

Reactivity of a Triruthenium Acetylide Complex toward Alkynes and the Silica-Mediated Dehydration of Cluster-Bound Alkynols: X-ray Crystal Structures of the Novel Butadienylic Species

$[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ and the Unusual Complex $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{-OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$

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The lightly ligated complex $[\text{Ru}_3(\text{CO})_8(\text{MeCN})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**4**), derived from $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**1**), reacts with terminal alkynes and alkynols under very mild conditions to give high yields of products derived from addition of three molecules of alkyne/alkynol. More interestingly, complex **4** also reacts with diphenylacetylene to form the novel butadienylic species $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ (**6**), stabilized by an uncommon interaction between a phenyl substituent and a cluster metal atom. Its formation represents a key step in understanding the reaction mechanism leading to tri- and tetra-alkyne-substituted derivatives. The acetonitrile derivative of **6** reacts further with diphenylacetylene to afford the complex $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}\{\mu_3\text{-}\eta^4\text{-C}(\text{Ph})=\text{C}(\text{Ph})\}]$ (**7**), which, upon heating, isomerizes to give $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{Ph})\text{H}\}\{\mu_3\text{-}\eta^4\text{-C}(\text{Ph})=\text{C}(\text{Ph})\}]$ (**2**) in high yield. The analogous complex $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{CPh}_2\text{OH})\text{H}\}\{\mu_3\text{-}\eta^4\text{-C}(\text{CPh}_2\text{OH})=\text{C}(\text{Ph})\}]$ (**8**) is formed directly from **4** through reaction with 1,1,3-triphenyl-2-propyn-1-ol. Finally, the tetra-alkyne-substituted metallacyclic complex $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CC}(\text{CPh}_2\text{OH})\text{CH}_2\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**5a**), obtained from reaction of 1,1-diphenyl-2-propyn-1-ol with **4**, undergoes facile dehydration in the presence of silica gel to yield the cluster complex $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**9**), a process that involves formation of an unusual heterocycle. In addition, complex **9** contains a terminal carbene unit, one of the first examples of such a ligand in a cluster complex. The structures of complexes **6**, **8**, and **9** have been determined crystallographically and are discussed in association with possible reaction mechanisms.

Introduction

The ease of synthesis of the acetylide complex $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**1**) has led to numerous studies being carried out into its reactivity and catalytic behavior.¹ Investigations into the reactivity of complex **1** toward alkynes have led to the isolation of the clusters **2** and **3** (see Scheme 1) via addition of two or three molecules of alkyne, carbon–carbon bond formation, hydride migration, and, in some cases, CO insertion.^{2–4} The isolation of complex **2**, containing a butadienic chain

common to all of the alkyne linkage products and a “lone” molecule of diphenylacetylene coordinated to the opposite face of the Ru_3 triangle, led to the suggestion that formation of the dienic ligand occurs first and that further alkyne addition takes place in a second step. However, formation of a complex in which only one molecule of alkyne has added to form a butadienic chain was never effected under the reaction conditions (Δ , heptane). Loss of carbonyl groups can be effected at room temperature (or below) via addition of trimethylamine-*N*-oxide and the resulting species stabilized by a weakly coordinating ligand.⁵ Reactions with suitable two-electron donor molecules can then be carried out under mild conditions, often leading to the isolation of

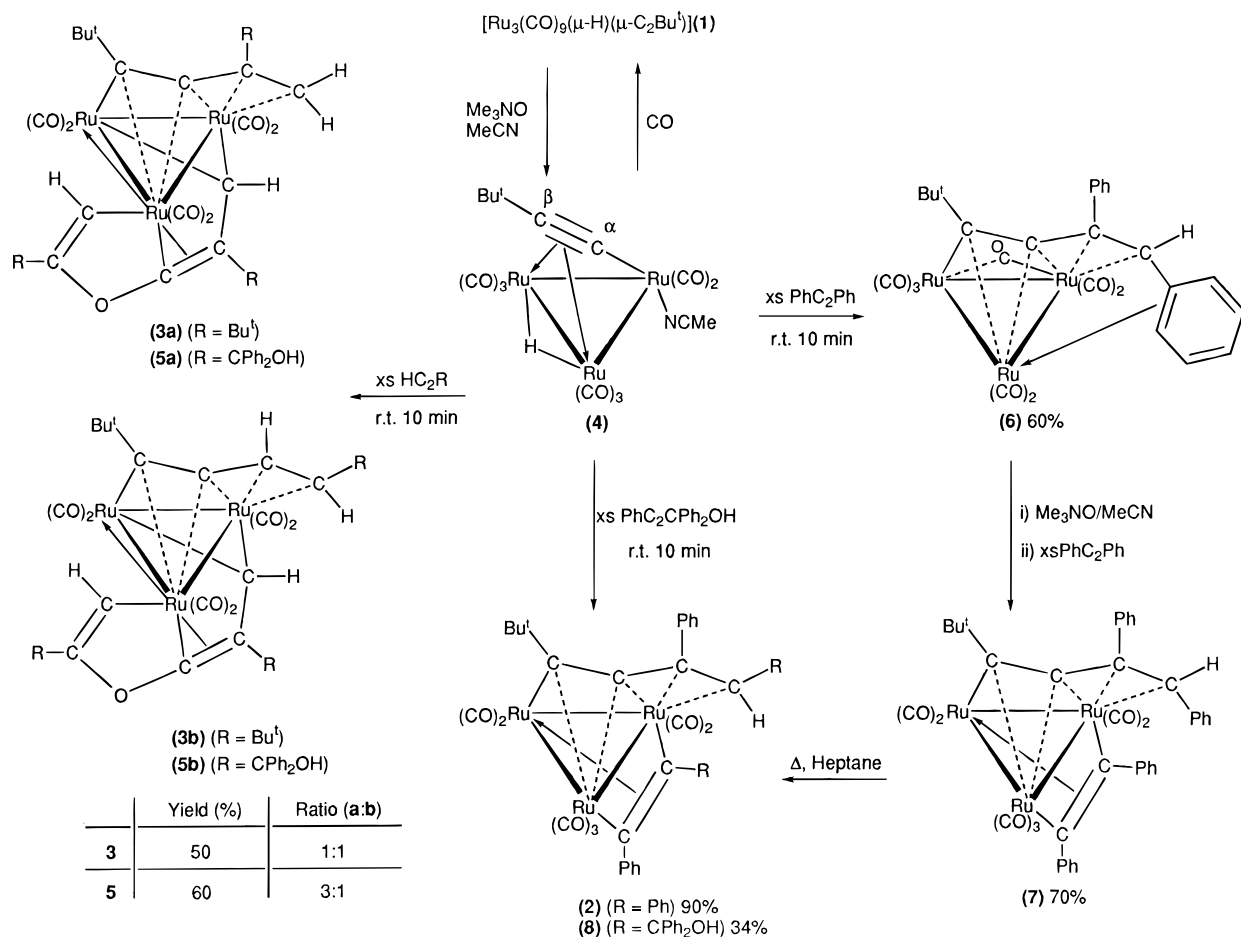
(1) Sappa, E. *J. Cluster Sci.* **1994**, 5, 211.

(2) Aime, S.; Gervasio, G.; Milone, L.; Sappa, E.; Franchini-Angela, M. *Inorg. Chim. Acta* **1978**, 26, 223.

(3) Aime, S.; Gervasio, G.; Milone, L.; Sappa, E.; Franchini-Angela, M. *Inorg. Chim. Acta* **1978**, 27, 145.

(4) Gervasio, G.; Sappa, E.; Lanfredi, A.; Tiripicchio, A. *Inorg. Chim. Acta* **1982**, 61, 217.

(5) See, for example, Foulds, G. A.; Johnson, B. F. G.; Lewis, J. J. *Organomet. Chem.* **1985**, 296, 147.

Scheme 1. Reactivity of **4** toward Alkynes

intermediates that are not seen in the corresponding thermal reactions of the parent carbonyl clusters.⁶ We report here on the synthesis of the acetonitrile derivative of **1**, i.e., $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**4**), and its reactivity toward alkynes at room temperature. The reactivity of **4** toward terminal alkynes follows the same pattern observed for the unsubstituted complex **1** although under much milder conditions. In addition, when $\text{HC}_2\text{CPh}_2\text{OH}$ is used in the reaction, an interesting dehydration process is observed for one of the products. In contrast, reaction of **4** with diphenylacetylene affords the title complex **6**, containing a butadienic fragment, the complex being stabilized through an unusual phenyl interaction with one of the ruthenium atoms. Subsequent reactions show this complex to be the “missing link” in the formation of complexes derived from two and three molecules of alkyne. Reaction of **4** with the asymmetric alkyne $\text{PhC}_2\text{CPh}_2\text{OH}$ results in formation of the bis-alkyne species **8**.

Results and Discussion

Synthesis of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (4**).** Complex **4** was obtained by displacement of a carbonyl ligand from the acetylide complex **1** using trimethylamine-*N*-oxide in acetonitrile solvent.

The reverse reaction can be readily effected by purging a dichloromethane solution of **4** with carbon mon-

oxide gas, which affords the parent carbonyl species **1** in 95% yield after 5 min.

It was not possible to obtain a ^1H NMR spectrum of good quality, and therefore, without a crystallographic study of complex **4** it is not clear which of the several possible sites in complex **1** is being occupied by the acetonitrile. However, previous studies on monophosphine-substituted derivatives of **1** have shown that the phosphine ligands occupy a “radial” site, approximately cis to C_α of the acetylide unit,⁷ and it is likely that the acetonitrile ligand is in an analogous position in **4**.

Reactivity of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (4**) toward Terminal Alkynes ($\text{HC}\equiv\text{CR}$).** Complex **4** reacts with an excess of *tert*-butyl acetylene, at room temperature, to afford the green complexes $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CC}(\text{Bu}^t)\text{CH}_2\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{Bu}^t)\text{COC}(\text{Bu}^t)\text{-CH}\}]$ (**3a**) and $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CCH}(\text{Bu}^t)\text{C}(\text{Bu}^t)\text{H}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{Bu}^t)\text{COC}(\text{Bu}^t)\text{CH}\}]$ (**3b**) in a combined yield of 50%. These complexes were previously synthesized from reaction of **1** or $[\text{Ru}_3(\text{CO})_{12}]$ with excess $\text{Bu}^t\text{C}\equiv\text{CH}$ in refluxing heptane (albeit in yields of less than 5%) and were readily characterized through comparison of their IR, NMR, and mass spectroscopic data.^{2,8} The isomers have been shown to arise from the asymmetry of the alkyne coupling to the α -carbon of the acetylide

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(8) Aime, S.; Gervasio, G.; Milone, L.; Sappa, E.; Franchini-Angela, M. *Transition Met. Chem.* **1976**, *1*, 96.

(6) See, for example: Aime, S.; Arce, A.; De Danctis, Y.; Gobetto, R.; Milone, L.; Osella, D.; Violano, L. *Organometallics* **1991**, *10*, 2854.

ligand and forming a butadienic chain. The ^1H NMR spectrum of **3a,b** showed the isomers to be present in a 1:1 ratio, which mirrors the result obtained previously from the thermal reaction.

It was previously found that thermolysis of complex **1** in the presence of excess $\text{Bu}^t\text{C}\equiv\text{CH}$ led to formation of a red complex, $[\text{Ru}_3(\text{CO})_5(\text{C}_{12}\text{H}_{20})(\text{C}_{19}\text{H}_{30}\text{O})]$, derived from addition of four molecules of alkyne.⁹ The isolation of trace amounts of a red substance from our reaction led to the suggestion that some of this complex may be being produced. However, IR spectroscopy failed to support this hypothesis, and employing longer reaction times did not appear to increase the yield of the unknown complex.

Interestingly, complex **4** reacts with an excess of 1,1-diphenyl-2-propyn-1-ol ($\text{HC}\equiv\text{CCPh}_2\text{OH}$) to afford the green complexes $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CC}(\text{CPh}_2\text{OH})\text{-CH}_2\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**5a**) and $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CCHC}(\text{CPh}_2\text{OH})\text{H}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**5b**) in a combined yield of 60% and a small amount of the black complex $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$, discussed later. The spectroscopic data for the new complexes **5a,b** agree well with those of complexes **3**, suggesting that complexes **5a** and **5b** are isomers with the structures shown in Scheme 1. Thus, both complexes contain two fused metallacycles on one face of the Ru_3 triangle (formally formed through head-to-head coupling of two propargyl alcohol units with CO insertion) and, on the opposite face, a butadienic chain. For complexes **3** the latter was shown to be formed through carbon–carbon bond formation between the incoming alkyne and the acetylide unit of **1** with hydride migration from the Ru–Ru vertex to the γ -carbon of the chain.²

The ^1H NMR spectrum of **5a,b** showed the isomers to be present in a ratio of ca. 3:1 (**5a:5b**), with the major isomer being that containing a butadienic chain formed through head-to-tail coupling of a propargyl alcohol with the acetylide unit of **4**, as indicated by the presence of signals due to a CH_2 group in the ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ DEPT NMR spectra. The minor isomer is that in which the butadienic chain has been formed through head-to-tail coupling of the alkyne and acetylide, with the unique proton held endo with respect to the metal center and appearing as a doublet in the ^1H NMR spectrum with $J = 8$ Hz, cf. $J = 11$ Hz for complex **3b**. This is expected on steric grounds, as it allows the bulky CPh_2OH group of the chain to be held pointing away from the metal center.

The disparity in the abundance of the isomers **5a,b** is puzzling given that complexes **3a,b** were formed in a 1:1 ratio regardless of the reaction conditions. Indeed, from steric considerations complex **5b** might be expected to be present in greater amounts than **5a**, as any steric interactions between the CPh_2OH and Bu^t groups would be minimized. It may be that the differences in the isomer ratios are due to electronic effects.

Isolation of the tetra-alkynic complexes **3a,b** and **5a,b** in good yields under the mild reaction conditions used (20 min, room temperature) suggests that, as expected, the acetonitrile-derived species **4** is more reactive than

the unsubstituted complex **1** toward alkynes. However, the facile nature of alkyne addition to the acetylide complex and of the carbon–carbon bond formation, CO insertion, and hydride migration processes that take place is surprising. Further, the failure to isolate any of the proposed intermediates in the formation of complexes such as **3a,b** and **5a,b** suggests that, for terminal alkynes, these processes occur very readily. Indeed, the use of equimolar amounts of alkyne and complex **4** in the above reactions gave the same products but in greatly reduced yields.

As was previously mentioned, heating complex **1** in the presence of diphenylacetylene gave the bis-diphenylacetylene species **2**, a supposed intermediate in the formation of the tris-alkyne complexes obtained from terminal alkynes. With this in mind the reactivity of **4** toward internal alkynes was investigated.

Reactivity of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (4**) toward Internal Alkynes ($\text{PhC}\equiv\text{CR}$).** Addition of diphenylacetylene to complex **4** results in formation of the novel butadienic species $[\text{Ru}_3(\text{CO})_8\{\mu\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ (**6**) in high yield. The structure of the product was confirmed by an X-ray diffraction study and is discussed later. The spectroscopic properties of complex **6** are consistent with the solid-state structure. The solution IR spectrum contains a band at 1953 cm^{-1} , indicative of an asymmetrically bridging carbonyl unit. The ^1H NMR spectrum shows a doublet at $\delta\ 5.6$ for the proton attached to the metal-bound ortho-carbon of the phenyl group on C_γ and a singlet at $\delta\ 5.5$ for the proton on C_γ , suggesting it is held in an exo position.

Ruthenium and osmium clusters containing C_4 butadienylic (or related) chains are known; they may be obtained from diynes¹⁰ or via C–C bond forming reactions between cluster-coordinated acetylenes or acetylides and free C_2 ligands¹¹ and also by coupling of the coordinated acetylide of **1** and a phenylacetylide originating from a diphenylphosphino ligand.¹²

However, organometallic complexes containing a metal–phenyl π -interaction analogous to that seen in **6** are rare. One example is the di-iron complex formed from deoxygenation of the alkynol $\text{HC}_2\text{C}(\text{Me})(\text{OH})\text{Ph}$.¹³ The most recent example involving a cluster is the alkyne complex $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-PhC}_2\text{-}$

(10) See, for example: (a) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1993**, *12*, 1365. (b) Corrigan, J. F.; Taylor, N. J.; Carty, A. J. *Organometallics* **1994**, *13*, 3378. (c) Blenkiron, P.; Enright, G. D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1996**, *15*, 2855. (d) Blenkiron, P.; Enright, G. D.; Low, P. J.; Corrigan, J. F.; Taylor, N. J.; Chi, Y.; Saillard, J.-Y.; Carty, A. J. *Organometallics* **1998**, *17*, 2447. (e) Blenkiron, P.; Enright, G. D.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1997**, 483. (f) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **1997**, *536*, 93. (g) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Organomet. Chem.* **1998**, *558*, 197.

(11) See, for example: (a) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans.* **1999**, 13. (b) Eveland, R. W.; Raymond, C. C.; Shriver, D. F. *Organometallics* **1999**, *18*, 534. (c) Carty, A. J.; Hogarth, G.; Enright, G.; Frapper, G. *J. Chem. Soc., Chem. Commun.* **1997**, 1883. (d) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1996**, 969. (e) Carty, A. J.; Chi, Y.; Blenkiron, P.; Delgado, E.; Enright, G. D.; Wang, W.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1996**, *15*, 5269. (f) Shiu, C.-W.; Chi, Y.; Chung, C.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1998**, *17*, 2970. (g) Delgado, E.; Chi, Y.; Wang, W.; Hogarth, G.; Low, P. J.; Enright, G. D.; Peng, S.-M.; Lee, G.-H.; Carty, A. J. *Organometallics* **1998**, *17*, 2936.

(12) Sappa, E.; Pasquini, G.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Dalton Trans.* **1989**, 601.

(13) Gervasio, G.; Sappa, E. *Organometallics* **1993**, *12*, 1458, and references therein.

(9) Gervasio, G.; Sappa, E.; Lanfredi, A.; Tiripicchio, A. *Inorg. Chim. Acta* **1993**, *68*, 171.

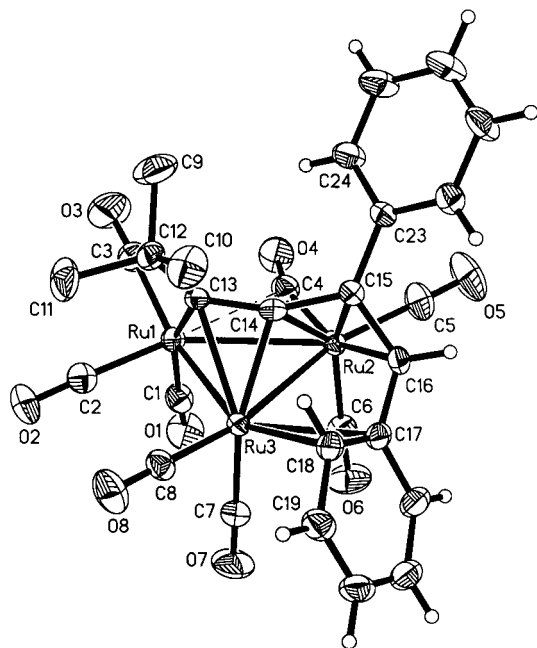


Figure 1. Molecular Structure of **6**, showing labeling scheme.

$\text{Bu}^t(\text{CO})_6]$ synthesized by Bruce and co-workers via phenyl transfer from a coordinated dpmm molecule of the acetylide complex $[\text{Ru}_3(\mu\text{-H})(\mu\text{-dpmm})(\mu_3\text{-C}_2\text{Bu}^t)(\text{CO})_7]$.¹⁴

Reaction of **6** with $\text{Me}_3\text{NO}/\text{MeCN}$ followed by addition of excess alkyne afforded the bis-diphenylacetylene complex $[\text{Ru}_3(\text{CO})_7\{\mu\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}\{\mu\text{-}\eta^4\text{-CPh}=\text{CPh}\}]$ (**7**) in 70% yield. The spectroscopic data for complex **7** suggested that it was an isomer of the previously isolated species **2**, but to allow a proper comparison the spectroscopic data of **2** were rerecorded. Pertinent differences in these data are as follows: in the IR spectrum an extra CO stretch at 2033 cm^{-1} is present for complex **2**; in the ^1H NMR spectra a lower field chemical shift for the unique proton of the butadienic chain is observed for complex **7** (δ 6.2 cf. δ 3.2 for complex **2**). All other data agree well.

We propose, therefore, that the complexes **2** and **7** are isomeric, differing only in the orientation of the Ph and H substituents on the γ -carbon of the C4-chain. The following observations support this:

i. The low-field chemical shift for the unique proton of **7** is close to that of the equivalent proton in complex **6**.

ii. Comparison of the X-ray structures of complexes **2**⁴ and **6** (the precursor of complex **7**) clearly shows the proton of **2** is held endo, whereas that of **6** is held exo (see Figure 2). The ^1H NMR spectra of the two complexes show that their structures in solution correspond with those found in the solid state.

iii. Thermolysis of complex **7** in heptane leads to formation of complex **2** in 80% yield, along with some decomposition. Presumably, such an isomerization is driven by the fact that it minimizes interactions between the bulky phenyl group and the rest of the cluster.

The last observation suggests that complex **2** is the thermodynamically favored isomer.

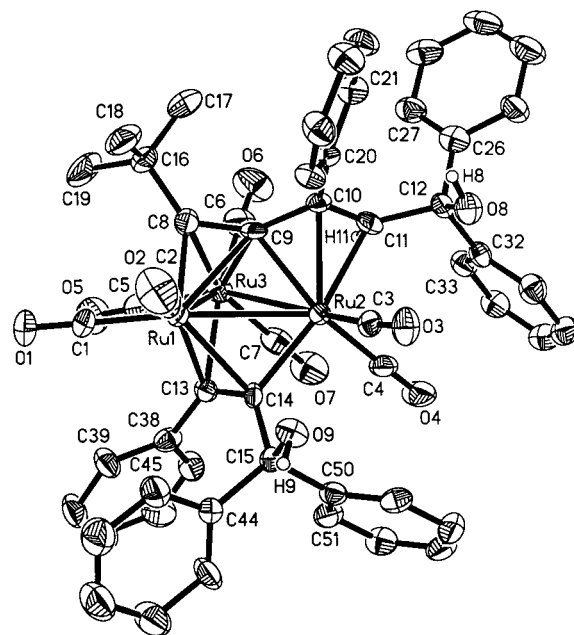


Figure 2. Molecular structure of **8**, showing labeling scheme.

Interestingly, addition of the alkynol $\text{PhC}\equiv\text{CCPh}_2\text{OH}$ to the acetonitrile derivative **4** afforded $[\text{Ru}_3(\text{CO})_7\{\mu\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{CPh}_2\text{OH})\text{H}\}\{\mu\text{-}\eta^4\text{-C}(\text{CPh}_2\text{OH})=\text{CPh}\}]$ (**8**), the structural analogue of complex **2**, and trace amounts of a red complex. Complex **8** was fully characterized through comparison of its spectroscopic data with those of complexes **2** and **7** and its structure firmly established through an X-ray diffraction study. The solid-state structure showed that the organic fragments in **8** were formed through linkage of the phenyl-substituted end of the incoming alkyne moiety with the acetylide ligand of **4** and addition of a second alkyne molecule on the opposite face of the triruthenium center, bound in the parallel fashion commonly seen for trimetallic μ_3 -alkyne complexes.¹⁵

It should be noted that for the asymmetric alkynes $\text{HC}\equiv\text{CBu}^t$ and $\text{HC}\equiv\text{CCPh}_2\text{OH}$ the products existed as isomers arising from the alkynes undergoing both head-to-tail and tail-to-tail linkage with the α -carbon of the acetylide unit in **4** to form a butadienylic chain. Conversely, for the bis-alkyne derived species **8**, only one form of the butadienylic chain is seen in the NMR spectra and the solid-state structure. This may mean that, of the asymmetric alkynes, only triphenyl-1-propyn-2-ol shows 100% regioselectivity in its linking, although such a result would be the opposite of that expected on steric grounds and thus tends to confirm that electronic effects control the linkage. However, in this regard it should be noted that trace amounts of an unstable red complex were isolated from the reaction of **4** with triphenyl-1-propyn-2-ol, the IR spectrum of which bears a striking resemblance to that of the butadienylic complex $[\text{Ru}_3(\text{CO})_8\{\mu\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ (**6**). Thus, bands at 2078s, 2046vs, 2011vs, 2007s, 1997vs, 1983m(sh), and 1950w cm^{-1} agree well with those seen at 2075vs, 2044vs, 2014vs, 2004vs, 1996m(sh), 1985w, and 1953m cm^{-1} for **8**. Further, the

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(15) Deabate, S.; Giordano, R.; Sappa, E. *J. Cluster Sci.* **1997**, *8*, 407.

IR spectrum of the reaction mixture indicates that this compound is formed in significant amounts during the reaction but apparently degrades rapidly on alumina, silica gel, and Florosil, even under an atmosphere of nitrogen. It is tempting to suggest that the unidentified red complex may be that containing a butadienylic chain formed via linkage of the CPh₂OH-substituted end of the alkyne with the acetylide fragment of **4** and stabilization of the complex through coordination of the phenyl substituent on the other alkyne carbon with the metal center. Such a result would be in keeping with all of our earlier observations and with the steric considerations mentioned above.

Several conclusions can be drawn from the above results. The fact that the alkynes RC≡CR' (R = Ph, R' = Ph or CPh₂OH) yield "unsubstituted" butadienylic complexes such as **6** strongly suggests that such intermediates are only isolated when a stabilizing phenyl-metal interaction is possible. Further, the failure to isolate such a complex from the reaction with HC≡CCPh₂OH implies that such interactions occur only when the incoming alkyne contains a terminal phenyl group.

Isolation of the butadienylic complex **6** from reaction of **4** with diphenylacetylene supports the earlier hypothesis that for complexes **2** and **5** alkyne addition has occurred via initial formation of the butadienylic chain common to all these clusters. That complex **2** (previously isolated from thermolysis of **1** in the presence of diphenylacetylene) can be formed from **6** further suggests that **6** is a true intermediate in alkyne oligomerization in this system. The reaction occurs in two steps, the first involving coordination of a molecule of diphenylacetylene in parallel fashion onto the unsubstituted face of the ruthenium triangle to form complex **7**; a molecule of CO is also lost during the process. The second step is a thermally induced isomerization of the butadienylic chain in complex **7**, suggesting that complex **2** represents the thermodynamically favored form of this species.

It is interesting to note that although complexes such as **3** and **5**, derived from addition of three molecules of alkyne to complex **4**, are readily isolated when terminal alkynes are used, no analogous species were obtained from the internal alkynes. One attempt was made at forming such complexes through formation of the acetonitrile derivative of complex **2** and addition of excess diphenylacetylene, but the reaction yielded only starting material and trace amounts of several brown products, the IR spectra of which were inconsistent with complexes **3** and **5**. Prolonged heating of complex **2** in the presence of excess diphenylacetylene also proved unsuccessful.

X-ray Structures of [Ru₃(CO)₈{μ-η⁸-C(Bu^t)=CC(Ph)=C(H)Ph}] (6**) and [Ru₃(CO)₇{μ-η⁶-C(Bu^t)=CC(Ph)=C(CPh₂OH)H}{μ-η⁴-C(CPh₂OH)=CPh}] (**8**).** The molecular structures of complexes **6** and **8** are shown in Figures 1 and 2, and their relevant structural parameters presented in Tables 1 and 2, respectively.

For both complexes **6** and **8** the three ruthenium atoms form an isosceles triangle, of which the Ru(1)–Ru(3) edge [2.6533(5) Å, **6**; 2.6823(10) Å, **8**] is significantly shorter than both the Ru(1)–Ru(2) and Ru(2)–Ru(3) edges [2.9728(5) and 2.8383(4) Å, **6**; 2.8672(10) and 2.8341(10) Å, **8**, respectively].

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **6**

| | | | |
|-------------------|------------|-------------------|-----------|
| Ru(1)–C(13) | 2.088(3) | C(12)–C(13) | 1.534(4) |
| Ru(1)–Ru(3) | 2.6533(5) | C(13)–C(14) | 1.348(4) |
| Ru(1)–Ru(2) | 2.9728(5) | C(14)–C(15) | 1.422(4) |
| Ru(2)–C(4) | 1.937(4) | C(15)–C(16) | 1.454(4) |
| Ru(2)–C(14) | 2.179(3) | C(15)–C(23) | 1.487(5) |
| Ru(2)–C(15) | 2.198(3) | C(16)–C(17) | 1.473(5) |
| Ru(2)–C(16) | 2.215(3) | C(17)–C(18) | 1.416(4) |
| Ru(2)–Ru(3) | 2.8383(4) | C(17)–C(22) | 1.423(4) |
| Ru(3)–C(14) | 2.120(3) | C(18)–C(19) | 1.412(5) |
| Ru(3)–C(13) | 2.343(3) | C(19)–C(20) | 1.358(5) |
| Ru(3)–C(18) | 2.439(3) | C(20)–C(21) | 1.392(6) |
| Ru(3)–C(17) | 2.538(3) | C(21)–C(22) | 1.362(6) |
| C(4)–O(4) | 1.143(4) | | |
| Ru(3)–Ru(1)–Ru(2) | 60.275(12) | C(16)–C(15)–Ru(2) | 71.38(18) |
| C(4)–Ru(2)–Ru(1) | 61.04(10) | C(23)–C(15)–Ru(2) | 120.9(2) |
| Ru(3)–Ru(2)–Ru(1) | 54.276(12) | C(15)–C(16)–C(17) | 123.1(3) |
| Ru(1)–Ru(3)–Ru(2) | 65.449(12) | C(15)–C(16)–Ru(2) | 70.15(18) |
| O(4)–C(4)–Ru(2) | 161.5(3) | C(17)–C(16)–Ru(2) | 108.5(2) |
| C(14)–C(13)–C(12) | 124.9(3) | C(18)–C(17)–C(22) | 117.5(3) |
| C(14)–C(13)–Ru(1) | 99.8(2) | C(18)–C(17)–C(16) | 122.6(3) |
| C(12)–C(13)–Ru(1) | 135.0(2) | C(22)–C(17)–C(16) | 119.2(3) |
| C(14)–C(13)–Ru(3) | 63.56(18) | C(18)–C(17)–Ru(3) | 69.66(18) |
| C(12)–C(13)–Ru(3) | 128.5(2) | C(22)–C(17)–Ru(3) | 114.0(2) |
| Ru(1)–C(13)–Ru(3) | 73.30(9) | C(16)–C(17)–Ru(3) | 95.0(2) |
| C(13)–C(14)–C(15) | 156.8(3) | C(19)–C(18)–C(17) | 119.4(3) |
| C(13)–C(14)–Ru(3) | 81.7(2) | C(19)–C(18)–Ru(3) | 109.1(2) |
| C(15)–C(14)–Ru(3) | 119.0(2) | C(17)–C(18)–Ru(3) | 77.36(19) |
| C(13)–C(14)–Ru(2) | 124.7(2) | C(20)–C(19)–C(18) | 121.0(4) |
| C(15)–C(14)–Ru(2) | 71.77(16) | C(19)–C(20)–C(21) | 120.3(4) |
| Ru(3)–C(14)–Ru(2) | 82.60(10) | C(22)–C(21)–C(20) | 120.3(3) |
| C(14)–C(15)–C(16) | 111.7(3) | C(21)–C(22)–C(17) | 121.4(3) |
| C(14)–C(15)–C(23) | 124.7(3) | C(28)–C(23)–C(15) | 120.4(3) |
| C(16)–C(15)–C(23) | 123.3(3) | C(24)–C(23)–C(15) | 121.1(3) |
| C(14)–C(15)–Ru(2) | 70.34(16) | | |

In complex **6** the Ru(1)–Ru(2) edge is asymmetrically bridged by the C(4)O(4) carbonyl unit having a Ru(2)–C(4)–O(4) angle of 161.5(3)° and Ru(1)–C(4) and Ru(2)–C(4) lengths of 2.648(5) and 1.937(4) Å, respectively. The remaining seven carbonyl groups are coordinated in a terminal fashion [three to Ru(1) and two to each of Ru(2) and Ru(3)]. The triruthenium center is bridged by an organic fragment formed through carbon–carbon bond formation between one end [C(15)] of a molecule of diphenylacetylene and the α-carbon [C(14)] of the acetylide unit of complex **4**, and hydride migration from the cluster to C(16) of the alkyne. The ligand bridges all three metal atoms, acting as a σ-donor to Ru(1) and π-donor to Ru(2) and Ru(3), formally donating eight electrons to the metal center. Some donation of the π-electron density between the phenyl carbons of C(17)–C(18) to Ru(3) is occurring, with Ru(3)–C(17) and Ru(3)–C(18) distances of 2.538(3) and 2.439(3) Å, respectively. This interaction results in localization of the π-bonding in the phenyl ring, with the C(19)–C(20) and C(21)–C(22) bonds [of length 1.358(5) and 1.362(6) Å] being significantly shorter than the remaining four C–C bonds (all greater than 1.390 Å). Similar results were obtained for [Ru₃(μ-H)(μ₃-PPhCH₂PPh₂)(μ₃-PhC₂-Bu^t)(CO)₆] by Bruce et al.¹⁴

The butadienic chain of complex **6** is isomeric with that found in complex **2**. The chains differ from each other only in the respective orientations of the phenyl and protonic substituents on C(16). Presumably, this difference is due to the fact that in complex **6** the phenyl group is coordinated to Ru(3) via carbons C(17) and C(18), acting as a two-electron donor ligand and so requiring to be held endo with respect to the metal center.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $8 \cdot \frac{1}{2} \text{H}_2\text{O}$

| | | | |
|-------------------|------------|-------------------|-----------|
| Ru(1)–C(8) | 2.038(8) | C(8)–C(16) | 1.523(10) |
| Ru(1)–C(13) | 2.109(7) | C(9)–C(10) | 1.441(10) |
| Ru(1)–C(14) | 2.223(6) | C(10)–C(11) | 1.414(10) |
| Ru(1)–C(9) | 2.422(7) | C(10)–C(20) | 1.495(9) |
| Ru(1)–Ru(3) | 2.6823(10) | C(11)–C(12) | 1.528(10) |
| Ru(1)–Ru(2) | 2.8672(10) | C(12)–O(8) | 1.437(9) |
| Ru(2)–C(14) | 2.127(7) | C(12)–C(32) | 1.525(10) |
| Ru(2)–C(9) | 2.147(7) | C(12)–C(26) | 1.536(11) |
| Ru(2)–C(10) | 2.246(7) | C(13)–C(14) | 1.377(11) |
| Ru(2)–C(11) | 2.295(7) | C(13)–C(38) | 1.491(10) |
| Ru(2)–Ru(3) | 2.8341(10) | C(14)–C(15) | 1.555(10) |
| Ru(3)–C(9) | 2.176(7) | C(15)–O(9) | 1.428(8) |
| Ru(3)–C(8) | 2.298(7) | C(15)–C(44) | 1.537(10) |
| Ru(3)–C(13) | 2.395(8) | C(15)–C(50) | 1.555(9) |
| C(8)–C(9) | 1.358(10) | O(10)···H(9) | 2.0411 |
| Ru(3)–Ru(1)–Ru(2) | 61.31(3) | C(32)–C(12)–C(26) | 108.1(6) |
| Ru(3)–Ru(2)–Ru(1) | 56.13(2) | C(11)–C(12)–C(26) | 111.5(6) |
| Ru(1)–Ru(3)–Ru(2) | 62.56(3) | C(14)–C(13)–C(38) | 131.8(7) |
| C(9)–C(8)–C(16) | 131.0(7) | C(14)–C(13)–Ru(1) | 76.0(4) |
| C(9)–C(8)–Ru(1) | 88.6(5) | C(38)–C(13)–Ru(1) | 132.4(5) |
| C(16)–C(8)–Ru(1) | 135.8(6) | C(14)–C(13)–Ru(3) | 108.9(5) |
| C(9)–C(8)–Ru(3) | 67.5(4) | C(38)–C(13)–Ru(3) | 116.2(5) |
| C(16)–C(8)–Ru(3) | 131.5(5) | Ru(1)–C(13)–Ru(3) | 72.8(2) |
| Ru(1)–C(8)–Ru(3) | 76.2(2) | C(13)–C(14)–C(15) | 127.7(6) |
| C(8)–C(9)–C(10) | 146.3(6) | C(13)–C(14)–Ru(2) | 108.0(5) |
| C(8)–C(9)–Ru(2) | 134.2(6) | C(15)–C(14)–Ru(2) | 122.5(5) |
| C(10)–C(9)–Ru(2) | 74.6(4) | C(13)–C(14)–Ru(1) | 67.0(4) |
| C(8)–C(9)–Ru(3) | 77.3(4) | C(15)–C(14)–Ru(1) | 128.5(4) |
| C(10)–C(9)–Ru(3) | 131.6(5) | Ru(2)–C(14)–Ru(1) | 82.4(2) |
| Ru(2)–C(9)–Ru(3) | 81.9(2) | O(9)–C(15)–C(44) | 107.9(5) |
| C(8)–C(9)–Ru(1) | 57.3(4) | O(9)–C(15)–C(50) | 108.9(6) |
| C(10)–C(9)–Ru(1) | 139.5(5) | C(44)–C(15)–C(50) | 112.3(6) |
| Ru(2)–C(9)–Ru(1) | 77.5(2) | O(9)–C(15)–C(14) | 104.4(5) |
| Ru(3)–C(9)–Ru(1) | 71.1(2) | C(44)–C(15)–C(14) | 115.6(6) |
| C(11)–C(10)–C(9) | 116.9(6) | C(50)–C(15)–C(14) | 107.3(5) |
| C(11)–C(10)–C(20) | 124.9(6) | C(21)–C(20)–C(10) | 120.3(6) |
| C(9)–C(10)–C(20) | 117.9(6) | C(25)–C(20)–C(10) | 121.4(6) |
| C(11)–C(10)–Ru(2) | 73.7(4) | C(27)–C(26)–C(12) | 123.5(7) |
| C(9)–C(10)–Ru(2) | 67.2(4) | C(31)–C(26)–C(12) | 117.5(8) |
| C(20)–C(10)–Ru(2) | 124.8(5) | C(33)–C(32)–C(12) | 120.4(7) |
| C(10)–C(11)–C(12) | 126.5(6) | C(37)–C(32)–C(12) | 121.2(6) |
| C(10)–C(11)–Ru(2) | 70.0(4) | C(43)–C(38)–C(13) | 121.7(7) |
| C(12)–C(11)–Ru(2) | 126.2(5) | C(39)–C(38)–C(13) | 121.7(6) |
| O(8)–C(12)–C(32) | 106.8(6) | C(49)–C(44)–C(15) | 124.6(6) |
| O(8)–C(12)–C(11) | 110.2(6) | C(45)–C(44)–C(15) | 117.4(6) |
| C(32)–C(12)–C(11) | 109.4(6) | C(51)–C(50)–C(15) | 121.3(7) |
| O(8)–C(12)–C(26) | 110.7(6) | C(55)–C(50)–C(15) | 120.1(6) |

The solid-state structure of complex **8** contains seven carbonyl groups all of which are bound in a terminal fashion to the ruthenium atoms [three to Ru(3) and two to each of Ru(1) and Ru(2)] despite the fact that the IR spectrum of **8** clearly shows a band at 1934 cm^{-1} , in the range normally associated with asymmetrically bridging carbonyl groups.¹⁶ A similar situation was seen for the analogous complex $[\text{Ru}_3(\text{CO})_7\{\mu\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{Ph})\text{H}\}\{\mu\text{-}\eta^4\text{-CPh}=\text{CPh}\}]$ (**2**).⁴ Once again, the butadienylic moiety of **8** has been formed through linkage of C(10) of the incoming alkyne unit and the α -carbon C(9) of the acetylide group. The resulting chain acts as a six-electron donor, bridging all three metal atoms through a combination of σ - and π -interactions. On the opposite side of the triangular cluster is found a molecule of $\text{PhC}_2\text{CPh}_2\text{OH}$, of which the CPh_2OH -substituted carbon C(14) is σ -bound to Ru(2), the phenyl-substituted carbon C(13) is σ -bound to Ru(3), and the C(13)–C(14) bond is π -bound to Ru(1). This bonding mode, in which the alkyne is oriented nearly parallel to a metal–metal edge, has been described for

numerous homo- and hetero-trinuclear species and comparisons have been made between the structural parameters for such compounds.¹⁰ Interestingly, the alkyne molecule in **8** matches that of the equivalent diphenylacetylene ligand in **2**, in being slightly asymmetric in its bonding to the ruthenium atoms. Thus, Ru(2)–C(14), Ru(3)–C(13), Ru(1)–C(13), and Ru(1)–C(14) bond lengths of 2.127(7), 2.395(8), 2.109(7), and 2.223(6) Å, respectively, are found for **8** [cf. the corresponding lengths of 2.07(2), 2.33(2), 2.10(2), and 2.21(2) Å previously found for **2**].

In principle, an alternative isomer of **8**, in which the C(13) and C(14) substituents were exchanged, could exist. That this is not the case may be due to the observed structure having interactions between the alkyne molecule and the carbonyl groups of the cluster at a minimum.

The butadienylic chains of both **6** and **8** are best represented by the allenyl–allyl description previously used for the analogous organic fragments in the solid-state structures of complexes **2** and **3a**. Thus, the C(13)–C(16) chain of **6** and the C(8)–C(11) chain of **8** both show extensive delocalization, with C–C bond distances in the range 1.348(4)–1.454(4) Å (**6**) and 1.358(10)–1.441(10) Å (**8**). Carbons C(14), C(15), and C(16) in complex **6** and C(9), C(10), and C(11) of complex **8** form allylic fragments coordinated to Ru(2) with metal–carbon distances in the range 2.179(3)–2.215(3) Å (**6**) and 2.147(7)–2.295(7) Å (**8**) [cf. 2.12(1)–2.32(1) Å for **2** and 2.163(7)–2.253(7) Å for **3a**]. Carbon C(14) of complex **6** has distorted sp -hybridization and, along with carbons C(13) and C(15), forms an allenyl fragment coordinated in a σ -fashion to Ru(1) [Ru(1)–C(13) 2.088(3) Å: cf. 2.04(1) and 2.058(6) Å for **2** and **3a**, respectively] and in a π -fashion to Ru(2) and Ru(3) with Ru–C distances in the range 2.120(3)–2.343(3) Å [cf. 2.12(1)–2.27(2) Å for **2** and 2.163(7)–2.287(6) Å for **3a**]. Carbons C(8)–C(9)–C(10) form a similar allenyl moiety in **8**, having a distance of 2.038(8) Å for the Ru(1)–C(8) σ -bond and Ru–C distances in the range of 2.147(7)–2.298(7) Å for the π -interactions with Ru(2) and Ru(3). The large central angles within these two C_3 -chains [156.8(3)° and 146.3(6)° for **6** and **8**, respectively] are also in keeping with the angles seen for the corresponding allenyl fragments in complexes **2** [146°], **3a** [151.8(7)°], and other allenyl complexes.¹⁷

Silica-Mediated Dehydration of $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CC}(\text{CPh}_2\text{OH})\text{CH}_2\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (5a**).** Coordination of propargyl alcohols at tri-iron centers is usually accompanied by spontaneous dehydration of the alkynol moiety.^{18,19} In contrast, such dehydration processes at Ru_3 and Os_3 centers are only observed under acidic conditions.^{20–23}

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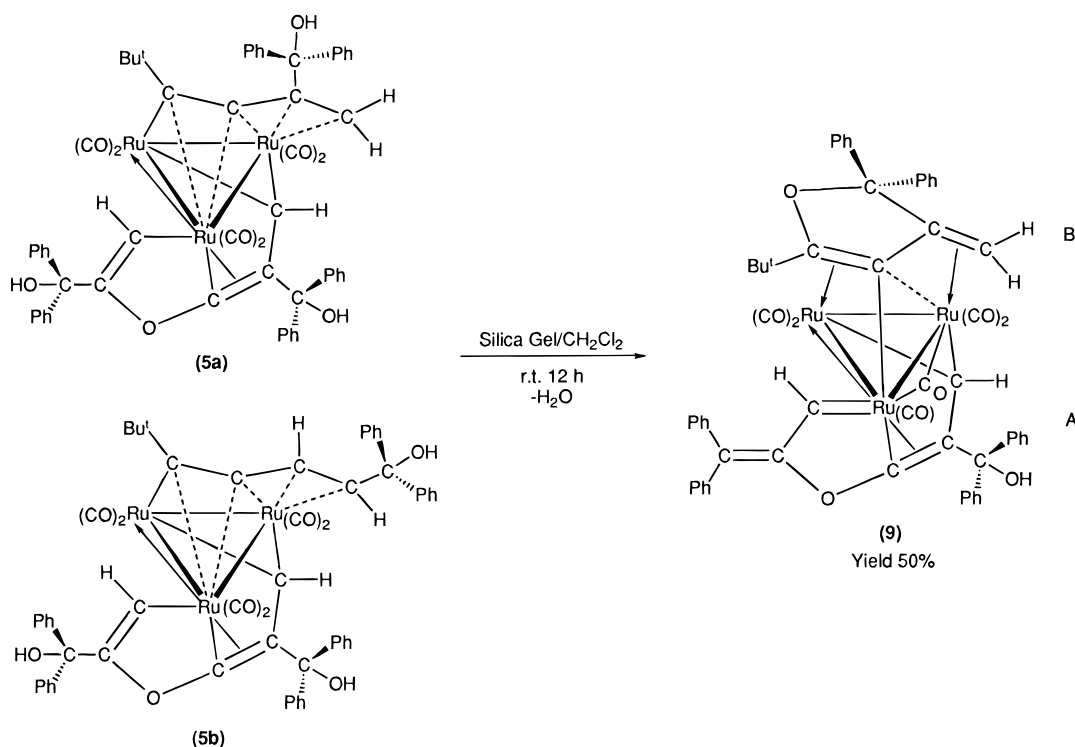
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Scheme 2. Silica-Mediated Dehydration of **5a**

There have been several reports on the effect of supports, such as silica gel, in promoting hydration and dehydration reactions,^{24,25} and we have recently shown how the HCCC(Me)(Ph)OH-derived acetylide complex $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})\{\mu_3\text{-}\eta^5\text{-C}_2\text{C}(\text{Me})(\text{Ph})\text{OH}\}]$ undergoes dehydration on TLC silica plates, albeit at high temperature.²³

We now report that reaction of the isomers **5** with silica gel results in dehydration and formation of $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2)\text{CH}\}]$ (**9**) (see Scheme 2). Thus, complex **9** can be afforded either during chromatography of **5** on silica gel or stirring of a dichloromethane slurry of **5** and silica gel (the yield varying according to the amount of time spent on the silica support but never exceeding 40%). The dehydration is concomitant with decomposition of most of the starting material.

The molecular structure of **9** was determined via a single-crystal X-ray diffraction study (discussed below) and agrees well with the spectroscopic data for solutions. In the IR spectrum a stretching frequency of 1857 cm^{-1} is observed, indicative of a bridging carbonyl. The organic fragment A of **9** is a dehydroxylated version of the metallacycles in **5**, the loss of OH having altered the bonding slightly. Thus, in the ^1H NMR spectrum only one OH group is observed (δ 4.4) and there is a signal at δ 11.7 (s, 1H) typical of a carbene type proton.²⁶ The presence of a carbene unit is supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, in which a signal at 236.7 ppm is seen for the CH unit. A second signal at 233.3 ppm is observed for the CO carbon of A, suggesting that it too

may have some carbene type character. A heterocyclic ligand B is found on the opposite face of the metal center from A. This ligand is best described as a furan ring with exocyclic double bond and is clearly derived from the butadienyl ligand of **5** through loss of a proton and ring formation. The presence of a CH_2 unit in B implies that **9** is the dehydration product of complex **5a** and not **5b**, notwithstanding the fact that, presumably, similar dehydration of **5b** would afford a six-membered heterocycle and not the five-membered one found in **9**. The lack of a dehydration product for **5b** may be because the oxygen atom involved in cyclization is held too far away from the Bu^t -substituted carbon for ring formation to occur. In contrast, the CPh_2OH unit of **5a** is much closer and orientated toward the relevant carbon atom.

The failure to retrieve any significant amounts of complex **5b** from the silica-mediated reactions leads us to propose that this isomer undergoes dehydration, but, in the absence of ring formation, decomposition occurs.

Overall, the formation of **9** from **5a** requires loss of one water molecule via abstraction of H and OH from organic fragments on opposing faces of the Ru_3 triangle, ring formation, and movement of a carbonyl unit from a terminal to a bridging position. The good yield (over 50%, based on **5a**) and the fact that the reaction is surface mediated add to its interest.

X-ray Structure of $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2)\text{-CH}\}]$ (9**).** The molecular structure of complex **9** is shown in Figure 3, with the two bridging organic fragments shown individually in Figures 4 and 5. The relevant structural parameters are given in Table 3.

The three ruthenium atoms form a triangle with bond lengths of 2.8511(5) [Ru(1)–Ru(2)], 2.7661(5) [Ru(1)–Ru(3)], and 2.8065(5) Å [Ru(2)–Ru(3)]. There are two

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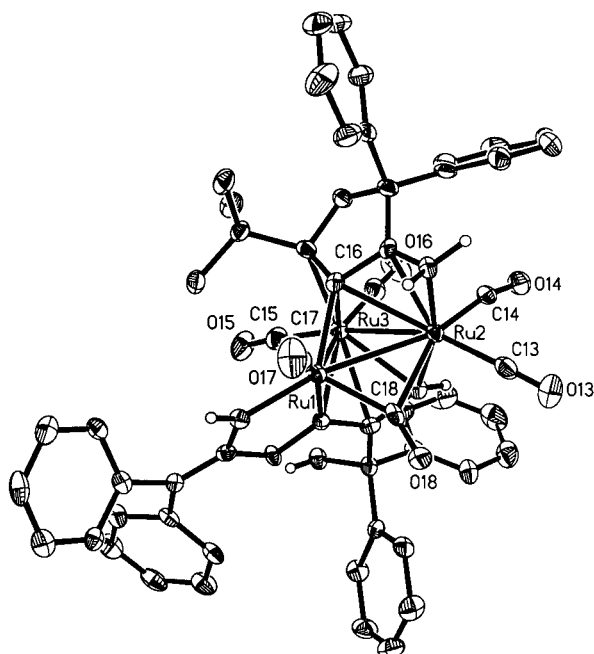


Figure 3. Molecular structure of **9**.

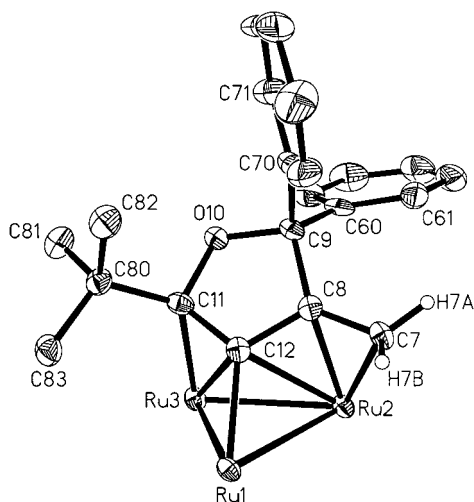


Figure 4. Heterocyclic unit of **9**. Other ligands removed for clarity.

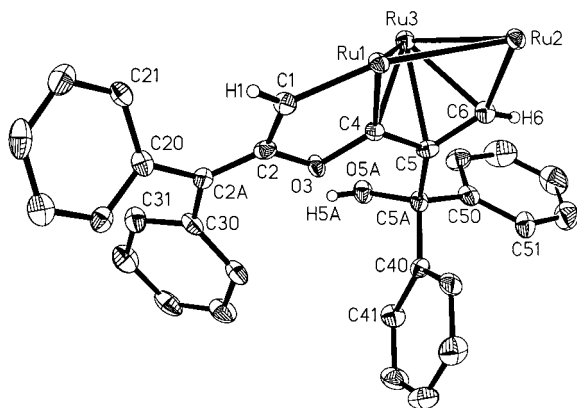


Figure 5. Metallacyclic unit of **9**. Other ligands removed for clarity.

terminal carbonyl ligands on each of Ru(2) and Ru(3) and one on Ru(1). The longer Ru(1)–Ru(2) bond is asymmetrically bridged by a carbonyl ligand [Ru(1)–

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **9**·CH₂Cl₂

| | | | |
|-------------------|-----------|-------------------|-----------|
| Ru(1)–C(1) | 1.944(4) | C(2A)–C(30) | 1.479(6) |
| Ru(1)–C(18) | 1.950(5) | C(2A)–C(20) | 1.479(5) |
| Ru(1)–C(4) | 2.027(4) | C(4)–O(3) | 1.390(4) |
| Ru(1)–C(12) | 2.086(4) | C(4)–C(5) | 1.441(5) |
| Ru(1)–Ru(3) | 2.7639(9) | C(5A)–O(5A) | 1.427(5) |
| Ru(1)–Ru(2) | 2.8486(8) | C(5A)–C(40) | 1.533(5) |
| Ru(2)–C(6) | 2.082(4) | C(5A)–C(50) | 1.537(5) |
| Ru(2)–C(8) | 2.246(4) | C(5A)–C(5) | 1.558(5) |
| Ru(2)–C(7) | 2.262(4) | C(5)–C(6) | 1.408(5) |
| Ru(2)–C(18) | 2.316(4) | C(7)–C(8) | 1.387(5) |
| Ru(2)–C(12) | 2.485(4) | C(8)–C(12) | 1.454(5) |
| Ru(2)–Ru(3) | 2.8032(8) | C(8)–C(9) | 1.558(5) |
| Ru(3)–C(6) | 2.244(4) | C(9)–O(10) | 1.454(5) |
| Ru(3)–C(11) | 2.244(4) | C(9)–C(60) | 1.515(6) |
| Ru(3)–C(4) | 2.254(4) | C(9)–C(70) | 1.553(6) |
| Ru(3)–C(5) | 2.304(4) | C(11)–O(10) | 1.441(4) |
| Ru(3)–C(12) | 2.341(4) | C(11)–C(12) | 1.442(6) |
| C(1)–C(2) | 1.420(5) | C(11)–C(80) | 1.543(6) |
| C(2)–C(2A) | 1.376(5) | C(18)–O(18) | 1.172(5) |
| C(2)–O(3) | 1.398(5) | | |
| C(18)–Ru(1)–Ru(2) | 53.86(12) | O(10)–C(9)–C(60) | 109.0(3) |
| Ru(3)–Ru(1)–Ru(2) | 59.91(2) | O(10)–C(9)–C(70) | 107.2(3) |
| C(18)–Ru(2)–Ru(1) | 42.85(11) | C(60)–C(9)–C(70) | 109.4(3) |
| Ru(3)–Ru(2)–Ru(1) | 58.55(2) | O(10)–C(9)–C(8) | 103.3(3) |
| Ru(1)–Ru(3)–Ru(2) | 61.55(2) | C(60)–C(9)–C(8) | 117.1(4) |
| C(2)–C(1)–Ru(1) | 117.8(3) | C(70)–C(9)–C(8) | 110.1(3) |
| C(2A)–C(2)–O(3) | 117.2(4) | O(10)–C(11)–C(12) | 107.9(3) |
| C(2A)–C(2)–C(1) | 128.5(4) | O(10)–C(11)–C(80) | 108.5(3) |
| O(3)–C(2)–C(1) | 114.3(4) | C(12)–C(11)–C(80) | 128.9(4) |
| C(2)–C(2A)–C(30) | 123.8(4) | O(10)–C(11)–Ru(3) | 112.8(2) |
| C(2)–C(2A)–C(20) | 118.9(4) | C(12)–C(11)–Ru(3) | 75.4(2) |
| C(30)–C(2A)–C(20) | 117.2(4) | C(80)–C(11)–Ru(3) | 119.9(3) |
| O(3)–C(4)–C(5) | 115.4(3) | C(11)–C(12)–C(8) | 109.1(3) |
| O(3)–C(4)–Ru(1) | 117.7(3) | C(11)–C(12)–Ru(1) | 126.1(3) |
| C(5)–C(4)–Ru(1) | 126.6(3) | C(8)–C(12)–Ru(1) | 123.9(3) |
| O(3)–C(4)–Ru(3) | 126.4(3) | C(11)–C(12)–Ru(3) | 68.1(2) |
| C(5)–C(4)–Ru(3) | 73.5(2) | C(8)–C(12)–Ru(3) | 119.9(3) |
| Ru(1)–C(4)–Ru(3) | 80.24(13) | Ru(1)–C(12)–Ru(3) | 77.03(13) |
| O(5A)–C(5A)–C(40) | 110.2(3) | C(11)–C(12)–Ru(2) | 124.6(3) |
| O(5A)–C(5A)–C(50) | 105.2(3) | C(8)–C(12)–Ru(2) | 63.3(2) |
| C(40)–C(5A)–C(50) | 110.7(3) | Ru(1)–C(12)–Ru(2) | 76.56(13) |
| O(5A)–C(5A)–C(5) | 110.2(3) | Ru(3)–C(12)–Ru(2) | 70.96(11) |
| C(40)–C(5A)–C(5) | 110.0(3) | O(18)–C(18)–Ru(1) | 147.0(3) |
| C(50)–C(5A)–C(5) | 110.4(3) | O(18)–C(18)–Ru(2) | 129.5(3) |
| C(6)–C(5)–C(4) | 115.6(4) | Ru(1)–C(18)–Ru(2) | 83.30(17) |
| C(6)–C(5)–C(5A) | 122.7(4) | C(25)–C(20)–C(2A) | 118.4(4) |
| C(4)–C(5)–C(5A) | 121.6(4) | C(21)–C(20)–C(2A) | 123.7(4) |
| C(6)–C(5)–Ru(3) | 69.7(2) | C(31)–C(30)–C(2A) | 119.0(4) |
| C(4)–C(5)–Ru(3) | 69.7(2) | C(35)–C(30)–C(2A) | 123.4(4) |
| C(5A)–C(5)–Ru(3) | 128.7(3) | C(45)–C(40)–C(5A) | 123.1(4) |
| C(5)–C(6)–Ru(2) | 129.3(3) | C(41)–C(40)–C(5A) | 119.1(4) |
| C(5)–C(6)–Ru(3) | 74.3(2) | C(51)–C(50)–C(5A) | 121.1(4) |
| Ru(2)–C(6)–Ru(3) | 80.69(14) | C(55)–C(50)–C(5A) | 119.7(4) |
| C(8)–C(7)–Ru(2) | 71.5(2) | C(65)–C(60)–C(9) | 121.3(4) |
| C(7)–C(8)–C(12) | 124.1(4) | C(61)–C(60)–C(9) | 120.9(4) |
| C(7)–C(8)–C(9) | 128.8(4) | C(75)–C(70)–C(9) | 124.9(4) |
| C(12)–C(8)–C(9) | 107.0(4) | C(71)–C(70)–C(9) | 116.9(4) |
| C(7)–C(8)–Ru(2) | 72.7(2) | C(4)–O(3)–C(2) | 111.7(3) |
| C(12)–C(8)–Ru(2) | 81.3(2) | C(11)–O(10)–C(9) | 110.9(3) |
| C(9)–C(8)–Ru(2) | 123.7(3) | | |

C(18) 1.950(8) Å, Ru(2)–C(18) 2.316(4) Å; Ru(1)–C(18)–O(18) 147.0(3)°, Ru(2)–C(18)–O(18) 129.5(3)°].

One face of the Ru₃ triangle is capped by a heterocyclic ring derived by loss of a proton from the hydroxyl group of the C₄-chain in **5a** and carbon–oxygen bond formation between O(10) and C(11). The atoms C(8), C(9), O(10), C(11), and C(12) make up a furan ring with an exocyclic double bond [C(7)–C(8)]. The ring and the double bond are approximately coplanar, with none of the constituent atoms deviating more than 0.092 Å from the mean plane. The plane of the organic ligand forms an angle of 41.4° with the Ru₃ plane.

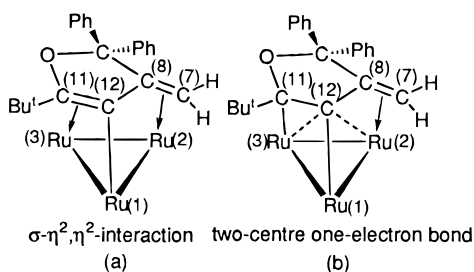


Figure 6. Alternative bonding modes of heterocyclic fragment of **9**.

The heterocycle bridges all three ruthenium atoms, formally donating five electrons to the metal center, although the exact mode of bonding is unclear. The Ru(1)–C(12) distance of 2.086(4) Å is typical of a Ru–C σ -bond, whereas Ru(2)–C(7), Ru(2)–C(8), and C(7)–C(8) lengths of 2.262(4), 2.246(4), and 1.387(5) Å, respectively, are suggestive of an η^2 -type interaction. Given the Ru(3)–C(11), Ru(3)–C(12), and Ru(2)–C(12) distances of 2.244(4), 2.341(4), and 2.485(4) Å, it is suggested that the C(11)–C(12) bond is interacting with Ru(3) in a η^2 -manner with C(12) being held accidentally within bonding distance of Ru(2) (see Figure 6a). However, the Ru(3)–C(12) bond is longer than expected for a simple π -interaction, and a bonding scheme in which C(12) interacts with both Ru(2) and Ru(3) as part of a two-center one-electron bond may be more accurate (see Figure 6b). This would be in keeping with the C(11)–C(12) and C(8)–C(12) bond lengths, which imply some delocalization of the electron density across C(11)–C(12)–C(8).

Structures containing a carbon interacting with all three metals of a trimetallic center, although rare, are known and have been the subject of theoretical studies.^{27,28}

The other face of the Ru₃ triangle is capped by an organic ligand derived from that of **5a** via loss of OH from C(2A). The C(4)–C(5)–C(6) chain forms two σ -bonds [Ru(1)–C(4) 2.027(4) and Ru(2)–C(6) 2.082(4) Å] and an allylic π -interaction with Ru(3) [Ru(3)–C(4) 2.254(4), Ru(3)–C(5) 2.304(4), and Ru(3)–C(6) 2.244(4) Å]. However, the C(4)–C(5) and C(5)–C(6) bond lengths of 1.441(5) and 1.408(5) Å, respectively, suggest the C(5)–C(6) bond contains the greater double-bond character. The atoms Ru(1), C(1), C(2), O(3), C(4), and C(2A) form a metallacycle with an exocyclic double bond, with all of the atoms being approximately coplanar (none of the atoms deviating more than 0.067 Å from the mean plane). This, together with the short Ru(1)–C(1) and Ru(1)–C(4) distances [1.944(4) and 2.027(4) Å, respectively] and the distinctly trigonal planar configuration of both C(1) and C(4), suggests that both these carbons can be considered as carbene carbon atoms.

Experimental Section

General Comments. [Ru₃(CO)₉(μ -H)(μ -C₂Bu^t)] (**1**) was prepared according to the literature method.²⁹ Alkynes, CO

gas, silica gel, and trimethylamine-*N*-oxide are all commercial products and were used as supplied.

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by distillation over the following reagents: hexane, heptane, toluene, and diethyl ether from sodium; acetonitrile and dichloromethane from calcium hydride.

Column chromatography was carried out on alumina (Brockmann activity II), under nitrogen, unless otherwise stated. Products were eluted using hexane and dichloromethane in variable v/v proportions according to the alkyne substituents. The products were recrystallized from heptane or hexane–CH₂Cl₂ mixtures at –20 °C.

Solution IR spectra were recorded with a Perkin-Elmer 1710 Fourier transform spectrometer, using calcium fluoride cells of 1 mm path length. ¹H and ¹³C{¹H} NMR were obtained using JEOL GX-270, GX-400 and Lambda-300 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemistry, University of Bristol. Fast atom bombardment mass spectra were recorded on a Fisons Autospec instrument.

Synthesis of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (4**).** A dichloromethane solution (150 cm³) of complex **1** (360 mg; 0.58 mmol) was cooled to –78 °C, by means of an acetone/dry ice slush bath, and 9.8 cm³ of a solution of (CH₃)₃NO (0.50 g) in acetonitrile (100 cm³) was added dropwise over 5 min. The mixture was stirred and allowed to warm to room temperature. Removal of solvent, under reduced pressure, and chromatography of the residue, eluting with hexane/dichloromethane/acetonitrile (14:5:1), yielded two yellow bands corresponding to the starting complex **1** (ca. 10%) and [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (**4**) (ca. 80%), respectively. Compound **4** was collected from the chromatography column and the solvent removed, under reduced pressure, until precipitation commenced, upon which it was placed in the freezer to facilitate further precipitation. The solvent was decanted from the yellow microcrystalline solid produced. It should be noted that [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (**4**) decomposes and ought to be used immediately or stored as a solid in the freezer for no longer than 24 h.

Complex 4. IR (ν_{CO}) in heptane: 2080m, 2051s, 2042vs, 2019vs, 2010vs, 1987 m, 1966m, 1953m cm^{–1}.

Reaction of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (4**) with CO.** A dichloromethane solution (20 cm³) of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (**4**) (0.10 g; 0.16 mmol) was purged with CO gas for 5 min. The solvent was removed, under reduced pressure, and the residue washed with 2 \times 10 cm³ portions of diethyl ether to afford yellow crystalline [Ru₃(CO)₉(μ -H)(μ -C₂Bu^t)] (**1**) (94 mg; 95%).

Reaction of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (4**) with HC \equiv CBu^t.** To a mixture of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (**4**) (0.40 g; 0.63 mmol) and *tert*-butyl acetylene (0.10 cm³; 0.82 mmol) was added dichloromethane (30 cm³). The mixture was stirred for 20 min, during which time the solution changed color from yellow to brown. Chromatography resulted in the isolation of [Ru₃(CO)₉(μ -H)(μ -C₂Bu^t)] (**1**) (0.04 g; 10%) and the known green complexes [Ru₃(CO)₆{ μ_3 - η^6 -C(Bu^t)CC(Bu^t)CH₂}-{ μ_3 - η^6 -CHC(Bu^t)COC(Bu^t)CH}] (**3a**) and [Ru₃(CO)₆{ μ_3 - η^6 -C(Bu^t)CCH(Bu^t)C(Bu^t)H}-{ μ_3 - η^6 -CHC(Bu^t)COC(Bu^t)CH}] (**3b**) (0.26 g; 50%). A trace amount of a red complex was also isolated but could not be characterized.

Complexes 3a,b. IR (ν_{CO}) in heptane: 2045vs, 2024vs, 1996vs, 1870w cm^{–1}. ¹H NMR (CDCl₃): **3a** δ 8.4 (s, 1H), 7.0 (s, 1H), 3.9 (s, 1H), 2.2 (s, 18H), 1.5 (s, 9H), 1.2 (s, 9H) and 0.9 (s, 1H); **3b** δ 8.2 (s, 1H), 6.8 (s, 1H), 4.8 (δ , J = 10 Hz, 1H), 2.7 (δ , J = 10 Hz, 1H), 2.2 (s, 18H), 1.4 (s, 9H), and 1.2 (s, 9H).

Reaction of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (4**) with HC \equiv CC(Ph)₂OH.** To a mixture of [Ru₃(CO)₈(NCMe)(μ -H)(μ -C₂Bu^t)] (**4**) (1.0 g; 1.58 mmol) and 1,1-diphenyl-2-propyn-1-ol (3.28 g; 15.75 mmol) was added dichloromethane (30 cm³). The mixture was stirred for 20 min, during which time the solution

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changed color from yellow to brown. Chromatography afforded 3 bands. The first, yellow, yielded 32 mg of $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**1**) (10%); the second, black, gave 94 mg of $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**9**) (5%); the third, green, afforded 1.14 g of the inseparable mixture of isomers $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CC}(\text{CPh}_2\text{OH})\text{CH}_2\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**5a**) and $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CCHC}(\text{CPh}_2\text{OH})\text{H}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**5b**) (60%).

Complex 9. IR (ν_{CO}) in heptane: 2051s, 2025vs, 2002m, 1980m, 1857m cm^{-1} . ^1H NMR (CDCl_3): δ 11.7 (s, 1H, Ru=CH), 8.1 (s, 1H, $\mu\text{-CH}$), 7.2 (m, 30H, 6 \times Ph), 4.4 (s, 1H, OH), 4.0 (δ , J = 2 Hz, 1H, CH_2), 3.0 (δ , J = 2 Hz, 1H, CH_2) and 0.9 (s, 9H, Bu^t). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 236.7 (Ru=CH), 233.3 (Ru=C), 220.1 ($\mu\text{-CO}$), 199.8–188.9 (all CO), 161.0 (CH), 147.5–140.0 (all ipso Ph), 130.8–124.8 (all Ph), 45.1 (CH_2), 39.2 (CMe_3), 32.7 (3 \times Me), 170.6, 170.2, 110.8, 97.4, 90.9, and 83.1 (all quaternary carbons). Assignments were aided by a DEPT 135° experiment. FAB mass spectrum: P^+ 1189 m/z + peaks for consecutive loss of 6 carbonyls. Anal. Found: C% 58.24, H% 3.54. Calc: C% 58.60, H% 3.70.

Complexes 5a,b. IR (ν_{CO}) in heptane: 2052m, 2031vs, 2023vs(sh), 1996vs, 1983s cm^{-1} . ^1H NMR (CDCl_3): **5a** δ 8.1 (s, 1H, $\mu\text{-CH}$), 7.5–6.5 (m, 30H, 6 \times Ph), 6.4 (s, 1H, CH), 3.8 (s, 1H, OH), 3.6 (s, 1H, CH_2), 2.6 (s, 1H, OH), 2.3 (s, 1H, OH), 1.3 (s, 1H, CH_2) and 1.1 (s, 9H, Bu^t); **5b** δ 8.3 (s, 1H, $\mu\text{-CH}$), 7.5–6.5 (m, 30H, 6 \times Ph), 6.4 (s, 1H, CH), 4.9 (δ , J = 8 Hz, 1H, $\text{CH}=\text{C}(\text{H})\text{CPh}_2\text{OH}$), 3.9 (s, 1H, OH), 2.9 (δ , J = 8 Hz, 1H, $\text{CH}=\text{C}(\text{H})\text{CPh}_2\text{OH}$), 2.5 (s, 1H, OH), 2.2 (s, 1H, OH) and 1.6 (s, 9H, Bu^t). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): **5a** δ 232.3 (C–O), 202.9–189.9 (all CO), 160.5 ($\mu\text{-CH}$), 148.2 ($\text{Bu}^t\text{C}=\text{C}$), 147.4–140.7 (all ipso Ph), 134.4–126.9 (all Ph), 124.8 (CH), 119.1 ($\text{Bu}^t\text{C}=\text{C}$), 86.6 (CCPh_2OH), 50.0 (CH_2), 43.7 (CMe_3), 34.1 (3 \times Me), 165.4, 84.6, 81.9, 79.7, and 77.4 (all quaternary carbons); **5b** δ 230.1 (C–O), 202.9–189.9 (all CO), 162.5 ($\mu\text{-CH}$), 150.0 ($\text{Bu}^t\text{C}=\text{C}$), 147.4–140.7 (all ipso Ph), 134.4–126.9 (all Ph), 124.6 (CH), 114.2 ($\text{Bu}^t\text{C}=\text{C}$), 87.4 ($\text{CH}=\text{CCPh}_2\text{OH}$), 50.0 ($\text{CH}=\text{CCPh}_2\text{OH}$), 41.8 (CMe_3), 33.5 (3 \times Me), 166.2, 82.1, 80.3, 78.7, and 77.0 (all quaternary carbons). Assignments were aided by a DEPT 135° experiment. FAB mass spectrum: P^+ 1207 m/z + peaks for loss of H_2O and then peaks for loss of up to 6 carbonyls. Anal. Found: C% 58.10, H% 3.95. Calc: C% 57.80, H% 3.80.

Dehydration of Complexes 5a and 5b on Silica Gel. To a dichloromethane solution (15 cm^3) of the mixture of isomers **5a,b** (100 mg; 0.08 mmol) was added silica gel (280 mg) and the mixture stirred for 24 h, during which time a color change from dark green to black was observed. The products were washed from the silica using dichloromethane and chromatographed on alumina to yield 40 mg of $[\text{Ru}_3(\text{CO})_5(\mu\text{-CO})\{\mu_3\text{-}\eta^5\text{-CC}(\text{Bu}^t)\text{OC}(\text{Ph})_2\text{CCH}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**9**) (40%) and 4 mg of complex $[\text{Ru}_3(\text{CO})_6\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)\text{CCHC}(\text{CPh}_2\text{OH})\text{H}\}\{\mu_3\text{-}\eta^6\text{-CHC}(\text{CPh}_2\text{OH})\text{COC}(\text{CPh}_2\text{OH})\text{CH}\}]$ (**5b**) (4%).

Reaction of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (4**) with $\text{PhC}\equiv\text{CPh}$.** To a mixture of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**4**) (500 mg; 0.76 mmol) and diphenyl acetylene (675 mg; 3.80 mmol) was added dichloromethane (40 cm^3). The mixture was stirred for 30 min, during which time the solution changed color from yellow to red. Chromatography afforded 3 bands. The first, yellow, yielded a trace amount of $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**1**); the second, red, gave trace amounts of a red solid, which was not characterized; the third, red, afforded 360 mg of complex $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ (**6**) (60%).

Complex 6. IR (ν_{CO}) in heptane: 2075vs, 2044vs, 2014vs, 2004vs, 1996m(sh), 1985w, 1953m cm^{-1} . ^1H NMR (CDCl_3): δ 7.3–6.8 (m, 9H, 2 \times Ph), 5.6 (δ , J = 6 Hz, 1H, ortho-H), 5.5 (s, 1H, CH), 1.2 (s, 9H, Bu^t). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 202.2 (CO), 200.2 (CO), 197.1 (br, CO), 146.3 and 146.2 (both ipso-Ph), 138.7 (CBu^t), 133.1–123.7 (all Ph), 122.1 ($\text{C}=\text{CBu}^t$), 86.0 (CHPh), 58.9 (CPh), 56.9 (ortho-C), 41.4 (CMe_3) and 32.0 (3 \times Me). Assignments were aided by a DEPT 135° experiment.

FAB mass spectrum: P^+ 789 m/z + peaks for consecutive loss of 7 carbonyls. Anal. Found: C% 42.73, H% 2.49. Calc: C% 42.70, H% 2.60.

Reaction of the Acetonitrile Derivative of $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ (6**) with $\text{PhC}\equiv\text{CPh}$.** To a dichloromethane solution (20 cm^3) of $[\text{Ru}_3(\text{CO})_8\{\mu_3\text{-}\eta^8\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]$ (**6**) (200 mg; 0.25 mmol) was added 4.6 cm^3 of a solution of Me_3NO (500 mg) in acetonitrile (100 cm^3). The mixture was stirred for 30 min, after which time IR spectroscopy showed only the presence of a new complex having bands at 2072w, 2061w, 2041vs, 2023s(sh), 2012vs, 2006vs(sh), 1997s, 1988s, 1972m, 1951m, 1935m, and 1908w cm^{-1} , which were attributed to formation of the acetonitrile derivative of complex **6**. The solvent was removed, under reduced pressure, and the residue redissolved in dichloromethane (40 cm^3) and diphenyl acetylene (228 mg; 1.27 mmol) added. After stirring at room temperature for 18 h removal of solvent and chromatography afforded two bands. The first, red, yielded a trace amount of the starting complex **6**. The second, brown, gave 164 mg of $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}\{\mu_3\text{-}\eta^4\text{-CPh}=\text{CPh}\}]$ (**7**) (70%).

Complex 7. IR (ν_{CO}) in heptane: 2071s, 2041vs, 2019s, 2005vs, 1997s, 1986m, 1935s cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.4–7.0 (m, 20H, 4 \times Ph), 6.2 (s, 1H, CH), 1.5 (s, 9H, Bu^t). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 202.3 (CO), 201.4 (CO), 198.2 (CO), 193.4 (CO), 180.1 ($\mu\text{-CPh}$), 164.1 ($\mu\text{-CPh}$), 152.5 (CBu^t), 149.3, 148.7, 143.2 and 141.8 (all ipso-Ph), 131.4–126.0 (all Ph), 111.3 ($\text{C}=\text{CBu}^t$), 72.3 (CPh), 71.8 (CH), 40.4 (CMe_3), and 34.3 (3 \times Me). Assignments were aided by a DEPT 135° experiment. FAB mass spectrum: P^+ 939 m/z + peaks for consecutive loss of 7 carbonyls. Anal. Found: C% 52.67, H% 3.23. Calc: C% 52.51, H% 3.22.

Isomerization of $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]\{\mu_3\text{-}\eta^4\text{-CPh}=\text{CPh}\}]$ (7**).** A heptane solution of $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]\{\mu_3\text{-}\eta^4\text{-CPh}=\text{CPh}\}]$ (**7**) (50 mg; 0.05 mmol) was heated at reflux for 17 h, after which time the IR spectrum showed a peak at 2033 cm^{-1} , indicative of complex **2**. Chromatography led to isolation of the brown complex $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{H})\text{Ph}\}]\{\mu_3\text{-}\eta^4\text{-CPh}=\text{CPh}\}]$ (**2**) (45 mg) in 90% yield.

Complex 2. IR (ν_{CO}) in heptane: 2068s, 2042s, 2033s, 2015s, 2003s, 1996vs, 1980m, 1938m cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.3–6.8 (m, 20H, 4 \times Ph), 3.2 (s, 1H, CH), 1.4 (s, 9H, Bu^t). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 201.4 (CO), 198.5 (CO), 195.4 (CO), 178.9 ($\mu\text{-CPh}$), 160.2 ($\mu\text{-CPh}$), 157.1 (CBu^t), 153.3, 152.5, 139.8 and 136.9 (all ipso-Ph), 132.4–128.1 (all Ph), 78.2 (CH), 77.4 (CPh), 40.1 (CMe_3), and 34.6 (3 \times Me). Assignments were aided by a DEPT 135° experiment. FAB mass spectrum: P^+ 939 m/z + peaks for consecutive loss of 7 carbonyls. Anal. Found: C% 52.75, H% 3.24. Calc: C% 52.51, H% 3.22.

Reaction of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (4**) with $\text{PhC}\equiv\text{C}(\text{Ph})_2\text{OH}$.** To a mixture of $[\text{Ru}_3(\text{CO})_8(\text{NCMe})(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**4**) (1.00 g; 1.58 mmol) and 1,1,3-triphenyl-2-propyn-1-ol (2.69 g; 9.45 mmol) was added dichloromethane (50 cm^3). The mixture was stirred for 30 min, during which time the solution changed color from yellow to red. Chromatography afforded 3 bands. The first, yellow, yielded a trace amount of $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-C}_2\text{Bu}^t)]$ (**1**); the second, red, gave trace amounts of a red solid, which was not characterized; the third, brown, afforded 618 mg of complex $[\text{Ru}_3(\text{CO})_7\{\mu_3\text{-}\eta^6\text{-C}(\text{Bu}^t)=\text{CC}(\text{Ph})=\text{C}(\text{CPh}_2\text{OH})\text{H}\}]\{\mu_3\text{-}\eta^4\text{-CPh}=\text{C}(\text{Ph})_2\text{OH}\}]$ (**8**) (34%).

Red Complex. IR (ν_{CO}) in heptane: 2078s, 2046vs, 2011vs, 2007s, 1997vs, 1983m(sh), 1950w cm^{-1} .

Complex 8. IR (ν_{CO}) in heptane: 2070m, 2052vs, 2011vs(sh), 2004vs, 1993vs(sh), 1934m cm^{-1} . ^1H NMR (CDCl_3): δ 7.8–6.8 (m, 30H, 6 \times Ph), 3.4 (s, 1H, OH), 3.0 (s, 1H, CH), 1.2 (s, 9H, Bu^t). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 202.4 (CO), 200.1 (CO), 194.5 (CO), 193.1 (CO), 180.9 ($\mu\text{-CPh}$), 158.9 ($\mu\text{-CCPh}_2\text{OH}$), 147.8 (CBu^t), 151.9, 149.9, 148.4, 147.3, 145.6 and 136.4 (all ipso-Ph), 131.7–123.7 (all Ph), 103.4 ($\text{C}=\text{CBu}^t$), 87.2 (CHPh), 83.2

Table 4. Details of Structural Analyses for Complexes **8**, **9**, and **6**^a

| | 8 ·1/2H ₂ O | 9 ·CH ₂ Cl ₂ | 6 |
|---|---|---|--|
| Formula | C ₅₅ H ₄₂ O ₉ Ru ₃ ·1/2H ₂ O | C ₅₈ H ₄₆ O ₉ Ru ₃ ·CH ₂ Cl ₂ | C ₂₈ H ₂₀ O ₈ Ru ₃ |
| recrystallized from | heptane | hexane/CH ₂ Cl ₂ | hexane/CH ₂ Cl ₂ |
| habit | plate | plate | block |
| cryst syst | triclinic | triclinic | monoclinic |
| space group (no.) | <i>P</i> $\bar{1}$ (2) | <i>P</i> $\bar{1}$ (2) | <i>P</i> 2 ₁ /c (14) |
| <i>a</i> /Å | 9.816(2) | 10.578(2) | 14.212(2) |
| <i>b</i> /Å | 12.972(3) | 15.541(3) | 11.948(1) |
| <i>c</i> /Å | 19.602(3) | 17.914(5) | 16.337(2) |
| α /deg | 81.76(3) | 100.44(1) | 90 |
| β /deg | 78.65(2) | 96.00(2) | 96.91(1) |
| γ /deg | 87.88(2) | 108.79(2) | 90 |
| <i>U</i> /Å ³ | 2421.8(8) | 2699.5(11) | 2753.8(7) |
| <i>Z</i> | 2 | 2 | 4 |
| <i>D</i> _c /g cm ⁻³ | 1.589 | 1.566 | 1.900 |
| <i>F</i> (000) | 1162 | 1276 | 1536 |
| <i>T</i> /K | 193 | 173 | 193 |
| <i>m</i> (Mo K α)/cm ⁻¹ | 9.82 | 9.84 | 16.73 |
| cryst dimens/mm | 0.30 × 0.15 × 0.01 | 0.15 × 0.10 × 0.02 | 0.5 × 0.4 × 0.2 |
| total data | 7639 | 23 006 | 4955 |
| no. of unique data | 7223 | 9461 | 4779 |
| no. of obsd data, <i>N</i> _o ^b | 5380 | 6377 | 4493 |
| abs corr | empirical | multiscan | empirical |
| max. and min. transmn | 1.000, 0.774 | 0.934, 0.744 | 0.986, 0.737 |
| no. of least-squares variables, <i>N</i> _v | 622 | 662 | 360 |
| <i>R</i> 1 ^c | 0.044 | 0.038 | 0.025 |
| <i>wR</i> 2 ^d | 0.103 | 0.054 | 0.066 |
| weighting scheme ^e <i>a</i> , <i>b</i> | 0.0480, 17.43 | 0.0128, 0 | 0.0248, 3.6235 |
| <i>S</i> ^f | 1.051 | 0.921 | 1.178 |
| largest diff map features/e Å ⁻³ | 0.703, -0.827 | 0.537, -0.499 | 0.465, -0.393 |
| extinction corr ^g <i>x</i> | 0.0021(2) | none | 0.00040(6) |

^a Data common to all: wavelength (λ) = 0.71073 Å, 2θ range 3–55°. ^b Observation criterion: $F_o^2 > 2\sigma F_o^2$. ^c $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed reflections. ^d $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^e $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. ^f $S = \{ \sum [w(F_o^2 - F_c^2)^2] / (N_o - N_v) \}^{1/2}$. ^g All F_c multiplied by $1/[1 + 0.001F_c^2\lambda^3/\sin 2\theta]^{1/4}$.

(CPh), 77.9 and 75.1 (both CPh₂OH), 40.3 (CMe₃), and 33.3 (3×Me). Assignments were aided by a DEPT 135° experiment. FAB mass spectrum: P⁺ 1150 *m/z* + peaks for loss of 3–7 carbonyls. Anal. Found: C% 57.05, H% 3.88. Calc: C% 57.39, H% 3.77.

X-ray Analysis of Complexes **6, **8**, and **9**.** Many of the details of the structure analyses carried out on complexes **8**, **9**, and **6** are listed in Table 4. In each case a single crystal was mounted in vacuum grease on a glass fiber.

Data Collection for **8 and **6**.** X-ray diffraction measurements were made using a Bruker P4 diffractometer. Cell dimensions were determined from the setting angle values of 20–30 centered reflections. Intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarization, and long-term intensity fluctuations on the basis of check reflections repeatedly measured during the data collection. Corrections for X-ray absorption effects were applied on the basis of azimuthal scan data.³⁰

Data Collection for **9.** X-ray diffraction measurements were made using a Bruker SMART CCD area-detector diffractometer. Cell dimensions were determined from three sets of 30 exposures. Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω , and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.³⁰

Solution and Refinement. The structures were solved by heavy-atom (Patterson and Fourier difference) methods and refined by least squares against F^2 . All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms H(11)

for **8** and H(16) for **6** were located in the electron density difference map and refined without positional constraints with isotropic displacement parameters. All other hydrogen atoms were assigned fixed isotropic displacement parameters and constrained to ideal geometries. Final difference syntheses showed no chemically significant features, the largest being close to the metal. Refinements proceeded smoothly to give the residuals listed in Table 4. All calculations were made using programs of the Bruker SHELXTL packages.³⁰ Complex neutral-atom scattering factors were used.³¹

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Supporting Information Available: Complete structure reports including atomic coordinates, thermal parameters, and bond lengths for the crystal structures of **6**, **8**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>. Complete atomic coordinates, thermal parameters, and bond lengths have been deposited at the Cambridge Crystallographic Data Centre. CCDC refs: 138796, 138797, and 138798. This information is also available free of charge via the Internet at <http://pubs.acs.org>.

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(30) SHELXTL program system version 5.1; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(31) *International Tables for Crystallography*, Kluwer: Dordrecht, 1992; Vol. C.