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

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Summary: The PPh_3 ligands of the cluster complex $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$ (1) (ampy = 2-amino-6-methylpyridinate) undergo carbon–phosphorus bond scission on reaction with hydrogen (110 °C, 1 atm) or diphenylacetylene (110 °C) to give $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu\text{-}PPh_2)_2(\mu\text{-}Ph)(CO)_6]$ (2) or $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu\text{-}PPh_2)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}(Ph)(CO)_5(PPh_3)]$ (3), which have been characterized by X-ray crystallography. Complex 2 represents the first example in ruthenium chemistry of a bridging η^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.[2] In this context, studies carried out during the last 20 years have demonstrated that triphenylphosphine–metal complexes are liable to undergo carbon–hydrogen[3] and/or carbon–phosphorus[2e,4] 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 on the activity and stability of homogeneous catalysts.[2e,4,5]

Metal-mediated P–Ph cleavage reactions generally lead to phosphido-bridged derivatives as well as to benzene,[6,7] benzaldehyde,[7,8] or biphenyl.[7,9] However, although σ-phenyl-μ-diphenylphosphido derivatives have been claimed as intermediates in the above cited processes,[8b,9] they have been isolated in very few occasions,[10] and to our knowledge, the cluster compound $[Os_3(\mu\text{-}PPh_2)(\mu_3,\eta^2\text{-}PPh_2C_6H_4)(\mu\text{-}Ph)(CO)_8]$, which was reported some 20 years ago,[11] is so far the only known transition-metal complex containing a bridging η^1-phenyl group arising from a P–C bond cleavage.[12,13]

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 phosphine-substituted derivatives[14] of $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9]$[15] (ampy = 2-amino-6-methylpyridinate) in the homogeneous hydrogenation of alkynes, a reaction for which $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_9]$ is an efficient catalyst precursor.[16] During the course of this work, we found that the cluster complex $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(CO)_7(PPh_3)_2]$[14b] (1) is a bad catalyst precursor for the homogeneous hydrogenation of diphenylacetylene (toluene, 80 °C, 1 atm). However, it reacts with hydrogen to give a mixture of products from which the μ-phenyl-bis(μ-diphenylphosphido) derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu\text{-}PPh_2)_2(\mu\text{-}Ph)(CO)_6]$ (2) (Scheme I) was separated by chromatographic methods and isolated as an air-stable compound.[17] On the other hand, complex 1 also reacts with diphenylacetylene to give the air-stable σ-phenyl–μ-diphenylphosphido derivative[18] $[Ru_3(\mu_3,\eta^2\text{-ampy})(\mu\text{-}PPh_2)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}(Ph)(CO)_5(PPh_3)]$ (3) (Scheme I). The spectroscopic data of clusters 2 and 3 were not

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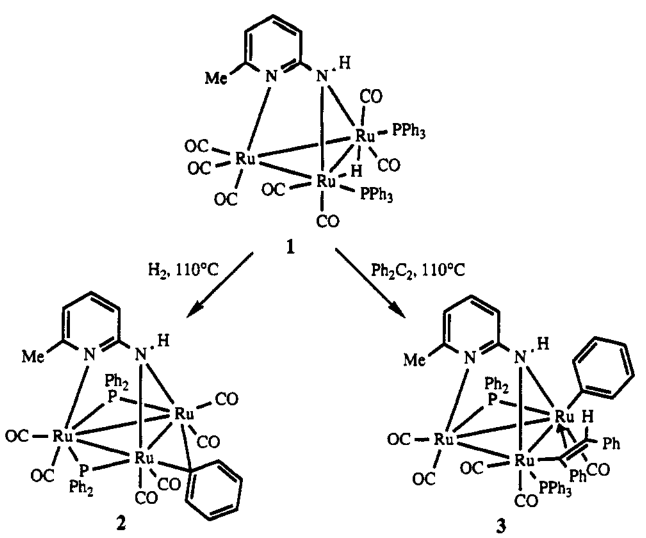
Scheme I



enough to unequivocally assign their structures; therefore, both compounds were studied by X-ray diffraction methods.[19]

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 PPh_2 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 Ru_3 plane (dihedral angle 89.3(3)°), the phosphido bridges are almost coplanar with the metal triangle (the dihedral angles between the Ru_3 plane and the Ru1–P1–Ru2 and Ru1–P2–Ru3 planes are 5.5(3) and 9.4(2)°, respectively). The μ,η^1-phenyl ring is planar and essentially orthogonal to the Ru2–Ru3 vector, involving a Ru2–C31–Ru3 bond angle of 69.0(4)°, Ru2–C31 and Ru3–C31 bond distances of 2.32(1)and 2.34(1) Å, respectively, and a dihedral angle between the metal triangle and the Ru2–C31–Ru3 plane of 9.8(3)°. The ipso carbon atom of the phenyl ring (C31) is at 0.33(1) Å from the metal triangle on the site opposite the ampy ligand. The short Ru2–Ru3 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 $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}anpy)(CO)_9]$ (anpy = 2-anilinopyridinate) is longer: 2.7531(4) Å.[15] A three-center two-electron bond model, similar to that described for $[Al_2Ph_6]$,[20] 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.

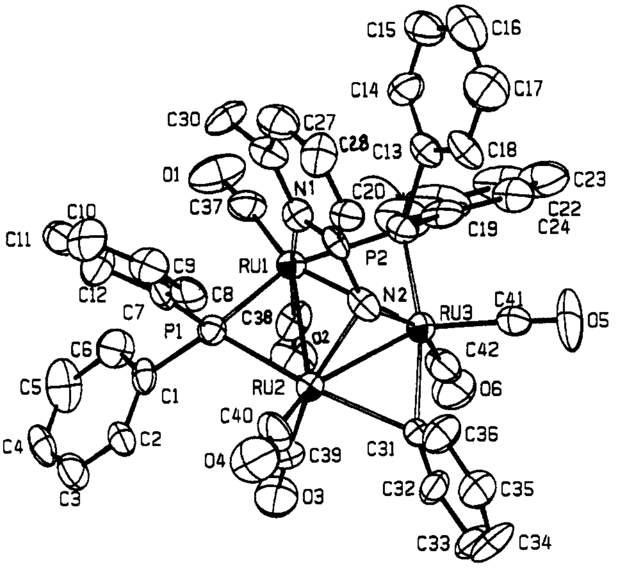


Figure 1. ORTEP view of the molecular structure of complex **2**. Selected bond distances (Å) and angles (deg) are as follows: Ru1–Ru2 2.970(2), Ru1–Ru3 2.980(2), Ru2–Ru3 2.637(2), Ru1–P1 2.347(3), Ru2–P1 2.290(4), Ru1–P2 2.347(4), Ru3–P2 2.297(4), Ru2–C31 2.32(1), Ru3–C31 2.34(1); Ru1–Ru2–Ru3 63.87(4), Ru1–Ru3–Ru2 63.50(4), Ru2–Ru1–Ru3 52.63(4), Ru1–P1–Ru2 79.7(1), Ru1–P2–Ru3 79.8(1), Ru2–C31–Ru3 69.0(4).

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 PPh_2 and η^1:η^2-PhC=C(H)Ph ligands. The cluster coordination shell is com-

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(17) Synthesis of **2**: Hydrogen was bubbled through a toluene solution (40 mL) of complex **1** (50 mg, 0.045 mmol) at reflux temperature for 70 min. The solution was concentrated under reduced pressure and chromatographed by TLC silica gel (5:2, hexane/dichloromethane) to yield 15 mg of **2**·CH_2Cl_3 as a red solid (31%). Anal. Calcd (found) for $C_{42}H_{32}N_2O_6P_2Ru_3$·$CH_2Cl_2$: C, 46.45 (46.53); H, 3.17 (3.21); N, 2.52 (2.40). IR (THF): 2026 (s), 2001 (vs), 1990 (s), 1951 (s), 1935 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (acetone-d_6, 121.7 MHz, external 85% H_3PO_4): 192.3 (s) ppm. ^1H NMR (C_6D_6, 300 MHz, internal $SiMe_4$): 9.0–6.5 (complex mixture of signals), 6.10 (t, 7.5 Hz, ampy), 5.53 (d, 7.5 Hz, ampy), 5.04 (d, 7.5 Hz, ampy), 4.20 (s, NH), 1.55 (s, ampy Me) ppm. Selected $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 75.5 MHz, internal $SiMe_4$): δ(CO) 205.8 (s, 2 CO), 201.2 (s, 1 CO), 197.3 (s, 1 CO), 193.6 (s, 2 CO); δ(ampy) 171.0, 159.1, 138.3, 118.0, 114.2, 30.9; δ(μ-phenyl *ipso* carbon) 142.3 (t, 17.4 Hz) ppm. Crystals of **2**·CH_2Cl_2 suitable for X-ray diffraction studies were obtained by diffusion of *n*-pentane layered on a solution of the complex in dichloromethane at −20 °C.

(18) Synthesis of **3**·C_7H_8: A toluene solution (10 mL) of complex **1** (49.4 mg, 0.044 mmol) and diphenylacetylene (8 mg, 0.045 mmol) was stirred under nitrogen at reflux temperature for 75 min. The solvent was removed under vacuum and the residue washed with diethyl ether (3 × 8 mL) to give **3**·C_7H_8 (40 mg, 71%) as a purple solid. Anal. Calcd (found) for $C_{61}H_{48}N_2O_5P_2Ru_3$·$C_7H_8$: C, 60.67 (61.47); H, 4.19 (4.07); N, 2.08 (2.00). IR (THF): 2003 (s), 1968 (w), 1941 (m), 1926 (m), 1912 (sh) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.7 MHz, external 85% H_3PO_4): 232.3 (d, J = 8.2 Hz), 42.7 (d, J = 8.2 Hz) ppm. ^1H NMR ($CDCl_3$, 300 MHz, internal $SiMe_4$): 8.3–5.8 (complex mixture of signals), 5.23 (s, alkenyl CH), 2.82 (s, NH), 2.28 (s, ampy Me), 2.17 (s, toluene Me) ppm. Crystals of **3**·$(CH_2Cl_2)_{0.5}$ suitable for the X-ray diffraction study were obtained by recrystallizing **3**·C_7H_8 from dichloromethane/hexane at −20 °C.

(19) (a) Crystal data for **2**·CH_2Cl_2: $C_{42}H_{32}N_2O_6P_2Ru_3$·$CH_2Cl_2$, fw = 1110.82, monoclinic, space group $P2_1/n$, a = 12.103(5) Å, b = 22.969(7) Å, c = 16.952(11) Å, β = 110.48(6)°, V = 4414.5(8) Å^3, Z = 4, μ(Mo Kα) = 12.344 cm^{-1}; R = 0.064, R_w = 0.079 for 3676 reflections ($I \geq 3\sigma(I)$) and 509 variables. Crystal data for **3**·$(CH_2Cl_2)_{0.5}$: $C_{61}H_{48}N_2O_5P_2Ru_3$·$(CH_2Cl_2)_{0.5}$, fw 1296.7, orthorhombic, space group $P2_12_12_1$, a = 10.729(6) Å, b = 19.844(3) Å, c = 28.137(7) Å, V = 5991(4) Å^3, Z = 4, μ(Mo Kα) = 8.756 cm^{-1}; R = 0.054, R_w = 0.066 for 3082 reflections ($I \geq 3\sigma(I)$) and 486 variables. Diffraction measurements at room temperature were made on an Enraf-Nonius CAD4 diffractometer. Absorption corrections were applied to the data.[19b] The structures were solved by direct methods[19c] and successive Fourier difference syntheses and refined by using the SDP program package.[19d] (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. (c) Main, P.; Fiske, S. J.; Hull, S. E.; Jessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN84 a System of Computer Programs for the Authomatic Solution of Crystal Structures from X-Ray Diffraction Data*; Universities of York and Louvain: U.K. and Belgium, 1984. (d) Frenz, B. A. & Associates Inc. *SDP Structure Determination Package*; Texas A & M University and Enraf-Nonius: College Station, TX and Delft, 1985.

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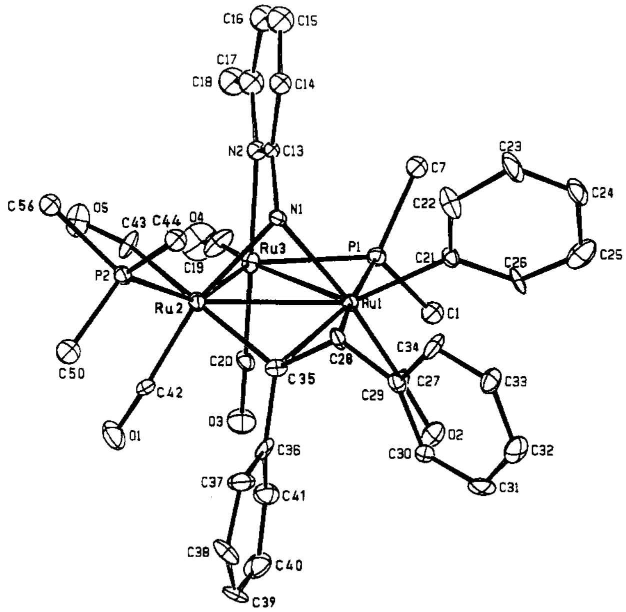

Figure 2. ORTEP view of the molecular structure of complex **3**. For clarity, only the *ipso* carbon atoms of the phenyl rings attached to phosphorus are shown. Selected bond distances (Å) and angles (deg) are as follows: Ru1–Ru2 2.775(2), Ru1–Ru3 2.828(2), Ru2–Ru3 2.741(2), Ru1–P1 2.327(5), Ru3–P1 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).

pleted by a PPh_3, a phenyl, and five terminal CO ligands. The arrangement of these ligands within the cluster is shown in Figure 2. The ampy ligand is nearly perpendicular to the Ru_3 plane (dihedral angle 93.7(3)°), and the phosphido bridge is almost coplanar with the metal triangle (the dihedral angle between the Ru_3 and Ru1–P1–Ru3 planes is 6.4(9)°). The alkenyl group spans the same metal–metal edge as the amido fragment of the ampy ligand, with the α- and β-carbon atoms occupying equatorial coordination sites cis to the PPh_3 and phenyl ligands, respectively. The structural features of this alkenyl group compare well with those found in other polynuclear ruthenium alkenyl complexes.[21]

The spectroscopic data for **2**[17] and **3**[18] are fully consistent with their X-ray structures. Those of complex **2** can be compared to those of $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$,[22] 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 stoichiometrically 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 PPh_3 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 $^{31}P\{^1H\}$ 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 PPh_2H 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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[21] See, for example: (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimata, E. W.; Bonnet, J.-J. *Organometallics* **1992**, *11*, 1351 and references therein. (b) García-Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1992**, *11*, 370 and references therein.

[22] Andreu, P. L.; Cabeza, J. A.; Riera, V. *Inorg. Chim. Acta* **1991**, *186*, 225.

[23] The conversion of μ-PPh_2 groups into terminal PPh_2H ligands has been described.[8a]

[24] In a related work on the hydrosilylation of alkynes promoted by an osmium cluster complex, the intermediate $[Os_3\{\mu,\eta^1:\eta^2\text{-}HC{=}C(H)\text{-}Bu^t\}\{Si(OEt)_3\}(CO)_{10}]$ decomposes, giving the silylated alkene 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.