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Reactivity of Diphenylbutadiyne with a Hexaruthenium Dihydride. Unusual 1,1- and *trans*-1,2-Additions of Two Hydrogen Atoms to an Internal CC Triple Bond[§]

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The reactions of the basal edge-bridged square pyramidal hexanuclear cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (**1**; H_2ampy = 2-amino-6-methylpyridine) with diphenylbutadiyne give mixtures of cluster compounds, the composition of which depends on the reaction time and temperature. The following products have been isolated and characterized: $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^3\text{-}PhCCCCH_2Ph)(\mu\text{-}CO)(CO)_{14}]$ (two isomers, **2** and **3**), $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^4\text{-}trans\text{-}PhCCCHCHPh)(\mu\text{-}CO)(CO)_{14}]$ (**4**), and $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-}trans\text{-}PhCCCHCHPh)(\eta^6\text{-}PhMe)(\mu\text{-}CO)(CO)_9]$ (**5**). In all products, the ampy ligand is attached to five metal atoms through its nitrogen atoms, in the same way as in complex **1**. These compounds represent unusual examples of 1,1- and *trans*-1,2-additions of two hydrogen atoms to an internal CC triple bond, since **2** and **3** contain a hydrocarbon ligand that arises from the migration of the original hydrides of **1** onto a terminal carbon atom of the diyne C_4 chain, and **4** and **5** contain a 1,4-diphenyl-*trans*-butenyne ligand. The reaction pathway **1** + PhC_2C_2Ph → **2** → **3** → **4** → **5** has been established by studying the individual thermolysis of compounds **2**−**4** and reactions of **1** with diphenylbutadiyne at different reaction times and temperatures.

Introduction

Many reactions of transition metal carbonyl cluster complexes with conjugated diynes have been reported over the last two decades. These studies have shown that the cluster chemistry of diynes is very rich and that it strongly depends on the nature of the metal cluster and the diyne used.[1−10]

Most metal clusters whose reactivity with diynes has been studied contain no hydride ligands. These clusters react with diynes to give products in which the diynes behave as alkyne ligands.[2,3] These diyne-containing clusters frequently undergo intramolecular (ligand cyclization) and/or intermolecular C−C coupling reactions with one or more additional diyne molecules to give products that often contain large unsaturated hydrocarbons as ligands.[3,4] Monohydrido[5,6] and some dihydrido[7,8] carbonyl metal clusters react with diynes, via migratory inser-

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[§] Dedicated to Prof. Víctor Riera on the occasion of his 70th birthday.

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tion, to give ynenyl derivatives, some of which are also prone to react with more diyne molecules to give large unsaturated hydrocarbyl ligands.[6] Diynes bound to osmium clusters are able to incorporate hydrogen atoms upon treatment with water.[5f]

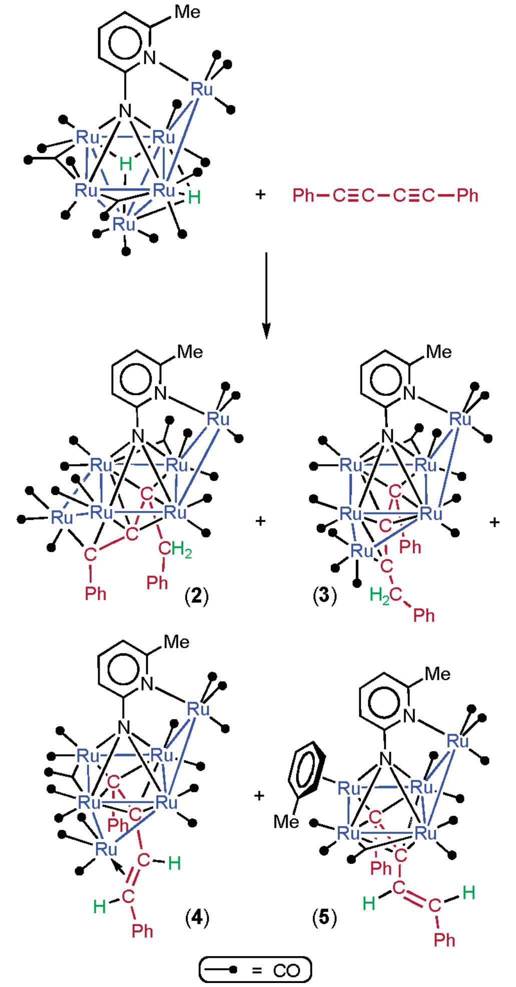
Of relevance to the investigation reported here is the key point that the reactions of diynes with di- and polyhydrido metal clusters may lead to hydrogenated diyne ligands. $[Os_3(\mu\text{-H})_2(CO)_{10}]$ induces diyne monohydrogenations (formation of ynenyl ligands),[7] cyclizations,[3e−h] and rearrangements,[7a] but no dihydrogenations. However, the reaction of $[Ru_4(\mu\text{-H})_2(\mu\text{-PPh})(CO)_{12}]$ with diphenylbutadiyne affords products with dihydrogenated diyne ligands that result from the addition of two hydrogen atoms in *cis*-1,2- and 1,4-positions,[9] while the reactions of $[Ru_4(\mu\text{-H})_4(CO)_{12}]$ with conjugated diynes give products that contain 1,1- and 1,4-hydrogenated diyne ligands.[10]

On the other hand, we have recently reported a high-yield synthesis of the hexaruthenium dihydride $[Ru_6(\mu_3\text{-H})_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-CO})_2(CO)_{14}]$ (**1**; H_2ampy = 2-amino-6-methylpyridine), which has a basal edge-bridged square pyramidal metallic skeleton.[11] Previous hexaruthenium cluster complexes with this metallic framework were very scarce, all being low-yield byproducts of processes that generally involve various steps from $[Ru_3(CO)_{12}]$.[12−14] The high-yield synthesis of complex **1**, in a one-pot reaction from $[Ru_3(CO)_{12}]$ and 2-amino-6-methylpyridine,[11] allowed us to undertake a systematic study of its reactivity. We have already reported the reactions of **1** with phosphanes,[11] $[PPN][BH_4]$,[15] and diphenylacetylene.[16]

Diphenylacetylene reacts with **1** to give *cis*-stilbene and a nonhydridic intermediate that reacts with more alkyne to give alkyne-containing cluster derivatives.[16] These results prompted us to study the reactivity of **1** with diphenylbutadiyne. We now report the results of that study, which include the isolation of new hexa- and pentanuclear cluster complexes containing ligands that arise from unusual hydrogenations of the diyne in 1,1- and *trans*-1,2-positions.

Results and Discussion

Scheme 1



Synthesis of Compounds 2−5. Mixtures of products were always obtained from reactions of compound **1** with diphenylbutadiyne in toluene at reflux temperature (110 °C). IR and qualitative TLC monitoring of the reactions indicated that the number of reaction products and the amount of each product varied with the reaction time and with the ratio of the reactants. In all cases, insoluble decomposition solids precipitated from the resulting solutions. Using a 1:1.5 cluster to diyne mol ratio, the complete consumption of the starting material **1** was observed after 1 h. From these reactions, the hexa- and pentanuclear derivatives $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^3\text{-PhCCCCH}_2\text{Ph})(\mu\text{-CO})(CO)_{14}]$ (**3**), $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^4\text{-}trans\text{-PhCCCHCHPh})(\mu\text{-CO})(CO)_{14}]$ (**4**), and $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-}trans\text{-PhCCCHCHPh})(\eta^6\text{-PhMe})(\mu\text{-CO})(CO)_9]$ (**5**) (Scheme 1) were isolated by chromatographic methods. In all cases, complex **3** was the major product (30−45%), but its yield decreased with the reaction time. Compound **4** was always a minor product (<14%), regardless of the reaction time. Compound **5** (3−7%) appeared only after long reaction times (>6 h). No attempts were made to isolate each product in the highest possible yield.

Aiming to isolate early reaction intermediates, complex **1** was also treated with diphenylbutadiyne at 50 °C. As expected, the rate of this reaction was very slow (IR and TLC monitoring). After 11 days, a new hexanuclear compound, $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^3\text{-PhCCCCH}_2\text{Ph})(\mu\text{-CO})(CO)_{14}]$ (**2**), could be isolated by chromatographic methods in 5% yield from a mixture that also contained the starting material **1** (12%) and a small amount of complex **3** (4%) (Scheme 1). Again, a considerable amount of untractable decomposition solid accompanied the resulting solution. We made no attempts to optimize the yield of compound **2**.

Characterization of Compounds 2−5. These compounds were analyzed by elemental microanalysis, FAB mass spectrometry, IR and ^{1}H NMR spectroscopies, and single-crystal X-ray diffraction.

Their ^{1}H NMR spectra confirmed the absence of hydride ligands and the incorporation of two hydrogen atoms to the hydrocarbon ligand. The J_{H-H} coupling constants between these two hydrogen atoms were very similar in all cases: 13.1 (**2**), 13.5 (**3**), 13.8 (**4**), and 15.4 Hz (**5**). These values ruled out the possibilities of *cis*-1,2- and 1,4-hydrogenations of the diyne, for which J_{H-H} couplings of 6−10 Hz[5a,9] and 0 Hz,[5a,9,10] respectively, should be expected. Coupling constants of

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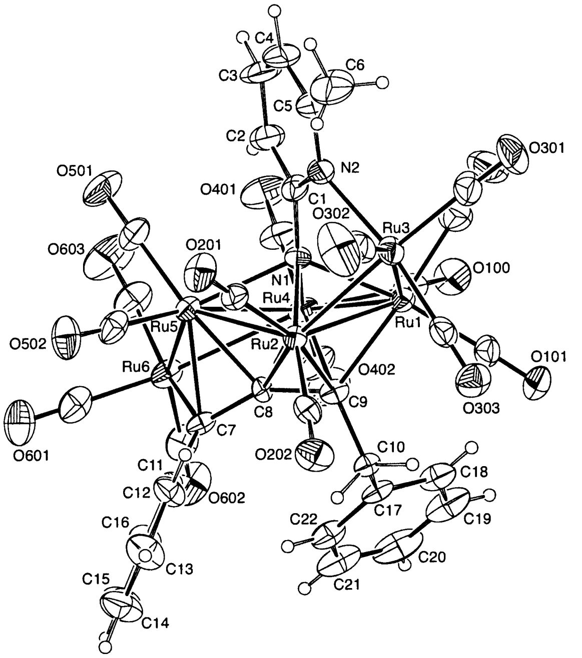

Figure 1. Molecular structure of compound **2**. The C and O atoms of each carbonyl ligand bear the same number.

Table 1. Selected Bond Distances (Å) in Compounds 2−5

	2	**3**	**4**	**5**
Ru(1)−Ru(2)	2.707(2)	2.716(1)	2.6856(4)	2.730(1)
Ru(1)−Ru(3)	2.767(2)	2.711(1)	2.6736(4)	2.687(1)
Ru(1)−Ru(4)	2.706(2)	2.673(1)	2.6956(4)	2.734(1)
Ru(2)−Ru(3)	2.660(2)	2.740(1)	2.7729(4)	2.741(1)
Ru(2)−Ru(5)	2.785(2)	2.744(1)	2.7590(4)	2.687(1)
Ru(2)−Ru(6)		3.008(1)	2.7959(4)	
Ru(4)−Ru(5)	2.802(2)	2.784(1)	2.7273(4)	2.744(1)
Ru(4)−Ru(6)	2.935(2)			
Ru(5)−Ru(6)	2.666(2)	2.668(1)	2.8154(4)	
N(1)−Ru(1)	2.152(9)	2.172(7)	2.179(3)	2.172(5)
N(1)−Ru(2)	2.164(9)	2.138(8)	2.150(3)	2.191(5)
N(1)−Ru(4)	2.269(9)	2.254(7)	2.198(3)	2.160(5)
N(1)−Ru(5)	2.337(9)	2.275(7)	2.205(3)	2.262(5)
N(2)−Ru(3)	2.24(1)	2.222(8)	2.230(3)	2.250(5)
C(7)−Ru(1)		2.171(9)	2.342(4)	2.319(6)
C(7)−Ru(2)		2.300(9)		
C(7)−Ru(4)		2.345(9)	2.148(4)	2.087(6)
C(7)−Ru(5)	2.30(1)		2.339(4)	2.386(6)
C(7)−Ru(6)	2.06(1)			
C(8)−Ru(1)			2.295(4)	2.262(6)
C(8)−Ru(2)	2.37(1)	2.227(8)	2.120(4)	2.219(6)
C(8)−Ru(4)	2.28(1)	2.383(9)		
C(8)−Ru(5)	2.11(1)	2.073(9)	2.370(4)	2.356(6)
C(9)−Ru(1)	2.20(1)			
C(9)−Ru(2)	2.26(1)			
C(9)−Ru(4)	2.38(1)			
C(9)−Ru(5)		2.287(9)		
C(9)−Ru(6)		2.062(10)	2.339(4)	
C(7)−C(8)	1.39(2)	1.405(12)	1.437(5)	1.456(8)
C(8)−C(9)	1.39(2)	1.376(13)	1.468(5)	1.489(8)
C(9)−C(10)	1.54(2)	1.508(14)	1.376(6)	1.348(9)

12−15 Hz have been reported for the CH_2 protons of Ru_4 clusters that contain a ligand that arises from a 1,1-hydrogenation of diphenylbutadiyne.[10]

Their molecular structures were determined by single-crystal X-ray diffraction. As far as possible, for comparison purposes, the four X-ray structures share a common atom-numbering scheme.

Figure 1 shows the molecular structure of compound **2**. A selection of intramolecular distances is given in Table 1. The structure can be described as derived from that of complex **1**, which has a basal edge-bridged square pyramidal metallic skeleton, with two face-capping hydrides and a μ_5-ampy ligand (Scheme 1).[11] The most relevant feature of **2** is that it contains a hydrocarbon ligand that results from the addition of two hydrogen atoms to the terminal carbon atom, C(10) in Figure 1, of the original diphenylbutadiyne ligand. The coordination of this new ligand induces the displacement of the apical Ru atom of **1** to an edge-bridging position (in **2**, the Ru(6) atom spans the Ru(4)−Ru(5) edge) and the distortion of the square defined by the Ru(1), Ru(2), Ru(4), and Ru(5) atoms toward an incipient butterfly arrangement. These four metal atoms are now attached to the C(7) and C(8) atoms of the ligand in such a way that the line defined by these atoms is almost parallel to the Ru(1)−Ru(5) vector. The values of the C−C and C−Ru distances in which the C(7), C(8), and C(9) atoms of the new ligand are involved suggest that this ligand may be considered as a resonance hybrid of two canonical forms: 1,4-diphenylbut-2-yn-1,1-diyl and 1,4-diphenylbuta-1,2-dien-1,3-diyl (Figure 2). In the first canonical form, the carbene carbon atom C(7) spans the Ru(5)−Ru(6) edge and the C atoms of the alkyne fragment are σ-bonded to Ru(1) and Ru(5) and π-bonded to Ru(2) and Ru(4). This type of coordination of an alkyne ligand to four metal atoms has been previously observed on many occasions, including some tetra-,[2e,17−19] penta-,[16−18] hexa-,[16,20] and heptaruthenium[16] complexes. The participation of the 1,4-diphenylbuta-1,2-dien-1,3-diyl canonical form is mainly evidenced by the fact that the C(7)−Ru(5) distance is 0.24(1) Å longer than the C(7)−Ru(6) distance and that the C(7)−C(8) distance, 1.39(2) Å, is shorter than expected for a single C−C bond (viz., 1.54(2) Å for C(9)−C(10)). The coordination of the ampy ligand is analogous to that found in complex **1**.[11] The cluster shell is completed with 14 terminal and one bridging CO ligand.

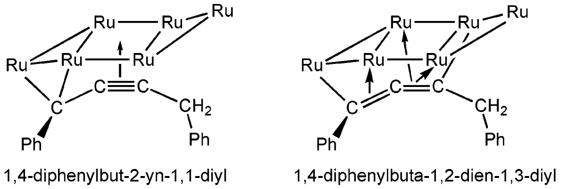

Figure 2. Schematic representation of the two canonical forms of the hydrocarbon ligand of compound **2**.

As expected for clusters having μ_4-alkyne ligands,[21] compound **2** disobeys the EAN rule, since it has eight metal−metal bonds and an electron count of 90 (two electrons less than the predicted 92). However, these clusters are well described by the polyhedral skeletal electron pair theory, considering the alkyne carbon atoms as part of the polyhedron.[21]

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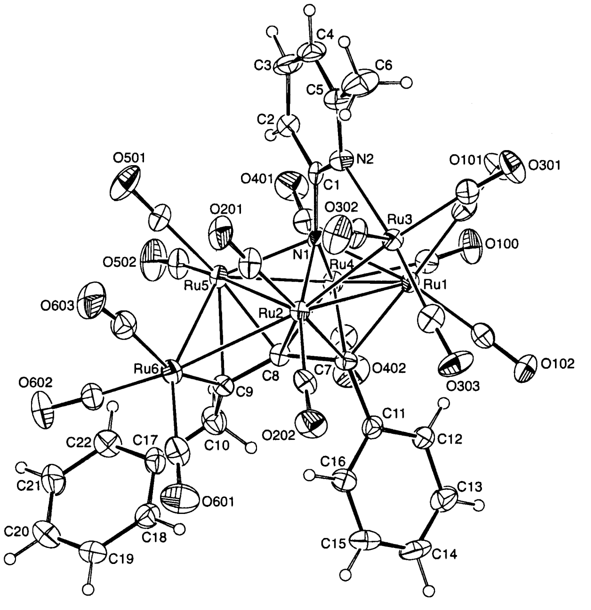

Figure 3. Molecular structure of compound **3**. The C and O atoms of each carbonyl ligand bear the same number.

As far as we are aware, there is only one previous report describing the 1,1-hydrogenation of a diyne C≡C bond. That paper reports the synthesis of [Ru$_4$(μ_4-RCH$_2$C$_3$R)(CO)$_{12}$] (R = Me, SiMe$_3$, Ph) from reactions of [Ru$_4$(μ-H)$_4$(CO)$_{12}$] with the corresponding diynes. Interestingly, the RCH$_2$C$_3$R ligands of these clusters are best described as allene-1,3-diyl ligands, since they bind the metal atoms of a butterfly Ru$_4$ arrangement in such a way that each terminal C atom of their nearly linear C$_3$ fragment is σ-attached to a metal atom and each allene C=C bond is π-bonded to another metal atom.[10] This contrasts with the structural situation found in compound **2**.

The molecular structure of compound **3** is shown in Figure 3. A selection of intramolecular distances is given in Table 1. The structure can be described as derived from that of complex **2**. It has the same hydrocarbon ligand as **2**, but now, the carbon atom that bridges the Ru(5)−Ru(6) edge is C(9), while C(7) and C(8) cap the distorted metallic square. Although the metallic skeleton is different from that of **2** (now the Ru(6) atom spans the Ru(2)−Ru(5) edge), the coordination of the hydrocarbon ligand to the metallic framework is comparable to that in compound **2**. Therefore, all the comments made above relative to the hydrocarbon ligand of compound **2** also apply for complex **3**.

The molecular structure of compound **4** is shown in Figure 4. A selection of bond distances is given in Table 1. The hexametallic skeleton and the arrangement of the ampy ligand in **4** are comparable to those of **3**. The most important difference between these two complexes is that the hydrocarbon ligand of **4** is *trans*-1,4-diphenylbutenyne. This ligand is bound through its alkene C(9)−C(10) fragment to Ru(6) and through the alkyne C(7)−C(8) fragment to the distorted metallic square in such a way that now the alkyne C(7)−C(8) bond is parallel to the Ru(2)−Ru(4) vector, the alkyne resulting σ-bonded to Ru(2) and Ru(4) and π-bonded to Ru(1) and Ru(5). It is interesting to note that, to our knowledge, metal complexes of conjugated *trans*-enynes are unprecedented and that the observation of metal complexes containing *trans*-alkene ligands is infrequent.[22]

Compound **5** is pentanuclear. Its molecular structure (Figure 5, Table 1) can be described as derived from that of compound **4**, resulting from the formal replacement of (a) a carbonyl ligand for the Ru(CO)$_3$ fragment that bridges the Ru(2)−Ru(5) edge and (b) an η^6-toluene solvent molecule for the three CO ligands that are attached to Ru(4). This structure is similar to that of [Ru$_5$(μ_5-κ^2-ampy)(μ_4-η^2-PhCCPh)(η^6-PhMe)(μ-CO)(CO)$_9$],[16] which contains diphenylacetylene instead of *trans*-1,4-diphenylbutenyne.

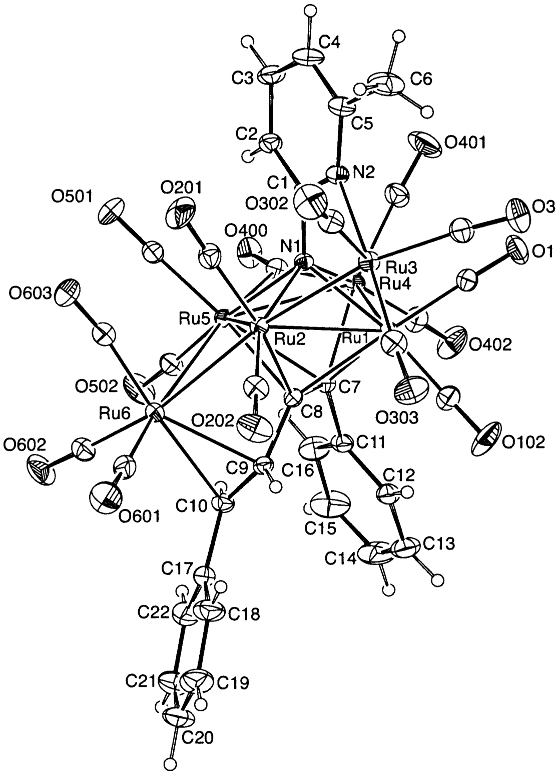

Figure 4. Molecular structure of compound **4**. The C and O atoms of each carbonyl ligand bear the same number.

Reaction Pathway. With the objective of gaining a deeper insight into the relationships between the compounds involved in the reaction of complex **1** with diphenylbutadiyne, the individual thermolysis of compounds **2**−**4** was studied. These reactions were monitored by analyzing the ^{1}H NMR spectra of the residues obtained after removing the solvent of aliquots taken from the reacting solutions at different reaction times.

The thermolysis of complex **2** at 83 °C gave, initially, a transient species that was completely converted into compound **3** after 24 h. No further evolution of complex **3** was observed at this temperature. At 110 °C, complex **3** slowly evolved into a mixture of compounds. After 10 h, the solution contained complexes **3** and **5** in ca. 1:1 ratio along with trace amounts of complex **4** and other unidentified species. In a parallel experiment, complex **4** was completely converted into complex **5** after 2.5 h at 110 °C.

These data indicate that the transformation of **2** into **3** has much lower activation energy than the transformation of **3** into **4**. In addition, the conversion of **3** into **4** is also slower than that of **4** into **5**. This explains why complex **3** is the major

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[22] See, for example: (a) Joy, J. R.; Orchin, M. *J. Am. Chem. Soc.* **1959**, *81*, 310. (b) Zambonelli, L.; Spagne, R. *J. Chem. Soc. (A)* **1971**, 2544. (c) Bilhou, J. L.; Basset, J. M.; Mutin, R.; Graydon, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 4083. (d) Clark, G. R.; Clark, P. W.; Marsden, K. *J. Organomet. Chem.* **1979**, *173*, 231. (e) Grevels, F. W.; Lindemann, M.; Benn, R.; Goddard, R.; Krueger, C. *Z. Naturforsch.* **1980**, *35B*, 1298. (f) Clark, G. R.; Cochrane, C. M.; Clark, P. W. *J. Organomet. Chem.* **1982**, *236*, 179. (g) Adams, R. D.; Che, G.; Yin, J. *Organometallics* **1991**, *10*, 2087. (i) Pu, J.; Peng, T. S.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2686.

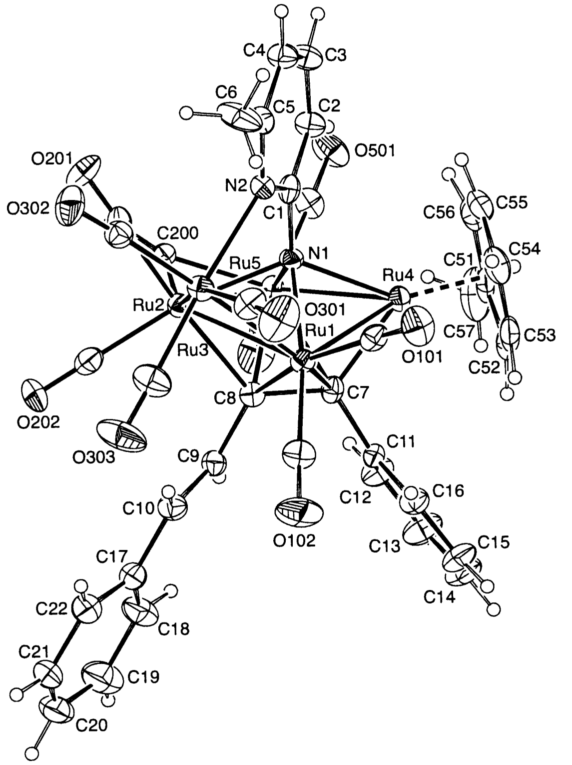
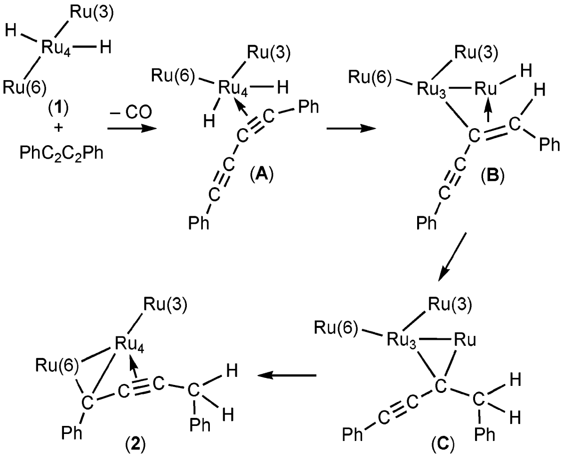


Figure 5. Molecular structure of compound **5**. The C and O atoms of each carbonyl ligand bear the same number.

Scheme 2. Proposed Reaction Pathway for the Formation of Compound 2 from 1 and Diphenylbutadiyne



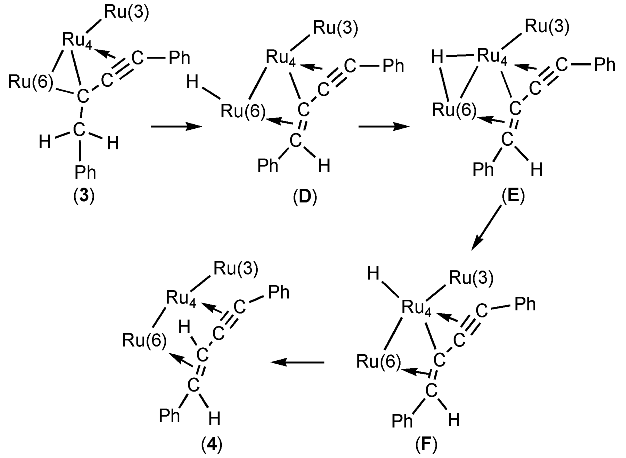
reaction product at any reaction time and why compounds **2** and **4** have been observed only in small amounts at any reaction time. These data, coupled with the results obtained from reactions of **1** with diphenylbutadiyne at different times and temperatures (commented upon above), allow us to propose the following reaction pathway:

$$\mathbf{1} + PhC_2C_2Ph \rightarrow \mathbf{2} \rightarrow \mathbf{3} \rightarrow \mathbf{4} \rightarrow \mathbf{5}$$

We have no doubt that the number of real intermediate species between compounds **1** and **5** is greater than three; in fact, some of them have been detected in small or very small amounts by ^{1}H NMR spectroscopy and/or TLC, but we have been unable to characterize them.

A simplistic proposal that would explain the formation of **2** from **1** and diphenylbutadiyne is shown in Scheme 2. In this and in the following schemes, the carbonyl and ampy ligands have been omitted for clarity, Ru_4 is the metallic square, Ru(3) is the metal atom attached to the pyridine N atom, and Ru(6) is the metal atom that is not attached to the ampy ligand (these two metal atoms maintain the same numbers as in the X-ray structures). The vacant sites necessary for the reaction of **1** with the diyne would arise from the loss of a CO ligand and from the displacement of the apical Ru(6) atom to an edge-bridging position, most probably that opposite the edge bridged by Ru(3), as found in complex **2**. In species **A**, it is also proposed that the diyne caps the Ru_4 metallic square through one of its alkyne moieties, as previously found in related alkyne complexes.[16-20] A migratory insertion process would give species **B**, which contains a bridging η^1:η^2-alkenyl-type ligand. A subsequent Markonikov migratory insertion process would lead to species **C**, which contains a CH_2Ph fragment. Finally, a multistep rearrangement of the ligand on the metallic framework would lead to compound **2**.

Scheme 3. Proposed Reaction Pathway for the Transformation of Compound 3 into 4



The isomerization process that transforms compound **2** into **3** implies a rearrangement of the metallic framework, since Ru(6) moves to an edge of the square adjacent to that spanned by Ru(3), and a profound change in the coordination of the diyne-derived ligand, which rotates nearly 180° over the metallic framework. We cannot suggest a mechanistic proposal for such a complicated isomerization.

The transformation of compound **3** into **4** is also an isomerization process that mainly implies the transformation of the organic ligand of **3** into a *trans*-enyne (in **4**). A proposal for such a transformation is depicted in Scheme 3. A β-hydrogen elimination of one of the H atoms of the CH_2Ph moiety of **3** would render a hydrido derivative containing an η^1:η^2-alkenyl-type ligand (**D**). Migration of this hydride to the atom of the metallic square that is σ-bonded to the alkenyl fragment (**E**, **F**) and a subsequent reductive elimination would lead to compound **4**, which has a *trans*-enyne ligand. This ligand-transformation process is accompanied by a subtle modification in the coordination of the alkyne moiety of the organic ligand, which rotates ca. 90° with respect to the atoms of the metallic square.[23] If the β-hydrogen elimination step had taken place with the other H atom of the CH_2Ph moiety (rotation of the $PhCH_2-C$ bond of **3** is possible), then a *cis*-enyne derivative would have been the final product. However, such a product has not been identified in the reaction solutions accompanying complex **4**.

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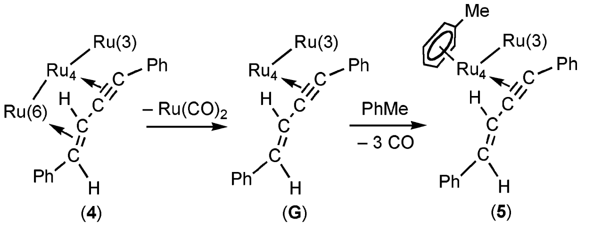
(23) The mobility of alkynes on M_4 faces is well known. See, for example: Lo, W. Y.; Lam, C. H.; Fung, W. K. M.; Sun, H. Z.; Yam, V. W. W.; Balcells, D.; Maseras, F.; Eisenstein, O. *Chem. Commun.* **2003**, 1260.

Scheme 4. Proposed Reaction Pathway for the Transformation of Compound 4 into 5



Only a few metal clusters containing *cis*-enyne ligands have been reported as products of reactions of hydrido clusters with conjugated diynes.[5a,9] However, no metal clusters containing *trans*-enyne ligands have been reported as products from these reactions.

Scheme 4 displays a proposal that would account for the transformation of compound **4** into **5**. We propose that, under the reaction conditions, complex **4** releases a $Ru(CO)_2$ fragment to give the pentanuclear complex $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-}trans\text{-}PhCCCHCHPh)(\mu\text{-}CO)(CO)_{12}]$ (**G**). A subsequent reaction of **G** with the toluene solvent would end in the pentanuclear η^6-toluene derivative **5**. This proposal is supported by the fact that a complex analogous to **G**, having diphenylacetylene instead of *trans*-1,4-diphenylbutenyne and characterized by X-ray diffraction, is a precursor of the η^6-toluene $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-}PhCCPh)(\eta^6\text{-}PhMe)(\mu\text{-}CO)(CO)_9]$, which is analogous to compound **5**.[16] Complex **G** would also be structurally related to $[Ru_5(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}PhCCH)(\mu\text{-}CO)(CO)_{13}]$[17,20] and $[Ru_5(\mu_4\text{-}NH)(\mu_4\text{-}\eta^2\text{-}PhCCH)(\mu\text{-}CO)(CO)_{13}]$.[18] These latter complexes have in common their metallic skeletons and the way the alkyne coordinates to the metals, but differ in the nature of the ancillary ligand that caps the metallic square. In addition, the excision of $Ru(CO)_n$ fragments from ruthenium carbonyl clusters is not unusual when working at high temperatures.[14b,17,20,24] For example, a cluster reduction process, similar to that described herein for the hexa- and pentanuclear compounds **4** and **5**, was observed to occur for the clusters $[Ru_6(\mu_4\text{-}S)(CO)_{18}]$ and $[Ru_5(\mu_4\text{-}S)(CO)_{15}]$.[14b] The formation of arene derivatives from arenes and ruthenium carbonyl clusters at high temperatures is well documented.[25]

Concluding Remarks

The reaction of compound **1** with diphenylbutadiyne is complicated. Nevertheless, a reaction pathway that implies the sequential transformation of compound **1** into four new products (**2**−**5**) has been established. In all cases, the new hydrocarbon ligands contain an alkyne fragment that prefers to cap a (distorted) square of metal atoms rather than to coordinate to a triangular metal face, even though this μ_4-coordination forces the metal atom that originally occupied such a site to move toward an edge-bridging position (**2**, **3**, and **4**) or to leave (**5**) the cluster.

As observed previously in the reactions of compound **1** with alkynes,[16] the present work also demonstrates that the ampy ligand behaves as a useful label to trace reaction products by ^1H NMR spectroscopy, behaving also as a reliable anchor that is able to maintain the pentanuclear edge-bridged square metal framework in reactions performed at high temperatures.

Certainly, the most important feature of this work is that it reports very unusual examples of addition of two hydrogen atoms to a internal CC triple bond of a conjugated diyne in 1,1- (compounds **2** and **3**) and *trans*-1,2-positions (compounds **4** and **5**). The latter process has never been observed previously. While the transformations of **2** into **3** and **4** into **5** maintain the nature of the diyne-derived ligand present in the corresponding initial product, the *trans*-1,2-addition product **4** arises from the 1,1-addition product **3**. Interestingly, for the 1,1-addition, at least two different metal atoms should be involved in the transfer of the two hydrides to the coordinated diyne (Scheme 2). Similarly, at least two metal atoms should be involved in the 1,2-hydrogen transfer that leads to **4** from **3** (Scheme 3). Therefore, it seems that these processes can take place only on polynuclear metal clusters.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, THF) or CaH_2 (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 spot TLC. Compound **1** was prepared as previously reported.[11] IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on a Bruker DPX-300 instrument, at room temperature, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

Reactions of Compound 1 with Diphenylbutadiyne. Reaction a. A solution of **1** (100 mg, 0.086 mmol) and diphenybutadiyne (26 mg, 0.129 mmol) in toluene (20 mL) was heated at reflux temperature for 1 h. The initial dark brown color was maintained. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (3 mL). The resulting solution was supported on preparative silica gel TLC plates. Repeated elution of the plates with hexane−diethyl ether (3:1) eluted several bands. The two major bands were worked up to afford, in order of elution, compounds **4** (16 mg, 14%, brown solid) and **3** (48 mg, 42%, brown solid). A black residue remained uneluted at the baseline of the plates.

Reaction b. A solution of **1** (100 mg, 0.086 mmol) and diphenylbutadiyne (26 mg, 0.129 mmol) in toluene (20 mL) was heated at reflux temperature for 10 h. The initial dark brown color was maintained. The solution was worked up as above. The three major TLC bands were extracted to afford, in order of elution, compounds **4** (4 mg, 3%, brown solid), **3** (32 mg, 28%, brown solid), and **5** (5 mg, 5%, dark green solid). A black residue remained uneluted at the baseline of the plates.

Reaction c. A solution of **1** (100 mg, 0.086 mmol) and diphenylbutadiyne (26 mg, 0.129 mmol) in 1,2-dichloroethane (20 mL) was heated at 50 °C for 11 days. After this time, some compound **1** still remained in the solution (IR spectroscopy). The original dark brown color acquired a greenish tone. The solution was worked up as above. The three major TLC bands were extracted to afford, in order of elution, compounds **2** (6 mg, 5%, dark green solid), **3** (5 mg, 4%, brown solid), and **1** (12 mg, 12%, dark brown solid). A black residue remained uneluted at the baseline of the plates.

Thermolysis of Compound 2. A solution of **2** (6 mg, 0.005 mmol) in 1,2-dichloroethane (5 mL) was stirred at reflux temperature. The reaction was monitored by ^1H NMR spectroscopy. After 6 h, the solution contained complex **3** and an unidentified species in ca. 1:1 ratio. After 24 h, complex **3** was the only product in the solution.

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[24] Cabeza, J. A.; da Silva, I.; del Río, I.; Martínez-Méndez, L.; Miguel, D.; Riera, V. *Angew. Chem. Int. Ed.* **2004**, *43*, 3464.

[25] For a review on η^6-arene ruthenium clusters, see: Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. *Chem. Rev.* **1994**, *94*, 1585.

Table 2. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction

	$\mathbf{2}\cdot0.5(CH_2Cl_2)$	**3**	$\mathbf{4}\cdot CH_2Cl_2$	**5**
formula	$C_{37}H_{18}N_2O_{15}Ru_6\cdot0.5(CH_2Cl_2)$	$C_{37}H_{18}N_2O_{15}Ru_6$	$C_{37}H_{18}N_2O_{15}Ru_6\cdot CH_2Cl_2$	$C_{39}H_{26}N_2O_{10}Ru_5$
fw	1379.42	1336.95	1421.88	1187.97
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	18.171(7)	17.567(4)	12.5797(1)	13.978(6)
b, Å	17.315(7)	12.218(3)	31.0551(4)	15.679(7)
c, Å	15.119(6)	18.911(4)	12.7125(2)	18.975(8)
β, deg	97.587(9)	97.009(4)	117.678(1)	111.098(8)
vol, Å^3	4715(3)	4028(1)	4398.0(1)	3880(3)
Z	4	4	4	4
$F(000)$	2636	2552	2720	2296
D_{calcd}, g cm^{-3}	1.943	2.204	2.147	2.034
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Cu Kα (1.54180)	Mo Kα (0.71073)
μ, mm^{-1}	1.993	2.264	17.991	1.962
cryst size, mm	0.04 × 0.21 × 0.36	0.26 × 0.16 × 0.14	0.20 × 0.15 × 0.13	0.13 × 0.23 × 0.26
temp, K	296(2)	296(2)	293(2)	296(2)
θ limits, deg	1.13 to 23.27	1.17 to 23.26	2.85 to 68.44	1.56 to 23.27
min./max. h, k, l	−20/14, −18/19, −12/16	−19/18, −12/13, −20/17	−15/15, −35/37, −15/15	−15/14, −13/17, −21/19
no. of collected rflns	20 715	17 410	39 853	16 847
no. of unique rflns	6768	5767	8077	5583
no. of reflns $I > 2\sigma(I)$	5030	4689	7470	4862
abs corr	SADABS	SADABS	XABS2	SADABS
max./min. transmn	1.000/0.662	1.000/0.783	0.105/0.070	1.000/0.779
no. of params/restraints	573/0	542/0	576/0	507/0
GOF on F^2	1.050	1.073	1.083	1.197
R1 (on F, $I > 2\sigma(I)$)	0.0630	0.0498	0.0302	0.0351
wR2 (on F^2, all data)	0.1699	0.1190	0.0801	0.0770
max./min. $\Delta\rho$, e Å^{-3}	1.379/−0.910	2.185/−0.869	0.860/−1.362	0.702 / −0.554

Thermolysis of Compound 3. A solution of **3** (15 mg, 0.011 mmol) in toluene (5 mL) was stirred at reflux temperature. After 10 h, the solution contained complexes **3** and **5** in ca. 1:1 ratio along with a trace amount (<3%) of complex **4** (^{1}H NMR spectroscopy) and other unidentified species.

Thermolysis of Compound 4. A solution of **4** (4 mg, 0.003 mmol) in toluene (5 mL) was stirred at reflux temperature. After 2.5 h, the solution contained only complex **5** (^{1}H NMR spectroscopy).

Data for [Ru_6(μ_5-κ^2-ampy)(μ_5-η^3-$PhCCCCH_2Ph$)(μ-CO)$(CO)_{14}$] (2). Anal. Calcd for $C_{37}H_{18}N_2O_{15}Ru_6$ (fw = 1336.96): C, 33.24; H, 1.36; N, 2.10. Found: C, 33.21; H, 1.34; N, 2.06. Positive FAB-MS: *m/z* 1338 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2084 (w, sh), 2068 (vs), 2032 (m), 2014 (m, sh), 2006 (s), 1976 (w, br), 1947 (w, sh), 1934 (w, br), 1855 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.75−7.60 (m, 2 H, Ph), 7.43−7.28 (m, 3 H, Ph), 7.13 (t, J = 7.8 Hz, 1 H, ampy), 7.00−6.83 (m, 3 H, Ph), 6.56 (d, J = 7.8 Hz, 1 H, ampy), 6.42 (d, J = 6.4 Hz, 2 H, Ph), 5.57 (d, J = 7.8 Hz, 1 H, ampy), 3.10 (d, J = 13.1 Hz, 1 H, CH), 2.77 (d, J = 13.1 Hz, 1 H, CH), 2.58 (s, 3 H, ampy).

Data for [Ru_6(μ_5-κ^2-ampy)(μ_5-η^3-$PhCCCCH_2Ph$)(μ-CO)$(CO)_{14}$] (3). Anal. Calcd for $C_{37}H_{18}N_2O_{15}Ru_6$ (fw = 1336.95): C, 33.24; H, 1.36; N, 2.10. Found: C, 33.64; H, 1.41; N, 2.05. Positive FAB-MS: *m/z* 1338 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2086 (m), 2067 (vs), 2035 (vs), 2020 (vs), 1998 (s), 1975 (m), 1950 (w), 1937 (w), 1848 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.17 (t, J = 7.7 Hz, 1 H, ampy), 7.02−6.73 (m, 6 H, Ph), 6.59 (d, J = 7.7 Hz, 1 H, ampy), 6.47−6.31 (m, 3 H, Ph + ampy), 6.22 (d, br, J = 6.7 Hz, 2 H, Ph), 3.72 (d, J = 13.5 Hz, 1 H, CH), 3.35 (d, J = 13.5 Hz, 1 H, CH), 2.54 (s, 3 H, ampy). ^{13}C NMR (DEPT-135, $CDCl_3$): δ 140.1 (CH_{ampy}), 129.2, 128.6, 128.3, 127.0, 126.7, 125.8 (10 CH_{Ph}), 120.4 (CH_{ampy}), 113.2 (CH_{ampy}), 57.1 (CH_2), 30.0 (Me_{ampy}).

Data for [Ru_6(μ_5-κ^2-ampy)(μ_5-η^4-*trans*-PhCCCHCHPh)(μ-CO)$(CO)_{14}$] (4). Anal. Calcd for $C_{37}H_{18}N_2O_{15}Ru_6$ (fw = 1336.95): C, 33.24; H, 1.36; N, 2.10. Found: C, 33.38; H, 1.40; N, 2.04. Positive FAB-MS: *m/z* 1338 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2082 (m), 2058 (vs), 2043 (s), 2017 (s), 1995 (s, br), 1977 (m, sh), 1969 (w, sh), 1946 (w, br), 1931 (w, sh) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.35−7.05 (m, 4 H, Ph + ampy), 7.00−6.70 (m, 6 H, Ph), 6.62 (d, J = 7.9 Hz, 1 H, ampy), 6.18 (d, br, J = 6.9 Hz, 1 H, Ph), 5.84 (d, J = 13.8 Hz, 1 H, CH), 5.72 (d, J = 7.9 Hz, 1 H, ampy), 3.41 (d, J = 13.8 Hz, 1 H, CH), 2.69 (s, 3 H, ampy). ^{13}C NMR (DEPT-135, $CDCl_3$): δ 139.4 (CH_{ampy}), 132.1, 129.5, 128.6, 128.3, 126.6, 123.6 (10 CH_{Ph}), 120.8 (CH_{ampy}), 113.7 (CH_{ampy}), 96.7 (CH), 79.5 (CH), 29.3 (Me_{ampy}).

Data for [Ru_5(μ_5-κ^2-ampy)(μ_4-η^2-*trans*-PhCCCHCHPh)(η^6-PhMe)(μ-CO)$(CO)_9$] (5). Anal. Calcd for $C_{39}H_{26}N_2O_{10}Ru_5$ (fw = 1187.97): C, 39.43; H, 2.21; N, 2.51. Found: C, 39.57; H, 2.41; N, 2.39. Positive FAB-MS: *m/z* 1189 [M$^+$]. IR (CH_2Cl_2): ν(CO) 2059 (s), 2016 (vs), 2001 (s), 1993 (s, br), 1980 (m, sh), 1968 (m), 1954 (m), 1945 (m, sh), 1918 (w, br), 1824 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.23−6.95 (m, 7 H, Ph + ampy), 6.83−6.67 (m, 4 H, Ph), 6.51 (d, J = 7.6 Hz, 1 H, ampy), 6.08 (d, J = 15.4 Hz, 1 H, CH), 5.78 (d, J = 7.6 Hz, 1 H, ampy), 5.57−5.41 (m, 3 H, PhMe), 5.36 (d, J = 5.8 Hz, 1 H, PhMe), 5.26 (d, J = 15.4 Hz, 1 H, CH), 5.02 (d, J = 5.8 Hz, 1 H, PhMe), 2.60 (s, 3 H, ampy), 2.07 (s, 3 H, PhMe).

X-ray Structures of $\mathbf{2}\cdot0.5(CH_2Cl_2)$, 3, and 5. A selection of crystal, measurement, and refinement data is given in Table 2. Diffraction data were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation. Raw frame data were integrated with SAINT.[26] Absorption corrections were applied with SADABS.[27] Structures were solved by direct methods and refined by full matrix least-squares against F^2 with SHELXTL.[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the PLATON program package.[29] WINGX program system[30] was used throughout the structure determinations. CCDC deposition numbers: 286872 ($\mathbf{2}\cdot0.5(CH_2Cl_2)$), 286873 (**3**), and 286875 (**5**).

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X-ray Structure of $4\cdot CH_2Cl_2$. A selection of crystal, measurement, and refinement data is given in Table 2. Diffraction data were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromated Cu Kα radiation. Raw frame data were integrated with DENZO and SCALEPACK.[31] Empirical absorption corrections were applied using XABS2.[32] The structures were solved by Patterson interpretation using the program DIRDIF-96.[33] Isotropic and full matrix anisotropic least-squares refinements against F^2 were carried out using SHELXL-97.[34] All non H atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the PLATON program package.[29] The WINGX program system[30] was used throughout the structure determination. CCDC deposition number: 286874.

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Supporting Information Available: Crystallographic data in CIF format for compounds **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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