Journal of Organometallic Chemistry, 426 (1992) 383–398
Elsevier Sequoia S.A., Lausanne
JOM 22187

Reactions of alkenyl and alkynyl ruthenium(II) complexes with isocyanides: synthesis of α,β-unsaturated η^1-acylruthenium(II) complexes and X-ray structure of $[Ru(C{\equiv}CPh)(CN^tBu)_3(PPh_3)_2]PF_6$

Julio Montoya, Amelia Santos, Javier López
Instituto de Ciencia de Materiales de Madrid, sede D, CSIC, Serrano 113, 28006 Madrid (Spain)

Antonio M. Echavarren
Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid (Spain)

Josep Ros
Departament de Química, Universitat Autónoma de Barcelona, 08193 Bellaterra, Barcelona (Spain)

and Antonio Romero
Instituto de Química Física Rocasolano, CSIC, Serrano 119, 28006 Madrid (Spain)

(Received June 24, 1991)

Abstract

Reaction of (*E*)-alkenyl complexes $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2$ and $Ru(CO)Cl(CH{=}CHR)(PPh_3)_2L$ (L = Me_2Hpz, py) with an excess of an isocyanide R'NC (R' = ^{t}Bu or cyclohexyl (Cy)) gives (*E*)-α,β-unsaturated-η^1-acyl complexes $[Ru(COCH{=}CHR)(CNR')_3(PPh_3)_2]Cl$ in good yield. The corresponding reactions with 1 equivalent of isocyanide give the hexacoordinate complexes $Ru(CO)Cl(CH{=}CHR)(CNR')(PPh_3)_2$. The reaction of $[Ru(CO)(CH{=}CHR)(NCMe)_2(PPh_3)_2]PF_6$ with ^{t}BuNC also affords η^1-acyl complexes $[Ru(COCH{=}CHR)(CN^tBu)_3(PPh_3)_2]PF_6$. On the other hand, treatment of alkynyl complexes $[Ru(CO)(C{\equiv}CR)(py)_2(PPh_3)_2]PF_6$ with an excess of ^{t}BuNC under forcing conditions promotes substitution of CO and pyridine ligands by the isocyanide, yielding alkynyl derivatives $[Ru(C{\equiv}CR)(CN^tBu)_3(PPh_3)_2]PF_6$. An X-ray diffraction study of one of the complexes (R = Ph) confirmed the proposed structure. Similarly, reaction of the alkynyl complexes with CO gives only the ligand-substitution products $[Ru(CO)_2(C{\equiv}R)(py)(PPh_3)_2]PF_6]$.

Correspondence to: Dr. A. Santos, Instituto de Ciencia de Materiales de Madrid, sede D, CSIC, Serrano 113, 28006 Madrid, Spain, or Dr. A.M. Echavarren, Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain.

Introduction

η^1- or η^2-Acyl complexes can be made by reaction of strongly coordinating ligands with transition metal complexes containing both carbonyl and σ-bonded carbon ligands. This proceeds by means of an intramolecular CO insertion reaction [1–3]. The isoelectronic isocyanide ligand usually undergoes migratory insertion more readily than the CO, yielding η^1- or η^2-iminoacyl complexes [4–6] and, in some cases, even polyinsertion products [7]. However, we recently reported in a preliminary communication that the reaction of several (*E*)-σ-alkenyl carbonyl Ru^{II} complexes with an excess of t-butyl isocyanide promoted the intramolecular CO insertion yielding η^1-acyl ruthenium(II) complexes [8] instead of η^1- or η^2-iminoacyl complexes [9]. A related insertion was recently observed in the synthesis of η^2-acyl complexes by reaction of some alkenyl ruthenium derivatives with CO [10]. We present below the results of a more extensive study on the synthesis of α,β-unsaturated η^1-acyl ruthenium(II) complexes, as well as the corresponding reactions of isocyanides with σ-alkynyl ruthenium(II) complexes containing one CO ligand. The related reaction of the σ-alkynyl complexes with CO has also been briefly examined.

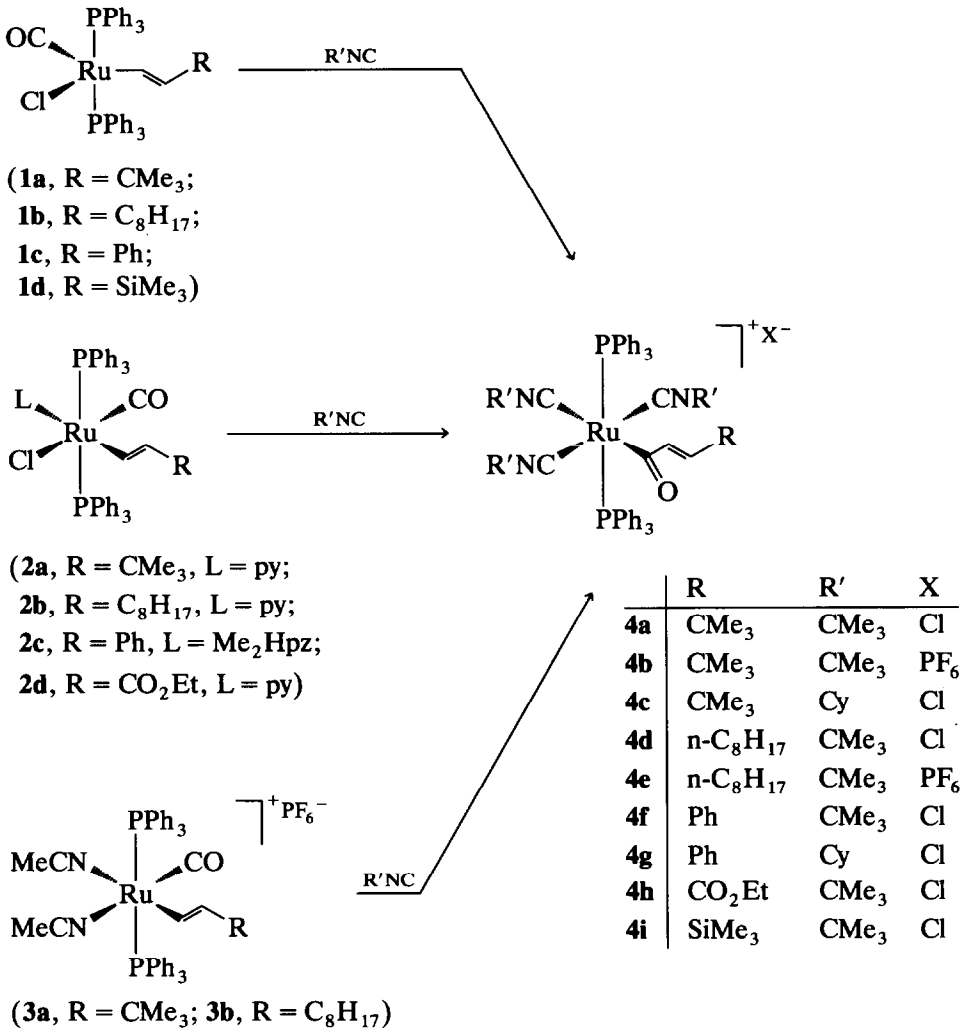
Results and discussion

Reactions of alkenyl complexes with isocyanides

The reaction of (*E*)-alkenyl complexes **1a–1d** [11], **2a–2d** [12,13], or **3a–3b** [14] with an excess of t-butyl or cyclohexyl isocyanide furnished hexacoordinated ruthenium(II) complexes **4a–4i** in excellent yields (Scheme 1) as moderately hygroscopic solids. The starting alkenyl complexes were rapidly converted into the acyl derivatives **4** within a few minutes at 23°C, as shown by monitoring the transformations by ^{1}H NMR spectroscopy in deuterochloroform or deuterobenzene solutions.

However, the ethoxycarbonyl ethenyl derivative **2d** required heating in ethanol under reflux for several hours to give **4h** in 72% yield. This is in keeping with the known lower activity in the migratory insertion of σ-bonded carbon ligands bearing electron-withdrawing substituents [1]. On the other hand, the more hindered $Ru(CO)Cl(CPh{=}CHPh)(PPh_3)_2$ (**1e**) [11] does not give the corresponding acyl derivative (see below) [15].

The ^{1}H NMR spectra of the acyl complexes **4** showed two sharp doublets corresponding to the olefinic protons, in contrast to the starting materials, that showed further splitting by coupling with the phosphorus atoms. The proton-decoupled ^{13}C NMR spectra of **4a**, **4d**, and **4f** showed a characteristic low field triplet 258.1–258.5 ppm [$^2J(^{13}C-^{31}P) = 9$ Hz] [16–18]. The ^{13}C NMR coupled spectrum of **4a** showed the expected coupling of the carbonyl carbon with the olefinic protons, supporting the assigned structures for complexes **4**. Other spectroscopic features were fully consistent with the assumed structures of the η^1-acyl complexes. Crystallization of complexes **4** was difficult because of their high solubilities in non-polar organic solvents and yielding crystals unsuitable for X-ray structure determination.



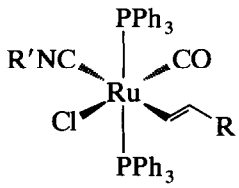
	R	R'	X
4a	CMe_3	CMe_3	Cl
4b	CMe_3	CMe_3	PF_6
4c	CMe_3	Cy	Cl
4d	n-C_8H_{17}	CMe_3	Cl
4e	n-C_8H_{17}	CMe_3	PF_6
4f	Ph	CMe_3	Cl
4g	Ph	Cy	Cl
4h	CO_2Et	CMe_3	Cl
4i	$SiMe_3$	CMe_3	Cl

Scheme 1.

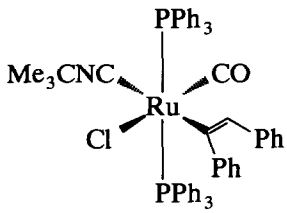
The η^1-acyl complexes **4** proved to be very unreactive and were recovered unchanged after exposure to a variety of conditions, including treatment at 23°C for several hours with trifluoracetic acid, iodine, or with nucleophiles such as methanol or *p*-toluidine. No hydrogenolysis was observed after treatment with H_2 (1 atm) at 80°C for 100 h.

The reaction of complexes **1** or **2** with 1 equivalent of isocyanide at 23°C gave the hexacoordinated complexes **5a**–**5g** in good yield. The stereochemistry shown was assigned in basis of the IR, ^1H, and ^{13}C NMR spectra and by comparison with data for related six-coordinate ruthenium complexes [11–13,19]. Thus, complexes **5** showed a $\nu(C{\equiv}O)$ between 1960 and 1940 cm^{-1}, similar to that observed for the neutral starting complexes **1** and **2**. Furthermore, the ^{13}C NMR spectra of **5a**, **5e**,

and **5f** showed a triplet at 200.4–199.8 ppm [$^2J(^{13}C-^{31}P) = 12$ Hz], within the usual range for CO ligands *trans* to Cl ligands.



(**5a**, R = CMe_3, R′ = CMe_3;
5b, R = CMe_3, R′ = Cy;
5c, R = Ph, R′ = CMe_3;
5d, R = Ph, R′ = Cy;
5e, R = CO_2Et, R′ = CMe_3;
5f, R = $SiMe_3$, R′ = CMe_3)



(**5g**)

Further reaction of complexes **5a–5f** with an excess of the isocyanide gave the corresponding η^1-acyl complexes **4**. The reaction of cyclohexyl isocyanide complex **5d** with an excess of t-butyl isocyanide gave the η^1-acyl complex **6** selectively in 74% yield. The ^1H NMR spectrum showed two t-butyl resonances at 1.09 and 1.06 ppm assigned to mutually *cis* t-butyl isocyanide ligands. In this example, the

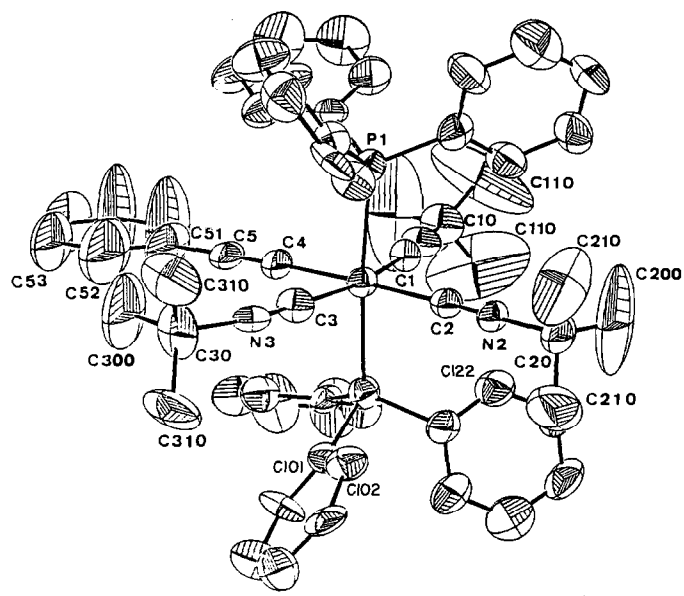
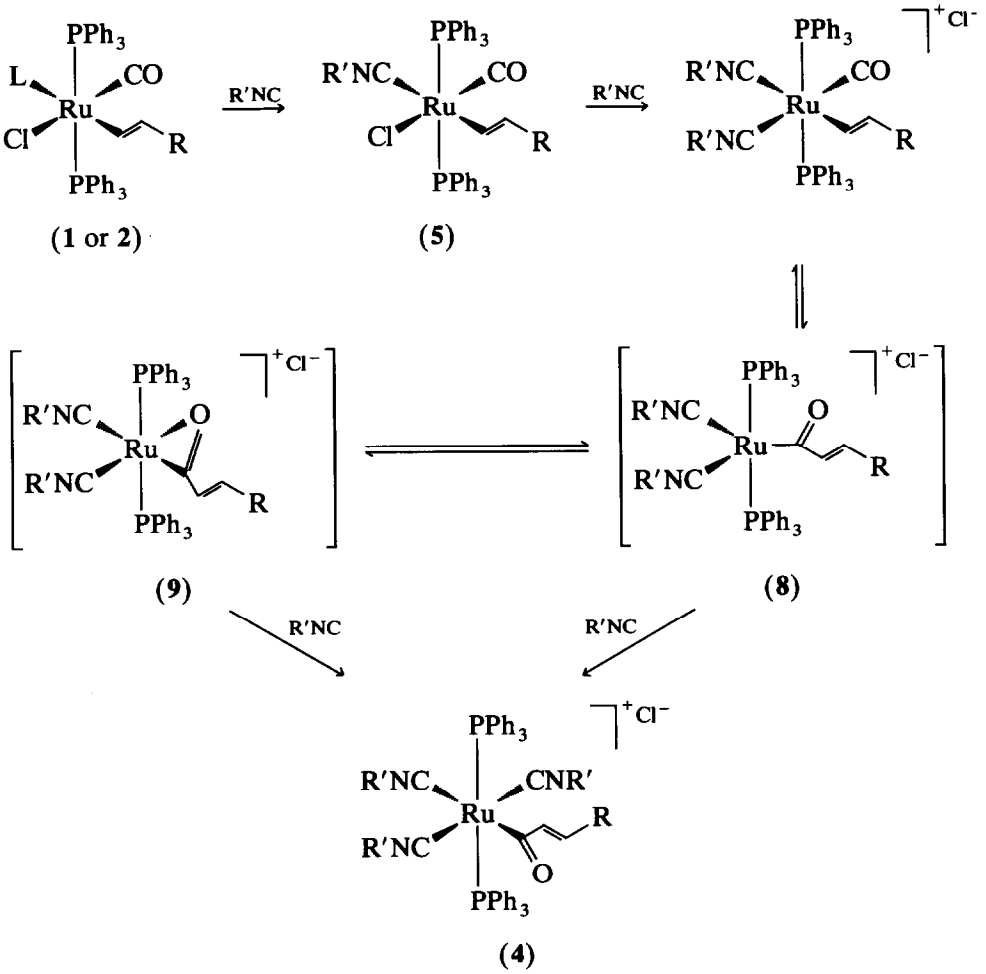
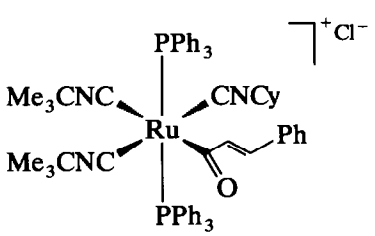


Fig. 1. ORTEP drawing of the structure of the cationic species $[Ru(C{\equiv}CPh)(CNCMe_3)_3(PPh_3)_2]^+$ (**16**) (atom numbering as in Tables 1 and 3). Numbering of the carbons of the phenyl rings omitted for clarity as are all the phenyl and methyl H atoms.



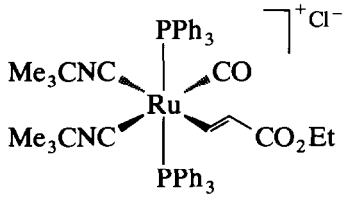
Scheme 2.

cyclohexyl isocyanide ligand in **6**, *trans* to the alkenyl ligand in the starting complex **5d**, is *cis* to the η^1-acyl ligand, as a result of the migratory insertion of the alkenyl into the Ru–CO bond [1] (see Scheme 2). Complex **5g**, being more hindered, behaved differently, yielding complex reaction mixtures under more forcing conditions.



(6)

When the less reactive complex **2d** was heated with t-butyl isocyanide in ethanol under reflux for 30 min, a second product, possibly **7**, was observed. This complex was not isolated as in pure form, and its structure was assigned on the basis of ^1H NMR data for samples containing small amounts of **2d**, **5e** and the acyl complex **4h**.

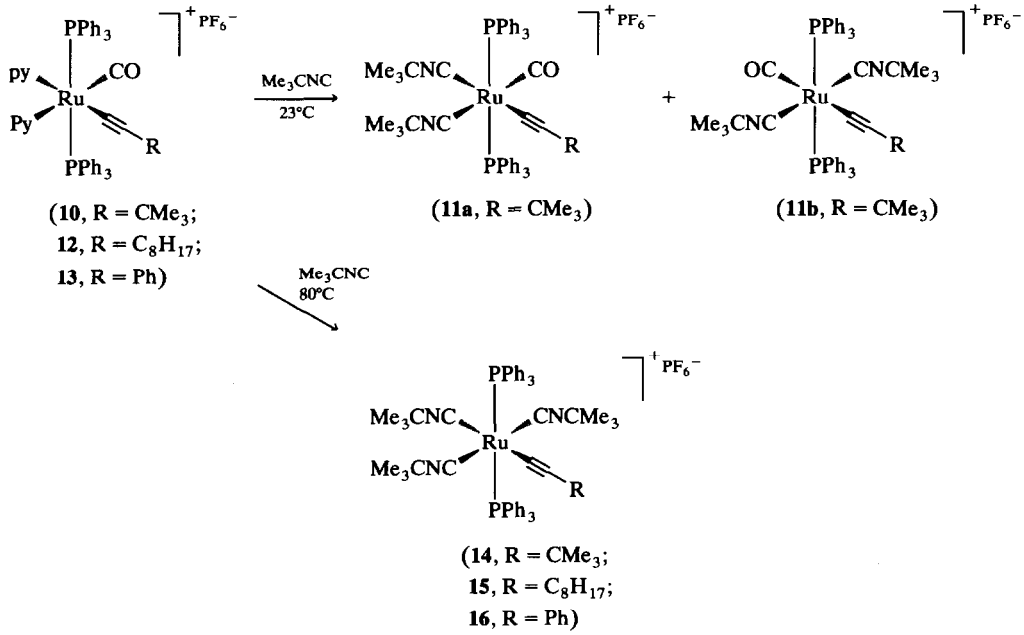


(7)

Complexes related to **7** are probably involved in the formation of η^1-acyl derivatives from **1–3** (Scheme 2). Presumably migratory insertion of the alkenyl ligand into the Ru–CO bond leads to the pentacoordinated η^1-acyl complex **8** or to a coordinatively saturated η^2-acyl complex **9**, both of which would react with the incoming ligand to yield the observed η^1-acyl complexes **4**. The selective formation of **6** from **5d** also supports this scheme. It is noteworthy that exclusive migratory insertion of the alkenyl ligand into the CO–Ru bond is observed even though both *cis* isocyanide and CO ligands are available in intermediates such as **7**.

Reactions of alkynyl complexes with isocyanides

The recently isolated alkynyl ruthenium complexes [20] proved to be rather unreactive towards isocyanides. Treatment of **10** with an excess of t-butyl iso-



(**10**, R = CMe_3;
12, R = C_8H_{17};
13, R = Ph)

(**11a**, R = CMe_3)

(**11b**, R = CMe_3)

(**14**, R = CMe_3;
15, R = C_8H_{17};
16, R = Ph)

Scheme 3.

cyanide in dichloromethane at 23°C for 24 h afforded a 1:3 mixture of *cis* **11a** and *trans* **11b** complexes in (a combined) 76% yield (Scheme 3). These isomers were partially separated by fractional recrystallization. Complex **11b**, which gave a singlet resonance at δ 0.96 for the two isocyanide ligands, showed an IR ν(C≡O) band at 1980 cm^{-1}, closer to the range observed for the starting materials (1950–1940 cm^{-1} [20]) than to the band at 2040 cm^{-1} observed for the *cis* isomer **11a** (Scheme 1). Complex **11a** gave a ^1H NMR spectrum containing two singlets for the isocyanide ligands, at 1.05 and 0.85 ppm.

Further reaction with isocyanide required forcing conditions. Thus, reaction of **10**, **12**, and **13** with t-butyl isocyanide in ethanol under reflux for 120–190 h afforded new complexes **14–16** in 47–81% yield as crystalline solids (Scheme 3). Surprisingly, neither carbonyl nor isocyanide insertion takes place in the reaction with the third equivalent of isocyanide, displacement of the carbonyl ligand occurring instead. The structures of **14–16** were tentatively assigned as shown by IR and NMR, and confirmed by the X-ray diffraction study of **16**.

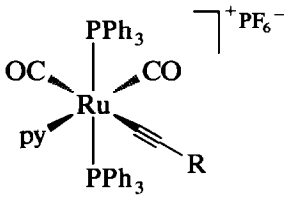
Similarly, reaction of **10** and **13** with CO (1 atm) failed to yield any insertion product, substitution of the pyridine *trans* to the alkynyl by CO taking place instead to yield complexes **17** and **18**, respectively. These *cis* dicarbonyl complexes showed two absorptions in the IR, at 2050 and 2000 cm^{-1}, and two triplet

Table 1

Selected bond lengths (Å) and angles (deg) for compound **16**

Bond lengths			
Ru–P1	2.379(4)	C2–N2	1.10(3)
Ru–C1	2.05(2)	N2–C20	1.47(3)
Ru–C2	2.02(3)	C20–C200	1.38(6)
Ru–C3	1.97(3)	C20–C210	1.44(4)
Ru–C4	2.03(3)	C3–N3	1.14(4)
C1–N1	1.07(3)	N3–C30	1.50(4)
N1–C10	1.49(3)	C30–C300	1.50(5)
C10–C100	1.29(8)	C30–C310	1.48(3)
C10–C110	1.32(6)	C4–C5	1.17(4)
		C5–C51	1.46(4)
Bond angles			
P1–Ru–P1	174.9(2)	C110–C10–C110	100(4)
P1–Ru–C1	88.0(1)	Ru–C2–N2	175(2)
P1–Ru–C2	88.7(1)	C2–N2–C20	179(3)
P1–Ru–C3	92.3(1)	N2–C20–C200	106(3)
P1–Ru–C4	91.4(1)	N2–C20–C210	108(2)
C1–Ru–C2	98.7(10)	C200–C20–C210	112(2)
C1–Ru–C3	166(1)	C210–C20–C210	110(3)
C1–Ru–C4	84.6(12)	Ru–C3–N3	177(2)
C2–Ru–C3	95.4(11)	C3–N3–C30	164(3)
C2–Ru–C4	176.7(12)	N3–C30–C300	106(3)
C3–Ru–C4	81.3(12)	N3–C30–C310	107(2)
Ru–C1–N1	173(3)	C300–C30–C310	110(2)
C1–N1–C10	180(2)	C310–C30–C310	115(2)
N1–C10–C100	107(4)	Ru–C4–C5	175(3)
N1–C10–C110	111(2)	C4–C5–C51	178(4)
C100–C10–C110	114(3)		

resonances in the ^{13}C NMR spectra, at δ 197 (J = 12–13 Hz) and 192 (J = 8–9 Hz).



(**17**, R = CMe_3;
18, R = Ph)

Structure for [Ru(C≡CPh)(CN^{t}Bu)$_3$(PPh$_3$)$_2$]PF$_6$ (16)

The structure of **16** revealed the $[Ru(C{\equiv}CPh)(CN^tBu)_3(PPh_3)_2]^+$ cations (Fig. 1) and the PF_6^- anions to be held together only by electrostatic interaction. Selected bond distances and angles are given in Table 1. The Ru atom displays distorted octahedral coordination, with the three isocyanides and the phenylethynyl ligand in the equatorial plane and the two triphenylphosphines in approximately axial positions. The six carbon atoms of the phenyl group of the alkynyl ligand lie in the equatorial plane. The C≡C bond distance (C4–C5) of 1.17(4) Å is within the range observed for σ-alkynylruthenium complexes [20,21].

Summary

The reaction of (*E*)-alkenyl ruthenium(II) complexes with alkyl isocyanides proceeds under mild conditions to yield (*E*)-α,β-unsaturated-η^1-acyl ruthenium(II) complexes. Although these complexes are obtained from intermediates with both CO and isocyanide ligands, exclusive migratory insertion of the alkenyl ligand into the Ru–CO bond is observed. The related alkynyl carbonyl ruthenium(II) complexes do not undergo insertion, reacting sluggishly with the isocyanides to yield new alkynyl ruthenium complexes in which the carbonyl ligand has been replaced by an isocyanide ligand. The corresponding reaction with CO leads to dicarbonyl alkynyl complexes by substitution of the pyridine *trans* to the alkynyl ligand.

Experimental

IR spectra were recorded with KBr discs on a Pye Unicam SP-3-300S spectrophotometer. Only the most significant frequencies are given. NMR spectra were recorded on Varian XL 300 (^1H NMR, 300 MHz), Bruker AM 200 (^{13}C NMR, 50 MHz), and Bruker WP-80 (^{31}P NMR, 32 MHz) spectrometers in $CDCl_3$. Elemental analyses were performed at the Instituto de Química Orgánica (CSIC). The presence of water molecules in several samples was demonstrated by integration of the ^1H NMR H_2O resonance at 1.60–1.50 ppm and/or by differential thermal and thermogravimetric analysis (Stanton–Redcroft (DTA-781) apparatus). Electric conductivities were performed with a Philips PW-9506 conductivity cell.

Dichloromethane was freshly distilled from CaH_2. All reactions were carried out under N_2 or Ar.

The following known ruthenium complexes were prepared by our previously described procedures: alkenyl complexes **1a**, **1c**, **1d**, **1e** [11], **2a**, **2b**, **2d** [12], **2c** [13], and **3a** [14]; alkynyl complexes **10**, **12**, and **13** [20]. **1b** and **3b** were prepared according to the general procedure: **1b** was prepared by the method described in ref. 11 in 40% yield. IR (cm^{-1}): ν(C≡O) 1925 vs, ν(C=C) 1582 m. ^1H NMR: δ 7.60–7.32 (m, 30 H), 6.96 (d, J = 12.6 Hz, 1 H), 4.62 (m, 1 H), 1.87 (m, 2 H), 1.30–1.01 (m, 12 H), 0.64 (t, J = 7.1 Hz, 3 H). Anal. Found: C, 68.25; H; 5.71. $C_{47}H_{49}ClO_2P_2Ru$ calc.: C, 68.15; H, 5.96%. **3b** was prepared by the procedure described in ref. 14 in 55% yield. IR (cm^{-1}): ν(C≡N) 2310 vw, 2290 vw, ν(C≡O) 1945 vs, $\nu(PF_6)$ 835 vs. ^1H NMR: δ 7.71–7.46 (m, 12 H), 7.51–7.37 (m, 18 H), 6.22 (dt, J = 16.1, 3.3 Hz, 1 H), 4.45 (dt, J = 16.1, 6.5 Hz, 1 H), 1.83 (q, J = 6.5 Hz, 2 H), 1.21–1.02 (m, 12 H), 0.84 (t, J = 6.9 Hz, 3 H).

Synthesis of η^1-acyl ruthenium complexes 4

General procedure. A mixture of alkenyl complexes **1–3** and the alkyl isocyanide (4 molar equivalents) in CH_2Cl_2 (200 mL/mmol alkenyl complex) was stirred at 23°C for 15 min. The solution was then evaporated and the residue triturated with hexane to yield crude complexes **4** as grey-yellow solids.

[Ru(COCH=CHCMe$_3$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]Cl ***(4a)***. This was prepared by the general procedure from **1a** or **2a** and t-butyl isocyanide in 77 and 95% yield, respectively. IR (cm^{-1}): ν(C≡N) 2185 m, 2130 vs, ν(C=O) 1615 w, ν(C=C) 1540 w. ^1H NMR: δ 7.55–7.35 (m, 30 H, PPh_3), 5.83 (d, J = 15.3 Hz, 1 H, HC=), 5.16 (d, J = 15.3 Hz, 1 H, =CH), 1.14 (s, 9 H, $CNCMe_3$), 1.08 (s, 18 H, 2 $CNCMe_3$), 0.67 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ NMR: δ 258.1 (t, J = 9.2 Hz, C=O), 148.8 (br s, 2 C≡N), 147.4 (br s, C≡N), 140.0 (s, *C*=C), 137.5 (s, C=*C*), 134.1 (t, J = 22.3 Hz, PPh_3), 133.7 (t, J = 5.4 Hz, PPh_3), 130.4 (s, PPh_3), 128.2 (t, J = 4.8 Hz, PPh_3), 57.8 (s, $CNCMe_3$), 57.6 (s, 2 $CNCMe_3$), 32.1 (s, CMe_3), 29.7 (s, $CNCMe_3$), 29.5 (s, 2 $CNCMe_3$), 28.8 (s, CMe_3). $^{31}P\{^1H\}$ NMR: δ 36.8 (s). Molar conductivity ($MeNO_2$): 52 Ω^{-1} cm^2 mol^{-1}. Anal. Found: C, 65.44; H, 6.95; N, 4.06. $C_{58}H_{68}ClN_3OP_2Ru \cdot 2H_2O$ calc.: C, 65.86; H, 6.86; N, 3.97%.

[Ru(COCH=CHCMe$_3$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]PF$_6$ ***(4b)***. This was prepared by the general procedure from **3a** and t-butyl isocyanide in 87% yield. IR (cm^{-1}): ν(C≡N) 2180 m, 2130 vs, ν(C=O) 1615 m, ν(C=C) 1540 m, $\nu(PF_6)$ 840 cm^{-1}. ^1H NMR is identical to that of **4a**. Anal. Found: C, 61.40; H, 5.93; N, 3.61. $C_{58}H_{68}F_6N_3OP_3Ru$ calc.: C, 61.58; H, 6.06; N, 3.71%.

[Ru(COCH=CHCMe$_3$)(CNCy)$_3$(PPh$_3$)$_2$]Cl ***(4c)***. This was prepared by the general procedure from **1a** and cyclohexyl isocyanide in 78% yield. IR (cm^{-1}): ν(C≡N) 2200 m, 2150 vs, ν(C=O) 1620 m, ν(C=C) 1540 m. ^1H NMR: δ 7.56–7.33 (m, 30 H, PPh_3), 6.17 (d, J = 15.3 Hz, 1 H, HC=), 5.47 (d, J = 15.3 Hz, 1 H, =CH), 3.40–3.17 (br, 3 H, 3 Cy), 1.58–1.39 (m, 15 H, 3 Cy), 1.21–1.09 (m, 15 H, 3 Cy), 0.74 (s, 9 H, CMe_3). Anal. Found: C, 69.63; H, 6.87; N, 3.74. $C_{64}H_{74}ClN_3OP_2Ru$ calc.: C, 69.90; H, 6.78; N, 3.82%.

[Ru(COCH=CHC$_8$H$_{17}$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]Cl ***(4d)***. This was prepared by the general procedure from **1b** or **2b** and t-butyl isocyanide in 72 or 85% yield, respectively. IR (cm^{-1}): ν(C≡N) 2185 m, 2130 vs, ν(C=O) 1615 w, ν(C=C) 1540 w. ^1H NMR: δ 7.60–7.25 (m, 30 H, PPh_3), 5.64 (d, J = 15.3 Hz, 1 H, HC=), 4.85 (dt, J = 15.3, 7.1 Hz, 1 H, =CH), 1.45–0.85 (m, 17 H, 7 CH_2 + CH_3), 1.13 (s, 9 H, $CNCMe_3$), 1.06 (s, 18 H, 2 $CNCMe_3$). $^{13}C\{^1H\}$ NMR: δ 258.1 (t, J = 9 Hz, C=O),

149.5 (br s, 2 C≡N), 147.5 (br s, C≡N), 142.6 (s, *C*=C), 133.9 (t, $J = 22.0$ Hz, PPh_3), 133.8 (t, $J = 5.2$ Hz, PPh_3), 130.5 (s, PPh_3), 128.2 (t, $J = 4.2$ Hz, PPh_3), 127.8 (s, C=*C*), 57.8 (s, CN*C*Me$_3$), 57.5 (s, 2 CN*C*Me$_3$), 31.8 (s, CH_2), 31.7 (s, CH_2), 29.7 (s, CNC*Me*$_3$), 29.5 (s, 2 CNC*Me*$_3$), 29.4 (s, 2 CH_2), 29.1 (s, CH_2), 28.5 (s, CH_2), 22.6 (s, CH_2), 14.0 (s, CH_3).

*[Ru(COCH=CHC$_8$H$_{17}$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]PF$_6$ (**4e**).* This was prepared by the general procedure from **3b** and t-butyl isocyanide in 86% yield. IR (cm^{-1}): ν(C≡N) 2190 m, 2135 vs, ν(C=O) 1615 m, ν(C=C) 1540 w, $\nu(PF_6)$ 840 vs. ^{1}H NMR is identical to that of **4d**. Anal. Found: C, 62.59; H, 6.18; N, 3.24. $C_{62}H_{76}F_6N_3OP_3Ru$ calc.: C, 62.72; H, 6.45; N, 3.54%.

*[Ru(COCH=CHPh)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]Cl (**4f**).* This was prepared by the general procedure from **1c** or **2c** and t-butyl isocyanide in 98 or 94% yield, respectively. IR (cm^{-1}): ν(C≡N) 2180 m, 2135 vs, ν(C=O) 1610 m, ν(C=C) 1540 m. ^{1}H NMR: δ 7.56–7.49 (m, 12 H, PPh_3), 7.47–7.39 (m, 18 H, PPh_3), 7.15–7.13 (m, 3 H, Ph), 6.82–6.79 (m, 2 H, Ph), 6.11 (d, $J = 15.6$ Hz, 1 H, *H*C=), 5.48 (d, $J = 15.6$ Hz, 1 H, =C*H*), 1.16 (s, 9 H, CNC*Me*$_3$), 1.02 (s, 18 H, 2 CNC*Me*$_3$). ^{13}C{^{1}H} NMR: δ 258.5 (t, $J = 9$ Hz, C=O), 148.2 (br s, 2 C≡N), 147.2 (br s, C≡N), 139.8 (s, *C*=C), 136.2 (s, Ph), 133.9 (t, $J = 18.0$ Hz, PPh_3), 133.8 (t, $J = 5.2$ Hz, PPh_3), 133.4 (s, Ph), 131.0 (s, Ph), 130.7 (s, PPh_3), 128.7 (s, Ph), 128.4 (t, $J = 4.6$ Hz, PPh_3), 125.2 (s, C=*C*), 58.0 (s, CN*C*Me$_3$), 57.7 (s, 2 CN*C*Me$_3$), 29.8 (s, CNC*Me*$_3$), 29.5 (s, 2 CNC*Me*$_3$). Anal. Found: C, 66.59; H, 6.35; N, 4.14. $C_{60}H_{64}ClN_3OP_2Ru \cdot 2H_2O$ calc.: C, 66.87; H, 6.36; N, 3.90%.

*[Ru(COCH=CHPh)(CNCy)$_3$(PPh$_3$)$_2$]Cl (**4g**).* This was prepared by the general procedure from **1c** and cyclohexyl isocyanide in 87% yield. IR (cm^{-1}): ν(C≡N) 2190 m, 2140 vs, ν(C=O) 1610 m, ν(C=C) 1540 w. ^{1}H NMR: δ 7.58–7.41 (m, 30 H, PPh_3), 7.23–7.19 (m, 3 H, Ph), 7.00–6.94 (m, 2 H, Ph), 6.66 (d, $J = 15.5$ Hz, 1 H, HC=), 5.94 (d, $J = 15.5$ Hz, 1 H, =CH), 3.46–3.20 (br, 3 H, 3 Cy), 1.50–1.39 (m, 15 H, 3 Cy), 1.29–0.99 (m, 15 H, 3 Cy). Anal. Found: C, 70.52; H, 6.55; N, 3.69. $C_{66}H_{70}ClN_3OP_2Ru$ calc.: C, 70.79; H, 6.30; N, 3.75%.

*[Ru(COCH=CHCO$_2$Et)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]Cl (**4h**).* This was prepared by a modification of the general procedure: a suspension of **2d** (104 mg, 0.12 mmol) and t-butyl isocyanide (0.068 mL, 0.60 mmol) was heated in EtOH (25 mL) under reflux for 48 h then cooled to room temperature. The solvent was evaporated and the residue triturated with hexane to give **4h** (121 mg, 72%). IR (cm^{-1}): ν(C≡N) 2200 m, 2150 vs, ν(C=O, ester) 1680 br m, ν(C=O) 1620 m. ^{1}H NMR: δ 7.30–6.55 (m, 30 H, PPh_3), 6.18 (d, $J = 16.0$ Hz, 1 H, HC=), 4.40 (d, $J = 16.0$ Hz, 1 H, =CH), 3.44 (q, $J = 7.0$ Hz, 2 H, CH_2), 1.17 (s, 9 H, CNCMe$_3$), 1.15 (t, $J = 7.0$ Hz, 3 H, CH_3), 1.09 (s, 18 H, 2 CNCMe$_3$).

*[Ru(COCH=CHSiMe$_3$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]Cl (**4i**).* This was prepared by the general procedure from **1d** and t-butyl isocyanide in 79% yield. IR (cm^{-1}): ν(C≡N) 2190 m, 2130 vs, ν(C=O) 1585 m, ν(C=C) 1540 w. ^{1}H NMR: δ 7.55–7.35 (m, 30 H, PPh_3), 6.05 (d, $J = 18.2$ Hz, 1 H, HC=), 5.08 (d, $J = 18.2$ Hz, 1 H, =CH), 1.17 (s, 9 H, CNCMe$_3$), 1.08 (s, 18 H, 2 CNCMe$_3$), −0.21 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR: δ 257.8 (t, $J = 9.4$ Hz, C=O), 153.1 (s, C=*C*), 148.3 (br s, 2 C≡N), 146.8 (br s, C≡N), 133.6 (t, $J = 22.0$ Hz, PPh_3), 133.4 (t, $J = 5.4$ Hz, PPh_3), 130.2 (s, PPh_3), 127.9 (t, $J = 4.6$ Hz, PPh_3), 126.7 (s, *C*=C), 57.6 (s, CN*C*Me$_3$), 57.3 (s, 2 CN*C*Me$_3$), 29.4 (s, CNC*Me*$_3$), 29.2 (s, 2 CNC*Me*$_3$), −1.70 (s, SiMe$_3$). ^{31}P{^{1}H} NMR: δ 36.8 (s). Anal. Found: C, 65.80; H, 6.61; N, 3.80. $C_{57}H_{68}ClN_3OP_2RuSi$ calc.: C, 65.97; H, 6.61; N, 4.05%.

[Ru(COCH=CHPh)(CNCMe$_3$)$_2$(CNCy)(PPh$_3$)$_2$]Cl (6). This was prepared by the general procedure from **5d** and t-butyl isocyanide in 74% yield. IR (cm^{-1}): ν(C≡N) 2180 m, 2135 vs, ν(C=O) 1610 m, ν(C=C) 1540 w. ^{1}H NMR: δ 7.54–7.50 (m, 12 H, PPh$_3$), 7.47–7.40 (m, 18 H, PPh$_3$), 7.18–7.15 (m, 3 H, Ph), 6.89–6.86 (m, 2 H, Ph), 6.35 (d, J = 15.5 Hz, 1 H, HC=), 5.64 (d, J = 15.5 Hz, 1 H, =CH), 3.26–3.22 (br, 1 H, Cy), 1.46–1.39 (m, 5 H, Cy), 1.09 (s, 9 H, CNCMe$_3$), 1.06 (s, 9 H, CNCMe$_3$), 1.03–0.96 (m, 5 H, Cy), Anal. Found: C, 66.30; H, 6.51; N, 4.06. $C_{62}H_{66}ClN_3OP_2Ru \cdot 3H_2O$ calc.: C, 66.38; H, 6.47; N, 4.07%.

Synthesis of Ru(CO)Cl(CH=CHR)(CNCR')(PPh$_3$)$_2$ (5)

General procedure. The alkyl isocyanide (1 molar equivalent) was added to a solution of alkenyl complex **1** or **2** in CH_2Cl_2 (approx. 250 mL/mmol). The mixture was stirred at 23°C for 5 min, the solvent then evaporated, and the residue triturated with hexane to yield complexes **5** as pale yellow solids.

Ru(CO)Cl(CH=CHCMe$_3$)(CNCMe$_3$)(PPh$_3$)$_2$ (5a). This was prepared by the general procedure from **1a** and t-butyl isocyanide in 70% yield. IR (cm^{-1}): ν(C≡N) 2135 s, ν(C≡O) 1945 vs. ^{1}H NMR: δ 7.89–7.80 (m, 12 H, PPh$_3$), 7.34–7.29 (m, 18 H, PPh$_3$), 6.69 (dt, J = 17.0, 3.0 Hz, 1 H, HC=), 4.82 (dt, J = 17.0, 1.9 Hz, 1 H, =CH), 1.02 (s, 9 H, CNCMe$_3$), 0.55 (s, 9 H, CMe$_3$). ^{13}C{^{1}H} NMR: δ 200.4 (t, J = 12.5 Hz, C≡O), 148.4 (br, C≡N), 146.1 (t, J = 3.3 Hz, C=*C*), 143.3 (t, J = 13.7 Hz, *C*=C), 134.8 (t, J = 21.4 Hz, PPh$_3$), 134.3 (t, J = 5.0 Hz, PPh$_3$), 129.1 (s, PPh$_3$), 127.5 (t, J = 4.5 Hz, PPh$_3$), 55.9 (s, CNC*Me*$_3$), 36.0 (s, *C*Me$_3$), 29.9 (s, CNC*Me*$_3$), 29.3 (s, C*Me*$_3$). Anal. Found: C, 67.18; H, 5.90; N, 1.35. $C_{48}H_{50}ClNOP_2Ru$ calc.: C, 67.40; H, 5.89; N, 1.64%.

Ru(CO)Cl(CH=CHCMe$_3$)(CNCy)(PPh$_3$)$_2$ (5b). This was prepared by the general procedure from **1a** and cyclohexyl isocyanide in 68% yield. IR (cm^{-1}): ν(C≡N) 2140 s, ν(C≡O) 1955 vs. ^{1}H NMR: δ 7.87–7.78 (m, 12 H, PPh$_3$), 7.32–7.29 (m, 18 H, PPh$_3$), 6.71 (dt, J = 17.4, 3.0 Hz, 1 H, HC=), 4.84 (dt, J = 17.4, 1.9 Hz, 1 H, =CH), 3.37–3.22 (br, 1 H, Cy), 1.45–1.42 (m, 5 H, Cy), 1.24–1.11 (m, 5 H, Cy), 0.54 (s, 9 H, CMe$_3$). Anal. Found: C, 65.10; H, 5.91; N, 2.02. $C_{50}H_{52}ClNOP_2Ru \cdot 2H_2O$: C, 65.46; H, 6.15; N, 1.53%.

Ru(CO)Cl(CH=CHPh)(CNCMe$_3$)(PPh$_3$)$_2$ (5c). This was prepared by the general procedure from **2c** and t-butyl isocyanide in 91% yield. IR (cm^{-1}): ν(C≡N) 2145 s, ν(C≡O) 1940 vs. ^{1}H NMR: δ 7.86 (dt, J = 17.9, 2.8 Hz, 1 H, HC=), 7.77–7.65 (m, 12 H, PPh$_3$), 7.34–7.22 (m, 18 H, PPh$_3$), 7.11 (t, J = 7.5 Hz, 2 H, Ph), 6.97–6.87 (m, 3 H, Ph), 5.86 (dt, J = 17.9, 1.9 Hz, 1 H, =CH), 1.00 (s, 9 H, CMe$_3$). Anal. Found: C, 65.55; H, 5.24; N, 1.95. $C_{50}H_{46}ClNOP_2Ru \cdot 2H_2O$ calc.: C, 65.89; H, 5.53; N, 1.54.

Ru(CO)Cl(CH=CHPh)(CNCy)(PPh$_3$)$_2$ (5d). This was prepared by the general procedure from **1c** and cyclohexyl isocyanide in 86% yield. IR (cm^{-1}): ν(C≡N) 2140 s, ν(C≡O) 1950 vs. ^{1}H NMR: δ 7.88 (dt, J = 17.9, 2.9 Hz, 1 H, HC=), 7.74–7.67 (m, 12 H, PPh$_3$), 7.32–7.23 (m, 18 H, PPh$_3$), 7.10 (t, J = 7.5 Hz, 2 H, Ph), 6.93 (t, J = 7.2 Hz, 1 H, Ph), 6.86 (t, J = 7.6 Hz, 2 H, Ph), 5.84 (d, J = 17.9 Hz, 1 H, =CH), 3.27–3.26 (br, 1 H, Cy), 1.45–1.35 (m, 5 H, Cy), 1.20–1.07 (m, 5 H, Cy). Anal. Found: C, 68.10; H, 5.65; N, 1.93. $C_{52}H_{48}ClNOP_2Ru \cdot H_2O$ calc.: C, 67.93; H, 5.48; N, 1.52%.

Ru(CO)Cl(CH=CHCO$_2$Et)(CNCMe$_3$)(PPh$_3$)$_2$ (5e). This was prepared by the general procedure from **2d** and t-butyl isocyanide in 98% yield. IR (cm^{-1}): ν(C≡N)

2170 s, ν(C≡O) 1960 vs, ν(C=O) 1680 w, ν(C=C) 1520 w, ν(C–O) 1145. ^{1}H NMR: δ 9.40 (dt, J = 17.9, 2.4 Hz, 1 H, HC=), 7.80–7.65 (m, 12 H, PPh_3), 7.40–7.25 (m, 18 H, PPh_3), 5.55 (dt, J = 17.9, 1.6 Hz, 1 H, HC=), 3.94 (q, J = 7.1 Hz, 3 H, CH_2), 1.15 (t, J = 7.1 Hz, 3 H, CH_3), 1.02 (s, 9 H, $CNCMe_3$). ^{13}C{^{1}H} NMR: δ 199.8 (t, J = 12.0 Hz, C≡O), 194.0 (t, J = 12.7 Hz, C=O), 163.9 (s, *C*=C), 147.0 (br, C≡N), 134.2 (t, J = 5.3 Hz, PPh_3), 133.7 (t, J = 22.1 Hz, PPh_3), 129.6 (s, PPh_3), 127.8 (t, J = 4.8 Hz, PPh_3), 127.6 (s, C=*C*), 58.5 (s, OCH_2), 56.5 (s, $CNCMe_3$), 29.7 (s, $CNCMe_3$), 14.7 (s, CH_3). Anal. Found: C, 65.00; H, 5.40; N, 1.50. $C_{47}H_{46}ClNO_3P_2Ru$ calc.: C, 64.79; H, 5.32; N, 1.61%.

Ru(CO)Cl(CH=CHSiMe$_3$)(CNCMe$_3$)(PPh$_3$)$_2$ (5f). This was prepared by the general procedure from **1d** and t-butyl isocyanide in 87% yield. IR (cm^{-1}): ν(C≡N) 2140 s, ν(C≡O) 1950 vs. ^{1}H NMR: δ 8.20 (dt, J = 20.0, 3.0 Hz, 1 H, HC=), 7.81–7.75 (m, 12 H, PPh_3), 7.30–7.28 (m, 18 H, PPh_3), 5.59 (dt, J = 20.0, 1.4 Hz, 1 H, HC=), 0.98 (s, 9 H, $CNCMe_3$), −0.36 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR: δ 200.4 (t, J = 12.3 Hz, C≡O), 179.7 (t, J = 13.0, *C*=C), 148.2 (br, C≡N), 141.2 (s, C=*C*), 134.4 (t, J = 21.6 Hz, PPh_3), 134.3 (t, J = 5.2 Hz, PPh_3), 129.2 (s, PPh_3), 127.5 (t, J = 4.5 Hz, PPh_3), 56.0 (s, CMe_3), 29.8 (s, $CNCMe_3$), −1.4 (s, $SiMe_3$). Anal. Found: C, 64.42; H, 5.93; N, 1.64. $C_{47}H_{50}ClNOP_2RuSi$ calc.: C, 64.78; H, 5.78; N, 1.61%.

Ru(CO)Cl(CPh=CHPh)(CNCMe$_3$)(PPh$_3$)$_2$ (5g). This was prepared by the general procedure from **5g** and t-butyl isocyanide in 54% yield. IR (cm^{-1}): ν(C≡N) 2150 s, ν(C≡O) 1950 vs. ^{1}H NMR: δ 7.72–7.65 (m, 12 H, PPh_3), 7.25–7.18 (m, 18 H, PPh_3), 6.90–6.68 (m, 7 H, 6 H Ph + 1 H HC=), 6.49 (d, J = 7.2 Hz, 2 H Ph), 5.82 (d, J = 7.2 Hz, 2 H Ph), 0.99 (s, 9 H, $CNCMe_3$).

Synthesis of bis(isocyanide)ruthenium complex [Ru(CO)(CH=CHCO$_2$Et)-(Me$_3$CNC)$_2$(PPh$_3$)$_2$]Cl (7)

This was obtained contaminated with starting material **2d**, **5e**, and acyl complex **4h**, from the reaction of **2d** with t-butyl isocyanide. ^{1}H NMR: δ 8.30 (dt, J = 17.9, 2.4 Hz, 1 H, HC=), 7.55–7.30 (m, 30 H, PPh_3), 5.30 (dt, J = 17.9, 1.6 Hz, 1 H, =CH), 3.68 (q, J = 7.1 Hz, 2 H, OCH_2), 1.15 (t, J = 7.1 Hz, 3 H, CH_3), 1.06 (s, 9 H, $CNCMe_3$), 1.04 (s, 9 H, $CNCMe_3$).

Synthesis of [Ru(CO)(C≡CCMe$_3$)(CNCMe$_3$)$_2$(PPh$_3$)$_2$]PF$_6$ (11a and 11b)

A solution of alkynyl complex **10** (132 mg, 0.13 mmol) and t-butyl isocyanide (0.043 mL, 0.38 mmol) in CH_2Cl_2 (15 mL) was stirred at 23°C for 24 h. The solvent was evaporated and the residue triturated with Et_2O to give a 1:3 mixture of *cis* and *trans* isomers **11a** and **11b** (101 mg, 76%). Fractional recrystallization from CH_2Cl_2–Et_2O–hexane gave *ca.* 80% pure samples of **11a** and **11b**. **11a** (*cis* isomer, white prismatic crystals). IR (cm^{-1}): ν(C≡N) 2190 s, 2160 vs, ν(C≡O) 2040 vs, ν(PF_6) 835 vs. ^{1}H NMR: δ 7.80–7.70 (m, 12 H, PPh_3), 7.50–7.45 (m, 18 H, PPh_3), 1.05 (s, 9 H, $CNCMe_3$), 0.92 (s, 9 H, CMe_3), 0.85 (s, 9 H, $CNCMe_3$). **11b** (*trans* isomer, white needles). IR (cm^{-1}): ν(C≡N) 2160 s, ν(C≡O) 1980 vs, ν(PF_6) 840 vs. ^{1}H NMR: δ 7.65–7.50 (m, 12 H, PPh_3), 7.40–7.30 (m, 18 H, PPh_3), 0.97 (s, 9 H, CMe_3), 0.96 (s, 18 H, 2 $CNCMe_3$). Anal. Found: C, 60.35; H, 5.90; N, 2.95. $C_{53}H_{57}F_6N_2OP_3Ru \cdot 0.5H_2O$: C, 60.34; H, 5.54; N, 2.66%.

Synthesis of tris(isocyanide)alkynyl complexes [Ru(C≡CR)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]PF$_6$ (14–16)

General procedure. A suspension of the alkynyl complex **10**, **12** or **13** and

t-butyl isocyanide (4 molar equivalents) was heated in ethanol (400 mL/mmol) under reflux for 120–190 h. The mixture was then cooled to room temperature, the solvent was evaporated, and the residue triturated with Et_2O to yield the title compounds as white crystalline solids.

[Ru(C≡CCMe$_3$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]PF$_6$ (14). This was prepared by the general procedure from **10** and t-butyl isocyanide in 62% yield. IR (cm^{-1}): ν(C≡N) 2210 m, 2185 vs, $\nu(PF_6)$ 840 vs. ^1H NMR: δ 7.89–7.85 (m, 12 H, PPh_3), 7.43–7.41 (m, 18 H, PPh_3), 0.97 (s, 18 H, $CNCMe_3$), 0.96 (s, 9 H, CMe_3), 0.74 (s, 9H, $CNCMe_3$). $^{13}C\{^1H\}$ NMR: δ 147.0 (br s, C≡N), 146.0 (br s, C≡N), 135.1 (t, $J = 23.6$ Hz, PPh_3), 134.1 (t, $J = 5.3$ Hz, PPh_3), 133.5 (s, C≡*C*), 130.8 (t, $J = 3.8$ Hz, *C*≡C), 130.2 (s, PPh_3), 128.1 (t, $J = 4.5$ Hz, PPh_3), 57.5 (s, 2 CN*C*Me$_3$), 57.2 (s, CN*C*Me$_3$), 31.9 (s, *C*Me$_3$), 29.6 (s, 2 CNC*Me*$_3$), 29.5 (s, CNC*Me*$_3$), 29.3 (s, C*Me*$_3$). Anal. Found: C, 59.76; H, 5.97; N, 3.95. $C_{57}H_{66}F_6N_3P_3Ru \cdot 2H_2O$ calc.: C, 60.20; H, 6.20; N, 3.70%.

Table 2

Crystal analysis parameters for compound **16**

Formula	$C_{58}H_{62}N_3F_6P_3Ru$
Crystal size (mm)	0.20×0.18×0.08
Unit cell dimensions (Å)	20.655(8), 16.607(5), 16.447(5)
Symmetry	Orthorhombic, *Pnma*
Packing: V (Å^3), Z	5641.61, 8
D_{calcd} (g cm^{-3}), M, F(000)	1.320, 1121.14, 2320
μ (cm^{-1})	4.126
Experimental data	
Technique	Four circle diffractometer CAD-4 Enraf Nonius, monochromated Mo-K_α, θ_{max} 25°
No. of reflections	
measured	5497
independent	5141
observed	1832 ($I \geqslant 3(I)$)
standard reflections	004 and 00$\bar{4}$ reflections every 90 min; no significant variation
Solution and refinement	
Solution	Patterson and Fourier synthesis
Refinement	Least squares on F_o with 1 block
H atoms	Difference Fourier synthesis
Parameters	
No. of variables	361
Computer and programs	VAX11/750, XRAY80, SYSTEM, DIRDIF [a]
Scattering factors and anomalous dispersion	Int. Tables for X-Ray Crystallography [b]
Final R	8.1%

[a] J.M. Stewart, F.A. Kundell and J.C. Baldwin, The XRAY80 System of Crystallographic Programs, Computer Science Center, University of Maryland, College Park, MD. P.T. Beurskens, W.P. Bosman, H.M. Doesburg, R.O. Gould, T.E.M. Van Der Hark, P.A. Prick, J.H. Noordik, G. Beurskens, V. Parthasarathi, H.J. Bruins Slot and R.C. Haltiwanger, DIRDIF System of Computer Programs, Technical Report 1983/1; Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1983.
[b] International Tables for X-ray Crystallography, Kynoch Press, Birmingham, UK, 1974.

[Ru(C≡CC$_8$H$_{17}$)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]PF$_6$ (15). This was prepared by the general procedure from **12** and t-butyl isocyanide in 47% yield. IR (cm^{-1}): ν(C≡N) 2210 m, 2185 vs, ν(PF$_6$) 840 vs. ^{1}H NMR: δ 7.74–7.72 (m, 12 H, PPh$_3$), 7.45–7.42

Table 3

Atomic coordinates and thermal parameters for compound **16**

Atom	x	y	z	U_{eq} [a]
Ru	0.2176(1)	0.2500(0)	0.0139(1)	38(1)
Cl	0.1182(11)	0.2500(0)	0.0096(17)	37(9)
N1	0.0667(11)	0.2500(0)	0.0149(16)	55(9)
C10	−0.0054(14)	0.2500(0)	0.0224(26)	76(14)
C100	−0.0189(28)	0.2500(0)	0.0988(40)	338(82)
C110	−0.0310(15)	0.3110(32)	−0.0182(39)	320(38)
C2	0.2357(13)	0.2500(0)	−0.1066(18)	39(10)
N2	0.2502(10)	0.2500(0)	−0.1714(13)	35(8)
C20	0.2680(18)	0.2500(0)	−0.2581(18)	63(13)
C200	0.2104(28)	0.2500(0)	−0.3013(23)	225(47)
C210	0.3060(18)	0.1787(20)	−0.2741(16)	151(17)
C3	0.3094(15)	0.2500(0)	0.0470(17)	45(10)
N3	0.3616(11)	0.2500(0)	0.0697(12)	33(7)
C30	0.4211(14)	0.2500(0)	0.1218(22)	76(16)
C300	0.3981(27)	0.2500(0)	0.2086(24)	164(29)
C310	0.4570(12)	0.1747(16)	0.1042(20)	117(13)
C4	0.2050(15)	0.2500(0)	0.1364(16)	45(12)
C5	0.2024(17)	0.2500(0)	0.2074(20)	65(13)
C51	0.1971(32)	0.2500(0)	0.2959(19)	108(24)
C52	0.2464(37)	0.2500(0)	0.3508(34)	185(40)
C53	0.2448(28)	0.2500(0)	0.4326(30)	132(27)
C54	0.1800(38)	0.2500(0)	0.4609(24)	144(28)
C55	0.1378(31)	0.2500(0)	0.4159(32)	279(49)
C56	0.1415(25)	0.2500(0)	0.3353(32)	237(47)
P1	0.2137(3)	0.1069(3)	0.0098(3)	45(2)
C101	0.2917(9)	0.0556(11)	0.0152(12)	49(6)
C102	0.3391(10)	0.0818(13)	−0.0405(12)	56(8)
C103	0.3976(11)	0.0418(13)	−0.0489(14)	60(9)
C104	0.4085(10)	−0.0241(14)	0.0032(15)	70(9)
C105	0.3633(13)	−0.0495(15)	0.0588(16)	83(11)
C106	0.3051(10)	−0.0107(13)	0.0631(14)	63(9)
C111	0.1651(11)	0.0627(12)	0.0907(11)	47(8)
C112	0.1852(11)	0.0641(13)	0.1709(12)	63(8)
C113	0.1457(15)	0.0338(16)	0.2311(14)	93(12)
C114	0.0879(14)	0.0011(21)	0.2116(20)	116(15)
C115	0.0656(12)	−0.0016(19)	0.1347(21)	120(15)
C116	0.1054(12)	0.0295(15)	0.0728(15)	75(10)
C121	0.1791(11)	0.0631(14)	−0.0817(11)	53(8)
C122	0.1349(10)	0.1039(13)	−0.1265(13)	65(9)
C123	0.1040(11)	0.0696(16)	−0.1947(14)	75(10)
C124	0.1213(14)	−0.0078(16)	−0.2177(15)	80(11)
C125	0.1671(16)	−0.0480(18)	−0.1699(20)	115(14)
C126	0.1967(12)	−0.0135(15)	−0.1041(16)	79(10)
P2	0.9990(5)	0.2500(0)	0.6664(9)	91(5)
F1	0.9363(11)	0.2500(0)	0.6176(17)	129(12)
F2	1.0577(16)	0.2500(0)	0.7289(26)	195(20)
F3	0.9697(11)	0.1893(16)	0.7216(17)	227(15)
F4	1.0279(12)	0.1842(16)	0.6224(19)	263(17)

[a] $U_{eq} = (1/3) \cdot \Sigma[U_{ij} \cdot a_i^* \cdot a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j \cdot \cos(a_i, a_j)] \cdot 10^3$.

(m, 18 H, PPh_3), 1.97–1.95 (m, 2 H, CH_2), 1.35–1.16 (m, 12 H, 6 CH_2), 0.92 (s, 18 H, 2 $CNCMe_3$), 0.86 (t, $J = 6.8$ Hz, CH_3), 0.78 (s, 9 H, CMe_3).

[Ru(C≡CPh)(CNCMe$_3$)$_3$(PPh$_3$)$_2$]PF$_6$ (16). This was prepared by the general procedure from **13** and t-butyl isocyanide in 81% yield. Recrystallization from CH_2Cl_2–hexane gave crystals suitable for a crystal structure determination. IR (cm^{-1}): ν(C≡N) 2235 m, 2185 vs, $\nu(PF_6)$ 840 vs. ^1H NMR: δ 7.72–7.71 (m, 12 H, PPh_3), 7.42–7.41 (m, 18 H, PPh_3), 7.28–7.26 (m, 1 H, Ph), 7.11–7.09 (m, 2 H, Ph), 6.80–6.77 (m, 2 H, Ph), 0.93 (s, 18 H, 2 $CNCMe_3$), 0.83 (s, 9 H, $CNCMe_3$).

[Ru(CO)$_2$(C≡C'Bu)(py)(PPh$_3$)$_2$]PF$_6$ (17). A solution of the alkynyl complex **10** (485 mg, 0.47 mmol) in 1,2-dichloroethane (15 mL) was heated under reflux under CO (1 atm) for 6.5 h. The solvent was evaporated and the residue triturated with Et_2O to yield **17** as a crystalline yellow solid (420 mg, 91%). IR (cm^{-1}): ν(C≡C) 2110 vw, ν(C≡O) 2050 vs, 2000 vs, ν(C=N) 1605 m, $\nu(PF_6)$ 840 vs. ^1H NMR: δ 8.28 (d, $J = 5.3$ Hz, 2 H, py), 7.55–7.50 (m, 13 H), 7.43–7.31 (m, 20 H), 1.04 (s, 9 H). $^{13}C\{^1H\}$ NMR δ 197.61 (t, $J = 12.6$ Hz, CO), 192.13 (t, $J = 8.4$ Hz, CO), 154.00 (s, py), 139.00 (s, py), 133.53 (t, $J = 5.3$ Hz, PPh_3), 131.21 (s, PPh_3), 130.04 (t, $J = 24.5$ Hz, PPh_3), 128.80 (t, $J = 5.1$ Hz, PPh_3), 126.32 (s, py), 124.90 (s, β C≡C), 93.45 (t, $J = 18.7$ Hz, α C≡C), 31.07 (s, CMe_3), 29.44 (s, C*Me*$_3$). Anal. Found: C, 59.35; H, 4.75; N, 1.76. $C_{49}H_{44}F_6NO_2P_3Ru$ calc.: C, 59.54; H; 4.49; N, 1.42%.

[Ru(CO)$_2$(C≡CPh)(py)(PPh$_3$)$_2$]PF$_6$ (18). A solution of the alkynyl complex **13** (384 mg, 0.36 mmol) in 1,2-dichloroethane (15 mL) was heated under reflux under CO (1 atm) for 6.5 h. The solvent was evaporated and the residue was triturated with Et_2O to yield **18** as a crystalline pale yellow solid (350 mg, 96%). IR (cm^{-1}): ν(C≡C) 2110 vw, ν(C≡O) 2050 vs, 2000 vs, ν(C=N) 1606 m, $\nu(PF_6)$ 840 vs. ^1H NMR: δ 8.30 (d, $J = 5.3$ Hz, 2 H, py), 7.62–7.45 (m, 13 H), 7.43–7.19 (m, 23 H), 6.97–6.92 (m, 2 H). $^{13}C\{^1H\}$ NMR δ 197.13 (t, $J = 12.3$ Hz, CO), 192.32 (t, $J = 8.8$ Hz, CO), 154.27 (s, py), 139.00 (s, py), 133.26 (t, $J = 5.3$ Hz, PPh_3), 131.30 (s, PPh_3), 130.30 (s, PPh_3), 129.80 (t, $J = 24.8$ Hz, PPh_3), 128.90 (t, $J = 5.1$ Hz, Ph), 128.22 (s, Ph), 126.73 (s, Ph), 126.51 (s, py), 116.51 (t, $J = 2.4$ Hz, β C≡C), 110.49 (t, $J = 18.5$ Hz, α C≡C) (one Ph carbon signal overlaps). Anal. Found: C, 60.57; H, 4.20; N, 1.60. $C_{51}H_{40}F_6NO_2P_3Ru$ calc.: C, 60.84; H; 4.00; N, 1.39%.

X-ray diffraction data for compound 16

Table 2 gives the crystal analysis parameters of compound **16**. Table 3 gives the final atomic coordinates and thermal parameters for all non-hydrogen atoms of this compound. Lists of structure factors and thermal parameters are available from the authors.

Acknowledgments

We gratefully acknowledge financial support of this work by the Dirección General de Investigación Científica y Técnica (DGICYT) (Project PB87-0201-C03-02). We also thank Dr. M.R. Torres for some preliminary studies and Dr. A. Vegas for helpful discussions concerning the X-ray structure.

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