Carbonyl−Metal Clusters with Mixed O,N-Donor Ligands: Reactivity of the Ureato Cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(CO)_9]$ with Phosphines. Structural Characterization of a Triphenylphosphine Derivative and of a Bis(diphenylphosphido) Derivative Which Also Contains a Bridging η^1-Phenyl Ligand

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The ureato-bridged carbonyl cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(CO)_9]$ (**1**) ($H_2NCONMe_2$ = *N*,*N*-dimethylurea) reacts with 1 equiv of triphenylphosphine or diphenylphosphine to give the isostructural derivatives $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(L)(CO)_8]$ (L = PPh_3, PPh_2H). The X-ray structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(PPh_3)(CO)_8]$ indicates that the substitution has taken place on an equatorial position *cis* to the bridging NH fragment. Treatment of **1** with bis(diphenylphosphino)methane (dppm) affords a mixture of the symmetric (C_s) and asymmetric (C_1) isomers of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(\mu\text{-}dppm)(CO)_7]$. All these reactions take place at room temperature. The phenyl-bridged bis(diphenylphosphido) derivative $[Ru_3(\mu\text{-}\eta^1\text{-}Ph)(\mu_3\text{-}HNCONMe_2)(\mu\text{-}PPh_2)_2(CO)_6]$ has been prepared by reaction of **1** with 2 equiv of PPh_3 in the presence of alumina and has been characterized by X-ray diffraction methods. The thermolysis of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(PPh_2H)(CO)_8]$ in refluxing THF leads to the phosphido-bridged derivatives $[Ru_3(\mu_3\text{-}HNCONMe_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(\mu\text{-}PPh_2)_2(CO)_6]$. It has been observed that carbonyl substitution reactions on compound **1** are easier than those previously reported on clusters containing *N*- and/or *P*-donor bridging ligands. This seems to be related to the hard−soft character of the bridging ligand: the harder the ligand the more reactive is the cluster in carbonyl substitution reactions.

Introduction

Ruthenium carbonyl cluster complexes containing O-donor ligands are relatively scarce in comparison with those containing N-, P-, or S-donor ligands.[1] In fact, as a consequence of the hard character of the oxygen-donor ligands and of the soft character of the ruthenium carbonyl species, the synthesis of such cluster compounds generally has to face two obstacles: (a) the reactions of $[Ru_3(CO)_{12}]$ with neutral O-donor ligands are favored little in a kinetic sense since they require high temperatures,[2] previous derivatization of $[Ru_3(CO)_{12}]$ to give more reactive intermediates,[3] or catalysis;[4] and (b) the formed compounds have little thermal stability, undergoing fragmentation of the cluster framework under the reaction conditions.[5−7] This is often the case for neutral clusters, while anionic clusters seem to be more stable; for example, the thermal reactions of $[Ru_3(CO)_{12}]$ with carboxylic acids generally lead to $[\{Ru_2(\mu\text{-}RCO_2)_2(CO)_4\}_n]$,[6] whereas the reactions with carboxylate anions render $[Ru_3(\mu\text{-}MeCO_2)(CO)_{10}]^-$.[8] Analogously, the thermal reaction of $[Ru_3(CO)_{12}]$ with

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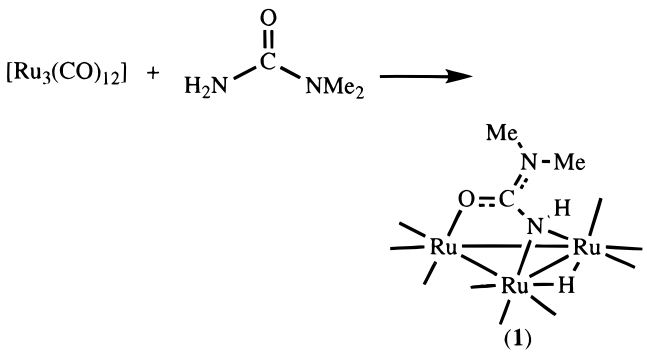
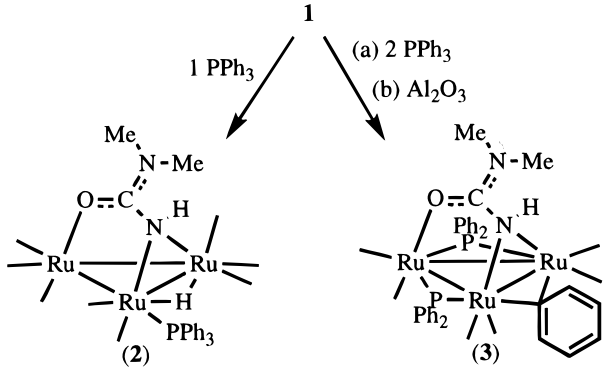
Scheme 1



Scheme 2



2-pyridone (HOpy) leads to $[\{Ru_2(\mu\text{-Opy})_2(CO)_4\}_n]$ and/or $[Ru_2(\mu\text{-Opy})_2(HOpy)_2(CO)_4]$ depending on the reaction conditions,[7] whereas the reaction with the pyridonate anion gives $[Ru_3(\mu\text{-Opy})(CO)_{10}]^-$.[9] Interestingly, protonation of $[Ru_3(\mu\text{-Opy})(CO)_{10}]^-$ at room temperature gives $[Ru_3(CO)_{12}]$ instead of the yet unknown $[Ru_3(\mu\text{-H})(\mu\text{-Opy})(CO)_{10}]$.[9]

It is curious that in spite of their expected high reactivity, the derivative chemistry of trinuclear ruthenium carbonyl clusters containing O-donor ligands remains nearly unexplored.[1] This statement also refers to ruthenium clusters containing mixed O,N-donor ligands, which are known for ligands derived from ureas,[10] carbamates,[11] aminophenol,[12] salicylaldimines,[13] and 8-hydroxyquinoline.[14]

We now describe the synthesis and reactivity with triphenylphosphine, diphenylphosphine, and bis(diphenylphosphino)methane ligands of the *N*,*O*-ureato cluster complex $[Ru_3(\mu\text{-H})(\mu_3\text{-HNCONMe}_2)(CO)_9]$ (**1**). These studies demonstrate that compound **1** is very reactive, undergoing not only easy carbonyl substitution reactions, but also easy P−C and P−H bond activation processes on coordinated ligands. Although the ureato derivatives $[Ru_3(\mu\text{-H})(\mu_3\text{-R}^1\text{NCONHR}^2)(CO)_9]$ ($R^1 = R^2 = H$; $R^1 = R^2 =$ Me; $R^1 = H$, $R^2 =$ Ph; $R^1 = H$, $R^2 =$ *cis*-CH=CHMe; $R^1 = H$, $R^2 =$ *trans*-CH=CHMe) were previously known,[10] we decided to carry out our reactivity studies on complex **1** because the presence of two methyl groups on the uncoordinated nitrogen atom increases the solubility of this type of compound and makes the assessment of the number of products of a reaction by ^{1}H NMR spectroscopy easier.

Results and Discussion

Synthesis and Characterization of Compound 1. Treatment of $[Ru_3(CO)_{12}]$ with an excess of *N*,*N*-dimethylurea in THF at reflux temperature led to the orange trinuclear complex $[Ru_3(\mu\text{-H})(\mu_3\text{-HNCONMe}_2)(CO)_9]$ (**1**), isolated in 75% yield. The structure proposed for this compound in Scheme 1 is supported by its analytical and spectroscopic data, which are comparable to those reported for the X-ray-characterized complex $[Ru_3(\mu\text{-H})(\mu_3\text{-HNCONHR})(CO)_9]$ (R = *cis*-CH=CHMe).[10] The observation of two diastereotopic methyl groups in the ^{1}H and ^{13}C NMR spectra of compound **1** indicates that rotation of the NMe_2 group is impeded and that the entire ureato group is planar in solution. The low wavenumber of the IR ν(CO) absorption of the ureato group (1602 cm^{-1}) also indicates some delocalization of the double bond between the C−O and C−N bonds.[10] In related triruthenium[15,16] and triosmium[17] thioureato clusters, the sulfur atom spans a metal-metal edge while the unique metal atom is attached to one of the nitrogen atoms.

Compounds Derived from Triphenylphosphine. Treatment of complex **1** with 1 equiv of triphenylphosphine in THF at room temperature allowed the isolation of a yellow solid, subsequently identified as $[Ru_3(\mu\text{-H})(\mu_3\text{-HNCONMe}_2)(PPh_3)(CO)_8]$ (**2**), in 70% yield (Scheme 2). Monitoring of a reaction in CD_2Cl_2 solvent by ^{1}H and ^{31}P{^{1}H} NMR indicated that compound **2** was not the only product formed, since a minor product (less than a 10%), characterized by a doublet at −10.84 ppm (J = 10.2 Hz) in the ^{1}H spectrum and a singlet at 28.8 ppm in the ^{31}P{^{1}H} NMR spectrum, was also observed, but it could not be isolated. The analytical and mass spectroscopic data of compound **2** were consistent with the proposed formulation, and its ^{1}H and ^{31}P{^{1}H} NMR spectra indicated the presence of a phosphine and a hydride ligand in a *cis* arrangement (J_{H-P} = 10.5 Hz).[18,19] However, as these data were insufficient to unequivocately determine the attachment of the phosphine ligand to the O-bonded or N-bonded Ru atom; the structure of **2** was determined by X-ray diffraction methods.

Figure 1 shows the molecular structure of compound **2**. A selection of bond distances and angles is given in Table 1. The structure resembles that of the starting material **1**, since the trinuclear cluster contains the hydride ligand spanning the same Ru−Ru edge as the

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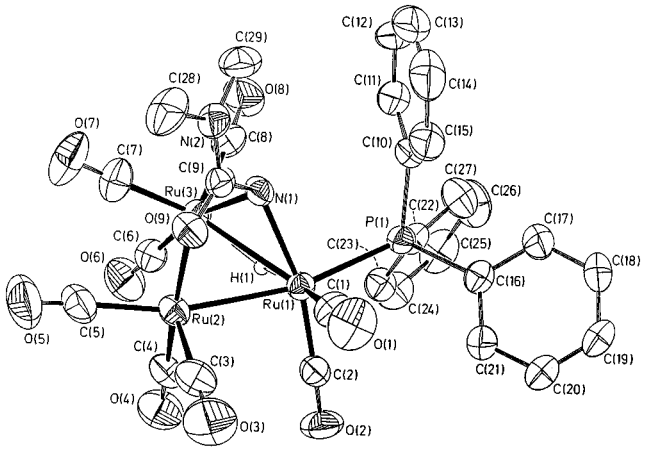

Figure 1. Molecular structure of compound **2**.

Table 1. Selected Bond Lengths and Bond Angles in Compound 2

Bond Lengths (Å)			
Ru(1)−Ru(2)	2.725(1)	Ru(1)−Ru(3)	2.798(4)
Ru(2)−Ru(3)	2.758(1)	Ru(1)−P(1)	2.386(2)
Ru(2)−O(9)	2.162(5)	Ru(1)−N(1)	2.146(6)
Ru(3)−N(1)	2.169(5)	Ru(1)−C(1)	1.872(8)
Ru(1)−C(2)	1.849(7)	Ru(2)−C(3)	1.907(8)
Ru(2)−C(4)	1.833(8)	Ru(2)−C(5)	1.942(8)
Ru(3)−C(6)	1.886(8)	Ru(3)−C(7)	1.914(8)
Ru(3)−C(8)	1.947(7)	C(1)−O(1)	1.146(8)
C(2)−O(2)	1.150(8)	C(3)−O(3)	1.143(9)
C(4)−O(4)	1.147(8)	C(5)−O(5)	1.123(9)
C(6)−O(6)	1.134(9)	C(7)−O(7)	1.137(8)
C(8)−O(8)	1.125(8)	C(9)−O(9)	1.243(7)
C(9)−N(1)	1.384(8)	C(9)−N(2)	1.327(8)
C(28)−N(2)	1.45(1)	C(29)−N(2)	1.44(1)

Bond Angles (deg)			
Ru(1)−Ru(2)−Ru(3)	61.37(7)	Ru(1)−Ru(3)−Ru(2)	58.75(4)
Ru(2)−Ru(1)−Ru(3)	59.89(4)		

NH fragment of the face-bridging ureato ligand, which is planar and perpendicular to the Ru_3 plane. The phosphine ligand occupies an equatorial position *cis* to both the NH fragment and the hydride ligand.

Therefore, the reactivity of compound **1** with 1 equiv of triphenylphosphine can be compared to that observed for the reference compounds $[Ru_3(\mu\text{-H})(\mu_3\text{-PhNCSNHPh})(CO)_9]$,[16] $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(CO)_9]$ (Hampy = 2-amino-6-methylpyridine),[18] and $[Ru_3(\mu\text{-H})(\mu_3\text{-Spy})(CO)_9]$ (HSpy = pyridine-2-thiol),[20] which also undergo carbonyl substitution in an equatorial position *cis* to both the bridging hydride and the bridging S or NH fragments. However, the reactions with these three cluster compounds are clean, giving single products, whereas, as commented above, that of compound **1** also gives a minor product (which may have the phosphine ligand attached to the O-bonded Ru atom). It should be noted that the three reference compounds have their unique Ru atoms attached to nitrogen atoms, whereas one metal atom of compound **1** is attached to oxygen, which is harder and, therefore, more *cis*-labilizing than nitrogen,[21] and this was expected to be reflected in its reactivity. A *cis*-directed substitution has been previously observed in ruthenium carbonyl clusters containing bridging amido ligands,[18,19] but recent kinetic studies on carbonyl substitution reactions in this type of clusters have pointed out that the mechanism governing the *cis*-substitution is associative[22] and, therefore, different from that operating in mononuclear complexes (dissociative).[21]

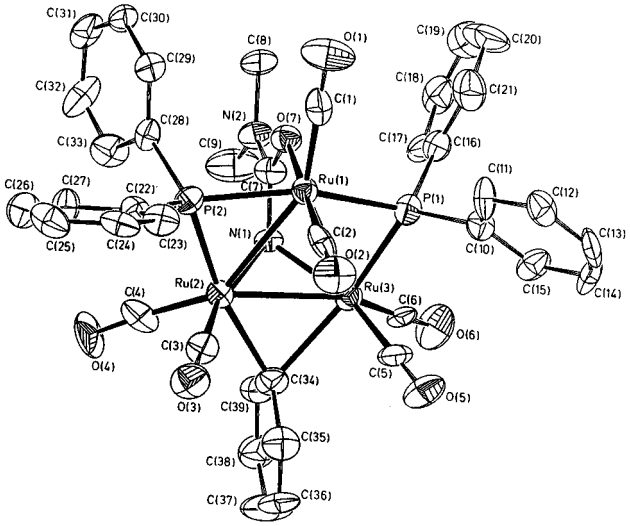

Figure 2. Molecular structure of compound **3**.

The reaction of compound **1** with 2 equiv of triphenylphosphine proved to be very complicated. Monitoring by $^{31}P\{^1H\}$ NMR spectroscopy of a reaction carried out in toluene-d_8 at room temperature showed the immediate formation of a mixture of at least six different species. After 30 min, the two major components of this mixture were responsible for a singlet resonance at 47.3 ppm and an AB spin system (19.3, 17.2 ppm, J = 28 Hz). Complex **2** was also observed as a minor product. Heating this mixture at 343 K for 3 h resulted in the appearance of a new singlet at 56.5 ppm, while the singlet at 47.3 ppm and that of compound **2** progressively disappeared and the AB system was maintained. Using an excess of triphenylphosphine (2-fold, toluene-d_8, 343 K, 30 min) resulted in the formation of a *ca.* 3:1 mixture of the same two compounds accompanied by minor impurities ($^{31}P\{^1H\}$ NMR). The ^1H NMR spectrum of this mixture contained a multiplet at −6.3 ppm. Unfortunately, we were unable to separate these two compounds by TLC on silica gel. Attempting a successful separation, we tried column chromatography on neutral alumina, and to our surprise, we observed that both compounds were transformed within the column into a different one, which was separated and subsequently identified as $[Ru_3(\mu\text{-}\eta^1\text{-Ph})(\mu_3\text{-HNCONMe}_2)(\mu\text{-PPh}_2)_2(CO)_6]$ (**3**) (Scheme 2). The ^1H NMR spectrum of this compound contains no hydride resonances and is complicated in the aromatic region, whereas the $^{31}P\{^1H\}$ NMR spectrum contains only a singlet at 198.8 ppm, indicating the transformation of the phosphine ligands into bridging diphenylphosphido groups.[23]

The molecular structure of compound **3** (Figure 2) was determined by an X-ray diffraction study on a crystal of the solvate **3**·CH_2Cl_2. A selection of bond distances and angles is given in Table 2. The cluster consists of an isosceles triangle of ruthenium atoms triply bridged

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Table 2. Selected Bond Lengths and Bond Angles in Compound 3·CH_2Cl_2

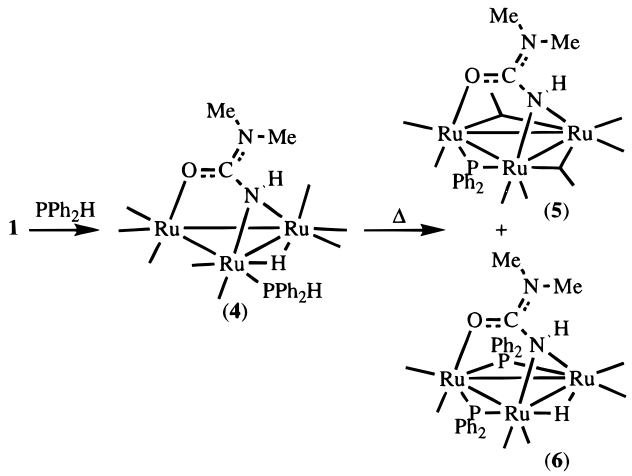
Bond Lengths (Å)			
Ru(1)−Ru(2)	2.969(3)	Ru(1)−Ru(3)	2.953(2)
Ru(2)−Ru(3)	2.661(3)	Ru(1)−P(1)	2.321(5)
Ru(1)−P(2)	2.338(5)	Ru(2)−P(2)	2.313(4)
Ru(3)−P(1)	2.289(5)	Ru(1)−O(7)	2.13(1)
Ru(2)−N(1)	2.15(1)	Ru(3)−N(1)	2.17(1)
Ru(1)−C(1)	1.91(2)	Ru(1)−C(2)	1.88(2)
Ru(2)−C(3)	1.84(2)	Ru(2)−C(4)	1.85(2)
Ru(3)−C(5)	1.85(2)	Ru(3)−C(6)	1.83(2)
Ru(2)−C(34)	2.29(2)	Ru(3)−C(34)	2.35(2)
C(1)−O(1)	1.15(2)	C(2)−O(2)	1.10(2)
C(3)−O(3)	1.15(2)	C(4)−O(4)	1.14(2)
C(5)−O(5)	1.12(2)	C(6)−O(6)	1.19(2)
C(7)−O(7)	1.29(2)	C(7)−N(1)	1.40(2)
C(7)−N(2)	1.33(2)	C(8)−N(2)	1.44(2)
C(9)−N(2)	1.44(2)		

Bond Angles (deg)			
Ru(1)−Ru(2)−Ru(3)	62.98(8)	Ru(1)−Ru(3)−Ru(2)	63.62(6)
Ru(2)−Ru(1)−Ru(3)	53.40(5)	Ru(1)−P(1)−Ru(3)	79.7(2)
Ru(1)−P(2)−Ru(2)	79.3(1)	Ru(2)−C(34)−Ru(3)	69.9(5)

by the ureato ligand, with the short edge spanned by the NH fragment of the ureato ligand and by the *ipso* carbon atom of the phenyl group, and with the two longest edges are also bridged by diphenylphosphido ligands. The bridging phenyl ligand is planar, essentially orthogonal to the metal triangle, and coplanar with the ureato ligand.

For comparison purposes, these results can be contrasted with those reported on the reactions of [Ru_3(μ-H)(μ_3-PhNCSNHPh)(CO)$_9$], [Ru_3(μ-H)(μ_3-mbim)(CO)$_9$] (Hmbim = 2-mercaptobenzimidazole), and [Ru_3(μ-H)-(μ_3-ampy)(CO)$_9$] with 2 equiv of triphenylphosphine, which give the symmetric disubstituted derivatives [Ru_3-(μ-H)(μ_3-L)(PPh_3)$_2$(CO)$_7$] (L = PhNCSNHPh,[16] mbim,[24] ampy[19]). The reaction of the thioureato complex takes place at room temperaure whereas those of the other two clusters require mild thermal activation (THF reflux). Interestingly, these three disubstituted compounds undergo P−C bond cleavage reactions under appropriate thermal activation (THF reflux for L = PhNCSNHPh and mbim, toluene reflux under H_2 for L = ampy) to give products containing bridging phenyl ligands, namely, [Ru_3(μ-η^1:η^2-Ph)(μ_3-S)(μ-PPh_2)(PPh_3)-(CO)$_6$][16] and [Ru_3(μ-η^1-Ph)(μ_3-L)(μ-PPh_2)$_2$(CO)$_6$] (L = mbim,[24] ampy[24,25]). The structures of the phenyl-bridged compounds with L = mbim and ampy are analogous to that of **3**; however, the mechanisms governing the formation of these clusters have to be different, since only **3** requires the presence of Al_2O_3. Other carbonyl clusters containing bridging η^1-phenyl groups are scarce,[26] being restricted to a few examples of ruthenium[27] and osmium.[28,29]

Scheme 3



Compounds Derived from Diphenylphosphine. Treatment of compound **1** with 1 equiv of diphenylphosphine in THF at room temperature led to instantaneous formation of the substituted derivative [Ru_3(μ-H)(μ_3-HNCONMe_2)(PPh_2H)(CO)$_8$] (**4**) (Scheme 3). Its analytical data and the comparison of its IR and NMR spectroscopic data with those of compound **2** indicated that both compounds are isostructural. The reactions of cluster **1** with 2 equiv or more of diphenylphosphine in THF solutions at room or reflux temperature led to mixtures of many compounds (spot TLC, ^{31}P NMR) which were not separated.

As it is known that carbonyl clusters containing diphenylphosphine ligands lead easily to diphenylphosphido derivatives under thermal conditions;[30−32] the thermolysis of compound **4** was studied. Heating a solution of compound **4** in THF at reflux temperature for 15 min resulted in the complete transformation of the cluster into a mixture of many compounds, from which the two major components, subsequently identified as [Ru_3(μ_3-HNCONMe_2)(μ-PPh_2)(μ-CO)$_2$(CO)$_6$] (**5**) and [Ru_3(μ-H)(μ_3-HNCONMe_2)(μ-PPh_2)$_2$(CO)$_6$] (**6**), were separated by chromatographic methods. The structures proposed for these compounds in Scheme 3 are based on their analytical and spectroscopic data. Both compounds show only one singlet in their respective ^{31}P-{^{1}H} NMR spectra, at chemical shifts which can be assigned to diphenylphosphido ligands spanning metal−metal bonds (401.3 ppm for **5**, 239.2 ppm for **6**).[23] The asymmetry of complex **5** was clearly evidenced by its ^{13}C{^{1}H} NMR spectrum, which shows eight carbonyl resonances, two of them (doublets) at chemical shifts characteristic of bridging CO ligands (238.0 and 230.7 ppm). For complex **6**, the fact that the ^{31}P{^{1}H} NMR spectrum is a singlet, that the hydride resonance of its ^{1}H NMR spectrum is a triplet, and that its ^{13}C{^{1}H} NMR spectrum only contains four CO resonances confirms that this compound is symmetric.

We have previously reported that the reactions of the cluster [Ru_3(μ-H)(μ_3-ampy)(CO)$_9$] with 1 or 2 equiv of diphenylphosphine give mono- or disubstituted derivatives as single products and that the respective ther-

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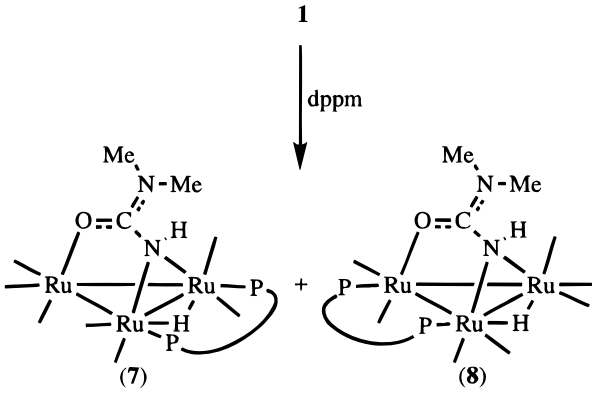
Scheme 4



molysis of these compounds lead to $[Ru_3(\mu_3\text{-ampy})(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_6]$ (analogous to complex **5**) and to a mixture of the symmetric and asymmetric isomers of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(\mu\text{-}PPh_2)_2(CO)_6]$ (the symmetric isomer is analogous to complex **6**).[30] A similar diphenylphosphine-based reactivity has also been reported for the cluster $[Ru_3(\mu\text{-PhCO})(\mu_3\text{-PhPpy})(CO)_9]$ (PhPpy = phenyl-2-pyridylphosphido).[32]

All these data suggest that the formation of many compounds in the reaction of complex **1** with 2 equiv of diphenylphosphine and in the thermolysis of compound **4** has to be a consequence of the presence of the *O*-bonded ureato ligand in the cluster.

Compounds Derived from Bis(diphenylphosphino)methane. Treatment of compound **1** with 1 equiv of bis(diphenylphosphino)methane (dppm) in dichloromethane at room temperature led to a 1:1 mixture of the symmetric (**7**) and asymmetric (**8**) isomers of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(\mu\text{-dppm})(CO)_7]$ (Scheme 4). Compound **7** is characterized by a singlet in its $^{31}P\{^1H\}$ NMR spectrum whereas that of compound **8** contains two doublets. The symmetry of complex **7** is also reflected by its ^1H NMR spectrum, which shows the hydride resonance equally coupled to both phosphorus atoms of the dppm ligand, whereas that of compound **8** is only coupled to one phosphorus atom. The fact that the hydride resonance of each compound also shows coupling to the proton of the NH fragment of the ureato ligand indicates that the NH-bridged Ru−Ru edges of both compounds are also spanned by the hydride ligands.

It is known that the reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ with dppm only gives the corresponding symmetric derivative.[33] This was explained on the basis of the harder character of the amido fragment of the ampy ligand as compared to that of the pyridine moiety.[18,19] The formation of the asymmetric isomer **8** in the reaction of compound **1** with dppm has to be related to the metal-bonded oxygen atom of the ureato ligand.

Concluding Remarks

Concerning the regioselectivity of the substitution reactions of compound **1**, the results described herein indicate that the first CO substitution takes place selectively on a ruthenium atom attached to the bridging amido moiety, whereas no selectivity between the two remaining ruthenium atoms is observed for the substitution of the second CO ligand. This contrasts with the results reported for the cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$, which undergo selective substitution of two CO ligands only on the metal atoms attached to the bridging amido moiety.[19,30,33] The mild conditions required by the reactions reported in this article indicate that compound **1** is more reactive than clusters containing N- and/or P-donor bridging ligands. This seems to be related to the hard−soft character of the bridging ligand: the harder the ligand, the more reactive is the cluster in carbonyl substitution reactions.

Finally, the results described herein have not only shed more light on the so far little-investigated area of the reactivity of carbonyl cluster compounds containing O-donor ligands but also include the preparation of a rare example of a cluster compound containing a bridging phenyl ligand which arises from an alumina-promoted P−C bond activation reaction.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (diethyl ether, tetrahydrofuran, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. Unless otherwise stated, the reactions were carried out under nitrogen at room temperature, using Schlenk vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC (silica gel). All reagents were obtained from Aldrich. 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 the matrix and cesium as the bombarding gas. Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(CO)_9]$ (1). A solution of *N*,*N*-dimethylurea (205 mg, 3.125 mmol) in methanol (2 mL) was added to a solution of $[Ru_3(CO)_{12}]$ (1 g, 1.565 mmol) in THF (40 mL). The resulting solution was stirred at reflux temperature for 4.5 h. During this time, the color changed from orange to greenish-yellow. The solvent was removed under reduced pressure, the solid residue was dissolved in dichloromethane (2 mL), and the solution was applied to a chromatography column (neutral alumina, activity I, 15 × 2 cm) packed in hexane. Dichloromethane eluted a yellow-orange band which gave compound **1** as an orange solid (755 mg, 75%). Anal. Calcd for $C_{12}H_8N_2O_{10}Ru_3$: C, 22.40; H, 1.25; N, 4.35. Found: C, 22.93; H, 1.13; N, 4.85. MS (*m*/*z*): 644 (M^+). IR ν(CO) (THF): 2081 (m), 2049 (vs), 2029 (vs), 1993 (s), 1966 (m), 1957 (w), 1602 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 3.64 (s br, 1 H, N*H*), 2.88 (s, 3 H, Me), 2.79 (s, 3 H, Me), −11.58 (s, 1 H, μ-H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 200.9 (s), 194.0 (br), 177.8 (s, HN*C*ONMe$_2$), 36.6 (s, Me of HNCONMe$_2$), 36.3 (s, Me of HNCONMe$_2$) ppm.

$[Ru_3(\mu\text{-}H)(\mu_3\text{-}HNCONMe_2)(PPh_3)(CO)_8]$ (2). A solution of compound **1** (200 mg, 0.311 mmol) and triphenylphosphine (82 mg, 0.313 mmol) in THF (15 mL) was stirred for 15 min. The solution was evaporated to dryness, and the residue was washed with pentane (2 × 5 mL) to give compound **2** as a yellow solid (190 mg, 70%). Anal. Calcd for $C_{29}H_{23}N_2O_9PRu_3$: C, 39.68; H, 2.64; N, 3.19. Found: C, 39.43; H, 2.58; N, 3.08. MS (*m*/*z*): 877 (M^+). IR ν(CO) (THF): 2060 (s), 2023 (vs), 1996 (s), 1978 (s), 1937 (sh), 1595 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): 7.64−7.41 (m, 15 H, PPh_3), 2.63 (s, 3 H, Me), 2.39 (s br, 1 H, N*H*), 2.09 (s, 3 H, Me), −11.15 (d, J = 10.5 Hz, 1 H, μ-H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 206.7 (d, J = 6.4 Hz, 1 *C*O),

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Table 3. Crystallographic and Refinement Data for 2 and 3·CH_2Cl_2

	2	**3**·CH_2Cl_2
formula	$C_{29}H_{23}N_2O_9PRu_3$	$C_{39}H_{32}N_2O_7P_2Ru_3{\cdot}CH_2Cl_2$
fw	877.67	1090.74
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	$P2_12_12_1$
a, Å	10.112(3)	10.285(5)
b, Å	20.221(5)	17.92(1)
c, Å	15.66(2)	22.79(2)
β, deg	91.15(3)	90
volume, Å^3	3201(4)	4200(5)
Z	4	4
F(000)	1720	2160
D_{calcd}, g/cm^3	1.821	1.725
μ, mm^{-1}	1.501	1.318
cryst size, mm	0.30 × 0.33 × 0.40	0.20 × 0.17 × 0.30
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
monochromator	graphite	graphite
temp, K	293(2)	293(2)
scan method	$\omega-2\theta$	$\omega-2\theta$
θ limits, deg	1.64−24.97	1.45−22.97
(*h*,*k*,*l*) ranges	(−11,0,0) to (12,24,18)	(0,0,0) to (11,19,24)
no. of reflns collected	7122	3526
no. of independent reflns	5602	3287
no. of reflns with $I > 2\sigma(I)$	3595	2300
restraints, parameters	0, 489	0, 506
$R(F)_{I>2\sigma(I)}$[a]	0.0302	0.0452
$R_w(F^2)_{\text{all data}}$[b]	0.1244	0.1429
GOF[c]	0.817	0.972
Δ/σ	0.03	0.03
max, min $\Delta\rho$, e/Å^3	0.407, −0.439	0.796, −0.752

[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) $= [\sum w (F_o^2 - F_c^2)^2/(N - P)]^{1/2}$.

203.9 (s br, 2 *C*O), 200.5 (s, 2 *C*O), 200.3 (s, 2 *C*O), 196.1 (d, *J* = 20.2 Hz, 1 *C*O), 178.2 (s, HN*C*ONMe$_2$), 135.1−128.7 (m, PPh$_3$), 37.8 (s, 2 Me of HNCON*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 30.7 (s) ppm.

[Ru$_3$(μ-η^1-Ph)(μ_3-HNCONMe$_2$)(μ-PPh$_2$)$_2$(CO)$_6$] (3). A solution of compound **1** (50 mg, 0.078 mmol) and triphenylphosphine (41 mg, 0.156 mmol) in THF (20 mL) was stirred at reflux temperature for 1 h. The solution was evaporated to dryness, and the residue was dissolved in dichloromethane (2 mL). This solution was passed through a column of neutral alumina (2 × 10 cm, activity IV), eluting with dichloromethane. The resulting solution was concentrated to *ca.* 2 mL and was applied to preparative TLC plates (silica gel). Elution with hexane−dichloromethane (1:1) afforded two major bands. The slower-moving band (yellow) contained a small amount (*ca.* 3 mg) of compound **2** (IR identification). The faster-moving band (red) afforded compound **3** as a dark-red solid (30 mg, 44%). Anal. Calcd for $C_{39}H_{32}N_2O_7P_2Ru_3$: C, 46.57; H, 3.21; N, 2.79. Found: C, 46.73; H, 3.35; N, 2.70. MS (*m*/*z*): 1005 (M^+). IR ν(CO) (THF): 2026 (m), 1998 (vs), 1957 (m), 1939 (m), 1646 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 8.39−6.97 (m, 25 H, 5 Ph), 3.18 (s br, 1 H, N*H*), 2.77 (s, 3 H, Me), 1.06 (s, 3 H, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 198.8 (s) ppm.

[Ru$_3$(μ-H)(μ_3-HNCONMe$_2$)(PPh$_2$H)(CO)$_8$] (4). Diphenylphosphine (13.5 μL, 0.078 mmol) was added to a solution of compound **1** (50 mg, 0.078 mol) in THF (10 mL). After the solution was stirred for 15 min, the solvent was removed under reduced pressure and the solid residue was washed with pentane (5 mL) to give compound **4** as an orange solid (45 mg, 72%). Anal. Calcd for $C_{23}H_{19}N_2O_9PRu_3$: C, 34.46; H, 2.39; N, 3.50. Found: C, 34.67; H, 2.51; N, 3.22. MS (*m*/*z*): 801 (M^+). IR ν(CO) (THF): 2061 (m), 2025 (vs), 1997 (s), 1979 (s), 1937 (sh), 1596 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): 7.62−7.43 (m, 10.5 H, 2 Ph, $^1/_2$ P*H*), 5.92 ($^1/_2$ d, $^1/_2$ H, $^1/_2$ P*H*), 2.62 (s, 3 H, Me), 2.36 (s br, 1 H, N*H*), 1.95 (s, 3 H, Me), −11.10 (d, *J* = 9.5 Hz, 1 H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −0.4 (s) ppm.

[Ru$_3$(μ_3-HNCONMe$_2$)(μ-PPh$_2$)(μ-CO)$_2$(CO)$_6$] (5) and [Ru$_3$(μ-H)(μ_3-HNCONMe$_2$)(μ-PPh$_2$)$_2$(CO)$_6$] (6). A solution of compound **4** (50 mg, 0.062 mmol) in THF (15 mL) was stirred at reflux temperature for 15 min (when the IR spectrum of the solution showed the complete disappearance of compound **4**). The color changed from orange to red. The solution was concentrated to *ca.* 1 mL and was applied to preparative TLC plates (silica gel). Hexane−dichloromethane (1:1) eluted seven bands, but only the two major ones were worked up. The seventh and slowest-moving band (red) gave compound **5** as a deep-red solid (20 mg, 40%). The fifth band (yellow) gave compound **6** as a yellow solid (10 mg, 17%). *Analytical and spectroscopic data for compound* ***5***. Anal. Calcd for $C_{23}H_{17}N_2O_9PRu_3$: C, 34.55; H, 2.14; N, 3.50. MS (*m*/*z*): 799 (M^+). Found: C, 34.70; H, 2.26; N, 3.37. IR ν(CO) (THF): 2048 (m), 2011 (vs), 1976 (m), 1958 (w), 1878 (w), 1824 (m), 1646 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): 7.76−7.34 (m, 10 H, PPh$_2$), 2.54 (s, 3 H, Me), 2.21 (s br, 1 H, N*H*), 1.79 (s, 3 H, Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 238.0 (d, *J* = 55.6 Hz, 1 *C*O), 230.7 (d, *J* = 53.4 Hz, 1 *C*O), 200.9 (s, 1 *C*O), 197.7 (d, *J* = 9.4 Hz, 1 *C*O), 197.6 (s, 1 *C*O), 195.0 (s, 1 *C*O), 194.6 (d, *J* = 7.8 Hz, 1 *C*O), 194.5 (s, 1 *C*O), 170.5 (s, HN*C*ONMe$_2$), 142.0 (d, *J* = 19.0 Hz, 1 C of PPh$_2$), 140.5 (d, *J* = 28.5 Hz, 1 C of PPh$_2$), 130.8−127.5 (m, 10 C of PPh$_2$), 36.9 (s, Me of HNCON*Me*$_2$), 36.1 (s, Me of HNCON*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 401.3 (s) ppm. *Analytical and spectroscopic data for compound* ***6***. Anal. Calcd for $C_{33}H_{28}N_2O_7P_2Ru_3$: C, 42.63; H, 3.04; N, 3.01. MS (*m*/*z*): 929 (M^+). Found: C, 42.85; H, 3.39; N, 2.89. IR ν(CO) (THF): 2028 (m), 1996 (vs), 1956 (m), 1939 (m), 1646 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 8.19−7.19 (m, 20 H, 2 PPh$_2$), 3.30 (s br, 1 H, N*H*), 2.59 (s, 3 H, Me), 1.09 (s, 3 H, Me), −7.80 (t, *J* = 29.3 Hz, 1 H, μ-H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 205.0 (t, *J* = 4.0 Hz, 1 *C*O), 204.5 (t, *J* = 7.1 Hz, 1 *C*O), 198.7 (t, *J* = 4.2 Hz, 2 *C*O), 198.3 (d, *J* = 2.3 Hz, 2 *C*O), 172.1 (s, HN*C*ONMe$_2$), 143−127 (m, 2 PPh$_2$), 38.0 (s, Me of HNCON*Me*$_2$), 36.5 (s, Me of HNCON*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 239.2 (s) ppm.

[Ru$_3$(μ-H)(μ_3-HNCONMe$_2$)(μ-dppm)(CO)$_7$] (Isomers 7 and 8). Bis(diphenylphosphino)methane (30 mg, 0.078 mmol) was added to a solution of compound **1** (50 mg, 0.078 mmol) in dichloromethane (20 mL). The solution was stirred for 15 min and then evaporated to dryness. The residue was dissolved in diethyl ether (5 mL). Addition of pentane (20 mL) led to the precipitation of an orange solid (60 mg, 80%), which

was a *ca.* 1:1 mixture of isomers **7** and **8**. This mixture could not be separated by chromatographic methods. Anal. Calcd for $C_{35}H_{20}N_2O_8P_2Ru_3$: C, 34.71; H, 2.10; N, 2.91. Found: C, 34.82; H, 2.27; N, 2.71. *Selected spectroscopic data for compound* **7**. ^{1}H NMR ($CDCl_3$): −11.15 (td, J = 13.2 and 4.5 Hz, 1 H, μ-H) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): 4.13 (s) ppm. *Selected spectroscopic data for compound* **8**. ^{1}H NMR ($CDCl_3$): −7.80 (dd, J = 35.0 and 3.9 Hz, 1 H, μ-H) ppm. ^{31}P-{^{1}H} NMR ($CDCl_3$): 19.8 (d, J = 42.4 Hz, 1 P), 7.40 (d, J = 42.4 Hz, 1 P) ppm.

Crystal Structures of 2 and 3·CH_2Cl_2. Orange (**2**) and red (**3**·CH_2Cl_2) crystals, obtained by layering pentane on a solution of the corresponding complex in dichloromethane at −20 °C, were used for the X-ray diffraction studies. A selection of crystal and refinement data for both compounds is given in Table 3.

The cell dimensions were determined by least-squares refinement of 25 high-order reflections with $0 \le \theta \le 25°$ (**2**) and $0 \le \theta \le 23°$ (**3**·CH_2Cl_2). The space groups $P2_1$ (**2**) and $P2_12_12_1$ (**3**·CH_2Cl_2) were 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 per reflection. Three standard reflections were monitored every 60 min, revealing no intensity fluctuations. Final drift correction factors were between 0.99 and 1.03 (**2**) and 0.98 and 1.13 (**3**·CH_2Cl_2). Profile analysis was performed on all reflections.[34] Lorentz and polarization corrections were applied.

The structures were solved by the Patterson method using DIRDIF.[35] Isotropic and full-matrix anisotropic least-squares refinements on F^2 were performed using SHELX93.[36] Additional empirical absorption corrections were applied at this stage, using the program XABS2.[37] The anisotropic refinement led to abnornally high anisotropy for C(40) of **3**·CH_2Cl_2, indicating disorder of the dichloromethane molecule. A Fourier synthesis map showed two alternative positions, to be denoted as C(40A) and C(40B). Subsequent least-squares refinement led to occupation factors of 0.63 for C(40A) and 0.37 for C(40B). All hydrogen atoms of **2** were located on a difference Fourier map and were refined isotropically. The hydrogen atoms of **3**·CH_2Cl_2 were geometrically placed and isotropically refined. Function minimized $[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, with $\sigma(F_o^2)$ from counting statistics and $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. Atomic scattering factors were taken from the literature.[38] Geometrical calculations were made with PARST.[39] The structure plots were drawn with the EUCLID package.[40] All calculations were carried out on DIGITAL workstations 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 **2** and **3**·CH_2Cl_2 (15 pages). Ordering information is given on any current masthead page.

OM9702946

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