Synthesis and Crystal Structure of $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2\{\mu\text{-}Cu(PPh_3)\}(CO)_9]$.* Hydrogenation–Dehydrogenation Reactions of Dienes and Alcohols with Heterogeneous Catalysts derived from $[NiM_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2(\mu\text{-}X)(CO)_9]$ [M = Ru, X = H; M = Os, X = $Cu(PPh_3)$]

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The complex $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2\{\mu\text{-}Cu(PPh_3)\}(CO)_9]$ has been synthesized in tetrahydrofuran (thf) by reaction of the anion $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2(CO)_9]^-$, generated *in situ* from $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_3(CO)_9]$ and NaH, with $[\{Cu(PPh_3)Br\}_4]$. Its structure has been determined by *X*-ray methods. Crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions a = 13.643(7), b = 14.120(6), c = 9.504(4) Å, α = 94.88(3), β = 105.77(4), and γ = 102.15(3)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.0462 for 2 191 observed reflections. The metal cluster can be described as a $NiOs_3$ tetrahedron with an Os–Os edge bridged by the Cu atom from the $Cu(PPh_3)$ group. This complex, supported on Chromosorb and thermally activated under H_2, forms a heterogeneous catalyst for the hydrogenation–dehydrogenation of several substrates, in particular alcohols. The behaviour of this catalyst is significantly different from that of systems derived from the parent cluster $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_3(CO)_9]$ or from $[NiRu_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_3(CO)_9]$. In particular, it shows high dehydrogenation ability.

The use of heterometallic clusters in catalysis is an expanding research area.[1,2] Of considerable interest are the possible correlations between the core compositions of heterometallic clusters and the catalytic properties of the corresponding mixed-metal cluster-derived (m.m.c.d.) particles which constitute a new generation of heterogeneous catalysts. In particular, we have been interested, as part of a collaborative project, in the tetrahedral complexes $[NiM_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_3(CO)_9]$ [M = Ru (**1**)[3] or Os (**2**)[4]]. When (**2**) is supported on $\gamma\text{-}Al_2O_3$ and thermally treated under H_2 a good heterogeneous system for the hydrogenation of CO, CO_2, and other small molecules is produced.[5] The nature of the metals, as well as the cluster core stoicheiometry, are expected to play an important role in the activity and selectivity of the corresponding m.m.c.d. catalysts.

In order to gain a better knowledge of the latter aspects, we have introduced copper in (**2**) by 'isolobal substitution'[6] of $Cu(PPh_3)$ for one bridging hydride. The complex obtained, $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2\{\mu\text{-}Cu(PPh_3)\}(CO)_9]$ (**3**), has been characterized by spectroscopy and its structure confirmed by an *X*-ray investigation. We also report here the use of (**3**) as a heterogeneous catalyst precursor which is, to our knowledge, the first such example for a copper-containing cluster. Copper-based catalysts, obtained in conventional ways or with new procedures, have been reported recently.[7] As substrates we have chosen dienes already studied in the presence of catalysts derived from (**1**) or (**2**) and some alcohols because the zeolite-catalyzed hydrogenation-dehydrogenation of methanol[8] is nowadays an increasingly important industrial process.

Experimental

Complexes (**1**) and (**2**) were synthesized and purified by established procedures.[3,4]

Preparation of $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2\{Cu(PPh_3)\}(CO)_9]$ (**3**).—To a tetrahydrofuran (thf) solution (20 cm^3) of $[NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_3(CO)_9]$ (**2**) (0.217 g, 0.23 mmol) was added a suspension of NaH (0.200 g, 8.50 mmol) in thf (5 cm^3). The purple solution was stirred for 3 d at room temperature. The reaction was stopped when the solution had turned green. The filtered solution containing the monoanion of (**2**) was evaporated to dryness under reduced pressure. A suspension of $[\{Cu(PPh_3)Br\}_4]$ (0.950 g, 0.058 mmol) in toluene (15 cm^3) was added to a suspension of the green monoanion of (**2**) in toluene (15 cm^3), and stirred at room temperature for 1 h. The solution was filtered and evaporated under reduced pressure. Crystallization of the solid residue in hexane afforded compound (**3**) as dark purple crystals (0.140 g, 47.8%). Analytical and spectroscopic data were as reported earlier.[9]

Crystal Structure Determination and Refinement of Complex

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* 2,2,2,3,3,3,4,4,4-Nonacarbonyl-1-η-cyclopentadienyl-2,3;2,4-di-μ-hydrido-3,4-μ-triphenylphosphinecuprio-*tetrahedro*-1-nickel-2,3,4-triosmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	2 727(1)	820(1)	8 613(1)	C(10)	945(27)	3 201(27)	7 673(43)
Os(2)	3 329(1)	2 470(1)	7 223(1)	C(11)	390(24)	2 195(23)	7 278(37)
Os(3)	3 844(1)	2 694(1)	10 315(1)	C(12)	401(24)	1 816(23)	8 609(38)
Ni	1 950(3)	2 320(3)	8 607(4)	C(13)	916(28)	2 604(28)	9 860(44)
Cu	5 266(3)	2 892(3)	8 939(4)	C(14)	1 235(24)	3 439(24)	9 186(39)
P	6 893(6)	2 918(5)	8 841(9)	C(15)	7 833(20)	2 926(19)	10 566(31)
O(1)	1 527(17)	165(15)	10 690(26)	C(16)	8 473(24)	2 254(23)	10 867(38)
O(2)	3 895(20)	−802(17)	8 685(30)	C(17)	9 145(28)	2 278(27)	12 192(45)
O(3)	843(18)	−233(17)	6 033(32)	C(18)	9 139(26)	2 949(26)	13 373(41)
O(4)	1 443(16)	1 821(18)	4 531(25)	C(19)	8 558(31)	3 638(31)	13 214(49)
O(5)	3 426(26)	4 653(21)	7 193(36)	C(20)	7 856(26)	3 623(25)	11 738(41)
O(6)	4 816(15)	2 463(19)	5 368(23)	C(21)	7 547(21)	3 900(20)	8 034(32)
O(7)	2 850(18)	2 474(18)	12 764(26)	C(22)	8 616(22)	4 143(21)	8 361(33)
O(8)	5 913(16)	2 867(19)	12 610(27)	C(23)	9 087(26)	4 925(25)	7 789(40)
O(9)	4 020(18)	4 878(15)	10 546(27)	C(24)	8 416(30)	5 349(27)	6 698(45)
C(1)	2 021(23)	449(22)	9 959(35)	C(25)	7 386(29)	5 094(27)	6 415(42)
C(2)	3 467(24)	−234(24)	8 720(36)	C(26)	6 885(23)	4 307(22)	7 086(35)
C(3)	1 528(22)	185(21)	7 046(34)	C(27)	6 837(23)	1 803(22)	7 671(35)
C(4)	2 159(23)	2 004(21)	5 602(35)	C(28)	7 417(29)	1 859(30)	6 704(46)
C(5)	3 375(22)	3 843(23)	7 243(35)	C(29)	7 380(35)	953(36)	5 878(54)
C(6)	4 275(22)	2 483(21)	6 083(34)	C(30)	6 702(33)	41(32)	6 017(49)
C(7)	3 180(22)	2 500(21)	11 795(35)	C(31)	6 056(26)	90(25)	6 805(40)
C(8)	5 167(24)	2 829(22)	11 679(36)	C(32)	6 124(24)	962(24)	7 756(38)
C(9)	3 925(23)	4 078(25)	10 477(36)				

(**3**).—Dark purple single crystals of complex (**3**) were obtained from hexane solution.

Crystal data. $C_{32}H_{22}CuNiO_9Os_3P$, M = 1 247.35, triclinic, space group $P\bar{1}$, a = 13.643(7), b = 14.120(6), c = 9.504(4) Å, α = 94.88(3), β = 105.77(4), γ = 102.15(3)°, U = 1 703(1) Å^3 (by least-squares refinement of the θ values of 28 accurately measured reflections), Z = 2, λ = 0.710 69 Å, D_c = 2.486 g cm^{-3}, F(000) = 1 172, μ(Mo-K_α) = 124.30 cm^{-1}.

A crystal of approximate dimensions 0.06 × 0.21 × 0.29 mm was used for the structure analysis. A correction for the absorption[10] was applied (maximum and minimum transmission factors 1.395 and 0.814 respectively) using the program ABSORB.[11] Siemens AED diffractometer, θ—2θ scan mode, using niobium-filtered Mo-K_α radiation; all reflections with θ in the range 3—23° were measured. Of 4 754 independent reflections, 2 191, having $I > 2\sigma(I)$, were considered observed and used in the analysis.

The structure was solved by direct and Fourier methods, and refined by full-matrix least squares with anisotropic thermal parameters in the last cycles for all the non-carbon and hydrogen atoms. The hydrogen atoms (excepting the hydrides) were placed at their geometrically calculated positions and included in the final structure-factor calculations with isotropic thermal parameters. Final R and R' values were 0.0462 and 0.0550. The SHELX system of computer programs was used.[12] Atomic scattering factors, corrected for anomalous dispersion of Os, Cu, Ni, and P, were taken from ref. 13. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, and on the GOULD 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Catalytic Experiments.—These were performed in a previously described catalytic–analytic gas chromatographic system;[14] the catalytic columns [1 m × 0.6 cm internal diameter (i.d.)] were filled respectively with (**1**) (35 mg per 12 g support), (**2**) (20 mg per 7 g support), and (**3**) (40 mg per 12 g support). The amounts of metals in the three systems were: (**1**), 0.025% Ni, 0.13% Ru; (**2**) 0.018% Ni, 0.17% Os; (**3**) 0.15% Ni, 0.15% Os, and 0.17% Cu.

The supporting material was Chromosorb P (Johns Manville, 60—80 mesh, superficial area 4 m^2 g^{-1}). The clusters were dissolved in light petroleum (b.p. 40—70 °C), under N_2, impregnated, and thermally treated on the support as previously described.[14] After 20 h at 155 °C under a current of H_2 (25 cm^3 min^{-1}), fully heterogeneous systems were obtained in all cases.

The substrates were injected either as vapours (as previously described[14]) or as liquids; no saturation of the catalytic column was observed. A glass-lined injection system was used for introducing the substrates into the catalytic column to avoid any contact with the metals of the introduction device; the activity of the column metal and of the chromatographic support was also checked by introducing ethanol into an empty 'catalytic column' or one containing only Chromosorb. In these experiments at 180 °C the formation of 2—4% aldehyde was observed.

The gaseous products from the catalytic experiments were analyzed on analytical columns filled with the materials, and operated under the following conditions and temperature programs using always 25 cm^3 min^{-1} of H_2 or N_2 as carrier (and reactant) gas: (*i*) pentadienes, 2.0 m × 0.6 cm i.d. n-octane-porasyl C (80—100 mesh), 75 °C (10 min) then 20 °C min^{-1} till 155 °C; (*ii*) empty catalytic column and column with support only, 2.5 m × 0.6 cm i.d., Chromosorb 101, 75 °C (3 min) then 20 °C min^{-1} till 155 °C; (*iii*) alcohols, as column and program (*ii*); (*iv*) alcohols (modified program), 2.5 m × 0.6 cm i.d., 155 °C then 20 °C min^{-1} till 230 °C.

For the alcohols, the injection procedure and the choice of the analytic programs were critical; we had observed that small amounts of the substrates were chemisorbed for long periods in the analytical columns, probably as alkoxides, and could be displaced by fresh substrate or by water. Thus, successive injections of alcohols were made after a sufficient interval of time for the analytical column to be purged completely.

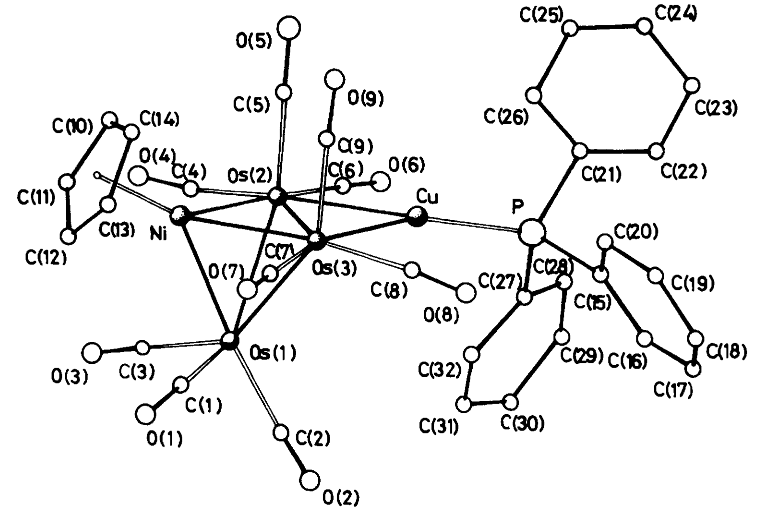

Figure. View of the complex [$NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2\{\mu\text{-}Cu(PPh_3)\}(CO)_9$] (**3**) showing the atomic numbering system. The hydride ligands bridging the Os(1)–Os(2) and Os(1)–Os(3) edges have been omitted

Table 2. Selected bond distances (Å) and angles (°) in complex (**3**)

Os(1)–Os(2)	2.856(2)	Cu–Os(3)	2.601(5)	Os(2)–C(6)	1.90(4)	C(4)–O(4)	1.17(3)
Os(1)–Os(3)	2.859(2)	Cu–P	2.240(10)	Os(3)–C(7)	1.88(4)	C(5)–O(5)	1.14(4)
Os(2)–Os(3)	2.803(2)	Os(1)–C(1)	1.85(4)	Os(3)–C(8)	1.88(3)	C(6)–O(6)	1.13(4)
Ni–Os(1)	2.560(5)	Os(1)–C(2)	1.96(4)	Os(3)–C(9)	1.92(4)	C(7)–O(7)	1.13(5)
Ni–Os(2)	2.557(5)	Os(1)–C(3)	1.88(2)	C(1)–O(1)	1.13(4)	C(8)–O(8)	1.14(4)
Ni–Os(3)	2.567(4)	Os(2)–C(4)	1.84(3)	C(2)–O(2)	1.09(5)	C(9)–O(9)	1.10(4)
Cu–Os(2)	2.613(4)	Os(2)–C(5)	1.92(3)	C(3)–O(3)	1.15(3)		
Os(2)–Os(1)–Os(3)	58.7(1)	Cu–Os(2)–Os(3)	57.3(1)	Os(2)–Os(3)–C(8)	128(1)	C(4)–Os(2)–C(6)	93(1)
Os(1)–Os(2)–Os(3)	60.7(1)	Cu–Os(3)–Os(2)	57.7(1)	Os(2)–Os(3)–C(9)	93(1)	C(5)–Os(2)–C(6)	94(1)
Os(1)–Os(3)–Os(2)	60.6(1)	Os(3)–Os(1)–C(1)	94(1)	Os(1)–Os(3)–C(7)	93(1)	C(7)–Os(3)–C(8)	91(1)
Os(1)–Ni–Os(2)	67.9(1)	Os(3)–Os(1)–C(2)	118(1)	Os(1)–Os(3)–C(8)	119(1)	C(7)–Os(3)–C(9)	94(1)
Os(2)–Ni–Os(3)	66.3(1)	Os(3)–Os(1)–C(3)	143(1)	Os(1)–Os(3)–C(9)	145(1)	C(8)–Os(3)–C(9)	95(1)
Os(1)–Ni–Os(3)	67.8(1)	Os(2)–Os(1)–C(1)	141(1)	Cu–Os(2)–C(4)	162(1)	Os(1)–C(1)–O(1)	174(3)
Ni–Os(1)–Os(2)	56.0(1)	Os(2)–Os(1)–C(2)	121(1)	Cu–Os(2)–C(5)	91(1)	Os(1)–C(2)–O(2)	175(3)
Ni–Os(1)–Os(3)	56.2(1)	Os(2)–Os(1)–C(3)	96(1)	Cu–Os(2)–C(6)	69(1)	Os(1)–C(3)–O(3)	175(3)
Ni–Os(2)–Os(3)	57.0(1)	Os(1)–Os(2)–C(4)	91(1)	Cu–Os(3)–C(7)	162(1)	Os(2)–C(4)–O(4)	172(3)
Ni–Os(2)–Os(1)	56.1(1)	Os(1)–Os(2)–C(5)	143(1)	Cu–Os(3)–C(8)	71(1)	Os(2)–C(5)–O(5)	176(3)
Ni–Os(3)–Os(1)	56.0(1)	Os(1)–Os(2)–C(6)	121(1)	Cu–Os(3)–C(9)	91(1)	Os(2)–C(6)–O(6)	178(3)
Ni–Os(3)–Os(2)	56.7(1)	Os(3)–Os(2)–C(4)	139(1)	C(1)–Os(1)–C(2)	97(1)	Os(3)–C(7)–O(7)	173(3)
Os(2)–Cu–Os(3)	65.0(1)	Os(3)–Os(2)–C(5)	91(1)	C(1)–Os(1)–C(3)	90(1)	Os(3)–C(8)–O(8)	172(3)
Os(2)–Cu–P	140.6(3)	Os(3)–Os(2)–C(6)	126(1)	C(2)–Os(1)–C(3)	98(1)	Os(3)–C(9)–O(9)	176(3)
Os(3)–Cu–P	151.9(3)	Os(2)–Os(3)–C(7)	139(1)	C(4)–Os(2)–C(5)	97(1)		

Results and Discussion

Crystal Structure of Complex (**3**).—The structure of complex (**3**) is shown in the Figure together with the atomic numbering system; selected bond distances and angles are given in Table 2.

Complex (**3**) is isostructural with the previously reported gold derivative [$NiOs_3(\eta\text{-}C_5H_5)(\mu\text{-}H)_2\{\mu\text{-}Au(PPh_3)\}(CO)_9$] (**4**)[9] and consists of a tetrahedral arrangement of three osmium and one nickel atom with an Os–Os edge bridged by the copper atom from the $Cu(PPh_3)$ group. The structure can be derived from that of the precursor (**2**) by replacing one of the equivalent hydrides by the $Cu(PPh_3)$ group on the basis of isolobal analogy.[6] The metal cluster can also be described as a Os_3Cu butterfly with the Os_3 wing nearly symmetrically capped by a $Ni(\eta\text{-}C_5H_5)$ fragment [dihedral angle between the two wings 113.7(1)°] or as a planar triangulated $NiOs_2Cu$ core [dihedral angle between the Ni,Os(2),Os(3) and Cu,Os(2),Os(3) triangles 178.5(2)°] with the $NiOs_2$ triangle capped by the third Os atom. The structural features of the $NiOs_3$ cluster of (**3**) are comparable to those of the precursor (**2**) and of the gold derivative (**4**), except for the Os–Os bond length bridged by the copper atom, which is significantly shorter in (**3**), 2.803(2) Å, with respect to the corresponding one in the gold derivative, 2.863(2) Å, this latter being practically unaltered with respect to those in the precursor (**2**). The most relevant structural parameters in complexes (**2**)—(**4**) are compared in Table 3.

As regards the Os–Cu bonds, those in (**3**), 2.601(5) and 2.613(4) Å, are shorter than the ones in [$Os_3H_3\{Cu(PPh_3)\}(CO)_{10}$], 2.695(5) and 2.726(5) Å,[15] where the $Cu(PPh_3)$ group also bridges an Os–Os edge of a triangular osmium cluster, but where bridging hydrides were hypothesized on all three edges of the Os_2Cu triangle.

Catalytic Results: Comparison of the Behaviour of Complexes (**1**)—(**3**).—(*a*) *Hydrogenation–dehydrogenation of dienes.* The results obtained in these experiments are collected in Table 4. They show that heterogeneous catalysts derived from complex (**3**) give lower amounts of C–C bond hydrogenolysis products[14a] compared with (**1**) or (**2**) and with increasing temperature increasing amounts of 2-pentene are formed. At 230 °C they represent the main products, especially when liquid substrates are injected. A better selectivity to monoenes is thus obtained with (**3**). This behaviour is probably the result of complex hydrogenation and dehydrogenation equilibria, as already suggested for (**1**) when using the same substrates under comparable conditions.[14] Nickel may be considered as responsible for the uptake of hydrogen and its storage in the catalytic system.[16] The dehydrogenation ability of (**3**) is much higher than that of (**1**), even under H_2; it is even more evident when alcohols are used as substrates.

Table 3. Comparison of bond distances (Å) and angles (°) in the clusters (**2**)—(**4**)

	(**2**)		(**3**)[c]	(**4**)[d]
Os–Os	2.859(1)[a]	2.866(2)[b]	2.856(2)	2.881(2)
	2.874(1)	2.866(2)	2.859(2)	2.875(2)
	2.874(1)	2.869(2)		
	2.873(1)			
	2.873(1)			
	2.873(1)			
Os–Os [M(PPh$_3$) bridged edge]			2.803(2)	2.863(2)
Ni–Os	2.578(2)	2.563(5)	2.560(5)	2.581(5)
	2.569(2)	2.564(5)	2.557(5)	2.581(4)
	2.569(2)	2.564(5)	2.567(4)	2.569(5)
	2.562(2)			
	2.563(2)			
	2.563(2)			
M–Os			2.613(4)	2.747(2)
			2.601(5)	2.775(2)
M–P			2.240(10)	2.292(8)
Dihedral angle between Os$_3$ and Os$_2$M triangles			113.7(1)	114.9(1)

[a] Ref. 4*a*; two independent molecules. [b] Ref. 4*b*. [c] This work. [d] Ref. 9.

(*b*) *Hydrogenation, dehydrogenation, and dehydration of alcohols.* The substrates studied were methanol, ethanol, n- and iso-propyl alcohol, the results obtained for methanol and ethanol are collected in Table 5 and those for Pr^nOH and Pr^iOH in Table 6.

Methanol and ethanol, in the presence of m.m.c.d. catalysts obtained from (**3**) give small amounts of C_1 or C_2 hydrocarbons and medium yields of formaldehyde or acetaldehyde, respectively. By contrast, the same substrates in the presence of catalysts derived from (**1**) or (**2**) give higher amounts of hydrocarbons (some probably due to oligomerization of C_2 units) and good yields of ethers as oxygenated products. The behaviour of complex (**3**) appears of interest; the formation of ethers during dehydration–hydrogenation sequences leading from methanol to hydrocarbons on zeolites[8] is well established, whereas aldehydes have been rarely reported in these reactions. The formation of aldehydes in the presence of (**3**) would hence represent an alternative route to (low molecular weight) hydrocarbons as well as a retrosynthetic path to syngas.

The dehydrogenation properties of complex (**3**) are again evident when Pr^nOH and Pr^iOH are reacted; acetone is formed, with better yields from Pr^iOH, whereas in the presence of (**2**) ethers are observed. Chemical equations (1)—(4) correspond to

$$2\,\mathrm{MeOH}\text{–}(\mathrm{NiOs_3}) \longrightarrow \mathrm{OMe_2} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{MeOH}\text{–}(\mathrm{NiOs_3Cu}) \longrightarrow \mathrm{HCHO} + \mathrm{H_2} \qquad (2)$$

$$2\,\mathrm{Pr^iOH}\text{–}(\mathrm{NiOs_3}) \longrightarrow \mathrm{OPr^i_2} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{Pr^iOH}\text{–}(\mathrm{NiOs_3Cu}) \longrightarrow \mathrm{Me_2CO} + \mathrm{H_2} \qquad (4)$$

these catalytic processes. A hydrogenation–dehydrogenation sequence for acetone, in the presence of complex (**2**), has been reported previously: Pr^iOH was the first hydrogenation product, followed by di-isopropyl ether and then propylene.[17] The hydrogenation properties of the catalyst derived from (**2**) and the dehydration properties of the support material were responsible for the observed results.

In conclusion, we have found considerable differences in the

Table 4. Hydrogenation–dehydrogenation of *cis*-1,3- and 1,4-pentadiene in the presence of catalysts derived from clusters (**1**) and (**3**); 100% conversion

Precursor and substrate	Reaction temperature (°C)	Selectivity				Ref.
		Cracking[a]	Pentane	1-Pentene	2-Pentenes[b]	
NiRu$_3$ (**1**)						
1,3-Pentadiene	80		100			14*b*
	150	2.9	97.1			
	230	18.6	81.4			
1,4-Pentadiene	80		100			14*b*
	150	2.4	97.6			
	230	18.1	81.9			
NiOs$_3$ (**2**)						
1,3-Pentadiene	80		100			14*a*
	150	27.4	72.6			This work[c]
CuNiOs$_3$ (**3**)						
1,3-Pentadiene	80		83.9		16.0	This work
	150		68.8	0.5	30.6	
	230	4.0	58.1	1.5	36.4	
	230[d]	1.3	49.9	2.3	46.5	
1,4-Pentadiene	80	0.8	90.5	1.5	7.1	This work
	150	1.2	73.4	1.8	23.6	
	230	4.2	57.8	1.7	36.2	
	230[d]	1.2	45.5	4.0	49.3	

[a] Cracking and/or C–C hydrogenolysis products (C_1 + C_2). [b] *cis* and *trans* isomers. [c] At higher temperatures (*e.g.* 230 °C) hydrogenolysis prevails. [d] Substrate injected as a liquid (see text).

Table 5. Hydrogenation–dehydrogenation of methanol and ethanol in the presence of cataysts derived from clusters (**1**)—(**3**)

Precursor and substrate (gas)[a]	Reaction temperature (°C)	Conversion (%)	Selectivity				
				$C_1 + C_2$[b]	OMe_2	HCHO	
Methanol							
$NiRu_3$(**1**)							
(H_2)	140	37.6		0.27	99.73		
$NiOs_3$ (**2**)							
(H_2)	200	25.0			100.0		
	230	60.0			100.0		
$CuNiOs_3$ (**3**)							
(H_2)	230	11.8		69.49[c]		30.51	
(N_2)	230	1.0		20.0		80.0	
			$C_1 + C_2$	C_3—C_8	OEt_2	MeCHO	HCHO
Ethanol							
$NiRu_3$ (**1**)							
(H_2)	200	29.30	30.72		69.28		
$NiOs_3$ (**2**)							
(H_2)	200	11.0	64.54		35.46		
	230	37.8	48.68	26.72[d]	24.60		
$CuNiOs_3$ (**3**)							
(H_2)	230	13.9	37.28—32.97[e]	4.82—2.33[e]		59.28—27.92[e]	
(N_2)	230	13.4[f]	5.97			82.84	11.19

[a] In parentheses, carrier and reactant. [b] Methane + ethane. [c] Methane only. [d] Mostly C_8. [e] Maximum and minimum values found in different experiments (see text). [f] Some ethylene was also present.

Table 6. Hydrogenation–dehydrogenation of Pr^nOH and Pr^iOH in the presence of catalysts derived from clusters (**2**) and (**3**)

Precursor and substrate (gas = H_2)	Reaction temperature (°C)	Conversion (%)	Selectivity				
			$C_1 + C_2$	$C_3 + C_9$	OPr^n_2	OPr^i_2	Me_2CO
Pr^nOH							
$NiOs_3$ (**2**)	200	36.8	33.15	32.61[a]	34.24		
	230	60.0	29.83	49.17[a]	21.0		
$CuNiOs_3$ (**3**)[b]	230	5.42					100
Pr^iOH							
$NiOs_3$ (**2**)	200	71.7	11.30	22.45[c]		66.25	
	230[d]	85.2	13.62	32.63[c]		53.64	
$CuNiOs_3$ (**3**)[b]	230	17.56	3.19	5.69[c]			91.11

[a] Saturated and unsaturated compounds: the C_9 fraction is about 25% of the total. [b] Mean values from several experiments. [c] Saturated and unsaturated compounds (mostly C_3). [d] Substrate injected as a liquid (see text).

behaviour of the catalyst derived from complex (**3**) with respect to those of (**1**) and (**2**) prepared and treated under similar conditions. Cluster (**3**) leads to a catalyst which shows dehydrogenation properties giving formaldehyde and acetaldehyde, respectively, from methanol and ethanol. The behaviour of Pr^nOH and Pr^iOH has also been considered; the catalytic activity of the column materials has also to be taken into account. The observed differences may be attributed to the presence of copper in (**3**); we also suspect the presence of copper(I) alkoxides[18] as reaction intermediates. Injection of water, immediately after that of the substrates, results in regeneration of alcohols; Cu^I could be formed by disproportionation between Cu^{II} obtained by oxidation by the support and Cu^0 upon reduction by H_2. Further investigations are in progress.

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