Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 801–810
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Oxidative addition capability of triphosphine iron and ruthenium complexes with methyl iodide

Piotr Jaunky, Helmut W. Schmalle, Montserrat Alfonso, Thomas Fox, Heinz Berke *

Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, Zürich CH-8057, Switzerland

Received 21 July 2003; accepted 10 November 2003

Abstract

The ruthenium and iron dicarbonyl complexes $Ru(MeP(CH_2CH_2PMe_2)_2)(CO)_2$ (**1**), $Ru(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$ (**2**) and $Fe(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$ (**3**) bearing strong donor tridentate phosphine ligands were prepared and fully characterised. The structures of the complexes have been established by X-ray diffraction studies. Oxidative addition of MeI to **1**–**3** proceeds instantaneously at room temperature and affords the corresponding octahedral cationic complexes *fac*,*cis*-[RuMe$(MeP(CH_2CH_2PMe_2)_2)(CO)_2$]I (**5a**) and *mer*,*cis*-[RuMe$(MeP(CH_2CH_2PMe_2)_2)(CO)_2$]I (**5b**), *mer*,*trans*-[MMe$(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$]I (**6a** (M = Ru); **7a** (M = Fe)) and *mer*,*cis*-[MMe$(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$]I (**6b** (M = Ru); **7b** (M = Fe)), respectively. The triphosphine preferentially adopts a facial arrangement in the case of the ethylene bridged tridentate ligand (**5a**) and a meridional arrangement in the case of the trimethylene bridged ligand (**6a**–**7b**). *mer*,*cis*-[RuMe$(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$]I (**6a**) undergoes CO insertion to the acetyl complex *mer*, *trans*-$[Ru(COMe)(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2]$I (**8**). Attempts to produce a ketene complex from the deprotonation of **8** were not successful. The acetyl protons in **8** show very low acidity and no reaction occurred when the complex was reacted with bases such as DBU, BEMP (2-tert-Butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine) or LDA.

Keywords: Oxidative addition; Tridentate phosphine ligand; CO insertions; Ketenes

1. Introduction

A catalytic metal-mediated build up of ketene moieties is currently under investigation in our group,

$$R_1R_2CHX + CO + Base \rightarrow [BaseH]X + R_1R_2C{=}C{=}O \quad (1)$$

The process has been established in parts in a stoichiometric transition metal mediated fashion [1]. The thermodynamically feasible catalytic reaction is still to be put into reality. It involves a metal carbonyl complex catalyst and is based on initial oxidative addition of an alkyl halide followed by a CO insertion step. Subsequent deprotonation [2–4] of the acyl complexes may readily afford the corresponding ketene complexes. Ultimately, the ketene ligand can be displaced by CO, regenerating the starting carbonyl complex, thus closing the catalytic cycle. Attempts to generate ketenes by this reaction sequence using $Fe(CO)_3(PMe_3)_2$ [2] or $Fe(CO)_3(PEt_3)_2$ [1] as the catalyst have failed although every single step of the cycle has been successfully tested with these species. The major drawback of it seemed to be the oxidative addition step, which appeared to be too slow [5] in comparison to the reaction of the bases with the alkyl halide. Ruthenium or iron dicarbonyl complexes bearing strong donor tridentate phosphine ligands are expected to be much more reactive towards oxidative addition reactions and thus should allow to circumvent the difficulties encountered with the iron tricarbonyl species.

1.1. Preparation of the Ru and Fe dicarbonyl complexes

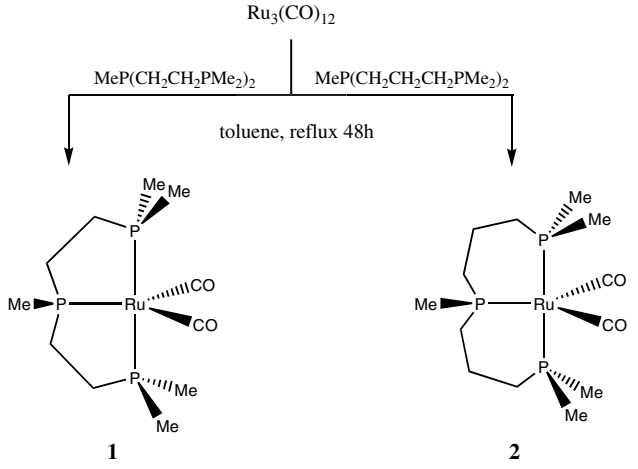
The tridentate phosphine ligands $MeP(CH_2CH_2PMe_2)_2$ [6] and $MeP(CH_2CH_2CH_2PMe_2)_2$ [7] were prepared according to published procedures. The

* Corresponding author. Tel.: +41-1-635-46-80; fax: +41-635-68-02.
E-mail address: hberke@aci.unizh.ch (H. Berke).

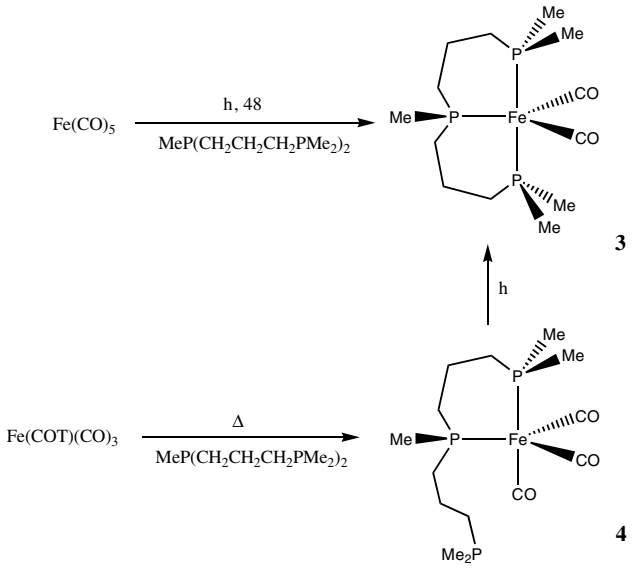
0022-328X/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2003.11.013

ruthenium dicarbonyl complexes **1** and **2** have been obtained from the thermal reaction of $Ru_3(CO)_{12}$ and the corresponding triphosphine ligand in refluxing toluene. The reactions proceed with a sequence of intermediates as indicated by ^{31}P NMR monitoring. Presumably, the ruthenium cluster is retained during the early stages of the reaction and slowly breaks down during the heating period to yield the dicarbonyl complexes **1** or **2** as the only product after 48 h (Scheme 1).

Attempts to prepare $Fe(MeP(CH_2CH_2CH_2\ PMe_2)_2)(CO)_2$ (**3**) from the thermal reaction of $Fe(CO)_5$ and $MeP(CH_2CH_2CH_2PMe_2)_2$ only led to the tricarbonyl iron complex $Fe(\eta^2\text{-}MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_3$ (**4**) where the triphosphine acts as a bidentate ligand. **4** could also be obtained from reaction of the triphosphine ligand and $Fe(COT)(CO)_3$ (Scheme 2). $Fe(COT)(CO)_3$ [8] (COT = cyclooctatetraene) or $Fe(BDA)(CO)_3$ [9] (BDA = benzylideneacetone) are efficient sources of $Fe(CO)_3$ and a variety of iron tricarbonyl complexes have been accessed by displacement of the labile [10] organic moieties with monodentate [11] or bidentate phosphine ligands [12]. The IR spectrum of **4** is consistent with the proposed structure and exhibits three ν_{CO} absorptions at 1871, 1903 and 1979 cm^{-1}. The bidentate coordination mode of the ligand was clearly evidenced by ^{31}P NMR spectroscopy. The coordinated phosphorus atoms exhibit doublet resonances (δ −13.2 and 20.8 ppm, $^2J_{PP} = 98$ Hz), while the uncoordinated terminal –PMe_2 group of the tridentate ligand gives rise to a singlet resonance at δ −53.4 ppm, the chemical shift being similar to that of the free ligand. When **4** is irradiated, further loss of carbon monoxide occurs leading to the formation of **3**, while prolonged heating affords only traces of the target dicarbonyl complex. The latter was more conveniently prepared by irradiation of a toluene solution of $MeP(CH_2CH_2CH_2PMe_2)_2$ and $Fe(CO)_5$ for 48 h at room temperature.



Scheme 1.



Scheme 2.

The IR spectra of the dicarbonyl complexes **1**–**3** exhibit two carbonyl stretching bands of similar intensities. The pattern indicates that the carbonyl groups are disposed *cis* in the pentacoordinated metal complexes [13]. The low wave numbers observed for the carbonyl bands suggest that the metal atom is rather electron rich consistent with the strong basic nature of the tridentate phosphine ligands. The ^{31}P NMR spectra of the complexes consist of an AM_2 spin system with a triplet resonance for the internal phosphorus nucleus of the tridentate ligand and a doublet resonance for the terminal phosphorus nuclei. The terminal phosphorus atoms of **1** exhibit a resonance at higher field than the internal phosphorus atom. The latter is at the bridgehead of two fused five-membered chelate rings which are known to cause low field ^{31}P chemical shifts relative to six-membered chelate rings [14]. Conversely, the complexes **2** and **3** possessing six-membered chelate rings show the opposite trend for the chemical shifts of the internal and terminal phosphorus nuclei. In the ^1H NMR spectra, the backbone protons of the tridentate phosphine ligands exhibit broad resonances in the region of δ 0.8–1.8 ppm. In the same chemical shift region there are also the sharp resonances of the methyl protons. The methyl groups bonded to the terminal phosphorus atoms show higher-order splitting patterns as reported earlier [15–17]. As observed in the ^1H NMR, the non-equivalence of the –PMe_2 methyl groups is also recognizable in the ^{13}C NMR spectra of the complexes **1**–**3**. The backbone carbon nuclei give rise to doublet of triplets resonances showing that coupling to all three phosphorus atoms occur. The central carbon atom of the trimethylene bridge has its resonance at higher field than the ones directly bonded to a phosphorus atom. The carbonyl resonances appear at low field (δ 218–220

ppm) displaying broad signals except in the case of **2**, where a quartet resonance was found at δ 218.1 ppm.

1.2. X-Ray diffraction studies on 1–3

The structures of **1**–**3** were unequivocally established by single crystal X-ray diffraction studies. Suitable crystals were obtained by slow cooling to −30 °C of a saturated toluene solution of the respective complex. Selected bond distances (Å) and bond angles (°) for the complexes **1**–**3** are listed in Table 1.

The X-ray diffraction studies on the dicarbonyl complexes **1**–**3** reveal distorted trigonal bipyramidal geometries at the metal centers (Figs. 1–3). The tridentate ligands span axial–equatorial–axial positions in the coordination polyhedron. The carbonyl ligands lie in the equatorial plane together with the internal phosphorus atom of the tridentate phosphine ligand. The chelate bite angle [18] of the ethylene bridged triphosphine ligand is obviously responsible for some strain occurring axially. As a consequence, the two axial ligands are bent towards the internal phosphorus atom, so that the P(2)–Ru(1)–P(3) angle in **1** is only 161.564(19)° which is significantly below the ideal 180° angle. The greater bite-angle of $MeP(CH_2CH_2CH_2PMe_2)_2$ compared to $MeP(CH_2CH_2PMe_2)_2$ is reflected by the almost absence of distortions in **2** (P(2)–Ru(1)–P(3) 178.90(2)°) and **3** (P(2)–Fe(1)–P(3) 171.21(2)°). The two five-membered chelate rings in the ruthenium complex **1** adopt an envelope conformation in order to minimise ring strain, while the two six-membered chelate rings in the complexes **2** or **3** are found in a boat conformation. The longest phosphine–metal bond is found for the equatorial phosphine P(1) as observed for the complexes **2** and **3**. This bond length pattern is in accord with the well-established [19] fact that strong σ-donor ligands (phosphine) are bound weakest in the equatorial plane of d^8 trigonal bipyramides.

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**–**3**

	1 (M = Ru)	**2** (M = Ru)	**3** (M = Fe)
Selected bond distances (Å)			
M(1)–P(1)	2.3009(5)	2.3386(6)	2.2125(6)
M(1)–P(2)	2.2999(5)	2.3167(6)	2.1789(6)
M(1)–P(3)	2.3281(5)	2.3166(6)	2.1815(6)
M(1)–C(1)	1.912(2)	1.890(2)	1.7394(19)
M(1)–C(2)	1.887(2)	1.896(2)	1.752(2)
C(1)–O(1)	1.150(3)	1.161(3)	1.180(2)
C(2)–O(2)	1.161(3)	1.163(3)	1.169(2)
Selected angles (°)			
P(1)–M(1)–P(2)	81.825(19)	89.58(2)	90.35(2)
P(1)–M(1)–P(3)	81.434(18)	91.30(2)	90.76(2)
P(2)–M(1)–P(3)	161.564(19)	178.90(2)	171.21(2)
P(1)–M(1)–C(1)	119.91(7)	119.91(7)	111.28(6)
P(1)–M(1)–C(2)	123.34(7)	116.82(7)	130.29(7)
C(1)–M(1)–C(2)	116.68(10)	125.84(9)	118.43(9)
C(1)–M(1)–P(2)	93.80(7)	90.15(8)	85.89(6)
C(1)–M(1)–P(3)	101.21(7)	90.03(8)	86.75(6)
C(2)–M(1)–P(2)	92.04(7)	89.60(7)	94.07(6)
C(2)–M(1)–P(3)	90.73(7)	89.41(7)	93.64(6)

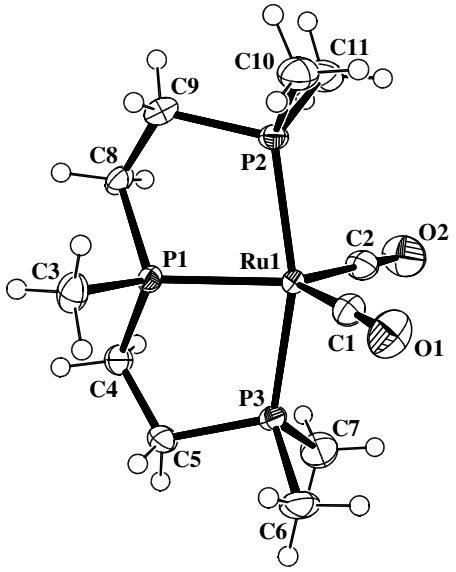


Fig. 1. Model of the X-ray diffraction study of **1** (ORTEP representation with selected atomic labels. Thermal ellipsoids are shown with a 50% probability level).

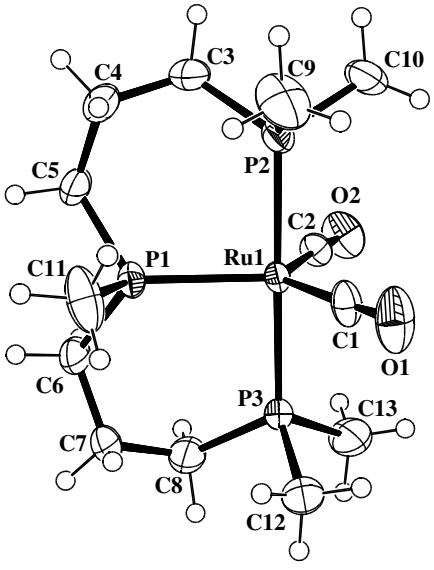


Fig. 2. Model of the X-ray diffraction study of **2** (ORTEP representation with selected atomic labels. Thermal ellipsoids are shown with a 50% probability level).

1.3. Oxidative addition reactions of MeI to the complexes 1–3

The addition of an excess of MeI to a benzene solution of **1** at room temperature resulted in an instanta-

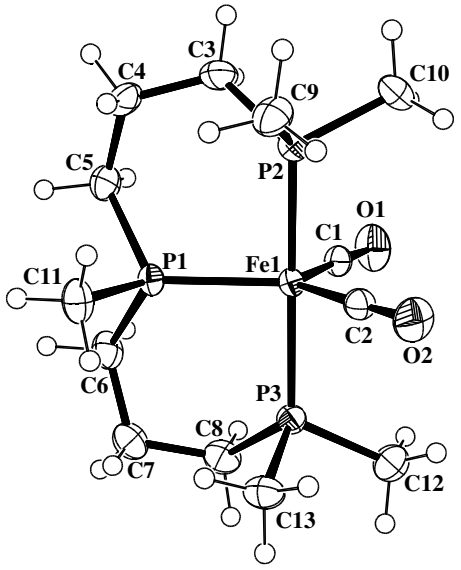
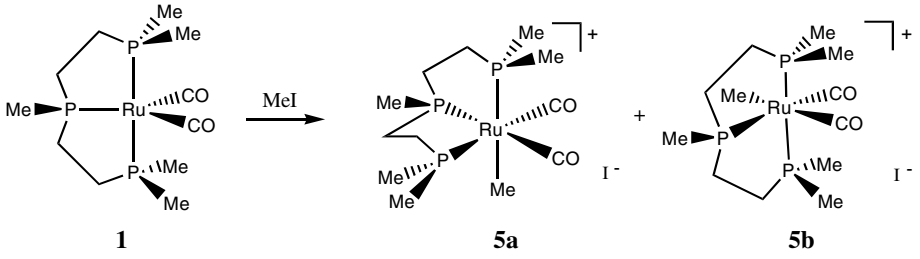


Fig. 3. Model of the X-ray diffraction study of **3** (ORTEP representation with selected atomic labels. Thermal ellipsoids are shown with a 50% probability level).

neous reaction. The benzene insoluble oxidative addition products consisted of a mixture of the cationic octahedral complexes *fac*, *cis*-[RuMe(MeP($CH_2CH_2PMe_2$)$_2$)$(CO)_2$]I (**5a**) and *mer*,*cis*-[RuMe(MeP($CH_2CH_2PMe_2$)$_2$)$(CO)_2$]I (**5b**) (Scheme 3).

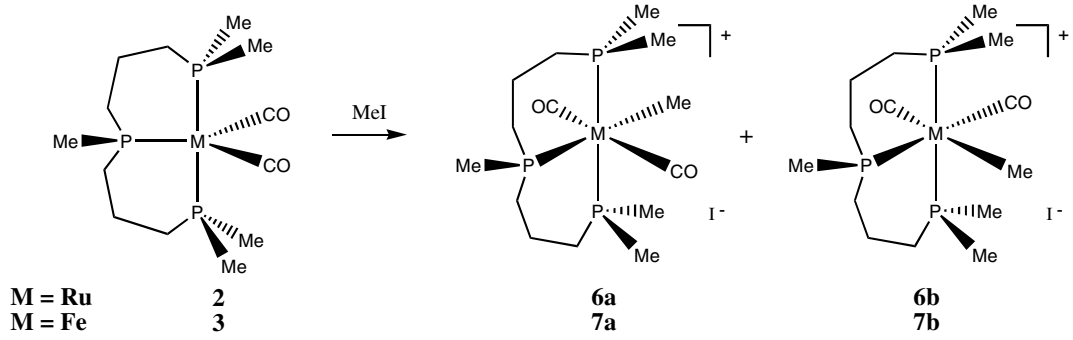
5a has been assigned structurally on the basis of IR and NMR data. The ^{31}P NMR spectrum of **5a** shows three doublet of doublets resonances indicating that the triphosphine ligand is facially bonded to the ruthenium center. The resonance at δ 86.3 ppm is assigned to the internal MeP– group, since it is the bridgehead of two five-membered chelate rings, thus a very low field chemical shift is expected. The resonances at δ 27.5 and δ 43.2 ppm are assigned to the PMe_2 group *trans* to a carbonyl ligand and *trans* to methyl, respectively. This assignment is based on the different *trans* influences of methyl and carbonyl groups on the phosphorus chemical shift [20]. The IR spectrum displays two strong carbonyl absorptions at 1996 and 2044 cm^{-1} for the carbonyl groups which are *cis* disposed. In the ^{1}H NMR spectrum, the resonance of the methyl group bonded to ruthenium appears at δ−0.4 ppm (ddd). The chemical shift is comparable with the chemical shift of the methyl group (δ−0.65 ppm) in *cis*,*fac*-[RuMe$(CO)_2$(etp)]I [21] (etp = PhP($CH_2CH_2PPh_2$)$_2$). Although a single [RuMe$(CO)_2$(etp)]I isomer was reported for the reaction of Ru$(CO)_2$(etp) with MeI, we observed that traces of a second isomer **5b** was present as detected by both ^{1}H and ^{31}P NMR spectroscopy. The ^{1}H NMR spectrum shows a quartet resonance at δ−0.92 ppm for the ruthenium bound methyl group. Thus, the methyl group is *cis* to the three phosphorus atoms of the triphosphine ligand. The ^{31}P NMR spectrum consists of an AB_2 spin system and indicates that the triphosphine ligand is meridionally coordinated to the ruthenium center. Therefore, the two carbonyl ligands are in *cis* position and occupy the remaining coordination sites, *trans* to the methyl group and *trans* to the internal –PMe group.

When a benzene solution of **2** was treated with an excess of MeI at room temperature, an instantaneous reaction occurred. An instantaneous reaction was even observed when the oxidative addition reaction was carried out in toluene at −78 °C. The precipitated oxidative addition products consisted of an isomeric mixture of the methyl complexes *mer*,*trans*-[RuMe(MeP($CH_2CH_2CH_2PMe_2$)$_2$)$(CO)_2$]I (**6a**) and *mer*,*cis*-[RuMe(MeP($CH_2CH_2CH_2PMe_2$)$_2$)$(CO)_2$]I (**6b**) (Scheme 4). The structure of the major isomer **6a** was assigned on the basis of IR and NMR evidence. The IR spectrum shows a single strong carbonyl absorption at 1990 cm^{-1}. The infrared data suggests that the carbonyl ligands are disposed *trans* to each other in the octahedral complex. The ^{31}P NMR spectrum of **6a** consists of an AB_2 spin system and this pattern is consistent with a meridional arrangement of the tridentate ligand around the ruthenium center. The methyl group therefore occupies the remaining coordination site *trans* to the –PMe group and exhibits the expected doublet of triplets (δ−0.32 ppm) resonance in the ^{1}H NMR spectrum. The *trans* coupling to phosphorus (3 Hz) is smaller than the *cis* coupling (6 Hz) and this trend has been previously observed in other related ruthenium complexes [22,23]. The Me–Ru moiety also exhibits a doublet of triplets resonance in the ^{13}C NMR spectrum. It is noteworthy that when an acetonitrile solution of **6a** and **6b** is kept at room temperature, the ratio **6a/6b** slowly increases



1 **5a** **5b**

Scheme 3.



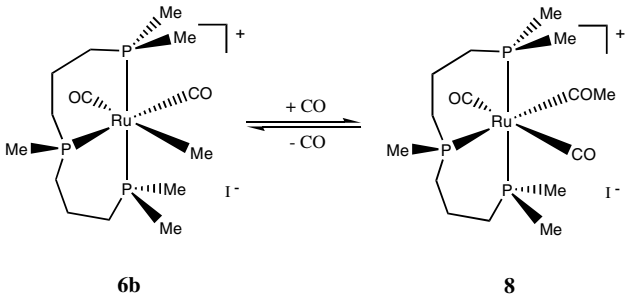
Scheme 4.

towards **6b.** The latter bears *cis* carbonyl ligands as indicated by the IR spectrum, which displays two strong carbonyl absorptions. The AB_2 spin system observed in the ^{31}P NMR spectrum is consistent with a meridional arrangement of the triphosphine around the metal center. Thus, the methyl group bonded to ruthenium is disposed *cis* to the three phosphorus atoms of the triphosphine and exhibits the expected quartet resonance in both the ^{1}H and the ^{13}C NMR spectra. Two related ruthenium complexes bearing trimethylene bridged triphosphine ligands can be found in the literature [21]. The oxidative addition of MeI to the complexes $Ru(CO)_2$(triphos), (triphos = ttp ($PhP(CH_2CH_2CH_2PPh_2)_2$) and cyttp ($PhP(CH_2CH_2CH_2PCy_2)_2$)) was reported to produce *mer*,*trans*-[RuMe(triphos)$(CO)_2$]I. The *mer*,*cis*-[RuMe(triphos)$(CO)_2$]I isomer could be detected only in the case where the triphosphine ligand was cyttp.

The iron complex **3** also reacted instantaneously with MeI when the oxidative addition reaction was carried out in benzene at room temperature to afford an isomeric mixture of the prevailing complex *mer*,*trans*-[FeMe($MeP(CH_2CH_2CH_2PMe_2)_2$)$(CO)_2$]I (**7a**) and of traces of *mer*,*cis*-[FeMe($MeP(CH_2CH_2CH_2PMe_2)_2$)$(CO)_2$]I (**7b**) (Scheme 4). The IR spectrum of **7a** shows a single strong ν_{CO} absorption and suggests that the carbonyl ligands occupy *trans* positions. The ^{31}P NMR spectrum indicates that the chelate phosphine ligand arranges in a *mer* configuration around the iron center. Therefore, the methyl group occupies the remaining coordination site *trans* to the central phosphorus atom of the triphosphine. The ^{1}H and ^{13}C NMR spectra did not show the expected doublet of triplets resonances for the Me–Fe moiety which appeared as simple triplets. One can rationalise the observed triplet resonances only if the *trans* coupling to phosphorus is assumed to be 0 or close to 0 Hz so that only the *cis* coupling is operative. The behaviour parallels the trend previously observed for related ruthenium complexes [22,23] (i.e., $^{3}J_{HP}$ (*trans*) $< {}^{3}J_{HP}$(*cis*)). To the best of our knowledge, similar observations have not been reported. The structure of the complex **7b** was assigned on the basis of ^{1}H and ^{31}P NMR data. IR spectroscopic data could not be recorded and the resonance for the iron bound methyl group could not be observed in the ^{13}C NMR spectrum owing to the low concentration of the complex in the isomeric mixture. The ^{31}P NMR spectrum indicates that the tridentate ligand occupies meridional positions around the central metal atom. The ^{1}H NMR spectrum shows a quartet resonance for the methyl group bonded to iron and implies that the latter is *cis* to the three phosphorus atoms of triphosphine. Therefore, the remaining carbonyl ligands are *cis* to each other.

1.4. Reactions with CO

Attempts to produce acetyl complexes by insertion of CO into the methyl–metal bonds of **5a** and **5b** were unsuccessful. It is noteworthy that a related methyl–ruthenium complex bearing a facially coordinated tridentate phosphine ligand was reported [23] not to react with carbon monoxide. Addition of methyl iodide to $Ru(CO)_2$(triphos) (triphos = $MeC(CH_2PPh_2)_3$) followed by treatment of the resulting methyl–ruthenium complex with carbon monoxide even under forcing conditions (270 atm over 15 h at 90 °C) failed to give the corresponding acetyl complex. It was also not possible to obtain acetyl complexes from the reaction of CO with the complexes **7a** and **7b**. However, when the isomers **6a** and **6b** are stirred under 1 bar of carbon monoxide for 48 h, the acetyl complex **8** was obtained. The presence of the acetyl moiety is confirmed by IR spectroscopy. The $\nu_{C=O}$ vibration is found at 1604 cm^{-1} as a medium intensity band and furthermore a strong absorption at 2003 cm^{-1} indicates the presence of *trans* CO groups. The ^{1}H NMR spectrum shows a singlet signal at δ 2.38 ppm for the acetyl protons. The ^{31}P NMR spectrum suggests a meridional phosphorus substitution pattern of the triphosphine ligand. The acetyl moiety was also detected in the ^{13}C NMR with the methyl group exhibiting a singlet resonance at δ 51.8 ppm and the C=O moiety showing a doublet of triplets resonance at very low field (δ 280.4 ppm). **6b** presumably converts to **8** in the presence of carbon monoxide via methyl migration



6b **8**

Scheme 5.

to the *cis* carbonyl [24–27], while driving the equilibrium between **6a** and **6b** towards the latter. Consistent with this observation is the fact that the acetyl complex **8** losses CO to give **6b** when the acetyl complex is stirred under a nitrogen atmosphere (Scheme 5).

*1.5. Attempts of deprotonation of **8***

In order to produce a ketene complex, deprotonation of the acetyl complex **8** was attempted using DBU or BEMP (2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine) [28] as the base. Whereas an immediate deprotonation of $Fe(PMe)_2(CO)_2(COMe)I$ occurred with BEMP [2], the acetyl protons of **8** show very low acidity and no deprotonation was observed even at the boiling point of acetonitrile. Stronger bases such as HMDS (hexamethyldisilazane) or LDA (lithium di-isopropylamide) also failed to react with the acetyl complex, which was left intact. It was also noted that decomposition occurred when *t*-BuLi was used as an example of a very strong base.

2. Experimental

All manipulations of air-sensitive compounds were carried out either in a dry glove-box under recirculating nitrogen or under dry nitrogen by conventional Schlenk techniques. Solvents were distilled from appropriate drying agents and freshly distilled under nitrogen prior to use (e.g., pentane, benzene and toluene were purified by refluxing over sodium/benzophenone, dichloromethane was refluxed either over calcium hydride or P_2O_5). The deuterated solvents (C_6D_6, CD_3CN) were obtained from commercial suppliers and distilled from appropriate drying agents and vacuum transferred for storage in Schlenk flasks fitted with Teflon stopcocks. ^1H, ^{31}P and ^{13}C NMR spectra were run on a *Varian Gemini-300* spectrometer operating at 300.1, 121.5 and 75.4 MHz, respectively. (δ (^1H), δ (^{13}C), rel. to $SiMe_4$, δ (^{31}P) rel. to 85% H_3PO_4). IR spectra were recorded on a *Bio-Rad FTS-45* instrument. Elemental analyses were measured on a *LECO CHNS-932* instrument. The irradiation experiments were carried out with a Philips HPK 125 high-pressure mercury lamp, cooled with a double-walled borosilicate water jacket.

The different transition metal carbonyl compounds $Fe(CO)_5$ (Alfa products), $Ru_3(CO)_{12}$ (Aldrich or Acros) and $Fe(COT)(CO)_3$ (Aldrich) were commercial products and used as received, $MePCl_2$ was graciously provided by Hoechst Knapsack. DBU and BEMP were purchased from Fluka. MeI was distilled over P_2O_5 under a nitrogen atmosphere before use. $MeP[CH_2CH_2PMe_2]_2$ [6] and $MeP[CH_2CH_2CH_2PMe_2]_2$ [7] were prepared according to reported procedures.

*2.1. General procedure for the preparation of the ruthenium dicarbonyl complexes **1** and **2***

The tridentate phosphine ligand was added to a suspension of $Ru_3(CO)_{12}$ (1/3 equiv.) in dry toluene. Slow CO evolution was observed and the mixture was heated to 40 °C during 4 h during which time the CO evolution stopped and all the $Ru_3(CO)_{12}$ had dissolved. The mixture was then heated to reflux for a period of 2 days during which time the colour changed from dark red to light yellow and all the free ligand was consumed, as observed by ^{31}P NMR monitoring. The toluene was then removed under vacuum to give a yellow solid. This residue was extracted with pentane. The pentane extracts were filtered over celite using a frit. Recrystallisation in cold (−30 °C) toluene afforded the air-sensitive ruthenium dicarbonyl complexes as light yellow solids.

*2.1.1. Ru(MeP(CH$_2$CH$_2$PMe$_2$)$_2$)(CO)$_2$ (**1**)*

According to the above general procedure, 710 mg (3 mmol) of $MeP(CH_2CH_2PMe_2)_2$ was reacted with 640 mg (1 mmol) of $Ru_3(CO)_{12}$ in 25 mL of dry toluene to give 730 mg (1.9 mmol, 64%) of **1** as a light yellow solid. Suitable crystals for X-ray diffraction were obtained from slow cooling to −30 °C of a saturated toluene solution. Anal. Calc. for $C_{11}H_{23}O_2P_3Ru$ (381.29): C, 34.65; H, 6.08. Found: C, 34.32; H, 6.11%. ^1H NMR (C_6D_6, 298 K): 0.9–1.4 (m, $-CH_2CH_2-$), 1.17 (d, $^2J_{HP} = 9$ Hz, $-P(CH_3)$), 1.25 and 1.36 (m, $-P(CH_3)_2$). $^{31}\{P\}^1\{H\}$ NMR (C_6D_6, 298 K): 45.5 (d, $^2J_{PP} = 34$ Hz, $-P(CH_3)_2$), 101.4 (t, $^2J_{PP} = 34$ Hz, $-P(CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): 19.1 (d, $J_{CP} = 21.4$ Hz, $-P(CH_3)$), 23 (t, $J_{CP} = 9.7$ Hz) and 25.9 (t, $J_{CP} = 14$ Hz, $-P(CH_3)_2$), 30.5 (dt, $J_{CP} = 14.4$ Hz, 26.3 Hz, $-CH_2CH_2-P(CH_3)$), 34.2 (dt, $J_{CP} = 13.7$, 21.4 Hz, $-CH_2CH_2-P(CH_3)_2$), 218.3 and 218.6 (m, CO). IR(C_6H_6, cm^{-1}): ν_{CO} 1860 (s) and 1937 (s).

*2.1.2. Ru(MeP(CH$_2$CH$_2$CH$_2$PMe$_2$)$_2$)(CO)$_2$ (**2**)*

According to the above general procedure, 1.2 g (4.7 mmol) of $MeP(CH_2CH_2CH_2PMe_2)_2$ was reacted

with 1 g (1.6 mmol) of $Ru_3(CO)_{12}$ in 25 mL of dry toluene. Recrystallisation in toluene at −30 °C gave 1.2 g (2.9 mmol, 62%) of **2** as a light yellow powder. Suitable crystals for X-ray diffraction were obtained from a saturated cold (−30 °C) toluene solution of **2**. Anal. Calc. for $C_{13}H_{27}O_2P_3Ru$ (409.34): C, 38.14; H, 6.65. Found: C, 38.47; H, 6.60%. ^1H NMR (C_6D_6, 298 K): 0.8–1.5 (m, $-CH_2CH_2CH_2-$), 1.1 (d, $^2J_{HP} = 9$ Hz, $-P(CH_3)$), 1.3 and 1.4 (m, $-P(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): −21.7 (t, $^2J_{PP} = 52$ Hz, $-P(CH_3)$), 1.6 (d, $^2J_{PP} = 52$ Hz, $-P(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): 20.1 (d, $J_{CP} = 5$ Hz, $-P(CH_3)$), 21.3 and 24 (m, $-P(CH_3)_2$), 23.6 (dt, $J_{CP} = 7$, 15.5 Hz, $-CH_2CH_2CH_2-$), 32.9 (dt, $J_{CP} = 9.6$, 15 Hz, $-CH_2CH_2CH_2-P(CH_3)$), 34 (dt, $J_{CP} = 4.7$, 21.6 Hz, $-CH_2CH_2CH_2-P(CH_3)_2$), 218.1 (q, $J_{CP} = 18$ Hz, CO). IR(C_6H_6, cm^{-1}): ν_{CO} 1834 (s) and 1886 (s).

2.1.3. $Fe(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$ (3)

$Fe(CO)_5$ (0.54 mL, 4 mmol) and $MeP(CH_2CH_2CH_2PMe_2)_2$ (1.2 g, 4.8 mmol) were mixed in 25 mL of toluene. The mixture was irradiated from the outside at room temperature with constant stirring during 48 h (^{31}P NMR spectroscopy monitoring) after which time the iron complex was the only compound present along with some free ligand. The toluene was then removed under vacuum to afford a brown solid which was washed with cold pentane. The crude reaction mixture was dissolved in 4 mL of toluene, filtered off over Celite and stored at −30 °C overnight during which time the complex precipitated as dark crystals suitable for X-ray diffraction (1 g, 2.7 mmol; 69%). Anal. Calc. for $C_{13}H_{27}O_2P_3Fe$ (364.12): C, 42.88; H, 7.47. Found: C, 42.75; H, 7.11%. ^1H NMR (C_6D_6, 298 K): 0.8–1.8 (m, $-CH_2CH_2CH_2-$), 1.0 (d, $^2J_{HP} = 6.3$ Hz, $-P(CH_3)$), 1.32 and 1.42 (m, $-P(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): 3.54 (t, $^2J_{PP} = 78.6$ Hz, $-P(CH_3)$), 35.9 (d, $^2J_{PP} = 78.6$ Hz, $-P(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): 19.8 (d, $J_{CP} = 3.2$ Hz, $-P(CH_3)$), 20.1 and 22.7 (m, $-P(CH_3)_2$), 22.1 (dt, $J_{CP} = 2$, 12.8 Hz, $-CH_2CH_2CH_2-$), 32.3 (m, $-CH_2CH_2CH_2-P(CH_3)$), 33.8 (dt, $J_{CP} = 6.3$, 23 Hz, $-CH_2CH_2CH_2-P(CH_3)_2$), 220.1 (br, CO). IR(C_6H_6, cm^{-1}): ν_{CO} 1817 (s), 1882 (s).

2.1.4. $Fe(\eta^2\text{-}MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_3$ (4)

$Fe(COT)(CO)_2$ (100 mg, 0.4 mmol) and $MeP(CH_2CH_2CH_2PMe_2)_2$ (100 mg, 0.4 mmol) were mixed in 2 mL of toluene and heated at 80 °C for 6 h. Recrystallisation from a cold (−30 °C) toluene/pentane mixture afforded 140 mg (0.36 mmol, 89%) of **4**. Anal. Calc. for $C_{14}H_{27}O_3P_3Fe$ (392.13): C, 42.88; H, 6.94. Found: C, 42.61; H, 6.87%. $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): −53.4 (s, uncoordinated $-P(CH_3)_2$), −13.2 (d, $^2J_{PP} = 97$ Hz, $-P(CH_3)$), 20.8 (d, $^2J_{PP} = 97$ Hz, coordinated $-P(CH_3)_2$). IR(C_7H_8, cm^{-1}): ν_{CO} 1871 (s), 1903 (s), 1979 (s).

2.2. General procedure for the oxidative addition of MeI to complexes 1–3

An excess of MeI (5 mmol) was added to 1 mmol of the metal carbonyl complex (**1**–**3**) in 5 mL of dry benzene at room temperature. An immediate precipitate appeared upon addition of the alkyl iodide. The reaction mixture was stirred for 10 min and filtered off over a frit under an inert atmosphere. The collected solid was washed with benzene and recrystallised from CH_2Cl_2/benzene.

2.2.1. Preparation of fac,cis-[RuMe(MeP(CH2CH2PMe2)2)(CO)2]I (5a) and mer,cis-[RuMe(MeP(CH2CH2PMe2)2)(CO)2]I (5b)

According to the above general procedure, treatment of 380 mg (1 mmol) of **1** with MeI (0.3 mL, 5 mmol) afforded 510 mg (0.97 mmol, 94%) of **5a** and **5b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{12}H_{26}O_2P_3RuI$ (523.23): C, 27.55; H, 5.01. Found: C, 27.36; H, 4.89%. **5a**: ^1H NMR (CD_3CN, 298 K): −0.4 (ddd, $^3J_{HP} = 3$, 5.8, 6.8 Hz, Ru–CH_3), 1.2–2.4 (m, $CH_3P[CH_2CH_2P(CH_3)_2]_2$). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): 27.5 (dd, $^2J_{PP} = 20$ Hz, $^2J_{PP} = 10$ Hz, $-P(CH_3)_2$ *trans* to CO), 43.2 (dd, $^2J_{PP} = 20$ Hz, $^2J_{PP} = 25$ Hz, $-P(CH_3)_2$ *trans* to Me), 86.3 (dd, $^2J_{PP} = 10$ Hz, $^2J_{PP} = 25$ Hz, $-P(CH_3)$). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K): −20.1 (m, Ru–CH_3), 19.8 (d, $J_{CP} = 21$ Hz, $-P(CH_3)$), 23 (m, $-P(CH_3)_2$), 32.3 (m, $-CH_2CH_2-P(CH_3)$), 36.1 (m, $-CH_2CH_2-P(CH_3)_2$), 199–200 (br, CO). IR(CH_2Cl_2, cm^{-1}): ν_{CO} 1996 (s) and 2044 (s). **5b** (selected data): ^1H NMR (CD_3CN, 298 K): −0.92 (q, $^3J_{HP} = 7$ Hz (*cis*), Ru-CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): 51.8 (d, $^2J_{PP} = 29$ Hz, $-P(CH_3)_2$), 78.7 (t, $^2J_{PP} = 29$ Hz, $-P(CH_3)$).

2.2.2. Preparation of mer,trans-[RuMe(MeP(CH2CH2CH2PMe2)2)(CO)2]I (6a) and mer,cis-[RuMe(MeP(CH2CH2CH2 PMe2)2)(CO)2]I (6b)

According to the above general procedure, treatment of 410 mg (1 mmol) of **2** with MeI (0.3 mL, 5 mmol) afforded 530 mg (0.96 mmol; 96%) of **6a** and **6b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{14}H_{30}O_2P_3RuI$ (551.28): C, 30.50; H, 5.49. Found: C, 30.70; H, 5.40%. **6a**: ^1H NMR (CD_3CN, 298 K): −0.32 (dt, $^3J_{HP} = 3$ Hz (*trans*), $^3J_{HP} = 6$ Hz (*cis*), Ru-CH_3), 1.4–2.2 (m, $CH_3P[CH_2CH_2CH_2\ P(CH_3)_2]_2$). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): −20 (t, $^2J_{PP} = 29$ Hz, $-P(CH_3)$), −9.4 (d, $^2J_{PP} = 29$ Hz, $-P(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K): −24.2 (dt, $J_{CP} = 25.9$ Hz (*trans*), $J_{CP} = 7$ Hz (*cis*), Ru-CH_3), 14.5 (t, $J_{CP} = 17.2$ Hz) and 16.9 (t, $J_{CP} = 15.6$ Hz, $-P(CH_3)_2$), 19.1 (d, $J_{CP} = 8.5$ Hz, $-P(CH_3)$), 20.7 (t, $J_{CP} = 16.9$ Hz, $-CH_2CH_2CH_2-$), 30.8 (dt, $J_{CP} = 29.2$, 2.2 Hz, $-CH_2CH_2CH_2-P(CH_3)$), 31.7 (dt, $J_{CP} = 6.3$, 16.8 Hz, $-CH_2$

CH_2CH_2–$P(CH_3)_2$), 199.2 (dt, $J_{CP} = 9.2$, 12.7 Hz, Ru–CO), 200 (dt, $J_{CP} = 8.5$, 14.6 Hz, Ru–CO). IR(CH_2Cl_2, cm^{-1}): ν_{CO} 1990 (s). **6b**: ^1H NMR (CD_3CN, 298 K): −0.47 (q, $^3J_{HP} = 8$ Hz, Ru–CH_3), 1.2–2.4 (m, $CH_3P[CH_2CH_2CH_2$ $P(CH_3)_2]_2$). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): −16 (d, $^2J_{PP} = 44$ Hz, –$P(CH_3)_2$), −15.8 (t, $^2J_{PP} = 44$ Hz, –$P(CH_3)$). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K): −9.4 (q, $^2J_{CP} = 9.3$ Hz, Ru–CH_3), 14.9 and 16 (t, $J_{CP} = 14.2$ Hz, –$P(CH_3)_2$), 19 (d, $J_{CP} = 7.6$ Hz, –$P(CH_3)$), 21 (m, –$CH_2CH_2CH_2$–), 28.3 (dt, $J_{CP} = 4.7$, 15.1 Hz, –$CH_2CH_2CH_2$–$P(CH_3)$), 29.7 (dt, $J_{CP} = 4.7$, 15.1 Hz, –$CH_2CH_2CH_2$–$P(CH_3)_2$), 194.3 (dt, $J_{CP} = 11$, 8 Hz, Ru–CO *trans* to Me), 195.5 (dt, $J_{CP} = 72$, 11.4 Hz, Ru–CO *trans* to –PMe). IR(CH_2Cl_2, cm^{-1}): ν_{CO} 1985 (s), 2043 (s).

2.2.3. Preparation of mer,trans-FeMe(MeP($CH_2CH_2CH_2PMe_2$)$_2$)(CO)$_2$]I (7a) and mer,cis-[FeMe(MeP($CH_2CH_2CH_2PMe_2$)$_2$)(CO)$_2$]I (7b)

According to the above general procedure, treatment of 365 mg (1 mmol) of **3** with MeI (0.3 mL, 5 mmol) afforded 440 mg (0.9 mmol, 89%) of a light brown powder as an isomeric mixture of **7a** and **7b**, which could not be separated. Anal. Calc. for $C_{14}H_{30}O_2P_3FeI$ (506.06): C, 33.23; H, 5.98. Found: C, 33.43; H, 6.06%. **7a**: ^1H NMR (CD_3CN, 298 K): −0.4 (t, $^3J_{HP} = 6.9$ Hz, Fe–CH_3), 1.2–2.3 (m, –$CH_2CH_2CH_2$–), 1.34–1.37 and 1.59–1.62 (m, –$P(CH_3)_2$), 1.64 (d, $^2J_{HP} = 8$ Hz, –$P(CH_3)$). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): 6.6 (t, $^2J_{PP} = 41$ Hz, –$P(CH_3)$), 18.8 (d, $^2J_{PP} = 41$ Hz, –$P(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K): −14.3 (t, $^2J_{CP} = 13$ Hz, Fe–CH_3), 13.3 (d, $J_{CP} = 12.2$ Hz, –$P(CH_3)$), 15.8 (t, $J_{CP} = 14.6$ Hz) and 17.9 (t, $J_{CP} = 14.9$ Hz, –$P(CH_3)_2$), 24.5 (dt, $J_{CP} = 29.6$, 4.6 Hz, –$CH_2CH_2CH_2$–), 25.5 (dt, $J_{CP} = 14$, 4.9 Hz, –CH_2CH_2 CH_2–$P(CH_3)$), 28.6 (dt, $J_{CP} = 24.4$, 6.1 Hz, –CH_2CH_2 CH_2–$P(CH_3)_2$), 214.7 (br, CO). IR(CH_2Cl_2, cm^{-1}): ν_{CO} 1961 (s). **7b** (selected data): ^1H NMR (CD_3CN, 298 K): −0.28 (q, $^3J_{HP} = 10$ Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): 4.8 (t, $^2J_{PP} = 70$ Hz, –$P(CH_3)$), 17.1 (d, $^2J_{PP} = 70$ Hz, –$P(CH_3)_2$).

2.2.4. Preparation of mer,trans-[Ru(COMe)(MeP($CH_2CH_2CH_2PMe_2$)$_2$)(CO)$_2$]I (8)

An acetonitrile solution of **6a/6b** (250 mg, 0.45 mmol) was stirred under a CO atmosphere for 48 h after which time only the acetyl complex **8** was present as indicated by ^1H NMR spectroscopy (absence of Me–Ru signals). Elemental analysis could not be obtained due to decarbonylation which readily occurred upon attempted isolation. ^1H NMR (CD_3CN, 298 K): 1.4–2.4 (m, $CH_3P[CH_2CH_2CH_2$ $P(CH_3)_2]_2$), 2.38 (s, Ru–C(O)CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): −23 (t, $^2J_{PP} = 42.7$ Hz, –$P(CH_3)$), −16.2 (d, $^2J_{PP} = 42.7$ Hz, –$P(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K): 16.3 (t, $J_{CP} = 23.6$ Hz) and 20 (t, $J_{CP} = 17$ Hz, –$P(CH_3)_2$), 18.6 (d, $J_{CP} = 6.6$ Hz, –$P(CH_3)$), 19.4 (m, –$CH_2CH_2CH_2$–), 26 (dt, $J_{CP} = 7.6$, 15.1 Hz, –$CH_2CH_2CH_2$–$P(CH_3)$), 26.9 (dt, $J_{CP} = 6.6$, 16 Hz, –$CH_2CH_2CH_2$–$P(CH_3)_2$), 51.8 (s, COCH_3), 192.9 (q, $J_{CP} = 9.6$ Hz, CO), 280.4 (dt, $J_{CP} = 8$, 11.2 Hz, C=O). IR(CH_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1604 (m), ν_{CO} 2003 (s).

Table 2
Crystal data and refinement details for complexes **1**, **2** and **3**

	1	2	3
Formula	$C_{11}H_{23}O_2P_3Ru$	$C_{13}H_{27}O_2P_3Ru$	$C_{13}H_{27}FeO_2P_3$
Formula weight	381.27	409.33	364.11
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group (No.)	$P2_1/c$	*Pbca*	$P2_1/n$
a (Å)	12.7115(7)	13.7722(8)	9.3587(7)
b (Å)	9.1954(6)	15.6410(9)	13.8308(7)
c (Å)	13.9253(8)	17.2327(13)	13.6717(7)
α, β, γ (°)	90, 99.616(6), 90	90, 90, 90	90, 97.673(9), 90
V (Å^3)	1604.82(17)	3712.1(4)	1753.80(18)
Z	4	8	4
Crystal dimensions (mm)	$0.32 \times 0.24 \times 0.18$	$0.53 \times 0.50 \times 0.44$	$0.30 \times 0.19 \times 0.18$
D_{calc} (g cm^{-3})	1.578	1.465	1.379
Absorption coefficient μ (mm^{-1})	1.265	1.099	1.129
$F(000)$	776	1680	768
2θ scan range (°)	$5.50 < 2\theta < 60.62$	$6.16 < 2\theta < 60.66$	$5.28 < 2\theta < 55.96$
Number of measured references	18,610	41,808	16,617
Unique data	4444	5533	4167
Transmission range	0.8043–0.6876	0.6434–0.5934	0.6366–0.4898
Number of parameters	246	177	177
R_1, wR_2 (%) all data	2.71, 6.28	4.01, 5.14	3.66, 3.87
R_1, wR_2 (observed) (%) [$I > 2\sigma(\sigma)$]	2.18, 5.79	2.44, 4.85	2.25, 3.82
Goodness-of-fit	1.065	0.998	1.229

2.3. X-ray structure analyses on *1*, *2* and *3*

Crystals of **1**, **2** and **3**, protected in hydrocarbon oil, were selected for the X-ray experiments using a polarizing microscope. They were mounted on top of a glass fibre and immediately transferred to the goniometer of an imaging plate detector system (Stoe IPDS diffractometer), where they were cooled to 183(2) K using an Oxford Cryo System. The crystal-to-image distances were set to 50, 50 and 60 mm for **1**, **2** and **3**, respectively ($\theta_{max} = 30.31$, 30.33 and 27.98°). The ϕ-rotation (**1**, **2**) or ϕ-oscillation (**3**) scan modes were applied according to the diffraction power (**1**, **2** strong, **3** weak) of the measured crystals. For the cell parameter refinements 7998, 8000 and 7998 reflections were selected out of the whole limiting spheres. A total of 18,610 (**1**), 41,808 (**2**) and 16,617 (**3**) diffraction intensities were collected [29], of which 4444, 5533 and 4167 were unique ($R_{int} = 0.0295$, 0.0395 and 0.0462) after data reduction. Numerical absorption corrections [30] based on 14, 21 and 18 crystal faces were applied with FACEitVIDEO and XRED [29]. The structures were solved by the Patterson method using the program SHELXS-97 [31]. Interpretation of the difference Fourier maps, preliminary plot generations and checking for higher symmetry were performed with PLATON [32] and the implemented program LEPAGE [33]. All heavy atoms were refined (SHELXL-97) [34] using anisotropic displacement parameters. Positions of H-atoms were calculated after each refinement cycle (riding model). Structural plots (Figs. 1–3) were generated using ORTEP [35]. Further crystallographic data and refinement results are presented in Tables 1 and 2.

3. Conclusion

The ruthenium or iron dicarbonyl complexes **1**–**3** bearing strong donor tridentate phosphine ligands show the expected high reactivity towards oxidative addition of methyl iodide. The geometries of the resulting octahedral cationic complexes **5a**–**7b** are dependent on the chelate bite angle [18] of the triphosphine ligands. Except for **6a** which inserts CO to give the acetyl complex **8**, it was observed that these cationic complexes do not react with CO (1 atm). Attempts to produce a ketene complex from the deprotonation of **8** were not successful. It is assumed that the low acidity of the acetyl complex arises from a too electron-rich metal fragment bearing the acetyl group.

4. Supporting material

Crystallographic data for structures **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 210755–210757 for compounds **1**–**3**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: + 44-1223-336033 or email: deposit@ccdc.cam.ac.uk or http://www.ccd.cam.ac.uk).

Acknowledgements

The financial support from the Swiss Science foundation and the funds of the University of Zurich is gratefully acknowledged.

References

[1] H. Berke, H. Kandler, W. Bidell, M. Janicke, D. Veghini, Organometallics 17 (1988) 960.
[2] M. Huttenloch, H. Berke, Unpublished results.
[3] D.A. Straus, R.H. Grubbs, J. Am. Chem. Soc. 104 (1982) 5499.
[4] B.D. Waymoith, R.M. Sanatarsiero, R.H. Grubbs, J. Am. Chem. Soc. 106 (1984) 4050.
[5] G. Cardachi, G. Bellachioma, A. Machioni, A. Madami, Inorg. Chem. 32 (1993) 554.
[6] R.B. King, J.C. Cloyd, J. Am. Chem. Soc. 97 (1975) 53.
[7] L. Dahlenburg, M. Antberg, C. Prengel, Inorg. Chem. 23 (1984) 4170.
[8] T.A. Manuel, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 366.
[9] J.A.S. Howell, B.F.G. Johnson, P.L. Josty, J. Lewis, J. Organomet. Chem. 39 (1972) 329.
[10] J.R. Sowa, V. Zanotti, G. Facchin, R.J. Angelici, J. Am. Chem. Soc. 113 (1991) 9185.
[11] L. Luo, S.P. Nolan, Organometallics 11 (1992) 3483.
[12] L. Luo, S.P. Nolan, Inorg. Chem. 32 (1993) 2410.
[13] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fourth ed., 1980, p. 1073.
[14] P.S. Pregosin, R.W. Kunz, ^{31}P and ^{13}C NMR Transit. Metal Complexes (1979).
[15] R.K. Harris, Can. J. Chem. 42 (1964) 2275.
[16] R.K. Harris, R.G. Hayter, Can. J. Chem. 42 (1964) 2282.
[17] E.G. Finer, R.K. Harris, Mol. Phys. 12 (1967) 457.
[18] P. Dierkes, P.W.N.M. Van Leeuwen, J. Chem. Soc., Dalton Trans. (1999) 1519.
[19] A.R. Rossi, R. Hoffmann, Inorg. Chem. 14 (1975) 365.
[20] D.W. Meek, T.J. Mazanec, Acc. Chem. Res. 14 (1981) 266.
[21] D.W. Meek, J. Guochen, Inorg. Chim. Acta 178 (1990) 195.
[22] S.I. Hommeltoft, M.C. Baird, Organometallics 2 (1986) 190.
[23] S.I. Hommeltoft, M.C. Baird, Organometallics 5 (1986) 1380.
[24] F. Calderazzo, Angew. Chem., Int. Ed. Engl. 16 (1977) 299.
[25] I.S. Butler, F. Basolo, R.G. Pearson, Inorg. Chem. 6 (1967) 2074.
[26] F. Calderazzo, Coord. Chem. Rev. 1 (1966) 118.
[27] G.M. Whitesides, J. Am. Chem. Soc. 96 (1974) 2814.
[28] R. Schwesinger, J. Willaredt, H. Schlemper, M. Keller, D. Schmitt, H. Fritz, Chem. Ber. 127 (1994) 2435.
[29] Stoe-IPDS Software package; version 2.92/1999. Stoe & Cie, GmbH, Darmstadt, Germany, 1999. Crystallographic data (excluding structure factors) for the structures given in this paper have been deposited with the Cambridge Crystallographic Data

Centre as supplementary publication nos. CCDC 210755, 210756 and 210757. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).
[30] P. Coppens, D. Leiserowitz, D. Rabinovich, Acta Crystallogr. 18 (1965) 1035.
[31] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[32] A.L. Spek, Acta Crystallogr., Sect. A 46 (1990).
[33] Y. Le Page, J. Appl. Crystallogr. 20 (1987) 264.
[34] G.M. Sheldrick, SHELX-97, Software package for Crystal Structure Determination and Refinement, University of Göttingen, Göttingen, Germany, 1997.
[35] C.K. Johnson, ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.