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Reactions of $[Ru(CO)ClH(Me_2Hpz)(PR_3)_2]$ (Me_2Hpz = 3,5-Dimethylpyrazole; R = Ph, *p*-Tolyl) with Acetylenes. The Crystal Structure of $[Ru(CO)Cl(HC{=}CHCMe_3)(Me_2Hpz)(PPh_3)_2]$ and $[Ru(CO)(MeO_2CC{=}CHCO_2Me)(HCO_3)(PPh_3)_2]$

Antonio Romero, Amelia Santos,* and Angel Vegas

Instituto Ciencias Materiales de Madrid, Sede D, Serrano, 113, 28006 Madrid, Spain

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Monosubstituted acetylenes $R'C{\equiv}CH$ (R' = *n*-C_3H_7, CMe_3, Ph, CO_2Me) react with the pyrazole hydrido complexes $[Ru(CO)ClH(Me_2Hpz)(PR_3)_2]$ (R = Ph, *p*-tolyl) in CH_2Cl_2 to yield alkenylpyrazole complexes $[Ru(CO)Cl(HC{=}CHR')(Me_2Hpz)(PR_3)_2]$ resulting from a cis insertion of the alkyne into the Ru–H bond. The X-ray crystal structure determination of the complex with R = Ph and R' = CMe_3 [monoclinic, $P2_1/n$, a = 10.413 (1) Å, b = 18.262 (1) Å, c = 23.861 (2) Å, β = 96.29 (1)°] shows a distorted octahedral geometry, with the ligands CO and Cl, alkenyl and pyrazole, and both phosphine molecules mutually trans. Bis-insertion derivatives $[Ru(CO)Cl\{MeO_2CC{=}C(CO_2Me)C(CO_2Me){=}CHCO_2Me\}(PR_3)]$ (R = Ph, *p*-tolyl) are formed in the reactions of both starting complexes with dimethyl acetylenedicarboxylate, and no reactions were observed with (trimethylsilyl)acetylene and diphenylacetylene. A secondary unexpected product of composition $[Ru(CO)(MeO_2CC{=}CHCO_2Me)(HCO_3)(PPh_3)_2]$ was isolated, along with the major alkenyl product, from the reaction of $[Ru(CO)ClH(Me_2Hpz)(PPh_3)_2]$ with methyl propiolate in CH_2Cl_2. The crystal structure of this compound has been determined by X-ray crystallography [monoclinic, $P2_1/n$, a = 11.556 (1) Å, b = 35.707 (2) Å, c = 10.386 (1) Å, β = 111.01 (2)°]. Reaction of the ruthenium hydrides with $PhC{\equiv}CH$ in EtOH yielded the unusual metallacycles $[\overline{Ru\{NH{=}C(Ph)OC}{=}CHPh\}(CO)Cl(PR_3)_2]$ (R = Ph, *p*-tolyl). The metallacycle with R = *p*-tolyl was also isolated from the reaction of the corresponding pyrazole alkenyl complex with $PhC{\equiv}CH$ in EtOH. However, the reaction of $[Ru(CO)Cl(HC{=}CHPh)(Me_2Hpz)(PPh_3)_2]$ with $PhC{\equiv}CH$ in EtOH affords an alkynyl complex, $[Ru(CO)Cl(C{\equiv}CPh)(Me_2Hpz)(PPh_3)_2]$. A similar product was obtained in the reaction of the alkenyl complex (R = Ph, R' = CMe_3) with $Me_3CC{\equiv}CH$ in EtOH. Mixtures of both pyrazole alkenyl and alkynyl complexes are formed in the reactions of $[Ru(CO)ClH(Me_2Hpz)(PPh_3)_2]$ with $Me_3CC{\equiv}CH$ and pent-1-yne in EtOH.

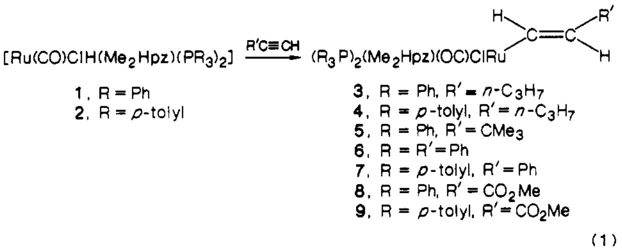
Introduction

In a preliminary communication,[1] we have reported on the reactions of $[Ru(CO)ClH(Me_2Hpz)\{P(p\text{-}MeC_6H_4)_3\}_2]$ with $PhC{\equiv}CH$, which were strongly dependent on the solvent nature. So, whereas in CH_2Cl_2 the expected insertion alkenyl complex was formed, reaction in EtOH leads to the metallacycle $[\overline{Ru\{NH{=}C(Ph)OC}{=}CHPh\}(CO)Cl\{P(p\text{-}MeC_6H_4)_3\}_2]$ as the only isolated product, which can be considered as formed from fragments of pyrazole, phenylacetylene, and EtOH in an anomalous bis-insertion reaction of $PhC{\equiv}CH$. Herein, we now report on a more general study of the reactivity of the pyrazole hydrido complexes $[Ru(CO)ClH(Me_2Hpz)(PR_3)_2]$ (R = Ph (**1**), *p*-tolyl (**2**)) with the mono- and disubstituted acetylenes $R'C{\equiv}CH$ (R' = n-C_3H_7, CMe_3, $SiMe_3$, Ph, CO_2Me) and $R'C{\equiv}CR'$ (R' = CO_2Me, Ph) in CH_2Cl_2 and in EtOH. An attempt to probe the first step of the early postulated mechanism for the anomalous insertion reaction[1] is also described.

Results and Discussion

Reactions in CH_2Cl_2. The reactions of the hydrido pyrazole complexes $[Ru(CO)ClH(Me_2Hpz)(PR_3)_2]$ (R = Ph (**1**), *p*-tolyl (**2**)) with monosubstituted acetylenes $R'C{\equiv}CH$ (R' = *n*-C_3H_7, CMe_3, Ph, CO_2Me) in CH_2Cl_2 give rise in all cases to simple insertion derivatives of one alkyne molecule into the Ru–H bond, according to eq 1. However, the pyrazole hydrido complexes were recovered unchanged in the reactions with $Me_3SiC{\equiv}CH$.

In all these products the alkenyl groups contain two trans hydrogen atoms, as deduced from the high ^1H NMR J values, in agreement with a cis insertion of the alkyne into the Ru–H bond. Complexes **3** and **5** are spectroscopically identical with those obtained by reaction of the five-coordinated alkenyl complexes $[Ru(CO)Cl(HC{=}CHR')(PPh_3)_2]$ with 3,5-dimethylpyrazole (Me_2Hpz),[2] which, on the basis of the crystal structure determination of the pentenyl derivative (R' = *n*-C_3H_7), contain the pyrazole and alkenyl ligands in a trans relationship, the CO and Cl ligands, and both phosphine molecules being also mutually trans. However, hydrido and pyrazole ligands were mutually cis in the starting complex **1**.[3] The crystal structure determination of complex **5** shows that the alkenyl and pyrazole ligands are also mutually trans in this



(1)

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complex. This fact shows that the insertion with these complexes is accompanied by a cis–trans isomerization.

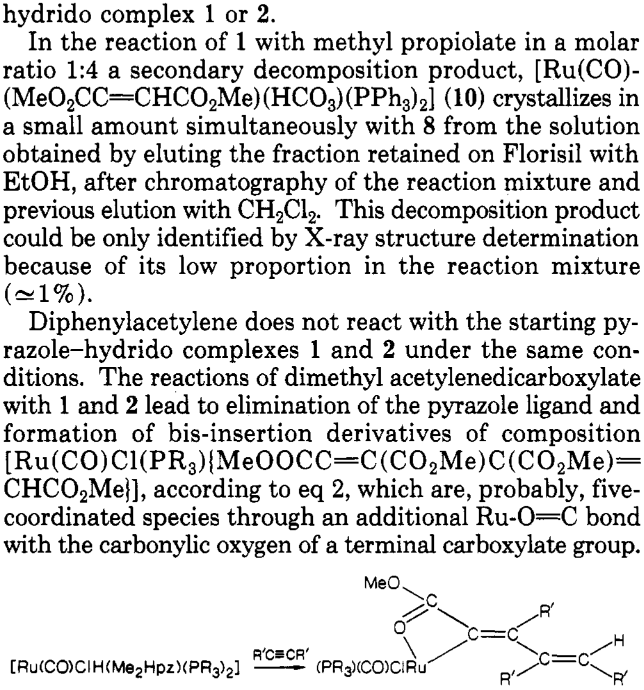
The most significative features of the IR and ^{1}H NMR spectra of these compounds are the shifts observed in the bands or signals involving the N–H bond of the pyrazole ligand with respect to those of the respective starting complex **1** or **2**. So the ν(NH) stretching frequency shifts toward higher values by 57 and 22 cm^{-1}, respectively, in the pentenyl complexes **3** and **4** and in 87 cm^{-1} in the complex **5**. The δ values for the iminic proton signals shift toward higher fields by 0.4–0.5 ppm in complexes **3**–**5**.

However, the reaction of **1** with PhC≡CH gives rise to a complex spectroscopically different from that obtained by reaction between the phenylethenyl complex and Me_2Hpz.[2] In this last complex the shift observed in the iminic proton signal of the pyrazole with respect to that of complex **1** toward higher fields is 0.43 ppm, and, therefore, the alkenyl and pyrazole ligands are likely mutually trans in this complex. The shift is considerably smaller in the compound **6** obtained from **1** (0.25 ppm toward higher fields). The IR ν(NH) values for the complexes obtained from the alkenyl and from the hydrido complex are also different (3210 and 3245 cm^{-1}, respectively). We conclude that very likely the alkenyl and pyrazole ligands occupy cis positions in complex **6**. Analogously, complex **7** shows $\Delta\ \nu$(NH) 32 cm^{-1} and $\Delta\delta$(NH) −0.26 ppm in agreement with a cis arrangement. On the other hand, we conclude that the pyrazole and alkenyl ligands are mutually trans in the complexes **8** and **9**, the shifts observed in the iminic proton signals being, respectively, 0.62 and 0.54 ppm toward higher fields.

It is to be noted that in all these alkenyl complexes the ^{1}H NMR methyl proton signals of Me_2Hpz shift toward lower fields with respect to those of the respective starting hydrido complex **1** or **2**.

In the reaction of **1** with methyl propiolate in a molar ratio 1:4 a secondary decomposition product, [Ru(CO)(MeO_2CC=$CHCO_2Me$)(HCO_3)(PPh_3)$_2$] (**10**) crystallizes in a small amount simultaneously with **8** from the solution obtained by eluting the fraction retained on Florisil with EtOH, after chromatography of the reaction mixture and previous elution with CH_2Cl_2. This decomposition product could be only identified by X-ray structure determination because of its low proportion in the reaction mixture ($\simeq$1%).

Diphenylacetylene does not react with the starting pyrazole–hydrido complexes **1** and **2** under the same conditions. The reactions of dimethyl acetylenedicarboxylate with **1** and **2** lead to elimination of the pyrazole ligand and formation of bis-insertion derivatives of composition [Ru(CO)Cl(PR_3){MeOOCC=C(CO_2Me)C(CO_2Me)=$CHCO_2Me$}], according to eq 2, which are, probably, five-coordinated species through an additional Ru–O=C bond with the carbonylic oxygen of a terminal carboxylate group.



(2)

Description of the Structure of Complex 5. The structure of **5** consists of discrete molecules (Figure 1) linked by van der Waals forces. Selected bond distances and angles are given in Table I. The Ru atom displays a distorted octahedral coordination, with Ru, Cl, C(1), N(1), and C(5) in the equatorial plane (largest deviation from mean plane = 0.0038 (5) Å in the Ru atom). Equation of least-squares plane passing through them is $-0.392\ (2)X - 0.326\ (2)Y - 0.8600\ (8)Z = -3.21\ (1)$. The two P atoms of PPh_3 molecules are in the apical sites, and a small deviation from linearity is observed for the P(1)–Ru–P(2) angle [176.05 (7)°]. In the equatorial plane Cl is trans to the carbonylic carbon C(1) and the pyrazole nitrogen N(1) is also trans to the alkenylic carbon C(5).

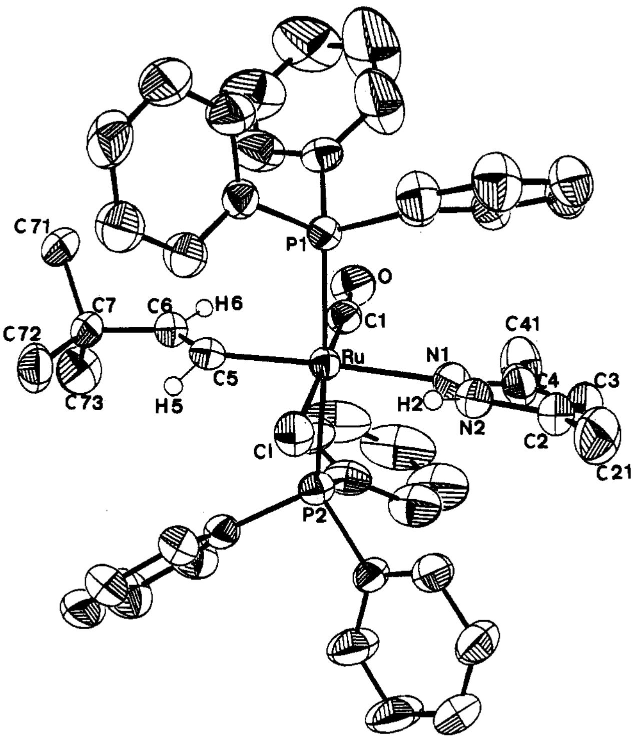


Figure 1. ORTEP[8] drawing of the molecular structure of [Ru(CO)Cl(HC=$CHCMe_3$)(Me_2Hpz)(PPh_3)$_2$] (**5**) (atom numbering as in Table V). Numbering of the carbons of the phenyl rings is omitted for clarity as are all the phenyl and methyl H atoms.

Table I. Selected Bond Lengths (Å) and Angles (deg) for Compound 5 (Esd's in Parentheses)

	Bond Lengths[a]		
Ru-P(1)	2.423 (5)	C(2)-C(21)	1.49 (1)
Ru-P(2)	2.396 (5)	C(3)-C(4)	1.41 (1)
Ru-Cl	2.495 (5)	C(4)-C(41)	1.51 (1)
Ru-C(1)	1.785 (8)	C(5)-H(5)	1.0 (1)
Ru-N(1)	2.228 (6)	C(5)-C(6)	1.33 (1)
Ru-C(5)	2.063 (7)	C(6)-H(6)	1.0 (1)
N(1)-N(2)	1.362 (9)	C(6)-C(7)	1.53 (1)
N(1)-C(4)	1.34 (1)	C(7)-C(71)	1.55 (1)
N(2)-H(2)	1.0 (1)	C(7)-C(72)	1.55 (1)
N(2)-C(2)	1.35 (1)	C(7)-C(73)	1.55 (1)
C(2)-C(3)	1.37 (1)		
	Bond Angles[b]		
P(1)-Ru-P(2)	176.05 (7)	Ru-C(1)-O	176.9 (6)
P(1)-Ru-Cl	88.70 (6)	N(2)-N(1)-C(4)	104.2 (6)
P(1)-Ru-C(1)	92.2 (2)	N(1)-N(2)-C(2)	113.7 (7)
P(1)-Ru-N(1)	93.3 (2)	N(2)-C(2)-C(3)	105.1 (8)
P(1)-Ru-C(5)	86.2 (2)	C(2)-C(3)-C(4)	107.1 (8)
P(2)-Ru-Cl	91.76 (6)	C(3)-C(4)-N(1)	110.0 (8)
P(2)-Ru-C(1)	87.3 (2)	Ru-C(5)-C(6)	133.4 (6)
P(2)-Ru-N(1)	90.6 (2)	C(5)-C(6)-C(7)	130.3 (7)
P(2)-Ru-C(5)	89.9 (2)	C(6)-C(7)-C(71)	108.7 (6)
Cl-Ru-C(1)	179.0 (3)	C(6)-C(7)-C(72)	108.2 (6)
Cl-Ru-N(1)	84.3 (2)	C(6)-C(7)-C(73)	112.1 (7)
Cl-Ru-C(5)	90.0 (2)	C(71)-C(7)-C(72)	108.5 (7)
C(1)-Ru-N(1)	96.1 (3)	C(71)-C(7)-C(73)	109.0 (7)
C(1)-Ru-C(5)	89.6 (3)	C(72)-C(7)-C(73)	110.2 (7)
N(1)-Ru-C(5)	174.2 (3)		

[a] Mean P–C in PPh_3 ligands = 1.832 (8) Å; mean C–C in Ph rings = 1.38 (1) Å. [b] Mean C–P–C in PPh_3 ligands = 101.9 (4)°; mean C–C–C in Ph rings = 120.0 (9)°; mean Ru–P–C = 116.3 (3)°.

As expected from the difference in the π-acceptor character of the carbonyl and alkenyl ligands, the Ru–C(1)

Table II. Selected Bond Lengths (Å) and Angles (deg) for Compound 10 (Esd's in Parentheses)

	Bond Lengths[a]		
Ru–P(1)	2.408 (3)	O(33)–H(33)	1.1 (1)
Ru–P(2)	2.395 (3)	C(4)–C(5)	1.49 (1)
Ru–C(1)	1.79 (1)	C(5)–O(51)	1.20 (1)
Ru–O(32)	2.262 (7)	C(5)–O(52)	1.31 (2)
Ru–O(33)	2.171 (7)	O(52)–C(52)	1.50 (1)
Ru–C(4)	2.044 (9)	C(4)–C(6)	1.33 (2)
C(1)–O(1)	1.15 (1)	C(6)–C(7)	1.47 (1)
C(2)–O(32)	1.28 (1)	C(7)–O(71)	1.17 (1)
C(2)–O(33)	1.26 (1)	C(7)–O(72)	1.35 (2)
C(2)–O(31)	1.19 (2)	O(72)–C(72)	1.48 (2)
	Bond Angles[b]		
P(1)–Ru–P(2)	171.38 (8)	O(31)–C(2)–O(32)	120.2 (8)
P(1)–Ru–C(1)	87.0 (4)	O(31)–C(2)–O(33)	124.4 (9)
P(1)–Ru–O(32)	88.8 (2)	O(32)–C(2)–O(33)	115.4 (9)
P(1)–Ru–O(33)	93.6 (2)	Ru–O(32)–C(2)	90.9 (5)
P(1)–Ru–C(4)	91.8 (3)	Ru–O(33)–C(2)	95.9 (6)
P(2)–Ru–C(1)	87.8 (4)	Ru–C(4)–C(6)	128.9 (7)
P(2)–Ru–O(32)	87.0 (2)	Ru–C(4)–C(5)	110.6 (7)
P(2)–Ru–O(33)	90.5 (2)	C(4)–C(5)–O(51)	124 (1)
P(2)–Ru–C(4)	95.1 (3)	C(4)–C(5)–O(52)	113 (1)
C(1)–Ru–O(32)	113.4 (3)	O(51)–C(5)–O(52)	123 (1)
C(1)–Ru–O(33)	171.2 (3)	C(5)–O(52)–C(52)	113 (1)
C(1)–Ru–C(4)	90.9 (4)	C(4)–C(6)–C(7)	123 (1)
O(32)–Ru–O(33)	57.8 (2)	C(6)–C(7)–O(71)	127 (1)
O(32)–Ru–C(4)	155.7 (4)	C(6)–C(7)–O(72)	110 (1)
O(33)–Ru–C(4)	97.9 (3)	O(71)–C(7)–O(72)	123 (1)
Ru–C(1)–O(1)	178.3 (9)	C(7)–O(72)–C(72)	115 (1)

[a] Mean P–C in PPh_3 ligands = 1.82 (1) Å; mean C–C in Ph rings = 1.37 (3) Å. [b] Mean Ru–P–C = 114.4 (4)°; mean C–P–C in PPh_3 ligands = 104.0 (6)°; mean C–C–C in Ph rings = 120 (2)°.

Table III. Crystal Analysis Parameters of Compound 5

	Crystal Data
formula	$[Ru(CO)Cl(HC{=}CHCMe_3)(Me_2Hpz)(PPh_3)_2]$, $C_{48}H_{49}ClN_2P_2Ru$
cryst habit	light yellow prisms
cryst size (mm)	0.18 × 0.15 × 0.10
symmetry	monoclinic, $P2_1/n$
unit cell dimens	10.413 (1), 18.262 (1), 23.861 (2) Å 90.00 (0), 96.29 (1), 90.00 (0)°
packing: V(Å^3), Z	4510.2 (6), 4
D(calcd) (g·cm^{-3}), M, F(000)	1.2062, 868.40, 1800
μ (cm^{-1})	43.81
	Experimental Data
technique	four-circle diffractometer Philips PW 1100 monochromated Cu Kα, θ_{max} = 65°
no. of reflctns	
measd	8146
independent	7676
obsd	6718 [$I \leq 3\sigma(I)$ criterion]
std reflctns	060 and 0$\bar{6}$0 reflections every 90 min variation no
soln and refinement	
soln	Patterson and Fourier synthesis
refinement	least squares on F_o with 2 blocks
absorptn correctn	yes; max and min, 1.435 and 0.885, respectively; mean, 1.002
parameters	
no. of variables	496
degrees of freedom	6222
ratio of freedom	12.5
H atoms	calculated positions for phenylic H and H(6)
computer and programs	VAX 11/750, XRAY80 System,[4] DIRDIF,[5] PARST[6]
scattering factors	ref 7
anomalous dispersion	ref 7
final R	5.6%

Table IV. Crystal Analysis Parameters of Compound 10

	Crystal Data
formula	$[Ru(CO)(MeOOCC{=}CHCOOMe)(HCO_3)(PPh_3)_2]$, $C_{44}H_{38}O_8P_2Ru$
cryst habit	light yellow prisms
cryst size (mm)	0.1 × 0.08 × 0.06
symmetry	monoclinic, $P2_1/n$
unit cell dimens	11.556 (1), 35.707 (2), 10.386 (1) Å 90.00 (0), 110.01 (2), 90.00 (0)°
packing: V (Å^3), Z	4000.7 (6), 4
D(calcd) (g·cm^{-3}), M, F(000)	1.42, 857.8, 1760
μ (cm^{-1})	44.4
	Experimental Data
technique	four-circle diffractometer PW 110 monochromated Cu Kα, θ_{max} = 65°
no. of reflctns	
measd	7355
independent	6824
obsd	4120 [$I \leq 4\sigma(I)$ criterion]
std reflctns	22$\bar{3}$ and $\bar{2}\bar{2}$3 reflections every 90 min variation no
soln and refinement	
soln	Patterson and Fourier synthesis
refinement	least squares on F_o with 2 blocks
absorptn correctn	none
parameters	
no. of variables	496
degrees of freedom	3624
ratio of freedom	7.3
H atoms	calcd positions for phenylic H
computer and programs	VAX 11/750, XRAY80 System,[4] DIRDIF,[5] PARST[6]
scattering factors	ref 7
anomalous dispersion	ref 7
final R	6.6%

bond length [1.79 (1) Å] is significantly shorter than the the Ru–C(5) distance [2.06 (1) Å]. In the alkenyl ligand, the C(5)–C(6) distance [1.33 (1) Å] corresponds clearly to a C=C double bond. The plane defined by the C(5), C(6), and C(7) atoms forms an angle of 175.6(3)° with the equatorial plane of the octahedron around the Ru atom.

Significant differences are observed in the Ru–Cl and Ru–N(1) distances [2.495 (5) and 2.228 (6) Å, respectively] of the alkenyl complex **5** if compared with those of the starting hydrido complex **1** [2.568 (3) and 2.174 (8) Å], the lengthening of the Ru–N(1) distance in the complex **5** and the Ru–Cl distance in the starting complex **1** being related to the predominant trans effect of both the hydrido and alkenyl lignds, respectively.

A final comment should be made about the short N(2)–Cl and C–H(2) contacts [2.986 (7) and 2.33 (1) Å, respectively] which could be regarded as an intramolecular N–H...Cl interaction, in spite of the small value of the N(2)–H(2)–Cl angle [120 (1)°]. A similar situation, which was not discussed in a previous report,[3] is observed in the starting hydrido complex **1**, where the N(2)–Cl and Cl–H(2) contact distances are 3.055 (6) and 2.37 (1) Å, respectively, and the angle at H(2) has a value of 124 (1)°. However, differences are observed in the relative conformation of their planar pyrazole rings. In the starting complex **1** the ring is almost parallel to the equatorial plane,[3] whereas in **5** the pyrazole is rotated around the Ru–N(1) bond up to form an angle of 19.4 (3)° with it. This rotation could be explained by the need to satisfying the correct N(2)–Cl and Cl–H-(2) contact distances in complex **5**.

Description of the Structure of Complex 10. The structure of **10** consists of discrete molecules (Figure 2) bonded by van der Waals forces. Selected bond lengths and angles are given in Table II. The Ru atom displays an irregular octahedral coordination, with Ru, C(1), C(4), O(32), and O(33) in the equatorial plane, and two P atoms of PPh_3 ligands are in approximately axial positions [P(1)–Ru–P(2) = 171.35 (8)°]. The compression of the O-

Table V. Atomic Parameters for $[Ru(CO)Cl(Me_2Hpz)(HC{=}CHCMe_3)(PPh_3)_2]$

atom	x/a	y/b	z/c	U_{eq}, Å^2
Ru	0.38013 (5)	−0.16674 (3)	0.13672 (2)	320 (2)
P(1)	0.2786 (2)	−0.2164 (1)	0.0486 (1)	384 (6)
P(2)	0.4862 (2)	−0.1259 (1)	0.2254 (1)	361 (5)
Cl	0.5642 (2)	−0.1254 (1)	0.0859 (1)	459 (6)
C(1)	0.2502 (7)	−0.1964 (4)	0.1741 (3)	396 (23)
O	0.1690 (5)	−0.2179 (3)	0.2003 (2)	590 (22)
N(1)	0.3038 (6)	−0.0544 (3)	0.1180 (3)	435 (21)
N(2)	0.3859 (6)	−0.0014 (3)	0.1033 (3)	472 (22)
C(2)	0.3273 (9)	0.0631 (5)	0.0895 (3)	550 (30)
C(3)	0.1999 (10)	0.0519 (5)	0.0962 (4)	624 (34)
C(4)	0.1883 (8)	−0.0210 (4)	0.1145 (4)	522 (28)
C(21)	0.4009 (11)	0.1277 (5)	0.0724 (5)	777 (42)
C(41)	0.0690 (9)	−0.0589 (6)	0.1307 (5)	765 (41)
C(5)	0.4660 (7)	−0.2680 (4)	0.1494 (3)	357 (22)
C(6)	0.4289 (7)	−0.3305 (4)	0.1715 (3)	406 (23)
C(7)	0.4942 (7)	−0.4054 (4)	0.1757 (3)	436 (25)
C(71)	0.5280 (9)	−0.4249 (5)	0.2389 (4)	628 (33)
C(72)	0.3967 (10)	−0.4628 (5)	0.1486 (4)	712 (38)
C(73)	0.6194 (9)	−0.4068 (5)	0.1461 (4)	655 (35)
C(101)	0.3556 (8)	−0.2964 (4)	0.0204 (3)	476 (27)
C(102)	0.4868 (9)	−0.2895 (5)	0.0131 (3)	595 (32)
C(103)	0.5511 (12)	−0.3459 (6)	−0.0124 (4)	810 (44)
C(104)	0.4827 (17)	−0.4080 (6)	−0.0301 (4)	974 (57)
C(105)	0.3540 (16)	−0.4156 (6)	−0.0223 (5)	951 (56)
C(106)	0.2943 (11)	−0.3596 (5)	0.0027 (4)	737 (40)
C(111)	0.2570 (7)	−0.1609 (4)	−0.0160 (3)	417 (24)
C(112)	0.2722 (9)	−0.0864 (5)	−0.0154 (3)	539 (30)
C(113)	0.2526 (9)	−0.0450 (5)	−0.0648 (4)	611 (33)
C(114)	0.2184 (10)	−0.0788 (6)	−0.1153 (4)	697 (38)
C(115)	0.2059 (14)	−0.1534 (6)	−0.1167 (4)	964 (53)
C(116)	0.2236 (12)	−0.1943 (5)	−0.0679 (4)	804 (43)
C(121)	0.1134 (8)	−0.2454 (5)	0.0554 (3)	535 (30)
C(122)	0.0927 (10)	−0.3037 (6)	0.0907 (4)	708 (37)
C(123)	−0.0331 (14)	−0.3206 (8)	0.1013 (5)	1050 (59)
C(124)	−0.1348 (12)	−0.2788 (11)	0.0780 (6)	1178 (73)
C(125)	−0.1158 (10)	−0.2214 (9)	0.0441 (5)	1043 (61)
C(126)	0.0073 (9)	−0.2041 (7)	0.0311 (4)	748 (41)
C(201)	0.4831 (7)	−0.0266 (4)	0.2333 (3)	367 (22)
C(202)	0.3648 (8)	0.0093 (4)	0.2337 (3)	465 (26)
C(203)	0.3575 (9)	0.0839 (5)	0.2369 (4)	562 (31)
C(204)	0.4693 (10)	0.1252 (5)	0.2395 (4)	654 (36)
C(205)	0.5868 (9)	0.0917 (5)	0.2382 (5)	680 (37)
C(206)	0.5939 (8)	0.0158 (5)	0.2355 (4)	544 (30)
C(211)	0.6563 (7)	−0.1486 (4)	0.2466 (3)	412 (24)
C(212)	0.7369 (7)	−0.1733 (5)	0.2083 (4)	556 (30)
C(213)	0.8651 (9)	−0.1861 (6)	0.2251 (4)	711 (38)
C(214)	0.9147 (9)	−0.1753 (6)	0.2801 (5)	735 (39)
C(215)	0.8352 (10)	−0.1528 (7)	0.3186 (4)	840 (44)
C(216)	0.7083 (9)	−0.1385 (6)	0.3020 (4)	697 (37)
C(221)	0.4136 (7)	−0.1591 (5)	0.2874 (3)	454 (26)
C(222)	0.4168 (13)	−0.2329 (5)	0.2975 (4)	812 (45)
C(223)	0.3651 (17)	−0.2616 (7)	0.3444 (5)	1118 (65)
C(224)	0.3119 (17)	−0.2179 (9)	0.3804 (6)	1215 (74)
C(225)	0.3028 (21)	−0.1463 (10)	0.3697 (7)	1675 (103)
C(226)	0.3552 (16)	−0.1166 (7)	0.3242 (5)	1196 (65)

[a] $U_{eq} = {}^1/_3[\sum(U_{ij}a_i{}^*a_j{}^*a_ia_j\cos(a_i,a_j))] \times 10^4$.

Table VI. Atomic Parameters for $[Ru(CO)(HCO_3)(MeOOCC{=}CHCOOMe)(PPh_3)_2]$

atom	x/a	y/b	z/c	U_{eq}, Å^2
Ru	0.37760 (7)	0.13155 (2)	0.12642 (8)	399 (2)
P(1)	0.2434 (2)	0.08257 (7)	0.1501 (3)	471 (10)
P(2)	0.4890 (3)	0.18124 (8)	0.0682 (3)	518 (11)
C(1)	0.3776 (9)	0.1076 (3)	−0.0256 (10)	450 (39)
O(1)	0.3804 (7)	0.0922 (2)	−0.1222 (7)	667 (35)
C(2)	0.2581 (9)	0.1821 (3)	0.2129 (10)	423 (38)
O(31)	0.2042 (8)	0.2053 (3)	0.2526 (9)	907 (46)
O(32)	0.2190 (6)	0.1725 (2)	0.0855 (7)	520 (28)
O(33)	0.3547 (6)	0.1655 (2)	0.2883 (6)	484 (27)
C(4)	0.5323 (9)	0.1030 (3)	0.2443 (10)	472 (39)
C(5)	0.5903 (10)	0.1209 (3)	0.3821 (12)	608 (48)
O(51)	0.6690 (9)	0.1446 (3)	0.4078 (10)	1050 (47)
O(52)	0.5427 (8)	0.1091 (2)	0.4717 (8)	732 (37)
C(52)	0.5946 (15)	0.1286 (4)	0.6078 (12)	1078 (72)
C(6)	0.5833 (11)	0.0725 (3)	0.2139 (10)	623 (47)
C(7)	0.6827 (11)	0.0507 (4)	0.3151 (12)	647 (50)
O(71)	0.7361 (8)	0.0589 (3)	0.4306 (8)	894 (41)
O(72)	0.7109 (9)	0.0204 (3)	0.2544 (9)	1010 (46)
C(72)	0.8001 (16)	−0.0058 (4)	0.3492 (16)	1222 (85)
C(101)	0.1132 (11)	0.0764 (3)	−0.0119 (12)	717 (52)
C(102)	0.0676 (10)	0.1053 (3)	−0.1005 (12)	655 (48)
C(103)	−0.0346 (11)	0.1009 (4)	−0.2188 (12)	781 (54)
C(104)	−0.0925 (13)	0.0671 (5)	−0.2543 (14)	1058 (70)
C(105)	−0.0469 (19)	0.0384 (5)	−0.1711 (20)	1886 (111)
C(106)	0.0532 (17)	0.0420 (5)	−0.0479 (18)	1545 (96)
C(111)	0.3108 (9)	0.0359 (3)	0.1864 (10)	485 (40)
C(112)	0.3418 (15)	0.0170 (3)	0.0863 (13)	856 (72)
C(113)	0.3992 (19)	−0.0175 (4)	0.1119 (19)	1262 (113)
C(114)	0.4265 (15)	−0.0333 (3)	0.2380 (18)	964 (85)
C(115)	0.3966 (12)	−0.0162 (3)	0.3390 (12)	691 (55)
C(116)	0.3382 (9)	0.0189 (3)	0.3124 (10)	536 (43)
C(121)	0.1719 (10)	0.0889 (3)	0.2777 (12)	593 (49)
C(112)	0.2429 (14)	0.1021 (4)	0.4059 (13)	843 (68)
C(123)	0.1915 (22)	0.1051 (5)	0.5051 (17)	1246 (116)
C(124)	0.0763 (35)	0.0981 (9)	0.4844 (31)	1850 (250)
C(125)	0.0055 (24)	0.0859 (9)	0.3600 (34)	1836 (209)
C(126)	0.0485 (13)	0.0804 (5)	0.2512 (19)	1174 (88)
C(201)	0.4258 (12)	0.1925 (3)	−0.1120 (12)	631 (54)
C(202)	0.3001 (15)	0.1881 (3)	−0.1857 (13)	857 (69)
C(203)	0.2475 (18)	0.1967 (4)	−0.3242 (14)	1151 (90)
C(204)	0.3156 (30)	0.2090 (6)	−0.3963 (17)	1601 (165)
C(205)	0.4444 (27)	0.2135 (6)	−0.3215 (25)	1587 (165)
C(206)	0.4937 (15)	0.2060 (4)	−0.1864 (16)	1071 (84)
C(211)	0.6519 (10)	0.1730 (3)	0.0948 (13)	685 (55)
C(212)	0.6785 (12)	0.1422 (4)	0.0256 (14)	804 (62)
C(213)	0.7994 (15)	0.1365 (4)	0.0333 (20)	1125 (95)
C(214)	0.8910 (15)	0.1607 (5)	0.1008 (25)	1315 (118)
C(215)	0.8656 (13)	0.1893 (5)	0.1716 (25)	1405 (116)
C(216)	0.7484 (13)	0.1970 (3)	0.1698 (17)	974 (76)
C(221)	0.4794 (10)	0.2256 (3)	0.1518 (12)	609 (50)
C(222)	0.4086 (13)	0.2547 (4)	0.0780 (14)	828 (63)
C(223)	0.3938 (18)	0.2867 (4)	0.1486 (20)	1239 (95)
C(224)	0.4460 (19)	0.2894 (4)	0.2848 (21)	1172 (102)
C(225)	0.5216 (16)	0.2612 (5)	0.3621 (15)	1013 (79)
C(226)	0.5359 (12)	0.2285 (3)	0.2944 (12)	735 (57)

[a] $U_{eq} = {}^1/_3[\sum(U_{ij}a_i{}^*a_j{}^*a_ia_j\cos(a_i,a_j))] \times 10^4$.

(32)–Ru–O(33) angle to 57.8 (2)° produces an increase of two of the remaining equatorial angles [C(1)–Ru–O(32) = 113.4 (3)°, C(4)–Ru–O(33) = 98.0 (3)°, C(1)–Ru–C(4) = 90.8 (4)°]. As in complex **5**, the bond length Ru–C is shorter for the carbonyl than for the alkenyl ligand.

The CO_3 group is completely planar (equation of least-squares plane passing through them is $0.672\ (4)X + 0.716\ (4)Y - 0.187\ (5)Z = 5.74\ (2)$) and almost parallel to the equatorial plane, the angle between them being 2.1 (3)°. However, the C(4), C(5), C(6), and C(7) atoms belonging to the alkenyl group deviate significantly from the plane defined by them (equation of least-squares plane is $0.784\ (4)X + 0.527\ (4)Y - 0.326\ (8)Z = 5.27\ (4)$, with deviations of −0.08 (1), 0.04 (1), 0.08 (1), and −0.04 (1) Å, respectively. This plane forms an angle of 15.4 (4)° with the equatorial plane.

These structural data indicate that, although methyl propiolate was the starting material for the preparation of **10**, this complex contains an alkenyl group resulting from the formal insertion of dimethyl acetylenedicarboxylate into the Ru–H bond. On the other hand, a planar tetraatomic bidentate ligand appears coordinated to the Ru atom. The geometry of this group is consistent with either a $CO_3{}^{2-}$ or a $HCO_3{}^-$ anion. In the first case, **10** should be a Ru^{III} complex, which seems to be improbable, so that the existence of a bicarbonate anion was assumed. Its H atom was searched in a ΔF synthesis, and a maximum was found in the vicinity of O(33) at a distance which is consistent with an OH bond.

Noteworthy is the difference observed in the two Ru–O distances: 2.263 (7) and 2.166 (7) Å. The first one, corresponding to the Ru–O(32) bond, is in good agreement

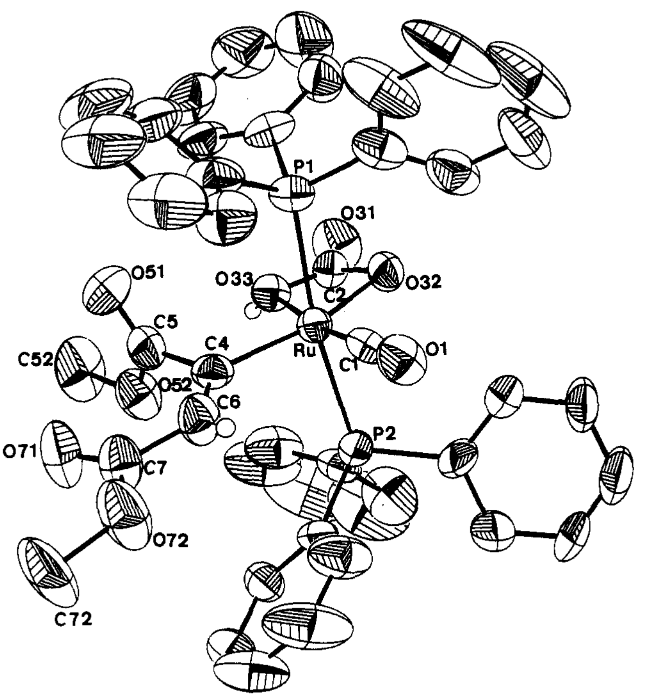
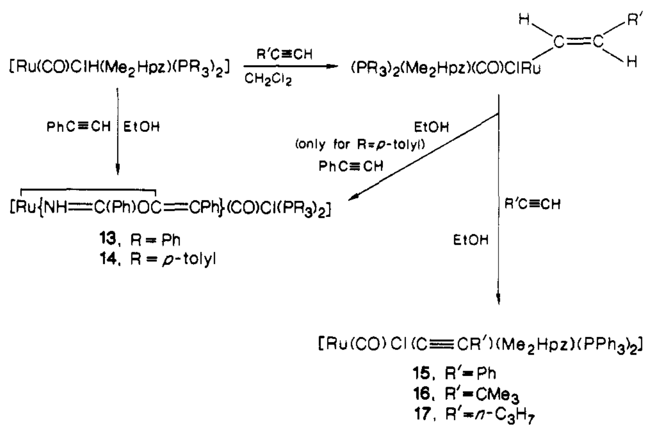


Figure 2. ORTEP[8] drawing of the molecular structure of [Ru(CO)(MeOOCC=CHCOOMe)(HCO$_3$)(PPh$_3$)$_2$] (**10**) (atom numbering as in Table VI). Numbering of the carbons of the phenyl rings is omitted for clarity as are all the phenyl and methyl H atoms.

with other reported Ru–O distances, but the Ru–O(33) distance lies in the range of Ru–N bond. Consequently the possibility of a carbamate ion was also considered. However, this possibility was disregarded because no change was observed when a final least-squares refinement was carried out by assuming that O(33) was a N atom, the geometry of the bidentate ligand resulting with a C–N bond length too short for a single bond. This led us to consider that the bidentate ligand is a bicarbonate anion and that the differences in both Ru–O distances could be attributed to the different trans effect of the carbonyl and alkenyl ligands.

Reactions in EtOH or EtOH/CH$_2$Cl$_2$. The starting complexes **1** and **2** react with PhC≡CH to give the unusual metallacycles [Ru{NH=C(Ph)OC=CHPh}(CO)Cl(PR$_3$)$_2$] (R = Ph, **13**; R = *p*-tolyl, **14**).[1] In the proposed mechanism for the formation of these metallacycles, we have postulated the formation of the mono-insertion alkenyl derivatives as intermediates. In an attempt to test the existence of such intermediates in the reaction in EtOH, the alkenyl mono-insertion derivatives **5**–**7** were allowed to react with the corresponding terminal acetylenes R′C≡CH in EtOH. Metallacycle **14** was obtained only in the reaction of complex **7** with PhC≡CH, alkynyl complexes [Ru(CO)Cl(C≡CR′)(Me$_2$Hpz)(PPh$_3$)$_2$] (R′ = Ph, **15**; R′ = CMe$_3$, **16**) being formed in the reactions with PhC≡CH and Me$_3$CC≡CH, respectively, according to (eq 3). In the reaction from **5**, the formation of **16** was incomplete.



13, R = Ph
14, R = *p*-tolyl

15, R′ = Ph
16, R′ = CMe$_3$
17, R′ = *n*-C$_3$H$_7$

(3)

Noteworthy is the fact that in the reaction of [Ru(CO)Cl(HC=CHPh)(PPh$_3$)$_2$] with Me$_2$Hpz in Et$_2$O/EtOH an alkynyl complex is formed of the same composition as **15** but with different IR and ^{1}H NMR spectra.[2] Both complexes must be isomers containing the pyrazole and alkynyl ligands in the equatorial plane in cis or trans positions. By using the spectral criterium based on the chemical shift values of the iminic pyrazole protons used above, we conclude that complex **15** is the cis isomer (δ(NH)11.07), the complex obtained from the five-coordinated alkenyl complex by reaction with Me$_2$Hpz in Et$_2$O/EtOH being the trans isomer (δ(NH) 10.93). The formation of these alkynyl complexes implies the displacement of an alkenyl by an alkynyl ligand, with formation of alkene (eq 4).

$$[\mathrm{Ru(CO)Cl(HC{=}CHPh)(Me_2Hpz)(PPh_3)_2}] + \mathrm{PhC{\equiv}CH} \rightarrow \textit{cis}\text{-}[\mathrm{Ru(CO)Cl(C{\equiv}CPh)(Me_2Hpz)(PPh_3)_2}] + \mathrm{PhHC{=}CH_2} \quad (4)$$

The reaction of Me$_3$CC≡CH with **1** in ethanol leads to the same mixture of the alkenyl complex **5** and the alkynyl complex **16** as that formed in the reaction of **5** with an excess of Me$_3$CC≡CH in EtOH, which was incomplete. A similar behavior was observed in the reaction of **1** with pent-1-yne, in which **3** and an alkynyl complex, **17**, were formed.

We cannot explain the different behavior observed for the reactions of the alkenyl complexes **6** and **7**, derived from PhC≡CH, in its reactions with an excess of PhC≡CH in EtOH.

Experimental Section

The complexes [Ru(CO)ClH(Me$_2$Hpz)(PR$_3$)$_2$] (**1**, **2**) were prepared according to a published procedure.[3] IR spectra were recorded with a PYE UNICAM SP-3-300S instrument using KBr disks. The ^{1}H NMR spectra were recorded on a Bruker WM spectrometer at 360 MHz; shifts are relative to Me$_4$Si (0.00 ppm), and the samples were dissolved in CDCl$_3$.

Mono-Insertion Derivatives [Ru(CO)Cl(HC=CHR′)(Me$_2$Hpz)(PR$_3$)$_2$] (3–9). General Preparation Method. The starting complex **1** or **2** (0.15 mmol) and 0.6 mmol of the alkyne were heated to reflux in CH$_2$Cl$_2$ (30 mL) for 4 h. The yellow solution was concentrated to 5 mL, and the complex was isolated by recrystallization or by precipitation with Et$_2$O or *n*-pentane (yield 75–80%).

[Ru(CO)Cl(HC=CHC$_3$H$_7$)(Me$_2$Hpz)(PPh$_3$)$_2$] (3) (Lemon Yellow). The complex was isolated as microcrystalline powder by precipitation with Et$_2$O: IR ν(NH) 3240 m, ν(C≡O) 1925vs, ν(C=N) 1560 cm^{-1}; ^{1}H NMR δ 0.53 (t, *J* = 6.8 Hz, Me), 0.89 (sex., *J* = 6.8 Hz, CH$_2$), 1.66 (s, 5 H, Me Me$_2$Hpz + CH$_2$), 1.80 (s, 3 H, Me Me$_2$Hpz), 4.65 (dt, *J* = 16.7, 7.8 Hz, 1 H, =CH), 5.34 (s, 1 H, CH Me$_2$Hpz), 7.09–7.33 (m, 31 H, CH Ph + HC=), 10.94 (s, 1 H, NH Me$_2$Hpz). Anal. Calcd for C$_{47}$H$_{47}$ClN$_2$OP$_2$Ru: C, 66.07; H, 5.55; N, 3.28. Found: C, 65.72; H, 5.62; N, 3.22.

[Ru(CO)Cl(HC=CHC$_3$H$_7$)(Me$_2$Hpz){P(*p*-MeC$_6$H$_4$)$_3$}$_2$] (4) (Light Yellow). The complex was isolated as microcrystalline powder after concentration to 5 mL and filtration and was washed with Et$_2$O: IR ν(NH) 3220 m, ν(C≡O) 1923 vs, ν(C=N) 1565 cm^{-1}; ^{1}H NMR δ 0.54 (t, *J* = 6.8 Hz, Me), 0.90 (sex., *J* = 6.8 Hz, CH$_2$), 1.61–1.69 (s, 5 H, Me Me$_2$Hpz + CH$_2$), 1.79 (s, 3 H, Me Me$_2$Hpz), 2.21 (s, 18 H, 6 Me *p*-tolyl groups), 4.66 (dt, *J* = 16.0, 7.0 Hz, 1 H, =CH), 5.30 (s, 1 H, CH Me$_2$Hpz), 6.89–6.91 (m, 10 H, CH *p*-tolyl groups), 7.18–7.21 (m, 15 H, CH *p*-tolyl groups + HC=), 10.90 (s, 1 H, NH Me$_2$Hpz). Anal. Calcd for C$_{53}$H$_{59}$ClN$_2$OP$_2$Ru: C, 67.83; H, 6.34; N,2.98. Found: C, 67.45; H, 6.30; N, 2.96.

[Ru(CO)Cl(HC=CHCMe$_3$)(Me_2Hpz)(PPh_3)$_2$] (5) (Light Yellow). The complex was isolated by precipitation with pentane as a crystalline solid, which was recrystallized from CH_2Cl_2/EtOH/Et_2O. Crystals adequate for an X-ray crystal structure determination were obtained: IR ν(NH) 3275 m, ν(C≡O) 1925 vs, ν(C=N) 1565 m cm^{-1}; ^{1}H NMR δ 0.50 (s, 9 H, 3Me), 1.67, 1.84 (s, 3 H, Me Me_2Hpz), 4.76 (d, J = 16.0 Hz, 1 H, =CH), 5.40 (s, 1 H, CH Me_2Hpz), 7.12–7.36 (m, 31 H, 6 Ph + HC=), 11.04 (s, 1 H, NH Me_2Hpz). Anal. Calcd for $C_{48}H_{49}ClN_2OP_2Ru$: C, 66.39; H, 5.69; N, 3.23. Found: C, 66.05, H, 5.80; N, 3.20.

[Ru(CO)Cl(HC=CHPh)(Me_2Hpz)(PPh_3)$_2$] (6) (Yellow). The complex was precipitated with n-pentane and recrystallized from CH_2Cl_2/n-pentane: IR ν(NH), 3245 m, ν(C≡O) 1923 vs, ν(C=N) 1565 m cm^{-1}; ^{1}H NMR δ 1.74, 1.85 (s, 3 H, Me Me_2Hpz), 5.40 (s, 1 H, CH Me_2Hpz), 5.85 (d, J = 15.0 Hz, 1 H, =CH), 6.60 (d, 2 H, Ph), 6.75 (t, 1 H, Ph), 6.96 (t, 2 H, Ph), 7.15–7.30 (m, 10 H, Ph PPh_3), 7.40–7.60 (m, 20 H, Ph PPh_3), 8.55 (d, J = 15.0 Hz, HC=), 11.20 (s, 1 H, NH Me_2Hpz). Anal. Calcd for $C_{50}H_{45}ClN_2OP_2Ru$: C, 67.60; H, 5.11; N, 3.15. Found: C, 67.24; H, 5.23; N, 3.13.

[Ru(CO)Cl(HC=CHPh)(Me_2Hpz){P(p-MeC$_6$H$_4$)$_3$}$_2$] (7) (Yellow). The complex was precipitated with pentane, filtered off, and washed with EtOH and pentane. recrystallization from CH_2Cl_2/pentane gives crystals of the pure product: IR ν(NH) 3230 m, ν(C≡O) 1912 vs, ν(C=N) 1568 m cm^{-1}; ^{1}H NMR δ 1.77, 1.92 (s, 3 H, Me Me_2Hpz), 2.29 (s, 18 H, 6 Me p-tolyl groups), 5.43 (s, 1 H, CH Me_2Hpz), 5.73 (d, J = 16.7 Hz, 1 H, =CH), 6.74 (d, 2 H, Ph), 6.88 (t, 1 H, Ph), 6.97 (d, 8 H, C_6H_4), 7.02 (t, 2 H, Ph), 7.27 (d, 16 H, C_6H_4), 8.70 (d, J = 16.7 Hz, 1 H, HC=), 11.07 (s, 1 H, NH Me_2Hpz). Anal. Calcd for $C_{56}H_{57}ClN_2OP_2Ru$: C, 69.16; H, 5.91; N, 2.88. Found: C, 69.04; H, 5.98; N, 2.75.

[Ru(CO)Cl(HC=CHCOOMe)(Me_2Hpz)(PPh_3)$_2$] (8) (Light Yellow). In this case the reaction was performedd in a molar ratio 1:1 (Ru/alkyne). Small crystals are formed by slow evaporation of the solvent (yield 80%): IR ν(NH) 3230 m, ν(C≡O) 1935 vs, ν(C=O) 1630 s, ν(C=N) 1560 m cm^{-1}; ^{1}H NMR δ 1.67, 1.83 (s, 3 H, Me Me_2Hpz), 3.42 (s, 3 H, Me COOMe), 5.45 (s, 1 H, CH Me_2Hpz), 5.65 (d, J = 17.5 Hz, 1 H, =CH), 7.13–7.35 (m, 30 H, Ph), 10.49 (d, J = 17.5 Hz, 1 H, HC=), 10.83 (s, 1 H, NH Me_2Hpz). Anal. Calcd for $C_{46}H_{43}ClN_2O_3P_2Ru$: C, 63.48; H, 4.98; N, 3.22. Found: C, 63.14; H, 4.96; H, 3.18.

Ru(CO)Cl(HC=CHCOOMe)(Me_2Hpz){P(p-MeC$_6$H$_4$)$_3$}$_2$] (9) (Light Yellow). In this case the reaction mixture was evaporated to dryness and the solid was washed with Et_2O, dissolved in CH_2Cl_2, precipitated with petroleum other, and washed with Et_2O (yield 78%): IR ν(NH) 3220m, ν(C≡O) 1930 vs, ν(C=O) 1685 vs, ν(C=N) 1565 cm^{-1}; ^{1}H NMR δ 1.65, 1.80 (s, 3 H, Me Me_2Hpz), 2.22 (s, 18 H, Me p-tolyl groups), 3.41 (s, 3 H, Me COOMe), 5.41 (s, 1 H, CH Me_2Hpz), 5.65 (d, J = 16.7 Hz, 1 H, =CH), 6.91–7.19 (m, 24 H, C_6H_4), 10.44 (d, J = 16.7 Hz, 1 H, HC=), 10.79 (s, 1 H, NH Me_2Hpz). Anal. Calcd for $C_{52}H_{55}ClN_2O_3P_2Ru$: C, 65.43; H, 5.81; N, 2.93. Found: C, 65.08; H, 5.90; N, 2.91.

[Ru(CO)(MeO$_2$CC=CHCO$_2$Me)(HCO$_3$)(PPh_3)$_2$] (10). The reaction of 1 with methyl propiolate in a molar ratio of 1:4 (Ru/alkyne) yields a strongly colored yellow solution, which was chromatographed in a short column packed with Florisil and eluted with CH_2Cl_2 (colorless fraction) and EtOH (yellow fraction). From the yellow fraction two crystalline solids were isolated: a light yellow complex in small crystals, identified as 6 (yield 60%), and a pale yellow, well crystallized compound, which, on the basis of the structure determination, corresponds to the composition [Ru(CO)(MeO$_2$CC=CHCO$_2$Me)(HCO$_3$)(PPh_3)$_2$] (yield 1%).

Bis-Insertion Derivatives [Ru(CO)Cl{MeOOCC=C(CO$_2$Me)C(CO$_2$Me)=CHCO$_2$Me}(PR$_3$)]. [Ru(CO)Cl{MeOOCC=C(CO$_2$Me)C(CO$_2$Me)=CHCO$_2$Me}(PPh_3)] (11). The starting complex 1 (0.15 mmol) reacts with MeO$_2$CC≡CCO$_2$Me (0.05 mL, 0.4 mmol) in CH_2Cl_2 (30 mL), and the mixture was heated to reflux for 4 h with formation of a red-orange solution, which was evaporated to dryness, extracted several times with Et_2O, and precipitated with n-pentane from the ethereal solution (yield 0.080 g): IR ν(C≡O) 1926 vs, ν(C=O) 1690 vs, ν(C=O) 1540 m cm^{-1}; ^{1}H NMR δ 3.19, 3.29, 3.81, 3.91 (s, 3 H, Me), 4.51 (s, 1 H, =CH), 7.10–7.50, 7.52–7.80 (m, 15 H, Ph). Anal. Calcd for $C_{31}H_{28}ClO_9PRu$: C, 52.29; H, 3.96. Found: C, 52.40; H, 4.11.

[Ru(CO)Cl{MeOOCC=C(CO$_2$Me)C(CO$_2$Me)=CHCO$_2$Me}{P(p-MeC$_6$H$_4$)$_3$}] (12). The reaction was performed as in the compound 11, but from the starting complex 2: IR ν(C≡O) 1936 vs, ν(C=O) 1710 vs, ν(C=O) 1540 m cm^{-1} ^{1}H NMR δ 2.22 (s, 9 H, Me p-tolyl groups), 3.22, 3.28, 3.81, 3.91 (s, 3 H, Me), 6.9–7.3, 7.3–7.7 (m, 12 H, C_6H_4). Anal. Calcd for $C_{34}H_{34}ClO_9PRu$: C, 54.15; H, 4.54. Found: C, 54.40; H, 4.78.

Anomalous Bis-Insertion Derivatives [Ru{NH=CPhOC=CHPh}(CO)Cl(PR$_3$)$_2$]. [Ru{NH=CPhOC=CHPh}(CO)Cl(PPh_3)$_2$] (13). An excess of PhC≡CH (0.6 mmol) was added to a suspension of the starting complex 1 (0.006 mmol) in 30 mL of EtOH/CH_2Cl_2 (2:1), and the mixture was heated with stirring at 40 °C. After 2 h the red-orange solution was evaporated to dryness and the solid was washed with Et_2O several times (yield 40%) to give a red-orange microcrystalline product: IR ν(NH) 3270 m, ν(C≡O) 1930 vs, ν(C=N) 1575 m cm^{-1}. ^{1}H NMR δ 4.70 (s, 1 H, =CH), 6.84–7.00 (m, 15 H, 3 Ph), 7.15–7.27 (m, 5 H, Ph), 7.34–7.50 (m, 20 H, 4Ph). Anal. Calcd for $C_{52}H_{42}ClNO_2P_2Ru$: C, 68.53; H, 4.64; N, 1.54. Found: C, 68.15; H, 4.50; N, 1.45.

[Ru{NH=CPhOC=CHPh}(CO)Cl{P(p-MeC$_6$H$_4$)$_3$}$_2$] (14). The reaction was performed as in the compound 13, but from the starting complex 2. In this case the complex could be recrystallized from CH_2Cl_2/EtOH (1:1) to give red-orange crystals which were adequate for a X-ray structure determination:[1] IR ν(NH) 3260 m, ν(C≡O) 1924 vs, ν(C=N) 1580 m cm^{-1}. ^{1}H NMR δ 2.18 (s, 18 H, 6 Me), 4.62 (s, 1 H, =CH), 6.70 (d, 2 H, Ph), 6.96 (m, 9 H, 2 C_6H_4 + 1 H, Ph), 7.00 (t, 2 H, Ph), 7.15 (d, 2 H, Ph), 7.19 (t, 1 H, Ph), 7.31 (t, 2 H, Ph), 7.53 (m, 16 H, 4 C_6H_4). Anal. Calcd for $C_{58}H_{54}ClNO_2P_2Ru$: C, 69.98; H, 5.47; N, 1.41. Found: C, 69.85; H, 5.61; N, 1.39.

[Ru(CO)Cl(C≡CR′)(Me_2Hpz)(PPh_3)$_2$] Compounds. [Ru(CO)Cl(C≡CPh)(Me_2Hpz)(PPh_3)$_2$] (15). An excess of PhC≡CH (0.5 mL, 5 mmol) was added to a solution of 6 (100 mg, 0.11 mmol) in EtOH (30 mL), and the mixture was refluxed for 4 h. The intense yellow solution that resulted was concentrated to dryness, and the solid was washed several times with Et_2O, redissolved in CH_2Cl_2, and precipitated with Et_2O, to give a brown-yellow microcrystalline solid (yield 63%): IR ν(NH) 3205 m, ν(C≡C) 2085 m, ν(C≡O) 1960 vs, ν(C=N) 1560 m cm^{-1}; ^{1}H NMR δ 1.57, 1.75 (s, 3 H, Me Me_2Hpz), 5.25 (s, 1 H, CH Me_2Hpz), 6.80–7.35, 7.55–7.90 (m, 35 H, Ph), 11.03 (s, 1 H, NH Me_2Hpz). Anal. Calcd for $C_{50}H_{43}ClOP_2Ru$: C, 67.75; H, 4.89; N, 3.16. Found: C, 67.59; H, 4.77; N, 2.98.

A similar reaction of 7 with phenylacetylene gives rise to formation of 14. However, the reaction of 5 with an excess of Me$_3$CC≡CH in EtOH after 2.5 h yields a mixture of the starting alkenyl complex 5 and an alkynyl complex 16, similar to 15, identified by IR and ^{1}H NMR spectroscopy. The same occurs in the reaction of 3 with pent-1-yne, which give rise to an orange complex, 17.

[Ru(CO)Cl(C≡CCMe$_3$)(Me_2Hpz)(PPh_3)$_2$] (16): IR ν(NH) 3280 m, ν(C≡C) 2120 w, ν(C≡O) 1955 s, ν(C=N) 1570 w cm^{-1}; ^{1}H NMR δ 0.96 (s, 9 H, 3Me), 1.54, 1.66 (s, 3 H, Me Me_2Hpz), 5.45 (s, 1 H, CH Me_2Hpz), 7.78 (m, 30 H, Ph), 10.98 (s, 1 H, NH). The complex is yellow.

[Ru(CO)Cl(C≡CC$_3$H$_7$)(Me_2Hpz)(PPh_3)$_2$] (17): IR ν(NH) 3220 m, ν(C≡C) 2060 w, ν(C≡O) 1945 s, ν(C=N) 1570 w cm^{-1}.

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Registry No. 1, 106583-99-7; 2, 106564-60-7; 3, 115461-99-9; 4, 115462-00-5; 5, 115462-01-6; 6, 115462-02-7; 7, 108296-48-6; 8, 115462-03-8; 9, 115462-04-9; 10, 115462-05-0; 11, 115462-10-7; 12, 115462-11-8; 13, 115462-06-1; 14, 108296-49-7; 15, 115462-07-2; 16, 115462-08-3; 17, 115462-09-4; n-C$_3$H$_7$C≡CH, 627-19-0; Me$_3$CC≡CH, 917-92-0; PhC≡CH, 536-74-3; MeO$_2$CC≡CH, 922-67-8; dimethyl acetylenedicarboxylate, 762-42-5.

Supplementary Material Available: Tables of thermal parameters and atomic coordinates and thermal parameters for hydrogen atoms for 5 and 10 (6 pages); listings of final observed and calculated structure factors for 5 and 10 (59 pages). Ordering information is given on any current masthead page.