Bis(keto-phosphane) and Bis(enolato-phosphane) Ruthenium Complexes − Synthesis and X-ray Structure Determination of RuCl(NO)[η^2-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$

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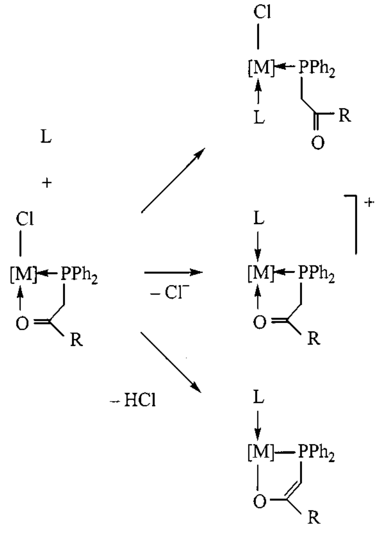
A slow reaction consisting of a cleavage of one Ru–Cl bond occurred when a mixture of $RuCl_2[Ph_2PCH_2C(tBu){=}O]_2$ (**1**) and $[NH_4][PF_6]$ was dissolved in methanol as shown by a subsequent reaction with carbon monoxide affording the stable cationic derivative $\{RuCl(CO)[Ph_2PCH_2C(tBu){=}O]_2\}[PF_6]$ (**2**). By contrast, the straightforward reaction of **1** with carbon monoxide yielded $RuCl_2(CO)[Ph_2PCH_2C(tBu){=}O][Ph_2PCH_2C({=}O)tBu]$ (**3**) which contains unreactive Ru–Cl bonds. The isomerization of **2**, which is induced under sun light exposure, is the preliminary step to the selective formation of the *all-cis* bis(enolato-phosphane) derivative *(ccc)*-$Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**9**). The isomeric bis(enolato-phosphane) derivative *(cct)*-$Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**10**), with *trans* phosphorus and *cis* carbonyl ligands, respectively, was selectively obtained under mild basic conditions, starting from *(cct)*-$RuCl_2(CO)_2[Ph_2PCH_2C({=}O)tBu]_2$ (**4**), which results from the reaction of **3** with carbon monoxide under thermal activation. Through an oxidative addition process, the reaction of **1** with $[NO][BF_4]$ yielded $\{RuCl_2(NO)[Ph_2PCH_2C(tBu){=}O][Ph_2PCH_2C({=}O)tBu]\}[BF_4]$ (**13**) with *trans* phosphorus and *trans* chloride ligands, respectively. Simple deprotonation of **13** generated the enolato-phosphane Ru^{IV} complex $RuCl_2(NO)[Ph_2PCH{=}C(tBu)O][Ph_2PCH_2C({=}O)tBu]$ (**14**) which retains the same geometry. Under basic conditions, the bis(enolato-phosphane) derivative $RuCl(NO)[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**15**) was obtained. The formation of **15** surprisingly showed a *trans* to *cis* rearrangement of the two phosphorus coordinating atoms, as further confirmed by an X-ray structure determination.

Introduction

Several pathways are available to the coordinatively saturated keto-phosphane complex $RuCl_2[\eta^2$-*(P,O)*-keto-phosphane$]_2$ for the incorporation of a donor ligand L (Scheme 1). These include: (i) a transformation of the coordination mode of the functional phosphane involving opening of the Ru-oxygen bond, (ii) the abstraction of one chloride generating a cationic derivative, or (iii) the formal (and nonreductive) elimination of HCl under basic conditions, facilitated by concomitant enolisation of the keto-phosphane ligand. To date, the first of these mechanistic possibilities, namely the change in coordination mode from η^2-*(P,O)* to η^1-*(P)* is well documented.[1−13] In order to emphasise the interest of an alternative preliminary cleavage of one Ru−Cl bond, the synthesis of a coordinatively unsaturated and highly reactive $\{RuCl[\eta^2$-*(P,N)*-functional phosphane$]_2\}^+$ species has been achieved starting from $RuCl_2[\eta^2$-*(P,N)*-functional phosphane$]_2$ complexes.[14] We report herein further comparison between these distinct reactivities, starting from a $RuCl_2[\eta^2$-*(P,O)*-keto-phosphane$]_2$ complex, namely $RuCl_2[Ph_2PCH_2C(tBu){=}O]_2$ (**1**)[11] and using carbon monoxide as an entering substrate L. The generation, under mild basic conditions, of rigid and strongly bound η^2-*(P,O)*-enolato-phosphane ligands leading to



Scheme 1

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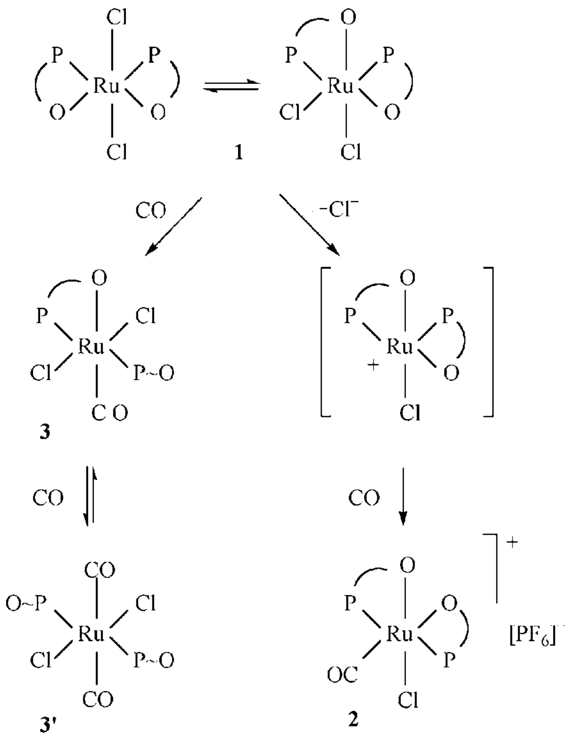
stability in stereoisomeric $Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(t Bu)O]_2$ derivatives is of interest. The reaction of $[NO][BF_4]$ with **1** afforded a new family of ruthenium(IV) derivatives. The bis(enolato-phosphane) complex $RuCl(NO)[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(t Bu)O]_2$ has been characterised by an X-ray structure determination.

Results and Discussion

1. Cationic (Keto-phosphane) Complexes Involving Carbon Monoxide

A cleavage of one Ru−Cl bond is likely to have occurred when $RuCl_2[Ph_2PCH_2C(t Bu){=}O]_2$ (**1**) (which behaves in solution as a mixture of two isomers with *cis* phosphorus and *trans* or alternatively *cis* chlorine coordinating atoms)[11] was reacted with a solution of $[NH_4][PF_6]$ in methanol. The examination of the resulting orange solution by $^{31}P\{^1H\}$ NMR spectroscopy showed a new set of resonances consisting of an AB spin system as expected for two inequivalent phosphorus *nuclei* and the observation of a low coupling constant value (^2J = 40.0 Hz) which indicated a retention of their mutual *cis* arrangement.[15] A subsequent admittance of a carbon monoxide atmosphere resulted in the formation of the cationic complex $\{RuCl(CO)[\eta^2$-*(P,O)*-$Ph_2PCH_2C(t Bu){=}O]_2\}[PF_6]$, **2**, which was isolated as orange-yellow crystals in 65% yield (Scheme 2). The structure of **2** was determined from a combination of elemental analysis, IR spectroscopy and ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^{13}C NMR spectroscopy. Elemental analysis indicated a retention of one chlorine atom *per* Ru. The $^{31}P\{^1H\}$ NMR spectrum consisted of an AB spin system and a high coupling constant value (^2J = 328 Hz) indicated a relative *trans* arrangement of the two phosphorus *nuclei*. The IR spectrum of **2** indicated that the two keto-phosphane ligands [ν(C=O): 1621 and 1596 cm^{-1}] are η^2-*(P,O)*-coordinated,[11] and produced a very strong absorption attributed to the carbon monoxide ligand [ν(C≡O): 1991, 1977 cm^{-1} (the absorption is slightly split at its summit, most likely due to a solid state effect)]. The examination of **2** by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy provided further evidence for one carbon monoxide ligand and two inequivalent keto-phosphane ligands, thus again indicating that the two coordinated oxygen atoms are located in a relative *cis* arrangement. The neutral complex $RuCl_2(CO)[\eta^2$-*(P,O)*-$Ph_2PCH_2C(t Bu){=}O][\eta^1$-*(P)*-$Ph_2PCH_2C({=}O)t Bu]$ (**3**)[11] was obtained when a solution of **1** and $[NH_4][PF_6]$ in methanol was stirred under a carbon monoxide atmosphere. Attempts to obtain **2** by reacting **3** with $[NH_4][PF_6]$ or $Ag[BF_4]$ failed.

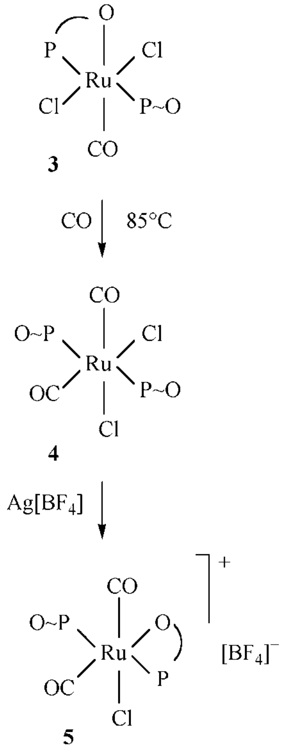


P–O: $Ph_2PCH_2C({=}O)t Bu$

Scheme 2

A preliminary cleavage of one Ru−Cl bond from **1** may account for the formation of **2** and not surprisingly, the reaction of $Ag[BF_4]$ with a solution of **1** in dichloromethane similarly generated a new species as shown by $^{31}P\{^1H\}$ NMR spectroscopy (see Exp. Sect.). Removal of the solvent resulted in the fast decomposition and further characterisation of the likely unsaturated species was not attempted. The distinct chemical pathways leading to **2** and **3** involve a *cis* to *trans* rearrangement of the phosphorus coordinating atoms. Requirement of an entrance of carbon monoxide *trans* relative to a coordinated oxygen atom may be responsible for the rearrangement achieving *trans* O−Ru−CO arrangements in **2** and **3**. Since complex **3** reversibly adds carbon monoxide to generate the fragile derivative *all-trans* $RuCl_2(CO)_2[\eta^1$-*(P)*-$Ph_2PCH_2C({=}O)t Bu]_2$ (**3′**)[11] (Scheme 2), we looked for a comparison between the hemilabile properties of the keto-phosphane ligands in complexes **2** and **3**.

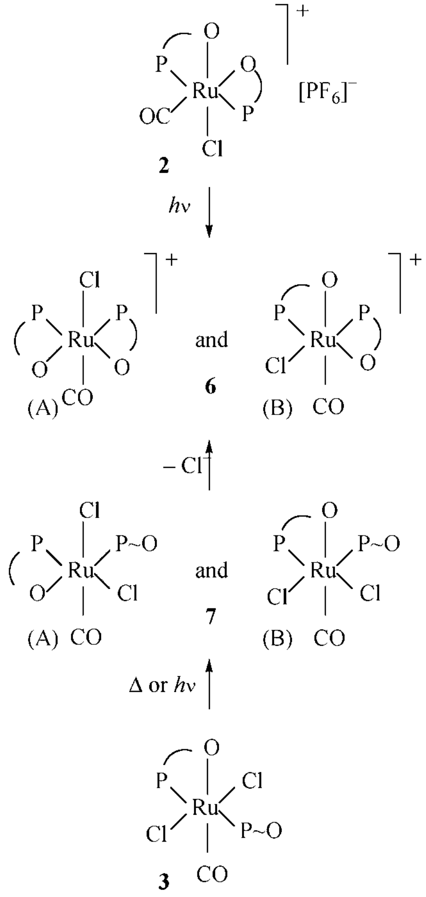
Under a moderate thermal activation, as previously reported, when starting from $RuCl_2$[ether-phosphane]$_2$ complexes,[10] complex **3** irreversibly added carbon monoxide to yield $RuCl_2(CO)_2[Ph_2PCH_2C({=}O)t Bu]_2$ the *cis,cis,trans* stereoisomer, **4** (Scheme 3) as it is thermodynamically favoured and stable. Thus, complex **4** was isolated as colourless crystals in 92% yield after a solution of **3** in hot toluene (85 °C) was stirred under a carbon monoxide atmosphere. The IR spectrum of **4** showed the two carbonyl ligands [ν(C≡O): 2056, 1992 cm^{-1}] to be in a relative *cis* arrangement besides a single absorption [ν(C=O): 1705 cm^{-1}] as expected for two equivalent η^1-*(P)*-coordinated keto-phosphanes. The $^{31}P\{^1H\}$ NMR spectrum consisted of a single resonance and the ^1H NMR spectrum showed the resonance attributed to the four equivalent PCH_2 protons as a virtual triplet. A clean reaction occurred when a stoichiometric amount of $Ag[BF_4]$ was added to a solution of **4** in dichloromethane and afforded the expected cationic derivative **5** which was also isolated as colourless crystals in 80% yield (Scheme 3). The formation of **5** merely consists of the removal of one chloride ligand from **4** allowing an η^2-*(P,O)*-coordination of one keto-phosphane ligand. As expected, the two keto-phosphane ligands in **5** were found inequivalent by $^{31}P\{^1H\}$ NMR spectroscopy and the observation of a high coupling constant value (^2J = 305 Hz) indicated a relative *trans* arrangement of the phosphorus *nuclei*. The IR spectrum of **5** showed that the two carbonyl ligands [ν(C≡O): 2072, 2015 cm^{-1}] are in a relative *cis* arrangement but that the distinct absorptions [ν(C=O): 1707, 1614 cm^{-1}] are attributable to the two keto-phosphane ligands, which are η^1-*(P)*- and η^2-*(P,O)*-coordinated, respectively.



Scheme 3

Complexes **2** and **5** are both stable and inert under a carbon monoxide atmosphere. Thus, a straightforward comparison of their structures is enough to emphasise an unusual strength of the O→Ru bonds in cationic complex **2**: an easy cleavage would allow carbon monoxide fixation by **2** resulting in formation of **5**.

Emphasising the easiness of photochemical activation, sun light exposure of a dichloromethane solution of **2** cleanly produced a pale precipitate of **6** which was collected in 82% yield (Scheme 4). In contrast, complex **2** decomposed under thermal activation (ethanol at reflux). The $^{31}P\{^1H\}$ NMR spectrum of **6** disclosed besides a single resonance, an AB spin system with a low coupling constant value (^2J = 24.0 Hz), thus suggesting a mixture of two species. At least one of them involves two phosphorus coordinating atoms in a relative *cis* arrangement. The ^1H NMR spectrum only allowed the determination of the relative abundance of the major unsymmetrical species in solution, and owing to a very low solubility, we failed to obtain a tractable $^{13}C\{^1H\}$ NMR analysis. Therefore, we sought for chemical evidence providing further information concerning the structure of **6**.

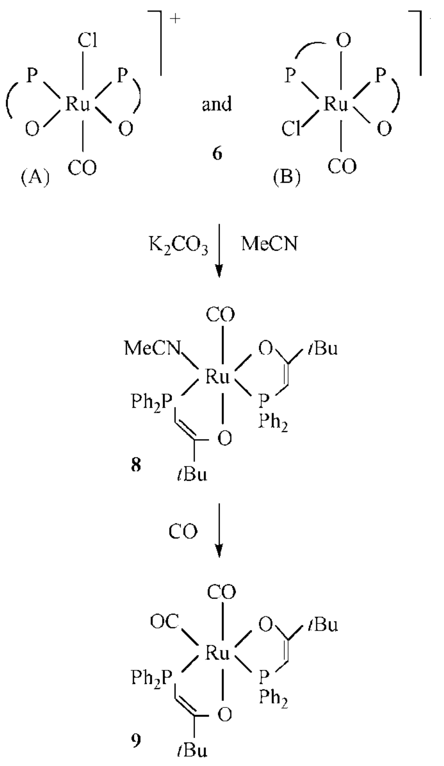


Scheme 4

A rearrangement of complex **3** similarly occurred under sun light exposure but also under thermal activation, to afford **7** as a mixture of two isomers both disclosing a relative *cis* arrangement of the phosphorus atoms by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 4). As expected for a mixture of two isomers, the $^{13}C\{^1H\}$ NMR spectrum disclosed two C≡O resonances and the observation of low $^2J_{PC}$ coupling constant values (^2J = 23 and 27 Hz, respectively) indicated that carbon monoxide was located in a *cis* position relative to the two phosphorus atoms. Only two structures, namely (A) and (B) in Scheme 4, remained conceivable on the basis of a *facial* arrangement of a carbon monoxide ligand and two phosphorus coordinating atoms. When compared to ether-phosphane complexes,[11] the relative abundance of the two isomers was also found to be solvent dependent by ^1H NMR spectroscopy (see Exp. Sect.), but no fluxional process between the coordinating modes of the two keto-phosphane ligands was observed at ambient temperature. Of further interest with respect to this study is the addition of $[NH_4][PF_6]$ to a solution of **7** in methanol which immediately resulted in the formation of a precipitate of **6.** Abstraction of one chloride ligand located *trans* relative to a phosphorus atom in **7**, affords the mixture of isomers which is assumed for **6** (Scheme 4).

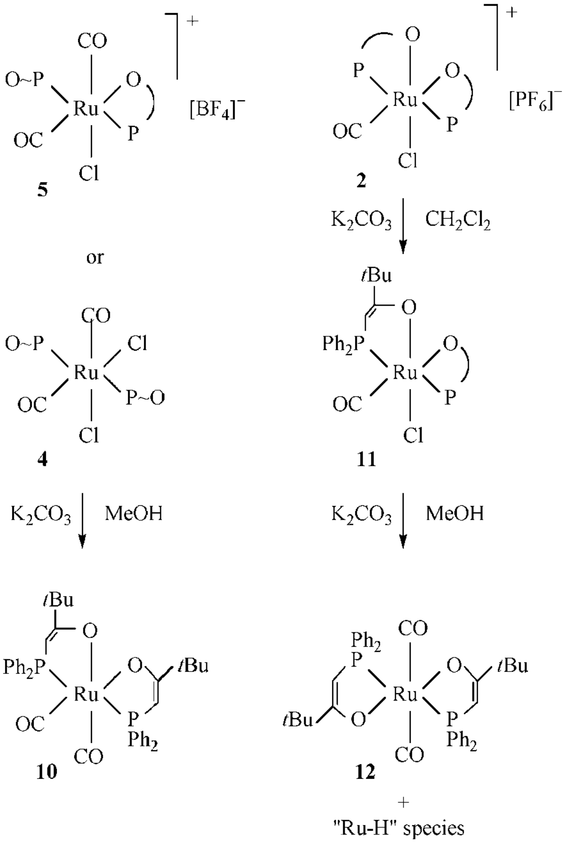
2. Neutral Bis(enolato-phosphane) Complexes Involving Carbon Monoxide

Owing to the very low solubility of **6** and the presence of two isomers for both **6** and **7**, some doubt remained concerning their structures. Complex **6** reacted with acetonitrile and K_2CO_3 resulting in a nearly quantitative formation of the neutral bis(enolato-phosphane) complex Ru(CO)(MeCN)[η^2-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**8**) and further reaction of **8** with carbon monoxide selectively led to the bis(enolato-phosphane) derivative *all-cis* $Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**9**) the structure of which was unambiguously determined (Scheme 5). $^{31}P\{^1H\}$ NMR spectroscopic studies were enough to specify the structure of **9** and indicated two inequivalent enolato-phosphane ligands and also showed that the phosphorus atoms are in a relative *cis* arrangement (^2J = 24.0 Hz). The ^1H NMR spectrum of **9** showed two distinct PCH= protons whereas a relative *cis* arrangement of the two carbonyl ligands was inferred from both IR and $^{13}C\{^1H\}$ NMR spectroscopy.



Scheme 5

The reaction of **4** or **5** with carbon monoxide under basic conditions (K_2CO_3 in methanol) was found to be very selective and afforded the bis(enolato-phosphane) derivative $Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**10**) with *cis* carbonyl ligands, *cis* oxygen and *trans* phosphorus coordinating atoms (Scheme 6). Complex **10** is a stereoisomer of **9**. Its IR spectrum indicated the relative *cis* arrangement of the two C≡O ligands and the conversion of both keto-phosphanes from **4** (or **5**), into enolato-phosphane ligands that were found to be equivalent by $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of **10** showed the resonance, attributed to the two equivalent PCH= protons, as a virtual triplet, as expected from a mutual *trans* arrangement of the two phosphorus coordinating atoms.

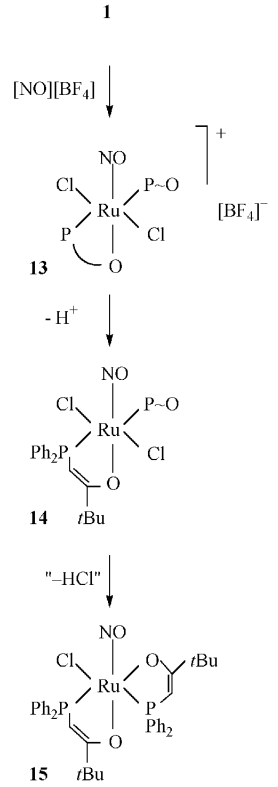


Scheme 6

Owing to its structure with *trans* phosphorus and *cis* oxygen coordinating atoms, the cationic complex **2** may appear as a precursor for the access to **10**. However, the reaction of **2** and K_2CO_3 in dichloromethane selectively afforded the *all-trans* derivative **11** (Scheme 6). We had previously reported the synthesis of **11** starting from **3** and allowing the access of a third stereoisomer of **9** and **10**, namely *all-trans* $Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH{=}C(tBu)O]_2$ (**12**).[11] When compared to the nearly quantitative synthesis of **9** and **10**, complex **12** was previously obtained in a markedly lower yield (24%). Therefore, the formation of **12** was re-investigated. Complex **11** was reacted with K_2CO_3 in methanol under a carbon monoxide atmosphere and the resulting crude material was examined by $^{31}P\{^1H\}$NMR spectroscopy that disclosed a mixture of **12** and of a second unidentified species but neither **9** nor **10** were detected. Fractional crystallization allows pure **12** to be obtained but we failed to isolate the second species which is likely a Ru−H complex as suggested by ^1H NMR spectroscopy (see Exp. Sect.).

3. Neutral Bis(enolato-phosphane) Complexes Involving Nitrogen Monoxide

The nitrosonium cation $[NO]^+$ is isoelectronic with carbon monoxide but also a strong oxidising reagent and the reaction of $[NO][BF_4]$ with a $RuCl_2$(ether-phosphane)$_2$ complex had proved to result in a Ru^{II} to Ru^{III} oxidation.[1] By contrast, the reaction of **1** with $[NO][BF_4]$ in dichloromethane afforded an orange solid that may be assumed to mainly contain *all-trans* (on the basis of two *trans* phosphorus and two *trans* chlorine coordinating atoms) $\{RuCl_2(NO)[Ph_2PCH_2C(tBu){=}O][Ph_2PCH_2C({=}O)tBu]\}[BF_4]$ (**13**). The structure of **13** was suggested by spectroscopic studies. The IR spectrum of **13** showed besides the characteristic absorption attributed to the $[BF_4]^-$ counter anion, a very strong absorption attributed to a nitrosyl ligand [ν(NO): 1884 cm^{-1}] and two absorptions [ν(C=O): 1701 cm^{-1} and 1595 cm^{-1}] emphasising two distinct keto-phosphane ligands, that are η^1-*(P)*- and η^2-*(P,O)*-coordinated, respectively. $^{31}P\{^1H\}$ NMR spectroscopy indicated a relative *trans* arrangement of the two inequivalent phosphorus *nuclei*, but ^1H NMR spectroscopy indicated two equivalent PCH_2 protons for each keto-phosphane, as may be expected when two chloride ligands are in a relative *trans* arrangement. Unfortunately, attempts of purification of **13** failed, instead affording the stable enolato-phosphane derivative *all-trans* $RuCl_2(NO)[Ph_2PCH{=}C(tBu)O][Ph_2PCH_2C({=}O)tBu]$ (**14**) (Scheme 7). The structure of **14** was similarly determined by spectroscopic studies but also elemental analysis and a peculiarly easy deprotonation of the η^2-*(P,O)*-coordinated keto-phosphane ligand in **13** straightforwardly accounts for the formation of **14**. A formal removal of HCl from **14** was achieved under basic conditions (KOH or K_2CO_3 in methanol) and afforded the bis(enolato-phosphane) complex $RuCl(NO)[Ph_2PCH{=}C(tBu)O]_2$ (**15**) which surprisingly showed a relative *cis* arrangement of the phosphorus coordinating atoms (Scheme 7). The spectroscopic data collected for **15** only allowed us to further specify a structure involving two distinct enolato-phosphane ligands but did not provide any information on the symmetry.



Scheme 7

A complete determination of the structure of **15** was achieved by an X-ray analysis that revealed a distorted octahedron (Figure 1). Examination of bond angles clearly indicated that the nitrosyl ligand behaves as a 3e-donor [O(1)−N(1)−Ru: 172.88(16)°] and is located *trans* relative to an oxygen atom [N(1)−Ru−O(3): 174.40(7)°].[16] The two phosphorus atoms are in a relative *cis* arrangement [P(1)−Ru−P(2): 101.685(18)°] and located *trans* relative to the oxygen [O(2)−Ru−P(1): 167.43(4)°] and chlorine [Cl(1)−Ru−P(2): 166.697(19)°] atoms. The two Ru−O bond lengths [Ru−O(3): 1.9930(13), Ru−O(2): 2.0820(13) Å] account for distinct *trans* influences from nitrosyl and phosphorus, whereas the two Ru−P bonds lengths [Ru−P(1): 2.3409(5), Ru−P(2): 2.3646(5) Å] remain close. The lengths of the C=C bonds involved in the two cycles [C(1)−C(2): 1.350(3), C(19)−C(20): 1.365(3) Å] are normal as expected for enolato-phosphane ligands.

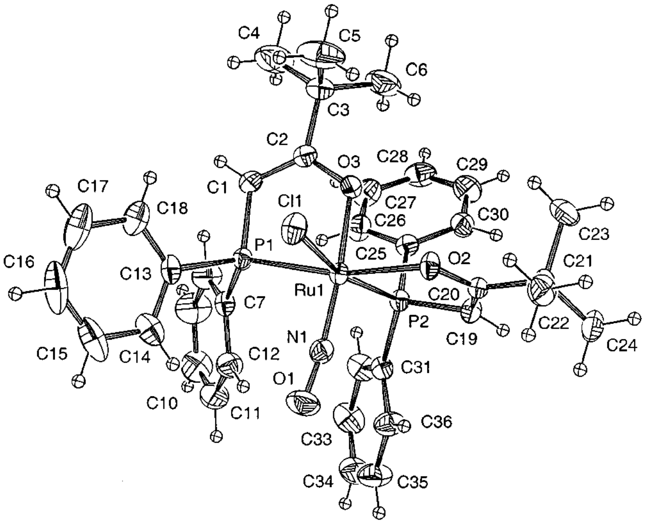


Figure 1. ORTEP drawing of $RuCl(NO)[Ph_2PCH{=}C(tBu)O]_2$ **(15)** showing 50% thermal ellipsoids; selected bond lengths (Å) and angles (°): Ru(1)−N(1) 1.7355(17), Ru(1)−O(3) 1.9930(13), Ru(1)−O(2) 2.0820(13), Ru(1)−P(1) 2.3409(5), Ru(1)−P(2) 2.3646(5), Ru(1)−Cl(1) 2.4193(5), O(1)−N(1) 1.162(2), C(1)−C(2) 1.350(3), C(19)−C(20) 1.365(3), N(1)−Ru(1)−O(3) 174.40(7), N(1)−Ru(1)−O(2) 99.30(7), O(3)−Ru(1)−O(2) 86.30(6), N(1)−Ru(1)−P(1) 92.74(5), O(3)−Ru(1)−P(1) 81.67(4), O(2)−Ru(1)−P(1) 167.43(4), N(1)−Ru(1)−P(2) 94.15(6), O(3)−Ru(1)−P(2) 86.65(4), O(2)−Ru(1)−P(2) 81.16(4), P(1)−Ru(1)−P(2) 101.685(18), N(1)−Ru(1)−Cl(1) 94.42(6), O(3)−Ru(1)−Cl(1) 85.82(4), O(2)−Ru(1)−Cl(1) 87.42(4), P(1)−Ru(1)−Cl(1) 88.051(18), P(2)−Ru(1)−Cl(1) 166.697(19), O(1)−N(1)−Ru(1) 172.88(16)

The *trans* to *cis* rearrangement of the two phosphorus coordinating atoms which is involved in the **14** to **15** transformation is intriguing because no pentacoordinated intermediate that still contains a strongly bonded enolato-phosphane ligand is expected from **14**. A possible pathway leading to **15** will consist of a preliminary deprotonation of the η^1-*(P)*-coordinated keto-phosphane in **14**. The coordination of the anionic oxygen atom may occur as a result of the ability of nitrosyl ligands to behave as either a 3e or 1e donor and this will generate an heptacoordinated intermediate transiently scrambling the octahedral structure.[17] Subsequent elimination of one chloride anion achieves the formation of **15**. From a steric point of view, complex **15** seems very close when compared to the bis(enolato-phosphane) complexes **9**, **10** and **12**, which seem equally stable, providing evidence for a lack of steric constraints.

Conclusion

The coordination of the oxygen atoms from the two keto-phosphane ligands leads to an unusually strong stabilization in the cationic complex $\{RuCl(CO)[Ph_2PCH_2C(tBu)=O]_2\}[PF_6]$ (**2**). The stereoisomeric *all-cis*, *cct,* and *all-trans* $Ru(CO)_2[\eta^2$-*(P,O)*-$Ph_2PCH=C(tBu)O]_2$ complexes, were selectively obtained under mild conditions and such a result indicates high energetic barriers between the three corresponding families of compounds. Thus, the behaviour of complex **2** under mild basic conditions clearly shows **2** to be an *all-trans* derivative. However, the families are strongly related to the number x of carbon monoxide ligands: the observation of the *cct* family requires $x = 2$ whereas only *all-trans* and *all-cis* derivatives are observed when $x = 1$, and a distinct geometry was observed when $x = 0$. As new evidence for synthetic usefulness, the precursor $RuCl_2[Ph_2PCH_2C(tBu)=O]_2$ (**1**) is able to coordinate not only carbon monoxide but also the isolelectronic nitrosonium cation. The coordination of $[NO]^+$ thus provides an entry to a family of octahedral ruthenium (IV) complexes such as $RuCl(NO)[\eta^2$-*(P,O)*-$Ph_2PCH=C(tBu)O]_2$, (**15**), the reactivity of which is under investigation.

Experimental Section

General: The reactions were performed according to Schlenk type techniques. Solvents were distilled under an inert atmosphere after drying according to conventional methods. Elemental analyses were performed by the "Service de Microanalyse du CNRS" Vernaison, France. Infrared spectra were recorded on a Nicolet 205 FT-infrared spectrometer as Nujol mulls. NMR spectra were recorded at 297 K on 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; vt, virtual triplet; m, unresolved multiplet. The precursor complex $RuCl_2[Ph_2PCH_2C(tBu)=O]_2$ (**1**) was synthesised as reported previously.[11]

Generation of the $\{RuCl[Ph_2PCH_2C(tBu)=O]_2\}^+$ Species: An aliquot of the solution resulting from the reaction of **1** with NH_4PF_6 in methanol (see synthesis of **2**) was examined by $^{31}P\{^1H\}$ NMR spectroscopy ($MeOH/CDCl_3$): δ = 62.8 (d), 70.7 (d), ^2J = 38 Hz. However, a second and minority species was detected: δ = 67.1 (d), 68.4 (d), ^2J = 37 Hz. In another experiment, an equivalent amount of $Ag[BF_4]$ was added to a solution of **1** in CH_2Cl_2. The mixture was stirred for 1 h and decanted. The supernatant solution was examined by $^{31}P\{^1H\}$ NMR spectroscopy (CH_2Cl_2/CD_2Cl_2): δ = 63.7 (d), 73.2 (d), ^2J = 39 Hz. Only one species was observed in CH_2Cl_2 suggesting that the observation of a second set of resonances in methanol indicated a solvated species.

***trans*-*(P,P)*-$\{RuCl(CO)[Ph_2PCH_2C(tBu)=O]_2\}[PF_6]$ (2):** A mixture consisting of sample **1** (5.20 g, 7.02 mmol) and NH_4PF_6 (1.20 g, 7.36 mmol) in methanol (80 mL), under an inert atmosphere, was stirred overnight to obtain an orange solution that was then stirred for 2 h under a carbon monoxide atmosphere. The resulting yellow precipitate was collected by filtration and then extracted with dichloromethane (40 mL). The solution was filtered and the filtrate was covered with methanol (20 mL) and diethyl ether (130 mL) to afford orange-yellow crystals. Yield: 4.00 g, 65%. IR: $\nu(C{\equiv}O)$ = 1991, 1977 cm^{-1}; $\nu(C=O)$ = 1621, 1596 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 35.0 (d), 48.4 (d, ^2J = 328 Hz). ^{1}H NMR (CD_2Cl_2): δ = 0.93 (s, 9 H, *t*Bu), 1.06 (s, 9 H, *t*Bu), 3.72 (dd, 1 H, $^2J_{H,H}$ = 18.7, $^2J_{PH}$ = 11.2 Hz, PCH_2, H_a), 3.97 (dd, 1 H, $^2J_{H,H}$ = 17.9, $^2J_{PH}$ = 11.1 Hz, $P'CH_2$, H_a), 4.74 (ddd, 1 H, $^2J_{H,H}$ = 17.9, $^2J_{PH}$ = 11.4, $^4J_{PH}$ = 3.1 Hz, $P'CH_2$, H_b), 4.83 (ddd, 1 H, $^2J_{H,H}$ = 18.7, $^2J_{PH}$ = 10.4 Hz, $^4J_{PH}$ = 1.5 Hz, PCH_2, H_b), 7.45−7.99 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 26.7 (s, CMe_3), 26.8 (s, CMe_3), 42.9 (d, $^1J_{PC}$ = 26.2 Hz, PCH_2), 43.4 (d, $^1J_{PC}$ = 26.9 Hz, PCH_2), 47.1 (d, $^3J_{PC}$ = 2.9 Hz, CMe_3), 47.7 (d, $^3J_{PC}$ = 3.4 Hz, CMe_3), 127.4−134.3 (m, 2 Ph_2P groups), 202.3 (dd, $^2J_{PC}$ = 13.6 and 11.4 Hz, $C{\equiv}O$), 235.9 (dd, $^2J_{PC}$ = 6.2, $^3J_{PC}$ = 4.9 Hz, C=O), 239.6 (dd, $^2J_{PC}$ = 5.5, $^3J_{PC}$ = 3.8 Hz, C=O). $C_{37}H_{42}ClF_6O_3P_3Ru$ (878.2): calcd. C 50.61, H 4.82, Cl 4.04, P 10.58; found C 50.82, H 4.89, Cl 4.03, P 10.23.

***ttt*-$RuCl_2(CO)[Ph_2PCH_2C(=O)tBu][Ph_2PCH_2C(tBu)=O]\cdot 2/3CH_2Cl_2$ (3):** The synthesis of **3** starting from **1** was reported previously.[11] A more straightforward synthesis starting from $[RuCl_2(p\text{-cymene})]_2$ is described herein. A mixture consisting of a sample of $[RuCl_2(p\text{-cymene})]_2$ (3.91 g, 6.38 mmol) and keto-phosphane $Ph_2PCH_2C(tBu)=O$ (7.26 g, 25.5 mmol) was dissolved in dichloromethane (60 mL) and methanol (140 mL) was then added. This mixture was stirred for 3 days under a carbon monoxide atmosphere and the resulting orange-yellow slurry was concentrated under vacuum. Diethyl ether was first added to collect the yellow precipitate. The solid was washed with diethyl ether then dried under vacuum and identified as *all-trans* $RuCl_2(CO)_2[Ph_2PCH_2C(=O)tBu]$, **3′**, by IR spectroscopy.[11] (Yield: 8.30 g, 82%). The crude product was dissolved in dichloromethane (50 mL) and the orange solution was stirred overnight in an open Erlenmeyer flask allowing the evolution of one mol of carbon monoxide. The solution was then covered with ethanol (250 mL) and the natural preferential evaporation of dichloromethane resulted in the formation of yellow crystals of **3**. Yield: 7.75 g, 74%. IR and NMR spectroscopic data as reported previously.[11]

***cct*-$RuCl_2(CO)_2[Ph_2PCH_2C(=O)tBu]_2$ (4):** A mixture consisting of a sample of **1** (4.06 g, 4.92 mmol) (or corresponding amounts of **3** or **3′**) and hot toluene (50 mL, 85 °C) was stirred for 2 days under a carbon monoxide atmosphere. The resulting colourless solution was evaporated under vacuum to leave a solid that was dissolved in dichloromethane (20 mL). Methanol (35 mL) was added and slow evaporation of the solution afforded colourless crystals of **4**. Yield: 3.59 g, 92%. IR: ν(C≡O) = 2056, 1992 cm^{-1}; ν(C=O) = 1705 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 19.2 (s). ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.82 (s, 18 H, 2 *t*Bu), 4.43 (vt, 4 H, $|^2J_{PH} + {}^4J_{PH}|$ = 7.7 Hz, 2 PCH$_2$), 7.38−7.84 (m, 20 H, Ph). C$_{38}$H$_{42}$Cl$_2$O$_4$P$_2$Ru (796.7): calcd. C 57.29, H 5.31, Cl 8.90, P 7.78; found C 57.40, H 5.29, Cl 8.85, P 7.76.

{RuCl(CO)$_2$[Ph$_2$PCH$_2$C(=O)*t*Bu][Ph$_2$PCH$_2$C(*t*Bu)=O]}[BF$_4$] (5): A mixture consisting of a sample of **4** (1.00 g, 1.26 mmol) and Ag[BF$_4$] (0.25 g, 1.28 mmol) in dichloromethane (30 mL) was stirred overnight. The resulting solution was decanted, then filtered and covered with diethyl ether (80 mL) to afford colourless crystals of **5**. Yield: 0.86 g, 80%. IR: ν(C≡O) = 2072, 2015 cm^{-1}; ν(C=O) = 1707, 1614 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 19.3 (d), 44.8 (d, ^2J = 305 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.02 (s, 9 H, *t*Bu), 1.05 (s, 9 H, *t*Bu), 4.04 (dd, 1 H, $^2J_{H,H}$ = 17.0, $^2J_{PH}$ = 10.2 Hz, P′CH$_2$, H$_a$), 4.15 (dd, 1 H, $^2J_{H,H}$ = 18.5, $^2J_{PH}$ = 11.8 Hz, PCH$_2$, H$_a$), 4.51 (dd, 1 H, $^2J_{H,H}$ = 16.8, $^2J_{PH}$ = 9.1 Hz, P′CH$_2$, H$_b$), 4.79 (dd, broad, 1 H, $^2J_{H,H}$ ≈ 18.5 Hz, $^2J_{PH}$ ≈ 12.0 Hz, PCH$_2$, H$_b$), 7.35−7.90 (m, 20 H, Ph). C$_{38}$H$_{42}$BClF$_4$O$_4$P$_2$Ru (848.0): calcd. C 53.82, H 4.99, Cl 4.18, P 7.30; found C 53.66, H 5.11, Cl 5.02, P 7.06, retention of some dichloromethane is likely to be responsible for the high chlorine value.

***cis-(P,P)*-{RuCl(CO)[Ph$_2$PCH$_2$C(*t*Bu)=O]$_2$}[PF$_6$] (6):** A Schlenk flask was filled with a solution consisting of a sample of **2** (4.11 g, 4.68 mmol) in dichloromethane (60 mL). The flask was then exposed to sunlight. After three weeks (corresponding to ≈ 70 h of exposure according to our feasibility) the resulting cream-coloured precipitate was collected by filtration, then washed with diethyl ether (50 mL). Yield: 3.39 g, 82%. IR: ν(C≡O) = 1995 cm^{-1}; ν(C=O) = 1613 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$), asterisk marked values for the unsymmetrical isomer: δ = 55.3* (d), 56.2 (s), 62.5* (d), ^2J = 24 Hz*. ^{1}H NMR (CD$_2$Cl$_2$), asterisk marked values for the unsymmetrical and major (3:1) isomer: δ = 1.15* (s, *t*Bu), 1.41 (s, *t*Bu), 1.45* (s, *t*Bu), 3.63* (dd, $^2J_{H,H}$ = 18.6 Hz, $^2J_{PH}$ = 9.9 Hz, 1 H from a PCH$_2$ group), 4.21−4.30 (m, 2 H from PCH$_2$* groups, and 4 H from the two equivalent PCH$_2$ that showed close chemical shifts of the inequivalent protons), 4.56* (dd, $^2J_{H,H}$ = 18.7 Hz, $^2J_{PH}$ = 10.2 Hz, 1 H from a PCH$_2$ group), 6.56−7.87 (m, 20 H, Ph, both isomers). C$_{37}$H$_{42}$ClF$_6$O$_3$P$_3$Ru (878.2): calcd. C 50.61, H 4.82, Cl 4.04, P 10.58; found C 50.71, H 4.92, Cl 4.18, P 10.69.

***ccc*-RuCl$_2$(CO)[Ph$_2$PCH$_2$C(=O)*t*Bu][Ph$_2$PCH$_2$C(*t*Bu)=O] (7):** A mixture consisting of a sample of **3** (7.53 g, 9.12 mmol) and toluene (80 mL), was heated to reflux for 20 h to afford a pale-yellow precipitate that was collected by filtration then washed with hexane and dried under vacuum. Yield: 5.63 g, 80%. Exposure of a solution of **3** in dichloromethane (as detailed for synthesis of **6**) to sunlight afforded a mixture of **6** and remaining **3**. Despite the fact that pale-yellow crystals were obtained upon addition of diethyl ether to a concentrated solution of the crude solid in dichloromethane, we failed to obtain **7** in a high state of purity as shown by elemental analyses. IR: ν(C≡O) = 1968 cm^{-1}; ν(C=O) = 1703, 1629 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$), asterisk marked values for the major isomer: δ = 41.7 (broad), 47.4* (d), 47.8* (d), 59.7 (d, ^2J = 23 and 27 Hz*). C$_{37}$H$_{42}$Cl$_2$O$_3$P$_2$Ru (768.7): calcd. C 57.82, H 5.51, Cl 9.22, P 8.06; found C 56.96, H 5.56, Cl 10.62, P 7.90. Attempts at recrystallization from hot acetonitrile yielded yellow crystals that retain acetonitrile (≈ 1.3 MeCN/Ru) but no significant change was observed from ^{31}P{^{1}H} NMR and IR spectroscopy. A concomitant crystallization of the two isomeric forms with only one retaining some solvent may account for the failure in obtaining a satisfactory elemental analysis. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$), asterisk marked values for the major isomer: δ = 39.9 (broad), 45.8* (d), 47.8* (d), 58.8 (d, ^2J = 23 and 27 Hz*). ^{1}H NMR (CD$_2$Cl$_2$), asterisk marked values for the major isomer: δ = 0.59 (s, *t*Bu), 0.70* (s, *t*Bu), 1.05 (s, *t*Bu), 1.28* (s, *t*Bu), 1.94 (s, MeCN), 2.62 (m, broad, 1 H from a PCH$_2$ group), 3.14 (m, broad, 1 H from a PCH$_2$ group), 4.02−4.30 (m, 5 H from PCH$_2$ groups), 4.67* (dd, $^2J_{H,H}$ = 17.2 Hz, $^2J_{PH}$ = 7.4 Hz, 1 H from a PCH$_2$ group), 6.75−7.86 (m, Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 2.2 (s, *Me*CN), 25.8 (s, C*Me*$_3$), 25.8 (s, C*Me*$_3$), 27.0 (s, C*Me*$_3$), 27.0 (s, C*Me*$_3$), 36.9 (d, $^1J_{PC}$ = 28.0 Hz, PCH$_2$), 37.4 (d, $^1J_{PC}$ = 33.4 Hz, PCH$_2$), 45.4 (d, $^3J_{PC}$ = 1.5 Hz, *C*Me$_3$), 45.9 (m, 2 *C*Me$_3$), 46.0 (d, $^3J_{PC}$ = 3.9 Hz, *C*Me$_3$), 47.2 (d, broad, $^1J_{PC}$ = 35.3 Hz, PCH$_2$), 49.0 (d, $^1J_{PC}$ = 31.5 Hz, PCH$_2$), 117.1 (s, Me*C*N), 127.7−137.5 (phenyl-groups resonances), 197.9 (dd, $^2J_{PC}$ = 17.7 and 13.0 Hz, C≡O), 204.3 (dd, $^2J_{PC}$ = 17.5 and 14.3 Hz, C≡O), 209.6 (d, $^2J_{PC}$ = 6.4 Hz, C=O), 209.7 (d, $^2J_{PC}$ = 10.7 Hz, C=O), 227.9 (d, $^2J_{PC}$ = 3.3 Hz, C=O), 228.4 (broad, C=O). Isomeric ratio as determined by ^{1}H NMR spectroscopy: 3:1 in CDCl$_3$, < 5:4 in CD$_2$Cl$_2$.

***ccc*-Ru(CO)(MeCN)[Ph$_2$PCH=C(*t*Bu)O]$_2$ (8):** A mixture consisting of a sample of **6** (3.39 g, 3.86 mmol), K$_2$CO$_3$ (1.20 g, 8.68 mmol) and acetonitrile (50 mL), was stirred overnight and then evaporated to dryness. The remaining solid was extracted with dichloromethane (50 mL). The solution was filtered and the clear filtrate was evaporated under vacuum to leave a cream-coloured powder that was found by NMR spectroscopy and elemental analysis to be pure. Yield: 2.62 g, 92%. IR: ν(C≡N) = 2325 cm^{-1}; ν(C≡O) = 1924 cm^{-1}; ν(C=CO) = 1506, 1493 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 45.3 (d), 48.8 (d), ^2J = 27. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.92 (s, 9 H, *t*Bu), 1.22 (s, 9 H, *t*Bu), 1.54 (s, 3 H, MeCN), 4.09 (d, 1 H, $^2J_{PH}$ = 3.5 Hz, PCH=), 4.46 (d, 1 H, $^2J_{PH}$ = 2.0 Hz, P′CH=), 6.83−7.66 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 3.1 (s, *Me*CN), 29.6 (s, C*Me*$_3$), 30.1 (s, C*Me*$_3$), 39.1 (dd, $^3J_{PC}$ = 12.6 Hz, $^4J_{PC}$ = 3.6 Hz, *C*Me$_3$), 39.2 (d, $^3J_{PC}$ = 12.6 Hz, *C*Me$_3$), 69.7 (d, $^1J_{PC}$ = 61.1 Hz, PCH=), 73.5 (d, $^1J_{PC}$ = 62.9 Hz, PCH=), 120.0 (d, $^3J_{PC}$ = 14.3 Hz, Me*C*N), 127.4−133.6 (m, phenyl-groups resonances), 134.2 (d, $^1J_{PC}$ = 51.5 Hz, PhP, *ipso*), 137.4 (d, $^1J_{PC}$ = 56.5 Hz, PhP, *ipso*), 138.9 (d, $^1J_{PC}$ = 53.1 Hz, PhP, *ipso*), 140.0 (d, $^1J_{PC}$ = 49.7 Hz, PhP, *ipso*), 198.9 (d, $^2J_{PC}$ = 17.1 Hz, =CO), 198.9 (d, $^2J_{PC}$ = 10.8 Hz, =CO), 202.7 (dd, $^2J_{PC}$ = 17.5 and 13.0 Hz, C≡O). C$_{39}$H$_{43}$NO$_3$P$_2$Ru (736.8): calcd. C 63.58, H 5.88, N 1.90, P 8.41; found C 63.28, H 6.12, N 1.96, P 8.72.

***ccc*-Ru(CO)$_2$[Ph$_2$PCH=C(*t*Bu)O]$_2$·1/6CH$_2$Cl$_2$ (9):** A solution consisting of a sample of **8** (2.50 g, 3.39 mmol) and dichloromethane (35 mL), was stirred under carbon monoxide for 20 h, and then evaporated under vacuum to dryness to leave a white solid. Yield: 2.38 g, 95%. IR: ν(C≡O) = 2051, 1972 cm^{-1}; ν(C=CO) = 1507, 1500 cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = 34.3 (d), 44.0 (d, ^2J = 24 Hz). ^{1}H NMR (C$_6$D$_6$): δ = 1.22 (s, 9 H, *t*Bu), 1.52 (s, 9 H, *t*Bu), 4.41 (dd, 1 H, $^2J_{PH}$ = 3.1 Hz, $^4J_{PH}$ = 0.7 Hz, PCH=), 4.65 (d, 1 H, $^2J_{PH}$ = 4.0 Hz, P′CH=), 6.84−7.63 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 30.0 (s, C*Me*$_3$), 30.5 (s, C*Me*$_3$), 39.8 (dd, $^3J_{PC}$ = 12.6, $^4J_{PC}$ = 2.7, *C*Me$_3$), 39.8 (d, $^3J_{PC}$ = 12.6 Hz, *C*Me$_3$), 70.8 (dd, $^1J_{PC}$ = 60.6 Hz, $^3J_{PC}$ = 3.1 Hz, PCH=), 71.8 (d, $^1J_{PC}$ = 64.6 Hz, PCH=), 128.1−140.8 (m, phenyl-groups resonances), 191.2 (dd, $^2J_{PC}$ = 102.3 and 11.7 Hz, C≡O), 199.7 (dd, $^2J_{PC}$ = 15.3 and 10.8 Hz, C≡O), 200.4 (dd, $^2J_{PC}$ = 15.3, $^3J_{PC}$ = 1.8 Hz, =CO), 200.8 (d, $^2J_{PC}$ = 14.4 Hz, =CO). C$_{38}$H$_{40}$O$_4$P$_2$Ru·1/6CH$_2$Cl$_2$ (737.9): calcd. C 62.12, H 5.51, Cl 1.60, P 8.40; found C 62.14, H 5.66, Cl 1.27, P 8.03.

***cct*-Ru(CO)$_2$[Ph$_2$PCH=C(*t*Bu)O]$_2$ (10):** A sample of **1** (4.60 g, 5.57 mmol) was converted into crude **4** (as detailed above) before adding K_2CO_3 (1.00 g, 7.24 mmol) and methanol (50 mL). This mixture was stirred for 7 days at room temperature. The solvent was then removed under vacuum to leave a white solid that was extracted with dichloromethane (30 mL). The solution was filtered and methanol (40 mL) was added to the colourless filtrate. Through slow evaporation, the mixture afforded colourless crystals of **10**. Yield: 3.04 g, 75%. IR: ν(C≡O) = 2029, 1963 cm^{-1}; ν(C=CO) = 1494 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 44.4 (s). ^1H NMR (CD_2Cl_2): δ = 0.97 (s, 18 H, 2 *t*Bu), 4.48 (vt, 2 H, $|^2J_{PH} + {}^4J_{PH}|$ = 5.8 Hz, 2 PCH=), 7.36−7.80 (m, 20 H, Ph). $C_{38}H_{40}O_4P_2Ru$ (723.8): calcd. C 63.06, H 5.57, P 8.56; found C 63.22, H 5.77, P 8.47.

Formation of *ttt*-RuCl(CO)[$Ph_2PCH=C(tBu)O$][$Ph_2PCH_2C(tBu)=O$] (11): The synthesis of **11** by reacting **3** with K_2CO_3 in dichloromethane has been reported previously.[11] Starting from **2**, complex **11** was selectively obtained also.

Formation of *ttt*-$Ru(CO)_2[Ph_2PCH=C(tBu)O]_2$ (12): A mixture consisting of a sample of **1** (0.77 g, 1.04 mmol) and K_2CO_3 (0.31 g, 2.24 mmol) in methanol (30 mL), was stirred for 4 days under a carbon monoxide atmosphere. The solvent was then removed under vacuum and the residue was extracted with dichloromethane (30 mL). A white powder was obtained after filtration of the solution and subsequent evaporation. The examination of the solid by NMR spectroscopy disclosed a mixture of two complexes when very weak additional resonances are omitted. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 27.1 (s, complex **12**)[11] and 29.9 (d), 51.5 (d) ^2J = 242 Hz (unidentified compound). ^1H NMR ($CDCl_3$), selected values attributed to the unidentified compound: δ = − 5.07 (dd, 1 H, $^2J_{PH}$ = 20.4 and 19.5 Hz, RuH), 3.92 (dd, 1 H, $^2J_{H,H}$ = 17.0 Hz, $^2J_{PH}$ = 6.8 Hz, PCH_2, H_a), 4.13 (dd, $^2J_{H,H}$ = 17.0 Hz, 1 H, $^2J_{PH}$ = 7.6 Hz, PCH_2, H_b), 4.62 (dd, 1 H, $^2J_{PH}$ = 3.5 Hz, $^4J_{PH}$ = 3.0 Hz, PCH=).

***ttt*-$RuCl_2(NO)[Ph_2PCH_2C(=O)tBu][Ph_2PCH_2C(tBu)=O][BF_4]$ (13):** A sample of **1** (5.00 g, 6.75 mmol) and $[NO][BF_4]$ (0.85 g, 7.28 mmol) were successively added to cold dichloromethane (60 mL, −80 °C). The mixture was allowed to reach ambient temperature and stirred overnight. The resulting solution was evaporated under vacuum to obtain an orange solid (5.52 g). The NMR spectroscopic analysis of this crude material indicated a mixture of several products and we failed to isolate a pure compound after recrystallization from a dichloromethane/diethyl ether mixture. When additional weak IR absorptions and NMR resonances are omitted, the collected spectroscopic data suggested the assumed structure. IR: ν(NO) = 1884 cm^{-1}; ν(C=O) = 1701 cm^{-1}, 1595 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 20.3 (d), 49.8 (d, ^2J = 371 Hz). ^1H NMR (CD_2Cl_2): δ = 0.84 (s, 9 H, *t*Bu), 1.05 (s, 9 H, *t*Bu), 4.39 (dd, 2 H, $^2J_{PH}$ = 9.1 Hz, $^4J_{PH}$ = 2.4 Hz, PCH_2), 4.70 (d, broad, 2 H, $^2J_{PH}$ = 10.0 Hz, $P'CH_2$), 7.00−7.70 (m, 20 H, Ph). Attempts at recrystallization of the compound from slow evaporation of its solution in a dichloromethane/ethanol mixture afforded orange crystals of the enolato-phosphane derivative **14** instead of **13**.

***ttt*-$RuCl_2(NO)[Ph_2PCH=C(tBu)O][Ph_2PCH_2C(=O)tBu]$ (14):** Complex **14** was obtained in 65% yield relative to **1** after recrystallization of **13** in a dichloromethane/ethanol mixture (see synthesis of **13**) or alternatively by reacting **13** with K_2CO_3 in dichloromethane. Further recrystallization from a dichloromethane/methanol mixture afforded orange needles. IR: ν(NO) = 1858 cm^{-1}; ν(C=O) = 1702 cm^{-1}; ν(C=CO): 1520 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 14.9 (d, PCH_2), 53.1 (d, PCH=, ^2J = 385 Hz). ^1H NMR (CD_2Cl_2): δ = 0.87 (s, 9 H, *t*Bu), 0.98 (s, 9 H, *t*Bu), 4.29 (dd, 2 H, $^2J_{PH}$ = 9.9 Hz, $^4J_{PH}$ = 1.8 Hz, PCH_2), 4.63 (dd, 1 H, $^2J_{PH}$ ≈ $^4J_{PH}$ ≈ 4.1 Hz, PCH=), 7.37−7.78 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 26.4 (s, C*Me*$_3$), 28.9 (s, C*Me*$_3$), 33.4 (d, $^1J_{PC}$ = 30.4 Hz, PCH_2), 38.6 (d, $^3J_{PC}$ = 12.3 Hz, *C*Me$_3$), 45.6 (d, $^3J_{PC}$ = 1.8 Hz, *C*Me$_3$), 72.1 (dd, $^1J_{PC}$ = 63.8 Hz, $^3J_{PC}$ = 1.8 Hz, PCH=), 128.5 (d, $^2J_{PC}$ = 10.9 Hz, Ph_2P, *ortho*), 128.6 (d, $^2J_{PC}$ = 10.0 Hz, Ph_2P, *ortho*), 129.8 (dd, $^1J_{PC}$ = 43.8 Hz, $^3J_{PC}$ = 2.4 Hz, Ph_2P, *ipso*), 130.9 (d, $^4J_{PC}$ = 2.7 Hz, Ph_2P, *para*), 131.1 (d, $^4J_{PC}$ = 2.3 Hz, Ph_2P, *para)*, 132.0 (dd, $^1J_{PC}$ = 57.2 Hz, $^3J_{PC}$ = 2.3 Hz, Ph_2P, *ipso*), 133.1 (dd, $^3J_{PC}$ = 9.1 Hz, $^5J_{PC}$ = 1.7 Hz, Ph_2P, *meta*), 134.3 (d, $^3J_{PC}$ = 8.8 Hz, Ph_2P, *meta*), 198.6 (dd, $^2J_{PC}$ = 16.9 Hz, $^3J_{PC}$ = 8.9 Hz, =CO), 209.8 (d, $^2J_{PC}$ = 5.4 Hz, C=O). ^{13}C NMR (CD_2Cl_2), selected values: δ = 33.4 (td, $^1J_{HC}$ = 130 Hz, PCH_2), 72.1 (ddd, $^1J_{HC}$ = 169 Hz, PCH=). $C_{36}H_{41}Cl_2NO_3P_2Ru$ (769.7): calcd. C 56.18, H 5.37, Cl 9.21, N 1.82, P 8.05; found C 55.84, H 5.43, Cl 9.85, N 1.84, P 7.79.

***ccc*-$RuCl(NO)[Ph_2PCH=C(tBu)O]_2$ (15):** **1** (5.30 g, 7.16 mmol) and $[NO][BF_4]$ (0.93 g, 7.96 mmol) produced crude complex **13** and this was added to ethanol (80 mL) and then KOH (0.80 g, 14.3 mmol) and the mixture was stirred at ambient temperature for 2 days. The resulting orange slurry was evaporated under vacuum to leave a solid that was extracted with dichloromethane (60 mL). The solution was filtered and the filtrate was covered with methanol (150 mL) to afford well-formed orange-red crystals. Yield: 3.02 g, 58%. Complex **15** may be similarly obtained starting from **14**. IR: ν(NO) = 1805 cm^{-1}; ν(C=CO) = 1507, 1497 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 40.7 (d), 46.5 (d), ^2J = 20. ^1H NMR (CD_2Cl_2): δ = 0.95 (s, 9 H, *t*Bu), 1.35 (s, 9 H, *t*Bu), 4.22 (dd, $^2J_{PH}$ = 6.3 Hz, 1 H, $^4J_{PH}$ = 1.4 Hz, PCH=), 4.63 (d, 1 H, $^2J_{PH}$ = 5.6 Hz, P′CH=), 7.00−7.64 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 29.0 (s, C*Me*$_3$), 29.7 (s, C*Me*$_3$), 39.1 (d, $^3J_{PC}$ = 12.6 Hz, *C*Me$_3$), 39.7 (dd, $^3J_{PC}$ = 12.6 Hz, $^4J_{PC}$ = 4.5 Hz, *C*Me$_3$), 71.1 (dd, $^1J_{PC}$ = 65.5 Hz, $^3J_{PC}$ = 1.8 Hz, PCH=), 73.5 (d, $^1J_{PC}$ = 66.4 Hz, PCH=), 128.2−137.0 (m, phenyl-groups resonances), 198.0 (d, $^2J_{PC}$ = 13.5 Hz, =CO), 201.3 (dd, $^2J_{PC}$ = 10.3 Hz, $^3J_{PC}$ = 3.1 Hz, =CO). $C_{36}H_{40}ClNO_3P_2Ru$ (733.2): calcd. C 58.97, H 5.50, Cl 4.84, N 1.91, P 8.45; found C 58.80, H 5.54, Cl 4.79, N 1.95, P 8.66.

Crystal Data for 15: $C_{36}H_{40}ClNO_3P_2Ru$, M = 733.15, crystal size 0.40 × 0.38 × 0.32, monoclinic, space group $P2_1/c$, $Z = 4$, a = 18.2203(2) Å, b = 10.9932(1) Å, c = 18.3698(3) Å, β = 109.1277(6)°, U = 3476.42(8) Å^3, $\delta_{calcd.}$ = 1.401 g cm^{-3}, T = 293(2) K, $F(000)$ = 1512, Mo-K_α radiation (λ = 0.71069 Å), μ = 0.655 mm^{-1}, 7952 reflections measured in the range 2.28° ≤ θ ≤ 27.50°, 7952 unique (R_{int} = 0.03%) which were used in all calculations. The structure was refined using full-matrix least-squares on F^2 to R_1 = 0.0296, wR_2 = 0.0745, S = 1.071, for 6891 reflections (>2σ) and 398 refined parameters, R_1(all data) = 0.0371, wR_2(all data) = 0.0805, goodness-of-fit on F^2 = 1.071. The sample was studied with a NONIUS Kappa CCD diffractometer with graphite monochromator. The cell parameters were obtained with Denzo and Scalepack.[18] The data collection ($2\theta_{max}$ = 60°, 148 frames via 1.9° ω rotation and 13 s per frame, index ranges $0 \le h \le 23$, $0 \le k \le 14$, $-23 \le l \le 22$) gave 19547 reflections.[19] The data reduction led to 7952 independent reflections from which 6891 had $I > 2\sigma(I)$. The structure was solved with SIR-97 which revealed the non hydrogen atoms.[20] After anisotropic refinement, many hydrogen atoms may be found with Fourier difference calculations. The whole structure was refined with SHELXL97 by full-matrix least-squares methods on F^2 [x, y, z, β_{ij} for Ru, P, Cl, O, C and N atoms; x, y, z in riding mode for H atoms; $w = 1/[\sigma^2(F_0^2) + (0.038P)^2 + 1.72P]$ where $P = (F_0^2 + 2F_c^2)/3$ with the resulting R = 0.029, wR = 0.075 and S = 1.071 (residual around solvent molecules); minimum and maximum final electron density: −0.619 and 0.695 eÅ^{-3}].[21] ORTEP views were prepared with PLATON98.[22]

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-165881. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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