Reactivity of $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}PhC{=}CHPh)(CO)_6]$ with Alkynes. Insertion Reactions of Nonactivated Alkynes into Ru−C and Ru−N Bonds

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The μ-1-azavinylidene−μ-alkenyl diruthenium complex $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}PhC{=}CHPh)(CO)_6]$ (**1**) reacts with excess 1-phenyl-1-propyne or 3-hexyne in 1,2-dichloroethane at reflux temperature to give *cis*-stilbene and the metallacyclic derivatives $[Ru_2\{\mu\text{-}\eta^3\text{:}\eta^4\text{-}R^1C{=}CR^2CR^1{=}CR^2N{=}CPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$ (**2**, $R^1 = Ph$, $R^2 = Me$; **3**, $R^1 = R^2 = Et$). These compounds contain ligands that result from the ortho metalation of a phenyl group of the original 1-azavinylidene ligand, the release of *cis*-stilbene, the insertion of the corresponding alkyne molecule into a Ru−N bond, and the insertion of a second alkyne molecule into a Ru−C bond. The reaction of compound **1** with phenylacetylene in 1,2-dichloroethane at reflux temperature gives *cis*-stilbene, $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu\text{-}\eta^2\text{:}\eta^4\text{-}PhC{=}CHCH{=}CPh)(CO)_5]$ (**4**), and $[Ru\{\eta^5\text{-}PhC{=}CHCPh{=}CHCPh{=}CHN{=}CPh(C_6H_4)\}(CO)_2]$ (**5**). The hydrocarbyl ligand of **4**, which can be described as a 1,4-diphenylbuta-1,3-diene-1,4-diyl ligand, arises from a head-to-head dimerization of phenylacetylene, whereas the organic ligand of **5** results from an unprecedented insertion of phenylacetylene into a Ru−N bond in addition to a head-to-tail trimerization of phenylacetylene. Thermolysis of compound **1** in refluxing 1,2-dichloroethane gives the tetranuclear derivative $[C_{48}H_{30}N_2O_8Ru_4]$ (**6**) and the binuclear product $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^3\text{:}\eta^4\text{-}PhCH{=}CPhCPh{=}CPh)(CO)_4]$ (**7**). The molecular structure of complex **6** remains unknown. Compound **7** contains a bridging dienyl ligand (with a phenyl substituent η^2-coordinated to a Ru atom) that arises from the coupling of diphenylacetylene with the diphenylalkenyl ligand of **1**. Mechanistic proposals that account for the formation of complexes **2**−**7** from compound **1** are given. The new C−N bonds of compounds **2**, **3**, and **5** are remarkable because they have been formed by migratory insertion of weakly electrophilic alkynes into Ru−N bonds, a process that has hitherto been very seldom observed only with internal alkynes and never with terminal alkynes.

Introduction

The past decade has experienced an increasing interest in the synthesis and reactivity of late-transition-metal amido complexes as a consequence of the relative scarcity of such compounds[1−10] and of their potential use in C−N bond-forming reactions.[6−10]

In this field, we have recently described a high-yield synthesis of $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(CO)_{10}]$,[5] a compound that contains a bridging amido ligand derived from benzophenone imine, which can be regarded as a 1-azavinylidene ligand.[11] As part of a general study of

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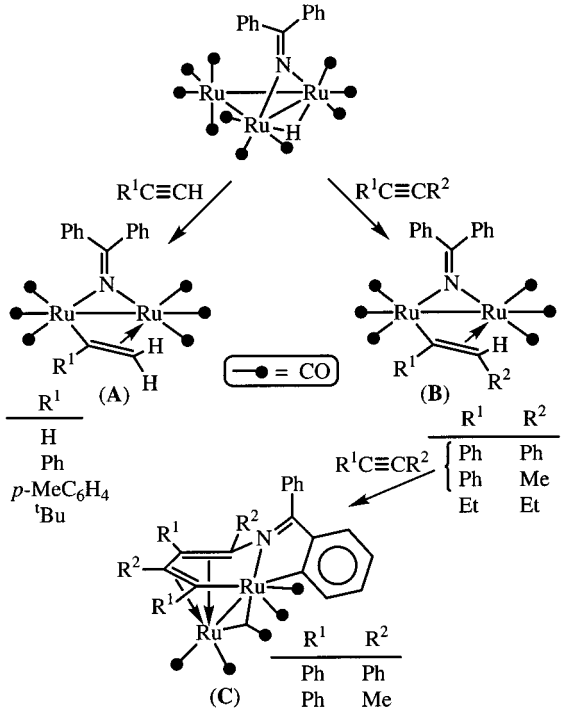
Scheme 1



the reactivity of this trinuclear cluster compound,[5−7,10,12] we have previously reported that its thermal reactions with alkyne reagents lead to the binuclear derivatives $[Ru_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}R^1C{=}CHR^2)(CO)_6]$ (**A** and **B** in Scheme 1).[7] These compounds contain alkenyl ligands that arise from the insertion of the alkynes into Ru−H bonds. Contrasting with the products derived from terminal alkynes (**A** in Scheme 1) and 3-hexyne (**B**; $R^1 = R^2 = Et$ in Scheme 1), which were thermally stable in the presence of more alkyne, the products derived from internal alkynes containing at least one phenyl group, such as diphenylacetylene and 1-phenyl-1-propyne, underwent a subsequent reaction with more alkyne, leading to the metallacyclic binuclear derivatives $[Ru_2\{\mu\text{-}\eta^3{:}\eta^4\text{-}R^1C{=}CR^2CR^1{=}CR^2N{=}CPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$ (**C** in Scheme 1) as the final products.[7] These metallacyclic compounds are remarkable because they contain new C−C and C−N bonds formed by insertion processes.

To date, the formation of C−N bonds via insertion of alkynes into the M−N bonds of amido complexes is unusual. In stoichiometric reactions, it has only been seldom achieved (a) with the highly electrophilic alkyne dimethyl acetylenedicarboxylate, for normal amido complexes,[8] and (b) with very few internal alkynes containing at least one phenyl group, when the N atom of the M−N bond belongs to a 1-azavinylidene ligand.[6,7,10] A few reports on catalytic hydroamination of alkynes with early-transition-metal, lanthanide, and actinide complexes invoke an alkyne insertion into a M−N bond as an important step of the corresponding catalytic mechanism.[13a−g] However, catalytic alkyne hydroaminations with late-transition-metal complexes are scarce and mechanistically far less studied.[13a,h−m]

Our interest in reactions leading to new C−N bonds by insertion processes[6,7,10] and the ready reaction of the compound $[Ru_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}PhC{=}CHPh)(CO)_6]$ (**1**) (**B**, $R^1 = R^2 = Ph$ in Scheme 1) with diphenylacetylene to give a product containing one such bond[7] (indicating an enhanced reactivity of compound **1** as compared with those of other structurally similar binuclear alkenyl derivatives derived from other alkynes), prompted us to study the reactivity of this binuclear compound (**1**) with a variety of alkyne reagents. We now describe that these reactions lead to products containing new ligands that result from alkyne insertion processes into Ru−C and Ru−N bonds. The first insertion of a terminal alkyne into a Ru−N bond is also reported.

Results

Reactions of Compound 1 with Internal Alkynes. Compound **1** was stirred with an excess (3−4-fold) of 1-phenyl-1-propyne and 3-hexyne in 1,2-dichloroethane at reflux temperature until the IR spectra of the solutions no longer showed the bands of the starting material (1.5−2 h). In both cases, GC analyses of the resulting solutions indicated the presence of *cis*-stilbene. Chromatographic workups allowed the isolation of two metallacyclic derivatives, the known $[Ru_2\{\mu\text{-}\eta^3{:}\eta^4\text{-}PhC{=}CMeCPh{=}CMeN{=}CPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$[7] (**2**) and the novel $[Ru_2\{\mu\text{-}\eta^3{:}\eta^4\text{-}EtC{=}CEtCEt{=}CEtN{=}CPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$ (**3**) (Scheme 2).

Compound **2** was characterized by comparing its spectroscopic data with those reported previously.[7] The structure of compound **3** was assigned on the basis of the similarity of its IR spectrum in the carbonyl region

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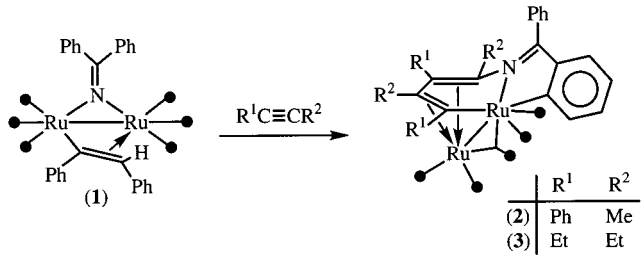
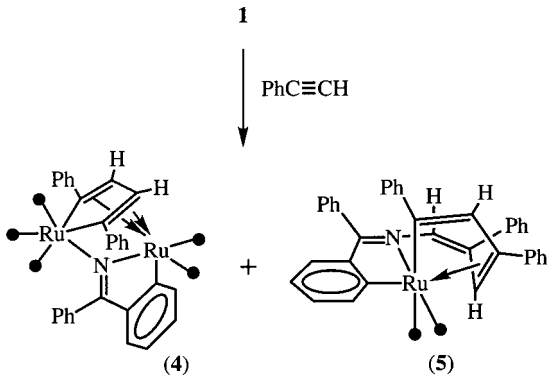
Scheme 2



Scheme 3



with that of complex **2** and was confirmed by its microanalysis, mass spectrum (which shows the corresponding molecular ion), and ^{1}H NMR spectrum (which shows four ethyl groups and the orthometalation of a phenyl ring).

It is interesting to note that the direct thermal reaction of the trinuclear precursor $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(CO)_{10}]$ with an excess of 3-hexyne leads to the binuclear alkenyl derivative $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}EtC{=}CHEt)(CO)_6]$, which does not react further with 3-hexyne (Scheme 1).[7]

To extend the results described above, the reactions of complex **1** with other internal alkynes were studied. Unfortunately, the reactions of complex **1** with the internal alkynes methyl phenylpropynate, dimethyl acetylenedicarboxylate, bis(trimethylsilyl)acetylene, 2-butyn-1-ol, 2,4-hexadiyne, 1,6-diphenoxy-2,4-hexadiyne, and diphenylbutadiyne gave mixtures of many products that we could not separate and/or identify.

Reactions of Compound 1 with Terminal Alkynes. Complex **1** reacted with phenylacetylene, under comparable reaction conditions with those commented above for the reactions with internal alkynes, to give a mixture of products from which the compounds $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu\text{-}\eta^2\text{:}\eta^4\text{-}PhC{=}CHCH{=}CPh)(CO)_5]$ (**4**) and $[Ru\{\eta^5\text{-}PhC{=}CHCPh{=}CHCPh{=}CHN{=}CPh(C_6H_4)\}(CO)_2]$ (**5**) were separated by chromatographic methods (Scheme 3). A qualitative GC analysis of the reaction solution indicated the presence of *cis*-stilbene. These two compounds were always obtained in medium to low yields (<30% for **4** and <20% for **5**). The use of longer reaction times and/or larger alkyne-to-metal ratios only increased the formation of intractable decomposition products. The microanalyses and spectroscopic data (MS, IR, ^{1}H NMR) of **4** and **5** did not provide enough information to make precise structure assignments for these compounds. The structures depicted in Scheme 3 are based on X-ray diffraction studies.

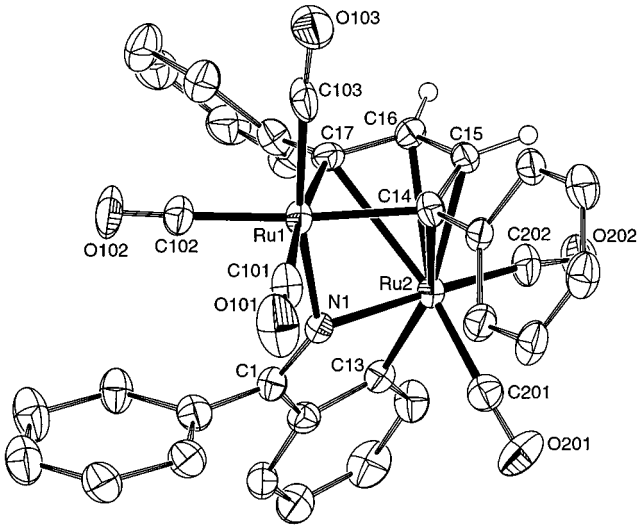


Figure 1. Molecular structure of compound **4** (phenyl H atoms omitted for clarity). Thermal ellipsoids represent the 40% probability level.

Figure 1 shows a view of compound **4**. Selected interatomic distances are given in Table 1. A 1,4-diphenylbuta-1,3-diene-1,4-diyl ligand, which undoubtedly arises from the coupling of two phenylacetylene molecules through their terminal carbon atoms, is η^2-attached to Ru(1) via two σ-interactions, forming a ruthenacyclopentadiene fragment, and η^4-attached to the Ru(2) atom through the four carbon atoms involved in the diene moiety.[14] Curiously, the bond length of the central C−C bond of the butadiene-1,4-diyl fragment, C(15)−C(16) = 1.33(1) Å, is between those found for the outer C−C bonds, C(14)−C(15) = 1.38(1) Å and C(16)−C(17) = 1.29(1) Å. In the literature, there are examples in which the central C−C bond of a η^4-butadiene fragment is shorter[15a−c] or longer[15c−e] than the outer C−C bonds. As found previously for related systems,[14,15] the distances associated with the σ-bonds Ru(1)−C(14) and Ru(1)−C(17), 1.954(7) and 2.129(7) Å, are shorter than those associated with the π-interactions between Ru(2) and the four C atoms of the butadiene-1,4-diyl fragment, which range from 2.292(7) to 2.520(7) Å, the two longest ones being those corresponding to the distances between Ru(2) and the outer C atoms. An ortho-metalated 2,2-diphenyl-1-azavinylidene ligand is attached to both Ru atoms through the nitrogen atom and to Ru(2) through the metalated phenyl ring.[16] The asymmetry imposed by this bulky ligand is responsible for the difference in the bond lengths of the outer C−C

(14) Related binuclear complexes containing $\mu\text{-}\eta^2\text{:}\eta^4$-buta-1,3-diene-1,4-diyl ligands are well-documented in the literature. See, for example: (a) Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 828. (b) Aime, S.; Tiripicchio, A.; Tiripicchio-Camellini, M.; Deeming, A. J. *Inorg. Chem.* **1981**, *20*, 2027. (c) Astier, A.; Daran, J. C.; Jeannin, Y.; Rigault, C. *J. Organomet. Chem.* **1983**, *241*, 53. (d) Bruce, M. I.; Matisons, J. C.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1983**, *251*, 249. (e) Aime, S.; Occhiello, E. *J. Chem. Soc., Dalton Trans.* **1988**, 1863. (f) Han, S. H.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 5621.

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Table 1. Selected Interatomic Distances (Å) in 4, 5, and 7

	4	5[a]	7
Ru(1)−Ru(2)	3.134(1)		2.7082(4)
Ru(1)−N(1)	2.057(6)	2.075(7)	2.051(3)
Ru(2)−N(1)	1.980(6)		2.065(3)
Ru(1)−C(101)	1.936(9)	1.93(1)	1.867(4)
Ru(1)−C(102)	1.778(8)	1.86(1)	1.913(4)
Ru(1)−C(103)	1.890(9)		
Ru(2)−C(201)	1.765(9)		1.847(4)
Ru(2)−C(202)	1.866(8)		1.882(5)
Ru(1)−C(13)		2.084(4)	
Ru(1)−C(14)	1.954(7)		2.415(3)
Ru(1)−C(15)			2.296(3)
Ru(1)−C(17)	2.129(7)		
Ru(1)−C(20)			2.499(3)
Ru(1)−C(22)		2.399(9)	
Ru(1)−C(23)		2.482(8)	
Ru(1)−C(31)		2.127(9)	
Ru(1)−C(35)			2.113(3)
Ru(2)−C(13)	2.023(7)		
Ru(2)−C(14)	2.426(7)		2.436(3)
Ru(2)−C(15)	2.292(7)		
Ru(2)−C(16)	2.343(7)		
Ru(2)−C(17)	2.520(7)		
Ru(2)−C(21)			2.182(3)
Ru(2)−C(28)			2.278(3)
Ru(2)−C(35)			2.205(3)
C(101)−O(101)	1.11(1)	1.12(1)	1.138(4)
C(102)−O(102)	1.018(9)	1.15(1)	1.117(4)
C(103)−O(103)	1.14(1)		
C(201)−O(201)	1.07(1)		1.141(4)
C(202)−O(202)	1.08(1)		1.139(5)
C(1)−N(1)	1.243(9)	1.31(1)	1.276(4)
C(14)−N(1)		1.41(1)	
C(14)−C(15)	1.38(1)	1.35(1)	1.474(4)
C(14)−C(21)			1.457(4)
C(15)−C(16)	1.33(1)		
C(15)−C(22)		1.47(1)	
C(16)−C(17)	1.29(1)		
C(21)−C(28)			1.438(4)
C(22)−C(23)		1.39(1)	
C(23)−C(30)		1.48(1)	
C(28)−C(35)			1.415(4)
C(30)−C(31)		1.34(1)	

[a] Data for only one of the two independent molecules of the asymmetric unit are given. Structural parameters for the two molecules are equivalent within the standard deviations.

bonds of the butadiene-1,4-diyl fragment as well as for the asymmetry in the distances between the metal atoms and the butadiene-1,4-diyl fragment carbon atoms (Table 1). The ligand shell of the molecule is completed with five carbonyl ligands. The long Ru(1)−Ru(2) distance, 3.134(1) Å, is in agreement with an electron count of 36, for which no metal−metal bond is expected.[17] In fact, the molecule can be considered as being formed by two octahedral ruthenium(II) fragments.

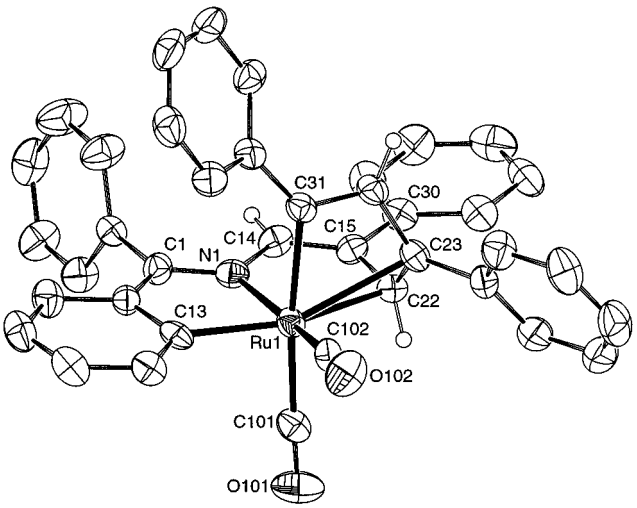


Figure 2. Molecular structure of compound **5** (phenyl H atoms omitted for clarity). Thermal ellipsoids represent the 40% probability level. Only one of the two independent molecules found in the asymmetric unit is shown.

Attempts to induce the formation of a C−N bond between the hydrocarbyl and the 1-azavinylidene ligands of complex **4**, by subjecting it to thermolysis in refluxing toluene, only led to extensive decomposition. This indicates that complexes of type **4** are not likely to be intermediates in the synthesis of complexes similar to **2** and **3**.

Figure 2 shows a view of compound **5**. Selected interatomic distances are given in Table 1. The compound is a mononuclear octahedral *cis*-dicarbonyl ruthenium(II) complex which contains an organic ligand that results from the coupling of four individual fragments: three phenylacetylene molecules and an ortho-metalated benzophenone imine-*N*-yl ligand. The three alkyne moieties are linked in a head-to-tail manner to render a hexatriene-1,6-diyl fragment that is attached to the nitrogen atom of the original 1-azavinylidene ligand through one of its ends, C(14), and to the ruthenium atom through the other end, C(31), and through both carbon atoms of its central C═C double bond. As expected, the distance associated with this bond, C(22)−C(23) = 1.39(1) Å, is longer than those associated with the two π-uncoordinated C═C double bonds, C(14)−C(15) = 1.35(1) Å and C(30)−C(31) = 1.34(1) Å.

The reactions of complex **1** with other terminal alkynes, such as acetylene, methyl propynate, (trimethylsilyl)acetylene, 2-methyl-3-butyn-2-ol, and 1,1-diphenyl-2-propyn-1-ol gave mixtures of many products that we could not separate and/or identify.

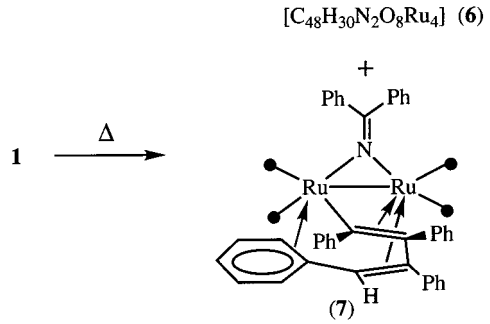
Thermolysis of Compound 1. To shed some light on the reaction pathways that lead to compounds **2**−**5** from **1**, and as the formation of *cis*-stilbene during these reactions seems to be associated with the ortho metalation of the 1-azavinylidene ligand of **1** (which would provide the hydride ligand required for the formation of *cis*-stilbene), we thought it of interest to study the thermolysis of compound **1**, since this could induce the ortho metalation of the 1-azavinylidene ligand of **1**.

A solution of **1** in 1,2-dichloroethane was stirred at reflux temperature until the complete disappearance of compound **1** was observed by IR spectroscopy (ca. 8 h).

(16) Previous examples of ortho metalation of 2,2-diphenyl-1-azavinylidene[5−7,10] and benzophenone imine[16a−k] ligands are known: (a) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1993**, *462*, 309. (b) Bohanna, C.; Esteruelas, M. A.; López, A. M.; Oro, L. A. *J. Organomet. Chem.* **1996**, *526*, 73. (c) Daniel, T.; Müller, M.; Werner, H. *Inorg. Chem.* **1991**, *30*, 3118. (d) Daniel, T.; Werner, H. *Z. Naturforsch., B* **1992**, *47*, 1707. (e) Daniel, T.; Knaup, M.; Dziallas, M.; Werner, H. *Chem. Ber.* **1993**, *126*, 1981. (f) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1994**, *480*, 145. (g) Daniel, T.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1994**, 221. (h) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 2496. (i) Barea, G.; Esteruelas, M. A.; Lledós. A.; López, A. M.; Oñate, E.; Tolosa J. I. *Organometallics* **1998**, *17*, 4065. (j) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **2000**, *19*, 275. (k) Cabeza, J. A.; del Río, I.; Grepioni, F.; Riera, V. *Organometallics* **2000**, *19*, 4643.

(17) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall International: Englewood Cliffs, NJ, 1990.

Scheme 4



At least six products were observed on preparative TLC plates, but only the two major ones, subsequently formulated as $[C_{48}H_{30}N_2O_8Ru_4]$ (**6**) and $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N{=}CPh_2)(\mu\text{-}\eta^3\text{:}\eta^4\text{-}PhCH{=}CPhCPh{=}CPh)(CO)_4]$ (**7**) could be satisfactorily isolated (yields: 46% and 11%, respectively) (Scheme 4). The presence of *cis*-stilbene in the reaction solution was identified by GC.

The microanalysis and FAB MS of compound **6** are fully consistent with a tetranuclear complex containing eight carbonyl ligands and either two metalated azavinylidene ligands and one stilbene ligand or one metalated azavinylidene ligand, one azavinylidene ligand, and one diphenylalkenyl ligand. These two possibilities, corresponding to the formulations $[Ru_4\{N{=}CPh(C_6H_4)\}_2(PhCH{=}CHPh)(CO)_8]$ and $[Ru_4\{N{=}CPh(C_6H_4)\}(N{=}CPh_2)(PhC{=}CHPh)(CO)_8]$, have the same microanalysis and molecular weight. The multiplicities and the low chemical shifts of some ^{1}H NMR resonances are compatible with the presence of at least one η^6-coordinated phenyl ring.[18] No additional structural information could be extracted from the IR and ^{1}H NMR spectra of complex **6**, and unfortunately, all attempts to obtain crystals of this compound suitable for X-ray diffraction studies were unsuccessful. These facts prevented the assignment of a molecular structure for this compound.

The structure of compound **7** was determined by an X-ray diffraction study. Figure 3 shows a view of the molecular structure. Selected interatomic distances are given in Table 1. The complex consists of two $Ru(CO)_2$ units spanned by the nitrogen atom of a 2,2-diphenyl-1-azavinylidene ligand and by a hydrocarbyl ligand that results from the coupling of diphenylacetylene and the alkenyl fragment of complex **1**. This new ligand behaves as a seven-electron donor, interacting with one metal atom through both C=C double bonds and with the remaining metal atom through the terminal carbon atom C(35) and through one of the edges, C(15)−C(20), of a phenyl ring. The Ru(2)−C(14) and Ru(1)−C(20) distances, 2.436(3) and 2.499(3) Å, respectively, are longer than expected for η^2 interactions between ruthenium atoms and C=C double bonds (for example, the distances between Ru(2) and the atoms C(21), C(28), and C(35) are in the range 2.182(3)−2.278(3) Å). This seems to be compensated by a long-distance interaction between Ru(1) and C(14), 2.415(3) Å. The metal−metal distance, 2.7082(4) Å, is within the range expected for 34-electron diruthenium(I) complexes.[2a]

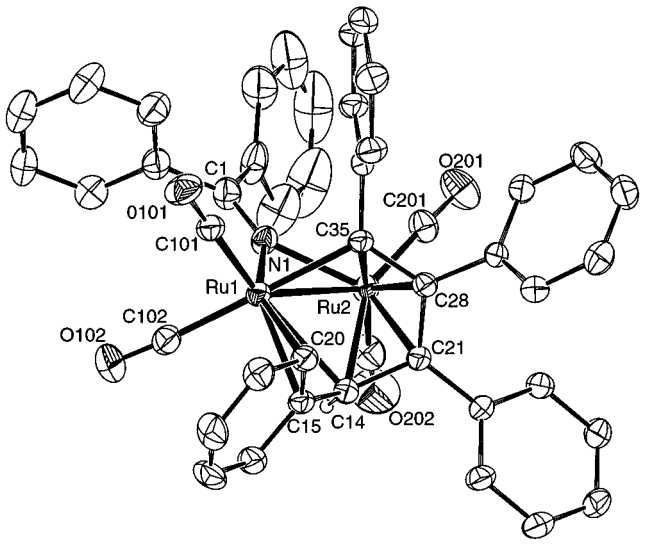
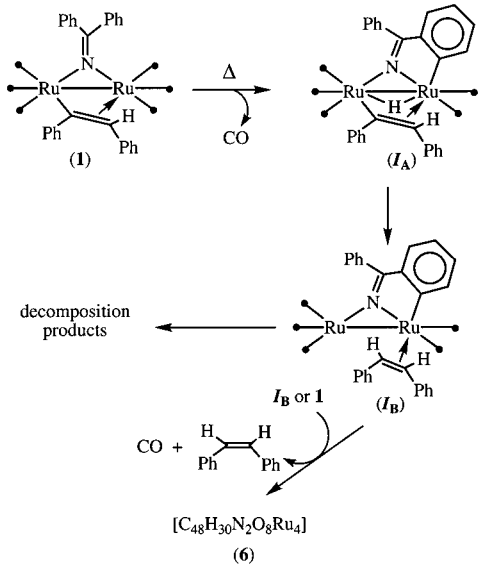


Figure 3. Molecular structure of compound **7** (phenyl H atoms omitted for clarity). Thermal ellipsoids represent the 30% probability level.

Scheme 5

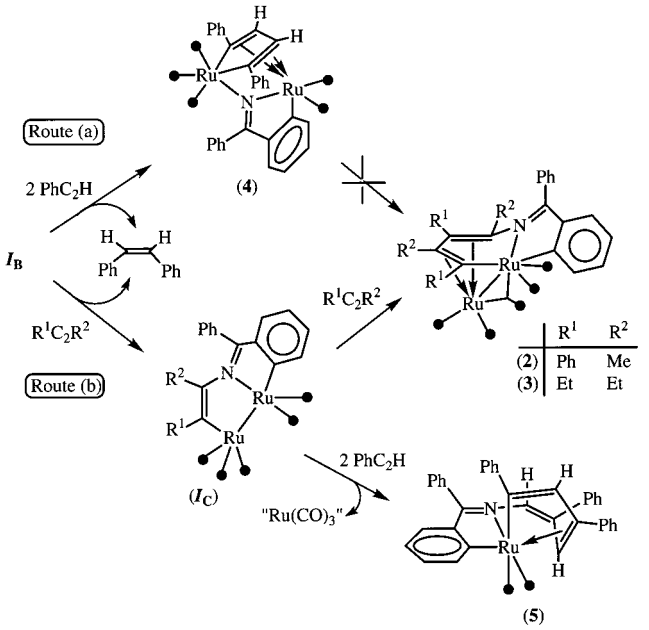


Discussion

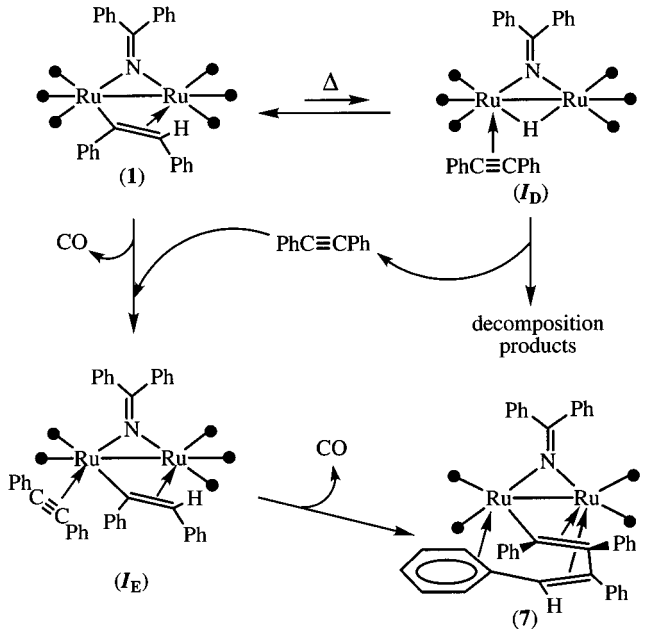
Most of the results described above shed some light on the reaction pathways that lead to compounds **2**−**5** from complex **1** and alkynes. The proposal made in Scheme 5 suggests that the thermal activation of compound **1** provokes the release of a CO ligand and the ortho metalation of a phenyl group of the diphenylazavinylidene ligand. However, it remains unknown whether the release of CO and the ortho metalation occur simultaneously with or subsequently to each other. The hydridoalkenyl species thus formed ($\boldsymbol{I_A}$) would be unstable and would reductively eliminate *cis*-stilbene to give an unsaturated intermediate containing a weakly bound *cis*-stilbene ligand ($\boldsymbol{I_B}$), prone to react with the alkyne present in solution. In the absence of alkyne reagents, as occurs during the thermolysis of **1**, most of $\boldsymbol{I_B}$ would relieve its unsaturation, undergoing

(18) The proton resonances of an η^6-coordinated phenyl ring appear at chemical shifts lower than those of an uncoordinated phenyl ring. For examples of ruthenium η^6-arene complexes, see: Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163 and references therein.

Scheme 6



Scheme 7



either dimerization or coupling with the remaining complex **1** present in solution. The tetranuclear intermediate thus formed (not represented in Scheme 5) would be thermally unstable and would lead, upon releasing *cis*-stilbene and carbon monoxide, to the tetranuclear product $[C_{48}H_{30}N_2O_8Ru_4]$ (**6**). A minor part of I_B would end up as uncharacterized decomposition products.

This mechanistic proposal is strongly supported by the following facts: (a) no reaction is observed at room temperature, indicating thermal activation, (b) compounds **2**−**6** contain an ortho-metalated phenyl ring belonging to the original 2,2-diphenyl-1-azavinylidene ligand, (c) compounds **2**−**5** do not contain any fragment arising from the original alkenyl ligand of **1**, (d) free *cis*-stilbene is obseved in all reaction solutions, and (e) complex **6** has been isolated as the major product of the thermolysis of compound **1**.

Regarding the formation of compounds **2**−**5**, two different routes starting from the intermediate I_B can be considered (Scheme 6). Route a would imply the addition of two alkyne molecules to I_B prior to any C−N bond-forming step, while route b would imply the formation of a C−N bond, by insertion of the first alkyne molecule into a Ru−N bond (intermediate I_C), prior to any C−C bond-forming step. It is clear that the synthesis of compound **4** follows route a, but we believe that the syntheses of compounds **2**, **3**, and **5** follow route b for the reasons stated below.

The new C−C bond of complex **4** should be formed by coupling of two coordinated alkyne ligands. Probably for steric reasons, the coupling seems to occur between the carbon atoms containing the smallest substituents. A hypothetical coupling of this hydrocarbyl ligand with the N atom would lead to a complex similar to **2**, but with a different sequence of R groups on the C_4 fragment of the metallacycle. Moreover, the fact that all attempts to synthesize a complex similar to **2** and **3** from compound **4** failed indicates that the formation of a C−N bond between the hydrocarbyl ligand and the N atom of complex **4** is a disfavored process. On the other hand, the presence of new C−N bonds and the alternation of the substituents (when they are different) in the hydrocarbyl fragments of compounds **2**, **3**, and **5** indicate that, during the synthesis of these compounds, the insertion of an alkyne molecule into a Ru−N bond of I_B, to give the intermediate I_C, is preferred over the coupling of the first alkyne with a second alkyne molecule. The subsequent C−C bond-forming steps (from the intermediate I_C) are insertion processes of alkynes into Ru−C bonds. It seems that the insertions that lead to new C−C or C−N bonds take place in such a way that the C atom of the entering alkyne that ends up bonded to the C or N atoms originally attached to ruthenium is that containing the smaller substituent, thereby leading to alternate substituents along the final hydrocarbyl fragment.

A reaction pathway that would account for the formation of complex **7**, a minor product of the thermolysis of compound **1**, is depicted in Scheme 7. Its hydrocarbyl ligand has to be the result of the insertion of diphenylacetylene into the Ru−C σ-bond of an alkenyl intermediate. As the only possible source of diphenylacetylene is complex **1**, we propose that, under thermal conditions, some molecules of compound **1** undergo a deinsertion of diphenylacetylene to give the alkyne intermediate I_D, which decomposes, releasing the alkyne. A concurrent thermal decarbonylation of **1** would give an intermediate (not represented in Scheme 7) prone to take up the free alkyne present in solution. The resulting intermediate (I_E) would render compound **7** after an insertion process and the release of CO.

Kinetic arguments may account for the fact that complex **7** is not observed in any of the reactions of compound **1** with alkynes. Although the rates of the reactions that lead to compounds **6** and **7** (Schemes 5 and 7) have to be of comparable magnitude (in fact, both compounds are formed together in the thermolysis of **1**), the processes shown in Scheme 6, which take place in the presence of an excess of alkyne reagents, seem to be much faster than those leading to complex **7** (Scheme 7). This reasoning would also explain why the

thermal reaction of compound **1** with an excess of diphenylacetylene gives $[Ru_2\{\mu\text{-}\eta^3\text{:}\eta^4\text{-PhC=CPhC-Ph=CPhN=CPh(C}_6H_4)\}(\mu\text{-CO})(CO)_4]$ as the major product.[7] In the thermolysis of compound **1**, the very small amount of diphenylacetylene available in solution would prevent the formation of $[Ru_2\{\mu\text{-}\eta^3\text{:}\eta^4\text{-PhC=CPhC-Ph=CPhN=CPh(C}_6H_4)\}(\mu\text{-CO})(CO)_4]$ in a characterizable amount.

Although all these mechanistic arguments are reasonable, the lack of mass balances in these reactions (decomposition products are always observed) suggests that caution should be taken when interpreting these mechanisms.

Insertion reactions of alkynes into M−C bonds are frequent in carbonyl ruthenium cluster chemistry.[19] However, as stated in the Introduction, insertion reactions of alkynes into M−N bonds are very rare. The examples in the literature are restricted to the highly electrophilic alkyne dimethyl acetylenedicarboxylate for normal amido complexes[8] and a few internal alkynes containing at least one phenyl group for complexes in which the N atom of the M−N bond belongs to a 1-azavinylidene ligand.[6,7,10] Therefore, although normal amido complexes have no tendency to insert weakly electrophilic alkynes into their M−N bonds,[3a−e] the results described herein support the suggestion that this is not the case for 1-azavinylidene complexes. In fact, in the present work we have extended the type of alkyne reagents that can be inserted into Ru−N bonds to 3-hexyne (a very weakly electrophilic alkyne) and to phenylacetylene (a terminal alkyne). It seems that 1-azavinylidene ligands have a "softer" character than normal amido ligands, since they may be able to accept electron density into the empty π^* orbitals associated with the C=N double bond. However, the previous statement, as well as how the "soft−hard" character of the N-donor ligands affects the insertion of alkynes into M−N bonds, needs to be investigated by theoretical calculations, which are out of the scope of this work.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk−vacuum-line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC (silica gel). Compound **1** was prepared as described previously.[7] The alkyne reagents were obtained from Aldrich. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run at room temperature with Bruker AC-200, AC-300, or DPX-300 instruments, using $SiMe_4$ as internal standard. GC analyses were carried out with a Perkin-Elmer 8600 gas chromatograph (flame ionization detector), equipped with a 30 m Supelcowax-10 capillary column (i.d. 0.25 mm). FAB-MS were obtained from the University of Santiago de Compostela Mass Spectroscopic Service; data given refer to the most abundant molecular ion isotopomer. Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Ru_2\{\mu\text{-}\eta^3\text{:}\eta^4\text{-PhC=CMeCPh=CMeN=CPh(C}_6H_4)\}(\mu\text{-CO})(CO)_4]$ (2). A solution of **1** (70 mg, 0.095 mmol) and 1-phenyl-1-propyne (50 μL, 0.399 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 2 h. The color changed from yellow to brownish yellow. The solution was concentrated under reduced pressure to ca. 2 mL, and the concentrate was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane eluted a yellow band, which gave compound **2** after solvent removal (45 mg, 65%). Its analytical and spectroscopic data matched those previously published.[7]

$[Ru_2\{\mu\text{-}\eta^3\text{:}\eta^4\text{-EtC=CEtCEt=CEtN=CPh(C}_6H_4)\}(\mu\text{-CO})(CO)_4]$ (3). A solution of **1** (70 mg, 0.096 mmol) and 3-hexyne (33 μL, 0.290 mmol) in 1,2-dichloroethane (15 mL) was stirred at reflux temperature for 1.5 h. The color changed from yellow to brownish yellow. The solution was concentrated under reduced pressure to ca. 2 mL, and the concentrate was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane eluted a yellow band, which gave compound **3** after solvent removal (15 mg, 22%). Anal. Found: C, 51.39; H, 4.38; N, 2.08. Calcd for $C_{30}H_{29}NO_5Ru_2$: C, 52.55; H, 4.26; N, 2.04. MS (*m*/*z*): 687 [M^+]. FW: 685.73. IR (THF): ν(CO) 2065 (w), 2037 (s), 2011 (s), 1989 (m), 1966 (vs), 1932 (sh), 1872 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.4−6.7 (m, 7 H), 6.68 (d, 7.6 Hz, 1 H), 6.63 (d, 8.1 Hz, 1 H), 2.6−1.8 (m, 8 H, 4 CH_2), 1.5−0.5 (m, 12 H, 4 CH_3) ppm.

$[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-N=CPh(C}_6H_4)\}(\mu\text{-}\eta^2\text{:}\eta^4\text{-PhC=CHCH=CPh)(CO)}_5]$ (4) and $[Ru\{\eta^5\text{-PhC=CHCPh=CHCPh=CHN=CPh(C}_6H_4)\}(CO)_2]$ (5). A solution of **1** (70 mg, 0.096 mmol) and phenylacetylene (40 μL, 0.364 mmol) in 1,2-dichloroethane (15 mL) was stirred at reflux temperature for 2 h. The color changed from yellow to brown. The solution was concentrated under reduced pressure to ca. 2 mL, and the concentrate was placed on preparative TLC plates (silica gel). Elution with hexane−dichloromethane (3:1) allowed the separation of compound **4** (20 mg, 30%) from the first band (yellow) and compound **5** (12 mg, 19%) from the second band (orange). A brown residue remained uneluted in the baseline.

Analytical and Spectroscopic Data for Compound 4. Anal. Found: C, 56.80; H, 3.08; N, 1.91. Calcd for $C_{34}H_{21}NO_5Ru_2$: C, 56.47; H, 3.02; N, 1.80. MS (*m*/*z*): 727 [M^+]. FW: 725.68. IR (THF): ν(CO) 2085 (s), 2031 (vs), 2005 (s), 1976 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.9−6.7 (m, 19 H), 5.99 (d, 2.2 Hz, 1 H), 5.90 (d, 2.2 Hz, 1 H) ppm.

Analytical and Spectroscopic Data for Compound 5. Anal. Found: C, 72.50; H, 4.13; N, 2.07. Calcd for $C_{39}H_{27}NO_2Ru$: C, 72.88; H, 4.23; N, 2.18. MS (*m*/*z*): 643 [M^+]. FW: 642.73. IR (CH_2Cl_2): ν(CO) 2022 (vs), 1968 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.00 (d, 7.4 Hz, 1 H), 7.8−6.7 (m, 22 H), 6.65 (d, 7.9 Hz, 1 H), 6.57 (dd, 7.6 and 2.0 Hz, 1 H), 6.47 (s, 1 H), 6.12 (d, 7.9 Hz, 1 H) ppm.

$[C_{48}H_{30}N_2O_8Ru_4]$ (6) and $[Ru_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-N=CPh}_2)(\mu\text{-}\eta^3\text{:}\eta^4\text{-PhCH=CPhCPh=CPh)(CO)}_4]$ (7). A solution of **1** (250 mg, 0.339 mmol) in 1,2-dichloroethane (50 mL) was stirred at reflux temperature for 8 h. The color changed from yellow to brown. The solution was concentrated under reduced pressure to ca. 3 mL, and the concentrate was placed on preparative TLC plates (silica gel). Multiple elution with hexane−dichloromethane (7:2) allowed the isolation of compounds **7** (32 mg, 11%) and **6** (90 mg, 46%) from the first (yellow) and fourth (green) bands, respectively.

Analytical and Spectroscopic Data for Compound 6. Anal. Found: C, 49.66; H, 2.71; N, 2.23. Calcd for $C_{48}H_{30}N_2O_8Ru_4$: C, 49.40; H, 2.59; N, 2.40. MS (*m*/*z*): 1168 [M^+]. FW: 1167.10. IR (CH_2Cl_2): ν(CO) 2085 (m), 2029 (vs), 2009 (m), 2003 (m), 1969 (m), 1947 (sh) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.49 (br, 2 H), 7.9−7.0 (m, 23 H), 6.89 (td, 7.4 and 1.2 Hz, 1 H), 6.22 (dd, 6.6, 6.0, and 1.2 Hz, 1 H), 6.13 (td, 6.0 and 1.2 Hz, 1 H), 4.93 (dd, 6.6 and 1.2 Hz, 1 H), 4.55 (dd, 6.0 and 1.2 Hz, 1 H) ppm.

Analytical and Spectroscopic Data for Compound 7. Anal. Found: C, 63.67; H, 3.87; N, 1.50. Calcd for $C_{45}H_{31}NO_4Ru_2$: C, 63.45; H, 3.67; N, 1.64. MS (*m*/*z*): 824 [M^+ − CO]. FW: 851.91. IR (CH_2Cl_2): ν(CO) 2028 (s), 1996 (vs), 1973 (m),

(19) Smith, A. K. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Shriver, D. F., Bruce, M. I., Vol. Eds.; Pergamon: Oxford, U.K., 1995; Vol. 7, p 747, and references therein.

Table 2. Crystal Data and Measurement Details for 4·CH_2Cl_2, 5, and 7·0.5Me_2CO

	4·CH_2Cl_2	**5**	**7**·0.5Me_2CO
formula	$C_{35}H_{23}Cl_2NO_5Ru_2$	$C_{39}H_{27}NO_2Ru$	$C_{46.5}H_{34}NO_{4.5}Ru_2$
fw	810.58	642.69	880.89
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	9.320(8)	13.344(4)	15.278(1)
b, Å	17.770(9)	15.089(8)	12.315(1)
c, Å	16.396(3)	16.088(8)	21.953(1)
α, deg	90	78.35(4)	90
β, deg	95.34(4)	82.92(3)	90.75(1)
γ, deg	90	73.35(3)	90
V, Å^3	2704(3)	3032(2)	4130.1(5)
Z	4	4	4
F(000)	1608	1312	1776
D_{calcd}, g/cm^3	1.366	1.408	1.417
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	1.366	0.553	0.775
cryst size, mm	0.34 × 0.22 × 0.20	0.25 × 0.24 × 0.20	0.32 × 0.24 × 0.22
temp, K	223(2)	293(2)	293(2)
θ limits, deg	3.0−31.4	3.0−23.0	2.0−34.4
min/max *h*, *k*, *l*	−12/+12, 0/26, 0/19	−14/+14, −16/+16, 0/17	−23/+19, −19/+19, −34/+33
no. of rflns collected	7221	8749	58660
no. of unique rflns	6979	8397	15738
no. of rflns with $I > 2\sigma(I)$	4093	4647	5063
abs cor	*ψ* scan	*ψ* scan	Bruker-SMART
max/min transmissn	1.00/0.76	1.00/0.85	1.00/0.78
refinement method	full-matrix l-s on F^2	full-matrix l-s on F^2	full-matrix l-s on F^2
no. of params	356	655	434
GOF on F^2	0.969	0.886	0.916
final R1 (on *F*, $I > 2\sigma(I)$)	0.0600	0.0367	0.0440
final wR2 (on F^2, all data)	0.1931	0.0985	0.1104

1933 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): *δ* 7.76 (dd, 8.0 and 1.5 Hz, 1 H), 7.6−6.7 (m, 27 H), 6.44 (dd, 8.0 and 1.5 Hz, 1 H), 5.47 (d, 5.9 Hz, 1 H), 5.11 (s, 1 H) ppm.

Crystal Structure Characterization of 4·CH_2Cl_2, 5, and 7·Me_2CO. X-ray diffraction data were collected on Nonius CAD-4 (**4**·CH_2Cl_2 and **5**) and Bruker-SMART (**7**·Me_2CO) diffractometers. Crystal data and details of measurements are summarized in Table 2. SHELXL97[20] was used for structure solution and refinement based on F^2. All non-H atoms were refined anisotropically. The H atoms were added in calculated positions and refined as riding on their respective C atoms. Only one Cl atom of the CH_2Cl_2 solvent molecule of **4**·CH_2Cl_2 could be detected (disordered over three positions with occupancies 0.5, 0.25, and 0.25). Compound **5** contains two very similar but crystallographically independent molecules in the asymmetric unit.

(20) Sheldrick, G. M. SHELXL97, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.

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Supporting Information Available: Diagrams with the complete numbering schemes and tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters for compounds **4**·CH_2Cl_2, **5**, and **7**·Me_2CO. This material is available free of charge via the Internet at http://pubs.acs.org.

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