New Octahedral $RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] Complexes Containing One Hemilabile Ketophosphane Ligand

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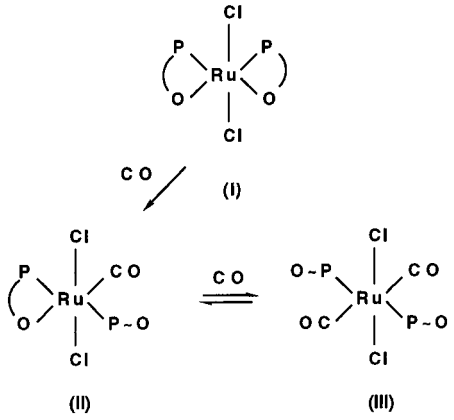
The reaction of the ketophosphanes $Ph_2PCH_2C(=O)t$Bu (**1**), $Ph_2PCMe_2C(=O)i$Pr (**1′**), or $Ph_2PCMe_2CH_2C(=O)$Me (**1′′**) with a precursor complex $RuCl_2(L)(\eta^6$-*p*-cymene) [L = PMe_3 (**a**), $PMePh_2$ (**b**), P*i*PrPh$_2$ (**c**), PPh_3 (**d**), $P(OMe)Ph_2$ (**e**), $P(OMe)_3$ (**f**)] in methanol and under carbon monoxide, provides an access to a novel family of complexes (*ttt*)-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] (**2a–e**, **2′a**,**e**,**f**, and **2′′a**) with *trans*-chlorine and *trans*-phosphorus atoms. Further reaction with carbon monoxide or acetonitrile under thermal activation yields the *cis*,*cis*,*trans* derivatives (*cct*)-$RuCl_2(CO)_2(L)[\eta^1$-(*P*)-ketophosphane] **4a**,**b** and **4′a**, and (*cct*)-$RuCl_2(CO)(MeCN)(L)[\eta^1$-(*P*)-ketophosphane] **5a**,**b**,**d**. Complexes **2a**,**b** and **2′a** rearrange under thermal activation, or after exposure to sunlight, into the (*ctc* and *ccc*)-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] isomers, with *cis*-chlorine and *cis*-phosphorus atoms, **6a**,**b** and **6′a**, respectively. Complexes **6a**,**b** reversibly add one molecule of carbon monoxide when forming the all-*cis* derivatives (*ccc*)-$RuCl_2(CO)_2(L)[\eta^1$-(*P*)-ketophosphane] **7a**,**b**, respectively. The removal of one chloride ligand in complexes **4a**, **4′a**, or **5a** with silver tetrafluoroborate affords the stable cationic derivatives $\{RuCl(CO)(L')(PMe_3)[\eta^2$-(*P*,*O*)-ketophosphane]$\}[BF_4]$, **8a** and **8′a** (L′ = CO) and **9a** (L′ = MeCN), respectively. Mild basic conditions are sufficient to allow the synthesis of the enolatophosphane derivatives (*ttt*)-$RuCl(CO)_2(L)[\eta^2$-(*P*,*O*)-$Ph_2PCH{=}C(t$Bu)O], **10a**,**c**,**e**, and of the analogous (*ccc*) and (*cct*) isomers, **11a**,**b** and **12a**, respectively.

Introduction

The discovery of the hemilabile behaviour of an ether−phosphane ligand,[1] in which the ether functionality coordinates at a ruthenium centre, has undoubtedly stimulated the interest of organometallic chemists with regard to functional phosphanes. The complexation of such ligands is of interest since the oxygen−metal bond is weak, thus providing facile access to coordinative unsaturation.[2,3] The series of $RuCl_2[\eta^2$-(*P*,*O*)-functional phosphane]$_2$ complexes, in which the organic function consists of an ether,[1,4−8] an ester,[9−11] or a keto group, have been largely studied.[12,13] Interestingly, their geometry is of type **I** (see Scheme 1), consisting of *trans*-chlorine, *cis* phosphorus, and *cis*-oxygen atoms, respectively. The preferred *cis* arrangement of the phosphorus atoms is unusual, as emphasised by the ability of complexes **I** to trap carbon monoxide through an irreversible process involving a *cis*-to-*trans* rearrangement of the phosphorus atoms (Scheme 1). The resulting complexes **II** exhibit a noteworthy fluxional behaviour through easy exchange between the coordinating modes of the oxygen atoms (not depicted in Scheme 1) and are able to interconvert with type-**III** complexes by reversible addition of carbon monoxide. We report herein a convenient route to new hybrid (*ttt*)-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] complexes with *trans*-chlorine and *trans*-phosphorus atoms. They are analogous of both type-**II** and all-*trans* $RuCl_2(CO)_2L_2$ complexes, and their study will allow further comparison. Furthermore, under basic conditions they are suspected of generating coordinatively unsaturated η^2-(*P*,*O*)-enolatophosphane derivatives by a formal HCl abstraction.



Scheme 1

Results

Synthesis of (*ttt*)-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] Complexes 2−2′′

An equimolar mixture consisting of a precursor complex $RuCl_2(L)(\eta^6$-*p*-cymene) [L = PMe_3 (**a**), $PMePh_2$ (**b**), P*i*PrPh$_2$ (**c**), PPh_3 (**d**), $P(OMe)Ph_2$ (**e**), $P(OMe)_3$ (**f**)] and a ketophosphane [$Ph_2PCH_2C(=O)t$Bu (**1**), $Ph_2PCMe_2C(=O)i$Pr (**1′**), $Ph_2PCMe_2CH_2C(=O)$Me (**1′′**)] in methanol was stirred at ambient temperature under carbon monoxide. Subsequent workup allowed all-*trans* (based on two *trans*-

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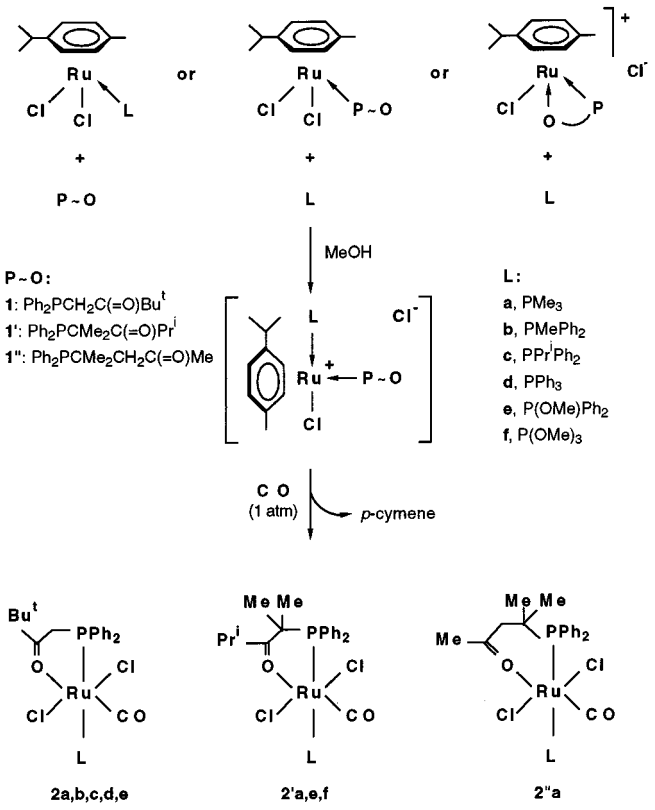
chlorine and two *trans*-phosphorus atoms, respectively) complexes (*ttt*)-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] **2a**−**e**, **2′a**,**e**,**f**, and **2′′a**, to be isolated in moderate to high yields (49−84%) as orange air-stable crystals (except for **2d**) (Scheme 2). The reaction formally consists of the substitution of a 6e-donor ligand (*p*-cymene) by one molecule of carbon monoxide and one molecule of ketophosphane acting as a 4e-donor. The generality of the reaction is not only shown by the involvement of a β- (**1**, **1′**) or a γ-ketophosphane (**1′′**), but also by the ability of the precursor complex $RuCl_2(\eta^6$-*p*-cymene)$[\eta^1$-(*P*)-$Ph_2PCH_2C(=O)t$Bu][14] in providing an alternative route to complexes of type **2**, when reacting with a ligand L such as $P(OMe)Ph_2$ and with carbon monoxide, to afford the expected derivative **2e** (see Scheme 2). The permethylated β-ketophosphane **1′** is unable to form a similar $RuCl_2(\eta^6$-*p*-cymene)$[\eta^1$-(*P*)-$Ph_2PCMe_2C(=O)i$Pr] derivative, but reacts with dimeric $[RuCl_2(\eta^6$-*p*-cymene)$]_2$ in methanol to generate a cationic species $\{RuCl(\eta^6$-*p*-cymene)$[\eta^2$-(*P*,*O*)-$Ph_2PCMe_2C(i$Pr)=O]$\}^+$, which has previously been characterised as its PF_6 salt.[14] Such solutions of $\{RuCl(\eta^6$-*p*-cymene)$[\eta^2$-(*P*,*O*)-$Ph_2PCMe_2C(i$Pr)=O]$\}$Cl in methanol may also be used to synthesise complexes **2′**. As summarised in Scheme 2, these distinct pathways leading to complexes **2**−**2′′** may be rationalised in terms of the formation of a transient cationic species $\{RuCl(\eta^6$-*p*-cymene)(L)$[\eta^1$-(*P*)-ketophosphane]$\}^+$ that will further react with carbon monoxide. Such a mechanism accounts for the requirement of methanol as the solvent, which allows a transient cleavage of one Ru−Cl bond. The reaction does not work in a solvent such as CH_2Cl_2. This strongly suggests the key role of methanol in the labilisation of the Ru−Cl bond.

The structures of complexes **2**−**2′′** were determined from a combination of elemental analysis, IR spectroscopy and ^{1}H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^{13}C NMR spectroscopy. Elemental analysis indicates the retention of two chlorine atoms per Ru atom. The IR spectra (Table 1) exhibit a very strong absorption close to 1940 cm^{-1} assigned to the carbon monoxide ligand, as well as a strong absorption close to 1640 cm^{-1} (1673 cm^{-1} for **2′′a**) indicating the coordination of the oxygen atom of the ketophosphane.[14] The $^{31}P\{^1H\}$ NMR spectra (Table 1) consist of an AB spin system and the large coupling constant values (> 300 Hz) indicate a mutual *trans* arrangement of the two phosphorus nuclei.[15] The ^{1}H and $^{13}C\{^1H\}$ NMR spectra both indicate a plane of symmetry requiring a relative *trans* arrangement of the two chloride ligands. Accordingly, the PCH_2 protons in complexes **2** and the $PCMe_2$ methyl groups in complexes **2′** and **2′′** are found to be equivalent by ^{1}H NMR spectroscopy. Furthermore, the two phenyl groups of the Ph_2P fragment are found to be equivalent by $^{13}C\{^1H\}$ NMR spectroscopy. The ^{13}C NMR resonances assigned to the C=O and C≡O carbon nuclei are close, but a simple comparison between the $^{13}C\{^1H\}$ and ^{13}C NMR spectra allows an unambiguous determination, since only the keto resonance is affected by far ^1H-^{13}C coupling.

The thermal stability of complexes **2**−**2′′** depends on the nature of the ancillary ligand L. The most stable complexes



Scheme 2

are **2a**, **2′a**, and **2′′a** (in which L = PMe_3). They were unaffected when thermally treated under reflux in methanol for several hours. In contrast, **2e** [in which L = $P(OMe)Ph_2$] decomposed in hot methanol as indicated by the formation of $RuCl_2(CO)[\eta^1$-(*P*)-$Ph_2PCH_2C(=O)t$Bu][η^2-(*P*,*O*)-$Ph_2PCH_2C(t$Bu)=O].[12] This latter complex was detected by $^{31}P\{^1H\}$ NMR spectroscopy.

Reversible and Irreversible Carbon Monoxide Binding by Complexes 2−2′

The $^{31}P\{^1H\}$ NMR spectrum of a solution of **2a** (or **2b**) in CD_2Cl_2 that was kept under carbon monoxide disclosed a new species, besides the minor presence of **2a** (or **2b**). After removal of the carbon monoxide, recovery of pure **2a** (or **2b**) is indicated by the corresponding NMR spectrum. The set of $^{31}P\{^1H\}$ NMR resonances corresponding to the new species still consists of an AB spin system and large coupling constant values (> 300 Hz), thus indicating a mutual *trans* arrangement of the two phosphorus nuclei. Attempts to isolate the species failed, but such reversible carbon monoxide binding by **2a** (or **2b**) is very similar to the reversible formation of complexes **III** from complexes **II**, as depicted in Scheme 1. Therefore, the reversible formation of the all-*trans* derivatives (*ttt*)-$RuCl_2(CO)_2(L)[\eta^1$-(*P*)-$Ph_2PCH_2C(=O)t$Bu] (**3a**,**b**) may be reasonably assumed (Scheme 3). In contrast, an irreversible binding of carbon monoxide by toluene solutions of complexes **2a**,**b** and **2′a** occurs upon thermal activation (≥ 80 °C), yielding the colourless *cis*,*cis*,*trans* derivatives (*cct*)-$RuCl_2(CO)_2(L)[\eta^1$-(*P*)-

Table 1. IR and $^{31}P\{^1H\}$ NMR data of the new complexes

Compound	IR[a] ν(C≡O)	ν(C=O) or (C=CO)	$^{31}P\{^1H\}$ NMR δ(PO)	δ(L)	$^2J_{PP}$
(*ttt*)-$RuCl_2(CO)(L)[\eta^2\text{-}(P,O)$-ketophosphane)] complexes **2a**−**e**, **2′a**,**e**,**f**, **2′′a**					
2a	1948, 1929	1635, 1624	45.3	5.6	356[b]
2b	1939	1630	48.5	19.8	353[b]
2c	1946, 1938	1633, 1627	49.0	41.9	343[c]
2d	1941	1624	49.4	33.0	357[c]
2e	1942	1620	45.1	131.8	389[c]
2′a	1936	1634	65.1	4.5	344[c]
2′e	1938	1637	65.1	131.6	374[b]
2′f	1965	1637	64.0	128.4	508[c]
2′′a	1942	1673	38.2	2.5	347[c]
(*ttt*)-$RuCl_2(CO)_2(L)[\eta^1\text{-}(P)$-ketophosphane)] complexes **3a**,**b**					
3a			10.9	−4.1	269[b]
3b			13.5	10.1	272[b]
(*cct*)-$RuCl_2(CO)_2(L)[\eta^1\text{-}(P)$-ketophosphane)] complexes **4a**,**b**, **4′a**					
4a	2056, 1988	1705	16.5	−2.2	339[c]
4b	2052, 1991	1694	20.5	13.4	336[b]
4′a	2045, 1992	1699	21.8	1.0	346[c]
(*cct*)-$RuCl_2(CO)(MeCN)(L)[\eta^1\text{-}(P)$-ketophosphane)] complexes **5a**,**b**,**d**					
5a	1957	1702	23.7	−1.0	364[c]
5b	1950	1701	26.5	18.0	359[c]
5d	1966	1708	27.5	21.9	362[c]
(*ccc*)-$RuCl_2(CO)(L)[\eta^2\text{-}(P,O)$-ketophosphane)] complexes **6a**,**b**, **6′a**					
6a	1972	1624	52.7	23.1	31[c]
6a, minor isomer in solution:			63.8	16.8	24[c]
6b	1951	1632	49.6	38.3	28[b]
6b, minor isomer in solution:			60.9	34.5	22[b]
6′a	1960	1620	74.2	21.3	30[b]
(*ccc*)-$RuCl_2(CO)_2(L)[\eta^1\text{-}(P)$-ketophosphane)] complexes **7a**,**b**					
7a	2078, 1988	1706	14.8	5.6	28[c]
7a, minor isomer in solution:			28.6	−9.7	29[c]
7b	2077, 1994	1706	26.1	12.4	29[b]
7b, minor isomer in solution:			28.7	3.4	28[b]
Cationic derivatives **8a**, **8′a**, **9a**					
8a	2081, 2018	1610	41.8	2.3	291[c]
8′a	2076, 2016	1622	58.6	1.8	285[c]
9a	1987	1615	45.4	3.7	324[c]
(*ttt*)-$RuCl(CO)_2(L)[\eta^2\text{-}(P,O)$-enolatophosphane)] complexes **10a**,**c**,**e**					
10a	1989	1510	25.0	−3.8	222[c]
10c	1991	1498	26.4	36.0	219[c]
10e	2006	1505	23.8	123.8	255[c]
(*ccc*)-$RuCl(CO)_2(L)[\eta^2\text{-}(P,O)$-enolatophosphane)] complexes **11a**,**b**					
11a	2070, 1968	1498	47.0	−5.6	31[c]
11b	2065, 1980	1500	46.6	7.8	31[c]
11b, minor isomer in solution:			42.6	21.9	31[c]
(*cct*)-$RuCl(CO)(L')(L)[\eta^2\text{-}(P,O)$-enolatophosphane)] complexes **12a** (L′ = CO), **13a** (L′ = MeCN)					
12a	2034, 1977	1505	41.4	−1.1	302[c]
13a	1940	1493	43.8	0.8	333[c]

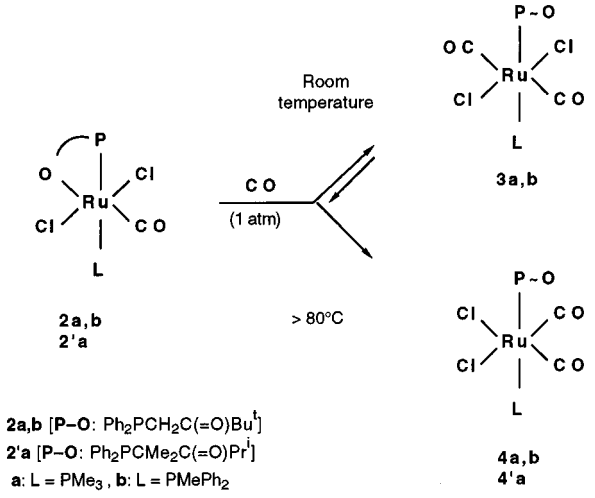
[a] $\tilde{\nu}$ in cm^{-1}. – [b] In $CDCl_3$. – [c] In CD_2Cl_2.

ketophosphane] (**4a**,**b** and **4′a**) (Scheme 3). The formation of **4a**,**b** and **4′a** involves an additional *trans*-to-*cis* rearrangement of the chloride ligands, relative to the $\eta^2\text{-}(P,O) \rightarrow \eta^1\text{-}(P)$ transformation of the coordination of the ketophosphane, therefore allowing the entrance of one carbon monoxide molecule.

The $^{31}P\{^1H\}$ NMR spectra of **4a**,**b** still consist of an AB spin system and the large coupling constant values ($^2J_{PP} >$ 300 Hz, Table 1) indicate the retention of the mutual *trans* arrangement of the two phosphorus nuclei. Both the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4a**,**b** and **4′a** indicate a plane of symmetry. Their IR spectra exhibit two strong absorptions (close to 2055 and 1990 cm^{-1}) as expected for a relative *cis* arrangement of two carbonyl ligands, as well as an absorption close to 1700 cm^{-1} assigned to the uncoordinated keto functionality. A relative *cis* arrangement of the two carbonyl ligands obviously requires a relative *cis* arrangement of the two chlorine atoms.

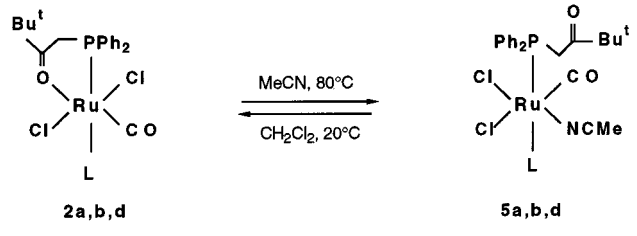
Reversible Acetonitrile Binding by Complexes 2

A *trans*-to-*cis* rearrangement of the chloride ligands is also involved when complexes **2a**,**b**,**d** are heated under reflux in acetonitrile, yielding the lemon-yellow *cis*,*cis*,*trans* complexes (*cct*)-$RuCl_2(CO)(N{\equiv}CMe)(L)[\eta^1\text{-}(P)$-ketophos-



Scheme 3

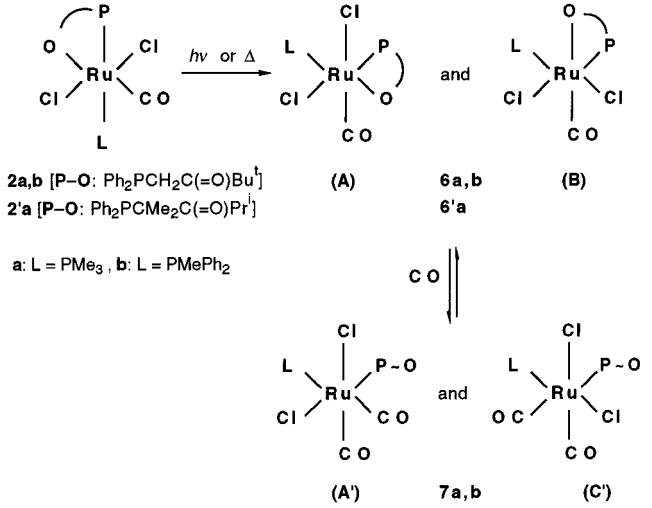
phane] (**5a**,**b**,**d**) (Scheme 4). The η^2-(*P*,*O*) → η^1-(*P*) modification of the coordination of the ketophosphane allows one acetonitrile ligand to enter. The $^{31}P\{^1H\}$ NMR spectra of complexes **5a**,**b**,**d** exhibit large $^2J_{PP}$ coupling constant values, indicating a retention of the relative *trans* arrangement of the phosphorus atoms. However, their ^1H NMR spectra show the two PCH_2 protons of the ketophosphane to be diastereotopic. Their $^{13}C\{^1H\}$ NMR spectra also indicate a loss of symmetry. This lack of a plane of symmetry suggests a relative *cis* arrangement of the two chloride ligands. Complexes **5a**,**b**,**d** were found to be stable in the solid state but not in dichloromethane solutions, as monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Thus, after standing for 1 d at room temperature, an NMR-spectroscopic sample of pure **5a** in CD_2Cl_2 shows a substantial presence of free acetonitrile, as well as the recovery of **2a**. The reaction of acetonitrile with crude **2d** (L = PPh_3), that was obtained as an insoluble precipitate which retained several impurities, allows the preparation of **5d** as analytically pure yellow crystals. Furthermore, a concentrated solution of **5d** in dichloromethane deposited orange crystals of pure **2d**, merely by standing for several days. A simple substitution of the weakly bonded acetonitrile ligand by carbon monoxide (instead of the formation of **2a** or **2d**) was not observed when a solution of **5a** or **5d** in dichloromethane was kept under carbon monoxide. This result is likely to be related to the kinetically favoured formation of *trans* derivatives in such processes.[16]



Scheme 4

Isomerisation of Complexes 2−2′

A slow reaction occurred when an orange solution of **2a** in toluene was heated at 80 °C under an inert gas, as indicated by the formation of a pale-yellow precipitate. After heating for 2 d and subsequent removal of the volatiles, the ^1H and $^{31}P\{^1H\}$ NMR analysis of the resulting material revealed a mixture consisting of a new species, **6a**, as well as unreacted **2a**, in a 2:1 ratio (Scheme 5). It is worth noting the thermal stability of complex **6a** which was successfully isolated in a 75% yield as an analytically pure precipitate after a solution of **2a** in toluene was heated under reflux. Thus, this procedure was used to synthesize **6b** starting from **2b**, while **6′a** was conveniently obtained after heating **2′a** in ethanol under reflux. The isomerisation of complexes **2a**,**b** and **2′a** into complexes **6a**,**b** and **6′a** also occurred when solutions of **2a**,**b** and **2′a** in dichloromethane were exposed to sunlight. Similar treatment of a solution of **2a** or alternatively **6a**, both led to mixtures of **2a** and **6a** in a 15:85 ratio, indicating a reversible process. This was determined by ^1H NMR spectroscopy. From the ratio it can be seen that **6a** is highly favoured. Irradiation from sunlight proved useful in synthesising **6a** and **6′a**, as detailed in the Exp. Sect. Complexes **6a**,**b** and **6′a** were characterised by elemental analysis and spectroscopic studies. The $^{31}P\{^1H\}$ NMR spectrum of **6′a** exhibits a small $^2J_{PP}$ coupling constant value (Table 1), indicating a relative *cis* arrangement of the phosphorus atoms.[15] The ^1H NMR spectrum shows two inequivalent $PCMe_2$ methyl groups. IR spectroscopy indicates the coordination of the keto functionality, and this η^2-(*P*,*O*) coordination of the ketophosphane obviously requires a relative *cis* arrangement of the corresponding oxygen and phosphorus coordinating atoms. Furthermore, the $^{13}C\{^1H\}$ NMR resonance assigned to the carbon monoxide ligand in **6′a** discloses two small $^2J_{PC}$ coupling constant values ($^2J_{PC}$ = 19.8 and 12.6 Hz), indicating a *cis* position of the carbon monoxide ligand relative to both phosphorus atoms. Therefore, only two octahedral structures, namely **A** and **B** as depicted in Scheme 5, remain conceivable. The NMR- and IR-spectroscopic study of **6a** leads to the same conclusion when some additional weak resonances are omitted. These resonances are too weak to allow further characterisation of the corresponding species; however, $^{31}P\{^1H\}$ NMR spectroscopy does show a small $^2J_{PP}$ coupling constant value. The NMR-spectroscopic study of **6b** was more informative and shows the presence of two isomers in a 3:2 ratio. These two isomers involve both a mutual *cis* arrangement of the phosphorus atoms and a *cis* arrangement of the carbon monoxide ligand relative to the phosphorus atoms, as expected for a mixture of **A** and **B**. To summarise these results, complex **6′a**, which involves the bulkiest ketophosphane **1′** and a small ligand L = PMe_3, shows only one isomer in solution, **A** or **B**. Complex **6b**, which involves the smaller ketophosphane **1** but a bulkier ligand L = $PMePh_2$, shows a mixture of **A** and **B** isomers in solution. Complex **6a**, which involves the ketophosphane **1** and L = PMe_3, will also show a mixture of **A** and **B** isomers, but one is highly favoured.



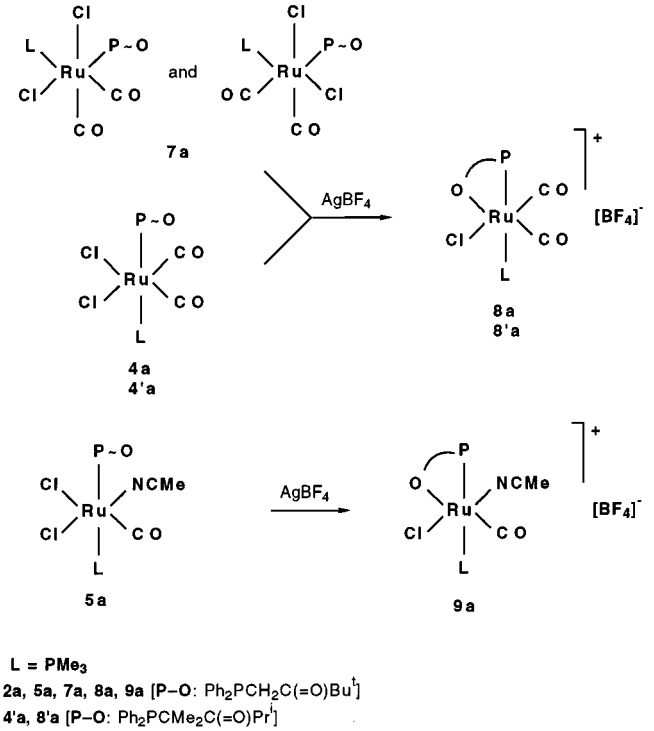
Scheme 5

Binding of Carbon Monoxide by Complexes 6−6′

Dichloromethane solutions of **6a** and **6b** were found to bind carbon monoxide (1 atm, ambient temperature) affording **7a** and **7b**, respectively (Scheme 5). Complexes **6a** and **6b** were recovered in the absence of carbon monoxide, indicating a reversible reaction. It should be noted that this process does not affect the **A/B** ratio (in **6a** and **6b**). In contrast, **6′a** irreversibly adds carbon monoxide affording the *cct* derivative **4′a**. This involves a *cis*-to-*trans* rearrangement of the phosphorus atoms. The NMR spectra of both **7a** and **7b** show a mixture of two isomers, namely **A′** and **C′** (Scheme 5). The small $^2J_{PP}$ coupling constant values (Table 1) clearly indicate the retention of the *cis* arrangement of the phosphorus atoms. The ^1H NMR spectrum shows the PCH_2 protons of the ketophosphane **1** to be inequivalent and rules out a *trans* mutual arrangement of the two chlorine atoms. The $^{13}C\{^1H\}$ NMR spectra indicate, for each molecule **A′** and **C′** that one carbon monoxide ligand is located in a *cis* position relative to the two phosphorus atoms and the second one in a *trans* P−Ru−CO arrangement.[15] Thus, only the two octahedral structures **A′** and **C′** remain conceivable. The isomeric structures **A′** and **C′** both show *cis* mutual arrangements of the two chlorine atoms and of the two carbonyl ligands, respectively, and are thus the two conceivable structures for an all-*cis*-$RuX_2(CO)_2(L)(L')$ complex. It is interesting to note that a simple substitution of the coordinated oxygen atom in **A** by an entering carbon monoxide molecule will lead to **A′**. However, a similar exchange of the coordinated oxygen atom in **B** by carbon monoxide will result in the formation of a symmetrical structure with *trans* carbon monoxide ligands, rather than **C′**. This is not experimentally detected. The stability of complexes **7a**,**b** is related to the nature of the ancillary ligand L. Complex **7a** (L = PMe_3) was found to be stable in a dichloromethane solution, or alternatively in a methanol solution, at ambient temperature and under carbon monoxide, but is converted into **4a** in hot methanol (see Exp. Sect.). In contrast, **7b** (L = $PMePh_2$) is stable in a dichloromethane solution, but is converted into **4b** on dissolution in methanol, even at ambient temperature. The straightforward formation of **4′a** on treatment of **6′a** with carbon monoxide, is indicative of the steric effect of the bulky ketophosphane **1′**, favouring a *cis*-to-*trans* rearrangement of phosphorus atoms.

Formation of Cationic Derivatives

Halide abstraction from **7a** using silver tetrafluoroborate creates an unsaturated centre that was found to trigger a *cis*-to-*trans* rearrangement of phosphorus atoms. This produces the cationic derivative **8a** in which the oxygen atom from the ketophosphane ligand completes the coordination at the ruthenium centre (Scheme 6). Complexes **4a** and **4′a** are also convenient precursors for the synthesis of such cationic derivatives, and afford the expected derivatives **8a** and **8′a**, respectively, through the removal of a chloride ligand (Scheme 6). In contrast, attempts to obtain cationic derivatives starting from a complex **2**, such as **2a**, invariably failed, even under carbon monoxide.



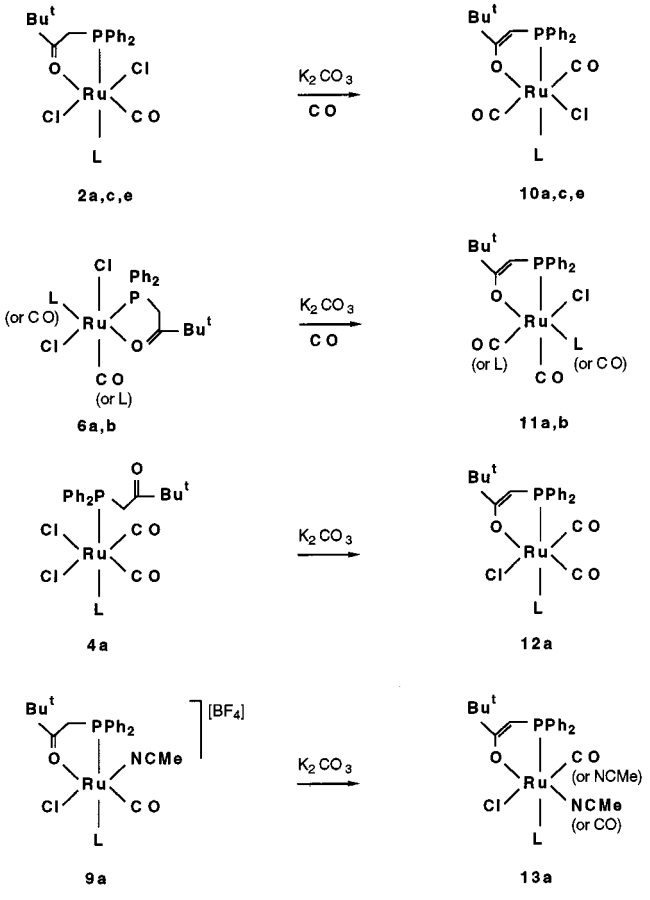
Scheme 6

The structures of complexes **8a** and **8′a** are unambiguously deduced from their $^{31}P\{^1H\}$ NMR spectra, which exhibit large $^2J_{PP}$ coupling constant values (Table 1) indicating a *trans* arrangement of the phosphorus atoms, and from their IR spectra which indicate a *cis* arrangement of the carbonyl ligands and the coordination of the keto functionality. The observation of two inequivalent PCH_2 protons by ^1H NMR spectroscopy also suggests a relative *cis* arrangement of the two carbonyl ligands. The substitution of one chloride ligand by the oxygen atom from the ketophosphane was also achieved starting from the fragile (pre-

sumably owing to its labile acetonitrile ligand) complex **5a**, which reacts with silver tetrafluoroborate to yield the more stable cationic derivative **9a** (Scheme 6).

Stereoselective Synthesis of Enolatophosphane Derivatives

Complexes **2a**,**c**,**e** were found to be rather robust under basic conditions (K_2CO_3 in dichloromethane or KOH in methanol). However, the consumption of the starting material was detected by $^{31}P\{^1H\}$ NMR spectroscopy after prolonged reaction times (several days at ambient temperature), but the observation of very numerous new resonances indicated an intractable mixture. Under such basic conditions and under carbon monoxide, a fast and selective process occurred, resulting in the formation of the enolatophosphane complexes **10a**,**c**,**e**. It is worth noting that the complexes **10a**,**c**,**e** retain an all-*trans* structure based on two *trans*-coordinating phosphorus atoms, two *trans*-carbonyl ligands and two *trans*-X-type coordinating atoms (Scheme 7). The process formally consists of the removal of one HCl molecule and the coordination of one molecule of carbon monoxide. Derivatives **6a**,**b** reacted in a similar manner and afforded the enolatophosphane derivatives **11a**,**b**, respectively, which retain a relative *cis* arrangement of the phosphorus atoms. The NMR-spectroscopic study of **11a**,**b** discloses one isomer for **11a**, but a mixture of two isomers for **11b**. These isomers involve both a relative *cis* arrangement of the phosphorus atoms and of the carbon monoxide ligands, respectively. For each structure, one carbon monoxide ligand is located in a *cis* position relative to the two phosphorus atoms, whereas the second carbon monoxide ligand is located in a *trans* position relative to a phosphorus atom, but three structures remain conceivable (vide infra). The formation of the enolatophosphane derivatives **12a** and **13a**, starting from the neutral *cct* isomer **4a** and from the cationic derivative **9a**, respectively, formally consists solely of the removal of one molecule of HCl or $H[PF_6]$ (Scheme 7), and was also found to be very stereoselective. This was monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

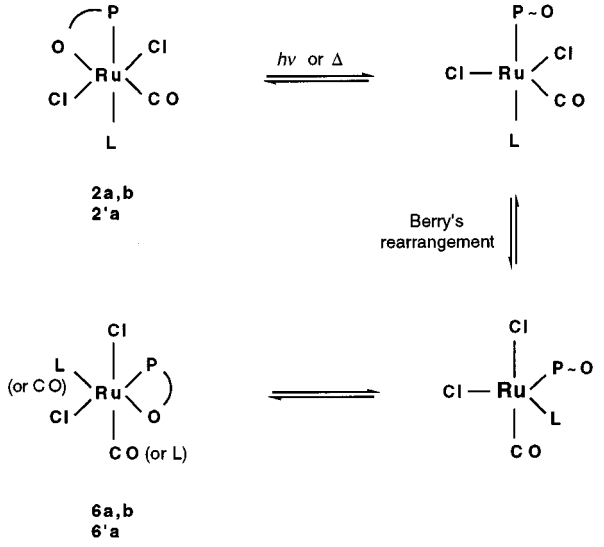


a, L = PMe_3; **b**, L = $PMePh_2$; **c**, L = PPr^iPh_2; **e**, L = $P(OMe)Ph_2$

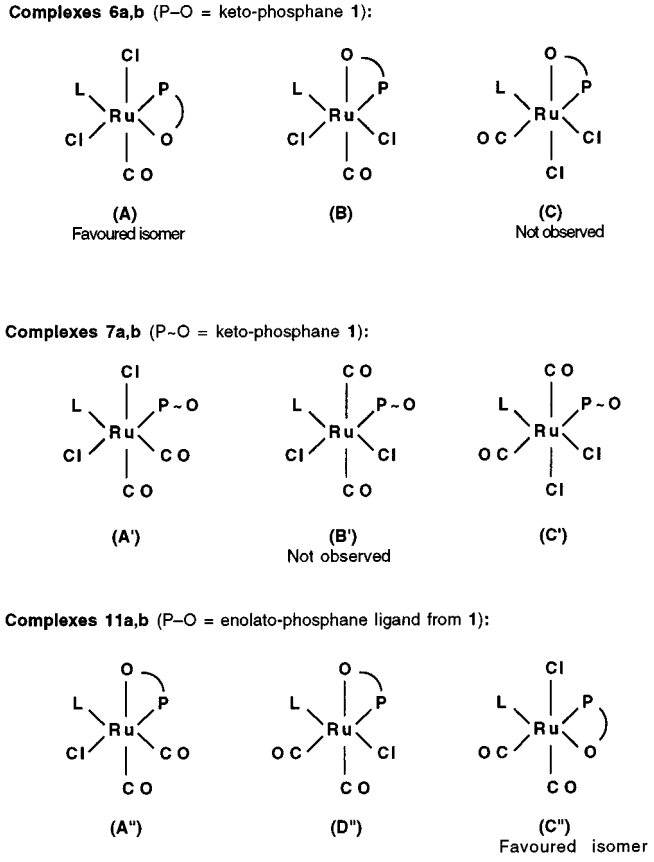
Scheme 7

Discussion

The removal of the arene ligand from $RuCl_2(L)(\eta^6$-*p*-cymene) complexes allows the coordination of a ketophosphane along with a CO ligand, thus providing access to a new family of octahedral Ru complexes bearing two distinct phosphorus-containing ligands. The process selectively leads to all-*trans* complexes based on of two *trans*-chlorine and *trans*-phosphorus atoms. The hemilabile character of the ketophosphane ligand allows the reversible formation of new all-*trans*-$RuX_2(CO)_2L_2$-type complexes (but with distinct L ligands) by reversible uptake of carbon monoxide. Previous studies concerning $RuX_2(CO)_2L_2$ complexes have proved that all-*trans* complexes easily rearrange under thermal activation into their thermodynamically favoured *cct* isomers through a preliminary cleavage of one Ru−CO bond. The mechanism of this transformation has been thoroughly elucidated.[16] Therefore, the formation of complexes of type **4** and **5** under thermal activation and in the presence of an entering ligand such as carbon monoxide or acetonitrile might be expected, and this accounts for the recovery of complexes of type **2** from **5** by loss of acetonitrile. The behaviour of complexes **2** under thermal activation and in the absence of an entering ligand was less predictable. Whereas all-*trans*-$RuX_2(CO)_2L_2$ complexes rearrange into their *cct* isomers, complexes of type **2** selectively afford the corresponding all-*cis* isomers **6**. This observation suggests that the formation of *cct* isomers of **2** (with *cis*-chlorine and *trans*-phosphorus atoms) is disfavoured due to the requirement of a (C=)O→Ru−Cl *trans* arrangement (only O→Ru−Cl *cis* arrangements are observed in complexes **2** and **6**). In contrast, the coordination of carbon monoxide is stabilised through the *trans* effect of a chloride ligand in (*cct*)-$RuX_2(CO)_2L_2$ complexes. As depicted in Scheme 8, the transformation of complexes **2** into complexes **6** may be assumed to involve a pentacoordinated intermediate arising from the cleavage of the oxygen−ruthenium bond. Such a Berry rearrangement[17] through a dissociative pathway already accounts for the isomerisation of all-*trans*-$RuX_2(CO)_2L_2$ complexes into their all-*cis* isomers.[16]



Scheme 8. Rationale accounting for the reversible isomerisation of complexes **2a**,**b** and **2′a** into complexes **6a**,**b** and **6′a**

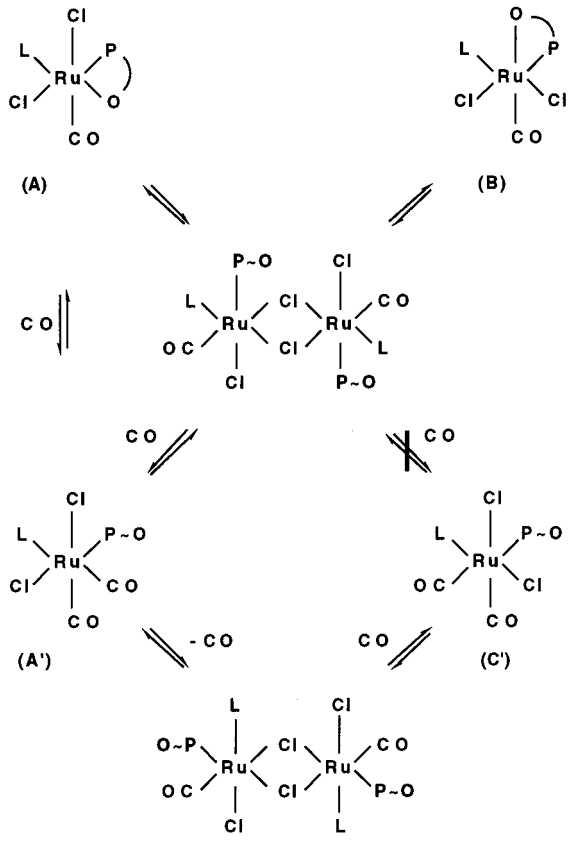


Scheme 9. Comparison between the distinct structures of complexes **6a**,**b**, **7a**,**b**, and **11a**,**b**

The formation of complexes **6** preserves the hemilabile property of the ketophosphane ligand as emphasised by the reactivity of complexes **6** towards carbon monoxide. Complexes **6a** and **6b** reversibly bind carbon monoxide to afford **7a** and **7b**, respectively. Solutions of **7a** and **7b** in dichloromethane both reveal a mixture of two all-*cis* isomers. As depicted in Scheme 9, a comparison of the structures of type **6** and **7** complexes excludes a mechanism based on the CO displacement of the weakly bound oxygen atom in complexes **6**, despite the fact that the structure **A′** of **7** may arise from **A** of **6**. The structure **C′** which is also observed in complexes **7**, is unexpected when compared with **A** and **B** of complexes **6**. The expected structure **B′** (Scheme 9) was not detected experimentally.

Moreover, the **A′**/**C′** ratio in a complex of **7** is unambiguously distinctly related to the **A**/**B** ratio in the parent complex **6**. Thus, the complete reversibility of the transformation of **6** to **7** provides further evidence for a dynamic equilibrium between **A** and **B**, and between **A′** and **C′**. The facile recovery of **6a** (or **6b**) from **7a** (or **7b**) illustrates the easy loss of carbon monoxide by **7**. However, preliminary cleavage of one Ru−CO bond in **7** (dissociative mechanism) will transiently generate a coordinatively unsaturated intermediate favouring a *cis*-to-*trans* rearrangement of the phosphorus atoms.[16] Therefore, an associative mechanism will more likely account for the retention of the all-*cis* geometry. The reversible **A** ⇄ **B** and **A′** ⇄ **C′** transformations are also easy. They may formally involve the exchange of the positions of the chlorine atom and the oxygen atom for the **A** ⇄ **B** isomerisation, and of the chlorine atom and the carbon monoxide ligand for the **A′** ⇄ **C′** isomerisation. As depicted in Scheme 10, all these reversible transformations may be achieved without any involvement of coordinatively unsaturated species. Associative pathways consisting of the transient formation of halogen-bridged dinuclear species easily account for the experimental observations. The formation of analogous dinuclear compounds by halogen-bridge formation from $RuX_2(CO)_2L_2$ complexes, which has been previously reported,[15,16] further supports such a mechanism.

The formation of the enolatophosphane derivatives **10a**,**c**,**e**, **11a**,**b**, and **12a** (Scheme 7) was found to be highly stereoselective. Preliminary coordination of the entering ligand, subsequent deprotonation of the η^1-(P)-coordinated ketophosphane and substitution of one chloride ligand by an anionic oxygen atom are the steps of a simple mechanism which account for the stereoselective formation of **10a**,**c**,**e** and **11a**,**b**. The formation of **12a** starting from **4a**, in which the ketophosphane is already η^1-(P)-coordinated, clearly provides the experimental support to such a mechanism. The formation of **13a** starting from the cationic complex **4a**, involves the simple deprotonation of the ketophosphane ligand. The NMR-spectroscopic study of **10a**,**c**,**e** allows an unambiguous structural determination. The structural determination is less accurate in the case of **11a**,**b**, but only *cis*-phosphorus and *cis*-carbonyl arrangements are observed. Thus, three structures, namely **A″**, **D″**, and **C″** (Scheme 9), remain conceivable after the examination of the NMR-spectroscopic data. Only one of them is involved in the case of **11a**, but two in the case of **11b** which reveals a mixture of two isomers. The **A″** and **D″** structures show an O−Ru−CO *trans* arrangement which may arise from **A′** and **C′** in the corresponding parent compound **7**.



Scheme 10. Simple rationale accounting for the easy isomerisation of complexes **6a**,**b** and **7a**,**b**

Only **C**′ may lead to the third structure **C**′′, which shows a Cl−Ru−CO *trans* arrangement. It should be noted that a chloride ligand is more labile when *trans* to a phosphorus atom. Therefore, the **C**′ → **C**′′ transformation will be a favoured pathway and the observation of only one isomer when starting from **7a** will thus suggest the structure **C**′′ for **11a**. The precursor **7b** involves a bulkier ancillary ligand L = $PMePh_2$ than L = PMe_3 in **7a**. For steric reasons, a slower **C**′ → **C**′′ transformation may result and a **C**′ → **D**′′ remains highly disfavoured, however, the **A**′ → **A**′′ transformation may become more competitive. This will result in a mixture of the two isomers **C**′′ and **A**′′ in the case of **11b**. This behaviour emphasises the high stability of the Cl−Ru−CO *trans* arrangement, and therefore also suggests that the favoured isomer in complexes **6a**,**b** and **6**′**a** is **A**. The observation of isomer **B** is related to steric hindrance.

Conclusion

This study of the new family of complexes *trans*-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] (**2**) emphasises the stability of the O→Ru bond in a *trans*-(C)=O→-Ru←(C≡O) arrangement, and the inability of the oxygen atom of the ketophosphane to coordinate *trans* to the chloride ligand. Due to this inability, the *cct* isomers of complexes **2** remain the speculative species. From this point of view, $RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] complexes remarkably differ from $RuX_2(CO)_2L_2$ compounds in which the *cct* isomers are thermodynamically favoured. The cleavage of the O→Ru bond in complexes **2**, that occurs under thermal activation or sunlight irradiation, results in a true coordinatively unsaturated species which allows the formation of stable *cis*-$RuCl_2(CO)(L)[\eta^2$-(*P*,*O*)-ketophosphane] derivatives according to a Berry rearrangement. Under less drastic conditions, the substitution of the coordinated oxygen atom by an entering ligand such as carbon monoxide probably occurs through an associative mechanism, allowing the geometry to be retained. The easy deprotonation of the ketophosphane $Ph_2PCH_2C(=O)t$Bu allows the generation of $RuCl(CO)_2(L)[\eta^2$-(*P*,*O*)-enolatophosphane] derivatives, and this transformation also preserves the geometry of the corresponding precursor complexes.

Experimental Section

General: The reactions were performed using Schlenk-type techniques, but only the handling of ketophosphanes required a rigorous exclusion of oxygen. Solvents were distilled under an inert gas after drying according to conventional methods. − Elemental analyses were performed by the Service de Microanalyse du CNRS, Vernaison, France. − Infrared spectra were recorded with a Nicolet 205 FT infrared spectrometer as Nujol mulls. − NMR spectra were recorded at 297 K with an AC 300 FT Bruker instrument (^{1}H: 300.13; ^{13}C: 75.47; ^{31}P: 121.50 MHz; absolute values of coupling constants in Hz) and referenced internally to the solvent peak. The following abbreviations are used: s: singlet; d: doublet; t: triplet; t_a: apparent triplet; q_4: quadruplet; m, unresolved multiplet. − The precursor complexes $RuCl_2(L)(\eta^6$-*p*-cymene) were obtained by treating $[RuCl_2(\eta^6$-*p*-cymene)]$_2$ with a stoichiometric amount of the corresponding phosphorus derivative L.[18] The ketophosphanes $Ph_2PCH_2C(=O)t$Bu (**1**), $Ph_2PCMe_2C(=O)i$Pr (**1**′), and $Ph_2PCMe_2CH_2C(=O)$Me (**1**′′), were prepared as previously reported.[12,14]

Synthesis of Complexes 2−2′′

(*ttt*)-$RuCl_2(CO)(PMe_3)[Ph_2PCH_2C(t$Bu)=O] (2a): $RuCl_2(PMe_3)$(*p*-cymene) (13.3 g, 34.8 mmol) was added to a solution of ketophosphane **1** (9.90 g, 34.8 mmol) in methanol (200 mL). As for the preparation of the other complexes **2−2**′′, the Schlenk tube was protected from light with aluminium foil and the mixture was then stirred under carbon monoxide at room temperature. After 2 d, the resulting slurry was heated and then filtered to obtain an orange solution that deposited orange crystals on cooling. Yield 13.6 g, 70%. − ^{1}H NMR ($CDCl_3$): δ = 7.60−7.39 (m, 10 H, Ph), 4.04 (dd, 2 H, $^2J_{PH}$ = 10.1, $^4J_{PH}$ = 1.4, PCH_2), 1.70 (dd, 9 H, $^2J_{PH}$ = 10.3, $^4J_{PH}$ = 2.3, PMe_3), 1.33 (s, 9 H, *t*Bu). − ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 229.5 (dd, $^2J_{PC}$ = 8.6, $^3J_{PC}$ = 4.9, C=O), 205.8 (dd, $^2J_{PC}$ = 17.1 and 11.0, C≡O), 133.6 (d, $^3J_{PC}$ = 11.0, Ph_2P, *meta*), 131.2 (dd, $^1J_{PC}$ = 42.1, $^3J_{PC}$ = 7.3, Ph_2P, *ipso*), 131.0 (d, $^4J_{PC}$ = 2.4, Ph_2P, *para*), 128.9 (d, $^2J_{PC}$ = 9.8, Ph_2P, *ortho*), 46.3 (d, $^3J_{PC}$ = 3.5, CMe_3), 43.0 (d, $^1J_{PC}$ = 23.8, PCH_2), 27.1 (s, CMe_3), 13.8 (d, $^1J_{PC}$ = 28.9, PMe_3). − ^{13}C NMR (CD_2Cl_2, selected values): δ = 229.5 (broad, C=O), 205.8 (dd, $^2J_{PC}$ = 17.1 and 11.0, C≡O), 43.0 (td, $^1J_{HC}$ = 131, $^1J_{PC}$ = 23.8, PCH_2), 13.8 (q_4d, $^1J_{HC}$ = 130, $^1J_{PC}$ = 28.9, PMe_3). − $C_{22}H_{30}Cl_2O_2P_2Ru$ (560.4): calcd. C 47.15, H 5.40, Cl 12.65, P 11.05; found C 47.48, H 5.49, Cl 12.60, P 11.00. − Probably due to a solid-state effect, the IR absorptions (Table 1)

assigned to the carbon monoxide ligand and to the keto functionality are split.

(*ttt*)-$RuCl_2(CO)(PMePh_2)[Ph_2PCH_2C(tBu)=O]$ (2b): A mixture consisting of $RuCl_2(PMePh_2)$(*p*-cymene) (7.00 g, 13.8 mmol) and ketophosphane **1** (4.00 g, 14.1 mmol) was dissolved in dichloromethane (30 mL), and methanol (70 mL) was then added. The mixture was stirred for 3 d (under carbon monoxide) and the resulting yellow slurry was concentrated under vacuum and diethyl ether was then added. The yellow precipitate was collected by filtration and then dissolved in dichloromethane (50 mL). The solution was filtered and the orange filtrate was covered with ethanol (250 mL) in an open flask allowing natural evaporation. Orange crystals were obtained. Yield 6.40 g, 68%. – ^{1}H NMR ($CDCl_3$): δ = 7.82–7.36 (m, 20 H, Ph), 4.06 (dd, 2 H, $^2J_{PH}$ = 10.5, $^4J_{PH}$ = 1.3, PCH_2), 2.23 (dd, 3 H, $^2J_{PH}$ = 9.2, $^4J_{PH}$ = 1.9, PMe), 1.08 (s, 9 H, *t*Bu). – $C_{32}H_{34}Cl_2O_2P_2Ru$ (684.5): calcd. C 56.15, H 5.01, Cl 10.36, P 9.05; found C 56.18, H 4.92, Cl 10.31, P 9.06.

(*ttt*)-$RuCl_2(CO)(PiPrPh_2)[Ph_2PCH_2C(tBu)=O]\cdot CH_2Cl_2$ (2c): Complex **2c** was similarly obtained in a 49% yield starting from $RuCl_2(PiPrPh_2)$(*p*-cymene) and ketophosphane **1**. – ^{1}H NMR (CD_2Cl_2): δ = 7.69–7.30 (m, 20 H, Ph), 3.97 (dd, 2 H, $^2J_{PH}$ = 10.2, $^4J_{PH}$ = 0.7, PCH_2), 3.46 (m, 1 H, C*H*Me$_2$), 1.04 (dd, 6 H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 14.8, CH*Me*$_2$), 0.87 (s, 9 H, *t*Bu). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 228.0 (dd, $^2J_{PC}$ = 7.1, $^4J_{PC}$ = 4.6, C=O), 206.8 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 13.4, C≡O), 135.2 (d, $^3J_{PC}$ = 8.2, Ph_2P, *meta*), 133.6 (dd, $^3J_{PC}$ = 9.9, $^5J_{PC}$ = 1.5, Ph_2P, *meta*), 131.1 (d, $^4J_{PC}$ = 2.1, Ph_2P, *para*), 130.9 (dd, $^1J_{PC}$ = 44.0, $^3J_{PC}$ = 4.4, Ph_2P, *ipso*), 130.2 (d, $^4J_{PC}$ = 1.7, Ph_2P, *para*), 130.1 (dd, $^1J_{PC}$ = 35.6, $^3J_{PC}$ = 3.3, Ph_2P, *ipso*), 128.8 (d, $^2J_{PC}$ = 9.8, Ph_2P, *ortho*), 128.1 (d, $^2J_{PC}$ = 8.8, Ph_2P, *ortho*), 45.9 (d, $^3J_{PC}$ = 2.9, *C*Me$_3$), 43.1 (d, $^1J_{PC}$ = 24.2, PCH_2), 26.8 (s, C*Me*$_3$), 22.6 (dd, $^1J_{PC}$ = 23.9, $^3J_{PC}$ = 1.8, *C*HMe$_2$), 18.1 (s, CH*Me*$_2$). – Easy loss of dichloromethane from the crystals occurs as seen by the elemental analysis results, which indicated the retention of only 0.8 CH_2Cl_2 per Ru; $C_{34}H_{38}Cl_2O_2P_2Ru\cdot$(0.8 CH_2Cl_2) (712.6 + 67.9 = 780.5): calcd. C 53.55, H 5.11, Cl 16.35, P 7.94; found C 53.56, H 5.15, Cl 16.47, P 7.95. – Probably due to a solid-state effect, the IR absorptions (Table 1) assigned to the carbon monoxide ligand and to the keto functionality are split.

(*ttt*)-$RuCl_2(CO)(PPh_3)[Ph_2PCH_2C(tBu)=O]\cdot{}^2/_3CH_2Cl_2$ (2d): A mixture was prepared starting from $RuCl_2(PPh_3)$(*p*-cymene) (9.50 g, 16.7 mmol), ketophosphane **1** (4.84 g, 17.0 mmol), dichloromethane (25 mL), and methanol (130 mL). It was stirred for 3 d. The resulting yellow precipitate was collected by filtration and washed with diethyl ether (100 mL). Yield 9.70 g, 72%. The low solubility of the compound precludes further purification.

Recovery of 2d from 5d: A solution of **5d** (4.00 g, 5.08 mmol) in dichloromethane (50 mL) was kept in the dark at room temperature. Orange crystals were collected after 10 d. Yield 1.58 g, 39%. – ^{1}H NMR (CD_2Cl_2): δ = 7.75–7.35 (m, 25 H, Ph), 4.12 (dd, 2 H, $^2J_{PH}$ = 10.7, $^4J_{PH}$ = 1.4, PCH_2), 1.11 (s, 9 H, *t*Bu). – $C_{37}H_{36}Cl_2O_2P_2Ru\cdot({}^2/_3\ CH_2Cl_2)$ (746.6 + 56.6 = 803.2): calcd. C 56.32, H 4.69, Cl 14.71, P 7.71; found C 56.06, H 4.69, Cl 15.12, P 7.33.

(*ttt*)-$RuCl_2(CO)[P(OMe)Ph_2][Ph_2PCH_2C(tBu)=O]$ (2e): Methanol (120 mL) was added to a solution consisting of $RuCl_2[Ph_2PCH_2C(=O)tBu]$(*p*-cymene)[14] (5.47 g, 9.26 mmol) and $P(OMe)Ph_2$ (3.20 mL, 16.0 mmol) in dichloromethane (60 mL). This mixture was stirred for 3 d. The resulting yellow slurry was concentrated under vacuum and diethyl ether was added. The yellow precipitate was collected by filtration and washed with diethyl ether. Yield 3.40 g, 52%. This crude product was found pure by NMR-spectroscopic analysis. Fractional crystallisation from a dichloromethane/ethanol mixture allowed the formation of orange-yellow crystals of analytical quality. – ^{1}H NMR (CD_2Cl_2): δ = 7.93–7.40 (m, 20 H, Ph), 4.07 (dd, 2 H, $^2J_{PH}$ = 10.5, $^4J_{PH}$ = 1.5, PCH_2), 3.65 (d, 3 H, $^3J_{PH}$ = 13.0, OMe), 0.99 (s, 9 H, *t*Bu). – $C_{32}H_{34}Cl_2O_3P_2Ru$ (700.5): calcd. C 54.86, H 4.89, Cl 10.12, P 8.84; found C 54.59, H 4.87, Cl 10.30, P 8.50.

(*ttt*)-$RuCl_2(CO)(PMe_3)[Ph_2PCMe_2C(iPr)=O]$ (2′a): A mixture consisting of $RuCl_2(PMe_3)$(*p*-cymene) (2.37 g, 6.20 mmol), ketophosphane **1′** (1.85 g, 6.20 mmol) and methanol (40 mL), was stirred for 2 d. The resulting yellow slurry was cooled to –20 °C and the yellow crystalline precipitate was then collected by filtration and washed with cold methanol (20 mL). Yield 3.00 g, 84%. Orange-yellow crystals were obtained by recrystallisation from hot methanol. – ^{1}H NMR (CD_2Cl_2): δ = 7.61–7.40 (m, 10 H, Ph), 3.33 (m, 1 H, C*H*Me$_2$), 1.67 (dd, 9 H, $^2J_{PH}$ = 10.4, $^4J_{PH}$ = 2.2, PMe_3), 1.54 (d, 6 H, $^3J_{PH}$ = 9.9, $PCMe_2$), 1.27 (d, 6 H, $^3J_{HH}$ = 6.6, CH*Me*$_2$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 229.8 (dd, $^2J_{PC}$ = 13.2, $^3J_{PC}$ = 3.9, C=O), 205.2 (dd, $^2J_{PC}$ = 16.4 and 10.0, C≡O), 136.1 (dd, $^3J_{PC}$ = 10.3, $^5J_{PC}$ = 1.1, Ph_2P, *meta*), 131.1 (d, $^4J_{PC}$ = 2.3, Ph_2P, *para*), 128.4 (dd, $^1J_{PC}$ = 38.6, $^3J_{PC}$ = 1.7, Ph_2P, *ipso*), 128.1 (d, $^2J_{PC}$ = 9.7, Ph_2P, *ortho*), 55.3 (d, $^1J_{PC}$ = 17.2, P*C*Me$_2$), 36.9 (d, $^3J_{PC}$ = 2.9, *C*HMe$_2$), 24.4 (s, PC*Me*$_2$), 20.9 (s, CH*Me*$_2$), 13.7 (dd, $^1J_{PC}$ = 29.8, $^3J_{PC}$ = 1.5, PMe_3). – $C_{23}H_{32}Cl_2O_2P_2Ru$ (574.4): calcd. C 48.09, H 5.62, Cl 12.34, P 10.78; found C 48.10, H 5.63, Cl 12.11, P 10.93.

(*ttt*)-$RuCl_2(CO)[P(OMe)Ph_2][Ph_2PCMe_2C(iPr)=O]$ (2′e): A mixture consisting of $RuCl_2[P(OMe)Ph_2]$(*p*-cymene) (5.20 g, 9.95 mmol), ketophosphane **1′** (3.08 g, 10.3 mmol), dichloromethane (15 mL), and methanol (90 mL), was stirred for 4 d. The resulting mixture was concentrated under vacuum and diethyl ether was then added. A yellow precipitate (6.20 g) was collected by filtration and washed with diethyl ether. This solid was dissolved in dichloromethane (40 mL) and the orange solution was covered with methanol (40 mL) and diethyl ether (100 mL) to obtain orange crystals. Yield 5.15 g, 72%. – ^{1}H NMR ($CDCl_3$): δ = 7.98–7.39 (m, 20 H, Ph), 3.63 (d, 3 H, $^3J_{PH}$ = 12.9, OMe), 3.09 (m, 1 H, C*H*Me$_2$), 1.52 (d, 6 H, $^3J_{PH}$ = 9.9, $PCMe_2$), 0.80 (d, 6 H, $^3J_{HH}$ = 6.7, CH*Me*$_2$). – $C_{33}H_{36}Cl_2O_3P_2Ru$ (714.6): calcd. C 55.47, H 5.08, Cl 9.92, P 8.67; found C 55.38, H 5.06, Cl 10.12, P 8.47.

(*ttt*)-$RuCl_2(CO)[P(OMe)_3][Ph_2PCMe_2C(iPr)=O]$ (2′f): A solution obtained from $RuCl_2[P(OMe)_3]$(*p*-cymene) (4.66 g, 10.8 mmol), ketophosphane **1′** (3.23 g (10.8 mmol) and methanol (60 mL), was stirred for 7 d. The resulting orange-yellow slurry was heated to obtain an orange solution that was filtered. The filtrate was slowly cooled to –20 °C to afford orange crystals. Yield 4.10 g, 61%. – ^{1}H NMR (CD_2Cl_2): δ = 7.59–7.38 (m, 10 H, Ph), 3.86 (d, 9 H, $^3J_{PH}$ = 11.1, OMe), 3.34 (m, 1 H, C*H*Me$_2$), 1.56 (d, 6 H, $^3J_{PH}$ = 10.1, $PCMe_2$), 1.28 (d, 6 H, $^3J_{HH}$ = 6.7, CH*Me*$_2$). – ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 234.6 (dd, $^2J_{PC}$ = 12.9, $^3J_{PC}$ = 4.5, C=O), 204.0 (dd, $^2J_{PC}$ = 23.1 and 10.6, C≡O), 136.2 (dd, $^3J_{PC}$ = 9.8, $^5J_{PC}$ = 1.7, Ph_2P, *meta*), 131.3 (d, $^4J_{PC}$ = 1.9, Ph_2P, *para*), 128.1 (d, $^2J_{PC}$ = 9.9, Ph_2P, *ortho*), 127.4 (dd, $^1J_{PC}$ = 41.6, $^3J_{PC}$ = 3.2, Ph_2P, *ipso*), 54.6 (d, $^1J_{PC}$ = 18.0, P*C*Me$_2$), 53.2 [d, $^2J_{PC}$ = 3.8, $P(OMe)_3$], 36.9 (d, $^3J_{PC}$ = 2.7, *C*HMe$_2$), 24.5 (s, PC*Me*$_2$), 20.8 (s, CH*Me*$_2$). – $C_{23}H_{32}Cl_2O_5P_2Ru$ (622.4): calcd. C 44.38, H 5.18, Cl 11.39, P 9.95; found C 44.48, H 5.21, Cl 11.43, P 9.90.

(*ttt*)-$RuCl_2(CO)(PMe_3)[Ph_2PCMe_2CH_2C(Me)=O]$ (2′′a): Methanol (80 mL) was added to a mixture of $RuCl_2(PMe_3)$(*p*-cymene) (2.70 g, 7.06 mmol) and ketophosphane **1′′** (2.65 g, 9.32 mmol),

and this mixture was stirred for 2 d. The volatiles were evaporated under vacuum. The resulting solid was dissolved in dichloromethane (30 mL). The solution was filtered and methanol (50 mL) was added to the orange filtrate. The slow concentration of this solution afforded orange crystals. Yield 2.35 g, 59%. − ^{1}H NMR (CD_2Cl_2): δ = 7.84−7.30 (m, 10 H, Ph), 3.50 (d, 2 H, $^3J_{PH}$ = 20.3, CH_2), 2.50 (s, 3 H, MeCO), 1.57 (dd, 9 H, $^2J_{PH}$ = 10.2, $^4J_{PH}$ = 2.1, PMe_3), 1.30 (d, 6 H, $^3J_{PH}$ = 11.3, $PCMe_2$). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 221.7 (s, C=O), 205.7 (dd, $^2J_{PC}$ = 16.5 and 13.0, C≡O), 135.8 (d, $^3J_{PC}$ = 9.0, Ph_2P, *meta*), 133.4 (d, $^1J_{PC}$ = 38.8, Ph_2P, *ipso*), 130.1 (d, $^4J_{PC}$ = 2.2, Ph_2P, *para*), 127.7 (d, $^2J_{PC}$ = 9.3, Ph_2P, *ortho*), 52.8 (d, $^2J_{PC}$ = 6.4, CH_2), 36.2 (s, MeCO), 30.3 (dd, $^1J_{PC}$ = 12.6, $^3J_{PC}$ = 1.7, P*C*Me_2), 25.6 (s, PC*Me*$_2$), 13.2 (d, $^1J_{PC}$ = 28.8, PMe_3). − $C_{22}H_{30}Cl_2O_2P_2Ru$ (560.4): calcd. C 47.15, H 5.40, Cl 12.65, P 11.05; found C 47.35, H 5.38, Cl 12.84, P 11.00.

Reactivity of Complexes 2 towards Carbon Monoxide

(*ttt*)-$RuCl_2(CO)_2(PMe_3)[Ph_2PCH_2C(=O)tBu]$ (3a): A solution of **2a** (0.15 g) in $CDCl_3$ (2.0 mL) was stirred for 2 h under carbon monoxide. The ^{1}H NMR spectrum of the resulting solution shows a 1:4 mixture of **2a** and **3a**, but the addition of hexane to such a solution selectively led to the recovery of **2a**. − ^{1}H NMR ($CDCl_3$, available values for **3a** from such a mixture of **2a** and **3a**): δ = 4.04 (dd, 2 H, $^2J_{PH}$ = 9.4, $^4J_{PH}$ = 1.4, PCH_2), 1.69 (dd, 9 H, $^2J_{PH}$ = 10.1, $^4J_{PH}$ = 2.1, PMe_3), 1.05 (s, 9 H, *t*Bu).

(*ttt*)-$RuCl_2(CO)_2(PMePh_2)[Ph_2PCH_2C(=O)tBu]$ (3b): A solution of **2b** (0.15 g) in $CDCl_3$ (2.0 mL) was treated similarly, and the ^{1}H NMR spectrum of the resulting solution shows a ca. 1:1 mixture of **2b** and **3b**. − ^{1}H NMR ($CDCl_3$, mixture of the two complexes): δ = 7.82−7.36 (m, 20 H, Ph), ca. 4.10 (2 H, PCH_2), ca. 2.20 (m, 3 H, PMe), 1.08 and 1.05 (2 s, 9 H, *t*Bu).

(*cct*)-$RuCl_2(CO)_2(PMe_3)[Ph_2PCH_2C(=O)tBu]$ (4a): An orange solution of **2a** (1.00 g, 1.78 mmol) in hot toluene (80 °C, 40 mL) was stirred for 2 d under carbon monoxide and the resulting colourless solution was concentrated under vacuum to leave the crude product. Recrystallisation from hot methanol afforded colourless crystals of **4a**. Yield 0.79 g, 75%. − ^{1}H NMR (CD_2Cl_2): δ = 7.78−7.34 (m, 10 H, Ph), 4.28 (d, 2 H, $^2J_{PH}$ = 7.6, PCH_2), 1.60 (dd, 9 H, $^2J_{PH}$ = 10.8, $^4J_{PH}$ = 2.4, PMe_3), 0.76 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 210.0 (dd, $^2J_{PC}$ = 10.0, $^4J_{PC}$ = 1.9, C=O), 193.4 (dd, $^2J_{PC}$ = 11.5 and 10.0, C≡O), 133.6 (d, $^3J_{PC}$ = 9.8, Ph_2P, *meta*), 131.2 (dd, $^1J_{PC}$ = 44.9, $^3J_{PC}$ = 1.4, Ph_2P, *ipso*), 131.1 (d, $^4J_{PC}$ = 2.3, Ph_2P, *para*), 128.5 (d, $^2J_{PC}$ = 10.0, Ph_2P, *ortho*), 46.0 (s, *C*Me_3), 31.8 (d, $^1J_{PC}$ = 25.0, PCH_2), 26.0 (s, C*Me*$_3$), 15.3 (dd, $^1J_{PC}$ = 33.3, $^3J_{PC}$ = 1.2, PMe_3). − ^{13}C NMR (CD_2Cl_2, selected values): δ = 31.8 (td, $^1J_{HC}$ = 130, $^1J_{PC}$ = 25.0, PCH_2). − $C_{23}H_{30}Cl_2O_3P_2Ru$ (588.4): calcd. C 46.95, H 5.14, Cl 12.05, P 10.53; found C 46.63, H 5.33, Cl 11.83, P 10.16.

(*cct*)-$RuCl_2(CO)_2(PMePh_2)[Ph_2PCH_2C(=O)tBu]\cdot CH_2Cl_2$ (4b): Complex **4b** was similarly obtained as colourless crystals in a 70% yield starting from **2b**. − ^{1}H NMR ($CDCl_3$): δ = 7.90−7.37 (m, 20 H, Ph), 4.50 (d, 2 H, $^2J_{PH}$ = 8.0, PCH_2), 2.30 (dd, 3 H, $^2J_{PH}$ = 10.6, $^4J_{PH}$ = 1.6, PMe), 0.79 (s, 9 H, *t*Bu). − $C_{33}H_{34}Cl_2O_3P_2Ru\cdot CH_2Cl_2$ (712.6 + 84.9 = 797.5): calcd. C 51.21, H 4.55, Cl 17.78, P 7.77; found C 51.21, H 4.64, Cl 16.98, P 7.71; the low chlorine value is attributed to an easy partial loss of CH_2Cl_2.

(*cct*)-$RuCl_2(CO)_2(PMe_3)[Ph_2PCMe_2C(=O)iPr]\cdot MeOH$ (4′a): A solution of **2′a** (3.00 g, 5.22 mmol) in hot toluene (85 °C, 60 mL) was stirred for 20 h under carbon monoxide, and the resulting colourless solution was concentrated to dryness under vacuum. Recrystallisation from hot methanol afforded colourless crystals. Yield 2.86 g, 86%. − ^{1}H NMR (CD_2Cl_2): δ = 7.87−7.28 (m, 10 H, Ph), 3.38 (s, 3 H, MeOH), 3.26 (m, 1 H, C*H*Me_2), 1.66 (dd, 9 H, $^2J_{PH}$ = 10.9, $^4J_{PH}$ = 2.4, PMe_3), 1.47 (d, 6 H, $^3J_{PH}$ = 12.9, $PCMe_2$), 1.19 (d, 6 H, $^3J_{HH}$ = 6.7, CH*Me*$_2$). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 218.0 (s, C=O), 193.9 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$11.3, C≡O), 136.4 (d, $^3J_{PC}$ = 7.9, Ph_2P, *meta*), 132.8 (d, $^1J_{PC}$ = 35.8, Ph_2P, *ipso*), 130.5 (d, $^4J_{PC}$ = 2.2, Ph_2P, *para*), 127.8 (d, $^2J_{PC}$ = 9.4, Ph_2P, *ortho*), 53.2 (dd, $^1J_{PC}$ = 17.2, $^3J_{PC}$ = 2.3, P*C*Me_2), 50.8 (s, MeOH), 35.7 (s, *C*HMe_2), 22.0 (s, PC*Me*$_2$), 20.7 (s, CH*Me*$_2$), 15.3 (d, $^1J_{PC}$ = 35.4, PMe_3). − $C_{24}H_{32}Cl_2O_3P_2Ru\cdot MeOH$ (602.4 + 32.0 = 634.5): calcd. C 47.33, H 5.72, Cl 11.18, P 9.76; found C 47.26, H 5.85, Cl 10.93, P 9.54.

Reactivity of Complexes 2 towards Acetonitrile

(*cct*)-$RuCl_2(CO)(MeCN)(PMe_3)[Ph_2PCH_2C(=O)tBu]$ (5a): **2a** (1.96 g, 3.50 mmol) was heated in acetonitrile (25 mL) to obtain a pale-yellow solution. On standing overnight at room temperature, lemon-yellow crystals formed. They were collected and then washed with acetonitrile (10 mL). Yield 1.75 g, 83%. − ^{1}H NMR (CD_2Cl_2): δ = 7.97−7.36 (m, 10 H, Ph), 4.40 (dd, 1 H, $^2J_{HH}$ = 17.1, $^2J_{PH}$ = 8.6, PCH_2, H_a), 4.25 (dd, 1 H, $^2J_{HH}$ = 17.0, $^2J_{PH}$ = 5.0, PCH_2, H_b), 1.64 (s, 3 H, MeCN), 1.54 (dd, 9 H, $^2J_{PH}$ = 10.3, $^4J_{PH}$ = 2.3, PMe_3), 0.74 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 211.0 (dd, $^2J_{PC}$ = 10.7, $^4J_{PC}$ = 2.5, C=O), 199.5 (dd, $^2J_{PC}$ = 13.6 and 11.5, C≡O), 135.2 (d, $^3J_{PC}$ = 10.8, Ph, *meta*), 133.2 (d, $^3J_{PC}$ = 9.0, Ph, *meta*), 131.5 (d, $^1J_{PC}$ = 38.6, Ph, *ipso*), 130.9 (d, $^4J_{PC}$ = 2.7, Ph, *para*), 130.7 (d, $^1J_{PC}$ = 38.6, Ph, *ipso*), 129.6 (d, $^4J_{PC}$ = 1.8, Ph, *para*), 128.2 (d, $^2J_{PC}$ = 9.9, Ph, *ortho*), 128.0 (d, $^2J_{PC}$ = 9.0, Ph, *ortho*), 122.7 (s, Me*C*N), 45.9 (s, *C*Me_3), 31.4 (d, $^1J_{PC}$ = 19.9, PCH_2), 25.8 (s, C*Me*$_3$), 14.1 (d, $^1J_{PC}$ = 30.5, PMe_3), 3.6 (s, *Me*CN). − $C_{24}H_{33}Cl_2NO_2P_2Ru$ (601.5): calcd. C 47.93, H 5.53, Cl 11.79, N 2.33, P 10.30; found C 48.20, H 5.69, Cl 11.69, N 2.45, P 10.33.

(*cct*)-$RuCl_2(CO)(MeCN)(PMePh_2)[Ph_2PCH_2C(=O)tBu]$ (5b): Similarly, **2b** (2.12 g, 3.10 mmol) was heated in acetonitrile (30 mL) to obtain a pale-yellow solution that deposited lemon-yellow crystals. Yield 1.83 g, 81%. − ^{1}H NMR (CD_2Cl_2): δ = 8.00−7.32 (m, 20 H, Ph), 4.48 (dd, 1 H, $^2J_{HH}$ = 17.1, $^2J_{PH}$ = 8.9, PCH_2, H_a), 4.40 (dd, 1 H, $^2J_{HH}$ = 17.1, $^2J_{PH}$ = 5.8, PCH_2, H_b), 2.21 (dd, 3 H, $^2J_{PH}$ = 9.9, $^4J_{PH}$ = 1.7, PMe), 1.05 (s, 3 H, MeCN), 0.75 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 210.9 (dd, $^2J_{PC}$ = 10.6, $^4J_{PC}$ = 1.7, C=O), 199.8 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 12.5, C≡O), 135.6−127.8 (m, 4 Ph groups), 122.0 (s, Me*C*N), 46.0 (s, *C*Me_3), 31.3 (d, $^1J_{PC}$ = 21.3, PCH_2), 25.8 (s, C*Me*$_3$), 12.5 (dd, $^1J_{PC}$ = 30.4, $^3J_{PC}$ = 1.4, PMe), 2.7 (s, *Me*CN). − $C_{34}H_{37}Cl_2NO_2P_2Ru$ (725.6): calcd. C 56.28, H 5.14, Cl 9.77, N 1.93, P 8.54; found C 56.16, H 5.18, Cl 9.76, N 2.12, P 8.25.

(*cct*)-$RuCl_2(CO)(MeCN)(PPh_3)[Ph_2PCH_2C(=O)tBu]$ (5d): Crude **2d** (5.05 g, ≈ 6.29 mmol) was heated in a mixture of acetonitrile (60 mL) and dichloromethane (15 mL) to obtain a pale-yellow solution. On standing overnight at room temperature, lemon-yellow crystals (3.23 g) were obtained. The concentration of the mother liquor afforded a supplementary crop of crystals. Overall yield 3.92 g, 79%. − ^{1}H NMR (CD_2Cl_2): δ = 8.03−7.33 (m, 25 H, Ph), 4.59 (dd, 1 H, $^2J_{HH}$ = 17.0, $^2J_{PH}$ = 8.4, PCH_2, H_a), 4.52 (dd, 1 H, $^2J_{HH}$ = 17.0, $^2J_{PH}$ = 6.5, PCH_2, H_b), 1.03 (s, 3 H, MeCN), 0.76 (s, 9 H, *t*Bu). − $C_{39}H_{39}Cl_2NO_2P_2Ru$ (787.7): calcd. C 59.47, H 4.99, Cl 9.00, N 1.78, P 7.86; found C 59.54, H 4.97, Cl 9.24, N 1.83, P 7.67.

Isomerisation of Complexes 2−2′

(*ccc*/*ctc*)-RuCl$_2$(CO)(PMe$_3$)[Ph$_2$PCH$_2$C(*t*Bu)=O] (6a). − Photo-Isomerisation of 2a: In a typical experiment, **2a** (2.00 g, 3.57 mmol) was dissolved in dichloromethane (50 mL) in a Schlenk flask. The flask was closed and placed behind a window where it was exposed to sunlight. After standing for two weeks (corresponding to ca. 50 h of exposure to sunlight), the solvent was removed under vacuum. The resulting solid was analysed by ^{1}H NMR spectroscopy, which indicated a 85% formation of **6a**. The solid was then dissolved in hot ethanol (60 mL) to obtain a solution that deposited pale-yellow crystals of **6a** on cooling. Yield 1.35 g, 68%. − **Thermally Induced Isomerisation of 2a:** A mixture of **2a** (2.00 g, 3.57 mmol) and toluene (30 mL) was heated under reflux for 20 h. The resulting cream-coloured precipitate was collected by filtration and dried under vacuum. Yield 1.54 g, 77%. − ^{1}H NMR (CD_2Cl_2): δ = 7.92−7.29 (m, 10 H, Ph), 4.26 (dd, 1 H, $^2J_{HH}$ = 17.9, $^2J_{PH}$ = 11.4, PCH_2, H_a), 4.09 (dd, 1 H, $^2J_{HH}$ = 17.9, $^2J_{PH}$ = 10.8, PCH_2, H_b), 1.51 (d, 9 H, $^2J_{PH}$ = 11.2, PMe_3), 1.29 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 227.2 (t_a, $^2J_{PC} \approx {}^3J_{PC} \approx$ 2.0, C=O), 197.5 (dd, $^2J_{PC}$ = 19.5 and 12.8, C≡O), 134.4 (d, $^3J_{PC}$ = 10.4, Ph, *meta*), 133.9 (d, $^1J_{PC}$ = 50.1, Ph, *ipso*), 132.2 (d, $^4J_{PC}$ = 2.4, Ph, *para*), 131.7 (d, $^4J_{PC}$ = 2.4, Ph, *para*), 131.2 (d, $^2J_{PC}$ = 10.4, Ph, *ortho*), 130.2 (d, $^1J_{PC}$ = 24.4, Ph, *ipso*), 129.7 (d, $^3J_{PC}$ = 9.8, Ph, *meta*), 129.2 (d, $^2J_{PC}$ = 11.0, Ph, *ortho*), 47.2 (d, $^1J_{PC}$ = 30.5, PCH_2), 46.0 (t_a, $^3J_{PC} \approx {}^4J_{PC} \approx$ 3.0, *C*Me_3), 27.1 (s, C*Me*$_3$), 19.2 (d, $^1J_{PC}$ = 37.3, PMe_3). The second but very minor isomer was only detected by $^{31}P\{^1H\}$ NMR spectroscopy (Table 1). − $C_{22}H_{30}Cl_2O_2P_2Ru$ (560.4): calcd. C 47.15, H 5.40, Cl 12.65, P 11.05; found C 47.41, H 5.43, Cl 12.21, P 10.77.

(*ccc*/*ctc*)-RuCl$_2$(CO)(PMePh$_2$)[Ph$_2$PCH$_2$C(*t*Bu)=O] (6b). − Photo-Isomerisation of 2b: A solution of **2b** (11.3 g, 16.5 mmol) in dichloromethane (150 mL) was treated as above. After 3 weeks of exposure to sunlight, the solvents were evaporated and the remaining solid was dissolved in methanol (100 mL) to obtain a solution that slowly deposited pale-yellow crystals of **6b**. Yield 5.95 g, 53%. The mother liquor was stirred under carbon monoxide for 20 h to afford a colourless precipitate of **4b** (3.08 g, overall yield 79%, with respect to the recovery of ruthenium). − **Thermally Induced Isomerisation of 2b:** A mixture of **2b** (3.54 g, 5.17 mmol) and toluene (50 mL) was heated as above to obtain a cream-coloured precipitate. Yield 2.60 g, 73%. − ^{1}H NMR (CD_2Cl_2, asterisk-marked values for the major ca. 3:2 isomer): δ = 7.90−7.60 (m, 20 H, Ph), 4.24* and 4.32 (2 dd, 1 H, $^2J_{HH}$ = 17.9* and 18.0, $^2J_{PH}$ = 10.8* and 10.9, PCH_2, H_a), 4.15 and 4.11* (2 dd, 1 H, partially overlapped, $^2J_{PH}$ = 10.8*, PCH_2, H_b), 2.19* and 1.15 (2 d, 3 H, $^2J_{PH}$ = 10.9* and 9.5, PMe), 1.30* and 1.12 (2 s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, asterisk-marked values for the major isomer): δ = 227.4* (t_a, $^2J_{PC} \approx {}^3J_{P'C} \approx$ 1.7, C=O), 227.2 (d, $^2J_{PC}$ = 2.9, C=O), 203.9 (dd, $^2J_{PC}$ = 19.1 and 14.5, C≡O), 197.4* (dd, $^2J_{PC}$ = 19.0 and 12.9, C≡O), 137.8−127.6 (m, Ph resonances for both isomers), 48.7* (d, $^1J_{PC}$ = 31.5, PCH_2), 48.5 (d, $^1J_{PC}$ = 33.9, PCH_2), 45.6* (d, $^3J_{PC}$ = 3.4, *C*Me_3), 45.6 (d, $^3J_{PC}$ = 2.9, *C*Me_3), 27.0* (s, C*Me*$_3$), 26.7 (s, C*Me*$_3$), 17.9* (d, $^1J_{PC}$ = 36.1, PMe), 16.6 (d, $^1J_{PC}$ = 37.0, PMe). − $C_{32}H_{34}Cl_2O_2P_2Ru$ (684.5): calcd. C 56.15, H 5.01, Cl 10.36, P 9.05; found C 55.86, H 5.10, Cl 10.40, P 9.29.

(*ccc*/*ctc*)-RuCl$_2$(CO)(PMe$_3$)[Ph$_2$PCMe$_2$C(*i*Pr)=O] (6′a). − Photo-Isomerisation of 2′a: Exposure to sunlight of a solution of **2′a** (3.00 g, 5.22 mmol) in dichloromethane (50 mL) resulted in a pale-yellow solution. Toluene (150 mL) was then added and partial slow evaporation of the solvents afforded pale-yellow crystals of **6′a·toluene**. Yield 2.36 g, 68%. − **Thermally Induced Isomerisation of 2′a:** A mixture of **2′a** (4.00 g, 6.96 mmol) and ethanol (60 mL) was heated under reflux for 3 d. The resulting solution was concentrated to dryness to leave a pale-yellow solid that was identified as pure **6′a** by NMR spectroscopy and elemental analysis. − ^{1}H NMR ($CDCl_3$): δ = 8.16−7.20 (m, 10 H, Ph), 3.28 (m, 1 H, C*H*Me_2), 1.52 (d, 9 H, $^2J_{PH}$ = 11.0, PMe_3), 1.49 (d, 3 H, $^3J_{PH}$ = 9.5, PC*Me*), 1.39 (d, 3 H, $^3J_{PH}$ = 12.8, PC*Me*), 1.39 (d, 3 H, $^3J_{HH}$ = 6.8, CH*Me*), 1.32 (d, 3 H, $^3J_{HH}$ = 6.6, CH*Me*). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 232.4 (dd, $^2J_{PC}$ = 7.2, $^3J_{PC}$ = 1.8, C=O), 197.6 (dd, $^2J_{PC}$ = 19.8 and 12.6, C≡O), 136.4 (d, $^2J_{PC}$ = 9.0, Ph, *ortho*), 133.0 (d, $^1J_{PC}$ = 46.7, Ph, *ipso*), 133.0 (d, $^3J_{PC}$ = 9.0, Ph, *meta*), 132.7 (s, Ph, *para*), 131.5 (s, Ph, *para*), 129.1 (d, $^3J_{PC}$ = 10.8, Ph, *meta*), 128.7 (d, $^2J_{PC}$ = 10.8, Ph, *ortho*), 125.9 (d, $^1J_{PC}$ = 43.1, Ph, *ipso*), 58.6 (d, $^1J_{PC}$ = 25.1, P*C*Me_2), 37.1 (d, $^3J_{PC}$ = 3.6, *C*HMe_2), 24.4 (s, CH*Me*), 23.0 (s, CH*Me*), 20.7 (s, PC*Me*), 20.5 (s, PC*Me*), 18.8 (d, $^1J_{PC}$ = 37.7, PMe_3). − $C_{23}H_{32}Cl_2O_2P_2Ru$: calcd. C 48.09, H 5.62, Cl 12.34, P 10.78; found C 48.10, H 5.70, Cl 12.26, P 10.67. − $C_{23}H_{32}Cl_2O_2P_2Ru$·toluene (574.4 + 92.1 = 666.5): calcd. C 54.06, H 6.05, Cl 10.64, P 9.29; found C 53.93, H 6.13, Cl 10.67, P 9.23.

Reactivity of Complexes 6−6′ towards Carbon Monoxide

(*ccc*)-RuCl$_2$(CO)$_2$(PMe$_3$)[Ph$_2$PCH$_2$C(=O)*t*Bu] (7a): A pale-yellow solution of **6a** (2.50 g, 4.46 mmol) in dichloromethane (30 mL) was stirred for 20 h under carbon monoxide, and the resulting clear solution was covered with hexane (100 mL) under the carbon monoxide, to obtain **7a** as colourless crystals. Yield 2.28 g, 87%. Alternatively, a solution of **6a** (2.00 g, 3.57 mmol) in methanol (40 mL) was stirred for 20 h under carbon monoxide to afford **7a** (as determined by NMR and IR spectroscopy) as a white precipitate that was collected by filtration and dried. Yield 1.73 g, 82%. Attempts to recrystallise from hot methanol afforded colourless crystals, but of the *cct* isomer **4a**. − ^{1}H NMR (CD_2Cl_2, asterisk-marked values for the major 3:1 isomer): δ = 7.86−7.41 (m, 10 H, Ph), 4.72* and 4.33 (2 dd, 1 H, $^2J_{HH}$ = 17.8* and 17.3, $^2J_{PH}$ = 7.5* and 6.8, PCH_2, H_a), 4.39* and 4.02 (2 dd, 1 H, $^2J_{PH}$ = 7.5* and 9.9, PCH_2, H_b), 1.24* and 1.23 (2 d, 9 H, $^2J_{PH}$ = 10.6* and 10.3, PMe_3), 1.06 and 0.81* (2 s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, asterisk-marked values for the major isomer): δ = 209.9* (d, $^2J_{PC}$ = 10.4, C=O), 208.7 (d, $^2J_{PC}$ = 6.1, C=O), 194.9 (dd, $^2J_{PC}$ = 15.9 and 12.2, C≡O), 194.0* (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 13.4, C≡O), 190.1* (dd, $^2J_{PC}$ = 115.4 and 11.6, C≡O), 189.7 (dd, $^2J_{PC}$ = 118.4 and 11.0, C≡O), 134.3−128.5 (m, Ph resonances for both isomers), 46.1* (d, $^3J_{PC}$ = 1.8, *C*Me_3), 45.8 (d, $^3J_{PC}$ = 2.4, *C*Me_3), 36.4 (d, $^1J_{PC}$ = 35.5, PCH_2), 32.0* (d, $^1J_{PC}$ = 28.5, PCH_2), 26.7* (s, C*Me*$_3$), 26.0 (s, C*Me*$_3$), 18.9* (d, $^1J_{PC}$ = 36.0, PMe_3), 14.3 (d, $^1J_{PC}$ = 33.0, PMe_3). − $C_{23}H_{30}Cl_2O_3P_2Ru$ (588.4): calcd. C 46.95, H 5.14, Cl 12.05, P 10.53; found C 46.80, H 5.12, Cl 11.91, P 10.73.

(*ccc*)-RuCl$_2$(CO)$_2$(PMePh$_2$)[Ph$_2$PCH$_2$C(=O)*t*Bu] (7b): Complex **7b** was studied by NMR spectroscopy after a solution of **6b** in $CDCl_3$ (or CD_2Cl_2) was stirred overnight under carbon monoxide. − ^{1}H NMR ($CDCl_3$, asterisk-marked values for the major 4:1 isomer): δ = 7.80−7.13 (m, 20 H, Ph), 4.88* and 4.47 (2 dd, 1 H, $^2J_{HH}$ = 18.0* and 17.4, $^2J_{PH}$ = 6.2* and 4.8, PCH_2, H_a), 4.35* and 1.98 (2 dd, 1 H, $^2J_{PH}$ = 7.9* and 10.2, PCH_2, H_b), 2.36 and 1.35* (2 d, 3 H, $^2J_{PH}$ = 10.9 and 10.5*, PMe), 0.82* and 0.71 (2 s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, asterisk-marked values for the major isomer): δ = 209.9* (d, $^2J_{PC}$ = 10.6, C=O), 208.2 (d, $^2J_{PC}$ = 9.9, C=O), 194.4* (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 12.4, C≡O), 193.6 (dd, $^2J_{PC}$ = 13.4 and 11.1, C≡O), 188.8 (dd, $^2J_{PC}$ = 117.4 and 10.8, C≡O), 187.7* (dd, $^2J_{PC}$ = 116.0 and 10.3, C≡O), 139.5−127.8 (m, Ph resonances for both isomers), 45.8* (d, $^3J_{PC}$ = 1.6, *C*Me_3), 45.6 (d, $^3J_{PC}$ = 1.3, *C*Me_3), 32.3* (d, $^1J_{PC}$ = 28.9, PCH_2), 31.3 (d, $^1J_{PC}$ = 26.8, PCH_2), 26.0 (s, C*Me*$_3$), 25.8* (s, C*Me*$_3$), 11.9 (d, $^1J_{PC}$ = 35.9,

PMe), 11.6* (d, $^1J_{PC}$ = 33.8, PMe). − The removal of the solvent from such solutions left a white solid consisting of a mixture of **7b** and **6b**, but allowing the determination of the main IR absorptions of **7b** in the solid state (Table 1).

Formation of 4b in Methanol: See synthesis of **6b**.

Reaction of 6′a with Carbon Monoxide: A solution of **6′a** in dichloromethane was stirred for 20 h under carbon monoxide and then examined by $^{31}P\{^1H\}$ NMR spectroscopy which indicated a complete conversion of **6′a** into **4′a**.

Cationic Derivatives

(*cct*)-{RuCl(CO)$_2$(PMe$_3$)[Ph$_2$PCH$_2$C(*t*Bu)=O]}(BF$_4$)·$^1/_2$CH$_2$Cl$_2$ (8a): A mixture consisting of **4a** (3.50 g, 5.95 mmol) and $AgBF_4$ (1.16 g, 5.95 mmol) in dichloromethane (60 mL) was stirred overnight. The resulting solution was decanted, then filtered and the filtrate was covered with diethyl ether (150 mL) to afford colourless crystals. Yield 3.15 g, 78%. Complex **8a** was obtained in a similar manner when starting from **6a** instead of **4a**. − ^1H NMR (CD_2Cl_2): δ = 7.84−7.33 (m, 10 H, Ph), 4.79 (ddd, 1 H, $^2J_{HH}$ = 18.7, $^2J_{PH}$ = 11.2, $^4J_{PH}$ = 2.9, PCH$_2$, H$_a$), 4.11 (dd, 1 H, $^2J_{HH}$ = 18.7, $^2J_{PH}$ = 10.9, PCH$_2$, H$_b$), 1.84 (dd, 9 H, $^2J_{PH}$ = 11.3, $^4J_{PH}$ = 2.6, PMe$_3$), 1.36 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 238.0 (t$_a$, $^2J_{PC} \approx {}^3J_{P'C} \approx$ 4.9, C=O), 195.5 (dd, $^2J_{PC}$ = 13.3 and 9.0, C≡O), 190.0 (dd, $^2J_{PC}$ = 11.6 and 9.2, C≡O), 134.4 (dd, $^3J_{PC}$ = 11.7, $^5J_{PC}$ = 1.5, PhP, *meta*), 133.3 (d, $^4J_{PC}$ = 2.6, PhP, *para*), 132.7 (d, $^4J_{PC}$ = 2.3, PhP, *para*), 131.6 (d, $^1J_{PC}$ = 47.7, PhP, *ipso*), 130.9 (d, $^3J_{PC}$ = 11.4, PhP, *meta*), 130.4 (d, $^2J_{PC}$ = 10.7, PhP, *ortho*), 130.0 (d, $^2J_{PC}$ = 11.6, PhP, *ortho*), 125.2 (dd, $^1J_{PC}$ = 53.5, $^3J_{PC}$ = 2.6, PhP, *ipso*), 47.9 (d, $^3J_{PC}$ = 3.5, *C*Me$_3$), 44.0 (d, $^1J_{PC}$ = 30.5, PCH$_2$), 27.0 (s, C*Me*$_3$), 14.9 (dd, $^1J_{PC}$ = 33.9, $^3J_{PC}$ = 1.4, PMe$_3$). − $C_{23}H_{30}BClF_4O_3P_2Ru\cdot{}^1/_2CH_2Cl_2$ (639.7 + 42.6 = 682.2): calcd. C 41.37, H 4.58, Cl 10.39, P 9.08; found C 41.16, H 4.49, Cl 10.38, P 9.22.

(*cct*)-{RuCl(CO)$_2$(PMe$_3$)[Ph$_2$PCMe$_2$C(*i*Pr)=O]}(BF$_4$) (8′a): Complex **8′a** was obtained as colourless crystals in a 84% yield, as above, starting from **4′a**. − ^1H NMR (CD_2Cl_2): δ = 7.94−7.20 (m, 10 H, Ph), 3.47 (m, 1 H, C*H*Me$_2$), 1.86 (dd, 9 H, $^2J_{PH}$ = 11.3, $^4J_{PH}$ = 2.6, PMe$_3$), 1.71 (d, 3 H, $^3J_{PH}$ = 10.1, PCMe), 1.51 (d, 3 H, $^3J_{PH}$ = 12.9, PCMe), 1.41 (d, 3 H, $^3J_{HH}$ = 6.8, C*H*Me), 1.23 (d, 3 H, $^3J_{HH}$ = 6.6, C*H*Me). − $C_{24}H_{32}BClF_4O_3P_2Ru$ (653.8): calcd. C 44.09, H 4.93, Cl 5.42, P 9.48; found C 43.95, H 4.83, Cl 5.66, P 9.60.

(*cct*)-{RuCl(CO)(MeCN)(PMe$_3$)[Ph$_2$PCH$_2$C(*t*Bu)=O]}(BF$_4$) (9a): Compound **5a** (1.67 g, 2.78 mmol) was added to a cold mixture (−60 °C) of $AgBF_4$ (0.54 g, 2.78 mmol), dichloromethane (50 mL), and acetonitrile (5 mL). After stirring overnight at room temperature, the solvents were evaporated leaving a solid that was extracted with dichloromethane (20 mL). The solution was filtered and the yellow filtrate was then covered with diethyl ether (100 mL) to afford lemon-yellow crystals. Yield 1.58 g, 87%. − ^1H NMR (CD_2Cl_2): δ = 7.88−7.23 (m, 10 H, Ph), 4.62 (ddd, 1 H, $^2J_{HH}$ = 18.4, $^2J_{PH}$ = 11.0, $^4J_{PH}$ = 2.9, PCH$_2$, H$_a$), 3.82 (dd, 1 H, $^2J_{HH}$ = 18.4, $^2J_{PH}$ = 10.2, PCH$_2$, H$_b$), 1.82 (t$_a$, 3 H, $^5J_{PH} \approx {}^5J_{P'H} \approx$ 0.8, MeCN), 1.69 (dd, 9 H, $^2J_{PH}$ = 10.7, $^4J_{PH}$ = 2.5, PMe$_3$), 1.38 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 234.7 (dd, $^2J_{PC}$ = 7.0, $^3J_{PC}$ = 4.6, C=O), 201.9 (dd, $^2J_{PC}$ = 14.8 and 9.8, C≡O), 135.0 (dd, $^3J_{PC}$ = 12.0, $^5J_{PC}$ = 1.8, Ph, *meta*), 132.8 (d, $^4J_{PC}$ = 2.5, Ph, *para*), 131.5 (d, $^4J_{PC}$ = 1.9, Ph, *para*), 131.1 (d, $^3J_{PC}$ = 10.8, Ph, *meta*), 130.4 (dd, $^1J_{PC}$ = 41.4, $^3J_{PC}$ = 1.5, Ph, *ipso*), 130.0 (d, $^2J_{PC}$ = 10.0, Ph, *ortho*), 129.7 (d, $^2J_{PC}$ = 10.9, Ph, *ortho*), 122.4 (s, Me*C*N), 127.0 (dd, $^1J_{PC}$ = 49.7, $^3J_{PC}$ = 2.3, Ph, *ipso*), 47.3 (d, $^3J_{PC}$ = 3.2, *C*Me$_3$), 43.0 (d, $^1J_{PC}$ = 27.0, PCH$_2$), 27.1 (s, C*Me*$_3$), 13.7 (dd, $^1J_{PC}$ = 31.3, $^3J_{PC}$ = 1.5, PMe$_3$), 3.5 (s, *Me*CN). − $C_{24}H_{33}BClF_4NO_2P_2Ru$ (652.8): calcd. C 44.16, H 5.10, Cl 5.43, N 2.15, P 9.49; found C 43.93, H 5.25, Cl 5.12, N 2.08, P 9.37.

Enolatophosphane Complexes

(*ttt*)-RuCl(CO)$_2$(PMe$_3$)[Ph$_2$PCH=C(*t*Bu)O] (10a): A mixture consisting of **2a** (3.00 g, 5.35 mmol) and K_2CO_3 (0.75 g, 5.43 mmol) in dichloromethane (30 mL) was stirred for 2 d under carbon monoxide. The resulting mixture was filtered and the yellow filtrate was concentrated leaving a crude product that was recrystallised from a mixture of benzene (10 mL) and hexane (100 mL). Lemon-yellow crystals were obtained. Yield 1.93 g, 65%. − ^1H NMR (CD_2Cl_2): δ = 7.87−7.37 (m, 10 H, Ph), 4.78 (dd, 1 H, $^2J_{PH}$ = 2.7, $^4J_{PH}$ = 1.7, PCH=), 1.66 (dd, 9 H, $^2J_{PH}$ = 9.9, $^4J_{PH}$ = 1.9, PMe$_3$), 1.11 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 203.1 (dd, $^2J_{PC}$ = 16.4, $^3J_{PC}$ = 5.2, =CO), 196.6 (t$_a$, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 13.9, C≡O), 139.1 (dd, $^1J_{PC}$ = 48.9, $^3J_{PC}$ = 2.1, Ph, *ipso*), 131.5 (dd, $^3J_{PC}$ = 10.5, $^5J_{PC}$ = 1.6, Ph, *meta*), 130.0 (d, $^4J_{PC}$ = 2.3, Ph, *para*), 128.7 (d, $^2J_{PC}$ = 10.1, Ph, *ortho*), 71.7 (dd, $^1J_{PC}$ = 61.5, $^3J_{PC}$ = 1.8, PCH=), 39.7 (d, $^3J_{PC}$ = 11.8, *C*Me$_3$), 29.6 (s, C*Me*$_3$), 15.6 (dd, $^1J_{PC}$ = 29.4, $^3J_{PC}$ = 1.6, PMe$_3$). − $C_{23}H_{29}ClO_3P_2Ru$ (552.0): calcd. C 50.05, H 5.30, Cl 6.42; found C 49.88, H 5.36, Cl 6.03.

(*ttt*)-RuCl(CO)$_2$(P*i*PrPh$_2$)[Ph$_2$PCH=C(*t*Bu)O]·CH$_2$Cl$_2$ (10c): A mixture consisting of **2c** (1.41 g, 1.77 mmol) and K_2CO_3 (0.30 g, 2.17 mmol) in dichloromethane (25 mL), was stirred for 20 h under carbon monoxide. The resulting mixture was filtered and the filtrate was covered with methanol to afford yellow crystals. Yield 0.81 g, 65%. − ^1H NMR (CD_2Cl_2): δ = 7.83−7.27 (m, 20 H, Ph), 4.69 (dd, 1 H, $^2J_{PH}$ = 3.2, $^4J_{PH}$ = 2.1, PCH=), 3.16 (m, 1 H, C*H*Me$_2$), 1.10 (dd, 6 H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 15.7, CH*Me*$_2$), 1.01 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 203.5 (dd, $^2J_{PC}$ = 15.7, $^4J_{PC}$ = 5.2, =CO), 196.8 (dd, $^2J_{PC}$ = 14.0 and 12.1, C≡O), 138.3 (dd, $^1J_{PC}$ = 50.4, $^3J_{PC}$ = 2.5, Ph$_2$P, *ipso*), 134.2 (d, $^3J_{PC}$ = 9.4, Ph$_2$P, *meta*), 132.1 (dd, $^1J_{PC}$ = 37.7, $^3J_{PC}$ = 1.4, Ph$_2$P, *ipso*), 131.5 (dd, $^3J_{PC}$ = 10.0, $^5J_{PC}$ = 1.2, Ph$_2$P, *meta*), 130.6 (d, $^4J_{PC}$ = 1.8, Ph$_2$P, *para*), 130.1 (d, $^4J_{PC}$ = 2.4, Ph$_2$P, *para*), 128.7 (d, $^2J_{PC}$ = 10.5, Ph$_2$P, *ortho*), 128.6 (d, $^2J_{PC}$ = 9.1, Ph$_2$P, *ortho*), 70.9 (d, $^1J_{PC}$ = 62.7, PCH=), 39.5 (d, $^3J_{PC}$ = 12.2, *C*Me$_3$), 29.7 (s, C*Me*$_3$), 24.4 (d, $^1J_{PC}$ = 22.6, *C*HMe$_2$), 17.9 (s, CH*Me*$_2$). − ^{13}C NMR (CD_2Cl_2, selected values): δ = 70.9 (dd, $^1J_{HC}$ = 164, $^1J_{PC}$ = 62.7, PCH=). − $C_{35}H_{37}ClO_3P_2Ru$ (704.1): calcd. C 59.70, H 5.30, Cl 5.03, P 8.80; found C 59.64, H 5.44, Cl 5.46, P 8.52.

(*ttt*)-RuCl(CO)$_2$[P(OMe)Ph$_2$][Ph$_2$PCH=C(*t*Bu)O]·CH$_2$Cl$_2$ (10e): A mixture consisting of **2e** (4.14 g, 5.91 mmol) and K_2CO_3 (0.82 g, 5.93 mmol) in dichloromethane (60 mL), was stirred for 3 d under carbon monoxide. The resulting mixture was filtered and the yellow filtrate was concentrated leaving a yellow solid. Yield 3.20 g, 70%. Yellow crystals were obtained after recrystallisation from dichloromethane/methanol. − ^1H NMR (CD_2Cl_2): δ = 7.83−7.30 (m, 20 H, Ph), 4.72 (t$_a$, 1 H, $^2J_{PH} \approx {}^4J_{PH} \approx$ 2.6, PCH=), 3.63 (d, 3 H, $^3J_{PH}$ = 13.3, OMe), 1.04 (s, 9 H, *t*Bu). − $C_{33}H_{33}ClO_4P_2Ru\cdot CH_2Cl_2$ (692.1 + 84.9 = 777.0): calcd. C 52.56, H 4.54, Cl 13.69, P 7.97; found C 52.16, H 4.61, Cl 12.46, P 7.92; the low chlorine value is likely to be due to to the easy loss of dichloromethane.

(*ccc*)-RuCl(CO)$_2$(PMe$_3$)[Ph$_2$PCH=C(*t*Bu)O] (11a): A mixture consisting of **6a** (3.43 g, 6.12 mmol) and K_2CO_3 (0.85 g, 6.15 mmol) in dichloromethane (40 mL), was stirred for 20 h under carbon monoxide. The resulting slurry was filtered and the filtrate was covered with toluene (30 mL) and then hexane (100 mL), to afford pale-yellow (almost colourless) crystals. Yield 2.86 g, 85%. − ^1H NMR (CD_2Cl_2): δ = 7.73−7.33 (m, 10 H, Ph), 4.74 (d, 1 H, $^2J_{PH}$ = 4.4,

PCH=), 1.27 (s, 9 H, *t*Bu), 1.06 (d, 9 H, $^2J_{PH}$ = 10.4, PMe_3). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 201.7 (d, $^2J_{PC}$ = 14.4, =CO), 199.4 (dd, $^2J_{PC}$ = 14.4 and 10.8, C≡O), 189.3 (dd, $^2J_{PC}$ = 113.1 and 10.8, C≡O), 141.1 (dd, $^1J_{PC}$ = 58.8, $^3J_{PC}$ = 2.2, Ph, *ipso*), 136.4 (dd, $^1J_{PC}$ = 56.1, $^3J_{PC}$ = 3.6, Ph, *ipso*), 131.5 (d, $^3J_{PC}$ = 9.9, Ph, *meta*), 131.1 (d, $^4J_{PC}$ = 2.7, Ph, *para*), 130.3 (d, $^2J_{PC}$ = 10.8, Ph, *ortho*), 130.3 (part of d, Ph, *para*), 129.6 (d, $^3J_{PC}$ = 10.8, Ph, *meta*), 129.1 (d, $^2J_{PC}$ = 10.8, Ph, *ortho*), 69.5 (d, $^1J_{PC}$ = 64.6, PCH=), 39.9 (d, $^3J_{PC}$ = 12.6, *C*Me_3), 29.7 (s, C*Me*$_3$), 13.3 (d, $^1J_{PC}$ = 31.4, PMe_3). − ^{13}C NMR (CD_2Cl_2, selected values): δ = 69.5 (dd, $^1J_{HC}$ = 164, $^1J_{PC}$ = 64.6, PCH=). − $C_{23}H_{29}ClO_3P_2Ru$ (552.0): calcd. C 50.05, H 5.30, Cl 6.42, P 11.22; found C 50.02, H 5.42, Cl 6.36, P 11.28.

(*ccc*)-RuCl(CO)$_2$(PMePh$_2$)[Ph$_2$PCH=C(*t*Bu)O] (11b): A mixture consisting of **6b** (2.04 g, 2.98 mmol) and K_2CO_3 (0.45 g, 3.26 mmol) in dichloromethane (40 mL), was stirred for 20 h under carbon monoxide. The resulting slurry was filtered and the filtrate was concentrated to dryness. The resulting solid was dissolved in a hot mixture of toluene (30 mL) and dichloromethane (15 mL) to obtain a clear solution that was covered with hexane (130 mL). Colourless crystals were obtained. Yield 1.69 g, 84%. − ^1H NMR (CD_2Cl_2, asterisk-marked values for the major 9:1 isomer): δ = 7.55−7.28 (m, 20 H, Ph), 4.89* and 4.84 (2 d, 1 H, $^2J_{PH}$ = 4.4* and 2.0, PCH=), 1.38* and 1.35 (2 s, 9 H, *t*Bu), 1.22 and 1.20* (2 dd, 3 H, $^2J_{PH}$ = 10.7 and 9.5*, $^4J_{PH}$ = 1.2 and 0.9*, PMe). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, asterisk-marked values for the major isomer): δ = 201.8* (d, $^2J_{PC}$ = 14.5, =CO), 199.4 (d, $^2J_{PC}$ = 17.4, =CO), 199.5 (dd, $^2J_{PC}$ = 13.7 and 10.7, C≡O), 198.5* (dd, $^2J_{PC}$ = 12.6 and 11.1, C≡O), 190.9 (dd, $^2J_{PC}$ = 105.3 and 11.4, C≡O), 189.4* (dd, $^2J_{PC}$ = 114.1 and 11.4, C≡O), 141.5−127.9 (m, Ph resonances for both isomers), 70.6* (d, $^1J_{PC}$ = 64.9, PCH=), 68.5 (d, $^1J_{PC}$ = 61.8, PCH=), 40.2* (d, $^3J_{PC}$ = 12.2, *C*Me_3), 39.7 (d, $^3J_{PC}$ = 12.2, *C*Me_3), 29.9 (s, C*Me*$_3$ for both isomers), 11.6 (dd, $^1J_{PC}$ = 23.0, $^3J_{PC}$ = 1.5, PMe), 11.2* (d, $^1J_{PC}$ = 28.2, $^3J_{PC}$ = 2.3, PMe). − $C_{33}H_{33}ClO_3P_2Ru$ (676.1): calcd. C 58.63, H 4.92, Cl 5.24, P 9.16; found C 58.35, H 4.98, Cl 5.42, P 9.33.

(*cct*)-RuCl(CO)$_2$(PMe$_3$)[Ph$_2$PCH=C(*t*Bu)O] (12a): A mixture consisting of **4a** (1.50 g, 2.20 mmol) and K_2CO_3 (0.31 g, 2.24 mmol) in dichloromethane (20 mL), was stirred for 7 d as required to complete the reaction, and then concentrated to dryness. The remaining solid was extracted with toluene (25 mL). The solution was filtered and the filtrate was covered with hexane (100 mL) to afford colourless crystals. Yield 0.90 g, 74%. − ^1H NMR (CD_2Cl_2): δ = 7.70−7.35 (m, 10 H, Ph), 4.58 (t_a, 1 H, $^2J_{PH} \approx {}^4J_{PH} \approx$ 3.0, PCH=), 1.66 (dd, 9 H, $^2J_{PH}$ = 10.6, $^4J_{PH}$ = 2.1, PMe_3), 1.20 (s, 9 H, *t*Bu). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 200.6 (dd, $^2J_{PC}$ = 18.0, $^3J_{PC}$ = 7.2, =CO), 198.2 (dd, $^2J_{PC}$ = 11.2 and 8.5, C≡O), 193.9 (t_a, $^2J_{PC} \approx {}^2J_{P'C} \approx$ 11.2, C≡O), 138.7 (d, $^1J_{PC}$ = 51.2, Ph, *ipso*), 133.6 (dd, $^1J_{PC}$ = 44.0, $^3J_{PC}$ = 3.6, Ph, *ipso*), 133.2 (dd, $^3J_{PC}$ = 9.9, $^5J_{PC}$ = 1.8, Ph, *meta*), 131.5 (dd, $^3J_{PC}$ = 10.8, $^5J_{PC}$ = 1.8, Ph, *meta*), 130.1 (d, $^4J_{PC}$ = 2.7, Ph, *para*), 130.0 (d, $^4J_{PC}$ = 2.7, Ph, *para*), 128.9 (d, $^2J_{PC}$ = 9.9, Ph, *ortho*), 128.4 (d, $^2J_{PC}$ = 10.8, Ph, *ortho*), 69.8 (dd, $^1J_{PC}$ = 61.0, $^3J_{PC}$ = 1.8, PCH=), 39.5 (d, $^3J_{PC}$ = 12.6, *C*Me_3), 29.8 (s, C*Me*$_3$), 14.8 (d, $^1J_{PC}$ = 30.4, PMe_3). − $C_{23}H_{29}ClO_3P_2Ru$ (552.0): calcd. C 50.05, H 5.30, Cl 6.42, P 11.22; found C 49.98, H 5.31, Cl 6.34, P 10.77.

(*cct*)-RuCl(CO)(MeCN)(PMe$_3$)[Ph$_2$PCH=C(*t*Bu)O] (13a): A mixture consisting of **9a** (1.00 g, 1.53 mmol) and K_2CO_3 (0.26 g, 1.90 mmol) in dichloromethane (25 mL), was stirred for 6 d and then concentrated to dryness. The remaining solid was extracted with toluene (15 mL). The solution was filtered and acetonitrile (1.0 mL) was added to the filtrate that was then covered with hexane (100 mL) to afford pale-yellow crystals. Yield 0.44 g, 50%. − ^1H NMR (CD_2Cl_2): δ = 7.80−7.29 (m, 10 H, Ph), 4.52 (dd, 1 H, $^2J_{PH}$ = 3.3, $^4J_{PH}$ = 1.1, PCH=), 1.58 (t_a, 3 H, $^5J_{PH} \approx {}^5J_{P'H} \approx$ 0.9, MeCN), 1.53 (dd, 9 H, $^2J_{PH}$ = 9.9, $^4J_{PH}$ = 2.1, PMe_3), 1.21 (s, 9 H, *t*Bu). − $C_{24}H_{32}ClNO_2P_2Ru$ (565.0): calcd. C 51.02, H 5.71, Cl 6.27, N 2.48, P 10.96; found C 51.03, H 5.78, Cl 6.14, N 2.49, P 10.84.

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