Cluster-Mediated Conversion of Diphenylacetylene into α-Phenylcinnamaldehyde. Construction of a Catalytic Hydroformylation Cycle Based on Isolated Intermediates

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Received August 6, 1998

The present paper deals with a rational attempt to achieve the hydroformylation of diphenylacetylene onto a hydrido triruthenium cluster complex incorporating the 2-(methylamino)pyridyl group (abbreviation: MeNpy) as a hemilabile ancillary ligand [note: in all species discussed below, the bridgehead μ_2-N atom is linked to the centers labeled as Ru(1) and Ru(2), whereas the pyridyl nitrogen is bound to Ru(3)]. The complex $Ru_3(\mu\text{-H})(\mu\text{-MeNpy})(CO)_9$ (**1**) is shown to react cleanly with diphenylacetylene to give the alkenyl complex $Ru_3(\mu\text{-MeNpy})(\mu\text{-PhC=CHPh})(CO)_8$ (**2**), the structure of which is reported. The reaction of **2** with 1 equiv of PPh_3 proceeds to completion within less than 3 min at 25 °C, giving two propenoyl complexes, namely, $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(PPh_3)(CO)_7$ (**3**) (48% yield) and $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(PPh_3)_2(CO)_6$ (**4**) (19% yield), both fully characterized by spectroscopic methods and X-ray analysis. Complex **3** is an adduct of **2** with PPh_3. The incorporation of the phosphine has caused a migratory CO insertion of the alkenyl group. The phosphine occupies an equatorial coordination site on Ru(1), in cis position relative to the nitrogen atom of the amido bridge. The newly formed propenoyl group occupies an equatorial bridging position across the Ru(1)−Ru(3) edge, with the acyl oxygen bound to Ru(1), in cis position relative to both the bridgehead nitrogen atom and the phosphine. The molecular structure of the second propenoyl compound, $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(PPh_3)_2(CO)_6$ (**4**), is formally derived from the previous one, **3**, by a simple substitution of an equatorial CO of Ru(2) by PPh_3. The use of a 2-fold amount of phosphine for the above reaction modifies only slightly the relative abundance of **3** (30%) and **4** (44%). This indicates that **3** is not the kinetic product of the reaction between **2** and a phosphine. Further reaction of **4b** with CO induces loss of one PPh_3 and incorporation of two CO ligands. This produces the open 50e cluster $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(PPh_3)(CO)_8$ (**5**), in which the bridging propenoyl group now spans the open edge Ru(1)−Ru(2) (the remaining phosphine occupies an equatorial site cis to the acyl oxygen). Treatment of **2b** with CO (1 atm, 25 °C, 20 min) also promotes migratory CO insertion, giving the 50e propenoyl complex $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(CO)_9$ (**6b**), whose structure has been determined. The propenoyl group spans the open edge Ru(1)−Ru(2). Although stable in CO-saturated solutions under CO atmosphere, the complex reverts rapidly to **2** within 30 s under inert atmosphere. Treatment of **6** with CO/H_2 gas mixtures under ambient conditions produces α-phenylcinnamaldehyde with concomitant recovery of **1**, showing that the hydroformylation of diphenylacetylene can be achieved in a stepwise manner through the cyclic reaction sequence **1** → **2** → **6** → **1**. Under nonoptimized catalytic conditions, the amount of α-phenylcinnamaldehyde obtained corresponds to about eight cycles. The metal-containing species recovered in the reactor through the catalytic runs is isolated and formulated as the bimetallic carboxamido complex $[Ru\{-C(O)-MeNpy\}(CO)_3]_2$ (**7**). Thus, it appears that deactivation of the system has taken place via CO insertion into the metal−amide bond.

Introduction

The ability of certain transition-metal clusters to reversibly coordinate CO[1,2] constitutes a desirable property in view of bringing this reagent into reaction with organic compounds. Although CO can cause cluster degradation, there is still the possibility to observe truly *cluster-mediated* carbonylations, provided we work under the mildest possible conditions with cluster prototypes exhibiting enhanced kinetic lability.[3] The present paper deals with a rational attempt to achieve the hydroformylation of diphenylacetylene onto a hydrido triruthenium cluster complex modified by a hemilabile ancillary ligand.

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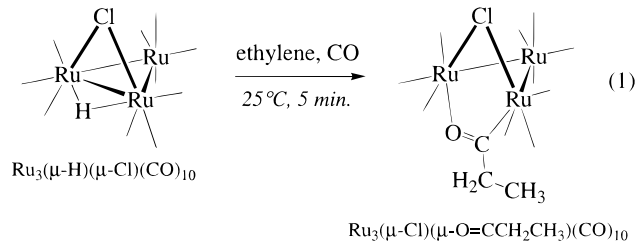
(2) For leading references in the case of ruthenium, see: (a) Lugan, N.; Bonnet, J.-J.; Ibers, J. A. *Organometallics* **1988**, *7*, 1538. (b) Lugan, N.; Lavigne, G.; Bonnet, J.-J.; Réau, R.; Neibecker, D.; Tkatchenko, I. *J. Am. Chem. Soc.* **1988**, *110*, 5369.

10.1021/om9806747 CCC: $18.00
Publication on Web 12/24/1998

The catalytic hydroformylation of olefins in the presence of $K[Ru_3(\mu\text{-}H)(CO)_{11}]$ reported some years ago by Süss-Fink and co-workers[4] remains an interesting example where the results of a reliable mechanistic study including labeling experiments were at least *consistent* with the hypothesis of a cluster-catalyzed reaction.[5] However, as it is often the case for numerous active systems in homogeneous catalysis, no direct evidence for the proposed intermediates could be obtained from the actual working catalyst's solution.

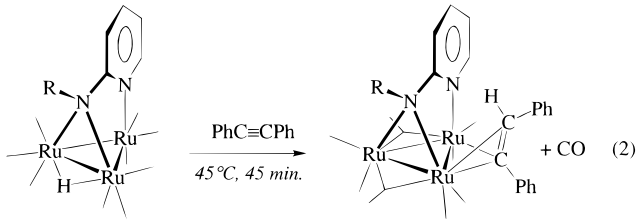
Valuable mechanistic information on the initial elementary steps involved in a typical "cluster-mediated" olefin hydroformylation is found in Kaesz's pioneering work on the reactivity of the complex $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$.[6] Indeed, as shown in eq 1, the latter incorporates both ethylene and CO within minutes at 25 °C to produce the 50e propionyl derivative $Ru_3\{\mu\text{-}O{=}C(CH_2CH_3)\}(\mu\text{-}Cl)(CO)_{10}$ as a result of ethylene insertion into a Ru−H bond, followed by migratory CO insertion.



$Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ $Ru_3(\mu\text{-}Cl)(\mu\text{-}O{=}CCH_2CH_3)(CO)_{10}$ (1)

A transient opening of the chloride bridge favoring the coordination of ethylene was originally proposed to account for the mild conditions of this reaction.[3a] Adducts bearing terminal halide ligands were effectively isolated later upon reaction of anionic triruthenium carbonyl halide complexes with various ligands.[3c,7,8]

On the basis of the model of the reactive prototype $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$ previously developed by Kaesz, we were led to devise the more robust derivatives $Ru_3(\mu\text{-}H)(\mu_3\text{-}RNpy)(CO)_9$ (**1a,b**) (**a**, R = Ph; **b**, R = Me),[9] in which the bridging amido group of the ancillary amidopyridyl ligand was also exhibiting a hemilabile behavior.[9,10] The hydrido species **1** was originally found to react cleanly with alkynes to afford the alkenyl species $Ru_3(\mu_3\text{-}PhNpy)(\mu\text{-}R'C{=}CHR'')(CO)_8$ (**2**) (see an example in eq 2).[9]



(**1**) (**2**), >90% yield (2)

Both **1** and **2**,[9a] as well as relevant complexes bearing modified amidopyridyl ligands,[11] were shown to act as catalyst precursors in the hydrogenation of diphenylacetylene. More recently, several alkyne oligomerization and co-oligomerization reactions were found to take place in the presence of **1a**.[12] Whereas this seemed to indicate a remarkable ability of this complex to accommodate *several* molecules of the reactants in its coordination shell, the systematic detection of the alkenyl complex $Ru_3(\mu_3\text{-}PhNpy)(\mu\text{-}R'C{=}CHR'')(CO)_8$ (**2a**) under catalytic conditions revealed only how the *first* of these alkyne molecules was interacting with the cluster. To identify the more accessible coordination site for further reaction with a second hypothetical incoming substrate molecule, we treated the alkenyl complex $Ru_3(\mu_3\text{-}MeNpy)(\mu\text{-}PhC{=}CHPh)(CO)_8$ (**2b**) with triphenylphosphine, regarded as a model two-electron donor ligand. To our surprise, this not only confirmed the existence of a privileged reaction site in this complex but also revealed a remarkable aptitude of its alkenyl group to undergo migratory CO insertion. With a view to possible implications in the hydroformylation of alkynes,[13] the parallel reaction of **2b** with CO was also examined. This led to the isolation of a novel trinuclear propenoyl derivative, later shown to participate in a cyclic cluster-mediated transformation of diphenylacetylene into α-phenylcinnamaldehyde.

Results

Phosphine-Induced Migratory CO Insertion onto the Alkenyl Complex 2. Whereas nucleophilic attack of triphenylphosphine onto the amidopyridyl complex $Ru_3(\mu\text{-}H)(\mu\text{-}RNpy)(CO)_9$ (**1**) leads to regioselective CO substitution at one of the two equivalent metal centers bearing the bridging nitrogen of the amido group, the corresponding sites in $Ru_3(\mu\text{-}MeNpy)(\mu\text{-}PhC{=}CHPh)(CO)_8$ (**2b**) are differentiated by the ligand environment: whereas the alkenyl group is π bound to the

(3) For specific reviews dealing with cluster activation, see: (a) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter 4, p 43. (b) Lavigne, G. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990; Chapter 5, p 201, and references therein; (c) Lavigne, G.; de Bonneval, B. In *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds: John Wiley & Sons: New York, 1998, Chapter 2, p 39.

(4) (a) Süss-Fink, G.; Herrmann, G. *J. Chem. Soc., Chem. Commun.* **1985**, 735. (b) Langenbahn, K.; Bernauer, K.; Süss-Fink, G. *J. Organomet. Chem.* **1989**, *379*, 165.

(5) For general recent reviews dealing with cluster-catalyzed reactions, see: (a) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990; Chapter 7, p 329, and references therein. (b) Süss-Fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. (c) Süss-Fink, G.; Jahncke, M.*Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; John Wiley & Sons: New York, 1998; Chapter 6, p 167.

(6) (a) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896. (b) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 4646.

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(9) (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E. W.; Bonnet, J.-J. *J. Am. Chem. Soc.* **1990**, *112*, 8607. (b) Lugan, N.; Laurent, F.; Lavigne, G.; Bonnet, J.-J. *Organometallics* **1992**, *11*, 1351.

(10) Shen, J.-K.; Basolo, F.; Nombel, P.; Lugan, N.; Lavigne, G. *Inorg. Chem.* **1996**, *35*, 755.

(11) Cabeza, J. A.; Fernandez-Colinas, J. M.; Llamazares, A.; Riera, V. *Synlett.* **1995**, 579.

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(13) Johnson, J. R.; Cuny, G. D.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *16*, 1760.

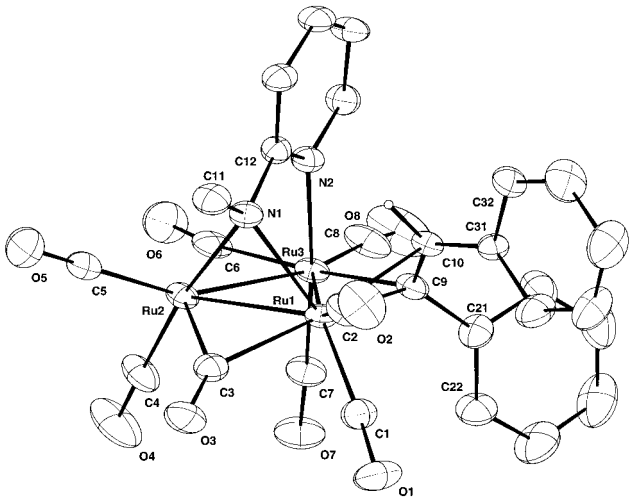
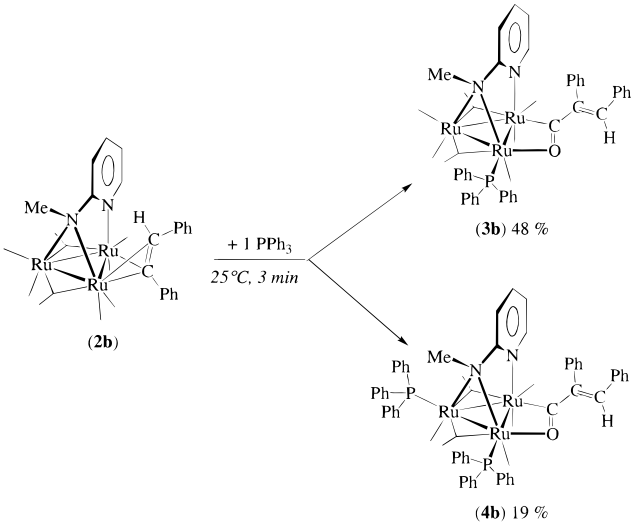


Figure 1. Perspective view of the alkenyl complex **2b**. Selected interatomic distances (Å) and bond angles (deg): Ru(1)−Ru(2) = 2.7229(6); Ru(1)−Ru(3) = 2.8107(6); Ru(2)−Ru(3) = 2.7701(6); Ru(1)−N(1) = 2.237(4); Ru(2)−N(1) = 2.175(4); Ru(3)−N(2) = 2.159(4); Ru(1)−C(9) = 2.289(5); Ru(1)−C(10) = 2.309(5); Ru(3)−C(9) = 2.112; C(9)−C(10) 1.392(7); Ru(3)−C(9)−C(10) = 121.4(4).

Scheme 1



center referred to as Ru(1), Ru(2) is surrounded only by carbonyl groups (see the perspective view displayed in Figure 1).[14]

The addition of 1 equiv of triphenylphosphine to **2b** was found to proceed rapidly to completion within less than 3 min at 25 °C (Scheme 1), giving two new complexes that were both fully characterized by spectroscopic methods as well as by X-ray diffraction analyses.

The first complex, $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(PPh_3)(CO)_7$ (**3b**), recovered in 48% yield, is an adduct resulting from the incorporation of PPh_3 *without* loss of CO. Its molecular structure is shown in Figure 2. The phosphine occupies an equatorial coordination site onto Ru(1), in cis position relative to the bridgehead nitrogen atom. Nucleophilic attack by the phosphine has triggered a migratory CO insertion. The newly formed

(14) The determination of the structure of **2b** was found necessary to ascertain the nature of the isomer we had in hand, which proved to be the same as for **2a**.[9b]

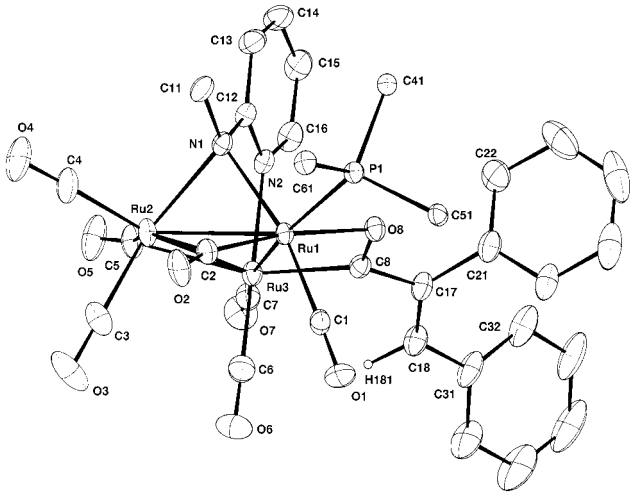


Figure 2. Perspective view of the propenoyl complex **3b**. The phenyl groups of the triphenylphosphine ligand are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Ru(1)−Ru(2) = 2.7169(6); Ru(1)−Ru(3) = 2.7792(6); Ru(2)−Ru(3) = 2.7354(6); Ru(1)−N(1) = 2.210(4); Ru(2)−N(1) = 2.186(5); Ru(3)−N(2) = 2.150(5); Ru(1)−O(8) = 2.180(4); Ru(3)−C(8) = 2.046(6); C(8)−O(8) = 1.254(6); C(8)−C(17) = 1.494(8); C(17)−C(18) = 1.339(9); Ru(1)−P(1) = 2.420(1); Ru(3)−C(8)−O(8) = 110.4(4); Ru(3)−C(8)−C(17) = 133.4(4); O(8)−C(8)−C(17) = 115.4(5).

propenoyl group occupies an equatorial bridging position accross the Ru(1)−Ru(3) edge, which is also supported by the N−C=N bridge of the ancillary ligand. The acyl type carbon is σ bound to Ru(3), whereas the acyl oxygen is bound to the ruthenium center Ru(1), in cis position relative to both the bridgehead nitrogen atom and the phosphine. Such a geometrical situation might be consistent with the occurrence of a *remote CO insertion* (vide infra), provided the derivative detected here is the *kinetic* isomer.

The structure of the second propenoyl compound, $Ru_3(\mu\text{-MeNpy})(\mu\text{-O=C−PhC=CHPh})(PPh_3)_2(CO)_6$ (**4b**), is shown in Figure 3. This complex is formally derived from the previous one, **3b**, by a simple phosphine-induced CO displacement taking place at the metal center Ru(2). The new phosphine occupies an equatorial coordination site in cis position relative to the bridgehead nitrogen atom, whereas the global arrangement of all other ligands remains unchanged.

At first sight, the formation of the latter bisphosphine derivative **4b** in reasonable yield (19%) from a stoichiometric reaction based upon a 1:1 ratio might be indicative of a low kinetic barrier for CO dissociation from the adduct **3b**, enabling it to compete favorably with its precursor **2b** for the capture of the phosphine. Quite surprisingly, however, the use of a 2-fold amount of phosphine under otherwise identical conditions (see Experimental Section) affected only moderately the relative abundance of **3b** and **4b** [a modification of the phosphine/triruthenium ratio from 1 to 2 caused the yields to vary from 48% to 30% for **3b** and from 19% to 44% for **4b**], thus ruling out the preceding working hypothesis. In an additional experiment, it was effectively found that the reaction of **3b** with PPh_3 does not work under ambient conditions, although the substituted derivative **4b** is obtained within 30 min at 50−60 °C.

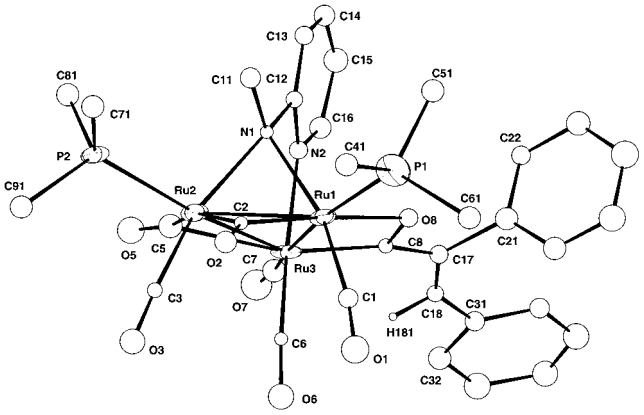


Figure 3. Perspective view of the propenoyl complex **4b**. The phenyl groups of the two triphenylphosphine ligands are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Ru(1)−Ru(2) = 2.638(4); Ru(1)−Ru(3) = 2.758(4); Ru(2)−Ru(3) = 2.721(4); Ru(1)−N(1) = 2.18(2); Ru(2)−N(1) = 2.17(2); Ru(3)−N(2) = 2.11(3); Ru(1)−O(8) = 2.23(2); Ru(3)−C(8) = 1.97(3); C(8)−O(8) = 1.35(4); C(8)−C(17) = 1.41(4); C(17)−C(18) = 1.21(4); Ru(1)−P(1) = 2.40(1); Ru(2)−P(2) = 2.36(1); Ru(3)−C(8)−O(8) = 111(2); Ru(3)−C(8)−C(17) = 138(3); O(8)−C(8)−C(17) = 110(3).

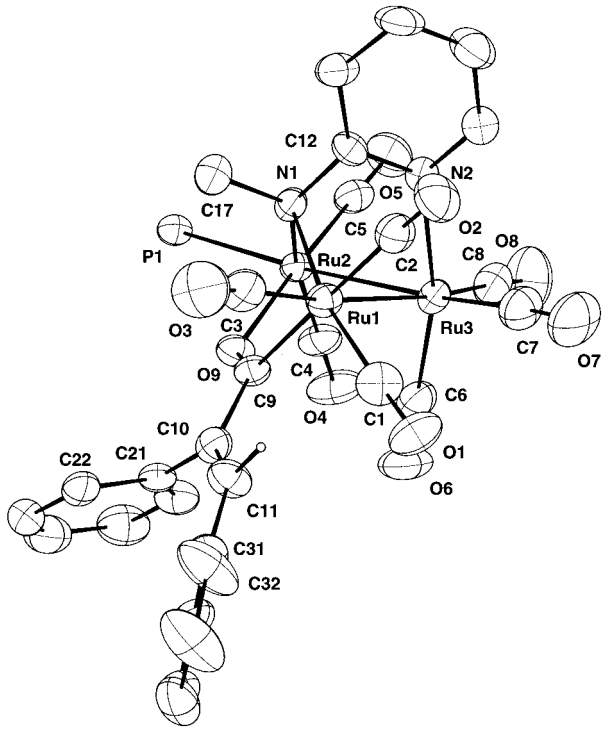


Figure 4. Perspective view of the propenoyl complex **5b**. The phenyl groups of the triphenylphosphine ligand are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Ru(1)−Ru(3) = 2.7742(9); Ru(2)−Ru(3) = 2.7623(8); Ru(1)−N(1) = 2.269(6); Ru(2)−N(1) = 2.202-(6); Ru(3)−N(2) = 2.172(6); Ru(2)−P(1) = 2.457(2); Ru(1)−C(9) = 2.073(7)); Ru(2)−O(9)= 2.093(5); C(9)−O(9) = 1.243(8); C(9)−C(10) 1.515(9); C(10)−C(11) = 1.35(1); Ru-(1)−Ru(3)−Ru(2) = 76.11(2); Ru(1)−C(9)-O(9) = 118.2(5); O(9)−C(9)−C(10) = 112.0(6); C(9)−C(10)−C(11) = 120.6-(7).

Such a behavior indicates that **3b** is *not* the kinetic product of the reaction between **2b** and a phosphine. There must be a transient metastable phosphine adduct **A** that may statistically decay via one of two competing pathways, namely, either (i) an intramolecular rearrangement leading to the adduct **3b** or (ii) the capture of a second phosphine ligand followed by intramolecular rearrangement and loss of CO to produce **4b**.

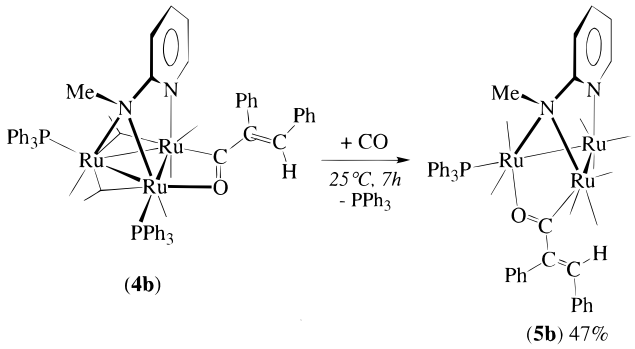
A kinetic study was undertaken[15] in order to gain further insight into the mechanism. The results indicate that the rate for disappearance of the reactant is first-order in complex and first-order in PPh_3 concentration. The second-order kinetics, as well as the activation parameters (low $\Delta H^{\ddagger}$, negative $\Delta S^{\ddagger}$), indicate that the initial reaction step is an associative nucleophilic addition of the ligand to the metal cluster complex.

Observation of a CO-Induced Migration of the Propenoyl Ligand at the Periphery of the Cluster. Direct attempts to intercept the above-mentioned adduct **A** at low temperature remained unsuccessful. So, while observing that the formation of **4b** involved loss of one carbonyl ligand, we reasoned that treatment of the latter with CO gas might constitute a retrosynthetic route to the intermediate **A**. Complex **4b** was effectively found to react with CO under ambient temperature conditions to produce the new derivative $Ru_3(\mu$-MeNpy)-(μ-O=C−PhC=CHPh)(PPh_3)$(CO)_8$ (**5b**) (Scheme 2, Figure 4). However, the latter is not the intermediate **A** we are looking for since it results from the incorporation of *two* carbonyls.

When a stream of nitrogen gas was bubbled through a solution of the newly formed compound **5b** under ambient conditions, a mixture of **2**, **3**, and **4** was obtained.

From the above experiments, we learn that the phosphine ligands are labile in these complexes and that the cluster **4b** is prone to accommodate an incoming substrate like CO via metal−metal bond opening (the open edge in **5b** is the one supporting the amido bridge (Ru(1)···Ru(2) = 3.413(1) Å)).

Scheme 2



The interconvertibility of the compounds **4b** and **5b** reveals an interesting aptitude of the bridging propenoyl group to migrate reversibly between the edge supported by the N−C=N bridge and the one supported by the μ-N atom.

Facile and Reversible Migratory CO Insertion under Carbon Monoxide. Following the observation that the addition of triphenylphosphine to **2b** causes migratory CO insertion, it was of interest to determine whether the addition of CO would have the same effect. Thus, a stream of CO gas was bubbled through a solution of **2b** at 20 °C. Infrared monitoring indicated

(15) Shen, J.-K.; Basolo, F.; Lugan, N.; Lavigne, G. Unpublished observations.

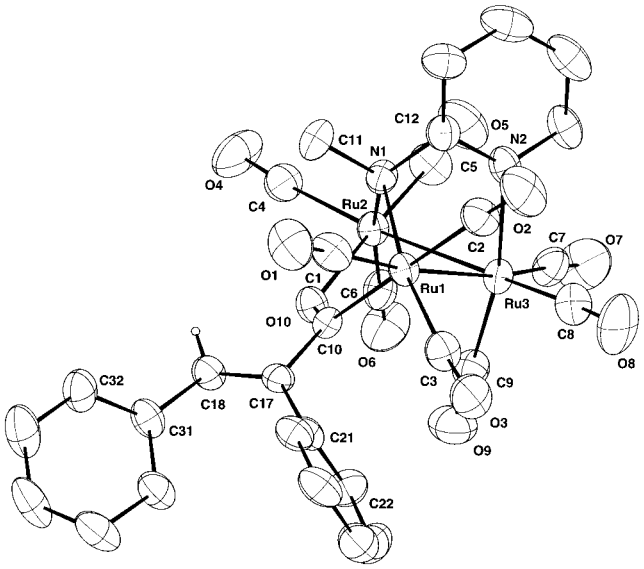
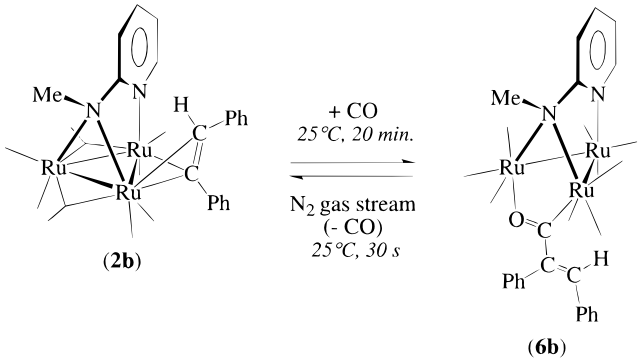


Figure 5. Perspective view of the propenoyl complex **6b**. Selected interatomic distances (Å) and bond angles (deg): Ru(1)−Ru(3) = 2.7948(7); Ru(2)−Ru(3) = 2.7559(7); Ru(1)−N(1) = 2.233(5); Ru(2)−N(1) = 2.194(5); Ru(3)−N(2) = 2.159(6); Ru(1)−C(10) = 2.075(6)); Ru(2)−O(10) = 2.103(4); C(10)−O(10) = 1.251(8); C(10)−C(17) 1.510(8); C(17)−C(18) = 1.332(9); Ru(1)−C(10)−O(10) = 121.3(4); O(10)−C(10)−C(17) = 113.3(5); C(10)−C(17)−C(18) = 118.0(5).

Scheme 3



the quantitative formation of the new adduct $Ru_3(\mu$-MeNpy)(μ-O=C−PhC=CHPh)$(CO)_9$ (**6b**) *without observable intermediate* (see Scheme 3).

Although stable in CO-saturated solutions under CO atmosphere, the complex was found to revert rapidly to the alkenyl complex **2b** under inert atmosphere. Nevertheless, we succeeded in growing suitable crystals of **6b** from CO-saturated solutions at low temperature. The structure of the compound is shown in Figure 5. Clearly, *two* carbonyl groups have been incorporated, causing (i) an opening of the trinuclear structure, (ii) a migratory CO insertion of the alkenyl group, and (iii) a migration of the resulting propenoyl ligand from the site where it was originally formed (namely, Ru(3)), toward the open edge Ru(1)···Ru(2) of the cluster.

Treatment of the Propenoyl Complex 6b with CO/H_2 Mixtures; Formation of α-Phenylcinnamaldehyde. Following the isolation of the propenoyl adduct $Ru_3(\mu$-MeNpy)(μ-O=C−PhC=CHPh)$(CO)_9$ (**6b**), it was of interest to investigate its reaction with hydrogen. Experiments carried out directly in an NMR tube on CO-presaturated solutions of this complex

Scheme 4

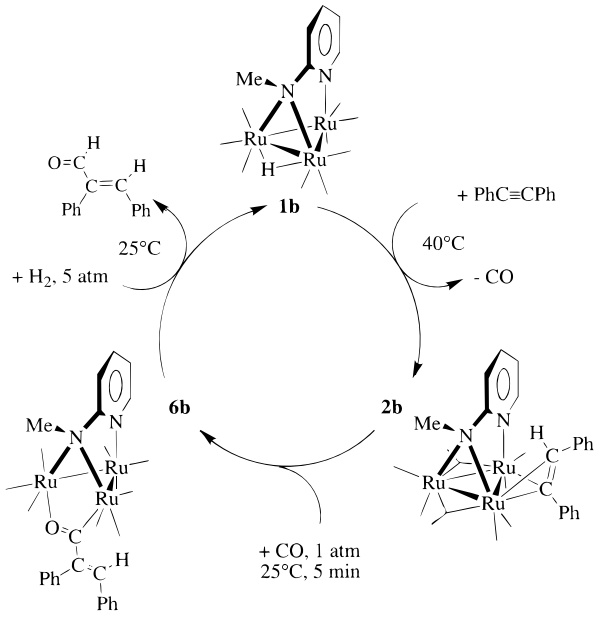
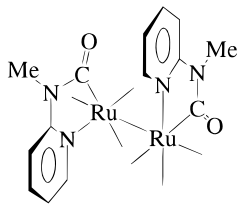


Chart 1



indicated that hydrogenolysis of the propenoyl ligand takes place under ambient temperature conditions under 3 atm of hydrogen to yield α-phenylcinnamaldehyde with concomitant recovery of the starting complex **1b**. Thus, the hydroformylation of diphenylacetylene is achieved in a stepwise manner through the cyclic reaction sequence **1b** → **2b** → **6b** → **1b** (Scheme 4).

Catalytic Runs and Analysis of the Metal-Containing Species Recovered in the Reactor. In preliminary catalytic runs, it was found that the production of α-phenylcinnamaldehyde is effective, even though the turnover numbers did not exceed 8−10 under nonoptimized standard experimental conditions. The principal metal-containing species present in the reactor through these catalytic runs was isolated, crystallized, and subject to an X-ray diffraction analysis that allowed its formulation as the bimetallic carboxamido complex $[Ru\{-C(O)-MeNpy\}(CO)_3]_2$ (**7**). Its structure is shown both in Chart 1 and in Figure 6.

The complex consists of the fusion of two identical mononuclear Ru fragments linked together through a metal−metal bond allowing the metal centers to achieve an octahedral environment. Each Ru center possesses a carbamoyl ligand derived from the original amidopyridyl moiety by CO insertion into the metal−amide bond. This newly formed ligand is also bound to the same Ru center by its pyridyl group, thus forming a five-membered metallacycle which is roughly located in the plane perpendicular to the unique Ru−Ru bond. The octahedral environment of each center is completed by three carbonyl groups adopting a *fac* arrangement.

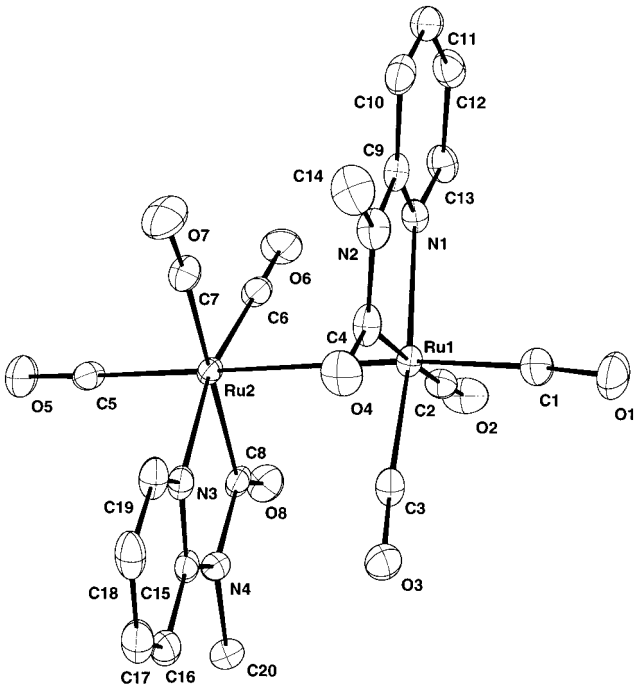


Figure 6. Perspective view of the complex **7b**. Selected interatomic distances (Å): Ru(1)−Ru(2) = 2.9395(3); Ru(1)−N(1) = 2.119(3); Ru(1)−C(4) = 2.074(3); C(4)−O(4) = 1.223(4); Ru(2)−N(3) = 2.124(3); Ru(1)−C(8) = 2.068(3); C(8)−O(8) = 1.223(4)

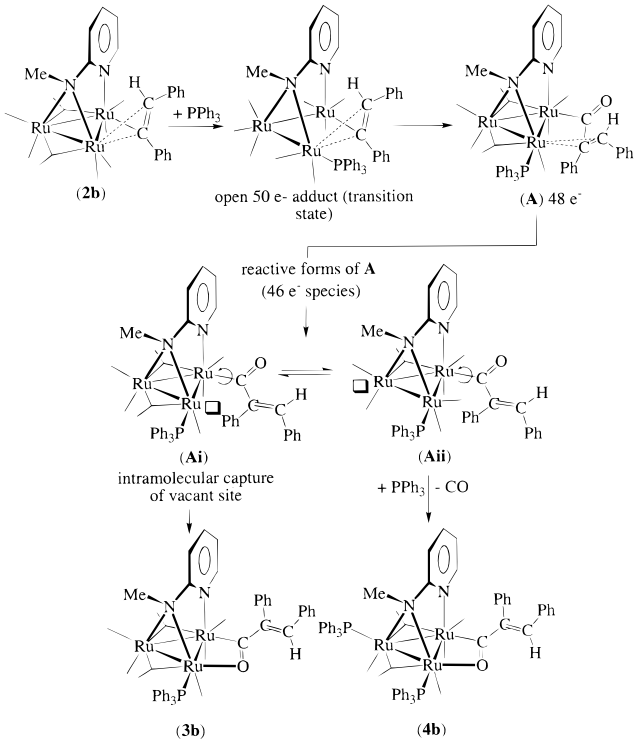
Attempts to initiate the catalysis by using **7** as a catalyst precursor were unsuccessful.

Thus, insertion of CO into the Ru−N bond of the trinuclear species may have affected the linkage of the supporting ancillary ligand, thereby facilitating a degradation of the cluster followed by recombination of some of its mononuclear fragments.

Discussion

Phosphine-Induced Migratory CO Insertion. The observation of an associative nucleophilic addition of the phosphine to the alkenyl complex **2b** suggests that the formation of the first metal−phosphine bond is assisted by a concomitant opening of a particularly weak *metal−ligand* or *metal−metal* bond. In fact, there are several of such bonds that are supposed to be weak: these include (i) the metal−nitrogen bonds that constitute the amido bridge,[9,10] (ii) the π bond connecting the alkenyl group to the metal, and (iii) the metal−metal bonds. Hypotheses considering the rupture of any of these bonds are equally reasonable, although reality may be more complex: indeed, the possibility of *a global expansion of the structure via lengthening of several of these bonds without localized rupture*[17] may also account for the remarkable ability of this complex to accommodate extra ligands. One may reasonably expect that the metal center connected to the rest of the molecule through the largest number of weak bonds, namely, Ru(1), will be the more accessible one.

Scheme 5



An interesting point is that the phosphine apparently triggers a *remote* CO insertion. A speculative mechanism suggesting how this could work is given in Scheme 5, where the proposed intermediates (or transition states) are based on known structural types (vide infra). While we believe such a mechanistic proposal is useful to rationalize the observed behavior, it should be considered with care, since there is no absolute evidence that the species we have identified are effectively the reacting *kinetic* isomers.

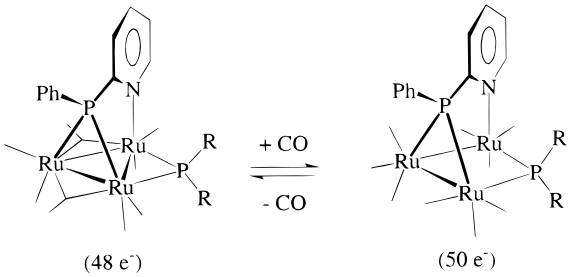
Here, it is assumed that nucleophilic attack of the phosphine onto Ru(1) (to which the alkenyl group is π bound) is assisted by opening of the metal−metal bond Ru(1)···Ru(3) and involves a concomitant shift of the two equatorial edge-bridging carbonyls in terminal position to give a 50e adduct. The subsequent migratory CO insertion into the Ru−C(alkenyl) bond may be regarded as the means by which the cluster relieves its supersaturation to recover a stable 48e configuration.[18] We suggest that such a migration process does not require opening of the alkenyl-to-metal π bond. The reduction in the number of electrons available to the cluster causes the reformation of the metal−metal bond Ru(1)−Ru(3) accompanied by a simultaneous shift of two equatorial carbonyls back to edge-bridging positions. This gives a metastable 48e intermediate **A** being *lightly stabilized* by coordination of the π bond of its propenoyl

(16) (a) An independent examination by Cabeza et al.[16b] of the parallel reaction between closely related alkenyl complexes (prepared from 2-amino-6-methylpyridine) and CO led to an erroneous formulation of the reaction product as a terminal σ-alkenyl derivative. The compound was subsequently re-formulated[16c] as a propenoyl complex similar to the one originally identified in our preliminary communication.[12] (b) Cabeza, J. A.; Fernandez-Colinas, J. M.; Llamazares, A.; Riera, V.; Garcia-Granda, S.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 4352. (c) Cabeza, J. A.; Fernandez-Colinas, J. M.; Llamazares, A.; Riera, V.; Garcia-Granda, S.; Van der Maelen, J. F. *Organometallics* **1995**, *14*, 3120.

(17) Lugan, N.; Fabre, P. L.; de Montauzon, P. L.; Lavigne, G.; Bonnet, J.-J.; Saillard, J.-Y.; Halet, J. F. *Inorg. Chem.* **1994**, *33*, 434.

(18) (a) There are several reported examples where a cluster relieves its supersaturation by reductive formation of CN[18b] or CC[18c] bonds, see: (b) Ramage, D. L.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1992**, *11*, 1242. (c) Rivomanana, S.; Mongin, C.; Lavigne, G. *Organometallics* **1996**, *15*, 1195.

Chart 2



group to the metal center Ru(1). The kinetic lability of this bond will favor the formation of an unsaturated intermediate **Ai** bearing a terminal propenoyl ligand. The latter may enter in equilibrium with an isomeric form **Aii** in which the unsaturation that originally appeared onto Ru(1) has been transferred onto Ru(2) by a simple migration of a bridging carbonyl into a terminal position. Each of these isomers is susceptible to decay by a different pathway: on one hand, free rotation around the Ru−C(acyl) bond in **Ai** allows intramolecular capture of the vacant coordination site by the acyl oxygen atom to produce **3b**. On the other hand, the vacant site available in **Aii** may be intercepted by a second incoming phosphine prior to the intramolecular rearrangement of the propenoyl group. Further rearrangement of this group then takes place in the final reaction step and involves geminal CO labilization by the propenoyl oxygen atom to produce **4b**.

Arguments that are consistent with the proposed reaction scheme are the following.

(a) Models for the nucleophilic addition of various ligands to a species of type **2** are found in the chemistry of the isostructural complex $Ru_3(\mu\text{-PhPpy})(\mu\text{-PR}_2)(CO)_8$[2b] (see Chart 2, in which a phosphido group is seen to occupy the same edge-bridging equatorial position as the alkenyl group in **2**).

Indeed, it was previously found[2b] that CO addition to $Ru_3(\mu\text{-PhPpy})(\mu\text{-PR}_2)(CO)_8$ results in an opening of the metal−metal bond bearing the equatorial diphenylphosphido ligand and a concerted shift of edge-bridging carbonyls to terminal positions, to produce the 50e adduct $Ru_3(\mu\text{-PhPpy})(\mu\text{-PR}_2)(CO)_9$.

(b) The recent report of a triruthenium complex bearing a $\sigma-\eta^1$ propenoyl ligand[19] strengthens our proposal of a similar structural arrangement in the transient species **Ai** and **Aii**.

(c) Propenoyl ligands stabilized by π donation from their carbon−carbon double bond to the metal are known in the chemistry of mononuclear complexes.[20] Bridged forms of these have been independently postuladed by Ojima[21] and Seyferth[22] as intermediates in multicentered migratory CO insertion processes. Finally, while the present paper was reviewed, the first cluster compound bearing a π-bound α,β-unsaturated acyl group was effectively reported by Hogarth.[23]

Questions Regarding the Reversible Migration of Propenoyl Groups at the Periphery of the Cluster. It is noteworthy that the reaction of **4b** with CO (Scheme 3) not only results in the opening of a metal−metal bond but also induces a migration of the propenoyl group at the periphery of the cluster. Also, in the reaction of **2b** with CO, the observed isomer for the propenoyl derivative **6b** is not the one that would result from a simple migratory CO insertion. At the present stage of our investigation, we do not understand why such migrations do occur and why they are so cleanly reversible.

Satisfactory models for the migration of acyl groups at two metal centers have been proposed by Kaesz and co-workers[24] on the basis of the existence of a bimetallic acyl species in which both C and O atoms were seen to occupy edge-bridging positions.[25] Alternatively, migration of the acyl from its original equatorial position to an axial position may be also considered. This would favor the interaction of the acyl C═O bond with three metal centers, as previously observed with other trimetallic cluster species.[26] A "windshield wiper" motion of the propenoyl group onto the face opposed to the amidopyridyl group would account for the formation of the observed isomer in which the propenoyl ligand is effectively adopting a pseudoaxial position. In addition to the above hypotheses, however, we cannot exclude the alternate possibility of a rotation of the anilinopyridyl group itself onto the metal triangle, although evidence for such a process would be difficult to obtain.

Formation of α-Phenylcinnamaldehyde. The stepwise stoichiometric production of α-phenylcinnamaldehyde from **1b** via the intermediacy of **2b** and **6b** is of some practical interest on a laboratory scale since (i) the reaction can be carried out under very mild conditions, (ii) α-phenylcinnamaldehyde is easily separated by simple crystallization from the solution in which it has been prepared, and (iii) the starting cluster can be recovered in solution. Unfortunately, the limited viability of the cluster under catalytic conditions (8−10 cycles) constitutes a drawback to more extensive applications of this system. It may be that a precise optimization of the CO and H_2 pressures as well as the use of more reactive alkynes would give better results. However, we are now convinced that the domain of experimental conditions under which the reaction can cycle catalytically without alteration of the metal framework will remain too narrow for intensive exploitation.

Conclusion

The triruthenium cluster complex $Ru_3(\mu_3\text{-RNpy})(\mu\text{-PhC═CHPh})(CO)_8$ exhibits an interesting behavior enabling its use as a prototype in model studies of cluster-mediated carbon−carbon bond forming reactions involving an alkenyl group. Indeed, this cluster undergoes associative nucleophilic addition of electron donor substrates such as PPh_3 or CO under very mild conditions. The supersaturation of the resulting adduct is

(19) Kabir, S. E.; Rosenberg, E.; Milone, L.; Gobetto, R.; Osella, D.; Ravera, M.; McPhillips, T.; Day, M. W.; Carlot, D.; Hajela, S.; Wolf, E.; Hardcastle, K. *Organometallics* **1997**, *16*, 2674.
(20) Mitsudo, T.; Fujita, K.; Nagano, S.; Suzuki, T.; Watanabe, Y.; Masuda, H. *Organometallics* **1995**, *14*, 4228.
(21) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38
(22) Seyferth, D.; Archer, C. M.; Ruschke, D. P. *Organometallics* **1991**, *10*, 3363
(23) Doherty, S.; Hogarth, G. *Inorg. Chem. Commun.* **1998**, *1*, 257.
(24) Jensen, C. M.; Chen, Y.-J.; Knobler, C. B.; Kaesz, H. D. *New J. Chem.* **1988**, *12*, 649.
(25) Sunkel, K.; Schloter, K.; Beck, W.; Ackerman, K.; Schubert, U. *J. Organomet. Chem.* **1983**, *241*, 333.
(26) Blake, A. J.; Dyson, P. J.; Johnson, B. F. G.; Martin, C. M. *J. Organomet. Chem.* **1995**, *492*, C17

then spontaneously relieved by a facile migration of the alkenyl group to a coordinated carbonyl ligand. Hydrogenolysis of the newly formed propenoyl group under CO/H_2 gas mixtures leads to the liberation of the corresponding α,β-unsaturated aldehyde, which can be easily separated. Unfortunately, the viability of such a system under catalytic conditions is limited by competitive CO insertion into the Ru−N bond of the bridging methylamidopyridyl group, converting the latter into a carboxamido group. Such a change in the ancillary ligand's anchorage to the cluster inevitably leads to a deadend with the liberation of mononuclear fragments that further reaggregate into a stable but inactive bimetallic species.

A tantalizing observation in this work is that *the cluster exhibits its most attractive and valuable properties under mild experimental conditions that are yet still very close to those susceptible to cause its degradation.*

Experimental Section

General Comments. All synthetic manipulations were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Tetrahydrofuran was distilled under argon from sodium benzophenone ketyl just before use. Dichloromethane, pentane, and hexane were distilled under nitrogen from CaH_2 and stored under nitrogen. The following reagent grade chemicals were used without further purification: $RuCl_3 \cdot nH_2O$ (Johnson Matthey), phenylacetylene (Fluka), diphenylacetylene (Lancaster), 2-(methylamino)pyridine (Aldrich).

$Ru_3(CO)_{12}$ was prepared according to a published procedure.[27] The syntheses of methylamidopyridyl complexes $Ru_3(\mu\text{-H})(\mu_3\text{-MeNpy})(CO)_9$ (**1b**) and $Ru_3(\mu_3\text{-MeNpy})(\mu\text{-PhC=CHPh})(CO)_8$ (**2b**) described below are slight modifications of relevant procedures published for the corresponding anilinopyridyl complexes.[9b] Chromatographic separations of the complexes were carried out either on Silicagel 60 (SDS, 70−230 mesh) or on aluminum oxide 90 active neutral (Merck, 70−230 mesh astm), as specified in the detailed procedures (vide infra).

The reactions were monitored by IR spectroscopy, following the evolution of ν(CO) absorptions. These spectra were recorded on a Perkin-Elmer 225 grating spectrophotometer and calibrated against water vapor absorptions. NMR spectra were recorded on Bruker AC 200 and Bruker WM 250. Mass spectra were recorded on a Ribermag R10-10.

Preparation of $Ru_3(\mu\text{-H})\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}(CO)_9$ (1b). The complex $Ru_3(C0)_{12}$ (1.0 g, 1.6 mmol) and 2-(methylamino)-pyridine (1.0 g, 1.6 mmol) were dissolved in benzene (90 mL) in a Schlenk flask equipped with a reflux condenser and connected to a vacuum line. The solution was heated under reflux until complete disappearance of the characteristic absorption bands of $Ru_3(CO)_{12}$ (ca. 3 h). It was then allowed to cool to room temperature. After complete evaporation of the solvent under vacuum, the solid residue was recovered with the minimum amount of dichloromethane and chromatographed on a silicagel column. Traces of residual $Ru_3(CO)_{12}$ were eluted first with pure hexane, whereas further elution with a 1:3 dichloromethane/hexane mixture resulted in a unique orange fraction containing the pure reaction product, which was recrystallized from the same reaction mixture at −30 °C (yield 85−90%).

$Ru_3(\mu\text{-H})\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}(CO)_9$ (1b): orange crystals; IR (heptane) ν [cm^{-1}] = 2076(m), 2046(s), 2026(s), 1999(s), 1988(vs), 1972(w), 1965(mw) (ν CO); ^1H NMR (200 MHz, $CDCl_3$) δ 8.16−6.47 (aromatic protons), 3.08 (s, C*H*$_3$), −10.68 (s, *hydride*).

(27) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1972**, *16*, 47.

Preparation of $Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}(C_6H_5)C{=}CH(C_6H_5)\}(CO)_8$ (2b). Crystals of the complex **1b** (200 mg, 0.30 mmol) and diphenylacetylene (54 mg, ca. 0.30 mmol) were dissolved in heptane (20 mL). The solution was heated at 60 °C for 45 min. This initially caused a gradual color change from orange to red, followed by a lightening of the solution accompanying the progressive formation of a garnet-red precipitate. The resulting suspension was then allowed to cool to room temperature, and the precipitate was subsequently recovered by filtration under nitrogen, washed several times with heptane, and dried under vacuum (yield 85−95%). It is noteworthy that this complex (unlike alkenyl species of the same type obtained with other alkynes) is only very slightly soluble in most usual solvents, which prevents the recording of its NMR spectrum.

$Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}(C_6H_5)C{=}CH(C_6H_5)\}(CO)_8$ (2b). Anal. Calcd (found) for $C_{28}H_{18}N_2O_8Ru_3$: C, 41.33 (41.11); H, 2.23 (2.40); N, 3.44 (3.37).

Reaction of the Alkenyl Complex $Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}(C_6H_5)C{=}CH(C_6H_5)\}(CO)_8$ (2b) with 1 equiv of Triphenylphosphine: Preparation of the Addition Product $Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}(CO)_7$ (3b). In a typical experiment, a suspension of complex **2b** (250 mg, 0.31 mmol) was stirred in 20 mL of dichloromethane. The addition of triphenylphosphine (80 mg, 0.31 mmol) caused the rapid dissolution of the suspension within less than 3 min, giving a limpid solution exhibiting an intense dark red color. This solution was reduced in volume under vacuum and chromatographed on alumina. Elution with pure pentane allowed the separation of trace amounts of a yellow oil (insufficient amount for proper characterization). Further elution with 2:3 pentane/dichloromethane allowed the separation of two distinct fractions. The first one, of pink color, contained small amounts of unreacted starting complex **2b**, whereas the second one, of red color, gave a red oil after solvent evaporation. Further recrystallization of this oil from dichloromethane/pentane at −30 °C gave red crystals of a new complex subsequently characterized as **3b** (160 mg, 0.15 mmol, 48% yield). A third fraction, of black color, was eluted with 1:2 pentane/dichloromethane. After solvent evaporation, it was recovered as a red oil, subsequently characterized as **4b** (85 mg, 0.06 mmol, 19%). Larger amounts of the latter species were subsequently obtained by using a more appropriate metal/ligand ratio, as described in the following paragraph.

$Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}(CO)_7$ (3b): red color; IR (CH_2Cl_2) ν [cm^{-1}] = 2030(vs), 1994(vs), 1969(m), 1935(m), 1860(vw), 1817(m), 1610(vw) (C=O); ^1H NMR ($CDCl_3$) δ = 8.15−6.20 (m, aromatic protons), 8.10 (s, vinylic C*H*), 2.58 (s, NC*H*$_3$); ^{31}P NMR {^1H} ($CDCl_3$) δ = 21.13 (*P*Ph$_3$); $^{13}C\{^1H\}$ NMR δ = 263.74 (*C*O, acyl), 239.53 229.10 (μ-*C*O), 203.96−196.82 (*C*O), 170.46, 152.97, 115.22, 112.23 (*pyridyl carbons*), 56.40 (N*C*H$_3$). Anal. Calcd (found) for $C_{47}H_{35}N_2O_8Cl_2P_1Ru_3$ (**3b**·CH_2Cl_2): C, 48.63 (48.52); H, 3.04 (2.73); N, 2.41 (2.33).

Reaction of $Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}(C_6H_5)C{=}CH(C_6H_5)\}(CO)_8$ (2b) with 2 equiv of Triphenylphosphine: Preparation of $Ru_3\{\mu_3\text{-}(CH_3)N(C_5H_4N)\}\{\mu\text{-}O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}_2(CO)_6$ (4b). The preceding reaction was reproduced under the same experimental conditions, but using a 2-fold amount of triphenylphosphine in a typical experiment, where the exact quantities of reagents were the following: **2b** (220 mg, 0.27 mmol), PPh_3 (139 mg, 0.53 mmol), dichloromethane (20 mL). The reaction was complete within 7−10 min. The solvent was then reduced in volume and chromatographed in the same way as in the previous experiment (vide supra). Chromatographic workup revealed the absence of any trace of starting material, whereas the relative abundance of **3b** and **4b** was modified: the complex **3b** (90 mg, 0.08 mmol, 30% yield) was still present in unexpectedly large amounts, whereas **4b** (160 mg, 0.12 mmol, 44% yield) was the major species obtained under these experimental conditions. Suitable

Table 1. Crystal Data, Data Collection, and Refinement Parameters for Compounds 2b−7b

	2b	3b	4b	5b	6b	7b
			Crystal Data			
chemical formula	$C_{28}H_{18}N_2O_8Ru_3$	$C_{47}H_{35}Cl_2N_2O_8PRu_3$	$C_{63}H_{48}N_2O_7P_2Ru_3$	$C_{48}H_{33}Cl_2N_2O_9PRu_3$	$C_{30}H_{18}O_{10}N_2Ru_3$	$C_{20}H_{14}O_8N_4Ru_2$
solvent molecules			0.5 CH_2Cl_2			
molecular weight	813.67	1158.88	1369.43	1186.89	869.69	640.49
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	12.037(2)	12.798(5)	14.579	10.130(1)	10.600(1)	8.983(4)
b (Å)	16.613(1)	22.290(4)	16.763	21.545(3)	10.002(1)	10.653(3)
c (Å)	14.466(2)	16.328(2)	27.174	22.088(2)	29.721(6)	12.043(3)
α (deg)	90.00	90.00	90.00	90.00	90.00	104.23(2)
β (deg)	104.34(1)	93.54(2)	100.87	93.98(1)	99.13(1)	101.14(3)
γ (deg)	90.00	90.00	90.00	90.00	90.00	93.90(3)
V (Å^3)	2803(1)	4649(3)	6522	4809(1)	3111(1)	1087.9(7)
Z	4	4	4	4	4	2
ρ_{calcd} (g cm^{-3})	1.93	1.66	1.39	1.64	1.85	1.96
μ (mm^{-1})	16.2	11.5	10.2	11.1	14.7	14.2
			Data Collection			
radiation			graphite monochromated, Mo Kα (λ = 0.710 73 Å)			
data collection method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
no. of obsd reflns	2896	4497	1837	3969	4706	3821
observation criterion	$F_o^2 > 3\sigma F_o^2$	$F_o^2 > 3\sigma F_o^2$	$F_o^2 > 3\sigma F_o^2$	$F_o^2 > 3\sigma F_o^2$	$F_o^2 > 3\sigma F_o^2$	$F_o^2 > 3\sigma F_o^2$
θ max (deg)	23	23	23	23	23	23
range of h, k, l	$0 \le h \le 13$ $0 \le k \le 18$ $-15 \le l \le 15$	$0 \le h \le 15$ $0 \le k \le 26$ $-19 \le l \le 19$	$-14 \le h \le 13$ $0 \le k \le 16$ $0 \le l \le 26$	$-12 \le h \le 12$ $0 \le k \le 25$ $0 \le l \le 26$	$0 \le h \le 12$ $0 \le k \le 11$ $-35 \le l \le 35$	$0 \le h \le 10$ $-12 \le k \le 12$ $-14 \le l \le 314$
scan range θ (deg)	0.8 + 0.35 tan θ	0.9 + 0.35 tan θ	0.9 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ	0.9 + 0.35 tan θ
			Refinement			
R	0.0293	0.0262	0.0939	0.0350	0.0721	0.0342
R_w	0.0342	0.0296	0.1062	0.0402	0.0772	0.0313
weighting scheme	Chebyshev	Chebyshev	Chebyshev	Chebyshev	Chebyshev	Chebyshev
coeff A_r	1.02, 0.525, 0.628	2.58, −0.813, 1.84	1.25, 0.693, 0.834	0.744, 0.183, 0.471	3.80, 2.59, 2.62	1.520, 0.208, 0.165
no. of reflns used	2896	4497	1837	3969	4706	3821
no. of params refined	370	568	201	586	406	307
GOF[a]	0.8836	0.9622	1.11	1.0837	0.9968	1.2422
residual electron density (e.Å^{-3})	−0.887/0.750	−0.647/0.608	−0.811/1.552	−0.474/0.970	−1.575/0.867	−1.63/0.99

[a] Goodness of fit = $[\sum w(|F_o| - |F_o|)^2/(N_{obs} - N_{params})]^{1/2}$.

crystals for an X-ray structure analysis of the latter compound were grown from a benzene/hexane mixture.

$Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}$-$\{P(C_6H_5)_3\}_2(CO)_6$ (4b): black color; IR (CH_2Cl_2) ν [cm^{-1}] = 2008(vs), 1955(m), 1940(vs), 1853(w), 1755(m), 1608(vw) (C=O);^{1}H NMR ($CDCl_3$) δ = 8.46−5.88 (m, aromatic protons), 8.04 (s, vinylic C*H*), 1.61 (s, NCH_3); ^{31}P NMR {^{1}H} ($CDCl_3$) δ = 44.07 (d, *P*Ph$_3$, $^3J_{(PP)}$ = 25.8 Hz); ^{13}C{^{1}H} NMR δ = 257.89 (*C*O, acyl), 240.55, 237.39 (μ-*C*O), 204.74−198.00 (*C*O), 170.86, 154.06, 113.81, 112.18 (*pyridyl carbons*), 22.48 (NCH_3). Anal. Calcd (found) for $C_{63}H_{48}N_2O_7P_2Ru_3$ (**3b**·CH_2Cl_2): C, 57.77 (57.75); H, 3.69 (3.70); N, 2.14 (2.12).

Reaction of the Adduct 3b with Triphenylphosphine Under Thermal Activation: Synthesis of the Disubstituted Derivative 4b. Crystals of the complex **3b** (130 mg, 0.12 mmol) and 1 equiv of triphenylphosphine (32 mg, 0.12 mmol) were dissolved in 15 mL of toluene. No reaction was observed when this solution was stirred at room temperature for 1 h. However, the formation of **4b** started when the temperature was raised to 50 °C; the reaction was then spectroscopically quantitative within 30 min.

Reaction of $Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}_2(CO)_6$ (4b) with Carbon Monoxide: Synthesis of $Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}(CO)_8$ (5b). Crystals of the complex **4b** were dissolved in dichloromethane (15 mL) in a Schlenk tube. A continuous stream of gaseous carbon monoxide was bubbled through this solution for 6 h at room temperature. A progressive lightening of the solution was observed, whereas IR monitoring indicated the formation of a new compound. After partial evaporation of the solution to a third of its volume under the influence of the gas stream, 10 mL of hexane was added, causing the precipitation of orange crystals of the new compound **5b** (40 mg, 0.036 mmol, 47% yield).

$Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}(CO)_8$ (5b): orange color: IR (CH_2Cl_2) ν [cm^{-1}] = 2051(s), 2019(vs), 1990(s), 1965(m), 1950(m) (C=O);^{1}H NMR ($CDCl_3$) δ = 8.14−6.20 (m, aromatic protons and vinylic C*H*), 1.57 (s, NCH_3); ^{31}P NMR {^{1}H} ($CDCl_3$)d = 15.50 (s, *P*Ph$_3$).

Transformation of $Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}\{P(C_6H_5)_3\}(CO)_8$ (5b) under a Stream of Inert Gas. Crystals of the complex **5b** (50 mg, 0.05 mmol) were dissolved in dichloromethane (5 mL). A continuous stream of nitrogen gas was then bubbled through the solution at room temperature. IR monitoring indicated the progressive transformation of the initial complex over a period of 15 min. Evaporation of the resulting solution under reduced pressure produced a red oil, which was dried under vacuum. NMR analysis of the redissolved product showed it to consist of a mixture of **3b**, **4b**, and **2b**.

Reaction of $Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$(C_6H_5)C{=}CH(C_6H_5)\}(CO)_8$ (2b) with Carbon Monoxide: Preparation of $Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$(C_6H_5)C{=}CH(C_6H_5)\}(CO)_9$ (6b). A suspension of **2b** (100 mg, 0.12 mmol) in 10 mL of dichloromethane was stirred at room temperature in a Schlenk tube under nitrogen. A continuous stream of gaseous carbon monoxide was bubbled into the liquid through a gas inlet. Total dissolution of the initial suspension was obtained within 20 min. At that stage, the CO gas inlet was raised above the solution, and magnetic agitation was stopped. The addition of 10 mL of hexane caused the slow crystallization of the new complex **6b** recovered as yellow crystals (85 mg, 0.10 mmol,

83% yield) directly suitable for an X-ray structure analysis. Although the complex is fairly stable as a solid, its solutions must be kept under carbon monoxide (1 atm). Otherwise, it reverts to the starting alkenyl complex within less than 1 min.

$Ru_3\{\mu_3$-$(CH_3)N(C_5H_4N)\}\{\mu$-$O{=}C{-}(C_6H_5)C{=}CH(C_6H_5)\}$-$(CO)_9$ (6b): yellow color; IR (CH_2Cl_2) ν [cm^{-1}] = 2070(vw), 2047(s), 2017(s), 1992(m), 1978(m), 1955(sh) (C=O);^{1}H NMR ($CDCl_3$) δ = 8.02−6.30 (m, aromatic protons and vinylic C*H*), 3.09 (s, NC*H*$_3$); ^{13}C NMR {^{1}H} ($CDCl_3$) δ = 302.17 (*C*O, *acyl*), 204.54−199.46 (*C*O (terminal ligands)), 180.67, 153.42, 138.82, 117.69, 106.02 (*C*, pyridine), 155.76 (Ph*C*(CO)), 136.77, 135.17 (*C*, ipso), 133.76 (*C*(H)Ph), 60.30 (N*C*H$_3$).

Treatment of 6b with H_2/CO: Formation of α-Phenylcinnamaldehyde. The reaction was first carried out in an NMR tube and then reproduced on a preparative scale.

(a) NMR Experiment. A suspension of **2b** (70 mg, 0.08 mmol) in deuterated chloroform was subject to treatment with CO gas in the same way as described above. The resulting limpid CO-saturated solution was then introduced in an NMR tube. ^{1}H NMR indicated the presence of **6b** as the only species in solution. The tube was then charged with hydrogen (1 atm). A new NMR spectrum taken after 24 h indicated the presence of a mixture of **1b**, **6b**, and α-phenylcinnamaldehyde.

(b) Stoichiometric Synthesis of α-phenylcinnamaldehyde. A suspension of complex **2b** (150 mg, 0.18 mmol) in dichloromethane (5 mL) was introduced in a glass reactor. The complex **6b** was then generated in situ by treatment with CO gas in the same way as described above. A limpid CO-saturated solution of **6b** was thus obtained. The reactor was then closed, pressurized with 5 atm of hydrogen, and stirred at 40 °C overnight. After evaporation of the solvent, the residue was characterized as a mixture of complex **1b** and α-phenylcinnamaldehyde.

PhHC=CPhCHO: IR (CH_2Cl_2) ν [cm^{-1}] = 1685(s) (C=O); ^{1}H NMR ($CDCl_3$) δ = 9.78 (s, C*H*O), 7.45−7.18 (m, aromatic protons and vinylic protons); ^{13}C {^{1}H} NMR ($CDCl_3$) δ = 193.8 (*C*HO), 150.1 (Ca), 141.6 (ipso α-Ph), 133.8 (ipso β-Ph)

Catalytic Hydroformylation of Diphenylacetylene. The catalyst precursor **1b** (70 mg, 0.11 mmol), diphenylacetylene (940 mg, 5.30 mmol), and 15 mL of dichloromethane were introduced in an autoclave, which was subsequently pressurized with 5 atm of CO and 15 atm of hydrogen. The solution was continuously stirred with a magnetic agitator, and the temperature was raised to 70 °C. After 24 h, the reaction was stopped and the residue was chromatographed on an aluminum column. Elution with hexane gave a first fraction containing diphenylacetylene, followed by a second fraction containing α-phenylcinnamaldehyde subsequently recovered as white crystals (178 mg, 0.82 mmol), corresponding to a turnover of 8. Further elution with 2:1 hexane/dichloromethane allowed the recovery of a yellow fraction from which crystals of the new dimeric complex **7** (27 mg, 0.043 mmol) were isolated and subject to an X-ray structure analysis.

$[Ru\{C(O)N(CH_3)(C_5H_4N)\}]_2$: yellow; IR ($CH_2Cl_2$) ν [cm^{-1}] = 2077(s), 2072(sh), 2043(vs), 2008(s), 1983(s) (C=O).

X-ray Structure Determinations. Table 1 summarizes crystal and intensity data for compounds **2b**, **3b**, **4b**, **5b**, **6b**, and **7b**. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer. The cell constants were obtained by least-squares refinement of the setting angles of 25 reflections in the range 24° < 2θ(Mo Kα_1) < 28°. Data reductions were carried out using the CRYSTALS package.[28] The structures were solved by direct methods, using SIR92,[29] and refined with CRYSTALS. Perspective views of the molecules were drawn with the program CAMERON.[30] Selected bond distances and angles for the compounds **2b**−**7b** are included in the captions of the corresponding Figures 1−6.

Note: Due to the limited number of reflections available for **4b**, inherent to the poor quality of the crystal, only a few atoms were refined with anisotropic thermal parameters, whereas phenyl rings were treated as rigid groups.

Acknowledgment. Financial support of this work by the CNRS is gratefully acknowledged. We also thank Herbert D. Kaesz for discussion of this work under support of NATO Grant 931414, and Fred Basolo for the personal communication of his kinetic study.

Supporting Information Available: Crystallographic data for compounds **2b**−**7b** including tables of atomic coordinates, hydrogen coordinates, anisotropic thermal parameters, and interatomic distances and bond angles (44 pages). Ordering information is given on any current masthead page.

OM9806747

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