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Phosphine-substituted and phosphido-bridged metal clusters in homogeneous catalysis

II *. Behaviour of $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ (M = Ru, n = 1, 2, L = PPh_3, PCy_3; M = Os, n = 1, 2, L = PPh_3, PPh_2H, PEt_3, PCy_3), $M_3(CO)_{12-n}L_n$ (M = Ru, n = 1–3, L = PPh_3, PPh_2H, PEt_3, PCy_3; M = Os, n = 1, 2, L = PPh_3) and related complexes in the hydrogenation-isomerization of 1,4-pentadiene

Mario Castiglioni, Roberto Giordano and Enrico Sappa★

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

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Abstract

$(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9\text{-}n}L_n$ (M = Ru, $n = 1$, 2, L = PPh_3, PCy_3; M = Os, $n = 1$, 2, L = PPh_3, PPh_2H, PEt_3, PCy_3), $M_3(CO)_{12\text{-}n}L_n$ (M = Ru, $n = 1$–3, L = PPh_3, PPh_2H, PEt_3, PCy_3; M = Os, n = 1, 2, L = PPh_3) and related complexes have been examined as catalysts under homogeneous conditions, for isomerization-hydrogenation reactions of 1,4-pentadiene. All the clusters examined are active catalysts; their activities depend on the nature and the number of the phosphine substituents on the clusters. Attempts have been made to compare the effects on the catalytic activity of the donor properties and basicities of the phosphines. Some intermediates and/or side products have been isolated during the catalytic experiments; in particular the PPh_2H derivatives give phosphido-bridged bi- and tri-metallic complexes. The latter also show catalytic activity.

Introduction

In previous papers we have described the behaviour of the tetrahedral clusters $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_9$, (M = Ru, complex **1** [1]; M = Os, complex **2** [2]) as heterogeneous catalyst precursors [3–9] and as selective homogeneous catalysts for

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* For part I see Ref. 12.

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the hydrogenation and/or isomerization of alkynes, alkenes, and linear or cyclic dienes [1,10,11]. The "intact" clusters, stabilized by the capping (Cp)Ni, preferentially promote hydrogenation of the substrates, whereas, when homo-trimetallic fragments, such as $M_3(CO)_{12}$, are formed multisite coordination of the substrates occurs and isomerization predominates [10,11].

The substituted derivatives $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8L$ (L = PPh_2H, $P(o\text{-tolyl})_3$) are more active than the parent cluster [11]. This feature prompted us to undertake a more detailed study of the effect of phosphine ligands on the title clusters under homogeneous conditions.

Initially, we synthesized some new $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ (M = Ru, Os) phosphine derivatives as well as $M_3(CO)_{12-n}L_n$ (M = Ru, Os) complexes, and studied their reactivities under conditions comparable with those used in the catalytic experiments described below; thermal modification and disproportionation reactions, CO and phosphine displacement and formation of metallic fragments were observed [12]. In particular, thermal modifications of the PPh_2H substituted complexes were found to lead to phosphido-bridged derivatives, such as $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ and $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ [13].

We report here on catalytic hydrogenation and/or isomerization of 1,4-pentadiene under homogeneous conditions in the presence of "phosphine modified" $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ derivatives or "phosphine modified fragments" $M_3(CO)_{12-n}L_n$ (M = Ru, Os); some nickel-containing complexes have also been examined, and the behaviour of the phosphido-bridged derivatives has been studied. The phosphine ligands choosen are characterized by different steric effects, donor–acceptor abilities, and basicities (pK_a values).

We have found that all of the clusters and fragments studied are active either in hydrogenation or, mainly, in isomerization; the phosphido-bridged complexes also show a good catalytic activity. The observed activities are related to the nature and number of the phosphine substituents on the clusters, and in particular to their pK_a values. Some reaction intermediates (or side products) have been isolated and partially characterized.

In general the phosphine-substituted complexes are more active than the unsubstituted parent clusters, but isomerization rather than hydrogenation occurs. Phosphine modified organometallic derivatives are currently used in industrially important reactions such as hydroformylation and diene oligomerization [14], because of their enhanced stability and, more especially, their selectivity. Recent developments have involved the use of water-soluble clusters of the type $Ru_3(CO)_{12-n}L_n$ (n = 1, 3; L = tris(m-sulphonato-phenyl)phosphine) [15], very similar to the "fragments" considered in this work.

Experimental

Phosphine-substituted and phosphido-bridged complexes have been obtained and purified as previously reported [12]. The solvents used in the catalytic experiments were distilled over sodium. The H_2 and N_2 were high purity gases (SIAD, Bergamo) and were dried before use.

The organometallic products in the solutions after catalytic experiments were analyzed where possible with a F&M 185 C, H, N Analyzer or a Perkin–Elmer 303 AAS apparatus; some metal analyses were performed by F. Pascher Laboratories

Table 1

Catalyst concentrations and substrate/catalyst molar ratios used in the hydrogenation-isomerization reactions of 1,4-pentadiene [a]

Complex	Concentration ($\times 10^{-6}$) (mmol/l)	Substrate/catalyst molar ratio
$(Cp)NiOs_3H_3(CO)_8(PPh_3)$	3.38	574
$(Cp)NiOs_3H_3(CO)_8(PPh_2H)$	3.61	537
$(Cp)NiOs_3H_3(CO)_8(PCy_3)$	3.33	582
$(Cp)NiOs_3H_3(CO)_8(PEt_3)$	3.85	504
$(Cp)NiOs_3H_3(CO)_7(PEt_3)_2$	5.58	348
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$	4.36	445
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$ [b]	5.09	381
$(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$	3.48	557
$(Cp)NiRu_3H_3(CO)_8(PCy_3)$	5.35	363
$Os_3(CO)_{11}(PPh_3)$	3.50	554
$Os_3(CO)_{10}(PPh_3)_2$ [c]	7.27×10^{-1}	2668
$Os_3(CO)_{12}$	4.41	440
$Ru_3(CO)_{11}(PPh_3)$	4.58	424
$Ru_3(CO)_{10}(PPh_3)_2$	3.61	537
$Ru_3(CO)_{10}(PPh_3)_2$ [d]	2.71	716
$Ru_3(CO)_{10}(PPh_3)_2$ [e]	2.41	805
$Ru_3(CO)_{10}(PPh_3)_2$	1.51 [f]	1344
$Ru_3(CO)_9(PPh_3)_2$	2.23	870
$Ru_3(CO)_{11}(PPh_2H)$	5.01	387
$Ru_3(CO)_{10}(PPh_2H)_2$ [c]	1.05	1848
$Ru_3(CO)_9(PPh_2H)_3$	6.28	309
$Ru_3(CO)_{11}(PCy_3)$	3.70	524
$Ru_3(CO)_9(PEt_3)_3$	5.49	353
$HRu_3(CO)_7(PPh_2)_3$	3.79	512
$Ru_2(CO)_6(PPh_2)_2$	5.81	334
$(CO)_2Ni(PPh_3)_2$	7.82	248

[a] Reaction conditions: 1 atm H_2, 2 ml octane solvent, 1–7 mg complex for each vial; always 0.200 ml of substrate (1.94×10^{-3} mmol). [b] Under 1 atm of CO/H_2 (75/25 v/v). [c] Complexes very poorly soluble in octane. [d] In the presence of a 70.5 molar excess of PPh_3 with respect to the cluster. [e] Under 1 atm of CO/H_2 (75/25 v/v). [f] Substrate *cis*-1,3-pentadiene (2.03×10^{-3} mmol).

(Remagen, W. Germany). The ^1H and ^{31}P NMR spectra were obtained on a JEOL JNM GX 270 FT spectrometer, and the IR spectra on a Perkin–Elmer 580B spectrometer. The mass spectra were obtained by electron impact (70 eV) with a Kratos MS 50 spectrometer fitted with a direct inlet system.

Homogeneous catalysis. GLC analyses of the reaction solutions

The reactions were performed in sealed glass vials (volume 25 ml), each containing an n-octane solution of the cluster and the substrate. Details are given in Table 1. The vials were filled with hydrogen to 0.9–1.0 atm by standard vacuum techniques and then kept at 120 °C for the appropriate time.

The organic products in the solutions after the catalytic experiments were analyzed with a Carlo Erba 4200 FID gas-liquid chromatograph equipped with 2 m × 0.6 i.d. n-octane/Porasil C (80–100 mesh) columns, operated with N_2 (25 ml/min) as carrier gas and with the following temperature program: 75 °C (10 min), then 20 °C/min till 155 °C, and a further 15 min at this temperature.

Attempts to identify the organometallic products in the reaction solutions

The hydrogenation-isomerization solutions were also checked by TLC preparative plates to detect decomposition of the catalysts and identify intermediates or side products. The degree of decomposition of the clusters after the catalytic experiments, and the organometallic products observed (either fully or partially characterized) are given in Table 2.

Full characterization of these complexes was difficult because of the small amounts generally available. In a selected example a blank experiment was carried out in order to confirm the identification of some compounds. Thus a 250 ml vial was filled with a 50 ml solution (10 ml toluene, 40 ml octane) of $Ru_3(CO)_{10}(PPh_2H)_2$ (300 mg, 0.314 mmol) with 1 ml of 1,4-pentadiene under 0.9 atm. H_2. The vial was then kept at 120 °C for 1 h; TLC analysis of the solution revealed that considerable decomposition had occurred and showed the presence of seven products, two yellow (complexes **A**, **B**), one purple (complex **C**), one deep green (complex **D**), and one

Table 2

Decomposition (%) [a] of the catalyst complexes and organometallic derivatives [b] detected in the reaction solutions

Complex	Decomposition (%)	Organometallic derivatives [c]
$(Cp)NiOs_3H_3(CO)_8(PPh_3)$	15	parent complex (75%)
$(Cp)NiOs_3H_3(CO)_8(PPh_2H)$	35	$(Cp)NiOs_3H_3(CO)_9$ (tr) [d]; parent complex (40%); $(Cp)NiOs_3H_3(CO)_7(PPh_2H)_2$ (tr) [e]
$(Cp)NiOs_3H_3(CO)_8(PCy_3)$	5	parent complex (90%)
$(Cp)NiOs_3H_3(CO)_8(PEt_3)$	5	parent complex (90%)
$(Cp)NiOs_3H_3(CO)_7(PEt_3)_2$	90	parent complex (10%)
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$	60	$(Cp)NiRu_3H_3(CO)_9$ (tr)
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$ (CO/H_2)	30	parent complex (tr); $(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$ (40%)
$(Cp)NiRu_3H_3(CO)_8(PCy_3)$	50	parent complex (35%); $(Cp)NiRu_3H_3(CO)_7(PCy_3)_2$
$Ru_3(CO)_{11}(PPh_3)$	35	Complex **F** [e] (tr)
$Ru_3(CO)_{10}(PPh_3)_2$	30	Complex **F** (5%); complex **G** (15%)
$Ru_3(CO)_{10}(PPh_3)_2$ (excess PPh_3)	100	
$Ru_3(CO)_{10}(PPh_3)_2$ (*cis*-1,3-pentadiene)	20	Complex **H**
$Ru_3(CO)_{10}(PPh_3)_2$ (CO/H_2)	40	two unidentified products
$Ru_3(CO)_{11}(PPh_2H)$	40	$Ru_2(CO)_6(\mu\text{-}PPh_2)_2$; $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$; complex **J** (5% each)
$Ru_3(CO)_{10}(PPh_2H)_2$	60	Unidentified product; complex **J** (tr)
$Ru_3(CO)_9(PPh_2H)_3$	50	$HRu_3(CO)_7(\mu\text{-}PPh_2H)_3$ (25%)
$Ru_3(CO)_{11}(PCy_3)$	60	Complex **K** (tr)
$Ru_3(CO)_9(PEt_3)_3$	70	Complex **L** (tr); one unidentified product

[a] Maximum decomposition observed. [b] Identified and tentatively identified. [c] Spectroscopic data, when available, in Table 3. [d] tr = traces. [e] Not previously reported (see ref. 12).

deep red (complex **E**), together with considerable amounts of $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ and $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ [13].

The physical, analytical, and spectroscopic properties of these and other organometallic compounds found in the reaction solutions are shown in Table 3.

Results and discussion

This study was aimed at finding out whether "phosphine modified" clusters were better catalysts than the unsubstituted parent derivatives. We found that this is indeed, the case at least on the basis of the turnover data. Once this aspect had been confirmed, the factors affecting the catalytic activities were studied; namely (a) the number and nature of the phosphine substituents and their effects on the cluster dimensions; (b) (in selected cases) the influence of CO and of free phosphine. Finally the nature of the organometallic complexes present in the reaction solutions was investigated, when possible, in order to throw light on the reaction patterns.

Behaviour of the $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ *derivatives*

The results obtained in the presence of these complexes are listed in Table 4. The clusters with M = Ru require very short reaction times and tend to decompose, so that with longer reaction times the activity is lost; the monosubstituted PPh_3 derivative is less active than the parent cluster, and the same is observed for its osmium homologue. These two complexes represent the only exceptions to the observation of greater activity of the substituted products. The complex with M = Ru and two PPh_3 ligands is one of the most active, but when considering the products, however, it is necessary to remember that isomerization to 1,3-pentadiene is the main process, and that hydrogenation products represent only a small portion of the total. This is observed for nearly all the catalysts examined (see also Table 7, below); apparently, isomerization to 1,3-pentadiene is the first process, and is followed by hydrogenation. Indeed, comparison of the behaviour of $(Cp)NiOs_3H_3(CO)_9$ and of its PPh_2H monosubstitution product towards *cis*-1,3-pentadiene and 1,4-pentadiene shows that, in the case of *cis*-1,3-pentadiene, hydrogenation occurs readily.

In the case of unsubstituted clusters, the presence of CO apparently inhibits the activity [11].

Unfortunately, comparisons between osmium and ruthenium clusters can only be made for PPh_3 and PCy_3 derivatives (PPh_2H and PEt_3 are too reactive towards $(Cp)NiRu_3H_3(CO)_9$ [12]). Also noteworthy is the high activity of the PPh_2H derivatives of the osmium-nickel cluster, and activity is also high for the homometallic osmium "fragments" discussed below (see Table 5, below).

Also of interest is that in the reaction solutions, especially for the ruthenium-nickel clusters, we could find only insoluble decomposition products, or hetero-tetrametallic disproportionation derivatives; no $M_3(CO)_{12-n}L_n$ "fragments" were detected. This confirms the catalytic role of the "intact" clusters.

Behaviour of the $M_3(CO)_{12-n}L_n$ *"fragments"*

The results obtained with homotrimetallic derivatives are listed in Table 5. We have found that, once again, the phosphine-substituted derivatives are (without exception) more active than the unsubstituted parent clusters: the ruthenium

(*Continued on p. 121*)

Table 3

Physical and spectroscopic properties, and tentative identifications of the organometallic compounds detected in the reaction solutions (for the letters indicating the complexes, see text and Table 2)

Complex	Colour	IR (in C_6H_{14}) ν(CO) (cm^{-1})	^1H NMR (in $CDCl_3$) δ (ppm)	^{31}P NMR (in $CDCl_3$, H_3PO_4) δ (ppm)	Tentative identification
A	yellow	2107m, 2076sh, 2064vs 2040vs, 2021vs, 2010vs, 1998sh, 1988vs, 1955m	7.53–6.76 (Ph); 5.31 m, 1.48 s, 0.88–0.77 m (aliphatic H); −19.11 d (hydride)	–	$HRu_3(CO)_8(PPh_2H)$-(C_xH_y) [b]
B	yellow [a]	2072vs, 2042vs, 2010vs, 1988vs (vb)	7.58–6.71 m (Ph); 1.28 b, 0.89 t (aliphatic H)	–	Unidentified
C	purple [c]	2074vs, 2044vs, 2012vs, 1988vs, 1978sh	7.21 s, 7.08 m, 6.48 m	+166.7 s	Unidentified
D	green	2086m, 2060sh, 2042s(sh) 2022vs, 1988s(b)	–	–	Unidentified [d]
E	red	2080w, 2056sh, 2050s, 2024vs, 1988s(b), 1973sh	–		Unidentified [d]
F	yellow	2078m, 2048vs, 2039s(sh) 2004s, 1988s	–	–	See **G**.

G	yellow	2078m, 2042vs, 2024vs, 2008m, 1998m, 1988m(b)	7.45–7.25 mm (Ph); 6.70 d 2.87 s, 2.21 d (aliphatic H); −19.37 d (hydride)	–	$HRu_3(CO)_8(PPh_3)(C_xH_y)$
H	yellow	2078s, 2042vs, 2024vs, 1998s, 1980m	–	–	$HRu_3(CO)_8(PPh_3)(C_yH_z)$ [e]
K	yellow	2076s, 2051s, 2035vs, 2016vs, 1998s, 1992s	–	–	$HRu_3(CO)_8(PCy_3)(C_xH_y)$
J	yellow	2107m, 2076s, 2042vs, 2022s, 2018vs, 1996s(b), 1990s, 1954m	–	–	Compare with **A** [b]
L	yellow	2078m, 2039vs, 2022vs, 2006m, 1994s	–	–	$HRu_3(CO)_8(PEt_3)(C_xH_y)$

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[a] White as a solid; limpid yellow solution in $CHCl_3$. IR spectrum and ^1H NMR very close to those of $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$. [b] $HRu_3(CO)_8(C_6H_9)$ (allylic isomer) for comparison; yellow orange: IR; 2078s, 2040vs, 2022vs, 1999m, 1978w, cm^{-1}; ^1H NMR: 7.42 m (Ph), 6.62 d, 2.89 m, 2.52 d, 1.38 t (aliphatic H); −19.2 d (hydride). See: S. Aime, L. Milone, D. Osella and M. Valle, J. Chem. Res. (M), (1978) 782. [c] Ru 33.4, P 5.0%. IR spectrum very close to that of $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$. No aliphatic hydrogens in the ^1H NMR spectrum. [d] IR spectra similar to those of Ru_3 complexes with organic moieties derived by acetylide condensation: see: G. Gervasio, E. Sappa, A.M. Manotti Lanfredi and A. Tiripicchio, Inorg. Chim. Acta, 68 (1983) 171 and references therein. [e] These complexes can exist in different isomeric forms; the organic ligand can be acetylide, allenyl or allyl.

Table 4

Hydrogenation-isomerization of 1,4-pentadiene in the presence of clusters $(Cp)NiM_3H_3(CO)_{9-n}L_n$

Complex	Reaction time (min)	Turnover	Composition of the effluent gases (%)					Reference
			pentane	1-pentene	2-pentenes	*cis*-1,3-pentadiene	unchanged substrate	
$(Cp)NiRu_3H_3(CO)_9$	10	12	tr	0.2	–	1.9	97.8	10
	20	27	1.1	1.2	–	2.8	94.9	
	30	42	1.4	1.7	–	4.7	91.3	
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$	10	1	–	tr	–	–	99.8	this work
	20	9	tr	tr	–	1.9	97.9	
	30	39	tr	2.3	–	6.2	91.2	
	40	54	tr	4.4	–	7.6	89.7	
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$ [a]	10	0.5	–	tr		tr	99.9	this work
	20	3	–	tr		0.8	99.2	
	30	11	–	tr	–	2.8	97.2	
$(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$	10	52	tr	1.0		8.2	90.7	this work
	20	215	0.1	3.5	–	34.8	61.5	
	30	337	0.2	6.1	–	54.2	39.5	
	40	356	0.4	8.0	–	55.4	36.1	
$(Cp)NiRu_3H_3(CO)_8(PCy_3)$	10	130	0.1	3.3	–	32.4	64.1	this work
	20	167	0.2	9.3	–	36.5	54.0	
	40	184	0.4	10.7	–	39.6	49.3	

	Reaction time (h)							
$(Cp)NiOs_3H_3(CO)_9$	1	77	0.2	5.5	15.1	–	79.2	11
	2	119	4.7	20.8	6.7	–	67.8	
	4	106	3.2	22.4	3.3	–	71.1	
$(Cp)NiOs_3H_3(CO)_9$[b]	1	21	0.3	1.3	3.9	*94.5*[c]	94.5	11
	2	29	0.3	1.9	5.1	*92.6*	92.6	
	4	231	0.6	11.1	48.1	*40.2*	40.2	
$(Cp)NiOs_3H_3(CO)_8(PPh_3)$	1	36	tr	0.8	–	5.5	93.7	this work
	2	45	tr	1.2	–	6.6	92.2	
	4	74	0.6	4.9	–	7.4	87.1	
$(Cp)NiOs_3H_3(CO)_8(PPh_2H)$	1	177	tr	9.3	–	23.7	67.0	this work
	2	272	0.6	9.9	tr	40.2	49.3	
	4	442	1.1	5.3	12.3	63.7	17.5	
$(Cp)NiOs_3H_3(CO)_8(PPh_2H)$[b]	1	7	0.2	0.6	3.4	*98.5*	98.5	11
	2	43	0.4	1.4	7.7	*90.4*	90.4	
	4	337	1.3	25.0	48.5	*25.2*	25.2	
$(Cp)NiOs_3H_3(CO)_8(PCy_3)$	1	33	0.3	0.7	–	4.6	94.4	this work
	2	79	0.8	1.6	–	11.2	86.4	
	4	186	2.1	4.0	–	25.9	68.0	
$(Cp)NiOs_3H_3(CO)_8(PEt_3)$	1	42	0.3	1.3	–	6.7	91.7	this work
	2	110	1.1	5.3	–	15.5	78.1	
	4	125	1.3	6.6	–	16.9	75.2	
$(Cp)NiOs_3H_3(CO)_7(PEt_3)_2$	1	86	1.5	4.3	–	18.9	75.3	this work
	2	130	2.6	11.7	–	23.0	62.7	
	4	139	2.7	11.9	–	25.4	60.0	

[a] Under CO/H_2 (75/25). [b] Substrate *cis*-1,3-pentadiene, by comparison. [c] When italicised, the same as the substrate.

Table 5

Hydrogenation-isomerization reactions of 1,4-pentadiene in the presence of clusters $M_3(CO)_{12-n}L_n$ (M = Ru, Os: n = 1–3)

Cluster	Reaction time (min)	Turn-over	Composition of the effluent gases (%)					Reference
			pen-tane	1-pen-tene	2-pen-tenes	*cis*-1,3-penta-diene	unchanged substrate	
$Ru_3(CO)_{12}$	40	113	–	6.5	–	38.9	54.5	10
$Ru_3(CO)_{11}(PPh_3)$	10	167	–	1.6	–	37.9	60.5	this work
	20	173	–	2.9	–	38.0	59.1	
	40	221	tr	3.3	–	48.8	47.9	
$Ru_3(CO)_{10}(PPh_3)_2$	10	208	tr	2.5	–	36.1	61.4	this work
	20	228	tr	3.7	–	38.7	57.5	
	40	250	tr	4.4	–	42.1	53.5	
$Ru_3(CO)_{10}(PPh_3)_2$ [a]	10	66	1.0	0.6	3.3	95.7 [b]	95.1	this work
	20	114	1.1	0.8	6.6	97.5	91.5	
	40	141	1.1	0.9	8.5	89.5	89.5	
$Ru_3(CO)_{10}(PPh_3)_2$ [c]	10	28	–	0.7	–	3.2	96.1	this work
	20	82	–	2.1	–	9.3	88.6	
	40	190	–	5.2	–	21.3	73.5	
$Ru_3(CO)_{10}(PPh_3)_2$ [d]	10	103	tr	tr	–	12.8	87.2	this work
	20	351	–	0.4	–	43.2	56.4	
	40	422	–	0.5	–	51.9	47.6	
$Ru_3(CO)_9(PPh_3)_3$	10	293	tr	1.7	–	32.0	66.3	this work
	20	613	tr	6.1	6.8	57.4	29.6	
	40	631	tr	6.6	8.1	57.7	27.5	
$Ru_3(CO)_{11}(PPh_2H)$	10	142	tr	7.8	–	28.8	63.3	this work
	20	229	tr	6.7	0.7	51.8	40.7	
	40	250	tr	5.2	5.0	54.4	35.3	
$Ru_3(CO)_{10}(PPh_2H)_2$	10	170	tr	1.9	–	7.3	90.8	this work
	20	493	tr	5.7	–	20.9	73.3	
	40	636	tr	13.3	–	21.1	65.6	
$Ru_3(CO)_9(PPh_2H)_3$	10	21	0.1	1.3	–	5.3	93.3	this work
	20	58	0.3	3.6	–	14.8	81.3	
	40	115	0.3	6.9	–	30.1	62.7	
$Ru_3(CO)_{11}(PCy_3)$	10	284	–	2.3	–	51.9	45.8	this work
	20	287	–	2.1	tr	52.5	45.3	
	40	229	–	1.8	tr	55.2	42.9	
$Ru_3(CO)_9(PEt_3)_3$	10	195	–	1.3	–	53.9	44.8	this work
	20	245	–	2.1	5.4	61.8	30.7	
	40	253	–	2.3	7.0	62.4	28.2	
	Reaction time (h)							
$Os_3(CO)_{12}$	1	54	–	4.6	–	9.6	87.7	this work
	2	123	tr	5.2	–	22.6	72.1	
	4	128	tr	5.4	–	23.7	70.8	

Table 5 (continued)

Cluster	Reaction time (h)	Turnover	Composition of the effluent gases (%)					Reference
			pentane	1-pentene	2-pentenes	*cis*-1,3-pentadiene	unchanged substrate	
$Os_3(CO)_{11}(PPh_3)$	1	39	tr	1.5	–	5.4	93.0	this work
	2	158	tr	1.8	–	26.6	71.5	
	4	220	tr	1.9	–	37.6	60.4	
$Os_3(CO)_{10}(PPh_3)_2$	1	200	–	0.2	–	7.3	92.5	this work
	2	243	tr	0.4	–	8.6	90.9	
	4	283	tr	0.8	–	9.7	89.4	

[a] *cis*-1,3-pentadiene as substrate. [b] When italicized, the same as the substrate. [c] In the presence of a 70 to 1 molar excess of PPh_3. [d] Under 1 atm CO/H_2 (75 to 25 v/v).

derivatives show turnovers comparable to those of the heterometallic Ru_3Ni clusters. Isomerization to *cis*-1,3-pentadiene is the main process observed, and this was predictable in the light of previous experience [10,11].

The activity of the PPh_3 derivatives, either for M = Ru, or M = Os, increases with the degree of substitution of the clusters; the same is true for the PPh_2H derivatives (M = Ru, $n = 1$, 2), which again are considerably more active than the other complexes. However, for $n = 3$, there is a sudden decrease of activity; this could be explained in terms of either competitive formation of phosphido-bridged derivatives [12] or of cluster fragmentation induced by the presence of several ligands.

In order to examine the effect of excess phosphine, of CO, and of use of *cis*-1,3-pentadiene in place of 1,4-pentadiene, we carried out some experiments in the presence of $Ru_3(CO)_{10}(PPh_3)_2$. In the presence of excess PPh_3 considerable inhibition is observed initially, but after longer times the turnovers are comparable to those for the cluster alone; interestingly, the activity is considerably lower than that of $Ru_3(CO)_9(PPh_3)_3$.

In the presence of CO, the turnovers and, proportion of isomerization products are increased; this contrasts with the "inhibition" observed for the $(Cp)NiRu_3H_3(CO)_{9-n}L_n$ complexes. However, the observed "inhibition" or isomerization could also be due to a low $P(H_2)$ in the system, resulting in slow hydrogenation rates. The possibility that the presence of CO might also favour formation of fragments of low nuclearity cannot be ruled out, but, a trinuclear organometallic species was detected in considerable amounts in the final reaction solutions.

Finally, *cis*-1,3-pentadiene gives mainly 2-pentenes rather than 1-pentene, the turnovers being comparable for both of the substrates.

Behaviour of phosphido-bridged derivatives and of nickel-containing "fragments"

In the presence of 1,4-pentadiene, $(Cp)_2Ni(CO)_2$ was found to be an active hydrogenation catalyst [10]; by contrast $(CO)_2Ni(PPh_3)_2$ is totally inactive, although it is known to be a very efficient system for the cyclo-oligomerization of alkynes [14,16].

We previously found that the complexes $Ru_3(CO)_{12-n}(PPh_2H)_n$ undergo thermal modification reactions [12] leading mainly to $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ and

Table 6

Hydrogenation-isomerization of 1,4-pentadiene in the presence of phosphido-bridged complexes, or of nickel-containing "fragments"

Complex	Reaction time (min)	Turn-over	Composition of the effluent gases (%)					Reference
			pen-tane	1-pen-tene	2-pen-tenes	*cis*-1,3-penta-diene	unchanged substrate	
$HRu_3(CO)_7(\mu\text{-}PPh_3)_3$	10	39	–	3.4	–	4.1	92.4	this work
	20	95	tr	3.9	–	14.6	81.5	
	40	240	1.2	13.7	–	31.8	53.2	
$Ru_2(CO)_6(\mu\text{-}PPh_2)_2$	10	122	0.1	3.8	–	32.7	63.4	this work
	20	175	0.3	7.7	2.2	42.3	47.5	
	40	206	0.3	3.6	1.3	56.4	38.4	
$(Cp)_2Ni_2(CO)_2$	40	17	0.3	12.9	–	0.8	85.9	10
$(CO)_2Ni(PPh_3)_2$	10	–	–	tr		tr	99.8	this work
	20	–	–	tr	–	tr	99.7	
	40	–	–	tr	–	tr	99.5	

$HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ [13]. The latter derivatives were also identified in the blank experiments described in the Experimental section. We thus tested these complexes under catalytic conditions, and observed a considerable activity. In particular the amount of hydrogenation products is considerably high. Further studies are in progress on these derivatives.

The results obtained in these experiments are listed in Table 6.

Some thoughts on the factors which could influence the catalytic behaviour of the complexes

The above results show that: (i) with some exceptions, the phosphine-substituted clusters show increased turnovers with respect to the unsubstituted parent clusters; (ii) the activity increases when more than one phosphine is coordinated; and (iii) the activity depends on the pK_a of the phosphine. Attempts to correlate the steric and electronic properties of the clusters and of the phosphines with the observed catalytic activities are summarized in Table 7.

As shown in this table, isomerization is an important process for the $(Cp)NiM_3H_3(CO)_{9-n}L_n$ clusters, and the main process for the trimetallic derivatives. Other points of interest: (i) during the reactions the $(Cp)NiM_3H_3(CO)_{9-n}L_n$ complexes partly decompose to insoluble products, and partly disproportionate; (ii) the homo-trimetallic derivatives tend to disproportionate, but, in the presence of substrates, also give products in which hydrocarbyls replace CO rather than phosphine ligands; (iii) the PPh_2H derivatives give phosphido-bridged complexes, some of which are still catalytically active; and (iv) formation and reassembly of metal fragments could occur during the disproportionation reactions, as well as axial–equatorial isomerism [18].

The role of clusters

There are many cases known in which the apparent catalytic activity of clusters under homogeneous conditions, is due to formation (and reassembly) of metal fragments. Equilibria between phosphine-substituted clusters and fragments of lower nuclearity have been observed for ruthenium [17]. We previously showed that (Cp)Ni can be displaced by ligands during long reaction times under catalytic conditions [10,11]. By contrast, $Ru(CO)_3(PPh_3)_2$ is a precursor for the selective hydrogenation of cyclododecatriene [19]; the formation of polymetallic species could occur in the reactions.

In the reactions discussed here, however, we suggest that "intact" clusters act as true catalytic species; evidence for this hypothesis had been found for the parent complexes [10,11], and is indirectly supported by the following considerations: (a) the $(Cp)(NiM_3H_3(CO)_{9-n}L_n$ clusters, although giving some isomerization products, generally give higher hydrogenation/isomerization ratios (Table 7) than the trimetallic clusters; this corresponds to what was found for the parent, unsubstituted clusters. (b) The observed effect of the number of phosphine substituents cannot be accounted for unless the phosphines favour the formation of metal fragments; however, there are cases where coordinated phosphines tend to suppress the dissociation of clusters [19]. (c) The organometallic derivatives isolated after the catalytic experiments are still phosphine-containing substituted *clusters*. (d) It has been found that tetrahedral $H_4Ru_4(CO)_{11}L$ derivatives hydrogenate pentynes under conditions even milder than those we used and apparently act as intact cluster catalysts [20]; the formation of $H_4Ru_4(CO)_{12-n}L_n$ ($n = 0$–3) complexes from $Ru_3(CO)_{12-n}L_n$, probably via formation and reassembly of fragments occurs at 80 °C under 20 atm H_2 [21]. We could not detect such derivatives in our reaction solutions.

The attachment of the phosphines could also influence the cluster size and electron density, and hence the coordination of substrates, as discussed below. Finally, the presence of phosphines and phosphites strongly lowers the acidity of the hydride ligands, as shown by the pK_a values [22].

The role of phosphines

A tentative explanation of the increased activity of phosphine-substituted clusters [11] involved the possibility of ready release of the ligands and formation of free coordination sites. However, the results obtained here do not support this hypothesis; most of the organometallic products observed in the reaction solutions still contain phosphine ligands, and reactivity experiments [12] have shown that unsaturated hydrocarbyls displace CO more easily than phosphines in the complexes under consideration. Also, the catalytic activity observed for $(Cp)NiOs_3H_3(CO)_{9-n}L_n$ does not correspond to the order with which the phosphines displace each other from the complexes [12].

Another effect of phosphines could be to modify the dimensions, as well as the electron density on the clusters. Thus, for instance, the difficulties in obtaining the $(Cp)NiM_3H_3(CO)_6(PR_3)_3$ derivatives could be ascribed to the reciprocal *trans*-influence between the (always axial) phosphines [23] and the stabilizing (Cp)Ni. Unfortunately there are few studies dealing with these effects; in particular, the "*trans*-effect" should be considered only for square-planar derivatives and, in some instances, octahedral complexes. Comparable effects should be much more difficult to evaluate in more complex structures. Quantitative measurements on $Cr(CO)_4(PPh_3)L$ complexes [24] have shown that $Cr{-}PPh_3$ bonds are shorter when there is a stronger donor ligand in *trans* position; apparently, however, transition state effects dominate the reactivity of these monometallic complexes.

Table 7

Attempts to correlate structural, electronic parameters and ^{31}P NMR chemical shifts of the clusters or of the phosphines with the catalytic activities observed

Complex	Reaction time [a] (h [min])	Turnover [b]	Cluster size (Å)	Phosphine pK_a	^{31}P NMR
$(Cp)NiOs_3H_3(CO)_9$	4	106 [c]	2.867(2) [d], 2.564(5) [e,f] 2.869(1) [d], 2.572(2) [e,g] 2.873(1) [d], 2.565(2) [e,g,h]	–	–
$(Cp)NiOs_3H_3(CO)_8(PPh_3)$	4	74 (0.74) [i]	–	2.73	+ 25.69 s
$(Cp)NiOs_3H_3(CO)_8(PEt_3)$	4	125 (0.47)	–	8.69	+ 18.11 s
$(Cp)NiOs_3H_3(CO)_8(PCy_3)$	4	186 (0.27)	–	9.70	+ 44.87 s
$(Cp)NiOs_3H_3(CO)_8(PPh_2H)$	4	442 (0.28)	2.865(2) [d], 2.556(3) [e,l]	0.03	– 7.4, – 12.0 d
$(Cp)NiOs_3H_3(CO)_7(PEt_3)_2$	4	139 (0.57)		(8.69)	+ 15.85 s
$(Cp)NiRu_3H_3(CO)_9$	[30]	42 (0.67)	–	–	–
$(Cp)NiRu_3H_3(CO)_8(PPh_3)$	[40]	54 (0.58)	–	–	+ 31.30 s
$(Cp)NiRu_3H_3(CO)_8(PCy_3)$	[40]	184 (0.28)	–	9.70	+ 50.51 s
$(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$	[40]	356 (0.15)	–	(2.73)	+ 28.93 s
$Os_3(CO)_{12}$	4	128 (0.23)	2.877 [m]	–	–
$Os_3(CO)_{11}(PPh_3)$	4	220 (0.02)	2.869 [m]	2.73	– 0.54 s
$Os_3(CO)_{10}(PPh_3)_2$	4	283 (0.08)	–	(2.73)	– 8.68 s
$Ru_3(CO)_{12}$	[40]	113 (0.17)	2.854(1) [m]	–	–
$Ru_3(CO)_{11}(PPh_3)$	[40]	221 (0.07)	2.886(3) [m]	2.73	+ 29.81 s
$Ru_3(CO)_{10}(PPh_3)_2$	[40]	250 (0.10)	2.842(4)	(2.73)	+ 40.67 s
$Ru_3(CO)_9(PPh_3)_3$	[40]	631 (0.11)	–	(2.73)	–
$Ru_3(CO)_{11}(PCy_3)$	[40]	299 (0.03)	2.880(2) [h,m] 2.890(2)	9.70	–
$Ru_3(CO)_9(PEt_3)_3$	[40]	253 (0.15)	–	8.69	+ 11.71, + 32.69
$Ru_3(CO)_{11}(PPh_2H)$	[40]	250 (0.19)		0.03	+ 2.65 s
$Ru_3(CO)_{10}(PPh_2H)_2$	[40]	636 (0.63)		(0.03)	+ 4.87 s
$Ru_3(CO)_9(PPh_2H)_3$	[40]	115 (0.23)		(0.03)	+ 19.92 s

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[a] Maximum reaction time. [b] Maximum turnover observed at that time. [c] Only hydrogenation products. [d] Os–Os. [e] Os–Ni. [f] See ref. 2b. [g] See ref. 2a. [h] Two independent molecules. [i] In parentheses hydrogenation/isomerization products ratio. [l] See ref. 23a. [m] See ref. 25.

X-Ray studies on trimetallic, phosphine-substituted clusters [25] show that the average M–M bond lengths increase with the degree of substitution within a common structural type, and that the ligands coordinate at equatorial sites even in polysubstituted compounds, where they adopt a configuration which minimizes steric interactions. Finally, for a given metal the M–P bond lengths increase with decreasing π-acidity of the phosphine. It thus cannot be ruled out that the phosphine can influence the coordination (and release) of the substrates by steric and/or electronic effects.

Unfortunately, few results are available for the tetrahedral complexes [2,23]; those that are, indicate that phosphines do not significantly affect the cluster bonding parameters.

Finally, the electronic effects of the phosphines and their sterical effects should be considered; the latter effects seem not to be important, in the example reported here. On the other hand, the catalytic activities of the complexes seem to be related to the pK_a [26] of the phosphine ligands (Table 7). Examples of relationships between phosphine basicities and their catalytic properties are well known, especially for monometallic species [14]. A good example is given by phosphine-modified iridium catalysts, which, in the presence of triaryl-phosphines hydrogenate CO mainly to give ethylene glycol, whereas with trialkyl-phosphines, with their more powerful σ-donor ability, methanol is obtained [27].

Some comments on the reaction pathways and on the role of the intermediate products

The catalytic activities observed for the complexes under consideration are probably due to a combination of different effects; the presence of clusters as catalytic species, although not unambiguously demonstrated, is probable, and the organometallic products isolated in the reaction solutions favour this hypothesis. Isomerization rather than hydrogenation is observed; this behaviour was found previously and for the homo-trimetallic "fragments" [10,11]. By contrast, the $(Cp)NiM_3H_3(CO)_9$ clusters showed only hydrogenating properties; a possible explanation of the different behaviour observed for their phosphine-substituted derivatives is that isomerization of 1,4-pentadiene to 1,3-pentadiene occurs as a first step, followed by hydrogenation. Indeed, in the presence of $(Cp)NiOs_3H_3(CO)_8$-(PPh_2H) 1,3-pentadiene gives hydrogenation products [11].

Reaction paths similar to those proposed for the unsubstituted clusters probably operate also for their phosphine-substituted derivatives [10,11]; the enhanced activity is, as discussed above, probably due to the electronic effects induced by the phosphines, which favour either the release of CO ligands or of the coordinated substrate molecule. A point worthy of mention is that with trimetallic derivatives isomerization probably occurs via coordination to several sites; for equatorially substituted complexes, especially, both sides of the cluster triangle are easily accessible. By contrast the $(Cp)NiM_3H_3(CO)_{9-n}L_n$ complexes, which are generally substituted in axial positions, offer very poor access to the basal metal triangle; with these complexes, isomerization presumably involves one coordination site only. However, the possibility of the presence of more than one coordination site cannot be completely ruled out when account is taken of the fact that disproportionation reactions can occur readily.

Unfortunately the thermal instability of the studied clusters [12] prevents kinetic studies which might confirm the proposed reaction pathways.

The organometallic intermediate and/or side products were identified by spectroscopy; their nature points to "intact" cluster catalysis, and indicates that loss of phosphines is not essential for the catalytic activity of the complexes. The (trimetallic) hydrocarbyl substituted intermediates are of a type comparable with these found for the unsubstituted clusters.

Behaviour of the phosphido-bridged compounds

These complexes have also shown catalytic activity, and, perhaps surprisingly, hydrogenating power; the reaction patterns for these complexes are probably different from those found for the derivatives considered earlier, and are under active investigation. Possible processes involving the substrate during these reactions could be: (i) insertion into M–H bonds (when available); (ii) insertion into M–P (phosphido) bonds; and (iii), reversible metal–metal bond cleavage giving rise to vacant coordination sites. The latter hypothesis is, in our opinion, the most probable, in the light of available knowledge on the chemistry of these derivatives.

Concluding remarks

The results discussed above indicate that "phosphine modified" clusters are more active in the isomerization of 1,4-pentadiene than their unsubstituted parent compounds, and that the activity is related to the pK_a values of the phosphines. Noteworthy is the shift from hydrogenation to isomerization observed on going to the substituted $(Cp)NiM_3H_3(CO)_{9-n}L_n$ derivatives, from the $(Cp)NiM_3H_3(CO)_9$ clusters. Unfortunately, the side reactions [12] observed for the complexes examined prevent definitive statements about the reaction pathways.

The phosphido-bridged derivatives show good activities, and will be subject of further investigations.

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