Acetylide Participation in Ligand Substitution and P−C Bond Cleavage in the Reaction between HRu₃(CO)₉(μ₃,η²,η²,η¹-C≡CPh) and 4,5-Bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd). Syntheses and X-ray Structures of

HRu₃(CO)₇[μ₃,η²,η²,η¹,η¹,η¹-Ph₂PC=CC(O)CH₂C(O)PPh₂C=CPh] and Ru₃(CO)₇(μ,η²,η¹-PhC=CHPh)[μ₂,η²,η¹-PPhC=CC(O)CH₂C(O)PPh₂]

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The triruthenium cluster HRu₃(CO)₉(μ₃,η²,η²,η¹-C≡CPh) (**1**) reacts with the diphosphine ligand bpcd in the presence of Me₃NO to afford the new cluster compounds HRu₃(CO)₇(bpcd)-(μ₃,η²,η²,η¹-C≡CPh) (**2**) and HRu₃(CO)₇[μ₃,η²,η²,η¹,η¹,η¹-Ph₂PC=CC(O)CH₂C(O)PPh₂C=CPh] (**3**). Cluster **2** is the sole product from the controlled thermolysis of **1** with bpcd. Both **2** and **3** have been isolated and characterized in solution by IR and NMR (¹H and ³¹P) spectroscopies, and by X-ray crystallography in the case of the latter cluster. The bpcd ligand in **2** chelates to the ruthenium center that is σ bound by the acetylide ligand, and in the zwitterionic compound **3** one of the PPh₂ moieties of the bpcd ligand coordinates to a hydride-bridged ruthenium atom while the other PPh₂ group exists as a phosphonium center due to attack on the acetylide Cα carbon. Whereas **3** slowly decomposes in solution at elevated temperatures, cluster **2** was found to undergo a clean conversion to the new cluster Ru₃(CO)₇(μ,η²,η¹-PhC=CHPh)[μ₂,η²,η¹-PPhC=CC(O)CH₂C(O)PPh₂] (**4**). The bridging alkenyl ligand in **4** results from the formal cleavage of one of the P−Ph bonds of the bpcd ligand, followed by the concomitant coupling of the phenyl and hydride groups with the acetylide ligand. Cluster **4** has been fully characterized in solution and the solid-state structure established by X-ray analysis. NMR data are presented from a labeling study employing HRu₃(CO)₇(bpcd)-(μ₃,η²,η²,η¹-C≡Ctol-*p*) that shows that the hydrogen in the μ,η²,η¹-RC=CHR′ moiety of Ru₃-(CO)₇(μ,η²,η¹-RC=CHR′)[μ₂,η²,η¹-PPhC=CC(O)CH₂C(O)PPh₂] is distributed between both the phenyl and tol-*p* groups. The scrambling of the alkenyl hydrogen between the phenyl- and tol-*p*-substituted carbon atoms in the μ,η²,η¹-RC=CHR′ moiety suggests that hydride transfer from the triruthenium frame occurs via a transient cluster compound that possesses a coordinated PhC≡Ctol-*p* ligand.

Introduction

The ligand substitution properties and coordination chemistry of the acetylide-bridged cluster HRu₃(CO)₉-(μ₃,η²,η²,η¹-C≡CBuᵗ) have been extensively examined over the last two decades. Monodentate phosphine ligands react with HRu₃(CO)₉(μ₃,η²,η²,η¹-C≡CBuᵗ) to give HRu₃(CO)₈P(μ₃,η²,η²,η¹-C≡CBuᵗ) derivatives where the P-ligand is coordinated to the ruthenium center that is σ bound by the acetylide Cα atom (mode A).[1,2] The

course of substitution is more diverse when bidentate phosphine ligands are used. Here the bidentate ligand may function as a chelating group via coordination at the unique Ru(CO)₃ center (mode B) and/or a bridging

(1) (a) Jangala, C.; Rosenberg, E.; Skinner, D.; Aime, S.; Milone, L.; Sappa, E. *Inorg. Chem.* **1980**, *19*, 1571. (b) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J.; Sappa, E. *Inorg. Chem.* **1981**, *20*, 4437. (c) Sappa, E. *J. Organomet. Chem.* **1988**, *352*, 327. (d) Sappa, E.; Pasquinelli, G.; Tiripicchio, A.; Camellini, M. T. *J. Chem. Soc., Dalton Trans.* **1989**, 601.
(2) For a recent report on the site of MeCN substitution in HRu₃-(CO)₉(μ₃,η²,η²,η¹-C≡CBuᵗ), see: Charmant, J. P.; Davies, G.; King, P. J.; Wigginton, J. R.; Sappa, E. *Organometallics* **2000**, *19*, 2330.

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group through the ligation of one of the non-hydride-bridged ruthenium−ruthenium bonds (mode C). These coordination modes are depicted below. Rigid diphosphines such as (Z)-Ph$_2$PCH=CHPPh$_2$ and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) prefer the former coordination mode,[3,4] while the more flexible diphosphine ligands dppm and dppe furnish bridged cluster species.[5]

mode A   mode B   mode C
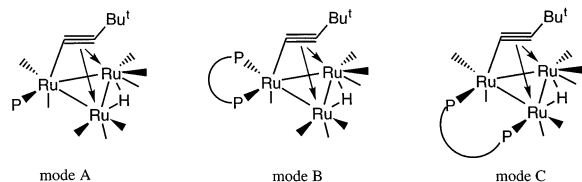
Besides the above commonly found patterns for CO substitution in HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CBu^t), there also exists the possibility for P-ligand attack at the multisite bound acetylide moiety. This particular course for nucleophilic attack is important if the reaction is governed by a charge-controlled rather than an orbital-controlled manifold. Earlier MO calculations carried out on HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CMe) have revealed that the LUMO is essentially an antibonding ruthenium−ruthenium-based orbital containing no acetylide contribution.[6] However, the calculated atomic charge on the acetylide C$_\alpha$ atom is positive and shows this carbon center to be an ideal site for nucleophilic attack. While no specific examples exist for P-ligand attack on the coordinated acetylide moiety in HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CBu^t), Carty and Sappa have reported that ^{t}BuNC adds regiospecifically to the acetylide C$_\alpha$ atom in the phenylacetylide-substituted cluster HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) to give the zwitterionic complex HRu$_3$(CO)$_9$-($\mu_3,\eta^2,\eta^2,\eta^1$-^{t}BuNCC=CPh).[7] Examples for the attack of a variety of 2e-donor ligands on both the C$_\alpha$ and C$_\beta$ atoms of the acetylide ligand in the related osmium analogues HOs$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CR) (where R = H, Me, Ph, CMe$_2$OH) are known.[8,9]

Wishing to explore the control, if any, that the acetylide R group might exert on the reaction of HRu$_3$-(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CR) with diphosphine ligands, we investigated the reaction between HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) (1) and bpcd. While both the Ph and Bu^t derivatives of HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CR) react with added bpcd to produce the chelated clusters HRu$_3$(CO)$_7$-

(3) Sappa, E.; Predieri, G.; Tiripicchio, A.; Vignali, C. *J. Organomet. Chem.* **1989**, *378*, 109.
(4) Shen, H.; Williams, T. J.; Bott, S. G.; Richmond, M. G. *J. Organomet. Chem.* **1995**, *505*, 1.
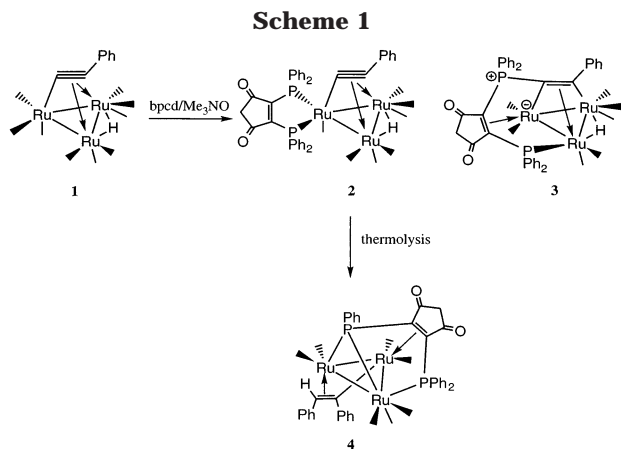(5) Predieri, G.; Tiripicchio, A.; Vignali, C.; Sappa, E. *J. Organomet. Chem.* **1988**, *342*, C33.
(6) Granozzi, G.; Tondello, E.; Bertoncello, R.; Aime, S.; Osella, D. *Inorg. Chem.* **1983**, *22*, 744.
(7) MacLaughlin, S. A.; Johnson, J. P.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1983**, *2*, 352.
(8) (a) Boyar, E.; Deeming, A. J.; Kabir, S. E. *J. Chem. Soc., Chem. Commun.* **1986**, 577. (b) Henrick, K.; McPartlin, M.; Deeming, A. J.; Hasso, S.; Manning, P. *J. Chem. Soc., Dalton Trans.* **1982**, 899. (c) Deeming, A. J.; Kabir, S. E.; Nuel, D.; Powell, N. I. *Organometallics* **1989**, *8*, 717.
(9) For examples of nucleophilic attack on a coordinated acetylide ligand in di- and trimetal complexes, see: (a) Jensen, M. P.; Shriver, D. F. *Organometallics* **1992**, *11*, 3385. (b) Norton, D. M.; Eveland, R. W.; Hutchison, J. C.; Stern, C.; Shriver, D. F. *Organometallics* **1996**, *15*, 3916. (c) Breckenridge, S. M.; Carty, A. J.; Pellinghelli, M. A.; Tiripicchio, A.; Sappa, E. *J. Organomet. Chem.* **1994**, *471*, 211. (d) Cherkas, A. A.; Hoffman, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1987**, *6*, 1466.

(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CR) under mild thermolysis conditions, we also observed a major difference in the thermal stability of these two cluster complexes. In refluxing toluene, HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CBu^t) is thermally stable,[4] while HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) (2) readily undergoes conversion to Ru$_3$(CO)$_7$(μ,η^2,η^1-PhC=CHPh)-[μ_2,η^2,η^1-PPhC=CC(O)CH$_2$C(O)PPh$_2$] (4). Moreover, disparate bpcd substitution reactivity was also found when Me$_3$NO was employed in the activation of the parent nonacarbonyl cluster. Whereas the expected cluster HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CBu^t) was the sole product obtained via the oxidative-decarbonylation route with HRu$_3$(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CBu^t), both the HRu$_3(CO)_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) and HRu$_3(CO)_7$[$\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-Ph$_2$PC=CC(O)CH$_2$C(O)PPh$_2$C=CPh] (3) were observed from 1 and bpcd. The critical influence demonstrated by the acetylide R group in determining the course of reactivity in HRu$_3$(CO)$_9$-($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CR) with bpcd is clearly seen in production of clusters 3 and 4. Herein we present our results on the synthesis and the spectral properties of the new clusters 2−4, along with the solid-state structures of clusters 3 and 4.

Results and Discussion

I. Syntheses and Spectral Data. Controlled thermolysis (<65 °C) of cluster 1 with the diphosphine ligand bpcd in a variety of solvents gives the disubstituted cluster HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) (2) in moderate to good isolated yields after column chromatography over silica gel. When the reaction between 1 and bpcd was carried out at in refluxing DCE or toluene, a new, slower moving red material was observed by TLC analysis in addition to 2. This new compound (cluster 4) was found to originate from 2 (vide infra). Cluster 2 was characterized spectroscopically in solution and by combustion analysis. The IR spectrum of 2 is unremarkable in comparison to the known clusters HRu$_3$(CO)$_7$-(P−P)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CBu^t) [where P−P = (Z)-Ph$_2$PCH=CHPPh$_2$, bpcd],[3,4] which possess a chelating diphosphine ligand, and the presence of a single, downfield ^{31}P resonance at δ 75.73 supports a cluster having idealized C_s symmetry where the phosphorus atoms of the bpcd ligand reside in the plane defined by the three ruthenium atoms.[10]

We next examined the Me$_3$NO activation of cluster 1 in the presence of bpcd as an alternative route for the high-yield production of 2. The use of this oxidative-decarbonylation reagent, as well as other related oxide derivatives, has the advantage of activating metalcarbonyl compounds toward ligand substitution under relatively mild reaction conditions.[11] Treatment of an equimolar mixture of 1 and bpcd in CH$_2$Cl$_2$ at room temperature with Me$_3$NO (2.0 equiv) furnishes two products, as revealed by TLC analysis, one of which corresponds to cluster 2. The top portion of Scheme 1 illustrates the course of this reaction.

(10) For chelating diphosphines that exhibit a large nuclear deshielding upon coordination, see: (a) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. (b) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, *6*, 254. (c) Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. *Inorg. Chem.* **1980**, *19*, 1277.
(11) (a) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53. (b) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227. (c) Darensbourg, D. J.; Darensbourg, M. Y.; Walker, N. *Inorg. Chem.* **1981**, *20*, 1918.

Scheme 1

Both products were subsequently isolated by chromatographic means and characterized spectroscopically. Cluster **2** was observed to be the minor product and was identified by its characteristic IR and NMR profiles. The zwitterionic cluster **3**, the major product of the reaction, results from the substitution of one of the hydrido-bridged $Ru(CO)_3$ moieties by a PPh_2 group, with the remaining PPh_2 becoming a phosphonium ligand via the formal attack on the acetylide C_α atom. Capture of the dione π bond at the non-hydrido-bridged $Ru(CO)_2$ center completes the sequence. Cluster **3** exhibits a well-populated IR spectrum with terminal $\nu(CO)$ stretching bands belonging to the triruthenium frame and two dione carbonyl bands of an intact bpcd moiety. The ^1H NMR spectrum of **3** shows a phenyl multiplet at δ 8.02–6.56 for the five aryl groups, an AB quartet at δ 3.33 for the diastereotopic dione protons, and a high-field singlet at δ −12.06 for the bridging hydride moiety. The ^{31}P NMR spectrum of **3** was particularly informative given the two ^{31}P doublets recorded at δ 12.89 and −0.17, which may be assigned to the ruthenium-bound PPh_2 and the phosphonium PPh_2 groups, respectively.

The reaction conditions leading to **2** and **3** were briefly explored as a function of temperature and Me_3NO stoichiometry. Carrying out the reaction either at 0 °C with 2.0 equiv of Me_3NO or at −78 °C in the presence of 1.0 equiv of Me_3NO, followed by warming to room temperature, afforded identical results in terms of the product distribution of **2** and **3**. The unexpected synthesis of zwitterionic **3** when the acetylide substituent is changed from a Bu^t to a Ph group suggests that further study of the phosphine substitution reactions in this genre of cluster as a function of the acetylide substituent are warranted in order to fully chart the scope and locale of ligand attack in $HRu_3(CO)_9(\mu_3,\eta^2,\eta^2,\eta^1\text{-}C\equiv CR)$.

II. Thermolysis Reactivity of Clusters 2 and 3. The thermal stability of clusters **2** and **3** was next examined as part of our interest in the P−C bond cleavage that often accompanies the thermolysis of bpcd-substituted clusters.[12] Batch thermolysis of **2** in refluxing DCE furnishes the cluster compound $Ru_3(CO)_7(\mu,\eta^2,\eta^1\text{-}PhC=CHPh)[\mu_2,\eta^2,\eta^1\text{-}PPhC=CC(O)\text{-}CH_2C(O)PPh_2]$ (**4**), whose formation derives from the

formal cleavage of one of the P−Ph bonds of the bpcd ligand, followed by the coupling of the phenyl and hydride groups with the acetylide ligand. Cluster **4** isolated from this thermolysis reaction corresponds to the same slower moving material found in the high-temperature thermolysis reactions of **1** and bpcd (vide supra). The reaction leading from **2** to **4** is depicted in the central portion of Scheme 1.

Besides the anticipated phenyl and dione methylene groups in **4**, the ^1H NMR spectrum revealed the presence of a singlet at δ 6.25 and, when taken together with the absence of a high-field, bridging ruthenium hydride signal, strongly supports the existence of a cluster-bound alkenyl moiety. The ^{31}P NMR spectrum of **4** provided valuable information concerning the nature of the phosphorus ligands in **4**. Besides the resonance at δ 19.77 that belongs to a ruthenium-bound PPh_2(dione) group, a phosphido moiety was observed at δ 116.63, which is consistent with a μ_2-phosphido ligand that spans a Ru−Ru bond.[13] The ^{31}P centers in **4** are coupled and appear as a pair of doublets.

A study on the conversion of **2** to **4** was also carried out by employing $^{31}P\{^1H\}$ NMR spectroscopy. Here a sealed NMR tube containing a ca. 0.034 M $CDCl_3$ solution of cluster **3** was heated in a temperature-controlled bath at 80 °C for a period of time sufficient to effect partial conversion to **4**. After the sample was quenched in an ice bath, the $^{31}P\{^1H\}$ NMR was recorded, and with the exception of starting cluster **2** the only other material observed was that of cluster **4**. Since no other cluster compounds were found by either ^{31}P or ^1H NMR spectroscopy in the sealed tube experiment, the relationship between these two clusters is unequivocally established as that shown in Scheme 1.

The thermal behavior of cluster **3** was examined in both DCE and toluene at temperatures in the range 80−90 °C. Only a gradual decomposition of **3** was found during the thermolysis reaction, yielding no observable carbonyl-containing species when the reaction was monitored by IR spectroscopy. These results prove that the alkenyl-bridged cluster **4** arises from only from the bpcd-chelated cluster **2** and not from the zwitterionic cluster **4**.

III. Labeling Data on the Regiochemistry for Phenyl and Hydride Transfer to the Coordinated Acetylide Ligand in $HRu_3(CO)_7(bpcd)(\mu_3,\eta^2,\eta^2,\eta^1\text{-}C\equiv Ctol\text{-}p)$. Having shown the formation of a $\mu,\eta^2,\eta^1\text{-}PhC=CHPh$ ligand in cluster **4**, we wished to explore the details concerning the regiochemistry for the transfer of the ruthenium-bound phenyl and bridging hydride groups ultimately to the coordinated phenylacetylide ligand. To accomplish this task, we prepared the labeled cluster $HRu_3(CO)_7(bpcd)(\mu_3,\eta^2,\eta^2,\eta^1\text{-}C\equiv Ctol\text{-}p)$ from $HRu_3(CO)_9(\mu_3,\eta^2,\eta^2,\eta^1\text{-}C\equiv Ctol\text{-}p)$[14] and bpcd. In the case of this tolyl derivative, $HRu_3(CO)_7(bpcd)(\mu_3,\eta^2,\eta^2,\eta^1\text{-}C\equiv Ctol\text{-}p)$,[15] two limiting extremes for alkenyl ligand formation may be envisioned. If hydride transfer to the acetylide ligand precedes the transfer of the bpcd-derived Ph group, one would ultimately expect an alkenyl moiety having one of the following compositions,

(12) (a) Shen, H.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, *14*, 4625. (b) Shen, H.; Bott, S. G.; Richmond, M. G. *Inorg. Chim. Acta* **1996**, *250*, 195. (c) Bott, S. G.; Shen, H.; Richmond, M. G. *Struct. Chem.* **2001**, *12*, 225.

(13) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: New York, 1987.

(14) Shen, H.; Bott, S. G.; Richmond, M. G. *J. Chem. Crystallogr.* **1997**, *27*, 25.

μ,η^2,η^1-PhC=CHtol-p or μ,η^2,η^1-PhHC=Ctol-p, depending on whether hydride attack takes place at the acetylide C$_\alpha$ or C$_\beta$ carbon atom. Alternatively, if the reductive elimination of the bpcd-derived Ru–Ph phenyl group precedes the hydride transfer, a symmetrically bound PhC≡Ctol-p ligand would result, followed by insertion into the metal–hydride bond. This scheme should produce isomeric alkenyl clusters having a scrambled hydride with no regiochemical preference. Implicit in these two scenarios is the absence of a reversible activation of the alkenyl C–H bond at the ruthenium cluster to furnish a hydrido-alkyne intermediate that could then equilibrate the hydride ligand between both alkyne carbon centers. A more likely fate for the once formed alkenyl ligand in our isomeric cluster products would involve a reversible dissociation of the alkenyl moiety from the cluster frame to afford a terminal alkenyl ligand, which in the absence of a suitable trapping ligand would simply revert back to a bridging alkenyl ligand.[16]

Refluxing samples of HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p$) in DCE led to the formation of the alkenyl-bridged clusters Ru$_3$(CO)$_7$(μ,η^2,η^1-RC=CHR′)[μ_2,η^2,η^1-PPhC=CC(O)CH$_2$C(O)PPh$_2$], as shown by eq 1. The two

                                                                                                    (1)

isomer A   isomer B
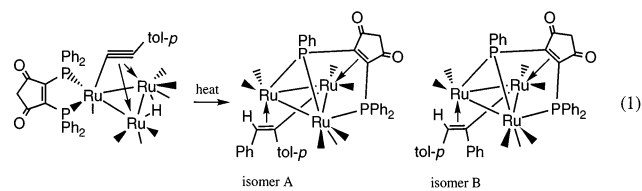
alkenyl-bridged clusters could not be separated by column chromatography and were, therefore, characterized in solution by IR and NMR spectroscopies.[17] Particularly informative concerning the isomeric composition of the two alkenyl-bridged clusters are the ^{1}H and ^{31}P NMR data. The ^{1}H NMR spectrum reveals the presence of two alkenyl CH protons at δ 6.25 and 6.18 and a doubling of the AB quartet belonging to the dione methylene groups for the two clusters. Integration of these two groups indicates that the ratio of the two

(15) The synthesis of HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p$) followed the same procedure as described for cluster **2**, with the yield of a typical thermolysis reaction being ca. 25%. The IR spectrum of HRu$_3$(CO)$_7$-(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p$) is indistinguishable from that of cluster **2**. HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p$) was characterized in solution by NMR. ^{1}H NMR (CDCl$_3$): δ 8.70–7.00 (24H, aromatic multiplet), 3.55 (2H, AB quartet, J_{H-H} = 22.3 Hz), 2.48 (3H, methyl), −20.81 (1H, s, bridging hydride). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 75.95 (s).

(16) For examples of bridged alkenyl clusters resulting from alkyne insertion into a metal–hydride bond and facile alkenyl decoordination/recoordination reactivity, see: (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E. W.; Bonnet, J.-J. *J. Am. Chem. Soc.* **1990**, *112*, 8607. (b) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *J. Mol. Catal.* **1992**, *71*, L7. (c) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 4352. (d) Alvarez, S.; Briard, P.; Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Mulla, F.; Ouahab, L.; Riera, V. *Organometallics* **1994**, *13*, 4360.

(17) (a) Chromatographic separation of Ru$_3$(CO)$_7$(μ,η^2,η^1-RC=CHR′)-[μ_2,η^2,η^1-PPhC=CC(O)CH$_2$C(O)PPh$_2$] afforded the isomeric compounds A and B in yields on the order of 40–60%. IR (CH$_2$Cl$_2$): ν(CO) 2064 (s), 2020 (vs), 1981 (s, sh), 1974 (s), 1715 (m, dione), 1684 (m, dione) cm^{-1}. (b) Thermolysis reactions of HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p$) in sealed NMR tubes afforded the isomeric alkenyl clusters Ru$_3$-(CO)$_7$(μ,η^2,η^1-RC=CHR′)[μ_2,η^2,η^1-PPhC=CC(O)CH$_2$C(O)PPh$_2$] in ca. a 45:55 ratio, which suggests that the chromatographic support used in the isolation of these clusters does not promote hydride scrambling over the alkenyl moiety.

Table 1. X-ray Crystallographic Data and Processing Parameters for HRu$_3$(CO)$_7$[$\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-Ph$_2$PC=CC(O)CH$_2$C(O)PPh$_2$C=CPh]·CH$_2Cl_2$ (3) and Ru$_3$(CO)$_7$(μ,η^2,η^1-PhC=CHPh)[μ_2,η^2,η^1-PPhC=CC(O)CH$_2$C(O)PPh$_2$] (4)

	3	4
space group	$P2_1/c$, monoclinic	$P2_1/n$, monoclinic
a, Å	18.799(2)	20.975(2)
b, Å	9.5012(6)	13.240(1)
c, Å	24.962(2)	32.480(2)
β, deg	101.162(7)	91.991(6)
V, Å^3	4374.2(6)	9015(1)
mol formula	C$_{45}$H$_{30}$Cl$_2$O$_9$P$_2$Ru$_3$	C$_{44}$H$_{28}$O$_9$P$_2$Ru$_3$
fw	1150.80	1064.86
formula units per cell (Z)	4	8
D_{calcd} (Mg/m^{-3})	1.747	1.569
λ(Mo K α), Å	0.71073	0.71073
abs coeff (mm^{-1})	12.53	10.93
total no. of reflns	5915	11 965
no. of ind reflns	3539	4714
no. of data/res/params	3539/0/429	4714/0/605
R	0.0400	0.0539
R_w	0.0460	0.0755
GOF	0.86	0.98
weights	$[0.04F^2 + (\sigma F)^2]^{-1}$	$[0.04F^2 + (\sigma F)^2]^{-1}$

isomers is 46:54. The methyl group for the two tolyl moieties appears as a singlet at δ 2.23, while the aromatic protons exhibit a complex multiplet from δ 8.05–6.80. The alkenyl chemical shift at δ 6.25 is identical to that found for cluster **4**, and we tentatively assign this to isomer A (μ,η^2,η^1-tol-pC=CHPh) in eq 1, with isomer B having the tol-p moiety at the proton-bearing alkenyl carbon. The ^{31}P NMR data for the thermolysis product of HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p$) parallels the ^{1}H NMR data in that two alkenyl-bridged clusters are observed. Here the PPh$_2$(dione) ligands appear as a set of doublets at δ 19.81 and 19.51 coupled with their respective μ_2-PPh(dione) group. The two expected phosphido resonances actually appear as a triplet at δ 116.36 due to overlapping of the two doublets. The $^2J_{P-P}$ values for both isomers are essentially the same and on the order of 20 Hz.

The above NMR data show that the μ_2-hydride is statistically scrambled between the phenyl- and tol-p-substituted carbon atoms in the μ,η^2,η^1-RC=CHR′ moiety. This suggests, subject to the above condition of irreversible alkenyl C–H bond activation in isomers A and B, that hydride transfer from the triruthenium frame occurs via a transient cluster compound that possesses a coordinated PhC≡Ctol-p ligand and that the reductive elimination of the bpcd-derived Ru–Ph phenyl group represents the first step involved in the formation of the alkenyl ligand.[18]

IV. X-ray Diffraction Structure of Clusters 3 and 4. The solid-state structures of clusters **3** and **4** were determined by X-ray crystallography in order to establish the disposition of the bpcd ligand about the cluster polyhedron and the fate of the alkenyl ligand in both clusters. The X-ray data collection and processing parameters for **3** and **4** are given in Table 1, with selected bond distances and angles listed in Table 2.

(18) Additional experiments are planned in order to investigate and resolve the sequence concerning the phenyl and hydride transfer in these acetylide clusters.

Table 2. Selected Bond Distances (Å) and Angles (deg) in

$HRu_3(CO)_7[\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1\text{-Ph}_2PC\!=\!CC(O)CH_2C(O)PPh_2C\!=\!CPh]\cdot CH_2Cl_2$ **(3)** and

$Ru_3(CO)_7(\mu,\eta^2,\eta^1\text{-PhC}\!=\!CHPh)[\mu_2,\eta^2,\eta^1\text{-PPhC}\!=\!CC(O)CH_2C(O)PPh_2]$ **(4)**[a]

$HRu_3(CO)_7[\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1\text{-Ph}_2PC\!=\!CC(O)CH_2C(O)PPh_2C\!=\!CPh]\cdot CH_2Cl_2$ **(3)**			
Bond Distances			
Ru(1)−Ru(2)	2.862(1)	Ru(1)−Ru(3)	2.732(1)
Ru(1)−P(1)	2.324(2)	Ru(1)−C(16)	2.15(1)
Ru(1)−C(17)	2.274(9)	Ru(2)−Ru(3)	2.961(1)
Ru(2)−C(11)	2.201(8)	Ru(2)−C(15)	2.232(9)
Ru(2)−C(16)	2.13(1)	Ru(3)−C(17)	2.065(9)
P(2)−C(16)	1.732(9)	C(11)−C(15)	1.46(1)
C(16)−C(17)	1.39(1)		
Bond Angles			
C(16)−Ru(1)−C(17)	36.6(3)	C(11)−Ru(2)−C(15)	38.4(4)
Ru(1)−C(16)−Ru(2)	83.9(3)	Ru(1)−C(16)−P(2)	124.6(4)
P(2)−C(16)−C(17)	144.3(8)	Ru(1)−C(17)−Ru(3)	77.9(3)
C(16)−C(17)−C(18)	124.5(8)		
$Ru_3(CO)_7(\mu,\eta^2,\eta^1\text{-PhC}\!=\!CHPh)[\mu_2,\eta^2,\eta^1\text{-PPhC}\!=\!CC(O)CH_2C(O)PPh_2]$ **(4)**			
Bond Distances, Molecule A			
Ru(1a)−Ru(2a)	2.981(3)	Ru(1a)−Ru(3a)	3.043(3)
Ru(1a)−P(1a)	2.380(6)	Ru(1a)−P(2a)	2.355(6)
Ru(2a)−Ru(3a)	2.693(3)	Ru(2a)−C(11a)	2.19(2)
Ru(2a)−C(15a)	2.24(2)	Ru(2a)−C(16a)	2.18(2)
Ru(3a)−P(2a)	2.252(6)	Ru(3a)−C(16a)	2.22(2)
Ru(3a)−C(17a)	2.39(2)	C(11a)−C(15a)	1.45(3)
C(16a)−C(17a)	1.41(3)		
Bond Angles, Molecule A			
P(1a)−Ru(1a)−P(2a)	84.4(2)	C(11a)−Ru(2a)−C(15a)	38.1(8)
P(2a)−Ru(3a)−C(16a)	122.0(6)	P(2a)−Ru(3a)−C(17a)	135.0(6)
C(16a)−Ru(3a)−C(17a)	35.5(8)	Ru(1a)−P(2a)−Ru(3a)	82.6(2)
Ru(2a)−C(16a)−Ru(3a)	75.4(7)	Ru(2a)−C(16a)−C(17a)	120.(2)
Ru(3a)−C(17a)−C(16a)	66.(1)		
Bond Distances, Molecule B			
Ru(1b)−Ru(2b)	2.968(3)	Ru(1b)−Ru(3b)	3.010(3)
Ru(1b)−P(1b)	2.387(7)	Ru(1b)−P(2b)	2.345(6)
Ru(2b)−Ru(3b)	2.678(3)	Ru(2b)−C(11b)	2.21(2)
Ru(2b)−C(15b)	2.25(2)	Ru(2b)−C(16b)	2.17(2)
Ru(3b)−P(2b)	2.260(6)	Ru(3b)−C(16b)	2.19(2)
Ru(3b)−C(17b)	2.34(2)	C(11b)−C(15b)	1.47(3)
C(16b)−C(17b)	1.39(3)		
Bond Angles, Molecule B			
P(1b)−Ru(1b)−P(2b)	84.9(2)	C(11b)−Ru(2b)−C(15b)	38.4(8)
P(2b)−Ru(3b)−C(16b)	122.5(6)	P(2b)−Ru(3b)−C(17b)	136.3(6)
C(16b)−Ru(3b)−C(17b)	35.5(8)	Ru(1b)−P(2b)−Ru(3b)	81.6(2)
Ru(2b)−C(16b)−Ru(3b)	75.7(7)	Ru(2b)−C(16b)−C(17b)	121.(2)
Ru(3b)−C(17b)−C(16b)	78.(1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Figure 1 shows the ORTEP diagram of cluster **3**. The structure of **3** consists of a planar array of three ruthenium atoms, whose Ru−Ru bond distances range from 2.732(1) Å [Ru(1)−Ru(3)] to 2.961(1) Å [Ru(2)−Ru-(3)] and are in full agreement with their single-bond designation.[19] The structural highlights of this 48e⁻ cluster rest with the disposition of the ancillary bpcd ligand about the cluster polyhedron and its role as an 8e⁻ donor ligand. Here the PPh₂ ligand attached to the Ru(1) center and dione π bond coordinated to the Ru(2) center both function as 2e⁻ donors, while the metalated alkyne moiety that bridges all three ruthenium centers via two formal σ bonds and one π bond completes the

8e⁻ count. The formation of the zwitterionic structure associated with **3** is the direct result of PPh₂ attack on the old acetylide C_α atom, giving rise to the phosphonium center P(2) that is balanced by a formal negative charge at the Ru(2) center.[20] The C(16)−C(17) and C(11)−C(15) bond distances of 1.39(1) and 1.46(1) Å, respectively, are lengthened slightly relative to the corresponding acetylide and noncomplexed dione π bond in $HRu_3(CO)_7(bpcd)(\mu_3,\eta^2,\eta^2,\eta^1\text{-C}\!\equiv\!CBu^t)$.[4] The remaining distances and angles are unexceptional and do not require comment. Cluster **4** contains 48 e⁻ and exists as two crystallographically independent molecules in the unit cell. The ORTEP diagrams for both molecules of **4**

(19) (a) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243. (b) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1988**, *7*, 503. (c) Voss, E. J.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1994**, *33*, 1087. (d) Shen, H.; Bott, S. G.; Richmond, M. G. *Inorg. Chim. Acta* **1996**, *241*, 71.

(20) For related examples involving the formation of a phosphonium moiety via diphosphine ligand attack on a coordinated alkyne, see: (a) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1994**, *13*, 3767. (b) Yang, K.; Bott, S. G.; Richmond, M. G. *J. Organomet. Chem.* **1996**, *516*, 65.
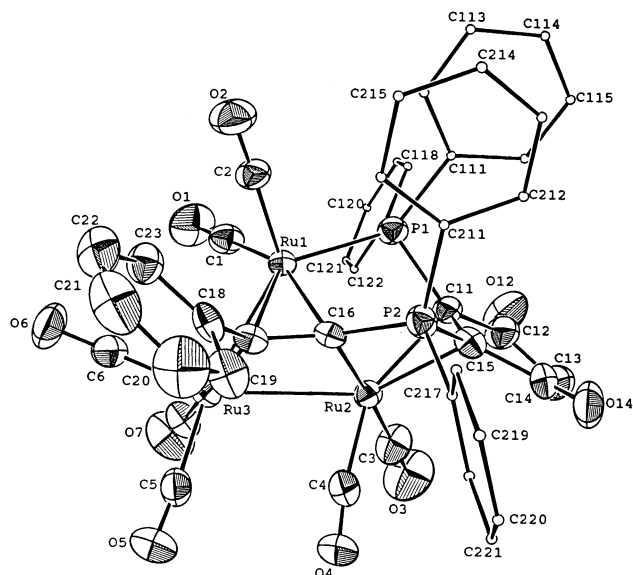
Figure 1. ORTEP drawing of the non-hydrogen atoms of HRu$_3$(CO)$_7$[$\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-Ph$_2$PC=CC(O)CH$_2$C(O)-PPh$_2$C=CPh]·CH$_2Cl_2$ (**3**) showing thermal ellipsoids at the 50% probability level. The hydride ligand that bridges the Ru(1)−Ru(3) vector and the solvent molecule have been omitted for clarity.

are shown in Figure 2, where the bridging phosphido and alkenyl moieties in **4** are readily discerned. The three ruthenium atoms in **4** form an isosceles triangle with the shorter Ru(2a)−Ru(3a) and Ru(2b)−Ru(3b) bonds of 2.693(3) and 2.678(3) Å, respectively, belonging to the alkenyl-bridged Ru−Ru vector. The other Ru−Ru bonds range from 3.043(3) Å [Ru(1a)−Ru(3a)] to 2.968(3) Å [Ru(1b)−Ru(2b)], with a mean distance of 3.001 Å. The phosphido linkage in **4** is asymmetrically tethered to the Ru(1a)−Ru(3a) and Ru(2a)−Ru(3a) vectors in molecules A and B, respectively. The asymmetric bonding of a phosphido ligand to a polynuclear core is a feature that is not unusual and that has been observed by us and others.[21] The seven ancillary CO groups in cluster **4** are all linear and exhibit bond distances and angles within normally acceptable limits. The dione π bond is coordinated to the Ru(2a) and Ru-(2b) centers in cluster **4** in a fashion analogous with that found in cluster **3**, leading to an elongation of the C(11a)−C(15a) [1.45(3) Å] and C(11b)−C(15b) [1.47(3) Å] bonds relative to the π bond distance of ca. 1.32 Å for free alkenes, in concert with the Dewar−Chatt−Duncanson model for alkene bonding.[22] Transfer of the bpcd phenyl group to the C$_\alpha$ atom of the acetylide ligand affords the observed bridging alkenyl moiety in **4** that is σ bound to the Ru(2a,b) centers and π bound to the Ru(3a,b) centers. The observed torsional angles of ca. 15° for the C(24a,b)−C(16a,b)−C(17a,b)−C(18a,b) linkages indicate that the two phenyls possess a *cis* disposition about the alkenyl moiety, as is often the case with stilbene-like alkenyl ligands.[16,23]
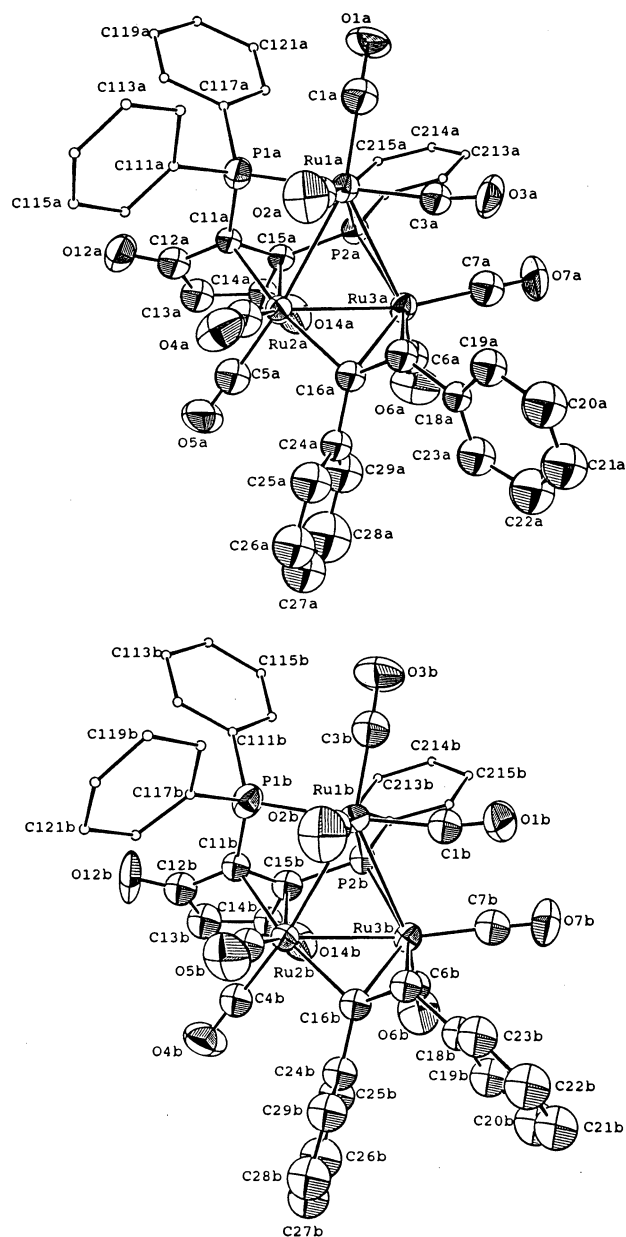

Figure 2. ORTEP drawing of the non-hydrogen atoms of the two molecules of Ru$_3$(CO)$_7$(μ,η^2,η^1-PhC=CHPh)[μ_2,η^2,η^1-PPhC=CC(O)CH$_2$C(O)PPh$_2$] (**4**) showing thermal ellipsoids at the 50% probability level.

Conclusions

Both the nature of the acetylide R group in HRu$_3$-(CO)$_9$($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CR) and the reaction conditions are shown to be important variables that control ligand substitution in this genre of cluster. Thermolysis of the parent cluster with bpcd promotes substitution to furnish the chelated product HRu$_3$(CO)$_7$(bpcd)($\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh), while cluster activation with Me$_3$NO changes the product distribution by affording the latter cluster as the minor product. The formation of the zwitterionic cluster HRu$_3$(CO)$_7$[$\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-Ph$_2$PC=CC(O)CH$_2$C-(O)PPh$_2$C=CPh] as the major product of the reaction is

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competitive with the formation of cluster **2**. X-ray structural elucidation of cluster **3** has confirmed the P-ligand attack on the coordinated acetylide in the parent cluster. We have also demonstrated that cluster **2** is a precursor to the alkenyl-bridged cluster **4** upon thermolysis, and the heating of the labeled cluster HRu_3-$(CO)_7$(bpcd)$(\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p)$ leads to a scrambled hydride ligand between the phenyl and tol-p groups in the bridging alkenyl group.

Experimental Section

General Procedures. The $Ru_3(CO)_{12}$ used in the synthesis of cluster **1** and $HRu_3(CO)_9(\mu_3,\eta^2,\eta^2,\eta^1$-C≡Ctol-$p)$ was prepared from hydrated $RuCl_3$ via the known carbonylation procedure.[24] The bpcd ligand was synthesized from 4,5-dichloro-4-cyclo-penten-1,3-dione according to the method described by Fenske.[25] The phenylacetylene and p-tolylacetylene used were purchased from Aldrich Chemical Co. and were used as received. All reaction and NMR solvents were distilled from an appropriate drying agent under argon and were handled and stored under inert atmosphere using Schlenk techniques.[26] The combustion analyses were performed by Atlantic Microlab, Norcross, GA.

Routine infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm NaCl cells. The ^1H NMR spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer, with the ^{31}P NMR data being obtained on a Varian 300 VXR-300 spectrometer operating at 121 MHz. The reported ^{31}P chemical shifts were referenced to external H_3PO_4 (85%), taken to have $\delta = 0$ and with positive chemical shifts to low field of the external standard.

Thermolysis Preparation of $HRu_3(CO)_7$(bpcd)-$(\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh). To 0.20 g (0.30 mmol) of $HRu_3(CO)_9$-$(\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) and 0.15 g (0.32 mmol) of bpcd in a Schlenk tube was added 30 mL of CH_2Cl_2 under argon flush. After the vessel was sealed, the reaction solution was heated at 50 °C for 3 days, at which time the solution gradually turned from yellow to brown-black in color. TLC analysis of the crude reaction solution using CH_2Cl_2 revealed the presence of three spots corresponding to unreacted **1** ($R_f = 0.90$; ca. <10%), $HRu_3(CO)_7$(bpcd)$(\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) ($R_f = 0.75$), and HRu_3-$(CO)_7[\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-$Ph_2PC{=}CC(O)CH_2C(O)PPh_2C{=}CPh]$ ($R_f = 0.40$, trace amount). The major product, cluster **2**, was isolated by column chromatography over silica gel using CH_2-Cl_2/petroleum ether as the eluant. Cluster **2** was recrystallized from CH_2Cl_2/hexane. Yield of **2**: 0.15 g (46.9%). IR (CH_2Cl_2): ν(CO) 2068 (s), 2050 (vs), 1994 (vs), 1935 (w), 1745 (w, dione), 1714 (m, dione) cm^{-1}. ^1H NMR (CDCl$_3$): δ 8.58–7.32 (25H, aromatic multiplet), 3.55 (2H, AB quartet, J_{H-H} = 21.3 Hz), −20.83 (1H, s, bridging hydride). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 75.73 (s). Anal. Calcd (found) for $C_{44}H_{28}O_9P_2Ru_3$: C, 49.59 (50.12); H, 2.65 (2.95).

Preparation of $HRu_3(CO)_7$(bpcd)$(\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) and $HRu_3(CO)_7[\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-$Ph_2PC{=}CC(O)CH_2C(O)-$$PPh_2C{=}CPh]$ via Me_3NO Activation. To 0.20 g (0.30 mmol) of $HRu_3(CO)_9(\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) and 0.14 g (0.30 mmol) of bpcd in a large Schlenk tube was added 40 mL of CH_2Cl_2, followed by 45.0 mg (0.60 mmol) of Me_3NO. The reaction solution was stirred for ca. 1 h under argon, after which time the solution was examined by IR and TLC analyses, which revealed the presence of two new products. After solvent removal under vacuum, the products were isolated by chro-

matography over silica gel. The first, yellow-brown band isolated using CH_2Cl_2/petroleum ether as the eluant afforded cluster **2** (vide supra) in ca. 10% yield (34.0 mg isolated). Changing the eluant to CH_2Cl_2/Et_2O (1:1) allowed for the isolation of a red band that corresponded to the zwitterionic cluster **3**. The analytical sample and single crystals of **3** suitable for X-ray diffraction analysis were grown from a CH_2-Cl_2 solution containing **3** that had been layered with hexane. Yield of **3**: 0.17 g (53.1%). IR (CH_2Cl_2): ν(CO) 2066 (s), 2001 (vs), 1965 (sh), 1719 (m, dione), 1687 (m, dione) cm^{-1}. ^1H NMR (CDCl$_3$): δ 8.02−6.56 (25H, aromatic multiplet), 3.33 (2H, AB quartet, J_{H-H} = 21.7 Hz), −12.06 (1H, s, bridging hydride). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 12.89 (d, J_{P-P} = 34.0 Hz), −0.17 (d, J_{P-P} = 34.0 Hz). Anal. Calcd (found) for $C_{44}H_{28}O_9P_2Ru_3{\cdot}1/2CH_2$-$Cl_2$: C, 48.23 (48.02); H, 2.64 (2.80).

Thermolysis of $HRu_3(CO)_7$(bpcd)$(\mu_3,\eta^2,\eta^2,\eta^1$-C≡CPh) to Give $Ru_3(CO)_7(\mu,\eta^2,\eta^1$-PhC=CHPh)$[\mu_2,\eta^2,\eta^1$-$PPhC{=}CC-$(O)CH_2C(O)PPh_2]$. To 0.20 g (0.19 mmol) of cluster **2** in a 100 mL Schlenk tube was added 20 mL of DCE, followed by refluxing for 5 h. Upon cooling, the reaction solution was examined by TLC and IR analyses, which indicated the presence of a new product. Purification by chromatography over silica gel using CH_2Cl_2/Et_2O (1:1) as the eluant afforded cluster **4** as a red solid. The analytical sample and single crystals of **4** suitable for X-ray diffraction analysis were grown from a CH_2Cl_2 solution containing **4** that had been layered with hexane. Yield of **4**: 84.0 mg (41.5%). IR (CH_2Cl_2): ν(CO) 2064 (s), 2022 (vs), 1989 (sh), 1972 (s), 1710 (m, dione), 1686 (m, dione) cm^{-1}. ^1H NMR (CDCl$_3$): δ 8.10−7.02 (25H, aromatic multiplet), 6.25 (1H, alkenyl CH), 3.48 (2H, AB quartet, J_{H-H} = 22.3 Hz). $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 116.63 (phosphido, d, J_{P-P} = 22.8 Hz), 19.77 (PPh$_2$, d, J_{P-P} = 22.8 Hz). Anal. Calcd (found) for $C_{44}H_{28}O_9P_2Ru_3$: C, 49.59 (50.12); H, 2.65 (2.95).

X-ray Diffraction Structures of $HRu_3(CO)_7$-$[\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-$Ph_2PC{=}CC(O)CH_2C(O)PPh_2C{=}CPh]{\cdot}CH_2Cl_2$ and $Ru_3(CO)_7(\mu,\eta^2,\eta^1$-PhC=CHPh)$[\mu_2,\eta^2,\eta^1$-$PPhC{=}CC(O)-$$CH_2C(O)PPh_2]$. Single crystals of **3** and **4** suitable for diffraction analysis were selected and sealed inside a Lindemann capillary, followed by mounting on the goniometer of an Enraf-Nonius CAD-4 diffractometer that employed Mo Kα radiation. Intensity data in the range $2.0 \le 2\theta \le 440$ were collected at room temperature using the ω-scan technique in the variable-scan speed mode and were corrected for Lorentz, polarization, and absorption (DIFABS). The structure of **3** was solved from the Patterson methods, while the structure of **4** was solved by using SHELX-86. In the case of cluster **3**, all non-hydrogen atoms were refined anisotropically, with the exception of the phenyl groups associated with the bpcd ligand and the chlorine atoms of the solvent. Refinement for **3** converged at $R = 0.0400$ and $R_w = 0.0460$ for 3539 unique reflections with $I > 3\sigma(I)$. All non-hydrogen atoms in cluster **4** were refined anisotropically, with the exception of the carbon atoms. The refinement for **4** converged at $R = 0.0539$ and $R_w = 0.0755$ for 4714 unique reflections with $I > 3\sigma(I)$.

Supporting Information Available: Textual presentations of the crystallographic and experimental details, listings of crystallographic data, bond distances, bond angles, and atomic and thermal parameters of $HRu_3(CO)_7[\mu_3,\eta^2,\eta^2,\eta^1,\eta^1,\eta^1$-$Ph_2PC{=}CC(O)CH_2C(O)PPh_2C{=}CPh]{\cdot}CH_2Cl_2$ (**3**) and $Ru_3(CO)_6$-$(\mu,\eta^2,\eta^1$-PhC=CHPh)$[\mu_2,\eta^2,\eta^1$-$PPhC{=}CC(O)CH_2C(O)PPh_2]$ (**4**).

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