Polynuclear Acetylide Chemistry: Acetylide to Acetylene Transformation at a Binuclear Center via C–C and C–N Bond-Forming Reactions. X-ray Structure of $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}\|\text{-}C(C(NHBu^t)(NEt_2))CPh](\mu\text{-}PPh_2)$

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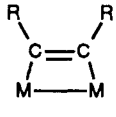
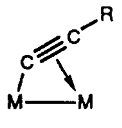
Transformation of the edge-bound acetylide complex $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (**1a**) to the electron-rich parallel acetylene derivative $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}\|\text{-}C(CNHBu^t)(NEt_2))CPh](\mu\text{-}PPh_2)$ (**4**) has been achieved by treatment of **1a** with the isonitrile $CNBu^t$, resulting in nucleophilic attack and C–C bond formation of C_α of the acetylide, followed by addition of the secondary amine $HNEt_2$ across the C–N multiple bond of the "carbon coordinated" isonitrile. Complex **4** exists in four isomeric forms in solution but as a single isomer in the solid state. An X-ray analysis shows that **4** crystallizes in the monoclinic space group $P2_{1/n}$ with $a = 16.174$ (6) Å, $b = 19.300$ (8) Å, $c = 11.745$ (6) Å, $\beta = 101.30$ (2)°, and $Z = 4$. The structure was solved and refined on the basis of 3998 observed ($I > 3\sigma(I)$) reflections to R and R_w values of 0.038 and 0.039, respectively. In the molecular structure the two alkyne carbon atoms of a dipolar $\mu\text{-}\eta^2$-acetylene with phenyl and amidinium $[C(NHBu^t)(NEt_2)]$ substituents, together with the diosmium fragment, constitute the dimetallacyclobutene $\overline{\text{Os–Os–C(R)–C}}\text{(R}')$. The Os–Os and C–C bond lengths within this four-membered ring are 2.829 (1) and 1.37 (1) Å. Similar conversions of **1a** (R = Ph), **1b** ($R = Pr^i$), and **1c** ($R = Bu^t$) to $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(C(NHPr^i)(NHBu^t))CPh](\mu\text{-}PPh_2)$ (**5a**), $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(C(NHPr^i)(NHBu^t))CPr^i](\mu\text{-}PPh_2)$ (**5b**), and $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(C(NHPr^i)(NHBu^t))CBu^t](\mu\text{-}PPh_2)$ (**5c**) with $CNBu^t$ and isopropylamine show the same reaction sequence observed for conversion of complex **1a** to complex **4**.

Introduction

The acetylide (–C≡CR) or alkynyl anion is formally derived from a monosubstituted acetylene HC≡CR by deprotonation, and simple organotransition-metal acetylides $L_nM{-}C{\equiv}CR$ can be considered as metal-substituted acetylenes with four π electrons available for coordination. Viewed in this light, close structural relationships[1] between acetylide and acetylene ligand bonding modes in polynuclear complexes are not unexpected. Thus, for example, at a binuclear center there are similarities in a structural sense between the so-called $\mu_2\text{-}\eta^2$ parallel interaction A of an acetylene with two metals[2] and the $\mu_2\text{-}\eta^2$ mode B of a dimetal acetylide, although structural data for binuclear acetylides[3] of type B show that the –C≡C– vector is neither perfectly coplanar with nor parallel to the M—M bond.



A



B

Despite the common structural and bonding features of acetylides and acetylenes relatively few methodologies have been described for converting acetylides to acetylenes or vice versa,[4] and in this paper we describe a strategy for the generation of a μ_2-∥-acetylene complex of type A from an acetylide of type B via successive carbon–carbon and carbon–nitrogen bond-forming reactions with $CNBu^t$ and NEt_2H. A single-crystal X-ray structural analysis of $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(C(NHBu^t)(NEt_2))C(Ph)](\mu\text{-}PPh_2)$ (**4**) has confirmed the presence of a novel dipolar acetylene ligand bearing an amidinium ion substituent. Similar transformations have been accomplished for the series of acetylides $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (**1a**, R = Ph; **1b**, $R = Pr^i$; **1c**, $R = Bu^t$) with $CNBu^t$ and isopropylamine.

Experimental Section

All manipulations were carried out on a double manifold by using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use (hexane and heptane over

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$LiAlH_4$, benzene and cyclohexane over $Na^+Ph_2CO^-$). Purification of products was attained by column chromatography with 100–200 mesh Florisil. IR spectra were measured on a Perkin-Elmer 180 instrument using sodium chloride cells of 0.5-mm path length. NMR spectra were recorded on Bruker AM-250 (^1H, 250 MHz; $^{31}P\{^1H\}$, 101.3 MHz) or WH-400 (^1H, 400 MHz; $^{31}P\{^1H\}$, 162.0 MHz; $^{13}C\{^1H\}$, 100.6 MHz) instruments. Chemical shifts are referenced to TMS and 85% H_3PO_4.

Synthesis of Complex 4. The syntheses of the binuclear acetylide complex $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (**1a**) and the isocyanide adduct $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(CNBu^t)CPh](\mu\text{-}PPh_2)$ (**2a**) were carried out as previously described.[3,5] Treatment of **2a** (130 mg, 0.142 mmol) with excess $HNEt_2$ (0.2 mL, 1.90 mmol) in *n*-hexane (5 mL) for 24 h resulted in a change in color of the solution from bright to pale yellow. Monitoring of the reaction by IR spectroscopy and thin-layer chromatography indicated complete consumption of starting material. The solvent was removed in vacuo and the residue washed with *n*-hexane (3 × 5 mL). Complex **4** (90 mg, 64%) was obtained on recrystallization from *n*-hexane. Anal. Calcd for $C_{35}H_{35}N_2O_6POs_2$: C, 42.42; H, 3.56; N, 2.83; P, 3.13. Found: C, 42.12; H, 3.65; N, 2.89; P, 3.10. IR (C_6H_{12}): ν(CO) 2050 s, 2013 vs, 1975 vs, 1954 w, 1945 w, 1924 s cm^{-1}. IR (Nujol): ν(NH) 3328 w cm^{-1}; $\nu(C{=}N)/\nu(C{=}C)$ 1581 w, 1542 m, 1525 w cm^{-1}. ^1H NMR (200.1 MHz, $CDCl_3$; δ, ranges only for four isomers): 7.99–6.47 (m, Ph H); 4.46, 4.40, 3.97 (br s, N–H); 3.7–2.2 (quartets, Et CH_2, $^3J_{H-H} \approx 7.0$ Hz); 1.22, 0.91, 0.81 (singlets, Bu^tCH_3); 0.62, 0.61 (t, Et CH_3, $^3J_{H-H} \approx 7.0$ Hz). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$; δ): 104.6 s, 102.8 (s), 102.6 (s), 98.3 (s, four isomers; μ-PPh_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$; δ, four isomers; ranges only): 188.6–175.7 (m, CO); 171.7, 170.5, 170.4 (singlets, C_α); 153.6, 152.2, 151.9, 151.4 (singlets, C_β); 147.4–118.4 (m, C Ph); 109.5, 109.4 (N–C–N); 53.5, 53.5, 52.1, 52.0 (singlets, t-Bu CMe_3); 47.4–39.7 (singlets, Et CH_2); 29.9, 29.0, 28.0, 28.5 (singlets, Bu^t CH_3); 14.4–10.8 (singlets, Et CH_3).

Synthesis of 5a–c. The acetylides **1b,c** and their isonitrile adducts were prepared as described elsewhere.[3,5] A common procedure as described below for **5b** was used to synthesize and isolate the three compounds **5a–c**. The complex $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(CNBu^t)CPr^i](\mu\text{-}PPh_2)$ (0.188 g, 0.21 mmol), prepared from **1b** by addition of $CNBu^t$, was dissolved in hexane (5 mL) and an excess of NH_2Pr^i (1 mL) added. The color changed from bright yellow to pale yellow over 24 h. The liquid was removed in vacuo and the solid washed with hexane (3 × 5 mL) and recrystallized from a 70:30 mixture of dichloromethane and hexane by slow evaporation of solvent, yielding 0.139 g (69.5%) of **5b**. Yields of **5a** and **5c** were 76.1% and 84.1%, respectively.

Complex 5a (R = Ph). Anal. Calcd for $C_{34}H_{33}NO_6POs_2$: C, 41.80; H, 3.40; N, 2.87; P, 3.17. Found: C, 41.70; H, 3.78; N, 2.53; P, 3.25. IR (C_6H_{12}): ν(CO) 2051 s, 2015 vs, 1978 s, 1956 w, 1947 m, 1924 m cm^{-1}. IR (Nujol): ν(NH) 3411 m, 3376 m cm^{-1}; $\nu(C{=}N)/\nu(C{=}C)$ 1566 s, 1562 sh, 1532 w cm^{-1}. ^1H NMR (250.1 MHz, $CDCl_3$; δ): 7.77–7.70 (m, Ph H); 7.29–7.14 (m, Ph H); 7.07–6.91 (m, Ph H); 6.47–6.43 (m, Ph H); 4.56 (d, N–H, $^3J_{H-H}$ = 10.3 Hz); 4.35 (s, N–H′); 3.60 (d, sept, Pr^i CH_3, J_{H-H} = 10.2 Hz, $^3J_{H-H}$ = 6.4 Hz); 1.17 (s, Bu^t CH_3); 1.08 (d, Pr^iCH_3, $^3J_{H-H}$ = 6.4 Hz); 0.05 (d, Pr^i CH_3', $^3J_{H-H}$ = 6.4 Hz). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$; δ): 102.7 (s, μ-PPh_2). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$; δ): 187.7 (d, CO, $^2J_{P-C}$ = 64.7 Hz); 186.9 (d, CO, $^2J_{P-C}$ = 62.6 Hz); 181.4 (d, CO, $^2J_{P-C}$ = 4.6 Hz); 180.8 (d, CO, $^2J_{P-C}$ = 7.1 Hz); 179.9 (d, CO, $^2J_{P-C}$ = 6.6 Hz); 179.6 (d, CO, $^2J_{P-C}$ = 4.7 Hz); 170.6 (s, C_α); 151.9 (s, C_i''); 147.1 (s, C_β); 142.0 (d, C_i, $^1J_{P-C}$ = 31.9 Hz); 136.2 (d, C_i', $^1J_{P-C}$ = 32.7 Hz); 135.1 (d, C_o, $^2J_{P-C}$ = 10.4 Hz); 134.4 (d, C_o', $^2J_{P-C}$ = 10.6 Hz); 129.1 (s, C_p); 128.8 (d, C_m, $^3J_{P-C}$ = 10.0 Hz); 128.6 (d, C_p', $^4J_{P-C}$ = 2.6 Hz); 128.0 (d, C_m', $^3J_{P-C}$ = 9.5 Hz); 127.2 (s, C_m''); 127.1 (s, C_o''); 125.1 (s, C_p'); 109.1 (s, N–*C*–N); 52.0 (s, Bu^tC); 47.3 (s, Pr^iCH); 29.0 (s, Bu^tCH_3); 24.0 (s, Pr^iCH_3); 21.9 (s, $Pr^iC'H_3$).

Complex 5b (R = Pr^i). Anal. Calcd for $C_{31}H_{35}N_2O_6Os_2P$: C, 39.48; H, 3.74; N, 2.97; P, 3.28. Found: C, 39.08; H, 3.68; N, 3.00; P, 3.58. Ir (C_6H_{12}): ν(CO) 2050 s, 2011 vs, 1976 vs, 1948 w, 1938 m, 1922 m cm^{-1}. ^1H NMR (250.1 MHz, $CDCl_3$; δ): 7.99–7.90 (m, Ph H); 7.74–7.67 (m, Ph H); 7.30–7.15 (m, Ph H); 4.97 (d, Pr^iNH, $^3J_{H-H}$ = 10.2 Hz); 4.91 (s, Bu^tNH); 3.95 (d, sept, Pr^iCH, $^3J_{H-H}$ = 10.2 Hz, $^3J_{H-H}$ = 6.4 Hz); 1.87 (sept, Pr^iCH', $^3J_{H-H}$ = 6.6 Hz); 1.34 (d, Pr^iCH_3, $^3J_{H-H}$ = 6.4 Hz); 1.13 (d, Pr^iCH_3', $^2J_{H-H}$ obscured); 1.11 (s, Bu^tCH_3); 0.84 (d, Pr^iCH_3'', $^3J_{P-H}$ = 6.5 Hz); 0.45 (d, Pr^iCH_3'', $^3J_{P-H}$ = 6.6 Hz). $^{31}P\{^1H\}$ NMR (62.8 MHz, $CDCl_3$; δ): 105.8 (s, μ-PPh_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$; δ): 188.4 (d, CO, $^2J_{P-C}$ = 61.9 Hz); 186.7 (d, CO, $^2J_{P-C}$ = 66.2 Hz); 181.7 (s, CO); 181.6 (s, CO); 180.8 (d, CO, $^2J_{P-C}$ = 7.6 Hz); 179.6 (d, CO, $^2J_{P-C}$ = 6.6 Hz); 171.7 (s, C_α); 154.8 (s, C_β); 143.6 (d, C_i, $^1J_{P-C}$ = 32.2 Hz); 136.4 (d, C_i', $^1J_{P-C}$ = 28.1 Hz); 135.5 (d, C_o, $^2J_{P-C}$ = 10.4 Hz); 134.3 (d, C_o', $^2J_{P-C}$ = 10.4 Hz); 129.0 (d, C_p, $^4J_{P-C}$ = 2.4 Hz); 128.8 (s, C_p'); 128.7 (d, C_m, $^3J_{P-C}$ = 9.8 Hz); 127.9 (d, C_m', $^3J_{P-C}$ = 9.3 Hz); 99.6 (s, N–C–N); 51.9 (s, *C*Me_3); 46.8 (s, Pr^iCH); 42.1 (s, Pr^iCH); 29.3 (s, Bu^tCH_3); 23.5 (s, Pr^iCH_3); 23.4 (s, Pr^iCH_3); 22.0 (s, Pr^iCH_3); 21.6 (s, Pr^iCH_3).

Table I. Summary of Crystallographic Data for 4

formula	$C_{35}H_{35}N_2O_6Os_2P$
mol wt	991.05
cryst syst	monoclinic
space group	$P2_1/n$
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)
a, Å	16.174 (6)
b, Å	19.300 (8)
c, Å	11.745 (6)
β, deg	101.30 (2)
V, Å^3	3595 (3)
Z	4
D_{calcd}, g cm^{-3}	1.831
$F(000)$	1896
cryst size, mm	0.25 × 0.27 × 0.32
μ(Mo Kα), cm^{-1}	71.58
diffractometer	Philips PW 1100
scan type	$\omega/2\theta$
scan speed, deg s^{-1}	0.100
scan width, deg	1.40
2θ range, deg	6–50
no. of rflns measd	$\pm h,k,l$
std rfln	1 measd after 50 rflns
no. of unique total data	6307
no. of unique obsd data ($I > 3\sigma(I)$)	3998
R	0.0382
R_w	0.0394

Complex 5c (R = Bu^t). Anal. Calcd for $C_{32}H_{37}N_2O_6POs_2$: C, 40.16; H, 3.90; N, 2.93; P, 3.24. Found: C, 39.87; H, 4.15; N, 3.19; P, 3.49. IR (C_6H_{12}): ν(CO) 2051 vs, 2012 vs, 1977 vs, 1949 w, 1938 m, 1921 s cm^{-1}. ^1H NMR (250.1 MHz, $CDCl_3$; δ): 8.01–7.92 (m, Ph H); 7.75–7.68 (m, Ph H); 7.28–7.15 (m, Ph H); 4.73 (d, Pr^iNH, $^3J_{H-H}$ = 10.4 Hz); 3.99 (s, Bu^tNH); 3.94 (d, sept, Pr^iCH, $^3J_{H-H}$ = 10.5 Hz, $^3J_{H-H}$ = 6.4 Hz); 1.52 (d, Pr^iCH_3, $^3J_{H-H}$ = 6.3 Hz); 1.25 (d, Pr^iCH_3', $^3J_{H-H}$ = 6.4 Hz); 1.14 (s, Bu^tCH_3); 0.89 (s, Bu^tCH_3'). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$; δ): 101.3 (s, μ-PPh_2). $^{13}C\{^1H\}$ (50.3 MHz, $CDCl_3$; δ): 189.1 (d, CO, $^2J_{P-C}$ = 61.1 Hz); 187.3 (d, CO, $^2J_{P-C}$ = 67.5 Hz); 182.4 (d, CO, $^2J_{P-C}$ = 7.5 Hz); 179.1 (d, CO, $^2J_{P-C}$ = 6.6 Hz); 172.6 (s, C_α); 158.0 (s, C_β); 143.8 (d, C_i, $^1J_{P-C}$ = 34.2 Hz); 135.6 (d, C_o, $^2J_{P-C}$ = 10.3 Hz); 135.3 (d, C_i', $^1J_{P-C}$ = 26.5 Hz); 134.3 (d, C_o', $^2J_{P-C}$ = 10.2 Hz); 129.1 (d, C_p, $^4J_{P-C}$ = 2.3 Hz); 128.7 (d, C_p', $^4J_{P-C}$ = 1.9 Hz); 128.7 (d, C_m, $^3J_{P-C}$ = 9.5 Hz); 127.9 (d, C_m', $^3J_{P-C}$ = 9.3 Hz); 99.7 (s, N–C–N); 51.9 (s, NBu^tC); 46.9 (s, Pr^iCH); 45.7 (s, Bu^tC'); 32.1 (s, Bu^tCH_3); 29.2 (s, $NBu^tC'H_3$); 23.4 (s, Pr^iCH_3); 23.0 (s, $Pr^iC'H_3$).

X-ray Crystal Structure Determination of 4. A pale yellow crystal of 4 for single-crystal X-ray diffraction was grown from a $CDCl_3$ solution in an NMR tube. The crystallographic data are summarized in Table I. Unit cell parameters were determined from the θ values of 25 carefully centered reflections, having $11 < \theta < 16°$. Data were collected at room temperature, the individual profiles having been analyzed by the method of Lehmann and Larsen.[6a] Intensities were corrected for Lorentz and polarization effects; a semiempirical absorption correction was applied (maximum and minimum values were 1.384 and 1.000).[6b]

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Table II. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms of 4

atom	x/a	y/b	z/c
Os(1)	1961 (1)	608 (1)	742 (1)
Os(2)	3618 (1)	1025 (1)	621 (1)
P	2411 (2)	1138 (1)	-844 (2)
O(1)	2579 (7)	-26 (5)	3158 (7)
O(2)	62 (5)	757 (5)	562 (8)
O(3)	1969 (6)	-801 (5)	-481 (9)
O(4)	4484 (7)	665 (6)	3128 (8)
O(5)	4941 (6)	1887 (5)	-215 (9)
O(6)	4078 (6)	-378 (5)	-321 (10)
N(1)	1261 (5)	2580 (5)	1183 (7)
N(2)	1300 (6)	1898 (5)	2821 (9)
C(1)	2329 (7)	205 (6)	2270 (10)
C(2)	783 (7)	696 (6)	614 (10)
C(3)	1951 (7)	-279 (7)	-16 (10)
C(4)	4184 (7)	796 (6)	2174 (12)
C(5)	4431 (8)	1562 (6)	106 (11)
C(6)	3917 (7)	139 (7)	13 (10)
C(7)	3015 (6)	1848 (5)	1384 (8)
C(8)	2224 (6)	1632 (5)	1470 (8)
C(9)	1587 (7)	2062 (6)	1875 (9)
C(10)	1825 (10)	1506 (7)	3760 (11)
C(11)	1955 (13)	1909 (10)	4902 (14)
C(12)	420 (12)	2011 (9)	2924 (16)
C(13)	23 (11)	1341 (11)	3318 (17)
C(14)	904 (8)	3279 (6)	1352 (10)
C(15)	1276 (11)	3727 (7)	518 (12)
C(16)	1224 (9)	3534 (7)	2572 (12)
C(17)	-60 (9)	3300 (9)	1074 (16)
C(18)	3379 (7)	2515 (5)	1829 (10)
C(19)	3676 (8)	3004 (6)	1144 (11)
C(20)	4028 (9)	3636 (8)	1571 (14)
C(21)	4116 (8)	3777 (7)	2714 (15)
C(22)	3866 (9)	3287 (8)	3439 (12)
C(23)	3492 (7)	2671 (7)	3002 (10)
C(24)	2314 (7)	640 (6)	-2189 (9)
C(25)	3006 (8)	507 (7)	-2708 (11)
C(26)	2946 (11)	137 (9)	-3694 (12)
C(27)	2209 (11)	-117 (8)	-4230 (11)
C(28)	1501 (10)	12 (8)	-3769 (11)
C(29)	1538 (9)	374 (7)	-2746 (11)
C(30)	2035 (6)	1977 (5)	-1455 (8)
C(31)	2582 (7)	2457 (7)	-1805 (10)
C(32)	2269 (10)	3048 (7)	-2411 (12)
C(33)	1439 (10)	3190 (7)	-2613 (12)
C(34)	875 (8)	2735 (8)	-2269 (12)
C(35)	1185 (7)	2142 (7)	-1679 (9)

Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. The hydrogen atoms were clearly localized in the final difference Fourier map and refined isotropically. The final cycles of refinement were carried out on the basis of 555 variables; after the last cycles, no parameters shifted by more than 0.30 esd. The largest remaining peak in the final difference map was equivalent to about 1.28 e/Å^3. In the final cycles of refinement a weighting scheme, $w = 1/[\sigma^2(F_o)]$, was used. The atomic scattering factors, corrected for anomalous dispersion, were taken from ref 7a.

All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CIENCA, Casalecchio Bologna) and on the GOULD POWERNODE 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 system of crystallographic computer programs.[7b]

The final atomic coordinates for the non-hydrogen atoms are given in Table II. The atomic coordinates of the hydrogen atoms (Table S1), the anisotropic thermal parameters (Table S2), the remaining bond lengths and angles (Table S3), and structure factors (Table S4) are available as supplementary material.

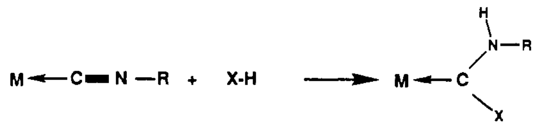
Table III. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for 4

Os(1)-Os(2)	2.829 (1)	C(6)-O(6)	1.12 (2)
Os(1)-P	2.362 (3)	P-C(24)	1.83 (1)
Os(2)-P	2.347 (3)	P-C(30)	1.83 (1)
Os(1)-C(1)	1.94 (1)	C(7)-C(8)	1.37 (1)
Os(1)-C(2)	1.89 (1)	C(7)-C(18)	1.47 (1)
Os(1)-C(3)	1.93 (1)	C(8)-C(9)	1.47 (2)
Os(1)-C(8)	2.162 (9)	C(9)-N(1)	1.33 (1)
Os(2)-C(4)	1.92 (1)	N(1)-C(14)	1.50 (2)
Os(2)-C(5)	1.86 (1)	C(14)-C(15)	1.52 (2)
Os(2)-C(6)	1.95 (1)	C(14)-C(16)	1.51 (2)
Os(2)-C(7)	2.15 (1)	C(14)-C(17)	1.53 (2)
C(1)-O(1)	1.13 (1)	C(9)-N(2)	1.32 (2)
C(2)-O(2)	1.16 (1)	N(2)-C(10)	1.46 (2)
C(3)-O(3)	1.15 (2)	C(10)-C(11)	1.53 (2)
C(4)-O(4)	1.16 (2)	N(2)-C(12)	1.47 (2)
C(5)-O(5)	1.16 (2)	C(12)-C(13)	1.55 (3)

Os(2)-Os(1)-P	52.84 (8)	Os(1)-P-C(24)	117.8 (4)
Os(2)-Os(1)-C(1)	92.3 (4)	Os(1)-P-C(30)	124.3 (4)
Os(2)-Os(1)-C(3)	98.8 (4)	Os(2)-P-C(24)	120.2 (4)
Os(2)-Os(1)-C(8)	69.2 (3)	Os(2)-P-C(30)	122.4 (4)
P-Os(1)-C(2)	111.1 (4)	C(24)-P-C(30)	99.3 (5)
P-Os(1)-C(3)	89.8 (4)	Os(1)-C(1)-O(1)	177 (1)
P-Os(1)-C(8)	81.3 (3)	Os(1)-C(2)-O(2)	178 (1)
C(1)-Os(1)-C(2)	103.3 (5)	Os(1)-C(3)-O(3)	178 (1)
C(1)-Os(1)-C(3)	92.6 (5)	Os(2)-C(4)-O(4)	176 (1)
C(1)-Os(2)-C(8)	90.0 (4)	Os(2)-C(5)-O(5)	179 (1)
C(2)-Os(1)-C(3)	97.2 (5)	Os(2)-C(6)-O(6)	178 (1)
C(2)-Os(1)-C(8)	93.8 (4)	Os(2)-C(7)-C(8)	108.3 (7)
Os(1)-Os(2)-P	53.31 (8)	Os(2)-C(7)-C(18)	127.8 (8)
Os(1)-Os(2)-C(4)	99.5 (4)	C(8)-C(7)-C(18)	123.8 (9)
Os(1)-Os(2)-C(6)	94.3 (4)	Os(1)-C(8)-C(7)	111.3 (7)
Os(1)-Os(2)-C(7)	71.2 (3)	Os(1)-C(8)-C(9)	123.2 (7)
P-Os(2)-C(5)	104.4 (4)	C(7)-C(8)-C(9)	125.1 (9)
P-Os(2)-C(6)	92.5 (4)	C(8)-C(9)-N(1)	116.5 (9)
P-Os(2)-C(7)	81.7 (3)	C(8)-C(9)-N(2)	121 (1)
C(4)-Os(2)-C(5)	101.6 (5)	N(1)-C(9)-N(2)	122 (1)
C(4)-Os(2)-C(6)	92.3 (5)	C(9)-N(1)-C(14)	135.5 (9)
C(4)-Os(2)-C(7)	86.9 (4)	C(9)-N(2)-C(10)	121 (1)
C(5)-Os(2)-C(6)	97.3 (5)	C(9)-N(2)-C(12)	123 (1)
C(5)-Os(2)-C(7)	97.6 (5)	C(10)-N(2)-C(12)	116 (1)
Os(1)-P-Os(2)	73.85 (9)		

Results and Discussion

The addition of activated X—H bonds (X = O, N, S) across the C≡N triple bond of a metal-coordinated isonitrile[8] is a well-established route to metal–carbene complexes (eq 1).



$$\mathrm{M \leftarrow C \equiv N - R \;+\; X{-}H \longrightarrow M \leftarrow C}\begin{smallmatrix} /\,\mathrm{N(H)-R} \\ \backslash\,\mathrm{X} \end{smallmatrix} \qquad (1)$$

Less well-known and appreciated is the observation[5a,9,10] that electrophilic hydrocarbyl ligands, particularly μ_2-η^2- and μ_3-η^2-acetylides, undergo attack at carbon by soft carbon nucleophiles such as isonitriles, generating carbon–carbon bonds (eq 2). These adducts contain "carbon coordinated" isonitriles that, like their metal complex counterparts, are susceptible to addition of activated X–H bonds (eq 2). This methodology constitutes a strategy for functionalizing acetylides via C—C and C—X bond-forming reactions. In the present case the X—H reagent is a

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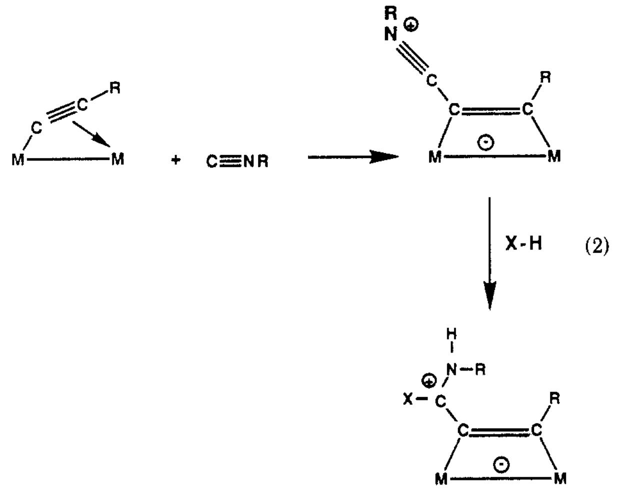
(7) (a) *International Tables for X-ray Crystallography*; Kynoch Press; Birmingham, England, 1974; Vol. IV. (b) Sheldrick, G. M. SHELX-76 Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(8) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209 and references therein.

(9) MacLaughlin, S. A.; Johnson, J. P.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1983**, *2*, 352.

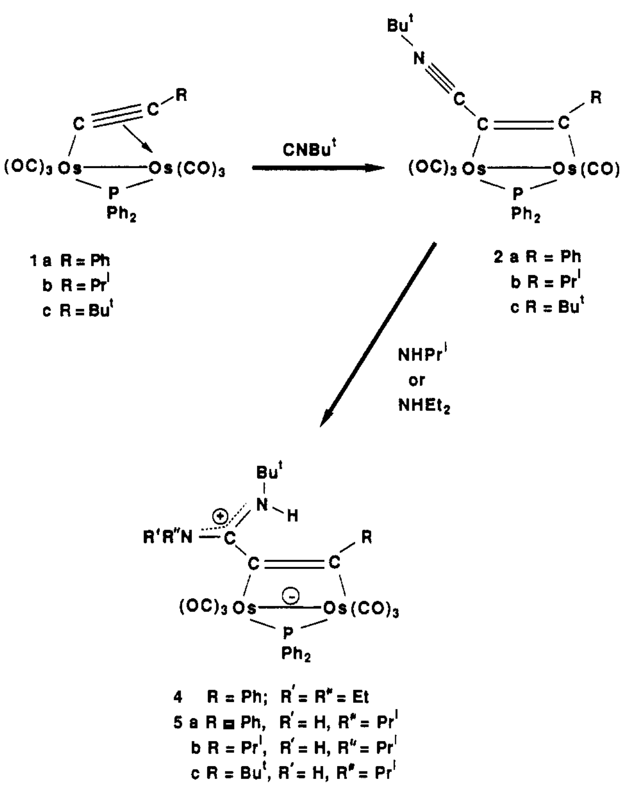
(10) Cherkas, A. A.; Carty, A. J.; Sappa, E.; Pellinghelli, M. A.; Tiripicchio, A. *Inorg. Chem.* **1987**, *26*, 3201.



primary (NH_2Pr^i) or secondary (Et_2NH) amine and the addition to the C≡N multiple bond of the carbon-coordinated isonitrile gives medium to high yields of the new parallel acetylene complexes $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(C(NHPr^i)(NHBu^t))CR](\mu\text{-}PPh_2)$ (R = Ph, Pr^i, Bu^t; **5a–c**) or $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(C(NEt_2)(NHBu^t))CPh](\mu\text{-}PPh_2)$ (**4**) containing an electron-rich amidinium ion substituent bearing two amino groups ($C(NRR')(NHBu^t)$) (Scheme I). This sequence of reactions can be compared with the use of a thiol RSH as the X—H reagent, in which case the product is a thioaminocarbenium phenylacetylene.[10] In a preliminary communication we have also described the generation of cluster-bound $\mu_3\text{-}\eta^2\text{-}\|$-acetylenes in a trinuclear osmium framework via a similar two-step nucleophilic addition sequence.[9]

Crystal Structure of 4. The principal structural features of 4 are illustrated in Figure 1, which also gives the atomic numbering system used. Complex 4 consists of a core of two osmium atoms with a short Os–Os distance (2.829 (1) Å), symmetrically bridged by a phosphido group (Os(1)–P = 2.362 (3) Å, Os(2)–P = 2.347 (3) A, Os(1)–P–Os(2) = 73.85 (9)°). The plane of this triangular Os_2P core forms a dihedral angle of 92.46° with the plane containing the diosmacyclobutene ensemble defined by Os(1), Os(2), C(7), and C(8). The four atoms of the diosmacyclobutene are almost planar, the maximum deviation from a best least-squares plane through these atoms being 0.02 Å for C(7). The C(7)–C(8) bond length of 1.37 (1) Å is in the normal range for an olefinic double bond, and the metal–carbon bond lengths to the ligand (Os(1)–C(8) = 2.162 (9) Å, Os(2)–C(7) = 2.15 (1) Å) are indicative of symmetrical η^1,η^1 bonding of the metals to the unsaturated ligand. For comparison the osmium–carbon distances in the diosmacyclobutene complex $Os_2(CO)_8[\mu\text{-}\eta^1,\eta^1\text{-}C(CO_2Me)C(CO)_2Me)]$ are 2.138 (5) Å.[11] Thus, the molecule 4 quite adequately conforms to the description of a $\mu_2\text{-}\|$-acetylene complex.[2] In addition, the near-equivalence of the Os(1)–C(8) and Os(2)–C(7) distances and the C(8)–C(9) single-bond length suggest that, unlike the iminium ion complexes $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C(NHR)CH(Ph)](\mu\text{-}PPh_2)$ formed from **1a** by addition of primary amines across the multiple bond[12] and recent examples of bi- and polynuclear carbonyl compounds derived from electron-rich acetylenes,[13] there is little carbene character in the Os(1)–C(8) and Os(2)–C(7) interactions.

Scheme I



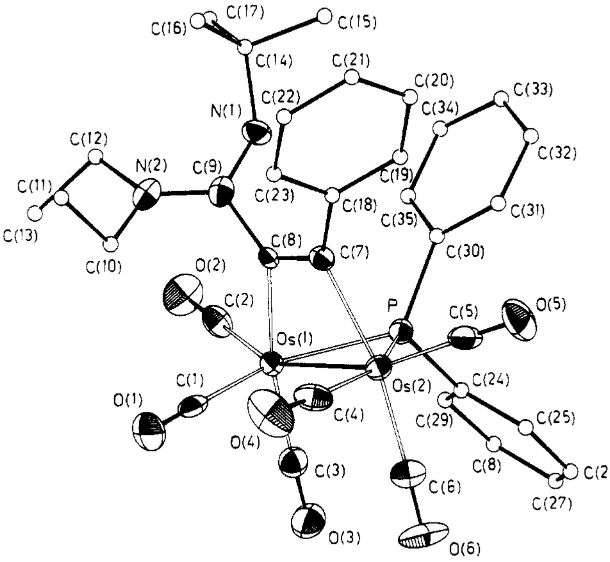


Figure 1. Perspective view of the molecular structure of $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}\|\text{-}C(C(NEt_2)(NHBu^t))CPh](\mu\text{-}PPh_2)$ showing the atomic numbering scheme used.

The nature of the substituent derived from the isonitrile and diethylamine and attached to C_α of the original acetylide is of some interest. The C(8)–C(9) bond length (1.47 (2) Å) is typical of a single bond between two sp^2-hybridized carbon atoms,[14] but the C(9)–N(1) (1.33 (1) Å) and C(9)–N(2) (1.32 (2) Å) distances are equivalent and indicative of multiple-bond character between carbon and nitrogen. In iminium ions of the type $R_2N{=}C$ where a full sp^2–sp^2 double bond is present, C–N bond distances lie in the range 1.28–1.38 Å.[15] The N(2)–C(9)–N(1)–C(8) moiety

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[11] Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25.

[12] Cherkas, A. A.; Randall, L. H.; Taylor, N. J.; Mott, G. N.; Yule, J. E.; Guinamant, J. L.; Carty, A. J. *Organometallics*, in press.

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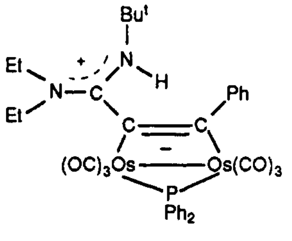
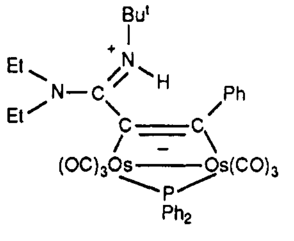
[15] Merenyi, R. Iminium Salts in Organic Chemistry, Part 1. In *Advances in Organic Chemistry: Methods and Results*; Bohme, H., Viehe, H. G., Eds.; Wiley: New York, 1976, *9*, 1.

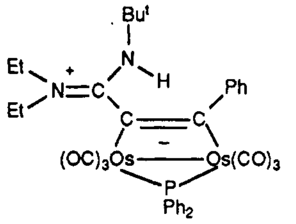
is practically planar (maximum deviation from the mean plane passing through the four atoms is 0.03 (1) Å for C(9)). All of this evidence points to the presence of two comparable bonds to the amidinium center C(9) with symmetrical multiple bonding from nitrogen lone pairs on sp^2-hybridized N(1) and N(2) into the formally vacant 2pπ orbital of C(9). Thus, the C(NEt$_2$)(NHPr^i) moiety may be considered as an electron-rich carbene substituent as in C or a resonance hybrid of the two limiting structures D and E. This situation contrasts with that found in the related complex derived from n-butanethiol Os$_2$(CO)$_6$[μ-η^2-C(SBu^n)(NHBu^t)CPh](μ-PPh$_2$), where electron delocalization to the amidinium center is limited to the CNHBu^t moiety.[10]



C



D

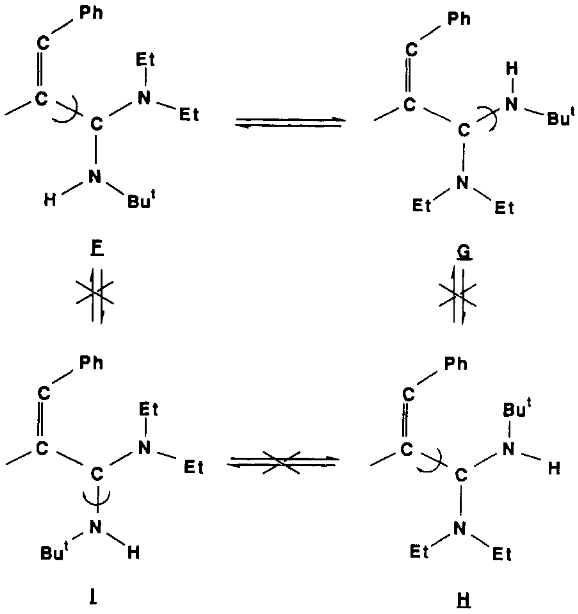


E

The C(8)–C(9)–N(1)–N(2) plane makes an angle of 70.6° with respect to the Os(1)–Os(2)–C(8)–C(7) metallacycle so that the carbene substituent lies roughly perpendicular to the C(7)–C(8) bond with N(1) oriented toward the bridging phosphido group. This arrangement presumably minimizes contacts with the phenyl substituent on C(7) and may indicate that free rotation about the single C(8)–C(9) bond is restricted (vide infra).

Spectroscopic Data. The IR spectra of 4 and **5a–c** in the ν(CO) region closely resemble those for the precursors, but the bands are shifted to slightly lower frequencies, consistent with greater charge transfer to the M$_2$(CO)$_6$ unit from the dipolar parallel acetylenes. In the isopropylamine adduct **5b** two ν(NH) bands were observed in Nujol mull spectra, indicating the presence of two different NH groups. The ^{13}C NMR spectra of **5a–c** in the ^{13}CO region are typical of static molecules on the NMR time scale, exhibiting six carbonyl resonances at 298 K, four of which are cis to the phosphido bridge and have small (0–10 Hz) $^2J_{\text{C-M-P}}$ couplings and two have large $^2J_{\text{C-M-P}}$ values (62–68 Hz) and are trans to the μ-PPh$_2$ group. The ^{31}P{^{1}H} NMR spectra of **5a–c** have a single phosphorus resonance downfield (101–106 ppm) of 85% H$_3$PO$_4$, characteristic of μ-PPh$_2$ groups bridging a strong osmium–osmium bond.[16]

Scheme II



For complex 4 the ^{31}P NMR spectra imply the presence of isomers in solution with four distinct signals present at 298 K. The major component of this pattern has a chemical shift of 106.02 ppm, while the remaining isomers (104.4, 104.3, 99.7 ppm) are present in lower concentrations. The ^{31}P NMR spectra of 4 were measured over the temperature range 298–373 K in an attempt to observe interconversion of the isomers. With increasing temperature the peak intensities of the isomers change with the two major peaks at 106 and 99.7 ppm broadening and disappearing as the two minor components at 104.4 and 104.3 ppm remain sharp. At 100 °C, the highest temperature accessible prior to decomposition, only the sharp resonances of the two minor isomers at 298 K remain. Unfortunately we were not able to obtain the high-temperature limiting spectrum, which would correspond to fast exchange of the two outer resonances in the ^{31}P spectrum. However, by using the equation $\Delta G^{\ddagger} = RT_c \ln [2K_BT_C/h\pi(\Delta\nu)]$,[17] we estimate the free energy of activation for the lower energy isomer conversion as 67.3 kJ mol^{-1}. In consideration of the structure of 4 the most likely rationale for the existence of isomers is restricted rotation about the C(8)–C(9) bond and about the C(9)–N(1) and C(9)–N(2) multiple bonds (Scheme II), which could give rise to the four isomers shown. Since the molecule possesses no axis or plane of symmetry, these isomers are diastereotopic. We suggest that the higher energy rotation in Scheme II is that corresponding to rotation about the C(9)–NHBu^t bond, since the X-ray data indicate that this is an iminium-like double bond. Rotation about the C(8)–C(9) bond, while sterically restricted, does not involve the breaking of a strong pπ–pπ interaction. Scheme II accounts for the possible existence of four isomers of 4, but the observation of only one interchanging pair in the ^{31}P NMR spectra implies that in one configuration, most likely H, the molecule is "locked" by the bulky *tert*-butyl group syn to the phenyl ring on C(7), preventing acess to isomer I. Thus, only two of the four isomers, F and G, related by a rotation about C(8)–C(9) when the *tert*-butyl group is anti to the phenyl ring, are interchangeable on the NMR time scale.

The same type of isomerism, leading to eight possible isomers, could in principle occur for **5a–c**. However, in these cases ^{31}P NMR studies showed only single-line spectra at 298 K and variable-temperature studies of **5b** provided no evidence for isomerism even over a wide temperature range. For these compounds either one predominantly stable isomer exists or the barriers to rotation are sufficiently low to permit fast equilibration of

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[16] Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *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, p 554.

[17] Binsch, G. *Top. Stereochem.* **1968**, *3*, 97.

isomeric species even at the lowest temperatures accessible.

The ^{13}C chemical shifts of the bound carbon atoms C(7) and C(8) of the acetylene as well as the amidinium center C(9) of the ligand are of some interest, since such shifts frequently provide an indication of the character of these atoms.[12] For 4 and **5a–c** the C_α and C_β resonances of the μ_2-‖-acetylene lie very close together in the range 147.1–171.7 ppm, in sharp contrast to the case for the precursor isonitrile adducts, which exhibit $\Delta(\delta_{C_\alpha}-\delta_{C_\beta})$ values of 172–142 ppm. The shifts in 4 and **5a–c** are somewhat downfield of the range for olefinic carbon signals (110–150 ppm)[18] but upfield of metal-bound carbenes. Clearly the electronic environments of C(7) and C(8) are not dramatically different in these compounds. The ^{13}C resonances for C(9) in 4 and **5a–c** were easily detected as nitrogen quadrupole broadened signals in the range 99–109 ppm.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work in the form of operating grants (A.J.C.), a postgraduate scholarship (A.A.C.), and an International Scientific Exchange Award (to E.S. and A.J.C.).

Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, and phenyl ring bond lengths and angles (4 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(18) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 289.

Distortions in the "Legs" of Four-Legged Piano-Stool Structures[†]

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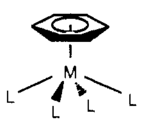
Received December 20, 1989

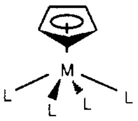
An analysis of existing four-legged piano-stool structures ($M(Ar)L_4$, $M(pd)L_4$; Ar = η^6-arene, pd = η^5-pentadienyl, L = two-electron-donor ligand) is presented. The dependency of the angle θ between the M–L and the M–Ar or M–pd vectors on the electronic structure and on the π-bonding ability of the ligand L is examined. The relevant conclusions from this analysis are that (i) the metal d_{z^2} orbital is a better base than the d_{xy} orbital, (ii) phosphine ligands exhibit distortions typical of π-acceptor ligands, (iii) halide ligands function as π donors in compounds with an electron count lower than 18, and (iv) the θ angle for a particular ligand strongly depends also on the nature of the ligand that is trans to it. The results of this anlysis can be used to qualitatively assess the π-bonding abilities of metals and ligands from structural data.

Introduction

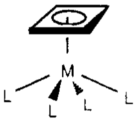
"Four-legged piano stool" is the commonly used terminology for structures of type I–III, i.e. containing a π-bonded cyclopolyene or cyclopolyenyl ligand and four additional σ-bonded two-electron-donor ligands (L). The structures may also be viewed as pseudo square pyramidal (sp) when the π-bonded ligand is considered to occupy a single coordination position.



I



II



III

A theoretical analysis of $MCpL_4$ compounds (Cp = η^5-cyclopentadienyl), type II, has been presented by Hoffmann.[1] In that work, the preference for the piano-stool structure over other possible isomers (isomeric pseudo-sp or pseudo-tbp geometries) was rationalized. The distortion of the Cp ring (tilting toward a η^3,η^2 conformation), which is sometimes observed experimentally, was also explained. However, the experimentally observed distortion of the four L ligands from the ideal pseudo-sp geometry (as measured by the angle L–M–Ct, θ; Ct = centroid of the Cp ligand) was not fully addressed.

We have recently prepared and structurally characterized a few members of the class of stable 17-electron radicals $MoCpX_2L_2$ (X = Cl, Br, I; L = phosphine)[2,3] and noticed distortions in the MoX_2L_2 moiety that differ substantially from those usually observed for 18-electron compounds of similar structure. This observation prompted us to analyze the origin of these distortions in more detail. We report here the results of this analysis, which allows the rationalization of our structural data and also of other data that are already available in the literature.

The Model

The electronic structures corresponding to the molecular structures I–III are expected to be qualitatively the same, since all three π ligands have a lower energy orbital involved in a σ interaction with the metal, followed at higher energy by two degenerate orbitals for a π donation (for the sake of homogeneity, we shall consider the cyclobutadiene ligand as an aromatic $C_4H_4^{2-}$, six-electron-donor system) and at least one orbital for a δ back-bonding interaction with the metal d_{xy} orbital (the arene and Cp ligands have two degenerate orbitals of this type, but only one can be used for δ back-bonding since the metal $d_{x^2-y^2}$ orbital is used up for the σ interaction with the four L ligands). Of the

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[†] Dedicated to Prof. F. Albert Cotton on the occasion of his 60th birthday.

(1) Kubácek, P.; Hoffman, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.
(2) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.
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