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Dimethyl Acetylenedicarboxylate (dmad) Reactivity with the Mixed-Metal Cluster $Co_2Rh_2(CO)_{12}$: Facile Cluster Fragmentation and Highly Specific Metal Redistribution to Give the Butterfly Cluster $Co_3Rh(CO)_{10}(\mu$-dmad) and the Planar Cluster $CoRh_3(CO)_9(\mu$-dmad$)_3$

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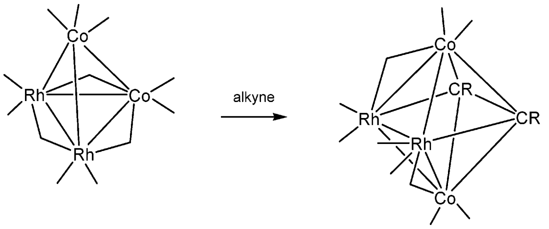
*Summary: The reaction between the tetrahedral cluster $Co_2Rh_2(CO)_{12}$ (**1**) and a 2-fold excess of dimethyl acetylenedicarboxylate (dmad) proceeds rapidly at room temperature to give alkyne-substituted clusters $Co_3Rh(CO)_{10}(\mu$-dmad) (**3**) and $CoRh_3(CO)_9(\mu$-dmad$)_3$ (**4**) as the major products in good yield. Cluster **3** was characterized in solution by IR and ^1H NMR spectroscopies and by comparison to an independently prepared sample of **3** from the reaction of dmad with the known tetrahedral cluster $Co_3Rh(CO)_{12}$ (**2**). Cluster **4** was characterized by IR and NMR (^1H and ^{13}C) spectroscopies and FAB mass spectrometry, and the solid-state structure was established by X-ray diffraction analysis. The structure of $CoRh_3(CO)_9(\mu$-dmad$)_3$ consists of a square planar array of metals where two of the three dmad ligands cap both of the $CoRh_3$ faces and the remaining dmad ligand bridges one of the Rh−Rh edges. The nine ancillary CO groups are all terminally bound, with one $Co(CO)_3$ and three $Rh(CO)_2$ moieties structurally found. The facile cluster fragmentation/metal redistribution observed upon reaction with dmad is briefly discussed relative to other alkyne ligands that react with cluster **1** to furnish the arachno clusters $Co_2Rh_2(CO)_{10}(\mu_4$-alkyne).*

Introduction

The reaction of the mixed-metal tetrahedrane cluster $Co_2Rh_2(CO)_{12}$ (**1**) with alkynes has been explored over the last two decades and found to proceed by a regiospecific alkyne insertion into the Co−Co bond of the cluster.[1−4] The resulting *arachno* or butterfly clusters $Co_2Rh_2(CO)_{10}(\mu_4$-alkyne), whose general structure is depicted in eq 1, have been thoroughly investigated for their stability and for their propensity to serve as precursors for the dinuclear alkyne-substituted compounds $CoRh(CO)_6(\mu$-alkyne). These latter alkyne compounds have elicited much recent interest due to their catalytic silylformylation reactivity that is presumed to derive from synergistic bimetallic catalysis.[5]



(1)

While a wide variety of the terminal and internal alkynes have been studied for their reactivity with cluster **1**, the vast majority of the alkynes employed have contained electron-donating substituents. Fewer examples exist concerning the reactivity pattern exhibited by electrophilic alkynes and their reaction with cluster **1**, with all reported reactions following the alkyne insertion chemistry depicted in eq 1.[1−5] This aspect has prompted us to probe the reaction between the electron-poor alkyne dimethyl acetylenedicarboxylate (dmad) and $Co_2Rh_2(CO)_{12}$. Herein we present our results that demonstrate that the simple and expected substitution product $Co_2Rh_2(CO)_{10}(\mu_4$-dmad) is not observed due to a facile cluster fragmentation and metal redistribution that furnishes the 60-electron cluster $Co_3Rh(CO)_{10}(\mu$-dmad) (**3**) and the 64-electron cluster $CoRh_3(CO)_9(\mu$-dmad$)_3$ (**4**) as the major isolable products. The molecular structure of **4** has been determined by X-ray crystallography, and the structural highlights are discussed within.

Experimental Section

Materials and Equipment. The starting cluster $Co_2Rh_2(CO)_{12}$ was prepared from $Co_2(CO)_8$ and $Rh_2(CO)_4Cl_2$ according to the published procedure,[6] with the former dimer obtained from Strem Chemical Co. and latter dimer synthesized from

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(1) Horváth, I. T.; Zsolnai, L.; Huttner, G. *Organometallics* **1986**, *5*, 180.

(2) Horváth, I. T. *Polyhedron* **1988**, *7*, 2345.

(3) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1991**, *10*, 3211.

(4) Zhu, B.-H.; Zhang, W.-Q.; Zhao, Q.-Y.; Bian, Z.-G.; Hu, B.; Zhang, Y.-H.; Yin, Y.-Q.; Sun, J. *J. Organomet. Chem.* **2002**, *650*, 181.

(5) (a) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (b) Ojima, I.; Li, Z. In *Catalysis by Di- and Polynuclear Metal Cluster Compounds*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998.

(6) Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F.; Salvatori, T. *J. Organomet. Chem.* **1973**, *59*, 379.

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hydrated $RhCl_3$ employing the known carbonylation route.[7] Thermolysis of $Co_2Rh_2(CO)_{12}$ in hexane afforded the known cluster $Co_3Rh(CO)_{12}$ employed in the control experiments.[6] The alkyne ligand dmad was purchased from Aldrich Chemical Co. and used as received, and the 99% ^{13}C-enriched CO used in the preparation of ^{13}CO-enriched $Co_2Rh_2(CO)_{12}$ was purchased from Isotec, Inc. All reaction and NMR solvents were distilled under argon from a suitable drying agent and stored in Schlenk storage vessels.[8]

The reported infrared data were recorded on a Nicolet 20 SXB FT-IR spectrometer in 0.1 mm amalgamated NaCl cells, using PC control and OMNIC software, while the ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini-200 spectrometer and the ^{13}C NMR spectrum of cluster **3** was recorded at 75 MHz on a Varian 300-VXR spectrometer. The high-resolution FAB mass spectrum was obtained at the Nebraska Center for Mass Spectrometry using 3-nitrobenzyl alcohol as the sample matrix.

Synthesis of $Co_3Rh(CO)_{10}(\mu$-dmad) and $CoRh_3(CO)_9(\mu$-dmad)$_3$. To 0.13 g (0.20 mmol) of $Co_2Rh_2(CO)_{12}$ (**1**) in 40 mL of hexane at room temperature was added 42 mg (0.30 mmol) of dimethyl acetylenedicarboxylate via syringe under agron. The solution was stirred for 3.0 h, during which time the solution changed color from brown to deep purple with accompanying precipitation of cluster **4** from solution. TLC analysis of the crude reaction solution using CH_2Cl_2 revealed the presence of three spots having R_f values of 0.90 (brown), 0.40 (purple), and 0.10 (dark purple). The hexane was removed under vacuum, the residue was dissolved in a minimum amount of CH_2Cl_2, and the three spots were separated by column chromatography using silica gel. Use of hexane as the eluent gave the fastest moving spot, while the second spot was obtained by using a mobile phase composed of CH_2Cl_2/hexane (3:1). Finally, changing the solvent system to CH_2Cl_2/ethyl acetate (9:1) afforded $CoRh_3(CO)_9(\mu$-dmad)$_3$. TLC and IR spectroscopic data from the fastest moving spot matched that of independently prepared $Co_3Rh(CO)_{12}$. Yield of $Co_3Rh(CO)_{12}$: ca. 20 mg (16% based on cluster **1**). The spectroscopic data suggest that the second spot corresponded to the alkyne-substituted cluster $Co_3Rh(CO)_{10}(\mu$-dmad). Yield of $Co_3Rh(CO)_{10}(\mu$-dmad): 47 mg (34% based on cluster **1**). IR (hexane): ν(CO) 2103 (m), 2073 (s), 2057 (vs), 2028 (m), 2009 (m), 1903 (m), 1882 (m), 1723 (w, CO_2Me) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.72 (s, CO_2Me). Yield of $CoRh_3(CO)_9(\mu$-dmad)$_3$: 60 mg (29% based on cluster **1**; 57% on dmad). IR (CH_2Cl_2): ν(CO) 2104 (vs), 2078 (vs), 2065 (s), 2043 (m), 2033 (m), 1742 (s, CO_2Me), 1723 (m, CO_2Me), 1707 (m, CO_2Me) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.98 (d, 3H, $J_{Rh-C} = 20$ Hz, CO_2Me), 3.87 (s, 9H, CO_2Me), 3.63 (s, 3H, CO_2Me), 3.50 (s, 3H, CO_2Me). ^{1}H NMR (C_6D_6): δ 3.44 (s, CO_2Me). ^{13}C NMR ($CDCl_3$): δ 183.70 (1C), 184.57 (1C), 184.92 (1C), 185.79 (1C), 186.99 (broad, Co$-$CO), 187.37 (1C), 188.69 (1C). FAB-MS (m/z): 1017.6928 ($M_4 - CO)^+$.

X-ray Structural Determination. Single crystals of $CoRh_3(CO)_9(\mu$-dmad)$_3$ suitable for X-ray crystallography were obtained by slowly evaporating a CH_2Cl_2/hexane solution containing **4** at room temperature. X-ray data were collected on a Bruker SMART 1000 CCD-based diffractometer at 213 K. The frames were integrated with the available SAINT software package using a narrow-frame algorithm,[9] and the structure was solved and refined using the SHELXTL program package.[10] The molecular structure was checked by using PLATON,[11] and all non-hydrogen atoms were refined anisotropically, with the hydrogen atoms assigned calculated positions and allowed to ride on the attached heavy atom. Refinement converged at $R = 0.0366$ and $R_w = 0.0972$ for 7996 independent reflections with $I > 2\sigma(I)$.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 260826 for $CoRh_3(CO)_9(\mu$-dmad)$_3$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ U.K. [fax: +44-(1223)336-033; e-mail: deposit@ccdc.ac.uk or http://www:ccdc.cam.ac.uk].

Results and Discussion

Our initial reactions between $Co_2Rh_2(CO)_{12}$ and dmad were conducted in hexane at room temperature using a cluster/alkyne stoichiometry of 1:1.5, conditions analogous to those employed in the first report dealing with alkyne substitution in $Co_2Rh_2(CO)_{12}$.[1] An immediate reaction leading to the complete consumption of the cluster **1** and the formation of three new species were confirmed by TLC analysis, which revealed one fast moving brown spot and two slower moving purple spots. These compounds were isolated by chromatography and subsequently identified in order of elution as $Co_3Rh(CO)_{12}$ (**2**), $Co_3Rh(CO)_{10}(\mu$-dmad) (**3**), and $CoRh_3(CO)_9(\mu$-dmad)$_3$ (**4**). Cluster **2** was unequivocally identified by its independent synthesis,[6] with the TLC and IR spectroscopic data exactly matching those obtained from the product of the reaction, while treatment of pure $Co_3Rh(CO)_{12}$ with dmad furnished cluster **3**, allowing us to establish the identity of the second compound isolated by chromatography. Structural precedent for the nature of cluster **3** derives from mixed-metal cluster $Co_3Rh(CO)_{10}(\mu$-PhCCPh), which has been isolated from the reaction of $Co_3Rh(CO)_{12}$ with diphenylacetylene.[12] The X-ray structure of $Co_3Rh(CO)_{10}(\mu$-PhCCPh) confirmed the position of the rhodium atom at the hinge position in the opened polyhedron. The independently prepared cluster **3** was found to be quite sensitive to heat, showing signs of decomposition during routine storage at room temperature.[13] The product distribution for the reaction of $Co_2Rh_2(CO)_{12}$ with dmad simplified to a 1:1 mixture of clusters **3** and **4** by employing a 2-fold excess of dmad relative to $Co_2Rh_2(CO)_{12}$. Scheme 1 illustrates the course of this reaction. Since the simple substitution product $Co_2Rh_2(CO)_{10}(\mu_4$-dmad) was not observed at any time in our reactions, unlike the corresponding clusters $Co_2Rh_2(CO)_{10}(\mu_4$-$RC_2R')$ containing electron-rich alkynes, we conclude that $Co_2Rh_2(CO)_{10}(\mu_4$-dmad) is labile and undergoes rapid transformation to the aforementioned clusters. The polyhedral structures adopted by both clusters **3** and **4** trace their parentage to the appropriate six-vertex *closo* $M_6(CO)_{16}$ cluster.[14] Here cluster **3**, with its 7 skeletal electron pairs (SEP), may be viewed as

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(7) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(8) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(9) *Saint* Version 6.02; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997–1999.

(10) *SHELXTL* Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

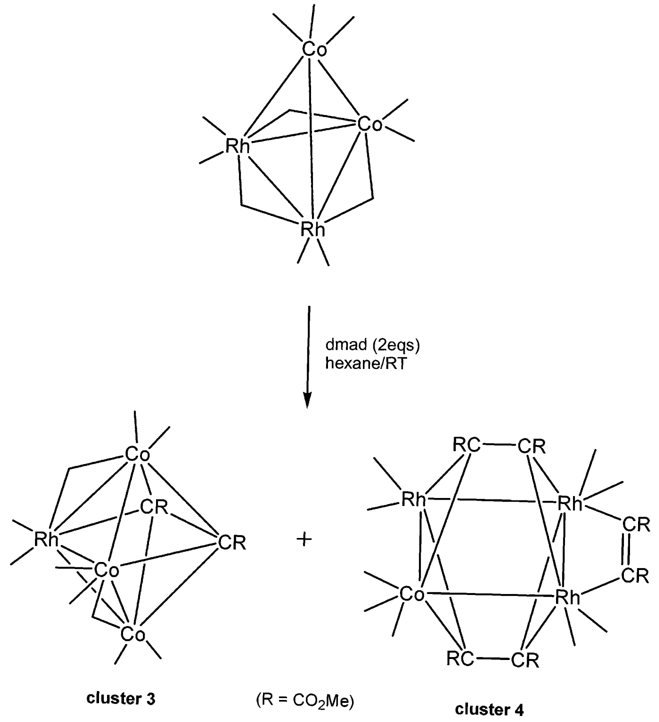
(11) Speck, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2001.

(12) For the synthesis and structural details on the butterfly cluster $Co_3Rh(CO)_{10}(\mu$-$PhC_2Ph)$, see: Tunik, S. P.; Krym, V. R.; Starova, G. L.; Nikol'skii, A. B.; Podkorytov, I. S.; Ooi, S.; Yamasaki, M.; Shiro, M. *J. Organomet. Chem.* **1994**, *481*, 83.

(13) The proposed structure of cluster **3** is furthered strengthened by data obtained from the reaction of $Co_3Rh(CO)_{12}$ with the terminal alkyne $HC_2C(O)OMe$. The product cluster $Co_3Rh(CO)_{10}[\mu_4$-$HC_2C(O)OMe]$ exhibits an IR spectrum identical to that of **3** and the preliminary X-ray structure reveals a disordered butterfly Co_3Rh core with respect to the coordinated alkyne ligand. Unpublished results.

(14) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Compounds*; Shriver, D. F., Kaesz, H. D., Adams, R. D.; Eds.; VCH Publishers: New York, 1990; Chapter 1.

Scheme 1



possessing *closo* or *arachno* polyhedral cores depending on whether the μ_4-dmad ligand is included in the vertex count or not. In the case of $CoRh_3(CO)_9(\mu\text{-dmad})_3$ with its 8 SEP, a *hypho* or square planar arrangement of the $CoRh_3$ atoms is predicted by polyhedral skeletal electron pair (PSEP) theory,[14,15] in accordance with the solid-state structure (vide infra).

Cluster **4** was characterized in solution by standard methods. Terminal carbonyl stretching bands from 2104 to 2033 cm^{-1} were found for the cobalt- and rhodium-bound CO groups, with the ν(CO) bands at 1742, 1723, and 1707 cm^{-1} ascribed to the carbomethoxy moieties of the dmad ligands.[16] The ^1H NMR spectrum of **4** in $CDCl_3$ exhibited four methyl resonances at δ 3.98, 3.87, 3.63, and 3.50 in a 1:3:1:1 integral ratio, consistent with the presence of six methyl groups but whose identities cannot be specifically assigned at this time. Changing the solvent to C_6D_6 afforded a single resonance at δ 3.44. A ^{13}C NMR spectrum of a ^{13}CO-enriched sample of $CoRh_3(CO)_9(\mu\text{-dmad})_3$ displayed six sharp carbonyl groups at δ 183.70, 184.57, 184.92, 185.79, 187.37, and 188.69 for the individual rhodium-CO groups and a broadened resonance at δ 186.99 for the $Co(CO)_3$ moiety. Finally, the FAB mass spectrum of **4**, while not showing the expected molecular ion at *m/z* 1045, does give a *m/z* peak at 1017.6928 [(parent − CO)$^+$] that corresponds to the loss of one CO ligand from cluster **4**.

Table 1. X-ray Crystallographic Data and Processing Parameters for the Tetrametallic Cluster $CoRh_3(CO)_9(\mu\text{-dmad})_3$

CCDC entry no.	260826
space group	monoclinic, *C*2/*c*
a, Å	40.981(5)
b, Å	9.185(2)
c, Å	21.368(3)
β, deg	120.569(2)
V, Å^3	6925(2)
mol formula	$C_{27}H_{18}CoO_{21}Rh_3$
fw	1046.07
formula units per cell (*Z*)	8
D_{calcd} (Mg/m^3)	2.007
λ(Mo Kα), Å	0.71073
abs coeff (mm^{-1})	1.963
abs corr	empirical
max./min. transmn	0.9073/0.8641
total no. of reflns	28 518
no. of indep reflns	7996
no. of data/res/params	7996/0/476
R	0.0366
R_w	0.0972
GOF on F^2	0.925
weights	$[0.04F^2 + (\sigma F)^2]^{-1}$

Table 2. Selected Bond Distances (Å) and Angles (deg) in the Tetrametallic Cluster $CoRh_3(CO)_9(\mu\text{-dmad})_3$[a]

Bond Distances			
Rh(1)−C(2)	2.062(4)	Rh(1)−C(10)	2.118(4)
Rh(1)−C(19)	2.121(4)	Rh(1)−Rh(2)	2.7397(6)
Rh(1)−Rh(3)	2.7589(5)	Rh(2)−C(3)	2.115(4)
Rh(2)−C(10)	2.126(5)	Rh(2)−C(19)	2.133(4)
Rh(1)−Co(1)	2.7241(7)	Rh(3)−C(11)	2.097(5)
Rh(18)−C(18)	2.108(5)	Rh(3)−Co(1)	2.7047(8)
Co(1)−C(11)	2.065(5)	Co(1)−C(18)	2.065(5)
C(2)−C(3)	1.290(7)	C(10)−C(11)	1.428(6)
C(18)−C(19)	1.411(6)		
Bond Angles			
Rh(2)−Rh(1)−Rh(3)	91.34(2)	Co(1)−Rh(2)−Rh(1)	87.90(2)
Co(1)−Rh(3)−Rh(1)	87.90(2)	Rh(3)−Co(1)−Rh(2)	92.86(2)
C(2)−Rh(1)−Rh(2)	70.8(2)	C(2)−Rh(1)−Rh(3)	162.0(1)
C(3)−Rh(2)−Rh(1)	68.6(2)	C(3)−Rh(2)−Co(1)	156.5(1)
Rh(1)−C(10)−Rh(2)	80.4(2)	Rh(1)−C(19)−Rh(2)	80.2(2)
Co(1)−C(11)−Rh(3)	81.1(2)	Co(1)−C(18)−Rh(3)	80.8(2)

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

The molecular structure of cluster **4** and the coordination of three dmad ligands to a $CoRh_3$ core were established by X-ray crystallography. Single crystals of **4** crystallize in the unit cell as independent molecules with no unusually short inter- or intramolecular contacts. Tables 1 and 2 report the X-ray data collection and processing parameters and selected bond distances and angles, respectively.

The thermal ellipsoid plot of $CoRh_3(CO)_9(\mu\text{-dmad})_3$ is shown in Figure 1. The principal structural features found for this square planar 64e$^-$ cluster include the coordination of three dmad ligands to the cluster frame and the fact that the cluster is composed of one cobalt atom and three rhodium atoms. The structure of $CoRh_3(CO)_9(\mu\text{-dmad})_3$ exhibits nine terminal carbonyl groups that are represented by three $Rh(CO)_2$ moieties and one $Co(CO)_3$ group. The two dmad ligands that cap the square $CoRh_3$ faces each donate 4e$^-$ to the total cluster valence electron count, while the remaining dmad ligand is edge-bound to the Rh(1)−Rh(2) vector and functions as a 2e$^-$ donor. The square planar arrangement of the $CoRh_3$ metals (σ_p = 0.010 Å) is confirmed by a mean metal−metal bond distance of 2.7313 Å, which is consistent with the Rh−Rh and Rh−Co bond lengths in other square motifs containing these metals.[17] The eight metal−carbon bond distances for the face-capping dmad ligands and the two Rh−C bond lengths for the μ_2-dmad group range from 2.062(4) Å [Rh(1)−C(2)]

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[15] Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990.

[16] Dolphin, D.; Wick, A. *Tabulation of Infrared Spectral Data*; Wiley-Interscience: New York, 1977.

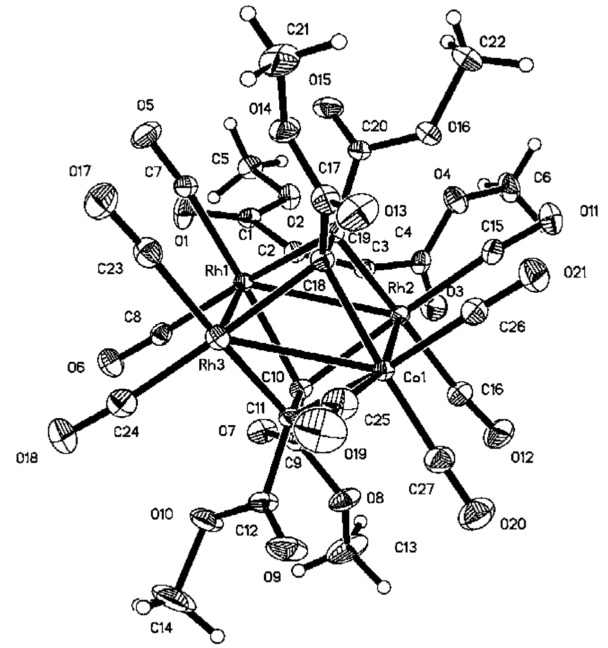

Figure 1. Thermal ellipsoid plot of $CoRh_3(CO)_9(\mu\text{-dmad})_3$ showing the thermal ellipsoids at the 50% probability level.

to 2.133(4) Å [Rh(2)−C(19)] and exhibit an average distance of 2.101 Å, in excellent agreement with other distances reported for coordinated alkyne compounds.[18] The remaining distances and angles are unexceptional.

Conclusions

The reaction between $Co_2Rh_2(CO)_{12}$ and the electrophilic alkyne dmad leads to cluster fragmentation and metal redistribution to give the new alkyne-substituted clusters $Co_3Rh(CO)_{10}(\mu\text{-dmad})$ (**3**) and $CoRh_3(CO)_9(\mu\text{-dmad})_3$ (**4**). The expected simple substitution product $Co_2Rh_2(CO)_{10}(\mu\text{-dmad})$ is unstable relative to metal scrambling. Our future efforts will concentrate on the study of other electrophilic alkyne ligands with cluster **1**, with the hope of gaining a firm understanding of the factors responsible for controlling the final product composition.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) (a) Martinengo, S.; Giani, C.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1577. (b) Albano, V. G.; Braga, D.; Grepioni, F.; Della Pergola, R.; Garlaschelli, L.; Fumagalli, A. *J. Chem. Soc., Dalton Trans.* **1989**, 879. (c) Lei, X.; Shang, M.; Fehlner, T. P. *Chem. Commun.* **1999**, 933.

(18) (a) Mague, J. T. *Inorg. Chem.* **1989**, *28*, 2215. (b) Targos, T. S.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 12. (c) Adams, R. D.; Huang, M. *Organometallics* **1996**, *15*, 4437.