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

I. Synthesis and reactivity of $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ (M = Ru, Os, n = 1,2: L = PPh_3, PPh_2H, PCy_3, PEt_3) and $M_3(CO)_{12-n}L_n$ (M = Ru, n = 1–3: L = PPh_3, PPh_2H, PCy_3, PEt_3; M = Os, n = 1,2: L = PPh_3)

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Abstract

The complexes $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ (M = Ru, Os, n = 1,2: L = PPh_3, PPh_2H, PCy_3, PEt_3) and $M_3(CO)_{12-n}L_n$ (M = Ru, n = 1–3: L = PPh_3, PPh_2H, PCy_3, PEt_3; M = Os, n = 1,2: L = PPh_3) have been synthesized by new or known procedures. Reactions of the complexes, relevant to their catalytic behaviour, have been examined; viz. ligand exchange, disproportionation, thermal decomposition or modification, reactions with metal fragments and selected ligands. The PPh_2H-substituted derivatives have been shown to give phosphido-bridged species.

Introduction

An investigation of the catalytic activity of homo- and hetero-metallic clusters in homogeneous and heterogeneous conditions revealed that tetrahedral derivatives $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_9$ (M = Rh, complex **1** [1]; M = Os, complex **2** [2,3]) are active and selective catalysts for the homogeneous hydrogenation and isomerization of linear and cyclic unsaturated hydrocarbons [4,5], as well as interesting precursors for supported heterogeneous catalysts [6–10]. We suggested a reaction pathway for the homogeneous hydrogenation-isomerization of dienes [4,5] based on the observation that, when the "intact" cluster is present in solution, hydrogenation occurs and the substrate coordinates to one metal centre only. The "capping" (Cp)Ni would stabilize the tetrahedral cluster core, and when trimetallic $M_3(CO)_{12}$ "fragments" are formed in solution, isomerization occurs preferentially [4] and the substrate is likely to coordinate to several metal centres.

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We also observed that some mono-phosphine substituted derivatives of **2** gave better turnovers than the parent cluster in reactions with dienes [5]. This prompted us to undertake a more detailed study of "phosphine modified" clusters **1** and **2** and of their possible homometallic fragments still bearing phosphine substituents.

Substituted derivatives of **2** have been reported previously. The monosubstitution products $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8L$ (L = PPh_3, **2a**; PPh_2H, **2b**; P(*o*-tolyl)$_3$, **2c**; PPh_2C_2Ph, **2d**; $PPh_2C_2Pr^i$, **2e**; PMe_2Ph, **2f**; $PPhH_2$, **2g**; $AsPh_3$, **2h**; $SbPh_3$, **2i**; dppm, **2l**) have been characterized spectroscopically [11,12]. Some disubstituted derivatives, $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_7L_2$ (L = PMe_2Ph, **2ff**; $SbPh_3$, **2ii**) have also been described [13]. However, we were unable to obtain trisubstituted derivatives, and furthermore, of the many possible axial or equatorial isomers, only those with ligands in axial positions (or "*trans-*" to the capping (Cp)Ni) could be obtained, as shown by X-ray structural studies for **2g** [12], **2d** [14] and **2ff** [13].

In this paper we describe the synthesis and reactions of some known and new phosphine-substituted derivatives $M_3(CO)_{12-n}L_n$ (M = Os, L = PPh_3, $n = 1,2$, complexes **3a, 4a**; M = Ru, L = PPh_3, PPh_2H, $n = 1$–3, complexes **5a, 5b, 6a, 6b, 7a, 7b**, respectively; M = Ru, L = PEt_3, $n = 3$, complex **7c**; M = Ru, L = PCy_3, $n = 1$, complex **5c**) and $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_{9-n}L_n$ M = Ru, L = PPh_3, $n = 1,2$, complexes **1a, 1aa**; L = PCy_3, **1m**; M = Os, L = PPh_3, $n = 1$, complex **2a**; M = Os, L = PPh_2H, $n = 1$, complex **2b**; M = Os, L = PCy_3, $n = 1$, **2m**; L = Et, $n = 1,2$, complexes **2n, 2nn**).

The reactions of these derivatives under conditions similar to those used in homogeneous catalytic experiments [5] have been examined, and ligand exchange, thermal decomposition, modification, or disproportionation was found to occur for several derivatives. We have also examined reactions with unsaturated hydrocarbons comparable with the substrates used in catalytic experiments. Finally, we have found that thermal treatment of the $Ru_3(CO)_{12-n}(PPh_2H)_n$ complexes in the presence or absence of other ligands leads mainly to phosphido-bridged derivatives, which have already been reported as the products of the photochemical treatment of $Ru_3(CO)_9(PPh_2H)_3$ [15].

Most of the complexes here described show considerable catalytic activity in homogeneous hydrogenation; this aspect is discussed in an accompanying paper [16].

Experimental

General experimental details: materials, purification and analysis of the products

The carbonyls $M_3(CO)_{12}$ (M = Ru, Os), $(CO)_2Ni(PPh_3)_2$ (Strem Chemicals) and $(Cp)_2Ni_2(CO)_2$ (Pressure Chemicals), and the phosphine and organic ligands (Fluka, Strem) were commercial products used as received after spectroscopic or GLC purity checks. Anhydrous Me_3NO was obtained by sublimation in vacuo of commercial $Me_3NO \cdot 2H_2O$ (Fluka). Complex **2** was obtained as previously described [2]. Complex **1** was prepared by a modification [4] of an established procedure [17].

All solvents were distilled over sodium and saturated with N_2 or H_2 prior to use. Reactions were carried out under dry N_2 or H_2 in standard three-necked flasks fitted with gas inlet, cooler, and mercury control valve.

The reaction solutions were filtered and concentrated to small volume under reduced pressure then subjected to preparative TLC (Kieselgel P.F. Merck; eluants mixtures of light petroleum and diethyl ether). When possible the products were recrystallized from aliphatic hydrocarbons or from hydrocarbon/$CHCl_3$ mixtures. Cluster **1** is more conveniently recrystallized from acetone.

The products were analyzed with a F&M C, H, N Analyzer; phosphorus and metal analyses were performed by Pascher Laboratories (Remagen, W. Germany). The ^1H and ^{31}P spectra were recorded on a JEOL JNM GX 280 FT instrument. Except for the unsubstituted parent clusters, the complexes decompose in the inlet system of the mass spectrometer (E.I. technique, direct inlet system, 70 eV).

Synthesis of the $M_3(CO)_{12-n}L_n$ derivatives

(a) Reactions of $Os_3(CO)_{12}$ with $(CO)_2Ni(PPh_3)_2$ and Me_3NO. Treatment of $Os_3(CO)_{12}$ (150 mg, 0.165 mmol) with $(CO)_2Ni(PPh_3)_2$ (200 mg, 0.313 mmol) in refluxing heptane, under N_2 in the presence of Me_3NO (50 mg) for 3 min yielded ca. 30% of the light yellow monosubstituted product **3a** and 30% of the orange **4a**, and ca. 30% of the osmium carbonyl was recovered unchanged. In hexane, after 10 min reflux, the yields of **3a** were 50%.

(b) Reactions of $Ru_3(CO)_{12}$ with PPh_3 and Me_3NO. Treatment of $Ru_3(CO)_{12}$ with a 1.5 to 1 molar excess of PPh_3 in refluxing hexane, under N_2 * in the presence of Me_3NO (50 mg) for 1 min gave a dark red solution and a considerable amount of a dark violet residue insoluble in common solvents and slowly decomposing under air. The solution was filtered and concentrated to small volume in vacuo; considerable amounts of $Ru_3(CO)_{12}$ were recovered as a precipitate. TLC of the solution afforded the monosubstituted **5a** (about a 10% yield) and the di- and tri-substituted **6a**, **7a** (50 and 30% yield, respectively). The quoted yields were averaged for several reactions, in which the unreacted $Ru_3(CO)_{12}$ was recovered and re-used.

(c) Reactions of $Ru_3(CO)_{12}$ with $(CO)_2Ni(PPh_3)_2$ and Me_3NO. Treatment of $Ru_3(CO)_{12}$ (200 mg, ca. 0.300 mmol) with $(CO)_2Ni(PPh_3)_2$ (300 mg, ca. 0.470 mmol) and Me_3NO (50 mg) in refluxing hexane for 2 min gave the following yields of substituted complexes; **5a**, 5%: **6a**, 50%: **7a**, 30% and left about 10% of unchanged $Ru_3(CO)_{12}$. In refluxing hexane for 5 min the yields were **5a**, 15%; **6a**, 60%; **7a**, traces.

(d) Reactions of $Ru_3(CO)_{12}$ with PPh_2H, PCy_3, PEt_3 and Me_3NO. Treatment of 250 mg (0.391 mmol) of $Ru_3(CO)_{12}$ with 0.5 ml of liquid PPh_2H and Me_3NO (50 mg) in refluxing hexane for 2 min gave a dark red suspension. This was concentrated small volume under reduced pressure, during, which ca. 5–10% of unchanged $Ru_3(CO)_{12}$ precipitated out. The soluble fraction yielded complexes **5b** (10%), **6b** (40%) and **7b** (40%).

Treatment of $Ru_3(CO)_{12}$ with a 2 to 1 molar excess of PCy_3 in the presence of Me_3NO (50 mg) in refluxing hexane for 2 min gave a red solution, from which after concentration unchanged $Ru_3(CO)_{12}$ separated (about 60%). TLC purification of the solution with light petroleum as eluant, gave an ca. 15% yield of **5c**.

Treatment of 250 mg (0.391 mmol) of $Ru_3(CO)_{12}$ with 0.5 ml of liquid PEt_3 and Me_3NO (50 mg) in refluxing hexane for 30 s gave a dark red solution, which, after

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* Unless otherwise specified, all the reactions described were performed under N_2 atmospheres.

filtration and TLC yielded about 75% of **7c** and 10–15% of a yellow, unidentified derivative.

Synthesis of the $(Cp)NiM_3H_3(CO)_{9-n}L_n$ derivatives

The new complexes **2m, 2n, 2nn** were obtained by the method used previously for the analogous osmium derivatives [11–14]. The new substituted derivatives of **1** were obtained by two procedures, as follows.

(a) Reactions of 1 with PPh_3, PPh_2H, PCy_3, PEt_3 and Me_3NO. Treatment of **1** with a two-fold molar excess of PPh_3 in the presence of Me_3NO in refluxing heptane for 2 min resulted in extensive decomposition. The main soluble product was $(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$ (**1aa**) (20%), together with traces of $Ru_3(CO)_{10}(PPh_3)_2$. In 3 min in refluxing hexane about 10% of $(Cp)NiRu_3H_3(CO)_8(PPh_3)$ (**1a**) and 70% of **1aa** are formed.

The reaction of PPh_2H with **1** and Me_3NO in hexane, with gentle warming for 5 min below the reflux temperature, yielded a red green solution, containing some unchanged **1**, ca. 10% of $Ru_3(CO)_{10}(PPh_2H)_2$, and 30% of $Ru_3(CO)_9(PPh_2H)_3$.

Treatment of **1** (200 mg, 0.283 mmol) with 0.5 ml of liquid PEt_3 and Me_3NO (50 mg) in refluxing for 30 s yielded a green-red solution containing some $Ru_3(CO)_9(PEt_3)_3$, and a green product tentatively identified as $(Cp)NiRu_3H_3(CO)_6(PEt_3)_3$.

Treatment of **1** (250 mg 0.366 mmol) with 0.5 g (1.78 mmol) of PCy_3 and Me_3NO (50 mg) in refluxing hexane for 4 min yielded about 40% of $(Cp)NiRu_3H_3(CO)_8(PCy_3)$ (**2m**) and 40% of (tentatively identified) $(Cp)NiRu_3H_3(CO)_7(PCy_3)_2$ (**2mm**).

(b) Reactions of $Ru_3(CO)_{12-n}(PPh_3)_n$ ($n = 1–3$) with $(Cp)_2Ni_2(CO)_2$. *($n = 1$)* The conditions used were similar to those for the synthesis of **1** [4,17]. Treatment of $Ru_3(CO)_{11}(PPh_3)$ (100 mg, 0.114 mmol) with $(Cp)_2Ni_2(CO)_2$ (100 mg, 0.329 mmol) in refluxing diglyme for 20 min under a current of H_2 gave a dark brown solution. This was reduced to small volume and subjected to TLC to give traces of the unchanged nickel substrate, about 20% of **1a**, 20% of **1aa**, and several unidentified trace products.

($n = 2$) Treatment of $Ru_3(CO)_{10}(PPh_3)_2$ (100 mg, 0.090 mmol) with $(Cp)_2Ni_2(CO)_2$ (100 mg, 0.329 mmol) in diglyme at 100 °C for 55 min under a current of H_2 yielded only 15% of **1aa**, a dark yellow unidentified derivative, and the products of extensive decomposition.

($n = 3$) Treatment of $Ru_3(CO)_9(PPh_3)_3$ (100 mg, 0.075 mmol) with $(Cp)_2Ni_2(CO)_2$ (100 mg, 0.329 mmol) in diglyme at 110 °C for 35 min under a current of H_2 gave only traces of **1a**, about 30% of **1aa**, and trace amounts of a dark-green unstable product, tentatively identified as $(Cp)NiRu_3H_3(CO)_6(PPh_3)_3$. Extensive decomposition also occurred.

(c) Reactions of $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 2,3$) with $(Cp_2Ni_2(CO)_2$. The ruthenium derivatives are sparingly soluble in aliphatic hydrocarbon solutions of the nickel dimer. Suspensions were formed, which gave clear solutions at reflux temperatures.

Addition of a 10 ml toluene solution of 50 mg (0.052 mmol) of $Ru_3(CO)_{10}(PPh_2H)_2$ to a hexane solution of 100 mg (0.329 mmol) of the nickel complex under N_2 followed by 30 min reflux gave a dark purple suspension. The reaction yielded seven species identified as: small amounts of unchanged $Ru_3(CO)_{12}$ and nickel dimer along with $H_2Ru_3(CO)_8(\mu\text{-}PPh_2)_2$ (complex **A**) [15], $H_2Ru_3(CO)_7(PPh_2H)(\mu\text{-}PPh_2)_2$ (complex **B**) [15], $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$ (complex

C) [15] and $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ (complex **D**) [15]; and with traces of an unidentified derivative. Yields of **A** and **B** were 5–10%, and those of **C** and **D** 10–20%. The same result was obtained after only 2 min in refluxing heptane. Complexes **A**–**D** were difficult to separate and isolate pure by TLC.

Addition of a 10 ml toluene solution of 75 mg (0.067 mmol) of $Ru_3(CO)_9(PPh_2H)_3$ to a heptane solution of 100 mg of nickel dimer followed by 10 min reflux under N_2 gave a dark purple solution containing the same products as above.

Other reactions. Reactions of $Ru_3(CO)_{12-n}L_n$ *(*$L = PPh_2H$, $n = 1\text{–}3$; $L = PPh_3$, $n = 2$*) with 3,3-dimethyl-but-1-yne*

A 10 ml toluene solution of $Ru_3(CO)_{11}(PPh_2H)$ with a 100 ml heptane solution containing 0.5 ml of the alkyne was refluxed under N_2 for 5 min to yield a dark yellow solution containing nine products, namely: $HRu_3(CO)_9(C_2Bu^t)$ (5%) [19]; $HRu_3(CO)_8(PPh_2H)(C_2Bu^t)$ (1%); $HRu_3(CO)_7(PPh_2H)_2(C_2Bu^t)$ (1%) *; **A** (5–10%); **B** (5–10%); **C** (10–20%); **D** (10–20%); an unidentified deep red complex (**E**); and an unidentified green complex (**F**) **.

The reaction of $Ru_3(CO)_{10}(PPh_2H)_2$ under similar conditions with 6 min reflux gave the same products in comparable yields.

$Ru_3(CO)_9(PPh_2H)_3$ after 15 min in refluxing heptane yielded a brown solution containing $Ru_3(CO)_{10}(PPh_2H)_2$ and products **A**–**D**. However, after 10–15 min reflux in octane the product distribution above was observed.

In refluxing heptane, $Ru_3(CO)_{10}(PPh_3)_2$ gave three products identified as $HRu_3(CO)_{9-n}(L)_n(C_2Bu^t)$ ($n = 2,3$) [20] and $Ru_3(CO)_9(PPh_3)_3$.

Thermal modification and/or disproportionation reactions of the phosphine-substituted derivatives

Refluxing of octane suspensions of $Ru_3(CO)_9(PPh_2H)_3$ (initially dissolved in a few ml of toluene) for 40 min under N_2 in the absence of other ligands yielded solutions containing complexes **A** and **B** in ca. 5–10% and **C** and **D** in ca. 10–20% yields.

Complexes of $(Cp)NiOs_2H_3(CO)_8L$ ($L = PPh_3$, PPh_2H) slowly disproportionated when their solutions were kept for 12–24 h at room temperature under N_2. The reaction occurred in a few minutes in refluxing hexane, and 5% of $(Cp)NiOs_3H_3(CO)_9$ and of $(Cp)NiOs_3H_3(CO)_7L_2$ were formed.

Refluxing of a solution $(Cp)NiRu_3H_3(CO)_8(PPh_3)$ in hexane for 30 s yielded 15% of $(Cp)NiRu_3H_3(CO)_9$ and 40% of $(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$.

Thermal disproportionation reactions are probably likely to occur during the syntheses described above.

Ligand exchange reactions on $(Cp)NiOs_3H_3(CO)_8L$ *complexes*

All the reactions were performed under N_2 in refluxing hexane in the presence of

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* $HRu_3(CO)_8(PPh_2H)(C_2Bu^t)$ IR: 2077s, 2055vs, 2049sh, 2044sh, 2025s, 2016vs, 1990m, 1970w. ^1H NMR: 7.60–7.18 mm (Ph): 1.29 t (Bu^t); -21.14 s (hydride). ^{31}P NMR: $+11.16$ s. $HRu_3(CO)_7(PPh_2H)_2(C_2Bu^t)$. IR: 2062s, 2024vs, 2014vs, 1996vs, 1982s, 1960m. ^1H NMR: 7.53–7.38 m (Ph): 1.99 s(Bu^t): -20.50 d (hydride). ^{31}P NMR: $+1.14$ s. Satisfactory C and H analyses were obtained for both complexes.

** See Discussion.

Table 1

Ligand exchange reactions of $(Cp)NiOs_3H_3(CO)_8L$ complexes
$(Cp)NiOs_3H_3(CO)_8L + L' \rightarrow (Cp)NiOs_3H_3(CO)_8L' + L$

L	L′	Reaction time (min)	Yield of L′ (%)
CH_3CN	CO	3	100
CH_3CN	PPh_3	3	100
CH_3CN	$C_2(PPh_2)_2$	3	90 [a]
CH_2CN	$SbPh_3$	2	80 [a]
$SbPh_3$	PPh_3	5	99 [a]
$SbPh_3$	$C_2(PPh_2)_2$	5	no exchange (30% decomposition)
$PPh_2C_2Pr^i$	PPh_3	5	no exchange (3% decomposition)
PPh_2H	PPh_3	6	90
PEt_3	PPh_3	2	no exchange

[a] Some decomposition and some $(Cp)NiOs_3H_3(CO)_9$ were observed.

a slight excess of the free ligand (1.2 to 1 molar ratio), except when CO was used (as a slow current). Details of these reactions are given in Table 1.

Results and discussion

Synthesis and characterization of the complexes

(a) Trimetallic derivatives. Phosphine-substituted carbonyl clusters are nowadays readily made by various methods: (a) thermal or photochemical substitution of phosphines for CO: (ii) displacement of labile ligands (e.g. acetonitrile): and (iii) labilization of coordinated CO's by various reactants.

These methods were employed for the synthesis of complexes $M_3(CO)_{12-n}L_n$ (M = Ru [21]; M = Os [22]). Thermal substitution reactions require high temperatures and generally give products only with $n = 3$ [23]. Greater selectivity is achieved by displacing CH_3CN [24]. A selective high yield synthesis of Ru derivatives with $n = 1,2,3$ (depending on the phosphine/cluster ratio) is obtained with Na-benzophenylketyl as a radical-ion initiator [25].

We have found that use of Me_3NO as a labilizing agent leads to fair yields of the products with $n = 1-3$, except when the weakly reactive PCy_3 or the very reactive PEt_3 are involved. The reaction stoichiometry and time also influence the yields; disproportionations are likely to occur, since the $n = 2$ products are generally favoured for most of the phosphines.

We have also confirmed that phosphine exchange between metals can be used in synthesis; $Ru_3(CO)_9(PPh_3)_3$ was previously made from $Ru_3(CO)_{12}$ and Pt(stilbene)$(PPh_3)_2$ [26]. Use of commercially available $(PPh_3)_2Ni(CO)_2$ also gives the $M_3(CO)_{12-n}(PPh_3)_3$ (M = Ru, Os) derivatives. Phosphine exchange between metals under relatively mild conditions is evidently significant in view of the disproportionation reactions observed.

Several $M_3(CO)_{12-n}L_n$ derivatives discussed here had previously only been partially characterized (see ref. 21–26) and, in particular ^{31}P NMR data were lacking. Full data for the derivatives are listed in Table 2.

Except for $Ru_3(CO)_9(PEt_3)_3$, each complex apparently gave only one isomer of the many axial–equatorial species possible; this could be the result of the failure of the TLC technique to effect their separation or to rapid equilibration in solution. Bruce and coworkers were also able to identify only one isomer for each complex [25a].

By contrast $Os_3(CO)_{12-n}L_n$ ($L = PPhMe_2$) gives separable isomers [27]; for $n = 2$, 1,1- and 1,2-species were separated on silica, and for $n = 3$, two C_s, non-interconvertible, 1,2,3- and 1,1,2-isomers were observed. It is noteworthy that intramolecular phosphine transfer was not observed.

(b) Heterometallic derivatives. These syntheses were performed as previously described [11–14], starting from clusters **1** or **2**, and the appropriate ligand, in the presence of Me_3NO. Details of the new osmium and ruthenium derivatives are given in Table 3.

The type and yields of the products depend on the nature (and hence on the reactivity) of the phosphine, as well as on the cluster metals; thus $(Cp)NiOs_3H_3(CO)_9$ usually gives $n = 1$ derivatives [11], and relatively long reaction times are required to obtain $n = 2$ complexes [13]. The behaviour of PEt_3 is unusual, as the $n = 2$ derivative is obtained in good yield in a very short time. Derivatives with $n = 3$ could not be obtained even after long reaction time or by use of a large excess of ligand, and only decomposition products were formed.

$(Cp)NiRu_3H_3(CO)_9$ is considerably more reactive and generally gives $n = 2$ products; with PPh_2H and PEt_3 in particular, fragmentation of the cluster occurs under very mild conditions. The latter ligand, however, gives small amounts of an unstable green product, which could not be crystallized, but which was tentatively identified as $(Cp)_3NiRu_3H_3(CO)_6(PEt_3)_3$.

Attempts to increase the selectivity and obtain $n = 3$ derivatives were made by using the $Ru_3(CO)_{12-n}(PPh_3)_n$ ($n = 1$–3) complexes, which were treated with $(Cp)_2Ni_2(CO)_2$ under H_2 under conditions similar to those adopted for the synthesis of cluster **1** [4,17]; these conditions are, however, rather drastic, so that some disproportionation occurs. Once again the $n = 2$ product is favoured, and only traces of the (assumed) $n = 3$ derivatives are obtained. This behaviour confirms that the trisubstituted derivatives are unstable, probably for steric as well as electronic reasons.

Reactions of $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 1$–3) with $(Cp)_2Ni_2(CO)_2$ were also examined, under conditions more closely similar to those used in the hydrogenation experiments described elsewhere [16]. Under these conditions no formation of substituted derivatives of **1** was observed; furthermore we did not observe reductive coupling and/or elimination of the phosphine hydrogen atoms with nickel containing fragments. Under a N_2 atmosphere, only gradual loss of phosphine hydrogen atoms occurs, leading to complexes **A**–**D**, observed previously by Geoffroy and coworkers [15] as stable products of the photochemical reaction of $Ru_3(CO)_9(PPh_2H)_3$; the same products are obtained, under N_2 and in comparable conditions, by simple thermal treatment in the absence of nickel dimer.

For the $(Cp)NiRu_3H_3(CO)_{9-n}L_n$ derivatives, reported here for the first time, we suggest the same structure and isomerism as found for the homologous osmium compounds. Indeed, the IR, ^1H and ^{31}P NMR of the two classes of complexes are closely comparable (see Table 3).

Other phosphine-substituted tetrahedral heterometallic clusters have been reported; $HRuCo_3(CO)_{11}(PPh_3)$, obtained by "metal selective" substitution of PPh_3 on one basal cobalt atom, has the ligand in an axial position, at least in the solid

(*Continued on p. 106*)

Table 2

Physical, analytical and spectroscopic data for complexes $M_3(CO)_{12-n}L_n$

Complex		Colour	Analysis (Found (calc) (%))				IR, ν(CO) (cm^{-1}) (C_6H_{14})	^{31}P NMR (δ (ppm)) ($CDCl_3$, H_3PO_4)
L	*n*		C	H	Os	P		
M = *Os*								
PPh_3 **(3a)**	1	yellow	30.8 (30.5)	1.4 (1.3)	51.2 (50.0)	2.8 (2.7)	2109m, 2057s, 2038s, 2022vs, 2004w, 1992w, 1980w, 1954w(b)	−0.54 s
PPh_3 **(4a)**	2	orange	41.1 (40.2)	2.1 (2.2)	41.8 (41.5)	4.6 (4.5)	2090s, 2053vs, 2012vs, 2005 vs(sh), 1998s(sh), 1985s(b)	−8.68 s
M = *Ru*								
			C	H	Ru	P		
PPh_3 **(5a)**	1	orange	40.0 (39.9)	1.8 (1.7)	35.1 (34.7)	3.6 (3.5)	2098s, 1062s, 2048vs, 2026– (3.5)	+28.91 s −2012vs(b) [a]
PPh_3 **(6a)**	2	red	50.1 (49.9)	2.9 (2.7)	27.2 (27.4)	5.5 (5.6)	2079s, 2046w, 2012vs, 1997vs(b) 1960w [a]	+40.67 s
PPh_3 **(7a)**	3	purple	57.1 (56.4)	3.5 (3.4)	23.0 (22.6)	7.01 (6.9)	2046s, 1980vs(b), 1967vs(b) [a]	
PPh_2H **(5b)**		yellow	35.0 (34.6)	1.5 (1.4)	38.5 (38.0)	4.0 (3.9)	2100m, 2062s, 2048vs, 2032vs, 2016vs, 1998sh, 1980m	+2.65 s
PPh_2H **(6b)**	2	red	43.0 (42.7)	2.4 (2.3)	31.3 (31.7)	6.7 (6.5)	2062vs, 2026vs, 2008vs(b), 1978 m(b)	+4.87 s
PPh_2H **(7b)**	3	purple	49.1 (48.5)	3.2 (3.0)	28.0 (27.2)	8.6 (8.3)	2062vs, 2028vs, 1988vs(vb)	+19.92 s
PCy_3	1	red	39.1 (39.1)	3.9 (3.7)	33.8 (34.0)	3.6 (3.5)	2096m, 2055sh, 2046vs, 2028sh, 2016vs, 1985m(b)	–
PEt_3	3	purple	36.1 (35.6)	5.2 (5.0)	33.4 (33.3)	10.2 (10.2)	2061s, 2016w, 1986s, 1968s, 1947vs	+11.71 s, +32.69 s [b]

[a] In hexane/$CHCl_3$ solution. [b] Intensity 1/1.

Table 3

Physical, analytical and spectroscopic data for complexes $(Cp)NiM_3H_3(CO)_{9-n}L_n$

Complex	Colour	Analysis (Found (calc) (%))						IR ν(CO) (cm^{-1}) (C_6H_{14})	^1H NMR (δ (ppm)) ($CDCl_3$)	^{31}P NMR (δ (ppm)) ($CDCl_3$,H_3PO_4)
		C	H	Ni	P	Ru	Os			
$(Cp)NiRu_3H_3(CO)_8PPh_3$	dark green	41.0 (40.6)	2.6 (2.5)	6.7 (6.4)	3.2 (3.4)	33.3 (33.1)		2073m, 2052vs, 2017vs, 2005s, 1961m(b)	7.40–7.25 mm (12H,Ph) [a]; 5.06 s (5H,Cp); −15.25 dd (2H), −15.29 t (1H, hydrides)	+31.30 s
$(Cp)NiRu_3H_3(CO)_8PCy_3$	green	40.3 (39.8)	4.4 (4.4)	6.5 (6.3)	3.5 (3.3)	33.1 (32.4)		2074s, 2053vs, 2010vs, 1998vs, 1980m(sh), 1949 s(b)	5.68 s (5H,Cp); 1.86, 1.26 m (33H, Cy); −15.86 (br,2H), −15.88 (br,1H, hydrides)	+50.51 s
$(Cp)NiOs_3H_3(CO)_8PCy_3$	dark purple	31.5 (31.0)	3.6 (3.4)	4.9 (4.9)	46.8 (47.5)	2.7 (2.6)		2067vs, 2056s, 2010vs, 1995s, 1986s, 1943m	5.92s (5H,Cp);2.08–1.31 mm (33H, Cy); −17.16 d, −17.19 d (2H), −17.56 t (1H, hydrides)	+44.87 s
$(Cp)NiOs_3H_3(CO)_8PEt_3$	dark purple	22.1 (21.9)	2.4 (2.2)	5.8 (5.6)	55.0 (54.9)	3.2 (3.0)		2078m–s, 2056vs 2016vs, 1996s(b),m 1987vs(b), 1950 m–s	6.06 s (5H,Cp); 2.07m,1.05 (15H,Et); −17.36 d, −17.39 (2H), −17.80 t (1H,hydrides)	+18.11 s
$(Cp)NiRu_3H_3(CO)_7(PPh_3)_2$	dark green	50.7 (50.1)	3.5 (3.3)	5.3 (5.1)	9.8 (9.7)	27.0 (26.61)		2055vs, 2014vs (sh), 2008vs, 1986 m(b), 1960m(b) [a]	7.69–7.15 mm (30H,Ph); 5.71 s (5H,Cp); −13.99 t(1H), −15.07 d (2H, hydrides)	+28.93 s
$(Cp)NiOs_3H_3(CO)_7(PEt_3)_2$	purple	25.5 (25.5)	3.4 (3.4)	5.7 (5.2)	51.0 (50.5)	5.7 (5.5)		2058s, 2010s(sh) 2001vs, 1967s(b) 1949s(b)	5.63 s (5H,Cp); 2.02 m, 1.04 m (30H,Et); −16.94 t (1H), −17.40 br, −17.43 br (2H, hydrides)	+15.85 s
$(Cp)NiRu_3H_3(CO)_6(PEt_3)_3$ [b]	green	37.0 (36.6)	5.8 (5.6)					2012m, 2004m, 1979vs, 1963m (b), 1945s	5.69–5.59 d (5H,Cp); 1.70 m 1.20 m (45H,Et); −15.46 s (ca. 3H, hydrides)	–

[a] In hexane/$CDCl_3$ solution. [b] Tentative identification.

state [28]. The first substitution of PPh_3 on $H_2FeRu_3(CO)_{13}$ occurs in an axial position on one of the basal ruthenium atoms, whereas the second substitution, on another ruthenium, can be either axial or equatorial [29]. ^1H and ^{31}P NMR data are available for the latter compounds; the monosubstituted species shows a hydridic signal at -17.98 d (J(P–H) 8.6 Hz) and a ^{31}P NMR signal at $+43.23$ s; the disubstituted complex shows complex hydridic signals at -17.12 m, -18.05 m, and ^{31}P NMR chemical shifts at $+41.9$ s, $+36.7$ s(all of the spectra being recorded in $CDCl_3$ at $-30\,°C$). These values fall in the range found at room temperature for the $(Cp)NiRu_3H_3(CO)_{9-n}L_n$ derivatives; the main difference is that the $n = 2$ complexes show only one ^{31}P signal owing to equivalence of the phosphines.

Thus, axial substitution is always observed for the first phosphine ligand attaching to a tetrahedral cluster formed by a triangle of identical metals capped by a heterometal. By contrast, when $M_2M'_2$ tetrahedral clusters are substituted, as for $H_2Ru_2Rh_2(CO)_{11}(PPh_3)$ [30], the position of the phosphine becomes a matter of choice of the basal triangle.

Thermal reactions

(a) Disproportionation reactions. These have been observed for nearly all the derivatives; $Ru_3(CO)_{12-n}L_n$ undergo this process quite easily, and apparently the statistically expected $n = 2$ complexes are the favoured products. Ready thermal disproportionation of $Ru_3(CO)_{12}$ or $Ru_3(CO)_{11}(P(OMe)_3)$ with $Ru_3(CO)_9(P(OMe)_3)_3$ has been reported [25]; it is probable that these reactions occur via intra- or inter-molecular phosphine exchange rather than by break-up into metal fragments followed by recondensation; the phosphine exchange observed between nickel and ruthenium favours this suggestion. However, kinetic studies on $Ru_3(CO)_9(PPh_3)_3$ and related compounds [31] have shown that fragmentation can also occur, and that there are complex equilibria between the tri-, bi- and mono-metallic species *.

Disproportionation reactions also occur during the synthesis of the $(Cp)NiRu_3H_3(CO)_{9-n}L_n$ derivatives; it is impossible to discriminate between disproportionation of the starting materials during the reaction and rearrangement of the products. The latter have shown a tendency to disproportionate, the process being faster for the ruthenium derivatives.

In addition to disproportionation, the $Ru_3(CO)_{12-n}(PPh_2H)_n$ ($n = 1$–3) complexes undergo thermal modification reactions; in the absence of ligands these occurs slowly, but the process is faster in the presence of $(Cp)_2Ni_2(CO)_2$ or of t-butyl-acetylene (see section b, below). Clusters **A**–**D** are formed, the same products that are obtained upon photochemical treatment of $Ru_3(CO)_9(PPh_2H)_3$ [15]. The formation of phosphido-bridged derivatives, from PPh_2H substituted clusters involves oxidative addition of the "fragments" PPh_2 and H together with some loss of hydrogen; the higher reaction rates observed in the presence of ligands show that these must assist the process, probably by accepting hydrogen. This is relevant to the catalytic behaviour of the PPh_2H substituted complexes.

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* We examined the reactions of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ or of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ with $(Cp)_2Ni_2(CO)_2$ under H_2 in diglyme. Preliminary results indicate that the clusters $(Cp)NiM_2M'(CO)_9H_3$ are formed, and these are under investigation.

(b) Reactions with 3,3-dimethyl-but-1-yne. This ligand has been chosen because of its well known coordinating ability [32]. Furthermore, phosphine-substituted, acetylide-bridged triruthenium clusters have already been reported [20], making easier the identification of new complexes of comparable structure.

The reactions of this alkyne with $(Cp)NiM_3H_3(CO)_9$ clusters have been discussed previously [4,5]. Displacement of the capping (Cp)Ni generally occurs. Cluster opening to give butterfly structures is dis-favoured.

Clusters $Ru_3(CO)_{12-n}L_n$ ($L = PPh_3$, PPh_2H) react with the alkyne in a complex way; when $n = 2$, $L = PPh_3$, $HRu_3(CO)_7(PPh_3)_2(C_2Bu^t)$ [20] and disproportionation products containing three phosphines, with or without the acetylide, are found. This shows that the alkyne or the derived acetylide displace the coordinated CO ligands rather than PPh_3.

When $L = PPh_2H$ and $n = 1$–3, some selectivity is observed; indeed, the same products are obtained in increasingly drastic conditions (for $n = 1,2,3$ solvents were refluxing heptane (short time), heptane (longer reaction time) and octane, respectively). The nature of the products deserves some comments. Small amounts of $HRu_3(CO)_9(C_2Bu^t)$ [19] are found, and this indicates that the alkyne can displace the phosphine ligands, although with considerable difficulty; $HRu_3(CO)_{9-n}(PPh_2H)_n(C_2Bu^t)$ ($n = 1,2$) derivatives are also found, and were identified by comparison of the spectroscopic data with those for known derivatives [20]. The main products of these reactions are, however, the phosphido-bridged complexes **A**–**D**, the thermal decomposition products. Finally, two unidentified products are also formed, but only under rather drastic conditions; they may possibly be derived from the reaction of complexes **C** or **D** with the alkyne *.

(c) Ligand exchange on $(Cp)NiOs_3H_3(CO)_8L$. The results of these reactions are in Table 1; apparently the sequence in which ligands displace each other depends on their π-donor abilities; the following series of ease of displacement have been observed [33]:

(a) $CH_3CN \gg SbPh_3 \simeq dppm \simeq C_2(PPh_2)_2 > PPh_3 > CO$

(b) $PPh_2H \simeq PCy_3 \simeq PEt_3 > PPh_3 > CO$

The positions of CO in the series may be deceptive, since the reactions were performed under a slow current of the gas, and hence with a considerable excess of it. Moreover the reactions described earlier indicate that CO is displaced more easily than the phosphine ligands by organic ligands.

Concluding remarks

An investigation of the reactions of $(Cp)NiM_3H_3(CO)_{9-n}L_n$ ($M = Ru$, Os) derivatives has shown that warming in the presence of ligands or of "metal

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* Reactions of complexes **C** or **D** with t-butyl-alkyne, by refluxing in octane for about 20 min were examined. Complex **C** gave a turquoise-green derivative (complex **F**) showing only terminal carbonyls and signals in the ^{31}P NMR typical of phosphido bridges; the ^{1}H NMR data indicate the presence of an organic ligand. Complex **D** gives a ruby-red derivative (complex **E**) with only terminal carbonyls and giving a ^{31}P NMR spectrum typical of phosphido-bridged derivatives; the ^{1}H NMR indicates the presence of an organic ligand. Hydridic signals were found for both compounds.

The green and red complexes are identical to those obtained by treating $Ru_3(CO)_{12-n}L_n$ with t-butyl-alkyne. Unfortunately, attempts to obtain X-ray grade crystals gave only crystalline powders. The nature of the complexes is still under investigation.

fragments" similar to those used in catalytic experiments gives rise to several processes which may be parallel or competitive.

The alkyne displaces (Cp)Ni and CO from the tetrahedral clusters and mainly CO from the trimetallic derivatives; displacement of phosphines from the latter is harder than that of CO. This behaviour may have implications for the catalytic behaviour of the clusters. With the tetrahedral complexes exchange of the phosphine occurs readily, the ease being determined by the π-donor abilities of the ligands. However, all the clusters examined undergo disproportionation, with preferential formation of the $n = 2$ derivatives. Whether this behaviour involves the formation and recombination of metal fragments is still uncertain.

The behaviour of the PPh_2H derivatives is noteworthy. Thermal treatment of the $Ru_3(CO)_{12-n}L_n(PPh_2H)_n$ complexes with or without other ligands gives phosphido-bridged derivatives. Thus, phosphine ligands tend to loose hydrogen and to give the more stable phosphido-bridging units; the phosphido-bridged derivatives still react with t-butyl-acetylene, probably by CO displacement and/or insertion into M–P or M–H bonds.

This behaviour must be taken into account when considering the homogeneous catalytic properties of the complexes [16].

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References

1 M. Castiglioni, E. Sappa, M. Valle, M. Lanfranchi and A. Tiripicchio, J. Organomet. Chem., 241 (1983) 99, and references therein.
2 S.G. Shore, W.S. Hsu, C.R. Weisenberger, M.L. Castle, M.R. Churchill and C. Bueno, Inorg. Chem., 22 (1983) 510.
3 G. Lavigne, F. Papageorgiou, C. Bergounhou and J.J. Bonnet, Inorg. Chem., 22 (1983) 2485.
4 M. Castiglioni, R. Giordano and E. Sappa, J. Organomet. Chem., 319 (1987) 167.
5 M. Castiglioni, R. Giordano, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, J. Chem. Soc., Dalton Trans., (1986) 23.
6 P. Moggi, G. Albanesi, G. Predieri and E. Sappa, J. Organomet. Chem., 252 (1983) C89.
7 G. Albanesi, R. Bernardi, P. Moggi, G. Predieri and E. Sappa, Gazz. Chim. Ital., 116 (1986) 385.
8 M. Castiglioni, R. Giordano, E. Sappa, G. Predieri and A. Tiripicchio, J. Organomet. Chem., 270 (1984) C7.
9 M. Castiglioni, R. Giordano, E. Sappa and P. Volpe, J. Chromatogr., 349 (1985) 173.
10 M. Castiglioni, R. Giordano and E. Sappa, J. Mol. Catal., 39 (1986) 287; idem, ibid., 40 (1987) 65.
11 E. Sappa, M. Valle, G. Predieri and A. Tiripicchio, Inorg. Chim. Acta, 88 (1984) L23.
12 G. Predieri, A. Tiripicchio, C. Vignali, E. Sappa and P. Braunstein, J. Chem. Soc., Dalton Trans., (1986) 1135.
13 E. Sappa, M.L. Nanni Marchino, G. Predieri, A. Tiripicchio and M. Tiripicchio Camellini, J. Organomet. Chem., 307 (1986) 97.
14 E. Sappa, G. Predieri, A. Tiripicchio and M. Tiripicchio Camellini, J. Organomet. Chem., 297 (1985) 103.
15 R.P. Rosen, G.L. Geoffroy, C. Bueno, M.R. Churchill and R.B. Ortega, J. Organomet. Chem., 254 (1983) 89.
16 M. Castiglioni, R. Giordano and E. Sappa, J. Organomet. Chem., the next, 342 (1988) 111.
17 G. Lavigne, F. Papageorgiou, C. Bergounhou and J.J. Bonnet, Inorg. Synth., XXV, in press.

18 E. Sappa, O. Gambino, L. Milone and G. Cetini, J. Organomet. Chem., 39 (1972) 169.

19 M. Catti, G. Gervasio and S.A. Mason, J. Chem. Soc., Dalton Trans., (1977) 2260.

20 C. Jangala, E. Rosenberg, D. Skinner, S. Aime, L. Milone and E. Sappa, Inorg. Chem., 19 (1980) 1571.

21 (a) M.A. Bennett, M.I. Bruce and T.W. Matheson, in E.W. Abel, F.G.A. Stone and G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982; Ch. 32.5, p. 872 et seq; (b) S.C. Tripathi, S.C. Srivastava, R.P. Mani and A.K. Shrimal, Inorg. Chim. Acta, 15 (1975) 249.

22 R.D. Adams and J.P. Selegue, in E.W. Abel, F.G.A. Stone and G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982; Ch. 33, p. 977 et seq.

23 (a) C.W. Bradford, Platinum Met. Rev., 11 (1967) 104; (b) F. Piacenti, M. Bianchi, E. Benedetti and G. Sbrana, J. Inorg. Nucl. Chem., 29 (1967) 1389; (c) B.F.G. Johnson, R.D. Johnston, P.L. Josty, J. Lewis and I.G. Williams, Nature, 213 (1967) 901; (d) F. Piacenti, M. Bianchi, E. Benedetti and C. Braca, Inorg. Chem., 7 (1968) 1815; (e) A.J. Deeming, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., 17 (1969) 40; idem, J. Chem. Soc. (A), (1970) 897; (f) J.P. Candlin and A.C. Shortland, J. Organomet. Chem., 16 (1969) 289; (g) R.J.H. Clark, C.W. Bradford, R.S. Nyholm and W. van Bronswijk, J. Chem. Soc. (A), (1970) 2889; (h) C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland and R. Mason, J. Chem. Soc., Chem. Commun., (1972) 87; (i) G.J. Gainsford, J.M. Guss, P.R. Ireland, R. Mason, C.W. Bradford and R.S. Nyholm, J. Organomet. Chem., 40 (1972) C70; (l) C.W. Bradford and R.S. Nyholm, J. Chem. Soc., Dalton Trans., (1973) 529; (m) A.J. Deeming, R.E. Kimber and M. Underhill, J. Chem. Soc., Dalton Trans., (1973) 2589; (n) M.I. Bruce, J.G. Matisons, R.C. Wallis, J.M. Patrick, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1983) 2365; (o) B.F.G. Johnson, J. Lewis, B.E. Reichert and K.T. Schorpp, J. Chem. Soc., Dalton Trans., (1976) 1403.

24 G.A. Foulds, B.F.G. Johnson and J. Lewis, J. Organomet. Chem., 296 (1985) 147.

25 (a) M.I. Bruce, Coord. Chem. Rev., 76 (1987) 1, and references therein; (b) M.I. Bruce, J.G. Matisons and B.K. Nicholson, J. Organomet. Chem., 247 (1983) 321.

26 M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1972) 2094.

27 A.J. Deeming, S. Donovan-Mtunzi, S.E. Kabir and P.J. Manning, J. Chem. Soc., Dalton Trans., (1985) 1037.

28 M. Hidai, H. Matsuzaka, Y. Koyasu and Y. Uchida, J. Chem. Soc., Chem. Commun., (1986) 1451.

29 J.R. Fox, W.L. Gladfelter, T.G. Wood, J.A. Smegal, T.K. Foreman, G.L. Geoffroy, I. Tavanaiepour, V.M. Day and C.S. Day, Inorg. Chem., 20 (1981) 3214.

30 J. Pursiainen and T.A. Pakkanen, J. Organomet. Chem., 315 (1986) 353.

31 A. Poe, Chemistry in Britain (1983) 997, and references therein.

32 E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., 83 (1983) 203.

33 Preliminary results have been reported: E. Sappa, G. Predieri and A. Tiripicchio, XII International Conference on Organometallic Chemistry, Vienna Sept. 8–13 (1985) paper 98.