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Hexaruthenium Carbonyl Cluster Complexes with Basal Edge-Bridged Square Pyramidal Metallic Skeleton: Efficient Synthesis of 2-Imidopyridine Derivatives and Determination of Their Reactive Sites in Carbonyl Substitution Reactions

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The reactions of $[Ru_3(CO)_{12}]$ with half equivalent of 2-amino-6-methylpyridine (H_2ampy) or 2-aminopyridine (H_2apy) in refluxing xylene give the hexanuclear products $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}L)(\mu\text{-}CO)_2(CO)_{14}]$ (L = ampy, **1**; apy, **2**). These reactions represent the first high-yield syntheses of hexanuclear complexes with a basal edge-bridged square pyramidal metallic skeleton. Five metal atoms of these complexes are bridged by the N-donor ligand in such a way that the edge-bridging metal atom is attached to the pyridine nitrogen, while the basal atoms of the square pyramid are capped by an imido fragment that arises from the activation of both N–H bonds of the NH_2 group. The reactive sites of these complexes in CO substitution reactions have been determined by studying the reactivity of **1** with triphenylphosphine. Two kinetically controlled monosubstitutions take place on the edge-bridging metal atom in positions *cis* to the pyridine nitrogen, leading to a mixture of two isomers of formula $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{13}(PPh_3)]$ (**3** and **4**). On heating at 80 °C, these monosubstituted isomers are transformed, via a dissociative pathway, into the product of thermodynamic control (**5**), which has the PPh_3 ligand on the apical Ru atom. The di- and trisubstituted derivatives $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{12}(PPh_3)_2]$ (**6**) and $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{11}(PPh_3)_3]$ (**7**) are stepwise formed from **3**–**5** and PPh_3. Compound **6** has the PPh_3 ligands on the edge-bridging and apical Ru atoms, and compound **7** has an additional PPh_3 ligand on an unbridged basal Ru atom. The compound $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{12}(\mu\text{-dppm})]$ (**8**), in which a basal and the apical Ru atoms are spanned by the dppm ligand, has been isolated from the reaction of **1** with bis(diphenylphosphino)methane.

Introduction

The synthesis and reactivity of carbonylruthenium clusters derived from 2-aminopyridines have been thoroughly studied.[1,2] Most of these clusters and their derivatives are trinuclear and contain a face-capping ligand that results from the activation of an N−H bond, to give an edge-bridging amido fragment and a hydride ligand, and from the coordination of the pyridine N atom to the remaining metal atom. Some of these complexes have been recognized as catalytic precursors for the hydrogenation,[3,4] dimerization,[5] polymerization,[5] and hydroformylation[6] of selected alkynes.

Working in this field, while studying the reactivity of $[Ru_3(CO)_{12}]$ with 2-amino-6-phenylpyridine (H_2apyPh), we were able to isolate the hexanuclear cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apyPh})(\mu\text{-}CO)_2(CO)_{14}]$ and its orthometalated derivative $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-apyC}_6H_4)(\mu\text{-}CO)_3(CO)_{13}]$, both having

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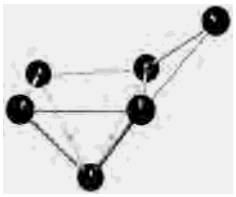


Figure 1. Basal edge-bridged square pyramidal metallic skeleton.

basal edge-bridged square pyramidal metallic skeletons (Figure 1). These complexes were always obtained in low yields after tedious chromatographic separations because, in addition to being formed together, they were always accompanied by the trinuclear orthometalated derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^3\text{-}apyC_6H_4)_2(CO)_6]$.[2e]

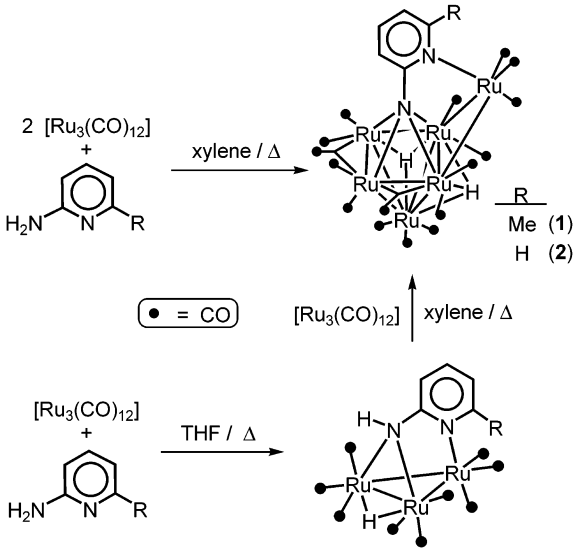
After a literature search, we ascertained that hexaruthenium cluster complexes with a basal edge-bridged square pyramidal metallic skeleton are very scarce.[7−9] They all have been prepared from $[Ru_3(CO)_{12}]$, generally in various steps, in low overall yields. Their inefficient preparation has so far prevented the study of their reactivity. Therefore, high-yield syntheses of hexaruthenium cluster complexes of this type were necessary.

Our results with 2-amino-6-phenylpyridine, commented above, led us to infer that the treatment of $[Ru_3(CO)_{12}]$ with nonorthometalable 2-aminopyridines, under analogous conditions to those that led to $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}apyPh)(\mu\text{-}CO)_2(CO)_{14}]$ and $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\eta^3\text{-}apyC_6H_4)(\mu\text{-}CO)_3(CO)_{13}]$,[2e] would be an appropriate approach to a high yield synthesis of hexaruthenium cluster complexes with a basal edge-bridged square pyramidal metallic skeleton. We now report that such an approach has been successful and that its efficiency has opened up the possibility of exploring the reactivity of this type of cluster complexes. Thus, a study of the reactivity of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ (**1**; H_2ampy = 2-amino-6-methylpyridine) with triphenylphosphine, reported herein, has allowed the identification of the metal atoms of these complexes that are prone to undergo CO substitution processes. Some of the results reported in this article have been briefly communicated in a preliminary form.[10]

Results and Discussion

Synthesis of Compounds 1 and 2. Treatment of $[Ru_3(CO)_{12}]$ with half equivalent of 6-methyl-2-aminopyridine or 2-aminopyridine (H_2apy) in refluxing xylene for 1 h allowed the isolation of the hexanuclear clusters $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}ampy)(\mu\text{-}CO)_2(CO)_{14}]$ (**1**) and $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}apy)(\mu\text{-}CO)_2(CO)_{14}]$ (**2**; H_2apy = 2-aminopyridine) in high yields (77 and 70%, respectively) (Scheme 1).

Scheme 1. Synthesis of Compounds **1** and **2**



When these reactions were monitored by IR spectroscopy and spot TLC, it was observed that the previously known[11] trinuclear complexes $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}ampy)(CO)_9]$ and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}apy)(CO)_9]$ are early intermediates (they appear after the first 5 min) in the formation of compounds **1** and **2**. In fact, in subsequent experiments, we proved that **1** and **2** can also be made by treating the corresponding trinuclear complexes with one equivalent of $[Ru_3(CO)_{12}]$ in xylene at reflux temperature for 1 h (Scheme 1). Therefore, what we have here is a thermally induced aggregation between the triangular amidopyridine clusters and $[Ru_3(CO)_{12}]$, where the N−H fragment of the former undergoes an oxidative N−H addition to give an imido ligand that ultimately serves as a bridgehead atom holding the newly formed square pyramidal base.

Compound **1** was characterized by X-ray diffraction (Figure 2, Table 1). It is noteworthy that, although the plane of the ampy ligand cuts the metal framework into two identical halves, the positions of the two edge-bridging CO ligands and the two face-capping hydrides result in the complex being asymmetric. While the pyridine N atom is

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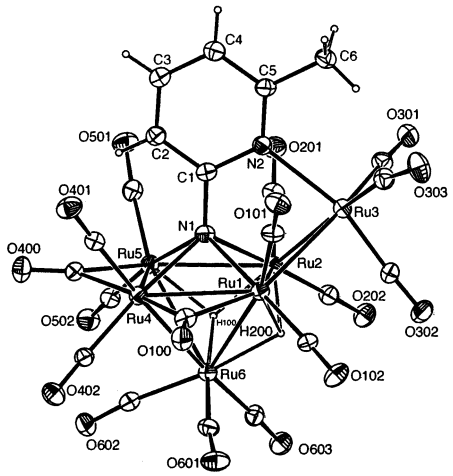


Figure 2. Molecular structure of compound **1**. The C and O atoms of each CO group bear the same number.

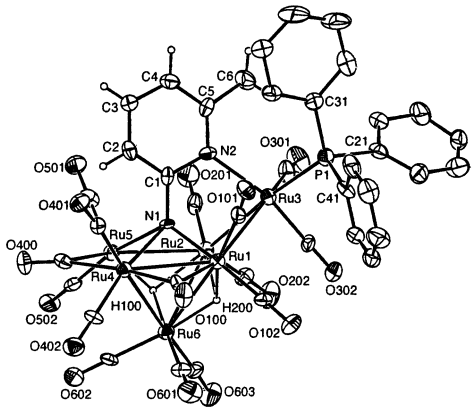


Figure 3. Molecular structure of compound **3**. The C and O atoms of each CO group bear the same number. Phenyl H atoms have been omitted for clarity.

attached to the edge-bridging Ru atom, the imido N atom symmetrically caps the four basal Ru atoms. It is interesting that the lengths of the four bonds that connect the apical Ru atom, Ru(6), with the basal Ru atoms are 0.1−0.2 Å longer than the remaining Ru−Ru bonds, an observation that is repeated in all the X-ray structures reported in this paper, that, for comparison purposes, have a common atom numbering scheme.

Overall, this structure is comparable to that of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}NCO_2Me)(\mu\text{-}CO)_2(CO)_{14}]$ (reported yield 5%), in which an imido N atom also caps the metallic square but a carbonyl oxygen atom is attached to the edge-bridging Ru atom.[8] Complexes having imido groups spanning four metal atoms are scarce.[2e,8,12] Among them, those whose imido fragment arises from the activation, via oxidative addition, of both N−H bonds of an NH_2 group are only represented by compounds derived from 2-aminopyridines.[2e]

It is also interesting to note that all the hitherto reported hexaruthenium cluster complexes with an edge-bridged square pyramidal metallic skeleton have an additional structural feature in common. That is, they have a ligand, C-,[7] N-,[2e,8] or S-donor,[9] capping the basal atoms of the square pyramid. It seems that the stability of this particular hexametallic framework requires the presence of such a bridging ligand.

The successful synthesis of complexes **1** and **2** enabled us to undertake a general study of the reactivity of this class of compounds. We chose compound **1** as an appropriate starting material because the presence of the methyl group on the pyridine ring facilitates the monitoring of the reactions by NMR spectroscopy, without affecting the reactivity of the complexes.[1]

Reactions Compound 1 with Triphenylphosphine: Monosubstituted Derivatives. The reaction of **1** with triphenylphosphine occurred readily (THF, reflux temperature, 10 min) to give, initially, a mixture of two isomeric monosubstituted products (**3** and **4**), corresponding to the formula $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{13}(PPh_3)]$ (Scheme 2), in a ca. 5:1 mol ratio (^{1}H NMR integration), which could not be separated by column chromatography or TLC. Different preparations and repeated recrystallizations did not lead to variations in the ratio of these products (^{1}H NMR analysis).

A crystal of this mixture was analyzed by X-ray diffraction (Figure 3, Table 1). The isomer contained in the crystal had

Table 1. Selected Intramolecular Interatomic Distances (Å) in Compounds **1**, **3**, **5**, **6**, **7** and **8**

	1	**3**	**5**	**6**	**7**	**8**
Ru(1)−Ru(2)	2.780(2)	2.760(2)	2.770(2)	2.7585(8)	2.7611(9)	2.798(1)
Ru(1)−Ru(3)	2.748(2)	2.803(1)	2.754(2)	2.8240(8)	2.8012(8)	2.769(2)
Ru(1)−Ru(4)	2.746(2)	2.750(1)	2.752(2)	2.7673(8)	2.7677(9)	2.757(2)
Ru(1)−Ru(6)	2.971(2)	2.965(2)	2.976(3)	2.9784(8)	2.9617(9)	2.983(2)
Ru(2)−Ru(3)	2.690(2)	2.710(2)	2.682(2)	2.7096(8)	2.6990(9)	2.705(2)
Ru(2)−Ru(5)	2.777(2)	2.783(1)	2.771(2)	2.7588(8)	2.7636(9)	2.751(1)
Ru(2)−Ru(6)	2.777(2)	2.893(2)	2.934(3)	2.9177(8)	2.9303(8)	2.872(2)
Ru(4)−Ru(5)	2.742(2)	2.739(2)	2.747(2)	2.7465(8)	2.7559(8)	2.739(2)
Ru(4)−Ru(6)	2.872(2)	2.871(2)	2.853(3)	2.8465(8)	2.8969(9)	2.882(2)
Ru(5)−Ru(6)	2.924(2)	2.942(2)	2.947(3)	2.9626(8)	2.9443(9)	2.955(1)
N(1)−Ru(1)	2.22(1)	2.13(1)	2.155(6)	2.141(6)	2.145(7)	2.174(9)
N(1)−Ru(2)	2.20(2)	2.14(1)	2.172(6)	2.172(6)	2.184(7)	2.180(9)
N(1)−Ru(4)	2.23(1)	2.285(9)	2.263(6)	2.269(6)	2.330(7)	2.27(1)
N(1)−Ru(5)	2.20(1)	2.23(1)	2.226(5)	2.248(6)	2.214(6)	2.25(1)
N(2)−Ru(3)	2.30(1)	2.20(1)	2.206(6)	2.226(6)	2.221(8)	2.21(1)
P(1)−Ru(2)						2.280(3)
P(1)−Ru(3)		2.446(4)		2.448(2)	2.431(2)	
P(1)−Ru(6)			2.368(3)			
P(2)−Ru(6)				2.367(2)	2.356(2)	2.364(3)
P(3)−Ru(4)					2.425(2)	

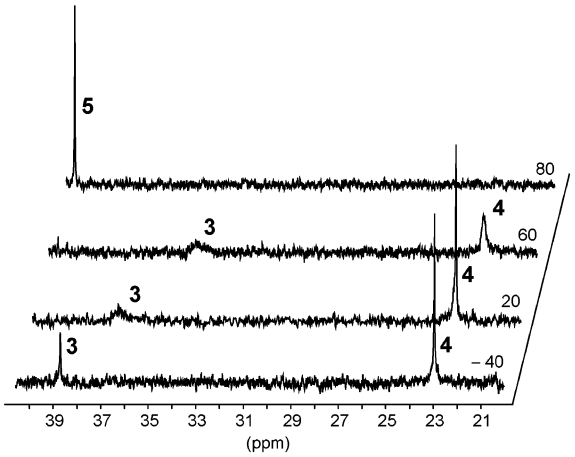


Figure 4. $^{31}P\{^1H\}$ NMR spectra of the mixture of compound **3** and **4** in CD_2Cl_2 (−40 and 20 °C) and toluene-d_8 (60 °C). At 80 °C (toluene-d_8), both compounds are transformed into complex **5**.

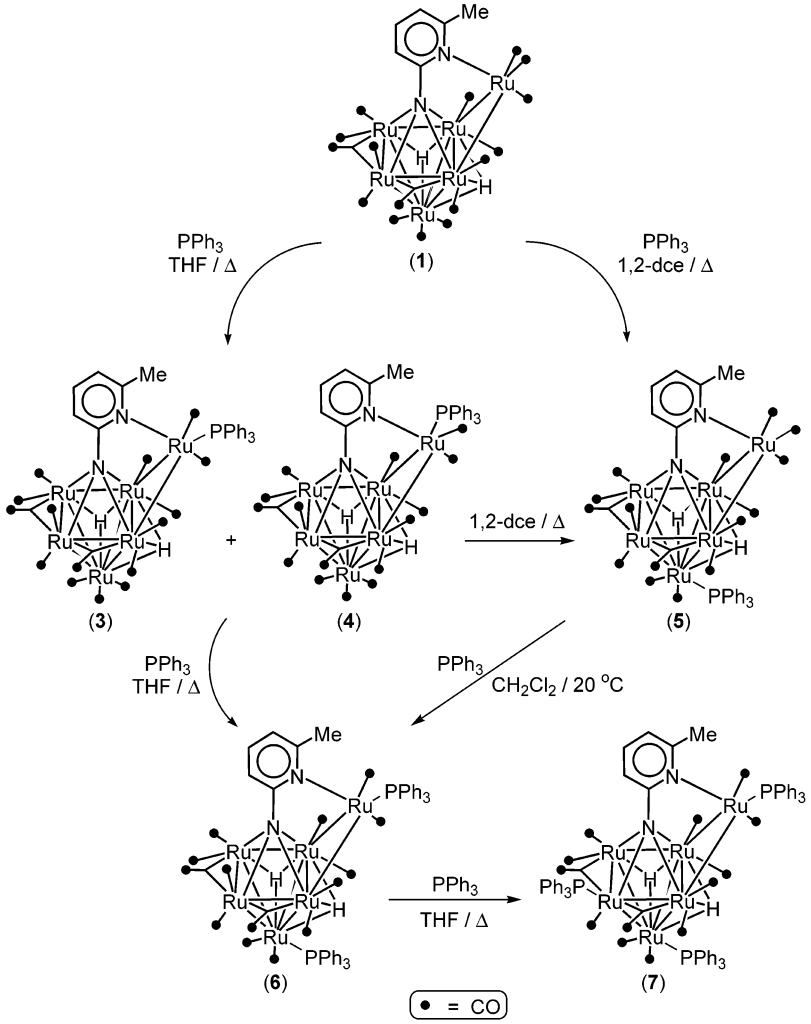
the PPh_3 ligand on the edge-bridging Ru atom, Ru(3), in a position *cis* to the pyridine N atom, and lined up with the Ru(2)−Ru(3) bond.

The −40 °C ^1H NMR spectrum of the mixture of **3** and **4** (at room temperature, the resonances of the minor isomer are broad) shows that both hydrides of the major isomer are coupled to the P atom with coupling constants of 6.4 and 2.0 Hz, whereas only one hydride of the minor isomer is coupled to the P atom, $J_{H-P} = 2.0$ Hz. The larger $^3J_{H-P}$ coupling constant (6.4 Hz) observed for the major isomer is compatible with a linear H−Ru−Ru−P arrangement,[13] which is indeed observed in the structure shown in Figure 3. Therefore, this structure corresponds to the major isomer, complex **3**.

A variable temperature $^{31}P\{^1H\}$ NMR study (Figure 4) revealed that the resonances of both isomers are sharp at −40 °C. The resonance of the minor component of the mixture is broad at room and higher temperatures, whereas the resonance of the major isomer broadens just above room temperature. After a few minutes at 80 °C, both compounds were transformed into a different product (**5**), characterized by a singlet at 40 ppm. The irreversibility of the latter transformation was checked by going back to room temperature, where the singlet that corresponds to complex **5** was the only resonance observed.

Complex **5** was subsequently prepared by heating the mixture of **3** and **4** in refluxing 1,2-dichloroethane and also by treating **1** with one equivalent of triphenylphosphine in 1,2-dichloroethane at reflux temperature (Scheme 2). The same transformations were observed in refluxing THF

Scheme 2. Reactivity of Compound **1** with Triphenylphosphine



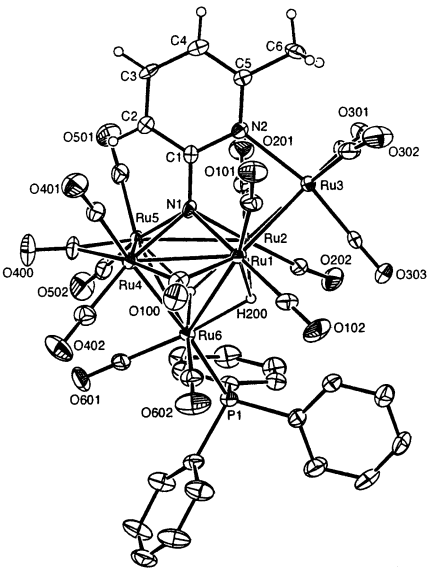


Figure 5. Molecular structure of compound **5**. The C and O atoms of each CO group bear the same number. Phenyl H atoms have been omitted for clarity.

(although slower due to its lower boiling point), indicating that solvent effects other than the temperature of reflux have little importance in these processes. The X-ray structure of **5** (Figure 5, Table 1) determined that this compound corresponds to the formula $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{13}(PPh_3)]$, being therefore a new monosubstituted isomer that bears the PPh_3 ligand on the apical Ru atom, Ru(6), in the position *cis* to both hydrides.

Our interpretation of these data is that the substitution of PPh_3 for CO in complex **1** is kinetically directed by the positions *cis* to the pyridine N atom, leading to a mixture of two isomers, **3** and **4**. Hence, we propose that the minor isomer (**4**) has the structure depicted in Scheme 2. The asymmetry of the starting material **1** may account for the different proportions of both isomers. The variable temperature NMR study, the fact that different preparations and recrystallizations led to the same ratio of **3** to **4**, and the impossibility of their separation, indicate that both isomers are in equilibrium at temperatures close to ambient and higher. The interconversion of **3** and **4** is probably due to a tripodal motion of the two carbonyls and the phosphine on Ru(3), a well-known process in carbonylmetal chemistry.[14] Alternatively, or concomitantly, a ligand rotation (involving hydrides and CO ligands) on the pyramidal part of the metal framework would also account for the interconversion of these two isomers.

A mechanistic study by Basolo et al.[15] on PPh_3 for CO substitution on tririutenium carbonyl clusters face-capped by 2-amidopyridine ligands concludes that the CO ligands adjacent to the amido group are more substitutionally labile than those adjacent to the pyridyl group. The apparent contradiction between this statement and our results can be explained if the mechanisms operating in both systems are different. In fact, the substitution reaction in Basolo's system follows an associative pathway that involves the simultaneous entering of the phosphine and the opening of one $N_{amido}-Ru$ arm, maintaining intact the remaining bonds in which the N_{amido} atom is implicated. In our system, such a selective bond opening is impossible because the imido fragment caps four metal atoms and the lengthening of one $N_{imido}-Ru$ bond would also modify the remaining $N_{imido}-Ru$ bonds. In our case, we think that it is more likely a common thermally induced dissociative pathway involving the release of CO from Ru(3) prior to the uptake of the phosphine ligand.

To check whether the isomerization of **3** and **4** to **5** is an intermolecular process, this rearrangement was studied in the presence of a different uncoordinated phosphine. An NMR tube charged with the mixture of **3** and **4**, tri-(*p*-anisyl)-phosphine (one phosphine per cluster), and toluene-d_8 was placed in the probe of an NMR spectrometer preheated to 80 °C. $^{31}P\{^1H\}$ NMR spectra were recorded at different reaction times. After 30 min at 80 °C, a complex mixture of products as well as free tripheylphosphine and tri-(*p*-anisyl)-phosphine was observed. The complexity of the mixture and the observation of free tripheylphosphine strongly support a dissociative pathway. This proposal is further substantiated by the fact that compound **1** was observed as a minor product of the thermolysis of **3** + **4** in refluxing in 1,2-dichloroethane for 75 min, that led to compound **5** as the major product.

Reactions Compound 1 with Triphenylphosphine: Di- and Trisubstituted Derivatives. The reaction of compound **1** with 2.5 equivalents of triphenylphosphine in refluxing 1,2-dichloroethane for 1 h led to a mixture of products from which the disubstituted derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{12}(PPh_3)_2]$ (**6**) was isolated in 40% yield. The monosubstituted products **3**-**5** and the trisubstituted derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{11}(PPh_3)_3]$ (**7**) were minor components of this mixture.

The positions of the PPh_3 ligands in complex **6** were determined by X-ray diffraction techniques. Figure 6 shows that the PPh_3 ligands of this complex occupy the same positions as the PPh_3 ligands in the monosubstituted derivatives **3** and **5**, that is, on the edge-bridging and apical Ru atoms. As expected from its structure, the $^{31}P\{^1H\}$ NMR spectrum of complex **6** consists of two uncoupled resonances.

Compound **6** was also prepared by treating the monosubstituted derivative **5** or the mixture of **3** and **4** with one equivalent of triphenylphosphine. Interestingly, while the reaction of **5** took place at room temperature, the reaction of the mixture of **3** and **4** required heating to the reflux temperature of THF (Scheme 2). This different reactivity exhibited by the monosubstituted complexes can be explained, once the structure of complex **6** is known, assuming that the substituted CO ligand of complex **5** is more labile (due to the labilizing effect of the pyridine fragment) than the CO ligands attached to the apical Ru atom of complexes

(13) See, for example, Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4611.
(14) For examples of tripodal motion of ligands of $M(CO)_2(PR_3)$ fragments, see (a) Cooke, J.; McClung, R. E. D.; Takats, J.; Rogers, R. D. *Organometallics* **1996**, *15*, 4459 and references therein. (b) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437. (c) Adams, H.; Agustinho, S. C. M.; Chombe, K.; Mann, B. E.; Smith, S.; Squires, C, Spey, S. E. *Can. J. Chem.* **2001**, *79*, 760.
(15) Shen, J. K.; Basolo, F.; Nombel, P.; Lugan, N.; Lavigne, G. *Inorg. Chem.* **1996**, *35*, 755.

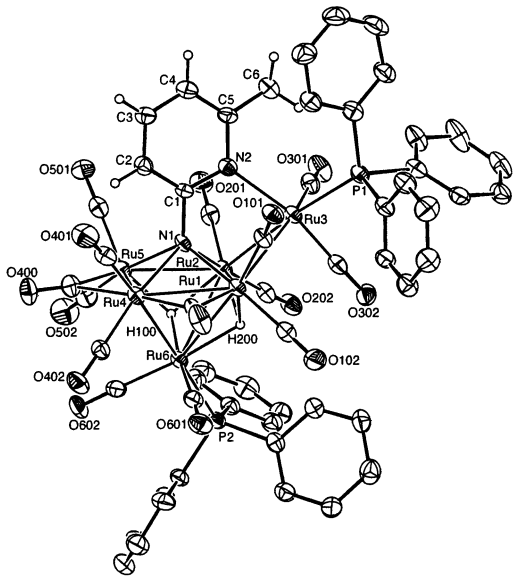


Figure 6. Molecular structure of compound **6**. The C and O atoms of each CO group bear the same number. Phenyl H atoms have been omitted for clarity.

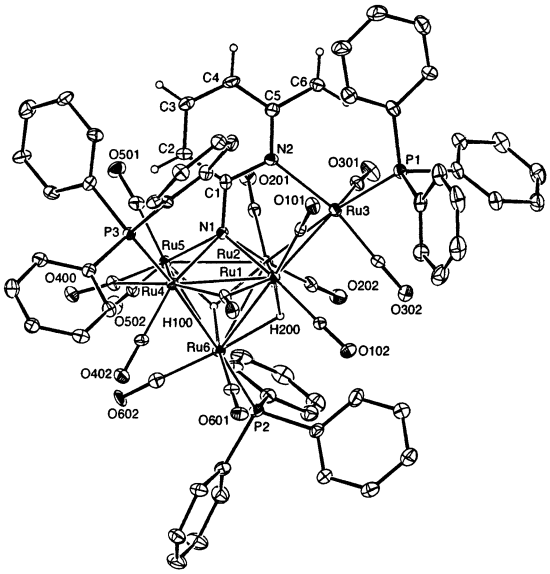
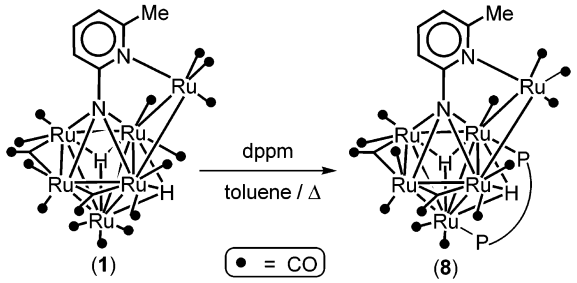


Figure 7. Molecular structure of compound **7**. The C and O atoms of each CO group bear the same number. Phenyl H atoms have been omitted for clarity.

3 and **4**. As the isomerization of **3** and **4** into complex **5** should be a dissociative process (the coordination sites involved are too far away for an intramolecular rearrangement), we believe that in the synthesis of complex **6** from **3** + **4** and tripenylphosphine such an isomerization should be inhibited to a great extent by the presence of triphenylphoshine in the reaction solution.

The most convenient method to prepare the trisubstituted derivative **7** was in the treatment of compound **1** with a large excess of triphenylphosphine (six equivalents) in refluxing 1,2-dichloroethane for 3 h. Under these conditions, a small amount of the disubstituted product **6** was still present in the reaction mixture. Longer reaction times led to mixtures of many products, some of them containing phosphide ligands ($\delta_{31P} > 200$), which were not investigated further.

Scheme 3. Synthesis of Compound **8**



An X-ray diffraction study (Figure 7, Table 1) revealed the positions of the PPh_3 ligands in complex **7**. Two such ligands are in the same positions as in the disubstituted derivative **6**, while the additional PPh_3 ligand is attached to Ru(4), the basal Ru atom that is not bonded to any of the hydrides.

The $^{31}P\{^1H\}$ NMR spectrum of this complex shows two doublets at 41.4 and 25.3 ppm ($^3J_{P-P} = 17.4$ Hz) and one singlet at 20.2 ppm. It is clear that the doublets correspond to the PPh_3 ligands attached to the square pyramid (their coupling is due to the fact that the P(3)−Ru(4)−Ru(6)−P(2) arrangement is nearly linear[13]).

A comparison of the ^{31}P chemical shifts of compounds **3**−**8** allowed us to establish a correlation between the observed ^{31}P chemical shift of a phosphine ligand with the coordination site it occupies on the cluster. Thus, PPh_3 ligands on the edge-bridging Ru atom, Ru(3) (with a linear P−Ru−Ru−H arrangement), appear at ca. 20 ppm (compounds **3**, **6**, and **7**), PPh_3 ligands on the apical Ru atom, Ru(6), appear at ca. 41 ppm (compounds **5**, **6** and **7**), and the PPh_3 ligand on the basal Ru(4) atom of complex **7** appears at 25.3 ppm.

Reaction of Compound 1 with Bis(diphenylphosphino)-methane. Complex **1** reacted with bis(diphenylphosphino)-methane (dppm) (1:1 molar ratio) in refluxing THF to give intricate mixtures of products. Monitoring these reactions by $^{31}P\{^1H\}$ and ^1H NMR, it was observed that at short reaction times (10−15 min) the major products contained monodentate dppm ligands, that some unreacted starting complex was still present and that all the dppm had been consumed. Longer reaction times (3−4 h) favored the formation of a major product, reducing the number of minor products. A reaction of complex **1** with dppm in refluxing toluene for 20 min allowed us to isolate, after a chromatographic workup, the disubstituted complex $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{12}(\mu\text{-dppm})]$ (**8**) in 16% yield (Scheme 3).

The $^{31}P\{^1H\}$ NMR spectrum of this complex consists of two doublets, $J_{P-P} = 66.1$ Hz, at positive chemical shifts (indicating that both P atoms are coordinated) and coincides with that of the major product observed in the reaction carried out in refluxing THF at long reaction times. Its molecular structure, which was determined by X-ray diffraction methods, is depicted in Figure 8. It shows a bidentate dppm ligand spanning the two ruthenium atoms that are attached to both hydride ligands, that is, the apical Ru(6) and the basal Ru(2).

The structure of complex **8** may give the impression that the experiment with dppm brings no support to the mecha-

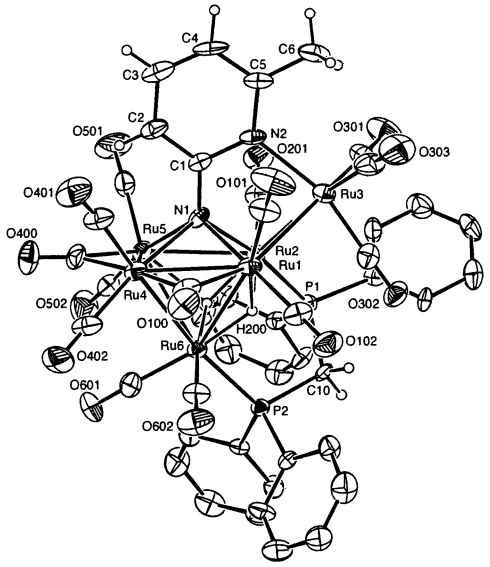


Figure 8. Molecular structure of compound **8**. The C and O atoms of each CO group bear the same number. Phenyl H atoms have been omitted for clarity.

nistic proposal given above for the case of triphenylphosphine. However, there is evidence that indicates that the dppm ligand might coordinate first as a monodentate ligand to Ru(3), as in **3** or **4**. A subsequent dissociative rearrangement would place a P atom on the apical Ru(6), as in **5**. Finally, coordination of the free P atom to Ru(2) would give the isolated product. The evidence for this proposal is as follows: (a) intermediates containing monodentate dppm ligands were detected when the reaction was monitored by $^{31}P\{^1H\}$ NMR, (b) compound **8** is a product of thermodynamic control since its synthesis requires long reaction times at high temperature, and (c) one of the P atoms of **8** occupies the same coordination site on Ru(6) as that occupied by the phosphine ligands of compounds **5**−**7**.

Concluding Remarks

The present work reports the first high-yield preparation of hexaruthenium carbonyl clusters complexes having a basal edge-bridged square pyramidal metallic skeleton. This has been accomplished by heating $[Ru_3(CO)_{12}]$ with half equivalent of nonorthometalable 2-aminopyridines in refluxing xylene. This efficient synthetic procedure has opened up the possibility of exploring the so-far unknown reactivity of this uncommon class of compounds.

Studying the reactivity of complex **1** with triphenylphosphine, we determined that its most labile CO ligands are those on the edge-bridging Ru atom, *cis* to the pyridine N atom (its substitution leads to compounds **3** and **4**), but the most stable monosubstituted product is complex **5**, which has the PPh_3 ligand on the apical Ru atom, *cis* to both hydride ligands. Once these two Ru atoms are occupied, as occurs in the disubstituted derivative **6**, the next substitution takes place on the basal Ru atom that is not bonded to any of the hydrides (compound **7**). All these compounds are 88-electron cluster complexes that obey the EAN rule, having therefore 10 metal−metal bonds.

As CO substitution processes are important steps in the reactivity of carbonyl cluster complexes, it is anticipated that the results reported herein will help rationalize some aspects of the reactivity of this type of hexaruthenium carbonyl clusters that undoubtedly will be investigated soon.

The 2-aminopyridine-derived ligands are not innocent in this chemistry. On the contrary, they play important roles, such as (a) promoting the formation of the basal edge-bridged square pyramidal metallic skeleton, (b) helping to maintain this metallic framework during the reactions, preventing cluster degradation, and (c) facilitating the monosubstitution of carbonyl ligands, providing pathways of accessible activation energy.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or CaH_2 (dichloromethane, 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. The xylene used was a mixture of isomers. All solvents and starting materials were purchased from commercial suppliers. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. NMR spectra were run on a Bruker DPX-300 instrument, at room temperature (unless otherwise stated), using the dichloromethane solvent resonance as the internal standard for ^1H ($\delta = 5.30$) or 85% aqueous H_3PO_4 as the external standard for ^{31}P ($\delta = 0$). 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.

$[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (1). A solution of $[Ru_3(CO)_{12}]$ (1 g, 1.565 mmol) and 2-amino-6-methylpyridine (85 mg, 0.786 mmol) in xylene (30 mL) was heated at reflux temperature for 1 h. The color changed from orange to dark brown. The reaction mixture was cooled to room temperature. Hexane (30 mL) was added with stirring, and the Schlenk tube was kept at −20 °C for 24 h. The solvent was decanted off and the solid residue was dissolved in THF (80 mL). The solution was filtered and the filtrate was evaporated to dryness to give a dark brown, nearly black, solid that was washed with hexane (3 × 10 mL) and dried under vacuum (704 mg, 77%). Calcd for $C_{22}H_8N_2O_{16}Ru_6$ (fw = 1162.72): C, 22.73; H, 0.69; N, 2.41. Found: C, 22.46; H, 0.70; N, 2.35. Positive FAB MS: $m/z = 1163$ [M^+]. IR (CH_2Cl_2): ν(CO) = 2094 (m), 2068 (s), 2049 (s), 2033 (vs), 2014 (m), 1995 (w, sh), 1973 (m, br), 1954 (w, sh), 1860 (w, br), 1828 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta = 7.21$ (t, $J = 7.8$ Hz, 1 H), 6.64 (d, $J = 7.8$ Hz, 1 H), 5.76 (d, $J = 7.8$ Hz, 1 H), 2.56 (s, 3 H), −11.46 (d, $J = 2.2$ Hz, 1 H), −15.90 (d, $J = 2.2$ Hz, 1 H).

$[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-apy})(\mu\text{-}CO)_2(CO)_{14}]$ (2). This complex was prepared from $[Ru_3(CO)_{12}]$ (272 mg, 0.425 mmol) and 2-aminopyridine (20 mg, 0.213 mmol) following the procedure described above for complex **1** (171 mg, 70%). Calcd for $C_{21}H_6N_2O_{16}Ru_6$ (fw = 1148.70): C, 21.96; H, 0.53; N, 2.44. Found: C, 21.86; H, 0.54; N, 2.43. Positive FAB MS: $m/z = 1149$ [M^+]. IR (CH_2Cl_2): ν(CO) = 2095 (m), 2071 (s), 2049 (s), 2033 (vs), 2019 (s, sh), 1996 (m, sh), 1973 (m, br), 1954 (w, sh), 1861 (w, br), 1828 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta = 7.77$ (dd, $J = 5.5$, 1.4 Hz, 1 H), 7.22 (ddd, $J = 8.8$, 7.2, 1.4 Hz, 1 H), 6.59 (ddd, $J = 7.2$, 5.5, 1.1 Hz, 1 H), 5.77 (d, br, $J = 8.8$ Hz, 1 H), −11.73 (d, $J = 2.4$ Hz, 1 H), −16.04 (d, $J = 2.4$ Hz, 1 H).

$[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\eta^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{13}(PPh_3)]$ (Isomers 3 and 4). A solution of compound **1** (50 mg, 0.043 mmol) and

triphenylphosphine (13 mg, 0.050 mmol) was stirred in THF (20 mL) at reflux temperature for 10 min. The color changed from dark brown to ruddy brown. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (8 mL). After adding silica gel (ca. 4 g), the solvent was evaporated under reduced pressure. The solid residue was placed into a silica gel column (2 × 20 cm) packed in hexane. Hexane-dichloromethane (3:1) eluted three bands. The first band, dark brown, contained a trace amount of compound **1**. The third band, blood red, contained a small amount of complex **6** (4 mg). The second band afforded a 5:1 mixture (by NMR) of compounds **3** and **4** as a ruddy brown solid after solvent removal (27 mg, 45%). Calcd for $C_{39}H_{23}N_2O_{15}PRu_6$ (fw = 1397.00): C, 33.53; H, 1.66; N, 2.01. Found: C, 33.61; H, 1.80; N, 2.15. Positive FAB MS: m/z = 1398 [M^+]. IR (CH_2Cl_2): ν(CO) = 2081 (m), 2072 (w), 2043 (m, sh), 2031 (vs), 2023 (s, sh), 1989 (w, br), 1967 (w, br), 1941 (w, br), 1849 (w, br), 1818 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.60−7.20 (m, Ph of **3** and **4**), 7.10 (t, J = 7.6 Hz, ampy of **3**), 6.85 (br, ampy of **4**), 6.34 (d, J = 7.6 Hz, ampy of **3**), 5.89 (br, ampy of **4**), 5.64 (d, br, ampy of **4**), 5.51 (d, J = 7.6 Hz, ampy of **3**), 2.01 (s, Me of ampy of **3**), 1.95 (s, Me of ampy of **4**), −11.53 (br, μ-H of **4**), −11.68 (dd, J = 6.4 and 2.0 Hz, μ-H of **3**), −13.55 (br, μ-H of **4**), −15.19 (t, J = 2.0 Hz, μ-H of **3**). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 37.1 (br, **4**), 23.2 (s, **3**).

[Ru$_6$(μ_3-H)$_2$(μ_5-η^2-ampy)(μ-CO)$_2$(CO)$_{13}$(PPh$_3$)] (Isomer 5). *Method (a):* A solution of compound **1** (100 mg, 0.086 mmol) and triphenylphosphine (23 mg, 0.086 mmol) was stirred in 1,2-dichloroethane (20 mL) at reflux temperature for 3 h. No color change was observed. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (8 mL). After adding silica gel (ca. 2 g), the solvent was removed under reduced pressure. The solid residue was placed into a silica gel column (2 × 20 cm) packed in hexane. Hexane-dichloromethane (5:1) eluted a small amount of compound **1** (6 mg) and a trace amount of an unidentified product. Hexane-dichloromethane (3:1) eluted two bands. The last band, dark green, contained a trace amount of an unidentified product. The fastest moving band, dark brown, afforded compound **5** as a brown solid after solvent removal (38 mg, 32%). *Method (b):* A solution of **3** + **4** (24 mg, 0.017 mmol) in 1,2-dichloroethane (15 mL) was stirred at reflux temperature for 75 min. The solvent was removed under reduced pressure. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the residue indicated the presence of compounds **1** and **5** in a 1:10 ratio together with small amounts of unidentified compounds. Calcd for $C_{39}H_{23}N_2O_{15}PRu_6$ (fw = 1397.00): C, 33.53; H, 1.66; N, 2.01. Found: C, 33.55; H, 1.57; N, 2.05. Positive FAB MS: m/z = 1398 [M^+]. IR (CH_2Cl_2): ν(CO) = 2077 (w), 2049 (s), 2021 (vs), 2000 (m, sh), 1987 (w, sh), 1975 (w), 1960 (m, br), 1948 (w, sh), 1852 (w, br), 1814 (w, br) cm^{-1}.^{1}H NMR ($CDCl_3$): δ = 7.60−7.00 (m, 16 H), 6.48 (d, J = 7.7 Hz, 1 H), 5.76 (d, J = 7.7 Hz, 1 H), 2.47 (s, 3 H), −11.18 (dd, J = 8.1, 2.6 Hz, 1 H), −14.84 (dd, J = 5.7, 2.6 Hz, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 40.7 (s).

[Ru$_6$(μ_3-H)$_2$(μ_5-η^2-ampy)(μ-CO)$_2$(CO)$_{12}$(PPh$_3$)$_2$] (6). *Method (a):* A solution of compound **1** (50 mg, 0.043 mmol) and triphenylphosphine (28 mg, 0.107 mmol) was stirred in 1,2-dichloroethane (20 mL) at reflux temperature for 1 h. The color changed from dark brown to red brown. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (8 mL). After adding silica gel (ca. 2 g), the solvent was removed under reduced pressure. The solid residue was placed into a silica gel column (2 × 20 cm) packed in hexane. Hexane-dichloromethane (4:1) eluted three bands. The first band, dark brown, contained a mixture of compounds **3**−**5** in trace amounts. The third band, brownish orange, contained a small amount of complex **7** (5 mg). The second band afforded compound **6** as a red brown solid after solvent removal (28 mg, 40%). *Method (b):* A solution of compound **5** (15 mg, 0.010 mmol) and triphenylphosphine (3 mg, 0.011 mmol) in dichloromethane (10 mL) was stirred at room temperature for 42 h. The solvent was removed under reduced pressure. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the residue indicated the complete transformation of the starting materials into complex **6**. Calcd for $C_{56}H_{38}N_2O_{14}P_2Ru_6$ (fw = 1631.27): C, 41.23; H, 2.35; N, 1.72. Found: C, 41.44; H, 2.41; N, 1.63. Positive FAB MS: m/z = 1632 [M^+]. IR (CH_2Cl_2): ν(CO) = 2053 (m), 2024 (vs), 2011 (vs), 1998 (m, sh), 1981 (w, sh), 1957 (m, br), 1933 (w, sh), 1841 (w, br), 1806 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.90−6.80 (m, 31 H), 6.26 (d, J = 7.6 Hz, 1 H), 5.59 (d, J = 7.6 Hz, 1 H), 1.95 (s, 3 H), −11.44 (m, 1 H), −14.08 (m, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 41.2 (s, 1 P), 20.7 (s, 1 P).

[Ru$_6$(μ_3-H)$_2$(μ_5-η^2-ampy)(μ-CO)$_2$(CO)$_{11}$(PPh$_3$)$_3$] (7). A solution of compound **1** (80 mg, 0.069 mmol) and triphenylphosphine (109 mg, 0.414 mmol) was stirred in 1,2-dichloroethane (30 mL) at reflux temperature for 3 h. The color changed from dark brown to dark orange. After cooling to room temperature, silica gel (ca. 4 g) was added and the solvent was removed under reduced pressure. The solid residue was placed into a silica gel column (2 × 20 cm) packed in hexane. Hexane-dichloromethane (3:1) eluted a small amount of complex **6** (8 mg). Hexane-dichloromethane (1:1) eluted compound **7**, which was isolated as a brown orange solid after solvent removal (74 mg, 57%). Calcd for $C_{73}H_{53}N_2O_{13}P_3Ru_6$ (fw = 1865.55): C, 47.00; H, 2.86; N, 1.50. Found: C, 47.26; H, 2.82; N, 1.33. Positive FAB MS: m/z = 1866 [M^+]. IR (CH_2Cl_2): ν(CO) = 2034 (m), 2013 (s), 1999 (vs), 1986 (m, sh), 1950 (m), 1940 (m), 1908 (w, br), 1818 (w, br), 1772 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.10−6.80 (m, 45 H), 5.93 (d, J = 7.4 Hz, 1 H), 5.84 (t, J = 7.4 Hz, 1 H), 5.10 (d, J = 7.4 Hz, 1 H), 1.96 (s, 3 H), −11.81 (m, 1 H), −13.35 (m, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 41.4 (d, J = 17.4 Hz, 1 P), 25.3 (d, J = 17.4 Hz, 1 P), 20.2 (s, 1 P).

[Ru$_6$(μ_3-H)$_2$(μ_5-η^2-ampy)(μ-CO)$_2$(CO)$_{12}$(μ-dppm)] (8). A solution of compound **1** (81 mg, 0.070 mmol) and bis(diphenylphosphino)methane (32 mg, 0.084 mmol) was stirred in toluene (20 mL) at reflux temperature for 20 min. The color changed from dark brown to dark red. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (10 mL). Silica gel (ca. 4 g) was added and the solvent was removed under reduced pressure. The solid residue was placed into a silica gel column (2 × 20 cm) packed in hexane. Hexane-dichloromethane (3:1) eluted four bands. The first contained a small amount of starting material **1**. The second and fourth bands were very weak and were not identified. The third band, dark red, afforded compound **8** after solvent removal (17 mg, 16%). Calcd for $C_{45}H_{30}N_2O_{14}P_2Ru_6$ (fw = 1491.09): C, 36.25; H, 2.03; N, 1.88. Found: C, 36.41; H, 2.17; N, 1.99. Positive FAB MS: m/z = 1492 [M^+]. IR (CH_2Cl_2): ν(CO) = 2062 (m), 2039 (vs), 2012 (vs), 1981 (m, br), 1950 (w, br), 1919 (w, br), 1842 (w, br), 1806 (w, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.00−6.80 (m, 21 H), 6.44 (d, J = 7.7 Hz, 1 H), 6.04 (d, J = 7.7 Hz, 1 H), 3.95 (ddd, J = 21.5, 11.5, 3.5 Hz, 1 H), 3.63 (ddd, J = 24.4, 12.1, 3.5 Hz, 1 H), 2.39 (s, 3 H), −11.82 (ddd, J = 11.8, 9.8, 2.0 Hz, 1 H), −15.03 (m, 1 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 48.8 (d, J = 66.1 Hz, 1 P), 31.9 (d, J = 66.1 Hz, 1 P).

X-ray Structures of Compounds 1, 3·2H$_2$O, 6, and 7·CH$_2$Cl$_2$. 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 radia-

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

	1	**3**·2H$_2$O[a]	**5**	**6**	**7**·CH$_2$Cl$_2$	**8**·0.5C$_7$H$_8$
formula	$C_{22}H_8N_2O_{16}Ru_6$	$C_{39}H_{23}N_2O_{15}PRu_6$·2O	$C_{39}H_{23}N_2O_{15}PRu_6$	$C_{56}H_{38}N_2O_{14}P_2Ru_6$	$C_{73}H_{53}N_2O_{13}P_3Ru_6$·$CH_2Cl_2$	$C_{45}H_{30}N_2O_{14}P_2Ru_6$·0.5$C_7H_8$
crystal system	orthorhombic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$Pc2_1b$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	8.8607(2)	18.4425(18)	11.998(13)	13.4886(4)	13.9447(6)	11.354(3)
b, Å	16.7448(4)	13.3512(13)	12.108(13)	14.8157(4)	15.1141(6)	23.584(6)
c, Å	20.6625(5)	19.6015(19)	16.396(18)	18.3555(5)	18.9417(8)	20.941(5)
α, deg	90	90	84.826(18)	69.068(2)	90.276(3)	90
β, deg	90	104.417(6)	77.902(18)	74.458(2)	95.087(3)	95.471(5)
γ, deg	90	90	68.341(18)	63.290(2)	104.990(3)	90
vol, Å^3	3065.7(2)	4674.5(8)	2164(4)	3035.1(2)	3839.5(3)	5582(3)
Z	4	4	2	2	2	4
radiation (λ, Å)	Cu Kα (1.54180)	Cu Kα (1.54180)	Mo Kα (0.71073)	Cu Kα (1.54180)	Cu Kα (1.54180)	Mo Kα (0.71073)
μ, mm^{-1}	24.033	16.251	2.148	12.812	11.049	1.701
temp, K	293(2)	293(2)	293(2)	200(2)	150(2)	299(2)
min/max h, k, l	0/10, 0/20, −24/24	−20/21, −16/14, −23/23	−7/13, −13/13, −18/17	−15/16, −16/17, 0/22	−16/16, −17/18, −22/21	−12/12, −26/25, −17/23
collected reflns	42734	33036	8379	80528	62023	20435
unique reflns	5707	7648	5588	11107	14041	7755
reflns with $I > 2\sigma(I)$	5376	3620	5228	9066	11643	6477
parameters/restraints	415/1	589/0	578/0	723/0	945/4	647/7
R_1 (on F, $I > 2\sigma(I)$)	0.0642	0.0644	0.0356	0.0648	0.0764	0.0729
wR_2 (on F^2, all data)	0.1250	0.1556	0.0802	0.2060	0.2642	0.1650

[a] Only the O atoms of the water molecules were observed and, therefore, their H atoms were not included in the refinement process.

tion. Empirical absorption corrections were applied using XABS2[16] for **1**, **3**·2H$_2$O, and **7**·CH$_2$Cl$_2$, or SORTAV[17] for **6**. The structures were solved by Patterson interpretation using the program DIRDIF-96.[18] Isotropic and full-matrix anisotropic least squares refinements against F^2 were carried out using SHELXL-97.[19] All non-H atoms were refined anisotropically. The oxygen atoms of two disordered water molecules were found in the asymmetric unit of **3**·2H$_2$O. Their hydrogen atoms were not included in the final model. The H100 and H200 atom positions of **3**·2H$_2$O were located in the corresponding Fourier maps. Their thermal parameters and the coordinates of H200 were fixed. For compounds **1**, **6**, and **7**·CH$_2$Cl$_2$, the positions of H100 and H200 were calculated using the program XHYDEX[20] and their coordinates and thermal parameters were fixed. The remaining hydrogen atom positions of the four compounds were geometrically calculated and refined riding on their parent atoms. The molecular plots were made with the EUCLID program package.[21] The WINGX program system[22] was used throughout the structure determinations.

X-ray Structures of Compounds 5 and 8·0.5C$_7$H$_8$. 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. Semiempirical absorption corrections were applied with SADABS.[23] Structures were solved by direct methods and refined by full-matrix least-squares method against F^2 with SHELXTL.[24] All non-hydrogen atoms were refined anisotropically except for the solvent toluene of **8**·0.5C$_7$H$_8$, whose carbon atoms were refined as a rigid group, with isotropic thermal factors, and with an occupancy factor of 0.5. The hydride ligands of both compounds were located in difference maps. Those of complex **5** were fully refined (both coordinates and isotropic thermal parameters), while those of **8** were refined with a fixed thermal parameter. The remaining hydrogen atoms were set in calculated positions and refined as riding atoms. The molecular plots were made with the EUCLID program package.[21] The WINGX program system[22] was used throughout the structure determinations.

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Supporting Information Available: Crystallographic data in CIF format for **1**, **3**·2H$_2$O, **5**, **6**, **7**·CH$_2$Cl$_2$, and **8**·0.5C$_7$H$_8$. This material is available free of charge via the Internet at http://pubs.acs.org.

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