Synthesis and Reactivity of Indenyl Ruthenium(II) Complexes Containing the Labile Ligand 1,5-Cyclooctadiene (COD): Catalytic Activity of [Ru(η^5-C_9H_7)Cl(COD)]

Patricia Alvarez,[†] José Gimeno,*[,†] Elena Lastra,[†] Santiago García-Granda,[‡] Juan Francisco Van der Maelen,[‡] and Mauro Bassetti[§]

Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Instituto de Química Universitaria "Enrique Moles" (Unidad Asociada al CSIC), 33006 Oviedo, Spain, Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain, and Centro CNR di Studio sui Meccanismi di Reazione, c/o Dipartimento di Chimica, Universitá "La Sapienza", 00185 Roma, Italy

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The treatment of $[RuCl_2(COD)]_n$ with KC_9H_7 in THF leads to the formation of [Ru(η^5-C_9H_7)Cl(COD)] (**1**) (80% yield) in a one-pot synthesis. Complex **1** is also formed by the reaction of $[RuCl_2(COD)]_n$ with NaC_9H_7 in THF followed by treatment of the intermediate complex [Ru(η^5-C_9H_7)(η^2-η^3-C_8H_{11})] (**2**) with HCl. Substitution of the labile COD ligand by bulky phosphines PR_3 (R = Cy, $^iPr_3$) can be achieved at room temperature in THF to give 16-electron species [Ru(η^5-C_9H_7)Cl(PR_3)], which react with CO (1 atm) to afford complexes [Ru(η^5-C_9H_7)Cl(CO)(PR_3)] (R = Cy (**3a**), ^{i}Pr (**3b**)). Chelate complexes [Ru(η^5-C_9H_7)Cl{(κ^2-*P,N*)-*o*-$Ph_2PC_6H_4C(H)$=N^{t}Bu}] (**4**) and [Ru(η^4-C_9H_7){κ^1-(*P*)-$Ph_2PCH_2C(O)^tBu$}{κ^2-(*P,O*)Ph_2PCH=$C(O)^tBu$}] (**5**) have been similarly prepared by reaction with the bidentate ligands. [Ru(η^5-C_9H_7)Cl(NBD)] (NBD = norbornadiene) (**6**) has been prepared through an exchange reaction of **1** with NBD and characterized by X-ray diffraction. Neutral complexes [Ru(η^5-C_9H_7)X(COD)] (X = FBF_3 (**7**), N_3 (**8**)) were prepared from complex **1** by metathesis reactions of the chloride ligand by $AgBF_4$ and NaN_3 respectively. The treatment of **7** in CH_2Cl_2 with an excess of pyridine and acetonitrile gives cationic complexes [Ru(η^5-C_9H_7)(COD)L][BF_4] in good yield (L = py (**9**), CH_3CN (**10**)). The structure of complex **9** has been determined by X-ray diffraction. Complex **1** catalyzes [2+2] and [4+2] cycloaddition reactions of norbornene and 1,5-cyclooctadiene with alkynes to give exotricyclic [4.2.1.0] coupling products and exotricyclo [4.2.2.0]dec-7-enes, respectively. These processes take place with high efficiency and selectivity. Complex **1** is also active in the catalytic hydration of terminal alkynes to afford ketones in high yield and selectivity.

Introduction

The most genuine role in coordination chemistry of carbocyclic η^4-dienes such as 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD), and tetrafluorobenzobarralene (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene) relies on their ability to act as labile ligands. This reactivity has been widely applied in numerous ligand exchange processes.[1] As the chemistry of organoruthenium(II) derivatives is concerned, the ready accessibility of the complexes $[RuCl_2(COD)]_x$ and $[RuCl_2(NBD)]_x$[2] has allowed them to be used as useful precursors of a wide series of derivatives, which have promoted the development of a chemistry rich both in stoichiometric and catalytic transformations.[3]

The growing interest during the past few years in the synthesis and reactivity of ruthenium(II) complexes has provided a variety of substrates. Among them, a series of stable semisandwich η^5-ring derivatives of the type [Ru(η^5-ring)X(η^4-diene)] (X = halide, H; ring = Cp, Cp*)[4a−e] and the analogous hydridotris(pyrazolyl)borate and hydridotris(3,5-dimethyl)pyrazolyl)borate complexes [RuTp(COD)X][4f] have attracted preferential attention. The lability of these η^4-coordinated ligands, which are able to undergo exchange reactions, is now well known. In general these reactions occur under very mild condi-

[†] Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo.

[‡] Departamento de Química Física y Analítica, Universidad de Oviedo.

[§] Universitá "La Sapienza".

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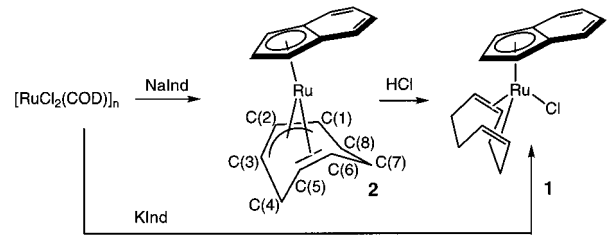
tions especially in Cp and Cp* derivatives.[5a−d] Despite this appealing behavior, which leads to the generation of free coordination sites under mild conditions, there have been only a few reports on the catalytic activity of these complexes, most of them containing COD as the diene ligand.[6] Catalytic transformations include (i) [2+2], [4+2], and [2+2+2] cycloadditions,[7] (ii) coupling reactions of alkynes with allyl alcohols,[8] propargyl alcohols,[9] and carboxylic acids[5c,10] (iii) Alder-ene type reactions,[11] (iv) cycloisomerization of enynes,[12] (v) allylation of thiols,[13] (vi) oligomerization of alkynes,[5c] and (vii) ketone reductions to alcohols via hydrogen transfer and hydrogenation reactions.[14]

It could be anticipated that the analogous semisandwich indenyl derivatives of the type [Ru(η^5-C_9H_7)X(η^4-diene)] should show an increased catalytic activity on the basis of the enhanced reactivity expected for the indenyl derivatives (indenyl effect).[15] However, as far as we know, no reaction catalyzed by these types of derivatives has been reported to date.[16]

We have recently reported that [Ru(η^5-C_9H_7)Cl-(PPh_3)$_2$] shows a dissociative indenyl effect giving rise to rate constants for the exchange of PPh_3 which are 1 order of magnitude greater than for the cyclopentadienyl complex.[17] These results have prompted us to study the reactivity of the known complex [Ru(η^5-C_9H_7)Cl(COD)][18] with the aim of exploring its catalytic activity. Here we report (a) the synthesis of novel neutral indenyl derivatives [Ru(η^5-C_9H_7)Cl(NBD))], [Ru(η^5-C_9H_7)Cl(CO)-(PR_3)] (PR_3 = PCy_3, P^iPr_3), [Ru(η^5-C_9H_7)Cl{κ^2-*(P,N)*-(*o*-$Ph_2P-C_6H_4-CH{=}N^tBu$}], and [Ru(η^5-C_9H_7){κ^1-*(P)*Ph_2-$PCH_2C(O)^tBu$}{κ^2-*(P,O)*-$Ph_2PCH{=}C(O)^tBu$}], which have been obtained via exchange reactions of COD in [Ru-(η^5-C_9H_7)Cl(COD)] under mild reaction conditions; (b) chloride metathesis reactions of [Ru(η^5-C_9H_7)Cl(COD)] with anionic and neutral ligands leading to the formation of either neutral [Ru(η^5-C_9H_7)(FBF_3)(COD)], [Ru-(η^5-C_9H_7)(N_3)(COD)] or cationic [Ru(η^5-C_9H_7)(COD)(py)]-[BF_4], [Ru(η^5-C_9H_7)(COD)(NCMe)][BF_4] complexes; (c) the first studies on the catalytic activity of the complex [Ru(η^5-C_9H_7)Cl(COD)] in C−C coupling reactions and the hydration of alkynes. An improved one-pot synthetic approach of the complex [Ru(η^5-C_9H_7)Cl(COD)] is also reported.

Scheme 1



Results and Discussion

Synthesis of [Ru(η^5-C_9H_7)Cl(COD)] (1). Although the starting material [Ru(η^5-C_9H_7)Cl(COD)] (**1**) has been previously prepared (40% yield),[18] we have used a modified synthetic approach which allows a one-pot synthesis of **1** (80% yield) by the reaction of [$RuCl_2$-(COD)]$_n$ with KC_9H_7 in THF at room temperature (Scheme 1). ^{1}H NMR data are in accordance with those published.[18] Unreported ^{13}C{^{1}H} spectral and mass data (FAB) are collected in the Experimental Section. However, the reaction of [$RuCl_2$(COD)]$_n$ with NaC_9H_7 in THF proceeds in a different way, leading instead to the formation of [Ru(η^5-C_9H_7)(η^2-η^3-C_8H_{11})] (**2**) (90% yield). Complex **2** is isolated as an air-sensitive dark orange oil by evaporation of the reaction mixture to dryness followed by extraction of the solid residue with CH_2Cl_2 and subsequent purification by column chromatography (Scheme 1).

Elemental analysis as well as NMR and mass spectrometry data support this formulation in which the original COD ligand has undergone a deprotonation (see Experimental Section for details). ^{1}H and ^{13}C{^{1}H} NMR spectra including DEPT experiments are consistent with a η^2-η^3 coordination mode of C_8H_{11}. Significantly, the ^{1}H NMR spectrum shows signals in the range δ 1.03−2.58 ppm assigned to the six unequivalent CH_2 protons, olefinic CH signals at δ 4.28 and 4.80, and allylic resonances at δ 1.89, 3.22, and 3.88 ppm. Furthermore,

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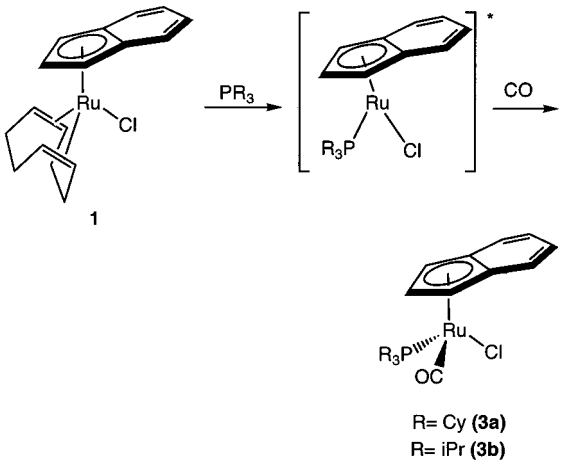
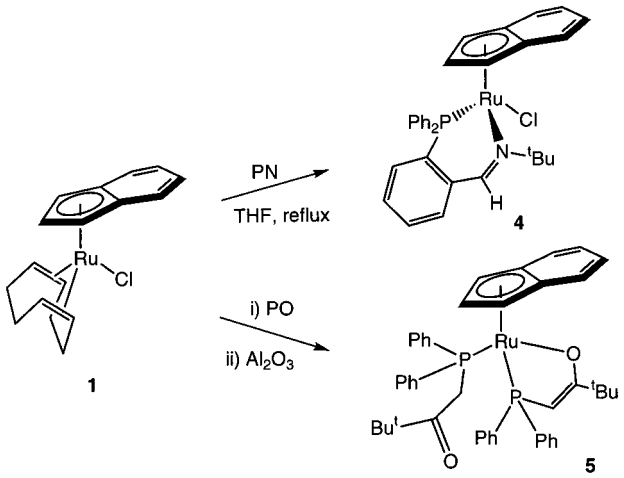
Scheme 2



Scheme 3



the $^1H-^1H$ COSY spectrum of complex **2** shows an interaction between the carbons C(6) and C(8). These data are consistent with the formation of the unsaturated η^2-η^3-cyclooctadienyl carbocycle. A similar η^2-η^3-coordination of the C_8H_{11} ring has been described in the complex [Ru(MeCN)((*R*)-BINAP)(η^2-η^3-C_8H_{11})][BF_4].[19a,b]

The chemical characterization of complex **2** is confirmed by its protonation. As expected, the addition to a solution of **2** in CH_2Cl_2 of 1.5 equiv of HCl (33% in water) leads to the formation of complex **1** (75%) in quantitative yield (Scheme 1).

Substitution Reactions in [Ru(η^5-C_9H_7)Cl(COD)] (1). (a) Exchange of COD. The lability of COD in complex **1** has been assessed in a series of substitution reactions including monodentate and bidentate ligands. Thus, the exchange of COD in complex **1** by PPh_3, $PMePh_2$, PMe_2Ph, and dppm proceeds instantaneously in refluxing THF to give quantitatively the known phosphine derivatives [Ru(η^5-C_9H_7)ClL_2].[17] It is noteworthy that the analogous exchange reaction of the two PPh_3 in the complex [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] by $PMePh_2$, PMe_2Ph, or dppm proceeds under refluxing toluene in preparative conditions. Significantly, the substitution of COD by the bulky phosphines PCy_3 and P^iPr_3 in complex **1** takes place at room temperature, leading to an instantaneous change of color from orange to purple. The reaction is monitored by $^{31}P\{^1H\}$ NMR, showing one single resonance at δ 45.7 (PCy_3) and 53.0 ppm (P^iPr_3). However, all attempts to isolate the phosphine complex have failed. The partial evaporation of the resulting THF solution followed by the addition of hydrocarbon solvents or the slow crystallization led to decomposition products. In contrast, the carbonyl complexes [Ru(η^5-C_9H_7)Cl(CO)(PR_3)] (R = Cy(**3a**); ^{i}Pr(**3b**)) are formed after bubbling CO (1 atm) through the original THF solution (Scheme 2). This seems to indicate that intermediate 16-electron complexes [Ru(η^5-C_9H_7)Cl(PR_3)] are generated which, although they could not be isolated,[20] readily react with CO to give the stable 18-electron species. Complexes **3a**,**b** have been isolated as air stable orange solids (75% and 80% yield, respectively) and characterized by analysis and spectroscopic methods. IR spectra (CH_2Cl_2) show the expected ν(CO) strong absorptions at 1935.5 (**3a**) and 1936.6 (**3b**) cm^{-1}. Proton, carbon, and phosphorus resonances in the NMR spectra are in accordance with this formulation (see the Experimental Section for details). In particular $^{31}P\{^1H\}$ NMR spectra exhibit one singlet resonance at δ 56.75 (**3a**) and 65.54 ppm (**3b**), the latter one appearing at a similar value shown by the analogous complex [Ru(C_5H_5)Cl(CO)(P^iPr_3)][21] (δ 66.4 ppm).

Reaction of complex **1** with 1 equiv of the iminophosphine *o*-$Ph_2PC_6H_4C(H)=N^tBu$[22] in THF yields the chelate complex [Ru(η^5-C_9H_7)(Cl){κ^2-*(P,N)*-*o*-$Ph_2PC_6H_4C(H)=N^tBu$}] (**4**) (80% yield). Elemental analysis along with IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data are in accordance with the presence of the iminophosphine group as a chelating ligand (see Experimental Section) (Scheme 3). It is noteworthy that complex **4** remains unchanged in the presence of an excess of the iminophosphine. The reluctance to incorporate one further ligand seems to indicate the strong chelate effect of the ligand and/or the steric hindrance arising from the two relatively close bulky ligands.

This behavior contrasts with that found in the reaction of complex **1** with the ketophosphine $Ph_2PCH_2C(O)^tBu$.[23a] Monitoring the reaction by $^{31}P\{^1H\}$ NMR, a mixture of substituted species (ca. 60/40%) is formed, namely, [Ru(η^5-C_9H_7)Cl{κ^1-*(P)*-$Ph_2PCH_2(CO)^tBu$}$_2$] (δ 51.0 and 49.0; $^2J_{PP}$ = 27.5) and [Ru(η^5-C_9H_7){κ^1-*(P)*-$Ph_2PCH_2C(O)^tBu$}{κ^2-*(P,O)*-$Ph_2PCH_2C(O)^tBu$}][Cl] (broad signals at δ 29.6 and 73.4). After working up the reaction mixture followed by a column chromatography (Al_2O_3), the neutral complex [Ru(η^5-C_9H_7){κ^1-*(P)*-$Ph_2PCH_2C(O)^tBu$}{κ^2-*(P,O)*-$Ph_2PCH=C(O)^tBu$}] (**5**) is isolated (80% yield) as an air stable solid (Scheme 3).

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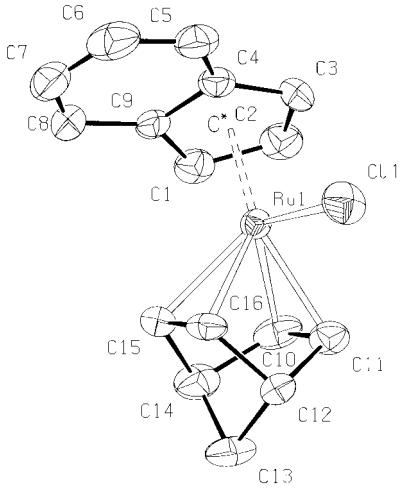


Figure 1. Structure of [Ru(η^5-C_9H_7)Cl(NBD)]. Selected bond distances (Å) are as follows: Ru−C*, 1.915 (4); Ru−C(15), 2.189(4); Ru−C(16), 2.172(4); Ru−C(11), 2.156(4); Ru−C(10), 2.164(4); Ru−Cl, 2.442(1). Selected bond angles (deg) are as follows: C*−Ru−C(10), 116.26(17); C*−Ru−C(15), 117.54(17); C*−Ru−C(11), 144.25(17); C*−Ru−C(16), 145.59(17); Cl−Ru−C*, 113.30(13). △ = 0.141(4); FA = 5.29(33); HA = 6.99(35). [a]△ = *d*(Ru−C(4),C(9)) − *d*(Ru−C(1),C(3)). [b]FA (fold angle) = angle between normals to least-squares planes defined by C(1), C(2), C(3) and C(4), C(5), C(6), C(7), C(8), C(9). [c]HA (hinge angle) = angle between normals to least-squares planes defined by C(1), C(2), C(3) and C(1), C(3), C(4), C(9). C* = centroid of C(1), C(2), C(3), C(4), C(9).

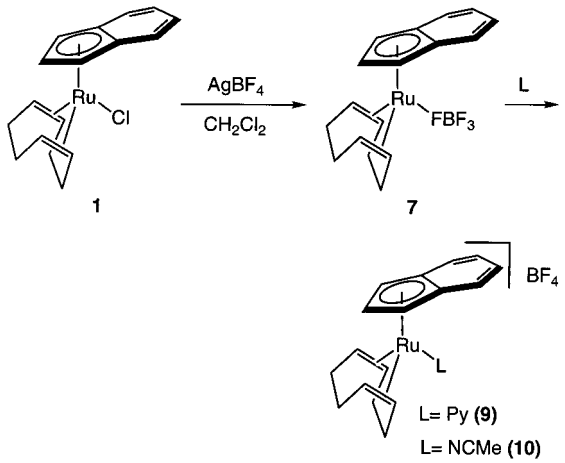
Complex **5** was characterized by elemental analyses and spectroscopic techniques. Thus, its IR spectrum shows two absorptions at 1701 ($\nu_{C=O}$) and 1495 ($\nu_{C=C-O}$) cm^{-1} as expected for the presence of the ketone and the enolate functionalities. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR are also in accordance with this formulation. In particular, its $^{31}P\{^1H\}$ NMR spectrum shows two doublet resonances at δ 69.9 and 41.4 ppm (d, J_{PP} = 36.9 Hz) assigned to the κ^2 (*P,O*) enolate phosphorus atom and the (κ-*P*) ketophosphine, respectively.[23]

The chelating enolate κ^2-*(P,O)*-$Ph_2PCH{=}C(O)^tBu$ complex **5** results from the deprotonation of one of the acid CH_2 protons in either κ^2-*(P,O)* and/or κ^1-(*P*) ketophosphine ligands, which takes place under the chromatography conditions. This type of transformation has been described previously as one that proceeds readily in the presence of a base.[23]

Complex **1** also undergoes a rapid exchange of COD by norbornadiene (NBD) in refluxing THF to give the analogous complex [Ru(η^5-C_9H_7)Cl(NBD)] (**6**).[24] Elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are in agreement with the proposed formulation (see Experimental Section). In addition, the structure of complex **6** has been confirmed by an X-ray diffraction study. An ORTEP-type view of the molecule is depicted in Figure 1, and selected bond distances and angles are listed in the caption.

The structure shows an approximately octahedral geometry at ruthenium. Although the indenyl group is bound to ruthenium in a typical η^5 fashion, there is a slight distortion of the five-carbon ring from planarity with a hinge angle (HA) of 7.0(3)° and a fold angle (FA) of 5.3(3)°. The characteristic slippage of the indenyl ring is also observed with a slip-fold (Δ) value of 0.141(4) Å. All of these values can be compared with those previously reported by us.[25] Norbornadiene is η^4-bonded to the ruthenium atom with an average Ru−C distance of 2.170(4) Å, which is typical for a π-olefin ruthenium bond and is in the range shown by the analogous complexes [Ru(η^5-C_5Me_5)(NBD)(H_2O)][BF_4] (2.201(8) Å)[26a] and [$RuCl_2$(NBD)(PPh_3)$_2$] (2.205 Å).[26b]

Scheme 4



(b) Synthesis of [Ru(η^5-C_9H_7)X(COD)] (X = FBF_3, N_3) Complexes. Chloride metathesis reactions have been carried out. Thus, [Ru(η^5-C_9H_7)(FBF_3)(COD)] (**7**) has been prepared by reacting **1** with $AgBF_4$ (1 equiv) in CH_2Cl_2 (Scheme 4). This complex is isolated (70% yield) as an air and water sensitive solid by evaporating to dryness the filtered reaction solution and has been characterized by elemental analysis and spectroscopic techniques (see Experimental Section). Mass spectrometry (FAB) shows the cation [M^+] (411) and fragmentations [$M^+ - F$] (392), [$M^+ - F_2$] (373), indicating the coordination of the BF_4^- fragment to the metal center. Moreover, conductivity measurements in CH_2Cl_2 show that complex **7** behaves as a nonelectrolite. The $^{19}F\{^1H\}$ NMR spectrum at room temperature shows signals that are consistent with the presence of an equilibrium between the coordinated and free BF_4^- anion in accordance with other reported data.[27]

Similarly, the treatment of complex **1** in THF/MeOH (10:1) with NaN_3 affords [Ru(η^5-C_9H_7)(N_3)(COD)] (85% yield) (**8**) as an air stable solid. Complex **8** has been characterized by elemental analyses, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and IR spectroscopy. In particular, the IR spectrum (Nujol) of **8** shows the expected ν_{N3} absorption at 2029 cm^{-1}. The rest of the data reveals the presence of the ligands but providing that there are no relevant features will not be further commented on (see Experimental Section for details).

(24) When an excess of NBD is used, a ring-opening metathesis polymerization of NBD takes place even at room temperature, indicating complex **1** is a ROMP catalyst. Unpublished results.

(25) The slight distortion toward an η^3 binding mode in the solid state of complex **6** appears to be maintained in solution, according to the value of $\Delta\delta$(C-3a, 7a) = −19.8(6) ppm obtained from the $^{13}C\{^1H\}$ NMR spectrum (see Experimental Section). (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 3178. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137.

(26) (a) Suzuki, H.; Kakigano, T.; Fukui, H.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1994**, *473*, 295. (b) Bergbreiter, D. E.; Bursten, B. E.; Cotton, F. A. *J. Organomet. Chem.* **1981**, *205*, 407.

(27) Beck, W.; Sünkel, K. *Chem. Rev.* **1998**, *88*, 1405.

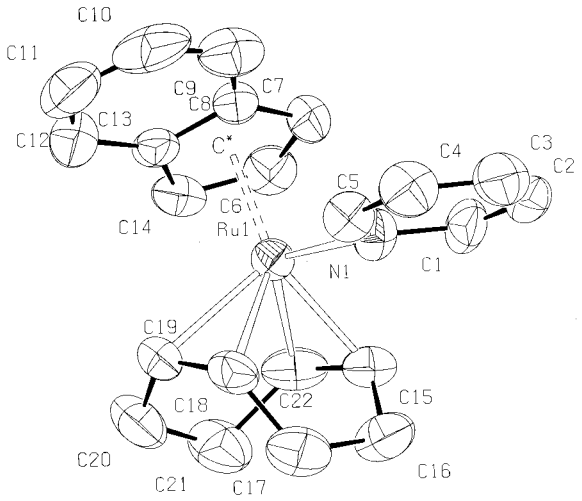


Figure 2. Structure of the cation of [Ru(η^5-C_9H_7)(py)(COD)]. Selected bond distances (Å) are as follows: Ru−C*, 1.913(11); Ru−C(15), 2.185(11); Ru−C(22), 2.206(11); Ru−C(18), 2.238(10); Ru−C(19), 2.240(11); Ru−N, 2.197(8); C(22)−C(15), 1.396(16); C(15)−C(16), 1.496(15); C(16)−C(17), 1.544(17); C(17)−C(18), 1.490(16); C(18)−C(19), 1.387(15); C(19)−C(20), 1.530(17); C(20)−C(21), 1.483(18); C(21)−C(22), 1.554(17). Selected bond angles (deg) are as follows: C*−Ru−C(22), 113.28(45); C*−Ru−C(19), 114.37(46); C*−Ru−C(18), 143.12(43); C*−Ru−C(15), 135.13(44); N−Ru−C*, 111.49(43); N−Ru−C(19), 115.1(4); N−Ru−C(18), 80.8(4); N−Ru−C(15), 83.6(4); N−Ru−C(22), 120.6(4). △ = 0.156(11); FA = 8.2(8); HA = 7.1(9). [a] △ = *d*(Ru−C(13),C(8)) − *d*(Ru−C(14),C(7)). [b] FA (fold angle) = angle between normals to least-squares planes defined by C(14), C(6), C(7) and C(8), C(9), C(10), C(11), C(12), C(13). [c] HA (hinge angle) = angle between normals to least-squares planes defined by C(14), C(6), C(7) and C(14), C(7), C(8), C(13). C* = centroid of C(14), C(6), C(7), C(8), C(13).

(c) Synthesis of Cationic Complexes [Ru(η^5-C_9H_7)(COD)L][BF_4] (L = py, NCMe). Treatment of complex **1** in CH_2Cl_2 with $AgBF_4$ followed by the addition of an excess of L (L = py, MeCN) to the filtered solution containing complex **7** yields [Ru(η^5-C_9H_7)(COD)(py)][BF_4] (**9**) and [Ru(η^5-C_9H_7)(COD)(MeCN)][BF_4] (**10**) in good yield (Scheme 4). The cationic complexes **9** and **10** are isolated as air stable tetrafluoroborate salts. The IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopic properties are in agreement with the presence of the ligands and are not further discussed here (details are given in the Experimental Section). The analytical and mass spectrometry data of **9** and **10** support the proposed formulation. In addition the structure of **9** has been confirmed by X-ray crystallography, and an ORTEP-type view of the structure of the cationic complex is shown in Figure 2. Selected bond distances and angles are given in the caption. [Ru(η^5-C_9H_7)(COD)(py)]$^+$ cations and [BF_4]$^-$ anions, separated by normal contacts, are present in the crystals. The cation shows a pseudoctahedral geometry around the ruthenium atom which is bonded to the indenyl group acting as an η^5 ligand, the two double bonds of COD, and the nitrogen atom of pyridine. As for the related NBD complex **7** the indenyl group shows a slight distortion of the five-carbon ring from planarity (see caption of Figure 2 for HA, FA, and Δ values).[28]

(28) The slight distortion toward an η^3 binding mode in the solid state of complex **9** appears to be maintained in solution, according to the value of $\Delta\delta$(C-3a, 7a) = −22.3(6) ppm.

Scheme 5

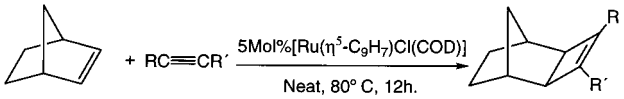


Table 1. Product Analysis of the [2+2] Cycloaddition Reaction of Norbornene with Alkynes, Catalyzed by [Ru(η^5-C_9H_7)Cl(COD)]

entry	alkyne	% conversion	% selectivity	% yield[a]
1	$MeO_2CC{\equiv}CCO_2Me$	100	99	99[b] (98)[c]
2	$HOH_2CC{\equiv}CCH_2OH$	90	77	63[b]
3	MeC≡CPh	95	97	93[b] (91)[c]
4	PhC≡CPh	95	97	92[b]
5	$HC{\equiv}C(CH_2)_5Me$	80	40	32[b]
6	$HC{\equiv}CCH_2OH$	90	16	15[b]

[a] Yield based on the alkyne. [b] GC data. [c] Yield of the isolated product obtained after complete transformation of the alkyne under preparative reaction conditions (see Experimental Section).

The COD ligand adopts a twist-boat or tub conformation showing an average Ru−C distance of 2.217(11) Å, both features being similar to those found in other ruthenium complexes.[5c,26a] The Ru−N distance is 2.197(8) Å.[29] It is interesting to note that C_9H_7 appears to be related more closely to C_5Me_5 and tris(pyrazolyl)borate than to C_5H_5 in the series of the related complexes [Ru(η^5-C_9H_7)X(COD)], [Ru(η^5-C_5Me_5)X(COD)], and [Ru(Tp)X(COD)] (Tp = $HB(pz)_3$), which afford similar cationic acetonitrile complexes in contrast to [Ru(η^5-C_5H_5)Cl(COD)].[5c,26a,30]

Catalytic Activity of [Ru(η^5-C_9H_7)Cl(COD)]. (a) [2+2] Cycloadditions of Norbornene with Alkynes. Internal alkynes are converted selectively into exo-tricyclic [4.2.1.0] coupling products (Scheme 5 and Table 1) essentially in quantitative yields under both analytical and preparative conditions (entries 1 and 3). On the other hand, cycloadditions of 1-heptyne and propargyl alcohol (entries 5 and 6) proceed with lower yield and selectivity. In fact, among other uncharacterized byproducts, the major components of the reaction mixture are the products of trimerization of the alkyne, which account for reduced selectivity of cycloaddition. Therefore, the presence of the terminal alkyne functionality drives the reaction toward trimerization, while the [2+2] cycloaddition process of internal alkynes appears insensitive to the nature of the substituents. As previously reported,[7a,f] in the case of [Ru(η^5-C_5Me_5)Cl(COD)] as precatalyst, the reaction of alkynes with norbornadiene does not proceed properly, most likely due to a chelation effect of this substrate hindering the catalysis.[31]

(b) [4+2] Cycloadditions of 1,5-Cyclooctadiene with Alkynes. The catalytic cycloadditions of 1,5-cycloctadiene with alkynes in the presence of [Ru(η^5-C_9H_7)Cl(COD)] (5 mol %) were also examined. The reactions led chemioselectively to the cycloaddition products exo-tricyclo [4.2.2.0]dec-7-enes (Scheme 6; Table 2). The presence of the sp^2-carbon substituents,

(29) This value compares well with other related pyridine ruthenium(II) complexes. (a) Stavrev, K.; Zerner, M. C. *J. Am. Chem. Soc.* **1995**, *117*, 8684 ([Ru($(NH_3)_5$(py)]$^{2+}$, 2.156 Å). (b) Faller, J. W.; Grimmond, B. J.; Curtis, M. *Organometallics* **2000**, *19*, 5174 ([Ru(*p*-$CH_3C_6H_4CH(CH_3)_2$)(κ^2-(P,P)-Ph_2PCH−(Me)Ph_2P(O)py][SbF_6]$_2$, 2.218(3) Å).

(30) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1164.

(31) [2+2] Cycloaddition of norbornadiene with diphenylacetylene using 5 mol % of [Ru(η^5-C_9H_7)Cl(COD)] as catalyst affords a 60% yield of the cycloadduct in 12 h.

Scheme 6

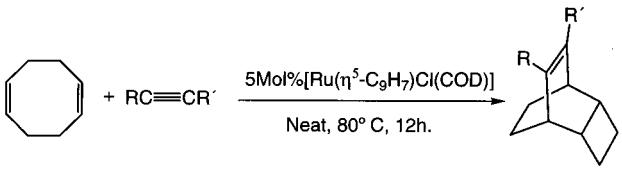


Table 2. Product Analysis of the [4+2] Cycloaddition Reaction of 1,5-Cyclooctadiene with Alkynes, Catalyzed by [Ru(η^5-C_9H_7)Cl(COD)]

entry	alkyne	% conversion	% selectivity	% yield[a]
1	$MeO_2CC{\equiv}CCO_2Me$	5	100	5[b]
2	$HOH_2CC{\equiv}CCH_2OH$	75	100	75[b]
3	$MeC{\equiv}CPh$	85	100	85[b] (95)[c]
4	$PhC{\equiv}CPh$	70	30	21[b]
5	$HC{\equiv}C(CH_2)_5Me$	95	100	95[b]
6	$HC{\equiv}CPh$	90	80	72[b]
7	$HC{\equiv}CCH_2OH$	50	60	30[b]

[a] Yield based on the alkyne. [b] GC data. [c] Isolated product obtained after complete transformation of the alkyne (20 h) under preparative reaction conditions (see Experimental Section).

carbomethoxy or phenyl, in the alkyne structure lowers the yield of the expected products (entries 1 and 4), as it was observed when using [Ru(η^5-C_5H_5)Cl(COD)] as catalyst.[7b] The data indicate stronger dependence of the [4+4] cycloaddition process on the steric and electronic properties of the alkyne than the corresponding [4+2] reactions. In both [2+2] and [4+2] cycloaddition reactions, the propargyl alcohol is a poor substrate.

(c) Water Addition to Alkynes. In the presence of complex **1** (5 mol %) aliphatic terminal alkynes and phenylacetylene (Table 3, entries 1−5) undergo addition of water, affording ketones (Scheme 7) in high yield and selectivity (Figure 3). No significant transformations were observed after 15 h of reaction. The presence of a hydroxy group in the α position of the alkyne (entry 6) does not seem to affect the efficiency of the reaction. When the temperature is increased by 10 °C, a small decrease of selectivity (97 to 94%) is observed in the reaction of 1-octyne. The formation of ketones via metal-catalyzed hydration of alkynes is a well-known process,[32] which occurs selectively due to the preferred addition of water in a Markovnikov fashion to the activated triple bond.[32b] While ruthenium(II) catalyst precursors have provided selective access to enol esters, dienes, ketoesters, and furans through electrophilic activation of terminal alkynes,[33] the hydration reaction has been reported only recently in the case of the complex [Ru(η^6-C_6Me_6)Cl_2{$Ph_2P(C_2H_3)$}] to form ketones with moderate yields and selectivities,[34] and in the case of [$RuCl_2$(η^6-C_6H_6)(PR_3)] (PR_3 = $PPh_2(C_6F_5)$, P{3-(C_6H_4-$SO_3Na)_3$}) to form ketones, or preferably aldehydes, in the presence of phosphine additives.[35] The addition of water to the triple bond has also been postulated in the reactions of terminal alkynes, water, and alkyl vinyl ketones to give 1,5-diketones, in the presence of a catalytic system involving the complex [Ru(η^5-C_5H_5)Cl(COD)].[36] It is known that the formation of carbon−heteroatom bonds from alkynes is catalyzed by electrophilic ruthenium centers,[32] whereas carbon−carbon bonds are formed with electron-rich metal centers, or in the presence of phosphine ligands which favor η^1-vinylidene species with respect to metal-η^2-alkyne complexes.[37,38] Since the lability of the COD ligand promotes the formation of an electrophilic ruthenium species, it is likely that nuclephilic attack of water in this hydration process occurs at a ruthenium-η^2-alkyne intermediate, formed by substitution/thermal release of COD from the complex [Ru(η^5-C_9H_7)Cl(COD)].

Conclusions

In this work the reactivity and catalytic applications of the complex [Ru(η^5-C_9H_7)Cl(COD)] (**1**) (COD = 1,5-cyclooctadiene) have been studied. It is shown that the labile COD ligand can be substituted under mild conditions. On the basis of this lability novel mixed carbonyl-phosphine complexes [Ru(η^5-C_9H_7)Cl(CO)(PR_3)] (R = Cy (**3a**), ^{i}Pr (**3b**)), bis-substituted complexes containing hemilabile ligands [Ru(η^5-C_9H_7)(Cl){κ^2-*(P,N)*-*o*-$Ph_2PC_6H_4C(H){=}N^tBu$}] (**4**) and [Ru(η^4-C_9H_7){κ^1-*(P)*-$Ph_2PCH_2C(O)^tBu$}{κ^2-*(P,O)*-$Ph_2PCH{=}C(O)^tBu$}] (**5**), and the analogous diene complex [Ru(η^5-C_9H_7)Cl(NBD)] (**6**) have been prepared via exchange processes in THF as solvent either at room or refluxing temperature. This lability contrasts with that found for the analogous complex [Ru{$HB(pz)_3$}(COD)Cl], in which the COD ligand can be substituted only by treating the reaction mixture above 100 °C.[5c] The lability of COD in complex **1** appears to be between that of [Ru(η^5-C_5Me_5)Cl(COD)] and [Ru($HB(pz)_3$)(COD)Cl].[4a,e,f]

The lability of COD in complex **1** has proved to be appropriate for the generation of 16 deficient electron species [Ru(η^5-C_9H_7)Cl(PR_3)]. Nevertheless these species appear to be unstable in the solid state in contrast to the analogous complex [Ru(η^5-C_5Me_5)Cl(P^iPr_3)], which has been isolated as a stable solid.[20] It is apparent that the C_5Me_5 ring proves to be a more electron releasing group than C_9H_7, therefore allowing the electronic deficiency in the metal atom to be compensated. Complex **1** is also a good precursor of novel COD derivatives which are obtained by the reaction with anionic and neutral ligands in the presence of a chloride abstractor to give complexes [Ru(η^5-C_9H_7)(FBF_3)(COD)] (**7**), [Ru(η^5-C_9H_7)(N_3)(COD)] **(8)**, [Ru(η^5-C_9H_7)(COD)(py)][BF_4] (**9**), and [Ru(η^5-C_9H_7)(COD)(NCMe)][BF_4] (**10**).

Complex **1** is an efficient catalyst in [2+2] and [4+2] cycloadditions of norbonene and 1,5-cyclooctadiene, respectively, and alkynes, with yields and selectivity in some cases higher than in the reactions catalyzed by

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(34) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *23*, 4740.
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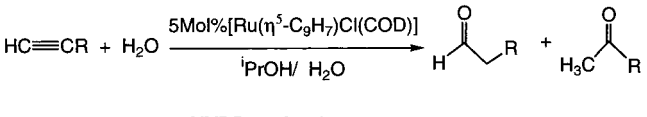
(37) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **1999**, *18*, 2821. (b) Bullock, R. M. J. *J. Chem. Soc., Chem. Commun.* **1986**, 165.
(38) Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 2483.

Table 3. Product Analysis of the Hydration Reaction of Alkynes to Ketones, Catalyzed by [Ru(η^5-C_9H_7)Cl(COD)]

entry	alkyne	*T* (°C)	*t* (h)	% ketone[a]	% aldehyde[a]	% selectivity
1	$CH_3(CH_2)_5C{\equiv}CH$	100	12	58	4	92
2	$CH_3(CH_2)_5C{\equiv}CH$	100	24	75	4	94
3	$CH_3(CH_2)_5C{\equiv}CH$	90	30	77	2	97
4	$PhC{\equiv}CH$	100	48	98	1	98
5	$CH_3(CH_2)_4C{\equiv}CH$	100	48	89	4	95
6	$(C_6H_{10})(OH)C{\equiv}CH$	90	24	93	2	97

[a] GC Data.

Scheme 7



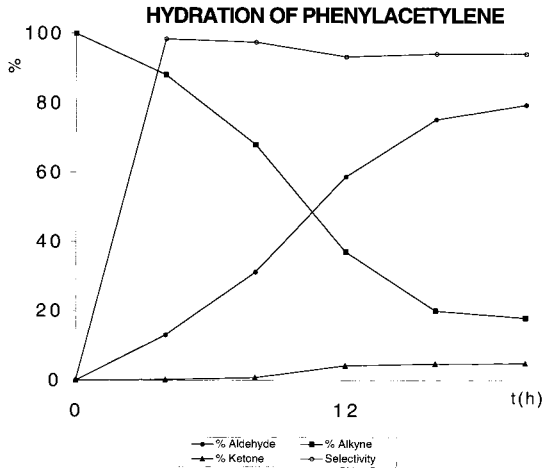


Figure 3. Hydration of phenylacetylene. GC data.

the analogous cyclopentadienyl and pentamethylcyclopentadienyl complexes.[7a,b] The formation of ketones via catalytic hydration of alkynes has been a synthetic approach of interest since the use of water as reagent and solvent is an important factor on the basis of economic safety and environment protection.[39] The use of complex [Ru(η^5-C_9Me_7)Cl(COD)] as catalyst not only offers an efficient and selective method to hydrate terminal alkynes but also is the first Ru(II) catalyst active in the hydration of α-hydroxy alkynes to form ketones.

Experimental Section

General Comments. All manipulations involving organoruthenium complexes were performed under an inert atmosphere of nitrogen, using standard Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. $[RuCl_2(COD)]_n$,[2] *o*-$Ph_2PC_6H_4C(H){=}N^tBu$,[22] and $Ph_2PCH_2C(O)^tBu$[23a] were prepared according to the literature procedure. All other chemicals were obtained from Aldrich Chemical Co. and used without further purification.

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. High-resolution mass spectra were recorded using a MAT-95 spectrometer. NMR spectra were recorded on a Bruker AC300 instrument, a AC200 instrument, or a 300 DPX instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), 188.3 MHz (^{19}F), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds.

Gas chromatography analyses were recorded on a HP 6890 GC (HP fused silica capillary column HP-INNOWAX cross-linked poly(ethylene glycol) 30 m × 0.25 mm). GC−MS analyses were obtained on a HP5890 GC (OV1 capillary column 12 m × 0.2 mm) coupled with a HP5970 MSD.

Synthesis of [Ru (η^5-C_9H_7)Cl(COD)] (1): Method A. A freshly prepared solution of KInd (1.5 mol) was added at room temperature to a solution of $[RuCl_2(COD)]_n$ (0.32 g, 1 mol) in THF (30 mL). The mixture was then stirred for 1 h and, after that, evaporated to dryness. The resulting solid residue was extracted with CH_2Cl_2 (20 mL) and filtered. The solution was evaporated to dryness and washed with hexane (2 × 20 mL). The volatiles were removed under vacuum to give **1** as an orange solid (0.338 g, 80% yield). ^{1}H NMR (δ, $CDCl_3$): 1.79 (m, 2H, CH_2), 1.96 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 3.75 (m, 2H, CH), 4.16 (m, 2H,CH), 5.25 (d, 2H, J_{HH} = 2.7 Hz, H-1,3), 5.47 (t, 1H, J_{HH} = 2.7 Hz, H-2), 6.90−7.45 (m, 4H, H-4,7 and H-5,6). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 28.1 (s, CH_2), 32.3 (s, CH_2), 77.6 (s, CH), 79.1 (s, CH), 94.9 (s, C-1,3), 83.6 (s, C-2), 111.1 (s, C-3a,7a), 124.0 and 129.0(s, C-4,7 and C-5,6). Anal. Calcd for $RuC_{17}H_{19}Cl$: (359.8): C, 56.7; H, 5.3. Found: C, 56.3; H 5.0. MS(FAB$^+$): *m/e* 360 (M^+), 323 (M^+ − HCl).

Method B. HCl (33% aqueous, 0.5 mL) was added to a solution of [Ru(η^5-C_9H_7)(C_8H_{11})] (**2**) (0.32 g, 1 mol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 10 min. Then, water (10 mL) was added and the organic phase was separated and dried with magnesium sulfate. Solvents were then removed, affording an orange solid (**1**) with 75% yield, which was washed with hexane (2 × 20 mL) and vacuum-dried.

Synthesis of [Ru(η^5-C_9H_7)(C_8H_{11})] (2). To a solution of $[RuCl_2(COD)]_n$ (0.32 g, 1 mol) in THF (30 mL) was added a freshly prepared solution of NaInd (0.19 g, 1.5 mol) at room temperature. The mixture was stirred for 4 h and then filtered. The solution was evaporated to dryness, and the resulting solid residue was extracted with CH_2Cl_2 (2 × 20 mL) and filtered. The solution was evaporated to dryness, resulting in a dark orange oil, which was purified using a silica column, recovering the orange fraction eluted with hexane. Evaporation affords **2** as a dark orange oil. Yield: 0.75 g, (90%). ^{1}H NMR (δ, $CDCl_3$): 1.03 (m, 1H, CH_2), 1.67 (m, 1H, CH_2), 1.89 (m, 1H, CH_2), 2.14 (m, 3H, CH-CH_2), 2.58 (m, 1H, CH_2), 2.91(m, 1H, CH), 3.22 (vt, 1H, J_{HH} = 6.8 Hz, CH), 3.88 (m, 1H, CH), 4.28 (m, 1H, CH), 4.80 (s, 1H, H-1), 5.28 (m, 1H, C-3), 5.33 (s, 1H, C-2), 6.90−7.31 (m, 4H, H-4,7 and H-5,6). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 10.4 (s, CH), 22.1 (s, CH_2), 24.1 (s, CH), 30.1 (s, CH_2), 36.5 (s, CH_2), 62.9 (s, CH), 68.6 (s, CH), 70.1 (s, C-1), 72.4 (s, C-3), 73.6 (s, CH), 84.8 (s, C-2), 102.0, 102.9 (both s, C-3a,7a), 122.7, 122.9, 123.5, and 124.0 (all s, C-4,5,6,7). MS(FAB$^+$): *m/e* 323 (M^+).

Synthesis of [Ru (η^5-C_9H_7)Cl(CO)(PR_3)] (R = Cy (3a), ^{i}Pr (3b)). To a solution of **1** (0.35 g, 1 mol) in THF (20 mL) was added the corresponding phosphine (1.2 mol) at room temperature. The solution was then monitored by ^{31}P NMR until a band at 53.7 ppm for **3a** and 45.7 ppm for **3b** appeared. Solvents were then reduced and CO was bubbled through the solution at room temperature for 5 min, yielding orange solids. Solvents were removed, and the solid was washed with hexane

(39) Tokunaga, M.; Larrow, J. F.; Kakivchi, F.; Jacovsen, E. N. *Science* **1997**, *277*, 936.

(2 × 20 mL) and vacuum-dried. **3a**: yield: 0.41 g (75%). IR (Nujol): ν 1935.5 cm^{-1} (CO). $^{31}P\{^1H\}$ (δ, $CDCl_3$): 56.75 (s). ^1H NMR (δ, $CDCl_3$): 1.07−2.10 (m, 33H, Cy), 5.06, 5.42, 5.54 (s, 1H, H-1,2,3), 7.29−7.44 (m, 4H, H-4,7 and H-5,6). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 26.8 (m, Cy), 27.4 (m, Cy), 29.4 (m, Cy), 30.5 (m, Cy), 35.8 (m, Cy), 64.1 (s, C1), 71.6 (s, C2), 90.4 (s, C3), 112.4, 116.0 (s, C3a,7a), 122.4, 124.6, 127.3 and 128.1 (all s, C-4,5,6,7), 205.3 (d, J_{PC} = 20.7 Hz, CO). Anal. Calcd for $RuC_{28}H_{40}ClOP$ (560.12): C, 60.0; H, 7.2. Found: C, 59.7; H, 6.9. **3b**: Yield: 0.34 g, 80%. IR (Nujol): ν 1936.6 cm^{-1} (CO). $^{31}P\{^1H\}$ (δ, $CDCl_3$): 65.54 (s). ^1H NMR (δ, $CDCl_3$): 1.02−1.45 (m, 18H, ^{i}Pr), 2.11−2.31 (m, 3H, ^{i}Pr), 5.11 (t, 1H, J_{HH} = 1.9 Hz, C-2), 5.53 (d, 2H, J_{HH} = 1.9 Hz, C-1,3), 7.22−7.31 (m, 4H, H-4,7 and H-5,6). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 19.2 (m, ^{i}Pr), 25.8 (m, ^{i}Pr), 62.9 (s, C-1), 72.5 (s, C-3), 89.7 (s, C-2), 112.7 and 113.7 (both s, C-3a,7a), 122.4, 123.0, 125.7, and 128.6 (all s, C-4,5,6,7), 205.5 (d, J_{PC} = 20.7 Hz, CO). Anal. Calcd for $RuC_{22}H_{34}ClOP$ (481.27): C, 54.8; H, 7.1. Found: C, 54.3; H, 7.2.

Synthesis of [Ru(η^5-C_9H_7)Cl{κ^2-(*P,N*)-*o*-$Ph_2PC_6H_4C(H)$=N^{t}Bu}] (4). *o*-$Ph_2PC_6H_4C(H)$=N^{t}Bu (1.5 mol) was added to a solution of **1** (0.359 g, 1 mol) in THF (25 mL). The solution was refluxed for 30 min. After cooling, solvents were removed under vacuum. The solid residue was purified by a silica gel column, recovering the red fraction eluted with Et_2O. **4** was obtained, removing all solvents under vacuum as a red solid in 80% yield. $^{31}P\{^1H\}$ (δ, $CDCl_3$): 82.25 (s). ^1H NMR (δ, $CDCl_3$): 1.11 (s, 9H, ^{t}Bu), 4.08 (s, 1H, H2), 4.57 (s, 2H, H1,3), 7.10, 7.23−7.50, 7.79 (m, 18H, H4,5,6,7, Ph), 8.14 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 32.1 (s, CCH_3), 59.2−62.4 (s, C1,3), 71.3 (s, CCH_3), 89.4 (s, C2), 120.5, 120.6 (s, C3a,7a), 124.4−140.8 (m, C-4,5,6,7, Ph), 164.4 (s, CH=N). Anal. Calcd for $RuC_{32}H_{31}ClNP$ (597.1): C, 64.3; H, 5.2. Found: C, 64.0; H, 4.5.

Synthesis of [Ru(η^5-C_9H_7){κ^1-(*P*)-$Ph_2PCH_2C(O)^tBu$}{κ^2-(*P,O*)-Ph_2PCH=C(O)^{t}Bu}] (5). $Ph_2PCH_2C(O)^tBu$ (0.6 g, 2.1 mol) was added to a stirred solution of **1** (0.53 g, 1 mol) in CH_2Cl_2 (25 mL) and the resulting solution refluxed for 1 h. The solution was then evaporated to dryness, and the solid residue was filtered through a column of Basic Alumine, recovering the fraction eluted with MeOH. Solvents were removed under vacuum, affording a red solid. Yield: 80%. IR (Nujol): ν 1701 (C=O), 1495 (C=CO) cm^{-1}. $^{31}P\{^1H\}$ (δ, $CDCl_3$): 69.9 (d, J_{PP} = 36.9 Hz), 41.4 (d, J_{PP} = 36.9 Hz). ^1H NMR (δ, $CDCl_3$): 0.45 (s, 9H, ^{t}Bu), 1.12 (s, 9H, ^{t}Bu), 2.25 (m, 1H, CH), 2.85 (m, 1H, CH), 3.51 (m, 1H, CH), 4.05 (m, 2H, H1,3), 4.79 (m, 1H, H2), 6.71−7.75 (m, 24H, Ph, H-4,5,6,7). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 27.7 (s, ^{t}Bu), 32.3 (s, ^{t}Bu), 33.9 (d, $^2J_{PC}$ = 10.8 Hz, CH_2), 40.8 (d, $^3J_{PC}$ = 11.6 Hz, CMe_3), 47.5 (s, CMe_3), 66.0 (d, $^2J_{PC}$ = 12.8 Hz, C2), 66.2 (s, C1), 77.6 (d, $^1J_{PC}$ = 57.9 Hz, CH=CO), 87.1 (s, C3), 107.1, 114.0 (s, C3a,7a), 124.4, 127.0, 127.3, 128.5 (all s, C4,5,6,7), 129.3 (d, J_{PC} = 9.1 Hz, *o,m*-Ph), 129.4 (d, J_{PC} = 10.0 Hz, *o,m*-Ph), 129.9 (d, J_{PC} = 9.7 Hz, *o,m*-Ph), 130.2 (d, J_{PC} = 2.4 Hz, *p*-Ph), 130.6 (d, J_{PC} = 2.2 Hz, *p*-Ph), 130.8 (d, J_{PC} = 1.8 Hz, *p*-Ph), 130.9 (d, J_{PC} = 2.1 Hz, *p*-Ph), 131.6 (d, J_{PC} = 2.2 Hz, *p*-Ph), 133.3 (d, J_{PC} = 10.0 Hz, *o,m*-Ph), 133.5 (d, J_{PC} = 9.8 Hz, *o,m*-Ph), 134.4 (d, J_{PC} = 10.2 Hz, *o,m*-Ph), 135.2 (d, J_{PC} = 9.9 Hz, *o,m*-Ph), 135.5 (d, J_{PC} = 34.7 Hz, *ip*-Ph), 136.2 (d, J_{PC} = 12.2 Hz, *o,m*-Ph), 140.0 (d, J_{PC} = 44.5 Hz, *ip*-Ph), 140.1 (dd, J_{PC} = 45.7 Hz, $^2J_{PC}$ = 4.9 Hz, *ip*-Ph), 146.9 (dd, J_{PC} = 39.2 Hz, $^2J_{PC}$ = 3.1 Hz, *ip*-Ph), 202.2 (d, J_{PC} = 15.2 Hz, C=CO), 212.8 (d, J_{PC} = 10.9 Hz, *C*=O). Anal. Calcd for $RuC_{28}H_{40}ClOP$ (560.12): C, 60.0; H, 7.2. Found: C, 59.8; H, 6.9.

Synthesis of [Ru(η^5-C_9H_7)Cl(NBD)] (6). Norbornadiene (0.1 g, 1 mol) was added at room temperature to a solution of **1** (0.35 g, 1 mol) in THF (20 mL). The solution was then refluxed for 30 min. After evaporation, the solid residue was extracted with dichloromethane (ca. 25 mL) and filtered (the excess of norbornadiene was separated as a polymer, characterized as the correspondent ROMP, not soluble in CH_2Cl_2). The extract was evaporated to dryness, yielding an orange solid, which was washed with hexane (2 × 20 mL) and dried under vacuum. **6**: Yield: 0.15 g, (40%). ^1H NMR (δ, $CDCl_3$): 1.22 (s, 1H, H-bridged-head), 3.60 (m, 1H, CH), 3.71 (m, 1H, CH), 3.78 (vt, 2H, J_{HH} = 3.9 Hz, =CH), 3.88 (vt, 2H, J_{HH} = 3.9 Hz, =CH), 5.44 (s, 1H, H-2), 5.53 (s, 2H, H-1,3), 7.22−7.38 (m, 4H, H-4,7 and H-5,6). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 45.3 (s, =CH), 48.6 (s, CH), 48.8 (s, CH), 60.2 (s, C-bridged-head), 65.1 (s, CH), 76.1 (s, C-1,3), 93.5 (s, C-2), 110.4 (s, C-3a,7a), 123.4 and 128.2 (both s, C-4,7 and C-5,6). Anal. Calcd for $RuC_{16}H_{17}Cl$ (345.8): C, 55.5; H, 5.0. Found: C, 55.3; H, 5.2.

Synthesis of [Ru(η^5-C_9H_7)(FBF_3)(COD)] (7): Method A. HBF_4·Et_2O (1.5 mol) was added dropwise at room temperature to a solution of **2** (0.323 g, 1 mol) in THF (20 mL). The solution was stirred for 10 min and then evaporated to dryness. The solid residue was washed with hexane (2 × 20 mL), affording a yellow-brown solid purified on a silica gel column, recovering the fraction eluted with Et_2O.

Method B. $AgBF_4$ (0.194 g, 1 mol) was added at room temperature to a solution of **1** in CH_2Cl_2 (15 mL). The solution was stirred at room temperature for 30 min. The solution was then filtered and evaporated to dryness, affording a brown solid. Yield: 70%. IR (Nujol): ν 1134, 870, 735 cm^{-1} (FBF_3). $^{19}F\{^1H\}$ NMR (δ, toluene/D_2O): −158.9 (s, free BF_4^-), −160.1 (s, br, F-B*F*$_3$), −301.1 (m, br, *F*-BF_3). ^1H NMR (δ, $CDCl_3$): 0.39 (m, 1H, CH_2), 0.75 (m, 1H, CH_2), 1.28−1.51 (m, 4H, CH_2), 2.51 (m, 2H, CH_2), 3.65 (m, 2H, CH), 4.61 (m, 2H,CH), 5.33 (m, 2H, H-1,3), 5.53 (m, H-2), 6.90−7.17 (m, 4H, H-4,7 and H-5,6). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 20.2 (s, CH_2), 29.2 (s, CH_2), 44.8 (s, CH), 75.2 (s, CH), 81.9 (s, C-2), 101.4 (s, C-3a,7a), 103.9, 107.6 (s, C-1,3), 122.4 and 123.5 (s, C-4,7 and C-5,6). Anal. Calcd for $RuC_{17}H_{19}BF_4$ (411.2): C, 49.6; H, 4.6. Found: C, 49.5; H, 4.9. MS(FAB$^+$): *m/e* 411 (M^+), 392 (M^+ − F), 373 (M^+ − F_2), 324 (M^+ − BF_4).

Synthesis of [Ru(η^5-C_9H_7)(N_3)(COD)] (8). NaN_3 (0.06 g, 1 mol, in 2 mL of MeOH) was added to a solution of **1** (0.359 g, 1 mol) in THF/MeOH (10:1) (20 mL). The solution was stirred at room temperature for 30 min. The solid residue was removed by filtration. Solvents were then removed, and the yellow solid was obtained, washed with hexane (2 × 20 mL), and vacuum-dried. Yield: 0.31 g (85%). IR (Nujol): ν 2029 cm^{-1} (N_3). ^1H NMR (δ, $CDCl_3$): 1.77 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 2.26 (m, 2H, CH_2), 3.37 (m, 4H, CH), 4.29 (m, 2H, CH), 5.37 (m, 1H, H-2), 5.47 (m, 2H, H-1,3), 7.29−7.44 (m, 4H, H-4,7 and H-5,6). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 27.87 (s, CH_2), 33.42 (s, CH_2), 75.07 (s, CH), 79.25 (s, CH), 83.76 (s, C-1,3), 97.32 (s, C-2), 110.19 (s, C-3a,7a), 123.46 and 128.66 (s, C-4,7 and C-5,6). Anal. Calcd for $RuC_{17}H_{19}N_3$ (366.43): C, 55.7; H, 5.2; N, 11.4. Found: C, 56.0; H, 5.5; N, 10.9.

Synthesis of [Ru(η^5-C_9H_7)(py)(COD)][BF_4] (9) (py = pyridine). $AgBF_4$ (0.194 g, 1 mol) was added to a solution of **1** (0.356 g, 1 mol) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 2 h in the dark. Then, pyridine (0.79 g, 1 mol) was added and the mixture stirred at room temperature for 20 min. The solution was then filtered and the solvents were removed, yielding an yellow solid, which was crystallized with CH_2Cl_2 (10 mL), vacuum-dried, and washed with hexane (2 × 20 mL). Removing all solvents afforded a yellow solid (0.35 g, 85%). IR (KBr): ν 1077 (BF_4^-). ^1H NMR (δ, $CDCl_3$): 1.64 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 2.43 (m, 2H, CH_2), 3.38 (m, 2H, CH), 5.45 (s, 2H, H-1,3), 5.80 (m, 2H, CH), 5.91 (s, 1H, H-2), 6.95−7.32 (m, 4H, H-4,7 and H-5,6), 7.48 (t, 2H, J_{HH} = 6.3 Hz, py), 7.98 (t, 1H, J_{HH} = 7.3 Hz, py), 8.42 (d, 2H, J_{HH} = 4.9 Hz, py). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 27.1 (s, CH_2), 32.6 (s, CH_2), 74.2 (s, CH), 85.3 (s, CH), 87.3 (s, C-1,3), 99.4 (s, C-2), 108.4 (s, C-3a,7a), 123.9 and 128.9 (both s, C-4,7 and C-5,6), 135.3 (s, py), 138.9 (s, py), 156.4 (s, py). Anal. Calcd for $RuC_{22}H_{24}F_4NB$ (452.2): C, 53.9; H, 4.9; N, 2.9. Found: C, 54.1; H, 4.7; N, 3.0.

Synthesis of [Ru(η^5-C_9H_7)(COD)(NCMe)][BF_4] (10). The same procedure as above was used with acetonitrile (1 mL). **10** was isolated as an orange solid. Yield: 0.40 g (85%). IR

(KBr): ν 2226 cm^{-1} (C≡N), 1069 (BF_4^-). ^{1}H NMR (δ, $CDCl_3$): 1.89 (m, 2H, CH_2), 2.06 (m, 2H, CH_2), 2.43 (m, 2H, CH_2), 2.54 (m, 2H, CH_2), 2.58 (s, 3H, Me), 3.67(m, 2H, CH), 4.61 (m, 2H, CH), 5.49 (s, 2H, H-1,3), 5.76 (s, 1H, H-2), 7.38−7.54 (m, 4H, H-4,7 and H-5,6). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 4.5 (s, 3H, Me), 27.6 (s, CH_2), 32.3 (s, CH_2), 73.9 (s, CH), 83.0 (s, CH), 85.0 (s, C-1,3), 96.13 (s, C-2), 101.1 (s, C-3a,7a), 124.4 and 130.0 (both s, C-4,7 and C-5,6), 131.45 (s, C≡N). Anal. Calcd for $RuC_{19}H_{22}F_4NB$ (452.2): C, 50.4; H, 4.9; N, 3.0. Found: C, 50.0; H, 4.7; N, 3.4.

[2+2] Cycloadditions Reactions of Norbornene, with Alkynes (General Procedure). A mixture of norbornene (0.018 g, 0.2 mol), the catalyst **1** (0.0017 g, 0.005 mol), and the alkyne (0.1 mol) under argon was heated in a sealed flask fitted with a Teflon septum at 80 °C in a thermostated bath. The reaction was monitored by gas chromatography−MS (nonane or undecane as internal standard). Formation of the coupling products was further confirmed by comparison with the literature NMR data.[40] Preparative conditions: Norbornene (0.18 g, 2 mol), complex **1** (0.017 g, 0.05 mol), and the alkyne were reacted at 80 °C. The reaction was monitored by GC until complete transformation of the alkyne (Table 1, entry 1: 20 h, entry 3: 24 h). The crude reaction mixture, after removal of solvent, was washed several times with hexane. The extracts were vacuum-dried, and the residue was purified by column chromatography (silica gel, hexane as eluant) (phenylacetilene) or vacuum distillation (1-octine), to give the pure products.

[4+2] Cycloadditions Reactions of 1,5-Cyclooctadiene with Alkynes (General Procedure). 1,5-Cyclooctadiene (0.021 g, 0.2 mol), complex **1** (1.7 mg, 0.005 mol), and the alkyne (0.01 mol) were reacted at 80 °C. Workup and analysis were carried out as indicated for the [2+2] cycloaddition reactions of norbonene. The formation of free COD during the reaction was detected by GC. Preparative conditions: 1,5-cyclooctadiene (0.21 g, 2 mol), complex **1** (0.017 g, 0.05 mol), and 1-phenyl-1-propyne (0.011 g, 0.1 mol) were reacted at 80 °C until complete conversion of the alkyne (Table 2, entry 3: 20 h). Once the reaction was finished, the mixture was extracted with diethyl ether (5 mL), solvents were removed under vacuum, and the oil was obtained vacuum distilled. ^{1}H and ^{13}C{^{1}H} NMR of the final product was in agreement with the literature data.[7b]

Hydration of Alkynes (General Procedure). A stirred solution of **1** (0.017 g, 0.05 mol) and the alkyne (1 mol) in 2-propanol/water (2.5/0.75 mL) was kept in a sealed vessel and heated in a thermostated bath. The reaction was monitored by gas chromatography−MS (nonane or undecane as internal standard). The product was purified by column chromatography on silica gel (hexane/Et_2O, 1:1) to give the pure products. Formation of ketones was confirmed by comparison of the NMR data (^{1}H NMR) and GC−mass data with those of commercially available samples or with those of the literature (Table 3, entry 6).[35]

X-ray Structure Determination of 6 and 9.[41] Crystal data, resolution, and refinement details are collected in Table 4. Unit cell dimensions were determined from the angular settings of 25 reflections (with 12.21° < θ < 15.26° (**6**) and 10.30° < θ < 12.29° (**9**)). A Nonius CAD4 single-crystal diffractometer provided with a Mo Kα radiation graphite crystal monochromator (λ = 0.71073 Å) was used for collecting data; ω−2θ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection was used. The intensity was checked throughout data collection by monitoring three standard reflections every 60 min. Final drift correction factors were between 1.00 and 1.03 (**6**) and 0.98 and 1.01 (**9**). On all reflections a profile analysis was performed.[41b,e] Both structures were solved by Patterson interpretation and phase expansion using the program DIRDIF92.[41a,i] A semiempirical absorption correction was applied for **6** by using the ψ-scan technique,[41g] while for **9**, an empirical absorption correction was applied using the program SHELXA.[41h] A full matrix anisotropic least-squares refinement over F^2, using the program SHELXL-97[41h] followed by a difference Fourier synthesis, allowed the location of every hydrogen atom of **6** and some H atoms for **9**. Positional parameters and anisotropic displacement parameters of the non-hydrogen atoms were refined. Hydrogen atoms were left free and isotropically refined for **6**, while H atoms were refined using geometrical and thermal restrictions for compound **9**.

Final conventional agreement factors were $R(F)$ = 0.028 for the 1792 "observed" reflections and 223 variables, and $wR(F^2)$ = 0.066 for the whole set of 2599 reflections for **6** and $R(F)$ = 0.057 for the 1560 "observed" reflections and 277 variables, and $wR(F^2)$ = 0.198 for the whole set of 3955 reflections for **9**.

Table 4. Crystallographic Data for Complexes 6 and 9

formula	$C_{16}H_{15}RuCl$ (**6**), $C_{22}H_{24}BF_4NORu$ (**9**)
fw	343.80 (**6**), 490.30 (**9**)
temp	293(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	(**6**) a = 7.171(3) Å, α = 90° b = 10.255(5) Å, β = 94.01(3)° c = 17.992(6) Å, γ = 90° (**9**) a = 8.483(2), Å α = 90° b = 24.966(7) Å, β = 105.34(4)° c = 9.880(8) Å, γ = 90°
volume	1320(1) Å^3 (**6**), 2018(2) Å^3 (**9**)
Z	4
density (calcd)	1.730 g/cm^3 (**6**), 1.614 g/cm^3 (**9**)
abs coeff	1.367 mm^{-1} (**6**), 0.821 mm^{-1} (**9**)
F(000)	688 (**6**), 992 (**9**)
cryst size	0.198 × 0.132 × 0.099 mm (**6**), 0.132 × 0.132 × 0.033 mm (**9**)
θ range for data collection	2.27−25.98° (**6**), 1.63−25.97° (**9**)
index ranges	$-8 \le h \le 8$, $-12 \le k \le 12$, $0 \le l \le 22$ (**6**), $-10 \le h \le 10$, $0 \le k \le 30$, $0 \le l \le 12$ (**9**)
no. of reflns collected	4827 (**6**), 4183 (**9**)
no. of ind reflns	2599 [R(int) = 0.035] (**6**) 3955 [R(int) = 0.067] (**9**)
abs corr	semiempirical (**6**), empirical over F^2 (**9**)
max. and min. transmn	0.906 and 0.675 (**6**), 0.871 and 0.577 (**9**)
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	2599/0/223 (**6**), 3955/0/277 (**9**)
goodness-of-fit on F^2	1.013 (**6**), 0.990 (**9**)
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0284, wR2 = 0.0560 (**6**) R_1 = 0.0568, wR2 = 0.1354 (**9**)
R indices (all data)	R_1 = 0.0689, wR2 = 0.0658 (**6**) R_1 = 0.2222, wR2 = 0.1982 (**9**)
largest diff peak and hole	0.464 and −0.603 e Å^{-3} (**6**) 1.018 and −1.512 e Å^{-3} (**9**)

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The refinement of the rather disordered BF_4^- group, present in structure **9**, was performed using procedures described elsewhere.[41k,l] Coordinates for the atoms of the BF_4^- group were first restrained to have similar 1,2 and 1,3 distances and then constrained and refined as a variable-metric rigid group.

Atomic scattering factors were taken from the International Tables for Crystallography.[41d] The plots in Figure 1 and Figure 2, showing the atomic numbering scheme, were made with the Xtal_GX package.[41c] Further geometrical calculations were made with PARST[41f] and the EUCLID program package.[41j] All calculations were made on an Alpha AXP200/166 workstation at the Scientific Computer Center, University of Oviedo.

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Supporting Information Available: Crystal structure data for **6** and **9**, including tables of atomic parameters, anisotropic displacement parameters, bond distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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