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SIMPLE, HIGH-YIELDS SYNTHESES OF NICKEL-OSMIUM CLUSTERS. SPECTROSCOPIC CHARACTERIZATION OF THE NEW $(\eta\text{-}C_5H_5)NiOs_3(CO)_9(\mu_2\text{-}H)_3$. THE REACTIVITY OF $(\eta\text{-}C_5H_5)NiOs_3(CO)_9(\mu_2\text{-}H)_3$ AND $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ TOWARDS H_2, CO, ALKYNES AND ALKENES

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Summary

The complexes $(\eta\text{-}C_5H_5)NiOs_3(CO)_9(\mu_2\text{-}H)_3$ and $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ can be obtained in high yield by treating $Os_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$ with $[(\eta\text{-}C_5H_5)\text{-}Ni(CO)]_2$ in refluxing hydrocarbons. The course of the reactions and the yields of the products can be modified by carrying out the reaction under nitrogen, hydrogen or carbon monoxide atmospheres.

A preliminary report of an X-ray study of the hexametallic, 87 e^- cluster was presented. The new tetrametallic derivative was characterized by spectroscopic techniques; a tetrahedral, tri-hydridic structure is proposed for this complex. The reactions of the heterometallic nickel-osmium complexes towards ligands, in particular alkenes and alkynes, are discussed. A preliminary investigation of homogeneous hydrogenation of these substrates is reported.

Introduction

Heterometallic cluster complexes receive much attention because of their potential catalytic importance [1]. Many such clusters have been obtained (usually in low yields or with low selectivity) by pyrolytic methods. We reported pyrolytic syntheses for nickel-iron [2] and nickel-ruthenium clusters [3]; in the latter reactions we obtained small yields of "$(\eta\text{-}C_5H_5)NiRu_3(CO)_9(H)$" (complex I), but disorder in the crystals and decomposition in solution prevented full characterization of this derivative [3].

The interest in I was mainly due to its formulation as a 58 e^- species (instead of the 60 e^- expected for tetrahedral clusters); electronically unsaturated species are of considerable catalytic interest, as with $H_2Os_3(CO)_{10}$ [4,5]. For this reason we attempted the synthesis of the osmium analogue of I; however, the main product (40% yield) obtained from $Os_3(CO)_{12}$ and $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ (compound A) under nitrogen was identified and characterized by X-rays as $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ (complex II) [6].

Another possible route to the analogue of I involved reaction of $H_2Os_3(CO)_{10}$ instead of $Os_3(CO)_{12}$; we previously showed that "condensation" of electron-rich species such as $(C_5H_5)Ni$ generated by A with electron-poor species is an efficient method of making heterometallic clusters [7,8].

We describe below the reaction of $H_2Os_3(CO)_{10}$ with A under nitrogen, in refluxing octane; the main products are complex II and $(\eta\text{-}C_5H_5)NiOs_3(CO)_9(\mu_2\text{-}H)_3$ (complex III), each in about 40% yield. The same reaction under hydrogen gives mainly III, and under CO mainly II. Hence, not only are high yields obtained in this simple pyrolytic synthesis, but there is also the possibility of increasing the selectivity towards one product.

The new complex III gives crystals unsuitable for X-ray analyses; it has been fully characterized by means of elemental analyses and spectroscopy; a tri-hydride, tetrahedral structure is proposed on the basis of the results and of the reactions of III as well as by comparison with other heterometallic osmium clusters. Complex I has spectroscopic characteristics similar to III and hence should be reformulated as a tri-hydride.

A reinvestigation of the spectroscopic characteristics of II is also reported: this complex is an 87 e^- species, as also shown by magnetic measurements.

Monometallic nickel complexes [9] as well as osmium clusters [5] have been reported to be active as catalysts in hydrogenations. We have carried out some preliminary experiments involving use of clusters II and III in homogeneous hydrogenation of t-butyl-alkynes and t-butyl-alkenes; these substrates were chosen because of related work [10] on ruthenium-alkyne clusters.

Experimental

Reactions of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with osmium clusters

A) $Os_3(CO)_{12}$. In a typical experiment, 300 mg (ca. 0.3 mmol) of $Os_3(CO)_{12}$ were refluxed in octane with 300 mg (ca. 1 mmol) of A for 40 min, under nitrogen. The mixture was then cooled and filtered under nitrogen; the recovered solid contained about 40% of the starting osmium carbonyl contaminated with dispersed metal powder *. The solution was evaporated under reduced pressure and purified by TLC; complex II was recovered in about 40% yield based on the amount of osmium carbonyl consumed, together with three trace products.

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* Attempts to purify the carbonyl by cyclohexane extraction in a Soxhlet apparatus gave still impure a product. Column chromatography led to the recovery of about one half of the carbonyl pure enough for further reaction.

The reaction of the same stoichiometric amounts of $Os_3(CO)_{12}$ and A in refluxing octane for 30 min, under hydrogen flow led to the deposition of a thick nickel mirror on the walls of the reaction vessel and of the condenser; about 20% of the osmium carbonyl was recovered unchanged. Two trace products, and III (about 60%) and II (about 10% yield, based on the osmium carbonyl consumed) were present in the reaction mixture.

B) $H_2Os_3(CO)_{10}$. The osmium di-hydride was obtained in almost quantitative yield by refluxing $Os_3(CO)_{12}$ in octane under hydrogen flow and monitoring the reaction by IR. It was treated with a 2 : 1 molar excess of A in refluxing octane for 30 min, under nitrogen. The reaction is fully reproducible and affords III and II each in about 40% yield, and four trace products.

This reaction can also be performed in a single step by adding the nickel reactant A directly to the $H_2Os_3(CO)_{10}$ solution without further purification; similar yields are obtained.

The same reaction, under CO flow affords about 60% of II and some trace products; III was not observed under these conditions.

Reactions of nickelocene (B) with osmium clusters

A) $Os_3(CO)_{12}$. Treatment of $Os_3(CO)_{12}$ with a 3 : 1 molar ratio of B in refluxing octane under nitrogen, for 50 min, leads to considerable decomposition. Cooling and filtration under nitrogen affords a green solution containing unchanged B and a small amount of $Os_3(CO)_{12}$. Treatment of the same reactants in refluxing octane, for 40 min under hydrogen flow leads to extensive decomposition; in the reaction mixture about 30% of unreacted B was found, together with about 5% of III.

B) $H_2Os_3(CO)_{10}$. When the osmium di-hydride is refluxed with a 3 : 1 ratio of B in heptane under nitrogen for 90 min, extensive decomposition is observed. Some unchanged B is recovered.

Reactions of II with H_2, CO and H_2O

Treatment of II under hydrogen flow for 90 min in refluxing heptane leaves about 85% of unreacted II; small amounts of III are detected. The same reaction in a sealed vial (see below) for 60 min at 110°C gives extensive decomposition to metal powder and ca. 5% of III. Complex III is also obtained from II, in high yield, when the latter is used in hydrogenation of alkynes and alkanes (see below).

Treatment of II in refluxing heptane for 120 min, under CO flow leaves 60% of unchanged II; some decomposition, about 4% of III, and traces of $Os_3(CO)_{12}$ were observed. The same reaction in a sealed vial at 100°C overnight gives metal powder, about 5% of III and small amounts of $Os_3(CO)_{12}$.

Treatment of II in octane solution with a 10:1 excess of water for 4 hours in a sealed vial at 110°C leads to a mixture of unreacted II (30%), III and $Os_3(CO)_{12}$ (5% each) and to decomposition products.

Reactions of III with H_2, CO, PPh_3 and A

Treatment of III under hydrogen flow for 6 hours in refluxing octane results in small decomposition and recovery of about 95% of unaltered complex.

Treatment of III under CO flow for 3 hours in refluxing octane, leads to the formation of small amounts of $Os_3(CO)_{12}$, $H_2Os_4(CO)_{13}$ and $H_4Os_4(CO)_{12}$ (2–5% each), metal powder, and recovery of about 40% of unchanged III.

Treatment of III with a 1.5:1 molar excess of PPh_3 in refluxing octane for 3 to 6 hours under nitrogen leads to increasing amounts of $(\eta\text{-}C_5H_5)NiOs_3(CO)_8(\mu_2\text{-}H)_3(PPh_3)$ together with phosphine-substituted osmium clusters and decomposition products; after 6 hours about a 15% yield of the phosphine-substituted III is achieved (complex IIIb).

Treatment of III with a 2:1 excess of A in refluxing octane, for 30 min under nitrogen leaves some unchanged A, about 30% of unreacted III and considerable decomposition; about 10% of II is obtained together with two yellow trace products.

Preliminary hydrogenation tests on t-butyl-alkyne and t-butyl-alkene

These experiments were performed in sealed glass vials, using a large amount of gas and substrate relative to the cluster compound. The conditions used and the results are shown in Table 3.

During these reactions it was observed that II is decomposed, giving partly complex III and partly alkyne-substituted derivatives of osmium; in contrast, III was general found to be unchanged after the reactions.

The organometallic compounds in solution after the reactions were investigated by IR spectroscopy; in several instances a strong band at 1641 cm^{-1} typical of aldehydes or ketones was also found. Unfortunately the heptanals obtained by hydroformylation of the substrates could not be separated, in the GLC mass spectrometer from the solvent used. Further investigations are in progress.

Purification, crystallization and analyses of the products

$Os_3(CO)_{12}$ and A were purchased from Strem. Hydrogen, nitrogen, and carbon monxide were commercial products, dried before use; a high purity 1/1 CO/H_2 mixture (SIAD analyzed gas) was also employed. The solvents were dried over sodium or molecular sieves.

Complex II is slightly soluble in heptane and well soluble in $CHCl_3$; crystals suitable for the X-ray analysis were obtained by cooling for several days a 30/70 (in volume) solution of $CHCl_3$/heptane at $-10°C$, under nitrogen.

Complex III is sometimes contaminated with $H_2Os_3(CO)_{10}$; purification by TLC, followed by cooling of its hexane-$CHCl_3$ solutions at $-10°C$ under nitrogen affords pure crystals of III. This complex slowly decomposes in $Os_3(CO)_{12}$ under these conditions.

Attempts to crystallize IIIb are in progress.

The products were purified by preparative TLC (Kiselgel PF Merck, with light petroleum-ethyl ether mixtures as eluant) and then crystallized.

Elemental analyses were obtained by F. Pascher Laboratory (Bonn, W. Germany). The mass spectra were recorded on a single focusing Hitachi-Perkin Elmer RMU 6 H operating with direct inlet system, at 70 eV.

The IR spectra were obtained on a Perkin Elmer 580 B spectrophotometer. The ^1H NMR on a JEOL C 60 HL and the ^{13}C NMR of III on a JEOL PS 100 FT in presence of $Cr(acac)_3$ as shift relaxation reagent.

The EPR spectra (on solid samples for II and III and on a CCl_4 solution for II were recorded on a Varian E 109 instrument * operating at a frequency of 9.517

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GHz, microwave power 90 mW, modulation amplitude 10 G.

The organic products in the solutions from the hydrogenation runs were analyzed on a Carlo Erba Fractovap 4200 GLC instrument equipped with FID. Operative conditions were: 2 m × 4 mm. column, n-octane/Porasil C (100/120 mesh), carrier N_2 25 cc/min., temperature program fro 6°C to 155°C.

The organic species in solution were also identified by means of a Carlo Erba-Kratos GC-mass spectrometer **.

Results and discussion

Spectroscopic data and structures for I, II, III

Analytic and spectroscopic data for I, II, III and IIIb are given in Table 1. The IR spectra of I and III and the calculated isotopic patterns for the ions Os_3^+, $NiOs_3^+$ and $Ni_3Os_3^+$ are presented in Fig. 1. The structure found for II [6] and those suggested for I and III are shown in Fig. 2.

The IR spectra of I and III are rather similar and indicate high local symmetry for the all-terminal CO ligands. In the ^1H NMR spectrum of III one singlet at 3.95 and one at 29.7 τ in integrated intensity ratio of 5:3 (media of several integrations on different samples) can be respectively assigned to one cyclopentadienyl and three edge-bridging hydrides. Values for hydridic chemical shifts in osmium-containing clusters are listed in Table 2.

The integration of the ^{13}C NMR spectrum of III indicates the presence of 9 CO ligands and one cyclopentadienyl. The presence of three sharp resonances in 1:1:1 integrated intensity for the CO's indicates stereochemical rigidity at room temperature.

Complex III is diamagnetic (EPR) and its mass spectrum shows a "parent ion" at *m/e* 920 instead of the expected *m/e* 950 value; apparently HCHO is lost immediately. Two main fragmentation pattern are then observed; (i) loss of 8 CO's and of C_5H_6 to leave $NiOs_3^+$, then loss of nickel and (ii) loss of C_5H_6, then of nickel and 8 CO's to leave Os_3^+.

The elemental analyses for III are in accord with the proposed formulation. The simple IR spectrum, the ^1H and ^{13}C NMR shifts (and integrations), as well as the ^1H data for IIIb, all point for a tri-hydridic, tetrahedral structure as shown in Fig. 2. The diamagnetism, the low reactivity of III and the well known stability of the Os_3 entity as well as the ready Ni–Ni rupture when A is brought into reaction under hydrogen [11] all point to this structure. The mass spectrum is compatible with this formulation.

Tetrahedral homo- and hetero-metallic clusters are quite common [12]; several tri-hydrides of ruthenium [10], osmium [13] and other metals [14] are also known in which the hydrides are edge-bridging on a metal atom triangle (see Table 2). The ^1H NMR spectrum of III is also in accord with those of the heterometallic osmium-containing tetrahedral hydrides $H_3CoOs_3(CO)_{12}$ [15], $H_2CoOs_3(CO)_{10}(C_5H_5)$ [16] and $H_2FeOs_3(CO)_{13}$ [17]; the last two were obtained by treating $H_2Os_3(CO)_{10}$ with electron-rich metal species, as discussed above. All these clusters and III are 60 e^- species.

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TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR COMPLEXES I, III AND II

Complex I
Gray-black fibrous crystals.
Found: C, 24.64; H, 0.83; Ni, 8.38; Ru, 45.33%
Calcd. for $C_{14}H_8O_9NiRu_3$: C, 24.76; H, 0.74; Ni, 8.65; Ru, 44.65%.
ν(CO) (heptane): 2060vs, 2011vs [3] cm^{-1}
(hexane): 2090w, 2060vs, 2012vs, 2001m (sh) cm^{-1}.
^1H NMR (CCl_4, τ): 4.50 s
EPR: diamagnetic substance.
Mass Spectrum; $P^+ = m/e$ 648, loss of 9 CO's.
(Isotopic pattern Ru_3Ni).

Complex III
Dark-violet fibrous crystals.
Found: C, 17.05; H, 0.71; Ni, 6.20; Os, 61.8%
Calcd. for $C_{14}H_8O_9NiOs_3$: C, 17.74; H, 0.64; Ni, 6.19; Os, 60.22%.
ν(CO) (hexane): 2092m-w, 2064vs, 2006vs, 1993m(sh) cm^{-1}
($CHCl_3$): 2092w, 2064vs, 2006s(b), 1980(sh,b) cm^{-1}
^1H NMR ($CDCl_3$, τ): 3.95 s (5H), 29.7 (3H) s.

^{13}C NMR ($CDCl_3$) (ppm, downfield positive with respect to
TMS): 86.95(5)^a (C_5H_5), 171.25(3)^a (CO),
178.84(3)^a (CO), 222.32(3)^a (CO). All singlets.

EPR: diamagnetic substance.
Mass spectrum: $P^+ = m/e$ 620, (fragmentation see text)
(Isotopic pattern Os_3Ni).

Complex IIIb.
Brown-violet solid.
Found: C, 32.15; Ni, 5.01; Os, 48.40;, P, 2.76%.
Calcd. for $C_{31}H_{23}O_8PNiOs_3$: C, 31.45; H, 1.96; O, 10.81; P, 2.62;
Ni, 4.96; Os, 48.20%,
ν(CO) (hexane): 2072m, 2052vs, 2014vs, 1995m, 1986s, 1953w, cm^{-1}.
^1H NMR ($CDCl_3$, τ): 2.70 m (15H), 4.0s (5H), 26.05–26.15dd (2H), 27.35m (1H).
Mass spectrum: decomposition.

Complex II
Brown-black crystals [6].
Found:C, 23.8; Ni, 13.5; Os 45.8%.
Calcd. for $C_{24}H_{15}O_9Ni_3Os_3$: C, 24.3; Ni, 14.7; Os, 48.1%.
ν(CO)(hexane): 2064w, 2042s, 2010(sh), 2008vs, 1969vs, 1956(sh) cm^{-1}
(Nujol): 2060w, 2040s, 2010(sh), 2004vs, 1996vs, 1965vs, 1950(sh), 1938s cm^{-1}.
^1H NMR ($CDCl_3$, τ): 3.20s, 4.75s (see text).
EPR: paramagnetic material
signal at 2.2384 g.
Mass Spectrum: $P^+ = m/e$ 822, loss of 9 CO's.

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[a] Integrated intensity.

In contrast, the electron count for II as previously formulated leads to 87 e^-, and hence to a paramagnetic electronically unsaturated compound. This prompted us to re-investigate all the spectroscopic properties of this complex. The IR spectra of the complex in solvents and in Nujol shows only terminal carbonyls. The ^1H NMR

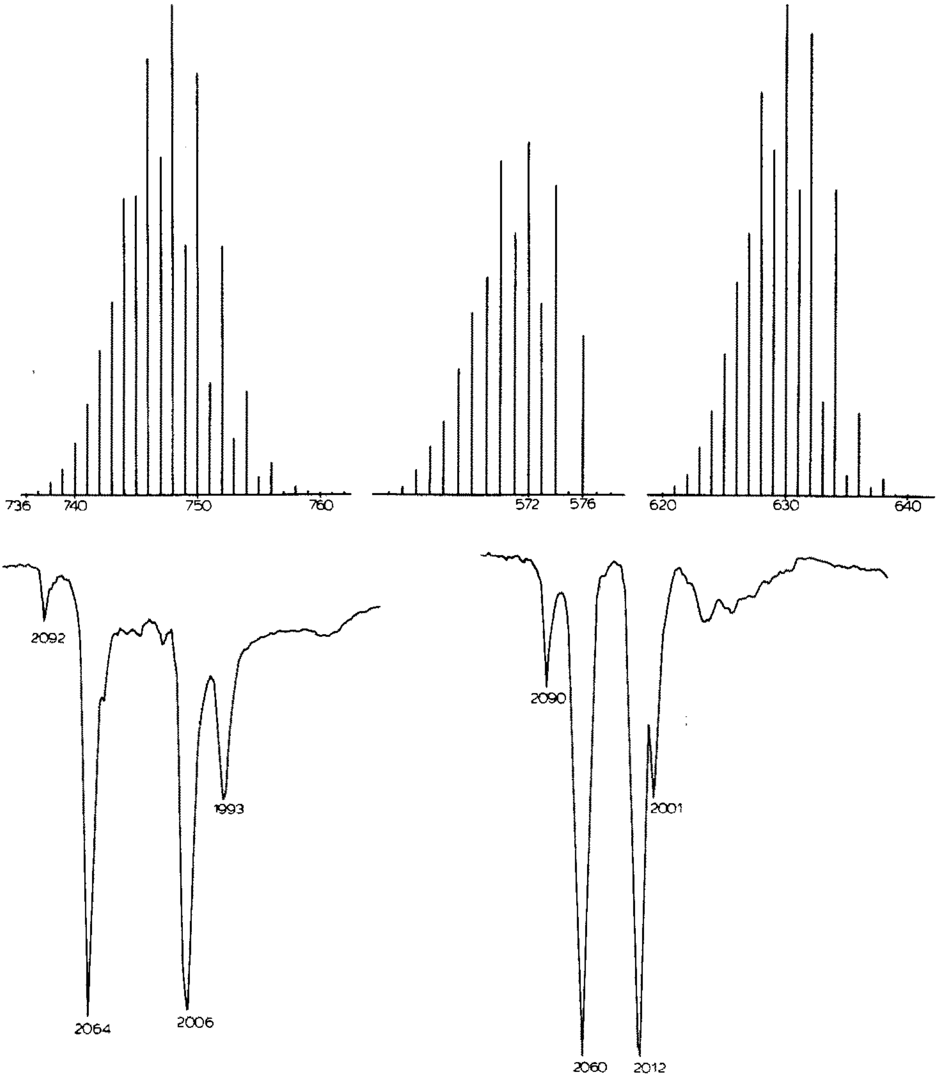

Fig. 1. IR Spectra of complexes III, left, and I, right. Mass spectra: isotopic patterns of the $NiOs_3$, Os_3 and Ni_3Os_3 ions (left to right).

spectrum * is not consistent with the solid state structure; only two signals at 3.20 τ and 4.75 τ, are observed, in an integration ratio of about 1:1. These can be assigned to two different cyclopentadienyls. The spectrum is not temperature dependent in the range $-50°$ to $+30°C$. A careful search for hydridic signals in the range $+10$ to $+35$ τ was unsuccessful, as was a search for low-field signals from -20 τ to 0 τ. The complex was found to be paramagnetic in the solid state and in CCl_4 solution. The mass spectrum shows a "parent ion" at *m/e* 822 corresponding to $Os_3(CO)_9^+$, and loss of 9 CO's.

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* Erroneously reported previously as 7.75 τ [6].

TABLE 2

^{1}H NMR DATA FOR HOMO- AND HETERO-METALLIC TETRAHEDRAL CLUSTERS CONTAINING OSMIUM, AND RELATED COMPLEXES

Complex	μ_2-H(τ)	(Cp)(τ)	Refs.
$H_2Os_4(CO)_{13}$	31.23	–	22
$H_4Os_4(CO)_{12}$	30.35	–	22
$H_2FeOs_3(CO)_{13}$	30.7	–	17
$H_2FeRuOs_2(CO)_{13}$	29.7	–	22
$(H_2)(Cp)CoOs_3(CO)_{10}$	27.17[a] 30.98 29.03	4.53	16, 17
$H_3Mn_3(CO)_{12}$	34.0	–	22
$H_3Re_3(CO)_{12}$	27.1	–	22
$H_3Ru_3(CO)_9CR$ ($R = CH_2Bu^t$)	27.5	–	10
$H_3Os_3(CO)_9CR$ ($R = Me$)	28.58	–	22
$H_3CoOs_3(CO)_{13}$	29.1	–	15
$H_3(Cp)NiOs_3(CO)_9$	29.7	3.95	This work

[a] At −80°C, coalesces at 22°C.

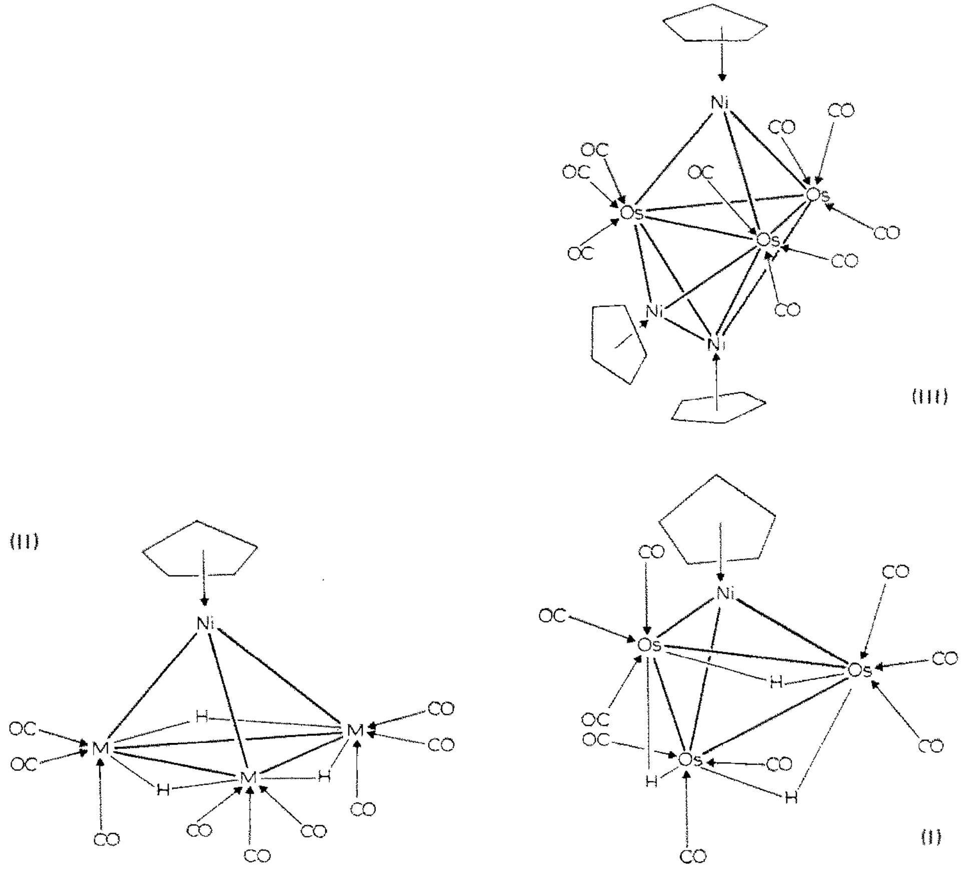


Fig. 2. Schematic structures for the complexes: (a) Complex II (X-ray crystallography); (b) complexes I and III, proposed structures.

All the above evidence point for the original formulation of II as non-hydridic, paramagnetic, 87 e^- species. The isostructural $Os_6(CO)_{18}$ cluster [18] is a 84 e^- structure and was considered unsaturated; in agreement with this, the complex readily adds alkyne (see below).

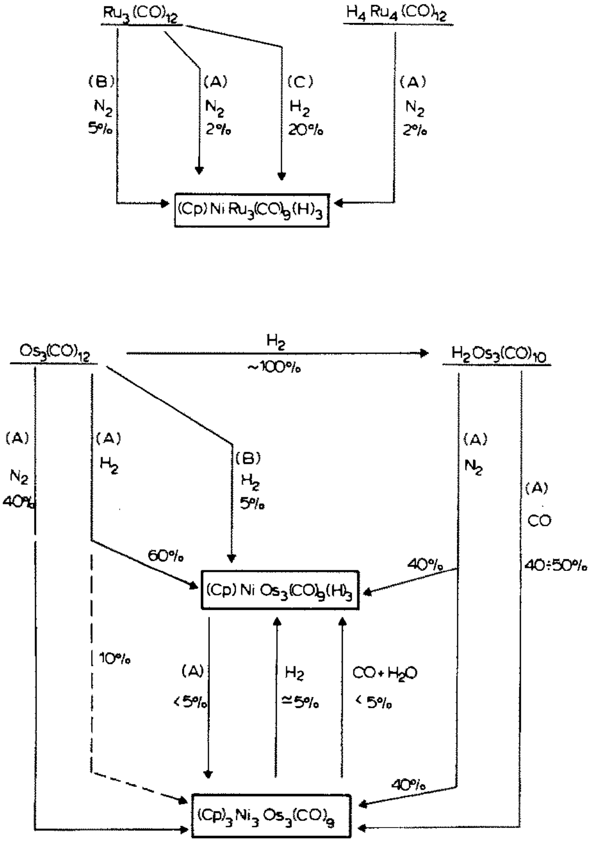
Some comments on the preparative procedures and formation mechanisms for II and III

The reactions leading to II and III represent examples of high-yield pyrolytic syntheses of heterometallic clusters, which can be conveniently modified by changing the reactants or the reaction atmosphere. The preparative methods for II and III and the chemical relationships within these complexes are shown in Scheme 1, and compared with those for I.

The newly reported reaction of $Os_3(CO)_{12}$ with A under hydrogen, and of $H_2Os_3(CO)_{10}$ with A under nitrogen, offer some advantages over the previously reported synthesis of II [6]. Thus in this latter "direct" synthesis, only half of the osmium carbonyl reacts, and only II is formed while considerable loss of $Os_3(CO)_{12}$

SCHEME 1

PREPARATIVE METHODS FOR COMPLEXES I, II AND III: RELATIONSHIPS BETWEEN II AND III



is observed. The use of hydrogen as reaction atmosphere directs this synthesis towards III, with less osmium loss. The time required for obtaining III is shorter than that employed for making $H_2Os_3(CO)_{10}$ under comparable conditions. Finally, the "indirect" synthesis, starting from $H_2Os_3(CO)_{10}$ can be performed in a single step and leads to high yields of both II and III; losses of osmium carbonyl are reduced and only a single purification is required. The use of a CO atmosphere diverts this synthesis towards II without increase in the yield.

The above evidence indicates a strong effect of the hydrogen in the synthesis of III; this has previously been observed for vinylidene osmium-nickel species [11]. Apparently the presence of hydrogen favours the formation of nucleophilic (Cp)Ni or (Cp)NiH species. In contrast, in the presence of CO or nitrogen, the stability of the bimetallic A seems to be increased.

The reaction of nickelocene with $H_2Os_3(CO)_{10}$ shows that saturated nickel species are not effective in the synthesis of heterometallic derivatives, and that the presence of "external" hydrogen is probably required; thus in the presence of H_2 the $Os_3(CO)_{12}$ reacts with nickelocene to give only small amounts of III.

The reactivity of II and III towards ligands and alkynes. Preliminary hydrogenation results

Complex III shows a very low reactivity towards hydrogen, CO and PPh_3. This is in accord with the electronic saturated formulation proposed. Complex III is also obtained from II in presence of hydrogen and alkynes and alkenes; it is also a by-product of the reactions of osmium hydrido-acetylide and -vinylidene clusters

SCHEME 2

RELATIONSHIPS WITHIN OSMIUM-ALKYNE DERIVATIVES AND COMPLEXES II AND III, OCTANE SOLUTIONS, UNDER HYDROGEN (SEE REF. 19).

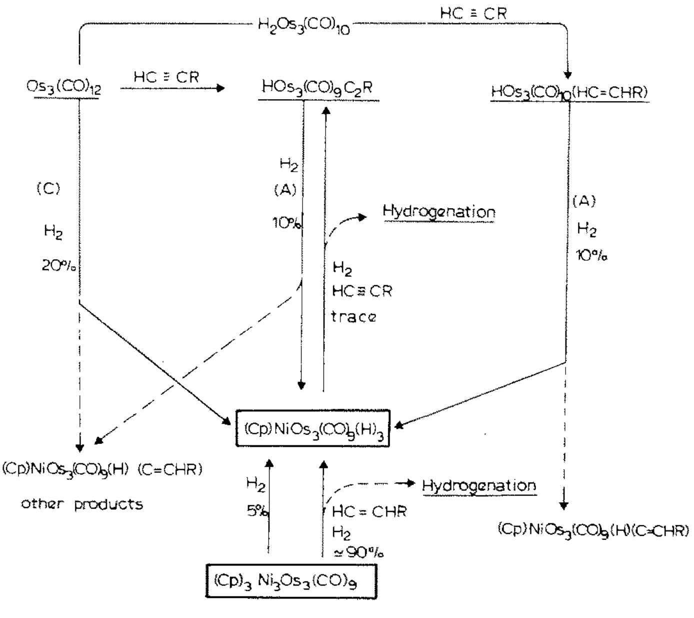


TABLE 3

HYDROGENATION OF t-BUTYL-ALKYNE AND -ALKENE IN THE PRESENCE OF COMPLEXES II AND III

Complex	Substrates	Gas	Reaction conditions and time (h)[a]		Organic products[b]			Species in solution[c]
II	t-butyl-alkyne	H_2	A	6	96.33	3.4	0.23	X
	t-butyl-alkyne	H_2	A	24	92.49	6.95	0.55	X, III
	t-butyl-alkyne	H_2	A	36	88.39	10.66	0.95	X, III
II	t-butyl-alkyne	H_2	B	6	54.70	39.82	5.48	X, Z
	t-butyl-alkyne	H_2	B	12	37.43	50.42	12.15	X, Z
	t-butyl-alkyne	H_2	B	36	32.37	56.27	11.4	X, Z
	t-butyl-alkyne	H_2	B	108	24.9	62.28	12.8	X, Z
II	t-butyl-alkyne	H_2/CO	C	8	99.06	0.94	–	X
	t-butyl-alkyne	H_2/CO	C	12	99.04	0.96	–	X
	t-butyl-alkyne	H_2/CO	C	56	99.0	1.0	–	X
II	t-butyl-ethylene	H_2	A	24	–	98.71	1.29	III
	t-butyl-ethylene	H_2	A	48	–	95.12	4.88	III
II	t-butyl-ethylene	H_2	B	12	–	92.29	7.71	III, Z
	t-butyl-ethylene	H_2	B	36	–	78.67	21.33	III, Z
	t-butyl-ethylene	H_2	B	108	–	56.8	43.2	III, Z
II	t-butyl-ethylene	H_2/CO	C	8	–	99.88	0.12	X, Z
	t-butyl-ethylene	H_2/CO	C	12	–	99.88	0.12	X, Z
	t-butyl-ethylene	H_2/CO	C	56	–	99.80	0.20	X, Z
III	t-butyl-alkyne	H_2	A	6	96.33	3.4	0.23	X
	t-butyl-alkyne	H_2	A	24	92.49	6.95	0.55	X, III
	t-butyl-alkyne	H_2	A	36	89.15	8.77	2.08	X, III
III	t-butyl-alkyne	H_2	B	12	95.5	4.1	0.3	X, Z
	t-butyl-alkyne	H_2	B	36	63.3	32.52	4.17	X, Z
	t-butyl-alkyne	H_2	B	108	53.79	39.49	6.7	X, Z
	t-butyl-alkyne	H_2/CO	C	8	98.8	1.20	–	X
	t-butyl-alkyne	H_2/CO	C	16	99.0	1.0	–	X
	t-butyl-alkyne	H_2/CO	C	56	98.5	1.5	–	X
III	t-butyl-ethylene	H_2	A	6	–	99.15	0.85	III
	t-butyl-ethylene	H_2	A	24	–	98.87	1.23	III
	t-butyl-ethylene	H_2	B	12	–	99.92	0.08	III
	t-butyl-ethylene	H_2	B	36	–	96.8	3.2	III, Z
	t-butyl-ethylene	H_2	B	108	–	94.54	5.78	III, Z
	t-butyl-ethylene	H_2/CO	C	8	–	99.9	0.1	III, Z
	t-butyl-ethylene	H_2/CO	C	16	–	99.9	0.1	III, Z
	t-butyl-ethylene	H_2/CO	C	56	–	99.8	0.20	III, Z

[a] All the reactions were performed in 100 ml sealed vials, with 3 ml of a solution of the complex.
(A) 90°C, pentane solution 1.10^{-3} mM for II and 1.5 10^{-3} mM for III, 0.6 atm H_2. Molar ratios: complex II 3×10^{-3}, gas 2.7, substrate 10 mM. complex III 4.5×10^{-3}, gas 2.7, substrate 10 mM.
(B) 110°C, octane solution, same molarities as A. 1 atm H_2. Molar ratios: II 3×10^{-3}, gas 4.5, substrate 10 mM. III 4.5×10^{-3}, gas 4.5, substrate 10 mM.
(C) 110°C, octane solution (same molarities as A). 1 atm CO/H_2 1/1 (volume). Molar ratios: II 3×10^{-3}, gas 2.25 (each), substrate 10 mM. III 3.5×10^{-3}, gas 2.25 (each), substrate 10 mM.

[b] The first figure refers to the percentage of alkyne, the second that of alkene, and the third that of C_6 alkane (expressed in percentage of the total C_6). GLC and GC-MS measurements.

[c] X = osmium-alkyne complexes, Z = presence of a strong IR signal at 1641 cm^{-1}.

with A under hydrogen [11,19]. In contrast, III does not react with alkynes and gives no substitution products.

Complex II is not formed in the above reactions; it reacts with alkyne yielding small amounts of homo- as well as hetero-metallic derivatives, among which are $(\eta\text{-}C_5H_5)NiOs_3(\mu_2\text{-}H)$ $(C=CHR)$ [8,11,19], 62 e^- butterfly clusters which might play an intermediate role in the alkyne hydrogenation *. These reactions may be of some interest for the catalytic hydrogenation of alkynes and alkenes, and are shown in Scheme 2. The results of the hydrogenation experiments in the presence of II and III are shown in Table 3.

As was predicted on the basis of its electron count and general reactivity, II was found to be more active in the hydrogenation. The reduction of the alkyne occurred more readily than that of the alkene. Carbon monoxide strongly inhibits the reaction; when this gas is present, III is not formed as by-product. This leads us to consider that the hydrogenation occurs via a species formed from II during the decomposition to III, and, indeed, after the reaction, all II has disappeared. The isostructural $Os_6(CO)_{18}$ was found to be reactive towards alkenes [20], and the ruthenium cluster $(PPh_2)Ru_5(CO)_{14}C_2R$, in presence of CO adds one molecule of ligand; the structure is modified from the square-pyramidal to an open "three triangle". This reaction is reversible [21], which could explain the inhibition by CO.

On the other hand, complex III shows lower reactivity and smaller selectivity, as a consequence of the electronic situation; however, this cluster can be recovered unaltered after several days of reaction at 110°C and thus might be a low-efficiency but very stable cluster catalyst.

Finally, as shown in Scheme 1, complexes II and III are structurally related, and their formation is affected by the presence of H_2 and CO. Possible uses of these clusters in homogeneous WGSR reactions are under investigation, as well as the nature of the species obtained by supporting II and III on heterogeneous substrates.

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References

1 W.L. Gladfelter and G.L. Geoffroy, Adv. Organometal. Chem., 18 (1980) 207. B.F.G. Johnson (Ed.), Transition Metal Clusters, J. Wiley, Interscience, 1980.

2 E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, J. Organometal. Chem., 199 (1980) 243.

3 E. Sappa, A.M. Manotti Lanfredi and A. Tiripicchio, J. Organometal. Chem., 221 (1981) 93.

4 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2697, and references therein.

5 A.J. Deeming and S. Hasso, J. Organometal. Chem., 114 (1976) 313; J.B. Keyster and J.R. Shapley, J. Amer. Chem. Soc., 98 (1976) 1056.

6 E. Sappa, M. Lanfranchi, A. Tiripicchio and M. Tiripicchio Camellini, J. Chem. Soc. Chem. Commun., (1981) 995.

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* An investigation on the reactivity of these clusters towards hydrogen and other ligands is in progress.

7 M. Lanfranchi, A. Tiripicchio, E. Sappa, S.A. McLaughlin and A.J. Carty, J. Chem. Soc. Chem. Commun., in press.

8 E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, Inorg. Chim. Acta, 41 (1980) 11.

9 G. Henrici Olivé and S. Olivé, Coordination and Catalysis, Monographs in Modern Chemistry, Verlag Chemie, 1977, see also ref. 5.

10 M. Castiglioni, G. Gervasio and E. Sappa, Inorg. Chim. Acta, 49 (1981) 217.

11 A.J. Carty, N.J. Taylor, E. Sappa and A. Tiripicchio, Inorg. Chem., submitted for publication.

12 P. Chini and B.T. Heaton, Topics in Current Chemistry, 71 (1977) 1–70, Springer Verlag.

13 Y.P. Yesinowski and D. Bailey, J. Organometal. Chem., 65 (1974) C27.

14 S.W. Kirtley, J.P. Olsen and R. Bau, J. Amer. Chem. Soc., 95 (1973) 4532.

15 S. Bhaduri, B.F.G. Johnson, J. Lewis, P.R. Raithby and D.J. Watson, J. Chem. Soc. Chem. Commun., (1978) 343.

16 M.R. Churchill, C. Bueno, S. Kennedy, J.C. Bricker, J.S. Plotkin and S.G. Shore, Inorg. Chem., 21 (1982) 627.

17 J.S. Plotkin, D.G. Alway, C.R. Weisenberger and S.G. Shore, J. Amer. Chem. Soc., 102 (1980) 6157.

18 C.R. Eady, W.G. Jackson, B.F.G. Johnson, J. Lewis and T.W. Matheson, J. Chem. Soc. Chem. Commun., (1975) 958.

19 A.J. Carty, E. Sappa and A. Tiripicchio, manuscript in preparation.

20 C.R. Eady, J.M. Fernandez, B.F.G. Johnson, J. Lewis, P.R. Raithby and G.M. Sheldrick, J. Chem. Soc. Chem. Commun., (1978) 421.

21 A.J. Carty, personal communication (to E.S.).

22 A.P. Humphries and H.D. Kaesz, S. Lippard (Ed.), Progr. in Inorganic Chemistry, 25 (1979) 146.