6.97 (m, 2 H), 5.48 (m, 2 H), 5.25 (m, 1 H), 1.4–1.1 (m, 5 H), 1.21 (d, $J = 10.2$ Hz, 9 H), 0.24 (d, $J = 5.5$ Hz, 3 H) ppm. $^{31}P\{^1H\}$ NMR for **14** (acetone-d_6): δ −39.5 ppm. $^{13}C\{^1H\}$ NMR for **14** (acetone-d_6): δ 123.7 (s), 123.4 (s), 121.8 (s), 121.6 (s), 112.6 (s), 110.4 (s), 97.7 (s), 70.3 (d, $J = 3.7$ Hz), 68.6 (d, $J = 13.1$ Hz), 23.2 (d, $J = 4.6$ Hz), 14.7 (d, $J = 37.0$ Hz), −13.9 (d, $J = 7.1$ Hz), −32.3 (d, $J = 8.7$ Hz) ppm. List of impurity peaks in the $^{13}C\{^1H\}$ NMR spectrum for **14** (acetone-d_6): δ 122.4 (s), 119.0 (s), 18.5 (d, $J = 36.1$ Hz), 9.9 (s) ppm. High-resolution MS (oil) (EI): m/e calcd for $C_{15}H_{24}PIr$, 428.1246/426.1222 (M^+, $^{193}Ir/^{191}Ir$); m/e found, 428.1230/426.1212 (M^+, $^{193}Ir/^{191}Ir$).

Kinetics of the Insertion Reaction of (η^5-C_9H_7)Ir(PMe_3)(CH_3)(H) (6a) with 3,3-Dimethyl-1-butyne. Samples were prepared in 5-mm thin-walled Wilmad 505-PS 8-in. NMR tubes. The volumes of the alkyne and cyclohexane-d_{12} were added to give a total volume of 0.60 mL, assuming a negligible (≤5%) change in the volume of mixing. For example, 4 mg (0.01 mmol) of **6a** was dissolved in 0.58 mL of cyclohexane-d_{12}, as measured by syringe, and the solution was loaded into an NMR tube fitted with a Cajon adaptor. Tetramethylsilane was vacuum-transferred (2.9×10^{-6} mol, 0.8 Torr, 66.34 mL, 293 K), into the NMR tubes as the internal standard for ^1H NMR spectra, and P(o-tol)$_3$ (6 mg, 2.0×10^{-5} mol) was added as a solid as the internal standard for $^{31}P\{^1H\}$ NMR spectra. The solution was degassed with three freeze–pump–thaw cycles, and 0.16 mmol (0.02 mL) of 3,3-dimethyl-1-butyne was condensed into the tube from a known-volume bulb. The tube was flame-sealed to give a solution with [**6a**] = 0.017 M and [alkyne] = 0.27 M. The tubes were heated in the appropriate Neslab constant-temperature baths and cooled rapidly in a 0 °C acetone bath. All NMR spectra were taken at 20 °C.

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Registry No. **4a**, 139377-84-7; **4b**, 139377-90-5; **4c**, 139377-91-6; **5a**, 139377-85-8; **5b**, 139377-92-7; **6a**, 139377-86-9; **8**, 139655-72-4; **9a**, 139655-73-5; **9b**, 139655-74-6; **9c**, 139655-75-7; **9d**, 139655-76-8; **9e**, 139655-77-9; **10a**, 139687-87-9; **10b**, 139687-86-8; **10c**, 139687-88-0; **13a**, 139687-89-1; **13b**, 139687-90-4; **13c**, 139687-91-5; **13d**, 139687-92-6; **14**, 139687-93-7; t-BuNC, 7188-38-7; acetylene, 74-86-2; *tert*-butylacetylene, 917-92-0; 2-butyne, 503-17-3; 3-hexyne, 928-49-4; ethylene, 74-85-1; 3,3-dimethyl-1-butyne, 917-92-0.

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Reaction of Cyclopentadiene with (Alkylidyne)triruthenium Clusters. Syntheses of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ and $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$. Crystal Structures of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ and $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$

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The reaction of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_{9-n}(NCMe)_n$ ($n = 1, 2$) with cyclopentadiene produces the new cluster $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$, in addition to $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$. Hydrogenation of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ gives $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$. The compound $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$, with $a = 9.039$ (2) Å, $b = 20.496$ (5) Å, $c = 11.896$ (3) Å, $\beta = 92.80$ (2)°, $V = 2201$ (1) Å^3, and $Z = 4$. Diffraction data (Mo Kα, $2\theta = 5$–$50°$) were collected with a Siemens R3m/V diffractometer, and the structure was solved and refined to $R = 5.09\%$ for all 3901 data ($R = 2.69\%$ for those 2659 data with $F > 6.0\sigma(F)$). The structure contains a triangular arrangement of ruthenium atoms (Ru–Ru = 2.738 (1)–2.749 (1) Å) capped by a μ_3-CPh ligand (Ru–C = 2.055 (5)–2.086 (5) Å). Atoms Ru(1) and Ru(2) are each bound to three terminal CO ligands, while Ru(3) is linked to an η^5-C_5H_5 ligand. The structure is completed by two bridging CO ligands bonded more strongly to Ru(3) and somewhat less strongly to the remaining Ru atoms (Ru(3)–C(31) = 1.993 (6) Å, Ru(1)–C(31) = 2.167 (6) Å; Ru(3)–C(32) = 1.972 (6) Å, Ru(2)–C(32) = 2.225 (6) Å). The compound $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, with $a = 10.465$ (2) Å, $b = 11.192$ (2) Å, $c = 18.444$ (3) Å, $\beta = 92.00$ (2)°, $V = 2158.8$ (7) Å^3, and $Z = 4$. Diffraction data (Mo Kα, $2\theta = 5$–$45°$) were collected with a Siemens R3m/V diffractometer, and the structure was solved and refined to $R_F = 3.24\%$ for all 2716 unique data ($R_F = 2.02\%$ for those 2110 data with $|F_o| > 6\sigma(|F_o|)$). The three ruthenium atoms in the structure form an almost perfect equilateral triangle (Ru–Ru = 2.690 (1)–2.705 (1) Å), which is capped by a μ_3-CPh ligand (Ru–C = 2.019 (4)–2.023 (4) Å). Each edge of the triangle has a symmetrically bridging carbonyl attached. The structure is then completed by one η^5-C_5H_5 ring bonded to each ruthenium.

The alkylidyne trimetallic clusters $(\mu\text{-}H)_3M_3(\mu_3\text{-}CX)(CO)_{9-n}L_n$ (M = Ru, Os; X = H, alkyl, aryl, halide, CO_2R, OMe, etc.) have proved to be valuable for studies of cluster reactivity because of the numerous derivatives available in good yield, allowing ready modification of steric and electronic character of the cluster.[1] Cyclopentadienyl derivatives $H_{4-2n}Ru_3(CX)(CO)_{6+n}Cp$ would be desirable because (1) the neutral clusters would contain even num-

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bers of hydride ligands, unlike the parent carbonyls, allowing for a comparison of reactivity vs hydride number, (2) ligand dissociation from one metal center would be blocked, and (3) the cyclopentadienyl ligand has been shown to stabilize oxidation processes. Examples of cyclopentadienyl complexes of alkylidyne trimetallic clusters of group 8 metals include $Fe_3(\mu_3\text{-}CR)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}Cp')$ ($Cp' = C_5H_5$, R = Me,[2] OMe;[3] $Cp' = C_5H_2Me_2(C_2H_3)$, R = Et[8]), $Fe_2M(\mu_3\text{-}COMe)(CO)_7(\eta^5\text{-}C_5H_5)$ (M = Co,[9a] Rh[9b]), and $Ru_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_3(\mu_3\text{-}CR)$.[4] A large number of mixed-metal and Co_3 or Rh_3 clusters have also been prepared. The synthetic procedures used for these clusters were not generally suitable for the desired class of alkylidynes. Therefore, we have undertaken to substitute directly onto $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CX)(CO)_9$ with cyclopentadiene or cyclopentadienide. In this paper we report the products from the reaction of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_{9-n}(NCMe)_n$ (n = 1, 2) with cyclopentadiene.

Experimental Section

$(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ was prepared by a modification of the previously reported method, using $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ (rather than $H_3Ru_3(\mu_3\text{-}CBr)(CO)_9$) for the reaction with benzene and $AlCl_3$.[5] Cyclopentadiene was prepared by thermal cracking of dicyclopentadiene. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer, and variable-temperature ^{13}C NMR spectra were obtained on a Varian VXR-400 spectrometer; chromium(III) acetylacetonate (0.02 M) was added as a relaxation agent for the ^{13}C NMR spectra. Infrared spectra of cyclohexane solutions were recorded on a Mattson Alpha Centauri Fourier transform spectrometer or a Beckman 4250 spectrophotometer. Mass spectra were recorded on a VG 70-SE mass spectrometer. Elemental analyses were performed by Galbraith Laboratories.

Reaction of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_8(NCMe)$ and Cyclopentadiene. A solution of trimethylamine *N*-oxide dihydrate (18.9 mg, 0.170 mmol) in acetonitrile (15 mL) was added dropwise via an addition funnel to a solution of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ (100 mg, 0.155 mmol) in 20 mL of acetonitrile in a 50-mL Schlenk flask under a nitrogen atmosphere. The mixture was stirred at room temperature for 30 min. The solvent was removed by vacuum transfer, leaving a red-purple residue. The residue was dissolved in 3 mL of cyclopentadiene. The resulting mixture was stirred under nitrogen at room temperature for 8 h. The solvent was removed by vacuum transfer, leaving a red-brown residue. Preparative TLC (silica gel; cyclohexane/dichloromethane, 2:1 v/v) yielded the following bands in order of elution: pale yellow $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ (contaminated with dicyclopentadiene), orange $(\mu\text{-}H)Ru_3(\mu_3\text{-}CPh)(CO)_8(\eta^4\text{-isoprene})$[10] (yield varied with the distillation cut of cyclopentadiene used), 3 mg (3%) of red $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$, 7 mg of brown, unidentified solid, and 24 mg (21%) of green $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. The red-brown bottom band was extracted and reapplied to a TLC plate, which was eluted with dichloromethane, to give two yellow bands and a red band. Extraction of the red band yielded $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ (13 mg, 11%).

Reaction of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_7(NCMe)_2$ and Cyclopentadiene. A solution of trimethylamine *N*-oxide dihydrate (38 mg, 0.34 mmol) in acetonitrile (20 mL) was added dropwise via an addition funnel to a solution of $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ (102 mg, 0.158 mmol) in 15 mL of acetonitrile in a 50-mL Schlenk flask under a nitrogen atmosphere. The mixture was stirred at room temperature for 15 min. The solvent was removed by vacuum transfer, leaving a red-purple residue. The residue was dissolved in 3 mL of cyclopentadiene. The resulting mixture was stirred under nitrogen at room temperature for 24 h. The solvent was evaporated under a stream of 1:1 CO/N_2 (to convert any unreacted acetonitrile complexes to the carbonyl), leaving a red-brown residue. Workup as described above yielded the following bands in order of elution: 30 mg (30%) of pale yellow $(\mu\text{-}H)_3Ru_3(\mu_3\text{-}CPh)(CO)_9$, 17 mg (15%) of orange $(\mu\text{-}H)Ru_3(\mu_3\text{-}CPh)(CO)_8(\eta^4\text{-isoprene})$ (yield varied with cut of cyclopentadiene used), 3 mg (3%) of red $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$, 7 mg of brown unidentified solid, and 10 mg (9%) of green $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. The red-brown bottom band was extracted and reapplied to a TLC plate, which was eluted with dichloromethane, to give two yellow bands and a red band. Extraction of the red band yielded $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ (9 mg, 8%).

Reaction of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ with Hydrogen. A solution of the cluster (25 mg, 0.0367 mmol) in cyclohexane was heated to 70 °C with hydrogen bubbling through the solution. After 2 h of heating the dark green solution had turned orange-red. The solvent was removed by rotary evaporation, and the resulting red oil was purified by thin-layer chromatography on silica gel, with cyclohexane/dichloromethane (2:1 v/v) as eluent. The only band on the plate yielded $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$ (22.6 mg, 0.0345 mmol, 94%), after extraction with dichloromethane.

$(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$. IR ($C_6H_{12}$): 2087 m, 2066 s, 2024 vs, 2001 s, 1998 sh, 1884 w, 1870 w cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): 7.66 (br, 2 H, Ph), 7.28 (br, 2 H, Ph), 7.12 (br, 1 H), 4.89 (s, 5 H, Cp), −17.91 (d, 1 H_a, RuHRu), −18.14 (d, 1 H_b, RuHRu) ppm; J_{ab} = 2.3 Hz. ^{13}C NMR ($CDCl_3$, 25 °C): 243.6 (1 C, s, μ_3-*C*Ph), 214.7 (1 C, s, semibridging CO), 193.2 (1 C, s, CO), 192.7 (1 C, s, CO), 192.6 (1 C, s, CO), 191.7 (1 C, s, CO), 191.4 (1 C, s, CO), 190.6 (1 C, s, CO), 163.7 (1 C, s, Ph), 130.5 (2 C, d, J = 160 Hz, Ph), 128.0 (2 C, d, J = 160 Hz, Ph), 125.6 (1 C, d, J = 161 Hz, Ph), 88.8 (5 C, d, J = 175 Hz, Cp) ppm. EI MS: m/z 658 ($^{102}Ru_3$). Anal. Calcd for $C_{19}H_{12}O_7Ru_3$: C, 34.81; H, 1.84. Found: C, 34.59; H, 1.90.

Brown Product, Band 4. IR (C_6H_{12}): 2085 m, 2079 m, 2067 w, 2040 s, 2025 vs, 2016 sh, 1988 w, 1978 m, 1969 sh, 1727 m cm^{-1}.

$Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. IR ($C_6H_{12}$): 2078 s, 2068 s, 2036 vs, 2020 vs, 1982 m, 1971 m cm^{-1}. ^{1}NMR ($CDCl_3$, 25 °C): 7.4 (m, 5 H), 4.99 (s, 5 H) ppm. ^{13}C NMR ($CDCl_3$, −60 °C): 277.3 (1 C, s, *C*Ph), 228.1 (2 C, s, μ-CO), 200.2 (2 C, s, CO), 199.0 (2 C, s, CO), 189.8 (2 C, s, CO), 160.9 (1 C, Ph), 130.8 (2 C, d, J = 160 Hz, Ph), 127.4 (2 C, d, J = 160 Hz, Ph), 127.0 (1 C, d, J = 160 Hz, Ph), 96.4 (5 C, d, 173 Hz, Cp) ppm. EI MS m/z 684 ($^{102}Ru_3$). Anal. Calcd for $C_{20}H_{10}O_8Ru_3$: C, 35.25; H, 1.48. Found: C, 34.35; H, 1.50.

$Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$. IR ($CH_2Cl_2$): 1808 vs, 1756 m cm^{-1} (lit.[5b] 1805 s and 1753 m cm^{-1}). ^1H NMR ($CDCl_3$, 25 °C): 7.3 (m, 5 H), 5.06 (s, 15 H) ppm (lit.[5b] 5.08 ppm). EI MS: m/z 674 ($^{102}Ru_3$).

Collection of X-ray Diffraction Data for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. A crystal with dimensions 0.25 mm × 0.25 mm × 0.15 mm was sealed into a 0.3-mm-diameter thin-walled capillary and aligned on a Siemens R3m/V single-crystal diffractometer. Determination of unit cell parameters and data

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[10] Characterization was by comparison of spectroscopic data with an authentic sample, prepared from $H_3Ru_3(CPh)(CO)_8(NCMe)$ and isoprene.[11] $(\mu\text{-}H)Ru_3(\mu_3\text{-}CPh)(CO)_8(\eta^4\text{-isoprene})$: IR ($C_6H_{12}$) 2090 s, 2068 vs, 2033 vs, 2024 s, 2019 sh, 2006 s, 1999 sh, 1942 w, 1879 w cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) 7.3 (m, 5 H, C_6H_5), 4.42 (br t, 1 H, J = 7.3 Hz), 2.12 (s, 3 H), 2.09 (m, 1 H, J = 2.3 Hz), 1.35 (dd, 1 H, J = 1.9, 6.6 Hz), 0.92 (br, 1 H), 0.18 (dd, 1 H, J = 1.6, 8.6 Hz), −17.00 (s, 1 H, RuHRu) ppm; ^{13}C NMR ($CDCl_3$, 25 °C) 241.4 (1 C, *C*Ph), 214.5 (1 C, semibridging CO), 212.2 (1 C, semibridging CO), 193.6 (1 C, CO), 192.6 (1 C, CO), 192.4 (1 C, CO), 192.3 (1 C, CO), 191.6 (1 C, CO), 191.4 (1 C, CO), 158.9 (1 C), 131.9 (2 C), 128.3 (2 C), 124.4 (1 C), 111.6 (1 C), 96.4 (1 C), 51.0 (1 C), 48.3 (1 C), 22.6 (1 C) ppm; EI MS m/z 688 ($^{102}Ru_3$). Anal. Calcd for $C_{20}H_{14}O_8Ru_3$: C, 35.14; H, 1.77. Found: C, 35.23; H, 2.15.

[11] Keister, J. B.; Nevinger, L. R. Unpublished results.

Table I. Crystallographic Data for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ and $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$

	$Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$	$Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$
(A) Crystallographic Parameters		
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14, var)	$P2_1/c$ (No. 14)
a, Å	9.039 (2)	10.465 (2)
b, Å	20.496 (5)	11.192 (2)
c, Å	11.896 (3)	18.444 (3)
β, deg	92.80 (2)	92.00 (2)
V, Å^3	2201.2 (9)	2158.8 (7)
T, K	298	298
formula	$C_{20}H_{10}O_8Ru_3$	$C_{25}H_{20}O_3Ru_3$
mol wt	681.5	671.6
Z	4	4
D(calcd), Mg/m^3	2.056	2.066
μ(Mo Kα), mm^{-1}	2.036	2.059
F(000)	1304	1304
(B) Data Collection		
diffractometer used	Siemens R3m/V	Siemens R3m/V
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
monochromator	highly oriented graphite cryst	highly oriented graphite cryst
2θ range, deg	5.0–50.0	5.0–45.0
scan type	2θ–θ	2θ–θ
scan speed, deg min^{-1}	constant; 3.97 in ω	constant; 2.00 in ω
scan range (ω), deg	0.60 plus Kα separation	0.60 plus Kα separation
bkdg measurement	stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time	stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time
index ranges	$0 \le h \le 10$, $0 \le k \le 24$, $-14 \le l \le 14$	$0 \le h \le 9$, $0 \le k \le 12$, $-19 \le l \le 19$
total no. of rflns collected	4295	3072
no. of indep rflns	3901 (R_{int} = 1.80%)	2716 (R_{int} = 1.28%)
no. of rflns ($R > 6.0\sigma(F)$)	2659	2110
abs cor	semiempirical	semiempirical
min/max transmissn	0.4819/0.5451	0.3404/0.4331

collection were carried out as described previously;[12] details appear in Table I. All data were corrected for the effects of absorption and for Lorentz and polarization effects. The crystal belongs to the monoclinic system (2/*m* diffraction symmetry); the systematic absences *h*0*l* for $h + l = 2n + 1$ and 0*k*0 for $k = 2n + 1$ uniquely define the centrosymmetric space group $P2_1/n$ (No. 14, var).

Solution and Refinement of the Crystal Structure of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. Crystallographic calculations were performed on a VAX3100 workstation, with use of the Siemens SHELXTL PLUS program set. Analytical scattering factors for neutral atoms were corrected for the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. The structure was solved by direct methods and refined to $R_F = 5.09\%$, $R_{wF} = 4.67\%$, and GOF = 0.93 for the 3901 reflections with $|F_o| > 0.3\sigma(|F_o|)$; $R_F = 2.69\%$ and $R_{wF} = 3.01\%$ for those 2659 data with $|F_o| > 6.0\sigma(|F_o|)$. Hydrogen atoms were included in calculated positions[13] based upon *d*(C–H) = 0.96 Å. The final model included a correction for secondary extinction of $\chi = [2.3\ (3)] \times 10^{-4}$, where $F^* = F[1 + 0.002\chi F^2/(\sin 2\theta)]^{-1/4}$. A final difference-Fourier map was clean, with residual electron density only in the range $\rho = -0.86$ to $+0.75$ e Å^{-3}. Final atomic coordinates are collected in Table II.

Collection of X-ray Diffraction Data for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$. A crystal with the dimensions 0.25 mm × 0.20 mm × 0.20 mm was selected for the structural analysis, which proceeded as before. The crystal belongs to the monoclinic crystal system (2/*m* diffraction symmetry). The systematic absences *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$ uniquely define the centrosymmetric space group $P2_1/c$ (No. 14). Determination of unit cell parameters and data collection were carried out as previously described;[12] details appear in Table I. All data were corrected for the effects of absorption and for Lorentz and polarization effects; the 3072 reflections were merged to a unique set of 2716 reflections (R_{int} = 1.28%).

Solution and Refinement of the Crystal Structure of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$. The structure was solved as described above and refined to $R_F = 3.24\%$ ($R_{wF} = 3.24\%$) for all 2716 unique observed reflections with $|F_o| > 0.3\sigma$ and $R_F = 2.02\%$ ($R_{wF} = 2.26\%$) for those 2110 reflections with $|F_o| > 6\sigma$.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$

	x	*y*	*z*	*U*(eq)[a]
Ru(1)	2256 (1)	6205 (1)	3358 (1)	52 (1)
Ru(2)	4976 (1)	5845 (1)	2625 (1)	43 (1)
Ru(3)	2669 (1)	6085 (1)	1103 (1)	40 (1)
O(11)	1790 (7)	5018 (3)	4901 (5)	117 (3)
O(12)	−666 (7)	6950 (4)	3278 (7)	147 (4)
O(13)	3536 (8)	7108 (4)	5176 (5)	129 (3)
O(21)	5360 (8)	4463 (3)	3634 (6)	127 (3)
O(22)	7571 (6)	6044 (3)	1111 (5)	96 (2)
O(23)	6634 (7)	6506 (3)	4586 (5)	101 (2)
O(31)	296 (5)	5217 (2)	1955 (4)	73 (2)
O(32)	3904 (6)	4735 (2)	947 (4)	73 (2)
C(1)	3707 (6)	6668 (3)	2305 (4)	41 (2)
C(2)	4071 (6)	7367 (3)	2196 (5)	46 (2)
C(3)	2994 (8)	7849 (3)	2301 (6)	71 (3)
C(4)	3332 (11)	8502 (4)	2178 (7)	88 (3)
C(5)	4741 (12)	8693 (4)	1970 (6)	85 (4)
C(6)	5803 (10)	8240 (3)	1903 (6)	71 (3)
C(7)	5503 (7)	7580 (3)	2016 (5)	57 (2)
C(11)	1928 (8)	5449 (4)	4335 (6)	76 (3)
C(12)	402 (9)	6668 (4)	3341 (7)	87 (3)
C(13)	3076 (9)	6766 (4)	4514 (6)	87 (3)
C(21)	5221 (8)	4973 (3)	3259 (6)	75 (3)
C(22)	6619 (7)	5947 (3)	1669 (6)	61 (2)
C(23)	6016 (8)	6259 (3)	3860 (6)	64 (2)
C(31)	1250 (6)	5605 (3)	2030 (5)	50 (2)
C(32)	3800 (6)	5265 (3)	1276 (5)	49 (2)
C(41)	3305 (9)	6323 (4)	−621 (5)	73 (3)
C(42)	2663 (11)	6891 (3)	−189 (6)	79 (3)
C(43)	1195 (11)	6713 (5)	27 (6)	90 (4)
C(44)	952 (10)	6084 (5)	−308 (7)	89 (4)
C(45)	2201 (12)	5844 (3)	−709 (5)	79 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Hydrogen atoms were placed in calculated positions[13] based upon *d*(C–H) = 0.96 Å. The final model included a correction for secondary extinction, by refining χ in the following expression: $F^* = F[1 + 0.002\chi F^2/(\sin 2\theta)]^{-1/4}$; χ was refined to a value of $[2.0\ (4)] \times 10^{-4}$. A final difference-Fourier map showed little residual

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Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$

	x	*y*	*z*	*U*(eq)[a]
Ru(1)	1185 (1)	2134 (1)	910 (1)	25 (1)
Ru(2)	3770 (1)	2105 (1)	924 (1)	30 (1)
Ru(3)	2534 (1)	1699 (1)	2154 (1)	34 (1)
O(12)	2405 (4)	528 (4)	−170 (2)	60 (2)
O(13)	694 (4)	−215 (3)	1647 (2)	54 (1)
O(23)	4236 (4)	−273 (4)	1642 (3)	70 (2)
C(12)	2431 (5)	1189 (4)	332 (3)	34 (2)
C(13)	1217 (5)	708 (5)	1572 (3)	38 (2)
C(23)	3734 (5)	665 (5)	1581 (3)	45 (2)
C(1)	2517 (4)	3107 (4)	1470 (2)	23 (1)
C(2)	2456 (5)	4423 (4)	1561 (3)	29 (2)
C(3)	2662 (5)	5188 (5)	989 (3)	43 (2)
C(4)	2577 (5)	6424 (5)	1047 (4)	52 (2)
C(5)	2241 (7)	6921 (5)	1698 (4)	69 (3)
C(6)	2002 (8)	6180 (6)	2257 (4)	84 (3)
C(7)	2112 (7)	4957 (5)	2205 (3)	64 (3)
C(41)	−913 (6)	1823 (6)	695 (4)	56 (2)
C(42)	−747 (5)	2942 (5)	1051 (3)	43 (2)
C(43)	−81 (5)	3721 (5)	599 (3)	42 (2)
C(44)	222 (5)	3079 (6)	−19 (3)	50 (2)
C(45)	−327 (6)	1924 (6)	27 (3)	58 (2)
C(51)	5761 (6)	1629 (6)	634 (5)	73 (3)
C(52)	5115 (7)	1968 (7)	17 (5)	74 (3)
C(53)	4750 (6)	3179 (6)	74 (4)	58 (2)
C(54)	5215 (5)	3576 (5)	753 (3)	51 (2)
C(55)	5817 (5)	2629 (6)	1119 (4)	61 (3)
C(61)	1641 (8)	1135 (7)	3180 (3)	72 (3)
C(62)	1841 (8)	2368 (6)	3232 (3)	66 (3)
C(63)	3155 (8)	2575 (8)	3221 (3)	72 (3)
C(64)	3752 (8)	1452 (8)	3151 (3)	80 (3)
C(65)	2788 (8)	553 (7)	3141 (3)	72 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

electron density remaining with $\rho = -0.45$ to $+0.38$ e $Å^{-3}$. Final atomic coordinates are provided in Table III.

Results and Discussion

In earlier work we had examined the reactions of cyclohexadiene with $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = OMe, Ph), which produced the cyclohexadiene complexes $HRu_3(\mu_3\text{-}CX)(CO)_8$(1,3-cyclohexadiene).[6] This reaction was believed to proceed via CO dissociation, diene coordination, hydrogenation, and finally complexation of a second diene molecule.

The reaction of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ with cyclopentadiene yielded only $HRu_3(\mu\text{-}COMe)(CO)_{10}$. We hypothesized that the propensity of the COMe ligand for μ-bridging rather than μ_3-bridging, combined with greater lability for the cluster, might indicate a lower stability for diene complexes when X = OMe, relative to other derivatives. Indeed, $HRu_3(\mu_3\text{-}COMe)(CO)_8$(1,3-cyclohexadiene) is significantly less stable than the benzylidyne analogue.

On the other hand, the slow rate of CO dissociation from $H_3Ru_3(\mu_3\text{-}CPh)(CO)_9$ and other alkylidyne derivatives[7] made the direct reaction with unstable cyclopentadiene unfeasible. Therefore, we prepared the "lightly stabilized" derivatives $H_3Ru_3(\mu_3\text{-}CPh)(CO)_{9-n}(NCMe)_n$ (n = 1, 2) through the reaction with 1 or 2 equiv of trimethylamine *N*-oxide in acetonitrile. These clusters readily lose NCMe.

Addition of cyclopentadiene to $H_3Ru_3(\mu_3\text{-}CPh)(CO)_{9-n}(NCMe)_n$ gave nine products in varying yields. Four of these products have been characterized as $(\mu\text{-}H)Ru_3(\mu_3\text{-}CPh)(CO)_8(\eta^4\text{-isoprene})$ (presumably derived from reaction with isoprene contamination of the cyclopentadiene),[10] $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$, $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$, and $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$.

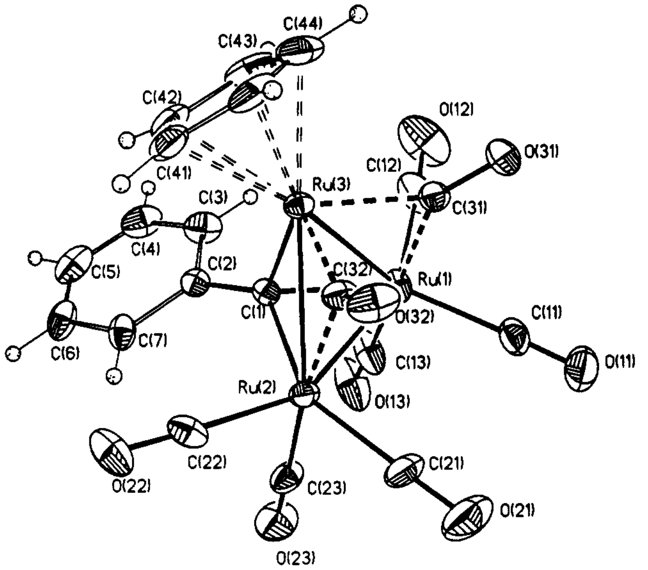

Figure 1. Structure and labeling of the atoms for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$.

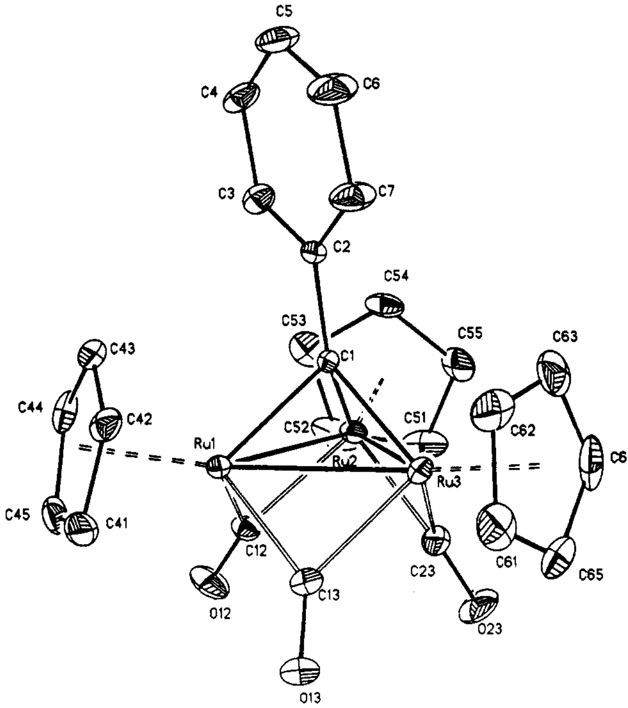

Figure 2. Structure and labeling of the atoms for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$.

$Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. The structure of this compound in the solid state was established by X-ray crystallography. The crystal consists of discrete molecular units of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$. There is one notable close contact between a hydrogen atom on the $\eta^5\text{-}C_5H_5$ ring and an oxygen atom of a carbonyl ligand on an adjacent molecule (H(43)···O(13)′ = 2.515 Å). Other than this, molecules are separated by normal van der Waals distances.

The molecular geometry is depicted in Figure 1; distances are collected in Table IV. The three ruthenium atoms define a triangle in which Ru(1)–Ru(2) = 2.749 (1) Å, Ru(2)–Ru(3) = 2.739 (1) Å, and Ru(3)–Ru(1) = 2.738 (1) Å. The slightly shorter Ru(2)–Ru(3) and Ru(3)–Ru(1) distances may be the result of "bridging" carbonyls (vide infra) about these bonds. The benzylidyne ligand (μ_3-CPh) caps one side of the triangular array, with Ru(1)–C(1) = 2.086 (5) Å, Ru(2)–C(1) = 2.065 (5) Å, and Ru(3)–C(1) = 2.055 (5) Å. The μ_3-CPh ligand does not lie vertically above

Table IV. Bond Lengths (Å) for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$

Ru(1)–Ru(2)	2.749 (1)	Ru(1)–Ru(3)	2.738 (1)
Ru(1)–C(1)	2.086 (5)	Ru(1)–C(11)	1.968 (8)
Ru(1)–C(12)	1.926 (8)	Ru(1)–C(13)	1.913 (8)
Ru(1)–C(31)	2.167 (6)	Ru(2)–Ru(3)	2.739 (1)
Ru(2)–C(1)	2.065 (5)	Ru(2)–C(21)	1.947 (7)
Ru(2)–C(22)	1.926 (7)	Ru(2)–C(23)	1.904 (7)
Ru(2)–C(32)	2.225 (6)	Ru(3)–C(1)	2.055 (5)
Ru(3)–C(31)	1.993 (6)	Ru(3)–C(32)	1.972 (6)
Ru(3)–C(41)	2.210 (7)	Ru(3)–C(42)	2.255 (7)
Ru(3)–C(43)	2.214 (9)	Ru(3)–C(44)	2.229 (8)
Ru(3)–C(45)	2.231 (7)	O(11)–C(11)	1.121 (11)
O(12)–C(12)	1.125 (11)	O(13)–C(13)	1.120 (10)
O(21)–C(21)	1.142 (9)	O(22)–C(22)	1.129 (9)
O(23)–C(23)	1.125 (9)	O(31)–C(31)	1.173 (7)
O(32)–C(32)	1.161 (7)	C(1)–C(2)	1.477 (8)
C(2)–C(3)	1.396 (9)	C(2)–C(7)	1.393 (9)
C(3)–C(4)	1.382 (10)	C(4)–C(5)	1.367 (14)
C(5)–C(6)	1.341 (12)	C(6)–C(7)	1.386 (9)
C(41)–C(42)	1.409 (11)	C(41)–C(45)	1.401 (12)
C(42)–C(43)	1.412 (13)	C(43)–C(44)	1.364 (14)
C(44)–C(45)	1.340 (13)		

the triruthenium plane but is tilted toward Ru(3) (viz., Ru(3)–C(1)–C(2) = 126.8 (4)° as compared to Ru(1)–C(1)–C(2) = 130.0 (4)° and Ru(2)–C(1)–C(2) = 133.2 (4)°).

Atoms Ru(1) and Ru(2) are each linked to three terminal carbonyl ligands, while Ru(3) is bonded to an η^5-cyclopentadienyl ligand. The structure is completed by two "bridging" carbonyl ligands which are more strongly bound to Ru(3) and somewhat less strongly bound (one each) to Ru(1) and Ru(2). Curtis[14] has associated values $\alpha = [d(M(2)\text{–}C) - d(M(1)\text{–}C)]/d(M(1)\text{–}C)$ in the range of 0.1–0.6 with semibridging carbonyls and α values less than 0.1 with bridging carbonyls. The ligand C(31)–O(31) is associated with distances of Ru(3)–C(31) = 1.993 (6) Å and Ru(1)–C(31) = 2.167 (6) Å (α = 0.087) and with the angles Ru(1)–C(31)–Ru(3) = 82.2 (2)°, Ru(3)–C(31)–O(31) = 141.6 (5)°, and Ru(1)–C(31)–O(31) = 136.1 (5)°. The other such ligand, C(32)–O(32), is associated with distances of Ru(3)–C(32) = 1.972 (6) Å and Ru(2)–C(32) = 2.225 (6) Å (α = 0.128) and with the angles Ru(2)–C(32)–Ru(3) = 81.3 (2)°, Ru(3)–C(32)–O(32) = 144.4 (5)°, and Ru(2)–C(32)–O(32) = 134.3 (5)°. Thus, the "bridging" carbonyls in this molecule are borderline examples between symmetrically bridging and semibridging. The purpose of these bridging carbonyl groups is, of course, to transfer charge from the otherwise electron-rich (20-electron) Ru(3) to the otherwise electron-poor (17-electron) Ru(1) and Ru(2). It should be noted that α values for the bridging carbonyls of the Fe_3 analogues range from 0.066 to 0.175.[2,3]

The six terminal carbonyl ligands are associated with Ru–CO distances of 1.904 (7)–1.968 (8) Å. These distances break into distinct sets: the longest (Ru(1)–C(11) = 1.968 (8) Å and Ru(2)–C(21) = 1.947 (7) Å are in axial sites, trans to the μ_3-CPh ligand; the shortest (Ru(1)–C(13) = 1.913 (8) Å and Ru(2)–C(23) = 1.904 (7) Å) are in equatorial sites, trans to the bridging carbonyl ligands; the intermediate pair (Ru(1)–C(12) = 1.926 (8) Å and Ru(2)–C(22) = 1.926 (7) Å) are in mutually trans, equatorial sites.

C–O distances range from 1.120 (10) to 1.142 (9) Å (average 1.127 Å) for the terminal carbonyl ligands and are 1.161 (7) and 1.173 (7) Å (average 1.167 Å) for the two bridging carbonyl ligands.

Atom Ru(3) is linked to an η^5-C_5H_5 ligand with Ru–C distances ranging from Ru(3)–C(41) = 2.210 (7) Å to Ru(3)–C(42) = 2.255 (7) Å; the centroid of the η^5-C_5H_5 ring is 1.891 Å from Ru(3) and is displaced from the Ru_3 plane by 15.4° toward the capping benzylidyne ligand.

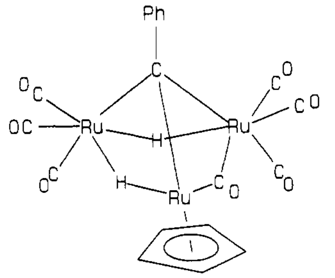

Figure 3. Proposed structure for $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$.

The spectroscopic data indicate that the same structure is maintained in solution. Of note are the resonance at 228.1 ppm due to bridging carbonyls and the shift of the μ_3-carbon atom (277.3 ppm). The compound is structurally analogous to $Fe_3(\mu_3\text{-}CX)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ (X = OMe,[3] Me[2]). The only Ru_3 derivative previously reported is $Ru_3(\mu_3\text{-}CCH_2CMe_3)(CO)_8(\eta^5\text{-}C_5H_5)$, prepared in "low" yield by reaction of cyclopentadiene with $HRu_3(CCCMe_3)(CO)_9$ and characterized by spectroscopic methods.[15]

$(\mu\text{-}H)_2Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)(CO)_6(\eta^5\text{-}C_5H_5)$. The proposed structure for this product is shown in Figure 3. The ^{13}C NMR spectrum indicates a μ_3-benzylidyne moiety (243.6 ppm) and a single semibridging CO ligand (214.7 ppm). The assignment of the latter resonance to a semibridging CO ligand is supported by the chemical shift, which is intermediate between values associated with symmetrically bridging (cf. 228 ppm for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$) and terminal carbonyls (190–200 ppm) and close to the chemical shifts for the semibridging carbonyls of $HRu_3(\mu_3\text{-}CX)(CO)_8$(diene) (X = OMe, diene = cyclohexadiene, α = 0.323, 0.449;[6] X = Cl, diene = cyclohexadiene, ^{13}C δ_{av} 213 ppm;[17] X = Ph, diene = isoprene, δ 214.5 and 212.2 ppm[10]). The low symmetry displayed by the ^1H and ^{13}C NMR spectra rules out the symmetrical arrangement with both hydrides bridging to the RuCp center, and the hydride–hydride coupling constant (2.3 Hz) is characteristic for hydrides bridging adjacent edges of Ru_3 clusters.

The pathway for formation of this product is still unknown. The yield is both low and irregular. However, the product can be formed in excellent yield by hydrogenation of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$.

$Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$. This compound had previously been prepared by Morris and Knox.[4b] Characterization is by comparison of spectroscopic data and, as no previous structural studies of analogous compounds have been performed, by an X-ray crystal structure determination.

The crystal consists of discrete molecular units of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ (Figure 2) which are all separated by normal van der Waals distances.

Each molecule of $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ contains a pseudo-3-fold axis, which is only disrupted by the capping benzylidyne ligand. Distances are tabulated in Table V.

The molecule contains a Ru_3 core that forms an almost perfect equilateral triangle with the following edges: Ru-

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(17) For $HRu_3(\mu_3\text{-}CCl)(CO)_8$(cyclohexadiene): ^{13}C NMR ($CDCl_3$, 25 °C): 245.3 (1 C, μ_3-C), 215.3 (2 C), 192.7 (2 C), 192.4 (2 C), 191.9 (2 C), 96.5 (2 C), 69.4 (2 C), 23.6 (2 C) ppm. Fluxional 4-fold rotation of the cyclohexadiene ligand generates a plane of symmetry in the molecule.[11]

Table V. Bond Lengths (Å) for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$

Ru(1)–Ru(2)	2.705 (1)	Ru(1)–Ru(3)	2.697 (1)
Ru(1)–C(12)	2.013 (5)	Ru(1)–C(13)	2.009 (5)
Ru(1)–C(1)	2.023 (4)	Ru(1)–C(41)	2.245 (6)
Ru(1)–C(42)	2.238 (5)	Ru(1)–C(43)	2.276 (5)
Ru(1)–C(44)	2.225 (6)	Ru(1)–C(45)	2.243 (6)
Ru(2)–Ru(3)	2.690 (1)	Ru(2)–C(12)	2.025 (5)
Ru(2)–C(23)	2.017 (6)	Ru(2)–C(1)	2.021 (4)
Ru(2)–C(51)	2.233 (7)	Ru(2)–C(52)	2.228 (8)
Ru(2)–C(53)	2.251 (7)	Ru(2)–C(54)	2.264 (6)
Ru(2)–C(55)	2.238 (6)	Ru(3)–C(13)	2.044 (5)
Ru(3)–C(23)	2.032 (6)	Ru(3)–C(1)	2.019 (4)
Ru(3)–C(61)	2.230 (7)	Ru(3)–C(62)	2.267 (6)
Ru(3)–C(63)	2.273 (7)	Ru(3)–C(64)	2.217 (7)
Ru(3)–C(65)	2.235 (7)	O(12)–C(12)	1.185 (6)
O(13)–C(13)	1.180 (6)	O(23)–C(23)	1.178 (7)
C(1)–C(2)	1.483 (6)	C(2)–C(3)	1.382 (7)
C(2)–C(7)	1.390 (8)	C(3)–C(4)	1.391 (8)
C(4)–C(5)	1.380 (10)	C(5)–C(6)	1.353 (10)
C(6)–C(7)	1.377 (9)	C(41)–C(42)	1.422 (8)
C(41)–C(45)	1.401 (9)	C(42)–C(43)	1.407 (8)
C(43)–C(44)	1.394 (8)	C(44)–C(45)	1.418 (9)
C(51)–C(52)	1.357 (12)	C(51)–C(55)	1.433 (11)
C(52)–C(53)	1.413 (10)	C(53)–C(54)	1.400 (9)
C(54)–C(55)	1.395 (9)	C(61)–C(62)	1.399 (11)
C(61)–C(65)	1.370 (12)	C(62)–C(63)	1.396 (12)
C(63)–C(64)	1.411 (13)	C(64)–C(65)	1.424 (12)

(1)–Ru(2) = 2.705 (1) Å, Ru(1)–Ru(3) = 2.697 (1) Å, and Ru(2)–Ru(3) = 2.690 (1) Å (average 2.697 Å). The bond angles within this triangular core are Ru(3)–Ru(1)–Ru(2) = 59.7 (1)°, Ru(1)–Ru(2)–Ru(3) = 60.0 (1)°, and Ru(1)–Ru(3)–Ru(2) = 60.3°.

The triangular Ru_3 core is capped by a benzylidyne ligand which is associated with the following ruthenium–carbon distances: Ru(1)–C(1) = 2.023 (4) Å, Ru(2)–C(1) = 2.021 (4) Å, and Ru(3)–C(1) = 2.019 (4) Å. The ipso carbon atom of the benzylidyne ligand, C(1), sits directly above the centroid of the Ru_3 triangle. However, the phenyl ring is not perpendicular to the Ru_3 plane but is bent away such that it makes an angle of 83.9° with the triangular Ru_3 plane.

Each edge of the Ru_3 triangle is associated with a symmetrically bridging carbonyl ligand. These carbonyl ligands have the following distances: Ru(1)–C(13) = 2.009 (5) Å and Ru(3)–C(13) = 2.044 (5) Å; Ru(1)–C(12) = 2.013 (5) Å and Ru(2)–C(12) = 2.025 (5) Å; Ru(2)–C(23) = 2.017 (6) Å and Ru(3)–C(23) = 2.032 (6) Å (average 2.023 Å). The carbon–oxygen distances are C(13)–O(13) = 1.180 (6) Å, C(12)–O(12) = 1.185 (6) Å, and C(23)–O(23) = 1.178 (7) Å (average 1.181 Å). All carbonyl ligands are located on the side of the Ru_3 plane away from the benzylidyne ligand.

Each of the three ruthenium atoms has an η^5-cyclopentadienyl ligand associated with it. These cyclopentadienyl ligands lie slightly above the Ru_3 plane on the side which is capped by the μ_3-benzylidyne ligand. The planes formed by the carbon rings of each of the cyclopentadienyl ligands are slanted toward the benzylidyne ligand. These three Cp planes form angles of 76.7°, 77.5°, and 81.0° with the Ru_3 plane. Distances from the ruthenium to the centroid of the appropriate Cp ring are as follows: Ru(1)–Cp = 1.899 Å, Ru(2)–Cp = 1.901 Å, and Ru(3)–Cp = 1.903 Å (average 1.901 Å).

This compound is a member of a series of (alkylidyne)triruthenium clusters which have been previously prepared in 10–20% yields by pyrolysis of $Ru_2(\mu\text{-}CHR)(CO)_3Cp_2$ (R = H, Me, Et, Pr, Ph, CO_2Et). One member of the series, $Ru_3(\mu\text{-}CMe)(\mu\text{-}CO)_3(\eta^5\text{-}C_5Me_5)_3$, has been shown to give stable mono- and dicationic oxidation products.[16] The synthetic route used here should provide derivatives such as chloromethylidyne, not previously available. The comparison of the chemistry of the radical cations derived from $H_3Ru_3(\mu_3\text{-}CX)(CO)_6(PPh_3)_3$[1c] and $Ru_3(\mu\text{-}CX)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ will be of some interest, as the HOMO for the former series is metal–carbon bonding in character while the HOMO for the latter is likely to be metal–metal bonding in character.

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Supplementary Material Available: Listings of anisotropic thermal parameters, calculated H atom positions, and interatomic angles for $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)$ and $Ru_3(\mu_3\text{-}CPh)(\mu\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3$ (8 pages). Ordering information is given on any current masthead page.

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