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Journal of Organometallic Chemistry 690 (2005) 1429–1455
Journal of Organometallic Chemistry
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Iron(0) and ruthenium(0) complexes with tridentate phosphonite ligands and their potential for ketene formation from methyl iodide, CO and a base

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Received 26 September 2004; accepted 18 November 2004
Available online 22 January 2005

Abstract

An efficient route to the novel tridentate phosphine ligands $RP[CH_2CH_2CH_2P(OR')_2]_2$ (**I**: R = Ph; R′ = *i*-Pr; **II**: R = Cy; R′ = *i*-Pr; **III**: R = Ph; R′ = Me and **IV**: R = Cy; R′ = Me) has been developed. The corresponding ruthenium and iron dicarbonyl complexes $M(triphos)(CO)_2$ (**1**: M = Ru; triphos = **I**; **2**: M = Ru; triphos = **II**; **3**: M = Ru; triphos = **III**; **4**: M = Ru; triphos = **IV**; **5**: M = Fe; triphos = **I**; **6**: M = Fe; triphos = **II**; **7**: M = Fe; triphos = **III** and **8**: M = Fe; triphos = **IV**) have been prepared and fully characterized. The structures of **1**, **3** and **5** have been established by X-ray diffraction studies. The oxidative addition of MeI to **1**–**8** produces a mixture of the corresponding isomeric octahedral cationic complexes *mer*,*trans*-(**13a**–**20a**) and *mer*,*cis*-[M(Me)(triphos)$(CO)_2$]I (**13b**–**20b**) (M = Ru, Fe; triphos = **I**–**IV**). The structures of **13a** and **20a** (as the tetraphenylborate salt (**21**)) have been verified by X-ray diffraction studies. The oxidative addition of other alkyl iodides (EtI, *i*-PrI and *n*-PrI) to **1**–**8** did not afford the corresponding alkyl metal complexes and rather the cationic octahedral iodo complexes *mer*,*cis*-[M(I)(triphos)$(CO)_2$]I (**22**–**29**) (M = Ru, Fe; triphos = **I**–**IV**) were produced. Complexes **22**–**29** could also be obtained by the addition of a stoichiometric amount of I_2 to **1**–**8**. The structure of **22** has been verified by an X-ray diffraction study. Reaction of **13a/b**–**20a/b** with CO afforded the acetyl complexes *mer*,*trans*-[M(COMe)(triphos)$(CO)_2$]I, **30**–**37**, respectively (M = Ru, Fe; triphos = **I**–**IV**). The ruthenium acetyl complexes **30**–**33** reacted slowly with 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) even in boiling acetonitrile. Under the same conditions, the deprotonation reactions of the iron acetyl complexes **34**–**37** were completed within 24–40 h to afford the corresponding zero valent complexes **5**–**8**. It was not possible to observe the intermediate ketene complexes. Tracing of the released ketene was attempted by deprotonation studies on the labelled species *mer*,*trans*-[Fe$(COCD_3)$(triphos)$(CO)_2$]I (**38**) and *mer*,*trans*-[Fe(^{13}COMe)(triphos)$(CO)_2$]I (**39**).

Keywords: Iron; Ruthenium; Phosphonite; Oxidative addition; Ketene

1. Introduction

A catalytic metal mediated build-up of ketene moieties is currently under investigation in our group [1]. The process involves a metal carbonyl catalyst and is based on initial oxidative addition of an alkyl halide followed by a CO insertion step. Subsequent deprotonation of the acyl complexes may afford the corresponding ketene complexes. Ultimately, the ketene ligand can be displaced by CO, regenerating the starting carbonyl complex, thus closing the catalytic cycle. In an earlier publication [1], we have reported that $Fe(CO)_3(PMe_3)_2$ or $Fe(CO)_3(PEt_3)_2$ were not suitable catalysts for the process owing to their poor reactivity towards oxidative addition reactions with alkyl halides. The ruthenium or iron dicarbonyl complexes $Ru(MeP(CH_2CH_2PMe_2)_2)(CO)_2$, $Ru(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2$, and Fe (MeP-

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doi:10.1016/j.jorganchem.2004.11.055

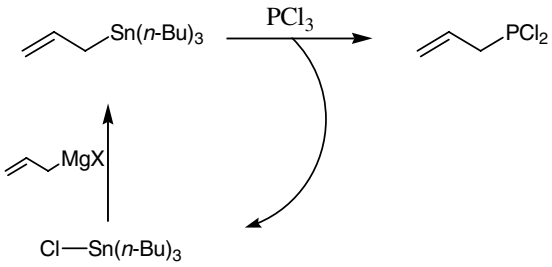
$(CH_2CH_2CH_2PMe_2)_2)(CO)_2$, bearing strong donor tridentate phosphine ligands, expectedly showed a much higher reactivity towards oxidative additions. In conjunction with these systems, problems were also encountered here for the reactions with CO or for the deprotonation reactions. Deprotonation of the acetyl species $[Ru(COMe)(MeP(CH_2CH_2CH_2PMe_2)_2)(CO)_2]I$ could not be effected with $P[MeN(CH_2)_3NMe](NEt_2)(N$*t*-Bu) (BEMP) or even stronger bases such as sodium hexamethyldisilazide (HMDS) or lithium diisopropylamide (LDA). It is assumed that the low acidity of the acetyl complex arises from a too electron-rich metal fragment bearing the acetyl group. Therefore, an electronic tuning of the triphosphine ligand was undertaken to enhance the acidity of the M-$COCH_3$ protons without losing on the ability of the metal center to accomplish oxidative additions. The ruthenium and iron complexes **1**–**8** bearing the novel tridentate phosphine ligands **I**–**IV** with terminal alkoxy groups were investigated and the results are presented hereafter.

2. Preparation of the tridentate phosphine ligands I–IV

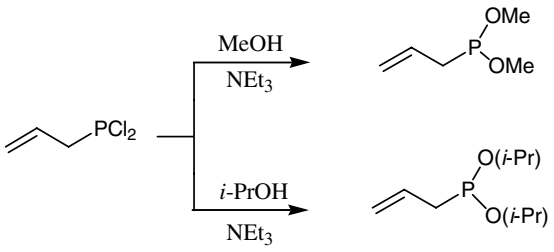
The polyphosphines containing terminal alkoxy groups provide chelating ligands with stronger π-accepting properties than polyphosphines containing terminal alkyl groups [2–4], owing to the greater electronegativity of the alkoxy substituents [5]. Essentially two methods have been applied to introduce alkoxy substituents on a phosphorus atom: the alcoholysis of aminophosphine derivatives [6–10] or the reaction of chlorophosphine derivatives with an alcohol in the presence of a tertiary amine base [11–15]. Triphosphine ligands of the type $RP[CH_2CH_2CH_2P(OR)_2]_2$ have not been reported previously. The tridentate phosphine ligands $RP[CH_2CH_2P(OMe)_2]_2$ (R = Me, Ph), prepared from alcoholysis of aminophosphine intermediates, have been reported by King and Masler [7]. The procedure involves a base catalysed addition [2,3,16,17,7] of dimethylvinylphosphonite to methyl- or phenylphosphine. The required vinyl phosphonite intermediate was obtained from the reaction of bis(dimethylamino)vinylphosphine with methanol. We have however observed that substitution of both amino groups did not occur when isopropanol was used instead of methanol, presumably owing to steric factors. Thus, the synthetic method is not suitable for triphosphines bearing terminal isopropoxy groups, which are valuable ligands, since they should be less sensitive to Arbuzov [18,19] type reactions than the triphosphines possessing methoxy groups. The conversion of the P–Cl bonds in chlorophosphine derivatives appears to have a wider scope than the alcoholysis of aminophosphines [20]. Approaches involving bis(primaryphosphine) derivatives of the type $RP[CH_2CH_2CH_2PH_2]_2$, where the P–H bonds can be converted to P–Cl bonds by a variety of methods [21–26] are restricted by the reactivity of the internal tertiary phosphine function, which readily quaternizes in the presence of P–Cl bonds. Protecting groups such as BH_3 or sulfur cannot be envisaged because of the alcoholysis conditions (tertiary amine base are typically used to deprotect phosphine borane adducts) [27–29] or the desulfuration conditions, respectively. We therefore envisaged next the synthesis of the trimethylene-bridged phosphine ligands from coupling of a primary phosphine with allylphosphonites which can be readily prepared from alcoholysis of allyldichlorophosphine. The synthetic approach should also be convenient for the synthesis of ethylene-bridged triphosphines $RP[CH_2CH_2P(OR)_2]_2$ by using vinylphosphonites, but the required vinyldichlorophosphine intermediate is difficult to prepare [30]. The reaction of PCl_3 with vinyltin derivatives failed to give dichlorovinylphosphine [31]. In contrast to this, allyldichlorophosphine was available from allyltributyltin and PCl_3 [32]. The reaction was carried out with irradiation and found to be faster in the presence of a radical initiator (AIBN), therefore a radical character of the substitution was proposed. However, the reaction was reported [33] later to also proceed without photolysis and in the presence of duroquinone or acrylonitrile. Thus, an anionic process cannot be excluded. We observed that the reaction of allyltributyltin and PCl_3, carried out on the pure compounds at room temperature and without irradiation, proceeded cleanly to afford high yields of allyldichlorophosphine (Scheme 1).

A slight excess of the allyltin derivative was always used to ensure complete conversion of PCl_3 into the allylphosphine, because the two chloro phosphines are difficult to separate. Tributyltinchloride is regenerated during the reaction and may be re-used. Conversion of allyldichlorophosphine to dimethyl- or diisopropylallylphosphonite [34] by alcoholysis with methanol or isopropanol, respectively, in the presence of triethylamine proceeded in excellent yields (Scheme 2).

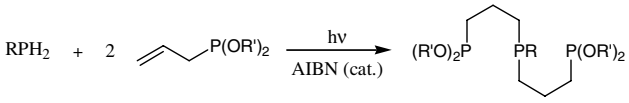
The AIBN catalysed free radical addition [35–38] of phenylphosphine or cyclohexylphosphine with either dimethyl- or diisopropylallylphosphonite afforded the triphosphine ligands **I**–**IV** in quantitative yields (Scheme 3).



Scheme 1.



Scheme 2.



I (R = Ph; R' = *i*-Pr)
II (R = Cy; R' = *i*-Pr)
III (R = Ph; R' = Me)
IV (R = Cy; R' = Me)

Scheme 3.

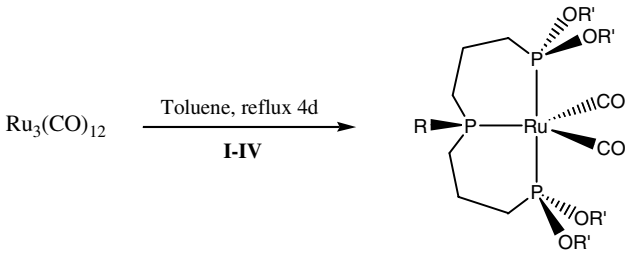
The irradiation was carried out on the pure intermediates and the ligands were obtained as colourless air-sensitive viscous liquids, which gave satisfactory elemental microanalysis. The NMR spectra were in accord with the given structures [39–41]. The compounds solidified upon storing at −30 °C.

3. Preparation of the Ru(0) and Fe(0) dicarbonyl complexes 1–8

Only a few reports of ruthenium complexes containing tridentate phosphine ligands have appeared in the literature [42–44]. Synthetic access to them involve either direct substitution on zerovalent ruthenium carbonyl complexes [45] or reduction of ruthenium(II) precursors in the presence of carbon monoxide [44,46,47]. The complexes **1**–**4** were prepared in good yields from the thermal reaction of the corresponding tridentate phosphine ligand with $Ru_3(CO)_{12}$ in refluxing toluene (Scheme 4).

The ruthenium dicarbonyl complexes **1**–**4** were all obtained as air-sensitive light yellow solids, which gave satisfactory elemental analysis. All complexes were fully characterized by IR and NMR spectroscopy.

In general, carbonyl complexes of iron ($Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$) react with monodentate phosphine ligands to give mixtures of the mono- and disubstituted derivatives $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$ [48,49]. This behaviour is expected to result from the intermediary $[Fe(CO)_4]$ [50,51]. Multidentate phosphine ligands allow substitution of three CO groups. Alternatively, tri(tertiary phosphine)dicarbonyliron(0) complexes are often prepared by reduction of iron(II) precursors [52–54].



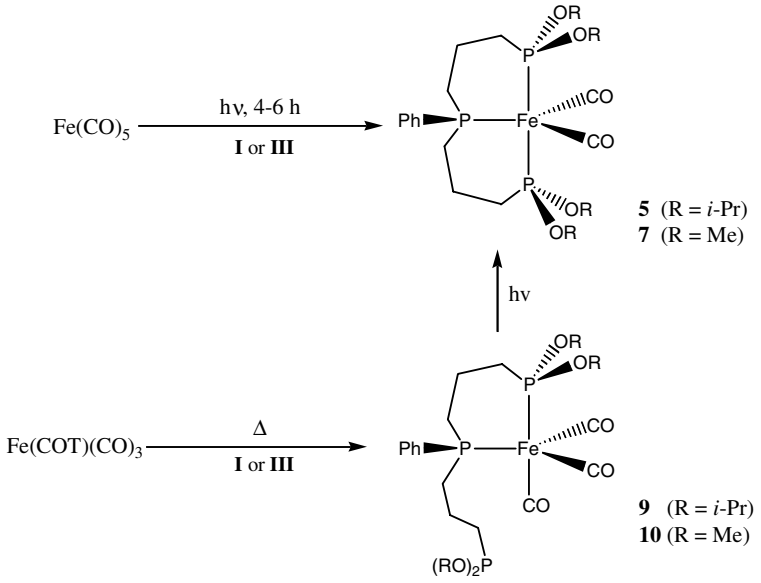
	R	R'
1	Ph	*i*-Pr
2	Cy	*i*-Pr
3	Ph	Me
4	Cy	Me

Scheme 4.

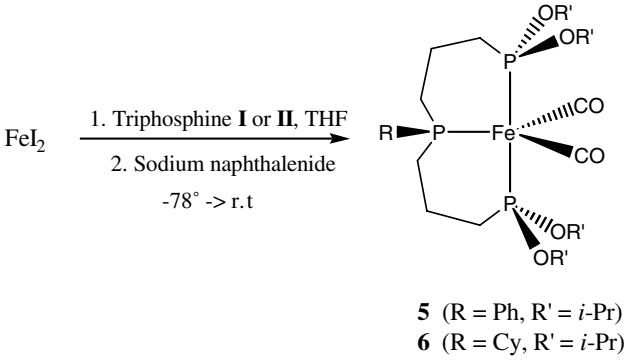
The thermal reaction of $Fe(CO)_5$ and the triphosphine ligands **I** or **III** afforded the corresponding iron tricarbonyl complexes **9** and **10**, respectively, where the triphosphine is η^2 coordinated together with minor amounts of the target iron dicarbonyl complexes (**5** or **7**). The iron tricarbonyl complexes could also be obtained by displacement of the cyclooctatetraene moiety from $Fe(COT)(CO)_3$ (Scheme 5).

Attempts to displace a carbonyl group by further heating were not successful. It was observed that the iron tricarbonyl complexes **9** and **10** could be converted to the corresponding dicarbonyl complexes **5** and **7**, respectively, upon irradiation, however, in these cases the reactions showed considerable amounts of decomposition products. When a toluene solution of iron pentacarbonyl is irradiated in the presence of the tridentate phosphine ligands **I**–**IV**, complexes **5** and **7** are formed in similar yields. ^{31}P NMR monitoring of the photochemical reactions according to Scheme 5 showed that the iron dicarbonyl complexes were the only compounds present along with the free phosphine ligands after 4–6 h. Complete decomposition occurred upon longer irradiation times (10 h or more). The synthesis of the iron dicarbonyl complexes (**5**–**8**) from the reduction of the corresponding Fe(II) precursors was examined next. $FeCl_2$ reacted with **I** to give $Fe(PhP[CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2)Cl_2$ (**11**) in high yield. The compound showed satisfactory elemental analysis. However, an attempted reduction of **11** with sodium amalgam did not lead to the dicarbonyl complex **5** presumably owing to the poor solubility of **11** in THF. Therefore, the analogous more soluble diiodo complex $Fe(PhP[CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2)I_2$ (**12**) was prepared in high yield from FeI_2 and **I** in THF at room temperature. Complex **12** was cleanly reduced to the target complex **5** under an atmosphere of CO with sodium naphthalenide. A similar procedure could be applied for the synthesis of **6** (Scheme 6).

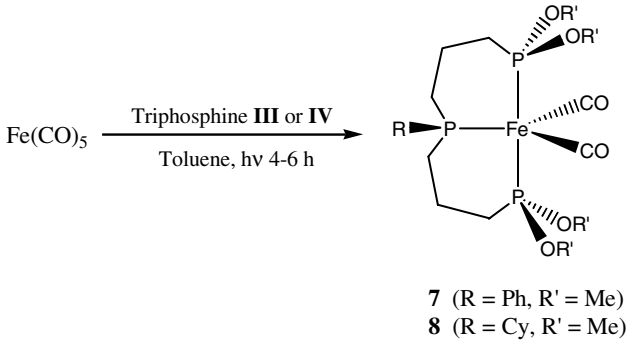
Surprisingly, the iron complexes **7** and **8** bearing the tridentate phosphine ligands **III** and **IV** with terminal



Scheme 5.



Scheme 6.



Scheme 7.

methoxy groups could not be prepared using a similar approach as for the synthesis of **5** and **6**. Brunnet et al. [55] published an extensive series of $Fe(CO)_2L_3$ complexes (L = phosphine, phosphite) involving a one-pot reaction of $K[FeH(CO)_4]$ and the corresponding ligands in a protic medium. The type of complexes $Fe(CO)_2(PR_3)_3$ and $Fe(CO)_2(P(OR)_3)_3$ were obtained in fair to high yields (depending on the ligand's cone angle). However, preparations of **7** or **8** starting from $K[FeH(CO)_4]$ [56–58] or $H_2Fe(CO)_4$ [59,60] failed. The Fe(0) dicarbonyl complexes **7** and **8** were finally obtained in low yields (~30%) from the short time irradiation of $Fe(CO)_5$ with the tridentate phosphine **III** and **IV**, respectively (Scheme 7). ^{31}P NMR monitoring of the reaction showed the optimum irradiation times for the reaction to be 4–6 h in dilute toluene solutions (0.1 M) of $Fe(CO)_5$ and the respective triphosphine ligand. Irradiation was stopped as soon as other unidentified broad signals started to appear around 35 and 220 ppm in the ^{31}P NMR spectrum.

4. X-ray diffraction studies on 1, 3 and 5

Suitable crystals for X-ray diffraction for **1, 3** and **5** were obtained from slow cooling of saturated toluene solutions to −30 °C. Selected bond distances (Å) and bond angles (°) are listed in Table 1. The complexes possess approximate trigonal bipyramidal geometry with the tridentate phosphine ligand spanning axial–equatorial–axial positions (Figs. 1–3). Axial distortions are more pronounced for the complexes bearing diisopropylphosphonite groups (**1** and **5**). The phosphonite groups located above the equatorial plane are eclipsed with those located below the equatorial plane. With respect to the P(2)–P(3) axis, the phosphonite groups and the equatorial carbonyl ligands appear staggered. The longest phosphine–metal bond is obtained for the equatorial phosphine P(1). This bond length pattern is in accord with the well-established fact [61] that σ-donor ligands are bound weakest in the equatorial positions in d^8 trigonal bipyramids.

Table 1
Comparison of selected related bond lengths (Å) and bond angles (°) in **1**, **3** and **5**

	1 (M = Ru)	**3** (M = Ru)	**5** (M = Fe)
Bond distances (Å)			
M(1)–P(1)	2.3608(6)	2.352(2)	2.2203(6)
M(1)–P(2)	2.2918(6)	2.268(2)	2.1601(6)
M(1)–P(3)	2.3025(6)	2.261(2)	2.1630(6)
M(1)–C(1)	1.905(3)	1.918(8)	1.7537(18)
M(1)–C(2)	1.888(2)	1.921(8)	1.747(2)
C(1)–O(1)	1.154(3)	1.149(10)	1.169(2)
C(2)–O(2)	1.166(3)	1.185(11)	1.173(2)
Angles (°)			
P(1)–M(1)–P(2)	89.62(2)	95.72(8)	91.42(2)
P(1)–M(1)–P(3)	88.99(2)	86.18(8)	90.40(2)
P(2)–M(1)–P(3)	171.46(2)	177.23(8)	169.35(2)
P(1)–M(1)–C(1)	96.62(8)	105.3(3)	96.96(7)
P(1)–M(1)–C(2)	142.20(8)	122.2(3)	144.93(6)
C(1)–M(1)–C(2)	121.17(11)	132.5(4)	118.11(9)
C(1)–M(1)–P(2)	93.19(8)	91.2(3)	93.85(6)
C(1)–M(1)–P(3)	95.35(8)	86.3(3)	96.34(6)
C(2)–M(1)–P(2)	87.81(8)	84.8(2)	86.06(6)
C(2)–M(1)–P(3)	88.12(8)	95.9(2)	86.41(6)

5. Reaction of 1–8 with alkyl iodides

The oxidative additions of MeI to the ruthenium centers of **1**–**4** are completed within 5 min when the reactions are performed in dichloromethane at room temperature. Under the same conditions, the reactions of the iron complexes **5** and **7** bearing ligands with a phenyl group on the internal phosphorus atom of the triphosphine take 48 h. Consistent with the increased basicity of the cyclohexyl triphosphine system, the iron complexes **6** and **8** react on a qualitative scale faster with MeI in comparison with the phenyl-substituted compounds. Furthermore, the ruthenium complexes react much faster with MeI than the iron complexes. A similar trend has been observed for the disubstituted phosphine derivatives of $Ru(CO)_5$ and $Fe(CO)_5$ [62–66]. The oxidative addition reactions of MeI with **1**–**8** are summarized in Scheme 8.

An isomeric mixture of the corresponding *mer*,*trans*- and *mer*,*cis*-[M(Me)(triphos)$(CO)_2$]I (M = Fe, Ru; triphos = **I**–**IV**) cationic octahedral complexes is formed.

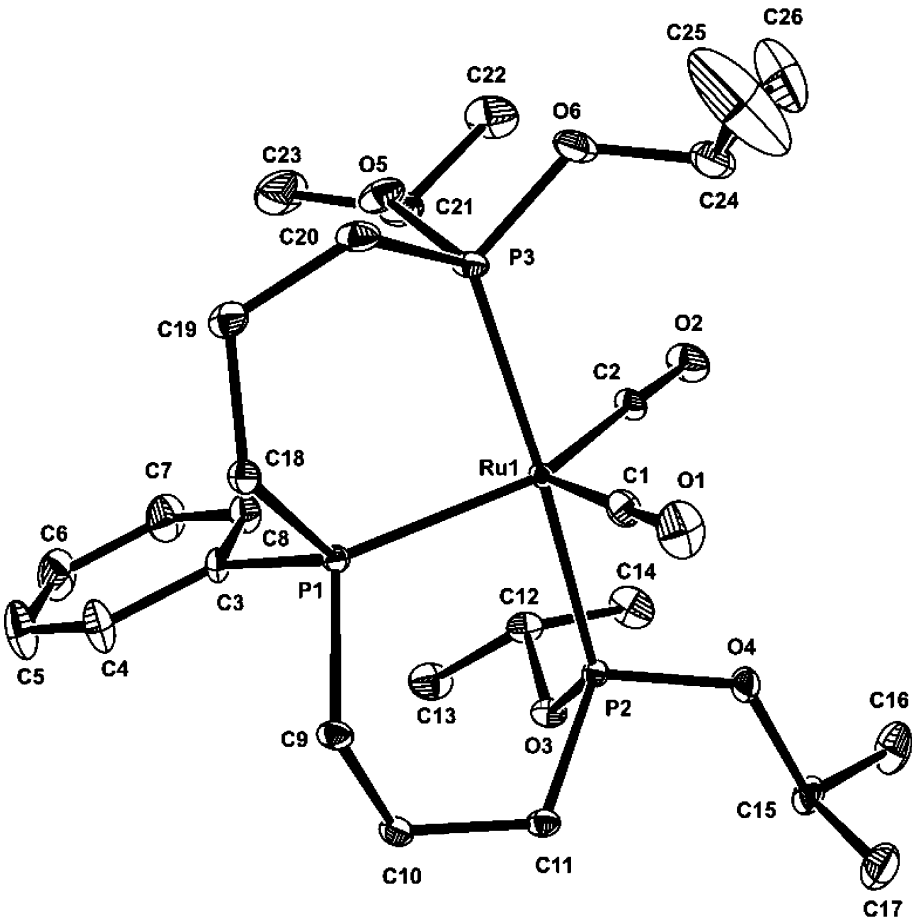


Fig. 1. Model of the structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown with a 30% probability level.

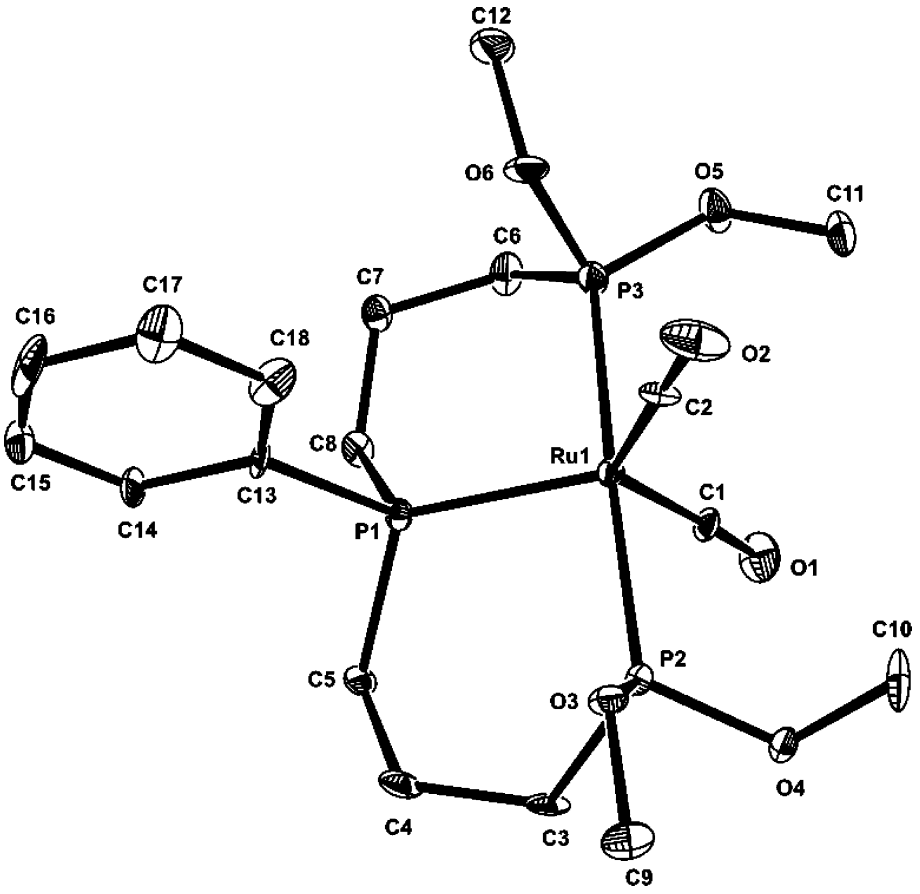


Fig. 2. Model of the structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown with a 30% probability level.

^{1}H NMR monitoring of the reactions shows that the *trans* CO isomers **13a**–**20a** are formed. Some of these complexes, seen in a most prominent way for **17a** and **19a**, are slowly converted further in an equilibration reaction to the corresponding *cis* CO isomers **13b**–**20b**. Similar observations have been made on the related ruthenium complexes [Ru(Me)(PhP($CH_2CH_2CH_2P$-Cy_2)$_2$(CO)$_2$]I [43] and [Ru(Me)(MeP($CH_2CH_2CH_2P$-Me_2)$_2$(CO)$_2$]I [1]. The isomerisation process was observed to occur faster with the iron complexes than with the ruthenium complexes. For a given metal (Ru or Fe), the isomerisation also proceeds faster for the complexes bearing a phenyl substituent instead of the cyclohexyl on the internal phosphorus atom of the tridentate phosphine ligand. For example, the oxidative addition of MeI to **5** is completed in 48 h at room temperature with concomitant equilibration to the *cis* CO isomer **17b**. However, reaction of **6** with MeI affords the equilibrium mixture of the isomers **18a/18b** only after five days of equilibrium at room temperature. It is remarkable that for all the cyclohexyl derivatives the *trans* isomers (**14a**, **16a**, **18a** and **20a**) are more stable, while for the phenyl derivatives the same is valid for M = Ru (**13a** and **15a**), but in the cases of M = Fe (**17b** and **19b**) there is an inverse preference.

Complexes **13a**–**20b** were structurally assigned on the basis of IR and NMR spectroscopic data of the isomeric mixtures in solution. The IR spectra of the *mer*,*trans*-[M(Me)(triphos)(CO)$_2$]I complexes (**13a**–**20a**, M = Ru, Fe; triphos = **I**–**IV**) are characterized by a single strong ν(CO) stretching band. This supports the *trans* disposition of the carbonyl ligands in these octahedral complexes. The ^{31}P NMR spectra indicate a meridional arrangement of the tridentate phosphine ligand in the complexes. The spectra show an AM_2 spin system with a triplet resonance for the internal phosphorus nucleus and a doublet resonance for the terminal phosphonite moieties. The ^{1}H NMR spectra are consistent with the proposed structures. The Me_{Ru} moieties exhibit doublet of triplet resonances.

The observation that the coupling constant to the *trans* phosphorus nucleus is smaller than the coupling to the *cis* phosphorus nuclei has precedence from related observations in the literature. A similar trend was reported on ruthenium complexes [42,43,67]. The resonance for the metal bound methyl group also appeared as doublet of triplets in the ^{13}C NMR spectra. *mer*, *trans*-Derivatives showed in some cases a greater tendency for crystallisation. Thus, it was possible to obtain suitable crystals for X-ray diffraction for **13a**

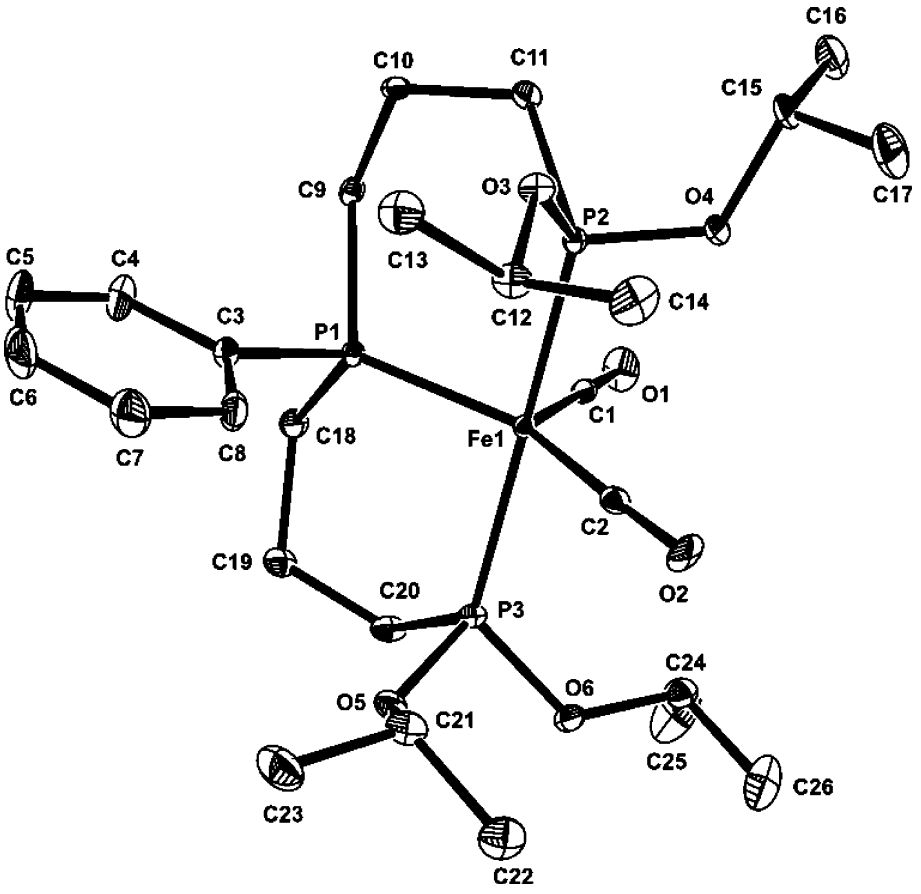
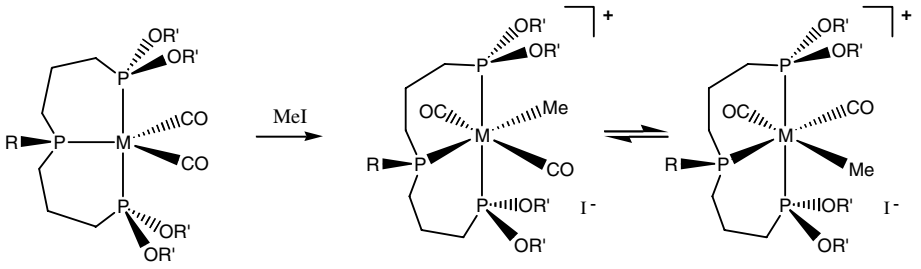


Fig. 3. Model of the structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown with a 30% probability level.



M	R	R'			
Ru	Ph	*i*-Pr	**1**	**13a** - 90%	**13b** - 10%
Ru	Cy	*i*-Pr	**2**	**14a** - 100%	**14b** - Traces
Ru	Ph	Me	**3**	**15a** - 98%	**15b** - 2%
Ru	Cy	Me	**4**	**16a** - 100%	**16b** - Traces
Fe	Ph	*i*-Pr	**5**	**17a** - Traces	**17b** - 100%
Fe	Cy	*i*-Pr	**6**	**18a** - 95%	**18b** - 5%
Fe	Ph	Me	**7**	**19a** - Traces	**19b** - 100%
Fe	Cy	Me	**8**	**20a**- 100%	**20b** - Traces

Scheme 8.

and **21**. Suitable crystals for **13a** were obtained by slow cooling of a saturated dichloromethane solution to −30 °C. The structure is shown in Fig. 4. Selected bond distances (Å) and bond angles (°) are listed in Table 2.

The X-ray diffraction study reveals a pseudo octahedral geometry at ruthenium, with a meridionally arranged triphosphine ligand and *trans* carbonyl groups.

The structure of **20a** was also unequivocally established by a single crystal X-ray diffraction study on the

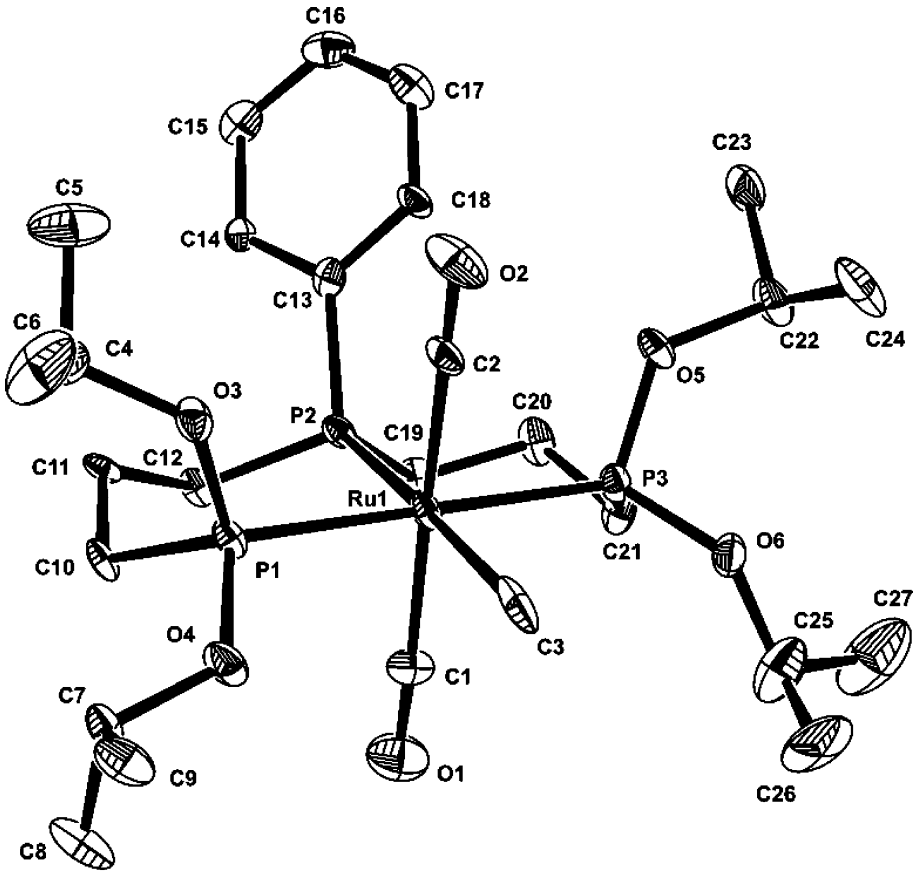


Fig. 4. Model of the structure of **13a**. Hydrogen atoms and iodine counter ion are omitted for clarity. Thermal ellipsoids are shown with a 30% probability level.

Table 2
Selected bond lengths (Å) and bond angles (°) in **13a**

Bond distance (Å)		Angle (°)	
Ru(1)–C(3)	2.225(14)	P(1)–Ru(1)–C(3)	175.8(4)
Ru(1)–P(1)	2.377(3)	P(2)–Ru(1)–P(3)	177.10(12)
Ru(1)–P(2)	2.335(3)	C(1)–Ru(1)–C(2)	172.2(5)
Ru(1)–P(3)	2.345(3)	P(1)–Ru(1)–C(1)	89.0(3)
Ru(1)–C(1)	1.919(15)	P(1)–Ru(1)–C(2)	98.4(4)
Ru(1)–C(2)	1.934(15)	C(1)–Ru(1)–C(3)	86.9(5)
C(1)–O(1)	1.132(15)	C(2)–Ru(1)–C(3)	85.7(5)
C(2)–O(2)	1.151(15)	C(1)–Ru(1)–P(2)	92.4(4)
		C(1)–Ru(1)–P(3)	88.8(4)
		C(2)–Ru(1)–P(2)	89.8(4)
		C(2)–Ru(1)–P(3)	88.6(4)
		C(3)–Ru(1)–P(2)	88.6(4)
		C(3)–Ru(1)–P(3)	88.8(3)

corresponding tetraphenylborate salt (**21**) (Fig. 5). Suitable crystals were obtained by slow cooling of a saturated dichloromethane solution of **21** to −30 °C. Selected bond distances (Å) and bond angles (°) are listed in Table 3.

The cation of **21** adopts a pseudo octahedral geometry. The triphosphine ligand is meridionally arranged around the metal atom. The structure confirms that the carbonyl ligands occupy *trans* positions and that the methyl group is located *trans* to the internal phosphorus atom of the tridentate phosphine ligand. The longest Fe–P distance is found for Fe(1)–P(1) *trans* to the methyl ligand, while Fe(1)–P(2) and Fe(1)–P(3) have comparable values.

The *cis* carbonyl complexes **13b**–**20b** exhibit two strong *ν*(CO) bands in the IR spectra indicating that the carbonyl ligands are disposed *cis* to each other in the octahedral complexes. The ^{31}P NMR spectra consist of a triplet and doublet resonance pattern and support the meridional arrangement of the tridentate ligands around the metal center.

6. Reactions with I_2 and the alkyl iodides EtI, *n*-PrI and *i*-PrI

The oxidative addition of alkyl iodides (EtI, *n*-PrI and *i*-PrI) to the ruthenium and iron complexes **1**–**8** did not produce the expected alkyl metal complexes. It is interesting to note that the oxidative addition of MeI to $RuL_2(CO)_3$ (L = phosphine) does even not take place when the phosphine ligand is different from PMe_3 [68–70]. No reactions were also observed with MeI when the starting compound $Fe(CO)_3L_2$ contained

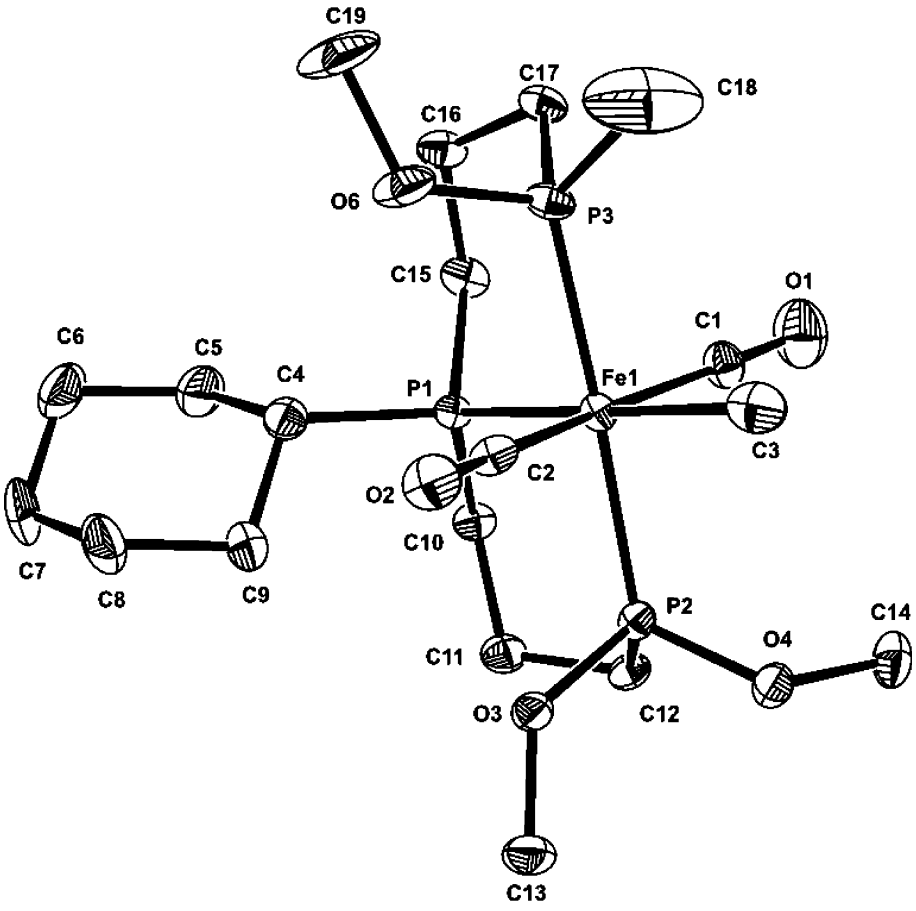


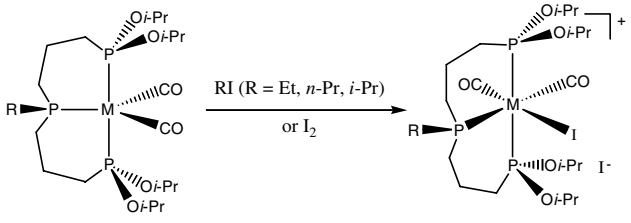
Fig. 5. Model of the structure of **21**. Hydrogen atoms and the BPh_4^- counter ion are omitted for clarity. Thermal ellipsoids are shown with a 30% probability level.

Table 3
Selected bond lengths (Å) and bond angles (°) in **21**

Bond distance (Å)		Angle (°)	
Fe(1)–C(3)	2.105(5)	P(1)–Fe(1)–C(3)	175.64(12)
Fe(1)–P(1)	2.2724(10)	P(2)–Fe(1)–P(3)	177.54(5)
Fe(1)–P(2)	2.2097(10)	C(1)–Fe(1)–C(2)	167.66(17)
Fe(1)–P(3)	2.2159(10)	P(1)–Fe(1)–P(2)	91.07(4)
Fe(1)–C(1)	1.832(4)	P(1)–Fe(1)–P(3)	87.93(4)
Fe(1)–C(2)	1.789(3)	P(1)–Fe(1)–C(1)	91.94(12)
C(1)–O(1)	1.079(4)	C(3)–Fe(1)–P(2)	89.21(11)
C(2)–O(2)	1.135(4)	C(3)–Fe(1)–P(3)	91.96(12)
		C(3)–Fe(1)–C(1)	83.70(16)
		C(3)–Fe(1)–C(2)	84.11(16)
		C(1)–Fe(1)–P(2)	92.35(12)
		C(1)–Fe(1)–P(3)	89.92(12)
		C(2)–Fe(1)–P(2)	89.34(11)
		C(2)–Fe(1)–P(3)	88.63(11)

triethylphosphine instead of trimethylphosphine [71]. This behaviour may be due to a notable steric hindrance of the ligand on the oxidative addition process.

The complexes bearing triphosphine ligands with terminal isopropoxy groups (**1**, **2**, **5** and **6**) react within one week with an excess of EtI, *n*-PrI or *i*-PrI in CH_2Cl_2 at room temperature to afford an iodo complex independent of the type of alkyl iodide used. The same products were obtained from the oxidative addition reaction of a stoichiometric amount of I_2 to the zero valent complexes, which proceeds instantaneously in dichloromethane at room temperature (Scheme 9).



	M	R
1	Ru	Ph
2	Ru	Cy
5	Fe	Ph
6	Fe	Cy

	M	R
22	Ru	Ph
23	Ru	Cy
26	Fe	Ph
27	Fe	Cy

Scheme 9.

The structures of the iodo complexes (**22**, **23**, **26** and **27**) were established by spectroscopic means. Furthermore iodo complex **22** could be characterized by an X-ray diffraction study. The complex was crystallized from the reaction mixture of **1** with *i*-PrI (Fig. 8). Similar

observations [64] have been made in the reaction of alkyl halides with $Fe(CO)_3L_2$ (L = PMe_3, PPh_3) which produced $Fe(CO)_2L_2I_2$ species. It has been shown that the reactions involve an initial step in which halogen radicals are formed from the alkyl halides either photochemically or thermally. These radicals react with $Fe(CO)_3L_2$ in an one-electron oxidation to give the radical cation $[Fe(CO)_3L_2]^{\cdot+}$ as shown for the reaction of halogens with $Fe(CO)_3L_2$ [72].

A further complication was observed for the complexes bearing ligands with terminal dimethylphosphonite groups. Reaction of EtI, *n*-PrI or *i*-PrI with **3**, **4**, **7** or **8** therefore also led to the corresponding iodo complexes (**24**, **25**, **28** and **29**, respectively) but also to additional products corresponding to the oxidative addition of MeI (**15a**, **16a**, **19a** and **20a**, respectively) (Scheme 10).

Although phosphine oxide moieties could not be detected by ^{31}P NMR spectroscopy, MeI is obviously generated from an Arbuzov type reaction at the coordinated $-P(OMe)_2$ groups of the tridentate phosphine ligands. Similar Arbuzov reactions were observed at the coordinated trimethylphosphite groups in the complex $[CpCo(dppe)P(OMe)_3]$ [73]. Consistent with the effect of increased sterics on Arbuzov reactions the highest amounts of methyl complexes were observed with EtI (6–8% by ^{31}P NMR spectroscopy) while only traces could be detected by ^1H NMR spectroscopy when *i*-PrI was used in the oxidative addition reactions. As observed for the oxidative addition reactions of MeI with **3**, **4**, **7** and **8**, isomerisation of the *trans* CO methyl complexes (**15a**, **16a**, **19a** and **20a**) to the corresponding *cis* CO isomers (**15b**, **16b**, **19b** and **20b**) could be observed in the cases where the concentration of the methyl complexes were sufficient to be detected by ^1H or ^{31}P NMR spectroscopy (essentially for the reactions with EtI).

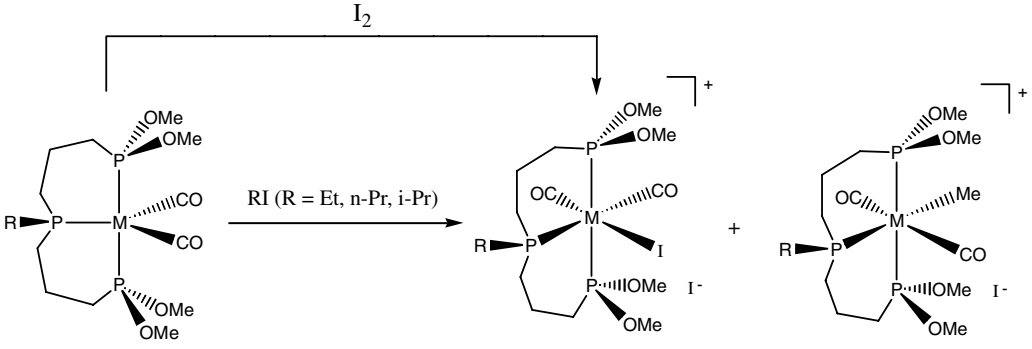
The iodo complexes **22**–**29** were structurally assigned on the basis of IR and NMR data. Furthermore, the structure of **22** was unequivocally established by a single crystal X-ray diffraction study (Fig. 6). Suitable crystals were obtained by slow cooling of a saturated dichloromethane solution of **22** to −30 °C. Selected bond distances (Å) and bond angles (°) are listed in Table 4.

The X-ray study confirms that **22** is an iodo complex. The cationic complex adopts an octahedral geometry with an iodide counter anion. The triphosphine ligand is meridionally arranged around the metal center. The structure shows that a carbonyl ligand is in *trans* position to the internal phosphorus atom of the triphosphine ligand and consequently the iodide is found *trans* to a carbonyl ligand. The Ru–I distance is consistent with such separations in other ruthenium iodo complexes [74].

7. Reactions with CO and deprotonation reactions

When **1**–**8** are reacted with MeI and the resulting isomeric mixtures of the methyl complexes (**13a/b**–**20a/b**) are stirred under 1 bar of carbon monoxide for 48 h. In all cases, the same single acetyl complex is obtained (Scheme 11).

This reactivity towards CO insertions parallels earlier observations on related ruthenium complexes and has been discussed previously [1]. The presence of the acetyl moiety is confirmed by IR spectroscopy. The corresponding ν(C=O) vibration is found as a band of medium intensity in the range between 1604 and 1616 cm^{-1} and further evidence for the presence of *trans* CO groups is provided by the appearance of one strong carbonyl absorption. The acetyl moieties are also indicated in the ^1H NMR spectra giving rise to singlet resonances (δ 2.4–2.7 ppm) for the acetyl protons. The ^{31}P NMR



M	R			
Ru	Ph	**3**	**24**	**15a**
Ru	Cy	**4**	**25**	**16a**
Fe	Ph	**7**	**28**	**19a**
Fe	Cy	**8**	**29**	**20a**

Scheme 10.

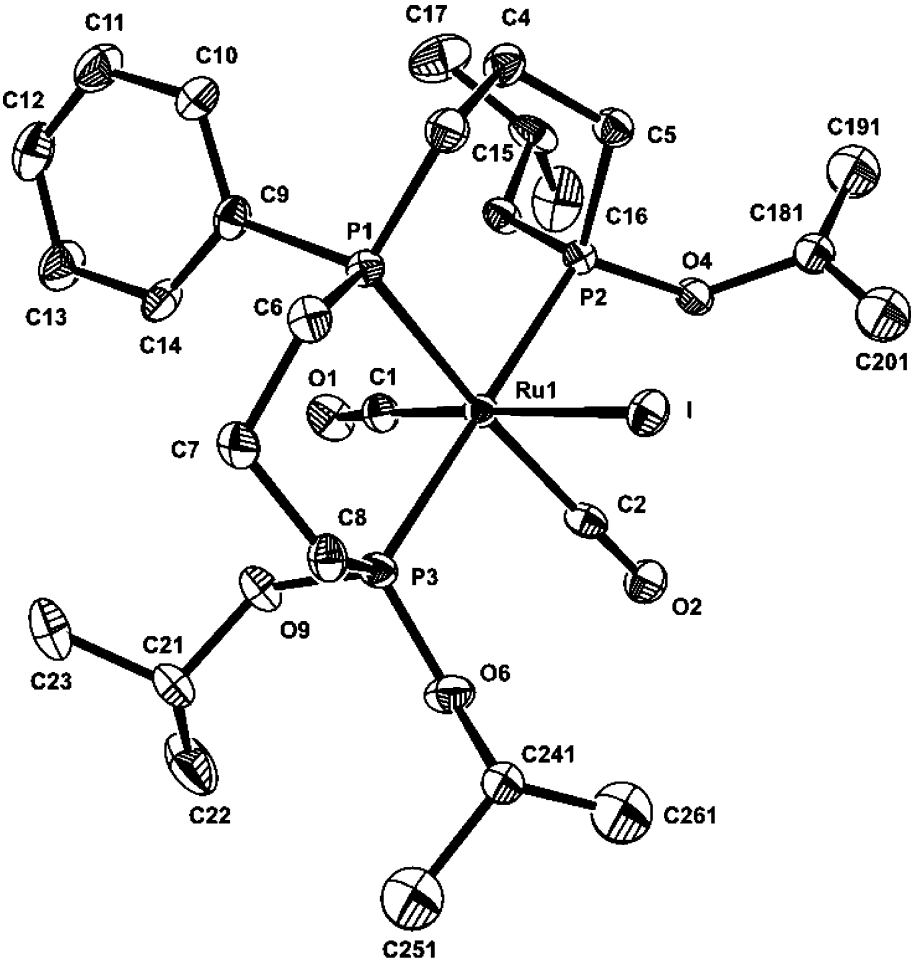
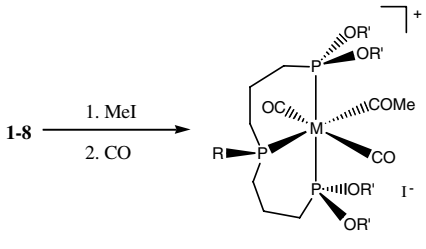


Fig. 6. Model of the structure of **22**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown with a 30% probability level.

Table 4
Selected bond lengths (Å) and bond angles (°) in **22**

Bond distance (Å)		Angle (°)	
Ru(1)–I(1)	2.7582(7)	P(1)–Ru(1)–C(2)	171.6(2)
Ru(1)–P(1)	2.3997(17)	P(2)–Ru(1)–P(3)	178.35(6)
Ru(1)–P(2)	2.350(2)	I(1)–Ru(1)–C(1)	177.6(2)
Ru(1)–P(3)	2.350(2)	P(1)–Ru(1)–P(2)	89.18(7)
Ru(1)–C(1)	1.890(7)	P(1)–Ru(1)–P(3)	89.79(7)
Ru(1)–C(2)	1.949(7)	P(1)–Ru(1)–C(1)	95.3(2)
C(1)–O(1)	1.125(9)	P(1)–Ru(1)–I(1)	87.05(4)
C(2)–O(2)	1.119(8)	I(1)–Ru(1)–P(2)	89.93(5)
		I(1)–Ru(1)–P(3)	88.73(5)
		I(1)–Ru(1)–C(2)	84.6(2)
		C(1)–Ru(1)–C(2)	93.1(3)
		C(1)–Ru(1)–P(2)	89.7(3)
		C(1)–Ru(1)–P(3)	91.7(3)
		C(2)–Ru(1)–P(2)	90.7(3)
		C(2)–Ru(1)–P(3)	90.1(3)

spectra of the acetyl complexes consist of an AM_2 system with a triplet resonance for the internal phosphorus atom of the triphosphine and a doublet resonance for the terminal phosphorus atoms, which suggests the given meridional phosphorus substitution pattern. In the



	M	R	R'
30	Ru	Ph	*i*-Pr
31	Ru	Cy	*i*-Pr
32	Ru	Ph	Me
33	Ru	Cy	Me
34	Fe	Ph	*i*-Pr
35	Fe	Cy	*i*-Pr
36	Fe	Ph	Me
37	Fe	Cy	Me

Scheme 11.

^{13}C NMR spectrum, the singlet resonance for the acetyl methyl group is found at around δ 50 ppm, and the ^{13}CO resonance is found at expected much lower field (δ 259–268 ppm) as a doublet of triplets in cases where the signal could be resolved. The splitting pattern is consistent with the acetyl moiety disposed *trans* to the internal phosphorus nucleus of the tridentate phosphine ligand, since the latter is meridionally arranged around the metal center. The carbonyl ligands usually exhibited broad resonances in the region of δ 200–210 ppm. In the case of **31**, the CO ligands give rise to a quartet resonance, showing the magnetic equivalence of all three

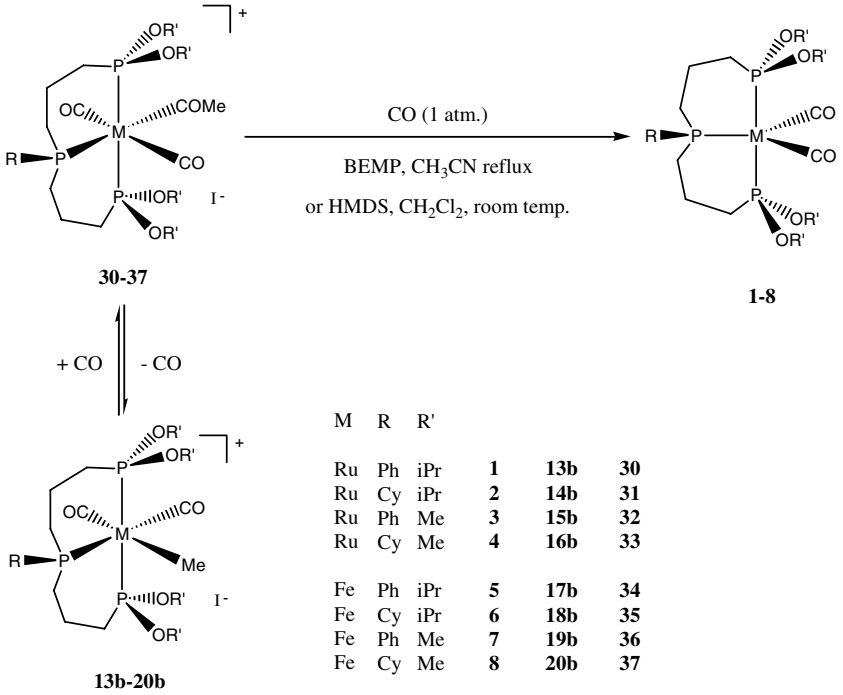
phosphorus ligands and an isochronous behaviour of the two ^{13}C nuclei. In the case of **34**, two signals for the two *trans* carbonyl groups were found as two distinct doublets of triplets. This is attributed to the rigid stereochemistry at the internal phosphorus atom of the triphosphines inducing distinction of the environments of the CO groups.

8. Deprotonation experiments

In order to access ketene complexes, deprotonation of the acetyl complexes **30**–**37** was attempted using BEMP as the base. The initial deprotonation experiments carried out in dichloromethane at room temperature and under a carbon monoxide atmosphere showed that no reaction occurred with the ruthenium acetyl complexes (**30**–**33**) and that the iron acetyl complexes (**34**–**37**) reacted very slowly as evidenced by the presence of a small amount of protonated BEMP in the ^{31}P NMR spectra after four days of reaction. The deprotonation experiments with BEMP can be conveniently monitored by ^{31}P NMR spectroscopy. The signal of the protonated base [BEMPH]I appears at δ 23 ppm, whereas the BEMP exhibits a resonance at δ 1 ppm. The dichloromethane was changed for acetonitrile and the deprotonation experiments with BEMP were carried out at reflux temperature of the solvent under an atmosphere of CO with ^{31}P NMR monitoring. Under these conditions, the deprotonation reactions were completed after 24 h for the iron acetyl complexes bearing a phenyl group on the internal phosphorus atom of the triphosphine ligand (**34** and **36**) and 40 h for those having a cyclohexyl substituent (**35** and **37**). Under the same reaction conditions, the ruthenium acetyl complexes **30**–**33** reacted much slower and the reaction was not completed even after 4 days. It is noteworthy that the use of the stronger base sodium hexamethyldisilazide (HMDS) effected instantaneous deprotonation of the ruthenium or iron acetyl complexes when the reaction was carried out in dichloromethane at room temperature. In all the deprotonation experiments, however, the products of the reactions of the acetyl complexes with either BEMP or HMDS were identified spectroscopically as the "starting" zero valent dicarbonyl metal complexes **1**–**8** (Scheme 12).

It should be noted that when the iron acetyl complex **34** was subjected for 48 h to the same conditions as those employed in the deprotonation reactions with BEMP (acetonitrile, reflux, CO atmosphere) in the absence of a base, the species proved to be stable apart from the traces of a decarbonylation product. This indicates that generation of the zero valent metal complex **5** from the corresponding acetyl complex does not occur in the absence of the base and rules out its formation from a decomposition pathway of the parent acetyl species.

However, despite that any ketene product could logically appear in Scheme 12 it was not possible to trace any ketene complex intermediate regardless whether the deprotonations were carried out under forcing conditions or at room temperature. It is also difficult to verify whether ketene complexes do form, but replacement of a



M	R	R'			
Ru	Ph	iPr	**1**	**13b**	**30**
Ru	Cy	iPr	**2**	**14b**	**31**
Ru	Ph	Me	**3**	**15b**	**32**
Ru	Cy	Me	**4**	**16b**	**33**
Fe	Ph	iPr	**5**	**17b**	**34**
Fe	Cy	iPr	**6**	**18b**	**35**
Fe	Ph	Me	**7**	**19b**	**36**
Fe	Cy	Me	**8**	**20b**	**37**

Scheme 12.

ketene ligand would anyway be expected to occur readily in the presence of carbon monoxide. When the deprotonation experiments were carried out under a nitrogen atmosphere decarbonylation of the acetyl complexes was observed in most cases, which confirms that the deprotonations of the acetyl moieties are slow reactions, significantly slower than the decarbonylation steps.

While deprotonation of the acetyl moieties become plausible by the appearance of the protonated BEMP resonance in the ^{31}P NMR spectra, it is likely that the intermediate ketene complexes are not stable and can therefore not be traced spectroscopically. In order to pursue the fate of any ketene product, labelling experiments with the D and ^{13}C labeled iron acetyl complexes **38** and **39** were carried out. These complexes were prepared from the reaction of **5** with CD_3I and $^{13}CH_3I$, respectively, followed by the reaction with natural abundance ^{12}CO. The deprotonation experiments of **38** and **39** with BEMP were pursued by ^{2}H, ^{13}C and ^{31}P NMR spectroscopy and the results are summarized in Scheme 13.

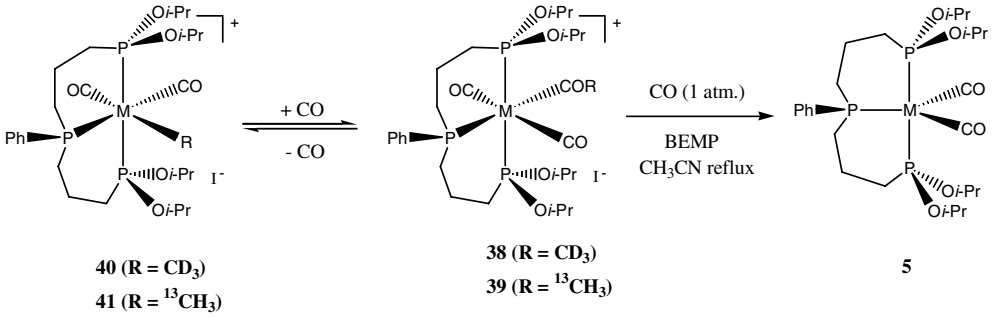
After 28 h of reaction at room temperature, the iron acetyl complexes **38** and **39** are the main species along with small amounts of the decarbonylated species **40** and **41**, while only traces of **5** can be detected in the ^{31}P NMR spectroscopy (Fig. 7).

The ^{2}H NMR spectrum shows an intense resonance for the acetyl moiety of **38** at 2.6 ppm and a broad signal at −0.2 ppm indicates the presence of a small amount of **40**. The ^{13}C NMR spectrum is consistent with the observations made from the ^{2}H NMR spectrum. The labelled carbon atom of the acetyl group of **39** exhibits a singlet at 48 ppm and the presence of decarbonylated **39** is evidenced by the quartet resonance for **41** at −11 ppm. Finally, the presence of acetyl and methyl iron complexes is confirmed by ^{31}P NMR, which also shows the presence of traces of **5** identified by the resonance at 216 ppm. Thus, significant deprotonation of the acetyl iron species with BEMP does not occur at room temperature.

After 12 h in refluxing acetonitrile, about half of the iron acetyl complexes have reacted with BEMP and the reaction is completed after 24 h (Fig. 8).

After 24 h of reaction in refluxing acetonitrile and under an atmosphere of CO, the ^{2}H NMR spectrum shows that **38** is no longer present in the reaction mixture as evidenced by the complete disappearance of the singlet resonance at δ 2.6 ppm corresponding to the Fe-$COCD_3$ moiety. Only one singlet resonance at δ 1.5 ppm can be observed in the ^{2}H NMR spectrum. This resonance actually corresponds to the signal of the deuterated base. The presence of [BEMPD]I is also confirmed by ^{31}P NMR spectroscopy with the observation of a singlet resonance at 23 ppm and apart from minor amounts of **38** and **39**, the ^{31}P NMR spectrum indicates that **5** is the predominant species. The ^{13}C NMR spectrum confirms that only traces of the acetyl species remain (singlet resonance at δ 48.5 ppm) and apart from some minor signals, no ^{13}C resonance of significant intensity is observed. Evidence for the formation of diketene resulting from a dimerisation of ketene, was also not obtained based upon the ^{13}C NMR analysis. Throughout the deprotonation experiments, the signals can be observed of the labelled iron acetyl and methyl complexes. However, while the ^{2}H and ^{13}C resonances of the acetyl species gradually disappear, no signals for labelled species appear as analysed both by ^{2}H and ^{13}C NMR spectroscopy. In fact, the ^{2}H experiment confirms that the base actually abstracts a proton from the Fe-$COCD_3$ group, as indicated by the formation of [BEMPD]I, and supports the formation of the zerovalent "starting" dicarbonyl complex **5** via deprotonation of the corresponding acetyl species with necessarily concomitant formation of a ketene moiety. However, tracing of the released ketene up to now remained unsuccessful and its chemical fate is as yet unclear in these reactions.

In order to support a mechanistic scheme involving free ketene species, an independent experiment with the reaction of free ketene with BEMP was investigated. Recently, BEMP was reported [75] to produce ketenes from the dehydrohalogenation reaction of a variety of acid chlorides. High yields of RHC=C=O (R = Br, ethyl, phenyl, phenoxy, benzyloxy, 1-naphthyl, 2-naphthyl, 2-thienyl) were obtained when THF solutions of the corresponding acid chlorides were passed through a column packed with polymer-supported BEMP and



Scheme 13.

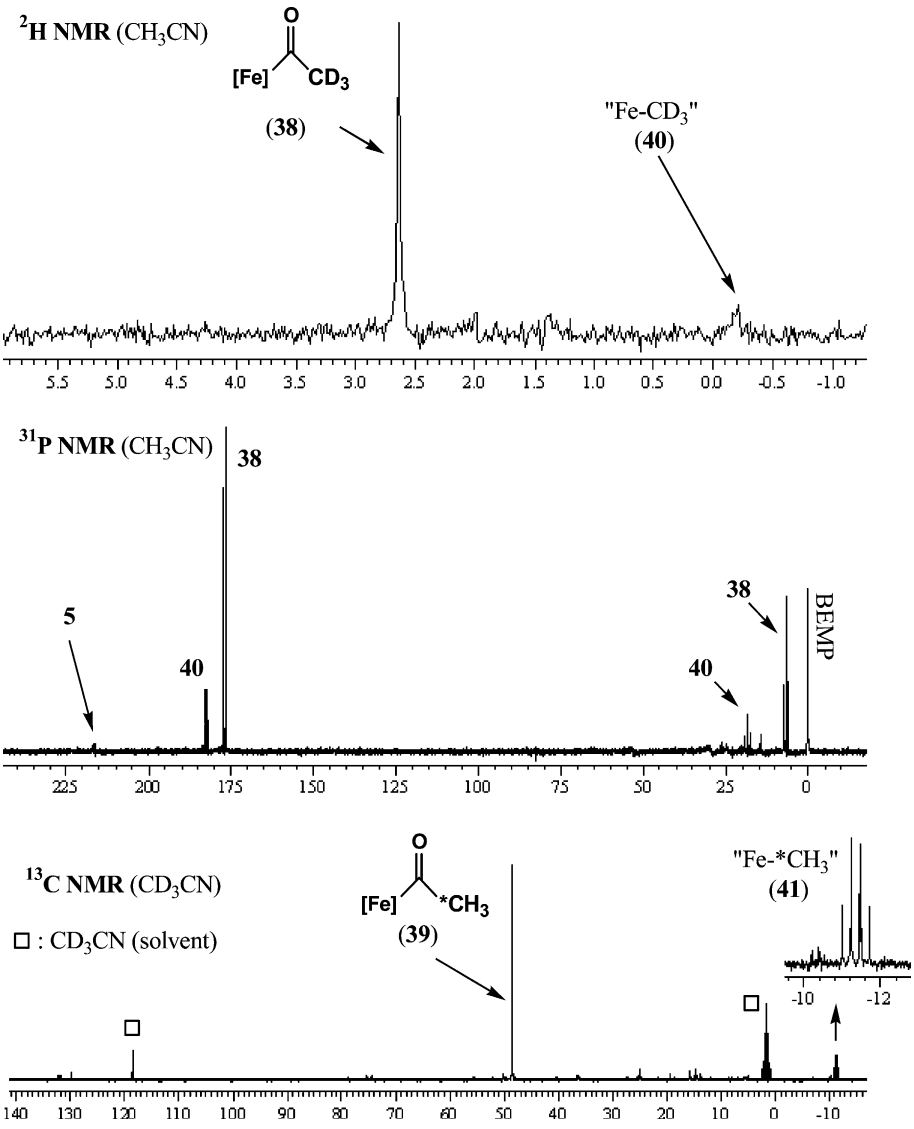
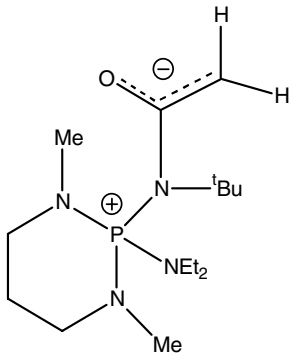


Fig. 7. NMR spectroscopy of the products of the deprotonation reaction of **38** and **39** with BEMP (28 h room temperature, CO atmosphere).

cooled to −78 °C. Although the approach is believed by the authors to be amenable to the formation of most reactive ketenes, exclusively preparation of mono-substituted ketenes was reported [76]. We have observed that a reaction occurs when ketene and BEMP are brought together, even at low temperatures. Ketene, generated by the dehydrohalogenation [74] of acetyl chloride with diisopropylethylamine (DIEA) catalysed by a Lewis acid ($Al(SbF_6)_3$), was condensed into a dichloromethane solution of BEMP cooled by means of a dry ice/acetone bath. A ^{31}P NMR spectrum of the light yellow solution carried out at −80 °C showed that an adduct is formed with a sharp resonance at δ 26 ppm. The signal then quickly disappeared upon warming to room temperature while the light yellow solution turned brown and only a very broad resonance around δ 33 ppm remained at 20 °C. Heating to 80 °C led to the formation of an insoluble sticky material with no phosphorus resonances in the ^{31}P NMR spectrum. It is proposed that at −80 °C, the ketene reacts with BEMP to give a base-ketene adduct:



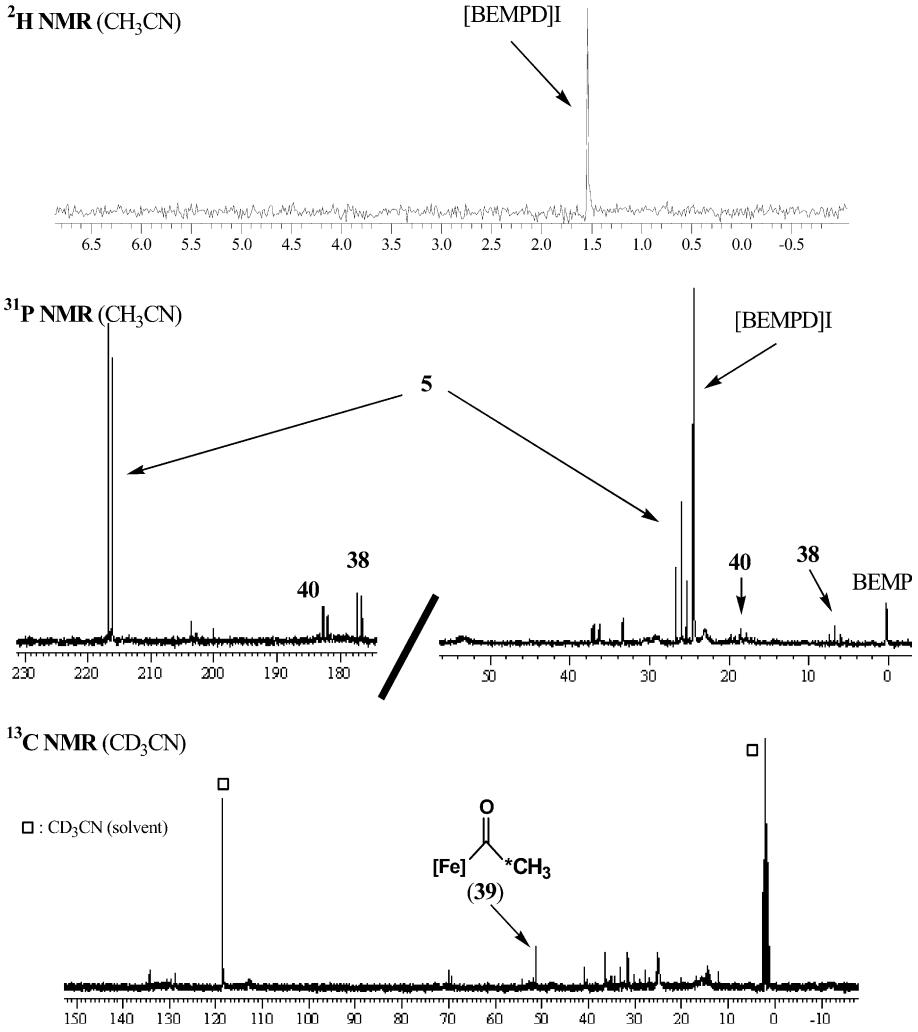


Fig. 8. NMR spectroscopic analysis pursuit of the products of the deprotonation reaction of **38** and **39** with BEMP after a 24-h reflux period in acetonitrile under an atmosphere of CO.

Upon warming, the latter presumably undergoes further reaction either with ketene or the ketene-BEMP adduct itself, resulting in insoluble polymeric material. This all prevented proper characterisation of any ketene released in the deprotonation reactions of Schemes 12 and 13.

9. X-ray structure analyses

The X-ray diffraction data were collected at measurement temperatures of 123(2) K for **1**, 153(2) K for **3**, **5** and **22**, and of 183(2) K for **13a** and **21**, using an imaging plate detector system (Stoe IPDS) with graphite-monochromated Mo Kα-radiation ($\lambda = 0.71073$ Å). A total of 200, 183, 190, 220, 205 and 209 images were exposed at constant times of 1.50, 3.00, 1.80, 7.00, 3.00 and 2.60 min per image for the structures **1**, **3**, **5**, **13a**, **21** and **22** [77]. The crystal-to-image distances were set to 50 mm for **1**, **3**, **5** and **21**, and to 60 mm for **13a** and **22** (θ_{max} range: 27.96–30.37°). ϕ-rotation (for **1** and **5**) and -oscillation modes (for **3**, **13a**, **21** and **22**) were necessary for the increments of 1.0°, 1.0° and 1.2°, 1.0°, 0.9°, and 0.7° per exposure in each case. Total exposure times were 19, 19, 22, 41, 27 and 28 h. The intensities were integrated by using a dynamic peak profile analysis and estimated mosaic spread (EMS) check was performed to prevent overlapping intensities. For the cell parameter refinements 7490 (**13a**) to 8000 reflections with intensities $I > 6\sigma(I)$ were selected out of the whole limiting spheres for the six structures. A total of 34,297, 29,400, 33,723, 39,215, 49,145 and 34,289 reflections were collected, of which 9168, 6432, 8319, 16,330, 13,263 and 10,409 were unique after performing absorption corrections and data reductions ($R_{int} = 4.90\%$, 14.60%, 7.22%, 20.27%, 13.51% and 8.86%). 15, 10, 13, 12, 7 and 8 indexed crystal faces were used for the numerical absorption corrections [78].

All crystals were embedded in polybutene oil within a glove box. The crystal quality was examined under polarized light. Sometimes crystals with intrusions

(holes or solvent) or with tiny intergrown pieces (**3**, **13a** and **21**) had to be accepted for the X-ray experiment. In general, the structures were solved with an incomplete data set (50% or less completeness) while the measurement was still executing, because the correct chemical formula cannot always be predicted when solvent molecules co-crystallize with the complex (**13a**, **21** and **22**). The corrected formula was then used for the final

Table 5
Crystallographic details of **1**, **3** and **5**

	1	**3**	**5**
Formula	$C_{26}H_{45}O_6P_3Ru$	$C_{18}H_{29}O_6P_3Ru$	$C_{26}H_{45}FeO_6P_3$
M_r (g mol^{-1})	647.6	535.39	602.38
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group [No.]	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
a (Å)	14.9483(9)	11.6423(8)	14.9087(7)
b (Å)	19.6736(14)	14.2702(8)	19.2328(12)
c (Å)	10.5705(6)	13.5705(9)	10.5482(5)
α, β, γ (°)	90, 92.508(7), 90	90, 90, 90	90, 91.292(6), 90
V (Å^3)	3105.7(3)	2254.6(2)	3023.8(3)
Z	4	4	4
Crystal dimensions (mm)	$0.43 \times 0.32 \times 0.29$	$0.26 \times 0.11 \times 0.09$	$0.37 \times 0.33 \times 0.13$
d(calcd) (g cm^{-3})	1.385	1.577	1.323
Absorption coefficient, μ (mm^{-1})	0.694	0.939	0.693
F(0 0 0)	1352	1096	1280
2θ scan range (°)	$5.66 < 2\theta < 60.54$	$6.0 < 2\theta < 60.74$	$5.74 < 2\theta < 60.72$
No. of measured ref.	34,297	29,400	33,723
No. of ref. $I > 2\sigma(I)$	6944	4869	4638
Unique data	9168	6432	8319
Transmission range	0.8530–0.7932	0.9195–0.8187	0.9206–0.8188
No. of parameters	333	257	333
R_1, wR_2 (%) all data	5.02, 10.57	9.08, 19.72	6.91, 5.12
R_1, wR_2 (obsd) (%)[a]	3.66, 10.19	7.41, 18.82	3.05, 4.72
Goodness-of-fit	1.001	1.246	0.889

[a] $R_1 = \sum(F_o - F_c)/\sum F_o;\ I > \sigma(I);\ wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Table 6
Crystallographic details of **13a**, **21** and **22**

	13a	**21**	**22**
Formula	$C_{28}H_{50}IO_{6.25}P_3Ru$	$C_{44}H_{60}BCl_2FeO_6P_3$	$C_{28}H_{49}Cl_4I_2O_6P_3Ru$
M_r (g mol^{-1})	807.56	915.39	1071.25
crystal system	Triclinic	Monoclinic	monoclinic
Space group [No.]	$P\bar{1}$	$P2_1$/n	$P2_1/c$
a (Å)	13.4296(7)	17.8454(13)	11.5653(8)
b (Å)	15.2303(9)	11.3696(6)	13.7235(5)
c (Å)	20.7337(15)	22.7120(18)	28.1248(16)
α, β, γ (°)	74.829(8), 71.419(8), 67.619(7)	90, 98.367(9), 90	90, 100.302(7), 90
V (Å^3)	3669.0(4)	4559.1(5)	4391.9(4)
Z	4	4	4
Crystal dimensions (mm)	$0.16 \times 0.10 \times 0.07$	$0.37 \times 0.21 \times 0.10$	$0.37 \times 0.22 \times 0.06$
d(calcd) (g cm^{-3})	1.462	1.334	1.620
Absorption coefficient, μ (mm^{-1})	1.434	0.598	2.148
F(0 0 0)	1640	1928	2112
2θ scan range (°)	$4.4 < 2\theta < 56.12$	$5.1 < 2\theta < 60.66$	$5.06 < 2\theta < 55.92$
No. of measured ref.	39,215	49,145	34,289
No. of ref. $I > 2\sigma(I)$	3363	5149	4932
Unique data	16,330	13,263	10,409
Transmission range	0.9222–0.8797	0.9447–0.8519	0.7967–0.5707
No. of parameters	723	520	383
R_1, wR_2 (%) all data	22.40, 17.85	13.64, 13.87	10.74, 14.34
R_1, wR_2 (obsd) (%)[a]	4.22, 9.14	5.44, 12.08	5.16, 12.75
Goodness-of-fit	0.422	0.715	0.799

[a] $R_1 = \sum(F_o - F_c)/\sum F_o;\ I > \sigma I);\ wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

absorption corrections. All measurement procedures were calculated by using the Stoe IPDS software [77]. The measurement temperatures were controlled by an Oxford cryogenic system. The absolute structure of **3** (non-centrosymmetric space group $P2_12_12_1$) was confirmed by refining the Flack parameter to −0.13(7) [79]. It should be noted that for compounds **13a**, **21** and **22** only about 20%, 39% and 47% of the unique reflections were observed by criterion $I > 2\sigma(I)$. This corresponds to the low goodness-of-fit values for these structures (Table of crystallographic details).

The structures were solved with the merged data sets after checking for correct space groups. The Patterson or direct methods were used to solve the crystal structures by applying the software options of the program SHELXS-97 [80]. The structure refinements were performed with the program SHELXL-97 [81]. The programs PLATON and PLUTON [82] were used to check the results of the X-ray analyses, they were also used for the completion of the structures by checking the difference electron density calculations. Relevant crystallographic data are collected in Tables 5 and 6.

10. Conclusion

The ruthenium dicarbonyl complexes (**1**–**4**) undergo fast oxidative addition reactions with MeI while the related iron complexes (**5**–**8**) react much slower. The oxidative addition of EtI, *n*-PrI or *i*-PrI to **1**–**8** did not produce the expected alkyl metal complexes. Instead the iodo complexes **22**–**29** were obtained. The iron-acetyl complexes (**34**–**37**) proved to be much more acidic than the related ruthenium-acetyl complexes (**30**–**33**). In all the deprotonation experiments, we were unable to observe any ketene–metal intermediate. Exemplary investigations with labelled (^{2}H and ^{13}C) acetyl complexes (**38** and **39**) were also performed. It was clearly established that deprotonation of the acetyl group occurs, but evidence for ketene–metal complexes or free ketene could not be obtained. On the basis of NMR studies, it is assumed that the ketene-complexes are not stable and that the released ketene reacts with the base added to non-identifiable, presumably polymeric compounds, as it was observed in an independent experiment involving the addition of free ketene to BEMP.

11. Supporting material

Crystallographic data for structures **1**, **3**, **5**, **13a**, **21** and **22** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 250413, 250414, 250415, 250416, 250417 and 250418. 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).

12. 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_2Cl_2) were obtained from commercial suppliers and distilled from appropriate drying agents and vacuum transferred for storage in Schlenk flasks fitted with Teflon stopcocks. ^{1}H, ^{31}P and ^{13}C NMR spectra were run on a *Varian Gemini-2000* spectrometer operating at 300.1, 121.5 and 75.4 MHz, respectively ($\delta(^1H)$, $\delta(^{13}C)$ rel. to $SiMe_4$, $\delta(^{31}P)$ 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. The alkyl iodides were purchased from Aldrich and distilled prior to use. CD_3I and $^{13}CH_3I$ were used as received from commercial suppliers (Aldrich or Fluka). Phenylphosphine and cyclohexylphosphine were commercially available (Strem). Diisopropylallylphosphonite and dimethylallylphosphonite were prepared following a literature procedure [34].

12.1. General procedure to obtain *I*–*IV*

A 20-mL schlenk was charged with 1 eq. of the required primary phosphine, 2 eq. of di-alkylallylphosphonite and 50 mg of AIBN. The mixture was irradiated from the outside for 48 h at room temperature with constant stirring. The ligands were obtained in quantitative yields as colourless viscous liquids sufficiently pure to be used directly without further purification.

12.1.1. $PhP[CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$ (*I*)

1.16 g (10.5 mmol) of phenylphosphine and 4 g (21 mmol) of diisopropylallylphosphonite. Anal. Calc. for $C_{24}H_{45}O_4P_3$ (490.6): C, 58.76%; H, 9.25%. Found: C, 58.90%; H, 9.50%. ^{1}H NMR (CD_2Cl_2, 298 K): 1.1 (d, $^3J_{HH}$ = 6 Hz, –CH(CH_3)$_2$), 1.6–1.8 (m,

–$CH_2CH_2CH_2$–), 4–4.2 (m, –$CH(CH_3)_2$), 7–7.6 (m, –$P(C_6H_5)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −25.7 (s, –$P(C_6H_5)$), 179.9 (s, –$P[OCH(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 19.5 ('t', $^2J_{CP}$ = 16 Hz, –$CH_2CH_2CH_2$–), 24.6 (s, –$CH(CH_3)_2$), 30 ('t', $^1J_{CP}$ = 11 Hz, $^3J_{CP}$ = 11 Hz, –$H_2CH_2CH_2$–$P(C_6H_5)$), 37.3 ('t', $^1J_{CP}$ = 11 Hz, $^3J_{CP}$ = 11 Hz, –$CH_2CH_2CH_2$–$P[OCH(CH_3)_2]_2$), 70.6 (d, $^2J_{CP}$ = 29 Hz, –$P[OCH(CH_3)_2]_2$), (Phenyl: 128.5 (d, $^3J_{CP}$ = 7 Hz, C *meta*), 128.7 (s, C *para*), 132.8 (d, $^2J_{CP}$ = 17 Hz, C *ortho*), 139.6 (d, $^1J_{CP}$ = 19 Hz, C *ipso*)).

12.1.2. $CyP[CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$ (**II**)

917 mg (7.9 mmol) of cyclohexylphosphine and 3 g (15.8 mmol) of diisopropylallylphosphonite. Anal. Calc. for $C_{24}H_{51}O_4P_3$ (496.6): C, 58.00%; H, 10.36%. Found: C, 57.85%; H, 10.15%. ^1H NMR (CD_2Cl_2, 298 K): 1.2 (d, $^3J_{HH}$ = 6 Hz, –$CH(CH_3)_2$), 1.6–1.9 (m, –$CH_2CH_2CH_2$– and –$P(C_6H_{11})$), 4–4.2 (m, –$CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −19.5 (s, –$P(C_6H_{11})$), 183.3 (s, –$P[OCH(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 19.9 ('t', $^2J_{CP}$ = 16.4 Hz, –$CH_2CH_2CH_2$–), 24.6 (s, –$CH(CH_3)_2$), 26 ('t', $^1J_{CP}$ = 11 Hz, $^3J_{CP}$ = 11 Hz, –$CH_2CH_2CH_2$–$P(C_6H_{11})$), 26.7 (s, cyclohexyl C *para*), 27.2 (d, $^3J_{CP}$ = 9 Hz, cyclohexyl C *meta*), 29.4 (d, $^2J_{CP}$ = 12 Hz, cyclohexyl C *ortho*), 35.2 (d, $^1J_{CP}$ = 12 Hz, cyclohexyl C *ipso*), 37.5 ('t', $^1J_{CP}$ = 10 Hz, $^3J_{CP}$ = 10 Hz, –$CH_2CH_2CH_2$–$P[OCH(CH_3)_2]_2$), 70.7 (d, $^2J_{CP}$ = 23 Hz, –$P[OCH(CH_3)_2]_2$).

12.1.3. $PhP[CH_2CH_2CH_2P(OMe)_2]_2$ (**III**)

990 mg (9 mmol) of phenylphosphine and 2.5 g (18 mmol) of dimethylallylphosphonite. Anal. Calc. for $C_{16}H_{29}O_4P_3$ (378.3): C, 50.80%; H, 7.73%. Found: C, 51.20%; H, 7.78%. ^1H NMR (CD_2Cl_2, 298 K): 1.55–1.80 (m, –$CH_2CH_2CH_2$–), 3.31 (d, $^3J_{HP}$ = 11 Hz, –$P(OCH_3)_2$), 7–7.55 (m, –$P(C_6H_5)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −26.3 (s, –$P(C_6H_5)$), 189.8 (s, –$P(OCH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 19.5 ('t', $^2J_{CP}$ = 16 Hz, –$CH_2CH_2CH_2$–), 29.9 (dd, J_{CP} = 13 Hz, J_{CP} = 10.6 Hz, –$CH_2CH_2CH_2$–$P(C_6H_5)$), 35.2 (dd, J_{CP} = 19.5 Hz, J_{CP} = 10.6 Hz, –$CH_2CH_2CH_2$–$P(OCH_3)_2$), 53.3 (d, $^2J_{CP}$ = 11.2 Hz, –$P(OCH_3)_2$), (Phenyl: 128.6 (d, $^3J_{CP}$ = 7.2 Hz, C *meta*), 128.9 (s, C *para*), 132.8 (d, $^2J_{CP}$ = 16.9 Hz, C *ortho*), 139.3 (d, $^1J_{CP}$ = 19.2 Hz, C *ipso*)).

12.1.4. $CyP[CH_2CH_2CH_2P(OMe)_2]_2$ (**IV**)

2.1 g (18 mmol) of cyclohexylphosphine and 5 g (36 mmol) of dimethylallylphosphonite. Anal. Calc. for $C_{16}H_{35}O_4P_3$ (384.3): C, 50.00%; H, 9.18%. Found: C, 50.13%; H, 9.48%. ^1H NMR (CD_2Cl_2, 298 K): 1.1–1.8 (m, –$CH_2CH_2CH_2$– and –$P(C_6H_{11})$), 3.37 (d, $^3J_{HP}$ = 11 Hz, –$P(OCH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6H_6, 298 K): −20.1 (s, –$P(C_6H_5)$), 190.2 (s, –$P(OCH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 19.5 ('t', $^2J_{CP}$ = 16.9 Hz, –$CH_2CH_2CH_2$–), 25.9 (dd, J_{CP} = 16.2 Hz, J_{CP} = 10.4 Hz, –$CH_2CH_2CH_2$–$P(C_6H_{11})$), 26.6 (s, cyclohexyl C *para*), 27.2 (d, $^2J_{CP}$ = 9.6 Hz, cyclohexyl C *meta*), 29.4 (d, $^3J_{CP}$ = 11.8 Hz, cyclohexyl C *ortho*), 35.2 (d, $^1J_{CP}$ = 12.6 Hz, cyclohexyl C *ipso*), 35.3 (dd, J_{CP} = 19.3 Hz, J_{CP} = 10.2 Hz, –$CH_2CH_2CH_2$–$P(OCH_3)_2$), 53.3 (d, $^2J_{CP}$ = 11.2 Hz, –$P(OCH_3)_2$).

12.2. General procedure for the preparation of the ruthenium dicarbonyl complexes **1**–**4**

The required tridentate phosphine ligand (**I**–**IV**) was added to a suspension of $Ru_3(CO)_{12}$ (1/3 eq.) 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 4 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.

12.2.1. $Ru(PhP[CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2)(CO)_2$ (**1**)

980 mg (2 mmol) of **I** and 430 mg (0.7 mmol of Ru) of $Ru_3(CO)_{12}$ in 20 mL of toluene. Recrystallisation from toluene/pentane at −30 °C gave 970 mg (1.5 mmol, 75%) of **1** as a light yellow powder. Suitable crystals for X-ray diffraction were obtained from a cold (−30 °C) toluene solution. Anal. Calc. for $C_{26}H_{45}O_6P_3Ru$ (647.6): C, 48.22%; H, 7.00%. Found: C, 48.60%; H, 7.21%. ^1H NMR (CD_2Cl_2, 298 K): 0.8–2.4 (m, –$CH_2CH_2CH_2$–), 0.92, 1.14, 1.4 and 1.45 (d, $^3J_{HH}$ = 6 Hz, –$P[OCH(CH_3)_2]_2$), 4.58 and 5.49 (sept., $^3J_{HH}$ = 6 Hz, –$P[OCH(CH_3)_2]_2$), 6.9–8 (m, –$P(C_6H_5)$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): 5.1 (t, $^2J_{PP}$ = 54 Hz, –$P(C_6H_5)$), 190.4 (d, $^2J_{PP}$ = 54 Hz, –$P[OCH(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 19.1 (m, –$CH_2CH_2CH_2$–), 24.3 (m, –$CH(CH_3)_2$), 32.5 (dt, J_{CP} = 4.7, 24 Hz, –$CH_2CH_2CH_2$–$P(C_6H_5)$), 37.1 (dt, J_{CP} = 3.7, 24.7 Hz, –$CH_2CH_2CH_2$-$P[OCH(CH_3)_2]_2$), 68.9 (m, –$P[OCH(CH_3)_2]_2$), (Phenyl: 127.8 (s, C *para*), 128.5 (d, $^3J_{CP}$ = 7 Hz, C *meta*), 133.6 (d, $^2J_{CP}$ = 16 Hz, C *ortho*), 138.3 (d, $^1J_{CP}$ = 22 Hz, C *ipso*)), 211 and 218 (m, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1851 (s) and 1912 (s).

12.2.2. $Ru(CyP[CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2)(CO)_2$ (**2**)

990 mg (2 mmol) of **II** and 430 mg (0.7 mmol) of $Ru_3(CO)_{12}$ in 20 mL of toluene. Recrystallisation from toluene/pentane at −30 °C gave 880 mg (1.35 mmol, 67%) of **2** as a light yellow powder. Anal. Calc. for $C_{26}H_{51}O_6P_3Ru$ (653.6): C, 47.77%; H, 7.86%. Found: C, 47.80%; H, 7.53%. ^1H NMR (CD_2Cl_2, 298 K):

0.8–2.4 (m, –PCH_2CH_2CH_2P–, –P[OCH(CH_3)$_2$]$_2$ and –P(C$_6H_{11}$)), 4.5 and 5.0 (sept., $^3J_{HP}$ = 6 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 4.5 (t, $^2J_{PP}$ = 51 Hz, –P(C$_6$H$_{11}$)), 192.2 (d, $^2J_{PP}$ = 51 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): 20.1 (m, –CH$_2$$CH_2CH_2$–), 24.5 (m, –CH($CH_3$)$_2$), 26.6 (dt, J_{CP} = 4.3, 21 Hz, –CH$_2$CH$_2$$CH_2$–P(C$_6H_{11}$)), 27 (s, Cyclohexyl C *para*), 28.1 (d, $^3J_{CP}$ = 11.3 Hz, Cyclohexyl C *meta*), 29.7 (d, $^2J_{CP}$ = 12,1 Hz, Cyclohexyl C *ortho*), 37.1 (dt, J_{CP} = 4, 24.6 Hz, –CH$_2$CH$_2$$CH_2$-P[OCH(CH$_3$)$_2$]$_2$), 38.4 (d, $^1J_{CP}$ = 14 Hz, Cyclohexyl C *ipso*), 69.2 (m, –P[OCH(CH$_3$)$_2$]$_2$), 215.4 (br, CO)). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1842 (s) and 1901 (s).

*12.2.3. Ru(PhP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$ (**3**)*

980 mg (2.6 mmol) of **III** and 560 mg (0.9 mmol of Ru) of $Ru_3(CO)_{12}$ in 20 mL of toluene. Recrystallisation from toluene/pentane at −30 °C gave 940 mg (1.7 mmol, 67%) of **3** as a light yellow powder. Anal. Calcd. for $C_{18}H_{29}O_6P_3Ru$ (535.4): C, 40.38%; H, 5.46%. Found: C, 40.20%; H, 5.60%. ^{1}H NMR (CD_2Cl_2, 298 K): 1.2–2.4 (m, –CH_2CH_2CH_2–), 3.4 and 3.73 (m, –P(OCH_3)$_2$), 7.4–7.8 (m, –P(C$_6H_5$)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 5.6 (t, $^2J_{PP}$ = 56.4 Hz, –P(C$_6$H$_5$)), 197.5 (d, $^2J_{PP}$ = 56.4 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 18.8 (m, –CH$_2$$CH_2CH_2$–), 32.8 (dt, J_{CP} = 24.6, 4.8 Hz, –CH$_2$CH$_2$$CH_2$–P(C$_6H_{11}$)), 33.8 (dt, J_{CP} = 4.7, 23.8 Hz, –CH$_2$CH$_2$$CH_2$–P(OCH$_3$)$_2$), 51.9 and 52.7 (m, –P(OCH$_3$)$_2$), (Phenyl: 128.2 (d, $^3J_{CP}$ = 9.7 Hz, C *meta*), 129.9 (s, C *para*), 133.7 (d, $^2J_{CP}$ = 16.3 Hz, C *ortho*), 137.8 (d, $^1J_{CP}$ = 25 Hz, C *ipso*)), 215.5 (br m, CO)). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1856 (s) and 1911 (s).

*12.2.4. Ru(CyP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$ (**4**)*

990 mg (2.6 mmol) of **IV** and 560 mg (0.9 mmol of Ru) of $Ru_3(CO)_{12}$ in 20 mL of toluene. Recrystallisation from toluene/pentane at −30 °C gave 1 g (1.84 mmol, 71%) of **4** as a light yellow powder. Anal. Calc. for $C_{18}H_{35}O_6P_3Ru$ (541.4): C, 39.93%; H, 6.52%. Found: C, 40.15%; H, 6.61%. ^{1}H NMR (CD_2Cl_2, 298 K): 0.8–2.2 (m, –CH_2CH_2CH_2– and –P(C$_6H_{11}$)), 3.52 and 3.69 (m, –P(OCH_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 4.9 (t, $^2J_{PP}$ = 55.8 Hz, –P(C$_6$H$_{11}$)), 201.6 (d, $^2J_{PP}$ = 55.8 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19.7 (m, –CH$_2$$CH_2CH_2$–), 26.2 (dt, J_{CP} = 26.2, 5.2 Hz, –CH$_2$CH$_2$$CH_2$–P(C$_6H_{11}$)), 26.9 (s, cyclohexyl C *para*), 28.1 (d, $^3J_{CP}$ = 11.2 Hz, cyclohexyl C *meta*), 28.6 (d, $^2J_{CP}$ = 12.6 Hz, cyclohexyl C *ortho*), 33.8 (dt, J_{CP} = 4.6, 25.1 Hz, –CH$_2$CH$_2$$CH_2$–P(OCH$_3$)$_2$), 38.6 (d, $^1J_{CP}$ = 16.4 Hz, cyclohexyl C *ipso*), 51.9 and 52.8 (m, –P(OCH$_3$)$_2$), 215.8 (q, $^2J_{CP}$ = 17.1 Hz, CO)). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1848 (s) and 1903 (s).

*12.2.5. Fe(PhP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$ (**5**)*

In a Schlenk, 1.4 g (1.6 mmol) of **12** was dissolved in 25 mL of THF and the mixture was cooled to −78 °C. The vessel was evacuated and refilled with CO three times. Sodium naphtalide (3.5 mmol, prepared from 450 mg of naphthalene and an excess of sodium in 5 mL of THF) was then added under CO atmosphere, the Schlenk was closed and the temperature was allowed to warm up slowly to room temperature. The reaction mixture was stirred overnight. Filtration over Celite® followed by removal of THF under vacuum gave a light orange solid. The residue was extracted with pentane and recrystallisation from toluene/pentane at −30 °C yielded 680 mg (1.1 mmol, 67%) of **5**. Suitable crystal for X-ray diffraction were obtained from a cold (−30 °C) saturated toluene solution. Anal. Calc. for $C_{26}H_{45}O_6P_3Fe$ (602.4): C, 51.84%; H, 7.53%. Found: C, 51.52%; H, 7.51%. ^{1}H NMR (CD_2Cl_2, 298 K): 0.8–2.4 (m, –CH$_2$CH$_2$CH$_2$–), 0.85, 0.95, 1.06 and 1.48 (m, –P[OCH(CH_3)$_2$]$_2$), 4.48 and 5.49 (sept., $^3J_{HP}$ = 6 Hz, –P[OCH(CH$_3$)$_2$]$_2$), 7–7.9 (m, –P(C$_6H_5$)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 25.6 (t, $^2J_{PP}$ = 79 Hz, –P(C$_6$H$_5$)), 215.1 (d, $^2J_{PP}$ = 79 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19.4 (m, –CH$_2$$CH_2CH_2$–), 24.5 (m, –CH($CH_3$)$_2$), 32.1 (dt, J_{CP} = 26, 7 Hz, –CH$_2$CH$_2$$CH_2$–P(C$_6H_5$)), 37.1 ('t', J_{CP} = 22 Hz, –CH$_2$CH$_2$$CH_2$–P[OCH(CH$_3$)$_2$]$_2$), 68.7 and 69.6 (m, –P[OCH(CH$_3$)$_2$]$_2$), (Phenyl: 129.6 (s, C *para*), 128 (d, $^3J_{CP}$ = 9 Hz, C *meta*), 133.5 (d, $^2J_{CP}$ = 14 Hz, C *ortho*), 138.8 (d, $^1J_{CP}$ = 27 Hz, C *ipso*), 217 and 221 (m, CO)). IR (C_6H_6, cm^1): ν_{CO} 1839 (s) and 1895 (s).

*12.2.6. Fe(CyP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$ (**6**)*

The phosphine ligand **II** (1.6 g, 3.2 mmol) was slowly added to a suspension of FeI_2 (1 g, 3.2 mmol) in 25 mL of THF. The red coloured mixture was stirred overnight at room temperature. The Schlenk was cooled to −78 °C, evacuated and refilled with CO three times. A 10-ml THF solution of sodium naphtalide (prepared from 900 mg (7 mmol) of naphthalene and an excess of sodium) was added to the mixture. The temperature was allowed to warm up slowly to room temperature and the reaction mixture was stirred overnight. Filtration over Celite® followed by removal of THF under vacuum gave a light brown solid. The residue was extracted with pentane and recrystallisation from toluene/pentane at −30 °C afforded 1.2 g of **6** (1.9 mmol; 62%). Anal. Calc. for $C_{26}H_{51}O_6P_3Fe$ (608.4): C, 51.32%; H, 8.45%. Found: C, 51.12%; H, 8.22%. ^{1}H NMR (CD_2Cl_2, 298 K): 0.9–2.2 (m, –PCH_2CH_2CH_2P– and –P(C$_6H_{11}$)), 1.18–1.51 (m, –P[OCH(CH_3)$_2$]$_2$), 4.5 and 5.5 (sept., $^3J_{HP}$ = 6 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 25.1 (t, $^2J_{PP}$ = 74.7 Hz, –P(C$_6$H$_{11}$)), 214.6 (d, $^2J_{PP}$ = 74.7 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): 19.6 (m, –CH$_2$$CH_2CH_2$–), 24.6 (m, –CH($CH_3$)$_2$), 25 (dt, J_{CP} = 21.6, 6.7 Hz, –CH$_2$CH$_2$$CH_2$–P(C$_6H_{11}$)), 27 (s, cyclohexyl C *para*), 28 (d, $^3J_{CP}$ = 10.9 Hz, cyclohexyl C *meta*), 29.8 (d,

$^2J_{CP}$ = 12.5 Hz, cyclohexyl C *ortho*), 35.1 (dt, J_{CP} = 2.7, 20.7 Hz, $-CH_2CH_2CH_2$-P[OCH$(CH_3)_2]_2$), 37.9 (d, $^1J_{CP}$ = 18.5 Hz, Cyclohexyl C *ipso*), 67.5 (m, –P[O*C*H-$(CH_3)_2]_2$), 218.1 (br, CO)). IR (C_6H_6, cm^{-1}): ν_{CO} 1828 (s), 1891 (s).

12.2.7. Fe(PhP[$CH_2CH_2CH_2P(OMe)_2]_2$)$(CO)_2$ (7)

The phosphine ligand **III** (760 mg, 2 mmol) and $Fe(CO)_5$ (0.27 mL, 2 mmol) in 20 mL of benzene were irradiated for 4–5 h after which time all free **III** was consumed (^{31}P NMR spectroscopy monitoring). The benzene was removed under vacuum and the residue was purified by column chromatography (benzene/THF). Recrystallisation from toluene/pentane at −30 °C afforded 351 mg (0.7 mmol, 36%) of **7**. Anal. Calc. for $C_{18}H_{29}O_6P_3Fe$ (490.2): C, 44.10%; H, 5.96%. Found: C, 44.27%; H, 6.35%. ^{1}H NMR (CD_2Cl_2, 298 K): 1.5–2.2 (m, –PCH_2CH_2CH_2P–), 3.39 and 3.78 (m, –P(OCH_3)$_2$), 7.35–7.82 (m, –P(C_6H_5)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 25.8 (t, $^2J_{PP}$ = 82.2 Hz, –P(C_6H_5)), 222 (d, $^2J_{PP}$ = 82.2 Hz, –P(OCH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19.7 (m, –CH_2*C*H_2CH_2–), 31–31.8 (m, –CH_2CH_2*C*H_2–P(C_6H_5) and –CH_2CH_2*C*H_2–P(OCH_3)$_2$), 50.6 and 51.3 (m, –P(O*C*H_3)$_2$), (Phenyl: 127.9 (d, $^3J_{CP}$ = 8.6 Hz, C *meta*), 129.5 (s, C *para*), 133.1 (d, $^2J_{CP}$ = 14.7 Hz, C *ortho*), 138.5 (d, $^1J_{CP}$ = 30.8 Hz, C *ipso*). IR (C_6H_6, cm^{-1}): ν_{CO} 1837 (s), 1895 (s).

12.2.8. Fe(CyP[$CH_2CH_2CH_2P(OMe)_2]_2$)$(CO)_2$ (8)

The phosphine ligand **IV** (1 g, 2.6 mmol) and $Fe(CO)_5$ (0.35 mL, 2.6 mmol) in 25 mL of benzene were irradiated from the outside for 5 h at room temperature with constant stirring. The benzene was removed under vacuum and the residue was purified by column chromatography (benzene/THF). Recrystallisation from toluene/pentane at −30 °C afforded 360 mg of **8** (0.68 mmol; 28%). Anal. Calcd. for $C_{18}H_{35}O_6P_3Fe$ (496.2): C, 43.57%; H, 7.11%. Found: C, 43.21%; H, 7.16%. ^{1}H NMR (CD_2Cl_2, 298 K): 1.1–2.2 (m, –PCH_2-CH_2CH_2P– and –P(C_6H_{11})), 3.62 and 3.87 (m, –P(OCH_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 24.7 (t, $^2J_{PP}$ = 82.2 Hz, –P(C_6H_{11})), 222.8 (d, $^2J_{PP}$ = 82.4 Hz, –P(OCH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19.4 (m, –CH_2*C*H_2CH_2–), 25.6 (dt, J_{CP} = 22.9, 7.3 Hz, –CH_2CH_2*C*H_2–P(C_6H_{11})), 27 (s, cyclohexyl C *para*), 28.2 (d, $^3J_{CP}$ = 12 Hz, cyclohexyl C *meta*), 29.3 (d, $^2J_{CP}$ = 10.2 Hz, cyclohexyl C *ortho*), 35.1 (dt, J_{CP} = 3.2, 21.5 Hz, -CH_2CH_2*C*H_2–P(OCH_3)$_2$), 38.7 (d, $^1J_{CP}$ = 19.3 Hz, cyclohexyl C *ipso*), 51.8 (m, –P(OCH_3)$_2$), 216.5 (br, CO)). IR (C_6H_6, cm^{-1}): ν_{CO} 1826 (s), 1888 (s).

12.2.9. Fe(η^2-PhP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)$(CO)_3$ (9)

$Fe(COT)(CO)_2$ (100 mg, 0.4 mmol) and the phosphine ligand **I** (200 mg, 0.4 mmol) were mixed in 2 mL of toluene and heated to 80 °C for 8 h. Recrystallisation from a cold (−30 °C) toluene/pentane mixture afforded 194 mg (0.31 mmol, 77%) of the product. Anal. Calc. for $C_{27}H_{45}O_7P_3Fe$ (630.4): C, 51.44%; H, 7.19%. Found: C, 51.47%; H, 7.19%. ^{31}P{^{1}H} NMR (C_6D_6, 298 K): 35.2 (d, $^2J_{PP}$ = 96.7 Hz, –P(C_6H_5)), 178.2 (s, uncoordinated –P[OCH$(CH_3)_2]_2$), 205.4 (d, $^2J_{PP}$ = 96.7 Hz, coordinated –P[OCH$(CH_3)_2]_2$).

12.2.10. Fe(η^2-PhP[$CH_2CH_2CH_2P(OMe)_2]_2$)$(CO)_3$ (10)

$Fe(COT)(CO)_2$ (100 mg, 0.4 mmol) and the phosphine ligand **III** (150 mg, 0.4 mmol) were mixed in 2 mL of toluene and heated to 80 °C for 8 hours. Recrystallisation from a cold (−30 °C) toluene/pentane mixture afforded 136 mg (0.26 mmol, 66%) of the product. Anal. Calc. for $C_{19}H_{29}O_7P_3Fe$ (518.2): C, 44.04%; H, 5.64%. Found: C, 44.21%; H, 5.78%. ^{31}P{^{1}H} NMR (C_6D_6, 298 K): 36.5 (d, $^2J_{PP}$ = 97.1 Hz, –P(C_6H_5)), 182.7 (s, uncoordinated –P(OCH_3)$_2$), 213 (d, $^2J_{PP}$ = 97.1 Hz, coordinated –P(OCH_3)$_2$).

12.2.11. $FeCl_2$(PhP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$) (11)

$FeCl_2 \cdot 4H_2O$ (400 mg, 2 mmol) was suspended in 20 mL of methanol. The phosphine ligand **I** (1 g, 2 mmol) was slowly added to the suspension resulting in an immediate dark blue colour. The mixture was stirred overnight at room temperature. The methanol was removed under vacuum, leaving a dark brown solid. The residue was recrystallized from methanol/ether. Complex **11** was obtained as a brown microcrystalline material (1.1 g, 1.7 mmol; 88%). The compound was paramagnetic and exhibited no ^{31}P NMR resonance. Anal. Calc. for $C_{24}Cl_2H_{45}O_4P_3Fe$ (617.3): C, 46.69%; H, 7.35%. Found: C, 46.83%; H, 7.14%.

12.2.12. FeI_2(PhP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$) (12)

The phosphine ligand **I** (1.6 g, 3.2 mmol) was slowly added to a suspension of FeI_2 (1 g, 3.2 mmol) in 40 mL of THF. The red coloured mixture was stirred overnight at room temperature. THF was removed under vacuum to leave a red-brown solid. The residue was recrystallized from THF/pentane and washed with pentane. Complex **12** was obtained as a red-brown microcrystalline material (2.3 g, 2.9 mmol; 92%). The compound was paramagnetic and exhibited no ^{31}P NMR resonance. Anal. Calc. for $C_{24}H_{45}I_2O_4P_3Fe$ (800.2): C, 36.02%; H, 5.67%. Found: C, 36.16%; H, 5.53%.

12.3. General procedure for the oxidative addition reaction of MeI to 1–8

The metal dicarbonyl complex (**1**–**8**, 0.5 mmol) in 2 mL of CH_2Cl_2 was treated with an excess of MeI (5 mmol) at room temperature and the reaction was

monitored by ^{31}P NMR spectroscopy. The excess MeI and CH_2Cl_2 was removed under vacuum. The residue was washed with pentane and recrystallized from CH_2Cl_2/pentane.

*12.3.1. mer,trans-[Ru(PhP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)-($CO)_2Me$]I (**13a**) and mer,cis- [Ru(PhP[CH_2CH_2-$CH_2P(Oi\text{-}Pr)_2]_2$)($CO)_2Me$]I (**13b**)*

Treatment of 330 mg (0.5 mmol) of **1** with MeI (0.15 mL, 2.5 mmol) gave 360 mg (0.46 mmol; 92%) of **13a** and **13b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{27}H_{48}O_6P_3RuI$ (789.6): C, 41.07%; H, 6.13%. Found: C, 41.28%; H, 6.26 %. (**13a**): ^1H NMR (CD_2Cl_2, 298 K): 0.17 (dt, $^3J_{HP}$ = 3 Hz (*trans*), $^3J_{HP}$ = 5 Hz (*cis*), Ru–CH_3), 1–2.8 (m, –$CH_2CH_2CH_2$–), 1.18–1.33 (m, –P[OCH(CH_3)$_2$]$_2$), 4.42 and 5.53 (sept., $^3J_{HP}$ = 6 Hz, –P[OC*H*$(CH_3)_2]_2$), 7.4–7.9 (m, –P(C_6H_5)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −4.5 (t, $^2J_{PP}$ = 33.6 Hz, –P(C_6H_5)), 155.7 (d, $^2J_{PP}$ = 33.6 Hz, –P[OCH$(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): −22.8 (dt, $^2J_{CP}$ = 25 Hz (*trans*), $^2J_{CP}$ = 6.6 Hz (*cis*), 24.3 (m, –CH(*C*H_3)$_2$), 24.5 (m, –CH_2*C*H_2CH_2–), 30.5 (dt, J_{CP} = 29, 2.1 Hz, –CH_2CH_2*C*H_2–P(C_6H_5)), 34.1 (dt, J_{CP} = 3.7, 17.3 Hz, –CH_2CH_2*C*H_2P[OCH$(CH_3)_2]_2$), 72.4 (m, –P[O*C*H$(CH_3)_2]_2$). (Phenyl: 128.4 (s, C *para*), 129.5 (d, $^3J_{CP}$ = 9.8 Hz, C *meta*), 131.6 (d, $^2J_{CP}$ = 13.1 Hz, C *ortho*), 133.8 (d, $^1J_{CP}$ = 21 Hz, C *ipso*), 199 (dt, $^2J_{CP}$ = 7.6, 15 Hz, CO) and 200.7 (dt, $^2J_{CP}$ = 6.8, 16.8 Hz, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2002 (s). (**13b**) (selected data): ^1H NMR (CD_2Cl_2, 298 K): −0.25 (q, $^3J_{HP}$ = 7.8 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −2.7 (t, $^2J_{PP}$ = 51 Hz, –P(C_6H_5)), 156.3 (d, $^2J_{PP}$ = 51 Hz, –P[OCH$(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): −18 (q, $^2J_{CP}$ = 11 Hz, Ru–*C*H_3). IR (CD_2Cl_2, cm^{-1}) 1968 (s), 2063 (s).

*12.3.2. mer,trans-[Ru(CyP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)-($CO)_2Me$]I (**14a**) and mer,cis-[Ru(CyP[$CH_2CH_2CH_2$-$P(Oi\text{-}Pr)_2]_2$)($CO)_2Me$]I (**14b**)*

Treatment of 330 mg (0.5 mmol) of **2** with MeI (0.15 mL, 2.5 mmol) gave 350 mg (0.45 mmol; 89%) of a **14a** and **14b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{27}H_{54}O_6P_3RuI$ (795.6): C, 40.76%; H, 6.82%. Found: C, 40.77%; H, 6.43 %. (**14a**): ^1H NMR (CD_2Cl_2, 298 K): 0.12 (dt, $^3J_{HP}$ = 2.8 Hz (*trans*), $^3J_{HP}$ = 5.2 Hz (*cis*), Ru–CH_3), 0.8–2.4 (m, –PCH_2CH_2CH_2P–, –O–CH(CH_3)$_2$ and –P(C_6H_{11})), 4.4–4.8 (m, –O–C*H*$(CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −3 (t, $^2J_{PP}$ = 32 Hz, –P(C_6H_{11})), 158 (d, $^2J_{PP}$ = 32 Hz, –P[OCH$(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): −23.9 (dt, $^2J_{CP}$ = 24 Hz (*trans*), $^2J_{CP}$ = 6.9 Hz (*cis*), Ru–*C*H_3), 19.1 (m, –CH_2*C*H_2CH_2–), 24.6 (m, –CH(*C*H_3)$_2$), 25.6 (m, –CH_2CH_2*C*H_2–P(C_6H_{11})), 26.4 (s, cyclohexyl C *para*), 27.4 (d, $^3J_{CP}$ = 10.8 Hz, cyclohexyl C *meta*), 31.4 (d, $^2J_{CP}$ = 12,2 Hz, cyclohexyl C *ortho*), 33.3 (dt, J_{CP} = 4, 17.5 Hz, –CH_2CH_2*C*H_2–P[OCH$(CH_3)_2]_2$), 38.7 (d, $^1J_{CP}$ = 23.7 Hz, cyclohexyl C *ipso*), 72.2 (m, –P[O*C*H$(CH_3)_2]_2$), 199.3 (q, $^2J_{CP}$ = 8 Hz, CO) and 201 (q, $^2J_{CP}$ = 8 Hz, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1997 (s). (**14b**) (selected data): ^1H NMR (CD_2Cl_2, 298 K): −0.41 (q, $^3J_{HP}$ = 7.6 Hz, Ru–*C*H_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −0.5 (t, $^2J_{PP}$ = 50 Hz, –P(C_6H_{11})), 158.1 (d, $^2J_{PP}$ = 50 Hz, –P[OCH$(CH_3)_2]_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): −17.1 (q, $^2J_{CP}$ = 10.2 Hz, Ru–*C*H_3). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2017 (s) and 2066 (s).

*12.3.3. mer,trans-[Ru(PhP[$CH_2CH_2CH_2P(OMe)_2]_2$)-($CO)_2Me$]I (**15a**) and mer,cis-[Ru(PhP[$CH_2CH_2CH_2$-$P(OMe)_2]_2$)($CO)_2Me$]I (**15b**)*

Treatment of 270 mg (0.5 mmol) of **3** with MeI (0.15 mL, 2.5 mmol) gave 290 mg (0.43 mmol, 86%) of **15a** and **15b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{19}H_{32}O_6P_3RuI$ (677.4): C, 33.69%; H, 4.76%. Found: C, 33.46%; H, 4.73%. (**15a**): ^1H NMR (CD_2Cl_2, 298 K): 0.24 (dt, $^3J_{HP}$ = 2.8 Hz (*trans*), $^3J_{HP}$ = 5 Hz (*cis*), Ru–CH_3), 1.4–2.6 (m, –$CH_2CH_2CH_2$–), 3.61 and 3.69 (m, –P(OCH_3)$_2$)), 7.2–7.8 (m, –P(C_6H_5)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −4.7 (t, $^2J_{PP}$ = 34.7 Hz, –P(C_6H_5)), 167.1 (d, $^2J_{PP}$ = 34.7 Hz, –P$(OCH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): −26.5 (dt, $^2J_{CP}$ = 23.7 Hz (*trans*), $^2J_{CP}$ = 6.8 Hz (*cis*), Ru–*C*H_3), 18.3 (m, –CH_2*C*H_2CH_2–), 25.0 (dt, J_{CP} = 25.7, 2.7 Hz, –CH_2CH_2*C*H_2–P(C_6H_{11})), 31.1 (dt, J_{CP} = 3.4, 19.7 Hz, –CH_2CH_2*C*H_2–P$(OCH_3)_2$), 54 (m, –P(O*C*H_3)$_2$), (Phenyl: 125.8 (s, C *para*), 128.1 (d, $^3J_{CP}$ = 9.6 Hz, C *meta*), 129.5 (d, $^2J_{CP}$ = 15.4 Hz, C *ortho*), 131 (d, $^1J_{CP}$ = 19.3 Hz, C *ipso*), 199.3 (dt, ^{2}Jcp = 6.8, 16.9 Hz, CO) and 199.5 (dt, ^{2}Jcp = 7.5, 15.6 Hz, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2012 (s). (**15b**) (selected data): ^1H NMR (CD_2Cl_2, 298 K): −0.21 (q, $^3J_{HP}$ = 8 Hz, Ru–CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −3.1 (t, $^2J_{PP}$ = 51 Hz, –P(C_6H_5)), 171 (d, $^2J_{PP}$ = 51 Hz, –P$(OCH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): −19.2 (q, $^2J_{CP}$ = 9.7 Hz, Ru–*C*H_3). IR (CD_2Cl_2, cm^{-}1): 1982 (s), 2048 (s).

*12.3.4. mer,trans-[Ru(CyP[$CH_2CH_2CH_2P(OMe)_2]_2$)-($CO)_2Me$]I (**16a**) and mer,cis-[Ru(CyP[$CH_2CH_2CH_2$-$P(OMe)_2]_2$)($CO)_2Me$]I (**16b**)*

Treatment of 270 mg (0.5 mmol) of **4** with MeI (0.15 mL, 2.5 mmol) gave 321 mg (0.47 mmol, 94%) of **16a** and **16b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{19}H_{38}O_6P_3RuI$ (683.4): C, 33.39%; H, 5.60%. Found: C, 33.52%; H, 5.73%. (**16a**): ^1H NMR (CD_2Cl_2, 298 K): 0.05 (dt, $^3J_{HP}$ = 2.8 Hz (*trans*), $^3J_{HP}$ = 5 Hz (*cis*), Ru–CH_3), 1.1–2.2 (m, –CH_2CH_2CH_2– and –PC_6H_{11}), 3.5–3.7 (m, –P(OC-H_3)$_2$), 7.5–7.8 (m, –P(C_6H_5)). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −2.8 (t, $^2J_{PP}$ = 34 Hz, –P(C_6H_5)), 168.9 (d,

$^2J_{PP}$ = 34 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −26.1 (dt, $^2J_{CP}$ = 24.5 Hz (*trans*), $^2J_{CP}$ = 6.9 Hz (*cis*), Ru–*C*H$_3$), 17.5 (m, –CH$_2$*C*H$_2$CH$_2$–), 26.4 (s, cyclohexyl C *para*), 27.8 (d, $^3J_{CP}$ = 10.2 Hz, cyclohexyl C *meta*), 28.7 (d, $^2J_{CP}$ = 14 Hz, cyclohexyl C *ortho*), 30.1 (dt, J_{CP} = 29.4, 2.8 Hz, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$H$_{11}$)), 31.7 (dt, J_{CP} = 3.8, 19.6 Hz, –CH$_2$CH$_2$*C*H$_2$–P(OCH$_3$)$_2$), 39.6 (d, $^1J_{CP}$ = 23.2 Hz, cyclohexyl C *ipso*), 54 (m, –P(O*C*H$_3$)$_2$), 198.7 (dt, $^2J_{CP}$ = 7.8, 15.8 Hz, CO) and 198.9 (dt, $^2J_{CP}$ = 7.4, 16.9 Hz, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2006 (s). (**16b**) (selected data): ^{1}H NMR (CD_2Cl_2, 298 K): −0.45 (q, $^3J_{HP}$ = 7.4 Hz, Ru–CH$_3$), 1.1–2.2 (m, –C*H*$_2$C*H*$_2$C*H*$_2$– and –PC$_6$*H*$_{11}$), 3.4–3.7 (m, –P(OC*H*$_3$)$_2$), 7.5–7.8 (m, –P(C$_6$*H*$_5$)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −2.1 (t, $^2J_{PP}$ = 51.9 Hz, –P(C$_6$H$_5$)), 171.8 (d, $^2J_{PP}$ = 51.9 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −20.1 (q, $^2J_{CP}$ = 10.1 Hz, Ru–*C*H$_3$). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1996 (s) and 2041 (s).

*12.3.5. mer,trans-[Fe(PhP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$Me]I (**17a**) and mer,cis-[Fe(PhP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$Me]I (**17b**)*

Treatment of 300 mg (0.5 mmol) of **5** with MeI (0.15 mL, 2.5 mmol) for 48 hours gave 366 mg (0.49 mmol, 99%) of **17a** and **17b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{27}H_{48}O_6P_3FeI$ (744.3): C, 43.54%; H, 6.45%. Found: C, 43.21%; H, 6.13%. (**17a**) (selected data): ^{1}H NMR (CD_2Cl_2, 298 K): 0.37 (t, $^3J_{HP}$ = 4.8 Hz, Fe-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 18 (t, $^2J_{PP}$ = 52 Hz, –P(C$_6$H$_5$)), 182 (d, $^2J_{PP}$ = 52 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −11.67 (t, $^2J_{CP}$ = 14.4 Hz, Fe-*C*H$_3$), 19.1 (m, –CH$_2$*C*H$_2$CH$_2$–), 27.1 (m, –CH(*C*H$_3$)$_2$) 29.9 (m, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$H$_5$)), 35.6 (m, –CH$_2$CH$_2$*C*H$_2$– P[OCH(CH$_3$)$_2$]$_2$), 68.9 and 72.6 (m, –P[O*C*H(CH$_3$)$_2$]$_2$), (Phenyl: 127.9–133.8), 212.1 and 213.9 (br, CO). IR (CD_2Cl_2, cm^1): ν_{CO} 1970(s). (**17b**): ^{1}H NMR (CD_2Cl_2, 298 K): −0.20 (q, $^3J_{HP}$ = 8.8 Hz, Fe-C*H*$_3$), 1.25–1.38 (m, –P[OCH(C*H*$_3$)$_2$]$_2$), 1.8–2.4 (m, –PC*H*$_2$C*H*$_2$C*H*$_2$P–), 4.49 and 4.6 (sept., $^3J_{HP}$ = 6 Hz, –P[OC*H*(CH$_3$)$_2$]$_2$), 7–7.9 (m, –P(C$_6$*H*$_5$)). ^{31}P {^{1}H} NMR (CD_2Cl_2, 298 K): 14 (t, $^2J_{PP}$ = 90 Hz, –P(C$_6$H$_5$)), 177.8 (d, $^2J_{PP}$ = 90 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −11.98 (q, $^2J_{CP}$ = 18.7 Hz, Fe-*C*H$_3$), 18.1 (m, –CH$_2$*C*H$_2$CH$_2$–), 24.1 (dt, J_{CP} = 5.5, 29.1 Hz, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$H$_5$)), 24.7 (m, –CH-(*C*H$_3$)$_2$), 25.1 ('t', J_{CP} = 13 Hz, –CH$_2$CH$_2$*C*H$_2$–P[OCH(CH$_3$)$_2$]$_2$), 72.6 and 73.9 (m, –P[O*C*H(CH$_3$)$_2$]$_2$), (Phenyl: 129.3 (s, C *para*), 131.5 (d, $^3J_{CP}$ = 9 Hz, C *meta*), 134 (d, $^2J_{CP}$ = 9 Hz, C *ortho*), 134.5 (d, $^1J_{CP}$ = 39 Hz, C *ipso*), 207.9 (dt, $^2J_{CP}$ = 16.6, 20 Hz, CO *trans* to –P(C$_6$H$_5$)), 210.3 (q, $^2J_{CP}$ = 31 Hz, CO *cis* to the three P atoms). IR (CD_2Cl_2, cm^1): ν_{CO} 1994 (s) and 2044 (s).

*12.3.6. mer,trans-[Fe(CyP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$Me]I (**18a**) and mer,cis-[Fe(CyP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$Me]I (**18b**)*

Treatment of 300 mg (0.5 mmol) of **6** with MeI (0.15 mL, 2.5 mmol) gave 324 mg (0.42 mmol, 86%) of **18a** and **18b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{27}H_{54}O_6P_3FeI$ (750.3): C, 43.22%; H, 7.25%. Found: C, 43.58%; H, 7.10%. (**18a**): ^{1}H NMR (CD_2Cl_2, 298 K): 0.21 (t, $^3J_{HP}$ = 5.4 Hz, Fe-C*H*$_3$), 1.1–2.5 (m, –PC*H*$_2$C*H*$_2$C*H*$_2$P– and –P(C$_6$*H*$_{11}$)), 1.3 (m, –P[OCH(C*H*$_3$)$_2$]$_2$), 4.5 and 4.7 (sept., $^3J_{HP}$ = 6 Hz, –P[OC*H*(CH$_3$)$_2$]$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 17.7 (t, $^2J_{PP}$ = 50.1 Hz, –P(C$_6$H$_{11}$)), 182.7 (d, $^2J_{PP}$ = 50.1 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −12.7 (t, ^2J_P = 14.6 Hz, Fe-*C*H$_3$), 19 (m, –CH$_2$*C*H$_2$CH$_2$–), 24.4 (m, –CH(*C*H$_3$)$_2$), 25.3 (dt, J_{CP} = 16.3, 4.8 Hz, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$*H*$_{11}$)), 26.4 (s, cyclohexyl C *para*), 27.5 (d, $^3J_{CP}$ = 11.5 Hz, cyclohexyl C *meta*), 28.8 (d, $^2J_{CP}$ = 14 Hz, cyclohexyl C *ortho*), 31.6 (dt, J_{CP} = 13.2, 2.1 Hz, –CH$_2$CH$_2$*C*H$_2$–P[OCH(CH$_3$)$_2$]$_2$), 38.7 (d, $^1J_{CP}$ = 23.5 Hz, cyclohexyl C *ipso*), 72.6 (m, –P[O*C*H(CH$_3$)$_2$]$_2$), 211.8 (dt, $^2J_{CP}$ = 13, 29.4 Hz, CO) and 214.1 (dt, $^2J_{CP}$ = 10.4, 32.5 Hz, CO). IR (CD_2Cl_2, cm^1): ν_{CO} 1968 (s). (**18b**) (selected data): ^{1}H NMR (CD_2Cl_2, 298 K): −0.31 (q, $^3J_{HP}$ = 9.1 Hz, Fe-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 14.4 (t, $^2J_{PP}$ = 88.8 Hz, –P(C$_6$H$_{11}$)), 181.9 (d, $^2J_{PP}$ = 88.8 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −11.64 (q, $^2J_{CP}$ = 20.6 Hz, Fe-*C*H$_3$), 207 (dt, $^2J_{CP}$ = 15.1, 19 Hz, CO *trans* to –P(C$_6$H$_{11}$)), 211.6 (q, $^2J_{CP}$ = 32 Hz, CO *cis* to the three P atoms). IR (CD_2Cl_2, cm^1): ν_{CO} 1997 (s) and 2046 (s).

*12.3.7. mer,trans-[Fe(PhP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$Me]I (**19a**) and mer,cis-[Fe(PhP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$Me]I (**19b**)*

Treatment of 245 mg (0.5 mmol) of **7** with MeI (0.15 mL, 2.5 mmol) gave 300 mg (0.48 mmol, 96%) of **19a** and **19b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{19}H_{32}O_6P_3FeI$ (632): C, 36.10%; H, 5.10%. Found: C, 36.36%; H, 5.01%. (**19a**) (selected data): ^{1}H NMR (CD_2Cl_2, 298 K): 0.37 (t, $^3J_{HP}$ = 4.8 Hz, Fe-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 18.8 (t, $^2J_{PP}$ = 56 Hz, –P(C$_6$H$_5$)), 196.4 (d, $^2J_{PP}$ = 56 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −14.8 (t, $^2J_{CP}$ = 14.1 Hz, Fe-*C*H$_3$). IR (CD_2Cl_2, cm^1): ν_{CO} 1976(s). (**19 b**): ^{1}H NMR (CD_2Cl_2, 298 K): −0.04 (q, $^3J_{HP}$ = 8.4 Hz, Fe-C*H*$_3$), 1.7–2.4 (m, –PC*H*$_2$C*H*$_2$C*H*$_2$P–), 3.3–3.6 (m, –P(OCH$_3$)$_2$), 7.4–7.7 (m, –P(C$_6$H$_5$)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 15.9 (t, $^2J_{PP}$ = 86 Hz, –P(C$_6$H$_5$)), 196.4 (d, $^2J_{PP}$ = 86 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −11.7 (q, $^2J_{CP}$ = 17.9 Hz, Fe-*C*H$_3$), 18.7 (m, –CH$_2$*C*H$_2$CH$_2$–), 30.1 (m, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$H$_5$)), 35.4 (m, –CH$_2$CH$_2$*C*H$_2$–P(OCH$_3$)$_2$), 52.9 and 54.1 (m, –P(O*C*H$_3$)$_2$), (Phenyl: 128.7 (s, C *para*), 131.2 (d,

$^3J_{CP}$ = 9 Hz, C *meta*), 132 (d, $^2J_{CP}$ = 9.6 Hz, C *ortho*), 133.2 (d, $^1J_{CP}$ = 36.8 Hz, C *ipso*), 217 (br, CO). IR (CD_2Cl_2, cm^1): ν_{CO} 1990 (s) and 2046(s).

*12.3.8. mer,trans-[Fe(CyP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$Me]I (**20a**) and mer,cis-[Fe(CyP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$Me]I (**20b**)*

Treatment of 247 mg (0.5 mmol) of **8** with MeI (0.15 mL, 2.5 mmol) gave 280 mg (0.44 mmol, 89%) of **20a** and **20b** as an isomeric mixture which could not be separated. Anal. Calc. for $C_{19}H_{38}O_6P_3FeI$ (638.1): C, 35.76%; H, 6.00%. Found: C, 35.58%; H, 5.82%. (**20a**): ^{1}H NMR (CD_2Cl_2, 298 K): 0.23 (t, $^3J_{HP}$ = 5.2 Hz, Fe-C*H*$_3$), 1–2.2 (m, –C*H*$_2$C*H*$_2$C*H*$_2$– and –P(C$_6$*H*$_{11}$)), 3.6 and 3.8 (m, –P(OC*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 20 (t, $^2J_{PP}$ = 55 Hz, –P(C$_6$H$_{11}$)), 198.3 (d, $^2J_{PP}$ = 55 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −15.1 (t, $^2J_{CP}$ = 14 Hz, Fe-*C*H$_3$), 18.7 (m, –CH$_2$*C*H$_2$CH$_2$–), 26 (m, CH$_2$CH$_2$*C*H$_2$–P(C$_6$*H*$_{11}$)), 27 (s, cyclohexyl C *para*), 27.7 (d, $^3J_{CP}$ = 3.3 Hz, cyclohexyl C *meta*), 29 (d, $^2J_{CP}$ = 10.6 Hz, cyclohexyl C *ortho*), 32.5 (m, –CH$_2$CH$_2$*C*H$_2$–P(OCH$_3$)$_2$), 39 (d, $^1J_{CP}$ = 26.4 Hz, cyclohexyl C *ipso*), 52.8 and 54.1 (m,–P(O*C*H$_3$)$_2$), 207 and 209 (br, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1972 (s). (**20b**) (selected data): ^{1}H NMR (CD_2Cl_2, 298 K): −0.18 (q, $^3J_{HP}$ = 8.5 Hz, Fe-C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 16.8 (t, $^2J_{PP}$ = 85.9 Hz, –P(C$_6$H$_{11}$)), 197.2 (d, $^2J_{PP}$ = 85.9 Hz, –P(OCH$_3$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): −11.7 (q, $^2J_{CP}$ = 20.6 Hz, Fe-*C*H$_3$) 19 (m, –CH$_2$*C*H$_2$CH$_2$–), 25.1 (m, CH$_2$CH$_2$*C*H$_2$–P(C$_6$*H*$_{11}$)), 33 (m, –CH$_2$CH$_2$*C*H$_2$–P(OCH$_3$)$_2$), 51–54 (m,–P(O*C*H$_3$)$_2$), 211 (br, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1996 (s), 2039 (s).

*12.3.9. mer,trans-[Fe(CyP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$Me]BPh4 (**21**)*

Treatment of 120 mg (0.25 mmol) of **8** with MeI (0.08 mL, 1.25 mmol) for 2 days. The solvent was removed under vacuum to leave a light brown solid. A solution of sodium tetraphenylborate (100 mg, 0.3 mmol) in 5 mL of methanol was added to the residue and the mixture was stirred for 2 h. The light yellow precipitate was filtered off over a frit and washed with methanol and dried under vacuum to give **21** (147 mg, 18 mmol, 71%). Suitable crystals for X-ray diffraction were obtained from crystallisation in a dichloromethane/pentane solution at room temperature. Anal. Calc. for $BC_{43}H_{58}O_6P_3Fe$ (830.5): C, 62.18%; H, 7.04%. Found: C, 62.20%; H, 7.21%.

*12.4. General procedure for the oxidative addition reaction of EtI, n-PrI, i-PrI and iodine to **1–8***

The metal dicarbonyl complex (**1**–**8**, 0.15 mmol) in 1 mL of CH_2Cl_2 was treated with an excess of alkyl iodide (EtI (10 eq., 0.12 mL, 1.5 mmol); *n*-PrI or *i*-PrI (10 eq., 0.15 mL, 1.5 mmol) at room temperature for four days, to yield the iodo complexes **22**–**29**. The latter were better prepared from the instantaneous reaction of **1**–**8** with a stoichiometric amount of iodine in dichloromethane at room temperature. Pentane was added to the reaction mixture. The precipitated material was washed with pentane and recrystallized from CH_2Cl_2/pentane or CH_2Cl_2/benzene.

*12.4.1. mer,cis-[Ru(PhP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$I]I (**22**)*

Complex **1** (100 mg, 0.15 mmol) was treated with one equivalent of I_2 (38 mg, 0.15 mmol). Recrystallisation from CH_2Cl_2/pentane afforded 120 mg (0.13 mmol, 88%) of **22** as a light yellow powder. Anal. Calc. for $C_{26}H_{45}I_2O_6P_3Ru$ (901.5): C, 34.64%; H, 5.03%. Found: C, 34.96%; H, 5.17%. ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −12.7 (t, $^2J_{PP}$ = 48 Hz, –P(C$_6$H$_5$)), 143.5 (d, $^2J_{PP}$ = 48 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 20.1 (m, –CH$_2$*C*H$_2$CH$_2$–), 23.3 (m, –CH(*C*H$_3$)$_2$), 27.7 (m, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$*H*$_5$)), 37.9 (m, –CH$_2$CH$_2$*C*H$_2$–P[OCH(CH$_3$)$_2$]$_2$), 72.9 (m, –P[O*C*H(CH$_3$)$_2$]$_2$). (Phenyl: 128 (s, C *para*), 129.1 (d, $^3J_{CP}$ = 11 Hz, C *meta*), 132 (d, $^2J_{CP}$ = 14.3 Hz, C *ortho*), 133.9 (d, $^1J_{CP}$ = 18.1 Hz, C *ipso*), 187.2 (dt, ^2J_P = 81.3, 12.4 Hz, CO *trans* to P) and 189.4 (q, ^2J_P = 11 Hz, CO *trans* to I). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2033 (s), 2086 (s).

*12.4.2. mer,cis-[Ru(CyP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$I]I (**23**)*

Complex **2** (100 mg, 0.15 mmol) was treated with one equivalent of I_2 (38 mg, 0.15 mmol). Recrystallisation from CH_2Cl_2/pentane afforded 130 mg (0.14 mmol, 96%) of **23.** Anal. Calcd. for $C_{26}H_{51}I_2O_6P_3Ru$ (907.5): C, 34.41%; H, 5.66%. Found: C, 34.48%; H, 5.52%. ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −10.2 (t, $^2J_{PP}$ = 48 Hz, –P(C$_6$H$_{11}$)), 145.5 (d, $^2J_{PP}$ = 48 Hz, –P[OCH(CH$_3$)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19.4 (m, –CH$_2$*C*H$_2$CH$_2$–), 24.6 (m, –CH(*C*H$_3$)$_2$), 26.1 (m, –CH$_2$CH$_2$*C*H$_2$–P(C$_6$*H*$_{11}$)), 27.2 (s, cyclohexyl C *para*), 28.3 (d, $^3J_{CP}$ = 3.5 Hz, cyclohexyl C *meta*), 29.9 (d, $^2J_{CP}$ = 10.9 Hz, cyclohexyl C *ortho*), 37.3 (dt, J_{CP} = 22.1, 5 Hz, –CH$_2$CH$_2$*C*H$_2$– P[OCH(CH$_3$)$_2$]$_2$), 38.2 (d, $^1J_{CP}$ = 27.3 Hz, cyclohexyl C *ipso*), 74.1 (m, –P[O*C*H(CH$_3$)$_2$]$_2$), 188.1 (dt, ^2J_P = 80, 11.4 Hz, CO *trans* to P) and 189.9 (q, ^2J_P = 11.2 Hz, CO *trans* to I). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2029 (s), 2084 (s).

*12.4.3. mer,cis-[Ru(PhP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$I]I (**24**)*

Complex **3** (80 mg, 0.15 mmol) was treated with one equivalent of I_2 (38 mg, 0.15 mmol). Recrystallisation from CH_2Cl_2/benzene afforded 110 mg (0.14 mmol, 93%) of **24** as a light yellow solid. Anal. Calc. for $C_{18}H_{29}I_2O_6P_3Ru$ (789.2): C, 27.39%; H, 3.70%. Found: C, 27.76%; H, 3.65%. ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K):

−13.4 (t, $^2J_{PP}$ = 47.3 Hz, –P(C_6H_5)), 155.5 (d, $^2J_{PP}$ = 47.3 Hz, –P(OCH_3)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 17.5 (m, –$CH_2CH_2CH_2$–), 24.3 (dt, J_{CP} = 3.8, 34.6 Hz, –$CH_2CH_2CH_2$–P(C_6H_{11})), 26.1 ('t', J_{CP} = 19.5 Hz, –$CH_2CH_2CH_2$-P[O(CH_3)]$_2$), 54.8 and 56.6 (m, –P(OCH_3)$_2$), (Phenyl: 130 (d, $^3J_{CP}$ = 9.1 Hz, C *meta*), 131.8 (d, $^2J_{CP}$ = 10.3 Hz, C *ortho*), 132.4 (s, C *para*), 132.9 (d, $^1J_{CP}$ = 34.1 Hz, C *ipso*)), 187.3 (dt, $^2J_{CP}$ = 83.2, 12.5 Hz, CO *trans* to –P(C_6H_5)) and 188.9 (q, $^2J_{CP}$ = 11.2 Hz, CO *trans* to I). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2014 (s) and 2072 (s).

*12.4.4. mer,cis-[Ru(CyP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$I]I (**25**)*

Complex **4** (81 mg, 0.15 mmol) was treated with one equivalent of I_2 (38 mg, 0.15 mmol). Recrystallisation from CH_2Cl_2/benzene afforded 95 mg (0.12 mmol, 81%) of **25** as a light yellow solid. Anal. Calc. for $C_{18}H_{35}I_2O_6P_3Ru$ (795.3): C, 27.18%; H, 4.44%. Found: C, 27.15%; H, 4.20%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): −10.6 (t, $^2J_{PP}$ = 45.8 Hz, –P(C_6H_5)), 156.7 (d, $^2J_{PP}$ = 45.8 Hz, –P(OCH_3)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 18.6 (m, –$CH_2CH_2CH_2$–), 24.9 (m, –$CH_2CH_2CH_2$–P(C_6H_{11})), 26.9 (s, cyclohexyl C *para*), 27.4 (d, $^3J_{CP}$ = 14 Hz, cyclohexyl C *meta*), 29.1 (d, $^2J_{CP}$ = 8.8 Hz, cyclohexyl C *ortho*), 29.7 (m, –$CH_2CH_2CH_2$–P(OCH_3)$_2$), 37.9 (d, $^1J_{CP}$ = 20 Hz, cyclohexyl C *ipso*), 54–55.8 (m, –P(OCH_3)$_2$), 189 (br, CO). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2024 (s) and 2084 (s).

*12.4.5. mer,cis-[Fe(PhP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$I]I (**26**)*

Complex **5** (100 mg, 0.17 mmol) was treated with one equivalent of I_2 (43 mg, 0.17 mmol). Recrystallisation from CH_2Cl_2/pentane afforded 100 mg (0.12 mmol, 69%). Anal. Calcd. for $C_{26}H_{45}I_2O_6P_3Fe$ (856.2): C, 36.47%; H, 5.30%. Found: C, 36.31%; H, 5.18%. *mer*, *cis*-[Fe**Lig3**(CO)$_2$I]I (**26**): $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): 5.8 (t, $^2J_{PP}$ = 85 Hz, –P(C_6H_5)), 172 (d, $^2J_{PP}$ = 85 Hz, –P[OCH(CH_3)$_2$]$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 18.9 (m, –$CH_2CH_2CH_2$–), 24.3–25.1 (m, –CH(CH_3)$_2$ and –$CH_2CH_2CH_2$–P(C_6H_5)), 29.1 (dt, J_{CP} = 4.2, 16.3 Hz, –$CH_2CH_2CH_2$–P[OCH(CH_3)$_2$]$_2$), 74.2 and 76.8 (m, –P[OCH(CH_3)$_2$]$_2$), (Phenyl: 127.9 (d, $^2J_{CP}$ = 9.3 Hz, C *ortho*), 131.1 (d, $^3J_{CP}$ = 7.9 Hz, C *meta*), 132.1 (s, C *para*), 133.5 (d, $^1J_{CP}$ = 41.9 Hz, C *ipso*), 206 (dt, $^2J_{CP}$ = 34.9, 26.3 Hz, Fe-CO *trans* to -PPh) and 210.8 (q, $^2J_{CP}$ = 21.6 Hz, Fe-CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2024 (s) and ν_{CO} 2067 (s).

*12.4.6. mer,cis- [Fe(CyP[CH$_2$CH$_2$CH$_2$P(Oi-Pr)$_2$]$_2$)(CO)$_2$I]I (**27**)*

Complex **6** (100 mg, 0.16 mmol) was treated with one equivalent of I_2 (40 mg, 0.16 mmol). Recrystallisation from CH_2Cl_2/pentane afforded 121 mg (0.14 mmol, 88%) of **27**. Anal. Calc. for $C_{26}H_{51}I_2O_6P_3Fe$ (862.3): C, 36.22%; H, 5.96%. Found: C, 36.40%; H, 6.07%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): 6.9 (t, $^2J_{PP}$ = 81.9 Hz, –P(C_6H_{11})), 169.9 (d, $^2J_{PP}$ = 81.9 Hz, –P[OCH(CH_3)$_2$]$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 18.7 (m, –CH_2-CH_2CH_2–), 24 (m, –CH(CH_3)$_2$), 26.6 (m, –CH_2-CH_2CH_2–P(C_6H_{11}), cyclohexyl C *para* obscured), 27.4 (d, $^3J_{CP}$ = 12.1 Hz, cyclohexyl C *meta*), 29 (d, $^2J_{CP}$ = 15.6 Hz, cyclohexyl C *ortho*), 32 (m, –CH_2CH_2-CH_2–P[OCH(CH_3)$_2$]$_2$), 39.9 (d, $^1J_{CP}$ = 19.3 Hz, cyclohexyl C *ipso*), 74–76 (m, –P[OCH(CH_3)$_2$]$_2$), 206–209 (br, CO). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 2016 (s) and ν_{CO} 2064 (s).

*12.4.7. mer,cis-[Fe(PhP[CH$_2$CH$_2$CH$_2$P(OMe)$_2$]$_2$)(CO)$_2$I]I (**28**)*

Complex **7** (80 mg, 0.16 mmol) was treated with one equivalent of I_2 (40 mg, 0.16 mmol). Recrystallisation from CH_2Cl_2/benzene afforded 114 mg (0.15 mmol, 96%) of **28** as a light yellow solid. Anal. Calc. for $C_{18}H_{29}I_2O_6P_3Fe$ (744): C, 29.06%; H, 3.93%. Found: C, 29.37%; H, 4.25%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): 5 (t, $^2J_{PP}$ = 82.8 Hz, –P(C_6H_5)), 183.2 (d, $^2J_{PP}$ = 82.8 Hz, –P(OCH_3)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 19 (m, –$CH_2CH_2CH_2$–), 28.8 (m, –$CH_2CH_2CH_2$–P(C_6H_5)), 34.1 (m, –$CH_2CH_2CH_2$–P(OCH_3)$_2$), 52 and 53.7 (m, –P(OCH_3)$_2$), (Phenyl: 127.3 (d, $^2J_{CP}$ = 9.3 Hz, C *ortho*), 130.6 (d, $^3J_{CP}$ = 8.2 Hz, C *meta*), 132.3 (s, C *para*), 133.5 (d, $^1J_{CP}$ = 40.1 Hz, C *ipso*), 207.1 and 211.4 (br, CO). IR (CH_2Cl_2, cm^1): ν_{CO} 2022 (s) and ν_{CO} 2065 (s).

*12.4.8. mer,cis- [Fe(CyP[CH$_2$ CH$_2$CH$_2$P-(OMe)$_2$]$_2$)(CO)$_2$I]I (**29**)*

Complex **8** (80 mg, 0.16 mmol) was treated with one equivalent of I_2 (40 mg, 0.16 mmol). Recrystallisation from CH_2Cl_2/benzene afforded 104 mg (0.14 mmol, 87%) of **29** as a light yellow solid. Anal. Calc. for $C_{18}H_{35}I_2O_6P_3Fe$ (750): C, 28.82%; H, 4.70%. Found: C, 29.11%; H, 4.79%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): 7.9 (t, $^2J_{PP}$ = 82 Hz, –P(C_6H_{11})), 184.1 (d, $^2J_{PP}$ = 82 Hz, –P(OCH_3)$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): 18.1 (m, –$CH_2CH_2CH_2$–), 25.2 (s, cyclohexyl C *para*), 27.6 (d, $^3J_{CP}$ = 9.4 Hz, cyclohexyl C *meta*), 28.4 (m, $CH_2CH_2CH_2$–P(C_6H_{11})), 32 (d, $^2J_{CP}$ = 13.2 Hz, cyclohexyl C *ortho*), 34.3 (m, –$CH_2CH_2CH_2$–P(OCH_3)$_2$), 39 (d, $^1J_{CP}$ = 18.3 Hz, cyclohexyl C *ipso*), 52.6 and 54 (m, –P(OCH_3)$_2$), 206.6 and 209 (br, CO). IR (CH_2Cl_2, cm^1): ν_{CO} 1997 (s) and ν_{CO} 2046 (s).

*12.5. General procedure for the reaction of **13a/b–20a/b** with CO*

The respective isomeric complexes **13a/b–20a/b** were dissolved in CD_2Cl_2 and stirred under an atmosphere of carbon monoxide at room temperature. The completeness of the reactions was monitored by ^1H NMR spectroscopy. Elemental analysis for **30–37** could not

be obtained due to decarbonylation on attempted isolation of the acetyl complexes.

*12.5.1. mer,trans-[Ru(PhP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)-($CO)_2$(COMe)]I (**30**)*

A dichloromethane solution of **13a/13b** (250 mg, 0.3 mmol) was stirred overnight under CO. ^{1}H NMR (CD_2Cl_2, 298 K): 0.8–2.8 (m, –$CH_2CH_2CH_2$–), 1.15 and 1.35 (m, –P[OCH(CH_3)$_2$]$_2$), 2.53 (s, C(O)CH_3), 4.48 and 4.64 (m, $^3J_{HP}$ = 6 Hz, –P[OCH(CH_3)$_2$]$_2$), 7.3–7.8 (m, –P(C_6H_5)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −10.7 (t, $^2J_{PP}$ = 51 Hz, –P(C_6H_5)), 153.3 (d, $^2J_{PP}$ = 51 Hz, –P[OCH(CH_3)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 17.8 (m, –$CH_2CH_2CH_2$–), 24 (m, –CH(CH_3)$_2$), 29.9 (m, –$CH_2CH_2CH_2$–P(C_6H_5)), 33.5 (m, –$CH_2CH_2CH_2$-P[OCH(CH_3)$_2$]$_2$), 50.4 (s, C(O)CH_3), 73 (m, –P[OCH(CH_3)$_2$]$_2$), (Phenyl: 129 (s, C *para*), 129.8 (d, $^3J_{CP}$ = 10.2 Hz, C *meta*), 130.9 (d, $^2J_{CP}$ = 16.1 Hz, C *ortho*), 133.1 (d, $^1J_{CP}$ = 19.6 Hz, C *ipso*), 194 (br, CO), 260 (br, *C*(O)CH_3). IR (CD_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1608 (m) and ν_{CO} 1997 (s).

*12.5.2. mer,trans-[Ru(CyP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)-($CO)_2$(COMe)]I (**31**)*

A dichloromethane solution of **14a/14b** (250 mg, 0.3 mmol) was stirred for 48 h. ^{1}H NMR (CD_2Cl_2, 298 K): 1–2.6 (m, –P$CH_2CH_2CH_2$P–, –O–CH(CH_3)$_2$ and –P(C_6H_{11})), 2.4 (s, –C(O)CH_3), 4.4–4.8 (m, –O–CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −4.1 (t, $^2J_{PP}$ = 50 Hz, –P(C_6H_{11})), 154.5 (d, $^2J_{PP}$ = 50 Hz, –P[OCH(CH_3)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 18.8 (m, –$CH_2CH_2CH_2$–), 24.6 (m, –CH(CH_3)$_2$), 25.5 (m, –$CH_2CH_2CH_2$–P(C_6H_{11})), 26.2 (s, cyclohexyl C *para*), 27.2 (d, $^3J_{CP}$ = 10.3 Hz, cyclohexyl C meta), 27.7 (m, –$CH_2CH_2CH_2$-P[OCH(CH_3)$_2$]$_2$), 28.3 (d, $^2J_{CP}$ = 3 Hz, cyclohexyl C *ortho*), 38.6 (d, $^1J_{CP}$ = 26.6 Hz, cyclohexyl C *ipso*), 49.9 (s, –C(O)-CH_3), 73.6 (m, –P[OCH(CH_3)$_2$]$_2$), 195.4 (q, ^2J_P = 10.4 Hz, CO), 258.8 (dt, $^2J_{CP}$ = 7, 13.1 Hz, –*C*(O)CH_3). IR (CD_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1612 (m) and ν_{CO} 1995 (s).

*12.5.3. mer,trans-[Ru(PhP[$CH_2CH_2CH_2P(OMe)_2]_2$)-($CO)_2$(COMe)]I (**32**)*

A dichloromethane solution of **15a/b** (400 mg, 0.6 mmol) was stirred for 48 hours. ^{1}H NMR (CD_2Cl_2, 298 K): 1.6–2.6 (m, –$CH_2CH_2CH_2$–), 2.47 (s, C(O)CH_3). 3.6–4.1 (m, –P(OCH_3)$_2$), 7.4–7.7 (m, –P(C_6H_5)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −12.3 (t, $^2J_{PP}$ = 51.9 Hz, –P(C_6H_5)), 168.5 (d, $^2J_{PP}$ = 51.9 Hz, –P(OCH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 17.6 (m, –$CH_2CH_2CH_2$–), 23.9 (dt, J_{CP} = 31.9, 3.3 Hz, –$CH_2CH_2CH_2$–P(C_6H_{11})), 27.4 (m, –$CH_2CH_2CH_2$–P(OCH_3)$_2$), 50.6 (s, C(O)CH_3), 54.3 (m, –P(OCH_3)$_2$), (Phenyl: 129.3 (d, $^3J_{CP}$ = 10.2 Hz, C *meta*), 129.6 (s, C *para*), 133 (d, $^2J_{CP}$ = 14.4 Hz, C *ortho*), 136.1 (d, $^1J_{CP}$ = 20.9 Hz, C *ipso*), 198 (br, CO), 259.2 (br, *C*(O)CH_3). IR (CD_2Cl_2, cm^{-}1): 1604 (m), 2003 (s).

*12.5.4. mer,trans-[Ru(CyP[CH_2CH_2 CH_2P-($OMe)_2]_2$)($CO)_2$(COMe)]I (**33**)*

A dichloromethane solution of **16a/b** (200 mg, 0.3 mmol) was stirred for 48 h. ^{1}H NMR (CD_2Cl_2, 298 K): 1.2–2.6 (m, –C$H_2CH_2CH_2$– and C_6H_{11}P–), 2.42 (s, –C(O)CH_3), 3.4–3.9 (m, –P(OCH_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): −5.2 (t, $^2J_{PP}$ = 51.7 Hz, –P(C_6H_{11})), 169.1 (d, $^2J_{PP}$ = 51.7 Hz, –P(OCH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 18.3 (m, –$CH_2CH_2CH_2$–), 26.1 (m, –$CH_2CH_2CH_2$–P(C_6H_{11}), cyclohexyl C *para* obscured), 27.4 (d, $^3J_{CP}$ = 11 Hz, cyclohexyl C *meta*), 28.7 (d, $^2J_{CP}$ = 8.4 Hz, cyclohexyl C *ortho*), 29.4 (m, –$CH_2CH_2CH_2$–P(OCH_3)$_2$), 39.3 (d, $^1J_{CP}$ = 24.7 Hz, cyclohexyl C *ipso*), 49.8 (s, C(O)CH_3), 54 (m, –P(OCH_3)$_2$), 196 (br, CO), 259 (br, *C*(O)CH_3). IR (CD_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1611 (m) and ν_{CO} 2002 (s).

*12.5.5. mer,trans-[Fe(PhP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)-($CO)_2$(COMe)]I (**34**)*

A dichloromethane solution of **17a/b** (400 mg, 0.5 mmol) was stirred under a CO atmosphere for 48 h. ^{1}H NMR (CD_2Cl_2, 298 K): 1.2–1.5 (m, –P[OCH(CH_3)$_2$]$_2$), 1.8–2.6 (m, –P$CH_2CH_2CH_2$P–), 2.68 (s, Fe-C(O)CH_3), 4.57 and 4.78 (sept., $^3J_{HP}$ = 6 Hz, –P[OCH(CH_3)$_2$]$_2$), 7–7.9 (m, –P(C_6H_5)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 4 (t, $^2J_{PP}$ = 90 Hz, –P(C_6H_5)), 175 (d, $^2J_{PP}$ = 90 Hz, –P[OCH(CH_3)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 18.9 (m, –$CH_2CH_2CH_2$–), 24.7 (m, –CH(CH_3)$_2$), 25.1 (m, –$CH_2CH_2CH_2$–P(C_6H_5)), 27.3 (dt, J_{CP} = 4.2, 16.3 Hz, –$CH_2CH_2CH_2$–P[OCH-(CH_3)$_2$]$_2$), 48.2 (m, Fe-C(O)CH_3), 73.8 and 74.6 (m, –P[OCH(CH_3)$_2$]$_2$), (Phenyl: 129.3 (d, $^2J_{CP}$ = 9 Hz, C *ortho*), 131.1 (d, $^3J_{CP}$ = 7.7 Hz, C *meta*), 131.4 (s, C *para*), 135.7 (d, $^1J_{CP}$ = 40.1 Hz, C *ipso*), 205.8 (dt, $^2J_{CP}$ = 17, 14 Hz, Fe-CO) and 208.8 (dt, $^2J_{CP}$ = 25, 27.6 Hz, Fe-CO), 268 (dt, $^2J_{CP}$ = 13, 25 Hz, Fe-*C*(O)CH_3)). IR (CD_2Cl_2, cm^1): $\nu_{C=O}$ 1612 (m) and ν_{CO} 1997 (s).

*12.5.6. mer,trans-[Fe(CyP[$CH_2CH_2CH_2P(Oi\text{-}Pr)_2]_2$)-($CO)_2$(COMe)]I (**35**)*

A dichloromethane solution of **18a/b** (370 mg, 0.5 mmol) was stirred under a CO atmosphere for 48 hours. ^{1}H NMR (CD_2Cl_2, 298 K): 1.1–2.1 (m, –P$CH_2CH_2CH_2$P– and –P(C_6H_{11})), 1.27 (m, –P[OCH(CH_3)$_2$]$_2$), 2.54 (s, –C(O)CH_3), 4.5 and 4.7 (sept., $^3J_{HP}$ = 6 Hz, –P[OCH(CH_3)$_2$]$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 10.7 (t, $^2J_{PP}$ = 88 Hz, –P(C_6H_{11})), 175.2 (d, $^2J_{PP}$ = 88 Hz, –P[OCH(CH_3)$_2$]$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19 (m, –$CH_2CH_2CH_2$–), 24.6 (m, –CH(CH_3)$_2$), 25.7 (s, cyclohexyl C *para*), 26.2 (dt, J_{CP} = 19.7, 6.3 Hz, –$CH_2CH_2CH_2$–P(C_6H_{11})), 27.9 (d, $^3J_{CP}$ = 3.6 Hz, cyclohexyl C *meta*), 28.6 (d,

$^2J_{CP}$ = 3.8 Hz, cyclohexyl C *ortho*), 31.8 (dt, J_{CP} = 12.5, 2.2 Hz, –$CH_2CH_2CH_2$–P[OCH(CH_3)$_2$]$_2$), 37.4 (d, $^1J_{CP}$ = 20.6 Hz, cyclohexyl C *ipso*), 50.1 (m, C(O)CH_3), 73.8 (m, -P[OCH(CH_3)$_2$]$_2$), 209.8 (dt, J = 13, 29.2 Hz, CO), 253.3 (dt, J = 10.7, 18.9 Hz, –C(O)CH_3). IR (CD_2Cl_2, cm^{-1}): ν_{CO} 1616 (m), 1989 (s).

*12.5.7. mer,trans- [Fe(PhP[$CH_2CH_2CH_2P(OMe)_2$]$_2$)($CO)_2$($COMe$)]I (**36**)*

A dichloromethane solution of **19a/b** (250 mg, 0.4 mmol) was stirred under a CO atmosphere for 48 h. ^{1}H NMR (CD_2Cl_2, 298 K): 1.7–2.7 (m, –PCH_2CH_2CH_2P–), 2.61 (s, Fe-C(O)CH_3), 3.5–4.0 (m, –P(OCH_3)$_2$), 7.4–7.7 (m, –P(C_6H_5)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 2.7 (t, $^2J_{PP}$ = 85.8 Hz, –P(C_6H_5)), 191.7 (d, $^2J_{PP}$ = 85.8 Hz, –P(OCH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 18.5 (m, –$CH_2CH_2CH_2$–), 23.9 (m, –CH(CH_3)$_2$), 25.6 (m, –$CH_2CH_2CH_2$–P(C_6H_5)), 50.1 (m, Fe-C(O)CH_3), 52–54 (m, –P(OCH_3)$_2$), (Phenyl: 129 (s, C *para*), 130.4 (d, $^3J_{CP}$ = 9 Hz, C *meta*), 134.1 (d, $^2J_{CP}$ = 9 Hz, C *ortho*), 136 (d, $^1J_{CP}$ = 40 Hz, C *ipso*), 208 (br, Fe-CO), 267.2 (m, Fe-C(O)CH_3)). IR (CD_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1614 (m), ν_{CO} 1984 (s).

*12.5.8. mer,trans-[Fe(CyP[$CH_2CH_2CH_2P(OMe)_2$]$_2$)($CO)_2$($COMe$)]I (**37**)*

A dichloromethane solution of **20a/20b** (250 mg, 0.4 mmol) was stirred under a CO atmosphere for 48 hours. ^{1}H NMR (CD_2Cl_2, 298 K): 1.1–2 (m, –PCH_2CH_2CH_2P– and –P(C_6H_{11})), 2.53 (s, Fe-C(O)CH_3), 3.5–4.0 (m, –P(OCH_3)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): 9.7 (t, $^2J_{PP}$ = 85.5 Hz, –P(C_6H_{11})), 192.3 (d, $^2J_{PP}$ = 85.5 Hz, –P(OCH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): 19 (m, –$CH_2CH_2CH_2$–), 25.9 (s, cyclohexyl C *para*), 26.6 (m, –$CH_2CH_2CH_2$–P(C_6H_{11})), 27.8 (d, $^3J_{CP}$ = 4.1 Hz, cyclohexyl C *meta*), 28 (d, $^2J_{CP}$ = 3.7 Hz, cyclohexyl C *ortho*), 33.2 (dt, J_{CP} = 12.5, 2.2 Hz, –$CH_2CH_2CH_2$–P(OCH_3)$_2$), 37.4 (d, $^1J_{CP}$ = 21.8 Hz, cyclohexyl C *ipso*), 48.7 (m, C(O)CH_3), 51–54 (m, –P(OCH_3)$_2$), 211 (br, Fe-CO), 259.2 (m, Fe-C(O)CH_3)). IR (CD_2Cl_2, cm^{-1}): $\nu_{C=O}$ 1616 (m), ν_{CO} 1973 (s).

*12.6. Preparation of the labeled compounds **38**–**41***

38 and **39** were prepared from the reaction of **40** and **41**, respectively, with CO. The D and ^{13}C labelled complexes **40** and **41** were prepared in an analogous fashion to compounds **17a/b**, in similar yields, from the reaction of **5** (300 mg, 0.5 mmol) with CD_3I or $^{13}CH_3I$ (0.15 mL, 2.5 mmol). *mer,trans-* [Fe(PhP[$CH_2CH_2CH_2$P(O*i*-Pr)$_2$]$_2$)($CO)_2$($COCD_3$)]I (**38**): 2D NMR (CH_3CN, 298 K): 2.6 (s, Fe-$COCD_3$). *mer,trans*-[Fe(PhP [$CH_2CH_2CH_2$P(O*i*-Pr)$_2$]$_2$)($CO)_2$($CO^{13}CH_3$)]I (**39**): ^{13}C{^{1}H} NMR (CD_3CN, 298 K): 48 (s, Fe-$^{13}COCH_3$). *mer,trans*-[Fe(CD_3)(PhP[$CH_2CH_2CH_2$P(O*i*-Pr)$_2$]$_2$)($CO)_2$]I (**40**): 2D NMR (CH_3CN, 298 K): – 0.2 (br, Fe-CD_3). *mer, trans*-[Fe($^{13}CH_3$)(PhP[$CH_2CH_2CH_2$P(O*i*-Pr)$_2$]$_2$)($CO)_2$]I (**41**): ^{13}C{^{1}H} NMR (CD_3CN, 298 K): −11 (q, $^2J_{CP}$ = 22.6 Hz, Fe-$^{13}CH_3$).

Acknowledgement

The financial support of the Swiss National Funds and the funds of the University of Zurich are gratefully acknowledged. Hoechst Knapsack is gratefully acknowledged for a generous gift of dichloromethylphosphine.

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