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Multisite-Bound Vinylidenes on Heterometallic Clusters. Reformulation of (η^5-$C_5H_5Ni)Ru_3(CO)_9(\mu_4$-$\eta^2$-C═CHR) (R = *t*-Bu) as Hydrido-Bridged (μ-H)(η^5-$C_5H_5Ni)Ru_3(CO)_9(\mu_4$-$\eta^2$-C═CHR). Molecular Structure of the Isopropyl Derivative (R = *i*-Pr) and an Improved Synthetic Method

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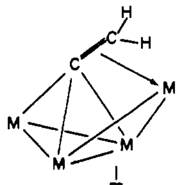
The mixed-metal vinylidene cluster (μ-H)(η^5-$C_5H_5Ni)Ru_3(CO)_9(\mu_4$-$\eta^2$-C═CH-*i*-Pr) has been synthesized via the reaction of (μ-H)$Ru_3(CO)_9(\mu_3$-η^2-C≡C-*i*-Pr) with $[\eta^5$-$C_5H_5Ni(CO)]_2$ and fully characterized by single-crystal X-ray diffraction. Crystals are monoclinic, space group $P2_1/n$ with $a = 9.131$ (1) Å, $b = 16.257$ (3) Å, $c = 15.751$ (3) Å, $\beta = 94.35$ (1)°, and $Z = 4$. The structure was solved and refined by using 3440 observed diffractometer data to R and R_w values of 0.034 and 0.040. The Ru_3Ni core has a butterfly configuration with the nickel atom occupying a wing-tip site. The unsaturated vinylidene ligand is σ-bonded to Ru(1), Ru(3), and Ni and η^2-coordinated to Ru(2). The dihedral angle between the two wings of the butterfly is 118.25°. The Ru(1)–Ru(3) edge is bridged by a single hydrogen atom. Location of the hydride in (μ-H)(η^5-$C_5H_5Ni)Ru_3(CO)_9(\mu_4$-$\eta^2$-C═CH-*i*-Pr) by X-ray and spectroscopic methods confirms that the related cluster previously described in the literature as (η^5-$C_5H_5Ni)Ru_3(CO)_9(\mu_4$-$\eta^2$-C═CH-*t*-Bu) should be reformulated as a hydride. A higher yield synthesis of these mixed $NiRu_3$ clusters using molecular hydrogen has been designed.

Introduction

Interest in the chemistry of multisite-, cluster-bound vinylidenes stems principally from the expectation that μ-C═CH_2 groups, formed via μ-methylene migration to a carbidic carbon atom, may be implicated in Fischer–Tropsch hydrocarbon synthesis.[2] In the specific context of tetranuclear butterfly clusters there are also rather close structural similarities between the prototype μ_4-vinylidene complex **1** and μ_4-carbido **2** (e.g., $Fe_4(CO)_{12}(\mu_4\text{-}C)^{2-}$),[3,4] μ_4-methylidyne **3** (e.g., (μ-H)$Fe_4(CO)_{12}(\mu_4$-CH)),[4] μ_4-CO **4** (e.g., $HFe_4(CO)_{13}^-$),[5] and μ_4-COMe **5** (e.g., $HFe_4(CO)_{12}(COMe)$)[6] clusters discussed as model intermediates in CO hydrogenation. Although vinylidenes are well-known as terminal and doubly bridging[7,8] ligands in organometallic chemistry, only a few examples of μ_4-bound C═CRR′ groups are known. The first cluster of this type to be described was formulated as (η^5-$C_5H_5Ni)Ru_3(CO)_9(\mu_4$-$\eta^2$-C═CH-*t*-Bu).[9] X-ray analysis showed a μ_4-C═CHR group σ-bonded to two ruthenium atoms and one nickel atom with the double bond η^2-coordinated to the remaining ruthenium atom. Similar μ_4-η^2-bonding modes were recently observed in the electron-precise homo-



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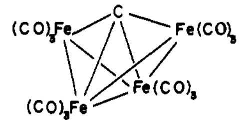

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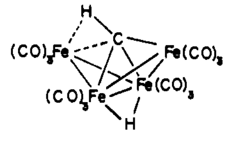

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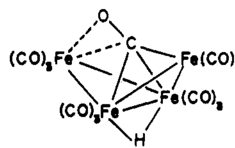

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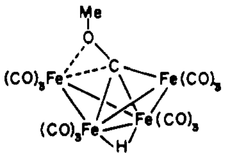

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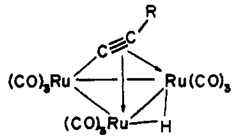

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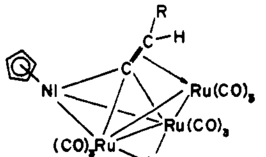

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tetranuclear butterfly clusters $Ru_4(CO)_{10}(\mu_3\text{-}OR)(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{=}CH\text{-}i\text{-}Pr)$[10] and the mixed butterfly $(\eta^5\text{-}C_5H_5Fe)Co_3(CO)_7(\mu\text{-}CO)_2(\mu_4\text{-}\eta^2\text{-}C{=}CH_2)$.[11] In the former the μ-vinylidene was derived from an alkyne; in the latter the cluster precursor was the dinuclear μ-vinylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$.

Since vinylidenes, C═CHR, are valence tautomers of acetylenes, RC≡CH, clusters containing μ-bound C═CHR ligands might be expected among the products of reactions between polynuclear carbonyls and acetylenes. In fact such evidence is generally lacking.[12] Thus for example the reaction of alkynes with $Ru_3(CO)_{12}$ leads to different clusters depending on the alkyne substitution, but vinylidenes are not among the products.[13,14] With terminal alkynes and phosphinoalkynes, C–H or C–P cleavage occurs but hydrido- or phosphido-bridged acetylides[14,15] rather than vinylidenes are formed.

An alternative route to cluster vinylidenes might involve transfer of hydrogen, probably as hydride ion, to the β-carbon atom of a carbocationic acetylide. Since there is now abundant evidence that μ-η-acetylides in binuclear and polynuclear carbonyls are exceedingly sensitive to nucleophilic attack,[16] hydride transfer to such an activated unsaturated ligand would be expected. In seeking to exploit the demonstrated electrophilicity of μ-acetylides in clusters, we are investigating the reactions of compounds such as $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)$,[14] $Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)$,[17] and $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CR)$[18] with transition-metal nucleophiles as a route to higher mixed-metal species.[19] As part of this work we have reexamined the reactions of $[\eta^5\text{-}C_5H_5Ni(CO)]_2$ with $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{—}C{\equiv}CR)$ (**6**) in an effort to extend the range of cluster vinylidene complexes. A careful X-ray structural analysis of "$(C_5H_5Ni)Ru_3(CO)_9(C{=}CH\text{-}i\text{-}Pr)$" revealed the presence of a bridging hydride ligand previously undetected[9] in the *tert*-butyl analogue. Thus, these vinylidene clusters must be reformulated as the hydrido species $(\mu\text{-}H)(C_5H_5Ni)Ru_3(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CHR)$ (**7**) (R = *t*-Bu, *i*-Pr). The presence of a hydrido ligand obviates the need to rationalize the diamagnetism of **7** (R = *t*-Bu) on the basis of 5-electron-donor character for the vinylidene. On the basis of knowledge of the correct structure of **7**, a logical and higher yield synthesis has been developed and is described herein.

Table I. Crystal and Intensity Data for $(\mu\text{-}H)(\eta^5\text{-}C_5H_5Ni)Ru_3(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CH\text{-}i\text{-}Pr)$

(A) Crystal Data at 21 ± 1 °C

space group $P2_1/n$
$a = 9.131\ (1)$ Å
$b = 16.257\ (3)$ Å
$c = 15.751\ (3)$ Å
$Z = 4$
mol wt = 748.33
$\beta = 94.35\ (1)^\circ$
$V = 2331.4\ (6)$ Å^3
ρ(calcd) = 2.132 g cm^{-3}
ρ(measd) = 2.12 g cm^{-3}
$F(000) = 1440$
μ(Mo Kα) = 26.97 cm^{-1}

(B) Data Collection

radiation: Mo Kα ($\lambda = 0.710\,69$ Å)
monochromator: highly oriented graphite
scan type: θ–2θ
scan speed: variable, 2.0–29.3° min^{-1}
bkgd measurements: stationary crystal, stationary counter at beginning and end of each scan for a time equal to half the scan time
reflcns measd: 4130 ($2\theta \leqslant 50^\circ$)
reflcns obsd: 3440 ($I \geqslant 3\sigma(I)$)
std reflcns: 2 measured after every 100 reflections

Experimental Section

Synthesis of Complex 6 (R = *i*-Pr). Treatment of $Ru_3(CO)_{12}$ (300 mg; 0.5 mM) with 0.5 mL (5 mM) of liquid HC≡C-*i*-Pr in refluxing heptane under nitrogen (15 min) gave a dark yellow solution. Thin-layer chromatography revealed the presence of small amounts of six other compounds in addition to **6** and $Ru_3(CO)_{12}$. Preparative TLC (silica gel) with mixtures of petroleum ether and ethyl ether as eluants separated **6**, slightly contaminated with $Ru_3(CO)_{12}$. Treatment with a small volume of heptane left $Ru_3(CO)_{12}$ undissolved and afforded on cooling overnight at −10 °C yellow crystals of **6** (20%). Anal. Calcd: C, 27.0; H, 1.3; Ru, 48.6. Found: C, 26.9; H, 1.2; Ru, 49.0. Ir (C_7H_{16}): ν(CO) 2096 m, 2070 vs, 2052 vs, 2024 vs, 2017 sh, 1991 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 0.80 (m, 1 H, –CH), −20.70 (s, 1 H, Ru–H–Ru).

Reaction of 6 (R = *i*-Pr) with $[\eta^5\text{-}C_5H_5Ni(CO)]_2$. A twofold excess of the nickel dimer was refluxed in *n*-octane (200 mL) with **6** (R = *i*-Pr) (300 mg) for 40 min. Removal of solvent followed by preparative thin-layer chromatography on silica gel (eluant petroleum ether–ether) afforded **7** (R = *i*-Pr) as an oily brown solid. Recrystallization from heptane–$CHCl_3$ (80:20) gave dark prisms in 20% yield. Anal. Calcd: C, 31.5; Ni, 8.4; Ru, 40.7. Found: C, 31.1; Ni, 8.1; Ru, 41.0. Ir (C_7H_{16}): ν(CO) 2082 s, 2056 vs, 2044 vs, 2012 s, 2006 sh, 1985 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.30 (s, 5 H, C_5H_5), 4.80 (s, 1 H, ═CH), 1.40 (m, 1 H, –CH), 1.25 (s, 3 H, CH_3), 0.75 (s, 3 H, CH_3), −21.3 (s, 1 H, Ru–H–Ru).

Reaction of 6 (R = *i*-Pr, *t*-Bu) with $[\eta\text{-}C_5H_5Ni(CO)]_2$ and Dihydrogen. Location of the hydride ligand in **7** (R = *i*-Pr) led us to attempt the reaction of **6** with $[\eta^5\text{-}C_5H_5Ni(CO)]_2$ under dihydrogen. In a typical experiment **6** was refluxed with a twofold excess of nickel reagent in heptane under rapid flow of H_2 for 80 min. The solution was cooled under H_2 and chromatographed as before. About 20% of **6** was recovered unreacted together with small amounts of metallic nickel and much improved yields of **7** (40–50%). Minute amounts of four other clusters were also evident.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 580 instrument and ^{1}H NMR spectra in $CDCl_3$ with Me_4Si as an internal standard on a JEOL C60 HL instrument. Microanalyses were carried out with an F & M 185, C, H, and N analyzer and a PE 303 atomic absorption spectrometer.

X-ray Crystal Structure Analysis. Collection and Reduction of X-ray Data. Brown crystals of **7** (R = *i*-Pr) were shown to be monoclinic from preliminary photography. A suitable prism of dimensions 0.26 × 0.28 × 0.32 mm was mounted on a glass fiber, attached to a eucentric goniometer head, which was transferred to a Syntex $P2_1$ automatic diffractometer. Accurate unit cell dimensions were determined from the setting angles of 15 strong reflections well dispersed in reciprocal space by employing the Syntex autoindexing and cell refinement routines. Details are given in Table I. The complex crystallizes in the same space group ($P2_1/n$) as the *tert*-butyl analogue, and the unit cell parameters confirm that the two structures are

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Table II. Atomic Coordinates (Fractional, $\times 10^4$) for $(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C=CH-}i\text{-Pr})$

A. Non-Hydrogen Atoms

	x	y	z
Ru(1)	3483.6 (5)	830.4 (3)	3071.6 (3)
Ru(2)	3228.2 (5)	1075.7 (3)	1315.1 (3)
Ru(3)	979.0 (5)	217.7 (3)	2088.8 (3)
Ni	839.9 (8)	1299.8 (5)	3270.7 (4)
O(1)	5009 (6)	2467 (3)	3401 (4)
O(2)	3356 (6)	285 (4)	4929 (3)
O(3)	6375 (5)	−34 (4)	2800 (4)
O(4)	5873 (6)	2195 (3)	1214 (4)
O(5)	1999 (6)	1198 (4)	−530 (3)
O(6)	4930 (6)	−486 (3)	918 (4)
O(7)	−634 (6)	−919 (4)	3256 (4)
O(8)	1615 (7)	−1142 (4)	846 (4)
O(9)	−1818 (6)	749 (4)	1084 (4)
C(1)	4442 (7)	1858 (4)	3302 (4)
C(2)	3374 (7)	485 (4)	4239 (4)
C(3)	5287 (7)	288 (4)	2889 (4)
C(4)	4883 (7)	1772 (4)	1218 (4)
C(5)	2455 (7)	1158 (4)	149 (4)
C(6)	4284 (7)	77 (4)	1080 (4)
C(7)	−56 (7)	−482 (4)	2824 (4)
C(8)	1395 (7)	−632 (4)	1300 (4)
C(9)	−754 (7)	556 (4)	1453 (4)
C(10)	1753 (6)	1448 (3)	2278 (3)
C(11)	1951 (6)	2137 (3)	1748 (4)
C(12)	806 (7)	2514 (4)	1114 (4)
C(13)	1556 (10)	3101 (5)	526 (5)
C(14)	−350 (10)	2979 (6)	1568 (6)
C(15)	214 (10)	1197 (7)	4546 (5)
C(16)	796 (11)	1983 (7)	4390 (6)
C(17)	−99 (12)	2374 (5)	3773 (7)
C(18)	−1177 (9)	1838 (6)	3506 (5)
C(19)	−1008 (9)	1101 (5)	3998 (5)

B. Hydrogen Atoms

	x	y	z	B, Å^2
H(1)	2498	−135	2748	6 (2)
H(11)	2768	2602	2042	5 (2)
H(12)	381	2077	710	4 (2)
H(13A)	2354	2864	185	7 (2)
H(13B)	988	3371	165	6 (2)
H(13C)	1936	3658	806	10 (2)
H(14A)	−875	2680	1942	4 (2)
H(14B)	−811	3323	1314	7 (2)
H(14C)	203	3435	1907	7 (3)
H(15)	650	880	5090	10 (4)
H(16)	1743	2419	4618	12 (3)
H(17)	78	3026	3637	12 (4)
H(18)	−2126	1851	3128	7 (2)
H(19)	−1603	569	3923	8 (3)

probably isomorphous. Intensity data were collected on the $P2_1$ diffractometer as indicated in Table I. Over the course of data collection the intensities of the standard reflections 206 and 251 declined by less than 2%. Data were reduced to structure factors in the normal way following application of Lorentz and polarization corrections. No absorption correction was necessary since examination of ψ scans revealed that a maximum error of 5% in intensities would be introduced by absorption effects ($\mu = 26.97\ \text{cm}^{-1}$).

Solution and Refinement of the Structure. The positions of all four heavy atoms were immediately evident from a Patterson synthesis. Following one cycle of positional refinement, Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement using isotropic temperature coefficients reduced the residual R ($R = \sum w|F_o| - |F_c|)/\sum|F_o|$) to 0.074. Conversion to anisotropic temperature coefficients and two cycles of refinement reduced R to 0.039. At this stage the detailed stereochemistry of the molecule, in particular the large angles Ru(1)–Ru(3)–CO and Ru(3)–Ru(1)–CO, suggested the possible presence of a bridging hydride along the Ru(1)–Ru(3) edge. Examination of a difference Fourier map revealed unmistakably the location of the bridging hydrogen atom. All other hydrogen atoms were similarly found. In a final calculation these hydrogen atoms were included and isotropic temperature factors refined. A weighting scheme of the type $w^{-1} = 2.84 - 0.0218|F_o| + 0.00034|F_o|^2$ was used in the final refinement cycles. At convergence R and R_w ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) values were 0.034 and 0.040. A final difference map was featureless. All computations were carried out by using programs already described[16e] on IBM 4341 or 370 systems in the University of Waterloo computing center. Scattering factors used were taken from the tabulations of ref 20 with the exception of those of the hydrogen atoms, which were taken from ref 21. Corrections for the real and imaginary components of anomalous dispersion were made for Ru and Ni atoms.[20] Atomic coordinates are listed in Table II, and a selection of bond lengths and bond angles is listed in Table III. Anisotropic thermal parameters are available as supplementary material (Table S1). Tables of observed and calculated structure factors have been deposited as supplementary data.

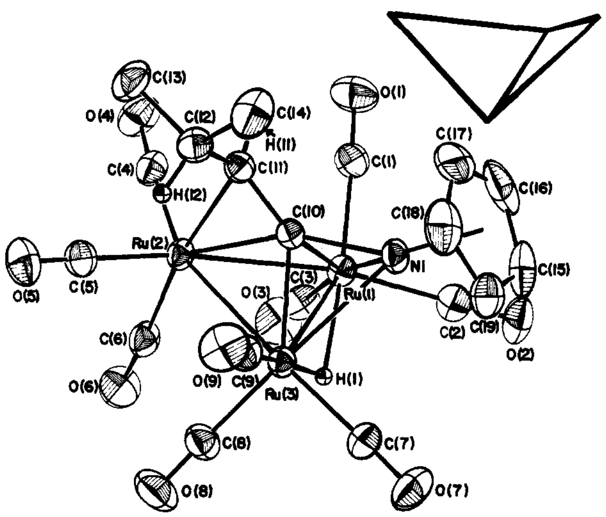

Figure 1. An ORTEP II perspective view of the molecular structure of $(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C=CH-}i\text{-Pr})$ showing the atomic numbering scheme used. The tetrametal skelton is shown as an inset.

Results and Discussion

The reaction of the terminal alkyne, HC≡C-*i*-Pr, with $\text{Ru}_3(\text{CO})_{12}$ in boiling heptane gives modest but reproducible yields of $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C≡C-}i\text{-Pr})$ (**6**) (R = *i*-Pr). This molecule exhibits a parent ion at m/e 626 in the mass spectrum and fragment ions corresponding to the loss of nine CO molecules. The pattern of ν(CO) bands in the IR spectrum corresponds closely to that of **6** (R = *t*-Bu). In the ^{1}H NMR spectrum a high-field ($\delta = -20.70$) singlet can be assigned to a bridging hydride. Thus **6** (R = *i*-Pr) is isostructural with the *tert*-butyl analogue, which has been fully characterized by X-ray and neutron diffraction.[22]

The reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ni(CO)}]_2$ with the hydride-bridged cluster **6** (R = *i*-Pr) affords small amounts of a mixed tetranuclear compound originally considered, by analogy with the *tert*-butyl analogue,[9] to be the μ_4-vinylidene cluster $(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C=CH-}i\text{-Pr})$. Subsequent to the X-ray analysis of this complex (vide infra), an examination of the high-field regions of the ^{1}H NMR spectrum revealed a broadened resonance at $\delta = -21.3$ corresponding to a bridging hydride. The *tert*-butyl cluster exhibits a similar ^{1}H resonance at $\delta = -22.1$. Thus both compounds are hydrido-bridged vinylidene clusters.

Description and Discussion of the Structure of 7 (R = *i*-Pr). An ORTEP II plot of the structure of $(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C=CH-}i\text{-Pr})$ is shown in Figure 1. The basic

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Table III. Selected Bond Lengths (Å) and Angles (deg) for $(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C=CH-}i\text{-Pr})$

A. Bond Lengths

Ru(1)-Ru(2)	2.7875 (6)	Ru(2)-C(10)	2.188 (5)	Ni-C(18)	2.097 (9)
Ru(1)-Ru(3)	2.8428 (6)	Ru(2)-C(11)	2.219 (6)	Ni-C(19)	2.134 (8)
Ru(1)-Ni	2.5735 (8)	Ru(3)-Ni	2.5715 (8)	C(1)-O(1)	1.123 (9)
Ru(1)-C(1)	1.908 (7)	Ru(3)-C(7)	1.922 (6)	C(2)-O(2)	1.135 (8)
Ru(1)-C(2)	1.933 (7)	Ru(3)-C(8)	1.915 (7)	C(3)-O(3)	1.140 (8)
Ru(1)-C(3)	1.910 (6)	Ru(3)-C(9)	1.890 (7)	C(4)-O(4)	1.136 (8)
Ru(1)-C(10)	2.183 (5)	Ru(3)-C(10)	2.134 (5)	C(5)-O(5)	1.120 (8)
Ru(1)-H(1)	1.86	Ru(3)-H(1)	1.76	C(6)-O(6)	1.128 (8)
Ru(2)-Ru(3)	2.8335 (6)	Ni-C(10)	1.843 (5)	C(7)-O(7)	1.140 (9)
Ru(2)-C(4)	1.903 (6)	Ni-C(15)	2.136 (7)	C(8)-O(8)	1.123 (9)
Ru(2)-C(5)	1.922 (6)	Ni-C(16)	2.087 (10)	C(9)-O(9)	1.137 (8)
Ru(2)-C(6)	1.938 (6)	Ni-C(17)	2.125 (9)	C(10)-C(11)	1.417 (8)

B. Bond Angles

Ru(2)-Ru(1)-Ru(3)	60.4 (0)	Ru(1)-Ru(2)-C(10)	50.3 (1)	Ni-Ru(3)-C(8)	170.5 (2)
Ru(2)-Ru(1)-Ni	94.0 (0)	Ru(1)-Ru(2)-C(11)	79.2 (1)	Ni-Ru(3)-C(9)	95.7 (2)
Ru(2)-Ru(1)-C(1)	93.8 (2)	Ru(3)-Ru(2)-C(4)	158.9 (1)	Ni-Ru(3)-C(10)	44.9 (1)
Ru(2)-Ru(1)-C(2)	168.4 (2)	Ru(3)-Ru(2)-C(5)	102.7 (1)	Ni-Ru(3)-H(1)	82.9
Ru(2)-Ru(1)-C(3)	85.7 (2)	Ru(3)-Ru(2)-C(6)	93.3 (1)	C(7)-Ru(3)-C(8)	95.5 (2)
Ru(2)-Ru(1)-C(10)	50.5 (1)	Ru(3)-Ru(2)-C(10)	48.2 (1)	C(7)-Ru(3)-C(9)	93.5 (2)
Ru(2)-Ru(1)-H(1)	81.1	Ru(3)-Ru(2)-C(11)	80.5 (1)	C(7)-Ru(3)-C(10)	130.0 (2)
Ru(3)-Ru(1)-Ni	56.4 (0)	C(4)-Ru(2)-C(5)	96.8 (2)	C(7)-Ru(3)-H(1)	81.6
Ru(3)-Ru(1)-C(1)	138.5 (2)	C(4)-Ru(2)-C(6)	94.3 (2)	C(8)-Ru(3)-C(9)	93.7 (2)
Ru(3)-Ru(1)-C(2)	108.6 (2)	C(4)-Ru(2)-C(10)	115.1 (2)	C(8)-Ru(3)-C(10)	133.3 (2)
Ru(3)-Ru(1)-C(3)	115.1 (2)	C(4)-Ru(2)-C(11)	90.1 (2)	Ru(1)-C(10)-Ru(2)	79.2 (0)
Ru(3)-Ru(1)-C(10)	48.1 (1)	C(5)-Ru(2)-C(6)	91.6 (2)	Ru(1)-C(10)-Ru(3)	82.4 (0)
Ru(3)-Ru(1)-H(1)	37.1	C(5)-Ru(2)-C(10)	116.2 (2)	Ru(1)-C(10)-Ni	79.0 (0)
Ni-Ru(1)-C(1)	98.0 (2)	C(5)-Ru(2)-C(11)	94.3 (2)	Ru(1)-C(10)-C(11)	125.6 (2)
Ni-Ru(1)-C(2)	81.6 (2)	C(6)-Ru(2)-C(10)	134.8 (2)	Ru(2)-C(10)-Ru(3)	81.9 (0)
Ni-Ru(1)-C(3)	169.5 (2)	Ru(1)-H(1)-Ru(3)	103.3	Ru(2)-C(10)-Ni	153.4 (0)
Ni-Ru(1)-C(10)	44.7 (1)	C(6)-Ru(2)-C(11)	172.2 (2)	Ru(2)-C(10)-C(11)	72.4 (2)
Ni-Ru(1)-H(1)	81.1	C(10)-Ru(2)-C(11)	37.5 (2)	Ru(3)-C(10)-Ni	80.2 (0)
C(1)-Ru(1)-C(2)	97.4 (2)	Ru(1)-Ru(3)-Ru(2)	58.8 (0)	Ru(3)-C(10)-C(11)	135.6 (2)
C(1)-Ru(1)-C(3)	92.6 (2)	Ru(1)-Ru(3)-Ni	56.5 (0)	Ni-C(10)-C(11)	133.5 (2)
C(1)-Ru(1)-C(10)	90.5 (2)	Ru(1)-Ru(3)-C(7)	106.9 (1)	Ru(2)-C(11)-C(10)	70.1 (2)
C(1)-Ru(1)-H(1)	174.7	Ru(1)-Ru(3)-C(8)	114.5 (2)	Ru(2)-C(11)-C(12)	117.6 (2)
C(2)-Ru(1)-C(3)	96.7 (2)	Ru(1)-Ru(3)-C(9)	142.5 (2)	C(10)-C(11)-C(12)	126.5 (3)
C(2)-Ru(1)-C(10)	126.2 (2)	Ru(1)-Ru(3)-C(10)	49.6 (1)	C(11)-C(12)-C(13)	109.5 (3)
C(2)-Ru(1)-H(1)	87.6	Ru(1)-Ru(3)-H(1)	39.6	C(11)-C(12)-C(14)	111.0 (4)
C(3)-Ru(1)-C(10)	136.2 (2)	Ru(2)-Ru(3)-Ni	93.0 (0)	C(13)-C(12)-C(14)	109.6 (4)
C(3)-Ru(1)-H(1)	88.5	Ru(2)-Ru(3)-C(7)	162.9 (1)	C(8)-Ru(3)-H(1)	87.8
C(10)-Ru(1)-H(1)	85.2	Ru(2)-Ru(3)-C(8)	83.7 (2)	C(9)-Ru(3)-C(10)	93.2 (2)
Ru(1)-Ru(2)-Ru(3)	60.8 (0)	Ru(2)-Ru(3)-C(9)	103.5 (2)	C(9)-Ru(3)-H(1)	175.1
Ru(1)-Ru(2)-C(4)	99.1 (1)	Ru(2)-Ru(3)-C(10)	49.9 (1)	C(10)-Ru(3)-H(1)	89.2
Ru(1)-Ru(2)-C(5)	162.9 (1)	Ru(2)-Ru(3)-H(1)	81.3	Ru(1)-Ni-Ru(3)	67.1 (0)
Ru(1)-Ru(2)-C(6)	93.7 (1)	Ni-Ru(3)-C(7)	85.1 (1)	Ru(1)-Ni-C(10)	56.4 (1)

skeletal stereochemistry of the tetrametal core of **7** (insert, Figure 1) consists of a butterfly arrangement of three ruthenium atoms and a nickel atom, the latter occupying a wing-tip site. The vinylidene ligand is σ-bonded via C(10) to Ni, Ru(1), and Ru(3) and η^2-coordinated to Ru(2) via C(10) and C(11). The most important structural feature is however the presence of a hydride ligand bridging the Ru(1)–Ru(3) edge. This hydrogen atom, located directly in a difference Fourier map, exerts a rather profound stereochemical influence on the adjacent metal atoms, forcing carbonyl groups C(2)–O(2), C(3)–O(3), C(7)–O(7), and C(8)–O(8) away from the internuclear ruthenium–ruthenium region. Thus, the C–Ru(1)–Ru(3) and C–Ru(3)–Ru(1) angles subtended at the metals by these equatorial CO groups are 111.9 (average) and 110.7° (average), respectively. For the non-hydrogen-bridged edges Ru(1)–Ru(2) and Ru(3)–Ru(2), corresponding angles subtended at Ru(2) by carbonyls C(4)–O(4), C(6)–O(6) and C(5)–O(5), C(6)–O(6) are considerably smaller [illegible]6.4 and 98.0°, respectively). Although the hydride was not located in the previous study of **7** (R = *t*-Bu),[9] an analysis of the bond angles involving Ru–Ru bonds and equatorial carbonyl groups (Ru(2)–Ru(1)–C = 110.3° (average); Ru(1)–Ru(2)–C = 108.9° (average)) leaves little doubt that in this cluster also there is a hydride bridge across the Ru(1)–Ru(2) edge. Reexamination of the X-ray data for **7** (R = *t*-Bu) has subsequently confirmed the presence of a bridging hydride. Originally the diamagnetism of **7** (R = *t*-Bu) was explained on the basis that the vinylidene ligand was contributing 5 electrons to the cluster framework. When reformulated as hydrides, the clusters **7** can be described as electron-precise 62-electron clusters with the μ_4-η^2-C=CHR ligand adopting a normal 4-electron-donor role. An alternative description of the structure in terms of the skeletal-electron-counting rules is as a nido square-pyramidal system with five vertices and seven electron pairs for skeletal bonding. Such a description places C(10), Ru(1), Ru(2), and Ni in basal sites with Ru(3) apical. As expected for a 62-electron butterfly structure, there are five metal–metal bonds. The longest Ru–Ru distance (Ru(1)–Ru(3) of 2.8428 (6) Å) is that bridged by the hydride. This edge is also the hinge of the butterfly. Lengthening of a metal–metal bond by bridging hydrogen is a not uncommon feature of ruthenium hydride chemistry,[23] but it should also be noted that the hinge edge is frequently the longest in other butterfly structures. In Table III structural data for some known ruthenium butterflies are presented. Several features of this compilation are noteworthy. Unlike Fe–Fe bonds in the iron butterfly structures,[3,4] the Ru–Ru bonds show considerable variation in length. Thus, for those clusters with five Ru–Ru bonds the average Ru–Ru distance changes from 2.813

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Table IV. Structural Parameters for Ruthenium Butterfly Clusters

compd	Ru–Ru bond lengths, Å				ϕ,[d] Å	ref
	a		*b*	*c*		
$PPN[Ru_4(CO)_{13}Cl]$	2.813 (1) 2.791 (1)	2.797 (1) 2.814 (1)	2.832 (1)	3.452	91.0	24
$Ru_4(CO)_{13}(PPh)$	2.833 (1) 2.861 (1)	2.784 (1) 2.924 (1)	2.974 (1)	4.012	111.24	28
$Ru_4(CO)_{11}(C_8H_{10})$	2.739 (2) 2.749 (2)	2.735 (2) 2.728 (2)	2.823 (2)	NR	112	29
$Ru_4(CO)_{12}(C_2Ph_2)$	2.74 (1) 2.71 (1)	2.71 (1) 2.74 (1)	2.81 (5)	NR	115.5	30
$Ru_4(CO)_{10}(C_{12}H_{16})$	2.775 (6) 2.776 (6)	2.775 (5) 2.811 (8)	2.850 (6)	3.664 (7)	NR	31
$(H)(C_5H_5Ni)Ru_3(CO)_9(C{=}CH\text{-}t\text{-}Bu)$[e]	2.788 (2) 2.833 (2)	2.572 (3)[f] 2.555 (3)[f]	2.825 (2)	3.892	116.6	9
$Ru_4(CO)_{12}(MeC_2Me)$	2.728 (1) 2.710 (1)		2.880 (1)	NR	116.9	32
$H(C_5H_5Ni)Ru_3(CO)_9(C{=}CH\text{-}i\text{-}Pr)$	2.7875 (6) 2.8335 (6)	2.5735 (8)[f] 2.5715 (8)[f]	2.8428 (6)	3.924	118.25	this work
$Ru_4(CO)_9(C_6H_6)(C_6H_8)$	2.702 (3) 2.643 (3)	2.700 (4) 2.655 (3)	2.809 (3)	3.912	118.5	33
$Ru_4(CO)_{10}(OH)(PPh_2)(C{=}CH\text{-}i\text{-}Pr)$	2.758 (1) 2.703 (1)	2.800 (1) 2.803 (1)	3.4559 (6)	4.1244 (6)	141.49	10
$Ru_4(CO)_8(DAB)_2$	2.848 (2) 2.838 (2)	2.838 (2) 2.846 (2)	2.994 (2)	NR	142.2	26
$Ru_4(CO)_{10}(OEt)(PPh_2)(C{=}CH\text{-}i\text{-}Pr)$	2.7398 (5) 2.6890 (5)	2.8110 (6) 2.7908 (5)	3.3670 (5)	4.150	143.69	10
$Ru_4(CO)_8(PPh_2)(C_2\text{-}t\text{-}Bu)_2(Ph_2PC_2\text{-}t\text{-}Bu)$	2.777 (1) 2.872 (1)	3.021 (1) 3.100 (1)	3.043 (1)	5.001	167.04	25
$Ru_4(CO)_{13}(PPh_2)(C_2\text{-}t\text{-}Bu)$	2.883 (1) 2.905 (1)	3.157 (1) 3.197 (1)	3.025 (1)	5.259	176.93	25
$Ru_3Fe(CO)_{13}(PPh_2)_2$	3.147 (1) 3.171 (1)	2.861 (1)[f] 2.868 (1)[f]	3.098 (1)	5.163	177.85	34
$(C_5H_5Ni)Ru_3(CO)_8(C_6H_9)$	2.693 (3) 2.708 (3)	2.611 (3)[f] 2.595 (5)[f]	2.664 (3)[f]	NR	NR	35
$FeRu_3(CO)_{12}(C_2Ph_2)$,[g] A	2.681 (1) 2.649 (1)	2.681 (1) 2.700 (1)	2.829 (1)	3.775 (1)	112.7	37
B	2.712 (1) 2.688 (1)	2.680 (1)[f] 2.646 (1)[f]	2.780 (1)[f]	3.910 (1)	117.0	37

[a] Bond lengths within the wings. [b] Hinge distance. [c] Wing-tip distance. [d] Dihedral angle between the wings. [e] Reformulated as the hydride. [f] Heteronuclear metal-metal distances. [g] A and B are isomers. Isomer A has the iron atom at a wing-tip site.

Å in $PPN[Ru_4(CO)_{13}Cl]$[24] up to 3.032 Å in $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$.[25] The range of dihedral angles between the planes defining the wings of the butterfly is also impressive, from 91.0° for $PPN[Ru_4(CO)_{13}Cl]$[24] through 142.2° for $Ru_4(CO)_8(DAB)_2$[26] up to 176.93° in $Ru_4(CO)_{13}(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$.[25] There is an apparent correlation between the "flatness" of the butterfly as defined by the magnitude of the dihedral angle and the average length of the Ru–Ru bonds, with the more electron-rich clusters exhibiting a selective lengthening of Ru–Ru bonds and larger dihedral angles.[27]

In electron-precise 64-electron clusters where arguably only four Ru–Ru bonds are present as in the μ_4-vinylidene species $Ru_4(CO)_{10}(\mu_3\text{-}OR)(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{=}CH\text{-}i\text{-}Pr)$,[10] the average Ru–Ru distances are quite short. Of the three mixed-metal ruthenium butterflies reported to date, the dihedral angles in $(\mu\text{-}H)(C_5H_5Ni)Ru_3(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CH\text{-}i\text{-}Pr)$ and the reformulated *tert*-butyl analogue (118.25 and 116.6°) are at the lower end of the range. The Ru–Ru bond lengths (average 2.8212 and 2.818 Å) are normal when compared to the values in $Ru_3(CO)_{12}$ (average 2.8542 Å).[36] The mixed cluster $Ru_3Fe(CO)_{13}(PPh_2)_2$ is formally an electron-rich 64-electron species; the molecule is almost flat and the average Ru–Ru distance (3.128 Å) is remarkably long.[34]

Despite the recent growth of metal cluster chemistry, very few mixed ruthenium–nickel compounds are known. Examples are $(C_5H_5Ni)Ru_3(CO)_8(C_6H_9)$,[35] $(C_5H_5)_2NiRu_2(CO)_4(C_2Ph_2)$,[19b] and $(C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)$.[19d] The Ru–Ni distances (average 2.563 and 2.573 Å for 7) (R = *t*-Bu, *i*-Pr) are consistent with the Ru–Ni bond length (~2.60 Å) predictable from the Ni–Ni and Ru–Ru distances in $[\eta^5\text{-}C_5H_5Ni(CO)]_2$ (2.345 (3) Å)[38] and $Ru_3(CO)_{12}$ (average

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Table V. Structural Parameters for μ_4-Vinylidene and μ_4-Acetylide Clusters

complex	C=C, Å	C(α)-M, Å	C(β)-M, Å	butterfly dihedral angle, deg	ref
$(H)(C_5H_5Ni)Ru_3(CO)_9(C{=}CH\text{-}t\text{-}Bu)$	1.436 (13)	1.834 (8)[a] 2.176 (9) 2.156 (8) 2.159 (8) av 2.162	2.227 (10)	116.6	9
$(H)(C_5H_5Ni)Ru_3(CO)_9(C{=}CH\text{-}i\text{-}Pr)$	1.417 (8)	1.843 (5)[a] 2.134 (5) 2.183 (5) 2.188 (5) av 2.168 (5)	2.219 (6)	118.25	this work
$Ru_4(CO)_{10}(OH)(PPh_2)(C{=}CH\text{-}i\text{-}Pr)$	1.415 (10)	2.183 (5) 2.237 (5) 2.178 (5) 2.105 (5) av 2.175	2.267 (5)	141.49	10
$(C_5H_5)FeCo_3(CO)_9(C{=}CH_2)$	1.431	1.933 (8)[b] 1.917 (6)[c] 1.917 (6)[c] 2.087 (8)[c]	2.085 (10)[c]	124.1	11
$NiRu_4(CO)_9(PPh_2)_2(C_2\text{-}i\text{-}Pr)_2$	1.34	2.06 (2) 2.25 (2) 2.02 (2)[a] av 2.15	2.44 (3) 1.99 (3)[a]		19a
	1.38	2.27 (4) 2.28 (3) 2.08 (4)[a] av 2.275	2.50 (3) 1.89 (3)[a]		
$Ru_5(CO)_{13}(PPh_2)(C_2Ph)$	1.342 (11)	2.114 (8) 2.095 (8) 2.190 (8) 2.340 (8) av 2.185	2.163 (8) 2.216 (8)		17

[a] Ni–C bond length. [b] Fe–C bond length. [c] Co–C bond length.

2.8542 Å).[36]

Several compounds are now known in which C_α of a vinylidene or acetylide ligand is multisite bound to four metal atoms. A selection of structural parameters for these μ_4–bond ligands is gathered in Table V. Such information should be pertinent to the activation of the unsaturated ligand in these clusters. It is evident that for the μ_4-vinylidenes, despite considerable structural variations in the cluster framework and dihedral angles, the C=C distances are remarkably invariant (1.415–1.436 Å). The range of Ru–C_α distances is 2.105–2.237 or 2.06–2.28 Å if the μ_4-acetylides are included. The average Ru–C_α distance covers the rather narrow range of 2.15–2.28 Å for these μ_4 species. Although the chemistry of these multisite-bound vinylidenes and acetylides has not yet been explored in detail, it is apparent that the unsaturated ligand can accommodate a wide variation in geometry for the M_4 fragment to which it is coordinated (Table V).

None of the carbonyl groups deviate substantially from linearity, the smallest M–C–O angle being Ru(2)–C(4)–O(4) (175.8 (2) Å). There are no intramolecular contacts of significance.

Comments on the Mode of Formation of Clusters 7. Clusters of type **7** are of interest for a number of reasons. First, surface-bound vinylidenes generated via methylene–carbide coupling are possible intermediates in Fischer–Tropsch syntheses; substituted vinylidene clusters **7** can constitute useful models for vinylidene reactivity. Furthermore, detection of a hydride in **7** (R = *i*-Pr, *t*-Bu) allows a closer analogy to be drawn between these vinylidene species and clusters of types **3**–**5**. It is notable that complexes **7** are the first hydrido–vinylidene clusters to be characterized. Thus, both the mechanism of formation of **7** and the chemistry of the μ_4-vinylidene are worthy of attention.

The mechanism initially proposed for the formation of the "hydride-free" cluster **7** (R = *t*-Bu) was a simple nucleophilic addition of a η^5-C_5H_5Ni fragment to C_α of **6** (R = *t*-Bu) followed by a hydride shift onto the acetylide. Location of a bridging hydride in the product **7** required a reassessment of the mechanism. When the reaction of **6** with nickel reagent is carried out under a hydrogen atmosphere, the yields of **7** are doubled. Since the initial reactions were carried out under purified nitrogen, solvent or organometallic decomposition are two probable sources of hydrogen. It is noteworthy that synthesis of **7** (R = *t*-Bu) under nitrogen always leads to the production of a small amount of white crystalline material, identified by IR and NMR spectrometry as a polyacetylene.

Previous work[39] has shown that in the presence of H_2 **6** gives $H_3Ru_3(CO)_9(HC_2\text{-}t\text{-}Bu)$, $H_2Ru_3(CO)_9(C{=}CH\text{-}t\text{-}Bu)$, and $H_3Ru_3(CO)_9(CCH_2CH_3)$. Possible routes to **7** thus could include nucleophilic attack by "C_5H_5Ni" on **6** followed by hydride migration to the acetylide, generating a coordinatively unsaturated vinylidene intermediate, which could then undergo oxidative addition of hydrogen, or, alternatively, generation of a dihydride intermediate $H_2Ru_3(CO)_9(C{=}CHR)$ followed by nucleophilic attack by "C_5H_5Ni" on the hydrido cluster. Further studies of these interesting reactions are in progress.

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Registry No. **6** (R = *i*-Pr), 73555-47-2; **6** (R = *t*-Bu), 57673-31-1; **7** (R = *i*-Pr), 85442-17-7; **7** (R = *t*-Bu), 71926-99-3; $Ru_3(CO)_{12}$, 15243-33-1; $[\eta^5\text{-}C_5H_5Ni(CO)]_2$, 12170-92-2; Ni, 7440-02-0; Ru, 7440-18-8.

Supplementary Material Available: Tables S1 and S2, showing anisotropic thermal parameters and remaining bond lengths and angles, and a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(39) Castiglioni, M.; Gervasio, G.; Sappa, E. *Inorg. Chim. Acta* **1981**, *49*, 217.