η^1-Aryl-Bridged Triruthenium Cluster Complexes

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Both triphenylphosphine ligands of the cluster complex $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(PPh_3)_2(CO)_7]$ (ampy = 2-amino-6-methylpyridinate; **1a**) undergo a carbon–phosphorus bond scission on reaction with hydrogen (toluene, 110 °C, 1 atm) to give the η^1-phenyl-bridged derivative $[Ru_3(\mu\text{-Ph})(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (**2a**). The compound **2a**·CH_2Cl_2 has been characterized by X-ray crystallography. An extended Hückel molecular orbital calculation describing the interaction of the bridging phenyl group with the trimetallic fragment is also reported. The new complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(ER_3)_2(CO)_7]$ (ER_3 = PMe_2Ph (**1b**), PCy_3 (**1c**), P(*p*-tolyl)$_3$ (**1d**), $AsPh_3$ (**1e**)) have been prepared in order to compare their behavior toward hydrogen with that of complex **1a**; only **1d** and **1e** gave products analogous to **2a**, whereas **1b** and **1c** (unlike the others, **1c** is not isostructural with **1a**) gave mixtures of unidentified products. Another η^1-phenyl-bridged compound, namely, $[Ru_3(\mu\text{-Ph})(\mu_3\text{-mbim})(\mu\text{-}PPh_2)_2(CO)_6]$ (mbim = 2-mercaptobenzimidazolate) has been obtained, without the use of hydrogen, from the reaction of $[Ru_3(\mu\text{-H})(\mu_3\text{-mbim})(CO)_9]$ with PPh_3 in refluxing THF.

Introduction

We have recently published[1,2] that the triruthenium cluster complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$[3] (ampy = 2-amino-6-methylpyridinate) and its monosubstituted derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(PPh_3)(CO)_8]$[4] are efficient catalyst precursors for the homogeneous hydrogenation of diphenylacetylene under mild conditions. In this context, in a preliminary communication,[5] we briefly reported that the disubstituted derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(PPh_3)_2(CO)_7]$[6] (**1a**) (Chart 1), a poor catalyst precursor for hydrogenation reactions, reacts with hydrogen, undergoing two P–C bond cleavages which gave rise to the first example in ruthenium chemistry of a complex containing a bridging η^1-phenyl ligand: $[Ru_3(\mu\text{-Ph})(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (**2a**). We now report, together with full details of the synthesis and characterization of complex **2a**, the preparation of other ruthenium cluster complexes containing bridging η^1-aryl ligands, starting not only from derivatives of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ containing triphenylarsine or triarylphosphine ligands, i.e. $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(L)_2(CO)_7]$ (L = $AsPh_3$, P(*p*-tolyl)$_3$), but also from trinuclear complexes containing μ_3 ligands different from ampy, i.e. $[Ru_3(\mu\text{-H})(\mu_3\text{-mbim})(CO)_9]$ (mbim = 2-mercaptobenzimidazolate). The results of a molecular orbital calculation (extended Hückel level) on a model compound analogous to complex **2a** are also included.

Many metal-mediated P–Ph cleavage reactions are now known.[7,8] They usually lead to phosphido-bridged derivatives as well as to benzene,[9,10] benzaldehyde,[10,11] or biphenyl.[10,12] However, very few σ-phenyl-μ-diphenylphosphido derivatives have been isolated[13] although they have often been claimed as intermediates in these reactions.[11b,12] Moreover, prior to this work, the cluster compound $[Os_3$-

Chart 1

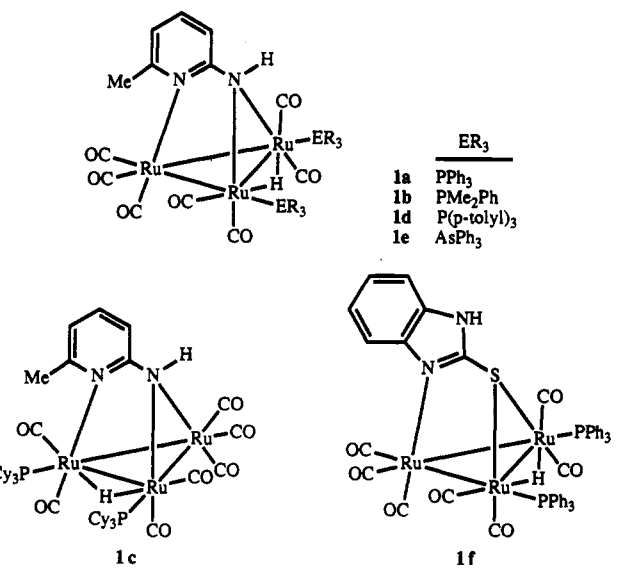

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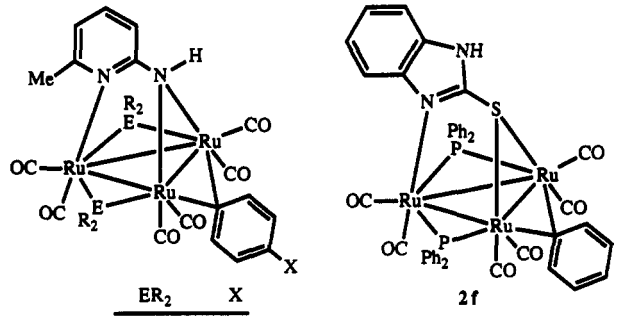
Chart 2



	ER_2	X
2a	PPh_2	H
2d	P(p-tolyl)$_2$	Me
2e	$AsPh_2$	H

2f

(μ-Ph)(μ_3-$PPh_2C_6H_4$)(μ-PPh_2)$(CO)_8$][14] was, as far as we are aware, the only known transition metal complex containing a bridging η^1-phenyl ligand arising from a P–C bond cleavage reaction.[15,16]

Results and Discussion

The reaction of compound **1a** with hydrogen (1 atm) in refluxing toluene (no reaction was observed in refluxing THF) gives [Ru_3(μ-Ph)(μ_3-ampy)(μ-PPh_2)$_2(CO)_6$] (**2a**) (Chart 2) as the major component of a mixture of products which was separated by chromatographic methods. The carbonyl region of its $^{13}C\{^1H\}$ NMR spectrum contains only four resonances and its $^{31}P\{^1H\}$ NMR spectrum consists of only one singlet resonance at a high chemical shift (192.3 ppm), indicating the transformation of the terminal PPh_3 ligands of **1a** into bridging PPh_2 ligands.[17] The simplicity of these spectra, which suggests a symmetric structure, contrasts with the ^1H NMR spectrum, which is much more complicated in the 9.0–6.5 ppm region than that of complex **1a** and which contains no hydride resonances. Since these spectroscopic data were insufficient to unequivocally assign the structure of complex **2a**, an X-ray diffraction study was carried out (Figure 1).[5]

The cluster consists of an isosceles triangle of ruthenium atoms triply bridged by the ampy ligand, with the short edge (Ru(2)–Ru(3) 2.637(2) Å) spanned by the amido fragment and by one carbon atom of the phenyl group, and with the two longest edges also bridged by PPh_2 ligands. The μ,η^1-phenyl ring is planar and essentially

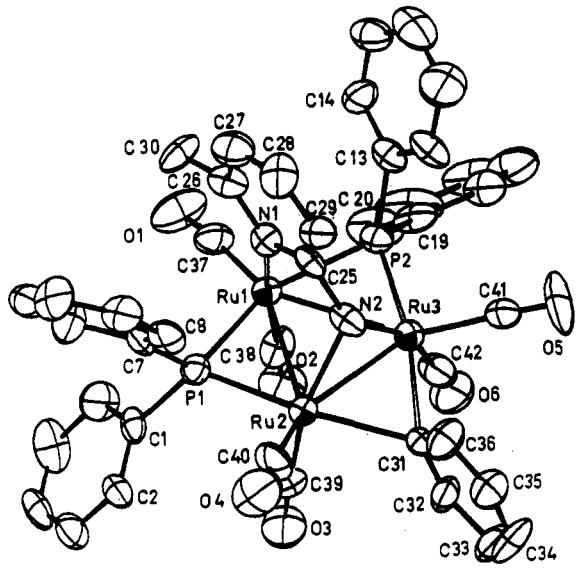


Figure 1. Molecular structure of [Ru_3(μ-Ph)(μ_3-ampy)(μ-PPh_2)$_2(CO)_6$] (**2a**).

orthogonal to the Ru(2)–Ru(3) vector, involving a Ru(2)–C(31)–Ru(3) bond angle of 69.0(4)°, Ru(2)–C(31) and Ru(3)–C(31) bond distances of 2.32(1) and 2.34(1) Å, respectively, and a dihedral angle between the metal triangle and the Ru(2)–C(31)–Ru(3) plane of 9.8(3)°. The ipso carbon atom of the phenyl ring (C(31)) is 0.33(1) Å away from the plane defined by the metal triangle, on the side opposite the ampy ligand. The Ru(2)–Ru(3) bond distance (2.637(2) Å) is shorter than the other Ru–Ru distances (Ru(1)–Ru(2) 2.970(2) Å; Ru(1)–Ru(3) 2.980(2) Å) and also shorter than the Os–Os distance (3.095(2) Å) of the phenyl-bridged edge of [Os_3(μ-Ph)(μ_3-$PPh_2C_6H_4$)-(μ-PPh_2)$(CO)_8$][14] and than the Ru–Ru distance (2.7531(4) Å) of the edge bridged by the amido and the hydrido ligands in the related cluster complex [Ru_3(μ-H)(μ_3,η^2-anpy)$(CO)_9$] (anpy = 2-anilinopyridinate).[3] Overall, this structure resembles that proposed for the symmetric isomer of [Ru_3(μ-H)(μ_3-ampy)(μ-PPh_2)$_2(CO)_6$],[18] a compound that may be described as the result of a hypothetical substitution of a hydride for the bridging phenyl ligand of **2a**.

A three-center–two-electron bond model, similar to that proposed for [Al_2Ph_6],[19] could be used to explain the interaction of the bridging phenyl ring with the Ru(2) and Ru(3) atoms of complex **2a**, but an interaction of the phenyl π-orbitals with the appropriate metal d orbitals might also contribute to the bonding, as suggested by the complexity of the aromatic region of the ^1H and $^{13}C\{^1H\}$ NMR spectra, which implies that in solution there is no free rotation of the phenyl group about the C(31)–C(34) axis. Therefore, theoretical calculations were needed to determine the bonding situation.

The compound [Ru_3(μ-Ph)(μ_3-ampy)(μ-PH_2)$_2(CO)_6$] was subjected to an extended Hückel molecular orbital calculation. As can be observed in Figure 2, the HOMO essentially corresponds to a bonding interaction between a sp^2 orbital (s, p_x, p_z) of the phenyl fragment ipso carbon and the appropriate metal d orbitals. Interestingly, an analysis of the overlap population between the [Ru_3(μ_3-

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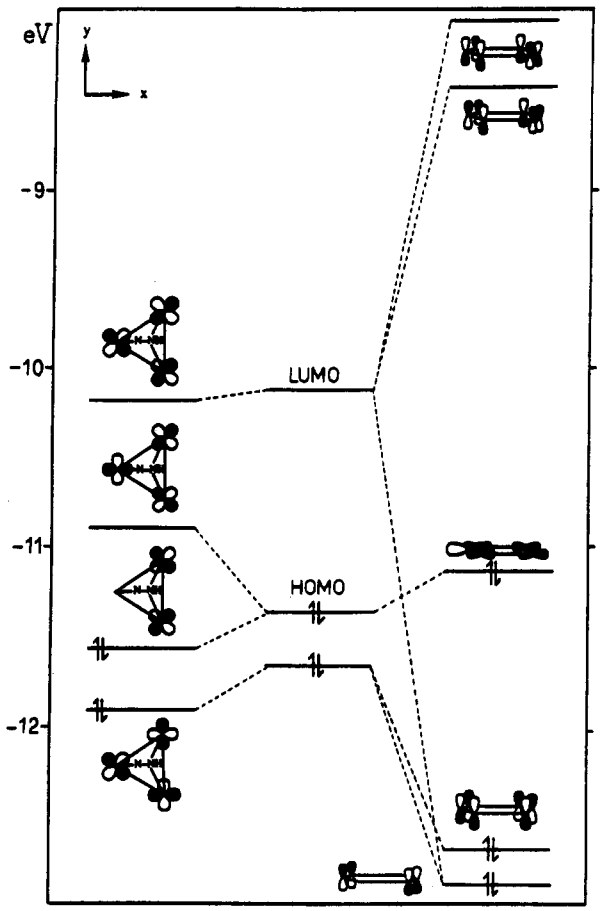

Figure 2. Interaction diagram of the fragments $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PH_2)_2(CO)_6]^+$ and $[C_6H_5]^-$, to give $[Ru_3(\mu\text{-Ph})(\mu_3\text{-ampy})(\mu\text{-}PH_2)_2(CO)_6]$, in the frontier orbital region. Only the most important contributions to each MO are shown.

ampy)$(\mu\text{-}PH_2)_2(CO)_6]^+$ and $[C_6H_5]^-$ fragments indicates that the $2p_y$ orbital of the phenyl fragment ipso carbon atom contributes 18% to the bonding of this fragment with the metal triangle. This contribution may be the responsible for the observed conformation of the phenyl group with respect to the metal triangle (the proximity of the equatorial CO ligands may also force the bridging phenyl group to be perpendicular to the Ru(2)–Ru(3) vector).

Although the elimination of one CO ligand and one benzene molecule from complex **1a** stoichiometrically leads to **2a** without the use of hydrogen, the thermolysis of **1a** does not give **2a** unless a hydrogen atmosphere is used; therefore, hydrido derivatives should be intermediates in this reaction. It is also interesting to note that complex **2a** is remarkably stable, since it does not eliminate benzene or transform the phosphido bridges into terminal PPh_2H ligands[20] when exposed to hydrogen in refluxing toluene.

In order to shed light on the general significance of this reaction, i.e. for the cleavage of P–C bonds of a variety of phosphine ligands, and considering the possibility of isolating intermediates that could help us to know the reaction mechanism, the new compounds $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(ER_3)_2(CO)_7]$ (ER_3 = PMe_2Ph (**1b**), PCy_3 (**1c**), P(*p*-tolyl)$_3$ (**1d**), $AsPh_3$ (**1e**)) were prepared and their reactions with hydrogen investigated.

Treatment of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ with 2 equiv of ER_3 in refluxing THF leads to the isolation of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(ER_3)_2(CO)_7]$ (ER_3 = PMe_2Ph (**1b**), PCy_3 (**1c**), P(*p*-tolyl)$_3$ (**1d**), $AsPh_3$ (**1e**)). Their spectroscopic data suggest that complexes **1b**, **1d**, and **1e** are isostructural with **1a** (Chart 1), which has been characterized by X-ray diffraction methods;[6] however, the $^{31}P\{^1H\}$ NMR spectrum of **1c** shows two singlets of equal intensity, indicating the presence of two different phosphorus atoms which do not couple with each other, and the ^1H NMR spectrum exhibits the hydride resonance as a triplet with a coupling constant of 7.8 Hz, indicating that the hydride is cis to both phosphine ligands,[6] as expected for the structure depicted in Chart 1. Steric arguments cannot explain why the structure of **1c** is different from that of **1a**; therefore, it seems reasonable that the difference should be caused by the higher basicity of tricyclohexylphosphine. If this is true, the compound $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(PEt_3)_2(CO)_7]$, which contains a small but basic phosphine ligand, should have the same structure as **1c**; in fact, the former was characterized by NMR spectroscopy[21] as the major component of the mixture obtained by the reaction of $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ with 2 equiv of triethylphosphine, but it could not be isolated in its pure form.

As expected, compounds **1b** and **1c**, which contain ligands more basic than those in **1a**, react with hydrogen (1 atm) more easily (1.5 h, 20 and 70 °C respectively) than **1a**. Unfortunately, they give complex mixtures of hydrido derivatives (NMR) that we were unable to separate and characterize.

The behavior of complexes **1d** and **1e** toward hydrogen was found to be very similar to that of complex **1a**. Both react with hydrogen, at 1 atm, in refluxing toluene to give mixtures of products from which the μ-η^1-aryl derivatives $[Ru_3\{\mu\text{-}(p\text{-tolyl})\}(\mu_3,\eta^2\text{-ampy})\{\mu\text{-P}(p\text{-tolyl})_2\}_2(CO)_6]$ (**2d**) and $[Ru_3(\mu\text{-Ph})(\mu_3,\eta^2\text{-ampy})(\mu\text{-}AsPh_2)_2(CO)_6]$ (**2e**) (Chart 2) could be isolated. Their spectroscopic data (see Experimental Section) are comparable to those of **2a**. Unfortunately, although other products (shown to be hydride derivatives by NMR spectroscopy) were also produced in these reactions, they could not be isolated and characterized.

In order to see whether or not these P–C bond cleavage reactions could be observed in other phosphine-substituted triruthenium clusters containing μ_3 ligands different from ampy, we attempted to make the complex $[Ru_3(\mu\text{-H})(\mu_3\text{-mbim})(PPh_3)_2(CO)_7]$ (mbim = 2-mercaptobenzimidazolate) (**1f**). However, the room temperature reaction of $[Ru_3(\mu\text{-H})(\mu_3\text{-mbim})(CO)_9]$ with 2 equiv of triphenylphosphine always afforded inseparable mixtures of **1f** and the monosubstituted derivative $[Ru_3(\mu\text{-H})(\mu_3\text{-mbim})(PPh_3)(CO)_8]$,[22] whereas the reactions at reflux temperature (THF) gave, within a few minutes, the phenyl-bridged derivative $[Ru_3(\mu\text{-Ph})(\mu_3\text{-mbim})(\mu\text{-}PPh_2)_2(CO)_6]$ (**2f**) (Chart 2).

Remarkably, unlike the synthesis of compounds **2a**, **2d**, and **2e**, the preparation of **2f** does not require the use of hydrogen and can be achieved at a lower temperature. Since all these complexes have comparable structures, the different reaction paths followed by the ampy- and the mbim-containing systems have to be related to electronic

(20) The conversion of μ-PPh_2 groups into terminal PPh_2H ligands by reaction with hydrogen has been described.[11a]

(21) Selected spectroscopic data for $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(PEt_3)_2(CO)_7]$: (a) ^1H NMR (C_6D_6) −10.42 (t, J = 10.0 Hz, μ-H) ppm; (b) $^{31}P\{^1H\}$ NMR (C_6D_6) 41.9 (s), 20.0 (s) ppm.

(22) (a) Selected spectroscopic data for **1f**: ^1H NMR ($CDCl_3$) −12.20 (t, br, J = 9.0 Hz, μ-H) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 28.8 (s) ppm. (b) Selected spectroscopic data for $[Ru_3(\mu\text{-H})(\mu_3\text{-mbim})(PPh_3)(CO)_8]$: ^1H NMR ($CDCl_3$) −12.94 (d, J = 14.3 Hz, μ-H) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 33.6 (s) ppm.

effects caused by these ligands. Unfortunately, we still know very little about these systems to rationalize their behavior.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. Unless otherwise stated, the reactions were carried out under nitrogen, using conventional Schlenk techniques and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). The compounds $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$[3] and $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(PPh_3)_2(CO)_7]$[6] (**1a**) were prepared as described previously. All other reagents (reagent or analytical grade) were used as received from commercial suppliers. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were run at 23 °C with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P) as standards (δ = 0 ppm). Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(PMe_2Ph)_2(CO)_7]$ (1b). A solution of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (52.2 mg, 0.079 mmol) and PMe_2Ph (23 μL, 0.180 mmol) in THF (10 mL) was stirred at reflux temperature for 30 min. The solvent was removed under reduced pressure and the residue washed with hexane (3 × 6 mL) to give complex **1b** as a red-orange solid (40 mg, 58%). Anal. Calcd for $C_{29}H_{30}N_2O_7P_2Ru_3$: C, 39.41; H, 3.42; N, 3.17. Found: C, 40.02; H, 3.78; N, 3.01. IR ν(CO) (THF): 2025 (s), 1987 (s), 1968 (m), 1950 (s), 1934 (w), 1919 (m) cm^{-1}. Selected ^1H NMR (C_6D_6): 6.63 (t, J = 7.4 Hz, 1 H), 5.99 (d, 1 H), 5.98 (d, 1 H), 5.20 (s, NH), 2.48 (s, 3 H), 1.20 (m, 12 H), −10.68 (t, J = 9.2 Hz, μ-H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): −5.01 (s) ppm.

Preparation of Complexes 1c, 1d, and 1e. These complexes were prepared from $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ and the appropriate ER_3 ligands, using the same synthetic procedure described above for **1b**.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(PCy_3)_2(CO)_7]$ (**1c**): reaction time 5 h; red solid, 46%. Anal. Calcd for $C_{49}H_{74}N_2O_7P_2Ru_3$: C, 50.38; H, 6.38; N, 2.40. Found: C, 51.01; H, 6.73; N, 2.19. IR ν(CO) (THF): 2016 (s), 1971 (s), 1942 (vs), 1922 (m), 1910 (sh), 1891 (w) cm^{-1}. Selected ^1H NMR (C_6D_6): 6.85 (t, J = 7.6 Hz, 1 H), 6.38 (d, 1 H), 5.02 (d, 1 H), 2.57 (s, 3 H), −9.08 (t, J = 7.8 Hz, μ-H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): 59.02 (s, 1 P), 34.87 (s, 1 P) ppm.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})\{P(p\text{-tolyl})_3\}_2(CO)_7]$ (**1d**): reaction time 15 min; orange solid, 92%. Anal. Calcd for $C_{55}H_{50}N_2O_7P_2Ru_3$: C, 54.32; H, 4.14; N, 2.30. Found: C, 55.01; H, 4.57; N, 2.23. IR ν(CO) (THF): 2027 (s), 1990 (s), 1972 (m), 1955 (s), 1937 (w), 1927 (m) cm^{-1}. Selected ^1H NMR (C_6D_6): 6.57 (t, J = 7.6 Hz, 1 H), 5.91 (d, 1 H), 5.28 (d, 1 H), 2.50 (s, 3 H), 1.96 (s, 18 H), −9.39 (t, J = 8.6 Hz, μ-H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): 29.18 (s) ppm.

$[Ru_3(\mu\text{-}H)(ampy)(AsPh_3)_2(CO)_7]$ (**1e**): reaction time 3.5 h; orange solid, 76%. Anal. Calcd for $C_{49}H_{38}As_2N_2O_7Ru_3$: C, 48.24; H, 3.14; N, 2.29. Found: C, 49.00; H, 3.27; N, 2.31. IR ν(CO) (THF): 2033 (s), 1992 (s), 1978 (m), 1961 (s), 1937 (w), 1926 (m) cm^{-1}. Selected ^1H NMR (C_6D_6): 6.85 (t, J = 7.6 Hz, 1 H), 6.38 (d, 1 H), 5.02 (d, 1 H), 2.59 (s, 3 H), −9.70 (s, μ-H) ppm.

$[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (2a). 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 the products were separated by TLC (silica gel, 5:2 hexane–dichloromethane). Bands one and two contained very small amounts of unidentified compounds. The third band (red) was worked up to give **2**·CH_2Cl_2 as a red solid (15 mg, 31%). Anal. Calcd for $C_{42}H_{32}N_2O_6P_2Ru_3\cdot CH_2Cl_2$: C, 46.45; H, 3.17; N, 2.52. Found: C, 46.53; H, 3.21; N, 2.40. IR (THF): 2026 (s), 2001 (vs), 1990 (s), 1951 (s), 1935 (s) cm^{-1}. ^1H NMR (C_6D_6): 9.0–6.5 (complex mixture of signals), 6.10 (t, J = 7.5 Hz, 1 H), 5.53 (d, 1 H), 5.04 (d, 1 H), 4.20 (s, NH), 1.55 (s, 3 H) ppm. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ(CO) 205.8 (2 CO), 201.2 (1 CO), 197.3 (1 CO), 193.6 (2 CO); δ(ampy) 171.0, 159.1, 138.3, 118.0, 114.2, 30.9; δ(μ-phenyl) 142.3 (t, J = 17.4 Hz, *ipso* carbon). $^{31}P\{^1H\}$ NMR (acetone-d_6): 192.3 (s) ppm.

$[Ru_3\{\mu\text{-}(p\text{-tolyl})\}(\mu_3\text{-ampy})\{\mu\text{-}P(p\text{-tolyl})_2\}_2(CO)_6]$ (2d). Hydrogen was bubbled through a toluene solution (40 mL) of complex **1d** (72 mg, 0.059 mmol) at reflux temperature for 1.5 h. The solution was concentrated, and the products were separated in a chromatography column (2 × 8 cm) of neutral alumina (activity IV). The first band (red), which was eluted with a mixture of hexane–dichloromethane (7:1), was worked up to give complex **2d** as a red solid (10 mg, 15%). Anal. Calcd for $C_{47}H_{42}N_2O_6P_2Ru_3$: C, 51.51; H, 3.86; N, 2.56. Found: C, 51.72; H, 3.86; N, 2.56. IR (THF): 2023 (s), 1998 (vs), 1987 (s), 1947 (s), 1931 (s) cm^{-1}. ^1H NMR (C_6D_6): 8.3–5.4 (complex mixture of signals), 4.28 (s, NH), 2.37 (s, 6 H), 2.28 (s, 3 H), 2.06 (s, 6 H), 1.59 (s, 3 H) ppm. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ(CO) 206.3 (t, J = 4.0 Hz, 2 CO), 201.6 (t, J = 4.1 Hz, 1 CO), 197.5 (t, J = 7.6 Hz, 1 CO), 193.9 (t, J = 2.3 Hz, 2 CO); δ(ampy) 171.0, 159.1, 138.1, 117.6, 114.0, 31.0; δ(μ-(*p*-tolyl)) 139.3 (t, J = 18.0 Hz, *ipso* carbon), 21.3 (Me); δ(P(*p*-tolyl)$_2$) 21.3 (2 Me), 21.1 (2 Me). $^{31}P\{^1H\}$ NMR (C_6D_6): 185.7 (s) ppm.

$[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}AsPh_2)_2(CO)_6]$ (2e). Hydrogen was bubbled through a toluene solution (25 mL) of complex **1e** (70 mg, 0.0457 mmol) at reflux temperature for 40 min. The solution was concentrated under reduced pressure, and the products were separated by TLC (silica gel, 2:1 hexane–dichloromethane). The first two bands contained trace amounts of compounds which were not identified. The third band (red) was worked up to give **2e** as a red solid (12 mg, 19%). Anal. Calcd for $C_{42}H_{32}As_2N_2O_6Ru_3$: C, 45.29; H, 2.90; N, 2.51. Found: C, 45.03; H, 3.15; N, 2.39. IR (toluene): 2024 (s), 1993 (vs), 1987 (s), 1952 (s), 1935 (s) cm^{-1}. ^1H NMR (C_6D_6): 8.4–6.8 (complex mixture of signals), 6.70 (t, J = 7.8 Hz, 1 H), 6.55 (d, 1 H), 5.40 (d, 1 H), 4.20 (s, NH), 1.58 (s, 3 H). Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ(CO) 204.5 (2 CO), 199.7 (1 CO), 195.9 (1 CO), 192.9 (2 CO); δ(ampy) 170.5, 158.1, 137.4, 116.9, 112.6, 30.2 ppm.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-mbim})(CO)_9]$. This complex was prepared by following the anionic route described by Lavigne and co-workers[23] for the synthesis of $[Ru_3(\mu\text{-}H)(\mu_3\text{-pyS})(CO)_9]$ (pyS = pyridine-2-thiolate): K-selectride (312 μL, 1 M in THF, 0.312 mmol) was added to a solution of 2-mercaptobenzimidazole (52 mg, 0.34 mmol) to give a white precipitate of Kmbim. After stirring for 30 min, a solution of $[Ru_3(CO)_{12}]$ (200 mg, 0.313 mmol) in THF (25 mL) was added. The mixture was stirred for 2.5 h and then evaporated to dryness. Dichloromethane (25 mL) and trifluoroacetic acid (27 μL) were added to the residue to give a red-orange solution and a white precipitate (KO_2CCF_3). The filtered solution was evaporated to dryness and the residue washed with hexane (2 × 5 mL) to give $[Ru_3(\mu\text{-}H)(\mu_3\text{-mbim})(CO)_9]$ as an orange solid (143 mg, 65%). Anal. Calcd for $C_{16}H_6N_2O_9Ru_3S$: C, 27.24; H, 0.86; N, 3.97. Found: C, 27.36; H, 1.02; N, 3.78. IR (THF): 2083 (m), 2051 (s), 2031 (vs), 2001 (s), 1995 (sh), 1964 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): 9.88 (br s, NH), 7.5–7.3 (m, 4 H), −13.14 (s, μ-H) ppm.

$[Ru_3(\mu\text{-}Ph)(\mu_3\text{-mbim})(\mu\text{-}PPh_2)_2(CO)_6]$ (2f). A THF solution (15 mL) of $[Ru_3(\mu\text{-}H)(\mu_3\text{-mbim})(CO)_9]$ (30 mg, 0.043 mmol) and PPh_3 (23 mg, 0.088 mmol) was stirred at reflux temperature for 45 min. The solvent was removed under reduced pressure and the residue introduced in a chromatography column (10 × 2 cm) of neutral alumina (activity IV). The first band (red), which was eluted with a mixture of hexane–dichloromethane (1:1), was worked up to give complex **2f** as a red solid (38 mg, 83%). Anal. Calcd for $C_{43}H_{30}N_2O_6P_2Ru_3S$: C, 48.36; H, 2.83; N, 2.62. Found: C, 48.23; H, 3.00; N, 2.48. IR (CH_2Cl_2): 2031 (s), 2004 (vs), 1997 (s), 1958 (m), 1939 (m) cm^{-1}. ^1H NMR (acetone-d_6): 8.4–6.4 (complex mixture of signals) ppm. $^{31}P\{^1H\}$ NMR (acetone-d_6): 195.4 (s) ppm.

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Molecular Orbital Calculations. Calculations were carried out at the extended Hückel level,[24] on the compound $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-}ampy)(\mu\text{-}PH_2)_2(CO)_6]$, using the weighted H_{ij} formula.[25] Standard atomic parameters were taken for H, C, N, O,[24] and P.[26] The exponents (ζ) and the valence shell ionization potentials (H_{ii}, in eV) for Ru were respectively 2.078 and −8.60 for 5s, 2.043 and −5.10 for 5p; a linear combination of two Slater-type orbitals (ζ_1 = 5.378, c_1 = 0.5340; ζ_2 = 2.303, c_2 = 0.6365) was used to represent the atomic d orbitals; the H_{ii} value for 4d was set equal to −12.20 eV. The X-ray determined atomic coordinates of compound **2a** were used in the calculations, except that hydrogen atoms were substituted for the phenyl groups of the phosphido ligands.

Crystal Structure of $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-}ampy)(\mu\text{-}PPh_2)_2(CO)_6]\cdot CH_2Cl_2$ ($2a\cdot CH_2Cl_2$). A red crystal of $2a\cdot CH_2Cl_2$, obtained by layering pentane on a solution of the complex in dichloromethane, was used for the X-ray diffraction study. The cell dimensions were determined by least-squares refinement from the setting angles of 25 centered reflections in the range $10 < 2\theta < 20°$. The intensities were collected using the θ–2θ scan method. The measurement of three standard reflections every 60 min revealed no intensity fluctuations. One set of reflections was collected up to $2\theta = 50°$. The intensities were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[27] and successive Fourier difference syntheses and was refined by weighted anisotropic full-matrix least-squares methods. After refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms, the positions of the hydrogen atoms were calculated (C–H = 0.95 Å, B_{iso} = 4 Å^2) and included as a fixed contribution to F_c. A CH_2Cl_2 molecule of solvation was refined isotropically. Scattering factors and corrections for anomalous dispersion were taken from ref 28. The drawing was made with ORTEP.[29] All calculations were performed on a MicroVAX 3100 computer using the SDP program package.[30] Tables of crystal and refinement data can be found as supplementary material in the preliminary communication of this work.[5]

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, positional parameters, and angles between least-squares planes (7 pages). Ordering information is given on any current masthead page.

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