The Replacement of One Hydrido-ligand in [(η-C_5H_5)NiOs_3(μ-H)$_3$(CO)$_9$] by $MPPh_3^+$ (M = Cu or Au). Crystal Structure of [(η-C_5H_5)NiOs_3(μ-H)$_2$(μ-$AuPPh_3$)(CO)$_9$],† the First Gold–Nickel–Osmium Cluster

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Abstraction by NaH in tetrahydrofuran of one hydride ligand of [(η-C_5H_5)NiOs_3(μ-H)$_3$(CO)$_9$] (3) leads to the anion [(η-C_5H_5)NiOs_3(μ-H)$_2$(CO)$_9$]$^-$, which upon reaction with M(PPh_3)Cl (M = Au or Cu) leads to the pentametallic clusters [(η-C_5H_5)NiOs_3(μ-H)$_2$(μ-$MPPh_3$)(CO)$_9$] [M = Au, (1); M = Cu, (2)]. The structure of (1) 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 = 13.923(3), b = 14.213(4), c = 9.544(4) Å, α = 93.81(4), β = 105.48(2), γ = 102.83(2)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.055 for 2 867 observed reflections. The structure of (1) can be derived from that of (3) by replacing one of the three equivalent hydride ligands by $AuPPh_3^+$. The metal cluster can be described as a NiOs_3 tetrahedron with an Os–Os edge bridged by an Au atom.

Numerous recent studies have concentrated on the synthesis of mixed-metal clusters containing the $AuPR_3^+$ unit (R = aryl or alkyl). Besides the enhanced reactivity which might be anticipated for these clusters, their study has also been motivated by recognition that the $AuPR_3^+$ fragment and a hydride have similar bonding characteristics.[1,2] As a result, knowledge of the structures of these complexes should allow an indirect evaluation of the position of the hydride in the parent compounds. This is particularly useful when the exact location of the hydride ligand has not been determined by *X*-ray or neutron diffraction. Conversely, the structure of the $AuPR_3^+$-containing clusters may often be predicted on the basis of the known geometry, when available, of the analogous hydrido-derivatives. So far, in all known cases but one,[3] no rearrangement of the precursor anionic metal core is observed upon addition of the $AuPR_3^+$ group(s), which is consistent with theoretical predictions since this 12-electron cation formally donates no electron to the cluster for skeletal bonding. However, skeletal rearrangements of the final cluster have been observed.[4] In complexes containing one $AuPR_3^+$ unit the co-ordination of the gold atom has been found very versatile,[5] as for the hydride ligand. Examples are known where $AuPR_3^+$ is in terminal, edge-bridging, or face-bridging position. When two or more $AuPR_3^+$ groups are present in the cluster, structural predictions may become more difficult because of the easy occurrence of direct Au–Au bonds.

Among the heterometallic gold clusters described previously, species containing four,[5–8] five,[2,4,9–13] six,[8–10,13,14] seven,[8,13,15] and eight [16] metal atoms have been most commonly encountered.

Cluster cores containing one gold atom and two different metals have been structurally characterized only for [FeCo_3(CO)$_{12}$($AuPPh_3$)],[2] [RuCo_3(CO)$_{12}$($AuPPh_3$)],[12] and [CoRu_3(CO)$_{13}$($AuPPh_3$)].[13] These clusters, together with six others having Fe_4Au,[10] Os_4Au,[11] Fe_3Au_2,[9] and Ru_3Au_2 [4] cores, represent the only examples reported so far of heteropentametallic gold clusters structurally investigated.

Here we report the synthesis of the new pentametallic clusters [(η-C_5H_5)NiOs_3(μ-H)$_2$(μ-$AuPPh_3$)(CO)$_9$] (1) and [(η-C_5H_5)NiOs_3(μ-H)$_2$(μ-$CuPPh_3$)(CO)$_9$] (2) and the crystal structure of (1), the first gold–nickel–osmium cluster.

Experimental

Air-sensitive reagents and products were manipulated in a nitrogen atmosphere using Schlenk techniques. Solvents were purified and dried by standard techniques. I.r. spectra were recorded in the region 4 000—400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer in tetrahydrofuran (thf) or toluene solution. The ^{1}H n.m.r. spectra were recorded on a FT-Brucker SY 200 instrument ($CDCl_3$ solution) (positive chemical shifts are downfield relative to H_3PO_4). The u.v. spectra were recorded on a Beckman Acta CIII spectrophotometer (hexane solutions).

Preparation of [(η-C_5H_5)NiOs_3(μ-H)$_2$(μ-$AuPPh_3$)(CO)$_9$] (1). —To a thf solution (10 cm^3) of [(η-C_5H_5)NiOs_3(μ-H)$_3$(CO)$_9$] (3)[17,‡] (0.063 g, 0.07 mmol) was added a suspension of NaH (0.100 g, 4.25 mmol) in thf (10 cm^3). The purple solution was stirred for 4 d at room temperature.

The i.r. bands [ν(CO) region] of the solution change during the reaction, and are shifted to lower wavenumbers.

A gradual change in colour was noticed and the reaction was stopped when the solution had turned green. The filtered solution, presumably containing the monoanion of complex

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† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-μ$_3$-(η-cyclopentadienyl)nickelio-1,2;1,3-di-μ-hydrido-2,3-μ-triphenylphosphineaurio-*triangulo*-triosmium.

Supplementary data available (No. SUP 23983, 20 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ The spectroscopic characterization of (3) and some catalytic experiments are described by M. Castiglioni, M. Valle, E. Sappa, M. Lanfranchi, and A. Tiripicchio, *J. Organomet. Chem.*, 1983, **241**, 99.

(3), was evaporated under reduced pressure. A suspension of $Au(PPh_3)Cl$ (0.099 g, 0.20 mmol) in toluene (15 cm^3) was added to a suspension of the green monoanion of (3) in toluene (20 cm^3), and stirred at 0 °C for 2 h. The solution became red-brown, and a new change in the i.r. bands was observed. The solution was filtered and evaporated under reduced pressure.

Extraction of the solid residue with hexane gave (1) (0.035 g, 36%) (not optimized), m.p. 208—210 °C (Found: C, 27.4; H, 2.1.* Calc. for $C_{32}H_{22}AuNiO_9Os_3P$: C, 27.3; H, 1.55%). I.r., ν(CO) (hexane): 2 073m, 2 065w, 2 046vs, 2 023vs, 2 006w, 1 997 (sh), 1 992vs, 1 983vs, 1 957s, and 1 949m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 7.43 (m, 15 H, PPh_3), 5.98 (s, 5 H, C_5H_5), −17.51 [d, 2 H, μ-H, $^3J(PH)$ = 1.5 Hz]. U.v., $\lambda_{max.}$ (hexane): 376, 516, 580 nm (sh).

Preparation of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}CuPPh_3)(CO)_9]$ (2).—This compound was prepared by the same procedure as that described previously for (1). Crystallization of the solid residue in hexane affords compound (2) as black crystals (0.050 g, 20%) (not optimized), m.p. 178—180 °C (Found: C, 30.5; H, 2.5.* Calc. for $C_{32}H_{22}CuNiO_9Os_3P$: C, 30.15; H, 1.75%). I.r., ν(CO) (hexane): 2 072m, 2 043s, 2 028vs, 1 998s, 1 980s, 1 942s, and 1 933m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 7.43 (m, 15 H, PPh_3), 5.95 (s, 5 H, C_5H_5), −17.57 (s, 2 H, μ-H). U.v., $\lambda_{max.}$ (hexane): 377, 505, 585 nm (sh).

Crystal Structure Determination of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}AuPPh_3)(CO)_9]$ (1).—Black crystals of (1), suitable for the *X*-ray analysis, were obtained by slow cooling of a hexane solution to −15 °C. A flattened crystal of approximate dimensions 0.10 × 0.20 × 0.30 mm was selected and mounted on a Philips PW 1100 diffractometer in a random orientation. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 carefully centred reflections chosen from diverse regions of reciprocal space. Intensities were collected at 295 K in the range $6 \leqslant 2\theta \leqslant 48°$ (θ—2θ scan) using the three-point technique. Of the total 5 503 independent intensities, 2 867 for which $I \geqslant 3\sigma(I)$ were used for the solution and refinement of the structure. Correction was made for Lorentz, polarisation, and *X*-ray absorption effects, the last by a semi-empirical method [18] with maximum and minimum corrections of 1.5213 and 1.0000 respectively.

Crystal data. $C_{32}H_{22}AuNiO_9Os_3P$, M = 1 407.77, triclinic, a = 13.923(3), b = 14.213(4), c = 9.544(4) Å, α = 93.81(4), β = 105.48(2), γ = 102.83(2)°, U = 1 759(1) Å^3, Z = 2, D_c = 2.658 g cm^{-3}, $F(000)$ = 1 272, space group $P\bar{1}$, Mo-K_α *X*-radiation, λ = 0.7107 Å, μ(Mo-K_α) = 155.87 cm^{-1}.

Structure solution and refinement for (1). The structure was solved by direct and Fourier methods and refined by full-matrix least squares using the SHELX system of computer programs [19] with initially isotropic and then anisotropic thermal parameters for Au, Os, Ni, and P only. The carbon atoms of the phenyl and cyclopentadienyl groups were treated as rigid groups with distances of 1.395 and 1.420 Å respectively. The hydrogen atoms (except the hydrides) were placed at their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The atomic scattering factors used, corrected for the anomalous dispersion of the Au, Os, Ni, and P atoms, were taken from ref. 20. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen in the first stages of the refinement, then weights were applied according to the scheme $w = K/[\sigma^2(F_o) + gF_o^2]$ with K = 1.2972 and g = 0.005. Refinement converged at R = 0.055 (R' = 0.061).

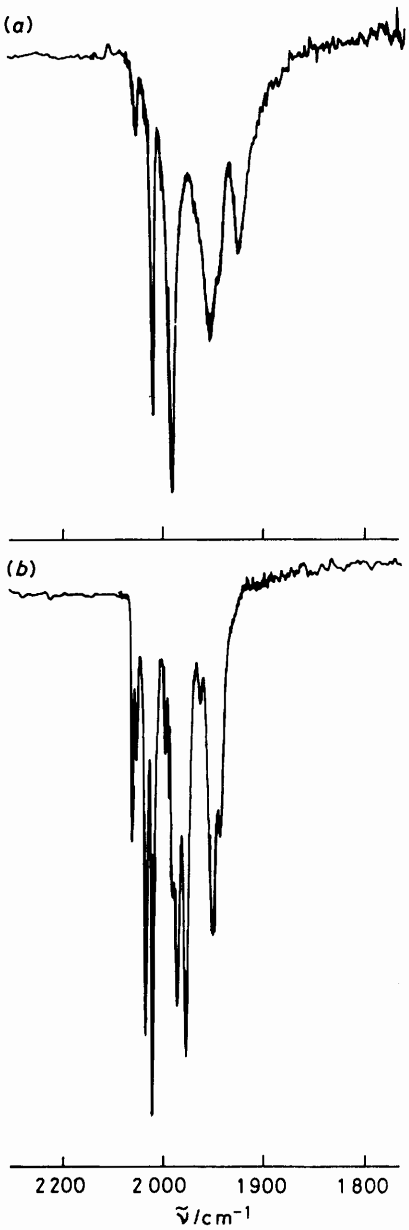

Figure 1. Infrared spectra in the ν(CO) region: (*a*) $Na[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(CO)_9]$ in thf and (*b*) $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}AuPPh_3)(CO)_9]$ in hexane

Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elletronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with the financial support from the University of Parma.

Results and Discussion

When a thf solution of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ (3) was treated with an excess of NaH, the mixture turned green, and the monoanion of (3) was obtained predominantly. When this was treated with an excess of $M(PPh_3)Cl$ (M = Au or Cu)

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* Experimental H analysis results which are higher than required by theory have also been found in related complexes (E. Sappa, unpublished results; G. Lavigne, F. Papageorgiou, C. Bergounhou, and J. J. Bonnet, *Inorg. Chem.*, 1983, **22**, 2485).

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
Au	5 332(1)	2 843(1)	8 974(1)	C(10)	972(24)	3 178(21)	7 613(30)
Os(1)	2 689(1)	799(1)	8 620(2)	C(11)	424(24)	2 185(21)	7 398(30)
Os(2)	3 308(1)	2 480(1)	7 239(1)	C(12)	421(24)	1 899(21)	8 795(30)
Os(3)	3 824(1)	2 633(1)	10 371(1)	C(13)	967(24)	2 716(21)	9 874(30)
Ni	1 969(3)	2 321(3)	8 668(5)	C(14)	1 308(24)	3 506(21)	9 143(30)
P	6 955(5)	2 875(6)	8 826(9)	C(15)	7 880(15)	2 895(16)	10 579(19)
O(1)	1 486(22)	110(22)	10 789(34)	C(16)	8 562(15)	2 297(16)	10 759(19)
O(2)	3 823(21)	−832(22)	8 620(33)	C(17)	9 196(15)	2 269(16)	12 154(19)
O(3)	857(21)	−226(21)	5 975(33)	C(18)	9 148(15)	2 840(16)	13 367(19)
O(4)	1 394(21)	1 910(20)	4 643(32)	C(19)	8 466(15)	3 439(16)	13 187(19)
O(5)	3 380(22)	4 637(24)	7 300(35)	C(20)	7 832(15)	3 467(16)	11 793(19)
O(6)	4 678(19)	2 430(20)	5 176(31)	C(21)	7 608(16)	3 906(16)	8 057(27)
O(7)	2 759(21)	2 348(21)	12 760(33)	C(22)	8 676(16)	4 227(16)	8 403(27)
O(8)	5 818(22)	2 744(21)	12 803(34)	C(23)	9 118(16)	4 972(16)	7 716(27)
O(9)	3 991(22)	4 797(23)	10 583(34)	C(24)	8 491(16)	5 395(16)	6 683(27)
C(1)	2 019(32)	386(32)	10 028(51)	C(25)	7 423(16)	5 073(16)	6 338(27)
C(2)	3 396(27)	−251(27)	8 561(42)	C(26)	6 981(16)	4 328(16)	7 025(27)
C(3)	1 560(31)	202(31)	7 041(48)	C(27)	6 915(16)	1 803(14)	7 628(25)
C(4)	2 168(28)	2 132(28)	5 648(45)	C(28)	7 530(16)	1 820(14)	6 686(25)
C(5)	3 385(26)	3 812(28)	7 316(42)	C(29)	7 443(16)	976(14)	5 779(25)
C(6)	4 176(27)	2 454(27)	6 043(43)	C(30)	6 741(16)	114(14)	5 813(25)
C(7)	3 143(28)	2 407(28)	11 811(44)	C(31)	6 127(16)	97(14)	6 755(25)
C(8)	5 114(29)	2 717(28)	11 826(45)	C(32)	6 213(16)	941(14)	7 662(25)
C(9)	3 933(27)	3 979(29)	10 583(43)				

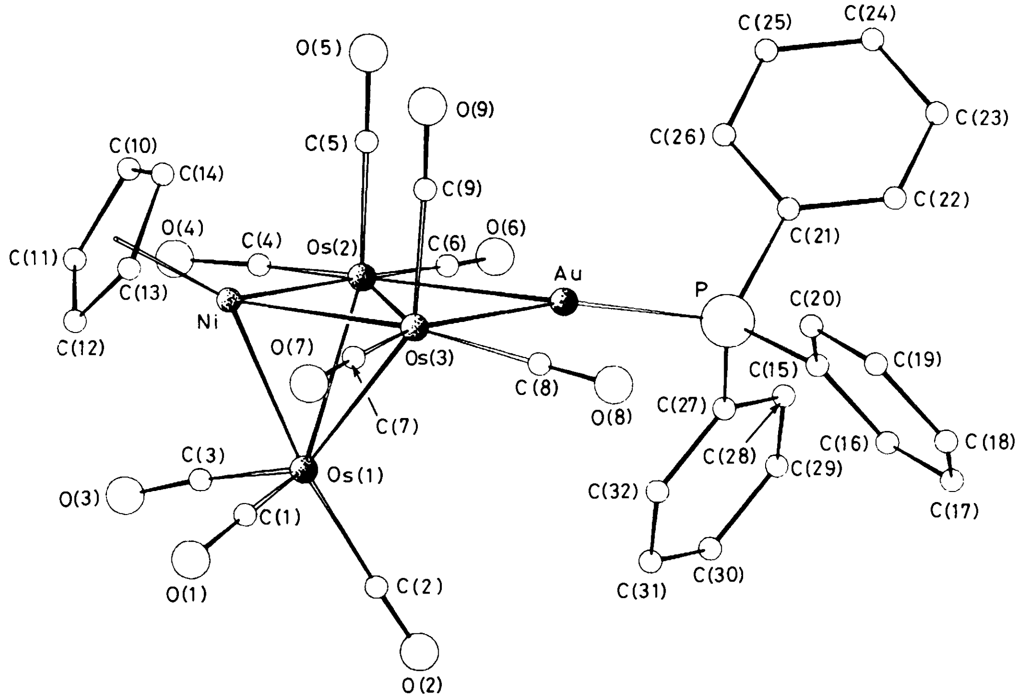


Figure 2. View of the molecule $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}AuPPh_3)(CO)_9]$ showing the atomic numbering scheme. The hydride ligands, which bridge the Os(1)–Os(2) and Os(1)–Os(3) bonds, are not represented

the complexes (1) and (2), respectively, were formed according to equation (i). The i.r. spectra of these clusters showed ν(CO) stretching absorptions characteristic of terminal carbonyls. A greater number of absorptions than in complex (3) was observed, because of the lowering of the symmetry due to the substitution of M (Au or Cu) for one of the three equivalent hydrides (Figure 1). The ^1H n.m.r. spectra are well resolved and three different types of hydrogen atoms are easily distinguished. The μ-H resonances appear at −17.51 p.p.m. (d) with a $^3J(PH)$ coupling of 1.5 Hz for (1), and −17.57 p.p.m. (s) for (2), whereas the hydride resonance for (3) appears at −19.7 p.p.m. (s). The C_5H_5 resonances are very similar in (1), (2), and (3): 5.98, 5.95, and 6.05 p.p.m., respectively.

$$Na[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(CO)_9] + M(PPh_3)Cl \xrightarrow{\text{thf}} [(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}MPPh_3)(CO)_9] + NaCl \quad (i)$$

The analogy between the spectroscopic data for (1) and (2)

Table 2. Selected bond distances (Å) and angles (°)

(*i*) Involving the metal atoms

Os(1)–Os(2)	2.881(2)	Ni–Os(3)	2.581(4)	Os(1)–C(1)	1.88(5)	Os(2)–C(6)	1.87(4)
Os(1)–Os(3)	2.875(2)	Au–Os(2)	2.775(2)	Os(1)–C(2)	1.97(4)	Os(3)–C(7)	1.87(4)
Os(2)–Os(3)	2.863(2)	Au–Os(3)	2.747(2)	Os(1)–C(3)	1.85(4)	Os(3)–C(8)	1.93(4)
Ni–Os(1)	2.581(5)	Au–P	2.292(8)	Os(2)–C(4)	1.83(3)	Os(3)–C(9)	1.88(4)
Ni–Os(2)	2.569(5)			Os(2)–C(5)	1.87(4)		

Os(2)–Os(1)–Os(3)	59.7(1)	Au–Os(2)–Os(3)	58.3(1)	Os(2)–Os(3)–C(8)	131(1)	Au–Os(2)–C(5)	91(1)
Os(1)–Os(2)–Os(3)	60.1(1)	Au–Os(3)–Os(2)	59.2(1)	Os(2)–Os(3)–C(9)	93(1)	Au–Os(2)–C(6)	70(1)
Os(1)–Os(3)–Os(2)	60.3(1)	Os(3)–Os(1)–C(1)	93(1)	Os(1)–Os(3)–C(7)	93(1)	Au–Os(3)–C(7)	161(1)
Os(1)–Ni–Os(2)	68.0(1)	Os(3)–Os(1)–C(2)	119(1)	Os(1)–Os(3)–C(8)	120(1)	Au–Os(3)–C(8)	72(1)
Os(2)–Ni–Os(3)	67.6(1)	Os(3)–Os(1)–C(3)	144(1)	Os(1)–Os(3)–C(9)	145(1)	Au–Os(3)–C(9)	92(1)
Os(1)–Ni–Os(3)	67.7(1)	Os(2)–Os(1)–C(1)	142(1)	Ni–Os(1)–C(1)	87(1)	C(1)–Os(1)–C(2)	98(2)
Ni–Os(1)–Os(2)	55.8(1)	Os(2)–Os(1)–C(2)	118(1)	Ni–Os(1)–C(2)	173(1)	C(1)–Os(1)–C(3)	94(2)
Ni–Os(1)–Os(3)	56.2(1)	Os(2)–Os(1)–C(3)	95(1)	Ni–Os(1)–C(3)	89(1)	C(2)–Os(1)–C(3)	95(2)
Ni–Os(2)–Os(3)	56.4(1)	Os(1)–Os(2)–C(4)	94(1)	Ni–Os(2)–C(4)	83(1)	C(4)–Os(2)–C(5)	95(2)
Ni–Os(2)–Os(1)	56.2(1)	Os(1)–Os(2)–C(5)	143(1)	Ni–Os(2)–C(5)	89(1)	C(4)–Os(2)–C(6)	91(2)
Ni–Os(3)–Os(1)	56.1(1)	Os(1)–Os(2)–C(6)	120(1)	Ni–Os(2)–C(6)	173(1)	C(5)–Os(2)–C(6)	96(2)
Ni–Os(3)–Os(2)	56.0(1)	Os(3)–Os(2)–C(4)	139(1)	Ni–Os(3)–C(7)	83(1)	C(7)–Os(3)–C(8)	90(2)
Os(2)–Au–Os(3)	62.5(1)	Os(3)–Os(2)–C(5)	91(1)	Ni–Os(3)–C(8)	171(1)	C(7)–Os(3)–C(9)	94(2)
Os(2)–Au–P	141.5(2)	Os(3)–Os(2)–C(6)	128(1)	Ni–Os(3)–C(9)	90(1)	C(8)–Os(3)–C(9)	95(2)
Os(3)–Au–P	154.1(2)	Os(2)–Os(3)–C(7)	138(1)	Au–Os(2)–C(4)	161(1)		

(*ii*) Involving the carbonyl and PPh$_3$ ligands

P–C(15)	1.81(2)	C(1)–O(1)	1.20(6)	C(4)–O(4)	1.20(4)	C(7)–O(7)	1.17(6)
P–C(21)	1.85(2)	C(2)–O(2)	1.12(5)	C(5)–O(5)	1.18(5)	C(8)–O(8)	1.15(5)
P–C(27)	1.82(2)	C(3)–O(3)	1.22(4)	C(6)–O(6)	1.22(5)	C(9)–O(9)	1.15(5)

Au–P–C(15)	114(1)	C(15)–P–C(27)	108(1)	Os(1)–C(3)–O(3)	176(4)	Os(3)–C(7)–O(7)	174(3)
Au–P–C(21)	118(1)	C(21)–P–C(27)	104(1)	Os(2)–C(4)–O(4)	177(4)	Os(3)–C(8)–O(8)	172(4)
Au–P–C(27)	110(1)	Os(1)–C(1)–O(1)	172(4)	Os(2)–C(5)–O(5)	176(3)	Os(3)–C(9)–O(9)	174(4)
C(15)–P–C(21)	103(1)	Os(1)–C(2)–O(2)	176(3)	Os(2)–C(6)–O(6)	175(3)		

Table 3. Comparison of bond distances (Å) and angles (°) in some related complexes

Complex	Os–Os	Os–Os [a]	Os–Ni	Os–Au	Os–Au–Os	Ref.
[$Os_4H(CO)_{13}(AuPEt_3)$]	2.812(2) 2.813(2) 2.820(2) 2.832(2) 2.952(2)	2.929(2)		2.745(2) 2.799(2)	63.8(1)	11
[$Os_4H_3(CO)_{12}(AuPEt_3)$]	2.816(2) 2.823(2) 2.944(1) 2.962(2) 2.982(2)	2.960(1)		2.783(2) 2.803(2)	64.0(1)	11
(1)	2.875(2) 2.881(2)	2.863(2)	2.569(5) 2.581(4) 2.581(5)	2.747(2) 2.775(2)	62.5(1)	*b*
(3) [c]	2.871(6)		2.567(6)			*d*

[a] AuPPh$_3$-bridged edge. [b] This work. [c] Mean values in two independent molecules. [d] M. R. Churchill and C. Bueno, *Inorg. Chem.*, 1983, **22**, 1510.

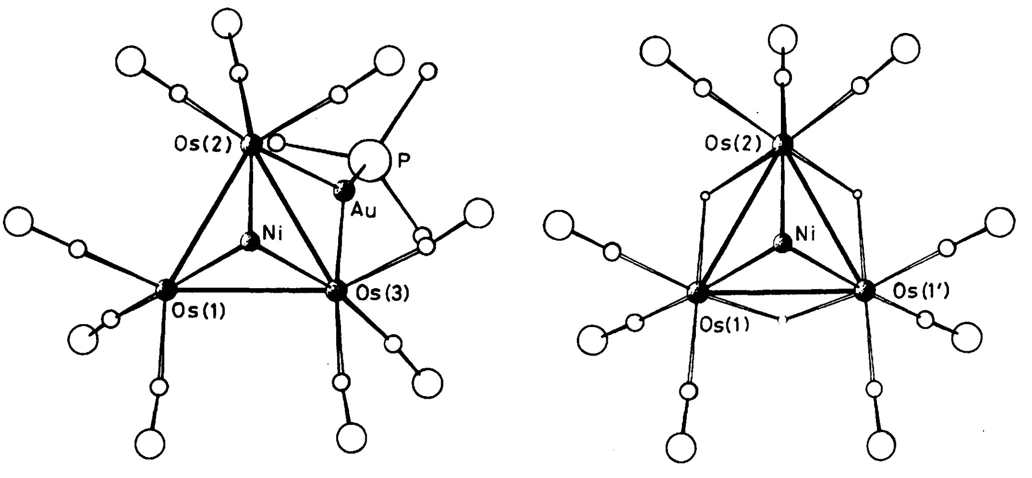
(i.r. and ^1H n.m.r., see Experimental section) suggests a very similar structure for these two complexes.

The structure of complex (1) has been determined by an *X*-ray diffraction study. A view of the molecule is shown in Figure 2; selected bond distances and angles are given in Table 2.

The structure of (1) can be regarded as derived from that of (3) [17] by replacing one of the three equivalent hydrides by the gold atom from the $AuPPh_3^+$ ligand. The metal cluster consists of a $NiOs_3$ tetrahedron with the Os(2)–Os(3) edge bridged by the Au atom. The structures of (1) and (3) are compared in Figure 3, in which the cyclopentadienyl rings are omitted for clarity. The substitution of a hydride in (1) leaves the structure virtually unaltered, except for some carbonyls undergoing slight deviations probably because of the steric hindrance of the bulky PPh$_3$ group. This fact supports once more the analogy between H and $AuPPh_3^+$.

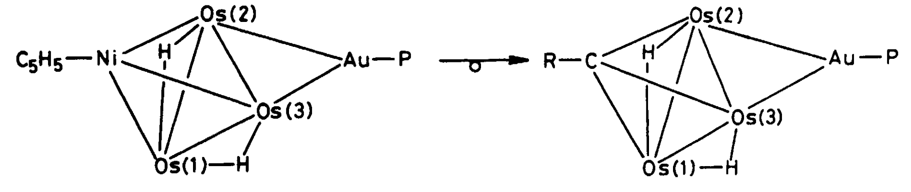
This type of structure is relatively rare for gold-containing clusters and has been reported previously only for [$Os_4(\mu\text{-}H)(CO)_{13}(AuPEt_3)$] and [$Os_4(\mu\text{-}H)_3(CO)_{12}(AuPEt_3)$].[11] A comparison of the structural parameters of (1) and (3) with those of these complexes is presented in Table 3.

Complex (1) is a 72-electron cluster, directly resulting from the $NiOs_3(\mu\text{-}H)_3$ unit by replacement of a μ-H with the $AuPPh_3^+$ group. The same electron count is found for the clusters [$M'Co_3(CO)_{12}(\mu_3\text{-}AuPPh_3)$] (M′ = Ru or Fe),[2,12] of trigonal-bipyramidal structure. This is expected since the

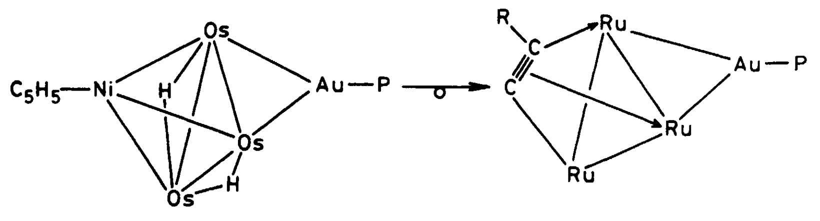


(1) (3)

Figure 3. Comparison of the structures of the complexes (1) and (3). The cyclopentadienyl rings are omitted for clarity



(1) (4)



(1) (5)

contribution of the AuPPh$_3$$^+$ group for skeletal bonding remains zero whether it is in a μ_2- or μ_3-bridging position.

The metal cluster in (1) can also be described as a planar triangulated NiOs$_2$Au core [the dihedral angle between the triangles Ni,Os(2),Os(3) and Au,Os(2),Os(3) is 179.1(1)°] with the NiOs$_2$ triangle triply bridged by the Os(CO)$_3$ group. A planar array of three different metal atoms such as that found in (1) appears unprecedented and is relevant to the model study of the interaction of small molecules or metallic fragments with metal surfaces.[21] The capping Os(CO)$_3$ fragment contributes two skeletal bonding electrons to the cluster and is equivalent to CH$^+$ or CO.

A further description of the metal cluster of (1) is as a Os$_3$Au 'butterfly' with the Os$_3$ 'wing' nearly symmetrically capped by a Ni(η-C$_5$H$_5$) fragment. The dihedral angle between the two wings [Os(1),Os(2),Os(3) and Os(2),Os(3),Au] is 113.7(1)°.

Considering the isolobal relationship between the CR (R = alkyl or aryl) and Ni(η-C$_5$H$_5$) groups,[22,23] the structure of (1) would be related to that of the hypothetical complex (4), which arrangement has indeed been observed in an analogous case with [Ru$_3$(μ_3-COMe)(μ-H)$_2$(AuPPh$_3$)(CO)$_9$].[8]

Cluster (1) is also related to the alkynyl butterfly complex [Ru$_3$Au(CO)$_9$(C$_2$Bu^t)(PPh$_3$)] (5)[5] in which the five-electron-donor ($\sigma + 2\pi$) $^-$C≡CBu^t ligand is formally equivalent to Ni(η-C$_5$H$_5$) + 2H (3 + 2 electrons).

In reaction (i), only one of the hydride ligands has been removed by NaH, allowing the synthesis of the first gold–nickel–osmium, (1), and copper–nickel–osmium, (2), clusters. They have a similar structure (see above), although the bonding modes of AuPR$_3$$^+$ and CuPR$_3$$^+$ may vary.[24] This is in part due to their differing bonding abilities. Evans and Mingos [1] have shown that for the AuPH$_3$$^+$ fragment, the p_x and p_y orbitals are relatively high lying and cannot accept electron density as effectively as CuPH$_3$$^+$.

Further work is in progress to substitute more than one hydride in (3). These clusters should be interesting in relation to the preparation of cluster-derived catalysts,[25] as shown with their precursor (3) which leads to a high-efficiency catalyst for hydrogenation and CO methanation when supported on alumina.[26]

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