A Triad of Stable, Cationic, μ-Hydrido, μ-Alkylidene Complexes, $[(\mu\text{-H})M_2(CO)_6\{\mu\text{-CHC(Ph)NEt}_2\}(\mu\text{-PPh}_2)]X$ (M = Fe, Ru, Os; X = BF_4, PF_6), via the Protonation of an Alkylidene-Bridged, Electron-Rich Metal–Metal Bond

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A triad of cationic μ-hydrido, μ-alkylidene complexes of the iron group $[(\mu\text{-H})M_2(CO)_6\{\mu\text{-CHC(Ph)NEt}_2\}(\mu\text{-PPh}_2)]BF_4$ (M = Fe, **3a**; M = Ru, **3b**; M = Os, **3c**) has been synthesized via the direct protonation of the electron-rich μ-alkylidene complexes $M_2(CO)_6\{\mu\text{-CHC(NEt}_2\text{)Ph}\}(\mu\text{-PPh}_2)$ (**2a–c**) with HBF_4. The complexes were characterized by IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and by a single-crystal X-ray analysis of **3b** with PF_6^- as the counterion. $[(\mu\text{-H})Ru_2(CO)_6\{\mu\text{-CHC(NEt}_2\text{)Ph}\}(\mu\text{-PPh}_2)]PF_6\cdot CH_2Cl_2$ crystallizes as triclinic crystals, space group $P\bar{1}$, with a = 11.324 (4) Å, b = 12.075 (3) Å, c = 14.999 (5) Å, α = 64.97 (2)°, β = 86.40 (3)°, γ = 87.97 (2)°, Z = 2, and D_{calcd} = 1.720 g·cm^{-3}. The structure was solved and refined to R and R_w values of 0.033 and 0.035 based on 3912 observed intensities measured with Mo Kα radiation on a Syntex P2$_1$ diffractometer. The binuclear cation, isoelectronic with $Ru_2(CO)_9$, has three different bridges, a μ-hydride, a μ-diphenylphosphide, and a μ-alkylidene across an Ru–Ru bond (Ru(1)–Ru(2) = 2.7860 (6) Å). The hydride is asymmetrically bound to the two metal atoms (Ru(1)–H(1) = 1.94 (4) Å; Ru(2)–H(1) = 1.77 (4) Å). The reactions of electron-rich **2a–c** with HBF_4 are compared to those of other μ-alkylidenes of ruthenium.

Transition-metal complexes containing hydrido and alkylidene ligands bridging the same metal–metal bond are rare,[1-4] in part because protonation of μ-alkylidene species may lead to μ-methyl or terminal methyl[5-7] or μ-alkylidyne compounds.[6,8] Such molecules are however of considerable current interest for the following substantive reasons. (i) They are plausible intermediates between μ-alkylidene and alkyl ligands.[9] The interrelationships of these and related μ-hydrocarbyl fragments are fundamental to an understanding of organometallic transformations at polynuclear centres.[10] (ii) The electronic structures, bonding, and reactivities of alkylidene complexes are the subject of intensive investigation at present.[11,12] Theoretical studies suggest that the μ-alkylidene carbon atom is electron rich;[12] alkylidene hydrides should be stabilized by increased electron density in the M–C(H)(R)–M system. In this paper we report results pertinent to these aspects. The synthesis of a triad of stable μ-hydrido, μ-alkylidene complexes, $[(\mu\text{-H})M_2(CO)_6\{\mu\text{-CHC(Ph)NEt}_2\}(\mu\text{-PPh}_2)]BF_4$ (**3a**, M = Fe; **3b**, M = Ru; **3c**, M = Os), via the protonation of

Table I. Further Experimental Data on Intensity Collection, Structure Solution, and Refinement for $[(\mu\text{-H})Ru_2(CO)_6\{\mu\text{-CHC(Ph)NEt}_2\}(\mu\text{-PPh}_2)]PF_6\bullet CH_2Cl_2$

mol formula	$[(\mu\text{-H})Ru_2(CO)_6\{\mu\text{-CHC(Ph)NEt}_2\}(\mu\text{-PPh}_2)]PF_6\cdot CH_2Cl_2$
mol wt	960.56
cryst color and habit	yellow prisms
cryst system	triclinic
a, Å	11.324 (4)
b, Å	12.075 (3)
c, Å	14.999 (5)
α, deg	64.97 (2)
β, deg	86.40 (3)
γ, deg	87.97 (2)
V, Å^3	1855 (1)
d_{calcd}, g·cm^{-3}	1.720
diffractometer	Syntex P2$_1$
space group	$P\bar{1}$
radiatn	Mo Kα (λ = 0.71069 Å)
$F(000)$	948
μ(Mo Kα), cm^{-1}	11.01
transmissn factors	0.72–0.84
scan method	$\theta/2\theta$
scan speed, deg/min	3.45–29.30
scan width, deg	0.85 below Kα_1 to 0.85 above Kα_2
2θ range, deg	≤45
temp, K	295 ± 1
std reflctns (every 100 measurements)	$534, 2\bar{6}\bar{4}$
std variatn, %	±2
independent reflctns	4858
obsd reflctns	3912
R (isotropic)	0.091
R (anisotropic)	0.033
R_w	0.035
max residuals about solv (e Å^{-3})	0.65
weighting scheme $w^{-1} = A - B\|F_o\| + C\|F_o\|^2$	
A	2.04
B	0.02
C	0.00042

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[1] For reviews see: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205.

[2] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[3] Churchill, M. R.; DeBoer, B. G.; Shapley, J. R.; Keister, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 2357.

[4] Hermann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63.

[5] Hursthouse, M. B.; Jones, R. A.; Abdul Malik, K. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1979**, *101*, 4128.

[6] Davies, D. L.; Gracey, B. P.; Guerchais, V.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 841.

[7] Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1400.

[8] Dimas, P. A.; Duesler, E. N.; Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7787.

[9] Mononuclear, cationic, alkylidene hydrides are known and are important intermediates in α-elimination reactions. See: Turner, H. W.; Schrock, R. R.; Fellman, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.

[10] For a selection of recent references in this area see: (a) Casey, C. P.; Roddick, D. M. *Organometallics* **1986**, *5*, 436. (b) Gracey, B. P.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans* **1985**, 1935 and earlier papers in this series. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464. (d) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783.

[11] See, for example, ref 1 and: Carter, E. A.; Goddard III, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 2180.

[12] (a) Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852. (b) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554.

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Table II. Atomic Positions (Fractional ×10^4) and Hydrogen Atom Thermal Parameters (×10^3) for [(μ-H)$Ru_2(CO)_6${μ-CHC(Ph)NEt_2}(μ-PPh_2)]PF_6•CH_2Cl_2

(a) Non-Hydrogen Atoms

	x	*y*	*z*		*x*	*y*	*z*
Ru(1)	373.3 (4)	4538.2 (4)	2291.5 (3)	C(11)	3272 (7)	580 (6)	3618 (5)
Ru(2)	2498.0 (4)	5704.2 (4)	1420.2 (3)	C(12)	2305 (10)	−355 (8)	3920 (7)
P(1)	1325.9 (13)	5979.4 (13)	2677.3 (10)	C(13)	2734 (5)	2421 (5)	1785 (4)
O(1)	−534 (4)	2667 (4)	4300 (3)	C(14)	1834 (7)	1849 (6)	1555 (5)
O(2)	−452 (4)	3348 (5)	985 (4)	C(15)	1963 (10)	1586 (8)	733 (7)
O(3)	−1987 (4)	5940 (4)	1891 (3)	C(16)	2961 (11)	1887 (9)	167 (6)
O(4)	2550 (5)	8438 (4)	29 (3)	C(17)	3902 (9)	2419 (8)	394 (6)
O(5)	3213 (7)	5215 (5)	−392 (3)	C(18)	3777 (6)	2691 (6)	1219 (5)
O(6)	4947 (4)	5550 (5)	2184 (4)	C(19)	1989 (5)	5596 (5)	3853 (4)
N	2829 (4)	1803 (4)	3518 (3)	C(20)	2993 (6)	6209 (6)	3868 (5)
C(1)	−221 (5)	3370 (5)	3555 (4)	C(21)	3484 (6)	5978 (7)	4744 (5)
C(2)	−107 (5)	3691 (6)	1503 (4)	C(22)	3002 (6)	5129 (7)	5604 (5)
C(3)	−1104 (5)	5437 (5)	2021 (4)	C(23)	2025 (6)	4510 (6)	5600 (4)
C(4)	2516 (6)	7428 (6)	526 (4)	C(24)	1514 (5)	4732 (5)	4729 (4)
C(5)	2986 (7)	5307 (5)	307 (4)	C(25)	545 (5)	7412 (5)	2427 (4)
C(6)	4048 (6)	5642 (5)	1888 (4)	C(26)	343 (6)	7857 (6)	3147 (5)
C(7)	2203 (5)	3878 (5)	2592 (4)	C(27)	−339 (6)	8887 (6)	2962 (5)
C(8)	2582 (4)	2704 (4)	2666 (4)	C(28)	−813 (6)	9515 (6)	2062 (5)
C(9)	2697 (6)	1921 (6)	4455 (4)	C(29)	−610 (6)	9103 (6)	1333 (5)
C(10)	3800 (7)	2397 (8)	4679 (6)	C(30)	41 (5)	8051 (6)	1520 (4)
				Anion			
P(2)	6881 (2)	1865 (2)	2997 (1)	F(4)	6386 (7)	569 (5)	3445 (6)
F(1)	6777 (5)	1845 (7)	4036 (4)	F(5)	5614 (4)	2435 (5)	2796 (4)
F(2)	6963 (5)	1856 (5)	1962 (4)	F(6)	8166 (5)	1313 (5)	3205 (4)
F(3)	7395 (5)	3156 (4)	2568 (5)				
				Solvent			
Cl(1)	6246 (3)	7960 (3)	2566 (2)	C(31)	5534 (9)	9320 (9)	1967 (9)
Cl(2)	4231 (3)	9084 (3)	1580 (3)				

(b) Hydrogen Atoms

	x	*y*	*z*	U_{iso}, Å^2		*x*	*y*	*z*	U_{iso}, Å^2
H(1)	108 (4)	564 (4)	103 (3)	37 (13)	H(16)	312 (7)	190 (8)	−44 (7)	138 (35)
H(7)	236 (4)	391 (4)	316 (3)	38 (14)	H(17)	458 (5)	254 (5)	15 (4)	71 (20)
H(9A)	253 (4)	126 (5)	487 (4)	46 (18)	H(18)	435 (4)	297 (4)	141 (3)	40 (16)
H(9B)	203 (4)	244 (4)	441 (3)	38 (14)	H(20)	326 (5)	685 (5)	332 (4)	55 (18)
H(10A)	443 (6)	191 (6)	467 (5)	85 (23)	H(21)	413 (5)	631 (5)	472 (4)	66 (19)
H(10B)	398 (6)	316 (6)	419 (5)	84 (24)	H(22)	347 (5)	508 (5)	612 (4)	76 (20)
H(10C)	371 (6)	254 (6)	519 (5)	101 (25)	H(23)	180 (4)	402 (4)	613 (4)	41 (15)
H(11A)	384 (4)	33 (4)	414 (4)	45 (15)	H(24)	84 (4)	439 (4)	474 (3)	39 (14)
H(11B)	371 (5)	79 (5)	303 (4)	72 (20)	H(26)	69 (4)	736 (4)	380 (4)	49 (15)
H(12A)	169 (6)	−32 (6)	440 (5)	79 (25)	H(27)	−43 (5)	914 (6)	348 (5)	80 (22)
H(12B)	173 (6)	−14 (6)	349 (5)	86 (23)	H(28)	−123 (4)	1023 (5)	192 (4)	58 (16)
H(12C)	255 (7)	−118 (8)	408 (6)	128 (30)	H(29)	−98 (5)	961 (5)	71 (4)	74 (20)
H(14)	100 (6)	157 (6)	205 (5)	101 (24)	H(30)	14 (4)	773 (5)	103 (4)	54 (16)
H(15)	118 (7)	145 (8)	52 (6)	146 (34)					

the electron-rich μ-alkylidenes $M_2(CO)_6${μ-CHC(Ph)-NEt_2}(μ-PPh_2) (**2a–c**) is described. To our knowledge compounds **3a–c** represent the first complete series of isostructural μ-H, μ-CHR compounds. An X-ray analysis of **3b** has revealed a novel structure related to that of $Fe_2(CO)_9$, but with three different (H, CH(R), PPh_2) bridging groups.

Experimental Section

General Procedures. Standard Schlenk line techniques were used and manipulations carried out under an atmosphere of nitrogen. Solvents were dried (CH_2Cl_2 over P_2O_5, hexane and heptane over $LiAlH_4$), deoxygenated, and distilled before use. Deuteriochloroform for NMR studies was stored over Linde molecular sieves. HBF_4·Et_2O was purchased from Aldrich Chemical Co. and used as received. IR spectra were recorded on a Perkin-Elmer 180 spectrometer as solutions in 0.5-mm matched sodium chloride cells. NMR spectra were measured on a Bruker AM-250 instrument (^1H, 250 MHz; $^{31}P\{^1H\}$, 101.3 MHz; $^{13}C\{^1H\}$, 62.8 MHz), and shifts are referenced to Me_4Si (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P). Microanalyses were carried out by Guelph Chemical Laboratories.

Syntheses. Complexes **2a–c** were prepared as described elsewhere.[13]

[(μ-H)$Ru_2(CO)_6${μ-CHC(Ph)NEt_2}(μ-PPh_2)]BF_4·CH_2Cl_2 (3b). Complex **2b** (0.448 g, 0.61 mmol) was dissolved in CH_2Cl_2 (6 mL). The solution was cooled to −78 °C in a dry ice–acetone bath. An excess of HBF_4 etherate was added to the stirring solution. The mixture was allowed to warm to room temperature and solvent removed in vacuo. The solids were extracted with heptane until the extract was colorless, and the residue was dissolved in a minimum of CH_2Cl_2. Crystals were grown by slow diffusion of hexane into the solution at −20 °C for 3 days; yield 0.371 g (67%). Anal. Calcd for $C_{31}H_{29}BCl_2F_4NO_6PRu_2$: C, 41.26; H, 3.24; N, 1.55; P, 3.43. Found: C, 41.89; H, 3.32; N, 1.62; P, 3.56. IR (CH_2Cl_2): 2104 m, 2086 vs, 2040 m, sh, 2027 s cm^{-1}. NMR ($CDCl_3$): ^1H δ 7.96–6.82 (m, 15 H, Ph), 3.43 (q, CH_2, J_{HH} = 7.2 Hz), 3.15 (q, CH_2, J_{HH} = 7.2 Hz), 3.09 (d, CH, J_{PH} = 29.7 Hz), 1.05 (t, CH_3, J_{HH} = 7.2 Hz), 0.63 (t, CH_3, J_{HH} = 7.2 Hz), −12.85 (d, Ru-*H*-Ru, J_{PH} = 27.2 Hz); $^{13}C\{^1H\}$, δ 198.1 (d, C_β, J_{PC} = 5.7 Hz), 192.4 (d, CO, J_{PC} = 7.1 Hz), 190.4 (d, CO, J_{PC} = 7.8 Hz), 188.4 (d, CO, J_{PC} = 68.5 Hz), 136.9–125.6 (17 peaks, C–Ph), 55.9 (d, μ-C, J_{PC} = 20 Hz), 52.5 (s, $CH_3\mathit{C}H_2$), 50.0 (s, $CH_3\mathit{C}H_2$), 13.3 (s, $\mathit{C}H_3CH_2$), 11.5 (s, $\mathit{C}H_3CH_2$); $^{31}P\{^1H\}$, δ +93.8 (s).

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[13] (a) Smith, W. F.; Yule, J. E.; Taylor, N. J.; Paik, H. N.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 1593. (b) Cherkas, A. A.; MacLaughlin, S. A.; Carty, A. J.; Taylor, N. J., submitted for publication.

[(μ-H)$Os_2(CO)_6${μ-CHC(Ph)NEt_2}(μ-PPh_2)]BF_4·CH_2Cl_2 (3c). The procedure was similar to that for **3b** above except that 0.341 g (0.37 mmol) of **2c** was used. Yield of **3c** was 0.242 g, 59.3%. Anal. Calcd for $C_{31}H_{29}BCl_2F_4NO_6POs_2$: C, 34.45; H, 2.70; N, 1.30; P, 2.87. Found: C, 34.65; H, 2.74; N, 1.30, P, 2.84. IR (CH_2Cl_2): 2104 m, 2085 vs, 2029 m, sh, 2016 s cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.96–6.85 (m, Ph), 3.39 (q, CH_2, J_{HH} = 7.0 Hz), 3.09 (q, CH_2, J_{HH} = 7.2 Hz), 2.86 (dd, CH, J_{HH} = 2.3 Hz, J_{PH} = 28.5 Hz), 1.04 (t, CH_3, J_{HH} = 7.0 Hz), 0.62 (t, CH_3, J_{HH} = 7.2 Hz), −14.93 (dd, Os–*H*–Os, J_{HH} = 2.3 Hz, J_{PH} = 18.2 Hz); $^{13}C\{^1H\}$, δ 199.0 (d, C_β, J_{PC} = 9.8 Hz), 170.6 (d, CO, J_{PC} = 7.2 Hz), 169.8 (d, CO, J_{PC} = 69.5 Hz), 169.4 (d, CO, $J_{PC} < 5$ Hz), 137.1–121.4 (17 peaks C–Ph), 52.5 (s, $CH_3\mathit{C}H_2$), 48.1 (s, $CH_3\mathit{C}H_2$), 25.6 (d, μ-C, J_{PC} = 10.5 Hz), 12.9 (s, $\mathit{C}H_3CH_2$), 11.0 (s, $\mathit{C}H_3CH_2$); $^{31}P\{^1H\}$, δ −0.25 (s).

[(μ-H)$Fe_2(CO)_6${μ-CH(Ph)NEt_2}(μ-PPh_2)]BF_4 (3a). Treatment of **2a** (0.501 g, 0.798 mmol) in CH_2Cl_2 (6 mL) as for **2b** above gave a clear orange solution with spectroscopic features [IR (CH_2Cl_2): 2076 m, 2064 vs, 2015 m sh, 2010 s cm^{-1}. NMR: ^1H, δ −14.0 (d, Fe–*H*–Fe, J_{PH} = 29.8 Hz); $^{31}P\{^1H\}$, δ +116.6 (s)] similar to those of **3b**. Although **3a** was stable in solution, attempts to obtain crystals led to impure orange powders.

X-ray Crystal Structure Analysis of [(μ-H)$Ru_2(CO)_6${μ-CHC(CPh)NEt_2}(μ-PPh_2)]PF_6·CH_2Cl_2. Yellow crystals of the hydrido diruthenium complex with PF_6^- as the cation were obtained from CH_2Cl_2/*n*-heptane solutions at −10 °C. Preliminary X-ray measurements using the Syntex $P2_1$ autoindexing and cell refinement procedures indicated no systematic absences and a triclinic cell. The space group $P\bar{1}$ was subsequently confirmed by the solution and refinement of the structure. Accurate cell constants were obtained by refinement of the setting angles of 15 reflections well dispersed in reciprocal space and input to the Data General Nova Computer. Crystal data and further details of the collection, reduction, and refinement of X-ray data are given in Table I. Intensity data were collected at 295 ± 1 K on a crystal of dimensions 0.20 × 0.20 × 0.28 mm^3 using graphite-monochromated Mo K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption (μ = 11.01 cm^{-1}).

The structure solution and refinement were based on 3912 observed intensities. The ruthenium and phosphorus atoms were located in a sharpened Patterson function and the remaining atoms including the dichloromethane of solvation in subsequent Fourier syntheses. Refinement of positions and isotropic thermal parameters for all non-hydrogen atoms gave an *R* value of 0.091. Conversion to anisotropic coefficients followed by several cycles of least-squares refinement to convergence, and calculation of a difference Fourier map revealed reasonable positions for all hydrogen atoms including the bridging hydride H(1). In final cycles of refinement positional parameters and individual isotropic coefficients for all hydrogen atoms were allowed to vary. With an appropriate weighting scheme, $w^{-1} = A - B|F_o| + C|F_o|^2$, introduced, the final *R* ($R = \sum|F_o| - |F_c|/\sum|F_o|$) and R_w ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$ values were 0.033 and 0.035, respectively. The function minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. A final difference map was featureless with maximum residual electron density at the level of 0.65 e Å^{-3}.

Scattering factors used, including corrections for the real and imaginary components of anomalous dispersion for the heavy atoms, were taken from ref 14a. Hydrogen atom scattering factors were those of Stewart et al.[14b] All calculations were carried out on linked IBM 4341 systems in the University of Waterloo, Department of Computer Services, using programs described elsewhere.[15] Tables II and III contain listings of atomic coordinates and important bond lengths and angles, respectively. Thermal parameters (Table S1), remaining bond lengths and angles (Table S2), and structure factors (Table S3) have been deposited as supplementary material.

Results and Discussion

Treatment of the σ-η-acetylides $M_2(CO)_6(\mu$-η-$C_2Ph)(\mu$-$PPh_2)$ **1**[13] in heptane/toluene with an excess of Et_2NH gives red (M = Fe) **2a**, yellow (M = Ru) **2b**, and pale yellow (M = Os) **2c** crystals of the mesoionic μ-alkylidene complexes which are formed by N–H addition across the triple bond of the acetylide. The ruthenium and osmium complexes[16] are isostructural with **2a**;[15] extremely high-field shifts for the ^{13}C NMR resonances of **2a** (δ 68.0 (J_{P-C} = 40.3 Hz), **2b** (δ 35.0 (J_{P-H} = 23.3 Hz)), **2c** (δ 29.1 (J_{P-H} = 13.6 Hz)) indicate that the bridging alkylidene carbon atom is electron rich. Indeed these ^{13}C shifts are well upfield of the normal range of values for μ-CHR ligands given by Herrmann,[1a] indicating that the zwitterionic nature of the hydrocarbyl places negative charge on the alkylidene carbon atom.[12a,b]

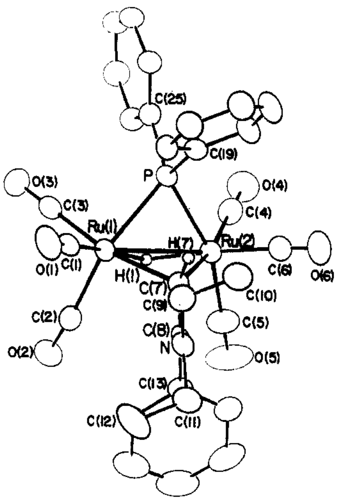
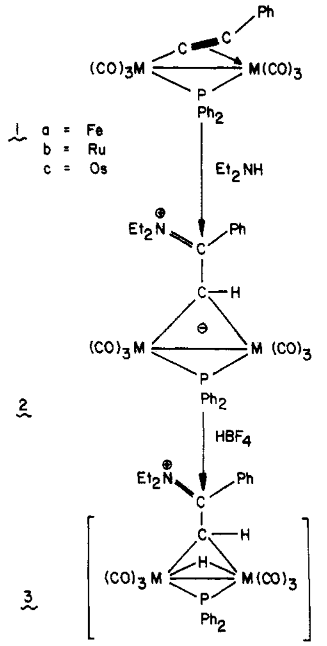


Figure 1. A perspective view of the molecular structure of the cation [(μ-H)$Ru_2(CO)_6${μ-CHC(Ph)NEt_2}(μ-PPh_2)]$^+$ showing the atomic numbering.



Reaction of **2a–c** with an excess of ethereal HBF_4 at −78 °C gave yellow or orange-yellow solutions from which **3b,c** were obtained as yellow microcrystalline solids. Cations identical with those in **3b,c** were obtained from reactions of **2b,c** with $Ph_3C^+PF_6^-$ in CH_2Cl_2/MeOH. Solutions of **3a–c** had only four terminal ν(CO) bands at higher frequency than those in **2a–c** and exhibited metal–hydride

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(14) (a) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(15) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

(16) The new complexes **2b** and **2c** have been characterized by elemental analysis, IR and NMR spectroscopy, and full single-crystal X-ray analyses.[13b]

Table III. Bond Lengths (Å) and Angles (deg) for $[(\mu\text{-H})Ru_2(CO)_6\{\mu\text{-CHC(Ph)NEt}_2\}(\mu\text{-PPh}_2)]\ PF_6 \bullet CH_2Cl_2$

	Bond Distances		
Ru(1)–Ru(2)	2.7870 (6)	Ru(1)–P(1)	2.364 (2)
Ru(1)–C(1)	1.918 (6)	Ru(1)–C(2)	1.970 (7)
Ru(1)–C(3)	1.931 (6)	Ru(1)–C(7)	2.197 (5)
Ru(1)–H(1)	1.94 (4)	Ru(2)–P(1)	2.369 (2)
Ru(2)–C(4)	1.942 (7)	Ru(2)–C(5)	1.966 (6)
Ru(2)–C(6)	1.919 (6)	Ru(2)–C(7)	2.182 (5)
Ru(2)–H(1)	1.77 (4)	P(1)–C(19)	1.828 (5)
P(1)–C(25)	1.817 (7)	C(1)–O(1)	1.125 (7)
C(2)–O(2)	1.119 (9)	C(3)–O(3)	1.134 (8)
C(4)–O(4)	1.128 (9)	C(5)–O(5)	1.114 (8)
C(6)–O(6)	1.118 (8)	C(7)–C(8)	1.428 (8)
C(8)–N	1.319 (6)	C(8)–C(13)	1.498 (8)
N–C(9)	1.470 (8)	N–C(11)	1.492 (9)
C(9)–C(10)	1.506 (11)	C(11)–C(12)	1.507 (13)
	Bond Angles		
Ru(2)–Ru(1)–P	54.00 (3)	Ru(2)–Ru(1)–C(1)	138.2 (2)
Ru(2)–Ru(1)–C(2)	106.8 (2)	Ru(2)–Ru(1)–C(3)	120.4 (2)
Ru(2)–Ru(1)–C(7)	50.2 (1)	Ru(2)–Ru(1)–H(1)	39 (1)
P–Ru(1)–C(1)	103.1 (2)	P–Ru(1)–C(2)	158.8 (2)
P–Ru(1)–C(3)	94.2 (2)	P–Ru(1)–C(7)	73.8 (1)
P–Ru(1)–H(1)	77 (1)	C(1)–Ru(1)–C(2)	97.7 (3)
C(1)–Ru(1)–C(3)	92.9 (3)	C(1)–Ru(1)–C(7)	92.5 (2)
C(1)–Ru(1)–H(1)	176 (1)	C(2)–Ru(1)–C(3)	88.7 (3)
C(2)–Ru(1)–C(7)	101.6 (2)	C(2)–Ru(1)–H(1)	82 (1)
C(3)–Ru(1)–C(7)	167.7 (2)	C(3)–Ru(1)–H(1)	91 (1)
C(7)–Ru(1)–H(1)	83 (1)	Ru(1)–Ru(2)–P	53.85 (3)
Ru(1)–Ru(2)–C(4)	120.6 (2)	Ru(1)–Ru(2)–C(5)	109.1 (2)
Ru(1)–Ru(2)–C(6)	133.8 (2)	Ru(1)–Ru(2)–C(7)	50.7 (1)
Ru(1)–Ru(2)–H(1)	43 (1)	P–Ru(2)–C(4)	94.7 (2)
P–Ru(2)–C(5)	161.8 (2)	P–Ru(2)–C(6)	100.4 (2)
P–Ru(2)–C(7)	74.0 (1)	P–Ru(2)–H(1)	80 (1)
C(4)–Ru(2)–C(5)	89.3 (3)	C(4)–Ru(2)–C(6)	96.5 (3)
C(4)–Ru(2)–C(7)	168.4 (2)	C(4)–Ru(2)–H(1)	88 (1)
C(5)–Ru(2)–C(6)	96.8 (3)	C(5)–Ru(2)–C(7)	100.8 (2)
C(5)–Ru(2)–H(1)	82 (1)	C(6)–Ru(2)–C(7)	88.0 (2)
C(6)–Ru(2)–H(1)	176 (1)	C(7)–Ru(2)–H(1)	88 (1)
Ru(1)–P–Ru(2)	72.15 (3)	Ru(1)–P–C(19)	123.5 (2)
Ru(1)–P–C(25)	116.9 (2)	Ru(2)–P–C(19)	117.9 (2)
Ru(2)–P–C(25)	120.8 (2)	C(19)–P–C(25)	104.3 (2)
Ru(1)–C(1)–O(1)	177.8 (2)	Ru(1)–C(2)–O(2)	171.0 (3)
Ru(1)–C(3)–O(3)	177.8 (2)	Ru(2)–C(4)–O(4)	177.5 (3)
Ru(2)–C(5)–O(5)	171.8 (3)	Ru(2)–C(6)–O(6)	176.9 (3)
Ru(1)–C(7)–Ru(2)	79.1 (1)	Ru(1)–C(7)–C(8)	122.2 (2)
Ru(2)–C(7)–C(8)	131.2 (2)	C(7)–C(8)–N	121.8 (3)
C(7)–C(8)–C(13)	122.2 (3)	N–C(8)–C(13)	116.0 (3)
C(8)–N–C(9)	122.8 (3)	C(8)–N–C(11)	123.3 (4)
C(9)–N–C(11)	113.9 (4)	N–C(9)–C(10)	112.3 (4)
N–C(11)–C(12)	112.8 (4)	Ru(1)–H(1)–Ru(2)	98 (1)

resonances at low field (δ −14.0, **3a**; δ −12.85, **3b**; δ −14.93, **3c**). Singlet ^{31}P shifts upfield of the values in **2a–c**[13b,15] and typical of μ-PPh_2 groups bridging a strong metal–metal bond[17] were observed. The structure of **3b** with PF_6^- as the counterion determined by X-ray diffraction is illustrated in Figure 1. Bond lengths and angles are given in Table III. The cation is remarkable in possessing three different bridging atoms: a hydride, a phosphide, and an alkylidene. We know of no other example of such a structure for a binuclear ruthenium carbonyl. Although the cation is formally isoelectronic with $Ru_2(CO)_9$, the latter, which has never been structurally characterized,[18] does not have the triply bridged $Fe_2(CO)_9$ structure. A significant lengthening of the Ru(1)–Ru(2) bond length in **3b** (2.7860 (6) Å) from that in the parent alkylidene **2b** (Ru(1)–Ru(2) = 2.7236 (6) Å)[13b] can be attributed to the presence of the bridging hydride. The alkylidene carbon atom C(7) is bonded almost symmetrically to the two ruthenium atoms (Ru(1)–C(7) = 2.197 (5) and Ru(2)–C(7) = 2.182 (5) Å), and the phosphido bridge–ruthenium distances are essentially identical. The Ru(1)–H(1) (1.94 (4) Å) and Ru(2)–H(1) (1.77 (4) Å) distances may indicate some asymmetry in the hydride bridge. As expected from the short Ru–Ru distance the angles subtended at the alkylidene carbon (Ru(1)–C(7)–Ru(2) = 79.1 (1)°) and the phosphorus atom (Ru(1)–P(1)–Ru(2) = 72.15 (3)°) are acute.

Although polynuclear ruthenium hydride complexes are well-known,[19] relatively few dinuclear μ-hydrido species have been characterized[20] and we are unaware of any μ-hydrido, μ-alkylidene diruthenium complexes. The closest comparison is with the μ-hydrido, μ-η^2-vinyl complex $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO_2(\mu\text{-H})(\mu\text{-CH}{=}\text{CHMe})]$ described by Knox and co-workers[20e] which has a somewhat longer Ru–Ru bond length (Ru(1)–Ru(2) = 2.857 (2) Å) and a significantly larger Ru(1)–H–Ru(2) (113.7°) angle.

In contrast to the μ-methylene complex $[Ru_2(CO)_2(\mu\text{-CO})(\mu\text{-CH}_2)(\eta\text{-}C_5H_5)_2]$ which yields the μ-methyl cation $[Ru_2(CO)_2(\mu\text{-CO})(\mu\text{-CH}_3)(\eta\text{-}C_5H_5)_2]^+$ on protonation,[6] **3a–c** show no evidence for conversion to μ-alkyls. Furthermore, attempts to remove H^- ion from the electron-rich alkylidene carbon atoms of **2a–c** (cf. ref 8) afforded only **3a–c**, presumably via solvent participation or trityl cation breakdown.[5] The particular stability of **3a–c** may reflect the extreme electron richness of the M–CHR–M system in **2a–c**, in agreement with an earlier suggestion[4] based on theoretical studies.[12] It is also worth noting that treatment of the triple methylene bridged complex $Ru_2(\mu\text{-CH}_2)_3(PMe_3)_6$ with HBF_4 affords the alkyl complex $[Ru_2(\mu\text{-CH}_2)_2(\mu\text{-CH}_3)(PMe_3)_6]BF_4$ whereas with molecular hydrogen the bis(μ-hydrido) compound $H_2Ru_2(\mu\text{-H})_2(PMe_3)_6$ is formed.[20b]

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Registry No. **2a**, 59584-64-4; **2b**, 108418-01-5; **2c**, 108418-02-6; **2a**·BF_4, 108418-04-8; **3b**·BF_4, 108418-06-0; **3b**·PF_6·ÅCH_2Cl_2, 108418-11-7; **3c**·BF_4, 108418-08-2; **3c**·PF_6, 108418-09-3.

Supplementary Material Available: Anisotropic thermal parameters (Table S1) and remaining bond lengths and angles for **3b** (Table S2) (3 pages); structure factors (Table S3) for **3b** (21 pages). Ordering information is given on any current masthead page.

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(17) (a) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (b) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1986, Chapter 16, pp 559–619.

(18) Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

(19) (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145. (b) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, **1982**; Vol. 4, Chapters 32.5 and 32.6, pp 843, 889.

(20) (a) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, Chapters 32.4, p 821. (b) Jones, R. A.; Wilkinson, G.; Colquohoun, I. J.; McFarlane, W.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2480. (c) Chaudret, B.; Devillers, J.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1983**, 641. (d) Ashworth, T. V.; Liles, D. C.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1984**, 1317. (e) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2099. (f) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727.