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Heterometallic Clusters of Ruthenium and the Group 11 Elements (Cu, Ag, and Au) Containing a COMe Ligand. X-ray Structure of $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-COMe})(CuPPh_3)$

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Deprotonation of $H_3Ru_3(CO)_9(\mu_3\text{-COMe})$ (1) with K-Selectride leads to formation of the cluster anion $[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]^-$ which was isolated as the PPN salt **2**. This anion reacts with $MPPh_3Cl$ (M = Cu, Ag, Au) to form the heterometallic clusters $H_2Ru_3(CO)_9(\mu_3\text{-COMe})(MPPh_3)$ [M = Cu (**3**), Ag (**4**), Au (**5**)]. Reaction of these clusters with PPh_3 results in rapid formation of the PPh_3-substituted derivatives $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-COMe})(MPPh_3)$ [M = Cu (**6**), Ag (**7**), Au (**8**)]. The X-ray structure of **6** is reported: the compound forms orange monoclinic crystals, space group $P2_1/a$ (No. 14), with lattice dimensions a = 45.824 (6) Å, b = 11.157 (5) Å, c = 9.026 (2) Å, β = 95.31 (1)°, V = 4594.8 Å^3, and Z = 4. The four metal atoms adopt a "butterfly" configuration with the Cu atom occupying a "wing tip" site and the three Ru atoms capped by the COMe ligand. Two of the CO ligands exhibit a semibridging relationship with the Cu atom. **3** and **4** are unstable in CH_2Cl_2 solution eventually giving the homometallic clusters $H_3Ru_3(CO)_8PPh_3(\mu_3\text{-COMe})$ (**9**) and $H_3Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-COMe})$ (**10**).

Introduction

The chemistry of mixed-metal ruthenium clusters incorporating MPR_3 moieties (M = Cu, Ag, Au; R = aryl or alkyl) in the metal framework is now well established having received considerable attention in recent years. Several such clusters have been prepared from triruthenium clusters containing μ_3-bridging ligands, e.g. μ_3-PPh, μ_3-S, $\mu_3\text{-}C_2Bu^t$, μ_3-COMe. Interest in clusters of this type is partly due to the expectation that the capping ligand will introduce an inherent stability, inhibiting cluster fragmentation during reactivity and catalytic studies. In particular, the heterometallic species resulting from the reactions of $MPPh_3X$ (M = Cu, Ag, or Au; X = Cl, I) with the cluster anions $[HRu_3(\mu_3\text{-PPh})(CO)_9]^-$,[1] $[Ru_3(CO)_9(\mu_3\text{-}C_2Bu^t)]^-$,[2] $[HRu_3(\mu_3\text{-S})(CO)_9]^-$,[3] and $[Ru_3(\mu_3\text{-S})(CO)_9]^{2-}$[4] have been reported.

Interest has also been directed toward comparing heterometallic clusters containing MPR_3 moieties in an effort to ascertain whether variation in the heterometal influences structure and chemical properties.

The aim of this work was to prepare the clusters $H_2Ru_3(CO)_9(\mu_3\text{-COMe})(MPPh_3)$ (M = Cu, Ag or Au) from $H_3Ru_3(CO)_9(\mu_3\text{-COMe})$ by formation of the anion $[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]^-$ and subsequent reaction with $MPPh_3Cl$. We now report our synthetic studies, compound characterization by spectroscopy, and X-ray diffraction together with a comparison of the chemical reactivity of the Cu, Ag, and Au derivatives.

Experimental Section

General Data. All reactions were performed under dry, oxygen-free nitrogen in nitrogen-saturated solvents. MeOH and CH_2Cl_2 were distilled under nitrogen from Mg turnings and CaH_2, respectively. Petroleum ether refers to the fraction of bp 40–60 °C. Infrared (IR) spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer. NMR spectra were recorded on a Brüker AM360, JEOL FX90Q, or JEOL GX270 spectrometer.

The following compounds were prepared by established methods: $CuPPh_3Cl$,[5] $AgPPh_3Cl$,[6] $AuPPh_3Cl$,[7] $H_3Ru_3(CO)_9(\mu_3\text{-COMe})$.[8] K-Selectride (potassium tri-*sec*-butylborohydride in THF) and (PPN)Cl (bis(triphenylphosphine)nitrogen(1+) chloride) were used as supplied by Aldrich. Product separation by column chromatography was performed on flash silica (Camlab silica gel (230–400 mesh)).

1. Preparation of the Anion $[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]^-$. (a) Methanol Solution of the Potassium Salt. A MeOH (40 mL) solution of $H_3Ru_3(CO)_9(\mu_3\text{-COMe})$ (1) (200 mg, 0.333 mmol) at 50 °C was treated with 0.33 mL of 1.0 M K-Selectride/THF. This mixture was then stirred for 15 min at 50 °C giving a deep orange-red solution which was cooled to room temperature. Quantitative conversion to the anion was observed by IR.

(b) Isolation of $[PPN][H_2Ru_3(CO)_9(\mu_3\text{-COMe})]$ (2). To a MeOH solution of the potassium salt from 1(a) was added (PPN)Cl (191 mg, 0.333 mmol). After stirring for 15 min the solution was reduced in volume under vacuum until an orange solid just began to precipitate from solution. Subsequent cooling to approximately −20 °C for approximately 30 min gave the required product by filtration in 60% yield after washing with MeOH (−20 °C) (3 × 10 mL portions). Anal. Calcd for $C_{47}H_{35}NO_{10}P_2Ru_3$: C, 49.5; H, 3.1; N, 1.2. Found: C, 49.4; H, 3.1; N, 1.1. **2** is very soluble in CH_2Cl_2 and $CHCl_3$, partially soluble in MeOH, and insoluble in nonpolar organic solvents.

2. Preparation of the Heterometallic Clusters $H_2Ru_3(CO)_9(\mu_3\text{-COMe})(MPPh_3)$ (M = Cu (3), Ag (4), Au (5)). To a solution of $K[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]$ (from 200 mg (**1**), 0.333 mmol) in MeOH (25 mL) at room temperature (vide infra 1(a)) was added solid $MPPh_3Cl$ (0.333 mmol, 120 mg (M = Cu); 135 mg (M = Ag); 165 mg (M = Au)). The required product began to precipitate from solution after ca. 1 min of stirring (M = Cu, Au, orange precipitate; M = Ag, yellow precipitate) and after 10 min was collected by filtration and washed with MeOH (3 × 10 mL portions). This gave the following: **3**, 222 mg, 72%; **4**, 204 mg, 63%; **5**, 265 mg, 75%. Anal. Calcd for $C_{29}H_{20}CuO_{10}PRu_3$ (**3**): C, 37.6; H, 2.2. Found: C, 37.7; H, 2.3. Anal. Calcd for $C_{29}H_{20}AgO_{10}PRu_3$ (**4**): C, 35.9; H, 2.1. Found: C, 35.7; H, 2.2. Anal. Calcd for $C_{29}H_{20}AuO_{10}PRu_3$ (**5**): C, 32.9; H, 1.9. Found: C, 33.0; H, 2.0.

3, **4**, and **5** are very soluble in CH_2Cl_2 and $CHCl_3$, fairly soluble in nonpolar organic solvents, and insoluble in MeOH.

3. Preparation of the Heterometallic Clusters $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-COMe})(MPPh_3)$ (M = Cu (6), Ag (7), Au (8)). A solution of $H_2Ru_3(CO)_9(\mu_3\text{-COMe})(MPPh_3)$ (0.16 mmol, 148 mg (M = Cu); 155 mg (M = Ag); 170 mg (M = Au)) and PPh_3 (44

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Table I. Summary of Crystal Data and Structure Solution

formula	$C_{46}H_{35}CuO_9P_2Ru_3$
mol wt	1160.49
system	monoclinic
space group	$P2_1/a$ (No. 14)
a, Å	45.824 (6)
b, Å	11.157 (5)
c, Å	9.026 (2)
β, deg	95.31 (1)
V, Å^3	4594.8
Z	4
D(calcd), g cm^{-3}	1.677
D(obsd), g cm^{-3}	1.71 (2)
F(000)	2296
μ(Mo Kα), cm^{-1}	14.96
cryst size, mm	0.55 × 0.35 × 0.07
radiatn	Mo Kα (λ = 0.71069 Å)
2θ range, deg	3 (min), 50 (max)
data measd	8371
data obsd ($F \geq 3\sigma(F)$)	5342
no. of variables	299
R	0.057
R_w	0.064

mg, 0.17 mmol) in CH_2Cl_2 (40 mL) was heated under reflux for 30 (M = Cu, Ag) or 60 min (M = Au). The resulting solution was cooled to room temperature and reduced in volume to ca. 1 mL. MeOH (40 mL) was added which resulted in precipitation of the required products as orange solids which after being washed with MeOH (3 × 10 mL portions) were isolated in yields of greater than 90%. Anal. Calcd for $C_{46}H_{35}CuO_9P_2Ru_3$ (**6**): C, 47.6; H, 3.0. Found: C, 47.5; H, 3.0. Anal. Calcd for $C_{46}H_{35}AgO_9P_2Ru_3$ (**7**): C, 45.9; H, 2.9. Found: C, 46.2; H, 3.0. Anal. Calcd for $C_{46}H_{35}AuO_9P_2Ru_3$ (**8**): C, 42.7; H, 2.7. Found: C, 42.8; H, 2.8.

6, **7**, and **8** are very soluble in CH_2Cl_2 and $CHCl_3$, practically insoluble in nonpolar organic solvents, and insoluble in MeOH.

4. Preparation of $H_3Ru_3(CO)_8PPh_3(\mu_3\text{-COMe})$ (9) and $H_3Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-COMe})$ (10). A solution of $H_3Ru_3(CO)_9(\mu_3\text{-COMe})$ (150 mg, 0.25 mmol) and PPh_3 (66 mg, 0.25 mmol) in CH_2Cl_2 (30 mL) was heated under reflux for 30 min. The resulting solution was cooled to room temperature and evaporated to dryness and the solid residue chromatographed on a silica gel column. The required products were isolated as orange solids from the second and third bands with a 1:1 v/v CH_2Cl_2/petroleum ether mixture as the eluant. This gave the following: **9**, 63 mg, 30%; **10**, 37 mg, 14%. Anal. Calcd for $C_{28}H_{21}O_9PRu_3$ (**9**): C, 40.3; H, 2.5. Found: C, 40.4; H, 2.6. Anal. Calcd for $C_{45}H_{36}O_8P_2Ru_3$ (**10**): C, 50.5; H, 3.4. Found: C, 50.8; H, 3.5.

9 and **10** are very soluble in CH_2Cl_2 and $CHCl_3$ and reasonably soluble in nonpolar organic solvents and MeOH.

5. Crystallographic Study. Crystals of $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-COMe})(CuPPh_3)$ were grown as orange air-stable rectangular plates by cooling a CH_2Cl_2 solution. Preliminary photographic examination established the crystal system and approximate cell dimensions. Accurate cell dimensions were obtained from 25 accurately centered reflections and intensity data recorded from the same crystal at room temperature mounted in a thin-wall glass capillary by using an Enraf-Nonius CAD-4 diffractometer. A total of 8371 reflections were recorded in two batches (7247 and 1124) due to instrumental problems. An empirical psi-scan absorption correction was applied to the data (transmission: mininum, 71.6; maximum, 100.0%) as well as the Lorentz and polarization correction. After systematically absent reflections ($0k0$, $k \neq 2n$; $h0l$, $h \neq 2n$) were removed and multiply measured reflections were averaged, there remained 7709 (R_{int} = 0.016). Omitting $F < 3\sigma(F)$ reflections left 5923 observed reflections. Additional details of the data collection are summarized in Table I. The direct methods facility (EEES) in the SHELX package[9] was used to locate the four metal atom positions, and repeated structure factor and difference electron density syntheses located the remaining non-hydrogen atoms. Inspection of the observed and calculated structure factors showed rather poor agreement for several reflections hkl for l = 0–2. This is due to the large value of the a cell dimension combined with the choice of radiation and scan mode ($\omega/2\theta$) and the finite detector aperture.[10] This $\omega/2\theta$ motion scans along a line passing through the reflection and the origin of the reciprocal lattice. For example, for the $hk0$ reflections the onset of the poor agreement occurred at larger values h as k increased (as would be expected). A total of 581 reflections were rejected on this basis leaving 5342 unique reflections used for the refinement. The phenyl ring carbon atoms were treated as regular hexagons (d(C–C) = 1.395 Å) with isotropic atoms. Hydrogen atoms on the phenyl rings were positioned geometrically (d(C–H) = 0.95 Å) with a common refined temperature factor. Full-matrix least-squares refinement with minimization of $\sum w(\Delta)^2$ converged to R = 0.057 and R_w = 0.064 [anisotropic (Ru, Cu, P, O, C) and isotropic (C(phenyl), H) atoms, $w = 1/[\sigma^2(F) + 0.0002F^2]$, maximum shift/error = 0.2]. The final difference electron density map showed features all within the range +1.32 to −1.31 e Å^{-3}, and no convincing evidence was noted to locate the hydride atoms. Atomic coordinates are shown in Table II with selected bond lengths and bond angles in Table III. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX[9] (P, O, C, H) and ref 11 (Ru, Cu). All calculations were carried out by using an IBM 3090 computer and the programs in ref 9 and 12.

Results and Discussion

(i) The Anion $[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]^-$. Reaction of $H_3Ru_3(CO)_9(\mu_3\text{-COMe})$ (**1**) with K-Selectride in MeOH at 50 °C leads to rapid deprotonation of **1** to give the anion $[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]^-$ which was isolated as the PPN salt $[PPN][H_2Ru_3(CO)_9(\mu_3\text{-COMe})]$ (**2**). The ^1H NMR for **2** (Table IV) is consistent with this formulation and shows unexceptional chemical shifts. The ^{13}C NMR (Table V) shows the CO ligands to be undergoing rapid exchange at room temperature (a single signal is observed in the carbonyl region at δ 200.0 ppm). At −90 °C this single resonance is replaced by four signals in the intensity ratio 2:2:3:2. A proposed structure for the anion is shown in Figure 1a, and we assign the signals of relative intensity 2 to the three pairs of CO's labeled a, b, and c and the signal of relative intensity 3 to the three CO's labeled d which we believe are averaged by rotation about their common Ru atom. For the synthesis of further compounds the anion was used directly as the potassium salt in MeOH.

(ii) The Heterometallic Clusters $H_2Ru_3(CO)_9(\mu_3\text{-COMe})(MPPh_3)$ (M = Cu (3), Ag (4), Au (5)). Reaction of $K[H_2Ru_3(CO)_9(\mu_3\text{-COMe})]$ with $MPPh_3Cl$ (M = Cu, Ag or Au) in MeOH at room temperature leads to the rapid precipitation of the heterometallic clusters **3**, **4**, or **5**. All three compounds are reasonably air stable, decomposing in the air at room temperature over a period of weeks. **5** has been previously prepared in a much lower yield (27%) by treating **1** with $AuPPh_3Me$, and its structure has been determined by X-ray diffraction.[13]

The ^1H NMR spectra (Table IV) for **3**, **4**, and **5** are very similar except for the multiplicity of the hydride signals. Whereas **5** shows a doublet (J = 1.5 Hz) due to coupling with the phosphorus of the PPh_3 ligand, **3** and **4** exhibit singlet features at room temperature and doublets (J = 1.4 Hz, (**3**), J = 2.1 Hz (**4**)) at −90 °C. This loss of coupling at temperatures above −90 °C suggests that **3** and **4** undergo fluxional processes in solution. Since (i) the ^{31}P NMR spectrum of **4** at room temperature retains coupling

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Table II. Atomic Coordinates and Isotropic Thermal Parameters (×10³ Å²) for $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)(CuPPh_3)$

	x	*y*	*z*	*U*[a]
Ru(1)	0.41419 (2)	0.38323 (6)	0.11960 (7)	31.3 (3) *
Ru(2)	0.36967 (2)	0.40294 (6)	−0.12365 (7)	32.3 (3) *
Ru(3)	0.35340 (2)	0.34477 (7)	0.16105 (7)	35.4 (4) *
Cu(1)	0.33931 (3)	0.2142 (1)	−0.0719 (1)	41.6 (6) *
P(1)	0.4484 (1)	0.2199 (2)	0.1035 (2)	33.9 (12) *
P(2)	0.3127 (1)	0.0665 (2)	−0.1795 (2)	38.1 (12) *
C(1)	0.4399 (2)	0.4927 (8)	0.0420 (10)	47.2 (55) *
O(1)	0.4548 (2)	0.5630 (7)	−0.0029 (9)	80.7 (57) *
C(2)	0.4255 (2)	0.4342 (10)	0.3143 (10)	57.7 (66) *
O(2)	0.4312 (2)	0.4655 (10)	0.4326 (9)	108.0 (73) *
C(3)	0.3684 (2)	0.2781 (9)	−0.2779 (10)	47.0 (55) *
O(3)	0.3705 (2)	0.2173 (7)	−0.3780 (7)	63.9 (46) *
C(4)	0.3336 (2)	0.4768 (10)	−0.1938 (10)	52.8 (61) *
O(4)	0.3121 (2)	0.5195 (9)	−0.2395 (9)	87.7 (62) *
C(5)	0.3928 (2)	0.5130 (8)	−0.2263 (9)	42.4 (51) *
O(5)	0.4068 (2)	0.5756 (7)	−0.2878 (9)	76.1 (53) *
C(6)	0.3443 (2)	0.1804 (11)	0.2110 (11)	59.1 (67) *
O(6)	0.3408 (2)	0.0872 (8)	0.2618 (10)	96.9 (68) *
C(7)	0.3143 (3)	0.3954 (11)	0.1181 (10)	58.3 (68) *
O(7)	0.2909 (2)	0.4266 (10)	0.0957 (9)	92.5 (69) *
C(8)	0.3546 (2)	0.4213 (10)	0.3514 (10)	55.9 (62) *
O(8)	0.3529 (2)	0.4732 (9)	0.4575 (8)	100.3 (68) *
C(9)	0.3776 (2)	0.4858 (8)	0.0828 (9)	36.9 (46) *
O(9)	0.3778 (1)	0.6068 (5)	0.1212 (7)	50.2 (39) *
C(10)	0.3508 (3)	0.6724 (10)	0.0861 (13)	135.7 (97) *
C(11)	0.4837 (1)	0.2298 (5)	0.2189 (6)	40.3 (20)
C(12)	0.4949 (1)	0.3430 (5)	0.2577 (6)	56.0 (25)
C(13)	0.5218 (1)	0.3537 (5)	0.3424 (6)	65.1 (29)
C(14)	0.5376 (1)	0.2512 (5)	0.3882 (6)	71.1 (31)
C(15)	0.5264 (1)	0.1380 (5)	0.3493 (6)	74.3 (33)
C(16)	0.4995 (1)	0.1273 (5)	0.2647 (6)	62.4 (28)
C(21)	0.4359 (2)	0.0681 (5)	0.1401 (7)	48.1 (23)
C(22)	0.4190 (2)	0.0556 (5)	0.2599 (7)	66.0 (30)
C(23)	0.4091 (2)	−0.0574 (5)	0.2982 (7)	93.8 (42)
C(24)	0.4161 (2)	−0.1580 (5)	0.2168 (7)	99.1 (44)
C(25)	0.4331 (2)	−0.1455 (5)	0.0970 (7)	95.0 (43)
C(26)	0.4430 (2)	−0.0324 (5)	0.0587 (7)	76.8 (34)
C(31)	0.4597 (2)	0.2110 (6)	−0.0833 (5)	44.4 (22)
C(32)	0.4391 (2)	0.1751 (6)	−0.1979 (5)	59.0 (27)
C(33)	0.4459 (2)	0.1798 (6)	−0.3453 (5)	80.5 (35)
C(34)	0.4733 (2)	0.2206 (6)	−0.3780 (5)	93.0 (41)
C(35)	0.4940 (2)	0.2565 (6)	−0.2634 (5)	104.5 (46)
C(36)	0.4872 (2)	0.2518 (6)	−0.1161 (5)	67.7 (30)
C(41)	0.3339 (1)	−0.0395 (5)	−0.2789 (7)	43.2 (21)
C(42)	0.3616 (1)	−0.0714 (5)	−0.2140 (7)	63.3 (29)
C(43)	0.3785 (1)	−0.1542 (5)	−0.2843 (7)	85.6 (38)
C(44)	0.3676 (1)	−0.2051 (5)	−0.4195 (7)	77.7 (35)
C(45)	0.3399 (1)	−0.1732 (5)	−0.4844 (7)	74.2 (33)
C(46)	0.3230 (1)	−0.0904 (5)	−0.4141 (7)	64.3 (29)
C(51)	0.2840 (1)	0.1154 (6)	−0.3205 (6)	44.9 (22)
C(52)	0.2904 (1)	0.2043 (6)	−0.4211 (6)	59.9 (27)
C(53)	0.2691 (1)	0.2415 (6)	−0.5317 (6)	69.9 (31)
C(54)	0.2413 (1)	0.1898 (6)	−0.5418 (6)	70.7 (32)
C(55)	0.2348 (1)	0.1009 (6)	−0.4413 (6)	70.0 (31)
C(56)	0.2561 (1)	0.0637 (6)	−0.3306 (6)	57.6 (26)
C(61)	0.2936 (1)	−0.0244 (5)	−0.0513 (6)	40.8 (21)
C(62)	0.2801 (1)	0.0359 (5)	0.0596 (6)	59.3 (27)
C(63)	0.2656 (1)	−0.0286 (5)	0.1628 (6)	71.6 (32)
C(64)	0.2644 (1)	−0.1534 (5)	0.1551 (6)	78.3 (34)
C(65)	0.2779 (1)	−0.2137 (5)	0.0442 (6)	77.8 (35)
C(66)	0.2924 (1)	−0.1492 (5)	−0.0590 (6)	55.9 (25)

[a] Parameters with an asterisk are equivalent isotropic temperature factor from anisotropic atom: $U_{iso} = {}^1/_3$(trace of diagonalized *U*).

Table III. Selected Bond Lengths (Å) and Angles (deg)

Ru(1)–Ru(2)	2.864 (1)	Ru(1)–P(1)	2.417 (2)
Ru(2)–Ru(3)	2.817 (1)	Cu(1)–P(2)	2.220 (2)
Ru(3)–Ru(1)	2.877 (1)		
Cu(1)–Ru(2)	2.590 (1)	C–O(min)	1.13 (1)
Cu(1)–Ru(3)	2.590 (1)	C–O(max)	1.15 (1)
Ru(1)–C(1)	1.876 (10)	P(1)–C(11)	1.845 (5)
Ru(1)–C(2)	1.874 (9)	P(1)–C(21)	1.827 (6)
Ru(2)–C(3)	1.966 (10)	P(1)–C(31)	1.812 (5)
Ru(2)–C(4)	1.902 (11)	P(2)–C(41)	1.818 (5)
Ru(2)–C(5)	1.917 (9)	P(2)–C(51)	1.828 (5)
Ru(3)–C(6)	1.944 (12)	P(2)–C(61)	1.823 (5)
Ru(3)–C(7)	1.882 (12)		
Ru(3)–C(8)	1.915 (9)	C–C(fixed)	1.395
C(9)–Ru(1)	2.033 (9)	C(9)–O(9)	1.39 (1)
C(9)–Ru(2)	2.082 (8)	O(9)–C(10)	1.45 (1)
C(9)–Ru(3)	2.085 (9)		
Ru(1)–Ru(2)–Ru(3)	60.8 (1)	Ru(1)–C(9)–Ru(2)	88.2 (3)
Ru(2)–Ru(3)–Ru(1)	60.4 (1)	Ru(1)–C(9)–Ru(3)	88.6 (3)
Ru(3)–Ru(1)–Ru(2)	58.8 (1)	Ru(2)–C(9)–Ru(3)	85.1 (3)
Ru(2)–Ru(3)–Cu(1)	57.1 (1)	Ru(1)–C(9)–O(9)	121.2 (6)
Ru(3)–Cu(1)–Ru(2)	65.9 (1)	Ru(2)–C(9)–O(9)	130.5 (6)
Cu(1)–Ru(2)–Ru(3)	57.1 (1)	Ru(3)–C(9)–O(9)	129.7 (6)
Ru(1)–P(1)–C(11)	117.5 (2)	P(1)–Ru(1)–Ru(2)	115.6 (1)
Ru(1)–P(1)–C(21)	118.2 (3)	P(1)–Ru(1)–Ru(3)	122.5 (1)
Ru(1)–P(1)–C(31)	109.9 (2)	P(2)–Cu(1)–Ru(2)	143.8 (1)
Cu(1)–P(2)–C(41)	113.7 (3)	P(2)–Cu(1)–Ru(3)	149.1 (1)
Cu(1)–P(2)–C(51)	114.5 (2)		
Cu(1)–P(2)–C(61)	114.3 (2)	C(9)–O(9)–C(10)	116.6 (8)
Ru(2)–C(3)–O(3)	169.2 (8)	Cu(1)...C(3)	2.49 (1)
Ru(3)–C(6)–O(6)	169.6 (10)	Cu(1)...C(6)	2.57 (1)
Ru–C–O(min)	169.2 (8)	C–P–C(min)	102.5 (3)
Ru–C–O(max)	178.4 (9)	C–P–C(max)	105.1 (3)

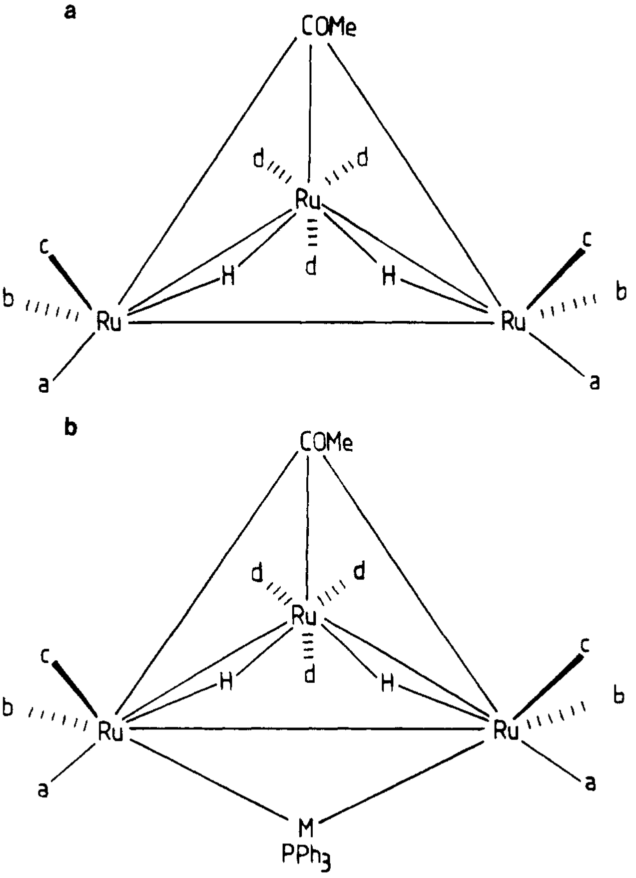

Figure 1. Proposed structures for (a) the anion $[H_2Ru_3(CO)_9(\mu_3\text{-}COMe)]^-$ and (b) compounds **3** and **4**.

to silver and (ii) the ^1H NMR spectrum of an equimolar mixture of **3** and **4** at room temperature leads to broadening of the hydride signals of both compounds, we suggest that an intermolecular exchange of $MPPh_3$ moieties occurs for **3** and **4**.

Comparison of the IR spectra for **3**, **4**, and **5** indicates that **3** and **4** are probably isostructural with **5**, i.e. with the $MPPh_3$ moiety edge-bridging a Ru–Ru bond.

Variable-temperature ^{13}C NMR studies on **3** and **4** show that whereas at −90 °C, four signals are seen for the CO

Table IV. Selected Spectroscopic Data

compound	$\nu(CO)^a/cm^{-1}$	$\delta(^1H)^d$	$\delta(^{31}P)^d$
$[PPN][H_2Ru_3(CO)_9(\mu_3\text{-}COMe)]$ (**2**)	2067 (w), 2028 (vs), 1999 (vs), 1965 (s), 1938 (m), 1919 (m)^b	7.3–7.6 (m, Ph, 30 H), 3.67 (s, OMe, 3 H), –16.97 (s, μ-H, 2 H)	
$H_2Ru_3(CO)_9(\mu_3\text{-}COMe)(CuPPh_3)$ (**3**)	2091 (m), 2084 (w), 2050 (s), 2034 (vs), 2022 (m), 2005 (w), 1991 (m), 1976 (w), 1959 (m), 1951 (sh, m)	7.1–7.6 (m, Ph, 15 H), 3.88 (s, OMe, 3 H), –17.75 (s, μ-H, 2 H)	4.4 (s, br)
$H_2Ru_3(CO)_9(\mu_3\text{-}COMe)(AgPPh_3)$ (**4**)	2090 (s), 2084 (w), 2050 (s), 2035 (vs), 2022 (s), 2019 (sh, s), 2001 (w), 1991 (s), 1986 (sh, m), 1963 (s), 1954 (s), 1938 (sh, w)	7.0–7.6 (m, Ph, 15 H), 3.85 (s, OMe, 3 H), –18.32 (s, μ-H, 2 H)	15.9 [2 × d, $J(^{109}Ag^P)$ = 423, $J(^{107}AgP)$ = 375]
$H_2Ru_3(CO)_9(\mu_3\text{-}COMe)(AuPPh_3)$ (**5**)	2091 (m), 2086 (sh, w), 2054 (s), 2039 (vs), 2023 (m), 2016 (sh, w), 2002 (sh, w), 1994 (s), 1982 (sh, w), 1974 (m), 1968 (m)	7.3–7.6 (m, Ph, 15 H), 3.90 (s, OMe, 3 H), –18.58 [d, J(PH) = 1.5, μ-H, 2 H]	
$H_2Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)(CuPPh_3)$ (**6**)	2053 (m), 2022 (s), 1977 (m), 1946 (m)^c	7.0–7.6 (m, Ph, 30 H), 3.89 (s, OMe, 3 H), –17.63 [d of d, J(Ru–PH), = 8.7 J(Cu–PH) = 0.9, μ-H, 2 H]	2.7 (s, br), 26.4 (s)
$H_2Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)(AgPPh_3)$ (**7**)	2054 (m), 2023 (s), 1977 (m), 1952 (m)^c	7.0–7.6 (m, Ph, 30 H), 3.91 (s, OMe, 3 H), –17.82 [d of d of d, J(Ru–PH) = 9.3, J = 2.8, 1.1, μ-H, 2 H]	14.1 [2 × (d of d), $J(^{107}AgP)$ = 353.5, $J(^{109}AgP)$ = 408.2, J(PP) = 0.7], 27.7 [d of d, J(AgP) = 2.0, J(PP) = 0.7]^e
$H_2Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)(AuPPh_3)$ (**8**)	2058 (m), 2029 (s), 2023 (sh, s), 1978 (m), 1963 (m)^c	7.0–7.7 (m, Ph, 30 H), 3.96 (s, OMe, 3 H), –18.08 [d of d, J(Ru–PH) = 8.8, J(Au–PH) = 2.0, μ-H, 2 H]	26.2 (d, J(PP) = 1), 61.7 (d, J(PP) = 1)^e
$H_3Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)$ (**9**)	2092 (s), 2067 (vs), 2033 (sh, s), 2027 (vs), 2023 (vs), 2016 (sh, s), 2006 (s), 1999 (s), 1994 (sh, m), 1977 (w), 1965 (m)	7.1–7.6 (m, Ph, 15 H), 3.88 (s, OMe, 3 H), –16.77 [d of d, J(PH) = 10.7, J(HH) = 2.9, μ-H, 2 H], –17.29 [t, J(HH) = 2.9, μ-H, 1 H]	23.4 (s)
$H_3Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}COMe)$ (**10**)	2079 (s), 2071 (s), 2033 (vs), 2027 (vs), 2021 (vs), 2006 (s), 1992 (m), 1975 (sh, m), 1969 (s), 1960 (sh, w)	6.9–7.6 (m, Ph, 30 H), 3.96 (s, OMe, 3 H), –15.73 [t of t, J(PH) = 9.3, J(HH) = 2.9, μ-H, 1 H], –16.30 [d of d, J(PH) = 9.3, J(HH) = 2.9, μ-H, 2 H]	22.2 (s)

[a] IR recorded in cyclohexane unless stated otherwise. [b] Recorded in MeOH. [c] Recorded in CH_2Cl_2. [d] All chemical shifts in ppm; coupling constants (J) given in Hz; ^1H chemical shifts relative to TMS; ^{31}P spectra hydrogen-1 decoupled with chemical shift relative to 85% H_3PO_4 as external reference; CD_2Cl_2 used as solvent unless otherwise stated. [e] Recorded in $CDCl_3$.

Table V. ^{13}C NMR Data^a for Compounds 2, 3, 4, and 6

compd	δ(*C*–OMe)	δ(*C*O)	$\delta(O\text{–}CH_3)$
2	258.9 (s)	207.0 (s, 2 C) 202.2 (s, 2 C) 195.9 (s, 3 C) 192.0 (s, 2 C)	67.7 (s)
3	274.2 (s)	205.4 (s, 2 C) 195.6 (s, 2 C) 192.2 (s, 3 C) 188.8 (s, 2 C)	68.8 (s)
4	269.2 (s)	208.0 (s, 2 C) 195.4 (s, 2 C) 193.6 (s, 3 C) 189.6 (s, 2 C)	69.1 (s)
6	280.7 [d, J(PC) = 39]	207.9 (s, 2 C) 196.6 (s, 2 C) 194.2 (s, 2 C) 194.0 (s, 2 C)	69.5 (s)

[a] All chemical shifts in ppm relative to TMS; coupling constant in Hz; CH_2Cl_2 solution at -90 °C; hydrogen-1 decoupled. Phenyl resonances omitted.

ligands (relative intensities 2:2:3:2) at higher temperatures, the signals begin to broaden and reveal the existence of fluxional processes. For **3** broadening is first observed at −80 °C, and as the temperature is raised further the four signals broaden further and by −10 °C have collapsed to a single resonance at δ 195.5 ppm. All four signals broaden to approximately the same degree at a particular temperature. For **4**, broadening is first observed at −30 °C with the two signals at higher δ broadening first. Due to the reactivity of **3** and **4** in solution, spectra at temperatures higher than −10 °C are complicated by the presence of signals from other compounds and hence were not recorded. At −10 °C, **4** shows four very broadened signals.

Although no attempt is made here to fully assign the ^{13}C spectra, we do propose that the signal of relative intensity 3 is an averaged signal due to the rotation of the three CO ligands bound to the unique Ru atom (labeled d in Figure 1b). Another possible explanation for this signal would be that the averaging is due to three CO ligands undergoing an internuclear migration around the Ru_3 triangle. The proposed rotation is preferred to an internuclear migration (requiring the making and breaking of bonds) since the latter would be expected to have a relatively high-energy barrier being inhibited by the other edge-bridging moieties. Having made this assignment, the remaining three signals of relative intensity 2 can be assigned to the three pairs of CO ligands labeled a, b, and c in Figure 1b.

Equivalence of all CO ligands as observed for **3** would then arise due to this rotation coupled with either (a) a CO migration around the Ru_3 unit, or, more likely, (b) dissociation of the $CuPPh_3$ group followed by hydride migration and recombination. Reasons against a mechanism as (a) are presented above whereas mechanism (b) is supported by the proposed intermolecular exchange of $MPPh_3$ moieties for **3** and **4**.

(iii) The Heterometallic Clusters $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)(MPPh_3)$ (M = Cu (6), Ag (7), Au (8)). Refluxing the clusters **3**, **4**, or **5** with PPh_3 in CH_2Cl_2 leads to the rapid formation of the PPh_3-substituted derivatives **6**, **7**, or **8** in near quantitative yield. The mild conditions required show the substitution to be facile and following the conversion by IR shows the process to be more rapid for **3** and **4** than for **5**. The X-ray crystal structure of **6** has been determined and shows the presence of discrete molecules (see Figure 2). The Ru_3Cu metal core forms a "butterfly" configuration with an interplanar

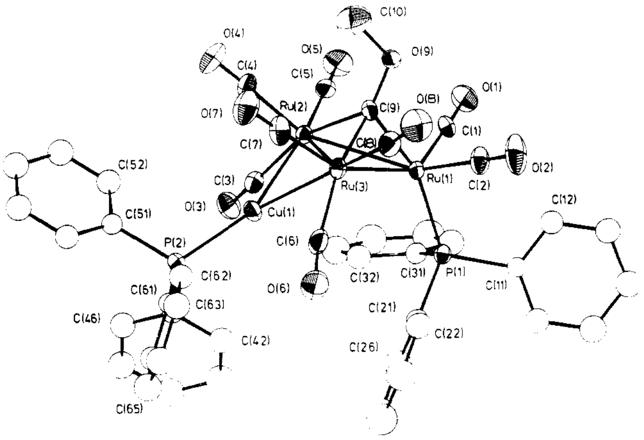

Figure 2. The molecular structure of $H_2Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)(CuPPh_3)$ showing the atom numbering scheme and excluding hydrogen atoms for clarity. The atoms are drawn at the 30% probability level.

angle of 125.0° and the Cu atom symmetrically edge bridging a Ru–Ru bond. The three Ru atoms are asymmetrically capped on the opposite side to the $CuPPh_3$ moiety by the carbon atom of the μ_3-COMe ligand. The Ru–Ru and Ru–Cu bond lengths are unexceptional with the shortest Ru–Ru bond (Ru(2)–Ru(3)) being the one bridged by the $CuPPh_3$ moiety. This is also observed for $CuRu_3(CO)_9(C_2Bu^t)(PPh_3)$.[2] The two hydrides not located by this X-ray study are believed to bridge the two longer Ru–Ru bonds. The Ru–C(O) bond lengths have an average value of 1.91 (1) Å which is normal, but it is worthwhile noting that the two longest of these bonds belong to the CO ligands trans to the μ_3-COMe ligand (Ru(2)–C(3) = 1.97 (1), Ru(3)–C(6) = 1.94 (1) Å). This supports other work[13] which shows the μ_3-COMe ligand to have a strong trans influence. The carbonyl ligands, which are all terminal, are essentially linear except for the two mentioned above which show Ru–C–O angles of 169.2 (8)° and 169.6 (10)°. This coupled with comparatively short C···Cu distances for these two CO ligands (C(3)···Cu(1) = 2.49 Å, C(6)···Cu(1) = 2.57 Å) indicates a semibridging relationship between these two CO ligands and the Cu atom. This semibridging relationship is not unusual and similar close Cu···C contacts of 2.30–2.73 Å have been reported in several other clusters.[14-16] Such a relationship has also been observed in the X-ray study of 5[13] where two CO ligands semibridge the Au atom with Au···C distances of 2.76 and 2.74 Å and Ru–C–O angles of 168 (1)° and 171 (1)°.

On the basis of the similarity of the IR spectra the three compounds **6**, **7**, and **8** are believed to be isostructural. This is supported by the ^1H NMR spectra (Table IV) where the expected multiplicities are observed for the μ-H signals. The largest coupling in each case is attributed to the phosphorus of the PPh_3 ligand bound to Ru and for **6** and **8** the smallest coupling to that of the PPh_3 bound to the heterometal. **7** also exhibits coupling to the Ag nuclei. These observations are in contrast with the ^1H NMR studies of **3**, **4**, and **5** where only **5** showed the expected multiplicity for a rigid system.

The ^{13}C NMR spectrum has been recorded for **6** which at –90 °C shows a doublet at δ 280.7 ppm (J = 39 Hz) due to the carbyne carbon coupling with the phosphorus of the transoid PPh_3 ligand and four signals (relative intensities 1:1:1:1) attributed to the CO ligands. These CO signals are consistent with the structure of **6** (Figure 2).

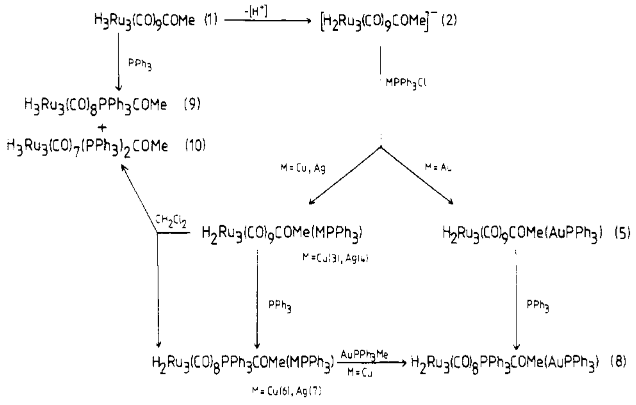

Figure 3. Reaction scheme.

The reaction of **6** with $AuPPh_3Me$ in diethyl ether at room temperature was attempted in an effort to prepare the trimetallic cluster $HRu_3(CO)_8PPh_3(\mu_3\text{-}COMe)(CuPPh_3)(AuPPh_3)$ but led instead to the formation of **8**. This suggests that a $AuPPh_3$-bridged Ru–Ru bond is the stronger.

(iv) The Homometallic Clusters $H_3Ru_3(CO)_8PPh_3(\mu_3\text{-}COMe)$ (9) and $H_3Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}COMe)$ (10). Refluxing **1** in CH_2Cl_2 with PPh_3 followed by chromatographic separation leads to the isolation of compounds **9** and **10**. These compounds are also formed in solutions of **3** and **4** in CH_2Cl_2 after several days. They are also found in small yields in the filtrate from the preparation of **3**, **4**, and **5**.

(v) Reactivity of 3, 4, and 5 in CH_2Cl_2. Both **3** and **4** are unstable in CH_2Cl_2 solution at room temperature with decay over a period of 4 days to essentially **9** and **10** for **4** and a wider range of products (including **9** and **10**) for **5**. This reactivity has been studied by ^1H and ^{31}P NMR and shows the decay to be complex involving a number of unidentified compounds, but in both cases the first new species observed are the PPh_3 derivatives **6** and **7**, respectively, which can be easily identified within 5 min for **3** and 15 min for **4**. After a day both solutions form insoluble deposits and **4** shows a silver mirror on the NMR tube wall. In comparison **5** is stable under similar conditions.

Conclusion

The reaction of the anion $[H_2Ru_3(CO)_9(\mu_3\text{-}COMe)]^-$ with $MPPh_3Cl$ (M = Cu, Ag, Au) forms the heterometallic clusters **3**, **4**, and **5** which are believed to be isostructural with the heterometal edge-bridging a Ru–Ru bond. This contrasts with the analogous series of compounds $H_3Ru_4(CO)_{12}(MPR_3)$ where the heterometal edge-bridges for M = Au (R = Ph)[17] and face-bridges for M = Cu (PR_3 = $PMePh_2$).[2] In solution at room temperature **3** and **4** are significantly more labile than **5** as observed by (i) the intermolecular exchange of $MPPh_3$ moieties is only seen for **3** and **4**, (ii) the stability in solution where **3** and **4** both undergo decomposition processes to a number of products whereas **5** is stable, and (iii) the rate of substitution of CO by PPh_3 where **3** > **4** > **5**. (The rate for **3** and **4** is approximately twice that for **5**). This substitution reaction is particularly selective and rapid for all three clusters. With PPh_3, **2** shows similar reactivity to **3**, **4**, and **5** in terms of the rate of reaction, but it does so with much less selectivity. It hence appears that the introduction of the

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$MPPh_3$ moiety in place of a hydride ligand leads to a more directed substitution.

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Registry No. **1**, 71562-47-5; **2**, 119503-09-2; **3**, 119503-10-5; **4**, 119503-11-6; **5**, 84076-21-1; **6**, 119528-79-9; **7**, 119503-13-8; **8**, 119503-14-9; **9**, 119503-15-0; **10**, 119503-16-1; $CuPPh_3Cl$, 22176-30-3; $AgPPh_3Cl$, 52495-09-7; $AuPPh_3Cl$, 14243-64-2; $K[H_2Ru_3(CO)_9(\mu_3\text{-}COMe)]$, 119503-17-2.

Supplementary Material Available: Tables of hydrogen atom positions (Table S1), anisotropic thermal parameters (Table S2), and bond lengths and angles (Table S3) (4 pages); a listing of observed and calculated structure factors (Table S4) (30 pages). Ordering information is given on any current masthead page.

Synthesis of [Alkenyl(dimethylamino)carbene]tungsten Complexes Using the Peterson Reaction: X-ray Crystal Structure of (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$

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Treatment of $(CO)_5W[C(NMe_2)CH_3]$ (**1**) with *n*-BuLi followed by Me_3SiCl produced $(CO)_5W[C(NMe_2)CH_2SiMe_3]$ (**2**) in 90% yield. $(CO)_5W[C(NMe_2)CHSiMe_3]Li$, which was formed in the reaction between **2** and *n*-BuLi, reacted with several nonenolizable aldehydes or ketones to afford moderate yields (45–61%) of the desired (alkenylaminocarbene)tungsten complexes $(CO)_5W[C(NMe_2)CH{=}CR^1R^2]$ (**3a–f**) (**a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, $R^2 = Ph$; **c**, $R^1 = H$, $R^2 =$ 2-furyl; **d**, $R^1 = H$, $R^2 =$ *trans*-$CH{=}CHPh$; **e**, $R^1 = H$, $R^2 = (\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$; **f**, $R^1 = R^2 = Ph$). For compounds **3b–e**, exclusive formation of the *E* isomer occurred. Treatment of **2** with *n*-BuLi followed by either $CF_3SO_3CH_3$ or $CH_2{=}CHCH_2Br$ afforded complexes **4a** and **4b** (70–90%), $(CO)_5W[C(NMe_2)CH(R)SiMe_3]$ (**4a**, $R = CH_3$; **4b**, $R = CH_2CH{=}CH_2$), respectively. Complexes **4a** or **4b** could not be obtained by reacting the corresponding complexes **5a** or **5b**, $(CO)_5W[C(NMe_2)CH_2R]$ (**5a**, $R = CH_3$; **5b**, $R = CH_2CH{=}CH_2$), with *n*-BuLi followed by Me_3SiCl. Furthermore, the lithium anions $(CO)_5W[C(NMe_2)C(R)SiMe_3]Li$ ($R = CH_3$, $CH_2CH{=}CH_2$) from **4a** or **4b** did not react with aldehydes or ketones to afford the desired α-substituted (alkenylaminocarbene)tungsten complexes. One example of such a complex, $(CO)_5W[C(NMe_2)C(CH_3){=}CH_2]$ (**7**), could, however, be prepared in 75–80% yield by treating $(CO)_5W[C(OCH_3)C(CH_3){=}CH_2]$ (**6**) with $HNMe_2$ in ether. $(CO)_5W[C(NMe_2)CHSiMe_3]Li$ was made to react with PhCOCl to yield the enol silyl ether derivative $(CO)_5W[C(NMe_2)CH{=}C(OSiMe_3)Ph]$ (**8**) (26%) along with a trace of an air-sensitive complex $(CO)_5W[C(NMe_2)CH_2C(O)Ph]$ (**9**). (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]$ (**3e**) was further characterized by single-crystal X-ray diffraction methods. Complex **3e** crystallizes in the monoclinic space group $P2_1/c$ with (at 20 °C) $a = 12.022$ (4) Å, $b = 12.857$ (8) Å, $c = 13.826$ (8) Å, $\beta = 102.19$ (4)°, and $D_{calcd} = 1.88$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 2604 independent observed $[F_o \geq 5\sigma(F_o)]$ reflections led to a final conventional *R* value of 0.044.

Introduction

Although Fischer-type carbene complexes have been studied extensively over the past 15 years,[1] research on these interesting species continues unabated. Of the many systems currently under investigation, aminocarbene complexes and alkenylcarbene complexes are receiving their proportional share of study. Organic synthetic applications of (aminocarbene)chromium complexes include reactions with alkynes, imines, or nucleophiles to afford indene derivatives,[2] β-lactams,[3] or α-amino acid derivatives,[3b] respectively. (Aminocarbene)iron complexes also react with alkynes to produce 5-aminofurans.[4] Moreover, Dötz and co-workers have recently described the synthesis and X-ray crystal structure of a novel Diels–Alder adduct obtained from an α,β-unsaturated (aminocarbene)tungsten complex.[5] On the other hand, alkenylcarbene complexes undergo many interesting transformations including Diels–Alder reactions,[6] cyclohexadienone annulations,[7] conversions to pyrroles,[8] δ-carbolines,[9] or 3-imidazoline complexes,[10] transmetalations,[11] formation of dimetallic

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