η²-Edge-Bridging and η³-Face-Capping Coordination of Conjugated Yenyl Ligands in Triruthenium Carbonyl Cluster Complexes Derived from 1,1-Dimethylhydrazine

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The reactions of the 1,1-dimethylhydrazine-derived cluster [Ru3(μ-H)(μ-η²-HNNMe2)(CO)9] with conjugated diynes, RCR (R = Me, Ph), afford the yenyl derivatives [Ru3(μ-η²-HNNMe2)(μ-η²-CCCCHR)(μ-CO)2(CO)9] (R = Me) and [Ru3(μ-η³-HNNMe2)(μ-η³-CCCCHR)-(μ-CO)(CO)] (R = Me, Ph), featuring η²-edge-bridging and η³-face-capping coordination modes for their yenyl ligands. DFT calculations have revealed that the face-capped products are slightly more stable than the edge-bridged ones. The regioselectivity of the reactions is affected by the nature of the R groups of the diynes.

Introduction

The studies reported over the last two decades on reactions of metal complexes with diynes have shown, as expected, that there is a rich organometallic chemistry resulting from the presence of two alkyne fragments in the organic reagents. Cluster chemists have actively participated in this research activity. 1−9

Reactivity studies involving conjugated diynes and amidopyridine-bridged hydrido-triruthenium carbonyl complexes of the type [Ru3(μ-H)(μ-η²-apy)(CO)9] (apy = 2-amidopyridine-type ligand) have shown that trinuclear products containing edge-bridging η²-yenyl ligands, namely, [Ru3(μ-η²-apy)(μ-η²-yenyl)(μ-CO)2(CO)9] (one of these compounds is shown at the left in Scheme 1), are selectively formed in these reactions. 12−14 These trinuclear yenyl derivatives are prone to undergo insertion reactions with unsaturated organic molecules leading to products that contain large unsaturated ligands. 12,13,15,16 The rearrangement of an yenyl ligand from an η²-edge-bridging to an η³-face-capping position on a triruthenium cluster has been observed on one occasion (Scheme 1). 14 For comparison purposes,

(14) Cabeza, J. A.; Grepaioni, F.; Moreno, M.; Riera, V. Organometallics 2000, 19, 5424.


it is worth mentioning here that the reactions of alkynes with complexes of the type [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-allyl](CO)\(_6\)] afford the edge-bridged alkenyl derivatives [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-allyl](CO)\(_6\)] with total regioselectivity.\(^{11,17}\)

Interestingly, the reactivity of the 1,1-dimethylhydrazine-derived cluster [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-1,1-dimethylhydrazino](CO)\(_6\)]\(^{18}\) (1) with alkynes differs considerably from that of [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-1,1-dimethylhydrazino](CO)\(_6\)] with the same reagents,\(^{11,17}\) despite the similarity of these clusters as far as structure and composition are concerned. In fact, in addition to edge-bridged alkenyl derivatives, the reactions of 1 with alkynes also give unusual face-capped alkenyl products (Scheme 2).\(^{19,20}\)

This different behavior observed for [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-1,1-dimethylhydrazino](CO)\(_6\)] and the 1,1-dimethylhydrazido-bridged cluster 1 in their reactions with alkynes, in addition to the above-commented remarkable results originated from the reactions of [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-1,1-dimethylhydrazino](CO)\(_6\)] with conjugated diynes, prompted us to study the reactivity of 1 with conjugated diynes. We now report the results of these studies, which have led us to observe two unusual coordination types for edge-bridging and face-capping ynenyl ligands in triruthenium clusters.

## Results and Discussion

Two trinuclear complexes, subsequently characterized as the edge-bridged and the face-capped ynenyl deriv-

tives [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-H\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-HNNMe\(_2\)](CO)\(_2\)(CO)\(_6\)] (2a) and [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-HNNMe\(_2\)](CO)\(_2\)(CO)\(_6\)] (2b), respectively, were the products of reactions of compound 1 with 1 equiv of hexa-2,4-diyne (Scheme 3). Compound 2a was the major product (65% isolated yield) of a 25 min reaction in refluxing THF. Longer reaction times and/or higher temperatures reduced the yield of 2a, increasing that of 3a; for example, a 77% yield of 3a was obtained from a 45 min reaction in refluxing 1,2-dichloroethane. Therefore, 2a is an intermediate in the synthesis of 3a.

The face-capped alkenyl derivative [Ru\(\mu\cdot\cdot\cdot\mu\cdot\cdot\cdot\mu\)-HNNMe\(_2\)](CO)\(_2\)(CO)\(_6\)] (3b) was the only product that could be isolated from reactions of compound 1 with 1 equiv of diphenylbutadiyne (Scheme 3). In refluxing dichloromethane and from the beginning of the reaction, complex 3b was the major reaction product, being accompanied by the starting material 1 and by trace amounts of two additional complexes (observed by TLC and \(^1\)H NMR spectroscopy) that could not be separated and characterized. At higher temperatures, complex 3b was the only observed reaction product.

Complex 2a was characterized by X-ray diffraction (Figure 1). Its most relevant structural feature is the way the ynenyl ligand coordinates to the trimetal core: edge-bridging through only the two C atoms of the alkenyl fragment. In all previous examples of trinuclear clusters containing conjugated ynenyl ligands in edge-bridging positions, these ligands interact with the metal atoms of the bridged edge through three C atoms (one of these compounds is shown at the left of Scheme 1).\(^{12–14}\) Therefore, in trinuclear clusters, the edge-bridging coordination type found for the ynenyl ligand of 2a, although common for alkenyl ligands,\(^{11,17,19–22}\) is unprecedented for conjugated ynenyl ligands.

The structure of 3b was also determined by X-ray diffraction (Figure 2). This time the ynenyl ligand caps...
Figure 1. Molecular structure of 2a. Thermal ellipsoids are drawn at the 20% probability level. Selected bond distances (Å) and angles (deg): C(3)–C(4) 1.426(6), C(3)–Ru(1) 2.224(4), C(3)–Ru(2) 2.261(4), C(3)–Ru(3) 2.367(4), C(4)–C(5) 1.337(7), C(4)–Ru(1) 2.111(4), C(4)–Ru(3) 2.247(4), C(5)–C(6) 1.344(7), C(5)–Ru(3) 2.263(4), Ru(1)–Ru(2) 2.8657(5), Ru(1)–Ru(3) 3.6255(5), Ru(2)–Ru(3) 2.8163(5), C(3)–C(4)–Ru(1) 75.2(2), C(3)–C(4)–C(5) 134.4(4), C(3)–C(4)–Ru(3) 76.7(2), C(4)–C(3)–C(101) 121.6(4), C(4)–C(3)–Ru(1) 66.6(2), C(4)–C(3)–Ru(2) 119.3(2), C(4)–C(3)–Ru(3) 67.4(2), C(4)–C(5)–C(6) 153.0(4), C(4)–C(5)–Ru(3) 72.1(3), C(5)–C(4)–Ru(1) 148.7(4), C(5)–C(4)–Ru(3) 73.4(3), C(5)–C(6)–C(201) 125.1(4), Ru(1)–C(3)–Ru(3) 104.2(2), Ru(1)–C(4)–Ru(3) 112.5(2), C(6)–C(5)–Ru(3) 135.0(3).

an open (two metal–metal bonds) triangle of ruthenium atoms in such a way that its alkyne moiety interacts with the three metal atoms in a “perpendicular” fashion, while the alkenyl moiety is σ-bound to one of the Ru atoms of the open edge. This latter interaction is responsible for the nonplanarity of the but-1-yn-3-yl fragment, the C(3)–C(4)–C(5)–C(6) dihedral angle being 127.6(9)°. Alternatively, this ligand can also be considered as having a buta-1,2,3-trien-1-yl fragment in which the C(3) atom is σ-bound to Ru(2), the C(3)=C(4) double bond is shared by Ru(1) and Ru(3), the C(4)=C(5) double bond is attached to Ru(3), and the C(5)=C(6) double bond is uncoordinated. In fact, the C(4)=C(5) and C(5)=C(6) distances are roughly similar. Therefore, the hydrocarbyl ligand of 3b would be more appropriately described as a resonance hybrid of the 1-yn-3-en-3-yl and 1,2,3-trien-1-yl canonical forms. Prior to this work, only three examples of triruthenium clusters containing face-capping ynenyl ligands were known; they are [Ru3(μ3-η2-appy)Ru3(μ3-η2)-PhOCH2CCCH2CH2OPh](CO)8 (Hapyr = 2-aminopyrimidine, depicted in Scheme 1),14 [Ru3(μ3-NS(O)MePh)(μ3-η2)-PhCCCH-Ph](CO)8,21 and [Ru3(μ3-NS(O)MePh)(μ3-η2)-PhCCCH-Ph](CO)8.21 While the butynenyl fragments of the first two complexes are planar and symmetrically cap the metallic plane, the butynyl fragment of the latter complex is similar to that of compound 3b. Curiously, the ynenyl ligands of the two sulfoximido clusters do not arise from a diyne but from a cluster-mediated coupling of two individual alkyne fragments.24 A few triruthenium carbonyl clusters containing butynyl ligands that asymmetrically cap a face of the metal triangle have been recently reported. In these cases, the butynecyl ligands are derived from bis(ferrocenyl)butadiyne.3b

Scheme 3 shows that the alkenyl moieties of compound 2a, 3a, and 3b have a hydrogen atom and an R group on the same carbon atom. In other words, all compounds arise from the Markovnikov-type insertion of an alkyne moiety into a Ru–H bond. This fact has been confirmed by X-ray diffraction for 2a and 3b and is clearly evidenced by the 1H NMR spectra of 2a and 3a, which show the resonances of a methyl group and the alkenyl proton coupled to each other (J = 5.9 and 6.4 Hz, respectively).

The similarity of the CO stretching regions of the IR spectra of compounds 3a and 3b indicates that both have similar structures. The absorptions of their bridging CO ligands are clearly observed as broad bands at 1788 cm⁻¹ (3a) and 1786 cm⁻¹ (3b).

Density functional theoretical calculations were carried out with the aim to compare the thermodynamic stabilities of the pairs of compounds 2a, 3a and 2b, 3b. These calculations also allowed us to confirm the structures of the compounds for which no X-ray diffraction data were available (2b and 3a). No simplified model compounds were used for the calculations.

For the cases in which both theoretical (DFT calculations) and experimental (X-ray diffraction) data were available (2a and 3b), the bond lengths and angles given by both methods are practically identical (this fact validates the calculations), the greatest diversences corresponding to the Ru–Ru bond distances, which are slightly longer (0.06–0.15 Å) in the calculated structures than in the experimental ones, but these diversences

are expected for calculations at the GGA level.24 The optimized structures of compounds 2b and 3a are very similar to those of 2a and 3b, respectively, except for the R groups of their ynnyl ligands (views of the four optimized structures and their corresponding atomic coordinates are given as Supporting Information).

Scheme 3 gives the relative thermodynamic stabilities of the two pairs of compounds, assigning 0.00 kcal/mol to the most stable compound of each pair. The values show that the face-capped compounds 3a and 3b are slightly more stable than the edge-bridged derivatives 2a and 2b. This may account for the fact that 2a is transformed into 3a upon heating, but it does not explain directly the lack of observation of the edge-bridged derivative 2b in the reaction of 1 with diphenylbutadiyne.

A previously reported kinetic analysis of the reaction of complex 1 with diphenylacetylene established that the reaction is first order in both cluster concentration and alkyne concentration and that the formation of the first intermediate, a hydrido-alkyne species, is the rate-limiting step.19 Assuming that a related hydrido-diyne intermediate is formed in the reaction of 1 with diynes, in the case of the reaction with hexa-2,4-diyne, the observation of the edge-bridged product 2a in higher amount than 3a at short reaction times implies that the formation of 2a from the corresponding hydrido-diyne intermediate has lower activation energy than the formation of the face-capped product 3a. Although it is clear that under the reaction conditions (THF at reflux) most of 3a arises from 2a (as commented above, such a transformation has been individually checked), it cannot be ruled out that a small amount of 3a may also be formed without the intermediacy of 2a (directly from the initial hydrido-diyne intermediate by a pathway different from that leading to 2a). The fact that 2b was not detected at any stage of the reaction of 1 with diphenylbutadiyne suggests that 2b is not an intermediate in the formation of the face-capped derivative 3b and, therefore, 3b should be formed from the hydrido-diyne intermediate by a pathway with a much lower activation energy than that which would lead to the edge-bridged product 2b. Therefore, the regioselectivity of the reactions reported herein also depends on kinetic aspects associated with the nature of the R groups of the used diynes.

Concluding Remarks

The reactions of the 1,1-dimethylhydrazine-derived cluster [Ru3(μ-H)(μ2-HNNMe2)(CO)]6 with conjugated diynes, RC=CHR (R = Me, Ph), afford the ynnyl derivatives [Ru3(μ2-HNNMe2)(μ-H)-RCCCHR)(μ-CO)2(CO)]6 (R = Me, 2a) and [Ru3(μ2-HNNMe2)(μ-H)-RCCCHR)-(μ-CO)(CO)]6 (R = Me, 3a; Ph, 3b), featuring η2-edge-bridging and η1-face-capping coordination modes for their ynnyl ligands. While the η2-edge-bridging coordination mode is unprecedented for conjugated ynnyl ligands in cluster chemistry, only one previous example of a cluster complex containing an η1-face-capping ynnyl ligand coordinated in a manner similar to that found in 3b is known. DFT calculations have revealed that the face-capped products are slightly more stable than the edge-bridged ones. These calculations, coupled to the experimental results obtained at different reaction times, allow us to conclude that the different R groups of the diynes affect considerably the regioselectivity of the reactions because, in addition to having a small effect on some thermodynamic parameters, they strongly influence the kinetics of key steps of the reaction pathway.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, THF) or CaH2 (dichloromethane) 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.18 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 (δ = 3.50). 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 isopomer.

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Conjugated Ynenyl Ligands on Ru3 Clusters

Theoretical Calculations. All the minimum-energy structures reported herein were optimized with density functional theory (DFT), within the Gaussian98 program,25 using the Becke’s three-parameter hybrid exchange–correlation functional26 containing the B3LYP nonlocal gradient correction.27 The LANL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.28 The basis set used for the remaining atoms was the 6-31G, with addition of (d,p)-polarization for all atoms. All optimized structures were confirmed as minima by calculation of analytical frequencies. For each calculation, the input model molecule was based on one of the X-ray-determined structures reported in this article, conveniently modified (if necessary) by changing the appropriate diff peak and hole 1.326 and 20.5C6H14.

X-ray Structures of 2a and 3b-0.5C6H14. Diffraction data were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromated Cu Kα radiation. Raw frame data were integrated with DENZO-SCALEPACK.29 Empirical absorption corrections were applied using SORTAV.30 The structures were solved by Patterson interpretation using the program DIRDIF-96.31 Isotropic and full matrix anisotropic least-squares refinements against F² were carried out using SHELXL-97.32 All non-H atoms were refined anisotropically. H atom positions were geometrically calculated and refined riding on their parent atoms. The molecular plots were made with the PLATON program package.33 The WINGX program system34 was used throughout the structure determinations. Selected crystal and refinement data are given as footnotes.35,36 CCDC deposition numbers: 255371 and 255372.

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Supporting Information Available: Crystallographic data in CIF format for compounds 2a and 3b-0.5C6H14 and computer-generated plots and atomic coordinates for the DFT-optimized molecular structures of 2a, 2b, 3a, and 3b. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049119X

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