Acknowledgment. We wish to thank Michelle Modrick of Exxon Research and Engineering Co. for help and advice with the X-ray measurements, and in particular with calculating the penetration depth of the X-rays into the FeO samples.

Registry No. Fe, 7439-89-6; H$_2$O, 7732-18-5; O$_2$, 7782-44-7; FeO, 1345-25-1.

Supplementary Material Available: A summary of X-ray diffraction data (Table II) and figures showing the rate of formation of FeO as a function of water flow (Figure 2), X-ray spectra of sample 125-5 and reference spectra of Fe$_3$O$_4$ and FeO (Figure 9 and 10), SEM photographs of the coked FeO surface (Figure 16), and SEM photographs of a fractured section of FeO after coking (Figure 17) (7 pages). Ordering information is given on any current masthead page.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus,
Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada,
Istituto di Chimica Generale ed Inorganica, Università di Torino, 10125 Torino, Italy,
and Istituto di Chimica Generale ed Inorganica, Università di Parma, and Centro di Studio
per la Strutturistica Diffrattometrica del CNR, 43100 Parma, Italy

Conversion of a μ-η^2-Acetylide to a μ-η^2-$\|$-Acetylene via Successive Nucleophilic Additions. X-ray Structure of Os$_2$(CO)$_6$[μ-η^2-C{C(NH-*t*-Bu)(S-*n*-Bu)}CPh](μ-PPh$_2$)

Andrew A. Cherkas,[1a] Arthur J. Carty,*[1a] Enrico Sappa,[1b] Maria Angela Pellinghelli,[1c] and Antonio Tiripicchio[1c]

Received March 24, 1987

The diosmium acetylide complex Os$_2$(CO)$_6$(μ-η^2-C≡CPh)(μ-PPh$_2$) (**1**) has been converted in two stages to the parallel acetylene derivative Os$_2$(CO)$_6$[μ-η^2-C{C(NH-*t*-Bu)(S-*n*-Bu)}CPh](μ-PPh$_2$) (**3**). Nucleophilic attack at carbon by *t*-BuNC afforded Os$_2$(CO)$_6$[μ-η^2-C{CN-*t*-Bu}CPh](μ-PPh$_2$) (**2**), and subsequent elaboration of **2** with *n*-BuSH gave, via S–H addition to the isocyanide C≡N bond, the compound **3**. Complex **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 18.276 (9) Å, b = 19.307 (8) Å, c = 10.265 (5) Å, V = 3622 (3) Å^3, Z = 4, $F(000)$ = 1928, and μ = 71.60 cm^{-1}. The structure was solved and refined to R and R_w values of 0.044 and 0.049 by using 2451 ($I \geq 2\sigma(I)$) unique observed data measured on a Siemens AED diffractometer. The molecular structure of the binuclear molecule (Os–Os = 2.813 (3) Å) contains a phosphido bridge (Os(1)–P–Os(2) = 74.1 (2)°) and a dipolar, disubstituted μ-η^2-$\|$-acetylene with substituents Ph and C(NH-*t*-Bu)(S-*n*-Bu). The acetylide triple bond length in **1** (1.228 (18) Å) increased to 1.28 (2) Å in **3**.

Introduction

The interrelationships and reactivity patterns of multisite-bound unsaturated ligands are currently the focus of considerable attention in organometallic chemistry.[2] The acetylide ligand –C≡C—R occupies a significant position in the hierarchy of small unsaturated molecules for a number of reasons: (i) the acetylide anion is isoelectronic with CO, and its coordination behavior in polynuclear systems frequently resembles that of multisite-bound CO;[3] (ii) as a two-carbon fragment, the acetylide is a potential source of other important hydrocarbyls including vinylidene, vinyl, alkylidene, and alkylidyne groups; (iii) the acetylide ligand is unrivaled in its versatility as a bridging hydrocarbyl, with symmetrical μ, μ-η^2, μ_3-η^2, and μ_4-η^2 bonding modes all well established.[4] We have recently documented a number of C–C,[5] C–N,[6] and C–P[7] bond-forming reactions on μ_n-η^2-acetylides, and in this paper we wish to report the conversion of Os$_2$(CO)$_6$(μ-η^2-C≡CPh)(μ-PPh$_2$) (**1**) to the acetylene complex Os$_2$(CO)$_6$[μ-η^2-C{C(NH-*t*-Bu)(S-*n*-Bu)}CPh](μ-PPh$_2$) (**3**) via the strategy of successive nucleophilic additions of *t*-BuNC and *n*-BuSH. We note that Shriver[8] has recently demonstrated the transformation of a ketenylidene via a μ_3-η^2-acetylide to a μ_3-η^2-$\perp$-acetylene on an Fe$_3$ cluster.

Experimental Section

All manipulations were carried out on a double manifold by using standard Schlenk techniques. Solvents were dried as follows and distilled under nitrogen prior to usage: hexane and heptane, over LiAlH$_4$; benzene and cyclohexane, over Na$^+$Ph$_2$CO$^-$. Column chromatography utilized 100–200-mesh Florisil. IR spectra were measured on a Perkin-Elmer 180 instrument using matched sodium chloride solution cells of 0.5-mm path length. NMR spectra were recorded on Bruker AM-250 (^{1}H, 250 MHz; ^{31}P, 101.3 MHz) or WH-400 (^{1}H, 400 MHz; ^{31}P, 162.0 MHz; ^{13}C, 100.6 MHz) instruments. Chemical shifts are referenced to TMS and 85% H$_3$PO$_4$.

Syntheses: Os$_2$(CO)$_6$[μ-η^2-C{CN-*t*-Bu}CPh](μ-PPh$_2$) (2). The binuclear acetylide **1**[9] (30 mg, 0.036 mmol) was dissolved in *n*-heptane (7 mL) and a solution of *tert*-butyl isocyanide (38.8 mg, 0.47 mmol) in heptane (5 mL) added. The pale yellow solution gradually darkened, and a yellow precipitate formed. When IR monitoring indicated complete consumption of **1**, a few drops of benzene were added to dissolve the precipitate, the solution was adsorbed onto Florisil, and the stained Florisil was added to the top of a 7 × 1.5 cm column of the same material. The only

---

(1) (a) Guelph-Waterloo Centre. (b) Università di Torino. (c) Università di Parma.

(2) For a selection of recent references 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. (c) Vites, J. C.; Jacobsen, G.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563. (d) Beanan, L. R.; Keister, J. B. *Organometallics* **1985**, *4*, 1713. (e) Sailor, M. J.; Shriver, D. F. *Organometallics* **1985**, *4*, 1476. (f) Nuel, D.; Dahan, F.; Mathieu, R. *J. Am. Chem. Soc.* **1985**, *107*, 1658. (g) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783. (h) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1985**, *4*, 793. (i) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5621.

(3) (a) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113 and references therein. (b) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.

(4) See for example: (a) μ: Carty, A. J.; Taylor, N. J.; Smith, W. F. *J. Chem. Soc., Chem. Commun.* **1979**, 750. (b) μ-η^2: Smith, W. F.; Yule, J.; Taylor, N. J.; Paik, H. N.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 1593. Nubel, P. O.; Brown, T. L. *Organometallics* **1984**, *3*, 29. (c) μ_3-η^2: Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *204*, C27. Sappa, E.; Gambino, O.; Milone, L.; Cetini, G. *J. Organomet. Chem.* **1972**, *39*, 169. (d) μ_4-η^2: MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 1194. (e) Weatherell, C.; Taylor, N. J.; Carty, A. J.; Sappa, E.; Tiripicchio, A. *J. Organomet. Chem.* **1985**, *291*, C9.

(5) (a) Carty, A. J.; Mott, G. N.; Taylor, N. J. *J. Organomet. Chem.* **1981**, *212*, C54. (b) MacLaughlin, S. A.; Johnson, J. P.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1983**, *2*, 352. (c) Nucciarone, D.; Taylor, N. J., Carty, A. J. *Organometallics* **1986**, *5*, 1179. (d) Gervasio, G.; Sappa, E.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1983**, *68*, 171.

(6) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726.

(7) Carty, A. J.; Ferguson, G.; Khan, M. A.; Mott, G. N.; Roberts, P. J.; Taylor, N. J. *J. Organomet. Chem.* **1978**, *149*, 345.

(8) Hriljac, J. A.; Shriver, D. F. *Organometallics* **1985**, *4*, 2225.

(9) Cherkas, A. A.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J., unpublished results.

0020-1669/87/1326-3201$01.50/0

Table I. Experimental Data for the X-ray Diffraction Study on $C_{35}H_{34}NO_6Os_2PS$ (**3**)

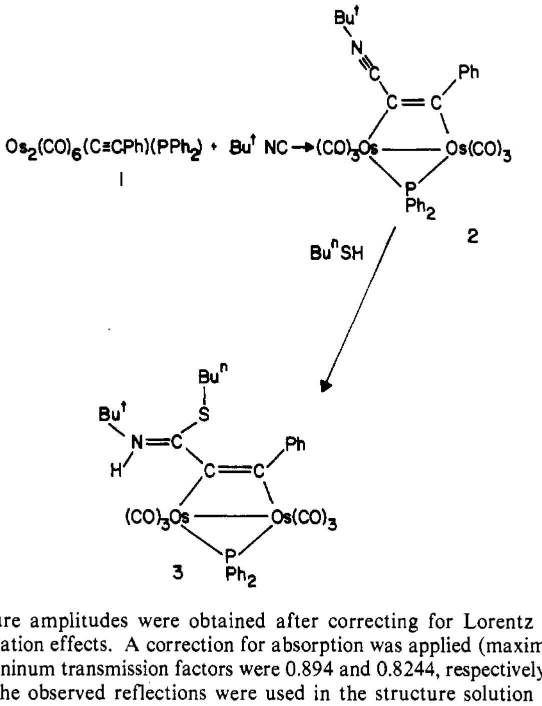
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	18.276 (9)
b, Å	19.307 (8)
c, Å	10.265 (5)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	3622 (3)
Z	4
$F(000)$	1928
D_{calcd}, g cm^{-3}	1.849
mol wt	1008.09
cryst dimens, mm	0.23 × 0.29 × 0.60
linear abs coeff, cm^{-1}	71.60
transmission factors	0.894–0.824
diffractometer	Siemens AED
scan type	$\theta/2\theta$
scan speed, θ/min	3–12
scan width, deg	$(\theta - 0.55)$–$(\theta + (0.55 + 0.346 \tan \theta))$
radiatn	Nb-filtered Mo Kα (λ = 0.71073 Å)
2θ range, deg	6–50
reflcns measd	$+h,+k,+l$
std reflcn	1 measd after every 50 reflcns
no. of unique tot. data	3743
no. of unique obsd data [$I \geq 2\sigma(I)$]	2451
no. of variables	249
R	0.044
R_w	0.049
final e Å^{-3} in diff map	0.80

movable band, bright yellow, was eluted with 50:50 heptane/benzene. After crystallization from n-C_7H_{16}/C_6H_6, 27.2 mg of **2** (~82%) was obtained. Anal. Calcd for $C_{31}H_{24}NO_6Os_2P$: C, 40.64; H, 2.80; N, 1.54. Found: C, 40.56; H, 2.64; N, 1.53. IR ν(CO) (C_6H_{12}): 2058 vs, 2024 vs, 1991 vs, 1967 w, 1958 s, 1937 w cm^{-1}. ^{1}H NMR (C_6D_6): δ 8.01–7.24 m (15 H, Ph), 0.6 s (9 H, t-Bu). ^{31}P NMR (C_6D_6): δ +103.5 s. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 211.5 (t-BuN*C*), 185.9 d (CO, J_{PC} = 72 Hz), 185.3 d (CO, J_{PC} = 65 Hz), 180.7 d (CO, J_{PC} = 5 Hz), 180.6 s (CO), 179.5 s (CO), 178.0 s (CO), 153.7 s (C–Ph ipso), 140.4 d (P–Ph ipso, J_{PC} = 36 Hz), 135.5 d (P–Ph ortho, J_{PC} = 9 Hz), 134–125 (C–Ph, 12 peaks), 69.7 s (C_α), 60.0 s (C_β), 29.9 (s, t-Bu *C*H_3), 29.3 (s, t-Bu *C*).

$Os_2(CO)_6[\mu$-η^2-C{C(NH-t-Bu)(S-n-Bu)}CPh](μ-PPh_2) (3). Treatment of **2** (100 mg, 0.109 mmol) in neat n-BuSH for 10 days at room temperature with continuous stirring gave a 50:50 mixture of **2** and product **3**, as indicated by IR monitoring. Solvent was removed in vacuo (*care*! vile odor); the orange oil was diluted with benzene (5 mL) and placed on a 10 × 1.5 cm Florisil column. Elution with 80:20 hexane/benzene removed the pale yellow band of **2**. The orange-yellow band of **3** was eluted with a 50:50 mixture of hexane and benzene. After crystallization from cyclohexane the yield of **3** was 38.1 mg (~35%). Approximately 40 mg of **2** was recovered. Anal. Calcd for $C_{35}H_{34}NO_6Os_2PS$: C, 41.73; H, 3.53; N, 1.20; P, 3.13; S, 3.58. Found: C, 41.70; H, 3.40; N, 1.39; P, 3.07; S, 3.18. IR ν(CO) (C_6H_{12}): 2053 s, 2012 s, 1979 s, 1958 w, 1949 m, 1927 m cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.7–6.3 m (15 H, Ph), 6.1 s br (1 H, NH), 2.8 m (2 H, CH_2), 2.1–2.0 m (2 H, CH_2), 1.2 s (9 H, t-Bu), 1.1 m (2 H, CH_2), 0.66 t (3 H, CH_3). ^{31}P NMR (C_6D_6): δ +98.8 s. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 199.5 s (BuN(H)*C*), 187.5 d (CO, J_{PC} = 64.2 Hz), 186.8 d (CO, J_{PC} = 71.6 Hz), 181.5 s (CO), 180.7 s (CO), 179.7 s (CO), 179.4 s (CO), 151.0 s (C–Ph ipso), 141.3 d (P–Ph ipso, J_{PC} = 7.9 Hz), 136.0 d (P–Ph ipso, J_{PC} = 9.5 Hz), 135–125 (Ph, 12 peaks), 57.4 s (C_α), 29.7 s (C_β), 27.8 s (t-Bu *C*H_3), 26.8 s (t-Bu *C*), 34.9 s (n-BuS*C*), 29.6 s (n-BuSC*C*), 21.9 s (n-BuSC$_2$*C*), 13.3 s (n-Bu*C*H_3).

X-ray Crystal Structure of 3. Crystals of **3** suitable for X-ray study were grown from cyclohexane as orange-yellow prisms. An appropriate crystal was selected, attached to a glass fiber, and mounted on a Siemens AED diffractometer. Crystal data and experimental parameters for data collection are given in Table I. Systematic absences (h00, h = 2n; 0k0, k = 2n; 00l, l = 2n) uniquely defined the space group as $P2_12_12_1$. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 carefully centered reflections (with θ in the range 10–15°). Intensities were measured at room temperatue, the individual reflection profiles having been analyzed according to Lehmann and Larsen.[10] The structure amplitudes were obtained after correcting for Lorentz and polarization effects. A correction for absorption was applied (maximum and mininum transmission factors were 0.894 and 0.8244, respectively).[11] Only the observed reflections were used in the structure solution and refinement.

Scheme I



The structure was solved by heavy-atom and Fourier methods and refined by full-matrix least squares (first with isotropic and then with anisotropic thermal parameters for the Os, S, P, O, N, and C(1)–C(9) atoms with the phenyl rings treated as rigid groups). At the end of the refinement an effort was made to locate a hydrogen atom on the two possible sites (N and S) of the new ligand through a difference Fourier map. A search of residual electron density in the region of the sulfur atom revealed no features consistent with the presence of a hydrogen atom. On the contrary, a peak (~0.33 e Å^{-3}) near the nitrogen atom at a distance of 0.79 Å was found attributable to a hydrogen atom. Its coordinates were not refined, but introduced, together with those of the other hydrogen atoms placed at their geometrically calculated positions in the final structure factor calculation with fixed isotropic thermal parameters (B = 7.0 Å^2). In an independent final cycle of refinement the coordinates $-x$, $-y$, $-z$ were used for the non-hydrogen atoms because of the acentric space group. No improvement in the R value was obtained [$R(x, y, z)$ = 0.045; $R(-x, -y, -z)$ = 0.053]. The former model was selected, and the reported data refer to this model. The function minimized in the refinement was $\sum w|\Delta F|^2$. The weighting scheme used in the last cycles was $w = K/[\sigma^2(F_o) + gF_o^2]$; at convergence the values for K and g were 0.6210 and 0.0016, respectively. The final R and R_w values were 0.044 and 0.049 ($R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. Scattering factors were taken from tabulations in ref 12a, with the exception of those for the hydrogen atoms.[12b] Data reduction, structure solution, and refinement were carried out on a CRAY X-MP/12 computer of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, and on a GOULD 32/77 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, by using the SHELX-76 system of crystallographic computer programs.[12c]

In Table II the atomic coordinates of the non-hydrogen atoms are given, and in Table III selected bond distances and angles are reported. The calculated (except for the H(1)N) coordinates of the hydrogen atoms (Table S1), the thermal parameters (Table S2), a complete listing of bond distances and angles (Table S3), and the listing of structure factors (Table S4) have been deposited.

Results and Discussion

Treatment of the μ-η^2-acetylide **1** with an excess of t-BuNC at ambient temperature results in exclusive attack of the latter at the α-carbon atom of the acetylide, generating a new car-

---

(10) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(11) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158. The program ABSORB was used, written by F. Ugozzoli, University of Parma.

(12) (a) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. (c) Sheldrick, G. M. "SHELX-76"; University of Cambridge: Cambridge, England, 1976.

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

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Os(1)	140 (1)	1584 (1)	1399 (1)	C(13)	−2286 (19)	−902 (17)	2817 (38)
Os(2)	703 (1)	238 (1)	1712 (1)	C(14)	−825 (13)	2505 (12)	5684 (22)
S	−1616 (3)	1302 (4)	4127 (8)	C(15)	−253 (16)	3005 (15)	6108 (28)
P	1275 (3)	1274 (3)	2281 (5)	C(16)	−1360 (16)	2965 (15)	4973 (29)
O(1)	−1265 (12)	1091 (12)	149 (25)	C(17)	−1101 (16)	2111 (15)	6775 (31)
O(2)	−88 (13)	3070 (9)	2293 (21)	C(18)	−79 (7)	92 (7)	4563 (10)
O(3)	746 (12)	1903 (14)	−1327 (19)	C(19)	−57 (7)	399 (7)	5792 (10)
O(4)	−612 (10)	−543 (10)	661 (20)	C(20)	−243 (7)	14 (7)	6893 (10)
O(5)	1598 (11)	−894 (11)	2961 (20)	C(21)	−452 (7)	−678 (7)	6764 (10)
O(6)	1562 (11)	175 (12)	−815 (19)	C(22)	−473 (7)	−985 (1)	5534 (10)
N	−463 (8)	2013 (8)	4730 (15)	C(23)	−287 (7)	−600 (7)	4434 (10)
C(1)	−740 (13)	1308 (12)	639 (19)	C(24)	2127 (6)	1488 (8)	1484 (15)
C(2)	−7 (12)	2483 (12)	1940 (22)	C(25)	2716 (6)	1039 (8)	1680 (15)
C(3)	542 (15)	1785 (15)	−249 (24)	C(26)	3394 (6)	1185 (8)	1121 (15)
C(4)	−126 (12)	−273 (14)	1001 (25)	C(27)	3484 (6)	1780 (8)	365 (15)
C(5)	1262 (14)	−481 (11)	2525 (24)	C(28)	2896 (6)	2229 (8)	169 (15)
C(6)	1259 (13)	171 (11)	142 (22)	C(29)	2217 (6)	2082 (8)	728 (15)
C(7)	63 (9)	501 (9)	3403 (16)	C(30)	1469 (8)	1499 (8)	3967 (12)
C(8)	−193 (9)	1110 (9)	3218 (17)	C(31)	1664 (8)	983 (8)	4853 (12)
C(9)	−702 (11)	1511 (10)	4046 (18)	C(32)	1866 (8)	1160 (8)	6120 (12)
C(10)	−1700 (14)	479 (14)	3290 (29)	C(33)	1874 (8)	1854 (8)	6502 (12)
C(11)	−2536 (15)	344 (15)	3125 (28)	C(34)	1679 (8)	2370 (8)	5616 (12)
C(12)	−2575 (16)	−278 (17)	2218 (30)	C(35)	1476 (8)	2193 (8)	4349 (12)

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

Os(1)–Os(2)	2.813 (3)	C(5)–O(5)	1.10 (3)
Os(1)–P	2.341 (6)	C(6)–O(6)	1.13 (3)
Os(2)–P	2.331 (6)	P–C(24)	1.81 (1)
Os(1)–C(1)	1.87 (2)	P–C(30)	1.82 (1)
Os(1)–C(2)	1.84 (3)	C(7)–C(8)	1.28 (2)
Os(1)–C(3)	1.88 (3)	C(7)–C(18)	1.45 (2)
Os(1)–C(8)	2.17 (2)	C(8)–C(9)	1.48 (3)
Os(2)–C(4)	1.95 (2)	C(9)–N	1.27 (2)
Os(2)–C(5)	1.92 (2)	N–C(14)	1.52 (3)
Os(2)–C(6)	1.91 (2)	C(9)–S	1.72 (2)
Os(2)–C(7)	2.15 (2)	S–C(10)	1.81 (3)
C(1)–O(1)	1.16 (3)	C(10)–C(11)	1.56 (4)
C(2)–O(2)	1.20 (3)	C(11)–C(12)	1.52 (4)
C(3)–O(3)	1.19 (3)	C(12)–C(13)	1.45 (5)
C(4)–O(4)	1.09 (3)		

Os(2)–Os(1)–P	52.8 (2)	C(5)–Os(2)–C(7)	96.3 (9)
Os(2)–Os(1)–C(1)	95.7 (7)	C(6)–Os(2)–C(7)	170.1 (8)
Os(2)–Os(1)–C(2)	152.8 (7)	Os(1)–P–Os(2)	74.1 (2)
Os(2)–Os(1)–C(3)	98.6 (8)	Os(1)–P–C(24)	122.0 (6)
Os(2)–Os(1)–C(8)	67.3 (5)	Os(1)–P–C(30)	118.7 (5)
P–Os(1)–C(1)	148.5 (7)	Os(2)–P–C(24)	118.0 (5)
P–Os(1)–C(2)	104.7 (7)	Os(2)–P–C(30)	122.1 (5)
P–Os(1)–C(3)	93.1 (8)	C(24)–P–C(30)	102.0 (7)
P–Os(1)–C(8)	78.9 (5)	Os(1)–C(1)–O(1)	175 (2)
C(1)–Os(1)–C(2)	105.6 (10)	Os(1)–C(2)–O(2)	179 (2)
C(1)–Os(1)–C(3)	91.1 (10)	Os(1)–C(3)–O(3)	175 (2)
C(1)–Os(1)–C(8)	89.9 (8)	Os(2)–C(4)–O(4)	176 (2)
C(2)–Os(1)–C(3)	97.7 (11)	Os(2)–C(5)–O(5)	178 (2)
C(2)–Os(1)–C(8)	95.6 (8)	Os(2)–C(6)–O(6)	175 (2)
C(3)–Os(1)–C(8)	165.9 (10)	Os(2)–C(7)–C(8)	107 (1)
Os(1)–Os(2)–P	53.1 (2)	Os(2)–C(7)–C(18)	129 (1)
Os(1)–Os(2)–C(4)	98.1 (7)	C(8)–C(7)–C(18)	124 (2)
Os(1)–Os(2)–C(5)	156.1 (7)	Os(1)–C(8)–C(7)	114 (1)
Os(1)–Os(2)–C(6)	99.3 (7)	Os(1)–C(8)–C(9)	117 (1)
Os(1)–Os(2)–C(7)	71.1 (5)	C(7)–C(8)–C(9)	129 (2)
P–Os(2)–C(4)	151.2 (7)	C(8)–C(9)–N	120 (2)
P–Os(2)–C(5)	105.9 (8)	C(8)–C(9)–S	121 (1)
P–Os(2)–C(6)	91.8 (7)	N–C(9)–S	119 (2)
P–Os(2)–C(7)	80.8 (5)	C(9)–N–C(14)	133 (2)
C(4)–Os(2)–C(5)	102.2 (10)	C(9)–S–C(10)	105 (1)
C(4)–Os(2)–C(6)	93.6 (10)	S–C(10)–C(11)	106 (2)
C(4)–Os(2)–C(7)	89.9 (9)	C(10)–C(11)–C(12)	104 (2)
C(5)–Os(2)–C(6)	92.0 (10)	C(11)–C(12)–C(13)	112 (3)

bon–carbon bond (Scheme I). The reaction is regiospecific, there being no evidence for nucleophilic addition to the β-carbon atom nor for CO displacement by the isocyanide. Thus under these conditions CO substitution is not competitive with adduct formation. In the corresponding iron system,[5a] nucleophilic attack also occurs at C_α, but CO substitution leading to $Fe_2(CO)_{6-n}(CN\text{-}t\text{-}Bu)_n(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (n = 1, 2) also occurs above 0 °C. Complex **2** was fully characterized analytically and spectroscopically. The pattern of ν(CO) frequencies and intensities closely resembles that of the iron analogue, for which an X-ray structure is available.[5a] The ^{31}P NMR spectrum exhibits a single resonance, typical of a μ-PPh_2 group across a short Os–Os vector.[13] The ^1H NMR spectrum shows only *t*-Bu and Ph proton resonances, and the ^{13}C NMR spectrum exhibits six nonequivalent CO resonances and signals at δ 69.7, 60.0, and 211.5 assignable to C_α and C_β of the acetylene and the carbon atom derived from the isocyanide. The molecule is thus nonfluxional at 298 K. Extended Hückel MO calculations on **1** show that, for the molecular geometry adopted in the crystal structure,[9] in which the acetylene triple bond lies almost parallel with the Os–Os bond, the LUMO is located principally on C_α. Thus regiospecificity in this case is orbital controlled.

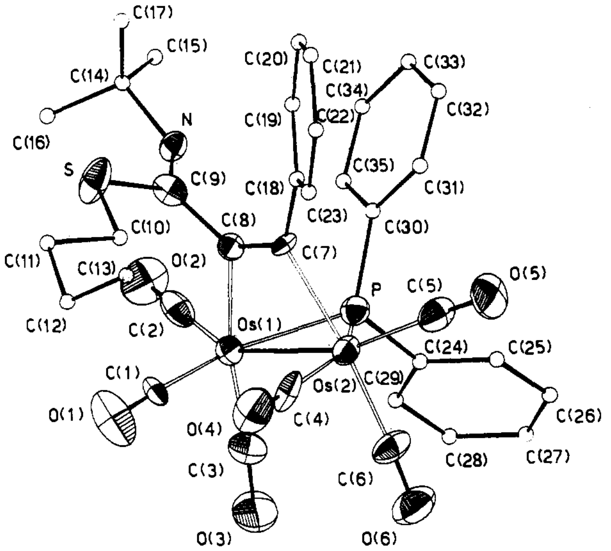


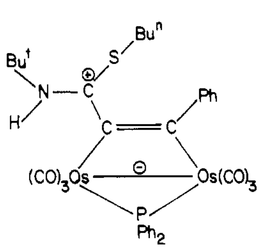
Figure 1. View of the structure of $Os_2(CO)_6[\mu\text{-}\eta^2\text{-}C\{C(NH\text{-}t\text{-}Bu)(S\text{-}n\text{-}Bu)\}CPh](\mu\text{-}PPh_2)$ (3) showing the atomic numbering. Phenyl ring and butyl group carbon atoms have been arbitrarily reduced in size for clarity.

---

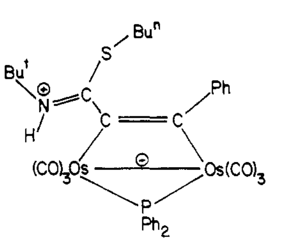
(13) (a) Carty, A. J. *Adv. Chem. Ser.* **1981**, *No. 196*, 163. (b) Carty, A. J.; MacLaughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Complexes*; Verkade, J. G., Quinn, L. D., Eds.; VCH: New York, 1986; Chapter II.

Further evidence for the structure of **2** comes from the nature of its reaction product **3** obtained via the addition of *n*-butyl mercaptan (Scheme I). Principal spectroscopic features of **3** are a ^{31}P shift at δ +98.8 for a μ-PPh_2 group with an acute M–P–M angle,[13] six nonequivalent ^{13}CO resonances, and a sharp ν(N–H) infrared band at 3280 cm^{-1} typical of a non-hydrogen-bonded N–H group.[14] The X-ray structure of **3**, depicted in Figure 1, consists of a pair of osmium atoms separated by a short Os–Os bond [2.813 (3) Å) and symmetrically bridged by a phosphido group [Os(1)–P = 2.341 (6) Å, Os(2)–P = 2.331 (6) Å]. The Os(1)–P–Os(2) angle is acute [74.1 (2)°]. Complex **3** is one of the few diosmium carbonyls to have been structurally characterized; the closest comparisons are with **1** [Os(1)–Os(2) = 2.7950 (6) Å, Os(1)–P–Os(2) = 72.61 (7)°][9] and with the μ-alkylidene complex $Os_2(CO)_6[\mu$-$CHC(Ph)NEt_2](\mu$-$PPh_2)$ [Os(1)–Os(2) = 2.741 Å, Os(1)–P–Os(2) = 70.8°].[15] In the recently reported $Os_2(CO)_6(\mu$-$PPh_2)(\mu$-I) complex[16] the Os–Os distance is 2.789 (1) Å; a somewhat longer distance, 2.8850 (5) Å, has been found in the dimetallacyclobutane complex $Os_2(CO)_8(\mu$-η^1,η^1-$CH_2CHCO_2CH_3)$.[17] All these distances are well within the range of values found for Os–Os single bonds.[18]

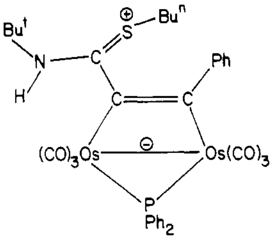
The new hydrocarbyl ligand, which is the principal source of interest, is bonded to the two osmium atoms via σ-interactions to C(7) [Os(2)–C(7) = 2.15 (2) Å] and C(8) [Os(1)–C(8) = 2.17 (2) Å]. The four-atom fragment Os(1)–Os(2)–C(7)–C(8) is planar, there being no statistically significant deviation from the mean plane through these atoms. The C(7)–C(8) distance, 1.28 (2) Å, compares well with the corresponding bond length of 1.33 (2) Å found in $Fe_2(CO)_6[\mu_2$-η^2-C{CN-*t*-Bu}CPh](μ-PPh_2)[5a] but is shorter than that of 1.424 (23) Å reported for the closely related triosmium cluster $Os_3(CO)_9[\mu_3$-η^2-C{C(NH-*t*-Bu)(NH-*n*-Bu}-CPh](μ-PPh_2).[5b] Thus the hydrocarbyl in **3** is a μ-η^2-‖-acetylene[19] with phenyl and C(R)(R′) substituents. Three possible descriptions for this zwitterionic acetylene ligand are those represented by A, where C(9) is a carbenium ion center, B, an iminium ion, and C, where the center of positive charge is a sulfonium ion. Although in principle the addition of *n*-BuSH to **2** could have occurred with retention of the hydrogen atom on sulfur, there are several other lines of evidence that suggest addition of S—H across the N═C bond of the "carbon-coordinated" isocyanide. An N—H bond is clearly indicated by solid-state IR and ^1H NMR data. Moreover, whereas the X-ray study did not reveal any evidence for an S—H hydrogen atom, there were some indications in an electron density difference map (see Experimental Section) for an N—H bond length of 0.79 Å. The C(14)–N–C(9) bond angle, 133 (2)°, is also consistent with an approximate sp^2 hybridization at the nitrogen atom. In the absence of multiple bonding to either of the heteroatoms, the carbenium ion form A might be expected to be a major contributor to the ground state of **3**. Consistent with this, the stereochemistry at C(9) is strictly planar. However, an examination of the bond lengths to C(9) clearly indicates that the fragment C(NH-*t*-Bu)(S-*n*-Bu) has iminium ion character. Thus the C(9)—N bond length of 1.27 (2) Å, although considerably longer than the C═N bond in coordinated isocyanides (values of 1.144 (5) and 1.148 (5) Å have been found in $Fe_2(CO)_4(t$-$BuNC)_2(\mu$-η^2-C≡CPh)(μ-PPh_2)),[5a] nevertheless has multiple-bond character. The S–C(9) distance, 1.72 (2) Å, on the other hand, is only marginally shorter than that predicted for a single bond on the basis of the covalent radii of sulfur (1.02 Å) and sp^2 carbon (0.74 Å). Thus, the correct description for the hydrocarbyl ligand [(*t*-BuNH)(S-*n*-Bu)CC═CPh] is that of an azene yne in its zwitterionic form, as represented by B. In this form the iminium nitrogen atom bears a formal positive charge with the negative charge delocalized into the $M_2(CO)_6(\mu$-$PPh_2)$ fragment. The plane containing the atoms C(9), N, S, and C(8) lies approximately perpendicular to the plane containing the μ-η^2-acetylene carbon atoms C(7) and C(8) and the metal atoms (the dihedral angle between these planes is 75.4 (4)°). Finally, it is worth noting that the C(8)–C(9) bond length, 1.48 (3) Å, is consistent with a single bond between two sp^2-hybridized carbon atoms.



A



B



C

The net effect of the sequence of reactions in Scheme I has been to convert an acetylide to a difunctionalized acetylene. This process has occurred via C–C and C–S bond-forming reactions. Complex **3** can also be regarded as a diosmacyclobutene, examples of which have recently been characterized.[20]

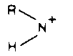
Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work in the form of operating grants (to A.J.C.) and an International Scientific Exchange Award (to E.S.).

Registry No. **1**, 109976-28-5; **2**, 109976-29-6; **3**, 109996-14-7; *n*-BuSH, 109-79-5; *t*-BuNC, 7188-38-7.

Supplementary Material Available: Tables of fractional coordinates (Table S1), anisotropic and isotropic thermal parameters (Table S2), and bond lengths and angles (Table S3) (6 pages); a listing of calculated and observed structure factors (Table S4) (14 pages). Ordering information is given on any current masthead page.

---

[14] ν(N–H) of



in $Fe_2(CO)_6[C(NH$-c-$C_6H_{11})CH(C_6H_5)][P(C_6H_5)_2]$ is at 3280 cm^{-1}.

[15] Cherkas, A. A.; MacLaughlin, S. A.; Granby, R. A.; Hoffman, D.; Taylor, N. J.; Carty, A. J., submitted for publication in *Organometallics*.

[16] Geoffroy, G. L.; Rosenberg, S.; Herlinger, A. W.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 2916.

[17] Burke, M. R.; Takats, J.; Grevels, F. W.; Reuvers, J. G. A. *J. Am. Chem. Soc.* **1983**, *105*, 4092.

[18] Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926.

[19] For recent reviews of metal–acetylene structural systematics see: (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Halet, J. F.; Saillard, J. Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, *24*, 218. (c) Einstein, F. W. B.; Tyers, K. G.; Tracey, A. S.; Sutton, D. *Inorg. Chem.* **1986**, *25*, 1631.

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