

**THE SYNTHESIS AND CRYSTAL STRUCTURE OF
 $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)$ AND OF
 $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8\{(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)\text{Co}_2(\text{CO})_6\}(\sigma\text{-P},\eta^2\text{-C}_2)$. THE
 REACTION OF UNSATURATED "LINEAR" LIGANDS ON CLUSTERS
 WITH METAL CARBONYL SPECIES**

ENRICO SAPPA,

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

GIOVANNI PREDIERI, ANTONIO TIRIPICCHIO and MARISA TIRIPICCHIO CAMELLINI

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

(Received May 20th, 1985)

Summary

The complex $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)$ (**2a**) has been obtained by treating $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_9$ (**1**) with $\text{PPh}_2\text{C}_2\text{Pr}^i$ in the presence of Me_3NO . Treatment of **2a** with $\text{Co}_2(\text{CO})_8$ in hexane at room temperature gives high yields of $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8\{(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)\text{Co}_2(\text{CO})_6\}$ (**3**). The complexes **2a** and **3** have been characterized by means of elemental analyses and IR, ^1H and ^{13}C NMR spectroscopies. Their structures have been determined by X-ray methods. Crystals of **2a** are triclinic, space group $P\bar{1}$ with $Z=4$ in a unit cell of dimensions a 16.543(7), b 16.578(7), c 16.461(6) Å, α 116.6(3), β 94.1(2), γ 118.8(3)°. Crystals of **3** are monoclinic, space group $P2_1/n$ with $Z=4$ in a unit cell of dimensions a 18.275(9), b 17.804(7), c 13.343(4) Å, β 106.46(3)°. Both structures were solved by direct and Fourier methods and refined by full-matrix least-squares to $R=0.055$ for 5882 observed reflections for **2a** and to $R=0.046$ for 1848 observed reflections for **3**. Both structures can be derived from that of **1** (having a tetrahedral NiOs_3 core with three hydridic hydrogen atoms bridging the Os–Os edges, a cyclopentadienyl group coordinated to the Ni atom, and nine terminal carbonyls bound to the Os atoms, three for each Os atom) by replacing one of the axial carbonyls by the $\text{Ph}_2\text{PC}\equiv\text{CPr}^i$ ligand. In **3** a $\text{Co}_2(\text{CO})_6$ unit interacts, through two π bonds, with the acetylenic C–C bond of the phosphino-alkyne ligand.

Introduction

We have synthesized and characterized the heterometallic $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_9$ (**1**) [1], which shows catalytic activity in hydrogenation of small molecules, under homogeneous [2] and heterogeneous conditions [3,4].

Complex **1**, whose structure is well known [5], is very stable and undergoes CO replacement with difficulty [1]; however, in the presence of Me_3NO and in hydrocarbon solutions, considerable yields of the monosubstituted derivatives $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8\text{L}$, where L can be a phosphine, arsine, stibine, phosphinoalkyne or bis(diphenylphosphino)methane (dppm) ligand (complexes **2**), can readily be obtained [6]. These complexes **2** (among which the derivative with $\text{L} = \text{Ph}_2\text{PC}\equiv\text{CPr}^i$, **2a**) have been characterized spectroscopically [6]; we report below the X-ray structure of **2a**, which, in accord with the spectroscopic evidence, has the phosphinoalkyne axially and linearly bound to one osmium atom.

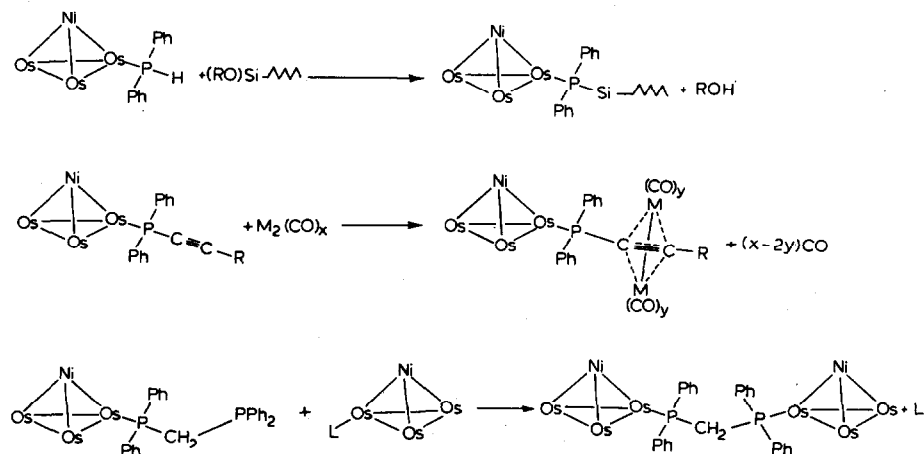
The behaviour of the phosphinoalkyne as a ligand is unexpected; indeed phosphinoalkynes usually undergo C-P bond cleavage under much milder conditions to give phosphido-bridged clusters with multi-site bound acetylides [7]. This "anomalous" behaviour led us to study the residual reactivity of some complexes **2**, specifically those with $\text{L} = \text{Ph}_2\text{PC}\equiv\text{CPr}^i$ (**2a**), PPh_2H and dppm, in the processes indicated in Scheme 1.

As a first part of this study, we now report the results of the reaction of **2a** with $\text{Co}_2(\text{CO})_8$; this gives the new complex $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8\{(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)\text{-Co}_2(\text{CO})_6\}$ (**3**) in high yield, and the product has been characterized by spectroscopy and by X-ray structural analysis. The preparative implications of this type of chemistry are briefly discussed.

Experimental

Materials

The hydrocarbon solvents (hexane, heptane) were dried over sodium. Reactions were carried out under dry nitrogen. Commercial $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (Fluka) was used



SCHEME 1

for the synthesis of the complex **2a** after being carefully dehydrated by sublimation in vacuo. The isopropyl-diphenylphosphino-acetylene was provided by Prof. A.J. Carty.

Complex **1** was prepared as previously described [1]; complex **2a** was obtained in over 50% yields (on **1**) by the method described in ref. 6.

Synthesis of the complex **3**

A hexane suspension of the complex **2a** and a twofold excess of $\text{Co}_2(\text{CO})_8$ (Strem Chemicals) was stirred for 90 min at room temperature under a N_2 stream; the colour of the solution changed from dark-grey violet to very dark brown. After filtration under N_2 and evaporation of the solvent in vacuo, the residue was dissolved in CHCl_3 and purified by preparative TLC (Kieselgel P.F. Merck; eluant diethyl ether 10% in light petroleum). A dark-grey band corresponding to the complex **3** was detected on the TLC plates together with small amounts of $\text{Co}_4(\text{CO})_{12}$ and another unidentified cobalt derivative. After elution from the plates, complex **3** was crystallized to give a final yield of about 60% (based on the amount of **2a** taken).

Analysis of the complexes **2a** and **3**

The elemental analysis of **2a** as well as its IR and ^1H NMR spectra have been previously reported [6]. The analysis for complex **3** was: C 29.35(29.62), H 1.55(1.73), Co 7.61(8.07), Ni 4.04(4.02), P 2.20(2.12), Os 38.5(39.09)% (Calculated values in parentheses; F. Pascher laboratory, Bonn, F.R.G.). Both **2a** and **3** decompose in the mass spectrometer. Their IR, ^1H and ^{13}C NMR data are listed in Table 1. The IR spectra were recorded on a Perkin-Elmer 580 B instrument (equipped with KBr optics) and the NMR spectra were obtained on a JEOL JNM-GX 270 FT Instrument.

TABLE 1
SPECTROSCOPIC DATA FOR COMPLEXES **2a** and **3**

Complex	IR ($\nu(\text{CO})$; C_6H_{14}) (cm^{-1})	^1H NMR (δ , CDCl_3)	^{13}C NMR (CDCl_3) ^a
2a	2074m, 2054vs, 2021vs, 1997s, 1988s(br), 1959m	7.39m (10H, Ph) ^b , 6.07s (5H, Cp), 3.01m (1H, CH), 1.36–1.33d (6H, CH_3); –16.61d, –16.66d (2H, hydrides), –17.79t (1H, hydride); $^2J(\text{PH})$ 9, $^2J(\text{HH})$ 2.5 Hz	21.70d, 22.50s (Pr^i), 86.30s (Cp); 128.45–128.59d, 130.39–130.42d, 131.53–131.55d (Ph); 136.0 (CH, Pr^i); 172.8–173.1d, 177.6d, 180.1s (CO's) ^c
3	2093w, 2074m, 2055vs, 2038m, 2020vs, 1997m, 1988s, 1960w	7.35m, 7.41m (10H, Ph), 6.03s (5H, Cp), 3.51m (1H, CH), 1.42d (6H, CH_3); –16.41d, –16.43d (2H, hydrides), –17.60t (1H, hydride); $^2J(\text{PH})$ 8.5, $^2J(\text{HH})$ 2.5 Hz	26.28–32.45 (Pr^i), 86.63s (Cp); 128.5d, 130.6d, 133.0d (Ph); 172.6s, 178.6s, 180.1s, 198.8 (br) (CO's).

^a ppm, downfield positive with respect of TMS. ^b In parentheses integration and attribution. ^c ^{13}C for **2a** not previously reported.

X-Ray data collections, structure solutions and refinements

Crystals of complex **2a** (dark violet) and **3** (dark grey) were obtained by keeping saturated solutions in heptane/ CH_3Cl at -15°C under nitrogen for several days. Those of **3** were very small, and repeated attempts to grow larger crystals were unsuccessful.

Crystal data and data collection parameters for both complexes are given in Table 2. Unit cell parameters were obtained by least-squares refinement of the θ values of 27 (**2a**) and 26 (**3**) carefully centered reflections chosen from diverse regions of the reciprocal space.

The intensity of one standard reflection was measured after 50 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection for either **2a** or **3**. The structure amplitudes were corrected for Lorentz and polarization effects. A correction for absorption effects was applied [8] (maximum and minimum transmission factor values: 1.2921 and 0.8284 for **2a**, 1.1837 and 0.8598 for **3**).

Both structures were solved by direct and Fourier methods and refined by full-matrix least-squares using the SHELX system of programs [9] with initially isotropic and then anisotropic thermal parameters for the metal and phosphorus

TABLE 2

CRYSTAL DATA AND DATA COLLECTION PARAMETERS

	2a	3
Formula	$\text{C}_{30}\text{H}_{25}\text{NiO}_8\text{Os}_3\text{P}$	$\text{C}_{36}\text{H}_{25}\text{Co}_2\text{NiO}_{14}\text{Os}_3\text{P}$
Mol. weight	1173.81	1459.74
Crystal system	triclinic	monoclinic
a , Å	16.543(7)	18.275(9)
b , Å	16.578(7)	17.804(7)
c , Å	16.461(6)	13.343(4)
α , deg	116.6(3)	—
β , deg	94.1(2)	106.46(3)
γ , deg	118.8(3)	—
V , Å ³	3290(3)	1246(1)
Z	4	4
D_{calcd} , g cm ⁻³	2.37	2.33
Crystal dimensions, mm	$0.55 \times 0.67 \times 0.80$	$0.05 \times 0.14 \times 0.24$
Space group	$P\bar{1}$	$P2_1/n$
$F(000)$	2160	2712
Diffractometer	Siemens AED	Siemens AED
Radiation	Mo- K_α (Nb-filtered), λ 0.7107 Å	
Linear abs. coeff., cm ⁻¹	122.26	104.57
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan range, deg	± 0.5 from the peak	± 0.5 from the peak
Scan speed, deg min ⁻¹	3–12	3–12
θ limits, deg	3–24	3–23
Reflections measured	$+h, +k, l$	$\pm h, k, l$
Total measured reflections	8552	5919
Total observed reflections	5882	1848
Criterion for observed reflections	$I \geq 2\sigma(I)$	$I \geq 2\sigma(I)$
R	0.055	0.046
R_w	0.078	0.055

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH, e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS OF THE COMPLEX **2a**

Atom	x	y	z
Os(11)	7770(1)	4393(1)	1741(1)
Os(21)	7357(1)	3316(1)	2762(1)
Os(31)	7433(1)	2270(1)	865(1)
Ni(1)	8928(2)	4036(2)	2386(2)
P(1)	6566(4)	4538(5)	1139(4)
O(11)	8977(14)	5104(16)	631(15)
O(21)	8939(12)	6664(14)	3542(13)
O(31)	7999(18)	2213(20)	3415(19)
O(41)	8552(15)	5448(17)	4782(16)
O(51)	5359(18)	2364(20)	2983(19)
O(61)	8168(14)	1083(17)	1220(15)
O(71)	5478(14)	235(16)	-789(15)
O(81)	8693(16)	2622(19)	-337(17)
C(11)	8535(16)	4824(19)	1062(17)
C(21)	8468(16)	5832(19)	2831(18)
C(31)	7753(24)	2564(27)	3138(25)
C(41)	8087(18)	4665(20)	4041(19)
C(51)	6122(18)	2729(20)	2921(18)
C(61)	7892(20)	1539(23)	1079(21)
C(71)	6219(22)	1045(25)	-140(23)
C(81)	8213(22)	2460(24)	109(23)
C(91)	5369(9)	3251(10)	282(11)
C(101)	4799(9)	3129(10)	-487(11)
C(111)	3872(9)	2139(10)	-1122(11)
C(121)	3515(9)	1272(10)	-989(11)
C(131)	4084(9)	1394(10)	-221(11)
C(141)	5011(9)	2383(10)	414(11)
C(151)	6248(13)	5361(14)	2029(12)
C(161)	6647(13)	6454(14)	2340(12)
C(171)	6403(13)	7063(14)	3048(12)
C(181)	5760(13)	6580(14)	3445(12)
C(191)	5361(13)	5487(14)	3134(12)
C(201)	5605(13)	4878(14)	2426(12)
C(211)	6893(16)	5143(18)	470(17)
C(221)	7167(18)	5630(21)	77(19)
C(231)	7461(29)	6215(32)	-427(30)
C(241)	8177(34)	6029(38)	-817(35)
C(251)	6564(40)	5690(44)	-1140(42)
C(261)	10121(16)	3909(15)	2285(15)
C(271)	10061(16)	4127(15)	3209(15)
C(281)	10193(16)	5160(15)	3730(15)
C(291)	10334(16)	5581(15)	3129(15)
C(301)	10290(16)	4808(15)	2236(15)
Os(12)	7349(1)	8972(1)	6742(1)
Os(22)	9447(1)	10406(1)	7762(1)
Os(32)	8596(1)	8430(1)	5864(1)
Ni(2)	8349(2)	8456(2)	7384(2)
P(2)	6596(4)	9582(4)	6139(4)
O(12)	5530(14)	6611(16)	5604(14)
O(22)	6867(14)	9580(16)	8548(15)
O(32)	11210(20)	10391(22)	8367(20)
O(42)	9353(14)	11222(16)	9766(15)

(continued)

TABLE 3 (continued)

Atom	x	y	z
O(52)	10605(17)	12629(19)	7970(17)
O(62)	10178(14)	8054(15)	6225(14)
O(72)	8990(14)	8739(16)	4216(15)
O(82)	7044(16)	5943(18)	4642(16)
C(12)	6206(34)	7481(38)	6018(34)
C(22)	7039(15)	9329(17)	7839(17)
C(32)	10523(22)	10447(24)	8217(22)
C(42)	9352(16)	10890(19)	8980(18)
C(52)	10212(17)	11813(20)	7957(18)
C(62)	9580(20)	8191(22)	6086(20)
C(72)	8813(19)	8552(22)	4781(21)
C(82)	7668(23)	6891(27)	5083(24)
C(92)	7026(10)	9908(13)	5275(10)
C(102)	6373(10)	9675(13)	4487(10)
C(112)	6725(10)	9951(13)	3842(10)
C(122)	7730(10)	10462(13)	3983(10)
C(132)	8383(10)	10695(13)	4771(10)
C(142)	8031(10)	10419(13)	5417(10)
C(152)	6690(13)	10812(12)	7048(12)
C(162)	5885(13)	10697(12)	7329(12)
C(172)	5952(13)	11629(12)	8025(12)
C(182)	6824(13)	12677(12)	8440(12)
C(192)	7629(13)	12792(12)	8159(12)
C(202)	7563(13)	11860(12)	7463(12)
C(212)	5336(16)	8581(18)	5482(17)
C(222)	4480(19)	7913(21)	5072(19)
C(232)	3436(28)	7088(31)	4492(29)
C(242)	3159(27)	5962(31)	4206(28)
C(252)	3112(36)	7189(40)	3836(39)
C(262)	8408(15)	7164(17)	7295(15)
C(272)	9080(15)	8162(17)	8217(15)
C(282)	8526(15)	8515(17)	8700(15)
C(292)	7512(15)	7736(17)	8075(15)
C(302)	7439(15)	6900(17)	7206(15)

atoms. During the refinement the cyclopentadienyl and phenyl rings were treated as rigid regular pentagons (C–C 1.42 Å) and hexagons (C–C 1.39 Å), respectively. The hydrogens of **3** (except for the hydridic ones) 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 metals and phosphorus atoms, were taken from ref. 10. The function minimized in the least-squares calculations was $\sum w |\Delta F|^2$; unit weights were chosen in the first stages of the refinement, then weights were applied according to the scheme $w = K/[\sigma^2(F_0) + gF_0^2]$ with $K = 0.9662$ and $g = 0.005$ in **2a** and $K = 0.6060$ and $g = 0.005$ in **3**.

Final atomic coordinates for the non-hydrogen atoms of **2a** are given in Table 3 and those of **3** in Table 4. Calculated coordinates for the hydrogen atoms in **3**, thermal parameters for atoms of **2a** and **3**, observed and calculated structure factors for both structures are available from the authors.

TABLE 4

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS OF THE COMPLEX 3

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Os(1)	2808(1)	1549(1)	855(1)
Os(2)	1961(1)	212(1)	81(1)
Os(3)	1230(1)	1432(1)	832(1)
Co(1)	4228(3)	1487(3)	-1485(4)
Co(2)	3677(3)	2576(3)	-2549(4)
Ni	2306(3)	634(3)	1985(4)
P	3056(5)	2437(5)	-324(7)
O(1)	4366(15)	836(14)	1511(21)
O(2)	3163(16)	2617(17)	2712(24)
O(3)	1016(16)	-965(19)	725(25)
O(4)	3357(17)	-797(16)	723(23)
O(5)	1395(15)	-130(15)	-2223(22)
O(6)	116(17)	391(17)	1522(23)
O(7)	1350(19)	2505(20)	2578(29)
O(8)	30(19)	2334(19)	-724(26)
O(9)	4098(18)	15(19)	-652(25)
O(10)	5557(19)	2050(18)	156(26)
O(11)	5011(21)	902(21)	-2983(31)
O(12)	4975(18)	3578(18)	-1584(25)
O(13)	3924(26)	2142(25)	-4547(38)
O(14)	2436(19)	3600(20)	-3360(26)
C(1)	3797(17)	1115(16)	1266(23)
C(2)	3046(22)	2180(22)	2003(32)
C(3)	1330(27)	-535(27)	471(36)
C(4)	2828(21)	-400(20)	457(29)
C(5)	1650(19)	-23(18)	-1319(28)
C(6)	547(28)	840(27)	1303(39)
C(7)	1301(25)	2039(27)	1880(37)
C(8)	452(27)	2020(25)	-161(36)
C(9)	4126(25)	622(27)	-1002(35)
C(10)	5009(23)	1880(22)	-499(33)
C(11)	4749(25)	1176(26)	-2371(36)
C(12)	4423(22)	3179(21)	-2010(28)
C(13)	3804(27)	2417(27)	-3774(40)
C(14)	2934(30)	3187(29)	-3026(39)
C(15)	3349(16)	2072(15)	-1394(23)
C(16)	3109(18)	1684(19)	-2261(25)
C(17)	2524(25)	1114(26)	-2940(35)
C(18)	2867(24)	492(23)	-3388(33)
C(19)	1962(23)	1546(25)	-3868(32)
C(20)	3279(14)	345(22)	3246(27)
C(21)	2811(14)	872(22)	3574(27)
C(22)	2082(14)	541(22)	3431(27)
C(23)	2099(14)	-191(22)	3016(27)
C(24)	2839(14)	-312(22)	2901(27)
C(25)	3774(11)	3162(11)	237(17)
C(26)	3730(11)	3872(11)	-217(17)
C(27)	4237(11)	4435(11)	271(17)
C(28)	4789(11)	4287(11)	1212(17)
C(29)	4833(11)	3576(11)	1666(17)
C(30)	4326(11)	3014(11)	1178(17)
C(31)	2210(10)	3008(11)	-784(17)

(continued)

TABLE 4 (continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(32)	1693(10)	2844(11)	-1749(17)
C(33)	1015(10)	3250(11)	-2090(17)
C(34)	854(10)	3820(11)	-1467(17)
C(35)	1371(10)	3984(11)	-502(17)
C(36)	2049(10)	3577(11)	-160(17)

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.

Results and discussion

The spectroscopic data for **3** and those of **2a** (as comparison) are listed in Table 1. Coordination between the $\text{Co}_2(\text{CO})_6$ entity and the alkyne carbons of **2a** affects only to a minor extent the spectroscopic properties of the complex; thus a predictable increase in the number of IR bands is observed, together with very small changes in the proton and ^{13}C NMR spectra, the main difference in the latter being the new

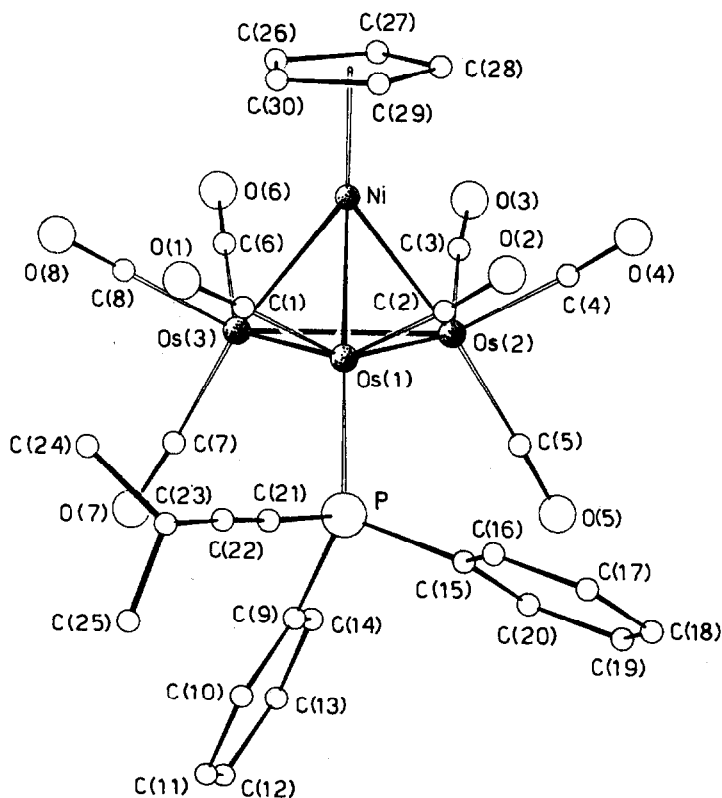


Fig. 1. View of the molecular structure of the complex $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)$ (**2a**) with the atomic numbering scheme.

TABLE 5

SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN THE TWO INDEPENDENT MOLECULES OF THE COMPLEX **2a**

	molecule 1	molecule 2
Os(1)–Os(2)	2.855(3)	2.856(3)
Os(1)–Os(3)	2.868(3)	2.863(3)
Os(2)–Os(3)	2.862(3)	2.870(3)
Os(1)–Ni	2.553(5)	2.552(5)
Os(2)–Ni	2.542(4)	2.552(4)
Os(3)–Ni	2.555(3)	2.548(4)
Os(1)–P	2.324(9)	2.345(9)
Os(1)–C(1)	1.85(3)	1.91(4)
Os(1)–C(2)	1.86(2)	1.83(3)
Os(2)–C(3)	1.95(5)	1.84(4)
Os(2)–C(4)	1.93(2)	1.85(3)
Os(2)–C(5)	1.89(3)	1.89(3)
Os(3)–C(6)	1.84(5)	1.90(4)
Os(3)–C(7)	1.87(2)	1.92(4)
Os(3)–C(8)	1.87(4)	1.88(3)
P–C(9)	1.82(1)	1.81(2)
P–C(15)	1.82(2)	1.83(2)
P–C(21)	1.75(3)	1.73(2)
C(21)–C(22)	1.20(5)	1.17(3)
C(22)–C(23)	1.48(7)	1.44(4)
C(1)–O(1)	1.14(4)	1.12(4)
C(2)–O(2)	1.13(2)	1.16(4)
C(3)–O(3)	1.07(7)	1.20(6)
C(4)–O(4)	1.12(3)	1.16(4)
C(5)–O(5)	1.14(4)	1.17(5)
C(6)–O(6)	1.14(6)	1.15(5)
C(7)–O(7)	1.18(3)	1.12(5)
C(8)–O(8)	1.14(5)	1.17(4)
Os(2)–Os(1)–Os(3)	60.0(1)	60.2(1)
Os(1)–Os(2)–Os(3)	60.2(1)	60.0(1)
Os(1)–Os(3)–Os(2)	59.8(1)	59.8(1)
Os(1)–Ni–Os(2)	68.2(1)	68.1(2)
Os(1)–Ni–Os(3)	68.3(1)	68.3(1)
Os(2)–Ni–Os(3)	68.3(1)	68.5(1)
Ni–Os(1)–Os(2)	55.7(1)	56.0(1)
Ni–Os(1)–Os(3)	55.9(1)	55.8(1)
Ni–Os(2)–Os(1)	56.1(1)	56.0(1)
Ni–Os(2)–Os(3)	56.1(1)	55.7(1)
Ni–Os(3)–Os(1)	55.8(1)	55.9(1)
Ni–Os(3)–Os(2)	55.6(1)	55.8(1)
Os(2)–Os(1)–P	118.4(3)	118.2(2)
Os(3)–Os(1)–P	119.4(2)	119.6(2)
Ni–Os(1)–P	173.4(3)	173.4(3)
Os(1)–P–C(9)	116.4(7)	116.0(7)
Os(1)–P–C(15)	117.0(6)	116.3(6)
Os(1)–P–C(21)	113.2(9)	112.0(9)
C(9)–P–C(15)	103(1)	104(1)
C(9)–P–C(21)	102(1)	102(1)
C(15)–P–C(21)	103(1)	105(1)
P–C(21)–C(22)	175(2)	177(2)
C(21)–C(22)–C(23)	178(4)	175(3)

TABLE 5 (continued)

	molecule 1	molecule 2
Os(1)–C(1)–O(1)	177(3)	179(4)
Os(1)–C(2)–O(2)	172(3)	178(3)
Os(2)–C(3)–O(3)	175(3)	170(3)
Os(2)–C(4)–O(4)	176(3)	176(3)
Os(2)–C(5)–O(5)	177(2)	172(2)
Os(3)–C(6)–O(6)	179(3)	180(3)
Os(3)–C(7)–O(7)	176(4)	173(3)
Os(3)–C(8)–O(8)	177(4)	174(3)

broad band in the CO region for **3**, which can be attributed to the carbonyls coordinated to the cobalt. The typical hydridic pattern of complexes **2** has been discussed elsewhere [11].

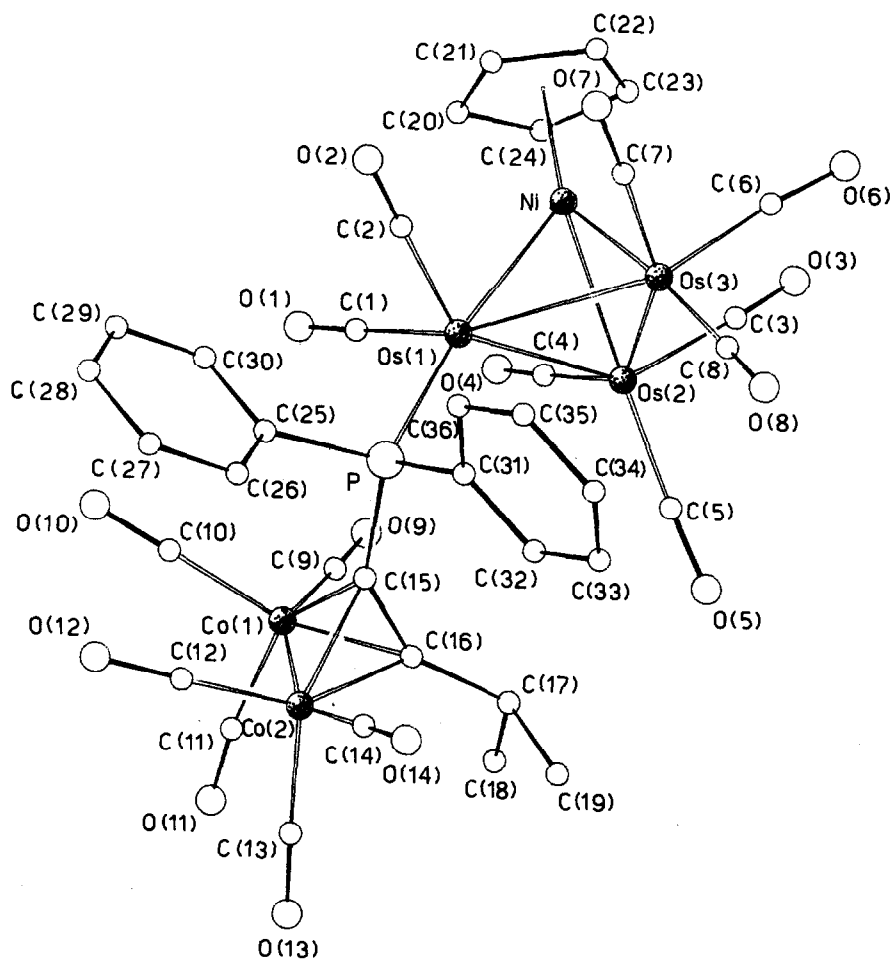


Fig. 2. View of the molecular structure of the complex $(\eta^5\text{-C}_5\text{H}_5)\text{NiOs}_3(\mu\text{-H})_3(\text{CO})_8\{(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)\text{Co}_2(\text{CO})_6\}$ (**3**) with the atomic numbering scheme.

Crystal structures of the complexes 2a and 3

The structures of the complexes **2a** and **3** are shown in Figs. 1 and 2, respectively. In the crystals of **2a** two crystallographically independent but practically identical molecules are present. Selected bond distances and angles in the complexes **2a** and **3** are given in Tables 5 and 6, respectively.

Both complexes **2a** and **3** consist of tetrahedral clusters of three osmium and one nickel atom. A cyclopentadienyl ligand is η^5 -coordinated to the nickel atom; three carbonyls are terminally bonded to Os(2) and Os(3) (two in equatorial and one in

TABLE 6
SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN **3**

Os(1)–Os(2)	2.868(3)	Co(1)–C(9)	1.70(5)
Os(1)–Os(3)	2.883(3)	Co(1)–C(10)	1.79(4)
Os(2)–Os(3)	2.875(3)	Co(1)–C(11)	1.80(5)
Os(1)–Ni	2.560(6)	Co(2)–C(12)	1.72(4)
Os(2)–Ni	2.551(5)	Co(2)–C(13)	1.74(6)
Os(3)–Ni	2.557(5)	Co(2)–C(14)	1.72(5)
Co(1)–Co(2)	2.445(7)	C(16)–C(17)	1.56(5)
Os(1)–P	2.363(9)	C(17)–C(18)	1.48(7)
Os(1)–C(1)	1.90(3)	C(17)–C(19)	1.57(6)
Os(1)–C(2)	1.85(4)	C(1)–O(1)	1.11(4)
Os(2)–C(3)	1.93(5)	C(2)–O(2)	1.20(5)
Os(2)–C(4)	1.87(4)	C(3)–O(3)	1.07(6)
Os(2)–C(5)	1.84(4)	C(4)–O(4)	1.17(5)
Os(3)–C(6)	1.87(5)	C(5)–O(5)	1.18(4)
Os(3)–C(7)	1.74(5)	C(6)–O(6)	1.21(6)
Os(3)–C(8)	1.95(4)	C(7)–O(7)	1.23(6)
P–C(15)	1.78(3)	C(8)–O(8)	1.07(5)
P–C(25)	1.84(2)	C(9)–O(9)	1.18(6)
P–C(31)	1.81(2)	C(10)–O(10)	1.17(5)
Co(1)–C(15)	1.95(3)	C(11)–O(11)	1.16(7)
Co(2)–C(15)	2.02(3)	C(12)–O(12)	1.23(5)
Co(1)–C(16)	2.04(3)	C(13)–O(13)	1.22(8)
Co(2)–C(16)	1.99(4)	C(14)–O(14)	1.16(6)
C(15)–C(16)	1.31(4)		
Os(2)–Os(1)–Os(3)	60.0(1)	C(25)–P–C(31)	101(1)
Os(1)–Os(2)–Os(3)	60.3(1)	P–C(15)–C(16)	143(3)
Os(1)–Os(3)–Os(2)	59.7(1)	C(15)–C(16)–C(17)	149(3)
Os(1)–Ni–Os(2)	68.3(2)	Os(1)–C(1)–O(1)	177(3)
Os(1)–Ni–Os(3)	68.6(2)	Os(1)–C(2)–O(2)	176(4)
Os(2)–Ni–Os(3)	68.5(2)	Os(2)–C(3)–O(3)	176(4)
Ni–Os(1)–Os(2)	55.7(1)	Os(2)–C(4)–O(4)	177(3)
Ni–Os(1)–Os(3)	55.7(1)	Os(2)–C(5)–O(5)	174(3)
Ni–Os(2)–Os(1)	56.0(1)	Os(3)–C(6)–O(6)	172(4)
Ni–Os(2)–Os(3)	55.8(1)	Os(3)–C(7)–O(7)	176(4)
Ni–Os(3)–Os(1)	55.8(1)	Os(3)–C(8)–O(8)	178(4)
Ni–Os(3)–Os(2)	55.7(1)	Co(1)–C(9)–O(9)	176(4)
Os(1)–P–C(15)	116.5(9)	Co(1)–C(10)–O(10)	172(4)
Os(1)–P–C(25)	116.6(8)	Co(1)–C(11)–O(11)	171(4)
Os(1)–P–C(31)	107.2(8)	Co(2)–C(12)–O(12)	176(3)
C(15)–P–C(25)	104(1)	Co(2)–C(13)–O(13)	165(4)
C(15)–P–C(31)	111(1)	Co(2)–C(14)–O(14)	179(5)

TABLE 7

STRUCTURAL PARAMETERS FOR COMPLEXES WITH P-BONDED PHOSPHINO-ALKYNES ($\text{Ph}_2\text{PC}\equiv\text{CR}$)

Complex	M-P (Å)	P-C (Å)	M-P-C (°)	C-C (Å)	C-R (Å)	P-C-C (°)	C-C-R (°)	Reference
2a (two independent molecules)	2.324(9) 2.345(9)	1.75(3) 1.73(2)	113.2(9) 112.0(9)	1.20(5) 1.17(3)	1.48(7) 1.44(4)	175(2) 177(2)	178(4) 175(3)	this work
3	2.363(9)	1.78(3)	116.5(9)	1.31(4)	1.56(5)	143(3)	149(3)	this work
4	2.3559(9)	1.760(4)	111.8(1)	1.174(6)	1.476(6)	176.0(2)	178.1(2)	7
5	2.342(1)	1.758(5)	114.2(1)	1.182(7)	1.447(8)	176.6(2)	178.6(3)	7
6	2.314(3)	1.748(11)	114.0(3)	1.199(16)	1.523(20)	176.3(8)	178.0(8)	12

axial positions), two are terminally bonded to Os(1) (in equatorial positions). The axial position on Os(1) is occupied by the phosphinoalkyne ligand, bonded to Os(1) through the phosphorus atom only. Three hydridic hydrogen atoms, not directly localized, bridge the Os–Os edges. Their presence is indicated by the ^1H NMR spectra and by the known structure of the starting complex **1**.

The replacement of one carbonyl in **1** by one phosphinoalkyne ligand leaves the NiOs_3 core virtually unaltered, as shown by the Os–Os and Os–Ni bond lengths (values range from 2.859(1) to 2.874(1) Å, averaging 2.871(6) Å, and from 2.562(2) to 2.578(3) Å, averaging 2.567(6) Å, have been reported for the two independent molecules of **1**, which have imposed C_s symmetry [5a]).

Complexes **2a** and **3** represent to our knowledge the first heterometallic examples of phosphino-alkynes coordinated only via the P atom to a cluster (even though in **3** the acetylenic C–C bond interacts with a $\text{Co}_2(\text{CO})_6$ unit, through two π bonds). A few homometallic examples (obtained under much milder conditions than those used for **2a**) have been reported by Carty and coworkers: $\text{Ru}_2(\text{CO})_5(\text{PPh}_2)(\text{C}_2\text{Pr}^i)-(\text{Ph}_2\text{PC}\equiv\text{CPr}^i)$ (complex **4**), $\text{Ru}_3(\text{CO})_{11}(\text{Ph}_2\text{PC}\equiv\text{CPh})$ (complex **5**) [7] and $\text{Ru}_3(\text{CO})_6-(\text{PPh}_2)_2(\text{C}_2\text{Bu}^i)_2(\text{Ph}_2\text{PC}\equiv\text{CBu}^i)$ (complex **6**) [12]. The structural parameters for these complexes are compared with those of **2a** and **3** in Table 7.

Complexes **2a**, **4**, **5** and **6** have comparable P–C(alkyne) and C–C(alkyne) distances and angles at phosphorus and the acetylenic carbons, but the distances and angles in the phosphino-alkyne ligand in **3** differ markedly, and follow the usual pattern observed for the coordinated alkynes [13]. As expected, coordination of the alkyne to the $\text{Co}_2(\text{CO})_6$ entity has a considerable effect on the linearity of the acetylenic group.

The bonding of the alkyne to the $\text{Co}_2(\text{CO})_6$ moiety in **3** is very similar to that observed in the well-known $\text{Co}_2(\text{CO})_6(\text{RC}_2\text{R}')$ derivatives [14] in which a tetrahedral Co_2C_2 core is obtained. A similar bonding of the $\text{Co}_2(\text{CO})_6$ moiety to an acetylide has been reported for $\text{Co}_2(\text{CO})_6[\text{PhC}\equiv\text{CMn}(\text{CO})_4(\text{PCy}_3)]$ [15].

Some comments on the formation and reactions of the complex 3

The reactions of $\text{Co}_2(\text{CO})_8$ with diynes have been described by Seyferth and Churchill [16]; the complex $\text{Co}_8(\text{CO})_{24}\text{C}_6 \cdot 1/2\text{C}_6\text{H}_6$ has been obtained in which the $\text{Co}_2(\text{CO})_6$ unit interacts, through two π bonds, with only one of the acetylenic C–C bonds of the $(\text{CO})_5\text{Co}_3\text{CC}\equiv\text{CC}\equiv\text{CCC}_3(\text{CO})_9$ system. The reactions of $\text{Co}_2(\text{CO})_8$

with phosphino- or diphosphino-alkynes to give, among others, products with $\text{Co}_2(\text{CO})_6(\text{RC}\equiv\text{CPR}'_2)$ units held together via Co-P bonds were described by Carty [17]. Finally, heterometallic non-clusters derivatives, in which the metals are held together by σ - and π -coordinated acetylides, were reported by Bruce and Churchill [18].

The reaction leading to **3** represents, to our knowledge, the first case in which a cluster-bound phosphino-alkyne with $\text{Co}_2(\text{CO})_8$ gives a specific and predictable "target" complex with high yield and selectivity. The possibility of bringing about reactions of other metal carbonyl species with cluster-bound phosphino-alkynes (or other unsaturated ligands) makes this synthetic approach potentially very versatile. The reactions of **3** with $(\text{Cp})_2\text{Ni}_2(\text{CO})_2$, $\text{Fe}_2(\text{CO})_9$ and other carbonyls are now under investigation.

The "tethering" of metal clusters of fragments via organic or inorganic bridges may have relevance in catalysis [19] and in the synthesis of organometallic polymers [20]. Moreover, controlled pyrolysis of complexes such as **3** could give new heterometallic clusters, eventually with carbon and phosphorus atoms in the frame. Further studies on this subject are in progress.

Acknowledgements

We thank Prof. A.J. Carty (University of Waterloo, Ontario, Canada) for helpful discussion and for access to unpublished results. The financial support of C.N.R. (Rome) for this work and a loan of OsO_4 from Johnson Matthey are also acknowledged.

References

- 1 M. Castiglioni, E. Sappa, M. Valle, M. Lanfranchi and A. Tiripicchio, *J. Organomet. Chem.*, 241 (1983) 99.
- 2 M. Castiglioni, R. Giordano, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc. Dalton Trans.*, in press.
- 3 M. Castiglioni, R. Giordano, E. Sappa, G. Predieri and A. Tiripicchio, *J. Organomet. Chem.*, 270 (1984) C7.
- 4 P. Moggi, G. Albanesi, G. Predieri and E. Sappa, *J. Organomet. Chem.*, 252 (1983) C89.
- 5 (a) M.R. Churchill and C. Bueno, *Inorg. Chem.*, 22 (1983) 1510; (b) G. Lavigne, F. Papageorgiou, C. Bergounhou and J.J. Bonnet, *Inorg. Chem.*, 22 (1983) 2485.
- 6 E. Sappa, M. Valle, G. Predieri and A. Tiripicchio, *Inorg. Chim. Acta*, 88 (1984) L23.
- 7 A.J. Carty, *Adv. in Chem. Ser.* 196 (1982) 163. A.J. Carty, *Pure and Appl. Chem.*, 54 (1982) 113.
- 8 N. Walker and D. Stuart, *Acta Cryst.*, A 39 (1983) 158. The program ASSORB was used (written by F. Uguzzoli, University of Parma).
- 9 G.M. Sheldrick, *System of Crystallographic Computer Programs*, University of Cambridge, 1976.
- 10 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, England, Vol. IV, 1974.
- 11 G. Predieri, A. Tiripicchio, C. Vignali, E. Sappa and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, in press.
- 12 A.J. Carty, N.J. Taylor and W.F. Smith, *J. Chem. Soc., Chem. Commun.*, (1979) 750.
- 13 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 83 (1983) 203.
- 14 D. Gregson and J.A.K. Howard, *Acta Cryst.*, C39 (1983) 1024, and references therein.
- 15 G.A. Carriedo, V. Riera, D. Miguel, A.M. Manotti Lanfredi and A. Tiripicchio, *J. Organomet. Chem.*, 272 (1984) C17.
- 16 D. Seyferth, R.J. Spohn, M.R. Churchill, K. Gold and F.R. Scholer, *J. Organomet. Chem.*, 23 (1970) 237.
- 17 H.A. Patel, A.J. Carty, and N.K. Hota, *J. Organomet. Chem.*, 50 (1973) 247.
- 18 O.M. Abu Salah, M.I. Bruce, M.R. Churchill and B.G. De Boer, *J. Chem. Soc., Chem. Commun.*, (1974) 688.
- 19 J. Evans and B.P. Gracey, *J. Chem. Soc., Chem. Commun.*, (1983) 247.
- 20 J.E. Sheats, C.U. Pittman Jr., and C.E. Carraher Jr., *Chemistry in Britain*, (1984) 709.