Clusters Containing a Quadruply Bridging CO Ligand. Syntheses, Crystal Structures, and Solution Dynamics of $CpWRu_4(CO)_{14}H$ and $Cp*MRu_4(CO)_{14}H$ (M = Mo, W)

Chi-Jung Su,[†] Yun Chi,^{*,†} Shie-Ming Peng,^{*,‡} and Gene-Hsiang Lee[‡]

Departments of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, Republic of China, and National Taiwan University, Taipei 10764, Taiwan, Republic of China

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The pentametal carbonyl cluster compounds $CpWRu_4(CO)_{14}(\mu_3-H)$ (4), $Cp^*MoRu_4(CO)_{14}$ (μ_3-H) (5), and Cp*WRu₄(CO)₁₄ (μ_3-H) (6) were obtained by condensation of Ru₃(CO)₁₂ with the corresponding anionic reagents $[CpW(CO)_3][PPN]$ and $[Cp^*M(CO)_3][PPN]$ (M = Mo, W) in the ratio 3:2 in refluxing THF solution, followed by treatment with excess CF_3CO_2H in CH_2Cl_2 at room temperature. The Cp derivative 4 possesses a trigonal-bipyramidal Ru_4W core in which the W atom is located at an equatorial position and the hydride lies on a WRu₂ triangular face. In contrast, the Cp* derivatives 5 and 6 adopt an edge-bridged tetrahedral geometry with a tentacle Cp*M fragment bridging a Ru-Ru edge, on which the novel μ_4 - η^2 -CO ligand is associated with the local butterfly Ru₃M array (M = Mo, W). The solution dynamics of these three cluster compounds are discussed.

Transition-metal clusters containing a quadruply bridging CO ligand form a very interesting class of organometallic compounds.¹ The unique μ_4 - η^2 -CO ligand of these clusters is bound to three metal atoms through the carbon atom and to one metal atom through its oxygen atom. Because of the multisite interaction with metal atoms, this bonding mode weakens the C-O bond substantially. As a result, it is implicated as a key intermediate for the reduction of CO on metal clusters² and the formation of carbido clusters through direct CO bond cleavage.³

The first structure of clusters containing a μ_4 -CO ligand was for the tetrairon anionic cluster $[HFe_4(CO)_{13}]^{-.4}$ From the variable-temperature ¹³C NMR data Shriver further demonstrated that it exists as two isomers in equilibrium.⁵ As indicated in Scheme 1, one isomer displays a butterfly framework with a μ_4 -CO ligand, while the other has a more crowded tetrahedral geometry. As revealed by the X-ray structures of the related complexes $[Fe_4(CO)_{13}(CuPPh_3)][PPN]$ and $[Fe_4(CO)_{13}(HgCH_3)]$ [PPN], the tetrahedral isomer contains 1 edge-bridging, 10 terminal, and 2 semibridging CO ligands on the coordination sphere with slightly elongated Fe-Fe bond distances.⁶

(2) (a) Muetterties, E. L.; Stein, J. Chem. Rev. 1979, 79, 479. (b) Whitmire, K. H.; Shriver, D. F. J. Am. Chem. Soc. 1980, 102, 1456.

(3) (a) Anson, C. E.; Bailey, P. J.; Conole, G.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. J. Chem. Soc., Chem. Commun. Dewis, J., Hiel artin, M., Jowell, H. H. S. Chem. Soc., Chem. Commun. 1989, 442. (b) Bailey, P. J.; Duer, M. J.; Johnson, B. F. G.; Lewis, J.; Conole, C.; McPartlin, M.; Powell, H. R.; Anson, C. E. J. Organomet. Chem. 1990, 383, 441. (c) Bailey, P. J.; Johnson, B. F. G.; Lewis, J. Inorg. Chim. Acta 1994, 227, 197. (d) Horwitz, C. P.; Shriver, D. F. J.

 Am. Chem. Soc. 1985, 107, 8147.
 (4) (a) Hieber, W.; Werner, R. Chem. Ber. 1957, 90, 286. (b) Manassero, M.; Sansoni, M.; Longoni, G. J. Chem. Soc., Chem. Commun. 1976, 919

(5) Horwitz, C. P.; Shriver, D. F. Organometallics 1984, 3, 756.

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Scheme 1



Recently, our research group has prepared a series of closely related tetranuclear carbonyl clusters, CpWRu₃- $(CO)_{12}H$ (1), Cp*WRu₃(CO)₁₂H (2), and Cp*MoRu₃- $(CO)_{12}H$ (3), which also showed the related tautomerization of butterfly and tetrahedral isomers (Scheme 2).7 In this cluster system, each individual isomer was fully identified according to its X-ray crystal structures, by the solution ¹H and ¹³C NMR spectral properties, and by comparison with the related crystal structure of osmium derivatives CpWOs₃(CO)₁₂H and Cp*WOs₃- $(CO)_{12}H.^8$ Our results not only allowed us to establish the exact core arrangement of each isomer and the location of its ancillary ligands but also enabled a profound understanding of the μ_4 -CO exchange process.^{7b} Thus, our system supplements what has not been found in the $[HFe_4(CO)_{13}]^-$ system⁴⁻⁶ and serves as an alternative model to probe the various factors that control the generation of the μ_4 -CO ligands in cluster compounds.

In this paper, we extend our studies of this subject to pentanuclear cluster compounds that possess the em-

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^{*} National Tsing Hua University.

[‡] National Taiwan University.

^{*} National Talwan University.
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(1) (a) Horwitz, C. P.; Shriver, D. F. Adv. Organomet. Chem. 1984, 23, 219. (b) Adams, R. D.; Babin, J. E.; Tasi, M. Angew. Chem., Int. Ed. Engl. 1987, 26, 685. (c) Wang, J.-C.; Lin, R.-C.; Chi, Y.; Peng, S.-H.; Lee, G.-H. Organometallics 1993, 12, 4061.

⁽⁶⁾ Horwitz, C. P.; Holt, E. M.; Brock, C. P.; Shriver, D. F. J. Am. Chem. Soc. 1985, 107, 8136.

<sup>Chem. Soc. 1985, 107, 8136.
(7) (a) Chi, Y.; Wu, F.-J.; Liu, B.-J.; Wang, C.-C.; Wang, S.-L. J.
Chem. Soc., Chem. Commun. 1989, 873. (b) Chi, Y.; Su, C.-J.; Farrugia,
L. J.; Peng, S.-M.; Lee, G.-H. Organometallics 1994, 13, 4167.
(8) (a) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D.
S. J. Chem. Soc., Chem. Commun. 1978, 534. (b) Peng, S.-M.; Lee, G.-H.; Chi, Y.; Peng, C.-L.; Hwang, L.-S. J. Organomet. Chem. 1989, 371, 197</sup> 197.



pirical formula LMRu₄(CO)₁₄H (L = Cp, Cp^{*}; M = Mo, W). The cluster compounds isolated, CpWRu₄(CO)₁₄H (4), Cp*MoRu₄(CO)₁₄H (5), and Cp*WRu₄(CO)₁₄H (6), also exhibit two different skeletal arrangements, namely the trigonal bipyramid and edge-bridged tetrahedron. Thus, their interchange provides an additional example of the formation of the μ_4 -CO ligand via reversible cluster equilibration. The chosen synthetic methodology was related to the redox-condensation procedures in the preparation of tetranuclear complexes 1-3,⁹ except that more vigorous conditions and a large excess of Ru₃(CO)₁₂ were required to improve the yields of pentametal complexes LMRu₄(CO)₁₄H.

Experimental Section

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on Bruker AM-400 and AMX-300 instruments; chemical shifts are quoted with respect to the internal standard tetramethylsilane (¹H and ¹³C NMR). Mass spectra were obtained on a JEOL-HX110 instrument operating in the fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of reactions was monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F₂₅₄, Merck), and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254} , Merck). The complexes $[Cp^*M(CO)_3][PPh_4]$ (M = Mo, W) were prepared from the reaction of Cp*Li slurry with Mo(CO)₆ or W(CO)₆ in refluxing THF solution, followed by addition of an aqueous solution of tetraphenylphosphonium chloride. The related Cp derivatives $[CpM(CO)_3][PPh_4]$ (M = Mo, W) were prepared under similar experimental conditions. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of [CpW(CO)_3][PPh₄] with Ru₃(CO)₁₂. A THF solution (40 mL) of Ru₃(CO)₁₂ (400 mg, 0.63 mmol) and [CpW-(CO)₃][PPh₄] (280 mg, 0.42 mmol) was heated at reflux for 1 h under nitrogen, during which time the color turned from orange to dark red. The solvent was removed in vacuo to produce an oily residue. This residue was dissolved in 30 mL of dichloromethane, after which 2 mL of trifluoroacetic acid was added with vigorous stirring. The resulting solution was continuously stirred for 1 h at room temperature. Then the solvent was removed in vacuo and the residue was separated by thin-layer chromatography. Development with a mixture of dichloromethane and hexane in a 2:3 ratio produced two bands, which were removed from the silica gel plates to yield 25 mg of the black pentanuclear cluster CpWRu₄(CO)₁₄H (4; 0.08 mmol, 5.6%) and 129 mg of the orange-red tetranuclear cluster CpWRu₃(CO)₁₂H (1; 0.145 mmol, 34%) after recrystallization.

Spectral data for 4: MS (FAB, 102 Ru, 184 W) m/z 1050 (M⁺); IR (C₆H₁₂) ν (CO) 2088 (w), 2061 (vs), 2038 (s), 2030 (m), 2011 (w), 1997 (w), 1968 (vw) cm^{-1}; {}^{1}H NMR (CD_2Cl_2, 230 K) \delta 6.24 (s, 5H), -14.83 (s, $J_{W-H} = 66$ Hz); ${}^{13}C$ NMR (CD₂Cl₂, 200 K) δ 234.0 (2C, $J_{W-C} = 155$ Hz), 201.5 (3C), 192.4 (2C), 189.2 (2C), 188.7 (2C). Anal. Calcd for C₁₉H₆O₁₄Ru₄W: C, 21.81; H, 0.58. Found: C, 21.71; H, 0.61.

Reaction of [Cp*Mo(CO)₃][PPh₄] with Ru₃(CO)₁₂. A THF solution (40 mL) of $Ru_3(CO)_{12}$ (237 mg, 0.37 mmol) and [Cp*Mo(CO)₃][PPh₄] (163 mg, 0.25 mmol) was heated at reflux for 6 h under nitrogen, during which time the color turned from orange to dark brown. The solvent was evaporated under vacuum, and the oily residue was redissolved in 30 mL of dichloromethane. After addition of 1 mL of trifluoroacetic acid, the solution was stirred at room temperature for 1 h. After the volatile components were removed under vacuum, the residue was subjected to thin-layer chromatographic separation (dichloromethane-hexane, 2:3), producing 82 mg of the black pentanuclear cluster Cp*MoRu₄(CO)₁₄H (5; 0.08 mmol, 32%) and 32 mg of the black tetranuclear cluster Cp*MoRu₃(CO)₁₂H (3; 0.038 mmol, 15%). The ¹³CO-enriched samples of 5 were prepared from the reactions of 50% enriched Ru₃(CO)₁₂ and regular [Cp*Mo(CO)₃][PPh₄] under similar conditions. Crystals of 5 suitable for an X-ray diffraction study were obtained from a layered solution of dichloromethanemethanol at room temperature.

Spectral data for 5: MS (FAB, 102 Ru, $^{98}Mo)$ m/z 1033 (M⁺); IR (C₆H₁₂) ν (CO) 2076 (m), 2062 (vw), 2043 (vs), 2034 (s), 2020 (s), 1996 (m, br), 1976 (w), 1856 (br, vw) cm⁻¹; ¹H NMR (CD₂Cl₂, 293 K) δ 2.01 (s, 15H, C₅Me₅), -15.08 (**5b**, 10%, 1H), -18.87 (**5a**, 90%, s, 1H); ¹³C NMR (THF-d₈, 205 K) isomer **5a**, δ 292.1 (μ_4 -CO), 240.6, 236.0 (br), 233.1 (Mo-CO), 228.6 (Mo-CO), 199.8 (3C), 199.5, 195.3, 194.9, 194.7, 193.5, 190.0. Anal. Calcd for C₂₄H₁₆O₁₄Ru₄Mo: C, 28.03; H, 1.57. Found: C, 27.88; H, 1.61.

Reaction of [Cp*W(CO)₃][PPh₄] with Ru₃(CO)₁₂. Condensation of $Ru_3(CO)_{12}$ with [Cp*W(CO)₃][PPh₄] in a 3:2 ratio under similar reaction conditions produced the analogous pentanuclear complex Cp*WRu₄(CO)₁₄H (6) and the tetranuclear cluster Cp*WRu₃(CO)₁₂H (2) in 17% and 23% yields, respectively.

Spectral data for **6**: MS (FAB, ¹⁰²Ru, ¹⁸⁴W) m/z 1120 (M⁺); IR (CCl₄) ν (CO) 2075 (m), 2042 (vs), 2035 (s), 2018 (s), 1996 (br, m), 1974 (w), 1889 (br, vw), 1844 (br, w) cm⁻¹; ¹H NMR (CDCl₃, 294 K) δ 1.98 (s, 15H, C₅Me₅), -14.25 (**b**, 33%, s, J_{W-H} = 68 Hz), -19.01 (**a**, s, 67%); ¹³C NMR (THF-d₈, 270 K) δ 302.0 (μ ₄-CO), 228.9, 227.1 (J_{W-C} = 176 Hz), 219.1 (J_{W-C} = 148 Hz), 199.9 (3C), 196.0 (J_{C-H} = 12 Hz), 194.3 (J_{C-H} = 10 Hz), 193.8

⁽⁹⁾ Cazanoue, M.; Lugan, N.; Bonnet, J.-J.; Mathieu, R. Organometallics 1988, 7, 2480.

and 192.7. Anal. Calcd for $C_{24}H_{16}O_{14}Ru_4W$: C, 25.82; H, 1.44. Found: C, 25.73; H, 1.49.

Hydrogenation of Cp*WRu₄(**CO**)₁₄**H.** A toluene solution (25 mL) of Cp*WRu₄(CO)₁₄H (42 mg, 0.038 mmol) was heated at reflux under 1 atm of dihydrogen for 20 min. The color turned slowly from dark brown to orange during the reaction. After the solution was cooled to room temperature, the solvent was removed and the residue separated by thin-layer chromatography (silica gel, dichloromethane-hexane, 1:4), giving 28 mg of Cp*WRu₃(CO)₁₁(μ -H)₃ (0.03 mmol, 79%) as red-orange needles after recrystallization from dichloromethane-methanol. Hydrogenation of the analogous pentanuclear clusters Cp*MoRu₄(CO)₁₄H and CpWRu₄(CO)₁₄H under similar conditions produced the trihydride complexes Cp*MoRu₃(CO)₁₁(μ -H)₃ in 61% and 63% yields, respectively.

Reaction of Cp*WRu₄(**CO**)₁₄**H with CO.** A toluene solution (20 mL) of Cp*WRu₄(CO)₁₄H (21 mg, 0.019 mmol) was heated at reflux under 1 atm of CO for 1 h. After the solution was cooled to room temperature, the solvent was removed and the residue separated by thin-layer chromatography (silica gel; dichloromethane-hexane, 2:3), giving 5.7 mg of Ru₃(CO)₁₂ and 8.4 mg of Cp*WRu₃(CO)₁₂H (0.009 mmol, 47%).

X-ray Crystallography. Diffraction measurements of complexes 4 and 5 were carried out on a Nonius CAD-4 diffractometer. All reflections were corrected for Lorentz, polarization, and absorption effects. Data reduction and refinement were performed using the NRCC-SDP-VAX packages. Lattice parameters for 4 were determined from 25 randomly selected high-angle reflections with 2θ angles in the range $19.00-32.62^{\circ}$. The space group *Pbca* was identified on the basis of systematic absences and confirmed by successfully solving the crystal structure. Absorption corrections were made by the Ψ scan method; the minimum and maximum transmission factors were 0.75 and 1.00, respectively. Anisotropic thermal parameters were introduced for all nonhydrogen atoms. The bridging hydride ligand was located from a difference Fourier map and was included in the structure factor calculation. Full-matrix least-squares refinement with 44 atoms and 348 parameters gave $R_F = 0.028$ and $R_w = 0.022$, for 3160 reflections with $I \ge 2\sigma(I)$. The residual electron density on the difference Fourier map is about 0.70 e/Å³.

Lattice parameters for 5 were determined from 25 selected reflections with 2θ angles in the range $16.12-34.64^{\circ}$. Empirical absorption corrections were performed, and the minimum and maximum transmission factors were 0.80 and 1.00, respectively. The structures were solved by using the NRCC-SDP-VAX packages and refined by least-squares cycles. The bridging hydride ligand was located from the difference Fourier map and was included in the structure factor calculation. The hydrogen atoms of the Cp* ligand were calculated at idealized positions with fixed temperature coefficients. Full-matrix least-squares refinement with 59 atoms and 393 parameters gave $R_F = 0.023$ and $R_w = 0.027$ for 4397 reflections with I > $2\sigma(I)$. The combined data collection and refinement parameters are summarized in Table 1. Atomic positional parameters for 4 and 5 are presented in Tables 2 and 3, whereas selected bond angles and lengths are listed in Tables 4 and 5, respectively.

Results and Discussion

The pentanuclear heterometallic cluster compound $CpWRu_4(CO)_{14}H$ (4) was isolated in ca. 6% yield from the reaction of a 3:2 molar ratio of $Ru_3(CO)_{12}$ and $[CpW-(CO)_3][PPh_4]$ in refluxing THF solution for 2 h, followed by addition of excess CF_3CO_2H in dichloromethane at room temperature. The related Cp^* derivatives $Cp^*MoRu_4(CO)_{14}H$ (5) and $Cp^*WRu_4(CO)_{14}H$ (6) were obtained in 15-17% yields under similar conditions from the related anionic complexes $[Cp^*M(CO)_3][PPh_4]$

 Table 1. Experimental Data for the X-ray

 Diffraction Studies^a

/		
compd	4	5
formula	$C_{19}H_6O_{14}WRu_4$	$C_{24}H_{16}O_{14}MoRu_4$
mol wt	982.38	1028.59
cryst syst	orthorhombic	monoclinic
space group	Pbca	$P2_{1}/c$
a(Å)	14.786(3)	10.468(1)
$b(\mathbf{A})$	16.624(5)	16.804(2)
$c(\mathbf{A})$	29.240(5)	17.251(3)
β (deg)		104.81(1)
$V(Å^3)$	4975(2)	2933(1)
Z	8	4
$D_c (g/cm^3)$	2.623	2.329
<i>F</i> (000)	3599	1960
$2\theta(\max)(\deg)$	50	50
hkl ranges	0-17, 0-19, 0-24	-12 to $+12$, $0-19$, $0-20$
cryst size (mm)	$0.10 \times 0.13 \times 0.17$	0.08 imes 0.25 imes 0.35
μ (Mo K α) (cm ⁻¹)	70.86	24.48
transmissn:	1.00, 0.75	1.00, 0.80
max, min	,	
no. of unique data	4362	5156
no. of data with	3160	4397
$I > 2\sigma(I)$		
no. of atoms and	44, 348	72, 452
params	,	
$\max \Delta \sigma$ ratio	0.040	0.003
$R_F; R_w$	0.028; 0.022	0.023; 0.027
GOF	1.58	2.41
D-map, max/min	+0.72/-0.66	+0.39/-0.53
(e/Å ³)		

^a Features common to all determinations: Nonius CAD-4 diffractometer, λ (Mo K α) = 0.709 30 Å, 25 °C; minimized function $\sum (w|F_o - F_c|^2)$, weighting scheme $(1/\sigma^2)(F_o)$, $w = 1/\sigma^2(F_o)$; GOF = $[\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables.

(M = Mo, W). The conditions used to prepare complexes 4-6 are identical with those used previously to obtain the tetranuclear anionic clusters $[LMRu_3(CO)_{12}]^-$ and neutral clusters 1-3,^{7b,9} except that we added 1.5 equiv of $Ru_3(CO)_{12}$ to maximize the yield of pentanuclear derivatives and to suppress the tetranuclear derivatives. Attempts to synthesize the CpMo derivative CpMoRu₄- $(CO)_{14}$ H were unsuccessful, presumably due to the poor thermal stability that caused unwanted decomposition during the reaction and workup. This result is consistent with the poor yield of complex 4.

The molecular formulas of these three pentanuclear clusters were obtained from FAB mass analyses. The solution IR spectrum of 4 shows the complex CO stretching bands in the region $2088-1968 \text{ cm}^{-1}$ due to the terminal and bridging CO ligands. However, IR spectra of the Cp* derivatives 5 and 6 are distinct, exhibiting an additional broad CO stretching band at 1396 and 1357 cm⁻¹ due to the quadruply bridging CO ligand. Encouraged by this finding, we carried out the single-crystal X-ray diffraction studies of both 4 and 5.

Crystal Structure of 4. An ORTEP diagram of 4 is shown in Figure 1, and selected bond parameters are presented in Table 4. The metal core consists of a Ru₄W trigonal-bipyramidal arrangement, with atoms Ru(1) and Ru(2) defining the axial positions and atoms Ru(3), Ru(4), and W located at the equatorial positions. In addition to the Cp ligand, this molecule contains 14 CO ligands: 2 CO ligands on the W atom and 3 CO ligands on each Ru atom. Among these 14 CO ligands, 3 CO ligands adopt the semibridging mode. These CO ligands include the C(1)O(1) and the C(2)O(2) ligands on the W atom and the C(11)O(11) ligand on Ru(3), which possess nonlinear M-C-O angles in the range 158-162°.

Table 2. Atomic Coordinates and EquivalentIsotropic Displacement Coefficients for 4

	_			
	x	У	z	$B_{ m eq}$ (Å ²) ^a
w	0.046387(22)	0.258646(23)	0.037099(17)	2.432(14)
Ru(1)	0.09697(5)	0.11133(4)	0.10349(4)	2.70(3)
Ru(2)	0.02908(5)	0.37807(4)	0.13881(4)	3.06(3)
Ru(3)	-0.01080(5)	0.21899(4)	0.17010(3)	2.49(3)
Ru(4)	0.17055(4)	0.26213(5)	0.15018(3)	2.39(3)
C(1)	-0.0278(6)	0.1597(6)	0.0321(5)	3.8(5)
C(2)	-0.0726(6)	0.3009(6)	0.0587(5)	3.9(5)
C(3)	0.1687(6)	0.0662(5)	0.0343(5)	3.3(4)
C(4)	0.0157(6)	0.0243(6)	0.0999(5)	4.0(5)
C(5)	0.1586(6)	0.0607(6)	0.1729(5)	3.9(5)
C(6)	0.0798(7)	0.4535(6)	0.0829(5)	5.3(6)
C(7)	-0.0779(7)	0.4394(6)	0.1387(5)	4.7(5)
C(8)	0.0706(7)	0.4336(6)	0.2136(5)	4.8(5)
C(9)	-0.1248(6)	0.1709(6)	0.1607(5)	4.1(5)
C(10)	0.0239(6)	0.1511(5)	0.2418(5)	4.0(5)
C(11)	-0.0563(6)	0.2997(6)	0.2291(5)	4.1(5)
C(12)	0.2730(6)	0.1948(6)	0.1591(5)	4.0(5)
C(13)	0.1740(6)	0.2874(6)	0.2423(5)	4.4 (5)
C(14)	0.2420(6)	0.3488(6)	0.1201(4)	3.4(4)
C(15)	0.0113(9)	0.2691(14)	-0.0715(6)	14.5(13)
C(16)	0.0897(11)	0.2196(8)	-0.0676(5)	10.2(10)
C(17)	0.1534(7)	0.2674(9)	-0.0463(5)	7.3(7)
C(18)	0.1217(8)	0.3418(7)	-0.0381(5)	6.2(6)
C(19)	0.0362(8)	0.3436(9)	-0.0532(6)	9.3(8)
O(1)	-0.0858(4)	0.1161(4)	0.0136(3)	5.2(4)
O(2)	-0.1496(4)	0.3200(4)	0.0538(4)	5.4(4)
O(3)	0.2095(4)	0.0415(4)	-0.0083(3)	5.2(4)
O(4)	-0.0298(5)	-0.0284(4)	0.0999(4)	6.1(4)
O(5)	0.1975(5)	0.0264(5)	0.2133(4)	6.5(4)
O(6)	0.1107(6)	0.5049(5)	0.0524(4)	8.5(5)
O(7)	-0.1449(5)	0.4733(5)	0.1394(4)	6.9(4)
O(8)	0.0958(5)	0.4692(5)	0.2588(4)	7.3(5)
O(9)	-0.1947(4)	0.1400(5)	0.1561(4)	7.0(5)
O(10)	0.0395(5)	0.1133(4)	0.2880(3)	6.0(4)
O(11)	-0.0871(5)	0.3302(4)	0.2750(3)	6.4(4)
O(12)	0.3387(4)	0.1591(5)	0.1637(4)	6.5(5)
O(13)	0.1804(5)	0.2991(5)	0.2977(3)	7.0(5)
O(14)	0.2888(5)	0.3986(4)	0.1020(4)	5.9(4)
H	0.143(4)	0.219(4)	0.074(3)	3.5(19)

 $^{a}B_{eq}$ is the mean of the principal axes of the thermal ellipsoid.

The metal-metal distances span the narrow range 2.935(1)-2.750(1) Å, with Ru-Ru distances (average 2.817 Å) being slightly shorter than the W-Ru distances (average 2.899 Å). The W-Ru(4) vector in the equatorial plane is the longest metal-metal bond within the whole molecule. The lengthening of this metal-metal bond is apparently due to the presence of the face-bridging hydride, which was located by difference Fourier synthesis. This hydride ligand is strongly associated with the W-Ru(4) edge (W-H = 1.75(6) Å and Ru(4)-H = 1.74(7) Å) but is weakly bonded to the opposite metal atom (Ru(1)-H = 2.00(7) Å).

Crystal Structure of 5. As indicated in Figure 2, compound 5 possesses a metal core of 1 Mo and 4 Ru atoms coordinated by 14 CO ligands, 1 face-bridging hydride, and a Cp* ligand. Selected bond distances are listed in Table 5. The skeleton consists of an edgebridged tetrahedral arrangement with a pendant Cp*Mo- $(CO)_2$ unit attached to the Ru₄ tetrahedron. All metalmetal bonds are normal, with Ru-Ru distances in the range 2.7448(7)-2.8720(7) Å and with Mo-Ru distances of 2.9445(8) and 2.9648(7) Å. As revealed by the difference Fourier synthesis, the hydride lies on the Ru(1)-Ru(2)-Ru(3) metal triangle. In addition, we observed three terminal CO ligands on the Ru(4) atom and two terminal CO ligands on each of the other three Ru atoms. The observed Ru-CO arrangement is completed by two bridging CO ligands on the Ru(1)-Ru(2)

Table 3. Atomic Coordinates and EquivalentIsotropic Displacement Coefficients for 5

	*	*		
	x	у	z	$B_{ m eq}({ m \AA}^2)^{lpha}$
Mo	0.32416(5)	0.12797(3)	0.19280(3)	1.805(19)
Ru(1)	0.04414(4)	0.16121(3)	0.11618(3)	1.902(18)
Ru(2)	-0.02036(4)	0.23953(3)	-0.03204(3)	2.056(18)
Ru(3)	0.24216(4)	0.22831(3)	0.04715(3)	1.847(19)
Ru(4)	0.07334(5)	0.32994(3)	0.10793(3)	2.165(19)
C(1)	0.2020(5)	0.2490(3)	0.1636(3)	2.09(24)
C(2)	0.2799(6)	0.0425(3)	0.1092(3)	2.5(3)
C(3)	0.1951(6)	0.0711(3)	0.2407(3)	2.8(3)
C(4)	-0.0353(6)	0.1701(4)	0.2006(3)	3.1(3)
C(5)	-0.0171(6)	0.0551(3)	0.0936(3)	2.46(25)
C(6)	-0.1462(6)	0.1979(3)	0.0303(3)	2.7(3)
C(7)	-0.0837(6)	0.1737(3)	-0.1239(3)	2.8(3)
C(8)	-0.1280(6)	0.3250(3)	-0.0797(3)	2.6(3)
C(9)	0.1449(6)	0.2832(3)	-0.0669(3)	2.7(3)
C(10)	0.3301(6)	0.1573(3)	-0.0073(3)	2.8(3)
C(11)	0.3811(6)	0.3016(3)	0.0613(3)	2.7(3)
C(12)	0.1303(6)	0.3888(4)	0.2068(4)	4.0(3)
C(13)	0.1129(7)	0.4146(4)	0.0441(4)	3.9(3)
C(14)	-0.1097(6)	0.3576(4)	0.1002(4)	3.8(3)
C(15)	0.5035(5)	0.1542(3)	0.3059(3)	2.35(23)
C(16)	0.4639(5)	0.0755(3)	0.3128(3)	2.58(25)
C(17)	0.4815(5)	0.0314(3)	0.2452(3)	2.36(23)
C(18)	0.5354(5)	0.0841(3)	0.1966(3)	2.27(24)
C(19)	0.5477(5)	0.1609(3)	0.2344(3)	2.32(24)
C(20)	0.5084(6)	0.2183(4)	0.3660(4)	3.7(3)
C(21)	0.4307(7)	0.0401(4)	0.3859(4)	4.2(4)
C(22)	0.4707(6)	-0.0571(3)	0.2365(4)	3.6(3)
C(23)	0.5924(6)	0.0600(4)	0.1286(4)	3.5(3)
C(24)	0.6090(6)	0.2340(4)	0.2099(4)	3.6(3)
O(1)	0.2835(3)	0.24344(21)	0.23167(20)	2.26(16)
O(2)	0.2639(4)	-0.00998(24)	0.06582(24)	3.92(22)
O(3)	0.1416(4)	0.02911(25)	0.27445(24)	3.73(21)
O(4)	-0.0869(5)	0.1750(3)	0.2516(3)	5.4(3)
O(5)	-0.0582(4)	-0.00785(24)	0.0828(3)	4.30(23)
O(6)	-0.2564(4)	0.1919(3)	0.0313(3)	4.01(22)
O(7)	-0.1228(5)	0.1371(3)	-0.1797(3)	5.1(3)
O(8)	-0.1930(4)	0.37718(25)	-0.1081(3)	4.21(22)
O(9)	0.1774(4)	0.3174(3)	-0.11677(25)	4.25(23)
O(10)	0.3829(5)	0.1186(3)	-0.0432(3)	5.0(3)
O(11)	0.4596(5)	0.3497(3)	0.0658(3)	4.72(24)
O(12)	0.1639(6)	0.4225(3)	0.2648(3)	7.4(3)
O(13)	0.1457(6)	0.4637(3)	0.0071(3)	6.5(3)
O(14)	-0.2163(5)	0.3732(3)	0.0988(3)	6.1(3)
Н	0.083(6)	0.152(3)	0.020(3)	5.5(16)

^{*a*} B_{eq} is the mean of the principal axes of the thermal ellipsoid.

and Ru(2)-Ru(3) edges. One CO ligand, C(9)O(9), is close to the symmetric bridging mode with Ru(2)-C(9) = 2.104(6) Å and Ru(3)-C(9) = 2.176(6) Å, while the second is more asymmetric with Ru(1)-C(6) = 2.243(6) Å and Ru(2)-C(6) = 2.027(6) Å.

The most important feature is the presence of the unique μ_4 -CO ligand. The carbon atom C(1) occupies the MoRu₃ butterfly crater of the cluster, and the oxygen atom O(1) is bonded to the bridging $Cp*Mo(CO)_2$ fragment. Thus, the orientation of the μ_4 -CO ligand differs from that revealed by the solid-state structure of clusters 1 and 2, in which the oxygen atom is tilted toward the wingtip $Ru(CO)_3$ fragment but is pointed away from the $CpW(CO)_2$ and $Cp^*W(CO)_2$ fragments. The CO distance, C(1)-O(1) = 1.266(6) Å, is much longer than that of other terminal CO ligands within the molecule, indicating a significant reduction in the C-O bond order. The small dihedral angle of $117.4(2)^{\circ}$ between the planes Mo-Ru(1)-Ru(3) and Ru(1)-Ru(3)-Ru(4) is undoubtedly due to the restriction imposed by the multiple-bonding interaction of the μ_4 -CO ligand. These features are observed in many other clusters containing the encapsulated μ_4 -CO fragment.^{10,11}

 Table 4. Selected Bond Distances (Å) and Bond

 Angles (deg) for 4

	_	<u> </u>	
	Intermetallic	Distances	
W-Ru(1)	2.892(1)	W-Ru(2)	2.871(1)
W-Ru(3)	2.898(1)	W-Ru(4)	2.935(1)
Ru(1)-Ru(3)	2.750(1)	Ru(1)-Ru(4)	2.892(1)
Ru(2)-Ru(3)	2.783(1)	Ru(2)-Ru(4)	2.854(1)
Ru(3)-Ru(4)	2.805(1)		
Paramet	ers Associated	l with CO Ligands	
W-C(1)	1.98(1)	Ru(1)-C(1)	2.48(1)
$\angle W - C(1) - O(1)$	157.9(8)	W-C(2)	1.94(1)
Ru(2) - C(2)	2.56(1)	$\angle W - C(2) - O(2)$	161.2(8)
Ru(1) - C(3)	1.91(1)	Ru(1) - C(4)	1.88(1)
Ru(1) - C(5)	1.88(1)	Ru(2) - C(6)	1.85(1)
Ru(2) - C(7)	1.88(1)	Ru(2) - C(8)	1.88(1)
Ru(3)-C(9)	1.88(1)	Ru(3) - C(10)	1.91(1)
Ru(2) - C(11)	2.58(1)	Ru(3) - C(11)	1.92(1)
$\angle Ru(3) - C(11) - O(1)$	1) 161.5(8)	Ru(4) - C(12)	1.89(1)
Ru(4) - C(13)	1.91(1)	Ru(4) - C(14)	1.89(1)
Bond Distan	ces Associated	d with the Cp Liga	nds
W - C(15)	2.27(1)	W-C(16)	2.31(1)
W - C(17)	2.32(1)	W - C(18)	2.34(1)
W-C(19)	2.32(1)		
N	letal-Hydride	• Distances	
W-H	1.75(6)	Ru(1)-H	2.00(7)
Ru(4)-H	1.74(7)		

 Table 5. Selected Bond Distances (Å) and Bond

 Angles (deg) for 5

Intermetallic Distances					
Mo-Ru(1)	2.9445(8)	Mo-Ru(3)	2.9648(7)		
Ru(1)-Ru(2)	2.8005(7)	Ru(1) - Ru(3)	2.8720(7)		
Ru(1)-Ru(4)	2.8592(7)	Ru(2)-Ru(3)	2.7448(7)		
Ru(2)-Ru(4)	2.8088(7)	Ru(3)-Ru(4)	2.8437(7)		
Parameters	Parameters Associated with the McCO Ligand				
Mo-C(1)	2.387(5)	$M_0 - O(1)$	2.131(3)		
Ru(1) - C(1)	2.210(5)	Ru(3)-C(1)	2.184(5)		
Ru(4) - C(1)	1.981(5)	C(1) - O(1)	1.266(6)		
$\angle \operatorname{Ru}(4) - \operatorname{C}(1) - \operatorname{O}(1)$	135.6(4)	$\angle Mo - C(1) - O(1)$	62.9(3)		
$\angle Ru(1) - C(1) - Ru(3)$) 81.6(2)				
M. C(0)	es Associated	With Other CO Lig	ands		
Mo - C(2)	2.004(5)	Mo - C(3)	1.998(6)		
$\operatorname{Ru}(1) - \operatorname{C}(4)$	1.859(6)	Ru(1) - C(5)	1.901(6)		
$\operatorname{Ru}(1) - \operatorname{C}(6)$	2.243(6)	Ru(2) - C(6)	2.027(6)		
Ru(2) - C(7)	1.906(6)	Ru(2) - C(8)	1.881(6)		
Ru(2) - C(9)	2.104(6)	Ru(3) - C(9)	2.176(6)		
Ru(3) - C(10)	1.896(6)	Ru(3) - C(11)	1.873(6)		
Ru(4) - C(12)	1.930(6)	Ru(4) - C(13)	1.909(6)		
Ru(4) - C(14)	1.943(6)				
Bond Distances Associated with the Cp* Ligands					
Mo - C(15)	2.377(5)	Mo-C(16)	2.377(5)		
Mo - C(17)	2.324(5)	Mo-C(18)	2.316(5)		
Mo-C(19)	2.332(5)	/			
Metal-Hydride Distances					
Ru(1)-H	1.82(6)	Ru(2)-H	1.90(6)		

NMR Analyses and Solution Fluxionality of 4. To acquire more information on the nature of these cluster complexes in solution, variable-temperature ¹H NMR spectra were recorded. At room temperature, complex 4 in CD_2Cl_2 exhibits a Cp signal at δ 5.76 and a very broad hydride signal at δ -15.36. Below 270 K the hydride signal broadens and turns into a sharp

2.05(6)

Ru(3) - (H)



Figure 1. Molecular structure and atomic numbering scheme of 4.



Figure 2. Molecular structure and atomic numbering scheme of 5.

singlet with clearly visible satellite peaks due to the coupling with the W atom (Figure 3). As the temperature increases, the hydride signal also sharpens and the tungsten satellites also become observable near 313 K. This behavior is consistent with a "hidden-partner" exchange process, and the failure to observe the hidden partner is apparently due to an equilibrium heavily favoring the major component, thus resulting in the signal of the minor isomer being lost in the base line of the NMR spectrum.¹²

Because we observe J_{W-H} coupling to the hydride signal at low temperature, we speculate that the major isomer in solution possesses a structure identical with that already determined by X-ray diffraction and that the exchange is due to hydride migration from a WRu₂ face to other triangular faces of the trigonal-bipyramidal

^{(10) (}a) Kwek, K.; Taylor, N. J.; Carty, A. J. J. Am. Chem. Soc. 1984, 106, 4636. (b) Field, J. S.; Haines, R. J.; Mulla, F. J. Organomet. Chem. 1990, 389, 227. (c) Chi, Y.; Chuang, S.-H.; Liu, L.-K.; Wen, Y.-S. Organometallics 1991, 10, 2485.

^{(11) (}a) Adams, R. D.; Babin, J. E.; Tasi, M. Inorg. Chem. 1988, 27, 2618. (b) Anson, C. E.; Bailey, P. J.; Conole, G.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Powell, H. R. J. Chem. Soc., Chem. Commun. 1989, 442. (c) Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Pearsall, M.; Sironi, A. J. Chem. Soc., Chem. Commun. 1984, 1089.

^{(12) (}a) Okazawa, N.: Sorenson, T. S. Can. J. Chem. 1978, 56, 2737.
(b) Anet, F. A. L.; Basus, V. J. J. Magn. Reson. 1978, 32, 339. (c) Nucciarone, D.; Taylor, N. J.; Carty, A. J. Organometallics 1988, 7, 127.



Figure 3. Variable-temperature ¹H NMR spectra of 4 in CD_2Cl_2 solution.



^{*a*} Legend: $Ru = Ru(CO)_2$; $Ru = Ru(CO)_3$. Three bridging CO ligands, located on the boldface metal-metal bonds, are omitted for clarity.

cluster arrangement (Scheme 3). Evidence for the occurrence of such exchange motion comes from the observation of facile hydride migration in hydride cluster compounds.¹³ The hydride exchange envisaged in Scheme 3 represents one such possibility, in which the hidden isomer **4b** is generated by hydride migration to a nearby Ru_3 triangular surface of the metal core.

In addition, the fluxionality of the major isomer is observed in the variable-temperature ¹³C NMR studies. The spectrum recorded at 200 K shows only 11 of the 14 expected CO signals at δ 234.0 ($J_{W-C} = 155$ Hz), 201.5, 192.4, 189.2, and 188.7 in the intensity ratio 2:3: 2:2:2. This pattern indicates the existence of a timeaveraged plane of mirror symmetry which coincides with the equatorial WRu₂ triangle, generated by hydride



Figure 4. Variable-temperature ¹³C NMR spectra of **6** in THF- d_8 solution. Signals marked with an asterisk are due to isomer **6b**.

migration between the adjacent WRu₂ faces. The existence of a mirror plane causes the bridging CO ligands on W-Ru edges to become equivalent and the terminal CO ligands on each axial Ru atom to possess an identical environment. Thus the signals occurring at δ 192.4, 189.2, and 188.7 are due to CO ligands on axial Ru atoms. Consistent with our hypothesis, these three signals broaden and coalesce into a very broad hump at δ 189.9 corresponding to six CO ligands when we raise the temperature to 253 K, due to the rapid threefold rotation. At 293 K, all CO resonances coalesce into the base line, indicating the coexistence of rapid isomerization with **4b** and CO scrambling between W and all Ru sites.

NMR Analyses and Solution Fluxionality of 5 and 6. The ¹H and ¹³C NMR spectra of the Cp^{*} derivatives 5 and 6 were recorded to illustrate its relationship with the Cp derivative. The ¹H NMR of 5 at 293 K shows, besides the Me signal due to the Cp^{*} ligand, two hydride signals at δ -15.08 and -18.87 in the ratio 1:9, suggesting the presence of two isomers in solution. Similarly, the Cp^{*}WRu₄ derivative 6 also exhibits two hydride signals at δ -14.25 ($J_{W-H} = 68$ Hz) and -19.01 in a ratio of 1:3 in both CD₂Cl₂ and THF- d_8 solution. Because of the lack of J_{W-H} coupling to the more downfield hydride signal, the predominant species 5a and 6a are assigned to possess a structure already determined by X-ray studies.

In accordance with this assignment, the ¹³C NMR spectrum of **6** at 270 K shows a series of nine CO signals at δ 302.0, 228.9, 227.1 ($J_{W-C} = 176$ Hz), 219.1 ($J_{W-C} = 148$ Hz), 199.9 (3C), 196.0, 194.3, 193.8, and 192.7 (Figure 4). The integrated intensity pattern is 1:1:1:1: 3:1:1:1:1 starting from left to right. We speculate that all these resonances derive from the isomer **6a**, and they account for 11 of the 14 expected CO ligands. The first

^{(13) (}a) Chen, C.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. J. Chem. Soc., Dalton Trans. **1993**, 1823. (b) Lin, R.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. Inorg. Chem. **1992**, 31, 3818. (c) Park, J. T.; Chi, Y.; Shapley, J. R.; Churchill, M. R.; Ziller, J. W. Organometallics **1994**, 13, 813.





5a, M = Mo; 6a, M = W



^a Legend: $Ru = Ru(CO)_2$; $Ru = Ru(CO)_3$. Two bridging CO ligands, located on the boldface Ru-Ru bonds, are omitted for clarity.

five signals are produced by the μ_4 -CO group, a bridging CO ligand, two CO ligands on the W atom, and the $Ru(CO)_3$ fragment located at the unique position opposite to the hydride ligand. The chemical shift of the μ_4 -CO ligand is exceptional. Its value appears compatible with that of the triply bridging CO ligand (δ 308.0) in $Cp*CpW_2Ru_2(CO)_6(CCPh)_2^{14}$ and is much lower field than that observed in the butterfly complexes [Fe₄(μ - $X)(CO)_{13}]^-$ (X = H, AuPPh₃, HgR; R = Me, CpFe(CO)₂, CpMo(CO)₃; δ 284.9-279.8)^{3d,15} and LWRu₃(CO)₁₂(μ -AuPPh₃) (L = Cp, Cp*; δ 272.8-255.1).¹⁶ Partial assignment of the four high-field Ru-CO resonances has been achieved by turning off proton decoupling. This treatment allowed the CO signals at δ 196.0 and 194.3 to appear as doublets in the undecoupled spectrum, indicating that they are due to CO ligands trans to the hydride.

The other three Ru–CO signals of **6a** and some CO signals of **6b** came into view at lower temperature. First, three broad CO signals surface at δ 236.1, 199.5, and 191.3 at 250 K. We believe that they are due to a "Ru(CO)₂(μ -CO)Ru" grouping of **6a**, for which the signal at δ 236.1 is due to the bridging CO ligand. By further cooling to 200 K, the CO signals of **6b** appear and the NMR spectrum becomes very complicated. Assignment of the CO resonance signals of **6b** is precluded because of their low intensity and high fluxionality. However, the slightly broad W–CO signal at δ 235.2, which exhibits a distinct coupling with the W atom ($J_{W-C} = 157$ Hz), the sharp Ru(CO)₃ resonance at δ 204.1, and several other broad peaks are definitely contributed by isomer **6b**.

On the basis of these limited ¹³C NMR spectral data, the key structure of the minor component **6b** can be deduced. The existence of only one W-CO resonance at δ 239.0 and the lack of the respective μ_4 -CO signal in the region below δ 239 strongly indicate that a trigonal-bipyramidal metal framework with nine M-M bonds is produced (Scheme 4), as formation of one additional M–M bond is required to compensate for the electronic unsaturation generated by removal of the μ_4 -CO ligand from the edge-bridged tetrahedral arrangement of **6a** (eight M–M bonds). The great fluxionality of the CO ligands confirms the attachment of CO ligands to the close-packed trigonal-bipyramidal metal framework. This behavior is in full accord with the ¹³C NMR fluxional behavior of the already discussed pentanuclear cluster **4** and the tetrahedral isomers **1–3**.

Although we are confident about the prediction of the skeletal arrangement, the exact disposition of the hydride and W atom in 6b cannot be determined from available data. Although the large J_{W-H} coupling implied that the hydride ligand is directly coordinated to the W atom, this ligand may adopt either a triply bridging or a doubly bridging mode; we have no experimental evidence to differentiate them. Similarly, the W atom may be located at either an axial or an equatorial site. We favor the structure with the W atom at the axial site, as the direct generation of M-M bonding between the pendant $Cp*W(CO)_2$ fragment and the $Ru(CO)_2$ fragment of **6a** is expected to lead readily to this trigonal-bipyramidal configuration. A subsequent cluster rearrangement following initial formation of the M-M bond might produce a more stable isomer with a W atom occupying an equatorial site, as shown in the alternative drawing 6b' in Scheme 4. The crystal structure of 4 supports the latter assignment.

Finally, the ¹³C NMR spectra of the Cp*MoRu₄ complex 5 were also recorded. The variable-temperature spectra exhibit similar fluxional behavior, and the respective diagnostics are less clear due to the lack of J_{W-C} coupling. By using our previous discussion, the 12 CO signals at δ 292.1, 240.6, 236.0 (br), 233.1, 228.6, 199.8 (3C), 199.5, 195.3, 194.9, 194.7, 193.5, and 190.0, observed in the spectrum at 205 K, are assigned to the μ_4 -CO group, two bridging CO ligands, two Mo-CO ligands, the CO ligands of a Ru(CO)3 fragment, and seven inequivalent terminal Ru-CO ligands of the predominant, edge-bridged tetrahedral isomer 5a, respectively. Three weak CO resonances at δ 219.2, 202.4, and 192.8 were also seen for the minor isomer 5b at this temperature. No attempt was made to identify these signals due to their low abundance.

Reactivity Studies. Limited studies have been conducted to reveal basic reactivities. Complexes 5 and 6 react with CO in refluxing toluene to afford complexes 3 and 2 in moderate yields, respectively. Upon switching to H₂, we obtain the corresponding hydride complexes Cp*MoRu₃(CO)₁₁H₃ and Cp*WRu₃(CO)₁₁H₃ in high yields, which adopt a tetrahedral framework with hydride ligands located on one Ru–Ru and two M–Ru edges.¹⁷ These results indicate that cluster degradation is the predominant pathway. The Cp derivative 4 follows the same reaction patterns presumably, but no attempt was made due to its scarcity.

Conclusion. In this work, we present the synthesis and structural characterization of neutral pentametal WRu₄ and MoRu₄ clusters with 1 hydride and 14 CO ligands. Their formation can be considered as a condensation between the tetranuclear anionic clusters $[LMRu_3(CO)_{12}]^-$ and $Ru_3(CO)_{12}$ to generate the penta-

⁽¹⁴⁾ Hwang, D.-K.; Lin, P.-J.; Chi, Y.; Peng, S.-M.; Lee, G.-H. J.
Chem. Soc., Dalton Trans. 1991, 2161.
(15) Wang, J.; Sabat, M.; Horwitz, C. P.; Shriver, D. F. Inorg. Chem.

⁽¹⁵⁾ Wang, J.; Sabat, M.; Horwitz, C. P.; Shriver, D. F. Inorg. Chem. 1988, 27, 552.

⁽¹⁶⁾ Chen, C.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. Unpublished results.

^{(17) (}a) Chi, Y.; Cheng, C.-Y.; Wang, S.-L. J. Organomet. Chem. 1989, 378, 45. (b) Housecroft, C. E.; Matthews, D. M.; Rheingold, A. L.; Song, X. J. Chem. Soc., Dalton Trans. 1992, 2855.

Clusters Containing a Quadruply Bridging CO Ligand

metal anionic clusters $[LMRu_4(CO)_{14}]^-$. These pentanuclear anions then react with a proton source to afford the isolated clusters $LMRu_4(CO)_{14}H$. The Cp derivative 4 shows a trigonal-bipyramidal core arrangement, in which the hydride ligand undergoes migration between the WRu₂ triangular faces and the Ru₃ faces. In contrast, the Cp* derivatives 5 and 6 show a different type of dynamic process, which involves a skeletal rearrangement between edge-bridged-tetrahedral and the trigonal-bipyramidal geometry and concurrent switching of one CO ligand between the novel μ_4 - η^2 mode and the regular C-bound mode. The Cp* ligand favors the edge-bridged-tetrahedral arrangement because it provides greater steric repulsion than does the Cp ligand. This argument is consistent with the trend observed in complexes 1-3, as the Cp* derivatives 2 and 3 contain more butterfly isomers ($\geq 85\%$) than the corresponding Cp derivative 1 (\sim 55%), and the Cp*-containing metal fragments invariably reside at the less congested wingtip positions. Finally, this enhanced steric interaction in the Cp* derivatives is confirmed by the observation that the C-Mo distances of the Cp* ligand in 6 (average 2.345 Å) are always longer than those of the C-W distances of the Cp ligand in 4 (average 2.31 Å).

Finally, these pentametal clusters are unstable relative to their tetrametal counterparts. Treatment of **5** and **6** with both CO and H₂ in refluxing toluene led to the formation of complexes **3** and **2** and the hydride complexes Cp*MoRu₃(CO)₁₁H₃ and Cp*WRu₃(CO)₁₁H₃. These degradation reactions formally proceed via expelling of the Ru(CO)₂ fragment and were confirmed by isolation of Ru₃(CO)₁₂ from the reaction mixture.

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Supporting Information Available: Tables of calculated positions of hydrogen atoms and anisotropic thermal parameters for 4 and 5 (6 pages). Ordering information is given on any current masthead page.

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