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MULTI-SITE BONDED HYDROCARBYLS ON OSMIUM CLUSTERS. THE REACTIONS OF HYDRIDOACETYLIDE AND HYDRIDOVINYLIDENE-OSMIUM CLUSTERS WITH $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ AND OF $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ WITH OSMIUM CARBONYLS. SYNTHESIS AND CRYSTAL STRUCTURE OF $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)Os_3(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CHBu^t)$

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Summary

The heterometallic cluster $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)Os_3(CO)_9(C{=}CHBu^t)$ has been obtained in low yield by treating hydridoacetylide- or hydridovinylidene-osmium clusters with $[(C_5H_5)Ni(CO)]_2$ under hydrogen. The structure of this complex has been determined by X-ray methods.

The crystals are monoclinic, space group $P2_1/n$ with a 15.412(9), b 16.916(10), c 9.088(6) Å, β 94.22(4)° and $Z = 4$. The structure was solved from diffractometer data by direct and Fourier methods and refined by full matrix least squares to a $R = 0.037$ for 2210 observed reflections.

The metal cluster consists of a butterfly arrangement with the Ni atom occupying the wing tip site. The vinylidene is σ-bonded to two Os and the Ni atoms and η-coordinated to the third Os atom. An Os–Os edge is bridged by a hydridic hydrogen atom. The structure of this complex is very similar to that of the previously reported Ru–Ni analogues; a comparison is made between the bonding parameters for the vinylidene and related ligands in the different clusters.

These butterfly complexes are structurally related to the iron clusters involved in the Fischer–Tropsch reaction; the formation mechanism of the vinylidene butterfly derivatives and the role of molecular hydrogen in their formation reactions are discussed.

Introduction

We found that the pyrolysis of cluster-bound hydrocarbyls with the electron-rich $(\eta\text{-}C_5H_5)Ni$ "fragment" provides an efficient method of obtaining tri-, tetra- and

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$$[(Cp)Ni(CO)]_2 + HOs_3(CO)_9C_2Bu^t \xrightarrow[60\ min]{E,N_2{}^a} HOs_3(CO)_9C_2Bu^t\ (20\%),\ (Cp)_2Ni_2(HC_2Bu^t)\ (25\%),\ \text{trace products (4)} \qquad \text{this work}$$

$$[(Cp)Ni(CO)]_2 + HOs_3(CO)_9C_2Bu^t \xrightarrow[40\ min]{E,H_2} Ni(CO)_4,\ HOs_3(CO)_9C_2Bu^t\ (10\%),\ (Cp)NiOs_3(CO)_9(H)(C{=}CHBu^t)\ (10\%),\ (Cp)NiOs_3(CO)_9(H)_3\ (5\text{–}10\%) \qquad \text{this work}$$

$$\begin{tikzcd}
{[(Cp)Ni(CO)]_2 + HOs_3(CO)_{10}(HC{=}CHBu^t)\,^c} \arrow[r, "E{,}N_2", "70\text{–}120\ min"'] & {(Cp)_2Ni_2(HC_2Bu^t)\ (20\%),\ HOs_3(CO)_9C_2Bu^t\ (10\%),\ Os_3(CO)_7(HC_2Bu^t)_3\ (3\%),\ Os_3(CO)_6(HC_2Bu^t)_4(CO)\ (3\%),\ \text{trace products (8)} \qquad \text{this work}} \\
{[(Cp)Ni(CO)]_2 + H_2Os_3(CO)_9(C{=}CHBu^t)} \arrow[ur, "E{,}N_2", "70\ min"'] &
\end{tikzcd}$$

$$\begin{tikzcd}
{[(Cp)Ni(CO)]_2 + HOs_3(CO)_{10}(HC{=}CHBu^t)} \arrow[r, "E{,}H_2", "30\ min"'] & {H_2Os_3(CO)_9(C{=}CHBu^t)\ (15\%),\ Ni(CO)_4,\ (Cp)NiOs_3(CO)_9(H)(C{=}CHBu^t)\ (10\%),\ (Cp)NiOs_3(CO)_9(H)_3\ (10\%) \qquad \text{this work}} \\
{[(Cp)Ni(CO)]_2 + H_2Os_3(CO)_9(C{=}CHBu^t)} \arrow[ur, "E{,}H_2", "30\ min"'] &
\end{tikzcd}$$

$$Os_3(CO)_{12} + (Cp)_2Ni_2(HC_2Bu^t) \xrightarrow[60\ min]{E,N_2} HOs_3(CO)_9C_2Bu^t\ (10\%),\ H_2Os_3(CO)_9(C{=}CHBu^t)\ (2\text{–}5\%),\ Os_3(CO)_7(HC_2Bu^t)_3\ (1\%),\ Os_3(CO)_6(HC_2Bu^t)_3(CO)\ (1\%) \qquad \text{this work}$$

$$Os_3(CO)_{12} + (Cp)_2Ni_2(HC_2Bu^t) \xrightarrow[30\ min]{E,H_2} H_2Os_3(CO)_9(C{=}CHBu^t)\ (15\%),\ HOs_3(CO)_9C_2Bu^t\ (5\%),\ (Cp)NiOs_3(CO)_9(H)_3\ (20\%),\ (Cp)NiOs_3(CO)_9(H)(C{=}CHBu^t)\ (10\%) \qquad \text{this work}$$

$$H_2Os_3(CO)_{10} + (Cp)_2Ni_2(HC_2Bu^t) \xrightarrow[100\ min]{E,N_2} HOs_3(CO)_9C_2Bu^t\ (5\%),\ HOs_3(CO)_{10}(HC{=}CHBu^t)\ (1\%),\ H_2Os_3(CO)_9(C{=}CHBu^t)\ (7\%),\ Os_3(CO)_7(HC_2Bu^t)_3\ (1\%),\ Os_3(CO)_6(HC_2Bu^t)_4(CO)\ (1\%) \qquad \text{this work}$$

$$HC_2Bu^t + (Cp)_3Ni_3Os_3(CO)_9 \xrightarrow[days]{F,H_2} (Cp)NiOs_3(CO)_9(H)_3,\ \text{osmium-alkyne complexes, alkyne hydrogenation} \qquad [13]$$

$$HC_2Bu^t + (Cp)NiOs_3(CO)_9(H)_3 \xrightarrow[6\ h]{E,N_2} HOs_3(CO)_9C_2Bu^t\ (tr),\ \text{trace products [2]},\ (Cp)NiOs_3(CO)_9(H)(C{=}CHBu^t)\ (tr) \qquad \text{this work}$$

$$HC_2Bu^t + (Cp)NiOs_3(CO)_9(H)_3 \xrightarrow[days]{F,H_2{}^b} \text{alkyne hydrogenation} \qquad [13]$$

$$HC_2Bu^t + (Cp)NiOs_3(CO)_9(H)_3 \xrightarrow[12\ h]{G,CO/H_2{}^b} HOs_3(CO)_9C_2Bu^t\ (tr),\ \text{alkyne hydrogenation},\ (Cp)NiOs_3(CO)_9(H)(C{=}CHBu^t)\ (tr) \qquad \text{this work}$$

$$HC_2Bu^t + (Cp)NiRu_3(CO)_9(H)_3 \xrightarrow[1\text{–}3\ h]{E,N_2} HRu_3(CO)_9(C_2Bu^t)\ (5\%),\ \text{trace products (5)}\,^d,\ (Cp)NiRu_3(CO)_9(H)(C{=}CHBu^t)\ (2\%) \qquad \text{this work}$$

$$HC_2Bu^t + (Cp)NiRu_3(CO)_9(H)_3 \xrightarrow[1\ h]{E,CO} HRu_3(CO)_9C_2Bu^t\ (tr),\ \text{trace products (7)}\,^d,\ (Cp)NiRu_3(CO)_9(H)(C{=}CHBu^t)\ (1\%) \qquad \text{this work}$$

SCHEME 1. [a] E = octane solution, 1.5/1 mol (the first figure is referred to the first reactant). [b] F = octane, 110°C, strong excess of alkyne. [c] Thermal decomposition of this species lead to complexes Ic and IVb. [d] Among these $H_3Ru_3(CO)_9(CCH_2Bu^t)$ [19]. [e] G = octane, 1.5/1 moles, 1 atm CO/H_2, sealed vials, 120°C.

penta-heterometallic nickel–iron and nickel–ruthenium clusters [1–5]. Whereas the iron derivatives are obtained in low yields and with low selectivity, the ruthenium complexes are usually formed in better yields and with greater selectivity, the latter depending upon the parent ruthenium hydrocarbyl clusters used [3].

The more commonly obtained ruthenium–nickel derivatives have Ru_3Ni butterfly structures [3]; in particular, from the $HRu_3(CO)_9C_2R$ ($R = Bu^t$, Pr^i) species (complexes I) the heterometallic clusters $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)Ru_3(CO)_9(C{=}CHR)$ are formed ($R = Bu^t$, complex IIa; $R = Pr^i$, complex IIb) [4,6]. The $\mu_4\text{-}\eta^2$ bound vinylidene-butterfly clusters II were the first reported examples of this structural arrangement for heterometallic derivatives; the only other known heterometallic butterfly complex is $(\eta\text{-}C_5H_5)FeCo_3(CO)_9(C{=}CH_2)$ [7], which also has the "hetero-metal" on a wing tip.

These clusters are of interest because their structures are closely comparable with those of the Fischer–Tropsch related iron butterfly derivatives $[Fe_4(CO)_{12}C]^{2-}$ [8], $HFe_4(CO)_{12}(CH)$ [9], $[HFe_4(CO)_{13}]^-$ [10] and $HFe_4(CO)_{12}(COMe)$ [11]. Therefore, improved synthetic methods based on the knowledge of the reaction patterns are highly desirable for complexes II, in order to facilitate the study of their reactivity and potential catalytic uses.

A considerable improvement in the yields of IIa, IIb was recently achieved by simply allowing the reactions to take place under hydrogen flow [6]. Possible intermediates in these reactions could be vinylidene clusters such as $H_2Ru_3(CO)_9(C{=}CHR)$ or mixed-metal species such as the tetrahedral $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)_3Ru_3(CO)_9$ [3,13], but these ruthenium derivatives were obtained in low yields. In contrast the hydridovinylidene osmium clusters are readily obtained in high yields from alkynes [12]. The complex $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)_3Os_3(CO)_9$ is also readily accessible in satisfactory yield [13].

As the proposed intermediates leading to complexes II are much more accessible for osmium, we investigated the synthetic pathways leading to the osmium homologue of complex IIa, the $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)Os_3(CO)_9(C{=}CHBu^t)$ (complex IIc). The reactions of $HOs_3(CO)_9(C_2Bu^t)$ (complex Ib) [14], $HOs_3(CO)_{10}(HC{=}CHBu^t)$ (complex III) and $H_2Os_3(CO)_9(C{=}CHBu^t)$ (complex IV) [14] with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ (complex A) were examined as well as the reactions of $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ (complex B) with $Os_3(CO)_{12}$. Finally, the reactions of $(\eta\text{-}C_5H_5)Ni(\mu\text{-}H)_3M_3(CO)_9$ ($M = Ru$, complex Va; $M = Os$, complex Vb) with HC_2Bu^t were attempted.

The structure of complex IIc has been confirmed by X-ray methods, and is compared with those found for IIa, IIb and with other vinylidene cluster derivatives.

Experimental

Reactions of Ib, II and IV with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$

The stoichiometry, yields and reaction conditions for the reactions within nickel complexes A, B and V and osmium carbonyls, and hydrido- or alkyne-carbonyls are shown in Scheme 1.

Conventional glass apparatus was used for all the reactions. When hydrogen flow was used, thick nickel mirrors were observed in the reaction vessels and reflux condensers, probably because of the formation and subsequent decomposition of

TABLE 1

SPECTROSCOPIC PROPERTIES OF THE (Cp)Ni$M_3(CO)_9(\mu$-H)(C=CHR) COMPLEXES AND OF THE "PARENT" $HM_3(CO)_9C_2R$ HYDRIDES

Complex	ν(CO) (hexane) (cm^{-1})	ν(CO) of hydrides I	$^1H(\delta, CDCl_3)$	^{1}H (hydride) of I	Ref.
IIb, M = Ru, R = Pr^i	2082s, 2056vs, 2044s, 2012s, 2006s(sh), 1985s	2096m, 2070vs, 2052vs, 2024s, 2017vs(sh), 1991m-s	5.30 s (5H) 4.80 s (1H) 1.40 s (1H) 0.85–1.25 (6H) −21.3 s (1H) (br)	−20.70 (s)	6
IIa, M = Ru, R = Bu^t	2079vs, 2058vs, 2040vs, 2008vs, 2000s(sh), 1979m-s	2097m, 2070vs, 2054vs, 2022vs, 1992m	5.40 s (5H) 4.50 s (1H) 2.0-2.15 (9H) −22.1 s (1H) (vbr)	−21.8 (s)	4
IIa, M = Os, R = Bu^t	2082m, 2057m, 2042vs, 2006vs, 1997s, 1974m	2029m, 2072vs, 2052vs, 2020vs, 2010s(sh), 1981m	6.35 s (1H) 5.60 s (5H) 2.10 s (9H) −24.3 s (1H) (br)	−23.5 (s)	this work

nickel hydridocarbonyls (indicated by "$Ni(CO)_4$" in Scheme 1.)

$Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$ were prepared by established procedures.

Reactions of complexes Va, Vb with t-butyl-acetylene

Complexes Va [3] and Vb [13] were obtained as previously reported. These complexes were also used for the hydrogenation of alkynes and alkenes in sealed vials and the results reported elsewhere [13]. In Scheme 1 are shown the results obtained under reaction conditions comparable with those used for complexes Ib–IV.

Reactions of $(\eta\text{-}C_5H_5)_2Ni_2(HC_2Bu^t)$ with $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$

Complex B was obtained by established procedures [15] and purified by filtering the reaction solutions under nitrogen, then reducing them to small volume and allowing the products to crystallize out at −10°C under nitrogen. Solutions containing B were also used without purification by simply adding the osmium reactants and allowing the reaction to proceed; the results were similar to those obtained with isolated samples.

Purification and analysis of the products

The reaction mixtures were separated on preparative TLC plates (Kieselgel P.F. Merck, eluant mixtures of light petroleum and ethyl ether). Complex B decomposes on the TLC plates. When possible, the products were crystallized from aliphatic hydrocarbons or from hydrocarbons/chloroform mixtures kept at −10°C under nitrogen.

The products were analyzed by means of an F & M C, H, N Analyzer and a Perkin–Elmer AAS; the mass spectra were obtained on a single focusing Hitachi–Perkin–Elmer RMU-6H instrument operating with direct inlet system, at 70 eV. The IR spectra were recorded on a Perkin–Elmer 580B instrument and the ^1H NMR spectra on a JEOL C 60 HL instrument.

Crystals and analysis of IIc

Crystals of this dark-brown complex were obtained as described above. The complex analyzes as follows: Found: C, 24.05; H, 1.64; Ni, 5.60; Os, 53.15. $C_{20}H_{16}NiO_9Os_3$ calcd: C, 23.33; H, 1.56; Ni, 5.70; O, 13.98; Os, 55.42%.

IIc decomposes in the mass spectrometer and gives the spectrum of Ib; similar behaviour has been observed for IIa, IIb. The IR and NMR spectra of IIc are compared with those of IIa, IIb in Table 1.

X-Ray data collection, structure determination and refinement of IIc

A small black crystal of IIc with dimensions ca. 0.06 × 0.09 × 0.20 was used for the data collection. The cell parameters were refined by a least-squares procedure applied to the θ values of 29 reflections accurately measured on a Siemens AED single crystal diffractometer.

Crystal data are as follows; $C_{20}H_{16}NiO_9Os_3$, $M = 1029.65$, monoclinic, a 15.412(9), b 16.916(10), c 9.088(6) Å, β 94.22(4)°; V 2363(2) Å^3; $Z = 4$; D_c 2.89 g cm^{-3}: $F(000) = 1856$, Mo-K_α radiation, $\bar{\lambda}$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha) = 169.42$ cm^{-1}; space group $P2_1/n$ from systematic absences.

Intensity data were collected on the same diffractometer using niobium-filtered

Mo-K_α radiation and the $\theta/2\theta$ scan technique. The intensity of a standard reflection was measured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A total of 4170 independent reflections was measured in the range $3 \leqslant \theta \leqslant 25°$; of these 2110, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. The structure amplitudes were obtained after the usual correction for Lorentz and polarization factors and the absolute scale was established by Wilson's method. No correction for absorption was applied.

The structure was solved by direct and Fourier methods and refinement was carried out by least squares full matrix cycles using the SHELX system of computing programs [16] with initially isotropic and then anisotropic thermal parameters for all the non hydrogen atoms. Not all the hydrogen atoms could be satisfactorily localized in a ΔF synthesis; they were placed in their geometrically calculated positions

TABLE 2

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

	x/a	y/b	z/c
Os(1)	1927(1)	4124(1)	1543(1)
Os(2)	2912(1)	4727(1)	4081(1)
Os(3)	3737(1)	3907(1)	1832(1)
Ni	1737(2)	3657(2)	4195(3)
O(1)	51(10)	4662(10)	1710(20)
O(2)	1520(11)	2592(9)	−58(18)
O(3)	2261(11)	4977(10)	−1311(17)
O(4)	1654(11)	5753(10)	5718(19)
O(5)	3971(12)	4399(9)	6925(17)
O(6)	4046(12)	6101(10)	3418(19)
O(7)	5613(10)	3782(9)	3003(17)
O(8)	3817(12)	2875(11)	−865(21)
O(9)	4099(11)	5434(10)	253(18)
C(1)	754(16)	4462(13)	1679(25)
C(2)	1664(12)	3148(11)	531(23)
C(3)	2126(13)	4666(12)	−257(20)
C(4)	2117(14)	5354(13)	5090(25)
C(5)	3599(15)	4503(14)	5836(26)
C(6)	3614(13)	5597(14)	3663(25)
C(7)	4911(13)	3810(11)	2565(19)
C(8)	3837(15)	3287(13)	139(27)
C(9)	3977(12)	4865(13)	878(25)
C(10)	2757(12)	3532(11)	3295(23)
C(11)	3224(14)	2828(15)	2930(28)
C(12)	3771(14)	2268(14)	3933(21)
C(13)	4477(15)	1878(12)	3172(27)
C(14)	4190(18)	2739(16)	5363(26)
C(15)	3162(17)	1664(16)	4592(32)
C(16)	1043(17)	2636(14)	4870(31)
C(17)	477(16)	3188(16)	4177(30)
C(18)	496(13)	3864(16)	5028(31)
C(19)	1115(19)	3760(16)	6191(25)
C(20)	1496(16)	2975(20)	6050(34)

TABLE 3

CALCULATED (except for H(1) and H(11) atoms) FRACTIONAL COORDINATES ($\times 10^4$) FOR THE HYDROGEN ATOMS

	x/a	y/b	z/c
H(1)	2197	4849	2620
H(11)	2831	2416	1871
H(131)	4887	2323	2728
H(132)	4196	1513	2286
H(133)	4861	1514	3949
H(141)	4635	3184	5017
H(142)	4537	2329	6102
H(143)	3678	3019	5925
H(151)	2845	1314	3716
H(152)	2677	1972	5173
H(153)	3536	1282	5350
H(16)	1112	2030	4522
H(17)	90	3101	3150
H(18)	97	4383	4822
H(19)	1287	4184	7052
H(20)	2025	2718	6736

(except for the H(1) and H(11) atoms placed in the found positions) and introduced into the final structure factor calculations. The final R was 0.037 for the observed reflections only. The atomic scattering factors used (corrected for the anomalous dispersion of Os and Ni) were taken from the ref. 17. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$. Unit weights were chosen in the first stages of the refinement, in the final cycles the weight used was calculated as $w = K/(\sigma^2(F_0) + gF_0^2)$ with $K = 0.2480$ and $g = 0.0057$.

Final atomic coordinates for non-hydrogen and hydrogen atoms are given in Tables 2 and 3, respectively. Lists of thermal parameters for the non-hydrogen atoms and of observed and calculated structure factors are available from the authors on request.

All the calculations were performed on the CYBER-76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

Results and discussion

Reaction paths leading to complex IIc. The easy synthesis of complexes IIa, IIb either under nitrogen or hydrogen, as well as the high yield syntheses of Vb [13] and of $(\eta\text{-}C_5H_5)_3Ni_3Os_3(CO)_9$ [18] led us to expect that preparation of IIc would be easy and give good yields. Instead, this complex was obtained only in moderate yields and only when hydrogen was used as the atmosphere. This is probably indicative of the fact that the parent osmium acetylide and vinylidene clusters are less prone to "addition" of $(\eta\text{-}C_5H_5)$Ni fragments than the ruthenium clusters. Also, the synthesis in low yields of polyalkyneosmium clusters (see Scheme 1) indicates easy oxidative addition of the ligand on osmium as does the easy alkyne transfer from nickel to osmium when complex B is used as the reactant.

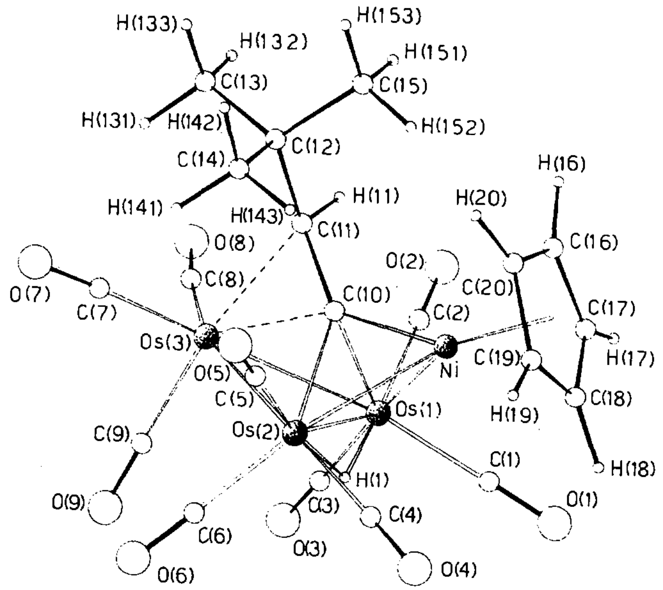
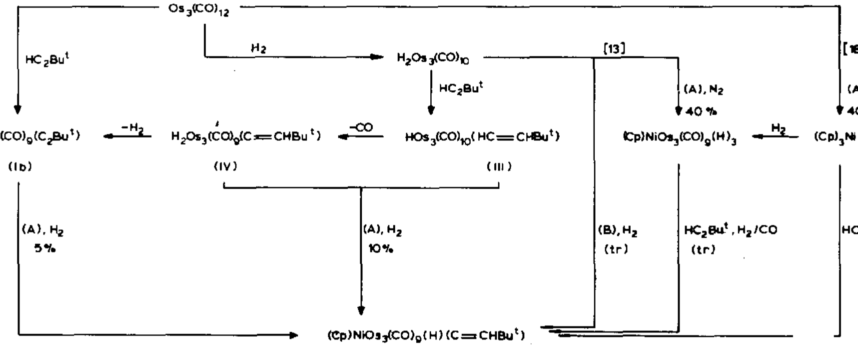


Fig. 1. View of the structure of the complex (η-C_5H_5)Ni(μ-H)$Os_3(CO)_9$(C=CHBu^t) with the atomic numbering scheme.

The presence of molecular hydrogen has been shown to be essential for the synthesis of IIc even when complexes III or IV are used as reactants. This is shown in Scheme 2 which shows all the reactions leading to IIc. This leads us to suggest that the role of molecular hydrogen consists in promoting Ni–Ni bond cleavage in complex A or B, rather than in forming hydrogenated and reactive osmium clusters. The low yields of IIc can also be explained in terms of the competition between "addition" of nickel fragments to Ib, III or IV and oxidative addition of alkynes to the same clusters to give polysubstituted homometallic osmium derivatives.



(A) = [(Cp)Ni(CO)]$_2$
(B) = (Cp)$_2$Ni$_2$(HC$_2$Bu^t)

SCHEME 2

The recent synthesis of Ni_2Ru_3 alkyne clusters [20] and the synthesis of (η-C_5H_5)$_2$$Ni_2Fe_2(CO)_6(C_2Et_2)$ [20] agree with the Ni–Ni bond rupture during the reactions leading to heterometallic derivatives: the observed formation of thick nickel mirrors in the reaction vessels in presence of H_2 also supports this hypothesis.

The results do not provide sound evidence for the participation of complex IV as a reaction intermediate in the following sequence:

$$\underset{(\mathrm{Ib})}{\mathrm{HOs_3(CO)_9(C{\equiv}CBu^t)}} \xrightarrow{(\mathrm{H_2})} \underset{(\mathrm{IV})}{\mathrm{H_2Os_3(CO)_9(C{=}CHBu^t)}}$$

$$\mathrm{IV} \xrightarrow{[(\eta\text{-}\mathrm{C_5H_5})\mathrm{Ni}]} \underset{(\mathrm{IIc})}{(\eta\text{-}\mathrm{C_5H_5})\mathrm{NiOs_3}(\mu\text{-H})\mathrm{(CO)_9(C{=}CHBu^t)}}$$

(Reaction path A).

However, some indirect evidence can be found in the slight increase in the yields of IIc observed when complexes III or IV are used instead of Ib. We have shown that thermal degradation of III with loss of CO and hydrogen gives, first complex IV and then Ib [14] (see also ref. 12). The presence of hydrogen may prevent, at least in part, the decomposition and increase the stability of IV in the reaction solution.

Another reaction sequence leading to low yields of either IIa, IIb and IIc is:

$$(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Ni_2(HC_2Bu^t)} \xrightarrow{(\mathrm{H_2})} \underset{(?)}{(\eta\text{-}\mathrm{C_5H_5})\mathrm{Ni(H)(C{=}CHBu^t)}} + \underset{(?)}{(\mathrm{H})(\eta\text{-}\mathrm{C_5H_5})\mathrm{Ni}}$$

$$\xrightarrow{\mathrm{M_3(CO)_{12}}} (\eta\text{-}\mathrm{C_5H_5})\mathrm{NiM_3(H)(CO)_9(C{=}CHBu^t)}$$

(Reaction path B).

The formation of nickel mirrors, as well as the synthesis of other clusters showing Ni–Ni bond rupture are in accord with this behaviour. Furthermore Ni–Ni bond breaking in presence of hydrogen has been observed for the complexes $(\eta\text{-}C_5H_5)_2$-$Ni_2(RC_2R')$ by Muetterties [21].

Finally, a third way leading to complexes II is the "opening" of the 60 electron species Va, Vb in the presence of alkyne, to give the 62 electron butterfly complexes II:

$$(\eta\text{-}\mathrm{C_5H_5})\mathrm{Ni}(\mu\text{-H})_3\mathrm{M(CO)_9} \xrightarrow{(+\mathrm{HC_2Bu^t}),(-\mathrm{H_2})} (\eta\text{-}\mathrm{C_5H_5})\mathrm{NiM_3(H)(CO)_9(C{=}CHBu^t)}$$

(Reaction path C).

In the case of similar reactions involving tetrahedral cobalt [22] and iron–ruthenium clusters [23], the resulting $Co_4(CO)_{10}(C_2Et_2)$ and $FeRu_3(CO)_{12}$-(C_2Ph_2) clusters show an acetylene coordinated along the hinge of the butterfly. The reaction described above is the first to give a vinylidene substituted butterfly structure.

From Scheme 2 one can see that complex Vb is formed from Ib, III and IV in the presence of $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ and hydrogen, and hence is a by-product of path A. However, the presence of hydrogen in excess would prevent the "opening" of clusters V since formation of II would involve release of some of the hydridic hydrogen; thus the overall yields of II via path C would be the result of two balancing effects, namely the formation of V via path A (favoured by hydrogen) and its "opening" in path C (disfavoured by the presence of hydrogen). The yields of complexes II via path C are, in fact, very low.

It is of interest that all three reaction paths leading to IIc discussed above require Ni–Ni bond rupture as one of the fundamental steps.

Spectroscopic results and crystal structure of IIc. The ^{1}H NMR and IR spectral data for IIc are shown in Table 1 along with data for IIa, IIb and of the parent hydrides I, Ib. The IR spectra of all the heterometallic complexes II are closely comparable with those of the homo-trimetallic complexes I, whereas complexes III and IV show quite different IR patterns. This is significant, especially in view of the fact that in complexes II the mutual positions of the ligand C(α) and of the hydride on the cluster are different from those in complexes I, so that a "rotation" of the ligand would have to occur during reaction by path A.

A similar change in the position of the ligands bridging one cluster edge with respect to the organic ligand is also observed when (μ-PPh$_2$)Ru$_3$(CO)$_8$(C$_2$R) is formed from (μ-PPh$_2$)Ru$_3$(CO)$_9$(C$_2$R) [24], when (μ-PPh$_2$)Ru$_3$(CO)$_8$[(Et)HNC=CHPr^i] [25] is formed by the same starting cluster and finally when HM$_3$(CO)$_9$(Ph-C=C–CNR) [26] (M = Ru, Os) are formed from HM$_3$(CO)$_9$(C$_2$R). This ligand rotation seems to be a general feature of these clusters; however, the symmetry properties of the (H)M$_3$(CO)$_9$ unit seem to be maintained in complexes I and II as shown by the spectra. Finally, the lowering of the ν(CO) frequencies by about 10–15 cm^{-1} and the slight increase in the chemical shifts of the hydride resonances in the ^{1}H NMR spectra of complexes II compared to complexes I may be due to the presence of the "electron rich" (η-C$_5$H$_5$)Ni.

The structure of complex IIc is shown in Fig. 1 and the bonding distances and angles in Table 4. The complex consists of a butterfly arrangement of three osmium atoms and one nickel atom, this latter occupying a wing-tip site; one t-butyl-vinylidene ligand is σ-coordinated to Os(1), Os(2) and Ni via C(10) and π-coordinated to Os(3) via C(10) and C(11). The approximate position of the hydridic hydrogen in IIc has been found in the Fourier difference map (Os(1)–H(1) and Os(2)–H(1), 1.60 and

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

(a) in the coordination sphere of the metal atoms			
Os(1)–Os(2)	2.855(2)	Os(2)–C(10)	2.15(2)
Os(1)–Os(3)	2.807(3)	Os(3)–C(7)	1.89(2)
Os(2)–Os(3)	2.846(2)	Os(3)–C(8)	1.88(2)
Os(1)–Ni	2.573(3)	Os(3)–C(9)	1.89(2)
Os(2)–Ni	2.568(4)	Os(3)–C(10)	2.18(2)
Os(1)–C(1)	1.91(2)	Os(3)–C(11)	2.25(2)
Os(1)–C(2)	1.92(2)	Ni–C(10)	1.84(2)
Os(1)–C(3)	1.92(2)	Ni–C(16)	2.14(2)
Os(1)–C(10)	2.21(2)	Ni–C(17)	2.10(2)
Os(2)–C(4)	1.91(2)	Ni–C(18)	2.14(2)
Os(2)–C(5)	1.89(2)	Ni–C(19)	2.12(2)
Os(2)–C(6)	1.88(2)	Ni–C(20)	2.10(3)
Os(2)–Os(1)–Os(3)	60.4(1)	C(4)–Os(2)–C(5)	92.6(9)
Os(3)–Os(2)–Os(1)	59.0(1)	C(4)–Os(2)–C(6)	93.5(9)
Os(1)–Os(3)–Os(2)	60.7(1)	C(4)–Os(2)–C(10)	128.5(8)
Os(2)–Os(1)–Ni	56.2(1)	C(4)–Os(2)–Os(1)	105.4(7)
Os(3)–Os(1)–Ni	93.0(1)	C(5)–Os(2)–C(6)	91.9(9)

Ni–Os(2)–Os(1)	56.4(1)	C(5)–Os(2)–C(10)	97.7(9)
Os(3)–Os(2)–Ni	92.2(1)	C(5)–Os(2)–Os(1)	147.5(7)
Os(2)–Os(1)–C(1)	106.9(7)	C(6)–Os(2)–C(10)	136.0(9)
Os(2)–Os(1)–C(2)	140.9(6)	C(6)–Os(2)–Os(1)	113.3(7)
Os(2)–Os(1)–C(3)	114.2(6)	C(10)–Os(2)–Os(1)	49.9(5)
Os(2)–Os(1)–C(10)	48.2(5)	C(7)–Os(3)–C(8)	96.1(9)
Os(3)–Os(1)–C(1)	166.6(7)	C(7)–Os(3)–C(9)	91.2(8)
Os(3)–Os(1)–C(2)	96.1(6)	C(7)–Os(3)–C(10)	116.7(7)
Os(3)–Os(1)–C(3)	85.5(6)	C(7)–Os(3)–C(11)	97.6(8)
Os(3)–Os(1)–C(10)	49.8(5)	C(7)–Os(3)–Os(1)	164.6(5)
Ni–Os(1)–C(1)	81.8(7)	C(7)–Os(3)–Os(2)	104.8(5)
Ni–Os(1)–C(2)	98.6(6)	C(8)–Os(3)–C(9)	94.2(9)
Ni–Os(1)–C(3)	168.9(6)	C(8)–Os(3)–C(10)	116.1(9)
Ni–Os(1)–C(10)	44.4(5)	C(8)–Os(3)–C(11)	87.9(9)
C(1)–Os(1)–C(2)	97.0(9)	C(8)–Os(3)–Os(1)	97.9(7)
C(1)–Os(1)–C(3)	97.1(9)	C(8)–Os(3)–Os(2)	158.2(7)
C(1)–Os(1)–C(10)	126.2(8)	C(9)–Os(3)–C(10)	134.3(8)
C(2)–Os(1)–C(3)	92.5(8)	C(9)–Os(3)–C(11)	170.7(8)
C(2)–Os(1)–C(10)	92.6(8)	C(9)–Os(3)–Os(1)	94.1(6)
C(3)–Os(1)–C(10)	135.3(8)	C(9)–Os(3)–Os(2)	91.4(7)
Os(3)–Os(2)–C(4)	162.5(7)	C(10)–Os(3)–C(11)	38.0(8)
Os(3)–Os(2)–C(5)	104.9(7)	C(10)–Os(3)–Os(1)	50.7(5)
Os(3)–Os(2)–C(6)	86.7(7)	C(10–Os(3)–Os(2)	48.5(5)
Os(3)–Os(2)–C(10)	49.3(5)	C(11)–Os(3)–Os(1)	76.6(6)
Ni–Os(2)–C(4)	83.8(7)	C(11)–Os(3)–Os(2)	83.5(6)
Ni–Os(2)–C(5)	100.3(7)	C(10)–Ni–Os(1)	57.2(6)
Ni–Os(2)–C(6)	167.7(7)	C(10)–Ni–Os(2)	55.5(6)
Ni–Os(2)–C(10)	44.7(5)		

(b) in the carbonyl groups

O(1)–C(1)	1.14(3)	O(6)–C(6)	1.11(3)
O(2)–C(2)	1.10(2)	O(7)–C(7)	1.13(2)
O(3)–C(3)	1.12(2)	O(8)–C(8)	1.15(3)
O(4)–C(4)	1.16(3)	O(9)–C(9)	1.14(3)
O(5)–C(5)	1.12(3)		
Os(1)–C(1)–O(1)	178(2)	Os(2)–C(6)–O(6)	178(2)
Os(1)–C(2)–O(2)	179(2)	Os(3)–C(7)–O(7)	177(2)
Os(1)–C(3)–O(3)	178(2)	Os(3)–C(8)–O(8)	173(2)
Os(2)–C(4)–O(4)	178(2)	Os(3)–C(9)–O(9)	177(2)
Os(2)–C(5)–O(5)	175(2)		

(c) in the organic ligands

C(10)–C(11)	1.44(3)	C(16)–C(17)	1.40(4)
C(11)–C(12)	1.52(3)	C(16)–C(20)	1.36(4)
C(12)–C(13)	1.49(3)	C(17)–C(18)	1.38(4)
C(12)–C(14)	1.62(3)	C(18)–C(19)	1.38(4)
C(12)–C(15)	1.54(3)	C(19)–C(20)	1.46(4)
Os(1)–C(10)–Os(2)	81.8(6)	C(11)–C(10)–Ni	130.9(1.5)
Os(1)–C(10)–Os(3)	79.6(7)	C(12)–C(11)–Os(3)	124.9(1.5)
Os(1)–C(10)–Ni	78.4(7)	Os(3)–C(11)–C(10)	68.3(1.2)
Os(2)–C(10)–Os(3)	82.2(7)	C(12)–C(11)–C(10)	129.7(2.1)
Os(2)–C(10)–Ni	79.9(7)	C(13)–C(12)–C(14)	109.3(1.9)
Os(3)–C(10)–Ni	153.2(1.1)	C(13)–C(12)–C(15)	112.0(2.0)
C(11)–C(10)–Ni	130.9(1.5)	C(13)–C(12)–C(11)	112.9(1.8)
C(11)–C(10)–Os(1)	118.8(1.5)	C(14)–C(12)–C(15)	103.5(1.8)
C(11)–C(10)–Os(2)	143.8(1.5)	C(15)–C(12)–C(11)	108.6(1.9)
C(11)–C(10)–Os(3)	73.7(1.2)		

1.67 Å, respectively) and is confirmed by the larger Os–Os–CO angles for the axial C(3)–O(3) compared with the equatorial C(1)–O(1) bonds (114.2(6)° and 106.9(7)°).

Complex IIc is a 62 electron cluster, in which the vinylidene ligand acts as a formal four electron donor; as expected the complex is diamagnetic (EPR, solid state and solution).

The cluster size is closely comparable with those of IIa, IIb, the mean M–M distances being 2.815(3) for IIa, 2.8213(6) for IIb and 2.835(3) Å for IIc. The mean M–Ni distances in these complexes are also very close: 2.563(3) for IIa, 2.5725(8) for IIb and 2.570(4) Å for IIc. The butterfly dihedral angles are 116.6° (IIa), 118.2° (IIb) and 117.1° (IIc), respectively, and fall in the relatively narrow range expected for 62 electron clusters [6].

The butterfly clusters can be regarded as models for surface "steps"; therefore the coordination and C–C "activation" of the vinylidene in clusters II is of interest both for comparisons between clusters and surfaces, and as a possible intermediate stage in the coordination–reduction of acetylides on clusters.

Although relatively few examples of μ_4-η^2 bound acetylides and vinylidenes have been reported previously (especially for heterometallic clusters), some general comments can be made. The "activation" of the μ_4-η^2 cluster bound vinylidenes seems to be independent of the nature of the cluster metals; indeed C–C distances of 1.42–1.44 Å are found in both the ruthenium (IIa, IIb) and the osmium (IIc) clusters as well as in $(\eta\text{-}C_5H_5)FeCo_3(CO)_9(C{=}CH_2)$ [7]. On the other hand, coordination to four metal centres results in a greater "activation"; thus, in the trimetallic $H_2Os_3(CO)_9(C{=}CH_2)$ [27] a C–C distance of 1.33 Å is found for the μ_3-η^2-bound vinylidene. Furthermore the C–C distances for the μ_4-η^2-bound vinylidenes are significantly longer than those in μ_4-η^2 and μ_5-η^2 bound acetylides in homo- and hetero-metallic frames; the values for the latter are in the range 1.34–1.39 Å [28–30]. Finally, the C–C distances for the μ_4-η^2 vinylidenes are slightly longer than those for the μ-η^2 ligands in the $HOs_3(CO)_{10}(RC{=}CHR')$ clusters in which the C–C distances are in the range 1.31–1.40 Å [14,31,32].

Thus, the formation of vinylidenes, with C–C distances close to the olefinic double bond, with clusters II seems to be an important step in the coordination-hydrogenation of acetylydes on clusters.

The role of clusters II as possible intermediates in the selective hydrogenation of alkynes and alkenes via clusters V is under investigation.

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