# Addition of $CH_3CO_2H$ and $HBF_4$ to Alkynyl Complexes of Ruthenium(II) and Osmium(II)

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The bis(alkynyl) complex $[Os(C_2Ph)_2(CO)(PiPr_3)_2]$ (**1**) reacts with $CH_3CO_2H$ to give the vinylacetato derivative $[Os(C_2Ph)\{C(=CHPh)OC(O)CH_3\}(CO)(PiPr_3)_2]$ (**3**). The protonation of **3** with $HBF_4$ in diethyl ether leads to the carbene compound $[Os(C_2Ph)\{=C(CH_2Ph)OC(O)CH_3\}(CO)(PiPr_3)_2]BF_4$ (**4**). On the other hand, reaction of the analogous ruthenium complex $[Ru(C_2Ph)_2(CO)(PiPr_3)_2]$ (**2**) with $CH_3CO_2H$ affords $[Ru(C_2Ph)(\eta^2\text{-}O_2CCH_3)(CO)(PiPr_3)_2]$ (**5**) and phenylacetylene. **5** reacts with $HBF_4$ in acetone to give $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]BF_4$ (**6**). The molecular structure of **6** has been determined by an X-ray investigation. **6** crystallizes in the monoclinic space group $C2/m$ with $a$ = 16.399(2) Å, $b$ = 14.870(5) Å, $c$ = 16.855(3) Å, $\beta$ = 105.98(2)°, and $Z$ = 4. The coordination geometry around the ruthenium atom could be described as based on a distorted octahedron with the two phosphine ligands occupying relative *trans* positions. The perpendicular coordination plane is formed by the atoms of the vinyl ester ligand (O and C), the oxygen atom of the acetone molecule, and the carbonyl ligand. The coordinated acetone molecule of **6** can be displaced by anions such as $[PhC{\equiv}C]^-$ and $Cl^-$ to give the complexes $[Ru(C_2Ph)\{C(=CHPh)OC(O)CH_3\}(CO)(PiPr_3)_2]$ (**9**) and $[Ru\{C(=CHPh)OC(O)CH_3\}Cl(CO)(PiPr_3)_2]$ (**10**), respectively. **9** reacts with $HBF_4$ in acetone as solvent to give **6** and phenylacetylene. The reaction of **10** with $HBF_4$ leads to the carbene cationic complex $[RuCl\{=C(CH_2Ph)OC(O)CH_3\}(CO)(PiPr_3)_2]BF_4$ (**11**). **10** also reacts with $CH_3CO_2H$; in this case the reaction affords *cis*-PhCH=CHOC(O)$CH_3$ and $[RuCl\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(PiPr_3)_2]$ (**12**). The compound $[Ru(\eta^2\text{-}O_2CCH_3)(CO)_2(PiPr_3)_2]BF_4$ (**13**) and *cis*-PhCH=CHOC(O)$CH_3$ were similarly obtained from **6** and $CH_3CO_2H$. The reactivity of the six-coordinate bis(alkynyl) complexes $[Ru(C_2Ph)_2(CO)(NCCH_3)(PiPr_3)_2]$ (**14**) and $[Ru(C_2Ph)_2(CO)_2(PiPr_3)_2]$ (**15**) toward $HBF_4$ was also investigated. These compounds react in coordinating solvents with $HBF_4$ to give $[Ru(C_2Ph)(CO)(NCCH_3)_2(PiPr_3)_2]BF_4$ (**16**) or $[Ru(C_2Ph)(CO)_2\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]BF_4$ (**17**) and phenylacetylene. In dichloromethane **17** releases the acetone ligand to give $[Ru(C_2Ph)(CO)_2(PiPr_3)_2]BF_4$ (**18**). Starting from **18** the hexacoordination can be achieved by addition of acetonitrile and carbon monoxide. These reactions lead to $[Ru(C_2Ph)(CO)_2(NCCH_3)(PiPr_3)_2]BF_4$ (**19**) and $[Ru(C_2Ph)(CO)_3(PiPr_3)_2]BF_4$ (**20**). Complexes **16** and **17** react with $CH_3CO_2H$ to give $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)(NCCH_3)(PiPr_3)_2]BF_4$ (**21**) and $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)_2(PiPr_3)_2]BF_4$ (**22**), which can be also prepared from **6** by reaction with acetonitrile and carbon monoxide, respectively.

## Introduction

Electronic structures and reactivities of organic fragments change, often dramatically, when they coordinate to transition metals to form organometallic complexes. Coordination of $[R{-}C{\equiv}C]^-$ to a metal center transfers the nucleophilicity from the $\alpha$-carbon atom to the $\beta$-carbon atom. Thus, the addition of electrophiles to the electron-rich $C_\beta$ of metal—alkynyls has been described on many occasions and is the best entry into the synthesis of vinylidene complexes.[1]

Previous studies of vinylidene complexes have identified the electron deficiency of the vinylidene ligand at the $\alpha$-carbon atom and the localization of electron density in the M=C double bond and at the $\beta$-carbon atom.[2,3] Chemical reactivity is thus oriented toward electrophiles at both $C_\alpha$[4] and $C_\beta$ and toward nucleophiles at $C_\alpha$. The reactions with nucleophiles generally result in the formation of vinyl derivatives.[1] Such compounds of electron-

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donating or electron-rich metals are nucleophilic at $C_\beta$, and their reactions with electrophiles lead to carbene complexes.[5]

With the notable exceptions of the formation of $\eta^2$-allene- or heteroketene-metal complexes, by addition of diazomethane or chalcogens to $[Rh(\eta^5\text{-}C_5H_5)(C{=}CHR)(P\textit{i}Pr_3)_2]$,[4] the reactions mentioned above have conformed to a simple rule:[2] nucleophiles add to the $\alpha$-carbon atoms in the terminal unsaturated organic ligands, whereas electrophiles add to the $\beta$-carbon atoms. Furthermore, it has been usually observed that the electrophilic complexes are cationic and the nucleophilic ones are electroneutral.[6]

We have previously reported that the tetrahydrido complex $[OsH_4(CO)(P\textit{i}Pr_3)_2]$ reacts with a stoichiometric amount of phenylacetylene to give molecular hydrogen and the hydrido-alkynyl-dihydrogen complex $[OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2]$. This compound by reaction with a second molecule of phenylacetylene affords the bis(alkynyl) derivative $[Os(C_2Ph)_2(CO)(P\textit{i}Pr_3)_2]$ (**1**).[7] The related ruthenium compound $[Ru(C_2Ph)_2(CO)(P\textit{i}Pr_3)_2]$ (**2**) can be prepared by starting from the octahedral tetrahydroborate $[RuH(\eta^2\text{-}H_2BH_2)(CO)(P\textit{i}Pr_3)_2]$[8] and phenylacetylene. The bis(alkynyl) complexes **1** and **2** react with Lewis bases such as $P(OMe)_3$, $PMe_3$, and CO to give the six-coordinate compounds $[M(C_2Ph)_2(CO)L(P\textit{i}Pr_3)_2]$ (M = Ru, Os).[7,8] Continuing with our work in this field, and as a part of a general study on the chemical properties of ruthenium and osmium complexes containing $\eta^1$-carbon ligands,[9] we have now investigated the addition of acetic acid ($H^+$ electrophile, $[CH_3COO]^-$ nucleophile) to the C≡C triple bond of one of the two alkynyl ligands of **1** and **2**. In addition, the protonation of the compounds formed in this way is also reported.

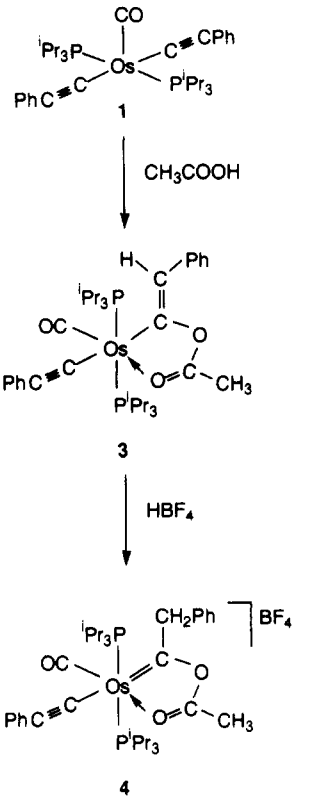
## Results

**$[Os(C_2Ph)_2(CO)(P\textit{i}Pr_3)_2]$ (1).** Treatment of **1** with a stoichiometric amount of acetic acid in methanol leads to a pink solid, analyzed as 1 $CH_3COOH$ in 90% yield. The spectroscopic data indicate that the solid is the vinyl ester compound **3** (Scheme 1).

The presence of the vinyl ester ligand in **3** can be inferred from the IR and $^1H$ and $^{13}C\{^1H\}$ NMR spectra. The IR spectrum in Nujol shows absorptions at 1625 and 1600 $cm^{-1}$, which are assigned to the $\nu$(C=O) and $\nu$(C=C) vibrations, respectively. The proposal that the ester unit coordinates to the osmium atom via the C=O oxygen is strongly supported by the value of the $\nu$(C=O) frequency. The $^1H$ NMR spectrum in $C_6D_6$ contains a singlet at 5.75 ppm, which is due to the vinylic proton, while the vinylic carbon atoms appear in the $^{13}C\{^1H\}$ NMR spectrum as triplets at 184.44 and 123.04 ppm with P-C coupling constants of 9.7 and 2.3 Hz, respectively.

Complex **3** reacts with $HBF_4$ in diethyl ether to give the cationic carbene derivative **4**.

**Scheme 1**




The IR spectrum of **4** shows the absorption due to the $[BF_4]^-$ anion with $T_d$ symmetry along with bands characteristic of the alkynyl and carbene ligands at 2100 ($\nu$(C≡C)) and 1625 ($\nu$(C=O)) $cm^{-1}$. The $^{13}C\{^1H\}$ NMR spectrum has the expected resonances for the carbene and alkynyl ligands. The Os=*C* carbon atom appears as a triplet at 285.62 ppm with a P—C coupling constant of 4.8 Hz, while *C*$H_2$Ph is observed as a singlet at 61.44 ppm. The alkynyl group is characterized by two triplets, one assigned to the $\alpha$-carbon atom at 96.65 ppm with a P—C coupling constant of 23.2 Hz and the second due to the $\beta$-carbon atom at 126.59 ppm with a P—C coupling constant of 2.8 Hz.

The $^{31}P\{^1H\}$ NMR spectra of **3** and **4** show singlets, indicating that the two phosphine ligands of these compounds are equivalent and are mutually *trans* disposed.

In addition, the selectivity of the reaction of **3** with $HBF_4$ should be noted. At first glance, **3** has two nucleophilic carbon atoms, the $\beta$-carbon atom of the vinyl ester ligand and the $\beta$-carbon atom of the alkynyl group. The exclusive formation of **4** indicates that the $\beta$-carbon atom of the vinyl ester is a stronger nucleophilic center than the $\beta$-carbon atom of the alkynyl group.

**$[Ru(C_2Ph)_2(CO)(P\textit{i}Pr_3)_2]$ (2).** Complex **2**, in contrast to **1**, reacts with a stoichiometric amount of acetic acid in methanol to give the alkynyl-acetato derivative **5** and phenylacetylene (Scheme 2).

Complex **5** was isolated as a yellow solid in 96% yield. **5** is formulated as an octahedral derivative containing a chelating acetato ligand on the basis of assignments for $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ at 1545 and 1430 $cm^{-1}$, respectively. In addition, the IR spectrum in Nujol shows a narrow $\nu$(C≡C) absorption at 2100 $cm^{-1}$ due to the alkynyl ligand. The characteristic signals of this ligand in the $^{13}C\{^1H\}$ NMR spectrum are a singlet at 115.63 ppm, assigned to the $\beta$-carbon atom, and a triplet at 109.92 ppm

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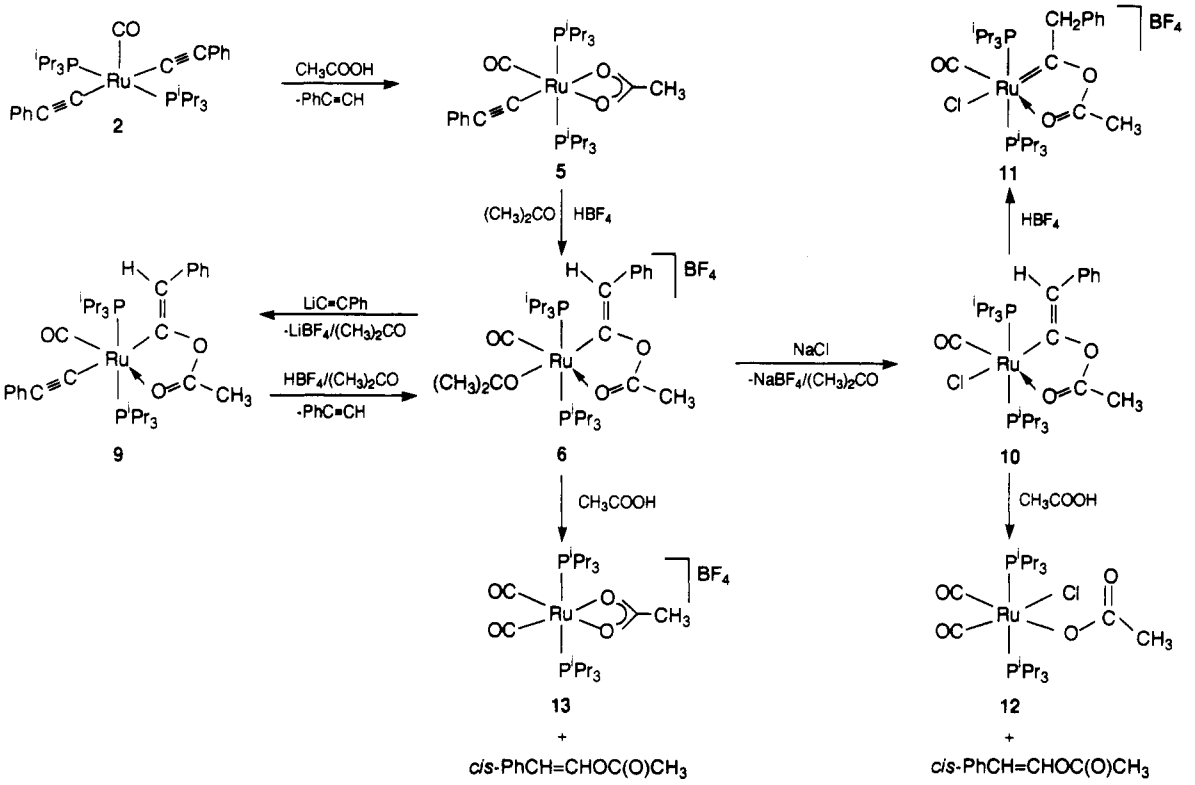
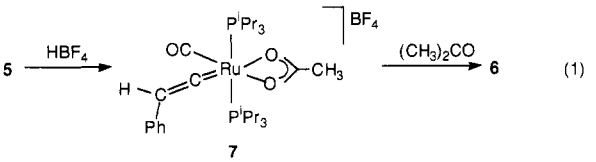
**Scheme 2**




with a P—C coupling constant of 15.7 Hz, due to the $\alpha$-carbon atom. In agreement with the mutually *trans* disposition of the triisopropylphosphine ligands, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 41.93 ppm.

The formation of **5** and phenylacetylene, from **2** and acetic acid, could be rationalized as the electrophilic attack of the proton at the $\alpha$-carbon atom of one of the two alkynyl ligands of **2** to afford a cationic $[Ru(C_2Ph)(\eta^2\text{-}HC{\equiv}CPh)(CO)(PiPr_3)_2]^+$ intermediate, which rapidly reacts with $[CH_3CO_2]^-$ by liberation of phenylacetylene to give **5**.

In contrast to the trend shown by **2**, the alkynyl ligand of **5** seems to undergo electrophilic attack at the $\beta$-carbon atom. Thus, the addition of $HBF_4$ to an acetone solution of **5** leads to the vinyl ester compound **6** (Scheme 2), which most probably is the result of the nucleophilic attack of the acetato group at the $\alpha$-carbon atom of the vinylidene ligand of an intermediate **7** (eq 1).




(1)

We note that the synthesis and X-ray crystal structure of the vinyl ester compound $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHCO_2CH_3)OC(O)CH_3\}(PPh_3)]$ have been recently reported. This complex was prepared by reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}O_2CCH_3)(PPh_3)]$ with methyl propiolate.[10]

The formation of **6** according to eq 1 is a process similar to that previously described for the synthesis of $[Fe\{\eta^3\text{-}C(=CHPh)C{\equiv}CPh\}(dmpe)]^+$ (dmpe = $(CH_3)_2PCH_2CH_2P(CH_3)_2$). The bis(alkynyl) complex $[Fe(C_2Ph)_2(dmpe)_2]$ is acid sensitive and is protonated by weak acids to form a vinylidene intermediate which rearranges into the butenyne derivative.[11] Butenyne compounds of ruthenium[12] and osmium[13] have also been reported. They are generally a result of the addition of alkynes to alkynyl complexes, via vinylidene intermediates.[14]

Complex **6**, which was isolated as a yellow solid in 92% yield, was characterized by IR, $^1H$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies, and X-ray diffraction. An ORTEP drawing of the molecular structure of the cation of **6** is presented in Figure 1. Selected bond distances and angles are listed in Table 1. The coordination geometry around the metal in the cation could be rationalized as derived from a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying opposite positions (P(1)—Ru-P(1)′ = 173.26(7)°). The perpendicular plane is formed by the atoms C(3) and O(1) of the vinyl ester ligand—defining with the ruthenium atom a five-membered ring (O(1)–Ru–C(3) = 79.2(3)°)—the oxygen atom of the acetone ligand, O(4), disposed *trans* to C(3) (O(4)–Ru–C(3) = 166.2(3)°) and the CO ligand located *trans* to the ketonic oxygen O(1).

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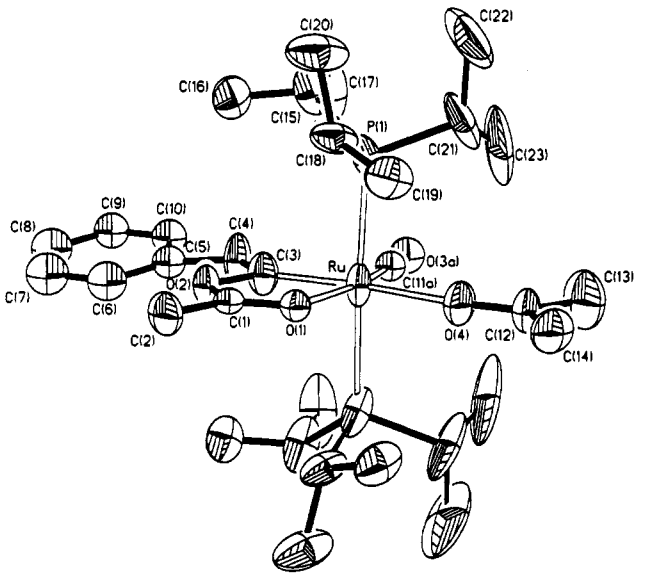



**Figure 1.** Molecular representation of the cationic complex $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]^+$ (cation of **6**) with the labeling scheme used.

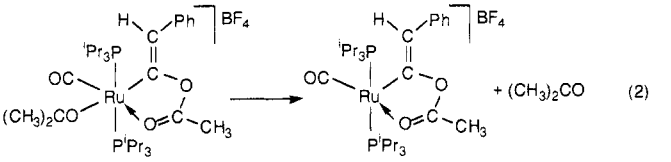
**Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Cationic Complex $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]^+$ (6)[a]**

| | | | |
|---|---|---|---|
| Ru–P(1) | 2.449(2) | C(1)–C(2) | 1.487(15) |
| Ru–O(1) | 2.131(6) | C(3)–O(2) | 1.466(13) |
| Ru–O(4) | 2.205(6) | C(3)–C(4) | 1.350(13) |
| Ru–C(3) | 1.967(8) | C(4)–C(5) | 1.498(10) |
| Ru–C(11a) | 1.83(4) | C(11a)–O(3a) | 1.11(5) |
| C(1)–O(1) | 1.225(9) | C(12)–O(4) | 1.235(10) |
| C(1)–O(2) | 1.331(10) | | |
| P(1)–Ru–P(1)′ | 173.26(7) | Ru–O(1)–C(1) | 112.0(5) |
| P(1)–Ru–O(1) | 87.91(6) | Ru–O(4)–C(12) | 164.7(6) |
| P(1)–Ru–O(4) | 87.26(5) | C(1)–O(2)–C(3) | 115.0(7) |
| P(1)–Ru–C(3) | 92.19(5) | O(1)–C(1)–O(2) | 122.0(8) |
| P(1)–Ru–C(11a) | 92.60(5) | O(1)–C(1)–C(2) | 123.1(8) |
| O(1)–Ru–O(4) | 87.0(2) | O(2)–C(1)–C(2) | 114.9(8) |
| O(1)–Ru–C(3) | 79.2(3) | Ru–C(3)–O(2) | 111.8(6) |
| O(1)–Ru–C(11a) | 168(1) | Ru–C(3)–C(4) | 136.0(8) |
| O(4)–Ru–C(3) | 166.2(3) | O(2)–C(3)–C(4) | 112.2(8) |
| O(4)–Ru–C(11a) | 105(1) | Ru–C(11a)–O(3a) | 178(3) |
| C(3)–Ru–C(11a) | 89(1) | | |

[a] The primed atom is related to the unprimed one by the symmetry transformation $x, -y, z$. The a-labeled atoms correspond to the disordered carbonyl group.

Figure 1 shows the acetone molecule coordinated to the ruthenium atom as an $\eta^1$-oxygen donor ligand. In keeping with the crystal structure, the IR spectrum of **6** in Nujol contains a band at 1680 $cm^{-1}$ assignable to the carbonyl group of this ligand. This value is typical for the $\eta^1$-coordination mode of the acetone molecule.[15]

The Ru–O(4) distance (2.205(6) Å) is long, and the distance O(4)–C(12) (1.235(10) Å) is quite similar to that observed in the free molecule acetone (1.20 Å).[16] This suggests that the Ru–acetone bond is weak. In fact, in dichloromethane solution, **6** dissociates the acetone molecule to give the five-coordinate complex **8** (eq 2), which is strongly supported by the IR spectrum in dichloromethane and the $^{13}C\{^1H\}$ NMR spectrum in chloroform-*d*. The IR spectrum shows the band of the carbonyl group




**6** **8**

at 1710 $cm^{-1}$, and the $^{13}C\{^1H\}$ NMR spectrum has the resonance of the carbon atom of the carbonyl group at 210 ppm.

The chelating five-membered ring is lying on the crystallographic symmetry plane. The Ru—C(3) distance (1.967(8) Å) is similar to those found in the related complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHCO_2CH_3)OC(O)CH_3\}(PPh_3)]$ (2.002(2) Å)[10] and $[Ru\{C(=C(CO_2CH_3)CH=CHC(CH_3)_3)C(O)OCH_3\}Cl(CO)(PPh_3)_2]$ (2.03(1) Å)[17] but significantly shorter than the Ru—C bond in the complexes $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHPh)OiPr\}(CO)(PPh_3)]$ (2.103(6) Å),[18] $[Ru\{C(=CHCO_2CH_3)CO_2CH_3\}(CO)(NCCH_3)_2(PPh_3)_2]ClO_4$ (2.12(5) Å),[19] and $[Ru\{CH=CHC(CH_3)_3\}Cl(CO)\{(CH_3)_2Hpz\}(PPh_3)_2]$ (2.063(7) Å),[20] where a Ru—C($sp^2$) single bond has been proposed. So, the Ru—C(3) distance shown in Table 1 suggests that for an adequate description of the bonding situation in **6** a second zwitterionic resonance form such as **6′** (Scheme 3) should be considered. Furthermore, the C(3)—O(2) bond length (1.466(9) Å), which is about 0.1 Å longer than the C—O single bond of the vinyl ligand in the complex $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHPh)OiPr\}(CO)(PPh_3)]$, seems to suggest that the vinyl ester ligand of **6** could be considered as an intermediate state between a normal chelate ring and the intermediate **7**. In this resonance form (**6″** in Scheme 3), the carbonyl oxygen atom of the acetato is on the way to nucleophilic attack at the $\alpha$-carbon atom of the vinylidene ligand. This proposal is also supported by the size of the Ru—C(3)—C(4) and O(2)—C(3)—C(4) angles of which the first one is widened to 136.0(8)° and the second one compressed to 112.2(8)° compared with the ideal value (120°) for an $sp^2$ carbon center. A similar situation has been found by Werner, in the complex $[Ru(\eta^5\text{-}C_5H_5)\{C(=CHCO_2CH_3)OC(O)CH_3\}(PPh_3)]$.[10]

Some contribution of the resonance forms **6′** and **6″** to the structure of **6** can also be proposed on the basis of the $^{13}C\{^1H\}$ NMR spectrum of this complex, which shows a triplet at 204.72 ppm with a coupling constant of 13.1 Hz. This signal, assigned to the $\alpha$-carbon atom of the vinyl ester group, appears about 80 ppm toward a lower field than the signal of the $\alpha$-carbon atom in the vinyl complex $[RuCl\{(E)\text{-}CH=CHPh\}(CO)(PiPr_3)_2]$[9a] where, beyond any doubt, there is a Ru—C single bond. A similar relationship is observed between the $^{13}C\{^1H\}$ NMR spectra of the complexes **3** and $[Os\{(E)\text{-}CH=CHPh\}Cl(CO)(PiPr_3)_2]$, suggesting that for an adequate description of the bonding situation in the vinyl ester of **3**, the resonance forms **6′** and **6″** should also be considered.

The acetone molecule of **6** can be displaced by anions such as $[PhC{\equiv}C]^-$ and $Cl^-$ to give the complexes **9** and

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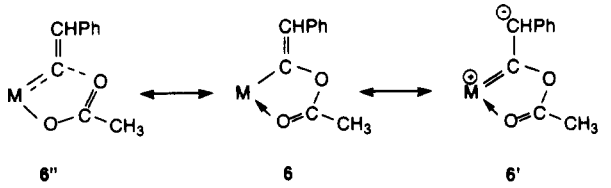
**Scheme 3**



6" 6 6'

10, respectively. In agreement with the structures shown in Scheme 2, the IR spectra in Nujol contain two bands of the vinyl ester ligands at about 1640 and 1590 $cm^{-1}$. Those centered around 1640 $cm^{-1}$ were assigned to the carbonyl groups; their values strongly support the coordination of the oxygen atoms to the metallic centers. The second ones were assigned to the vinylic carbon–carbon double bonds. In the $^{13}C\{^1H\}$ NMR spectra, the vinylic carbon atoms of the chelate ligands appear as triplets at about 209 ($C_\alpha$) and 122 ($C_\beta$) ppm, with P–C coupling constants of about 14 and 3 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectra show singlets, indicating that the phosphine ligands of **9** and **10** are chemically equivalent and consequently mutually *trans* disposed.

Complexes **3** and **9** are isoelectronic. Furthermore, they contain the same ligands in the same positions. However, between them, there is a pronounced difference in reactivity toward $HBF_4$. The osmium complex **3** reacts with $HBF_4$ by electrophilic attack at the $\beta$-carbon atom of the vinyl ester group to give the carbene complex **4** (Scheme 1), while the ruthenium complex **9** reacts with $HBF_4$ by electrophilic attack at the $\alpha$-carbon atom of the alkynyl ligand to afford **6** and phenylacetylene (Scheme 2).

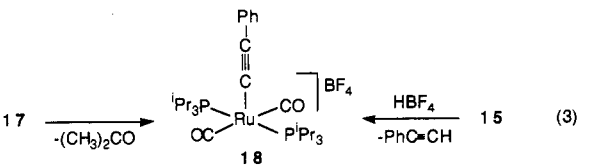
Complex **10**, in contrast to **9**, shows the same behavior as **3**. Thus, the addition of $HBF_4$ to a dichloromethane solution of **10** leads to the chloro–carbene complex **11**. This compound was isolated as a pale yellow solid in 55% yield. Its IR spectrum in Nujol shows the absorption due to the $[BF_4]^-$ anion with $T_d$ symmetry along with bands characteristic of the carbene ligand. In particular, one should note the $\nu$(CO) absorption at 1655 $cm^{-1}$, which strongly supports the coordination of the oxygen atom of the carbonyl group to the ruthenium. In the $^1H$ NMR spectrum, the most noticeable signal is a singlet at 4.77 ppm, due to the protons of the $CH_2Ph$ group.

Complex **10** also reacts with acetic acid under reflux. The reaction leads to *cis*-PhCH=CHOC(O)$CH_3$ and the monodentate acetato complex **12**. Compound **13** and *cis*-PhCH=CHOC(O)$CH_3$ were similarly obtained by reaction of **6** and acetic acid in acetone as solvent (Scheme 2). The source of the second carbonyl ligand of these compounds seems also to have its origin in the carboxylic acid. Although the decarbonilation of organic acids is not a general reaction, the process is known.[21]

The reaction of **10** with $HBF_4$ can be rationalized as the electrophilic attack of $H^+$ at the $\beta$-carbon atom of the vinyl acetato ligand, while the formation of *cis*-PhCH=CHOC(O)$CH_3$ from **10** and acetic acid could be rationalized as the electrophilic attack of the proton of the organic acid at the $\alpha$-carbon atom of the vinylacetato ligand. This seems to suggest that the source of the electrophile $H^+$ also determines the direction of the attack.

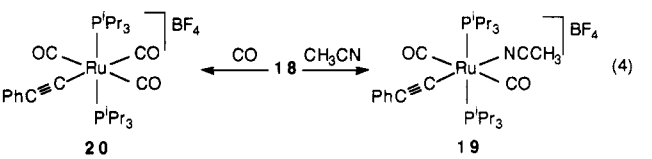
**Six-Coordinate Alkynyl Compounds.** The reactions aimed to elucidate the direction of the electrophilic attack on six-coordinate bis(alkynyl) complexes of ruthenium are summarized in Scheme 4. Compounds **14** and **15** were prepared by reaction of **2** with acetonitrile and carbon monoxide, respectively. As the IR spectra of these complexes only show one $\nu$(C≡C) band around 2090 $cm^{-1}$ and the IR spectrum of **15** contains only one $\nu$(CO) absorption at 1970 $cm^{-1}$, we assume that the two alkynyl ligands are symmetrically coordinated, and thus, the structures shown in Scheme 4 have been assigned. The same structures have been proposed for complexes of the type $[Fe(C_2R)_2L_2]$ ($L_2$ = diphosphine)[11] and $[Ru(CO)_2\{(C{\equiv}C)_nR\}_2(PEt_3)_2]$ ($n$ = 1, 2).[22]

In coordinating solvents, **14** and **15** react with $HBF_4$ to afford the solvento complexes **16** and **17** and phenylacetylene. The IR and NMR spectra of **16** and **17** are in good agreement with the proposed structures. The $^1H$ NMR spectrum of **16** has two singlets due to the methyl groups of two chemically inequivalent acetonitrile ligands at 2.48 and 2.45 ppm. The IR spectra in Nujol show the absorptions due to the $[BF_4]^-$ anion with $T_d$ symmetry, along with bands characteristic of coordinated ligands. In particular, the IR spectrum of **17** contains a $\nu$(CO) absorption at 1670 $cm^{-1}$, suggesting that the acetone coordinates to the ruthenium atom via the oxygen atom. In solution **17** releases the acetone ligand to afford the five-coordinate bis(carbonyl) derivative **18**. This is supported by the IR spectrum of **17** in dichloromethane, which shows the $\nu$(CO) absorption of the acetone at 1710 $cm^{-1}$. Complex **18** can be directly obtained by addition of $HBF_4$ to a tetrahydrofuran solution of **15** (eq 3).



(3)

The transformation of **18** into a hexacoordinated complex can be achieved by addition of acetonitrile and carbon monoxide. These reactions lead to the formation of **19** and **20**, respectively (eq 4).



(4)

Complexes **16** and **17** react with acetic acid to give the vinylacetato derivatives **21** and **22**, which can be prepared from **6** by reaction with acetonitrile and carbon monoxide, respectively. For these compounds the most distinctive spectroscopic data are, in the IR spectra, the absorptions due to the $[BF_4]^-$ anion with $T_d$ symmetry, at about 1100 $cm^{-1}$, and the $\nu$(CO) bands of the carbonyl group of the vinylacetate ligands observed between 1640 and 1620 $cm^{-1}$, which strongly support the coordination of the ketonic oxygen atom to the metallic center. From the $^{13}C\{^1H\}$ NMR spectra, one must note the triplets due to the vinylic carbon atoms of the vinylacetate group, which appear at about 200 and 130 ppm, with P–C coupling constants of about 11 and 5 Hz, respectively.

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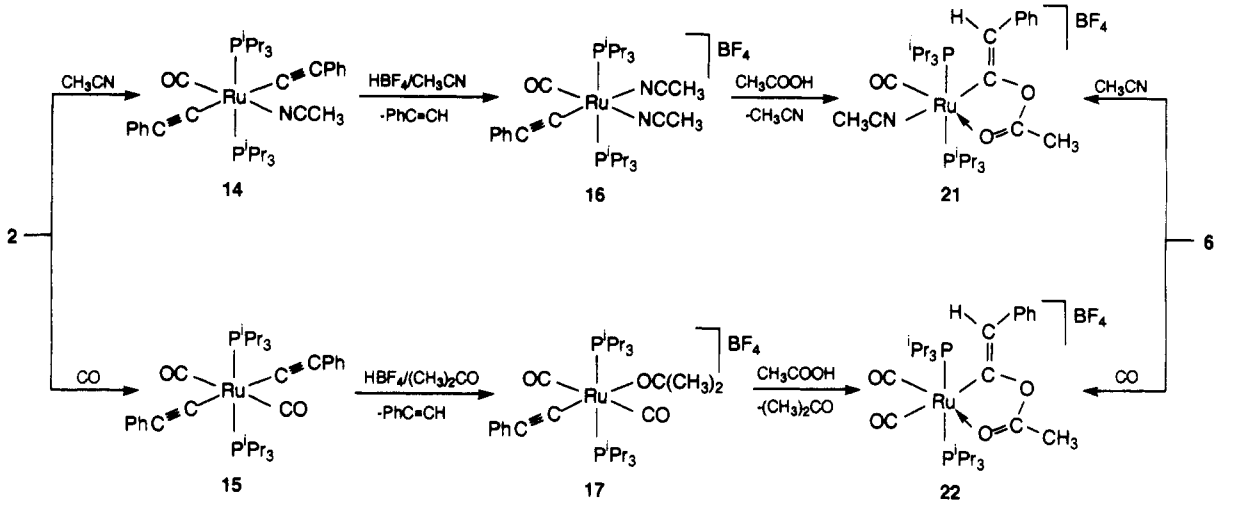
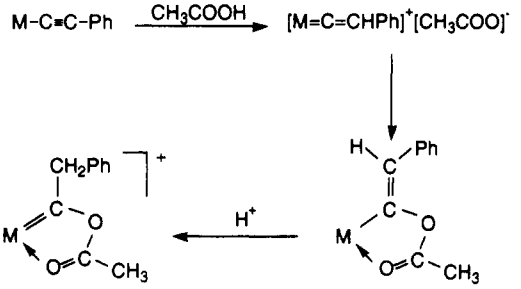
**Scheme 4**



**Scheme 5**



## Discussion

It is well-known that ligands can modify the properties of a given metal dramatically. However, it is also true that certain properties of a given complex are a result of the electronic nature of the metallic center. The study reported in this paper illustrates both phenomena.

On the basis of the previously mentioned simple rule, the addition of acetic acid to the C≡C triple bond of one of the two alkynyl ligands of **1** and **2**, and the subsequent protonation of the formed compounds, should afford carbene complexes of the type $[M{=}C(CH_2Ph)OC(O)CH_3]^+$, according to Scheme 5.

Complexes **1** and **2** are electroneutral, and therefore, they could be considered nucleophilic. Thus, the reactions should initially involve the addition of the electrophile $H^+$ at the nucleophilic β-carbon atom of one of the two alkynyl groups, to give cationic vinylidene intermediates. These species could undergo, on the α-carbon atom, nucleophilic attack of the acetate group. The resultant vinyl ester compounds should be nucleophilic at the β-carbon atom and, therefore, the reactions with $H^+$ should lead to cationic carbene derivatives.

The results obtained, in part, concordant with this approach, in particular for the case of the osmium complex **1** (Scheme 1). However, they also show noticeable divergences, mainly, when the behaviors of the ruthenium compounds **2**, **14**, and **15** are examined (Scheme 2 and 4).

The complexes $[M(C_2Ph)_2(CO)(PiPr_3)_2]$ (M = Os (**1**), Ru (**2**)) are isoelectronic and isostructural; furthermore, they contain the same ligands, and in the same positions. However, between them, there is a pronounced difference in reactivity toward acetic acid. The osmium complex **1** reacts with acetic acid to give the expected vinylacetato derivative $[Os(C_2Ph)\{C(=CHPh)OC(O)CH_3\}(CO)(PiPr_3)_2]$ (**3**) (Scheme 1). In contrast, the reaction of its analogous ruthenium complex **2** leads to phenylacetylene and $[Ru(C_2Ph)(\eta^2\text{-}O_2CCH_3)(CO)(PiPr_3)_2]$ (**5**) (Scheme 2). A similar relationship between the behaviors of **3** and its ruthenium analog $[Ru(C_2Ph)\{C(=CHPh)OC(O)CH_3\}(CO)(PiPr_3)_2]$ (**9**) is also observed. The osmium complex **3** affords the carbene cation $[Os(C_2Ph)\{=C(CH_2Ph)OC(O)CH_3\}(CO)(PiPr_3)_2]BF_4$ (**4**) by reaction with $HBF_4$ (Scheme 1), while the same reaction starting from **9** leads to phenylacetylene and $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]BF_4$ (**6**) (Scheme 2).

The behavior of **1** and **3** toward acetic acid and $HBF_4$ is in agreement with the general trend shown by the $\eta^1$-carbon unsaturated ligands. That is to say that nucleophiles add to the α-carbon atoms, whereas electrophiles add to the β-carbon atoms. The reactivity of **2** and **9**, that could be rationalized as the electrophilic attack at the α-carbon atom of an alkynyl group, however, is out of keeping with this simple rule. Furthermore, it indicates that the $\eta^1$-carbon unsaturated ligands do not always react with electrophile by attack at the β-carbon atom, in agreement with the Werner works.[4]

The behavior of the bis(alkynyl) complex $[Ru(C_2Ph)_2(CO)L(PiPr_3)_2]$ (L = $CH_3CN$ (**14**) and CO (**15**)) toward $HBF_4$ (Scheme 4) is similar to that of the bis(alkynyl) compound **2** toward acetic acid and different from the behavior previously observed for the iron complexes $[Fe(C_2R)_2L_4]$, where dimerization of the organic fragments takes place.[11] From a mechanistic point of view, the reactions of formation of **16** and **17** can be rationalized by electrophilic attack at the α-carbon atoms of the alkynyl groups of **14** and **15**. This implies acceptance of the fact that when the $[PhC{\equiv}C]^-$ group is coordinated to "$Ru(C_2Ph)(CO)(PiPr_3)_2$" and "$Ru(C_2Ph)(CO)L(PiPr_3)_2$" (L = $CH_3CN$, CO) fragments, the transfer of nucleophilicity from $C_\alpha$ to $C_\beta$ is not efficient, in contrast to that observed for the "$Os(C_2Ph)(CO)(PiPr_3)_2$" and "$Fe(C_2R)_2L_2$" (L = diphosphine) fragments. A similar situation has been described for anionic acetylide complexes of high-spin $d^5$ manganese (II) and for the $d^{10}$ metals of groups IB and

IIB, where the reactions with acids lead to the quantitative liberation of alkynes RC≡CH.[23]

In contrast to the behavior of **2**, **9**, **14**, and **15**, the alkynyl complex **5** reacts with $HBF_4$ by electrophilic attack at the β-carbon atom of the alkynyl group, and thus, the subsequent nucleophilic attack of the acetato group at the α-carbon atom affords the vinylacetato complex **6** (Scheme 2). The addition of acetic acid to the alkynyl cations **16** and **17** also follows the general trend shown by the $\eta^1$-carbon unsaturated ligands; in this way, the cationic vinylacetato derivatives $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)L(PiPr_3)_2]BF_4$ (L = $CH_3CN$ (**21**), CO (**22**)) are formed (Scheme 4).

The formation of **21** and **22** from **16** and **17** involves nucleophilic addition of the acetate group to the α-carbon atoms of the alkynyl ligands of **16** and **17**, and the electrophilic addition of $H^+$ to the β-carbon atoms. This is in agreement with the general trend shown by the $\eta^1$-carbon unsaturated ligands.

A particularly interesting case is the vinylacetato complex $[Ru\{C(=CHPh)OC(O)CH_3\}Cl(CO)(PiPr_3)_2]$ (**10**). This compound reacts with $HBF_4$ by electrophilic attack at the β-carbon atom of the vinylacetato ligand to give the carbene complex $[RuCl\{=C(CH_2Ph)OC(O)CH_3\}(CO)(PiPr_3)_2]BF_4$ (**11**). However, the reaction with acetic acid leads to PhCH=CHOC(O)$CH_3$ and $[RuCl\{\eta^1\text{-}OC(O)CH_3\}(CO)_2(PiPr_3)_2]$ (**12**) (Scheme 2). The formation of PhCH=CHOC(O)$CH_3$ is a result of the electrophilic attack of the proton of the acid at the α-carbon atom of the vinyl ligand of **10**, which seems to suggest that the source of the electrophile $H^+$ could also determine the direction of the addition.

## Concluding Remarks

This study has shown that the $\eta^1$-carbon unsaturated ligands do not always react with electrophiles by attack at the β-carbon atom. In this paper we report overwhelming evidence proving that the direction of the $H^+$ addition to alkynyl and vinylacetato complexes of ruthenium and osmium is determined by the electronic nature of the metallic center (Ru or Os), by the electronic properties of the ancillary ligands of the complexes, and also by the source of the electrophile.

## Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried using appropriate drying agents and freshly distilled under argon before use. Phenylacetylene (Merck) was distilled prior to use.

The starting materials $[Os(C_2Ph)_2(CO)(PiPr_3)_2]$ (**1**) and $[Ru(C_2Ph)_2(CO)(PiPr_3)_2]$ (**2**) were prepared by published methods.[7,8]

$^1H$ and $^{13}C$ NMR spectra were recorded on a Varian UNITY 300 spectrophotometer, and $^{31}P$ NMR spectra on either a Varian 200 XL (80.9 MHz) or a Varian UNITY 300 (121.4 MHz). Chemical shifts are expressed in ppm upfield from $Me_4Si$ ($^1H$ and $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). Coupling constants ($J$ and $N$ [$N = J(PH) + J(P'H)$ or $J(CP) + J(CP')$] are given in hertz. IR data were recorded on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectral analyses were performed with a VG Auto Spec. Ionization was by electron impact, operating at 70 eV.

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**Preparation of $[Os(C_2Ph)\{C(=CHPh)OC(O)CH_3\}(CO)(PiPr_3)_2]$ (3).** A suspension of complex **1** (150 mg, 0.2 mmol) in 5 mL of methanol was treated with glacial acetic acid (12 μL, 0.20 mmol). The mixture was stirred for 30 min at room temperature; during this period the initial dark red solid turned pink. The solid was filtered off, washed with methanol, and dried in vacuo. Yield: 145 mg (90%). Anal. Calcd for $C_{37}H_{56}O_3OsP_2$: C, 55.48; H, 7.05. Found: C, 55.64; H, 7.09. IR (Nujol): ν(C≡C) 2090 (s), ν(C≡O) 1900 (vs), ν(C=O) 1625 (s), ν(C=C) 1600 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.4–7.0 (m, 10 H, Ph), 5.75 (s, 1 H, =CHPh), 2.59 (m, 6 H, PCH), 2.36 (s, 3 H, $CH_3$), 1.37 (dvt, $J(HH) = 7.0$, $N = 13.7$, 18 H, $PCCH_3$), 1.25 (dvt, $J(HH) = 6.9$, $N = 12.7$, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 8.81 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $C_6D_6$): δ 187.88 (t, $J(CP) = 9.7$, CO), 184.44 (t, $J(CP) = 9.7$, Os—C=), 181.53 (s, OCO), 138.69 (t, $J(CP) = 1.6$, $C_{ipso}$ Ph), 130.88 (t, $J(CP) = 1.4$, $C_{ispo}$ Ph), 130.53, 128.55, 128.51, 127.90, 124.47, and 124.19 (all s, Ph), 123.04 (t, $J(CP) = 2.3$, =CHPh), 117.24 (s, ≡CPh), 111.21 (t, $J(CP) = 14.0$, Os—C≡), 24.69 (vt, $N = 24.9$, PCH), 20.49 and 19.07 (both s, $PCCH_3$), 18.08 (s, $CH_3CO_2$).

**Preparation of $[Os(C_2Ph)\{=C(CH_2Ph)OC(O)CH_3\}(CO)(PiPr_3)_2]BF_4$ (4).** A suspension of complex **3** (145 mg, 0.18 mmol) in 15 mL of diethyl ether was treated with a diethyl ether solution of $HBF_4$ ($HBF_4{\cdot}Et_2O$; 25 μL, 0.18 mmol). The mixture was stirred for 30 min at room temperature. The initial pink red solid slowly turned yellow. The solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 145 mg (90%). Anal. Calcd for $C_{37}H_{57}BF_4O_3OsP_2$: C, 50.00; H, 7.05. Found: C, 49.85; H, 6.91. IR (Nujol): ν(C≡C) 2100 (vw), ν(C≡O) 1955 (vs), ν(C=O) 1625 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.55–7.16 (m, 10 H, Ph), 4.40 (s, 2 H, $CH_2Ph$), 3.12 (s, 3 H, $CH_3$), 2.44 (m, 6 H, PCH), 1.30 (dvt, $J(HH) = 7.3$, $N = 14.9$, 18 H, $PCCH_3$), 1.19 (dvt, $J(HH) = 7.1$, $N = 14.2$, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 20.94 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 285.62 (t, $J(CP) = 4.8$, Os=C), 187.96 (s, OCO), 181.11 (t, $J(CP) = 8.3$, CO), 131.21 (s, Ph), 130.24 (s, Ph), 130.12 (t, $J(CP) = 1.6$, $C_{ipso}$ Ph), 128.91, 128.42, 128.16, and 126.69 (all s, Ph), 126.59 (t, $J(CP) = 2.8$, ≡CPh), 96.65 (t, $J(CP) = 23.2$, Os—C≡), 61.44 (s, $CH_2Ph$), 26.83 (vt, $N = 27.2$, PCH), 20.22 (s, $PCCH_3$), 19.35 (s, $CH_3CO_2$), 18.96 (s, $PCCH_3$).

**Preparation of $[Ru(C_2Ph)(\eta^2\text{-}O_2CCH_3)(CO)(PiPr_3)_2]$ (5).** A suspension of **2** (175 mg, 0.27 mmol) in 5 mL of methanol was treated with glacial acetic acid (16 μL, 0.27 mmol) and stirred for 30 min at room temperature. The resulting yellow solution was concentrated to dryness. The residue was treated with methanol, and the yellow solid obtained was filtered off, washed with methanol, and dried in vacuo. Yield: 158 mg (96%). Anal. Calcd for $C_{29}H_{50}O_3P_2Ru$: C, 57.13; H, 8.27. Found: C, 56.86; H, 8.43. IR (Nujol): ν(C≡C) 2100 (s), ν(C≡O) 1930 (vs), $\nu(OCO)_{asym}$ 1545 (m), $\nu(OCO)_{sym}$ 1430 (w) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.14–6.93 (m, 5 H, Ph), 2.54 (m, 6 H, PCH), 1.83 (s, 3 H, $CH_3$), 1.42 (dvt, $J(HH) = 7.0$, $N = 14.1$, 18 H, $PCCH_3$), 1.33 (dvt, $J(HH) = 6.9$, $N = 12.8$, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 41.93 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $C_6D_6$): δ 208.62 (t, $J(CP) = 13.1$, CO), 184.26 (s, OCO), 130.49, 130.30, and 124.30 (all s, Ph), 115.63 (s, ≡CPh), 109.92 (t, $J(CP) = 15.7$, Ru—C≡), 24.60 (vt, $N = 19.8$, PCH), 24.36 (s, $CH_3$), 20.63 and 19.70 (both s, $PCCH_3$).

**Preparation of $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]BF_4$ (6).** A solution of **5** (243 mg, 0.40 mmol) in 5 mL of acetone was treated with a diethyl ether solution of $HBF_4$ ($HBF_4{\cdot}Et_2O$; 54.5 μL, 0.40 mmol) and stirred for 1 h at room temperature. The solution was concentrated until the precipitation of a yellow solid (ca. 1 mL) and then diethyl ether was added to complete the precipitation. The solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 278 mg (92%). Anal. Calcd for $C_{32}H_{57}BF_4O_4P_2Ru$: C, 50.87; H, 7.60. Found: C, 51.01; H, 8.23. IR (Nujol): ν(C≡O) 1940 (vs), ν(C=O) 1680 (s), ν(C=O) 1640 (vs), ν(C=C) 1595 (s), $\nu(BF_4)$ 1050 (br, s) $cm^{-1}$. IR ($CH_2Cl_2$): ν(C≡O) 1950 (vs), ν(C=O) 1710 (s). $^1H$

NMR (300 MHz, $CDCl_3$): δ 7.21–7.00 (m, 5 H, Ph), 5.51 (t, $J$(HP) = 2.3, 1 H, =CHPh), 2.45 (s, 3 H, $CH_3CO_2$), 2.37 (m, 6 H, PCH), 2.13 (s, 6 H, $(CH_3)_2CO$), 1.32 (dvt, $J$(HH) = 7.1, $N$ = 14.6, 18 H, $PCCH_3$), 1.20 (dvt, $J$(HH) = 7.1, $N$ = 12.8, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 36.39 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 210.05 (br, $(CH_3)_2CO$), 204.72 (t, $J$(CP) = 13.1, Ru—C=), 178.91 (s, OCO), 175.65 (br, CO), 135.39 (t, $J$(CP) = 1.8, $C_{ipso}$ Ph), 128.33, 127.24, and 125.28 (all s, Ph), 122.29 (t, $J$(CP) = 3.5, =CHPh), 31.14 (s, $(CH_3)_2CO$), 23.69 (vt, $N$ = 19.8, PCH), 20.02 (s, $CH_3CO_2$), 19.80 and 18.69 (both s, $PCCH_3$).

**Preparation of [Ru(C₂Ph){C(=CHPh)OC(O)CH₃}(CO)(PiPr₃)₂] (9).** A solution of complex **6** (144 mg, 0.19 mmol) in 6 mL of tetrahydrofuran was treated with $LiC_2Ph$ (22 mg, 0.20 mmol) and stirred for 15 min at room temperature. The resulting red-brown solution was concentrated to dryness. The oily residue was treated with 10 mL of methanol and stirred until a pale orange solid precipitated, which was filtered off, washed with methanol, and dried in vacuo. Yield: 48 mg (35%). Anal. Calcd for $C_{37}H_{56}O_3P_2Ru$: C, 62.43; H, 7.93. Found: C, 61.95; H, 8.15. IR (Nujol): ν(C≡C) 2085 (m), ν(C≡O) 1915 (vs), ν(C=O) 1640 (vs), ν(C=C) 1590 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.44–7.03 (m, 10 H, Ph), 5.89 (br, 1 H, =CHPh), 2.50 (m, 6 H, PCH), 2.30 (s, 3 H, $CH_3$), 1.41 (dvt, $J$(HH) = 7.1, $N$ = 14.2, 18 H, $PCCH_3$), 1.26 (dvt, $J$(HH) = 6.4, $N$ = 12.7, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 40.33 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 209.25 (t, $J$(CP) = 13.8, Ru—C=), 195.99 (t, $J$(CP) = 12.2, CO), 178.64 (s, OCO), 137.74 (t, $J$(CP) = 1.6, $C_{ipso}$ Ph), 130.30 (t, $J$(CP) = 1.4, $C_{ipso}$ Ph), 129.89, 128.08, 127.81, 127.45, 123.90, and 123.47 (all s, Ph), 122.73 (t, $J$(CP) = 3.2, =CHPh), 116.04 (s, ≡CPh), 24.63 (vt, $N$ = 20.2, PCH), 20.44 (s, $PCCH_3$), 20.28 (s, $CH_3CO_2$), 19.08 (s, $PCCH_3$).

**Preparation of [Ru{C(=CHPh)OC(O)CH₃}Cl(CO)(PiPr₃)₂] (10).** A solution of complex **6** (174 mg, 0.23 mmol) in 10 mL of methanol was treated with NaCl (13.5 mg, 0.23 mmol) and stirred for 2 h at room temperature. A yellow microcrystalline solid precipitated, which was filtered off, washed with methanol, and dried in vacuo. Yield: 104 mg (70%). Anal. Calcd for $C_{29}H_{51}ClO_3P_2Ru$: C, 53.90; H, 7.96. Found: C, 54.12; H, 8.05. IR (Nujol): ν(C≡O) 1930 (vs), ν(C=O) 1640 (vs), ν(C=C) 1590 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.39 (d, $J$(HH) = 7.5, 2 H, $H_o$ Ph), 7.29 (t, $J$(HH) = 7.5, 2 H, $H_m$ Ph), 7.09 (t, $J$(HH) = 7.5, 1 H, $H_p$ Ph), 5.75 (br, 1 H, =CHPh), 2.58 (m, 6 H, PCH), 2.41 (s, 3 H, $CH_3$), 1.41 (dvt, $J$(HH) = 7.0, $N$ = 13.9, 18 H, $PCCH_3$), 1.31 (dvt, $J$(HH) = 6.5, $N$ = 12.5, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 33.75 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 208.08 (t, $J$(CP) = 13.8, Ru—C=), 186.32 (t, $J$(CP) = 12.4, CO), 178.20 (s, OCO), 137.00 (t, $J$(CP) = 1.6, $C_{ipso}$ Ph), 128.16, 127.28, and 124.24 (all s, Ph), 120.88 (t, $J$(CP) = 3.2, =CHPh), 23.81 (vt, $N$ = 19.4, PCH), 20.25 (s, $PCCH_3$), 19.97 (s, $CH_3CO_2$), 18.99 (s, $PCCH_3$).

**Preparation of [RuCl{=C(CH₂Ph)OC(O)CH₃}(CO)(PiPr₃)₂]BF₄ (11).** A solution of complex **10** (82 mg, 0.13 mmol) in 5 mL of dichloromethane was treated with a diethyl ether solution of $HBF_4$ ($HBF_4$·$Et_2O$; 17.5 μL, 0.13 mmol) and stirred for 20 min at room temperature. The solution was concentrated to ca. 0.5 mL, and addition of diethyl ether caused the precipitation of a pale yellow solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 52 mg (55%). Anal. Calcd for $C_{29}H_{52}BClF_4O_3P_2Ru$: C, 47.45; H, 7.14. Found: C, 47.15; H, 7.12. IR (Nujol): ν(C≡O) 1985 (vs), ν(C=O) 1655 (vs), ν($BF_4$) 1050 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 7.56–7.23 (m, 5 H, Ph), 4.77 (s, 2 H, $CH_2Ph$), 3.04 (s, 3 H, $CH_3$), 2.40 (m, 6 H, PCH), 1.26 (dvt, $J$(HH) = 6.8, $N$ = 13.9, 18 H, $PCCH_3$), 1.24 (dvt, $J$(HH) = 6.8, $N$ = 13.6, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 44.50 (s).

**Preparation of [RuCl{η¹-OC(O)CH₃}(CO)₂(PiPr₃)₂] (12).** A solution of complex **10** (90 mg, 0.14 mmol) in 8 mL of toluene was treated with an excess of glacial acetic acid (0.2 mL, 3.3 mmol) and stirred at reflux temperature. After 6 h the colorless solution was concentrated and a white solid precipitated, which was filtered off, washed with methanol, and dried in vacuo. Yield: 45.0 mg (56%). Anal. Calcd for $C_{22}H_{45}ClO_4P_2Ru$: C, 46.19; H, 7.93. Found: C, 46.16; H, 7.86. IR (Nujol): ν(C≡O) 2030 and 1965 (vs), ν(C=O) 1610 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.58 (m, 6 H, PCH), 1.91 (s, 3 H, $CH_3$), 1.37 (dvt, $J$(HH) = 7.4, $N$ = 14.8, 18 H, $PCCH_3$), 1.29 (dvt, $J$(HH) = 6.9, $N$ = 13.2, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 41.94 (s). The mass spectrum of the mother liquids of the solution shows a peak at $m/e$ 162, which can be assigned to PhCH=CHOC(O)$CH_3$.

Acetic acid (17 μL, 0.28 mmol) was added to a NMR tube containing a solution of complex **10** (9 mg, 0.014 mmol) in 0.6 mL of $C_6D_6$. The sample was shaken and immersed in a bath at 80 °C for 6 h. $^1H$ NMR (300 MHz, $C_6D_6$): Along with the signals due to the starting materials and complex **12**, two doublets can be recognized at 7.93 and 5.70 ppm with a coupling constant of 7.3 Hz, assigned to the olefin protons of *cis*-PhCH=CHOC(O)$CH_3$.

**Preparation of [Ru(η²-O₂CCH₃)(CO)₂(PiPr₃)₂]BF₄ (13).** A solution of complex **6** (83 mg, 0.11 mmol) in 5 mL of acetone was treated with an excess of glacial acetic acid (0.12 mL, 2.0 mmol) and stirred at reflux temperature. After 2 h the colorless solution was concentrated until a white solid precipitated (ca. 0.5 mL), and then diethyl ether was added to complete the precipitation. The solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 63 mg (91%). Anal. Calcd for $C_{22}H_{45}BF_4O_4P_2Ru$: C, 42.39; H, 7.28. Found: C, 42.36; H, 7.43. IR (Nujol): ν(C≡O) 2050 and 1990 (vs), ν($BF_4$) 1050 (br, s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): δ 2.55 (m, 6 H, PCH), 2.01 (s, 3 H, $CH_3$), 1.37 (dvt, $J$(HH) = 7.3, $N$ = 14.8, 36 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 50.93 (s). The mass spectrum of the mother liquids of the solution shows a peak at $m/e$ 162, which can be assigned to PhCH=CHOC(O)$CH_3$.

Acetic acid (10 μL, 0.17 mmol) was added to a NMR tube containing a solution of complex **6** (8.3 mg, 0.011 mmol) in 0.6 mL of $(CD_3)_2CO$. The sample was shaken and immersed in a bath at 60 °C for 4 h. $^1H$ NMR (300 MHz, $(CD_3)_2CO$): Along with the signals due to the starting materials and complex **13**, two doublets can be recognized at 7.65 and 5.76 ppm with a coupling constant of 7.3 Hz, assigned to the olefin protons of *cis*-PhCH=CHOC(O)$CH_3$.

**Preparation of [Ru(C₂Ph)₂(CO)(NCCH₃)(PiPr₃)₂] (14).** Acetonitrile (3 mL) was added to a Schlenk tube containing complex **2** (78.2 mg, 0.12 mmol). A white solid precipitated immediately, which was filtered off, washed with acetonitrile, and dried in vacuo. Yield: 81.5 mg (98%). Anal. Calcd for $C_{37}H_{55}NOP_2Ru$: C, 64.14; H, 8.00; N, 2.02. Found: C, 64.03; H, 8.44; N, 1.87. IR (Nujol): ν(C≡N) 2320 (vw), ν(C≡C) 2080 (s), ν(C≡O) 1935 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $(CDCl_3)$: δ 7.2–6.9 (m, 10 H, Ph), 2.85 (m, 6 H, PCH), 2.16 (s, 3 H, $CH_3$), 1.46 (dvt, $J$(HH) = 6.8, $N$ = 13.2, 36 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): δ 39.80 (s).

**Preparation of [Ru(C₂Ph)₂(CO)₂(PiPr₃)₂] (15).** Carbon monoxide was bubbled through a solution of complex **2** (100 mg, 0.15 mmol) in 20 mL of hexane for 20 min. The resulting white suspension was concentrated in vacuo. The white solid was filtered off, washed with hexane, and dried in vacuo. Yield: 66 mg (63%). Anal. Calcd for $C_{38}H_{52}O_2P_2Ru$: C, 63.61; H, 7.71. Found: C, 63.56; H, 7.64. IR (Nujol): ν(C≡C) 2090 (s), ν(C≡O) 1970 (vs) $cm^{-1}$. $^{13}C\{^1H\}$ NMR (75.43 MHz, $C_6D_6$): δ 202.51 (t, $J$(CP) = 12.3, CO), 130.74, 130.13, and 124.75 (all s, Ph), 114.47 (s, ≡CPh), 107.16 (t, $J$(CP) = 13.4, Ru—C≡), 26.22 (vt, $N$ = 22.6, PCH), 19.78 (s, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $C_6H_3$): δ 45.42 (s).

**Preparation of [Ru(C₂Ph)(CO)(NCCH₃)₂(PiPr₃)₂]BF₄ (16).** A suspension of **14** (139 mg, 0.20 mmol) in 4 mL of acetonitrile was treated with a diethyl ether solution of $HBF_4$ ($HBF_4$·$Et_2O$; 27.5 μL, 0.20 mmol) and stirred for 10 min at room temperature. The resulting yellow solution was concentrated, and addition of diethyl ether led to the formation of a white-off solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 92 mg (64%). Anal. Calcd for $C_{31}H_{53}BF_4N_2OP_2Ru$: C,

51.74; H, 7.42; N, 3.89. Found: C, 51.30; H, 7.16; N, 3.96. IR (Nujol): $\nu$(C≡N) 2340, 2290 (w), $\nu$(C≡C) 2110 (s), $\nu$(C≡O) 1960 (vs), $\nu(BF_4)$ 1050 (br, s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.2–7.0 (m, 5 H, Ph), 2.66 (m, 6 H, PCH), 2.48 (s, 3 H, $CH_3$), 2.45 (s, 3 H, $CH_3$), 1.42 (dvt, $J$(HH) = 6.8, $N$ = 13.0, 18 H, $PCCH_3$), 1.40 (dvt, $J$(HH) = 6.9, $N$ = 12.8, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 37.17 (s).

**Preparation of $[Ru(C_2Ph)(CO)_2\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]BF_4$ (17).** A suspension of **15** (111 mg, 0.16 mmol) in 4 mL of acetone was treated with a diethyl ether soultion of $HBF_4$ ($HBF_4{\cdot}Et_2O$; 29 μL, 0.21 mmol) and stirred for 15 min at room temperature. The resulting yellow solution was concentrated until a pale yellow solid precipitated (ca. 0.5 mL), and then diethyl ether was added to complete the precipitation. The solid was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 92 mg (79%). Anal. Calcd for $C_{31}H_{53}BF_4O_3P_2Ru$: C, 51.46; H, 7.38. Found: C, 51.52; H, 7.80. IR (Nujol): $\nu$(C≡C) 2120 (m), $\nu$(C≡O) 1995 (vs), $\nu$(C=O) 1670 (s), $\nu(BF_4)$ 1050 (br, s) $cm^{-1}$. IR ($CH_2Cl_2$): $\nu$(C≡C) 2120 (m), $\nu$(C≡O) 1995 (vs), $\nu$(C=O) 1710 (s). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.2–7.0 (m, 5 H, Ph), 2.7 (m, 6 H, PCH), 2.17 (s, 6 H, $(CH_3)_2CO$), 1.46 (dvt, $J$(HH) = 7.1, $N$ = 14.2, 36 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 45.28 (s).

**Preparation of $[Ru(C_2Ph)(CO)_2(PiPr_3)_2]BF_4$ (18).** A solution of **15** (68 mg, 0.10 mmol) in 5 mL of tetrahydrofuran was treated with a diethyl ether solution of $HBF_4$ ($HBF_4{\cdot}Et_2O$; 16 μL, 0.12 mmol) and stirred for 1 h at room temperature. The solution was concentrated to ca. 0.5 mL and addition of diethyl ether caused the precipitation of a yellow solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 42 mg (62%). Anal. Calcd for $C_{28}H_{47}BF_4O_2P_2Ru{\cdot}0.5H_2O$: C, 49.86; H, 7.32. Found: C, 49.67; H, 7.98. IR (Nujol): $\nu$(OH) 3400 (m, br), $\nu$(C≡C) 2120 (m), $\nu$(C≡O) 1995 (s), $\nu(BF_4)$ 1050 (br, s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.12–6.92 (m, 5 H, Ph), 3.1 (br, 1 H, $0.5H_2O$), 2.57 (m, 6 H, PCH), 1.33 (dvt, $J$(HH) = 7.3, $N$ = 14.2, 36 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 43.18 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): $\delta$ 198.67 (br, CO), 130.29, 128.32, 127.99, and 125.17 (all s, Ph), 127.77 (s, ≡CPh), 116.87 (t, $J$(CP) = 11.5, Ru—C≡), 25.23 (vt, $N$ = 21.6, PCH), 19.46 (s, $PCCH_3$).

**Preparation of $[Ru(C_2Ph)(CO)_2(NCCH_3)(PiPr_3)_2]BF_4$ (19).** A solution of **18** (67 mg, 0.1 mmol) in 4 mL of dichloromethane was treated with an excess of acetonitrile (0.1 mL). The resulting colorless solution was concentrated to ca. 0.5 mL, and addition of diethyl ether caused the precipitation of a white solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 57 mg (81%). Anal. Calcd for $C_{30}H_{50}BF_4NO_2P_2Ru$: C, 51.00; H, 7.13; N, 1.98. Found: C, 51.02; H, 7.32; N, 1.90. IR (Nujol): $\nu$(C≡N) 2295 (vw), $\nu$(C≡C) 2145 (m), $\nu$(C≡O) 2010 (s), $\nu(BF_4)$ 1060 (br, s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.2–7.0 (m, 5 H, Ph), 2.7 (m, 6 H, PCH), 2.51 (s, 3 H, $CH_3CN$), 1.44 (dvt, $J$(HH) = 7.21, $N$ = 14.4, 36 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 43.83 (s).

**Preparation of $[Ru(C_2Ph)(CO)_3(PiPr_3)_2]BF_4$ (20).** Carbon monoxide was bubbled through a solution of complex **18** (75 mg, 0.11 mmol) in 10 mL of dichloromethane for 15 min. The resulting colorless solution was concentrated to ca. 0.5 mL and addition of diethyl ether caused the precipitation of a white solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 60 mg (79%). Anal. Calcd for $C_{29}H_{47}BF_4O_3P_2Ru$: C, 50.23; H, 6.83. Found: C, 50.31; H, 6.85. IR (Nujol): $\nu$(C≡C) 2120 (w), $\nu$(C≡O) 2060 (br, vs), $\nu(BF_4)$ 1060 (br, s) $cm^{-1}$. IR ($CH_2Cl_2$): $\nu$(C≡C) 2110 (w), $\nu$(C≡O) 2050 and 2040 (vs). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.24–7.13 (m, 5 H, Ph), 2.80 (m, 6 H, PCH), 1.48 (dvt, $J$(HH) = 6.9, $N$ = 14.2, 36 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 48.35 (s).

**Preparation of $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)(NCCH_3)(PiPr_3)_2]BF_4$ (21). Route a.** Complex **6** (83 mg, 0.11 mmol) was dissolved in 0.5 mL of acetonitrile. Addition of diethyl ether to the resulting colorless solution caused the precipitation of a white solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 70 mg (86%).

**Route b.** A solution of **16** (72 mg, 0.1 mmol) in acetone (4 mL) was treated with glacial acetic acid (12 μL, 0.2 mmol). After being stirred for 24 h at room temperature, the solution was concentrated to ca. 0.5 mL and addition of diethyl ether led to the formation of a white solid. Yield: 45.2 mg (61%). Anal. Calcd for $C_{31}H_{54}BF_4NO_3P_2Ru{\cdot}0.5CH_3CN$: C, 50.63; H, 7.37; N, 2.77. Found: C, 50.59; H, 7.99; N, 3.00. IR (Nujol): $\nu$(C≡N) 2300, 2280 (vw), $\nu$(C≡O) 1950 (vs), $\nu$(C=O) 1640 (vs), $\nu$(C=C) 1595 (s), $\nu(BF_4)$ 1050 (br, s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.32–7.08 (m, 5 H, Ph), 5.71 (t, $J$(HP) = 2.4, 1 H, =CHPh), 2.57 (s, 3 H, $CH_3CN$), 2.44 (s, 3 H, $CH_3CO_2$), 2.36 (m, 6 H, PCH), 1.99 (s, 1.5 H, 0.5 free $CH_3CN$), 1.31 (dvt, $J$(HH) = 6.9, $N$ = 14.1, 18 H, $PCCH_3$), 1.27 (dvt, $J$(HH) = 7.2, $N$ = 13.5, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.9 MHz, $CDCl_3$): $\delta$ 35.43 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): $\delta$ 204.52 (t, $J$(CP) = 12.6, Ru—C=), 180.91 (br, CO), 179.84 (s, OCO), 135.7 (s, =CHPh), 129.78 (s, CN), 128.46, 127.58, 125.59, and 123.48 (all s, Ph), 24.12 (vt, $N$ = 20.2, PCH), 19.92 (s, $CH_3CO_2$), 19.73 and 18.76 (both s, $PCCH_3$), 3.51 (s, $CH_3CN$).

**Preparation of $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)_2(PiPr_3)_2]BF_4$ (22). Route a.** Carbon monoxide was bubbled through a solution of complex **6** (100 mg, 0.13 mmol) in 10 mL of dichloromethane for 10 min. The resulting colorless solution was concentrated to ca. 0.5 mL, and addition of diethyl ether caused the precipitation of a white solid, which was filtered off, washed with diethyl ether, and dried in vacuo. Yield: 80 mg (85%).

**Route b.** A solution of **17** (102 mg, 0.14 mmol) in 4 mL of dichloromethane was treated with an excess of glacial acetic acid (50 μL, 0.84 mmol). After being stirred for 9 h at room temperature, the solution was worked up as described in route a. Yield: 92 mg (90%). Anal. Calcd for $C_{30}H_{48}BF_4O_4P_2Ru$: C, 49.87; H, 6.70. Found: C, 49.58; H, 6.64. IR (Nujol): $\nu$(C≡O) 2040, 1970 (vs), $\nu$(C=O) 1620 (vs), $\nu$(C=C) 1590 (s), $\nu(BF_4)$ 1050 (br, s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.45–7.18 (m, 5 H, Ph), 5.99 (br, 1 H, =CHPh), 2.60 (s, 3 H, $CH_3$), 2.45 (m, 6 H, PCH), 1.31 (dvt, $J$(HH) = 6.9, $N$ = 14.1, 18 H, $PCCH_3$), 1.29 (dvt, $J$(HH) = 6.3, $N$ = 12.9, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): $\delta$ 40.34 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): $\delta$ 201.23 (t, $J$(CP) = 11.3, Ru—C=), 196.05 (t, $J$(CP) = 10.6, CO), 183.57 (s, OCO), 178.36 (t, $J$(CP) = 14.75, CO), 134.44 (t, $J$(CP) = 2.3, $C_{ipso}$ Ph), 128.7 and 128.05 (both s, Ph), 127.42 (t, $J$(CP) = 4.8, =CHPh), 126.8 (s, Ph), 25.27 (vt, $N$ = 21.6, PCH), 19.75 (s, $CH_3COO$), 19.64 and 18.89 (both s, $PCCH_3$).

**X-ray Structure Analysis of $[Ru\{C(=CHPh)OC(O)CH_3\}(CO)\{\eta^1\text{-}OC(CH_3)_2\}(PiPr_3)_2]BF_4{\cdot}0.25C_3H_6O$ (6).** Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of diethyl ether into a concentrated solution of **6** in acetone. Atomic coordinates are listed in Table 2. A summary of crystal data, intensity collection procedure, and refinement parameters is reported in Table 3. The crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 56 reflections in the range $20 \le 2\theta \le 43°$. Data were collected in two blocks using the same crystal in different orientations (6591 and 3764 reflections). The 10 355 recorded reflections were corrected for Lorentz and polarization effects. The data were merged and batch scale factors were applied on the base of 735 common reflections (0.9961, block 1; 1.0039, block 2). The internal consistency $R$ index was 0.0306. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed.

The structure was solved by Patterson (Ru atom) and conventional Fourier techniques in the monoclinic space group $C2/m$ (No. 12) with $Z = 4$. The cation in **6** was observed partially disordered around the crystallographic mirror plane (carbonyl and phenyl groups). Several attempts to refine the structure in the noncentrosymmetric space groups $C2$ and $Cm$ led to chemically unsatisfactory results. The carbonyl ligand was modeled by including two CO groups, one of them constrained to lie on the mirror plane, and refined with complementary

**Table 2. Atomic Coordinates (×10⁴) and Equivalent or Isotropic Displacement Coefficients (Å² × 10³) for the compound [Ru{C(=CHPh)OC(O)CH₃}(CO){η¹-OC-(CH₃)₂}(P*i*Pr₃)₂]BF₄·0.25C₃H₆O (6)**

| atom | *X/a* | *Y/b* | *Z/c* | $U_{eq}$[a]/$U_{iso}$ |
|---|---|---|---|---|
| Ru | 4516(1) | 0 | 2192(1) | 38(1) |
| P(1) | 4535(1) | 1644(1) | 2281(1) | 53(1) |
| O(1) | 3662(3) | 0 | 2944(3) | 31(2) |
| C(1) | 2920(5) | 0 | 2531(5) | 31(3) |
| C(2) | 2195(6) | 0 | 2900(7) | 51(4) |
| O(2) | 2704(3) | 0 | 1709(3) | 39(2) |
| C(3) | 3418(6) | 0 | 1343(6) | 47(3) |
| C(4) | 3159(6) | 0 | 510(6) | 59(4) |
| C(5)[c] | 2326(4) | −138(10) | −123(4) | 45(3)[b] |
| C(6)[c] | 1552 | −310 | 41 | 62(4)[b] |
| C(7)[c] | 806 | −325 | −603 | 73(5)[b] |
| C(8)[c] | 834 | −169 | −1412 | 71(5)[b] |
| C(9)[c] | 1608 | 3 | −1575 | 56(3)[b] |
| C(10)[c] | 2354 | 18 | −931 | 52(3)[b] |
| C(11a)[d] | 5044(22) | 0 | 1365(22) | 36(11)[b] |
| O(3a)[d] | 5344(16) | 0 | 850(15) | 54(7)[b] |
| C(11b)[d] | 5100(15) | 295(20) | 1434(13) | 19(6)[b] |
| O(3b)[d] | 5414(10) | 368(13) | 890(10) | 32(3)[b] |
| O(4) | 5553(4) | 0 | 3348(4) | 51(2) |
| C(12) | 6252(6) | 0 | 3865(5) | 44(3) |
| C(13) | 7049(8) | 0 | 3590(10) | 89(6) |
| C(14) | 6336(7) | 0 | 4754(6) | 58(4) |
| C(15) | 3966(5) | 2341(6) | 1375(4) | 69(3) |
| C(16) | 3003(5) | 2243(6) | 1168(4) | 60(3) |
| C(17) | 4260(6) | 2173(9) | 618(5) | 110(5) |
| C(18) | 4032(5) | 2027(4) | 3089(4) | 55(3) |
| C(19) | 4547(5) | 1704(5) | 3937(4) | 62(3) |
| C(20) | 3806(7) | 3025(5) | 3126(5) | 91(4) |
| C(21) | 5635(6) | 2095(8) | 2606(6) | 97(4) |
| C(22) | 5677(8) | 3102(10) | 2574(10) | 172(8) |
| C(23) | 6222(6) | 1688(11) | 2146(7) | 153(8) |
| B | 7419(22) | 2725(21) | 4810(19) | 129(12)[b] |
| F(1) | 8178(11) | 2862(12) | 5362(10) | 138(5)[b] |
| F(2) | 7311(11) | 1922(10) | 4423(9) | 128(5)[b] |
| F(3) | 7555(10) | 3165(10) | 4200(9) | 129(5)[b] |
| F(4) | 6770(16) | 3072(17) | 4960(16) | 219(10)[b] |
| O(30) | 127(21) | 0 | −3640(17) | 89(11)[b] |
| C(31) | −101(18) | 0 | −4380(18) | 50(9)[b] |
| C(32) | −1048(23) | 0 | −4835(33) | 208(48)[b] |
| C(33) | 554(31) | 0 | −4877(26) | 106(21)[b] |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor. [b] Isotropic displacement parameters are displayed for these atoms. [c] A constrained refinement has been applied to the phenyl group (C(5) to C(10)). [d] The carbonyl group was observed disordered in (a-labeled) and out (b-labeled) of the symmetry plane.

occupancy factors assigned on the basis of the thermal parameters. The phenyl group of the chelate ligand was allowed to refine out of the symmetry plane, with its geometry constrained to a regular hexagon. The $BF_4^-$ anion and the solvent molecules were refined with internal distances restrained to ideal geometries (B—F = 1.31(5), F···F = 2.14(5), C=O = 1.21(1), C—C = 1.54(1), and C···O 2.37(1) Å). The refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles for all non-hydrogen atoms, except those involved in disorder. Hydrogen atoms were geometrically calculated for those atoms not disordered and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Ru and P, were taken from ref 24. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weight defined as $w^{-1} = \sigma^2(F_o) + 0.001F_o^2$. Final *R* and $R_w$ values were 0.0629 and 0.0666, respectively. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[25]

**Table 3. Crystal Data and Data Collection and Refinement for [Ru{C(=CHPh)OC(O)CH₃}(CO){η¹-OC-(CH₃)₂}(P*i*Pr₃)₂]BF₄·0.25C₃H₆O (6)**

| | |
|---|---|
| **Crystal Data** | |
| formula | $C_{32}H_{57}BF_4O_4P_2Ru·0.25C_3H_6O$ |
| mol wt | 767.14 |
| color and habit | light yellow, laminar crystal |
| cryst size, mm | 0.376 × 0.152 × 0.472 |
| cryst syst | monoclinic |
| space group | *C*2/*m* (No. 12) |
| *a*, Å | 16.399(2) |
| *b*, Å | 14.870(5) |
| *c*, Å | 16.855(3) |
| *β*, deg | 105.98(2) |
| *V*, Å³ | 3951(2) |
| *Z* | 4 |
| *D*(calcd), g cm⁻³ | 1.290 |
| temp, K | 200 |
| **Data Collection and Refinement** | |
| diffractometer | 4-Circle Siemens-STOE AED |
| λ(Mo Kα), Å; technique | 0.710 73; bisecting geometry |
| monochromator | graphite oriented |
| $\mu$, mm⁻¹ | 0.52 |
| scan type | $\omega/2\theta$ |
| 2θ range, deg | $3 \le 2\theta \le 50$ |
| no. of data collect | 10 355 |
| no. of unique data | 3626 ($R_{int}$ 0.031) |
| no. of unique obsd data | 2719 ($F_o \ge 5.0\sigma(F_o)$) |
| no. of params refined | 218 |
| *R*, $R_w$[a] | 0.0629, 0.0667 |

[a] $w^{-1} = \sigma^2(F_o) + 0.001(F_o)^2$.

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, and interatomic distances (8 pages). Ordering information is given on any current masthead page.

OM930838D

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