at 1.32 ppm ($|^2J_{HP} + ^4J_{HP}| = 8.7$ Hz) due to PMe_3 and a triplet at -9.78 ppm ($^2J_{HP} = 61$ Hz) due to the two equivalent hydride protons, as observed in other similar complexes [17].

Complex *fac*-$[Os(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**3**) reacts with $NaBH_4$ in MeCN at 0°C to form *cis,trans*-$Os(CO)_2(PMe_3)_2(CH_3)H$ (**7**). No other compound was observed during the reaction. The structure of complex **7** was assigned on the basis of its IR and NMR spectra. The IR spectrum in *n*-hexane shows two CO stretching bands of equal intensity at 2003 and 1927 cm^{-1}, which indicate the *cis* position of the two CO ligands. The ^{1}H-NMR spectrum in CH_2Cl_2 shows a Harris triplet at 1.66 ppm, assigned to PMe_3, which indicates the equivalence of the two PMe_3 ligands; a triplet of doublet at -0.45 ppm, assigned to the methyl ligand which couples with the two phosphorus atoms of the phosphine ligands ($^3J_{HP} = 8.8$ Hz) and with the hydride ligand ($^3J_{HH} = 2.8$ Hz); and a triplet of quartet at -7.8 ppm assigned to the hydride ligand which couples with the two *cis* phosphorus atoms ($^2J_{HP} = 24.4$ Hz) and to the CH_3 protons ($^3J_{HH} = 2.8$ Hz). The structure is confirmed by the $^{13}C\{H\}$- and $^{31}P\{H\}$-NMR spectra. Complex **7** is very stable and does not exhibit reductive elimination even at 60°C, in contrast to similar complexes with other metals [18]. This behaviour is similar to the $Os(CO)_4(CH_3)H$ complex previously prepared by L'Eplattenier [19] and studied by Norton et al. [20].

The reduction of *fac*-$Os(CO)_3(PMe_3)CH_3I$ (**9**) with $NaBH_4$ in acetonitrile gives complex **10**. The structure of complex **10** (Chart 1) was assigned on the basis of the IR and NMR spectra. The IR spectrum shows three CO stretching bands of similar intensity at $\nu_{CO} = 2072$, 2011 and 1976 cm^{-1} in *n*-hexane, indicating a facial structure. The ^{1}H-NMR spectrum shows a doublet of doublet at -0.20 ppm (relative intensity 3) assigned to the methyl group, a doublet of quartet at -7.78 ppm (relative intensity 1) assigned to the hydride ligand and a doublet at 1.72 ppm (relative intensity 9), assigned to the PMe_3 ligand. The $^2J_{H-P}$ is 26.6 Hz in agreement with the *cis* structure between the hydride and the phosphine ligand [21].

In addition to the resonances of the methyl (-41.53 ppm) and the PMe_3 (19.08 ppm) groups, the $^{13}C\{^1H\}$-NMR spectrum also shows three doublets: one at 180.06 ppm, assigned to the COa group on the basis of the $^2J_{CO-P}$ coupling constant (83.5 Hz), characteristic of a *trans* structure of the CO and the phosphine ligand; [21] the second at 176.50 ppm ($^2J_{CO-P} = 8.25$ Hz) assigned to the COb group and the third at 179.39 ppm, with a coupling constant $^2J_{CO-P} = 8.03$ Hz, assigned to the COc group on the basis of the *trans* effect of the hydride ligand with respect to the methyl ligand [22].

cis,trans-$Fe(CO)_2(PMe_3)_2CH_3I$ (**2**) reacts with borohydrides in MeCN, giving $Fe(CO)_2(PMe_3)_2(MeCN)$ as the first product and then the hydride complex **8**. The behaviour is similar to complex **4** because complex **2** in MeCN is in equilibrium with the ionic derivative *cis,trans*-$[Fe(CO)_2(MeCN)(PMe_3)_2CH_3]^+I^-$ as previously described [23].

cis,trans-$Os(CO)_2(PMe_3)_2CH_3I$ (**1**) reacts very slowly with borohydrides in MeCN solution, but the product obtained is complex **7**. The reaction occurs via substitu-

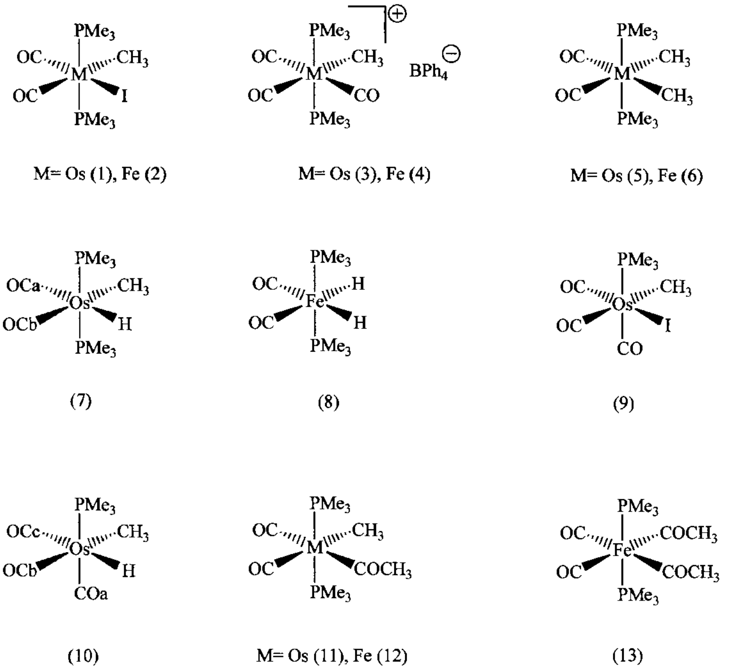
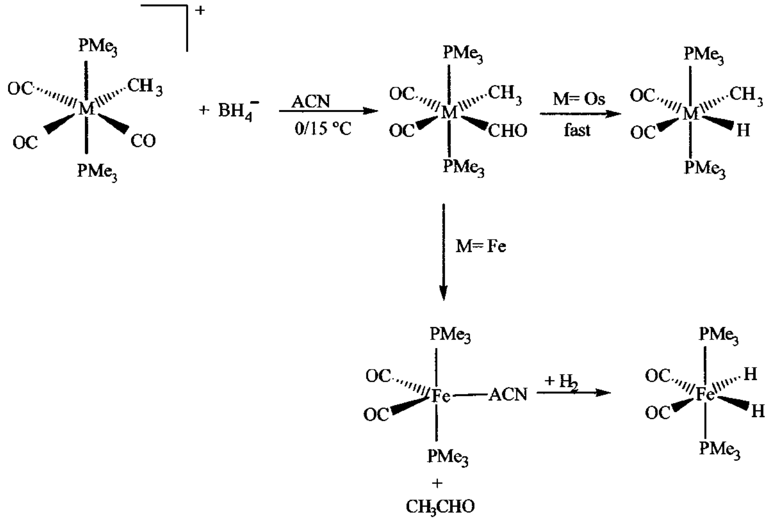

M= Os (1), Fe (2)
M= Os (3), Fe (4)
M= Os (5), Fe (6)
(7)
(8)
(9)
(10)
M= Os (11), Fe (12)
(13)

Chart 1.



Scheme 1.

tion of the iodide by the hydride anion as occurs in the reaction of some organometallic halide complexes with borohydrides [24].

3.2. Reactions with methyl lithium

The reaction of *cis,trans*-$Fe(CO)_2(PMe_3)_2CH_3I$ (**2**) with methyl lithium has already been described by Pankowski [25]. At −40°C in diethyl ether complex *cis,trans*-$Fe(CO)_2(PMe_3)_2(CH_3)_2$ (**6**) was obtained in 1% yield. We repeated the reaction in the same solvent at 0°C by using equimolar quantities of methyl lithium. The reaction was completed instantaneously. Complex **6** was obtained after crystallization from a *n*-hexane solution with a 55% yield.

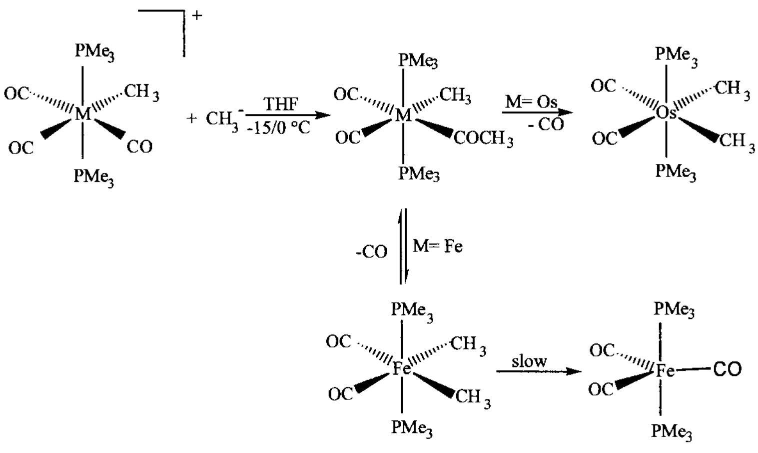
Complex *fac*-$[Fe(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**4**) reacts with methyl lithium in THF at −15°C giving *cis,trans*-$Fe(CO)_2(PMe_3)_2(CH_3)(COCH_3)$ (**12**) in the first step; complex **12** then decarbonylates to give complex **6**. $Fe(CO)_3(PMe_3)_2$ forms during this reaction always together with complex **6** due to the presence of free carbon monoxide. Complex **6** is stable at room temperature, but decomposes at temperatures higher than 40°C, giving $Fe(CO)_3(PMe_3)_2$ and other decomposition products. In the presence of carbon monoxide the decomposition also occurs at room temperature giving quantitatively $Fe(CO)_3(PMe_3)_2$; no acetyl complexes (either **12** or **13** (Chart 1)) were observed during this reaction, but $(COCH_3)_2$ formed and was identified by its IR spectrum.

cis,trans-$Os(CO)_2(PMe_3)_2CH_3I$ (**1**) reacts with methyl lithium in diethyl ether at room temperature to give complex *cis,trans*-$Os(CO)_2(PMe_3)_2(CH_3)_2$ (**5**), but the reaction does not go to completion. The preparation of complex **5** was obtained by reacting *fac*-$[Os(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ (**3**) with methyl lithium in THF at 0°C. The reaction was instantaneous and complex **5** was obtained quantitatively. Complex **5** shows two CO stretching bands of equal intensity at 1998 and 1930 cm^{-1} in THF, indicating the *cis* position of the two CO ligands, a Harris triplet in the ^{13}C- and ^{1}H-NMR spectrum, attributed to the PMe_3 ligands and a triplet attributed to the remaining equivalent CH_3 ligands. Complex **5** is very stable up to 60°C even in the presence of carbon monoxide or other nucleophilic ligands.

4. Discussion

The reduction of the ionic *fac*-$[M(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ complexes with borohydrides can be interpreted on the basis of Scheme 1. The first step of the reaction is the nucleoplilic attack of the hydride anion at the carbonyl ligand [26]. This reaction is well founded for a wide range of neutral and cationic carbonyl complexes [27]. The intermediate $M(CO)_2(PMe_3)_2(CH_3)(CHO)$ was never observed. The formation of this intermediate is supported by the experimental observation of CH_3CHO and $Fe(CO)_2(PMe_3)_2(MeCN)$ in the case of M = Fe. CH_3CHO could be formed by the reductive elimination of this intermediate. This indicates that reductive elimination is faster than the decarbonylation of the intermediate. Complex $Fe(CO)_2(PMe_3)_2(MeCN)$ reacts slowly to give complex **8**, which is very stable.

When M = Os, the decarbonylation of $Os(CO)_2(PMe_3)_2(CH_3)(CHO)$ is the most important process and complex **7** is formed. Complex **7** is also very stable in the presence of nucleophilic ligands. This behaviour is in agreement with the results obtained for complexes $Os(CO)_4(R)(H)$ described by Norton et al [20].



Scheme 2.

The different behaviours of Fe and Os can be easily explained on the basis of a fast reductive elimination in the iron complexes and a fast decarbonylation in the osmium complexes as observed previously [28].

cis,trans-$M(CO)_2(PMe_3)_2(CH_3)I$ (M = Fe, Os) reacts with borohydrides by the substitution of iodide with the hydride anion as observed in the literature [29]. $Fe(CO)_2(PMe_3)_2(CH_3)H$ eliminates CH_4 to give $Fe(CO)_2(PMe_3)_2(MeCN)$ whereas *cis,trans*-$Os(CO)_2(PMe_3)_2(CH_3)H$ is stable and is the final reaction product.

The reaction of *fac*-$[M(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ with CH_3Li in THF can be interpreted on the basis of Scheme 2.

The nucleophilic attack of CH_3^- at the carbonyl ligand forms $M(CO)_2(PMe_3)_2(CH_3)(COCH_3)$; this reaction is well founded in the literature [1b]. When M = Os, complex **11** decarbonylates very quickly to give the dimethyl complex **5**, which is also stable in the presence of nucleophilic ligands up to 60°C. When M = Fe complex **12** decarbonylates to complex **6**, which slowly gives $Fe(CO)_3(PMe_3)_2$. The decarbonylation of complex **12** to complex **6** is the equilibrium reaction; therefore the formation of complex **6** is not quantitative, because the free CO reacts with complex **12** to give $Fe(CO)_3(PMe_3)_2$.

Complexes **5** and **6** are also obtained when *cis,trans*-$M(CO)_2(PMe_3)_2(CH_3)I$ reacts with CH_3Li in diethyl ether. In this case, the reaction is quantitative for the iron derivative, due to the absence of free carbon monoxide. The reactions of complexes **5** and **6** with carbon monoxide were also studied. While complex **5** does not show reductive elimination up to 60°C, complex **6** shows quantitative formation of $Fe(CO)_3(PMe_3)_2$ at room temperature. Neither CH_3COCH_3 nor ethane formed. Diacetyl formed and was identified by comparison with a specimen. This behaviour indicates that the reaction of complex **6** proceeds via the formation of complex $Fe(CO)_2(PMe_3)_2(COCH_3)_2$ (**13**), which eliminates diacetyl quickly to give $Fe(CO)_3(PMe_3)_2$. Neither complex **12** nor complex **13** was observed as intermediates; this indicates that the reductive elimination in complex **13** is faster than the elimination in complexes **12** and **6**. This behaviour suggests the following order in the elimination reaction of methyl and acetyl complexes:

Diacetyl > acetyl,methyl > dimethyl

This order is in agreement with previous literature observations [30], regarding the behaviour of acetyl,methyl complexes with respect to dimethyl complexes.

In conclusion, the reduction of *fac*-$[M(CO)_3(PMe_3)_2CH_3]^+BPh_4^-$ and *cis,trans*-$M(CO)_2(PMe_3)_2(CH_3)I$ with methyl lithium leads to dimethyl complexes with both iron and osmium, while the reaction with borohydrides gives *cis,trans*-$M(CO)_2(PMe_3)_2(CH_3)H$ (M = Os) and dihydride complex (M = Fe). The different behaviours are due to the fast reductive elimination in the iron complex with respect to osmium and to the fast decarbonylation reaction of the osmium complexes, compared to the iron complexes.

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