Alkene and Alkyne Reactivity Toward a Bisruthenium(II) μ^2-Dinitrogen Complex Containing the "Pincer" Ligand 2,6-Bis[(dimethylamino)methyl]pyridine (NN′N). The X-ray Crystal Structures of [Ru(=C=CHPh)- Cl₂(NN′N)] and [Ru(=C=CHPh)(OTf)(NN′N)(PPh₃)][OTf] (OTf = Trifluoromethane Sulfonate)

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The binuclear Ru(II) μ^2-dinitrogen complex [{RuCl₂(η^3-NN′N)}₂(μ-N₂)] (**1**, NN′N = 2,6-bis-[(dimethylamino)methyl]pyridine) is an excellent starting material for the synthesis of mononuclear η^2-alkene complexes: *mer*,*trans*-[RuCl₂(η^3-NN′N)(η^2-H₂C=CHR)] (R = H, CH= CH₂, Ph, CH₂Ph, CH₂Br, CH₂OH, CHO, C≡N, CO₂Me; yields 73−93%). These new η^2-alkene Ru(II) compounds are stable at room temperature even when the alkene carbon atoms are substituted with potentially reactive functional groups. Of particular note is the reaction of **1** with allyl bromide, which leads to a rare example of a stable η^2-allyl bromide Ru(II) complex. Disubstituted alkenes are unreactive, but in contrast, maleic anhydride forms a stable η^2- alkene complex. Also with a terminal alkyne such as phenylacetylene, the μ^2-N₂ Ru(II) complex **1** reacts cleanly, leading to the formation of the neutral Ru(II) vinylidene complex *mer*,*cis*-[Ru(=C=CHPh)Cl₂(NN′N)] (**12**, X-ray structure). The corresponding η^2-alkyne complexes could not be detected. Via an alternative pathway, related mono- and dicationic vinylidene derivatives with phosphine ligands were synthesized using the neutral compound *mer*,*trans*-[RuCl₂(NN′N)(PPh₃)] (**13**) as starting material. Its treatment with silver salts in the presence of phenylacetylene yielded the complex *mer*-[Ru(=C=CHPh)(OTf)(NN′N)(PPh₃)]- [OTf] (**17**, OTf = trifluoromethane sulfonate; X-ray). Both Ru(II) starting materials, **1** and **13**, used in this study are unreactive toward internal alkynes such as diphenylacetylene, while the use of acetylene gas leads to the formation of complex product mixtures.

Introduction

The chemistry of metal vinylidenes has attracted considerable attention because of its relevance to several important stoichiometric and catalytic processes directed toward C−C bond formation.[1] For example, ruthenium complexes have been shown to be particularly efficient in promoting alkyne coupling reactions with high regio- and/or stereoselectivity,[2,3] coupling of alkynes and alkenes,[4,5] alkene co-cyclization[6] and Pauson−Khand type reactions.[7,8] Vinylideneruthenium(II) complexes have also been recently shown to be useful

catalysts for the ring-opening metathesis polymerization (ROMP) and ring-closure metathesis reaction (RCM) of cyclic or acyclic olefins, respectively.[9]

One of the primary reasons for the rapid development and applications of Ru-vinylidene complexes is that they are, in many cases, readily accessible from simple 1-alkynes.[10] Initial side-on coordination of the alkyne fragment to the metal center is typically followed by a 1,2-H-shift to give the corresponding vinylidene com-

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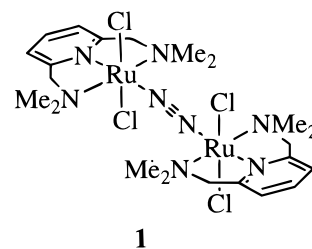
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plex.[11] This rearrangement is usually spontaneous at room temperature, although in some cases thermal activation is required.[12] The presence of strong donor ligands in the metal fragment favors this alkyne to vinylidene rearrangement.[13] Coordination of an unsaturated molecule to these vinylidene complexes may be followed by migratory insertion of the unsaturated fragment into the metal−carbon bond of the vinylidene ligand, coupling the two organic fragments.[14] The presence of readily available vacant coordination sites within the metal sphere is considered a prerequisite for this coupling process to take place. An additional advantage of Ru complexes when compared with early transition metal carbenes or vinylidenes is their tolerance of polar functional groups in the unsaturated fragment which permits, in some cases, the use of water as a solvent.[9d,15]

Recently, we reported the synthesis and structural characterization of the binuclear Ru(II) N_2-bridged complex [{RuCl$_2$(η^3-NN'N)}$_2$(μ-N$_2$)] (**1**, Figure 1), together with other complexes of the terdentate "pincer" ligand: 2,6-bis[(dimethylamino)methyl]pyridine (NN'N).[16] Several of these compounds have potent catalytic activity in the synthesis of piperidines and piperazines via

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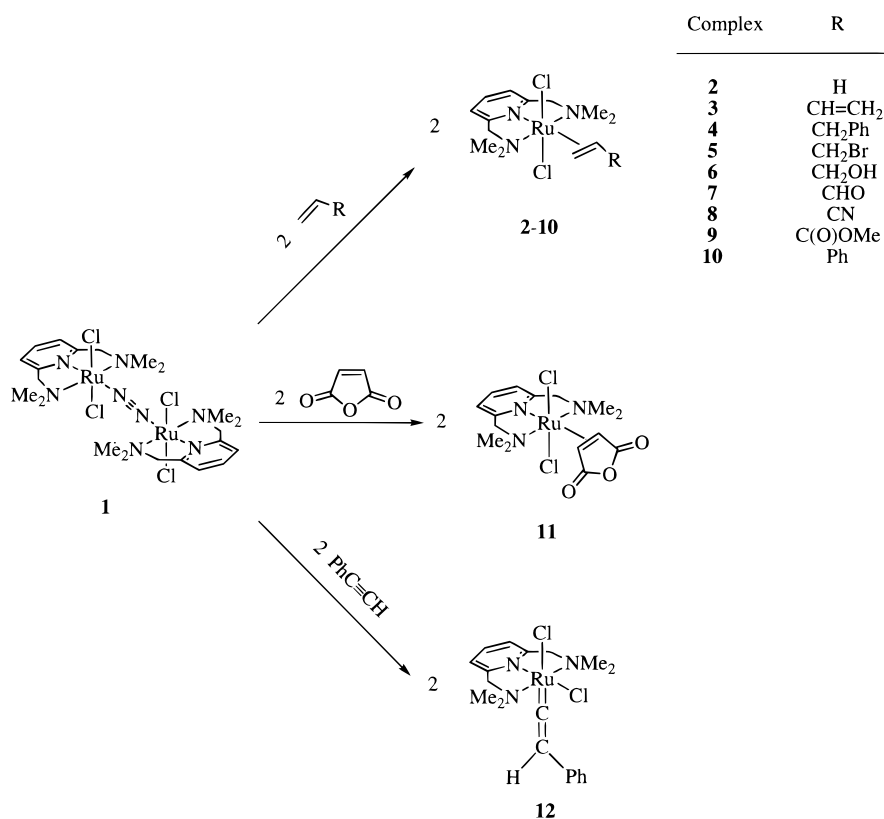(12) (a) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165. (b) Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518.
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Figure 1.

the (cyclo)alkylation of aromatic amines with alcohols.[17] The presence of the potentially labile N_2 ligand in complex **1** prompted us to study its reactivity toward unsaturated fragments, in an attempt to obtain derivatives that could find application in catalysis. In the first part of this work, the reactivity of **1** toward fuctionalized alkenes is described, while the second part deals with the synthesis of neutral and cationic vinylidene derivatives. We found that the presence of strong electron-donor groups such as the NMe$_2$ fragment assists in the tautomerization of a bound alkyne ligand. Moreover, the chloride ligands attached to the metal center can be easily removed by subsequent treatment with silver salts, thus generating vacant coordination sites on the metal which may permit the coordination of a second unsaturated fragment to the Ru center.

The presence of phosphine ligands in catalyst precursors may have an important influence on their properties.[2b,18] Therefore, the lack of P-donor ligands in complex **1** induced us to study the use of the related complex *mer,trans*-[RuCl$_2$(η^3-NN'N)(PPh$_3$)] (**13**) as a starting material. This resulted in the formation of both mono- and/or dicationic vinylidene complexes with triphenylphosphine ligands. In addition to the known activity of these types of complexes as catalysts in the (cyclo)alkylation reaction of aromatic amines with alcohols,[17] we found that the use of some of these complexes as catalysts in other organic transformations, i.e., coupling of alkynes and ring-opening metathesis polymerization of norbornene derivatives, is also possible.

Results and Discussion

Reaction of 1 with Monosubstituted Alkenes. Treatment of the binuclear complex **1** with ethylene in CH$_2$Cl$_2$ solution at room temperature (RT) affords *mer,trans*-[RuCl$_2$(η^3-NN'N)(η^2-CH$_2$=CH$_2$)] (**2**, Scheme 1) in 92% yield. The ^{1}H NMR spectrum of **2** shows one singlet at $\delta = 4.79$ for the four protons of the coordinated ethylene fragment (see Table 1). This indicates either a fixed geometry of the ethylene ligand, with the C=C fragment coplanar with one of the two mirror (symmetry) planes of the [RuCl$_2$(η^3-NN'N)] fragment, or free rotation of this alkene on the NMR time scale. The molecular C_{2v} symmetry of the [RuCl$_2$(η^3-NN'N)] fragment is confirmed by the signals observed for the CH$_2$

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Scheme 1

Complex	R
2	H
3	CH=CH₂
4	CH₂Ph
5	CH₂Br
6	CH₂OH
7	CHO
8	CN
9	C(O)OMe
10	Ph

Table 1. Selected ^{1}H and ^{13}C{^{1}H} NMR Data of 2−11^a

compound number, olefin	^{1}H NMR data				^{13}C{^{1}H} NMR data			
	Ar	C*H₂*	N*Me₂*	CH₂=CHR	*o*-, *m*-, *p*-C	*C*H₂	N*Me₂*	CH₂=CHR
2, CH₂=CH₂^b	7.78(t, 7.6) 7.46(d, 7.6)	4.25	2.39	4.79	159.4, 120.0, 135.8	72.6	53.9	74.4
3, CH₂=CH−CH=CH₂	7.79(t, 7.6)	4.92(d, 14.8)	2.47, 2.37	6.72(dt, 17.6, 8.2), 5.52(m), 5.34(d, 17.6), 5.13(m), 4.87(d, 10.8)	159.5, 120.0, 136.1	73.4	55.4	145.0, 111.4, 88.3, 76.3
4, CH₂=CH−CH₂Ph	7.47(d, 7.6) 7.82(t, 7.6)	3.39(d, 14.8) 5.00(d, 14.8)	2.50	5.16−5.03(m), 3.79(dd, 14.4, 10.2), 3.39(d, 9.0)	160.1, 120.5, 136.1	73.5	50.5 55.8	126.2, 89.0, 41.2
5, CH₂=CHCH₂Br	7.49(d, 7.6) 7.89(t, 7.6)	3.39(d, 14.8) 4.94(d, 14.8)	2.43	5.32−5.19(m), 5.04(d, 8.2), 4.79−4.61(m), 4.32−4.20(m)	160.0, 120.7, 137.4	73.6	51.7 56.1	83.3, 76.7, 52.7
6, CH₂=CHCH₂OH	7.55(d, 7.6) 7.83(t, 7.6)	3.42(d, 14.8) 4.91(d, 14.8)	2.43, 2.42	5.39(t, 8.8), 5.10−5.04(m), 4.77, 4.46(d, 14.0)	160.1, 120.1, 136.1	73.3	52.2 55.5	89.4, 72.0, 64.8
7, CH₂=CH−C(O)H	7.49(d, 7.6) 7.89(t, 7.6)	3.39(d, 14.8) 4.94(d, 14.8)	2.55, 2.41	9.76(d, 8.4), 5.72(d, 8.4), 5.57(d, 8.4), 5.06(t, 8.4)	159.3, 120.6, 137.6	73.4	51.7 55.7	209.4, 82.0, 80.9
8, CH₂=CH−CN	7.54(d, 7.6) 7.93(t, 7.6)	3.49(d, 14.8) 5.04(d, 14.8)	2.53	5.18(d, 9.8), 5.03(d, 9.8), 4.65(d, 9.8)	159.0, 120.6, 137.7	73.2	52.0 55.2	125.2, 76.0, 54.6
9, CH₂=CH−C(O)OMe	7.58(d, 7.6) 7.86(t, 7.6)	3.55(d, 14.8) 5.01(d, 14.8)	2.62, 2.50	5.52−5.46(m), 5.21(t, 9.8), 3.70	160.2, 120.7, 137.7	73.6	52.2 55.4	177.8, 76.0, 72.5, 50.6
10, CH₂=CHPh	7.51(d, 7.6) 7.80(t, 7.6)	3.39(d, 14.8) 5.01(d, 14.7)	2.54, 2.21	6.06(dd, 12.6, 9.3), 5.42(d, 9.3), 5.34(d, 12.6)	160.0, 120.0, 136.1	73.8	52.0 55.9	125.6, 89.4
11, C₄H₂O₃	7.44(t, 7.6) 8.00(t, 7.8) 7.61(d, 7.8)	3.42(d, 14.7) 4.39	2.67	6.03	159.6, 121.8, 139.5	74.5	52.0 55.2	176.0, 74.1

^{a} Spectra recorded using CD₂Cl₂ as a solvent. ^{b} All signals are singlets unless otherwise stated. ^{c} Key: d = doublet, t = triplet, m = multiplet, br = broad. ^{d} Coupling constants (parentheses) in hertz. ^{e} All spectra reported correct integration for the proposed structures. ^{f} All the signals corresponding to the phenyl rings have been omitted for simplicity. ^{g} Spectrum recorded using CDCl₃ as a solvent. The presence of 0.5 equiv of CH₂Cl₂ was confirmed by a signal at $\delta = 5.28$.

and NMe₂ groups of the pyridine ligand, both of which appear as singlets ($\delta = 4.25$ and 2.39, respectively). The small upfield shift of the resonance of the coordinated ethylene ligand relative to that of free ethylene ($\Delta\delta = 0.2$ ppm) reflects the retention of strong C−C double-bond character on coordination to the Ru center. Similar results have been found by Nishiyama et al. for the isostructural complex *mer,trans*-[RuCl₂(pybox-dihydro)-(η^2-CH₂=CH₂)] (pybox = bis(2-oxazolin-2-yl)pyridine).

This compound has been characterized by X-ray diffraction methods and contains the ethylene ligand orientated coplanar with the N−Ru−N vector, with an olefin C−C bond distance of 1.377(5) Å, which is in the expected range for a C−C double bond. The ^{1}H NMR resonances for the olefinic protons in this latter complex also appear as a singlet ($\delta = 4.95$).[19]

The ease with which ethylene displaces the N₂ ligand of **1** prompted us to carry out similar reactions with

diverse substituted olefins. Specifically, we tried alkenes with polar functional groups to study whether exclusive η^2-coordination of the olefinic fragment, without subsequent reaction of the functional substituent, would be possible. Treatment of **1** with 1,3-butadiene in CH_2Cl_2 solution at RT affords the complex *mer,trans*-[RuCl$_2$(η^3-NN'N)(η^2-CH$_2$=CHCH=CH$_2$)] (**3**, Scheme 1) in virtually quantitative yield. In **3**, only one of the two olefinic bonds is coordinated to the Ru center. No traces of the binuclear derivative *mer,trans*-[{RuCl$_2$(η^3-NN'N)}$_2$(μ-η^4-CH$_2$=CHCH=CH$_2$)] were observed in the course of this reaction (^{1}H NMR). Attempts to obtain the latter complex by the treatment of **3** with 0.5 equiv of **1** were also unsuccessful. The ^{1}H and ^{13}C{^{1}H} NMR data of **3** clearly show the presence of a η^2-coordinated and a free CH=CH$_2$ fragment (see Table 1). This coordination mode is atypical for transition metal complexes containing acyclic conjugated dienes. The two bonding motifs that are usually observed are the η^4-*cis*-diene and the enediyl bonding interactions.[20] Again, a relatively simple ^{1}H NMR pattern is observed for the NN'N ligand in **3**, i.e., one AB pattern for the CH$_2$ protons at $\delta = 4.92$ and 3.39 and two singlets for the NMe$_2$ methyl groups at $\delta = 2.37$ and 2.47.

When olefins such as allyl benzene, allyl bromide, allyl alcohol, or acrolein are used, pure products in good yields can be obtained (**4**–**7**, see Scheme 1 and Experimental Section). The presence of functional substituents at the alkene carbon atoms appears not to have a significant influence on the coordination mode of the ligands, since all give η^2-alkene derivatives similar to those described for the ethylene complex above. The resonances of the pyridine ligand in the corresponding ^{1}H NMR spectra of complexes **4**–**7** appear again as a simple AB pattern (Table 1).

Treatment of **1** with an excess of acrylonitrile or methyl acrylate in CH_2Cl_2 at RT affords the complexes *mer,trans*-[RuCl$_2$(η^3-NN'N)(η^2-CH$_2$=CHCN)] (**8**) and *mer,trans*-[RuCl$_2$(η^3-NN'N)(η^2-CH$_2$=CHCO$_2$Me)] (**9**, Scheme 1), respectively, in good yields. The ^{13}C{^{1}H} NMR spectrum of **8** shows the resonance of the nitrile group at $\delta = 125.2$, which indicates that it is not coordinated to the metal center. The IR spectrum of this complex shows one strong absorption band at 2210 cm^{-1}, which is assigned to the C≡N stretching frequency. A weak absorbance at 2232 cm^{-1} is probably due to a combination band resulting from the C–C (stretching) and C–H (deformation) vibrations. These data are similar to those of free acrylonitrile, which generates the corresponding bands at 2230 and 2279 cm^{-1}, respectively. These results again suggest that coordination of the nitrile fragment to Ru is not occurring.[21] Also for the methyl acrylate complex **9** it is strongly suggested that the carbonyl functionality is not coordinated. The increased back-donation from the metal fragment to the olefin ligand and subsequent donation to the carbonyl group
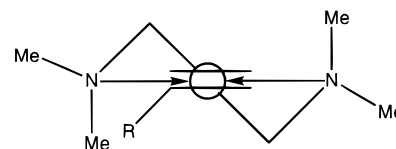
Figure 2. Newman projection along the mid-olefin–Ru–C_3 axis.

is reflected in the NMR and IR spectra of **9**. The resonance corresponding to the carbonyl group appears at $\delta = 177.8$ in its ^{13}C{^{1}H} NMR spectrum (vs 165.7 ppm in the free alkene), while its IR spectrum (CH_2Cl_2 solution) shows a ν(C=O) at 1692 cm^{-1}, which is shifted to lower wavenumbers with respect to free methyl acrylate (1725 cm^{-1}).

The reaction of styrene with **1** in CH_2Cl_2 solution, either in stoichiometric amounts or using an excess of alkene, yields the corresponding derivative *mer,trans*-[RuCl$_2$(η^3-NN'N)(η^2-CH$_2$=CHPh)] (**10**, Scheme 1) as the initial product. However, before all of **1** has reacted, complex **10** decomposes to give an unidentifiable mixture of compounds (^{1}H NMR). Hydride-containing products could be detected in the reaction mixture. However, when benzene is used as a solvent, **10** could be obtained as a pure product. This reaction appeared to be reversible, leading to completion only when a large excess of styrene is present in solution. When the excess of styrene is washed away under N$_2$ atmosphere, complex **1** is slowly reformed. The ^{1}H NMR spectrum of **10** shows the charasteristic AB pattern for the CH$_2$ fragment and two singlets for the methyl groups.

The diastereotopicity of the CH$_2$ protons and NMe$_2$ methyl groups in complexes **3**–**10** points to η^2-coordination of a prochiral alkene (CH$_2$=CHR) to the Ru(II) center (see Figure 2). However, the fact that a single AB resonance pattern is observed for both *ortho*-CH$_2$-NMe$_2$ substituents indicates that a fluxional process is operative which creates an apparent molecular symmetry plane. This fluxional process is present in all the complexes and could not be slowed or arrested at low temperature, no doubt due to a low energy barrier.[22] This would involve either a Ru-alkene dissociation–association process or olefin rotation. However, the ^{13}C{^{1}H} NMR data of these complexes allow us to discard the first process, since olefin dissociation would, for example, result in a single resonance for all the methyl groups, a fact that is not observed in any case. The fluxionality observed must be, therefore, due to alkene rotation around the metal–olefin bond. Similar fluxional processes involving rotation of alkene fragments on pentacoordinated Pt(II) metal centers containing chelating *N*-donor ligands have also been reported previously by our group.[23] The similarity between 5-coordinated Pt(II) and 6-coordinated Ru(II) complexes is not surprising, since both metal fragments afford the same electron count and display similar frontier molecular orbitals.

Treatment of 1 with Disubstituted Alkenes. No reaction takes place between **1** and the 1,1'-disubsti-

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Table 2. Selected ¹H and ¹³C{¹H} NMR Data of the Vinylidene Derivatives[a]

compound	¹H NMR data				¹³C{¹H} NMR data						
	Ar	CH_2	NMe_2	C=CHPh	o-C	m-C	p-C	CH_2	NMe_2	C_α	C_β
[Ru(=C=CHPh)Cl$_2$(NN′N)] (**12**)	7.89(t, 7.8)	4.62(d, 16.4)	2.83, 2.80	4.64	160.8	120.7	139.2	74.1	56.4	301.8	113.4
	7.41(d, 7.8)	3.98(d, 16.4)									
[Ru(=C=CHPh)Cl(NN′N)(PPh$_3$)][BF4] (**14**)	8.13(t, 7.8)	4.58(d, 15.6)	2.56, 2.48	3.10(d, 5.4)	158.7	122.2	141.6	75.1	56.6	356.4	113.4
	7.70(d, 7.8)	4.03(d, 15.6)							56.1	(d, 16.6)	
[Ru(=C=CHPh)(NN′N)(PPh$_3$)][BF$_4$]$_2$ (**15**)	8.26(t, 8.1)	4.36(d, 16.5)	2.49, 2.29	5.61(d, 2.4)	158.5	122.2	142.8	74.3	55.6	358.7	120.4
		4.12(d, 16.5)							53.2	(d, 12.9)	
[Ru(=C=CHPh)(OTf)(NN′N)(PPh$_3$)][OTf] (**17**)	8.24(t, 7.8)	4.53(d, 16.6)	2.56, 2.53	5.95(br)	159.2	122.7	142.7	74.8	56.7	363.0	117.0
	7.75(d, 7.8)	4.15(d, 16.6)								(d, 17.7)	

[a] Spectra recorded using CD$_2$Cl$_2$ as a solvent. [b] All signals are singlets unless otherwise stated. [c] Key: d = doublet, t = triplet, br = broad. [d] Coupling constants (parentheses) in hertz. [e] All spectra reported correct integration for the proposed structures. [f] All the signals corresponding to the phenyl rings have been omitted for simplicity.

tuted alkene methyl methacrylate in CH$_2$Cl$_2$ or in benzene at RT. Heating of the reaction mixture in benzene does not result in any spectral changes, while the heating of the CH$_2$Cl$_2$ solution leads to complex mixtures from which no pure products could be isolated.

As expected from the conditions used in the production of **1**,[16] treatment of this complex with a large excess of norbornadiene causes no change in the starting materials (NMR) under any reaction conditions. Similarly, when other cyclic olefins such as cyclopentene, cyclohexene, or norbornene are used, a reaction does not take place even at high temperatures and for extended reaction periods. Also, acyclic internal olefins, such as *cis*-2-buten-1,4-diol, are likewise unreactive and the only complexes detected are again the starting materials. However, treatment of **1** with a *cis*-1,2-disubstituted olefin containing strongly electron-withdrawing groups, namely maleic anhydride, leads to the formation of a stable and isolable complex: i.e., *mer,trans*-[RuCl$_2$(η³-NN′N)(η²-C$_4$H$_2$O$_3$)] (**11**, Scheme 1). The coordination of this alkene is likely due to its electronic properties, since its steric size is similar to that of the other internal olefins tested. The coordination of the olefin fragment is unequivocally reflected in its ¹³C{¹H} NMR spectrum, which shows a *C*H resonance at δ = 74.1. This value lies in the range of other coordinated olefins and is shifted upfield by 62.5 ppm with respect to the free ligand. The signal corresponding to the carbonyl groups appears at δ = 176.0 for **11**. The structure of this species is also confirmed by its IR spectrum in CH$_2$Cl$_2$ solution, which shows the absorptions corresponding to the ν$_s$-(C−O) (1753 cm⁻¹) and ν$_{as}$(C−O) (1828 cm⁻¹), respectively (cf. 1782 and 1852 cm⁻¹ in the free ligand). These data for **11** reflect an increased back-donation from the metal center to the alkene, which points to extensive σ-donation from the relatively hard *N*-donor atoms of the terdentate NN′N ligand.[23a,24]

Synthesis of Vinylidene Derivatives Using 1 as Starting Material. Treatment of the binuclear complex **1** with phenylacetylene in 1,2-dichloroethane at reflux temperature (86 °C) affords the vinylidene complex *mer,cis*-[Ru(=C=CHPh)Cl$_2$(η³-NN′N)] (**12**, Scheme 1). The ¹³C{¹H} NMR spectrum of **12**, which shows the resonance assigned to the Ru=*C* atom at δ = 301.8, unequivocally indicates the tautomerization of the alkyne derivative to give the corresponding vinylidene

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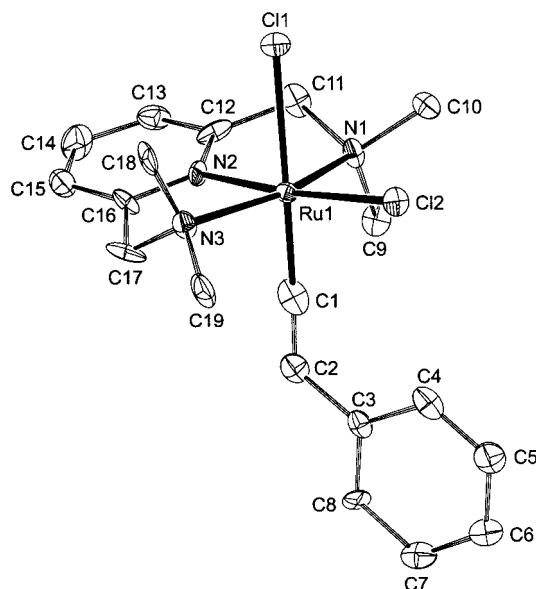
Figure 3. Molecular structure of compound **12**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

derivative.[1−3] The ¹H NMR spectrum of **12** shows the resonances of the diastereotopic C*H$_2$* and N*Me$_2$* groups of the pyridine ligand as doublets (δ = 4.62 and 3.98) and singlets (δ = 2.83 and 2.80), respectively, which points to the absence of a molecular symmetry plane as well as to rigid Ru−N coordination of both amine substituents. The signal assigned to the C*H* group of the vinylidene ligand appears as a singlet at δ = 4.64 (see Table 2).

To further confirm the structure proposed for this complex in solution, an X-ray diffraction study was carried out on a single crystal of **12** (Figure 3). Crystal and refinement data and a selection of bond distances and angles are given in Tables 3 and 4, respectively. The structure contains a hexacoordinated Ru center with the pyridine ligand occupying three meridional positions, while the chlorine ligands are positioned cis with respect to each other. If one assumes that the initial coordination site of the alkyne ligand is that which was previously occupied by the N$_2$ molecule, the ligand disposition shown in Figure 3 implies that a rearrangement process has taken place. The reason for this may be electronic in nature, although steric factors cannot be eliminated since the steric congestion is lower with the vinylidene ligand in the apical position. The Ru=C and C=C bond distances, 1.828(16) and 1.27(2) Å, respectively, are in the range of those expected for

Table 3. Crystal and Refinement Data of Complexes 12 and 17

	12	17
formula	$C_{19}H_{25}Cl_2N_3Ru$	$C_{38}H_{40}F_3N_3O_3PRuS,$ CF_3O_3S
fw	467.39	956.90
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a, Å	8.439(4)	13.647(2)
b, Å	13.450(6)	14.071(3)
c, Å	17.337(5)	23.267(3)
β, deg		116.316(10)
volume, Å^3	1967.8(14)	4004.8(12)
Z	4	4
$F(000)$	952	1952
D_{calc}, g/cm^3	1.578	1.587
μ, mm^{-1}	1.08	0.61
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
cryst size, mm^3	$0.13 \times 0.13 \times 0.43$	$0.08 \times 0.38 \times 0.55$
temp, K	150	150
θ limits, deg	1.9–27.5	1.7–25.0
min/max h, l, k	−7/10, −17/17, 0/22	−16/16, 0/16, −27/19
no. of reflns collected	6779	7909
no. of unique reflns	4505	7052
no. of reflns with $I > 2\sigma(I)$	3354	4848
no. of parameters	231	523
GOF on F^2	1.04	1.02
R_1 (on F, $I > 2\sigma(I)$)	0.0863	0.0634
wR_2 (on F^2, all data)	0.2463	0.1761

Table 4. Selected Bond Distances (Å) and Angles (deg) of Compound 12

Ru(1)−Cl(1)	2.539(3)	Ru(1)−Cl(2)	2.424(3)
Ru(1)−N(1)	2.168(11)	Ru(1)−N(2)	1.983(10)
Ru(1)−N(3)	2.194(9)	Ru(1)−C(1)	1.828(16)
C(1)−C(2)	1.27(2)	C(2)−C(3)	1.454(18)
Cl(1)−Ru(1)−Cl(2)	87.54(11)	Cl(1)−Ru(1)−N(1)	86.4(3)
Cl(1)−Ru(1)−N(2)	87.0(3)	Cl(1)−Ru(1)−N(3)	92.7(3)
Cl(1)−Ru(1)−C(1)	179.2(5)	Cl(2)−Ru(1)−N(1)	98.4(3)
Cl(2)−Ru(1)−N(2)	174.4(3)	Cl(2)−Ru(1)−N(3)	101.7(3)
Cl(2)−Ru(1)−C(1)	93.2(5)	N(1)−Ru(1)−N(2)	80.1(4)
N(1)−Ru(1)−N(3)	159.9(4)	N(1)−Ru(1)−C(1)	93.6(5)
N(2)−Ru(1)−N(3)	79.8(4)	N(2)−Ru(1)−C(1)	92.2(5)
N(3)−Ru(1)−C(1)	87.0(5)	Ru(1)−C(1)−C(2)	177.1(13)
C(1)−C(2)−C(3)	126.2(13)		

vinylidene−ruthenium(II) complexes.[1−3] Attempts to prepare similar Ru(II)-vinylidene compounds using the complex [Ru(PCP)Cl(PPh$_3$)] (PCP = [2, 6-(PPh$_2$CH$_2$)$_2$C$_6$-H$_3$]$^-$) have been reported previously by Jia et al.[25] However, these reactions do not lead to the expected vinylidene derivatives but to unusual coupling products of the alkyne fragment with C-ipso of the PCP ligand, a reaction that is not possible with the pincer ligand used in this study.

Synthesis of Vinylidene Derivatives Using [Ru-Cl$_2$(NN′N)(PPh$_3$)] as Starting Material. Attempts were performed to introduce a phosphine ligand in complex **12**, since it has been shown in many cases that P-donor ligands can play an important role in catalytic processes.[26] However, treatment of this compound with 1 or 2 equiv of Ag[BF$_4$] in the presence of an excess of phosphine leads to intractable mixtures of compounds. To obtain phosphine complexes similar to **12**, the compound *mer,trans*-[RuCl$_2$(NN′N)(PPh$_3$)] (**13**, Scheme

Scheme 2
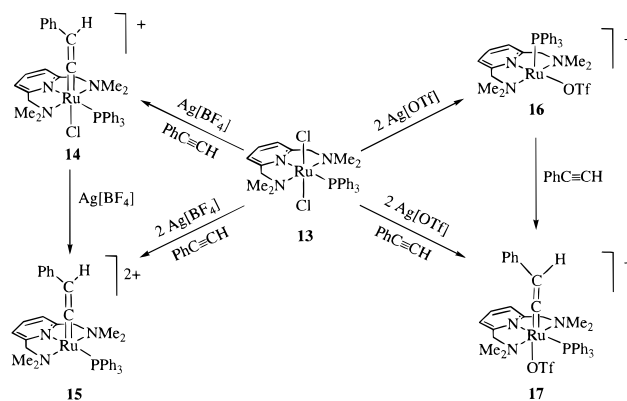
2) has been used as starting material to generate the corresponding vinylidene derivatives. Treatment of this complex with 1 equiv of Ag[BF$_4$] in CH$_2$Cl$_2$ in the presence of a large excess of phenylacetylene affords, in good yields, the monocationic vinylidene derivative *mer*-[Ru(=C=CHPh)Cl(NN′N)(PPh$_3$)][BF$_4$] (**14**, Scheme 2). The presence of the vinylidene ligand in **14** is clearly reflected by its ^{13}C{^{1}H} NMR spectrum, which shows the characteristic resonance of the Ru=C group at δ = 356.4 (d, $J_{C−P}$ = 16.6 Hz; Table 2). The value observed for the $J_{C−P}$ strongly suggests that the vinylidene and the phosphine ligand are positioned cis with respect to each other, as depicted in Scheme 2.[27,28] The presence of the other ligands and the absence of a symmetry plane in the complex are also clearly reflected by the ^{1}H and ^{31}P{^{1}H} NMR spectra (Table 2 and Experimental Section).

The use of these species as catalyst precursors in dimerization/polymerization processes requires the presence of a vacant coordination site on the metal center.[28] This vacant site can be easily generated in our vinylidene systems due to the presence of the chloride ligands, which can be removed by subsequent treatment with silver salts. Bearing these facts in mind, the monocationic complex **14** was treated with a second equiv of Ag[BF$_4$], to afford the dicationic, formally 16-electron complex [Ru(=C=CHPh)(NN′N)(PPh$_3$)][BF$_4$]$_2$ (**15**, Scheme 2). The dicationic nature of complex **15** is clearly reflected in its ^{31}P{^{1}H} NMR spectrum, which shows the resonance corresponding to the phosphine ligand shifted downfield with respect to the other monocationic vinylidene complexes reported (δ = 38.8). Related electron-deficient compounds containing the terdentate NN′N ligand have been isolated previously.[16] Treatment, for example, of **13** with 2 equiv of Ag[OTf] (OTf = trifluoromethane sulfonate) gives the monocationic, pentacoordinate derivative [Ru(OTf)(NN′N)-(PPh$_3$)][OTf] (**16**, Scheme 2).

A new vinylidene derivative, i.e., *mer*-[Ru(=C=CHPh)-(OTf)(NN′N)(PPh$_3$)][OTf] (**17**, Scheme 2), is formed when complex **16** is treated with an excess of phenylacetylene in CH$_2$Cl$_2$ at reflux temperature for 30 min. The Ru−C carbon atom of the vinylidene ligand appears in its ^{13}C{^{1}H} NMR spectrum as a doublet at δ = 363.0 ($J_{C−P}$ = 17.7 Hz). This suggests a cis-arrangement of

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(28) de los Ríos, I.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1998**, *17*, 3356.
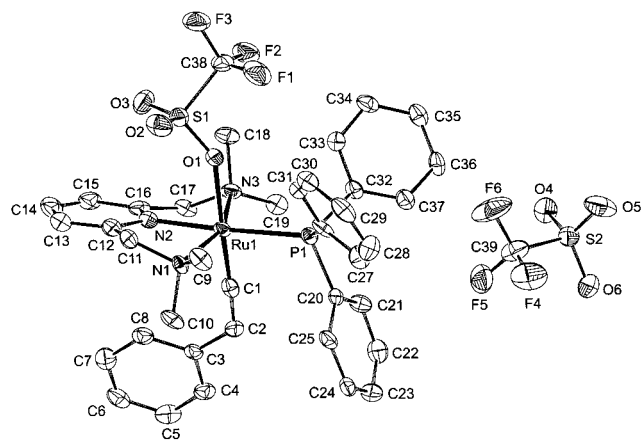
Figure 4. Molecular structure of compound **17**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) of Compound 17

Ru(1)−C(1)	1.796(7)	Ru(1)−N(1)	2.220(5)
Ru(1)−N(2)	2.043(6)	Ru(1)−N(3)	2.211(6)
Ru(1)−O(1)	2.229(5)	Ru(1)−P(1)	2.4358(18)
C(1)−C(2)	1.321(10)	C(2)−C(3)	1.454(10)
P(1)−Ru(1)−O(1)	89.27(12)	P(1)−Ru(1)−N(1)	100.81(15)
P(1)−Ru(1)−N(2)	176.13(17)	P(1)−Ru(1)−N(3)	102.77(16)
P(1)−Ru(1)−C(1)	89.6(2)	O(1)−Ru(1)−N(1)	87.88(19)
O(1)−Ru(1)−N(2)	86.9(2)	O(1)−Ru(1)−N(3)	91.45(19)
O(1)−Ru(1)−C(1)	177.7(2)	N(1)−Ru(1)−N(2)	78.5(2)
N(1)−Ru(1)−N(3)	156.4(2)	N(1)−Ru(1)−C(1)	94.3(2)
N(2)−Ru(1)−N(3)	77.9(2)	N(2)−Ru(1)−C(1)	94.2(3)
N(3)−Ru(1)−C(1)	86.8(2)	Ru(1)−C(1)−C(2)	175.0(6)
C(1)−C(2)−C(3)	126.4(7)		

the vinylidene and the phosphine ligands.[27,28] Moreover, a characteristic AB pattern was observed for resonances corresponding to the benzylic protons of the pyridine ligand (see Table 2). Although the analytical and spectroscopic data of **17** unequivocally confirm the schematic structure shown in Scheme 2, an X-ray crystallographic study was carried out on a single crystal of **17**. The molecular structure of **17** in the solid state is shown in Figure 4. Crystal and refinement data and a selection of bond distances and angles are given in Tables 3 and 5, respectively.

Complex **17** presents a Ru complex in an octahedral environment, with the NN′N ligand occupying three meridional positions, while a fourth position is occupied by the triphenylphosphine ligand. The vinylidene ligand is placed in an apical site, positioned cis with respect to the above-mentioned ligands. One of the two triflate molecules occupies the other apical site and is positioned trans with respect to the vinylidene ligand. The second triflate molecule is not coordinated. The Ru=C and C= C bond distances in the vinylidene ligand are 1.796(7) and 1.321(10) Å, respectively, in the range of those observed for similar complexes.[1−3] The ligand arrangement shown in Figure 4 involves a migration of the phosphine ligand from an apical position in **16** to a meridional position in **17**, showing that these isomerization processes can occur under mild conditions. The vinylidene ligand in complex **17** adopts an endo disposition with respect to the pyridine ring of the "pincer" ligand, in contrast with the exo in complex **12** (vide supra). These different dispositions of the vinylidene ligands in **12** and **17** are no doubt due to the bulkiness

Table 6.

catalyst	time (h)	temp (°C)	solvent	conversion (%)	dimeric products (%)			trimeric products (%)	other products (%)
					cis	trans	Z		
12	3	25	CH₂Cl₂	3	16	41	43		
12	4	110	toluene	8	12	43	45		
12	24	80	benzene	10	5	18	18	55	4

of the triphenylphosphine ligand in **17**, which may cause a strong interaction with the phenyl ring of the vinylidene ligand.

Attempts to use **12** as catalyst precursor for oligomerization of phenylacetylene were performed, although the results obtained were poor (see Table 6 and Experimental Section). The formation of the three possible isomers of the corresponding dimeric products (i.e., cis, trans, and *Z*) has been observed in all the runs (CG−MS, ¹H NMR), although the conversion appeared to be low (<10%). The use of more vigorous reaction conditions leads to the formation of small amounts of trimeric products together with the dimeric products observed previously (GC−MS). However, the large number of products and the low conversions observed in this case prevented their isolation and characterization. When acetylene gas is used in place of phenylacetylene, mixtures of many products were obtained, including dimeric products of phenylacetylene, which may arise from decomposition of the catalyst precursor. Addition of 1 or 2 equiv of Ag[BF₄] to the catalytic mixtures results in the decomposition of the precursor and does not increase the catalytic rate nor the product yields.

Treatment of the Olefin Derivatives with Carbon Monoxide. The olefin ligands in complexes **2**−**11** can be easily replaced by carbon monoxide (1 atm, 80 °C) to afford the previously known[16] monocarbonyl derivative *mer,trans*-[RuCl₂(η^3-NN′N)(CO)] (**12**; eq 1).

(1)

2-11
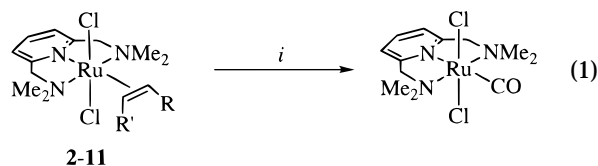
i: 86 °C in 1,2-dichloroethane under CO atmosphere; - alkene

This compound is also accessible from **1** by direct treatment with CO. The olefin substituents do not appear to have significant influence on this process, as reaction times (1.5−2 h) and yields are similar for all complexes tested. This reaction is irreversible and points to stronger binding of CO than alkenes to ruthenium.[24a]

Conclusions

The Ru(II) dinitrogen bridged complex **1** is a valuable starting material for the synthesis of new organometallic compounds because of its versatile reactivity patterns under mild conditions. A stabilizing effect on Ru−alkene bonding is exerted by the bis(ortho-diamino)pyridine "pincer" ligand, which accounts for the facile reactions of **1** with 1-alkenes and with *cis*-alkenes that have electron-withdrawing substituents. Better π-accepting ligands, i.e., carbon monoxide, however, easily displace the alkene ligands in **2**−**11**. These observations

are similar to those reported by Davies et al. for analogous reactions of [Ru(η^5-C$_5$H$_5$)Cl(dppe)] with alkenes.[29]

Vinylidene ligands can be juxtaposed with the neutral NN′N "pincer" ligand Ru(II) complexes. The facile accessibility and high-yield synthesis of these vinylidene derivatives facilitate their further study as catalyst precursors.[30] The presence of the chelating NN′N ligand arrays in these catalyst precursors may prevent the formation of byproducts which arise from metal framework ligand dissociation and subsequent catalyst deactivation. This ligand also facilitates the spectroscopic characterization of the species present during the catalytic runs.

Experimental Section

General. Solvents were dried over sodium benzophenone ketyl (Et$_2$O, hydrocarbons) or CaH$_2$ (CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl) and distilled under a nitrogen atmosphere prior to use. Unless otherwise stated, the reactions were performed under an atmosphere of nitrogen at room temperature. All reagents were obtained from commercial sources and were used without further purification. Complexes **1** and **13** were prepared as described previously.[16] Infrared spectra were recorded in solution on a UNICAM FT-IR 5000 spectrophotometer, using 0.1 mm NaCl cells. ^{1}H (200.133 and 300.103 MHz), ^{31}P{^{1}H} (81.018 and 121.486 MHz), and ^{13}C{^{1}H} (50.323 and 75.453 MHz) NMR spectra were recorded at room temperature with either a Bruker AC-200 or AC-300 instrument, using SiMe$_4$ as internal standard (δ_H or δ_C = 0.00) or external H$_3$PO$_4$ (85%, δ_P = 0.00). Fast atom bombardment mass spectra (FAB-MS) were obtained from the Analytical Chemical Department of Utrecht University on two different machines: (1) a JEOL JMS SX/SX 102A four-sector mass spectrometer, operated at 10 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 5 mA emission current, producing a beam of 6 keV xenon atoms; (2) a JEOL JMS AX 505 spectrometer, operated at 3 kV accelerating voltage, equipped with a JEOL MS-FAB 10 D FAB gun operated at a 10 mA emission current, producing a beam of 6 keV xenon. Nitrobenzyl alcohol was used as matrix. Data acquisition and processing were accomplished using JEOL Complement software. Microanalyses were obtained from H. Kölbe Mikroanalytisches Laboratorium (Germany). Pertinent ^{1}H and ^{13}C{^{1}H} NMR data are reported in Tables 1 and 2.

Syntheses of Alkene Derivatives. The synthesis of **2** will serve as a representative example. Complexes **3**−**11** were prepared in a similar fashion using an excess of the appropriate alkene. The synthesis of **10** was performed under an atmosphere of argon.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CH$_2$)] (2). Ethylene was gently bubbled through a solution of **1** (100 mg, 0.131 mmol) in CH$_2$Cl$_2$ (20 mL) for 30 min. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 20 mL) to give **2** as a green solid (95 mg, 92%). FAB-MS *m/z*: 393 [M$^+$]. Anal. Found: C, 38.84; H, 5.90; N, 10.09. Calcd for C$_{13}$H$_{23}$Cl$_2$N$_3$Ru·0.2 CH$_2$Cl$_2$ (410.34): C, 38.64; H, 5.75; N, 10.24. The presence of lattice CH$_2$Cl$_2$ was confirmed by ^{1}H NMR spectroscopy for a recrystallized sample of **2** (see Table 1).

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(30) Complexes **14**, **15**, and **17** show catalytic activity in the ring-opening metathesis polymerization of norbornene derivatives. For example, complex **15** polymerizes 800 equiv of norbornene in 1 h (CH$_2$-ClCH$_2$Cl, 80 °C) to afford 95% *trans*-polynorbornene. Complexes **14** and **17** present lower turnover numbers. Complex **12** is not active: del Río, I.; van Koten, G. *Tetrahedron Lett.*, in press (Ms. TETL/1998/871).

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CH−CH=CH$_2$)] (3). Yield: 91% (brown solid). FAB-MS *m/z*: 419 [M$^+$]. Anal. Found: C, 42.86; H, 5.89; N, 9.92. Calcd for C$_{15}$H$_{25}$Cl$_2$N$_3$Ru (419.39): C, 42.96; H, 6.01; N, 10.02.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHCH$_2$Ph)] (4). Yield: 95% (yellow solid). FAB-MS *m/z*: 483 [M$^+$]. Anal. Found: C, 50.12; H, 6.22; N, 8.43. Calcd for C$_{20}$H$_{29}$Cl$_2$N$_3$Ru (483.48): C, 49.69; H, 6.05; N, 8.69.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHCH$_2$Br)] (5). Yield: 94% (red solid). FAB-MS *m/z*: 406 [M$^+$ − Br]. Anal. Found: C, 34.38; H, 4.85; N, 8.66. Calcd for C$_{14}$H$_{24}$BrCl$_2$N$_3$Ru (486.28): C, 34.58; H, 4.97; N, 8.64.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHCH$_2$OH)] (6). Yield: 72% (pale green solid). FAB-MS *m/z*: 423 [M$^+$]. Anal. Found: C, 39.59; H, 5.96; N, 10.01. Calcd for C$_{14}$H$_{25}$Cl$_2$N$_3$ORu (423.38): C, 39.72; H, 5.95; N, 9.93.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHCHO)] (7). Yield: 73% (yellow solid). FAB-MS *m/z*: 421 [M$^+$]. IR (CH$_2$Cl$_2$) ν(CO): 1666 cm^{-1}. Anal. Found: C, 39.84; H, 5.50; N, 9.72. Calcd for C$_{14}$H$_{23}$Cl$_2$N$_3$ORu (421.36): C, 39.91; H, 5.50; N, 9.97.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHCN)] (8). Yield: 91% (pale red solid). FAB-MS *m/z*: 418 [M$^+$]. IR (CH$_2$Cl$_2$) ν-(CN): 2210 cm^{-1}. Anal. Found: C, 39.61; H, 5.32; N, 13.63. Calcd for C$_{14}$H$_{22}$Cl$_2$N$_4$Ru·0.05CH$_2$Cl$_2$ (422.61): C, 39.93; H, 5.27; N, 13.26.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHCO$_2$CH$_3$)] (9). Yield: 76% (yellow-green solid). FAB-MS *m/z*: 451 [M$^+$]. IR (CH$_2$Cl$_2$) ν(CO): 1692 cm^{-1}. Anal. Found: C, 37.64; H, 5.34; N, 9.06. Calcd for C$_{15}$H$_{25}$Cl$_2$N$_3$O$_2$Ru (451.39): C, 37.91; H, 5.58; N, 9.31.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-CH$_2$=CHPh)] (10). Yield: 80% (pale green solid). FAB-MS *m/z*: 469 [M$^+$]. Anal. Found: C, 48.88; H, 5.91; N, 8.78. Calcd for C$_{19}$H$_{27}$Cl$_2$N$_3$Ru (469.45): C, 48.61; H, 5.80; N, 8.95.

mer,trans-[RuCl$_2$(η^3-NN′N)(η^2-C$_4$H$_2$O$_3$)] (11). Yield: 87% (pale brown solid). FAB-MS *m/z*: 464 [M$^+$]. IR (CH$_2$Cl$_2$) ν(CO): 1828 (s), 1753 (s) cm^{-1}. Anal. Found: C, 38.72; H, 4.55; N, 8.89. Calcd for C$_{15}$H$_{21}$Cl$_2$N$_3$O$_3$Ru (463.36): C, 38.88; H, 4.57; N, 9.07.

Syntheses of Vinylidene Derivatives. mer,cis-[Ru(=C= CHPh)Cl$_2$(NN′N)] (12). Phenylacetylene (0.5 mL, 4.552 mmol) was added to a solution of complex **1** (300 mg, 0.393 mmol) in ClCH$_2$CH$_2$Cl (40 mL) and the resulting solution stirred at reflux temperature for 45 min. The solvent was removed under reduced pressure and the solid residue recrystallized from a mixture of CH$_2$Cl$_2$/pentane to give compound **12** as a brown solid (280 mg, 43%). Anal. Found: C, 48.61; H, 5.29; N, 8.85. Calcd for C$_{19}$H$_{25}$Cl$_2$N$_3$Ru (467.44): C, 48.82; H, 5.39; N, 8.99. FAB-MS *m/z*: 432 (M$^+$ − Cl).

mer-[Ru(=C=CHPh)Cl(NN′N)(PPh$_3$)][BF$_4$] (14). Phenylacetylene (0.1 mL, 0.911 mmol) was added to a solution of **13** (813 mg, 1.301 mmol) in CH$_2$Cl$_2$ (40 mL), and to this solution was added 257 mg (1.301 mmol) of Ag[BF$_4$]. The resulting mixture was then stirred at RT for 30 min. The formed solid was filtered off and the solvent removed under reduced pressure. The solid residue was washed with ether (3 × 25 mL) to give compound **14** as a pink solid (750 mg, 74%). ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): 10.0 ppm. Anal. Found: C, 56.98; H, 5.18; N, 5.32. Calcd for C$_{37}$H$_{40}$BClF$_4$N$_3$PRu (781.08): C, 56.90; H, 5.16; N, 5.38. FAB-MS *m/z*: 694 (M$^+$).

[Ru(=C=CHPh)(NN′N)(PPh$_3$)][BF$_4$]$_2$ (15). Phenylacetylene (0.5 mL, 4.552 mmol) was added to a solution of **13** (632 mg, 1.011 mmol) in CH$_2$Cl$_2$ (30 mL), and to this solution was added 399 mg (2.022 mmol) of Ag[BF$_4$]. The resulting mixture was then stirred at RT for 45 min. The solid formed was filtered off over Celite, the solvent was concentrated under reduced pressure to 5 mL, and 50 mL of ether was added. The solid residue was washed with ether (3 × 30 mL) to give compound **15** as a pale brown solid (800 mg, 95%). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 38.8 ppm. Anal. Found: C, 53.31; H, 4.84; N,

4.96. Calcd for $C_{37}H_{40}B_2F_8N_3PRu$ (832.43): C, 53.39; H, 4.84; N, 5.05. FAB-MS *m/z*: 678 (M$^+$ + F).

***mer*-[Ru(=C=CHPh)(OTf)(NN′N)(PPh₃)][OTf] (17).** A solution of **13** (400 mg, 0.640 mmol) in CH_2Cl_2 (40 mL) was treated with Ag[OTf] (500 mg, 1.946 mmol). The resulting mixture was then stirred at RT for 30 min, whereupon the color changed from orange to dark violet. Phenylacetylene (0.1 mL, 0.911 mmol) was added to the resulting solution after AgCl filtration, and the mixture was stirred at reflux temperature for 30 min. The solvent was then removed under reduced pressure and the solid residue washed with ether (2 × 20 mL) to give compound **17** as a pale brown solid (450 mg, 74%). ^{31}P-{^{1}H} NMR (CD_2Cl_2): 18.2 ppm. Anal. Found: C, 46.83; H, 4.08; N, 4.18. Calcd for $C_{39}H_{40}F_6N_3O_6PRuS_2 \cdot 0.75CH_2Cl_2$ (1020.65): C, 46.78; H, 4.10; N, 4.12. FAB-MS *m/z*: 808 (M$^+$).

General Procedure for the Reaction of the Alkene Derivatives with Carbon Monoxide. A 0.100 mmol portion of the alkene complex was dissolved in 40 mL of $ClCH_2CH_2Cl$ and heated to reflux temperature for ca. 2 h under a CO atmosphere. The solvent was removed under reduced pressure and the solid residue washed with pentane to give [RuCl₂(NN′N)(CO)] in quantitative yield. Its analytical and spectroscopic data matched those reported in the literature.[16]

General Procedure for the Catalytic Coupling of Alkynes. A 10 mg (0.021 mmol) sample of complex **12** was dissolved in 40 mL of the appropriate solvent, and 2.3 mL (21 mmol) of phenylacetylene and 4.4 µL (0.032 mmol) of Et_3N were added to this solution. When the catalytic run was completed, a portion of the reaction mixture was dried under reduced pressure and the residue analyzed by ^{1}H NMR. The remaining solution was filtered over neutral alumina (activity IV) and the solution analyzed by GC–MS. Conversions are given based on the amount of phenylacetylene that remained unreacted. Relative percentages of the products are based on GC integration.

Crystallographic Determinations. Crystal Structure of 12. A red crystal obtained by layering diethyl ether on a solution of the complex in dichloromethane/benzene was used for the X-ray diffraction study. Diffractometer: Enraf-Nonius CAD4T with rotating anode and graphite monochromator (Mo Kα, λ = 0.710 73 Å). Structure solution was performed with direct methods (SIR-97).[31] Structure refinement was done with SHELXL-97[32] against F^2. Non-hydrogen atoms were refined

with anisotropic temperature parameters; hydrogen atoms were refined as rigid groups. Structure graphics, checking for higher symmetry and absorption correction (routine DELABS, 0.33−0.76 transmission range), were performed with the program PLATON.[33] The absolute structure was determined by including the Flack *x* parameter[34] into the refinement, resulting in *x* = 0.00(13).

Crystal Structure of 17·CH₂Cl₂·C₆H₆. An orange crystal obtained by layering diethyl ether on a solution of the complex in dichloromethane/benzene was used for the X-ray diffraction study. Diffractometer: Enraf-Nonius CAD4T with rotating anode and graphite monochromator (Mo Kα, λ = 0.710 73 Å). Structure solution was done with direct methods (SIR-97).[31] Structure refinement was performed with SHELXL-97[32] against F^2. Non-hydrogen atoms were refined with anisotropic temperature parameters; hydrogen atoms were refined as rigid groups. Structure graphics, checking for higher symmetry and absorption correction (ψ-scans, 0.86−0.98 transmission range), were performed with the program PLATON.[33]

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **12** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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