The Crystal Structure and Reactivity of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PPh_2H)]$;† ^1H and ^{31}P Nuclear Magnetic Resonance Spectroscopic Characterization of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}HgBr)(CO)_8(PPh_2H)]$ and Related Complexes

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By reacting $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ (**1a**) with PPh_2H in the presence of Me_3NO, $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PPh_2H)]$ (**3a**) has been obtained. The crystal structure of (**3a**) has been determined by *X*-ray methods. Crystals are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 14.110(6)$, $b = 23.962(9)$, $c = 8.479(6)$ Å, and $\beta = 95.73(2)°$. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to $R = 0.033$ for 3 187 observed reflections. The structure consists of a tetrahedral arrangement of metal atoms with the three hydrides bridging the Os–Os edges; the phosphine ligand replaces an axial carbonyl of the starting complex. Both complexes (**1a**) and (**3a**) react with NaH in tetrahydrofuran to give the corresponding monoanions; these react with $HgBr_2$ affording μ-HgBr derivatives which have been characterized by i.r. and n.m.r. spectroscopy. Deuteriation experiments have shown that the faster rate of formation of the anion derived from (**3a**), with respect to that from (**1a**), is due to the presence of the P–H group, which is probably the site of attack by NaH.

The complex $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ (**1a**) is obtained in high yields by simple synthesis;[1] its structure consists of a tetrahedral framework of metal atoms, with a cyclopentadienyl ligand co-ordinated to the nickel atom, three terminal CO groups on each osmium atom, and three hydrides, each bridging an Os–Os edge.[2,3] Cluster (**1a**) is a homogeneous hydrogenation catalyst for alkynes, alkenes, and dienes[1,4] and is a heterogeneous catalyst precursor for the hydrogenation of CO, CO_2, and hydrocarbons.[5,6]

Complex (**1a**) is very stable in hydrocarbon solutions and undergoes CO substitution with difficulty.[1] However in the presence of Me_3NO, the substitution of one CO by a Group 5 donor ligand occurs easily, yielding complexes of general formula $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8L]$ [L = PhCN (**2a**), $NHPh_2$ (**2b**), PPh_2H (**3a**), PPh_3 (**3b**), $P(C_6H_4Me\text{-}o)_3$ (**3c**), $P(C_6H_{11})_3$ (**3d**), $AsPh_3$ (**3e**), $SbPh_3$ (**3f**), $PPh_2(C_2Pr^i)$ (**4a**), $PPh_2(C_2Ph)$ (**4b**), and $Ph_2PCH_2PPh_2$ (**5**)], which have been characterized by i.r. and n.m.r. spectroscopy.[7]

The reactivity of the hydride ligands was also explored and by reaction of (**1a**) with NaH, a solution of the anion $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(CO)_9]^-$ was obtained which upon treatment with $M(PPh_3)Cl$ (M = Au or Cu) gave the pentanuclear clusters $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}MPPh_3)(CO)_9]$ [M = Au (**6a**) or Cu (**6b**)]; the structure of (**6a**) has been determined by *X*-ray diffraction.[8]

Here we report the crystal structure of complex $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PPh_2H)]$ (**3a**), showing the phosphine co-ordinated to one osmium atom in an axial position, and describe its reactivity towards H^+ abstraction by NaH. In addition we describe the synthesis and spectroscopic characterization of the new monosubstituted complexes (**3g**) (L = $PPhH_2$), (**3h**) (L = $PPhMe_2$), (**3i**) [L = $P(OPr^i)_3$] and of the mercury derivatives $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}HgBr)(CO)_8L]$ [L = CO (**7a**) or PPh_2H (**7b**)] and $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}HgBr)_3(CO)_9]$ (**8**).

Experimental

The Group 5 donor ligands, $HgBr_2$, $Me_3NO{\cdot}2H_2O$, and $[N(PPh_3)_2]Cl$ were commercial products (Fluka, Janssen, Strem Chemicals) and were used without further purification, except for $Me_3NO{\cdot}2H_2O$, which was dehydrated by sublimation *in vacuo*. All the experiments were carried out under dry nitrogen, with the exception of some H/D exchange runs, for which ultra-pure hydrogen (SIAD) or deuterium (Carlo Erba) were used.

Complexes (**1a**) and (**3a**) were prepared as already reported.[1,7] The syntheses of the anions and the mercury derivatives were performed by standard Schlenk-tube techniques in rigorously dried and distilled tetrahydrofuran (thf). The other experiments were performed with standard glass apparatus in hydrocarbons, distilled over sodium before use.

Elemental analyses were performed with a Perkin-Elmer 204 automated analyzer (C, H, N), a Perkin-Elmer 303 atomic absorption spectrometer (Ni), and a Leeman Lab ICP 2.5 plasma emission spectrometer (Ni, Os, Hg). Satisfactory analyses were obtained for all the complexes. They do not

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† 2,2,2,3,3,3,4,4-Octacarbonyl-1-(η^5-cyclopentadienyl)-4-(diphenylphosphine)-2,3;3,4;2,4-tri-μ-hydrido-*tetrahedro*-nickeltriosmium.

Supplementary data available (No. SUP 56465, 4 pp.): H-atom coordinates, 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.

Table 1. Characterizing data for the new complexes

Complex	Colour	Analysis[a]/%	ν(CO)[b]/cm^{-1}	^{1}H(δ)[c,d]/p.p.m.	^{31}P(δ)[c,e]/p.p.m.	*J*/Hz
(**1b**)	Dark green	C, 39.8 (40.4); H, 2.1 (2.5); N, 0.8 (0.9)	2 051m, 2 015s, 1 987vs, 1 936ms, 1 915ms	7.48 (m, 30 H, Ph) 5.74 (s, 5 H, C_5H_5) 16.94 (s, 2 H, μ-H)	*f*	—
(**3a**)	Dark violet	C, 26.6 (27.1); H, 1.4 (1.7)	2 076m, 2 056vs, 2 021vs, 1 998s, 1 990vs, 1 959m, br	8.31 (t), 6.44 (t) (1 H, PH) 7.40 (m, 10 H, Ph) 7.44 (m), 608 (m) (2 H, PH) −16.97 (dd), −17.02 (dd) (2 H, μ-H) −17.81 (t, 1 H, μ-H)	−7.4 −12.0 (−41.4)[g]	1.8, $^3J(HH_P)$ 2.3, $^2J(HH)$ 10.5. $^2J(HP)$ 374, $^1J(H_PP)$
(**3g**)	Dark violet	C, 22.8 (22.1); H, 1.7 (1.5)	2 077m, 2 058vs, 2 023vs, 1 999s, 1 989vs, 1 962m,br	7.40 (m, 5 H, Ph) 7.44 (m), 6.08 (m) (2 H, PH) 6.06 (s, 5 H, C_5H_5) −17.11 (m), −17.28 (m) (2 H, μ-H) −17.80 (m, 1 H, μ-H)	*f*	*h*
(**3h**)	Dark violet	C, 23.6 (23.8); H, 1.5 (1.8)	2 074m, 2 055vs, 2 018vs, 1 996m, 1 986s, 1 954m,br	7.39 (m, 5 H, Ph) 6.03 (s, 5 H, C_5H_5) 2.26 (s), 2.22 (s) (6 H, Me) −17.01 (d), −17.05 (d) (2 H, μ-H) −17.94 (t, 1 H, μ-H)	−12.6 (−47)[g]	2.5, $^2J(HH)$ 9.8, $^2J(H_{Me}P)$ 10.5, $^2J(HP)$
(**3i**)	Dark violet	C, 23.1 (23.4); H, 2.4 (2.6)	2 076m, 2 056vs, 2 028vs, 1 998s, 1 994s, 1 986vs,br	6.06 (s, 5 H, C_5H_5) 4.46 (m, 3 H, CH) 1.29 (d, 18 H, Me) −17.33 (d), −17.38 (d) (2 H, μ-H) −17.70 (t, 1 H, μ-H)	*f*	2.6, $^2J(HH)$ 8.6, $^2J(HP)$
(**7a**)	Greenish brown	C, 13.2 (13.7); H, 0.4 (0.6); Hg, 16.5 (16.3); Ni, 4.7 (4.8); Os, 45.2 (46.4)	2 082m, 2 053vs, 2 025s, 2 002vs, 1 984vs	6.19 (s, 5 H, C_5H_5) −17.03 (s, 2 H, μ-H)	—	50, $^2J(HHg)$ (see text)
(**7b**)	Greenish brown	C, 21.3 (21.6); H, 1.5 (1.3); Hg, 15.3 (14.5); Ni, 4.5 (4.2); Os, 39.7 (41.1)	2 064m, 2 045vs, 2 018vs, 1 974vs,br, 1 956ms	8.27 (t), 6.36 (t) (1 H, PH) 7.46 (m, 10 H, Ph) 6.16 (s, 5 H, C_5H_5) −17.82 (d), −17.87 (d) (2 H, μ-H)	−6.3 −11.0 (−41.4)[g]	1.4, $^3J(HH_P)$ 10.5, $^2J(HP)$ 382, $^1J(H_PP)$
(**8**)	Green	C, 8.2 (9.4); H, 0.5 (0.3); Hg, 31.4 (33.7); Ni, 3.4 (3.3); Os, 30.5 (31.9)	2 080m (sh), 2 040vs, 2 000s, 1 980 (sh), 1 965s, 1 550 (sh)	6.58 (s, C_5H_5)	—	—

[a] Calculated values are given in parentheses. [b] KBr discs [(**1b**), (**7a**), (**7b**), (**8**)] or hexane solution [(**3a**), (**3g**), (**3h**), (**3i**)]. [c] $CDCl_3$ solution [(**1b**), (**3a**), (**3g**), (**3h**), (**3i**), (**7a**), (**7b**)] or [$^2H_6$]acetone [(**8**)]. [d] $SiMe_4$ as internal reference; s = singlet, d = doublet, t = triplet, m = multiplet. [e] Positive chemical shifts are downfield relative to external 83% H_3PO_4. [f] Not measured. [g] Free ligand. [h] See Figure 8.

sublime or decompose in the introduction system of the mass spectrometer [Kratos MS 50n direct inlet system, electron impact, 70 eV (*ca.* 1.1 × 10^{-17}J)]. I.r. spectra were recorded on a Beckman Acta C III and on a Perkin-Elmer 580 B instrument. The ^{1}H and ^{31}P n.m.r. spectra were obtained on Bruker CPX 200 or JEOL JNM GX 270 FT instruments.

Preparation of [(η-C_5H_5)$NiOs_3$(μ-H)$_3$(CO)$_8$L] [L = $PPhH_2$ (**3g**), $PPhMe_2$ (**3h**), *or* P(OPr^i)$_3$ (**3i**)].—These complexes were obtained by refluxing, for *ca.* 1 min, solutions of (**1a**) and the appropriate ligand in the presence of Me_3NO as described in ref. 7. Characterizing data are given in Table 1.

Preparation of [N(PPh$_3$)$_2$][(η-C_5H_5)$NiOs_3$(μ-H)$_2$(CO)$_9$] (**1b**).—The monoanion from (**1a**) was obtained by reacting (**1a**) with NaH in thf for 96 h according to the published procedure.[8] The thf solution containing the anion was treated with solid [N(PPh$_3$)$_2$]Cl, then filtered, and reduced to a small volume. Addition of pentane afforded a green solid, soluble in toluene, which was identified as (**1b**) (see Table 1).

Preparation of [(η-C_5H_5)$NiOs_3$(μ-H)$_2$(μ-HgBr)(CO)$_9$] (**7a**).—A green thf solution containing the monoanion (**1b**) was treated (1:1 molar ratio) with $HgBr_2$. The solution turned greenish brown and the i.r. spectrum showed major changes. Extraction with $CHCl_3$ gave a greenish brown solid which was identified as (**7a**) (see Table 1).

Preparation of [(η-C_5H_5)$NiOs_3$(μ-HgBr)$_3$(CO)$_9$] (**8**).—Addition of ethanol to a reaction mixture containing NaH in thf and (**1a**) resulted in a slight acceleration of the reaction rate and also in the appearance of a new species with two intense i.r. absorption bands at 1 939 and 1 896 cm^{-1} (Figure 1). The solution was filtered and allowed to react with $HgBr_2$, giving a deep green solution which was reduced to dryness and sequentially extracted with toluene, CH_2Cl_2, and thf. This latter extracted a green compound, also soluble in acetone, formulated as (**8**) (Table 1).

Preparation of [(η-C_5H_5)$NiOs_3$(μ-H)$_2$(μ-HgBr)(CO)$_8$(PPh$_2$H)] (**7b**).—Treatment of a thf solution of (**3a**) with NaH rapidly (0.5 h) resulted in a colour change from violet to green and in a significant shift of the CO stretching bands towards lower frequencies (Figure 2). Attempts to isolate the possible anion as a [N(PPh$_3$)$_2$]$^+$ salt were unsuccessful. Therefore a fresh thf solution was reacted with $HgBr_2$, then filtered and evaporated to dryness, giving a greenish brown solid, soluble in toluene, which was identified as (**7b**) (Table 1).

Figure 1. I.r. spectrum in the ν(CO) region of the hypothetical trianion derived from (**1a**) and NaH in thf in the presence of ethanol

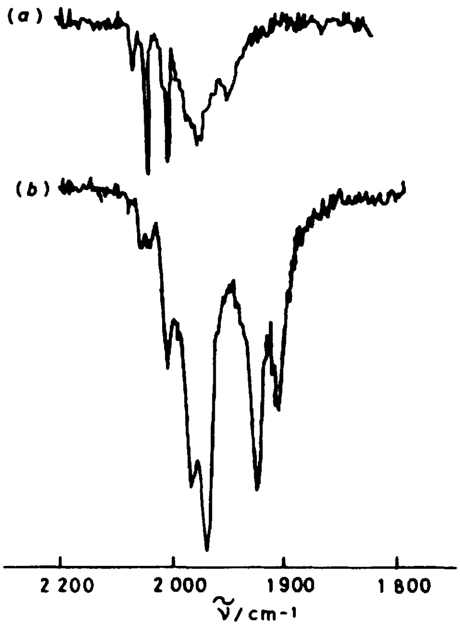

Figure 2. I.r. spectra in the ν(CO) region: (*a*) [(η-C_5H_5)$NiOs_3$(μ-H)$_3$(CO)$_8$(PPh_2H)] (**3a**) and (*b*) the corresponding monoanion in thf

Preparation of [(η-C_5H_5)$NiOs_3$(μ-D)$_3$(CO)$_8$(PPh_2H)] (**3a**-D_3) *and* H/D *Exchange Experiments*.—For the synthesis of (**3a**-D_3) the complex (**1a**-D_3) (obtained as in ref. 4) was used. Treatment of (**1a**-D_3) with PPh_2H in the presence of Me_3NO yielded *ca.* 70% of (**3a**-D_3) (^1H n.m.r.). This can be heated in a sealed vial (*in vacuo*, octane solution, 120 °C, 1 h) with only slight decomposition, but without H/D exchange processes occurring. Treatment of (**3a**) with D_2 (1 atm, octane solution, sealed vial, 3 h, 120 °C) gave almost quantitatively [(η-C_5H_5)$NiOs_3$(μ-H)$_3$(CO)$_8$(PPh_2D)] (**3a**-D′), identified by ^1H n.m.r. spectroscopy.

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of [(η-C_5H_5)$NiOs_3$(μ-H)$_3$(CO)$_8$(PPh_2H)] (**3a**)

Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	2 341(1)	1 677(1)	−1 777(1)
Os(2)	438(1)	1 423(1)	−3 055(1)
Os(3)	1 085(1)	1 096(1)	121(1)
Ni	857(1)	2 111(1)	−790(2)
P	3 590(2)	1 200(1)	−2 740(4)
O(1)	3 528(9)	2 192(6)	980(16)
O(2)	2 622(9)	2 680(5)	−3 844(16)
O(3)	−1 639(7)	1 545(5)	−2 462(14)
O(4)	369(8)	2 418(5)	−5 266(13)
O(5)	138(9)	571(5)	−5 694(13)
O(6)	−886(8)	1 199(6)	1 276(16)
O(7)	1 364(9)	−134(5)	981(16)
O(8)	2 079(9)	1 517(6)	3 197(13)
C(1)	3 089(9)	1 999(6)	−110(19)
C(2)	2 527(10)	2 306(6)	−3 063(19)
C(3)	−854(11)	1 503(6)	−2 698(17)
C(4)	404(9)	2 050(7)	−4 411(18)
C(5)	256(11)	893(6)	−4 658(18)
C(6)	−131(11)	1 158(6)	826(16)
C(7)	1 254(11)	317(7)	558(18)
C(8)	1 686(11)	1 362(7)	2 047(18)
C(9)	1 113(11)	2 684(7)	1 124(20)
C(10)	1 269(12)	2 964(7)	−371(21)
C(11)	411(11)	2 950(7)	−1 452(19)
C(12)	−274(11)	2 689(7)	−564(19)
C(13)	95(10)	2 506(7)	972(18)
C(14)	4 612(9)	1 027(6)	−1 318(16)
C(15)	5 534(10)	1 177(6)	−1 687(18)
C(16)	6 297(12)	1 124(7)	−601(21)
C(17)	6 207(13)	855(9)	829(23)
C(18)	5 281(14)	667(9)	1 208(25)
C(19)	4 483(11)	801(7)	94(20)
C(20)	3 317(9)	563(6)	−3 844(17)
C(21)	3 825(13)	464(9)	−5 172(24)
C(22)	3 590(16)	−41(11)	−6 041(28)
C(23)	2 877(14)	−394(8)	−5 635(24)
C(24)	2 414(11)	−282(7)	−4 407(20)
C(25)	2 599(10)	199(6)	−3 510(17)

In order to verify the possibility of 'base promoted' H/D exchange (**3a**) was reacted in sealed vials under the following conditions: (*a*) 250-cm^3 vial, 25 cm^3 octane solution of (**3a**) with 2 cm^3 of a saturated solution of NaOH in water–ethanol (50:50), 1 atm D_2, 120 °C, 1 h; *ca.* 2% of (**1a**) is formed, together with 7% of an unidentified product, and 90% of (**3a**) was recovered unchanged. The same results were obtained after 3 h, when only 80% of (**3a**) was recovered. (*b*) 250-cm^3 vial, 25 cm^3 octane solution of (**3a**) with 1 cm^3 of NaOD (40% in D_2O), 1 h, 120 °C; *ca.* 15% of (**1a**) and 5% of the unknown product were formed and 80% of (**3a**-D′) was recovered. (*c*) Finally, treatment of (**3a**-D_3) with NaH and subsequently with $HgBr_2$, as described above, led, as the final product, to [(η^5-C_5H_5)$NiOs_3$(μ-D)$_2$(μ-HgBr)(CO)$_8$(PPh_2D)] (**7b**-D_2D′).

Crystal Structure Determination of Complex (**3a**).—Dark grey-violet crystals of (**3a**) suitable for *X*-ray analysis were obtained by cooling n-heptane–$CHCl_3$ saturated solutions at −15 °C (kept under N_2) for several days.

Crystal data. $C_{25}H_{19}NiO_8Os_3P$, M = 1 107.70, monoclinic, a = 14.110(6), b = 23.962(9), c = 8.479(6) Å, β = 95.73(2)°, U = 2 852(3) Å^3 (by least-squares refinement from the θ values of 26 reflections accurately measured, λ = 0.710 69 Å), space group $P2_1/n$, Z = 4, D_c = 2.579 g cm^{-3}, $F(000)$ = 2 016. An elongated prismatic crystal of approximate dimensions 0.11 ×

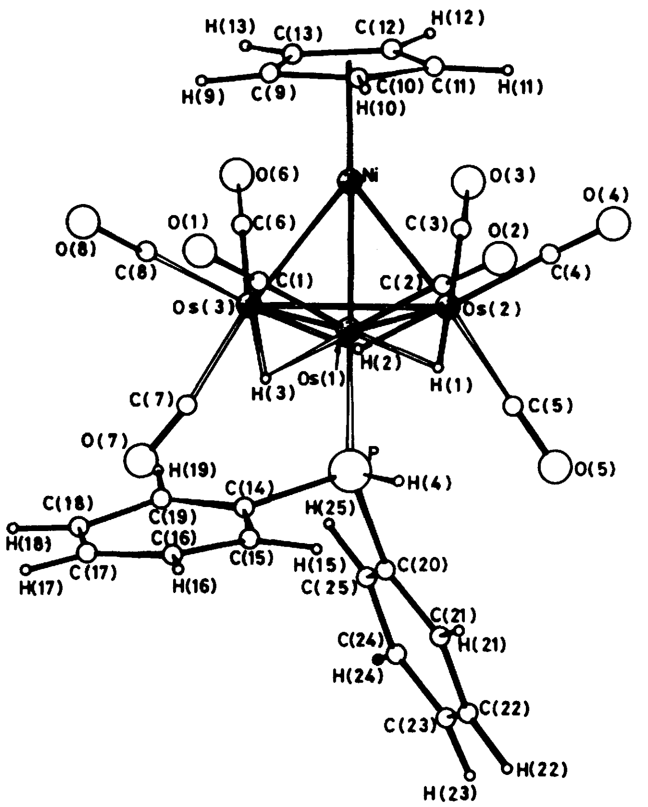

Figure 3. View of the molecular structure of $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PPh_2H)]$ (**3a**) with the atomic labelling scheme

0.30×0.58 mm was used for the structural analysis, $\mu(\text{Mo-}K_\alpha) = 140.95$ cm^{-1}. A correction for the absorption[9] was applied (max. and min. transmission factors 1.3673 and 0.8347) using the program ASSORB written by F. Ugozzoli, University of Parma.

Data collection and processing. Siemens AED diffractometer, $\theta/2\theta$ mode, using niobium-filtered Mo-K_α radiation; all the reflections in the range $3 \leqslant \theta \leqslant 26°$ were measured. Of 5 643 independent reflections, 3 187 having $I \geqslant 2\sigma(I)$ were considered observed and used in the analysis.

Structure analysis and refinement. Direct and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for Os, Ni, P, O atoms and carbon atoms of the carbonyl groups, hydrogen atoms H(1)—H(4) localized in the ΔF map, remaining hydrogen atoms placed at their geometrically calculated positions, all hydrogens not refined and introduced in the final calculations with isotropic thermal parameters. Weighting scheme used in the last cycles was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.7950$ and $g = 0.005$. Final R and R' values were 0.033 and 0.043 respectively. The SHELX system of computer-programs was used.[10] Atomic scattering factors, corrected for anomalous dispersion of Ni, Os, and P, are given in ref. 11. 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 coordinates for the non-hydrogen atoms are given in Table 2.

Results and Discussion

Crystal Structure of (**3a**).—The structure of complex (**3a**) is represented in Figure 3 and selected bond distances and angles are given in Table 3.

Table 3. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PPh_2H)]$

Os(1)–Os(2)	2.859(2)	Os(3)–C(7)	1.913(17)
Os(1)–Os(3)	2.870(2)	Os(3)–C(8)	1.875(15)
Os(2)–Os(3)	2.865(2)	C(1)–O(1)	1.156(19)
Ni–Os(1)	2.553(2)	C(2)–O(2)	1.130(20)
Ni–Os(2)	2.555(3)	C(3)–O(3)	1.150(19)
Ni–Os(3)	2.562(3)	C(4)–O(4)	1.139(20)
Os(1)–P	2.316(3)	C(5)–O(5)	1.168(19)
Os(1)–C(1)	1.846(14)	C(6)–O(6)	1.171(20)
Os(1)–C(2)	1.894(15)	C(7)–O(7)	1.144(20)
Os(2)–C(3)	1.887(16)	C(8)–O(8)	1.135(19)
Os(2)–C(4)	1.890(16)	P–C(14)	1.832(13)
Os(2)–C(5)	1.859(15)	P–C(20)	1.811(14)
Os(3)–C(6)	1.878(16)		

Os(2)–Os(1)–Os(3)	60.0(1)	Os(2)–C(4)–O(4)	178(1)
Os(1)–Os(2)–Os(3)	60.2(1)	Os(2)–C(5)–O(5)	178(1)
Os(1)–Os(3)–Os(2)	59.8(1)	Os(3)–C(6)–O(6)	179(1)
Os(1)–Ni–Os(2)	63.1(1)	Os(3)–C(7)–O(7)	173(1)
Os(1)–Ni–Os(3)	68.3(1)	Os(3)–C(8)–O(8)	177(1)
Os(2)–Ni–Os(3)	68.1(1)	Os(1)–P–C(14)	117.1(4)
Os(1)–C(1)–O(1)	177(1)	Os(1)–P–C(20)	117.9(4)
Os(1)–C(2)–O(2)	179(1)	C(14)–P–C(20)	105.2(6)
Os(2)–C(3)–O(3)	179(1)		

Complex (**3a**) is characterized by a tetrahedral cluster of three Os atoms and one Ni atom. A cyclopentadienyl ligand is η^5-co-ordinated to the Ni atom. The Os atoms Os(2) and Os(3) each bear three carbonyl groups (two equatorial and one axial). The remaining two carbonyls are bonded to Os(1) in equatorial positions. The PPh_2H ligand is axially bonded to Os(1). The three hydridic hydrogens, directly located, bridge the Os–Os edges.

The substitution of one carbonyl group in (**1a**) by the PPh_2H ligand leaves the structure practically unaltered, except that some of the carbonyls undergo slight deviations because of the steric hindrance of the bulky PPh_2H group, as already observed in the analogous complex (**4a**)[12] and in (**6a**), in which a hydridic hydrogen in (**1a**) was substituted by the $Au(PPh_3)$ group.[8]

Reactivity of (**1a**) *and* (**3a**).—The reactivity of (**1a**) is depicted in Figure 4. In reaction path (*i*) substitution of one or two carbonyls by Group 5 donor ligands is achieved in the presence of Me_3NO. The disubstituted derivatives have been obtained in slightly lower yields and will be described elsewhere.

Both (**1a**) and its monosubstituted phosphine derivative (**3a**) undergo hydrogen abstraction by NaH in thf giving the corresponding monoanions [path (*ii*)]. The former reacts with $M(PPh_3)Cl$ (M = Cu or Au) to give the pentametallic clusters (**6**) [path (*v*)].[8]

This method of increasing the nuclearity of these clusters by substitution of H by isolobal metal-containing fragments has also been used to obtain mercury derivatives. Thus the monoanions afford, by reaction with $HgBr_2$, the mercury derivatives (**7a**) and (**7b**) [paths (*vi*)] whose spectroscopic data indicate that the mercury atom replaces one hydride, as does the gold atom in (**6a**).[8] The spectroscopic evidence is also corroborated by previous literature findings[13] where again a HgBr group replaces one hydride ligand bridging a Ru–Ru edge of a triangular cluster. The resulting complex, $[Ru_3(CO)_9(C_2Bu^t)(HgBr)]$, is dimeric in the solid state, the Br atoms acting as asymmetric bridges between the mercury atoms, whereas it is monomeric in solution. The reaction of (**1a**) with NaH is very slow (*ca.* 96 h), but the same process for the PPh_2H derivative (**3a**) is complete after 30 min under the same conditions. If we exclude an electronic effect exerted by the phosphorus [since the PPh_3 derivative (**3b**) exhibits almost the same reaction time

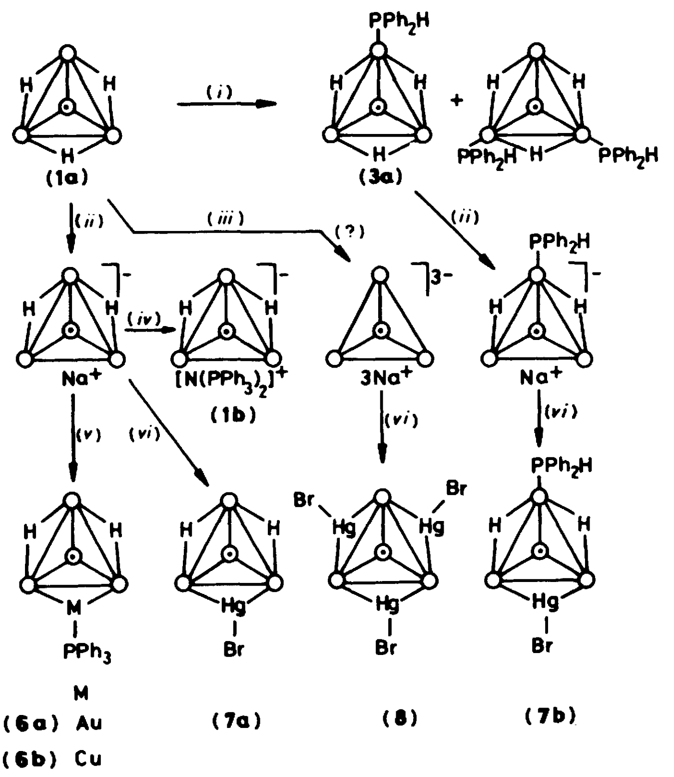

Figure 4. Scheme showing the reactivity of (**1a**) and (**3a**): ○ = Os atoms; ⊙ = (η-C_5H_5)Ni fragments; carbonyls have been omitted for clarity. (*i*) PPh_2H in heptane or octane with Me_3NO; (*ii*) NaH in thf; (*iii*) NaH in thf in the presence of EtOH; (*iv*) $[N(PPh_3)_2]Cl$ in thf; (*v*) $M(PPh_3)Cl$ (M = Cu or Au) in thf; (*vi*) $HgBr_2$ in thf

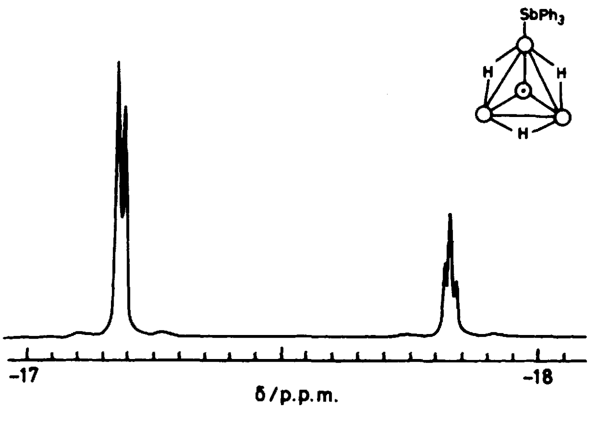

Figure 5. ^1H N.m.r. spectrum in the hydride region for [(η-C_5H_5)$NiOs_3(\mu$-$H)_3(CO)_8(SbPh_3)$] (**3f**)

as (**1a**)] the participation of the phosphine hydrogen in the process must be invoked. Probably this hydrogen is rapidly abstracted by NaH giving an unstable intermediate, which converts into the final monoanion through an internal rearrangement involving the hydrides. The experiments carried out with deuteriated clusters, described in the Experimental section, support this hypothesis. In particular the last one, reaction (*c*), shows that the deuterium atoms initially present only as hydrido-ligands, after reaction with NaH and $HgBr_2$, were found also on the phosphine. Another interesting feature of such reactions is provided by path (*iii*), where the presence of ethanol leads to an anionic intermediate, which gives, by

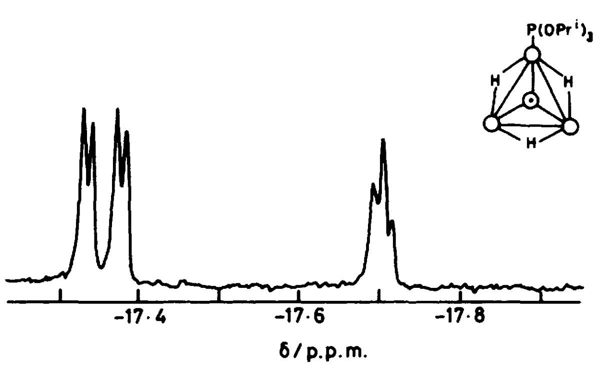

Figure 6. ^1H N.m.r. spectrum for [(η-C_5H_5)$NiOs_3(\mu$-$H)_3(CO)_8\{P(OPr^i)_3\}$] (**3i**)

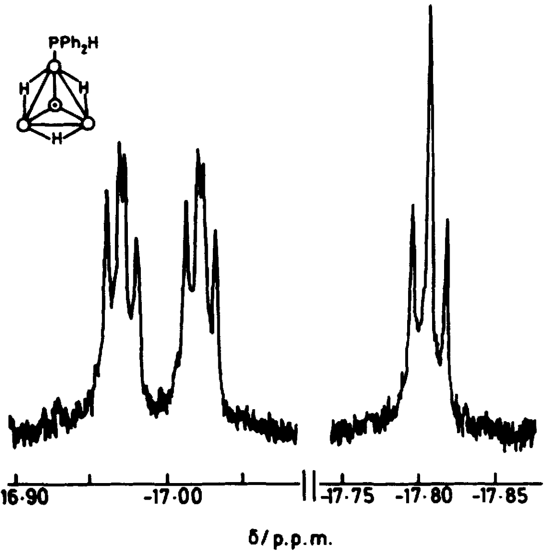

Figure 7. ^1H N.m.r. spectrum for [(η-C_5H_5)$NiOs_3(\mu$-$H)_3(CO)_8(PPh_2H)$] (**3a**)

reaction with $HgBr_2$, the trimercury derivative (**8**), formulated on the basis of spectroscopic evidence and accurate elemental determinations. The presence of this intermediate in solution is evidenced by new i.r. bands, which appear after the addition of ethanol (Figure 1). Its polyanionic nature is supported by the significant shift to lower frequencies of the major CO stretching bands.

N.M.R. Spectra.—The ^1H n.m.r. spectra of all these complexes in the hydridic region (see *e.g.* Figures 5—7) are very useful for the identification of these species, the multiplicities of the signals depending on the nature of the ligands, as recently observed by Churchill and co-workers[14] in the case of trihydridotriruthenium clusters. The ^1H n.m.r. spectrum of the monosubstituted cluster with $SbPh_3$, (**3f**), in the hydride region (Figure 5), consists of a triplet due to the hydride opposite the ligand and a doublet (2 H) to lower field due to the hydrides close to the ligand. The coupling constant $^2J(HH)$ is 2.2 Hz.

The presence of phosphorus-containing ligands produces a further splitting in such a way that the doublet becomes a doublet of doublets, whereas the triplet remains unchanged. The coupling constants are, in the case of $P(OPr^i)_3$, (**3i**) (Figure 6), $^2J(HH) = 2.6$ and $^2J(HP) = 8.6$ Hz.

Because of the presence of one hydrogen in the PPh_2H ligand of (**3a**), the doublets are further split (Figure 7): $^3J(HH_P) = 1.8$, $^2J(HH) = 2.3$, $^2J(HP) = 10.5$ Hz.

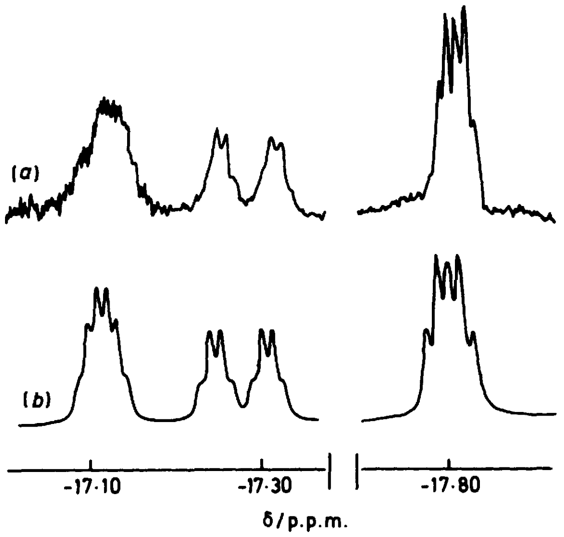

Figure 8. (*a*) ^{1}H N.m.r. spectrum for $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8\text{-}(PPhH_2)]$ (**3g**). (*b*) Computer simulated spectrum assuming, for a hypothetical 'equatorial' isomer $^2J(H_{cis}P)$ = 4.0, $^2J(H_{trans}P)$ = 10.6, and $^3J(H_{opposite}P)$ = 4.0 Hz

By substituting one hydrogen in (**3a**) by HgBr, complex (**7b**) is obtained, whose spectrum shows a doublet of doublets, without the triplet, thus confirming the substitution of the hydrogen opposite the phosphine by HgBr. Coupling constants are $^3J(HH_P)$ = 1.4 and ^2J(HP) = 10.5 Hz. In the case of the other HgBr derivative (**7a**), derived from (**1a**), the ^{1}H n.m.r. spectrum in the hydride region shows a singlet with two satellites derived from the coupling with ^{199}Hg [^2J(HHg) = 50 Hz].

The ^{1}H n.m.r. patterns of complexes (**3**) are consistent with axial isomers in solution, *i.e.* with the ligand occupying the 'symmetrical', sterically favoured axial position *trans* to the nickel atom, as found in the solid state for (**3a**) and (**4a**). The only exception is represented by (**3g**) (L = $PPhH_2$) which exhibits a more complex pattern from 25 to −50 °C, as shown in Figure 8. If we exclude the presence of a mixture of isomers (axial and equatorial; repeated attempts at separation by t.l.c., both on freshly prepared samples and after n.m.r. runs, were unsuccessful), we must invoke the existence of the equatorial isomer only (*i.e.*, with the phosphine *trans* to one adjacent hydride). This would be allowed by the relatively small cone angle[15] of $PPhH_2$ (101°) compared with those of PPh_2H (128°) and PPh_3 (145°). The computer simulated spectrum [obtained by using ^2J(HP) = 4 Hz for the adjacent *cis* hydrogen and ^2J(HP) = 10.6 Hz for the *trans* one] shows substantial similarities with the observed pattern (Figure 8).

As quoted in Table 1 the hydride chemical shifts fall in the usual range (δ −10 to −20) for hydrides bridging two osmium or ruthenium atoms.[14,16–21] Apparently no simple relationships exist between these shifts and the electronic or steric parameters of the ligands. However it is evident that the monosubstituted derivatives with Group 5 donor ligands exhibit the signals due to the hydrides, particularly those adjacent to the substituent, at lower field with respect to the corresponding unsubstituted derivative [complex (**1a**), δ −19.7 (s, 3 H, μ-H); see also ref. 14].

The values of the ^{31}P chemical shifts for certain complexes are quoted in Table 1. Other values for monosubstituted complexes with phosphines derived from (**1a**) are reported in ref. 7. By comparison of these values with the corresponding ones of the free ligands,[22] a significant shift towards lower field is generally observed upon co-ordination. Surprisingly, $Ph_2PCH_2PPh_2$ in (**5**) behaves as monodentate ligand,[7] the ^{31}P spectrum exhibiting two doublets [−16.6, −22.9 p.p.m.; ^2J(PP) = 100 Hz], due respectively to the co-ordinated and unco-ordinated phosphorus atoms.

Another significant feature is the increase in the coupling constant ^1J(HP) in (**3a**) (374 Hz) and (**7b**) (382 Hz) relative to that found in free PPh_2H (214—239 Hz),[22] which can be explained in terms of differing hybridization on complexation.[23]

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