Table III. Fractional Atomic Coordinates (×10^4) for (t-Bu_2InOEt)$_2$

	x	y	z
In	1255 (1)	1459 (1)	1851 (1)
C(1)	1492 (13)	1741 (12)	4311 (10)
C(11)	2251 (18)	287 (14)	4635 (15)
C(12)	2799 (20)	3062 (17)	5791 (13)
C(13)	−252 (17)	2174 (20)	4295 (18)
C(2)	2677 (15)	2711 (14)	1536 (13)
C(21)	2128 (21)	2308 (21)	−380 (14)
C(22)	4613 (15)	2367 (21)	2541 (22)
C(23)	2332 (23)	4467 (17)	2413 (24)
O(3)	−1335 (7)	950 (6)	−262 (7)
C(31)	−2883 (16)	1833 (17)	−538 (20)
C(32)	−2762 (18)	3393 (16)	290 (20)

correction was also applied (relative maximum and minimum transmission factors were 1.0 and 0.84, respectively). The structure was solved via the heavy-atom method and refined by full-matrix least squares. At the end of isotropic refinement, a further absorption correction was applied by using the DIFABS procedure.[14] All atoms were refined anisotropically, and no hydrogens were included. The final R and R_w values were 0.049 and 0.047, respectively, with 109 parameters and weights $w = 1/[\sigma^2(F) + 0.0005F_o^2]$. The maximum and minimum values on the final difference electron density map were 0.61 and −0.42 e Å^{-3}, respectively. The non-hydrogen coordinates are listed in Table III.

Acknowledgment. We thank the Director of Research at British Telecom Research Laboratories, Martlesham Heath, Ipswich, for financial support and permission to publish this work (D.M.F.), the SERC for financial support, P. Cook for the mass spectra, and G. Coumbarides for the variable-temperature NMR spectra, and Dr. K. D. Sales for the ESR spectra.

Registry No. t-Bu_3In, 113088-72-5; $InCl_3$, 10025-82-8; t-BuMgCl, 677-22-5; (t-Bu_2InCl)$_2$, 113088-74-7; t-BuLi, 594-19-4; (t-Bu_2InOEt)$_2$, 113088-75-8; $t\text{-}Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$, 113088-73-6; $\overline{NHCMe_2(CH_2)_3C}Me$, 768-66-1.

Supplementary Material Available: Tables of atomic coordinates, anisotropic temperature factors, and bond distances and angles (4 pages); a listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

---

[14] Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

A Triad of Electron-Rich μ_2-Alkylidene Complexes $M_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (M = Fe, Ru, Os) via the Addition of Diethylamine to the Acetylides $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$: Spectroscopic Properties and Structural Chemistry

Andrew A. Cherkas, Graham N. Mott, Ruthanne Granby, Shane A. Maclaughlin, John E. Yule,
Nicholas J. Taylor, and Arthur J. Carty*

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry,
University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received September 10, 1987

The synthesis, X-ray structures, and IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopic characterization of a triad of zwitterionic μ-alkylidene compounds, $M_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (**2a**, M = Fe; **2b**, M = Ru; **2c**, M = Os), are described. Complex **2** is formed by addition of diethylamine to the β-carbon atom of the μ_2-η^2-acetylide of **1**, $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (**1a**, M = Fe; **1b**, M = Ru; **1c**, M = Os), with hydrogen transfer across the acetylide triple bond. The ^1H and ^{13}C NMR chemical shifts for **2a–c** indicate a very electron-rich M–C–M core. Crystals of **2a–c** are monoclinic, space group $P2_1/n$, with unit cell dimensions: **2a**, a = 14.694 (7) Å, b = 13.653 (7) Å, c = 17.787 (7) Å, β = 99.03 (7)°; **2b**, a = 10.066 (1) Å, b = 20.297 (3) Å, c = 17.512 (2) Å, β = 105.90 (1)°; **2c**, a = 14.767 (2) Å; b = 14.174 (2) Å, c = 17.922 (3) Å, β = 99.92 (1)°. The structures were solved and refined to the following R and R_w values: **2a**, R = 0.035, R_w = 0.041, on 3760 observed ($I \geqslant 3\sigma(I)$) data; **2b**, R = 0.030, R_w = 0.037, on 3494 data; **2c**, R = 0.043, R_w = 0.050, on 3064 data. The three molecules are isostructural with a metal–metal bond bridged by a phosphido group and an electron-rich μ-alkylidene group. Structural changes down the triad are discussed in the context of metal–alkylidene bonding.

Introduction

Since the discovery of the first transition-metal μ-methylene complex by Herrmann and co-workers in 1975,[1] μ-alkylidene (or carbene) compounds in general have been the targets of considerable synthetic endeavour.[2] Much of the interest can be attributed to two factors: (i) the recognition that the alkylidene ligand is a key intermediate

---

[1] Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.

[2] For reviews see: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65. (c) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (d) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

0276-7333/88/2307-1115$01.50/0

in catalytic chemistry including the Fischer–Tropsch process,[3] olefin metathesis,[4] and alkyne oligomerization[5] and (ii) the analogy, based on isolobality,[6] between metal alkylidenes $L_nM{=}CRR'$ and olefins that has led to the development of rational strategies for the synthesis of polynuclear μ-alkylidenes.[7]

Theoretical studies[8] have suggested that μ-CH_2 groups bridging a strong metal–metal interaction where the M–CH_2–M angle is acute have relatively electron-rich carbon atoms. Carbon-13-NMR shifts for μ-CR_2 groups confirm this interpretation, these shifts being well upfield of terminal carbene resonances. The chemistry of such μ-CR_2 groups should therefore be dominated by reactions with electrophiles.

In earlier papers the synthesis of a series of μ-alkylidene complexes via the addition of primary or secondary amines across the triple bond of the acetylide $Fe_2(CO)_6(\mu_2$-η^2-$C{\equiv}CPh)(\mu$-$PPh_2)$ (**1a**, M = Fe) was described.[9,10a] We have now extended these studies to encompass the entire triad of μ-alkylidene complexes of formula $M_2(CO)_6[\mu$-$CHC(Ph)NEt_2](\mu$-$PPh_2)$ (**2a–c**, M = Fe, Ru, Os) which are hyperelectron rich by virtue of their mesoionic character. Single-crystal X-ray structure analyses on all three compounds of **2** (M = Fe, Ru, Os) have been carried out. The nucleophilic nature of the alkylidene carbon atom is dramatically illustrated by the ^{13}C NMR shift. In a separate paper[11] we have described the formation of stable μ-hydrido, μ-alkylidene complexes via the protonation of **2**.

Experimental Section

All manipulations were carried out under a blanket of nitrogen by using standard Schlenk tube procedures. Heptane and toluene were dried by refluxing over $LiAlH_4$ and collected just prior to usage. Diethylamine was purchased from J. T. Baker and was used without further purification. NMR solvents were from Merck, Sharp and Dohme Ltd. Infrared spectra were recorded on a Perkin-Elmer 180 spectrometer using 0.5-mm matched sodium chloride cells. FT NMR spectra were measured on a Bruker AM-250 spectrometer at the following frequencies: ^1H, 250 MHz; ^{13}C, 62.8 MHz; ^{31}P, 101.3 MHz; or for ^{13}C, a Bruker AC 200 at 50.3 MHz. Proton and carbon spectra used 5-mm tubes with TMS as a reference. ^{31}P spectra were obtained in 10-mm tubes and are relative to external 85% H_3PO_4. Microanalyses were carried out by Guelph Chemical Laboratories.

Synthesis. The syntheses of **1a–c** are described fully in ref 10b.

$Fe_2(CO)_6[\mu$-$CHC(Ph)NEt_2)](\mu$-$PPh_2)$ (**2a**) was prepared as previously described from **1** and the secondary amine.[10] Analytical and IR data for **2a** have been given previously. ^1H NMR ($CDCl_3$): δ 7.88–7.18 (Ph*H*, m, 15 H), 2.94 (CH_2, q, $^3J_{H-H}$ = 6.9 Hz, 2 H), 2.85 (CH_2', q, $^3J_{H-H}$ = 7.0 Hz, 2 H), 1.62 (C*H*, d, $^3J_{P-H}$ = 35.7 Hz, 1 H), 1.00 (CH_3, t, $^3J_{H-H}$ = 6.9 Hz, 3 H), 0.38 (CH_3', t, $^3J_{P-H}$ = 6.9 Hz, 3 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ +153.9 (s) $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.3 MHz): δ 215.3 (CO, s), 198.7 (C_β, d, $^3J_{P-C}$ = 7.8 Hz), 140.4 (C_i, d, $^1J_{P-C}$ = 30.3 Hz), 136.5 (C_i'', s), 136.3 (C_o, d, $^2J_{P-C}$ = 7.7 Hz), 135.4 (C_i', d, $^1J_{P-C}$ = 28.8 Hz), 133.3 (C_o', d, $^2J_{P-C}$ = 9.7 Hz), 129.7 (C_p, s), 129.6 (C_p', s), 128.7 (C_o'', Cp″, s), 128.2 (C_m, d, $^3J_{P-C}$ = 9.4 Hz), 127.8 (C_m'', s), 127.5 (C_m', d, $^3J_{P-C}$ = 10.6 Hz), 68.1 (C_α, d, $^2J_{P-C}$ = 40.9 Hz), 48.9 (*C*H_2Me, s), 45.4 (*C*′H_2Me, s), 13.8 (*C*H_3, s), 11.2 (*C*′H_3, s).

$Ru_2(CO)_6[\mu$-CHC(Ph)$NEt_2](\mu$-$PPh_2)$ (2b). To a slurry of **1b** (M = Ru) (0.5 g, 0.77 mmol) in heptane (30 mL) was added excess diethylamine (0.5 mL, 4.8 mmol), and the solution was stirred for 5 days. At the end of this time a bright yellow precipitate of product had formed leaving a brown supernatant which was syringed off. Concentration of the supernatant to a few milliliters provided further precipitate. The combined solids were washed with pentane and recrystallized from heptane/toluene to give 0.33 g of **2b** (60%). Attempts to recover more **2b** by chromatography of the supernatant resulted in a mixture of the starting material **1b** and the two carbon-bridged complexes $Ru_2(CO)_6[\mu$-C{NHEt}CH(Ph)]$(\mu$-$PPh_2)$ and $Ru_2(CO)_6[\mu$-C{NH-i-Pr}CH(Ph)]$(\mu$-$PPh_2)$. These products that are not due to ethylamine and isopropylamine impurities but rather result from intramolecular rearrangement and elimination processes which will be the subject of a forthcoming paper. Anal. Calcd for $C_{30}H_{26}NO_6PRu_2$: C, 49.38; H, 3.59; N, 1.92; P, 4.24. Found: C, 49.58; H, 3.98, N, 1.79; P, 4.34. IR (C_6H_{12}): ν(CO) 2052 m, 2021 vs, 1981 s, 1960 vs, 1951 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.88–7.03 (Ph*H*, m, 15 H), 2.73 (CH_2, q, $^3J_{H-H}$ = 7.1 Hz, 2 H), 2.66 (CH_2', q, $^3J_{H-H}$ = 7.1 Hz, 2 H), 1.37 (C*H*, d, $^3J_{P-H}$ = 31.5 Hz, 1 H), 0.83 (CH_3, t, $^3J_{H-H}$ = 7.1 Hz, 3 H), 0.22 (CH_3', t, $^3J_{H-H}$ = 7.1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ +136.7, s. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.8 MHz): δ 201.1 (CO, d, $^2J_{P-C}$ = 14.9 Hz), 196.0 (C_β, d, $^3J_{P-C}$ = 5.7 Hz), 140.0 (C_i, d, $^1J_{P-C}$ = 26.7 Hz), 137.5 (C_i'', s), 136.8 (C_o, d, $^2J_{P-C}$ = 9.5 Hz), 134.6 (C_i', d, $^1J_{P-C}$ = 25.8 Hz), 132.9 (C_o', d, $^2J_{P-C}$ = 12.3 Hz), 129.6 (C_p, s), 129.4 (Cp′, s), 129.1 (C_o'', s), 128.3 (C_m, d, $^3J_{P-C}$ = 9.7 Hz), 128.2 (C_p'', s), 127.7 (C_m'', s), 127.6 (C'_m, d, $^3J_{P-C}$ = 10.4 Hz), 55.0 (C_α, d, $^2J_{P-C}$ = 23.3 Hz), 48.5 (*C*H_2Me, s), 45.3 (*C*′H_2Me, s), 13.4 (*C*H_3, s), 10.5 (*C*′H_3, s).

$Os_2(CO)_6[\mu$-CHC(Ph)$NEt_2](\mu$-$PPh_2)$ (2c). The reaction was similar to that for **2b** above. From 0.51 g of **1c** (M = Os) in heptane (30 mL) and toluene (2 mL) with excess diethylamine (0.5 mL) was obtained **2c** (0.26 g, 47%). Anal. Calcd for $C_{30}H_{26}NO_6Os_2P$: C, 39.69; H, 2.89; N, 1.54; P, 3.41. Found: C, 39.85; H, 3.04; N, 1.65; P, 3.29. IR (C_6H_{12}): 2053 m, 2022 vs, 1974 s, 1951 s, 1941 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.88–7.02 (Ph*H*, m, 15 H), 2.68 (CH_2, q, $^3J_{H-H}$ = 7.2 Hz, 2 H), 2.61 (CH_2', q, $^3J_{H-H}$ = 7.1 Hz, 2 H), 1.44 (C*H*, d, $^3J_{P-H}$ = 29.6 Hz, 1 H), 0.84 (CH_3, t, $^3J_{H-H}$ = 7.1 Hz, 3 H), 0.22 (CH_3', t, $^3J_{H-H}$ = 7.1 Hz, 3 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ +57.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.3 MHz): δ 196.9 (C_β, d, $^3J_{P-C}$ = 10.4 Hz), 182.7 (CO, br, s), 138.7 (C_i, d, $^1J_{P-C}$ = 40.6 Hz), 137.6 (C_o, d, $^2J_{P-C}$ = 10.8 Hz), 137.1 (C_i'', s), 133.2 (C_o',

---

(3) See, for example: (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Rofer De Poorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. **1981**, *103*, 1287; (e) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (f) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roué, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862. (g) Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roué, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 537. (h) Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293. (i) Jones, R. A.; Wilkinson, G.; Galas, A. R. M.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1771. (j) Theopold, K. H.; Bergmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 2489. (k) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. E. *J. Chem. Soc., Chem. Commun.* **1981**, 809. (l) Nutton, A.; Vazquez de Miguel, A.; Isobe, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1983**, 166. (m) Laws, W. J.; Puddephatt, R. J. *J. Chem. Soc. Chem. Commun.* **1984**, 116. (n) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134. (o) Herrmann, W. A.; Bauer, C. *Chem. Ber.* **1982**, *115*, 14.

(4) (a) Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975**, *4*, 155. (b) Cardin, D. J.; Doyle, M. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 927. (c) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16* 283. (d) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (e) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (f) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (g) Schrock, R. R.; Rocklage, S.; Wengrovius, J.; Rupprecht, J. G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73.

(5) (a) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803. (c) Levisalles, J.; Rose-Munch, F.; Rudler, H.; Daran, J. C.; Dromzee, Y.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 152. (d) Levisalles, J.; Rose-Munch, F.; Rudler, H.; Daran, J. C.; Dromzée, Y.; Jeannin, Y.; Ades, D.; Fontanille, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1055. (e) Adams, P. Q.; Davies, D. L.; Dyke, S. F.; Knox, S. A. R.; Mead, K.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1983**, 222. (f) Han, C. C.; Katz, T. J. *Organometallics* **1985**, *4*, 2186.

(6) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *94*, 725.

(7) (a) Stone, F. G. A. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 89. (b) Stone, F. G. A. *ACS Symp. Ser.* **1983**, *No. 211*, 383.

(8) (a) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554. (b) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. (c) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

(9) (a) Carty, A. J.; Taylor, N. J.; Paik, H. N.; Smith, W.; Yule, J. G. *J. Chem. Soc., Chem. Commun.* **1976**, *41*. (b) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, 100, 3051.

(10) (a) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726. (b) Cherkas, A. A.; Randall, L. H.; MacLaughlin, S. A.; Mott, G. N.; Taylor, N. J.; Carty, A. J. *Organometallics*, in press.

(11) Cherkas, A. A.; Hoffman, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1987**, *6*, 1466.

Table I. Summary of Crystal Data, Intensity Collection Reduction, and Refinement for $M_2(CO)_6(\mu_2\text{-}PPh_2)[\mu_2\text{-}CHC(Ph)NEt_2]$ (2a, M = Fe; 2b, M = Ru; 2c, M = Os)

compound	**2a**	**2b**	**2c**
formula	$C_{30}H_{26}NO_6PFe_2{\cdot}C_6H_6$	$C_{30}H_{26}NO_6PRu_2{\cdot}0.5C_7H_8$	$C_{30}H_{26}NO_6POs_2{\cdot}C_6H_6$
mol wt (amu)	717.33	775.73	986.03
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	14.694 (7)	10.066 (1)	14.767 (2)
b, Å	13.653 (7)	20.297 (3)	14.174 (2)
c, Å	17.787 (7)	17.512 (2)	17.922 (3)
β, deg	99.03 (7)	105.90 (1)	99.92 (1)
Z	4	4	4
V, Å^3	3524.1	3441.0	3695.1
d(calcd), g·cm^{-3}	1.352	1.497	1.772
μ(Mo Kα), cm^{-1}	9.36	9.48	73.94
radiatn	Zr-filtered Mo Kα	graphite-monochromated (λ = 0.71069 Å) Mo Kα	
diffractometer	GE XRD-6	Syntex P2_1	Syntex P2_1
cryst size, mm	0.24 × 0.26 × 0.30	0.23 × 0.26 × 0.26	0.12 × 0.12 × 0.13
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	50	45	45
scan speed, deg min^{-1}	2	variable 2.93–29.3	
scan width	$\pm(0.9 + 0.43 \tan \theta)$	0.8° below Kα_1 to 0.8° above Kα_2	
std reflctns	040; 006 (every 100)	$43\bar{2}$ (every 50)	415; $42\bar{6}$ (every 100)
change in stds, %	±2	−4	±2
data measd	6216	4813	4867
data obsd ($I \geqslant 3\sigma(I)$)	3760	3494	3064
transmissn factors	0.72–0.84	0.74–0.84	0.32–0.52
no. of variables	520	424	416
$R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$	0.035	0.030	0.043
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.041	0.037	0.050
final electron density in diff map, e Å^{-3}	0.25	0.48	1.12
weighting scheme			
$w^{-1} = A - B\lvert F_o\rvert + C\lvert F_o\rvert^2$			
A	1.20	1.96	2.87
B	0.0398	0.013	0.0245
C	0.00055	0.00023	0.00012

d, $^2J_{P-C}$ = 11.4 Hz), 129.9 (C_i', d, $^1J_{P-C}$ = 40.1 Hz), 129.8 (C_p, d, $^4J_{P-C}$ = 2.5 Hz), 129.6 (C_p', $^4J_{P-C}$ = 4.5 Hz), 129.0 (C_o'', s), 128.7 (C_m, d, $^3J_{P-C}$ = 10.3 Hz), 128.6 (C_p'', s), 128.0 (C_m'', s), 127.8 (C_m', d, $^3J_{P-C}$ = 11.0 Hz), 48.9 (CH_2Me, s), 45.7 ($C'H_2Me$, s), 28.8 (C_α, d, $^2J_{P-C}$ = 13.5 Hz), 12.8 (CH_3, s), 9.8 ($C'H_3$, s).

X-ray Crystal Structure Analyses of 2a–c. Experimental procedures for **2b** and **2c** were similar, and data relating to X-ray measurements are given in Table I. Crystals of **2a** (from benzene–hexane) were dark red, of **2b** (from heptane–toluene) were yellow, and of **2c** (from cyclohexane–benzene) were pale yellow. An appropriate crystal was chosen, affixed to a glass fiber with epoxy glue and mounted on a goniometer head via a brass pin. The diffractometer used for **2b** and **2c**, a Syntex P2_1, is controlled by a Data General Nova computer. Preliminary measurements on the diffractometer using the Syntex polaroid rotation photography, autoindexing, and cell refinement procedures were used to identify crystal type and possible space groups. In each case a systematic check of zonal reflections was employed to confirm space group assignments. Intensity data were collected at 296 ± 2 K as described in Table I. Standard reflections were checked for decay after every 100 measurements. Background counts were taken at each end of the scan for half of the total scan time. No significant variations in standards were noted for either of the crystals of **2b,c**. Intensity data were corrected for Lorentz and polarization effects before conversion to structure factors in the normal way. An empirical absorption correction was applied to **2c** (μ = 73.94 cm^{-1}) but not to **2b** (μ = 9.48 cm^{-1}).

Intensity data for **2a** were collected on a GE-XRD6 automatic diffractometer. The unit cell was refined from the 2θ values of 25 reflections. Full details of experimental parameters for data collection and reduction are given in ref 9b.

The structures of **2a–c** were solved by the heavy-atom method using sharpened Patterson syntheses which revealed positions for the two metal and the phosphorus atoms. The remainder of the molecular skeleton became evident from Fourier maps. Refinements in each case were carried out first with isotropic thermal parameters and subsequently anisotropic temperature coefficients for all non-hydrogen atoms. Following two cycles of full-matrix least-squares refinement for **2a** and **2b**, hydrogen positions could be readily located in a difference map. These were subsequently refined with positions and isotropic temperature factors varying. For **2c** hydrogen atoms were not included. Final difference maps were featureless.

All calculations using a package of programs already described[9b] were carried out on the IBM 4341 or 360-75 systems in the University of Waterloo Computing Centre. The full matrix was employed in all least-squares refinements, and scattering factors, including anomalous dispersion corrections for heavy atoms, were taken from ref 12 and 13.

Positional parameters for all three compounds are given in Tables II–IV, and a comparison of pertinent bond lengths and angles is presented in Table V. Thermal parameters (Tables S1–S3), remaining bond lengths and angles (Table S4), and structure factors (Tables S5–S7) have been deposited as supplementary material.

Results and Discussion

The synthesis of **2a–c** involves the 1,2-addition of a nucleophile across the carbon–carbon triple bond of **1a–c** to form a dipolar μ-alkylidene (Scheme I). To the best of our knowledge the series **2a–c** constitutes the first complete isostructural triad of μ-alkylidene complexes. Compound **2c** is a rare example of a diosmium μ-alkylidene complex.[2] Nucleophilic addition of PMe_2Ph and other phosphines to the μ-η-vinyl triosmium clusters $HOs_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}CH{=}CH_2)$ has afforded zwitterionic alkylidene complexes typified by $HOs_3(CO)_{10}[CHCH_2PMe_2Ph]$ in which the bridging hydrocarbyl unit is related to that in **2c**.[14] The dehydrogenation of triethylamine by Os_3-

---

(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(13) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(14) (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *112*, C39. (b) Churchill, M. R.; DeBoer, B. G.; Shapley, J. R.; Keister, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 2357. (c) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewycz, R. A. *J. Organomet. Chem.* **1978**, *162*, C34. (d) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848.

Scheme I

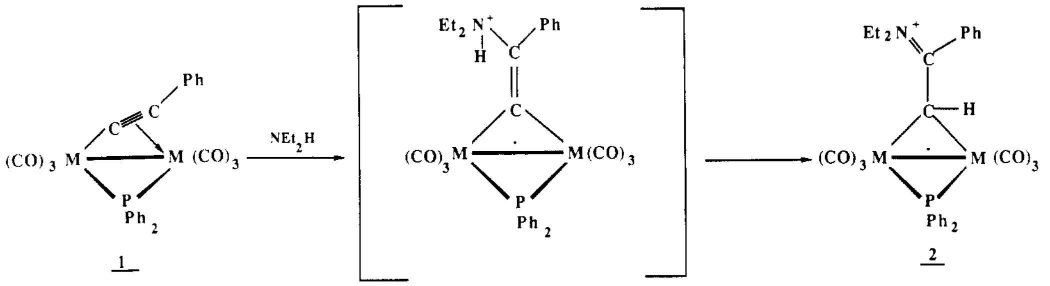


Table II. Atomic Coordinates (Fractional ×10⁴) for $Fe_2(CO)_6[\mu\text{-}CHC(Ph)\ NEt_2](\mu\text{-}PPh_2)\bullet C_6H_6$ (2a)

atom[a]	*x*	*y*	*z*
Fe(1)	3996.8 (3)	4356.3 (4)	2580.8 (3)
Fe(2)	5263.5 (3)	4902.7 (4)	1846.3 (3)
P	5377.1 (6)	4871.2 (7)	3107.7 (5)
O(1)	2608 (2)	5250 (3)	3356 (2)
O(2)	2998 (2)	3204 (2)	1312 (2)
O(3)	4163 (2)	2520 (2)	3442 (2)
O(4)	6869 (2)	3663 (3)	1835 (2)
O(5)	4604 (2)	3938 (3)	388 (2)
O(6)	6108 (3)	6684 (3)	1377 (2)
N	3553 (2)	7152 (2)	1408 (2)
C(1)	3162 (3)	4888 (3)	3060 (2)
C(2)	3370 (3)	3701 (3)	1775 (2)
C(3)	4126 (3)	3232 (3)	3101 (2)
C(4)	6234 (3)	4136 (3)	1865 (2)
C(5)	4792 (3)	4347 (3)	947 (2)
C(6)	5798 (3)	5977 (3)	1577 (2)
C(7)	4121 (2)	5685 (3)	2079 (2)
C(8)	3531 (2)	6180 (3)	1486 (2)
C(9)	4168 (3)	7786 (3)	1937 (2)
C(10)	3766 (4)	8048 (4)	2634 (3)
C(11)	2938 (3)	7708 (3)	812 (3)
C(12)	3435 (5)	8032 (5)	177 (3)
C(13)	2828 (2)	5647 (3)	934 (2)
C(14)	2010 (3)	5369 (3)	1169 (2)
C(15)	1347 (3)	4876 (3)	676 (3)
C(16)	1489 (3)	4662 (3)	−52 (3)
C(17)	2281 (3)	4948 (3)	−290 (2)
C(18)	2954 (3)	5444 (3)	193 (2)
C(19)	6194 (2)	4085 (3)	3697 (2)
C(20)	6713 (3)	4396 (4)	4384 (2)
C(21)	7334 (3)	3754 (4)	4810 (2)
C(22)	7450 (3)	2818 (4)	4553 (3)
C(23)	6945 (3)	2505 (4)	3876 (3)
C(24)	6316 (3)	3127 (3)	3458 (2)
C(25)	5466 (2)	6023 (3)	3645 (2)
C(26)	4932 (3)	6171 (3)	4209 (2)
C(27)	5022 (3)	7034 (4)	4633 (3)
C(28)	5648 (3)	7736 (3)	4506 (3)
C(29)	6187 (3)	7587 (3)	3953 (3)
C(30)	6103 (3)	6739 (3)	3521 (2)
C(31)S	5910 (7)	−91 (7)	2497 (5)
C(32)S	6190 (6)	−338 (7)	1814 (6)
C(33)S	5714 (7)	16 (8)	1152 (6)
C(34)S	5041 (8)	755 (9)	1189 (6)
C(35)S	4794 (6)	1029 (7)	1846 (6)
C(36)S	5213 (7)	600 (7)	2503 (5)

[a] S = solvent.

Table III. Atomic Positions (Fractional ×10⁴) for $Ru_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)\bullet 0.5C_7H_8$ (2b)

atom[a]	*x*	*y*	*z*
Ru(1)	624.8 (4)	2006.1 (2)	2497.8 (2)
Ru(2)	1290.6 (4)	2472.1 (2)	4013.8 (2)
P	2333.9 (12)	1572.8 (6)	3572.5 (8)
O(1)	1699 (6)	2018 (3)	1039 (3)
O(2)	−1030 (5)	732 (2)	2143 (3)
O(3)	−2176 (4)	2692 (2)	1868 (3)
O(4)	−1444 (4)	3215 (2)	3765 (3)
O(5)	3401 (5)	3324 (3)	5172 (3)
O(6)	464 (5)	1672 (2)	5278 (3)
N	3048 (4)	3870 (2)	2893 (3)
C(1)	1290 (6)	1991 (3)	1588 (3)
C(2)	−415 (5)	1207 (3)	2284 (3)
C(3)	−1097 (6)	2485 (3)	2102 (3)
C(4)	−399 (6)	2981 (3)	3835 (3)
C(5)	2628 (6)	2994 (3)	4755 (3)
C(6)	756 (6)	1968 (3)	4796 (3)
C(7)	1996 (5)	2825 (2)	2988 (3)
C(8)	1915 (5)	3507 (2)	2812 (3)
C(9)	4457 (6)	3588 (3)	3156 (4)
C(10)	4897 (8)	3300 (4)	2484 (6)
C(11)	3019 (6)	4583 (3)	2721 (4)
C(12)	3310 (8)	4993 (3)	3463 (5)
C(13)	579 (5)	3865 (2)	2492 (3)
C(14)	−55 (6)	3824 (3)	1690 (3)
C(15)	−1282 (7)	4190 (4)	1366 (4)
C(16)	−1812 (7)	4571 (4)	1858 (6)
C(17)	−1199 (7)	4609 (3)	2650 (5)
C(18)	11 (6)	4256 (3)	2971 (4)
C(19)	4161 (5)	1619 (2)	3583 (3)
C(20)	4591 (5)	1373 (3)	2957 (4)
C(21)	5998 (6)	1410 (3)	2973 (4)
C(22)	6925 (6)	1693 (3)	3598 (4)
C(23)	6501 (5)	1942 (3)	4227 (4)
C(24)	5129 (5)	1905 (2)	4223 (3)
C(25)	2201 (5)	738 (2)	3939 (3)
C(26)	910 (5)	511 (2)	3991 (3)
C(27)	765 (6)	−116 (3)	4257 (4)
C(28)	1888 (6)	−524 (3)	4491 (3)
C(29)	3174 (6)	−305 (3)	4454 (3)
C(30)	3320 (5)	318 (2)	4169 (3)
C(31)S	−1078 (18)	5207 (11)	4668 (7)
C(32)S	−1728 (21)	4604 (12)	4895 (9)
C(33)S	91 (32)	4325 (9)	5403 (9)
C(34)S*	−429 (30)	3793 (14)	5622 (11)

[a] S = solvent. The asterisk (*) = occupancy $^1/_2$.

$(CO)_{10}(CH_3CN)_2$ has also led to a dipolar μ-alkylidene cluster, $HOs_3(CO)_{10}$ (μ-CHCH=NEt$_2$).[14c]

The reaction of **1a** with diethylamine and dipropylamine affords **2a**, the product of addition of the NR_2 function to the β-carbon of the acetylide, quantitatively. For the iron system detailed variable-temperature NMR studies[10a] have shown that addition of intact R_2NH to the β-carbon atom of the acetylide afforded a dipolar μ_2-vinylidene complex, $Fe_2(CO)_6[\mu_2\text{-}C{=}C(Ph)\ NR_2H](\mu\text{-}PPh_2)$, at −35 °C which is converted at 25 °C via **1** into **2a** without any evidence for an intermediate enamine complex $Fe_2(CO)_6[\mu\text{-}\eta^2\text{-}CH{=}C(Ph)\ NEt_2](\mu\text{-}PPh_2)$. Isolated yields of **2a** are 90% or greater. Spectroscopically (^{31}P NMR) the conversion of **1a** to **2a** is quantitative. For **1b**, reaction with diethylamine afforded isolated yields of 60% **2b** and **1c** gave **2c** (47%). The solution product distributions by NMR were as follows: **2b** 50%, α-addition products, 25%, and unreacted **1b** 25%; **2c** 50%, α-addition products 30%, and unreacted **1c** 20%. Thus the ratio of β- to α-addition decreases down the triad with the major change occurring from iron to ruthenium. Complete structural characterization of another series of α-addition products $M_2(CO)_6[\mu\text{-}\eta^2\text{-}C(NHCy)CHPh](\mu\text{-}PPh_2)$ as well as an EHMO modeling study of the reactivity of **1** toward nucleophiles

Table IV. Atomic Positions (Fractional ×10^4) for $Os_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)\bullet C_6H_6$ (2c)

atom[a]	*x*	*y*	*z*
Os(1)	6012.9 (4)	768.9 (4)	2365.6 (3)
Os(2)	4673.1 (4)	173.6 (5)	3142.1 (3)
P	4579 (3)	125 (3)	1812 (2)
O(1)	7495 (10)	40 (11)	1544 (9)
O(2)	7073 (10)	1854 (10)	3713 (7)
O(3)	5755 (10)	2639 (9)	1507 (8)
O(4)	3011 (9)	1453 (11)	3132 (8)
O(5)	5418 (10)	1117 (11)	4658 (7)
O(6)	3720 (11)	−1571 (12)	3601 (8)
N	6483 (8)	−1997 (9)	3599 (7)
C(1)	6908 (11)	325 (12)	1828 (9)
C(2)	6719 (12)	1397 (12)	3230 (9)
C(3)	5841 (12)	1932 (15)	1852 (10)
C(4)	3602 (13)	998 (14)	3118 (10)
C(5)	5179 (12)	697 (16)	4107 (10)
C(6)	4083 (11)	−888 (15)	3433 (9)
C(7)	5899 (9)	−594 (10)	2892 (8)
C(8)	6492 (10)	−1056 (11)	3505 (8)
C(9)	5810 (12)	−2570 (12)	3071 (10)
C(10)	6211 (13)	−2872 (14)	2398 (12)
C(11)	7132 (11)	−2501 (12)	4193 (10)
C(12)	6644 (16)	−2828 (16)	4839 (12)
C(13)	7206 (11)	−530 (11)	4066 (9)
C(14)	7084 (12)	−332 (12)	4791 (9)
C(15)	7774 (14)	143 (14)	5285 (9)
C(16)	8588 (13)	419 (13)	5041 (12)
C(17)	8724 (12)	203 (15)	4320 (11)
C(18)	8025 (12)	−271 (14)	3808 (10)
C(19)	4539 (10)	−1028 (11)	1319 (8)
C(20)	3943 (10)	−1725 (11)	1489 (9)
C(21)	3897 (12)	−2566 (14)	1082 (10)
C(22)	4439 (12)	−2701 (12)	522 (10)
C(23)	5043 (12)	−1997 (13)	356 (10)
C(24)	5077 (11)	−1153 (14)	756 (9)
C(25)	3728 (10)	809 (11)	1196 (9)
C(26)	3597 (12)	1784 (13)	1420 (10)
C(27)	2936 (15)	2342 (15)	975 (12)
C(28)	2402 (15)	1980 (20)	325 (11)
C(29)	2562 (14)	1040 (18)	115 (11)
C(30)	3200 (11)	465 (14)	544 (8)
C(31)S	1091 (34)	−27 (32)	2435 (17)
C(32)S	1255 (33)	242 (35)	1763 (24)
C(33)S	861 (39)	−331 (43)	1190 (23)
C(34)S	45 (32)	−882 (37)	1158 (24)
C(35)S	26 (40)	−1232 (33)	1843 (28)
C(36)S	494 (50)	−701 (40)	2478 (27)

[a] S = solvent.

will be reported separately.[15] It is worth noting however in the present context that theoretical studies of reactivity patterns for terminal acetylides in *mononuclear* systems[16] suggest that nucleophilic additions to these alkynyl groups are frontier orbital controlled and that α-addition is unlikely. For the μ_3-η^2-acetylide in $(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)$ Granozzi et al.[17] have calculated that C_α of the acetylide carriers a positive atomic charge reflecting strong σ-donation to the σ-bound ruthenium atom. In this case the existence of a high-energy LUMO may dictate charge control of the reactivity. Thus for μ_2-η^2-acetylides that lie intermediate between the terminal and face bound μ_3-η^2-types a delicate balance between frontier orbital and charge control is likely.

X-ray Crystal Structures of 2a–c. The three molecules **2a–c** crystallize in the centrosymmetric space group $P2_1/n$. The unit cell parameters (Table I) are closely similar with the unit cell volume changing by only 254 Å^3

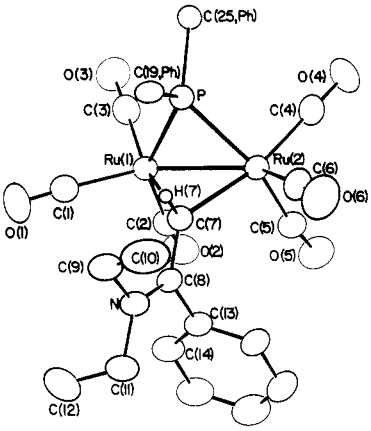
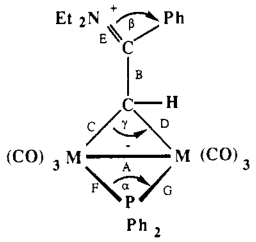


Figure 1. An ORTEP plot of the structure of $Ru_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (**2b**) showing the atomic numbering scheme used. The same numbering system is used for **2a** and **2c**.



2

	Fe	Ru	Os
Bond Distances (Å)			
A	2.5477 (6)	2.7234 (4)	2.7408 (8)
B	1.427 (5)	1.417 (7)	1.440 (20)
C	2.042 (4)	2.180 (5)	2.168 (14)
D	2.085 (4)	2.223 (5)	2.223 (14)
E	1.335 (5)	1.332 (7)	1.344 (20)
F	2.211 (1)	2.345 (1)	2.361 (4)
G	2.224 (1)	2.340 (1)	2.365 (4)
Bond Angles (deg)			
α	70.12 (2)	71.07 (3)	70.98 (9)
β	116.2 (1)	115.3 (3)	115.1 (8)
γ	76.2 (1)	76.4 (1)	77.2 (3)

Figure 2. Trends in structural parameters down the triad of $M_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (**2a–c**).

down the series. The molecules are isostructural; an ORTEP plot for the diruthenium complex **2b** (Figure 1) provides a perspective stereochemical view of the molecular structure. A compilation of bond lengths and angles is given in Table V. The principal skeletal features of the three molecules and the changes that occur down the triad are more readily compared via Figure 2. The structures of all three molecules have the following points in common. (i) The trigonal $M(CO)_3$ fragments are joined by a strong metal–metal bond. The M–M distances are at the lower end of the range of values for M–M single bonds. Relevant comparisons are as follows: for **2a**, Fe–Fe = 2.5477 (6) Å vs 2.5607 (5) Å in $Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}PPh_2)$;[18] for **2b**, Ru–Ru = 2.7234 (4) Å vs 2.7523 (8) Å in $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}C\text{-}t\text{-}Bu)(\mu\text{-}PPh_2)$[19] and 2.854 Å (av) in $Ru_3(CO)_{12}$;[20] for **2c** 2.7408 (8) Å vs 2.789 (1) Å in $Os_2(CO_6)(\mu\text{-}I)(\mu\text{-}PPh_2)$[21] and 2.877 Å (av) in $Os_3(CO)_{12}$.[22] (ii) The M–M vector is

---

(15) Carty, A. J.; Mott, G. N.; MacLaughlin, S. A.; Granby, R. A.; Taylor, N. J.; Cherkas, A. A., unpublished results.

(16) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

(17) Granozzi, G.; Tondello, E.; Bertoncello, R.; Aime, S.; Osella, D. *Inorg. Chem.* **1983**, *22*, 744.

(18) Taylor, N. J.; Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1980**, *19*, 560.

(19) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

(20) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

(21) Geoffroy, G. L.; Rosenberg, S.; Herlinger, A. W.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 2916.

(22) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

Table V. A Compilation of Important Bond Lengths (Å) and Angles (deg) for $M_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (2a–c)

	Fe	Ru	Os		Fe	Ru	Os
			(a) Bond Lengths				
M(1)–M(2)	2.5477 (6)	2.7234 (4)	2.7408 (8)	C(1)–O(1)	1.148 (5)	1.145 (8)	1.150 (22)
M(1)–P	2.211 (1)	2.345 (1)	2.361 (4)	C(2)–O(2)	1.139 (5)	1.131 (7)	1.134 (21)
M(1)–C(1)	1.757 (4)	1.891 (6)	1.874 (16)	C(3)–O(3)	1.142 (5)	1.137 (7)	1.174 (24)
M(1)–C(2)	1.814 (4)	1.942 (6)	1.930 (16)	C(4)–O(4)	1.144 (6)	1.138 (7)	1.090 (24)
M(1)–C(3)	1.787 (4)	1.911 (6)	1.883 (20)	C(5)–O(5)	1.135 (5)	1.129 (7)	1.155 (23)
M(1)–C(7)	2.042 (4)	2.180 (5)	2.168 (14)	C(6)–O(6)	1.148 (6)	1.129 (8)	1.171 (26)
M(2)–P	2.224 (1)	2.340 (1)	2.365 (4)	C(7)–C(8)	1.427 (5)	1.417 (7)	1.440 (20)
M(2)–C(4)	1.765 (4)	1.902 (6)	1.961 (19)	C(8)–N	1.335 (5)	1.332 (7)	1.344 (20)
M(2)–C(5)	1.808 (4)	1.941 (6)	1.912 (18)	C(8)–C(13)	1.497 (5)	1.495 (7)	1.521 (21)
M(2)–C(6)	1.766 (4)	1.914 (6)	1.858 (20)	N–C(9)	1.478 (5)	1.481 (8)	1.490 (22)
M(2)–C(7)	2.085 (4)	2.223 (5)	2.223 (14)	N–C(11)	1.488 (5)	1.477 (7)	1.487 (21)
P–C(19)	1.816 (4)	1.837 (5)	1.854 (16)	C(9)–C(10)	1.498 (7)	1.487 (11)	1.495 (27)
P–C(25)	1.834 (4)	1.830 (5)	1.806 (16)	C(11)–C(12)	1.505 (8)	1.502 (10)	1.538 (28)
			(b) Bond Angles				
M(2)–M(1)–P	55.18 (2)	54.37 (3)	54.61 (9)	C(5)–M(2)–C(6)	103.5 (1)	103.7 (2)	100.9 (8)
M(2)–M(1)–C(1)	138.6 (1)	141.1 (2)	142.4 (5)	C(5)–M(2)–C(7)	100.5 (1)	99.1 (2)	99.7 (7)
M(2)–M(1)–C(2)	93.4 (1)	97.6 (2)	94.1 (5)	C(6)–M(2)–C(7)	92.0 (1)	92.8 (2)	95.6 (7)
M(2)–M(1)–C(3)	119.3 (1)	117.5 (2)	118.0 (6)	M(1)–P–M(2)	70.12 (2)	71.07 (3)	70.98 (9)
M(2)–M(1)–C(7)	52.6 (1)	52.5 (1)	52.3 (4)	M(1)–P–C(19)	122.4 (1)	120.1 (1)	119.6 (5)
P–M(1)–C(1)	109.1 (1)	108.6 (2)	108.4 (5)	M(1)–P–C(25)	118.6 (1)	121.4 (1)	121.9 (5)
P–M(1)–C(2)	144.1 (1)	149.4 (2)	146.8 (5)	M(2)–P–C(19)	122.1 (1)	119.7 (1)	119.9 (5)
P–M(1)–C(3)	92.2 (1)	94.7 (2)	95.6 (6)	M(2)–P–C(25)	119.8 (1)	121.6 (1)	120.9 (5)
P–M(1)–C(7)	76.3 (1)	74.0 (1)	73.0 (4)	C(19)–P–C(25)	102.6 (1)	102.3 (2)	102.7 (7)
C(1)–M(1)–C(2)	106.3 (1)	101.2 (2)	103.7 (7)	M(1)–C(1)–O(1)	178.1 (1)	176.2 (3)	175.4 (8)
C(1)–M(1)–C(3)	97.4 (1)	97.0 (2)	95.2 (8)	M(1)–C(2)–O(2)	172.9 (1)	171.7 (2)	172.1 (7)
C(1)–M(1)–C(7)	87.8 (1)	90.7 (2)	92.2 (6)	M(1)–C(3)–O(3)	176.4 (1)	178.7 (2)	176.9 (7)
C(2)–M(1)–C(3)	89.2 (1)	88.1 (2)	89.9 (8)	M(2)–C(4)–O(4)	175.8 (1)	178.3 (2)	177.4 (8)
C(2)–M(1)–C(7)	99.3 (1)	99.6 (2)	97.6 (6)	M(2)–C(5)–O(5)	171.0 (1)	171.9 (2)	171.0 (7)
C(3)–M(1)–C(7)	168.4 (1)	167.9 (2)	167.9 (7)	M(2)–C(6)–O(6)	176.7 (2)	177.2 (3)	178.2 (8)
M(1)–M(2)–P	54.70 (2)	54.55 (3)	54.50 (9)	M(1)–C(7)–M(2)	76.2 (1)	76.4 (1)	77.2 (3)
M(1)–M(2)–C(4)	118.0 (1)	118.2 (2)	117.1 (5)	M(1)–C(7)–C(8)	131.2 (1)	131.8 (2)	131.0 (6)
M(1)–M(2)–C(5)	97.0 (1)	93.3 (2)	97.9 (6)	M(2)–C(7)–C(8)	120.7 (1)	118.6 (2)	118.6 (6)
M(1)–M(2)–C(6)	140.7 (1)	142.4 (2)	143.7 (5)	C(7)–C(8)–N	121.7 (1)	121.4 (3)	122.0 (8)
M(1)–M(2)–C(7)	51.1 (1)	51.1 (1)	50.5 (4)	C(7)–C(8)–C(13)	122.0 (1)	123.3 (3)	122.8 (8)
P–M(2)–C(4)	92.1 (1)	93.4 (2)	95.1 (6)	N–C(8)–C(13)	116.2 (1)	115.3 (3)	115.1 (8)
P–M(2)–C(5)	147.4 (1)	144.6 (2)	150.4 (6)	C(8)–N–C(9)	122.6 (2)	122.6 (3)	118.8 (9)
P–M(2)–C(6)	108.9 (1)	111.1 (2)	108.1 (6)	C(8)–N–C(11)	124.0 (2)	123.4 (3)	123.2 (9)
P–M(2)–C(7)	75.2 (1)	73.3 (1)	72.0 (4)	C(9)–N–C(11)	113.4 (2)	114.0 (3)	118.0 (9)
C(4)–M(2)–C(5)	87.9 (1)	89.7 (2)	88.7 (8)	N–C(9)–C(10)	112.7 (2)	112.0 (4)	110.8 (9)
C(4)–M(2)–C(6)	96.0 (2)	95.5 (2)	94.3 (8)	N–C(11)–C(12)	111.9 (2)	112.2 (4)	110.9 (10)
C(4)–M(2)–C(7)	166.7 (1)	166.2 (2)	165.7 (7)				

bridged by a μ-PPh_2 group with an acute M–P–M angle. (iii) A secondary alkylidene ligand $CHC(Ph)NEt_2$ bridging the two metals has a severely distorted tetrahedral geometry with very small M–C–M angles (76.2 (1)–77.2 (3)°). In **2a** and **2b** the hydrogen atom H(7) on the alkylidene carbon atom C(7), carbon atoms C(7) and C(8) lie in a plane almost perpendicular to the M–M vector with dihedral angles of 89.6° and 84.1°, respectively, between the planes defined by M(1), M(2), C(7) and C(7), C(8), H(7). The M_2PC framework has the expected folded butterfly configuration with the degree of folding increasing from iron to osmium [dihedral angles between the planes M(1), M(2), P and M(1), M(2), C(7) decrease from 99.74° (**2a**) to 96.96° (**2b**) to 95.49° (**2c**)] presumably as a result of longer metal–metal interactions in the heavier metals.

Within the dipolar alkylidene ligand the stereochemistry at the nitrogen atom and at C(8) is planar and the C(8)–N bond lengths are characteristic of $>C{=}N^+<$ bonds in iminium ion salts which lie within the range 1.287–1.38 Å.[23] The C(7)–C(8) bond lengths (1.417 (7)–1.440 (20) Å) are however short for what would normally be considered as a $C(sp^3)–C(sp^2)$ single bond (~1.51 Å). Thus despite the tetrahedral stereochemistry at C(7) there is some delocalization over the entire four-atom skeleton of the hydrocarbyl. The relative orientation of the C(13), C(8), N fragment with respect to the plane containing the alkylidene C–H group C(7), H(7), C(8) and that of the M(1), M(2), C(7) triangle can be judged by the small dihedral angles of 18.3° (**2a**) and 15.4° (**2b**) between C(13), C(8), N and C(7), H(7), C(8).

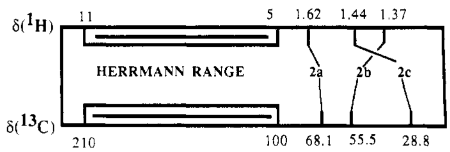
In terms of the changes in structural parameters down the triad, Figure 2 shows that while the M–M distance increases by almost 0.2 Å from **2a** to **2c**, this is accompanied by only a 0.9° increase in M–P–M angle at the phosphido bridge from **2a** to **2b** with the angles for **2b** and **2c** being essentially identical. An increase of 0.175 Å in M–M bond length and a smaller increment of 0.125 Å in the average M–P distances correspond to an M–P–M angle opening of 0.9° from **2a** to **2b** whereas the same parameters change by 0.0174 Å (M–M), 0.021 Å (M–P), and -0.1° (M–P–M) from **2b** to **2c**. One interpretation of these changes is that the increase in M–P bond length from **2b** to **2c** is not paralleled by a proportional increase in the metal–metal distance. Alternatively the metal–phosphorus interactions are weaker than expected in **2c**. Further examination of the data in Figure 2 indicates that there are corresponding trends in structural parameters at the μ-alkylidene which suggest that the two bridging systems communicate with one another.

The most notable feature of the M–C(R)H–M unit is that the bridge is unsymmetrical, with the asymmetry in the M–C bond lengths being 0.043 Å for **2a** and **2b** and 0.055 Å for **2c**. The magnitudes of the bond angles subtended by the metal atoms at the μ-CH(R) bridge are unexceptional and characteristic of bridging alkylidenes.

---

[23] For a compilation of C=N bond distances in iminium salts see: Merenyi, R. *Adv. Org. Chem.* **1976**, *9*, 90.

Chart I. ^1H and ^{13}C NMR Chemical Shifts for $M_2(CO)_6[\mu\text{-}CHC(NEt_2)Ph](\mu\text{-}PPh_2)$ Compared to the Herrmann Scale for μ-Alkylidenes μ-CHR



Thus in **2a** (Fe(1)–C(7)–Fe(2) = 76.2 (1)°) the angle is acute and comparable to values of 78.9 (1)° in $[\{(\eta^5\text{-}C_5H_5)Fe(CO)\}_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$[24a] and 76.81 (1)° in $Fe_2(CO)_8(\mu\text{-}CH_2)$.[24b] For **2b** (Ru(1)–C(7)–Ru(2) = 76.4 (1)°) relevant comparisons are with $Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6$ (Ru–C–Ru (av) = 78.1°)[25] and $[\{(\eta^5\text{-}C_5H_5)Ru(CO)\}_2(\mu\text{-}CO)(\mu\text{-}CH_2)]$ (Ru(1)–C–Ru(2) = 81.3°).[26] Direct comparison of metal–carbon bond lengths to bridging alkylidenes in complexes that are structurally unrelated is difficult in part because of wide fluctuations in metal–metal bond lengths. Thus for example **2a** has Fe–C(alkylidene) of 2.063 Å (av) while $Fe_2(CO)_8(\mu\text{-}CH_2)$ (Fe–Fe = 2.504 (1) Å) has Fe–C(alkylidene) of 2.015 (1) Å (av),[24b] but $[\{\eta^5\text{-}C_5H_5Fe(CO)_2\}(\mu\text{-}CO)(\mu\text{-}CHMe)]$ (Fe–Fe = 2.525 (1) Å) has a shorter Fe–C(alkylidene) bond length of 1.987 (1) Å.

In comparing changes in metal–carbon bond lengths down the triad, we see that the average M–C(alkylidene) bond distance increases by 0.147 Å from **2a** to **2b** and decreases by 0.006 Å from **2b** to **2c** although statistically the latter change is insignificant. Simultaneously the angle at the alkylidene carbon M–C–M increases fractionally from **2a** to **2b** (Δ = 0.2°) but much more from **2b** to **2c** (Δ = 0.8°). We attribute these trends to stronger metal–alkylidene bonding in the diosmium complex. Although there is an indication that the C(7)–C(8) and C(8)–N bond lengths in **2c** may be slightly longer than in **2a** and **2b**, the trend is marred by the higher estimated standard deviations in the diosmium complex. From the overall picture it is tempting to conclude that the mesoionic alkylidene ligand interacts more strongly with the dimetal fragment in **2c** presumably by increased delocalization of the formally negative charge on C(7) onto the metals. To compensate, the phosphido bridge interaction may be weakened. We are currently exploring the chemistry of **2a–c** with a range of electrophilic reagents to probe whether structural and bonding differences manifest themselves in patterns of reactivity.

^{31}P and ^{13}C NMR Spectral Features of 2a–c. The $^{31}P\{^1H\}$ NMR spectra of **2a–c** consist of a single sharp line. The chemical shifts (**2a**, δ 153.9; **2b**, δ 136.7; **2c**, δ 57.6) move increasingly upfield on descending the triad. This is a consistent feature of ^{31}P shifts for phosphido bridges in isostructural compounds of the iron group,[27] and the chemical shift differences $\Delta\delta(^{31}P)$ (Fe–Ru, 20–40 ppm; Ru–Os, 80–100 ppm) can be used to predict shifts for closely related phosphido-bridged complexes.

There are some interesting trends in $\delta(^{13}C)$ and $\delta(^1H)$ for the resonances of the μ-alkylidene carbon atoms and the hydrogen atom (H(7) in Figure 1) on this carbon in the ^{13}C and ^1H NMR spectra of **2a–c** (Chart I). For the C(7)–H proton resonances, the chemical shifts are in the order Fe > Os > Ru while for the ^{13}C resonances the order is Fe > Ru > Os. However, it is the position of the ^{13}C resonance of the alkylidene carbon atom in **2a–c** which is of principal interest. Herrmann has established a scale for ^{13}C NMR shifts in μ-alkylidene complexes and has pointed out that ^{13}C resonances for μ-*C*(H)(R) groups bridging M–M bonds fall in the range 100–200 ppm.[2a] The corresponding proton resonance for μ-C(*H*)R lies between 5 and 11 ppm. In **2a–c** the μ-*C* and μ-C*H* shifts are well upfield of these ranges. Indeed the ^{13}C chemical shifts appear to be unprecedented for μ-*C*(H)R ligands and indicate that these molecules have an exceptionally electron-rich M–C–M system. In support of this, protonation of **2a–c** readily affords isolable μ-hydrido, μ-alkylidene, μ-phosphido dimetal cations.[11]

Acknowledgment. We are grateful to NSERC for financial support of this work in the form of operating grants (A.J.C.) and scholarships (to A.A.C and S.A.M.).

Registry No. **1a**, 52970-25-9; **1b**, 82647-81-2; **1c**, 109976-28-5; **2a**, 64457-84-7; **2b**, 113132-32-4; **2c**, 113159-93-6; Fe, 7439-89-6; Ru, 7440-18-8; Os, 7440-04-2.

Supplementary Material Available: Anisotropic thermal parameters and hydrogen atom positions (Tables S1–S3) and remaining bond angles and distances (Table S4) (9 pages); structure factors (Tables S5–S7) (56 pages). Ordering information is given on any current masthead page.

---

[24] (a) Dyke, A. F.; Knox, S. A. R.; Naish, D. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1980**, 441. (b) Meyer, B. B.; Riley, D. E.; Davis, B. E. *Inorg. Chem.* **1981**, *20*, 3024.

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

[26] Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, D. *J. Chem. Soc., Dalton Trans.* **1984**, 2293.

[27] MacLaughlin, S. A.; Nucciarone, D.; Carty, A. J. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quinn, L. D., Eds.; VCH Publishers: New York, 1987; Chapter 16.