Homogeneous Catalysis on Metal Clusters. The Isomerization and Selective Hydrogenation of Dienes, Alkenes, and Alkynes in the Presence of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ and $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8L]$ [L = PPh_2H or $P(C_6H_4Me\text{-}o)_3$]. Spectroscopic Identification of the Reaction Intermediates and *X*-Ray Structure of $[Os_3(\mu\text{-}H)(CO)_9(MeCCHCMe)]$[†]

Mario Castiglioni, Roberto Giordano, and Enrico Sappa *
Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso M. D'Azeglio 48, 10125 Torino, Italy
Antonio Tiripicchio * **and Marisa Tiripicchio Camellini**
Istituto di Chimica Generale ed Inorganica, Universita di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

The complexes $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ and $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8L]$ [L = PPh_2H or $P(C_6H_4Me\text{-}o)_3$] catalyze under homogeneous conditions the hydrogenation of one double bond of dienes and show selectivity in the hydrogenation of triple and double C–C bonds; non-conjugated dienes are isomerized. Experimental evidence suggests that the cluster acts as a catalyst. Complexes $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(\text{diene})]$ and $[Os_3(\mu\text{-}H)(CO)_9(MeCCHCMe)]$ have been isolated in the reaction solutions. The former complexes have been identified by spectroscopy and the latter by *X*-ray diffraction methods. A reaction path is proposed. Crystals of $[Os_3(\mu\text{-}H)(CO)_9(MeCCHCMe)]$ are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 10.960(7), b = 17.064(8), c = 10.162(5) Å, β = 106.07(2)°, and Z = 4. The structure was determined from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.048. In the complex an allylic ligand (derived from a pentadiene) co-ordinated to a triangular osmium cluster has been found; although this type of structure has already been reported, this is the first osmium complex obtained by reaction with a diene.

The cluster complex $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ (**1**) is obtained in high yields by simple synthetic procedures;[1] its structure has been determined in two independent studies.[2,3] Monosubstituted derivatives of (**1**), of general formula $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8L]$ [L = nitrile, phosphine, phosphinoacetylene, or bis(diphenylphosphino)methane] are obtained in the presence of Me_3NO; these have been characterized by spectroscopy[4] and, for L = PPh_2H and $Ph_2PC{\equiv}CPr^i$, by *X*-ray methods.[5]

In n-octane solution, complex (**1**) is a low-efficiency, although selective, hydrogenation catalyst for alkynes and alkenes.[1] When supported and thermally treated on $\gamma\text{-}Al_2O_3$, it forms a heterogeneous catalyst for the methanation of CO and CO_2.[6] When supported onto silanized Chromosorb P (Johns Manville) the cluster (**1**) behaves as a homogeneous or heterogeneous hydrogenation catalyst for *cis*- and *trans*-penta-1,3-diene, depending on the pre-treatment conditions.[7]

In this paper we report on the catalytic activity of complex (**1**) and of its monosubstituted derivatives $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8L]$ [L = PPh_2H (**2a**), L = $P(C_6H_4Me\text{-}o)_3$ (**2b**)]. The following substrates were chosen: C_5 molecules, *cis*- and *trans*-penta-1,3-diene, penta-1,4-diene, pent-1-ene, pent-1-yne, and 3-methylbut-3-en-1-yne; C_6 molecules, *cis*-hexa-1,4-diene, *cis*, *trans*-hexa-2,4-diene, hexa-1,5-diene, hex-1-ene, *trans*-hex-3-ene, and hex-3-yne.

The results of the hydrogenation and isomerization[‡] experiments, in n-octane solution, agree with the behaviour of complexes (**1**), (**2a**) and (**2b**) as cluster catalysts. We could detect, in the reaction solutions, the isomeric complexes $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(CH_2{=}CH{-}CH{=}CHMe)]$ (**3**), which were characterized by spectroscopy.

For long reaction times the activity of complex (**1**) decreases, and in the reaction solutions the hydride $[Os_3(\mu\text{-}H)(CO)_9(MeCCHCMe)]$ (**4a**) is found. The structure of complex (**4a**) has been studied by *X*-ray diffraction methods; this complex is formed by a triangular cluster of osmium atoms, with a dimethylallyl ligand co-ordinated to all the metals. This structure has been reported for a limited number of iron, ruthenium, and osmium clusters, generally derived by reactions with alkynes. Complex (**4a**) is the first example of a similar structure obtained upon co-ordination and modification of a *diene* on an *osmium* cluster; according to the available literature (see above), the reactions of osmium clusters with dienes lead preferentially to 'allenyl' derivatives.

Experimental

Materials.—Complexes (**1**), (**2a**), and (**2b**) were prepared and purified as reported previously.[1,4] The dienes, alkenes, and alkynes were purchased from Fluka and Janssen and used without further purification, after ^1H n.m.r. purity checks. G.l.c. was employed either for detecting minor impurities in the ligands or for standardizing the gas-chromatographic operative conditions. The n-octane solvent was distilled over sodium; accurately dried, ultrapure hydrogen (Societa Italiana Acetilene e Derivati) or deuterium (Farmitalia–Carlo Erba) were used.

[†] 1,1,1,2,2,2,3,3,3-Nonacarbonyl-2,3-μ-hydrido-μ_3-[pentenylylidene-$C^2(Os^1,Os^2),C^3(Os^1),C^4(Os^1,Os^3)$]-*triangulo*-triosmium.

Supplementary data available (No. SUP 56322, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: atm = 101 325 Pa.

[‡] The isomerization reactions were studied only for the dienes and for pent-1-ene.

Table 1. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	1 850(1)	4 300(1)	1 841(1)	C(2)	558(21)	3 722(13)	559(22)
Os(2)	3 306(1)	2 990(1)	1 556(1)	C(3)	2 229(32)	5 007(19)	506(29)
Os(3)	1 721(1)	2 985(1)	3 451(1)	C(4)	3 536(24)	3 357(17)	−138(33)
O(1)	103(25)	5 414(12)	2 712(26)	C(5)	2 306(22)	2 097(14)	503(24)
O(2)	−232(17)	3 433(12)	−216(19)	C(6)	4 829(31)	2 422(15)	2 075(25)
O(3)	2 471(27)	5 407(13)	−234(27)	C(7)	2 288(34)	2 438(14)	5 115(28)
O(4)	3 759(22)	3 563(14)	−1 098(23)	C(8)	794(26)	2 119(14)	2 453(26)
O(5)	1 791(22)	1 591(12)	−39(24)	C(9)	198(26)	3 362(11)	3 823(21)
O(6)	5 788(17)	2 124(12)	2 393(21)	C(10)	2 344(29)	4 498(15)	5 246(24)
O(7)	2 687(21)	2 129(14)	6 131(19)	C(11)	2 636(23)	4 024(14)	4 140(25)
O(8)	216(25)	1 596(13)	1 866(24)	C(12)	3 600(26)	4 354(15)	3 638(23)
O(9)	−630(21)	3 558(13)	4 084(23)	C(13)	3 960(22)	4 022(14)	2 537(24)
C(1)	805(25)	5 024(15)	2 401(24)	C(14)	4 994(25)	4 509(13)	2 133(29)

Hydrogenation and Deuteriation Experiments.—Deuteriated complex (**1**). The reactions were performed in sealed glass vials (volume 25 cm^3). Each vial, containing an n-octane (1 cm^3) solution of complex (**1**), (**2a**), or (**2b**) (5.0 mg) and the substrate to be hydrogenated (0.20 cm^3), was filled with hydrogen or deuterium (0.9 atm unless otherwise stated) using standard vacuum techniques. Some isomerization experiments, and the reactions of deuteriated (**1**) with the dienes, were performed by using the same concentrations and procedure, but in the absence of any gas.

The deuteriated complex (**1**) was obtained upon exchange between complex (**1**) and D_2; complex (**1**) (50 mg) was dissolved in n-octane (25 cm^3) and introduced into a vial (volume 250 cm^3). Deuterium (0.9 atm) was then introduced, and the sealed vial was thermostatted at 120 °C for 4 h. After evaporation to dryness *in vacuo*, the residue was purified on preparative t.l.c. plates [Kiesel-gel P.F. Merck; eluant light petroleum (b.p. 40—70 °C)–ethyl ether (90:10)]; no decomposition was observed. The ^1H n.m.r. spectrum of deuteriated (**1**) showed only the cyclopentadienyl resonance, indicating a deuteriation yield of *ca.* 99.8%; the main difference between the i.r. spectra of non-deuteriated and deuteriated (**1**) is the shift of the band at 2 064 to 2 062 cm^{-1}.

Gas-chromatographic analyses of the reaction solutions. The organic products in the solutions from the hydrogenation experiments were analysed with a Carlo Erba 4200 FID gas–liquid chromatograph equipped with a n-octane–Porasil C (80/100 mesh) column (2 m × 0.6 cm) operated with N_2 (25 cm^3 min^{-1}) as carrier gas, with the following temperature programs: C_5 ligands, 75 °C (10 min), then 20 °C min^{-1} to 155 °C and a further 10 min at 155 °C; C_6 ligands, 70 °C (6 min), then 4 °C min^{-1} to 155 °C and a further 5 min at 155 °C.

The nature of the deuteriated organic products was detected by means of a Carlo-Erba 4200 and Kratos MS 50 gas-chromatographic mass-spectrometric system, and with a JEOL JNM-GX 270 FT n.m.r. instrument.

Identification (*and independent synthesis*) *of some organometallic products in the reaction solutions.* The hydrogenation solutions were also checked (by t.l.c.) both for incidental decomposition of the catalyst and for formation of new complexes.

After 4 h under hydrogen, in the solutions of (**2a**) and *cis*- or *trans*-penta-1,3-diene, four dark grey-violet complexes in very small amounts could be detected, together with >80% unaltered (**2a**); the new derivatives were identified as isomeric $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(CH_2{=}CH{-}CH{=}CHMe)]$ [complexes (**3a**), (**3b**), (**3c**), and (**3d**), in the order of elution on the t.l.c. plates]. Complexes (**3a**) and (**3c**) were also obtained (in 5—7% yields each, together with smaller amounts of a dark green, unidentified substance) by reacting complex (**1**) and Me_3NO with *cis*- or *trans*-penta-1,3-diene in refluxing heptane for 1 min, under N_2.[4]

After 4—6 h under hydrogen, in the solutions of (**1**) and *cis*- or *trans*-penta-1,3-diene, some decomposition occurred. After 24 h, however, the colour of the solutions turned to orange-yellow; in samples containing *cis*-penta-1,3-diene considerable decomposition was observed and three new products were detected, namely the yellow complex (**4a**) (*ca.* 5% yield), a light yellow solid, tentatively identified as $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}C_5H_7)]$ (**4b**) (structure probably similar to that given in ref. 8), and a red solid probably isomeric with (**4a**) [complex (**4c**)]. In the solutions containing *trans*-penta-1,3-diene very small amounts of (**4a**) and (**4c**) were observed.

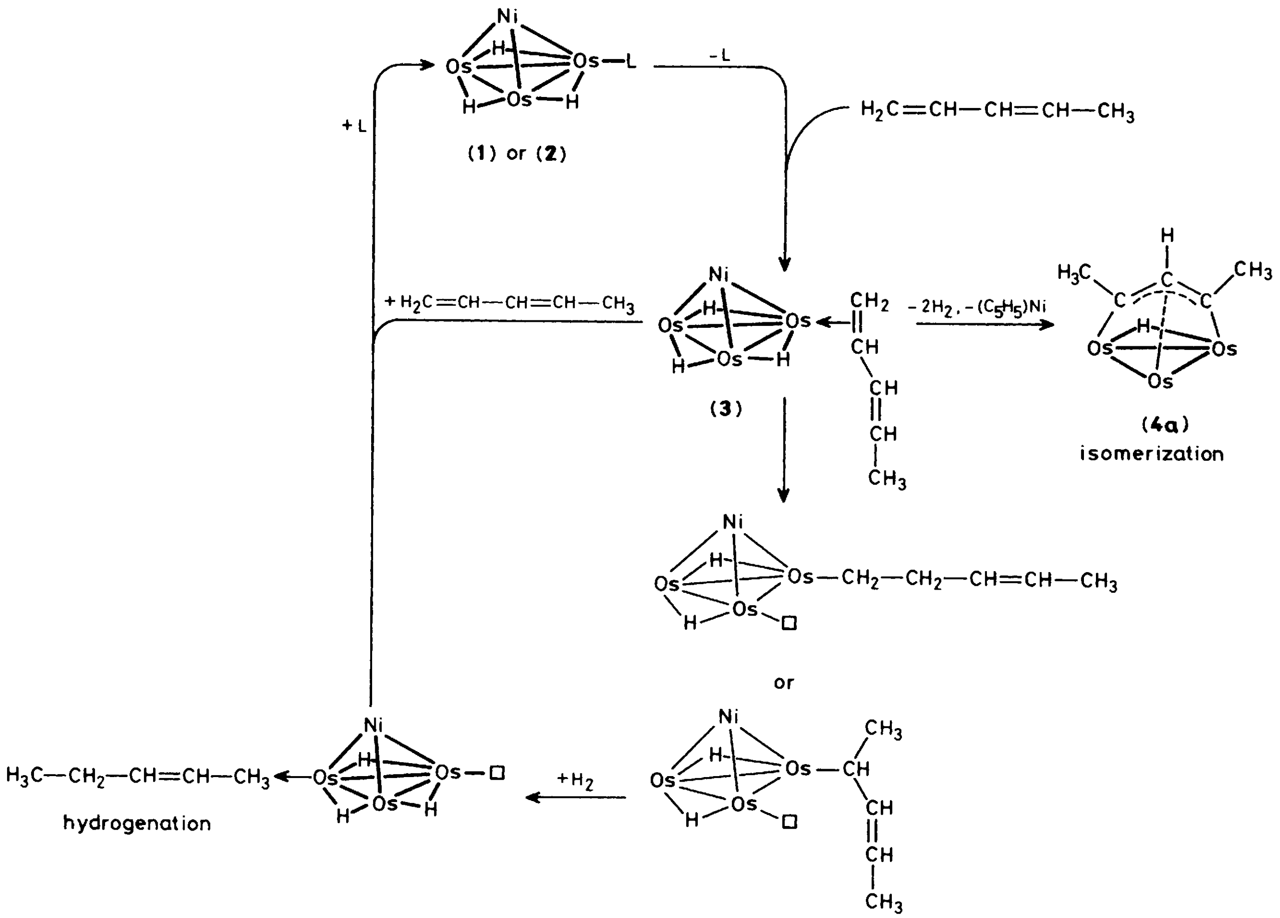
Hydrogenation (*and deuteriation*) *of complexes* (**3**). The clusters (**3a**) and (**3c**) are stable only for a few hours in solution under N_2; slow decomposition and formation of complex (**1**) occurs. This prevented the formation of crystals suitable for *X*-ray studies. When treated with hydrogen or deuterium in sealed vials as described above, the complexes release hydrogenated (or deuteriated) pentenes; decomposition and the formation of some complex (**1**) also occur.

Crystal Structure of the Complex (**4a**).—The yellow band observed on the preparative t.l.c. plates of the reaction solutions of (**1**) and *cis*-penta-1,3-diene (after 24 h) was collected, eluted with diethyl ether and taken to dryness *in vacuo*. The solid obtained was redissolved in n-heptane and the solution kept at −20 °C under N_2 for several days. Crystals of (**4a**) suitable for the *X*-ray analysis were obtained.

Crystal data. $C_{14}H_8O_9Os_3$, $M = 890.81$, monoclinic, $a = 10.960(7)$, $b = 17.064(8)$, $c = 10.162(5)$ Å, $\beta = 106.07(2)°$, $U = 1\,826(2)$ Å^3 (by least-squares refinement from the θ values of 27 reflections accurately measured, $\lambda = 0.710\,69$ Å), space group $P2_1/n$, $Z = 4$, $D_c = 3.240$ g cm^{-3}, $F(000) = 1\,568$. A yellow prismatic crystal, of approximate dimensions 0.21 × 0.26 × 0.33 mm, was used for the *X*-ray analysis, $\mu(\text{Mo-}K_\alpha) = 208.97$ cm^{-1}. A correction for the absorption was applied following ref. 9 (max. and min. transmission factors: 1.4413 and 0.7174) using the program ABSORB (F. Ugozzoli, University of Parma).

Data collection and processing. Siemens AED diffractometer, θ/2θ mode, niobium-filtered Mo-K_α radiation; all the reflections in the range $3 \leqslant \theta \leqslant 25°$ were measured. Of 3 216 independent reflections, 1 937 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis.

Structure analysis and refinement. Patterson and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms in the last cycles, hydridic hydrogen clearly localized in the ΔF map, remaining hydrogens placed at their geometrically calculated



Scheme. Proposed hydrogenation pattern for the dienes in the presence of complexes (**1**) or (**2**); L = CO, PPh_2H, or $P(C_6H_4Me\text{-}o)_3$

positions, all hydrogens not refined but introduced in the final calculations with isotropic thermal parameters. Weighting scheme used in the last cycles: $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 0.8623$ and $g = 0.005$. Final R and R' values 0.048 and 0.061. Programs and computer used are given in ref. 10*a*. Atomic scattering factors, corrected for the anomalous dispersion of Os, were taken from ref. 10*b*. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1.

Results and Discussion

Spectroscopic Data for Complexes (**3**) *and* (**4**).—The i.r., ^1H n.m.r., and mass spectra of (**3a**)—(**3d**) and (**4a**)—(**4c**) are in Table 2. The colours and i.r. spectra of the complexes (**3**) are closely comparable with those of the already reported complexes (**2**).[4] The mass spectra agree with the formulation as monosubstituted derivatives, in which the diene acts as a formal two-electron donor and replaces one CO ligand. We could not attribute unequivocally the multiplets of the dienic ligands in the ^1H n.m.r. spectra, probably because of easy isomerization in solution. However, the presence of a cyclopentadienyl singlet and of hydridic signals in integrated intensities 5:3, and the characteristic pattern of the hydridic resonances,[4,5] strongly support the proposed structure.

Complexes (**3**) (Scheme) would hence represent examples of diene ligands co-ordinated to one metal of a cluster *via* only one double bond. Generally, the dienes co-ordinate to one or two metal centres by using two double bonds, as in $[Os_3(CO)_{10}(C_4H_6)]$,[11] $[Ru_3H(CO)_7(C_2Bu^t)(C_6H_{10})]$,[12] and some derivatives from the reactions of $[Os_3(CO)_{12}]$ with hexa- or hepta-dienes[13] or alkynes;[14] derivatives such as $[Ru_3H(CO)_9(C_6H_9)]$ show an allenyl system bonded to the metal cluster.[15] However, some olefins co-ordinate through one double bond to osmium clusters, as in $[Os_3H(CO)_9(SMe)(C_2H_4)]$.[16]

X-*Ray Structure of* (**4a**).—The structure of (**4a**) is shown in the Figure together with the atomic numbering scheme; selected bond distances and angles are given in Table 3. The complex, having an idealized C_s-m symmetry [with the pseudo-mirror plane passing through C(12), Os(1), and the midpoint of the Os(2)–Os(3) edge] consists of an isosceles triangle of osmium atoms [Os–Os bonds: 2.808(2), 2.804(2) and 2.929(2) Å], with the longer side bridged by a hydridic hydrogen atom [Os(2)–H(1) 1.86, Os(3)–H(1) 1.94 Å]. The dihedral angle between the cluster plane and the Os(2)–Os(3)–H(1) plane is 152°.

Three terminal carbonyl groups are bonded to each osmium atom; two of these are approximately equatorial with respect to the cluster plane. The three remaining carbonyls (one on each osmium atom) occupy approximately axial positions on one side of the cluster. The other side of the cluster is occupied by a dimethylallyl ligand interacting with all the metal atoms; it is σ-bonded to Os(2) and Os(3) [2.05(2) and 2.06(2) Å respectively]

Table 2. Spectroscopic data for the complexes (**3**) and (**4**)

Complex	I.r. (ν_{CO}/cm^{-1})[a]	^{1}H N.m.r. (δ)[b]	Mass spectrum
(**3a**)	2 076s, 2 056vs, 2 007vs, 1 998vs, 1 990s br	6.44—6.02 (m, 3 H), 6.00 (s, 5 H, C_5H_5), 1.26—1.16 (m, 5 H), −15.67 (d, 2 H), −19.50 (t, 1 H, hydride)	P^+ *m/e* 994 (low intensity) Loss of 2 CO, diene, 6 CO
(**3b**)	2 074ms, 2 054vs, 2 007vs, 1 995m br, 1 986vs br	—	—
(**3c**)	2 076ms, 2 056vs, 2 011vs, 1 989vs br, 1 988vs br	5.90 (s, 5 H, C_5H_5), 3.23 (m, 5 H), 1.40—1.23 (m, 3 H), −14.74 (d, 2 H), −19.71 (t, 1 H, hydride)	Same as for (**3a**)
(**3d**)	2 074ms, 2 055vs, 2 020vs, 1 997m br, 1 988vs br	—	—
(**4a**)	2 096ms, 2 064vs, 2 046vs, 2 018vs, 2 006s, 1 998vs, 1 988vs	—	P^+ *m/e* 884 Loss of 9 CO
(**4b**)	2 098ms, 2 070vs, 2 050vs, 2 020vs, 2 006vs, 1 999vs	—	P^+ *m/e* 884 Loss of 9 CO
(**4c**)	2 096m, 2 068ms, 2 060ms, 2 048vs, 2 019s, 2 012s, 1 999s	—	Decomposes

[a] In n-heptane solution. [b] In $CDCl_3$ solution.

Table 3. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Co-ordination sphere of the metal atoms

Os(1)–Os(2)	2.808(2)	Os(1)–C(3)	1.94(3)	Os(2)–C(4)	1.91(3)	Os(3)–C(7)	1.88(3)
Os(1)–Os(3)	2.804(2)	Os(1)–C(11)	2.30(2)	Os(2)–C(5)	2.00(2)	Os(3)–C(8)	1.92(2)
Os(2)–Os(3)	2.929(2)	Os(1)–C(12)	2.25(2)	Os(2)–C(6)	1.88(3)	Os(3)–C(9)	1.92(3)
Os(1)–C(1)	1.88(3)	Os(1)–C(13)	2.27(2)	Os(2)–C(13)	2.05(2)	Os(3)–C(11)	2.06(2)
Os(1)–C(2)	1.91(2)						

Os(2)–Os(1)–Os(3)	62.9(1)	C(1)–Os(1)–C(3)	94.0(12)	C(5)–Os(2)–C(6)	94.0(11)	C(7)–Os(3)–C(9)	94.5(13)
Os(1)–Os(2)–Os(3)	58.5(1)	C(2)–Os(1)–C(3)	96.1(10)	C(13)–Os(2)–Os(1)	53.1(7)	C(8)–Os(3)–C(9)	90.0(12)
Os(1)–Os(3)–Os(2)	96.1(10)	C(4)–Os(2)–C(5)	87.6(11)	C(13)–Os(2)–Os(3)	82.5(7)	C(11)–Os(3)–Os(1)	54.0(7)
C(1)–Os(1)–C(2)	98.5(10)	C(4)–Os(2)–C(6)	95.4(13)	C(7)–Os(3)–C(8)	95.1(11)	C(11)–Os(3)–Os(2)	84.2(7)

(*b*) Carbonyl groups

C(1)–O(1)	1.13(4)	C(4)–O(4)	1.13(4)	C(6)–O(6)	1.13(4)	C(8)–O(8)	1.16(3)
C(2)–O(2)	1.11(3)	C(5)–O(5)	1.09(3)	C(7)–O(7)	1.13(3)	C(9)–O(9)	1.07(4)
C(3)–O(3)	1.10(4)						

Os(1)–C(1)–O(1)	174(2)	Os(2)–C(4)–O(4)	175(3)	Os(2)–C(6)–O(6)	176(2)	Os(3)–C(8)–O(8)	179(3)
Os(1)–C(2)–O(2)	175(2)	Os(2)–C(5)–O(5)	177(2)	Os(3)–C(7)–O(7)	176(3)	Os(3)–C(9)–O(9)	177(2)
Os(1)–C(3)–O(3)	178(3)						

(*c*) Organic ligand

C(10)–C(11)	1.49(4)	C(12)–C(13)	1.40(4)	C(10)–C(11)–C(12)	113(2)	C(12)–C(13)–C(14)	112(2)
C(11)–C(12)	1.41(4)	C(13)–C(14)	1.55(4)	C(10)–C(11)–Os(3)	122(2)	C(12)–C(13)–Os(2)	127(2)
				C(12)–C(11)–Os(3)	124(2)	C(14)–C(13)–Os(2)	121(2)
				C(11)–C(12)–C(13)	122(2)		

and is linked to the Os(1) atom through an η^3-bonding system [Os(1)–C(11) 2.30(2), Os(1)–C(12) 2.25(2), and Os(1)–C(13) 2.27(2) Å], so acting as a formal five-electron donor. The C(11)–C(12) and C(12)–C(13) bonds in the substituted allyl ligand are equal indicating an electron delocalization in the allyl moiety. All carbon atoms of this ligand and Os(2) and Os(3) are nearly coplanar [maximum deviation from the mean plane passing through them is 0.04(3) Å for C(14)]; the dihedral angle between this plane and the cluster plane is 51.2(3)°.

Complexes with allylic ligands similarly bonded to a triangle of metal atoms are known for iron, [$Fe_3(CO)_7(\eta^5\text{-}C_5H_2Et_3)(CHCHCEt)$],[17] ruthenium, [$Ru_3H(CO)_9(MeCCHCEt)$][18] and [$Ru_3H(CO)_9(PhCC_6H_4)$],[19] and osmium, [$Os_3(CO)_9(HCCPhCOCPhCH)$],[20] [$Os_3H(CO)_9(HCCHCOH)$], and [$Os_3H(CO)_9(HCCHCOMe)$].[21] All these complexes, excepting the ruthenium derivatives, were obtained upon reaction of alkynes on [$M_3(CO)_{12}$] clusters or their derivatives. Thus, complex (**4a**) is the first osmium example of this type of structure obtained upon co-ordination of a diene; all the available literature reports[13,14] indicate that the reactions of dienes with [$Os_3(CO)_{12}$] lead only to 'allenyl' complexes.[15]

Complex (**4a**) is probably obtained in a complex reaction,

Table 4. Hydrogenation and deuteriation experiments on *cis*-penta-1,3-diene (tr = trace amount)

			Composition (%) of the reaction mixtures (organic products)				
Complex	Time (h)	Turnover[a]	pentane	pent-1-ene	*trans*-pent-2-ene	*cis*-pent-2-ene	substrate
(1)[b]	1	—	—	tr	tr	tr	100
	2	—	—	tr	tr	tr	100
	4	6	—	0.30	0.90	0.40	98.40
	6	12	—	0.50	2.10	0.60	96.80
(1)[c]	1	21	0.26	1.27	2.26	1.65	94.55
	2	29	0.35	1.86	3.02	2.16	92.60
	4	231	0.59	11.15	27.03	21.07	40.16
	6	247	0.72	14.39	27.90	21.51	35.94
	24	357	1.30	17.00	41.90	32.50	7.40
(1)[d]	4	134	0.65	5.33	18.77	9.88	65.36
(1)[e]	4	282	1.60	15.90	34.80	20.90	26.90
	4	191	0.70	9.30	26.30	15.90	50.50
	4	143	0.50	5.80	19.60	11.10	63.00
	4	108	0.20	4.10	16.60	7.20	71.90
(1)[f]	4	203	1.10	11.10	25.00	15.40	47.40
	4	259	0.80	12.60	22.20	17.80	46.60
	4	337	1.00	12.40	22.60	16.60	47.40
	4	386	2.50	7.00	18.20	13.30	59.00
(1)[g]	4	216[h]	0.80	12.50	25.50	17.20	44.00
	4	37	0.80	1.90	4.70	2.20	90.40
	4	30	0.80	1.40	3.80	1.80	92.20
	4	19	0.50	0.90	2.30	1.20	95.10
(1)[i]	1	2	—	0.10	0.20	0.10	99.60
	2	2	—	0.10	0.20	0.10	99.60
	4	2	—	0.10	0.20	0.10	99.60
	6	5	—	0.50	0.60	0.30	98.60
(2a)[c]	1	7	0.17	0.58	2.54	0.89	98.51
	2	43	0.42	1.45	5.32	2.38	90.43
	4	337	1.26	25.03	27.51	21.03	25.17
	6	330	1.13	21.47	28.74	21.73	26.75
(2b)[c]	1	15	tr	0.50	1.60	0.90	97.00
	2	50	0.80	1.90	4.60	2.70	90.00
	4	283	2.50	9.70	24.90	19.60	43.20

[a] Moles of substrate reacted per mole of catalyst. [b] Without hydrogen or deuterium. [c] With hydrogen (0.9 atm). [d] Combined pressure of H_2 and O_2 (8:1 v/v, 0.9 atm). [e] Hydrogen pressure = 1.00, 0.75, 0.50, and 0.25 atm respectively for the four entries. [f] [Diene] = 1.70, 0.85, 0.42, and 0.21 mol dm^{-3} respectively for the four entries; [complex] = 4.4×10^{-3} mol dm^{-3}; hydrogen pressure = 0.9 atm. [g] [Complex] = 4.4×10^{-3}, 2.2×10^{-3}, 1.1×10^{-3}, and 4.4×10^{-4} mol dm^{-3} respectively for the four entries, diene (0.200 cm^3) and hydrogen (0.9 atm) added. [h] Corrected for the complex concentration. [i] Hydrogen and CO (1:1 v/v, 0.9 atm) added.

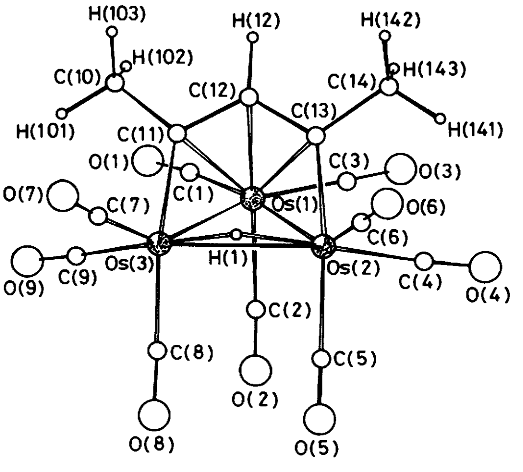


Figure. View of the molecular structure of the complex $[Os_3(\mu\text{-}H)(CO)_9(MeCCHCMe)]$ with the atomic numbering scheme

involving the 'substitution' of $(\eta\text{-}C_5H_5)Ni$ and two hydrides of (**1**) with the five-electron donor allyl ligand; an example of substitution of $(\eta\text{-}C_5H_5)Ni$ with a three-electron donor on cluster (**1**) has already been reported.[22]

Hydrogenation and Isomerization of the C_5 *and* C_6 *Molecules.*—The results of the hydrogenation and isomerization experiments for the C_5 molecules are collected in Tables 4 and 5, and those for the C_6 molecules in Table 6.

(*i*) *Selective hydrogenation of the double and triple bonds.* We found that complex (**1**) is more effective in the hydrogenation of 3,3-dimethylbut-1-yne than in that of 3,3-dimethylbut-1-ene.[1] The same is true for pent-1-yne compared to pent-1-ene; the former is easily hydrogenated to pent-1-ene, the latter is one of the hydrogenation products of *cis*- and *trans*-penta-1,3-diene. Analogous behaviour is observed for the C_6 molecules.

In the absence of isomerization, the internal triple bonds are hydrogenated more slowly than the terminal ones, as predictable from the 'classic' picture of homogeneous hydrogenation involving π-co-ordination of the substrate to one metal centre.[23] 3-Methylbut-3-en-1-yne gives isopentane and 2-methylbutadiene, that is preferential hydrogenation of the triple bond, in contrast with previous findings on ruthenium clusters,[22] probably because of different reaction mechanisms.

(*ii*) *Isomerization of mono- and di-enes in the presence of cluster* (**1**). The isomerization of the non-conjugated dienes occurs prior or competitively to the hydrogenation, in the presence of (**1**) (see in particular the behaviour of hexa-1,4-diene and of *cis*, *trans*-hexa-2,4-diene, Table 6); the final result is the selective hydrogenation of a terminal double bond.

Table 5. Hydrogenation experiments for *trans*-penta-1,3-diene and other C_5 molecules

			Composition (%) of the reaction mixtures (organic products)				
Reactants	Time (h)	Turnover[a]	pentane	pent-1-ene	*trans*-pent-2-ene	*cis*-pent-2-ene	substrate
(*a*) *trans*-Penta-1,3-diene							
(**1**)[b]	1	17	0.02	0.28	3.99	0.33	95.38
	2	19	0.06	0.40	4.22	0.45	94.78
	4	51	0.26	1.78	9.57	1.99	86.40
	6	193	0.41	13.53	28.31	9.17	48.74
(**2a**)[b]	1	28	0.10	0.35	5.54	0.35	93.66
	2	50	0.35	1.34	8.46	1.23	88.62
	4	70	0.51	1.99	11.16	2.21	84.12
	6	83	0.55	2.37	12.39	3.07	81.17
(*b*) Penta-1,4-diene							
(**1**)[b]	1	77	0.20	5.50	15.10	—	79.20
	2	119	4.70	20.80	6.70	—	67.80
	4	106	3.20	22.40	3.30	—	71.10
	6	265	4.10	11.20	38.20	18.40	28.10
(*c*) Pent-1-ene							
(**1**)[c]	1	81	—	76.70[d]	15.60	7.70	76.70
	2	111	—	68.00[d]	19.70	12.30	68.00
	4	133	—	61.70[d]	23.40	14.90	61.70
	6	142	—	59.10[d]	23.80	17.10	59.10
(*d*) Pent-1-yne							
(**1**)[b]	1	2	0.08	0.40	tr	tr	99.52
	2	7	0.10	1.40	0.10	0.20	98.20
	4	10	0.20	2.20	0.10	0.20	97.30
	24	183	2.70	43.00	1.90	2.70	49.70
(*e*) 3-Methylbut-3-en-1-yne			isopentane		2-methylbutadiene		substrate
(**1**)[b]	2	4	0.48		0.55		98.97
	4	19	0.53		4.19		95.28

[a] Moles of substrate reacted per mole of catalyst. [b] With hydrogen (0.9 atm). [c] Without hydrogen. [d] Compound is the same as the substrate.

The decrease of the hydrogenating efficiency and the formation of complex (**4a**) after a long time (24 h or more) under H_2 could indicate that isomerization occurs *via* allylic intermediates; this had been hypothesized for the isomerization of pentenes on $[Ru_4H_4(CO)_{12-n}(PR_3)_n]$[24] and evidenced when $[Ru_4H_2(CO)_{13}]$ was used as a catalyst.[25] In the latter study, the 'allylic' $[Ru_3H(CO)_9(C_6H_9)]$, proposed as an intermediate model, was found active in the isomerization of pent-1-ene; noteworthy is that the 'allylic' complex was obtained from the tetrahedral $[Ru_4H_2(CO)_{13}]$ upon substitution of one hydride and of $Ru(CO)_4$ with the formal five-electron donor ligand EtCCHCMe.[25]

Pent-1-ene isomerizes, in the presence of (**1**) and in the absence of hydrogen, yielding *trans*- and *cis*-pent-2-ene in the ratio of *ca.* 2:1. According to Wells and co-workers[26] this points to the presence of allylic intermediates.

(*iii*) *Hydrogenation of dienes in the presence of complexes* (**1**) *and* (**2**). Conjugated and non-conjugated dienes are converted to mono-enes with considerable efficiency and selectivity towards the terminal C=C bonds.

We have studied in detail the reactions of *cis*-penta-1,3-diene in the presence of (**1**); in the absence of hydrogen, the isomerization does not occur and only small amounts of hydrogenation products are formed. The same result is obtained when deuteriated (**1**) is used; deuterium was detected either in the reduced organic products* or in (**1**) recovered after reaction. This behaviour and the easy H/D exchange observed on (**1**) indicate that intramolecular hydride transfer occurs.

In the presence of hydrogen (4—6 h) the main reaction products are *trans*- and *cis*-pent-2-ene; some pent-1-ene is also found.* After 24 h the reaction slows down and (**4a**) is formed. Increased hydrogen pressure or greater concentration of complex (**1**) [or (**2**)], or of diene, influence favourably the reactions whereas the presence of CO exerts a strong inhibiting effect. Oxygen does not appreciably affect either the reaction rate or the product distribution; according to previous reports[27] this rules out the possibility of a radical mechanism.

Under comparable conditions, complexes (**2a**) and (**2b**) and *cis*-penta-1,3-diene give slightly better turnovers, with no dependence on the steric hindrance of the phosphine substituent. After some hours, however, the reactions become considerably slower than for (**1**) and the new complexes (**3**) are formed; these are probably obtained upon substitution of the phosphine with the diene. Noteworthy is the displacement of the phosphine instead of a CO ligand.[23] The modified reaction rate could hence be explained either by the difficulty for CO of displacing the diene co-ordinated on (**3**) or by the fact that CO substitution for the diene would lead to complex (**1**) [instead of the starting complex (**2**)] and hence to a different reaction rate and/or pathway.

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* $[3,4\text{-}D_2]$Pent-1-ene was found when deuterium was used; the same product was detected when deuteriated (**1**) was reacted with *cis*-penta-1,3-diene in the absence of hydrogen, and when the complexes (**3**) were reacted with deuterium. This result is probably due to isomerization, as discussed above.

Table 6. Hydrogenation of the C_6 molecules at 120 °C (n-octane as solvent)

			Composition (%) of the reaction mixtures (organic products)							
Reaction	Time (h)	Turnover[a]	C_3 or C_4 products	hexane	hex-1-ene	*trans*-hex-*n*-ene[b]	*cis*-hex-*n*-ene[b]	hexa-1,4-diene	hexa-2,4-diene	substrate
(*a*) *cis*-Hexa-1,4-diene										
(1)[c]	1	6	—	0.06	0.30	0.90	0.50[d]	98.30[e]	—	98.30
	2	20	—	0.30	0.90	3.20	1.60[d]	94.00[e]	—	94.00
	4	54	—	1.50	2.20	9.20	3.70[d]	83.40[e]	—	83.40
	6	47	—	1.40	2.10	7.60	3.40[d]	85.50[e]	—	85.50
(*b*) *cis, trans*-Hexa-2,4-diene										
(1)[c]	1	7	—	0.10	0.20	1.70	0.20[d]	—	97.80[e]	97.80
	2	14	—	0.10	0.20	3.30	0.50[d]	—	95.90[e]	95.90
	4	17	—	0.40	0.30	3.70	0.60[d]	—	95.00[e]	95.00
	6	22	—	1.00	0.50	4.40	0.80[d]	—	93.30[e]	93.30
(*c*) Hexa-1,5-diene										
(1)[f]	1	—	—	—	—	—	—	—	—	100
	2	11	—	—	—	—	—	3.50	—	96.50
	4	74	—	—	—	—	—	4.30	19.10	76.60
	6	42	—	—	—	—	—	13.30	—	86.70
(1)[c]	1	26	tr	—	1.40	1.10	—	5.50	—	91.90
	2	35	tr	tr	1.50	1.60	—	7.90	—	88.90
	4	183	0.20	0.40	6.20	18.90	—	31.70	—	42.50
	6	218	0.30	0.50	7.60	21.40	—	38.90	—	31.30
(*d*) *trans*-Hex-3-ene										
(1)[c]	1	3	—	0.41	—	—	0.45[d]	—	—	99.14
	2	7	—	0.55	—	—	1.67[d]	—	—	97.78
	4	60	—	1.30	—	—	5.21[d]	—	13.05	80.43
	24	114	—	6.89	—	—	10.40[d]	—	20.02	62.69
(*e*) Hex-3-yne										
(1)[c]	1	3	—	tr	tr	1.00	—	—	—	99.00
	2	6	—	tr	tr	1.80	—	—	—	98.10
	6	92	—	1.30	3.50	22.80	—	—	—	72.40

[a] Moles of substrate reacted per mole of catalyst. [b] The products (n = 2 or 3) could not be separated with the column and temperature program adopted for the analysis. [c] With hydrogen (1 atm). [d] *cis*-Hex-3-ene (detected by comparison with known standards). [e] Compound corresponds to the substrate. [f] Without hydrogen.

The results obtained with the other dienes can be compared to those discussed for *cis*-penta-1,3-diene; as predicted,[23] *trans*-penta-1,3-diene is hydrogenated more slowly. The non-conjugated dienes react readily and the hexadienes are hydrogenated with rates comparable to those observed for the pentadiene.

(*iv*) *Some remarks on the hydrogenation pathway.* Catalytic activity in the H/D exchange, together with site and product selectivity, have been indicated as criteria for identifying homogeneous catalytic reactions on clusters.[28] On these bases we propose that complexes (**1**) and (**2**) act as 'cluster catalysts'. The effects of hydrogen, cluster, and diene concentration, and of CO, and the nature of complexes (**3**) and (**4a**) suggest that a possible reaction path would be the one shown in the Scheme.

Cluster (**1**) is diamagnetic[1] and electronically saturated; vacant co-ordination sites or reactive species might be obtained only upon release of one CO or of two hydrides; alternatively, Ni–Os bond breaking would lead to 'butterfly' structures with co-ordinated alkynes or dienes.[22] This latter process has been proposed for the hydrogenation of ethylene on $[Ru_4H_4(CO)_{12}]$ where the H/D exchange was ascribed to competitive addition of H_2 or ethylene to a butterfly species.[29]

In the present study we did not detect butterfly intermediates; these are generally obtained from (**1**) in the presence of alkynes with a large excess of H_2 and their formation is favoured by CO.[22] The behaviour of the tetrahedral cluster $[PtOs_3H_2(CO)_{10}\{P(C_6H_{11})_3\}]$, which gives reversible Os–Pt bond cleavage (and butterfly structures) in the presence of CO, and addition of two hydrogen atoms onto the tetrahedral framework[30] accords with our findings.

The role of complexes (**3**) in the hydrogenation reactions has been established by reacting these derivatives with hydrogen or deuterium; pentane and pentenes (and not free pentadienes) were obtained, together with some complex (**1**) and slight decomposition.

The reaction pathway proposed in the Scheme shows considerable analogy with that proposed for $[Os_3H_2(CO)_{10}]$ anchored on silica,[31] the major difference being the nature of the first metal–ligand bond broken. Another example of a fully evidenced hydrogenation cycle on a cluster has been reported by Mays and co-workers[32] {hexafluorobut-2-yne on $[Os_3(CO)_{12}]$}; in this example, however, the CO plays a positive role, forming alkene intermediates and restoring the catalyst, so that a different mechanism is probably effective.

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