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The Reaction of $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9$ with Group V Donor Ligands:
Spectroscopic Characterization of the Monosubstituted Derivatives.
An Example of Monodentate Bis(diphenylphosphino)methane on a Heterometallic Cluster.*

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Introduction

$(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9$ (complex **1**) is obtained in good yields by treating under nitrogen $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ with $H_2Os_3(CO)_{10}$ [1, 2] or, alternatively by reacting under H_2 current $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ with $Os_3(CO)_{12}$ [1, 3]. The structure of **1** has been established by X-ray diffraction studies [2–4].

Interest for this complex comes from its potential use in homogeneous hydrogenation catalysis [1] and from its high efficiency as a CO and CO_2 methanation catalyst when supported on alumina [5].

All the available evidence indicates high stability for **1**; one could hence expect that it acts as a *true* cluster catalyst. This led us to carry out a detailed study of the reactivity of this complex.

Here we report the reactions of **1** towards Group V donor ligands; good yields of monosubstituted derivatives corresponding to the general formula $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(L)$ (L = Group V donor ligand) were obtained. These were characterized by means of elemental analyses, i.r. and ^1H N.M.R. spectroscopy; for some complexes F.A.B. mass spectrometry and ^{31}P N.M.R. runs were also performed.

Comments on the proposed structures of the complexes from spectroscopic data are made.

Experimental

All the reactions of complex **1** with the ligands were performed under dry N_2 in dehydrated, refluxing heptane in the presence of anhydrous Me_3NO obtained by sublimation of commercial $Me_3NO\cdot 2H_2O$ (Fluka).

The general procedure followed consisted of dissolving or suspending complex **1** and a 2 to 1 molar excess of ligand, together with some milligrams of Me_2NO, into the *cold* solvent under N_2 and then heating to reflux.

Blank experiments showed that decomposition only occurs when **1** is refluxed in the presence of Me_3NO, without any ligand. The water content in Me_3NO after sublimation was checked by ^1H N.M.R.

The following ligands were reacted with complex **1** (in parentheses are given the reflux time, the yields of the derivatives calculated on **1** and the numbering of the complexes):

Nitrogen Donors

Benzonitrile (70 min, 10%, complex **2a**), diphenylamine (1 min, 20%, complex **2b**).

Phosphines, Arsine and Stibine

Triphenylphosphine (70 min, 50%, complex **3a**); tri(*o*-tolyl)phosphine (5 min, 50%, complex **3b**); tris(cyclohexyl)phosphine (5 min, 60%, complex **3c**); diphenylchlorophosphine (no monosubstituted products); diphenylphosphine (15 min, 40%, complex **3d**); triphenylarsine (5 min, 10%, complex **3e**); triphenylstibine (5 min, 50%, complex **3f**).

Phosphinoacetylenes

Diphenylphosphinophenylacetylene (1 min, 70%, complex **4a**); diphenylphosphinoisopropylacetylene (5 min, 60%, complex **4b**).

Bis(diphenylphosphino)methane, DPPM

Reaction time 2 min, yields 60%, complex **5**.

The reaction mixtures were purified by preparative t.l.c. plates; satisfactory elemental analyses were obtained for all the complexes (except **2b**, because of the presence of excess of ligand) by means of an F & M 185 C, H, N Analyzer and a Perkin Elmer AAS spectrophotometer (See Table I).

The i.r. spectra were obtained on a Perkin Elmer 580 B (KBr optics) instrument; the ^1H N.M.R. spectra were obtained on a JEOL C 60 HL and on a Bruker CPX-200, this latter operating in F.T.; the ^{31}P N.M.R. were registered on the Bruker CPX 200.

Results and Discussion

The analyses and the physical and spectroscopic properties of complexes **2**–**5** are collected in Table 1.

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*This work is dedicated to the memory of Nerina Mossi Tortonese.

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TABLE I. Elemental Analyses, Physical and Spectroscopic Properties of Complexes **2**, **3**, **4** and **5**.

Complex	Physical Properties	Elemental Analysis	I.r. (ν_{CO}, C_7H_{16}), cm^{-1}	^{1}H and ^{31}P N.M.R.[a,b,c]
2a	dark grey-violet crystals	C% 23.70 (23.44)[d], H% 1.40 (1.28), N% 1.51 (1.37); Ni% 5.48 (5.73) Os% 56.12 (55.69)	2230vs, 2076m, 2054vs 2015vs, 1992vs(b), 1980s(sh,b), 1955m	*7.50–7.90 m (5H, Ph), 6.0 s (5H, Cp), –16.20, –16.80 m (3H, hydrides)
2b	dark grey green solid	C% 37.0 (27.53), H% 2.40 (1.76) N% 3.51 (1.28), Ni% 3.15 (5.38) Os% 40.12 (52.31) (see text)	2076m, 2064m(sh), 2056vs, 2015vs, 1980vs(b), 1935s(b)	
3a	dark grey-violet crystals	see ref. 1	2075m, 2056vs, 2018vs, 1997s, 1990s, 1950m	*7.30m (15H, Ph), 6.0s (5H, Cp), –16.05, –16.15d (2H, hydrides), –17.35s (1H, hydride)
3b	dark grey-violet crystals	C% 33.01 (33.23), H% 2.81 (2.62) Ni% 4.63 (4.78), Os% 46.90 (46.43)	2074m, 2055vs, 2014vs 1995s, 1988s, 1950 m(b)	7.45m (12H, Ph), 6.22s (5H, Cp), 2.15s (9H, Me), –16.30, –16.40 (d, 2H, hydrides), –16.80s (1H, hydride)
3c	dark grey-violet crystals	C% 31.15 (30.98), H% 3.71 (3.44) Ni% 4.65 (4.88), Os% 47.80 (47.47)	2075m, 2053vs, 2011vs, 1991s, 1983s(b), 1945m	*6.20s (5H, Cp), 1.20, 1.80m (33H, Cy), –17.30m (2H, hydrides), –17.60m (3H, hydride)
3d	dark grey-violet needle-like crystals	C% 27.60 (27.11), H% 1.88 (1.73) Ni% 5.10 (5.30), Os% 51.90 (51.51)	2076m, 2056vs, 2021vs, 1998s, 1990vs, 1959m(b)	7.46m (10H, Ph), 6.08s (5H, Cp), 8.32–6.45d (1H, P–H), –16.95, –17.00d (2H, hydrides), –17.78s (1H, hydride) ^{31}P (δ, $CHCl_3$) –7.4, –12.02 (d, PPh_2H)
3e	dark grey-violet crystals	C% 31.84 (30.33), H% 2.10 (1.89) Ni% 4.51 (4.78), Os% 47.0 (46.47)	2075m, 2056vs, 2014vs, 1996s, 1989s, 1950m(b)	*7.60m (15H, Ph), 6.30s(5H, Cp), –15.60m, –16.20m (3H, hydrides)
3f	dark grey-violet flat square crystals	C% 30.18 (29.21), H% 2.01 (1.82), Ni% 4.41 (4.61), Os% 45.15 (44.77)	2075m, 2056s, 2014vs, 1996s, 1980s, 1952m	*7.43m (15H, Ph), 6.17s (5H, Cp), –17.50 –17.78 (3H, hydrides)
4a	dark grey-violet solid	C% 33.02 (32.82), H% 2.50 (1.92), Ni% 4.61 (4.86), Os% 47.30 (47.24)	2076m, 2056vs, 2022vs, 1997s, 1989vs, 1961m	7.64, 7.44m (15H, Ph), 6.09s(5H, Cp), –16.61, –16.65d (2H, hydrides), –17.77s (1H, hydride) ^{31}P (δ, $CHCl_3$) –8.34 (Ph_2PC_2Ph)
4b	dark grey-violet prismatic crystals	C% 31.05 (30.70), H% 2.40 (2.15), Ni% 4.84 (5.00), Os% 49.50 (48.61)	2074m, 2054vs, 2021vs, 1997s, 1988s(b), 1959m	7.39m (10H, Ph), 6.07s (5H, Cp), 3.01m (1H, C–H), 1.36, 1.33d (6H, Me), –16.61, –16.66d (2H, hydrides) –17.79s (1H, hydride)
5	dark grey-violet solid	C% 35.12 (34.95), H% 2.51 (2.31) Ni% 4.26 (4.49), Os% 44.05 (43.69)	2075m, 2055vs, 2017vs, 1996s, 1988vs(b), 1954m	7.25s (20H, Ph), 6.07s (5H, Cp), 3.61, 5.56d (2H, CH_2), –16.57, –16.63d (2H, hydrides), –17.70s (1H, hydride) ^{31}P (δ, $CHCl_3$) 17.2, 15.95d (coordinated DPPM phosphorus), –22.33, –23.5d (free DPPM phosphorus)[e]

[a] In parentheses integrated intensities and attribution. [b] The ^{1}H (δ, ppm) were obtained in $CDCl_3$ solution. Internal standard for the ^{31}P, H_3PO_4. [c] The spectra marked (*) were obtained on the JEOL C 60 HL (single scansion); due to the low solubility of the samples high signal/noise ratio made difficult the attribution of the multiplicities. [d] In parentheses the calculated values. [e] Free DPPM ligand, –21.8s.

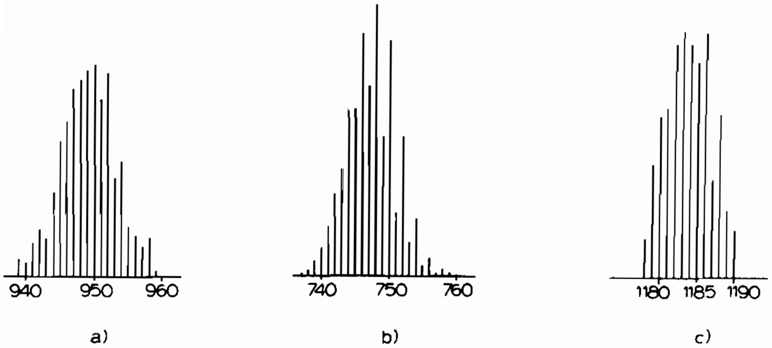

Fig. 1. Isotopic patterns for the parent ions of complexes **1** and **3a** (F.A.B. mass spectrometry). From left: (a) found, complex **1**; (b) calculated for $NiOs_3$ (ref. 1); (c) found, complex **3a**.

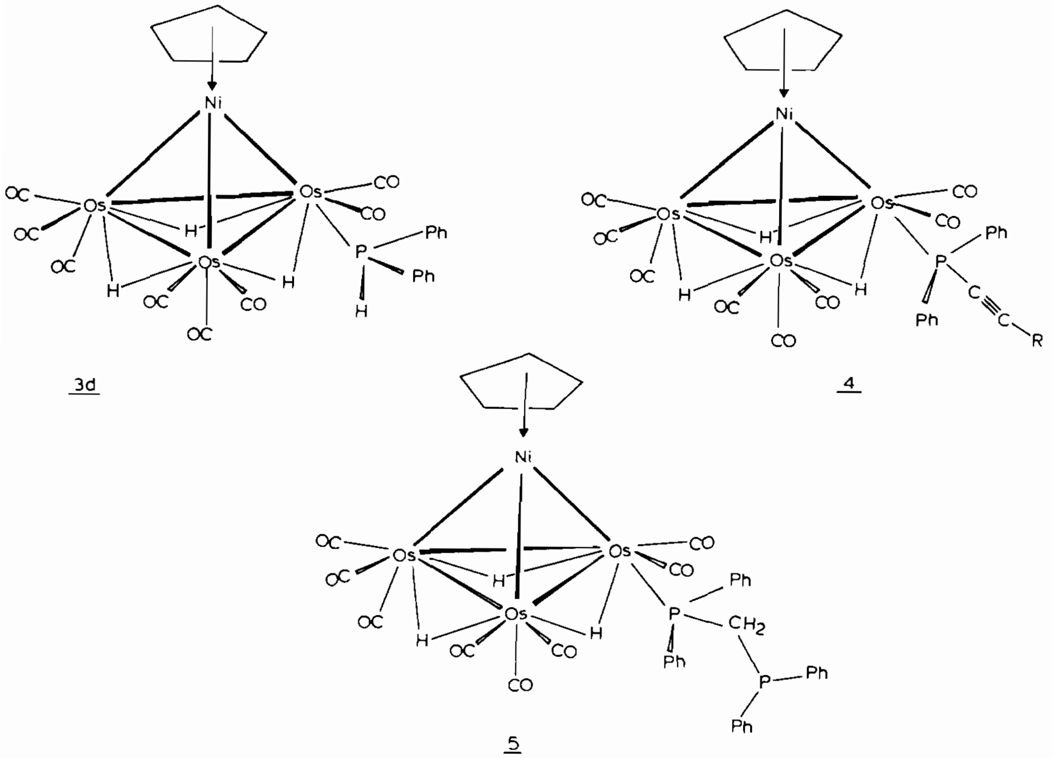

Fig. 2. Proposed structures for complexes **3d**, **4** and **5**.

The dark grey-violet colour (except for **2b**) and the low solubility in aliphatic hydrocarbons are a common characteristic for all the derivatives.

The i.r. spectra are very closely comparable; the same substitution and local symmetry is hence to be expected for compounds **2**–**5**.

The ^1H n.m.r. spectra are fully consistent with the proposed formulation of the complexes, either when considering the number of signals, and their integrated intensities. An examination of the X-ray structure of **1** [2–4] would indicate that – even in the presence of the hydrides – the less hindered position for the entering ligand is one of the three axial; preliminary X-ray results for complex **3d** confirm this hypothesis.

The formulation of complexes **2**–**5** as mono-substituted derivatives is also supported by the F.A.B. mass spectrum of complex **3a***, which shows the parent ion at 1184 m/e and the isotopic pattern shown in Fig. 1.

On the basis of the above spectroscopic evidence we propose for complexes **3**, **4** and **5** the structures shown in Fig. 2.

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*Obtained by Dr. Alan Hogg, Mass Spectrometry Laboratory, Dept. of Chemistry, University of Alberta, Edmonton (Canada).

The simple substitution of CO ligands by PhCN or phosphines is quite common; however, from the reaction of PPh_2H, μ-PPh_2 or μ_3-PPh bridged derivatives could also be expected [6]. To the best of our knowledge these have not been obtained, probably because the used reaction conditions are not favourable to the reductive elimination of H_2; further experiments on this subject are in progress.

Phosphinoacetylenes bonded only through phosphorous to clusters are relatively rare, as generally the unsaturated C–C bond also interacts with other metal centres. Among the few examples, all reported by A. J. Carty's group, there are $M_3(CO)_{11}(PPh_2C_2R)$ (M = Ru, Os) [7], $Os_3(CO)_9(COOEt)(OH)(PPh_2C_2R)$ [8] as well as the interesting $Ru_3(CO)_6(\mu\text{-}C_2Bu^t)(\mu,\eta^2\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(PPh_2C_2Bu^t)$ [9]. All these are homometallic derivatives, whereas complexes **4** represent the first examples for this coordination of the phosphinoacetylenes to heterometallic cores. Note that good yields of these derivatives in which the alkyne has not been split into μ-PPh_2 and acetylide ligands can be obtained in reaction conditions much more drastic than those adopted by Carty.

DPPM acts as a monodentate ligand on mono- and bi-metallic derivatives [10]; however, clusters showing this structural feature have not been previously reported. $Pt_4(\mu\text{-}CO)_2(\mu\text{-}DPPM)_3(Ph_2PCH_2P(O)Ph_2)$ indeed contains a mono-dentate, but partly oxidized DPPM [11].

Thus, complex **5** represents in our opinion the first example of monodentate DPPM on heterometallic clusters, the ^{31}P n.m.r. results, showing two distinct signals, only one of which is very close to that of free DPPM, strongly supporting the formulation of **5**.

Structural studies on some of the above derivatives, as well as the characterization of the other products obtained in the above reactions, are in progress.

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