

**MULTI-SITE BOUND HYDROCARBYLS ON OSMIUM CLUSTERS. THE REACTIONS OF t-BUTYLACETYLENE WITH  $\text{Os}_3(\text{CO})_{12}$  AND  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ . CHARACTERIZATION OF THE PRODUCTS AND CRYSTAL STRUCTURE OF  $\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CHBu}^t)$**

ENRICO SAPPA,

*Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso M. D'Azeglio 48, 10125 Torino (Italy)*

ANTONIO TIRIPICCHIO and ANNA MARIA MANOTTI LANFREDI

*Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffratometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma (Italy)*

(Received January 27th, 1983)

### Summary

As part of a study of the role of hydridoacetylide and hydridoalkenylosmium clusters as intermediates in the synthesis of heterometallic osmium-nickel derivatives, 3,3-dimethylbut-1-yne complexes of  $\text{Os}_3(\text{CO})_{12}$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  were synthesized and characterized. The structure of the hydridovinyl compound  $\text{HOs}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CH}=\text{CHBu}^t)$  has been determined by X-ray diffraction; the crystals are monoclinic, space group  $P2_1/n$  with  $a$  13.861(10),  $b$  17.177(11),  $c$  9.267(7) Å,  $\beta$  108.01(4)° and  $Z = 4$ . The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares to a  $R$  value of 0.052 for 2290 observed reflections.

This cluster is one of the few  $\mu\text{-}\eta^2$ -alkenyl compounds to have been structurally characterized. The alkenyl-ligand bridges the Os(2)–Os(3) edge forming a  $\sigma$ -bond to Os(2) and a  $\pi$ -bond to Os(3). The C(11)–C(12) bond length of the alkenyl ligand is 1.38(4) Å. The orientation of the ligand in the cluster and the NMR behaviour of the cluster are discussed. Relationships between the various clusters derived from t-butylacetylene are outlined.

### Introduction

We previously described the synthesis of the mixed-metal hydridovinylidene compounds  $(\eta^5\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_9(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}=\text{CHR})$  ( $\text{R} = \text{Bu}^t, \text{Pr}^i$ ) [1,2]. These clusters can be obtained in about 15% yield based on ruthenium by treating the complexes  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CR})$  [3] with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2$  under

nitrogen, and in lower yield (ca. 2%) by treating  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{HC}_2\text{R})$  with  $\text{Ru}_3(\text{CO})_{12}$ . The use of a hydrogen atmosphere in these reactions considerably improves the yields (45 and 10%, respectively). Two plausible mechanisms for the formation of these ruthenium-nickel butterfly clusters can be considered, one involves the intermediacy of hydrogenated derivatives of the acetylide cluster  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CR})$ , and the other requires the opening, in the presence of alkyne, of the 60-electron tetrahedral cluster  $(\eta^5\text{-C}_5\text{H}_5)\text{NiRu}_3(\text{CO})_9(\mu\text{-H})_3$  found as a by-product in the reactions under hydrogen.

Unfortunately, for ruthenium the proposed intermediates are accessible only in low yields. However, the analogous osmium complexes  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CHR})$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\text{CO})_9(\mu\text{-H})_3$  [4,5] can be obtained in good yields by the reaction of  $\text{Os}_3(\text{CO})_{12}$  with alkynes or with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2$  in the presence of hydrogen.

An investigation of the proposed reaction pathways for the mixed metal clusters was therefore undertaken with osmium complexes. The 3,3-dimethylbut-1-yne,  $\text{HC}\equiv\text{CBu}^t$ , was chosen as an appropriate unsaturated species, since it was used in earlier work [6]. Although complexes of this alkyne with  $\text{Os}_3(\text{CO})_{12}$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  have been very briefly mentioned in the literature [7,8] the reactions have not been fully described nor the products completely characterized.

In this paper we report a complete study of the reactions of  $\text{Os}_3(\text{CO})_{12}$  and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with  $\text{HC}\equiv\text{CBu}^t$ , spectroscopic characterization of the products, and a complete single crystal X-ray structure analysis of  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-HC}=\text{CHBu}^t)$ . In contrast to the large number of  $\mu\text{-}\eta$ -acetylide derivatives of the iron triad which have recently been characterized, cluster bound alkenyls are relatively rare [9–13]. The structure determination of  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-HC}=\text{CHBu}^t)$  affords the opportunity for a comparison of structural parameters for multi-site bound acetylide,  $\text{-C}\equiv\text{CBu}^t$ , vinylidene,  $=\text{C}=\text{CHBu}^t$ , and alkenyl,  $\text{-HC}=\text{CHBu}^t$ , ligands. A subsequent paper will deal with the conversion of the intermediates to the mixed vinylidene clusters.

## Experimental

*Reactions of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{HC}\equiv\text{CBu}^t$ .* In an earlier paper [14] 25% yields of  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CBu}^t)$  (I) were reported from the reaction of  $\text{HC}\equiv\text{CBu}^t$  with  $\text{Os}_3(\text{CO})_{12}$  in refluxing heptane for several hours. In our hands, satisfactorily reproducible yields were obtained by refluxing  $\text{Os}_3(\text{CO})_{12}$  with a 5/1 excess of alkyne in n-octane for 15 minutes under nitrogen. The resulting brown solution contains ca. 50% of unreacted osmium carbonyl; cooling, filtering, and TLC purification gave 25–30% yields of I, based on the osmium carbonyl taken. Small amounts of alkyne-tri- and tetra-osmium clusters (about 5% yield in each case) were also isolated. Physical and spectroscopic data for these derivatives are summarized in Table 1.

*Reactions of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with  $\text{HC}\equiv\text{CBu}^t$ .* These were performed as reported for other alkynes [7,8,12]. Treatment of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with a 1.2 to 1 molar excess of t-butylacetylene gave high yields of  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-HC}=\text{CHBu}^t)$  (II) as the sole product. Use of a greater excess of alkyne led to the formation of II together with  $\text{HOs}_3(\text{CO})_{10}(\text{C}=\text{CHBu}^t)$  (III), in small yield, and  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{HC}=\text{CBu}^t)$  (IV).

Refluxing of solutions of II in hexane or octane for 2 h gave, respectively, five and seven products; among these complex I was present in considerable amount, along with  $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CHBu}^t)$  (V) and  $\text{Os}_3(\text{CO})_{10}(\text{HC}=\text{CBu}^t)$  (VI), and approximately ca. 5% each of tri- and tetra-alkyneosmium clusters.

The physical and spectroscopic characteristics of complexes II–VI are listed in Table 1. Satisfactory elemental analyses were obtained for all the complexes.

*Purification and analyses of the products.* All reactions were performed in conventional glass apparatus under dry nitrogen. The products were purified on TLC preparative plates (Kieselgel P.F. Merck, the eluents were mixtures of light petroleum and diethyl ether). The products were crystallized when possible from heptane or heptane/chloroform mixtures kept at  $-10^\circ\text{C}$  under nitrogen.

Microanalyses of the products were performed with an F&M 185, C, H, N Analyzer and a Perkin–Elmer AAS. The mass spectra were obtained on a single focusing Hitachi–Perkin–Elmer RMU 6H instrument operating with a direct inlet system and E.I. equipment at 70 eV. The IR spectra were obtained on a Perkin–Elmer 580B instrument equipped with KBr optics; the  $^1\text{H}$  NMR spectra were recorded on a JEOL C 60 HL instrument.

#### *Crystal data and structure determination for complex II*

Bright orange crystals of II were obtained by cooling heptane solutions. A prismatic crystal having dimensions ca.  $0.16 \times 0.20 \times 0.44$  mm was used for data collection. The cell parameters were refined by a least-squares procedure applied to the  $\theta$  values of 29 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Crystal data are as follows:  $\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{Os}_3$ ,  $M = 934.86$ , monoclinic,  $a$  13.861(10),  $b$  17.177(11),  $c$  9.267(7) Å,  $\beta$  108.01(4) $^\circ$ ;  $V$  2098(3) Å $^3$ ;  $Z = 4$ ;  $D_c$  2.959 g cm $^{-3}$ ; Mo- $K_\alpha$  radiation ( $\lambda$  0.71069 Å),  $\mu(\text{Mo-}K_\alpha)$  181.98 cm $^{-1}$ ; space group  $P2_1/n$  from systematic absences.

Intensity data were collected on the same diffractometer using Nb-filtered Mo- $K_\alpha$  radiation and the  $\theta/2\theta$  scan technique. The intensity of a standard reflection was measured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A total of 3692 independent reflections was measured in the range  $3 \leq \theta \leq 25^\circ$ ; of these 2290, having  $I \geq 2\sigma(I)$ , were considered observed and used in the analysis. The structure amplitudes were obtained after the usual correction for Lorentz and polarization factors and the absolute scale was established by Wilson's method. No correction for absorption was applied.

The structure was solved by direct and Fourier methods and refinement was carried out by least squares full matrix cycles using the SHELX system of computing programs [15] with initially isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms. No attempts were made to localize the hydrogen atoms, which were placed in their geometrically calculated positions (except for the hydridic hydrogen atom) and introduced in the final structure factor calculations. The final  $R$  was 0.052 for the observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of Os atom) were taken from reference 16. The function minimized in the least-squares calculation was  $\sum w|\Delta F|^2$ . Unit weights were used in the first stages of the refinement, in the final cycles the weight used was calculated as  $w = K/(\sigma^2(F_0) + gF_0^2)$  with  $K = 0.5838$  and  $g = 0.009452$ .

(Continued on p. 397)

TABLE 1  
 PHYSICAL AND SPECTROSCOPIC CHARACTERISTICS FOR THE ALKYNE-, ACETYLIDE- AND VINYLIDENE-OSMIUM DERIVATIVES (WITH *t*-BUTYL SUBSTITUENTS)

Complex	$\nu(\text{CO})$ (hexane solution) ( $\text{cm}^{-1}$ )	$^1\text{H NMR}$ ( $\delta$ (ppm), $\text{CDCl}_3$ )	Mass spectrum ( $m/e$ )	Ref.
<i>(A) Reactions of <math>\text{Os}_3(\text{CO})_{12}</math></i>				
$\text{HOs}_3(\text{CO})_9(\text{C}_2\text{Bu}^t)$	2099m, 2079vs, 2052vs, 2020vs, 2010s(sh), 1981m <sup>a</sup> 2100m, 2072vs, 2052vs, 2010vs, 1984m-s	1.50 s (9H), -23.5s (1H)	$P^+$ 904 loss of 9 CO's	14 this work
$\text{Os}_3(\text{CO})_6(\text{HC}_2\text{Bu}^t)_4(\text{CO})^b$	2052m, 2034s, 2016vs, 1974s, 1962m	9.46s(1H), 6.46s(1H), 4.55d(1H), 2.60d(1H), 1.50d(18H), 1.15d(18H)	$P^+$ 1094 loss of 6 CO's	this work
$\text{Os}_3(\text{CO})_6(\text{HC}_2\text{Bu}^t)_4(\text{CO})^b$	2048m, 2021vs, 2010vs, 1974m-b, 1962m	9.28s(1H), 6.30s(1H), 3.50d(1H), 2.85d(1H), 1.55d(18H), 1.25s(9H), 1.15s(9H)	$P^+$ 1094 loss of 6 CO's	this work
$\text{Os}_3(\text{CO})_7(\text{HC}_2\text{Bu}^t)_3^c$	2084m, 2057m-s, 2033s, 2008vs, 1996vs, 1967s, 1925s	8.85s(1H), 5.25d(1H), 3.30d(1H), 1.30m(27H)	$P^+$ 1020 loss of 7 CO's	this work

$\text{Os}_3(\text{CO})_7(\text{HC}_2\text{Bu}^t)_3^c$	dark-yellow solid	2083m, 2058m, 2032s, 2008vs, 1996vs, 1967s, 1920s	8.90s(1H), 5.20d(1H), 4.80d(1H), 1.25m(27H)	$P^+$ 1020 loss of 7 CO's	this work
<i>(B) Reactions of <math>\text{H}_2\text{Os}_3(\text{CO})_{10}</math></i>					
$\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CHBu}^t)$	orange crystals	2108m, 2068vs, 2040s, 2020vs, 2000s(sh), 1982m	see below	$P^+$ 936 loss of 10 CO's	this work
$\text{HOs}_3(\text{CO})_{10}(\text{C}=\text{CHBu}^t)$	yellow crystals	2102m-w, 2065s, 2056vs, 2050s(sh), 2038vs, 2007s(sh), 1998s, 1992m	2.20s(1H), 1.40s(9H), -22.80s(1H)	$P^+$ 935 loss of 10 CO's	this work
$\text{H}_2\text{Os}_3(\text{CO})_9(\text{HC}=\text{CBu}^t)$	light yellow solid	2106m, 2076vs, 2057vs, 2028s, 2020s, 2010vs, 1995m-s, 1980m	8.45s(1H), 1.90s(9H), -22.75d(2H)	$P^+$ 906 loss of 9 CO's	this work
$\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CHBu}^t)$	light yellow solid	2105w, 2082s, 2060s, 2028s, 2022s, 2010vs, 2002s, 1993s	7.30s(1H), 2.10s(9H), -22.75d(2H)	$P^+$ 906 loss of 9 CO's	this work
$\text{Os}_3(\text{CO})_{10}(\text{HC}=\text{CBu}^t)$	orange solid	2100m, 2060vs, 2054vs(sh), 2022vs, 2006vs, 1998s, 1848m.	9.10s(1H), 1.25s.b(9H)	$P^+$ 934 loss of 10 CO's	this work

<sup>a</sup>  $\text{CCl}_4$  solution. <sup>b</sup> Isomers, see text. <sup>c</sup> Isomers, see text.

TABLE 2

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS

	$x/a$	$y/b$	$z/c$
Os(1)	3543(1)	1999(1)	3894(1)
Os(2)	2223(1)	785(1)	2385(1)
Os(3)	2047(1)	1365(1)	5132(1)
O(1)	5131(13)	811(11)	5718(23)
O(2)	1942(18)	3087(13)	1973(26)
O(3)	4764(16)	2248(13)	1738(22)
O(4)	4486(17)	3161(13)	6350(29)
O(5)	3911(18)	119(14)	1366(26)
O(6)	1325(17)	1737(14)	-561(27)
O(7)	787(17)	-569(12)	1308(22)
O(8)	1242(17)	3005(12)	4742(26)
O(9)	3450(17)	1704(12)	8278(24)
O(10)	178(14)	923(12)	5941(24)
C(1)	4478(16)	1258(14)	5028(23)
C(2)	2508(20)	2669(16)	2659(31)
C(3)	4291(19)	2123(18)	2538(36)
C(4)	4164(22)	2740(17)	5430(34)
C(5)	3294(19)	396(18)	1733(30)
C(6)	1681(19)	1402(18)	597(28)
C(7)	1286(18)	-5(16)	1608(25)
C(8)	1630(20)	2388(17)	5035(29)
C(9)	2920(20)	1554(15)	7108(26)
C(10)	890(18)	1065(14)	5595(32)
C(11)	2778(18)	280(12)	4543(29)
C(12)	2165(23)	-48(14)	5310(32)
C(13)	2600(19)	-508(15)	6771(29)
C(14)	3734(20)	-392(18)	7754(35)
C(15)	1891(27)	-373(17)	7782(35)
C(16)	2429(26)	-1364(16)	6233(32)

TABLE 3

CALCULATED ATOMIC COORDINATES ( $\times 10^4$ ) FOR THE HYDROGEN ATOMS (excepting the hydridic one)

	$x/a$	$y/b$	$z/c$
H(11)	3588	275	5088
H(12)	1353	25	4857
H(141)	3852	206	8129
H(142)	4224	-530	7082
H(143)	3907	-772	8729
H(151)	1975	219	8197
H(152)	2099	-771	8731
H(153)	1112	-474	7113
H(161)	2714	-1748	7194
H(162)	2826	-1475	5418
H(163)	1628	-1467	5711

TABLE 4

ANISOTROPIC THERMAL PARAMETERS ( $\times 10^4$ ) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS, IN THE FORM:  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})]$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Os(1)	311(5)	356(5)	428(6)	8(4)	136(4)	-31(4)
Os(2)	308(5)	421(5)	292(5)	-37(4)	79(4)	-10(4)
Os(3)	278(5)	389(5)	363(5)	-59(4)	122(4)	-31(4)
O(1)	387(102)	815(136)	641(128)	75(109)	-45(95)	157(96)
O(2)	1091(171)	829(149)	736(141)	406(124)	252(129)	410(135)
O(3)	913(147)	952(162)	532(112)	100(107)	442(110)	42(121)
O(4)	748(152)	790(147)	1047(186)	-310(134)	354(139)	-249(120)
O(5)	901(175)	942(177)	1036(172)	-265(142)	584(145)	92(141)
O(6)	718(146)	1173(181)	754(149)	434(134)	348(124)	221(132)
O(7)	1179(179)	793(147)	638(128)	-334(118)	138(123)	-541(137)
O(8)	860(157)	537(122)	954(166)	-159(114)	437(131)	64(110)
O(9)	797(149)	754(134)	560(127)	-291(107)	-85(111)	77(112)
O(10)	476(106)	1026(160)	855(155)	-37(129)	443(111)	-53(107)
C(1)	343(117)	684(155)	239(108)	-246(109)	122(93)	-328(114)
C(2)	531(157)	533(166)	475(162)	131(139)	59(128)	-21(131)
C(3)	365(139)	883(218)	742(189)	-58(161)	278(138)	-103(136)
C(4)	608(179)	658(191)	517(171)	-93(151)	60(139)	-317(151)
C(5)	427(145)	810(193)	450(156)	-4(143)	239(129)	22(136)
C(6)	420(146)	943(208)	369(143)	183(148)	158(119)	-53(147)
C(7)	564(151)	849(197)	400(129)	-452(142)	102(114)	-348(144)
C(8)	521(156)	552(170)	508(155)	-192(133)	211(127)	-226(139)
C(9)	399(166)	544(160)	428(121)	-137(115)	176(121)	14(127)
C(10)	338(140)	471(143)	652(186)	-195(133)	160(135)	-24(115)
C(11)	446(142)	201(108)	645(166)	-67(114)	179(125)	59(103)
C(12)	913(198)	268(138)	444(174)	-60(126)	68(150)	-121(131)
C(13)	485(151)	477(144)	474(153)	47(117)	176(124)	95(117)
C(14)	332(133)	771(192)	754(202)	124(164)	111(130)	50(128)
C(15)	1296(261)	477(166)	786(214)	196(158)	753(201)	202(170)
C(16)	1153(260)	449(151)	552(179)	105(137)	246(175)	80(158)

Final atomic coordinates for non-hydrogen atoms and for hydrogen atoms (in calculated positions) are given in Tables 2 and 3, respectively. The thermal parameters for the non-hydrogen atoms are given in Table 4. A list of observed and calculated structure factor calculations is available from the authors on request.

All the calculations were performed on the CYBER-76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with the financial support from the University of Parma.

## Results and discussion

*Spectroscopic properties and structures of the  $Os_3(CO)_{12}$  derivatives.* Complex I can be regarded as isostructural with  $(\mu-H)Ru_3(CO)_9(\mu_3-\eta^2-C\equiv CBu^1)$  [3] on the basis of closely comparable IR and  $^1H$  NMR spectra (Table 1). Reaction with excess of alkyne apparently leads to the products analogous with those from the ruthenium hydride. Thus the previously unreported  $Os_3(CO)_6(HC_2Bu^1)_4(CO)$  isomers (VIIa,

TABLE 5  
<sup>1</sup>H NMR FOR COMPLEX II

( $\delta$ (ppm), CDCl <sub>3</sub> )	Multiplicity	Intensity	Attribution
7.30	dd	1H	H(11) (C <sub><math>\alpha</math></sub> )
6.95	dd	1H	
4.85	d	1H	H(12) (C <sub><math>\beta</math></sub> )
4.70	d	1H	
1.30	d	9H	Bu <sup>t</sup>
1.10	d	9H	
-21.95	s	1H	Hydride
-24.75	d	1H	

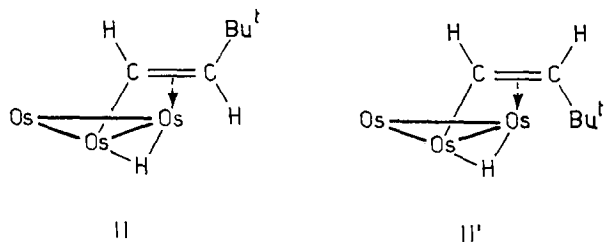
VIIb) and Os<sub>3</sub>(CO)<sub>7</sub>(HC<sub>2</sub>Bu<sup>t</sup>)<sub>3</sub> isomers (VIIIa, VIIIb) have colours, mass spectra, IR and NMR spectra strictly similar to those of the isomers Ru<sub>3</sub>(CO)<sub>6</sub>-(HC<sub>2</sub>Bu<sup>t</sup>)<sub>4</sub>(CO) [17] and of Ru<sub>3</sub>(CO)<sub>7</sub>(C<sub>2</sub>Ph<sub>2</sub>)[(C<sub>2</sub>Bu<sup>t</sup>)(PhC=CHPh)] [18]. On this basis we propose analogous structures and isomerism for VIIa, VIIb and the Ru<sub>3</sub>(CO)<sub>6</sub>(HC<sub>2</sub>Bu<sup>t</sup>)<sub>4</sub>(CO) derivatives; complexes VIIIa, VIIIb will likewise be isostructural with Ru<sub>3</sub>(CO)<sub>7</sub>(C<sub>2</sub>Ph<sub>2</sub>)[(C<sub>2</sub>Bu<sup>t</sup>)(PhC=CHPh)]. Isomerism was not observed for the ruthenium complex because of the presence of the "symmetrical" C<sub>2</sub>Ph<sub>2</sub> in the organic moiety; for VIIIa, VIIIb however, head-to-tail or tail-to-tail dimerization of the alkyne would lead to the presence of isomers.

*Spectroscopic properties and structures of the H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> derivatives.* The stoichiometries, colours, and the IR, <sup>1</sup>H NMR and mass spectra of the complexes derived from H<sub>2</sub>Os<sub>3</sub>(CO)<sub>10</sub> bear a remarkably close resemblance to those of the analogues previously described [7,8]. Thus, the corresponding structural formulae III–VI can be proposed for these compounds.

*Spectroscopic and structural data for Os<sub>3</sub>(CO)<sub>10</sub>( $\mu$ -II)( $\mu$ - $\eta^2$ -CH=CHBu<sup>t</sup>) (II).* The stoichiometry of this complex was established by microanalytical and mass spectral data. The latter show the sequential loss of 10 carbonyl groups; loss of hydrogen is a competing process. In the solution IR spectrum all the  $\nu$ (CO) bands are in the terminal region (Table 1). Unexpectedly the <sup>1</sup>H NMR shows twice as many resonances as expected for a molecule of structural formula II (Table 5). Moreover, the resonances appear in distinct pairs with equal intensities. Thus the two chemically distinct vinyl resonances appear as a pair of double doublets at  $\delta$  7.30, 6.95 ppm and a pair of doublets at  $\delta$  4.85, 4.70 ppm. The former is assigned to the proton on the  $\alpha$ -carbon,  $\sigma$ -bonded to osmium, on the basis of coupling to the hydridic hydrogen. The t-butyl proton resonance likewise appears as a doublet, and two upfield hydride resonances appear at  $\delta$  -21.95 and -24.75 ppm, one of which is a doublet.

Two explanations of this behaviour seem plausible. One of these is the existence of two isomers of II differing in the *cis* or *trans* stereochemistry of the olefinic hydrogen atoms across the coordinated double bond (structures II and II'). Evidence against such geometric isomerism is the fact that <sup>3</sup>J(H–H') for coupling between the olefinic hydrogens in II is essentially identical in the pairs of resonances attributed to H <sub>$\alpha$</sub> ; substantially different <sup>3</sup>J(H–H') are usually found for mutually *cis*- and





*trans*-olefinic hydrogens. Furthermore repeated attempts to separate the isomeric components by TLC were entirely unsuccessful.

An alternative explanation, and the one favoured, is that since II is inherently asymmetric, two non-interconverting enantiomers are present in solution. This suggests that flipping of the  $\mu$ - $\eta^2$ -alkenyl group from one configuration to another along the Os(2)–Os(3) edge is slow on the NMR time scale. Shapley has reported fluxional behaviour for the osmium derivative  $(\mu$ -H)Os<sub>3</sub>(CO)<sub>10</sub>( $\mu$ - $\eta^2$ -PhC=CHPh) which shows also different solid state structures [12]. It is possible that the bulky t-butyl group slows the interconversion process in II sufficiently to allow the observation of enantiomeric species at probe temperature. High temperature NMR runs were prevented by the rapid dehydrogenation of II to complex III.

A perspective view of the structure of II, determined by X-ray analysis, is shown in Fig. 1, together with the atomic numbering scheme. Bond distances and angles are listed in Table 6. The complex consists of a triangle of osmium atoms with ten terminal CO's, four of which are bonded to the Os(1) atom and three to the Os(2) and Os(3) atoms; the vinyl ligand bridges the Os(2)–Os(3) edge of the triangle forming a  $\sigma$ -bond to Os(2) and a  $\pi$ -bond to Os(3) atoms. A bridging hydride is also

(Continued on p. 402)

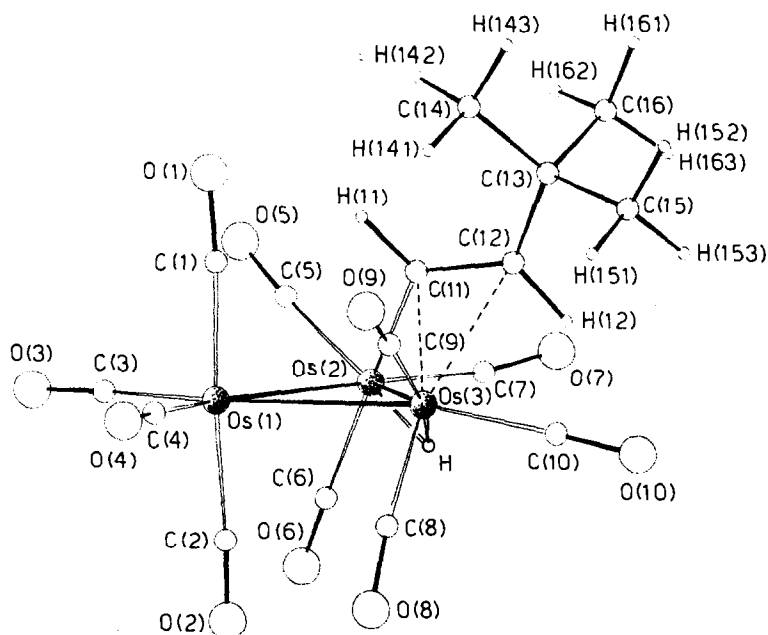


Fig. 1. Perspective view of the complex HOs<sub>3</sub>(CO)<sub>10</sub>(CH=CHBu<sup>t</sup>) with the atomic numbering scheme. The hydrogen atoms are in the idealized positions.

TABLE 6

## BOND DISTANCES (Å) AND ANGLES (°)

*(a) in the coordination sphere of the metal atoms*

Os(1)–Os(2)	2.841(2)	Os(2)–C(6)	1.91(3)
Os(1)–Os(3)	2.876(3)	Os(2)–C(7)	1.86(3)
Os(2)–Os(3)	2.814(2)	Os(2)–C(11)	2.10(2)
Os(1)–C(1)	1.89(2)	Os(3)–C(8)	1.84(3)
Os(1)–C(2)	1.92(3)	Os(3)–C(9)	1.88(2)
Os(1)–C(3)	1.87(3)	Os(3)–C(10)	1.86(3)
Os(1)–C(4)	1.91(3)	Os(3)–C(11)	2.27(2)
Os(2)–C(5)	1.89(3)	Os(3)–C(12)	2.43(2)
Os(2)–Os(1)–Os(3)	58.96(5)	C(6)–Os(2)–C(11)	170.2(9)
Os(1)–Os(2)–Os(3)	61.15(5)	C(6)–Os(2)–Os(1)	92.3(8)
Os(1)–Os(3)–Os(2)	59.89(5)	C(7)–Os(2)–C(11)	94.2(9)
Os(2)–Os(1)–C(1)	90.3(7)	C(7)–Os(2)–Os(1)	172.4(7)
Os(2)–Os(1)–C(2)	84.1(8)	C(11)–Os(2)–Os(1)	81.0(6)
Os(2)–Os(1)–C(3)	99.2(9)	C(8)–Os(3)–C(9)	88.9(10)
Os(2)–Os(1)–C(4)	158.7(9)	C(8)–Os(3)–C(10)	89.7(11)
Os(3)–Os(1)–C(1)	88.7(7)	C(8)–Os(3)–C(11)	158.2(9)
Os(3)–Os(1)–C(2)	88.1(9)	C(8)–Os(3)–C(12)	165.3(11)
Os(3)–Os(1)–C(3)	158.1(9)	C(8)–Os(3)–Os(1)	82.7(8)
Os(3)–Os(1)–C(4)	99.8(9)	C(8)–Os(3)–Os(2)	114.0(8)
C(1)–Os(1)–C(2)	174.4(9)	C(9)–Os(3)–C(10)	99.4(11)
C(1)–Os(1)–C(3)	91.3(9)	C(9)–Os(3)–C(11)	100.1(9)
C(1)–Os(1)–C(4)	87.7(9)	C(9)–Os(3)–C(12)	95.5(9)
C(2)–Os(1)–C(3)	89.9(9)	C(9)–Os(3)–Os(1)	89.8(8)
C(2)–Os(1)–C(4)	97.3(11)	C(9)–Os(3)–Os(2)	136.9(8)
C(3)–Os(1)–C(4)	102.1(12)	C(10)–Os(3)–C(11)	108.0(9)
Os(3)–Os(2)–C(5)	135.3(8)	C(10)–Os(3)–C(12)	75.7(9)
Os(3)–Os(2)–C(6)	117.8(9)	C(10)–Os(3)–Os(1)	168.0(8)
Os(3)–Os(2)–C(7)	111.3(7)	C(10)–Os(3)–Os(2)	115.7(8)
Os(3)–Os(2)–C(11)	52.6(6)	C(11)–Os(3)–C(12)	34.0(9)
C(5)–Os(2)–C(6)	93.2(10)	C(11)–Os(3)–Os(1)	77.5(6)
C(5)–Os(2)–C(7)	98.1(11)	C(11)–Os(3)–Os(2)	47.2(6)
C(5)–Os(2)–C(11)	93.8(9)	C(12)–Os(3)–Os(1)	111.3(8)
C(5)–Os(2)–Os(1)	88.1(8)	C(12)–Os(3)–Os(2)	71.7(7)
C(6)–Os(2)–C(7)	91.6(10)		

*(b) in the carbonyl groups*

O(1)–C(1)	1.21(3)	O(6)–C(6)	1.18(3)
O(2)–C(2)	1.11(4)	O(7)–C(7)	1.17(3)
O(3)–C(3)	1.15(4)	O(8)–C(8)	1.18(4)
O(4)–C(4)	1.10(4)	O(9)–C(9)	1.14(3)
O(5)–C(5)	1.12(4)	O(10)–C(10)	1.15(3)
Os(1)–C(1)–O(1)	175(2)	Os(2)–C(6)–O(6)	175(2)
Os(1)–C(2)–O(2)	176(2)	Os(2)–C(7)–O(7)	170(2)
Os(1)–C(3)–O(3)	176(3)	Os(3)–C(8)–O(8)	169(2)
Os(1)–C(4)–O(4)	176(3)	Os(3)–C(9)–O(9)	177(2)
Os(2)–C(5)–O(5)	176(3)	Os(3)–C(10)–O(10)	175(2)

*(c) in the organic ligand*

C(11)–C(12)	1.38(4)	C(13)–C(15)	1.57(4)
C(12)–C(13)	1.52(4)	C(13)–C(16)	1.55(4)
C(13)–C(14)	1.57(4)		
Os(2)–C(11)–C(12)	124(2)	C(12)–C(13)–C(15)	108(2)
Os(3)–C(11)–C(12)	80(1)	C(12)–C(13)–C(16)	103(2)
Os(2)–C(11)–Os(3)	80(1)	C(14)–C(13)–C(15)	110(2)
Os(3)–C(12)–C(13)	125(2)	C(14)–C(13)–C(16)	110(2)
C(11)–C(12)–C(13)	122(2)	C(15)–C(13)–C(16)	106(2)
C(12)–C(13)–C(14)	120(2)		

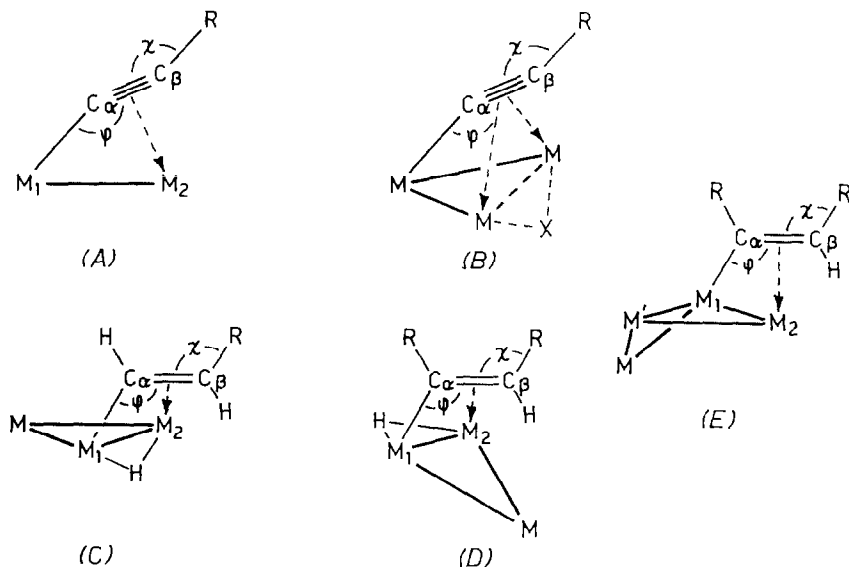
TABLE 7. COMPARISON OF THE BONDING PARAMETERS FOR  $\mu\text{-}\eta^2$  and  $\mu_3\text{-}\eta^2$  BOUND ACETYLIDES AND  $\mu\text{-}\eta^2$  ALKENYLS

Complex	Coordination of the ligand	$M_1\text{-}M_2$ <sup>a</sup>	M-C( $\alpha$ )	M-C( $\beta$ )	C-C	$\varphi$ <sup>d</sup>	$\chi$ <sup>d</sup>	Ref.
$\text{Fe}_2(\text{CO})_6(\text{PPh}_2)(\text{C}\equiv\text{CBu}^t)$	$\mu\text{-}\eta^2$ (A)	2.5959(6)	-	-	1.223(4)	162.4(1)	161.1(1)	21
$\text{Fe}_2(\text{CO})_4(\text{Bu}^t\text{NO})_2(\text{PPh}_2)(\text{C}\equiv\text{CBu}^t)$	$\mu\text{-}\eta^2$ (A)	2.5946(7)	-	-	1.225(5)	161(1)	161.3(1)	21
$\text{Ru}_2(\text{CO})_6(\text{PPh}_2)(\text{C}\equiv\text{CBu}^t)$	$\mu\text{-}\eta^2$ (A)	2.7523(3)	-	-	1.218(4)	158.9(1)	158.5(2)	21
$\text{Ru}_3(\text{CO})_6(\text{PPh}_2)_2(\text{C}_2\text{Bu}^t)(\text{PPh}_2)$ ( $\mu\text{-C}_2\text{Bu}^t)(\mu\text{-}\eta^2\text{-C}_2\text{Bu}^t)$	$\mu\text{-}\eta^2$ (A)	3.139(1)	2.046(9)	2.323(8)	1.24(3)	169.8	159.8	22
$\text{Ru}_4(\text{CO})_{13}(\mu\text{-PPh}_2)(\text{C}\equiv\text{CBu}^t)$	$\mu\text{-}\eta^2$ (A)	3.157(1)	2.044(8)	2.285(8)	1.199(12)	173.5(4)	159.9(5)	23
$\text{Ru}_4(\text{CO})_8(\text{PPh}_2)_2(\text{Ph}_2\text{C}_2\text{Bu}^t)$ ( $\mu\text{-}\eta^2\text{-C}\equiv\text{CBu}^t)(\mu_3\text{-}\eta^2\text{-C}_2\text{Bu}^t)$	$\mu\text{-}\eta^2$ (A)	-	2.041(7)	2.292(11)	1.228(1)	173.5(3)	163.3(4)	23
	$\mu_3\text{-}\eta^2$ (B)	-	1.961(7)	2.620(7)	1.315(9)	160.8(2)	138.3(1)	
$\text{HRu}_3(\text{CO})_9(\text{C}\equiv\text{CBu}^t)$	$\mu_3\text{-}\eta^2$ (B)	-	1.947(3)	2.210(3) <sup>d</sup>	1.315(6)	154.5(1)	140.2(3)	24
$(\text{PPh}_2)\text{Ru}_3(\text{CO})_9(\text{C}\equiv\text{CPr}^t)$	$\mu_3\text{-}\eta^2$ (B)	-	1.96(1)	2.219(3) <sup>d</sup>	1.284(8)	154.0(2)	145.2(3)	25
$(\text{PPh}_2)\text{Ru}_3(\text{CO})_8(\text{C}\equiv\text{CPr}^t)$	$\mu_3\text{-}\eta^2$ (B)	-	2.05(1)	-	1.24(1)	-	-	25
$(\text{PPh}_2)\text{Os}_3(\text{CO})_9(\text{C}\equiv\text{CPr}^t)$	$\mu_3\text{-}\eta^2$ (B)	-	-	-	1.28(1)	153.6(3)	142.0(8)	21
$\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CH}_2)$	$\mu\text{-}\eta^2$ (C)	2.845(2)	2.107(3)	2.273(3) <sup>b</sup>	-	-	-	9
				2.362(3) <sup>c</sup>				
$\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CHEt})$	$\mu\text{-}\eta^2$ (C)	2.834(1)	2.15(2)	2.28(2) <sup>b</sup>	1.40(3)	123.6(17)	112(4)	10
				2.46(3) <sup>c</sup>				
$\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CHBu}^t)$	$\mu\text{-}\eta^2$ (C)	2.814(2)	2.10(2)	2.27(2) <sup>b</sup>	1.38(4)	124(2)	122(2)	this work
				2.43(2) <sup>c</sup>				
$\text{HOs}_3(\text{CO})_{10}(\text{PhC}=\text{CHPh})$	$\mu\text{-}\eta^2$ (D)	2.820(3) <sup>d</sup>	2.11(4)	2.34(4)-2.21(4) <sup>b</sup>	1.40(5)	129(3)	131(3)	12
		2.821(3)	2.18(4)	2.44(4)-2.45(4) <sup>c</sup>	1.31(5)	126(3)	128(3)	
$\text{FeCo}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)(\text{PhC}=\text{CHPh})$	$\mu\text{-}\eta^2$ (E)	2.369(4)	1.98(2)	1.99(1) <sup>b</sup>	1.42(2)	116(1)	126(1)	13
				2.13(1) <sup>c</sup>				

<sup>a</sup> See structural formulae A-E on p. 402. <sup>b</sup> M-C( $\alpha$ ). <sup>c</sup> M-C( $\beta$ ). <sup>d</sup> Two independent molecules. <sup>e</sup> Mean of two values.

present according to the spectroscopic data; although it could not be located in the Fourier difference map, its position can nevertheless be inferred from several observations. (i) The Os(2)–Os(3) bond (2.814(2) Å) is shorter than the remaining Os(1)–Os(2) and Os(1)–Os(3) bonds (2.841(2) and 2.876(3) Å, respectively). A similar trend with the shortest side of the cluster involved in the double (hydride and alkenyl) bridge has been observed in  $\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CH}_2)$  (IIb) [9],  $\text{HOs}_3(\text{CO})_{10}(\text{HC}=\text{CHEt})$  (IIc) [10], and  $\text{HOs}_3(\text{CO})_{10}(\text{PhC}=\text{CHPh})$  (IId) [12]. (ii) The close relationships of II with IIb, IIc and IId also suggest that the hydride should be located along the same edge as the alkenyl group. Also the Os(1)–Os(3) side involving the Os of the  $\text{Os}(\text{CO})_4$  and the Os  $\pi$ -coordinated with the olefinic bond is the longest one. (iii) The location of the bridging hydride on the Os(2)–Os(3) edge of the cluster can be resolved by analysis of the carbonyl bond angles by comparison with those found in  $\text{Os}_3(\text{CO})_{12}$  [19] and  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  [20]. The Os–Os–CO bond angles (average value  $116^\circ$ ) relating the axial C(6)–O(6) and C(8)–O(8) and the equatorial C(7)–O(7) and C(10)–O(10) carbonyls suggest that the bridging hydride ligand lies in a plane midway between the planes defined by the axial and equatorial carbonyls, with the Os(2)–Os(3) edge as found in  $\text{HOs}_3(\text{CO})_{10}(\text{PhC}=\text{CHPh})$  [12].

The orientation of the alkenyl ligand is similar to that in the vinyl complexes  $\text{HOs}_3(\text{CO})_{10}(\text{CH}=\text{CHR})$  (R = H, Et) and differs from that in the stilbenyl complex  $\text{HOs}_3(\text{CO})_{10}(\text{CPh}=\text{CHPh})$ . In the vinyl derivatives the hydrogen atom on the  $\alpha$ -carbon of the ligand is *syn* with respect to the Os(1) atom, whereas in the stilbenyl derivative the substituent on the  $\alpha$ -carbon is *anti* with respect to the same Os atom; in other words, in the vinyl derivatives with the  $\alpha$ -carbon bridging one side of the triangle the  $\beta$ -carbon points outside the triangle, whereas in the stilbenyl derivative the  $\beta$ -carbon points inside the triangle. This is not the case for all the stilbenyl derivatives, since in the tetranuclear butterfly cluster  $\text{FeCo}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)-(\text{PhC}=\text{CHPh})$  [13] the disposition of the alkenyl ligand with respect to the triangular  $\text{FeCo}_2$  face is similar to that of the vinyl group. In Table 7 (and in formulae A–E)



the alkenyl complexes are compared with the  $\mu\text{-}\eta^2$  and  $\mu_3\text{-}\eta^2$  acetylide complexes; indeed the complexes I and II are related, and complex I could in principle be obtained from II by thermal dehydrogenation-decarbonylation. Although, unfortunately, few data are available for osmium-bridging acetylides, it can be seen that the C–C elongation does not depend on the M–M bond distance, whereas the angles around the C atoms of the ligand vary in the expected sense as a result of the change in the carbon hybridization. In particular complexes II, IIb, IIc and II d show comparable M–M, M–C $_{\alpha}$  and M–C $_{\beta}$  bonding parameters, whereas the C–C bonds are in a narrow range. These latter, as well as the angles at C $_{\alpha}$  and C $_{\beta}$ , point to the olefinic nature of the ligand.

It follows that the reactivity of II towards "electron-rich" metal species, such as ( $\eta^5\text{-C}_5\text{H}_5$ )Ni should reveal the differences between the electron-acceptor capability of the RC=CHR ligand (a formal 3 electron donor) and the acetylide (a formal 5 electron donor) in I (both I and II being 48 electron clusters). However, when the reactivities of I and II in thermal reactions are compared it must be kept in mind that heating of II readily gives the vinylidene-substituted clusters III–V, and then, by decarbonylation-dehydrogenation, the acetylide complexes I (see ref. 7, 8 and the Experimental).

The reactions of II and related clusters with [ $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})$ ] $_2$  are at present under investigation.

### Acknowledgements

We thank Professor A.J. Carty (University of Waterloo, Ontario, Canada) for helpful discussion and Johnson–Matthey for a loan of osmium tetroxide.

This work was financially supported by C.N.R. (Rome).

### References

- 1 E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini. *Inorg. Chim. Acta*, 41 (1980) 11.
- 2 A.J. Carty, N.J. Taylor, E. Sappa and A. Tiripicchio, *Inorg. Chem.*, in press.
- 3 E. Sappa, O. Gambino, L. Milone and G. Cetini, *J. Organomet. Chem.*, 39 (1972) 169.
- 4 This complex was reported as an incompletely characterized species by E. Sappa, A.M. Manotti Lanfredi and A. Tiripicchio, *J. Organomet. Chem.*, 221 (1981) 93. Full characterization of the ruthenium and osmium complexes is described in ref. 5.
- 5 Spectroscopic characterization: M. Castiglioni, E. Sappa, M. Valle, M. Lanfranchi and A. Tiripicchio, *J. Organomet. Chem.*, 241 (1983) 99. Structural characterization: S.G. Shore, W.L. Hsu, C.R. Weisenberger, M.L. Castle, M.R. Churchill and C. Bueno, *Organometallics*, 1 (1982) 1405 (for the osmium complex).
- 6 M. Castiglioni, G. Gervasio and E. Sappa, *Inorg. Chim. Acta*, 49 (1981) 217.
- 7 W.G. Jackson, B.F.G. Johnson, J.W. Kelland, J. Lewis and K.T. Schorpp, *J. Organomet. Chem.*, 87 (1975) C27.
- 8 A.J. Deeming, S. Hasso and M. Underhill, *J. Chem. Soc. Dalton Trans.*, (1975) 1614.
- 9 A.G. Orpen, A.V. Rivera, E.G. Bryan, D. Pippard, G.M. Sheldrick and K.D. Rouse, *J. Chem. Soc., Chem. Commun.*, (1978) 723.
- 10 J.J. Guy, B.E. Reichert and G.M. Sheldrick, *Acta Cryst. B*, 32 (1976) 3319.
- 11 M. Tachikawa, J.R. Shapley and C.G. Pierpoint, *J. Am. Chem. Soc.*, 97 (1975) 7172.
- 12 A.D. Clauss, M. Tachikawa, J.R. Shapley and C.G. Pierpoint, *Inorg. Chem.*, 20 (1981) 1528.
- 13 S. Aime, L. Milone, D. Osella and A. Tiripicchio, *Inorg. Chim. Acta*, in press
- 14 O. Gambino and E. Sappa, *Atti Acc. Sci. Torino*, 108 (1973–74) 305.
- 15 G.M. Sheldrick, *System of Computing Programs*, University of Cambridge, 1976.
- 16 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.

- 17 S. Aime, G. Gervasio, L. Milone, E. Sappa and M. Franchini Angela, *Inorg. Chim. Acta*, 26 (1978) 223.
- 18 E. Sappa, G. Predieri, A. Tiripicchio and A.M. Manotti Lanfredi, *Inorg. Chim. Acta*, 61 (1982) 217.
- 19 E.R. Corey and L.F. Dahl, *Inorg. Chem.*, 1 (1962) 521.
- 20 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, *Inorg. Chem.*, 16 (1977) 2697.
- 21 A.J. Carty, in E.C. Alyea and D.W. Meek Eds., *Adv. Chemistry Series* 196, p. 165, American Chemical Society, 1982.
- 22 A.J. Carty, N.J. Taylor and W.F. Smith, *J. Chem. Soc., Chem. Commun.*, (1979) 750.
- 23 A.J. Carty, S.A. MacLaughlin, J. Van Wagner and N.J. Taylor, *Organometallics*, 1 (1982) 1013.
- 24 M. Catti, G. Gervasio and S.A. Mason, *J. Chem. Soc., Dalton Trans.*, (1977) 2260.
- 25 A.J. Carty, S.A. MacLaughlin and N.J. Taylor, *J. Organomet. Chem.*, 204 (1981) C27.