Synthesis and Structural Characterization of Triruthenium Cluster Complexes Containing Bridging $\eta^1$-Phenyl and Terminal $\eta^1$-Phenyl Ligands Arising from the Cleavage of Triphenylphosphine Ligands

Pierrette Briard, Javier A. Cabeza, Angela Llamazares, Ladhène Ouahab, and Víctor Riera

Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo, Spain, and Laboratoire de Cristallochimie, Université de Rennes I, URA-CNRS 1495, Avenue du Général Leclerc, 35042 Rennes Cédex, France

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Summary: The $\text{PPh}_3$ ligands of the cluster complex $[\text{Ru}_3(\mu_3-H)(\text{CH}_3)(\text{PPh}_3)_2]_2$ (1) (amphi $= 2$-amino-6-methylpyridinidate) undergo carbon-phosphorus bond scission on reaction with hydrogen (100 °C, 1 atm) or diphenylacetylene (110 °C) to give $[\text{Ru}_3(\mu_3-H)(\text{PPh}_3)_2]_2$ (2) and $[\text{Ru}_3(\mu_3-H)(\text{PPh}_3)_2]_2$ (3), which have been characterized by X-ray crystallography. Complex 2 represents the first example in ruthenium chemistry of a bridging $\eta^1$-phenyl derivative.

The actual knowledge of fundamental cluster reactions is still insufficient to rationalize the transformations undergone by many organic substrates at adjacent metal centers. In this context, studies carried out during the last 20 years have demonstrated that triphenylphosphine-metal complexes are liable to undergo carbon-hydrogen and/or carbon-phosphorus bond cleavage reactions, depending on the conditions that they are exposed to, and that these reactions, which are still far from being predictable, may have important implications for the activity and stability of homogeneous catalysts.

Metal-mediated P-Ph cleavage reactions generally lead to phosphine-bridged derivatives as well as to benzene, benzaldehyde, or biphenyl. However, although $\sigma$-phenyl-$\mu$-diphenylphosphido derivatives have been claimed as intermediates in the above cited processes, they have been isolated in very few occasions, and to our knowledge, the cluster compound $[\text{Os}_8(\mu_2-\text{PPh}_3)(\mu_2^-\text{PPh}_2\text{CO}_2\text{H})(\mu^-\text{Ph})(\text{CO})_3]$, which was reported some 20 years ago, is so far the only known transition-metal complex containing a bridging $\eta^1$-phenyl group arising from a P-C bond cleavage.

We now communicate the syntheses and X-ray structures of the second example of such a class of compounds and of a rare triruthenium cluster complex containing a terminal phenyl ligand.

The original objective of this study was to investigate the catalytic activity of phosphate-substituted derivatives of $[\text{Ru}_3(\mu_3-H)(\text{PPh}_3)_2]_2$ (1) (amphi $= 2$-amino-6-methylpyridinidate) in the homogeneous hydrogenation of alkynes, a reaction for which $[\text{Ru}_3(\mu_3-H)(\text{PPh}_3)_2]_2$ (1) is an efficient catalyst precursor. During the course of this work, we found that the cluster complex $[\text{Ru}_3(\mu_3-H)(\text{PPh}_3)_2]_2$ (Scheme I) was separated by chromatographic methods and isolated as an air-stable compound. On the other hand, complex 1 also reacts with diphenylacetylene to give the air-stable $\sigma$-phenyl-$\mu$-diphenylphosphido derivative $[\text{Ru}_3(\mu_3-H)(\text{PPh}_3)_2]_2$ (2) (Scheme I), which have been isolated in very few occasions, and to our knowledge, the cluster compound $[\text{Os}_8(\mu_2-\text{PPh}_3)(\mu_2^-\text{PPh}_2\text{CO}_2\text{H})(\mu^-\text{Ph})(\text{CO})_3]$, which was reported some 20 years ago, is so far the only known transition-metal complex containing a bridging $\eta^1$-phenyl group arising from a P-C bond cleavage.


both compounds were studied by X-ray diffraction methods.

The molecular structure of compound 2 and its most relevant interatomic parameters are shown in Figure 1. The cluster consists of an isosceles triangle of ruthenium atoms triply bridged by the ampy ligand, with the two longest edges also bridged by PPh₂ ligands, and with the short edge spanned by the amido fragment of the ampy ligand and by one carbon atom of the phenyl group. The cluster coordination shell is completed by six terminal carbonyls, three in axial positions (trans to the nitrogen atoms of the ampy ligand) and three in equatorial positions. While the ampy ligand is nearly perpendicular to the Ru₃ plane (dihedral angle 89.3°), the phosphido bridges are almost coplanar with the metal triangle (the dihedral angles between the Ru₃ plane and the Ru₁-P₁-Ru₂ and Ru₂-P₂-R₃ planes are 5.3° and 9.4°, respectively). The μ₃-phenyl ring is planar and essentially orthogonal to the Ru₂-R₃ bond vector, involving a Ru₂-C₃-R₃ bond angle of 69.0°, Ru₂-C₃-R₃ and Ru₃-C₃ bond distances of 2.83(1) Å each, and a dihedral angle between the metal triangle and the Ru₂-C₃-R₃ plane of 9.8(3)°. The ipso carbon atom of the phenyl ring (C₃) is at 0.33(1) Å from the metal triangle on the site opposite the ampy ligand. The short Ru₂-R₃ bond distance (2.637(2) Å) may be a consequence of the presence of the bridging amido and phenyl groups on this edge, but, however, the edge bridged by the amido and the hydrido ligands in the related cluster complex [Ru₅(μ-H)(μ-η²-ampy)(CO)₃] (ampy = 2-anilinopyridine) is longer: 2.753(1) Å. A three-center two-electron bond model, similar to that described for [Al₆P₃H₃]²⁺, could explain the interaction of the phenyl ring with the two spanned ruthenium atoms of 2, but an interaction of the phenyl π-orbitals with the appropriate metal d-orbitals might also contribute to the bonding; therefore, theoretical calculations are needed to fully describe the situation.

The molecular structure of compound 3 and its most relevant interatomic parameters are shown in Figure 2. The cluster consists of a triangular array of ruthenium atoms triply bridged by the ampy ligand, with the two longest edges also bridged by PPh₂ ligands.
The spectroscopic data for 21 and 215 are fully consistent with their X-ray structures. Those of complex 2 can be compared to those of [Ru3(μ-H)(μ3,η6-ampy)(μ-PPh3)2(CO)4]2, a complex that may be described as the result of a hypothetical substitution of a hydride for the bridging phenyl ligand of 2.

The steps that lead to complex 2 from 1 have not been established. Although the elimination of one CO ligand and one benzene molecule from complex 1 could stochiometrically lead to 2 without the use of hydrogen, the thermolysis of 1 does not give 2 unless a hydrogen atmosphere is used; therefore, hydrido derivatives should be intermediates in this reaction. The formation of 3 from 1 and diphenylacetylene should also be a several-step process, which involves the elimination of two CO ligands, alkyne coordination and insertion into a Ru-H bond, and oxidative addition of a P-C bond of a PPh3 ligand, but the sequence of these reactions remains unknown.

Complex 3 reacts with hydrogen (1 atm, 1.5 h) in refluxing toluene (no reaction is observed at room temperature) to give 2 as the major component of a mixture of products (established by 31P{1H} NMR spectroscopy of the reaction solution), but it is remarkable that 2, under hydrogen in refluxing toluene, does not eliminate benzene or transforms the phosphido bridges into terminal PPh2H ligands.23 The great stability of 2 and 3 has to be related to the fact that they are coordinatively saturated 48-electron species and, in the case of compound 3, that the α-carbon atom of the alkenyl group is σ-bonded to a different Ru atom than the phenyl ligand.24

In conclusion, this work sheds light on the chemical reactivity of phosphine ligands in polynuclear complexes, describing the syntheses and structures of two uncommon derivatives arising from P-C bond cleavage reactions, and raises questions about the use of phosphine-substituted polynuclear complexes as homogeneous catalyst precursors. The general significance of the reactions described herein, i.e. for the cleavage of P-C bonds of a variety of phosphine ligands, is currently under investigation.

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Supplementary Material Available: Tables of crystal and refinement data, positional parameters, bond distances and angles, H-atom parameters, and anisotropic thermal parameters (16 pages). Ordering information is given on any current masthead page.

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(23) The conversion of μ-PPh3 groups into terminal PPh2H ligands has been described.26
(24) In a related work on the hydrosilylation of alkynes promoted by an osmium cluster complex, the intermediate [Os4(μ,η5-CsH3-phen)(CO)10] decomposes, giving the silylated alkenes because the alkenyl α-carbon and the silyl group are attached to the same Os atom. Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. Organometallics 1992, 11, 1.

Figure 2. ORTEP view of the molecular structure of complex 3. For clarity, only the ipso carbon atoms of the phenyl rings attached to phosphorus are shown. Selected bond distances (Å) and angles (deg) are as follows: Ru1-Ru2 2.775(2), Ru1-Ru3 2.828(2), Ru2-Ru3 2.741(2), Ru1-P1 2.327(5), Ru3-P1 2.258(6), Ru2-P2 2.409(6), Ru1-C21 2.13(2), Ru1-C28 2.27(2), Ru1-C35 2.25(2), Ru2-C35 2.11(2); Ru1-P1-Ru3 76.2(2), Ru1-C35-Ru2 78.9(6), C21-Ru1-C28 81.6(7), C21-Ru1-C35 119.1(7), Ru1-C28-C35 70(1), Ru2-C35-C28 124(1).