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Bis(diphenylphosphino)acetylene as a bridging ligand between homo- and hetero-metallic clusters

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Abstract

The reactions of $Ru_3(CO)_{11}L$, $HRu_3(CO)_8(C_2Bu^t)L$ (L = DPPA, CH_3CN) with $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_8L$ (M = Ru, Os; L = DPPA, CH_3CN) lead to "cluster interlinked" derivatives, with DPPA acting as a bridge (DPPA = bis(diphenylphosphino)acetylene). The complexes have been identified by elemental analyses and spectroscopy. Side reactions, such as displacement of ligands or thermal disproportionation, have been observed.

Introduction

Carbonyl clusters have been studied as models for the reactions of small molecules on surfaces [1], as potential homogeneous catalysts [2] and as heterogeneous catalyst precursors [3]. There is also some interest in the interlinking (or bridge-bonding) of similar or different metal fragments [4]. These reactions could lead to new precursors of heterogeneous catalysts [3], as well as to new molecules with interesting electron transfer [5] or redox [6] properties, and/or to building blocks for organometallic polymers [4].

Bridging ligands may be roughly divided in three main groups: (i) metal atoms [7], (ii) heteroatoms (e.g. carbon, sulphur, halogens) [8], and (iii) small organic molecules. Among the latter, substituted phosphines [9], diphosphines (e.g. DPPE, DPPM) * [10], acetylides [11], diynes [12], phosphaalkynes [13], phosphino- [14] and diphosphino-acetylenes [15,16] have been used.

We report here on some attempts to use bis(diphenylphosphinoacetylene), DPPA, as a bridge between metal clusters; this ligand has been extensively studied [15,16] because of its several bonding possibilities.

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* DPPM = bis(diphenylphosphino)methane
DPPE = bis(diphenylphosphino)ethane (also known as DIPHOS).

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For the present study, we chose as metal fragments the mono-substituted derivatives $Ru_3(CO)_{11}L$, $HRu_3(CO)_8(L)(\mu_3,\eta^2\text{-}C_2Bu^t)$ (L = CH_3CN, DPPA; complexes **1a**, **1b**, **2a**, **2b**, respectively) and $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_8$ (M = Ru, L = DPPA, complex **3b**; M = Os, L = CH_3CN, DPPA, complexes **4a**, **4b**). We have found that the complexes containing CH_3CN ligands readily undergo displacement of this ligand, and so interlinking of metal fragments may take place. However, only very low yields of products containing different metal "fragments" were obtained because of the occurrence of several side reactions, such as thermal decomposition or disproportionation; these reactions are also discussed.

Experimental

General experimental details

Materials and analysis of the products. The carbonyls $M_3(CO)_{12}$ (M = Ru, Os) and DPPA (Strem Chemicals), HC_2Bu^t and CH_3CN (Fluka) were commercial products, used as received after checks of their purity by IR spectroscopy and GLC. Anhydrous Me_3NO was obtained by sublimation in vacuo of commercial $Me_3NO \cdot 2H_2O$ (Fluka). Complexes $HRu_3(CO)_9(\mu_3,\eta^2\text{-}C_2Bu^t)$ [17] and $(\eta^5\text{-}C_5H_5)NiM_3(\mu\text{-}H)_3(CO)_9$ (M = Ru [18], M = Os [19]) were made and purified by published procedures.

All solvents were distilled over sodium and saturated with N_2 before use. Reactions were conducted under dry N_2 in standard three-necked flasks equipped with gas inlet, cooler, and mercury control valve. The reaction solutions were filtered under N_2, reduced to small volume under low pressure, and purified by preparative TLC (Kieselgel P.F. Merck, with mixtures of light petroleum and diethyl ether as eluents).

Analysis of products were carried out with a F & M 185 C, H, N Analyzer and a Perkin-Elmer 303 Atomic Absorption Spectrometer. Some analyses were carried out by the Pascher Laboratories (Remagen, W. Germany).

The IR spectra were recorded on a Perkin-Elmer 580B instrument. The NMR spectra were recorded on a JEOL JNM GX 270 FT multinuclear instrument.

Unfortunately, except for the parent derivatives all the complex decompose in the inlet system of the mass spectrometer (Kratos MS 50, operated in the E.I. mode at 70 eV at the lowest temperatures compatible with the stability of the complexes).

Synthesis of acetonitrile derivatives. (Complexes **1a**, **2a**, **4a**). Complex **1a** was obtained by a published method [20]; complex **2a** was obtained by refluxing for 2 min a suspension (ml) in hexane under N_2 of 75 mg of $HRu_3(CO)_9(C_2Bu^t)$ and 0.3 ml of CH_3CN in the presence of Me_3NO (20 mg). About 10% of pale yellow **2a** and 80% of the unchanged parent cluster were recovered after repeated TLC separations.

Complex **4a** was obtained by refluxing $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_9$ (100 mg) with 0.5 ml of CH_3CN in heptane (50 ml) under N_2 for 2 min in the presence of Me_3NO; an ca. 50% yield of the green-purple complex **4a** was obtained *. Some unchanged starting complex and decomposition products were recovered.

The same procedure with $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_9$ in refluxing hexane for 1-10 min, resulted only in extensive decomposition; apparently a light green substitution product was formed but decomposed immediately on the TLC plates.

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* See footnote ^{e} Table 1.

Synthesis of the DPPA derivatives. (Complexes **1b**, **2b**, **3b**, **4b**). Complex **1b** was obtained by stirring a suspension of 100 mg of $Ru_3(CO)_{12}$ with 100 mg of DPPA in hexane (50 ml), for 60 min at room temperature in the presence of Me_3NO; the resulting brick-red suspension contained about 30% of unchanged $Ru_3(CO)_{12}$, 30% of **1b**, and 10% of $Ru_3(CO)_{10}(DPPA)_2$.

Complex **2b** was obtained by refluxing for 1 min a suspension in hexane (50 ml) of 200 mg of $HRu_3(CO)_9(C_2Bu^t)$ and 100 mg of DPPA in the presence of Me_3NO; about 25% of unchanged starting material, 30% of orange **2b**, and 20% of a reddish derivative, tentatively identified as the disubstituted product, were isolated.

Complex **3b** was obtained in ca. 50% yield by refluxing a suspension $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_9$ in hexane (50 ml) with a small excess of DPPA in the absence of Me_3NO for 20 min; yields of ca. 50% of **3b** and ca. 20% of the disubstituted $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_7(DPPA)_2$ were obtained.

Complex **4b** was made by the above procedure but in heptane as a solvent and in the presence of Me_3NO; after only 2 min reflux yields of about 50% of **4b** and about 15% of the disubstituted $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_7(DPPA)_2$ were obtained. Interestingly, about 1% of $\{(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8\}_2$ (DPPA) (complex **4a**/**4b**) was also obtained.

Ligand exchange and thermal disproportionation reactions of clusters 1–4. As previously noted [21], CH_3CN is very easily displaced by CO and other ligands from all the complexes discussed here. In particular, complex **1a** is exceedingly unstable in the presence of CO. A few minutes are required for displacement of CH_3CN by DPPA in complexes **2a** or **4a** in refluxing hexane, and about 1 h in the same solvent at room temperature.

When a solution of complex $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(DPPA)$ in hexane was kept under N_2 at room temperature for 12 h small amounts of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_9$ and of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_7(DPPA)_2$ were formed. This reaction is much faster under reflux. Similarly when a solution of $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_8(DPPA)$ in hexane was refluxed for only 30 s ca. 40% of $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_7(DPPA)_2$ was formed along with decomposition products.

Cluster interlinking reactions

(a) Reactions of $Ru_3(CO)_{11}(CH_3N)$ (1a). When a small excess of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(DPPA)$ (**4b**) was added to a CH_2Cl_2 solution of freshly prepared **1a** kept at −78 °C and the stirred solution then allowed to warm to room temperature, no reaction occurred. Only after 40 min at 55 °C the solution had turned dark brown; considerable amounts of $Ru_3(CO)_{12}$ and small amounts (about 2% each) of two purple products were separated on the TLC plates, and identified as $\{(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8\}(DPPA)\{Ru_3(CO)_{11}\}$ (complex **1a**/**4b**) and $\{(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8\}_2(DPPA)$ (complex **4b**/**4b**).

(b) Reaction of $HRu_3(CO)_8(C_2Bu^t)(CH_3CN)$ (2a). A small excess of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8$ (DPPA) was added to a hexane solution of **2a**, at room temperature, and the solution was warmed to just below the reflux temperature. The mixture became brown-purple. Small amounts of $HRu_3(CO)_9C_2Bu^t$ and a yellow unidentified complex, and very small amounts (ca. 0.5%) of a brown-purple derivative, identified as $\{(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8\}(DPPA)\{HRu_3(CO)_8(C_2Bu^t)\}$ (complex **2a**/**4b**), were isolated. There was also extensive decomposition to give insoluble brown products.

(c) Reactions of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(CH_3CN)$ (4a). A small excess of $Ru_3(CO)_{11}(DPPA)$ was added to a hexane solution of **4a**; after 10 min reflux and TLC purification, considerable amounts of $Ru_3(CO)_{12}$ were isolated together with small yields (about 1% each) of complexes **1a/4b** and **4b/4b**.

A small excess of $HRu_3(CO)_8C_2Bu^t)(DPPA)$ was added to a hexane solution of **4a** and the solution was warmed to just below the reflux temperature. Work-up gave the products obtained from reaction (b) (above) again in ca. 1% yield.

A small excess of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(DPPA)$ was added to a hexane solution of **4a** and the solution was refluxed for 5 min. Small amounts of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_9$, about 30% of unchanged $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(DPPA)$, and about 3% of complex **4b/4b** were separated.

Complex **4a** was dissolved in hexane with a small excess of $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_8(DPPA)$ and a few ml of toluene were added to bring the ruthenium cluster into solution. The solution was refluxed for 30 s, during which extensive decomposition occurred. Small amounts of $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_9$, $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_9$, about 15% of $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_7(DPPA)_2$ were obtained, together with trace amounts of complex **4b/4b** and of a grey-purple derivative tentatively identified as $\{(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8\}(DPPA)\{(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_8\}$ (complex **4b/3b**).

Results and discussion

Spectroscopic characterization of the acetonitrile and DPPA derivatives. The analytical and spectroscopic data for the new derivatives $(\eta^5\text{-}C_5H_5)NiM_3H_3(CO)_{9-n}L_n$ (M = Ru, L = DPPA, $n = 1, 2$; M = Os, L = CH_3CN, DPPA, $n = 1, 2$), $Ru_3(CO)_{12}(DPPA)$ and $HRu_3(CO)_{9-n}L_n$ (L = CH_3CN, DPPA, $n = 1$) are listed in Table 1.

On the basis of the data for the complexes given in Table 1 we propose the structures shown schematically in Fig. 1.

The suggested structures are similar to those found for closely comparable derivatives; thus we previously synthesized several $(\eta^5\text{-}C_5H_5)NiM_3H_3(CO)_{9-n}L_n$ derivatives (M = Ru [21], M = Os [22]), some of which were studied by X-ray diffraction [23,24]. Moreover, the ^1H NMR signals from the hydridic nuclei for these derivatives are very useful for their unequivocal identification [24]. Bruce and coworkers have obtained and studied several $Ru_3(CO)_{11}L$ derivatives [25] showing spectroscopic features comparable with those of $Ru_3(CO)_{11}(DPPA)$. We have also previously made some $HRu_3(CO)_8L(C_2Bu^t)$ derivatives (L = PR_3 [26,27], PPh_2C_2R [28]) that can be compared with the substituted derivatives here discussed.

Some comments on the thermal disproportionation and ligand substitution reactions of complexes 1–4. During examination of homogeneous catalysis in the presence of $(\eta^5\text{-}C_5H_5)NiM_3H_3(CO)_{9-n}L_n$ and $Ru_3(CO)_{12-n}L_n$ [21] we found that these derivatives generally undergo disproportionations. We also observed that the ease of displacement of the ligands rises in the following sequence [21]: $CH_3CN \ll SbPh_3 < DPPM \simeq DPPA < PPh_3 < CO$. This observation was consistent with our finding in the present study, as DPPA readily displaces CH_3CN. However, the thermal disproportionation reactions mentioned above as well as the presence of CO, strongly reduces the yields of interlinked derivatives. Under CO, which is always present in small amounts, $Ru_3(CO)_{11}(CH_3CN)$ and $(\eta^5\text{-}C_5H_5)NiRu_3H_3(CO)_8$

Table 1. Analytical and spectroscopic data for complexes **1–4**

Complex	Physical properties	Elemental analysis (Found (calcd.)(%))				IR (ν(CO)), hexane (cm^{-1})	^{1}H NMR (δ, $CDCl_3$, 25 °C)	^{31}P NMR (δ, $CDCl_3$) [a]
		C	H	P(N)	Ru			
DPPA derivatives								
$Ru_3(CO)_{11}$(DPPA) (**1b**)	orange-red solid	45.1 (44.19)	1.88 (2.00)	6.15 (6.16)	29.8 (30.15)	2098m, 2061m, 2047vs, 2030vs, 2012vs	7.50–7.30 mm (Ph)	+7.50s(1) [c] −31.0s(1)
$HRu_3(CO)_8(C_2Bu^t)$-(DPPA) (**2b**)	orange solid	51.4 (51.35)	3.0 (2.81)	6.02 (5.76)	29.6 (28.18)	2077m-s, 2057vs, 2016vs, 2007vs, 1958m(b)	7.81–7.35 mm(20H,Ph): 1.36 s (9H,Bu^t): −21.20 t (1H,hydride)	+25.33s(1) −30.70s(1)
(Cp)$NiRu_3H_3(CO)_8$-(DPPA) (**3b**)	dark-green solid	45.2 (44.68)	2.8 (2.69)	6.2 (5.91)	28.0 (28.92)	2074m, 2050vs, 2024vs, 2006s, 1996w	7.60–7.11 mm(20H,Ph): 5.76 s(5H,Cp): −15.29 dd(2H), −15.46 t(1H, hydrides)	+4.43, +4.36d (1) −31.45s (1)
(Cp)$NiRu_3H_3(CO)_7$-$(DPPA)_2$	dark-green solid	55.0 (54.33)	3.5 (3.42)	9.1 (8.76)	21.1 (21.43)	2058s, 2021vs, 2016vs, (sh), 1987m(b), 1968m(b)	7.59–7.10 mm (40H,Ph): 5.68 s(5H,Cp): −14.55 tt(1H), −15.30 d(2H,hydrides).	+2.88s (1) −31.32s (1)
(Cp)$NiOs_3H_3(CO)_8$-(DPPA) (**4b**)	purple solid	37.0 (35.6)	2.3 (2.14)	5.1 (4.71)	44.1 (43.37)	2078s, 2058vs, 2022vs, 2000s, 1990s, 1961m	7.88–7.38 (20H,Ph) 6.06 s(5H,Cp): −16.88 dd(2H), −17.83 t(1H, hydrides)	+6.87s (1) −31.05s (1)
CH_3CN derivatives								
$HRu_3(CO)_8(C_2Bu^t)$-(CH_3CN) (**2a**)	light yellow solid	37.0 (36.57)	1.9 (1.81)	2.1 [b] (1.94)		2075vs, 2031vs, 2022s (sh), 2012vs	–	
(Cp)$NiOs_3H_3(CO)_8$-(CH_3CN) [d] (**4a**)	green-purple solid	19.1 (18.72)	1.33 (1.15) [e]			2076ms, 2057vs, 2016vs, 1994s, 1977s, 2250w (b) (CN)	5.92 s(5H,Cp): 3.24 s (3H,Me): −14.74 d (2H), −19.71 t (1H,hydrides)	–

[a] H_3PO_4, room temperature. [b] N. [c] Intensity in parentheses. [d] An accurate TLC separation revealed the presence of this product and of another green-purple band with a closely comparable elemental analysis: IR 2079m-s, 2056vs, 2011vs, 1990vs(b), 1944m-s(b): ^{1}H NMR, 5.86s(5H,Cp): 2.62s(3H,Me): −15.83s(1H), −16.95s(1H), −21.29s(1H, hydrides). Tentative identification, equatorial isomer. [e] The analysis of H in the presence of Os gives frequently uncorrect values.

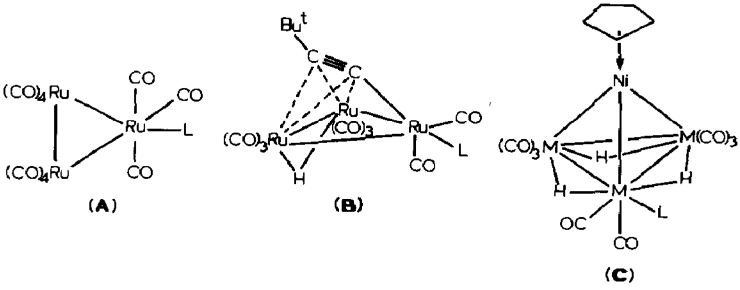

Fig. 1. Proposed structures for complexes **1a**,**1b** (A), **2a**,**2b** (B), **3b** (M = Ru) **4a**,**4b** (M = Os) (C).

(CH_3CN) are exceedingly unstable, and $HRu_3(CO)_8(C_2Bu^t)(CH_3CN)$ is only a little more resistant; thus, only $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(CH_3CN)$ is available in useful amounts for interlinking reactions.

Analytical and spectroscopic characterization of the cluster interlinking derivatives. The analytical and spectroscopic data for the complexes obtained from the reactions shown in Scheme 1 are listed in Table 2.

The yields of these products are usually very low, and for this reason sometimes complete spectroscopic characterization was impossible. Furthermore, rearrangements in solution made it very difficult to form crystals of the derivatives.

Identification of the interlinked derivatives was possible, however, especially when different metal fragments were present, by infrared analyses as well as by "cross reactions"; for instance, the identity of complex **1a**/**4b** was established by elemental analyses, comparison of the IR spectrum with those of the parent clusters (see discussion below), and by independent preparations of the complex via the reaction of $Ru_3(CO)_{11}(CH_3CN)$ with $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(DPPA)$ and comparison of this with the products obtained from $Ru_3(CO)_{11}(DPPA)$ and $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(CH_3CN)$. The identity of the products obtained was used as evidence for the interlinked nature of the product.

The same procedure was adopted for other derivatives. Finally, the identity of complex **4b**/**4b** was established from analytic results and spectroscopy; the slightly higher yields obtained for this derivative allowed recording of ^1H and ^{31}P NMR spectra and their integration. These showed the presence of two cyclopentadienyl ligands and of four phenyl groups, and a hydridic pattern close to that of the parent complex. A singlet in the ^{31}P NMR confirmed the equivalence of the two phos-

Scheme 1. Interlinking reactions described in the present work

$$\left.\begin{array}{l}\mathrm{Ru_3(CO)_{11}(CH_3CN) + (Cp)NiOs_3H_3(CO)_8(DPPA)}\\ \mathrm{Ru_3(CO)_{11}(DPPA) + (Cp)NiOs_3H_3(CO)_8(CH_3CN)}\end{array}\right\} \rightarrow \begin{array}{c}\mathrm{\{(Cp)NiOs_3H_3(CO)_8\}(DPPA)}\\ \mathrm{\{Ru_3(CO)_{11}\}}\\ \mathrm{\{(Cp)NiOs_3H_3(CO)_8\}_2(DPPA)}\end{array}$$

$$\left.\begin{array}{l}\mathrm{HRu_3(CO)_8(C_2Bu^t)(CH_3CN) + (Cp)NiOs_3H_3(CO)_8(DPPA)}\\ \mathrm{HRu_3(CO)_8(C_2Bu^t)(DPPA) + (Cp)NiOs_3H_3(CO)_8(CH_3CN)}\end{array}\right\} \rightarrow \begin{array}{c}\mathrm{\{(Cp)NiOs_3H_3(CO)_8\}(DPPA)}\\ \mathrm{\{HRu_3(CO)_8(C_2Bu^t)\}}\end{array}$$

$$\mathrm{(Cp)NiOs_3H_3(CO)_8(CH_3CN) + (Cp)NiOs_3H_3(CO)_8(DPPA) \rightarrow \{(Cp)NiOs_3H_3(CO)_8\}_2(DPPA)}$$

$$\mathrm{(Cp)NiOs_3H_3(CO)_8(CH_3CN) + (Cp)NiRu_3H_3(CO)_8(DPPA) \rightarrow} \begin{array}{c}\mathrm{\{(Cp)NiOs_3H_3(CO)_8\}(DPPA)}\\ \mathrm{\{(Cp)NiRu_3H_3(CO)_8\}}\end{array}$$

Table 2

Analytical and spectroscopic data for the interlinked derivatives

Complex	Physical	Elemental analysis (Found (calcd.)(%))				IR (ν(CO)), hexane (cm^{-1})	^{1}H, ^{31}P NMR [a]
		C	H	P	Ni		
(Cp)NiOs$_3$H$_3$(CO)$_8$(DPPA)-Ru$_3$(CO)$_{11}$ **(1a/4b)**	purple solid	31.9 (31.16)	1.8 (1.46)	3.3 (3.21)		2098m-s, 2078s, 2060s(sh), 2058vs, 2047s(sh), 2030s (sh), 2022vs(sh), 2012vs, 1994s, 1978s	–
(Cp)NiOs$_3$H$_3$(CO)$_8$(DPPA)-HRu$_3$(CO)$_8$(C$_2$Bu^t) **(2a/4b)**	grey solid	35.1 (35.48)	2.22 (1.92)	3.2 (3.10)		2077s, 2050vs, 2031s(sh), 2020vs, 2016s(sh), 2007m(sh), 1997s, 1979s, 1971m-w(b)	–
(Cp)NiOs$_3$H$_3$(CO)$_8$(DPPA)-CpNiRu$_3$H$_3$(CO)$_8$ **(4b/3b)**	grey-purple solid	31.9 (31.70)	2.12 (1.84) [b]			2076s, 2057vs, 2050(sh), 2024vs, 2016vs(sh), 2006m, 1997s, 1978s	–
(Cp)NiOs$_3$H$_3$(CO)$_8$(DPPA)-(Cp)NiOs$_3$H$_3$(CO)$_8$ **(4b/4b)**	purple solid	28.1 (27.91)	2.1 (1.62)	2.8 (2.77)	5.3 (5.29)	2078s, 2058vs, 2022vs, 2000s, 1990s, 1961m(b)	7.88–7.38mm (Ph): 6.06 (Cp): −16.92d, −17.83t (hydrides) [c]

[a] CDCl$_3$, room temperature. [b] The analysis of H in the presence of Os gives often incorrect values. [c] ^{31}P NMR (H$_3$PO$_4$): −6.93s(1), +6.87s(1). Several runs, on different samples gave always the same result; as equivalent P atoms are expected for this complex, the observed behaviour may be due to dissociation in solution.

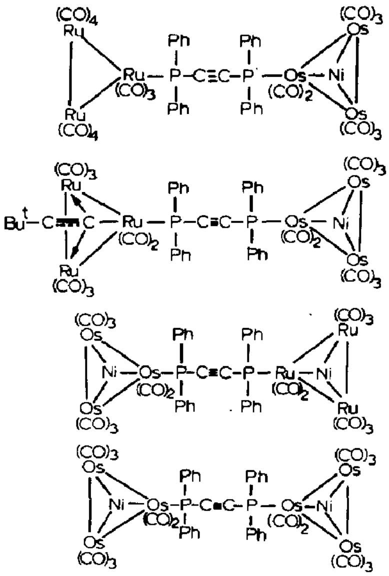

Fig. 2. Proposed structures for the interlinked derivatives (see Table 2 and Scheme 1). Hydridic hydrogens and (Cp) ligands on the $NiRu_3$ and $NiOs_3$ fragments have been omitted for clarity.

phorus atoms. Complex **4b/4b** was obtained in various reactions, as described in the experimental section, probably because of the stability of the parent fragments.

Further evidence for the identities of the complexes comes from the analysis of the infrared spectra (see Table 2); thus, for example the spectrum of **4b/4b** is very similar to that of the parent $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8L$ derivatives. Similar behaviour was previously observed for $\{Ru_3(CO)_{11}\}_2(DPPA)$ [26].

In contrast, the IR spectra of the products with two different fragments interlinked would be roughly the sum of those of the parent derivatives, the fragments being too far apart for significant interactions.

The structures of the interlinked complex reported in this work are shown schematically in Fig. 2; they are based on the reasoning given above and an analogy with known complexes of similar nature [16,26].

Concluding remarks

We have shown that it is possible to use the residual reactivity of phosphino-acetylenes and of diphosphino-acetylenes for interlinking of metal fragments; in particular, from $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(PPh_2C_2R)$ and $Co_2(CO)_8$ we obtained $(\eta^5\text{-}C_5H_5)NiOs_3H_3(CO)_8(PPh_2C_2R)Co_2(CO)_6$ [14] under mild conditions by using the alkyne triple bond to coordinate to $Co_2(CO)_6$.

In contrast, use of DPPA in comparable procedures gave only low yields of the expected products, and this approach, although possible, is not satisfactory, at least for the complexes described in this work. It is also noteworthy that diphosphines such as DPPM and DPPE tend to give better yields of interlinked products than does DPPA under comparable conditions [10b,10e]; this could be due either to steric effects (rigid steric requirements of the DPPA) or to electronic effects (too high an electron density on DPPA and low retrodonation to the clusters). Studies aimed at ascertaining whether metal fragments able to interact with the triple bond of DPPA give better yields of interlinked products are in progress.

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