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Reversible Thermal Activation of a Triphenylphosphine P−C Bond on a Cationic Non-Hydridic Triruthenium Carbonyl Cluster Complex. Structural Characterization of a μ-η^1:η^2-Benzoyl Derivative

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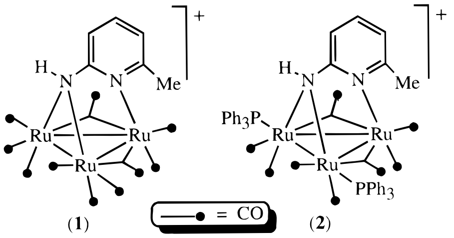
The thermal activation of a triphenylphosphine P−C bond of the 48-electron cationic cluster complex [$Ru_3(\mu_3$-ampy)$(PPh_3)_2(CO)_8][BF_4]$ (**2**; Hampy = 2-amino-6-methylpyridine) leads to the phenyl derivative [$Ru_3(\mu$-Ph)$(\mu_3$-ampy)$(\mu$-$PPh_2)(PPh_3)(CO)_7][BF_4]$ (**3**). Treatment of **3** with carbon monoxide regenerates **2** *via* the 50-electron intermediate [$Ru_3(\mu$-Ph)$(\mu_3$-ampy)$(\mu$-$PPh_2)$-$(PPh_3)(CO)_8][BF_4]$. These reactions represent the first reversible triphenylphosphine P−C bond activation reaction reported in carbonyl cluster chemistry. The neutral acyl derivative [$Ru_3(\mu$-PhCO)$(\mu$-Cl)$(\mu_3$-ampy)$(\mu$-$PPh_2)(PPh_3)(CO)_5]$, which arises from the reaction of **3** with [PPN]Cl, has been characterized by X-ray diffraction methods.

Introduction

Cationic trinuclear carbonyl cluster compounds containing no hydride ligands are uncommon.[1−10] Recently, we reported a high-yield synthesis of the first 48-electron triruthenium cluster of this kind, the face-bridged cluster [$Ru_3(\mu_3$-ampy)$(CO)_{10}][BF_4]$ (**1**; Hampy = 2-amino-6-methylpyridine) (Chart 1).[9] As far as we are aware, the only cationic, non-hydridic, trinuclear carbonyl clusters of ruthenium known prior to compound **1** are 50-, 47-, or 46-electron species.[4,5] Previous reactivity studies on **1** have revealed a unique chemical behavior as a result of the very high electrophilic character of this cluster.[11] These studies have allowed, for example, the preparation of the unusual hexanuclear compounds [$Ru_6(\mu_3$-ampy$)_2(CO)_{18}]$ (94 electrons)[11a] and [$Ru_6(\mu$-H)$(\mu_3$-ampy)$(\mu_4$-S)$(CO)_{17}]$ (92 electrons).[11b]

Chart 1



(**1**) (**2**)

As a continuation of these reactivity studies on cationic, non-hydridic, triruthenium cluster compounds, we now report that the thermolysis of the bis(triphenylphosphine) derivative of **1**, [$Ru_3(\mu_3$-ampy)$(PPh_3)_2$-$(CO)_8][BF_4]$ (**2**) (Chart 1),[9] leads to [$Ru_3(\mu$-Ph)$(\mu_3$-ampy)-$(\mu$-$PPh_2)(PPh_3)(CO)_7][BF_4]$ (**3**), a remarkable cationic

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cluster containing a phenyl ligand that arises from a P−C bond activation reaction. This reaction was found to be reversible, since **3** reacts with carbon monoxide to regenerate **2** *via* the 50-electron intermediate $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_8][BF_4]$ (**4**). We also report that the reaction of **3** with [PPN]Cl leads to the unusual μ-benzoyl derivative $[Ru_3(\mu\text{-}PhCO)(\mu\text{-}Cl)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_5]$ (**5**), which has been characterized by X-ray diffraction methods.

Results

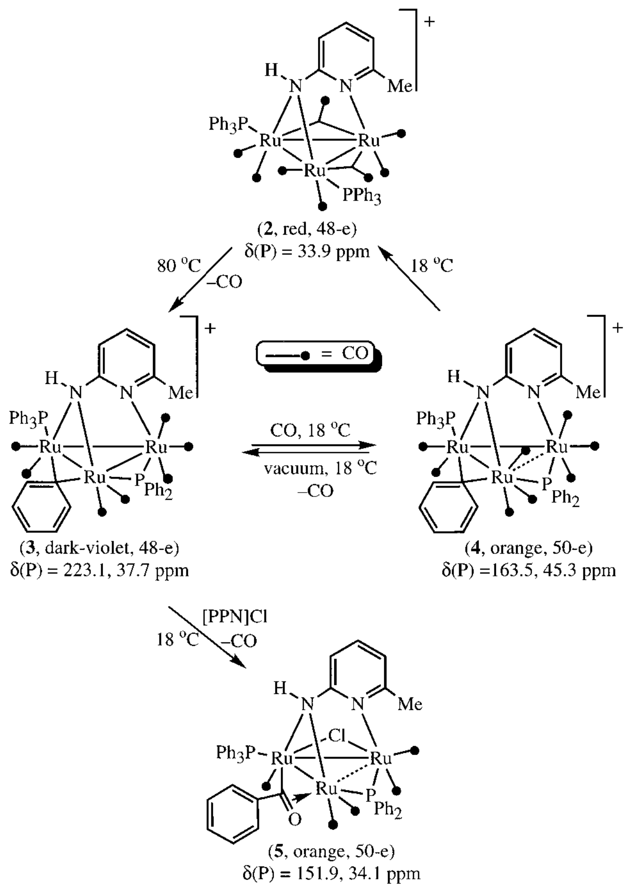
Triphenylphosphine P−C Bond Activation: Thermolysis of Compound 2. Stirring a 1,2-dichloroethane solution of **2** at reflux temperature for 1.5 h resulted in its quantitative transformation into the derivative $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_7][BF_4]$ (**3**). This compound is a violet solid which can be handled in air without appreciable decomposition.

The $^{31}P\{^1H\}$NMR spectrum of **3** displays two singlet resonances, one at a chemical shift close to that found for **2** (37.7 ppm in **3** *vs* 33.9 ppm in **2**), indicating a similar chemical environment of the PPh_3 ligand in **3** as that found in **2**, and the other at 223.1 ppm. The high chemical shift of this resonance confirms the transformation of one PPh_3 ligand of the starting compound **2** into a bridging diphenylphosphido ligand in **3**.[12] In addition, the fact that both resonances are singlets confirms that the PPh_3 and μ-PPh_2 ligands are attached to different ruthenium atoms.

Although the highest mass peak in the FAB mass spectrum of **3** is observed at $m/z = 1103$, corresponding to the hexacarbonyl fragment $[M - CO]^+$, the ^{13}C NMR spectrum shows seven CO resonances, confirming that the compound is actually a heptacarbonyl derivative. The IR spectrum verifies the absence of bridging CO ligands.

The presence of the phenyl ligand in **3** is also indicated by the ^1H and DEPT ^{13}C NMR spectra, which show the resonances of the corresponding atoms of the phenyl ligand spread over a wide range of chemical shifts (8.51−6.91 ppm in the ^1H spectrum, 152.2−124.5 ppm in the $^{13}C\{^1H\}$ spectrum), as observed previously for the cluster $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$, which contains a bridging η^1-phenyl ligand and which has been characterized by X-ray diffraction methods.[13] The other ruthenium cluster previously known to contain a bridging phenyl ligand is the trinuclear compound $[Ru_3(\mu,\eta^2\text{-}Ph)(\mu_3\text{-}S)(\mu\text{-}PPh_2)(PPh_3)(CO)_6]$.[14] However, the bridging phenyl ligand of this sulfur-capped 48-electron cluster is a three-electron donor, being coordinated to one metal atom in a σ-fashion and to another metal atom in a π-fashion. Such a coordination type for the phenyl ligand can be ruled out in the case of cluster **3**, since the high ^{31}P NMR chemical shift (223.1 ppm) observed for the diphenylphosphido ligand of **3** is within the range expected for 48-electron clusters (200−450 ppm)[12,15-17] and since, for **3** to be a 48-electron heptacarbonyl cluster, the phenyl ligand should contribute only one electron.

Scheme 1



The structure proposed for this compound in Scheme 1 is based on its spectroscopic data, since, despite many attempts, we could not grow single crystals suitable for an X-ray diffraction study. This structure is also supported by reactivity results and by the X-ray structure of one of its derivatives (*vide infra*), although the bridging situation of the phenyl ligand has not been unambiguously established.

Regeneration of the Triphenylphosphine Ligand: Reaction of Compound 3 with Carbon Monoxide. Exposure of a room temperature solution of **3** in 1,2-dichloroethane to carbon monoxide for a few minutes resulted in the quantitative formation of the orange 50-electron cationic derivative $[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_8][BF_4]$ (**4**). This compound could not be isolated, since it underwent a spontaneous transformation into **2** on being kept in solution at room temperature for 1 h (with and without a CO atmosphere), and it re-formed **3** within seconds when we attempted to evaporate the solvent under reduced pressure. As the solutions of cluster **4** proved to be indefinitely stable at temperatures below −50 °C, the compound could be characterized by NMR spectroscopy at low temperature (−60 °C).

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The ^{13}C NMR spectrum of **4** demonstrates the incorporation of a new CO ligand, since it shows eight carbonyl resonances in the range 205.3−198.8 ppm, as expected for terminal CO ligands. These resonances rule out the possibility of having an acyl ligand, which should present a higher chemical shift for its carbonyl resonance (see below the ^{13}C NMR data of the acyl compound **5**). As with that of **3**, the ^{13}C NMR spectrum of **4** also contains the resonances of the phenyl ligand spread over a wide range of chemical shifts (156.5−125.2 ppm), most of them overlapped with those of the other phenyl rings. The ^{1}H NMR spectrum is comparable with that of **3**. However, in the $^{31}P\{^{1}H\}$ NMR spectrum, the resonance of the diphenylphosphido group appears at 163.5 ppm, *ca.* 60 ppm lower than that of **3**. The addition of a CO ligand should transform **3** into a 50-electron derivative, and this should be accompanied by a considerable shift of the ^{31}P resonance of the μ-PPh_2 ligand toward lower frequencies;[12] for example, the ^{31}P chemical shifts of the μ-PPh_2 ligands in the 50-electron clusters $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]^+$,[4a] $[Ru_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_3(CO)_7]$,[4a] $[Ru_3(\mu_3\text{-}H)\{\mu_3\text{-}P(Ph)C_6H_4\}(\mu\text{-}PPh_2)_3(CO)_6]$,[18] and $[Ru_3\{\mu_3\text{-}P(Ph)C_5H_4N\}(\mu\text{-}PPh_2)_3(CO)_6]$[19] are in the range 148.5−1.4 ppm.

All these spectroscopic data support the structure proposed for **4** in Scheme 1, although, as occurs with **3**, the bridging situation of the phenyl ligand has not been unambiguously established.

Reaction of Compound 3 with [PPN]Cl: Synthesis and X-ray Structure of the Neutral Acyl Derivative 5. The structural characterization of a derivative of **3** would shed more light on the structure of this cluster. Therefore, some reactions of **3** were carried out in order to get single crystals of a derivative suitable for X-ray diffraction studies.

Treatment of a dichloromethane solution of **3** with [PPN]Cl resulted in an instantaneous color change from violet to orange. A chromatographic workup allowed the isolation of the neutral 50-electron acyl derivative $[Ru_3(\mu\text{-}PhCO)(\mu\text{-}Cl)(\mu_3\text{-}ampy)(\mu\text{-}PPh_2)(PPh_3)(CO)_5]$ (**5**).

The structure depicted for **5** in Scheme 1 is based on an X-ray diffraction study carried out on a crystal of the 1,2-dichloroethane solvate $\mathbf{5}\cdot 1.5C_2H_4Cl_2$. A selection of bond distances and angles is given in Table 1. Figure 1 shows a view of the molecular structure as well as of the coordination surroundings of the three metal atoms. The cluster consists of a triangle of ruthenium atoms triply bridged by the ampy ligand. A chloride, a benzoyl ligand, and a diphenylphosphido ligand act also as bridging ligands, spanning the three Ru−Ru edges, with the benzoyl ligand spanning the same edge as the amido fragment of the ampy ligand. The cluster shell is completed by one PPh_3 ligand and five terminal CO ligands (three in axial and two in equatorial positions).

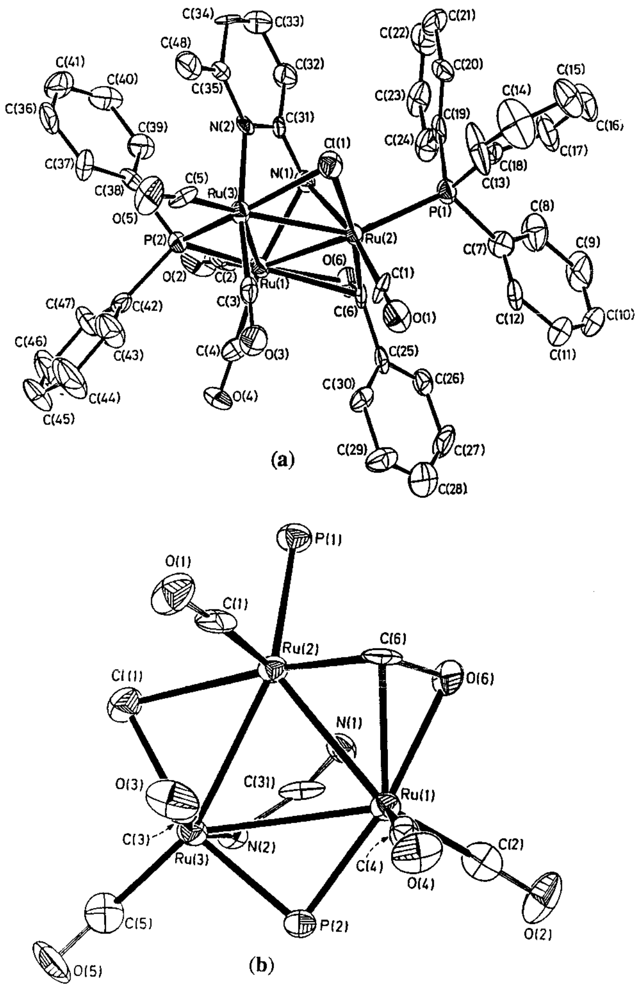

Figure 1. (a) Molecular structure of **5**. (b) Coordination shell of **5**, showing only the metal triangle and relevant atoms of each ligand.

Table 1. Selected Bond Lengths and Bond Angles in $\mathbf{5\cdot 1.5C_2H_4Cl_2}$

Bond Lengths (Å)			
Ru(1)−Ru(2)	2.848(2)	Ru(1)−Ru(3)	3.140(2)
Ru(2)−Ru(3)	2.836(2)	Ru(3)−Cl(1)	2.443(4)
Ru(1)−P(2)	2.277(4)	Ru(2)−P(1)	2.341(4)
Ru(3)−P(2)	2.265(4)	Ru(1)−N(1)	2.13(1)
Ru(2)−N(1)	2.18(1)	Ru(3)−N(2)	2.23(1)
Ru(2)−Cl(1)	2.591(4)	Ru(1)−C(2)	1.87(2)
Ru(1)−C(4)	1.89(2)	Ru(1)−C(6)	2.39(1)
Ru(2)−C(1)	1.85(2)	Ru(2)−C(6)	1.98(2)
Ru(3)−C(3)	1.83(2)	Ru(3)−C(5)	1.88(2)
Ru(1)−O(6)	2.219(9)	C(1)−O(1)	1.14(2)
C(2)−O(2)	1.16(2)	C(3)−O(3)	1.18(2)
C(4)−O(4)	1.13(2)	C(5)−O(5)	1.13(2)
C(6)−O(6)	1.26(2)		
Bond Angles (deg)			
Ru(1)−Ru(2)−Ru(3)	67.06(5)	Ru(1)−Ru(3)−Ru(2)	56.65(4)
Ru(2)−Ru(1)−Ru(3)	56.29(4)	Ru(2)−Cl(1)−Ru(3)	68.5(1)
Ru(1)−P(2)−Ru(3)	87.4(1)	Ru(1)−N(1)−Ru(2)	82.6(4)
Ru(1)−C(6)−O(6)	66.6(7)	Ru(2)−C(6)−O(6)	121(1)
O(6)−C(6)−C(25)	114(1)		

While the Ru−Ru distances of the edges associated with the chloride and acyl ligands (2.836 and 2.848 Å, respectively) are within the range expected for "normal" Ru−Ru bonds, the edge spanned by the diphenylphosphido ligand is considerably longer (3.140 Å). A similar situation has been found in the neutral 50-electron cluster $[Ru_3\{\mu_3\text{-}P(Ph)C_5H_4N\}(\mu\text{-}PPh_2)(CO)_9]$,[15] but in this case the diphenylphosphido-bridged edge (3.847 Å) is much longer than the other two (average 2.894 Å).

The benzoyl ligand of **5** interacts with two Ru atoms in a μ-η^1:η^2 manner, being σ-bonded to Ru(2) through the carbonyl carbon atom [Ru(2)−C(6) = 1.98(2) Å] and π-bonded to Ru(1) through the carbon and oxygen atoms [Ru(1)−C(6) = 2.39(1) Å, Ru(1)−O(6) = 2.219(9) Å]. Curiously, in other 50-electron triruthenium clusters

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containing bridging acyl ligands, for example in $[Ru_3(\mu\text{-}PhCO)\{\mu_3\text{-}P(Ph)C_5H_4N\}(CO)_9]$[20] and $[Ru_3(\mu\text{-}PhCH{=}CPhCO)\{\mu_3\text{-}N(Me)C_5H_4N\}(CO)_9]$,[21] the carbon atom of the acyl group is attached to only one Ru atom, while the oxygen atom closes the bridge binding the other Ru atom. It is also curious that, in contrast to **5** (in which the acyl-bridged Ru−Ru edge is closed, Ru(1)−Ru(2) = 2.848 Å), those of these two latter compounds are open, involving very long Ru−Ru distances (3.639 and 3.412 Å, respectively).

The FAB mass spectrum of **5** shows peaks due to the molecular ion and to ions resulting from the loss of up to five CO ligands. The IR (1605 cm^{-1}) and ^{13}C NMR (255.9 ppm) spectroscopic data of the acyl carbonyl group of this cluster are comparable to those reported for bridging acyl carbonyl groups of other 50-electron trinuclear clusters.[20−22] The fact that the ^{13}C NMR resonance of the acyl carbon atom is a singlet, although in the solid state it is attached to Ru(1) in a position approximately *trans* to the μ-PPh_2 ligand, suggests that the C(6)−Ru(1) interaction may be absent in solution, as found in other acyl clusters.[20,21] The remaining spectroscopic data of this compound are in agreement with the solid state structure.

The acyl group of **5** should be formed by a migratory insertion process which requires the attachment of the phenyl and carbonyl groups to the same metal atom. The fact that the carbonyl carbon atom of the acyl group of **5** is much closer to Ru(2) (1.98 Å) than to Ru(1) (2.39 Å) supports the attachment of the phenyl group of **3** to the ruthenium atom unbonded to the μ-PPh_2 ligand, as is, indeed, the case if the phenyl ligand of **3** is in a bridging position.

It is also worth noting that the $^{31}P\{^1H\}$NMR spectrum of **5** contains two singlet resonances at chemical shifts close to those of **4**. This fact confirms that **4** is a 50-electron cluster and that the Ru−Ru distance of its phosphido-bridged Ru−Ru edge should be similar to that of **5**.

Discussion

The cyclic reaction pathway shown in Scheme 1 represents a reversible P−C bond activation process occurring on cationic cluster complexes. The relevance of these results lies not only in the fact that a P−C bond activation reaction has never been observed previously on a cationic trinuclear carbonyl cluster compound but also in the fact that the reversibility of such a process has never been demonstrated previously.[23,24]

In addition, although the thermal activation of P−C bonds of coordinated triphenylphosphine ligands has been observed on many occasions,[13,14,16,23−29] these reactions generally lead to phosphido-bridged derivatives as well as to benzene,[28,29] benzaldehyde,[26,29] or biphenyl.[26,27] However, very few σ-phenyl-μ-diphenylphosphido derivatives have been isolated,[13,14,16,25] although they have often been claimed as intermediates in these processes.[24,26,27] Compounds containing bridging phenyl ligands arising from P−C bond cleavage reactions are even less common, being restricted to a few compounds of ruthenium[13,14,30] and to one of osmium.[16]

From a mechanistic point of view, although it is clear that **4** is an intermediate in the transformation of **3** into **2**, the involvement of **4** in the thermal transformation of **2** into **3** is unlikely. It seems more probable that, in the transformation of **2** into **3**, the P−C bond cleavage step is preceded by a CO dissociation step (which requires thermal activation) that would give rise to an unsaturated 46-electron species, which would undergo the oxidative addition of the P−C bond. As the phenyl and μ-PPh_2 ligands of **3** are not in a *cis* arrangement, a ligand rearrangement step should occur after the oxidative addition of the P−C bond. This mechanistic proposal is strongly supported by the fact that the reaction of **2** with triphenylphosphine in refluxing 1,2-dichloroethane renders the substituted derivative $[Ru_3(\mu_3\text{-ampy})(PPh_3)_3(CO)_7][BF_4]$ in quantitative spectroscopic yield. Therefore, as **3** is never observed when the reaction of **2** with triphenylphosphine is monitored by spectroscopic means, a CO dissociation step is expected to precede the formation of $[Ru_3(\mu_3\text{-ampy})(PPh_3)_3(CO)_7][BF_4]$ (when there is triphenylphosphine available in solution) or **3** (in the absence of additional ligands that could replace the released CO). Furthermore, we found that **3** does not react with triphenylphosphine in 1,2-dichloroethane at reflux temperature.

As far as the acyl derivative **5** is concerned, it should be noted that it is an uncommon type of compound in the sense that it is a 50-electron species containing an acyl ligand that spans a metal−metal bonded edge. All the other 50-electron triruthenium acyl clusters contain these ligands spanning open Ru−Ru edges.[20,21] The proximity of the acyl-bridged metal atoms of **5** may cause the acyl ligand to interact with the metal atoms in an η^1-*C*:η^2-*C,O* bridging type, whereas the acyl groups of the other known 50-electron triruthenium acyl clusters interact with the metal atoms in an η^1-*C*:η^1-*O* bridging type,[20,21] probably as a consequence of a longer Ru−Ru distance.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (diethyl ether, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. Unless otherwise stated, the reactions were carried out under nitrogen, using Schlenk vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compound **2** was prepared as described

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previously.[9] Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H, ^{13}C, and ^{31}P NMR spectra were run at room temperature with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ (for ^1H and ^{13}C) or external 85% H_3PO_4 (for ^{31}P) as standards ($\delta = 0$). Fast atom bombardment (FAB) mass spectra were obtained on a Finningan Mat-95 spectrometer, using nitrobenzyl alcohol as matrix and cesium as bombarding gas. Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_7][BF_4]$ (3). A solution of **2** (80 mg, 0.064 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 1.5 h. During this time, the color changed from red to violet. The solvent was removed under reduced pressure and the solid residue was washed with two 5-mL portions of diethyl ether and vacuum-dried to give **3** as a dark violet solid (70 mg, 89%). Anal. Calcd for $C_{49}H_{37}BF_4N_2O_7P_2Ru_3$: C, 48.33; H, 3.06; N, 2.30. Found: C, 47.84; H, 3.14; N, 2.29. MS (*m/z*): 1103 ($M^+ - CO$). IR ν(CO) ($C_2H_4Cl_2$): 2070 (m), 2053 (w), 2022 (vs), 1999 (w), 1964 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 23 °C): 8.51 (d, $J = 8.2$ Hz, 1 H, μ-Ph), 7.72−6.91 (complex mixture of signals, 30 H), 6.81 (t, $J = 7.3$ Hz, 1 H, ampy H^4), 6.36 (d, $J = 7.3$ Hz, 1 H, ampy H^3), 5.75 (s, br, 1 H, ampy NH), 2.38 (s, 3 H, ampy Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 23 °C, DEPT): 205.0 (d, $J = 7.8$ Hz), 204.6 (d, $J = 9.8$ Hz), 200.7 (d, $J = 8.2$ Hz), 198.8 (t, $J = 8.0$ Hz), 196.0 (d, $J = 12.6$ Hz), 193.8 (d, $J = 6.1$ Hz), 193.5 (d, $J = 5.2$ Hz) (7 CO ligands), 173.4 (s), 159.7 (s), 140.7 (s), 120.3 (s), 116.1 (s), 30.8 (s) (ampy carbon atoms), 152.2 (s, *C*H), 137.7 (d, $J = 46.2$ Hz, *C*), 136.3 (s, *C*H), 135.7 (d, $J = 29.2$ Hz, *C*), 133.9−129.0 (complex mixture of signals), 124.5 (s, *C*H) (6 phenyl groups) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C): 223.1 (s), 37.7 (s) ppm.

$[Ru_3(\mu\text{-}Ph)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_8][BF_4]$ (4). Carbon monoxide was bubbled for 2 min through a 1,2-dichloroethane solution (15 mL) of **3** (50 mg, 0.041 mmol) at room temperature. The color changed immediately from dark violet to orange. The IR spectrum of this solution showed the complete disappearance of **3** and the formation of a new product (**4**). IR ν(CO) ($C_2H_4Cl_2$): 2069 (vs), 2043 (s), 2000 (s), 1973 (sh) cm^{-1}. This compound was not isolated as a solid because **3** was re-formed within seconds when, in order to remove the solvent, the orange solution was exposed to vacuum. On the other hand, the orange solution of **4** turned red upon standing at room temperature for 1 h. The IR spectrum of this red solution indicated the quantitative transformation of **4** into **2**. The NMR spectra given below were obtained from a solution prepared by bubbling CO for 1 min through a CD_2Cl_2 solution of **3** in an NMR tube at −50 °C and transferring the tube quickly to the precooled spectrometer probe. ^1H NMR (CD_2Cl_2, −60 °C): 8.25−6.96 (m, 30 H), 6.82 (t, $J = 7.6$ Hz, 1 H, ampy H^4), 6.12 (d, $J = 7.6$ Hz, 1 H, ampy H^5), 5.45 (d, $J = 7.6$ Hz, 1 H, ampy H^3), 2.87 (s, br, 1 H, ampy NH), 2.31 (s, 3 H, ampy Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C, DEPT): 205.3 (s), 204.0 (d, $J = 13.9$ Hz), 196.8 (d, $J = 11.1$ Hz), 195.4 (d, $J = 9.6$ Hz), 194.8 (d, $J = 8.6$ Hz), 194.3 (d, $J = 7.1$ Hz), 190.1 (d, $J = 6.0$ Hz), 189.8 (d, $J = 6.0$ Hz) (8 CO ligands), 174.2 (s), 158.8 (s), 140.4 (s), 120.1 (s), 113.3 (s), 32.8 (s) (ampy carbon atoms), 153.5 (s, *C*H), 138.5 (d, $J = 47.2$ Hz, *C*), 133.6−128.6 (complex mixture of signals), 125.2 (s, *C*H) (6 phenyl groups) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C): 163.5 (s), 45.3 (s) ppm.

$[Ru_3(\mu\text{-}PhCO)(\mu\text{-}Cl)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(PPh_3)(CO)_5]$ (5). [PPN]Cl (23.6 mg, 0.041 mmol) was added to a solution of **3** (50 mg, 0.041 mmol) in dichloromethane (10 mL) at room temperature. The color changed from dark violet to orange. The solution was concentrated under reduced pressure to *ca.* 2 mL and introduced into a column (10 cm × 2 cm) of neutral alumina (activity IV) packed in hexane. Elution with dichloromethane afforded a single orange band. After evaporating to dryness the resulting solution, the residue was washed with diethyl ether (3 × 5 mL) and dried under vacuum to give **5** as an orange powder (35 mg, 75%). Anal. Calcd for $C_{48}H_{37}ClN_2O_6P_2Ru_3$: C, 50.64; H, 3.27; N, 2.46. Found: C, 51.31; H, 3.08; N, 2.32. MS (*m/z*): 1138 (M^+). IR ν(CO) (CH_2Cl_2): 2030 (s), 2001 (vs), 1964 (m), 1944 (m), 1927 (sh), 1605 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 23 °C): 7.77−6.87 (m, 30 H), 6.77 (t, $J = 7.7$ Hz, 1 H, ampy H^4), 6.04 (d, $J = 7.7$ Hz, 1 H, ampy H^5), 5.02 (d, $J = 7.7$ Hz, 1 H, ampy H^3), 2.98 (s, br, 1 H, ampy NH), 1.89 (s, 3 H, ampy Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 23 °C, DEPT): 255.9 (s) (acyl carbon), 210.5 (d, $J = 13.0$ Hz), 201.4 (d, $J = 13.1$ Hz), 200.5 (d, $J = 12.1$ Hz), 195.5 (s), 191.5 (t, $J = 5.5$ Hz) (5 CO ligands), 169.0 (s), 158.4 (s), 138.6 (s), 117.7 (s), 113.7 (s), 30.1 (s) (ampy carbon atoms), 152.3 (s, *C*), 140.5 (d, $J = 46.3$ Hz, *C*), 138.6 (d, $J = 34.2$ Hz, *C*), 135.1−125.7 (complex mixture of signals) (6 phenyl groups) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C): 151.9 (s), 34.1 (s) ppm.

Table 2. Crystallographic and Refinement Data for $5{\cdot}1.5C_2H_4Cl_2$

formula	$C_{48}H_{37}ClN_2O_6P_2Ru_3{\cdot}1.5C_2H_4Cl_2$
fw	1286.82
cryst syst	monoclinic
space group	$P2_1/c$
a, b, c, Å	14.998(4), 17.971(7), 19.615(10)
β, deg	105.14(4)
V, $Å^3$	5103(4)
Z	4
$F(000)$	2564
D_{calcd}, g/cm^3	1.675
μ, mm^{-1}	1.199
cryst size, mm	0.2 × 0.2 × 0.2
radiation (λ, Å)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
temp, K	293(2)
scan method	$\omega-2\theta$
θ limits, deg	1.41−22.98
h,k,l ranges	−16 to +15, 0 to +19, 0 to +21
reflns collected	7336
independent reflns	7092
$R_{int} = \sum(I - <I>)/\sum I$	0.086
reflns with $I > 2\sigma(I)$	3647
restraints, parameters	0, 614
$R(F)_{I>2\sigma(I)}{}^{a}$	0.0603
$R_w(F^2)_{\text{all data}}{}^{b}$	0.1941
GOF[c]	0.976
Δ/σ	0.009
max, min $\Delta\rho$, e/$Å^3$	1.207, −1.529

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] Goodness of fit (GOF) = $[\sum w(F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

Crystal Structure of $5{\cdot}1.5C_2H_4Cl_2$. An orange crystal, obtained by layering pentane on a solution of the complex in 1,2-dichloroethane at −20 °C, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 2.

The cell dimensions were determined by least-squares refinement of 25 reflections with $5 < \theta < 12°$. Space group $P2_1/c$ was determined from systematic absences. Intensities were collected with a scan angle of 1.5° and a variable scan rate with a maximun scan time of 60 s/reflection. Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.98 and 1.13. Profile analysis was performed on all reflections.[31] In view of the small size of the crystal, no absorption corrections were made. Lorentz and polarization corrections were applied.

The structure was solved by the Patterson heavy atom method using DIRDIF92.[32] Isotropic and full-matrix anisotropic least-squares refinements on F^2 were performed using

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SHELX93.[33] A difference Fourier synthesis allowed the location of two 1,2-dichloroethane solvent molecules, one lying on an inversion center (thus contributing one-half to the empirical fomula). After refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms, the hydrogen atoms were refined isotropically, using a riding model, with temperature factors fixed at 0.070 Å^2. Function minimization was carried out $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, with $\sigma(F_o^2)$ from counting statistics and $P = [\max(F_o^2, 0) + 2°F_c^2]/3$. Atomic scattering factors were taken from the literature.[34] Geometrical calculations were made with PARST.[35] The structure plot was drawn with the EUCLID package.[36] All calculations were carried out on VAX computers at the Scientific Computer Centre of the University of Oviedo.

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Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for **5**$\cdot 1.5C_2H_4Cl_2$ (11 pages). Ordering information is given on any current masthead page.

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