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Neutral and cationic diphenylphosphine and diphenylphosphido derivatives of a trinuclear ruthenium carbonyl cluster containing a bridging 1-azavinylidene ligand

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Abstract

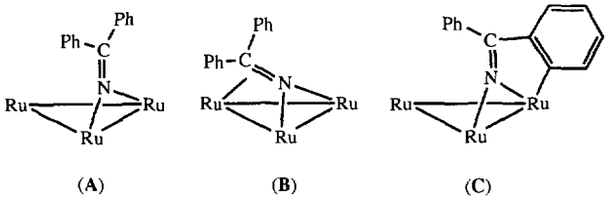
The synthesis and some reactivity of a number of neutral and cationic diphenylphosphine and/or diphenylphosphido derivatives of the 1-azavinylidene cluster compound $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**) are described. Compound **1** reacts with diphenylphosphine to give the substituted derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_2H)(CO)_9]$ (**2**). Thermolysis of compound **2** leads to the dihydrido-μ-phosphido derivative $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_8]$ (**3**), which on exposure to carbon monoxide is converted into the non-hydridic derivative $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_9]$ (**4**). Treatment of complex **3** with diphenylphosphine gives $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(PPh_2H)(CO)_7]$ (5). Compounds **2**, **4**, and **5** undergo protonation with $HBF_4 \cdot OEt_2$ to give the cationic derivatives $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(PPh_2H)(CO)_9][BF_4]$ (**8**), $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_9][BF_4]$ (**9**), and $[Ru_3(\mu\text{-}H)_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(PPh_2H)(CO)_7][BF_4]$ (**10**), respectively. The syntheses of these cationic complexes represent rare examples in which the protonation of neutral phosphido-bridged compounds has been achieved. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Clusters; Carbonyls; Diphenylphosphine; Diphenylphosphide; 1-Azavinylidene; Protonation reactions; Cationic clusters

1. Introduction

Mono- and binuclear complexes containing 1-azavinylidene ligands are currently being studied with interest. [1, 2] However, until recently, the presence of these ligands in trinuclear cluster compounds has been limited to a few old examples of iron [12–14], ruthenium [15–19], and osmium [20–23]. These clusters have generally been prepared in medium to low yields by reacting organic nitriles with molecular hydrogen in the presence of the appropriate cluster complex or by treating organic nitriles with hydrido trinuclear clusters. The low efficiency of these synthetic methods has probably prevented the development of the derivative chemistry of these trinuclear clusters.

Recently, we have described a high-yield synthesis of the 1-azavinylidene ruthenium cluster compound $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**) [24]. The preparation involves treatment of $[Ru_3(CO)_{12}]$ with the lithium salt of benzophenone imine followed by titration with a protic acid. We have also reported that reactions of compound **1** with bis(diphenylphosphino)methane and triphenylphosphine afforded substituted derivatives in which the 1-azavinylidene ligand displays different coordination modes, as shown below in Chart 1 [24].



We now report the synthesis and some reactivity of diphenylphosphine and diphenylphosphido derivatives of compound **1**. These studies have led, not only to new neutral trinuclear cluster complexes containing one or

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[1] For recent examples of mononuclear complexes containing 1-azavinylidene ligands, see Refs. [1–9].

[2] For recent papers on binuclear complexes containing 1-azavinylidene ligands, see Refs. [10,11].

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two diphenylphosphido bridges, but also to phosphido-bridged cationic derivatives. To date, although a few cationic complexes which contain phosphido ligands are known [25–33], those being carbonyl derivatives, such as $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]Cl$ [32] and $[M_2(\mu\text{-}PPh_2)(CO)_8][BF_4]$ (M = Fe, Ru) [33], are very rare [32–34].

2. Results and discussion

2.1. Neutral derivatives of compound 1

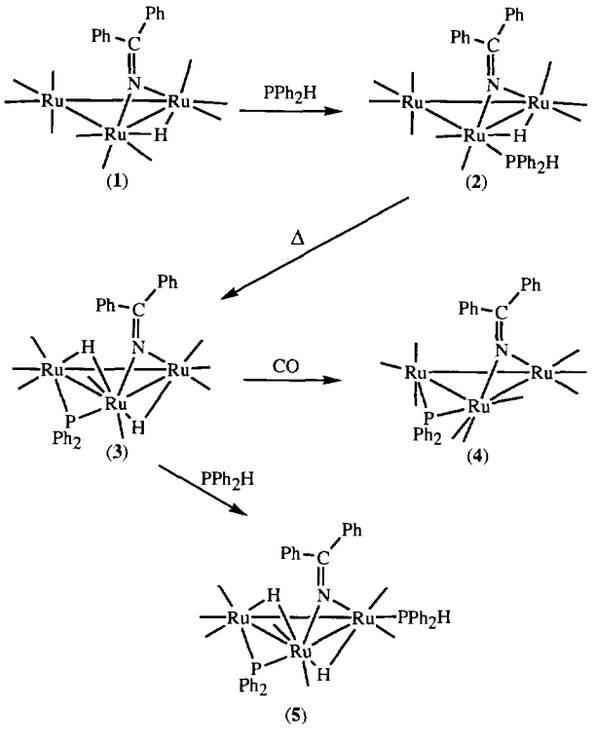
Treatment of compound **1** with diphenylphosphine in THF at room temperature led to the monosubstituted derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_2H)(CO)_9]$ (**2**). The use of an excess of diphenylphosphine at room temperature reduced the reaction time without formation of a disubstituted derivative. Attempts to make such disubstituted compound by increasing the temperature led to inseparable mixtures of complexes. The structure proposed for compound **2** in Scheme 1 is based on its spectroscopic IR (Table 1) and NMR (Table 2) data and on the similarity of these spectra with those of the related known compound $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_3)(CO)_9]$ [24].

Thermolysis of compound **2** in THF at reflux temperature led to the dihydrido-μ-phosphido derivative $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_8]$ (**3**). Its $^{13}C\{^1H\}$ NMR spectrum shows the presence of eight carbonyl ligands and its FAB mass spectrum contains the correct molecular ion. Since the phosphido and 1-azavinylidene ligands (as 3-electron donors) should have similar coordination properties, the structure proposed for complex **3** in Scheme 1 is similar to that of the related cluster of C_2 symmetry $[Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8]$ [35], in which the two hydride ligands

Table 1
Selected IR data

Compound	ν(CO) (cm^{-1})
2[a]	2081 (m), 2045 (vs), 2010 (vs), 1990 (m), 1979 (m), 1956 (w)
3[a]	2081 (m), 2044 (vs), 2028 (s), 2013 (m), 1985 (m), 1967 (w)
4[a]	2069 (w), 2041 (vs), 1998 (m), 1990 (m)
5[a]	2050 (s), 2020 (vs), 2007 (s), 1985 (s), 1973 (sh), 1956 (m)
6[a]	2060 (m), 2020 (sh), 2014 (vs), 2001 (m), 1989 (sh), 1958 (m)
7[a]	2077 (m), 2042 (vs), 2027 (m), 2013 (m), 1983 (m), 1970 (w)
8[b]	2130 (m), 2087 (s), 2074 (s), 2054 (vs), 2024 (m)
9[b]	2128 (w), 2114 (vs), 2073 (s), 2058 (s)
10[b]	2133 (w), 2115 (m), 2083 (sh), 2075 (s), 2058 (vs), 2017 (m), 1999 (sh)

[a] In THF. [b] In CH_2Cl_2.



Scheme 1.

span the same Ru–Ru edges as the phosphido ligands. This proposal is also supported by the ^1H NMR spectrum, which shows the hydride resonances as doublets with J(H–P) coupling constants of 19.3 and 28.7 Hz (Table 2). These values are within the respective ranges observed for cluster compounds having hydride and diphenylphosphido ligands spanning the same [35–39] or different [34,37–40] Ru–Ru edges.

We have previously reported that the thermolysis of $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-dppm})(CO)_8]$ leads to the derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(\mu\text{-dppm})(CO)_7]$, which contains the 1-azavinylidene in a face-bridging fashion (Chart 1, structure B) [24]. However, compound **3** remained unchanged when it was refluxed in THF for 2 h.

Exposure of a THF solution of complex **3** to carbon monoxide (gas bubbled, room temperature) led to the non-hydridic derivative $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_9]$ (**4**), in which a CO ligand has been substituted for the two hydride ligands. No evidence for the formation of compound **2** was observed by spot TLC and NMR spectroscopy, indicating that the transformation of **2** into **3** is irreversible.

Interestingly, the reaction of compound **3** with a 2-electron donor ligand different from CO, such as diphenylphosphine, did not lead to the substitution of dihydrogen, but to the CO-substituted dihydride derivative $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(PPh_2H)(CO)_7]$ (**5**). The structure proposed in Scheme 1 for this com-

Table 2
Selected ^{1}H and $^{31}P\{^{1}H\}$ NMR data

Compound	$\delta(\mu$-H) (ppm[a])	δ(P) (ppm[a])
2[b]	−13.60 (d) [7.1]	14.5 (s)
3	−13.96 (d) [19.3], −14.68 (d) [28.7]	142.4 (s)
4		100.1 (s)
5[c,d]	−14.02 (dd) [13.1, 5.2], −14.16 (dd) [6.2, 5.9]	154.5 (s), 22.1 (s)
6	−15.92 (dd) [19.9, 17.9]	178.9 (d), 164.9 (d) {123.3}
7[c]	−16.50 (t) [22.8]	164.0 (s)
8[e]	−13.23 (d) [11.5], −16.95 (d) [27.1]	24.6 (s)
9	−10.62 (d) [25.9]	75.0 (s)
10[c,f]	−13.95 (ddm) [17.8, 7.1], −14.09 (dm) [18.3], −20.33 (dm) [20.6]	147.0 (s), 34.3 (s)

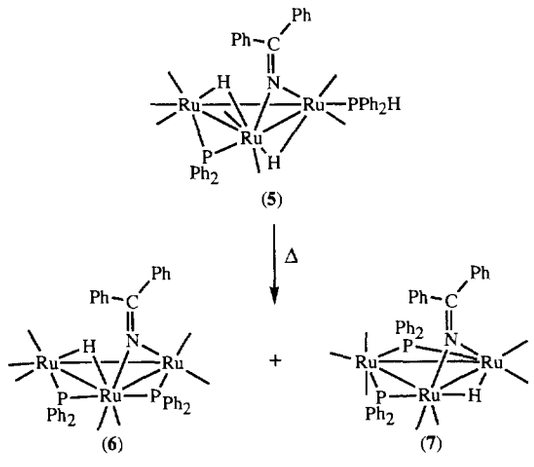
[a]Spectra were recorded in $CDCl_3$; multiplicities are given in parentheses; coupling constants (J, Hz) are given in square brackets [J(H–P)] or braces {J(P–P)}. [b]$\delta(PH) = 5.61$ (d, $J = 355.8$ Hz). [c]In CD_2Cl_2. [d]$\delta(PH)$ is obscured by the phenyl resonances. [e]$\delta(PH) = 6.16$ (d, $J = 355.8$ Hz). [f]$\delta(PH) = 5.91$ (d, $J = 374.8$ Hz).

plex is based on its $^{31}P\{^{1}H\}$ NMR spectrum, which does not show coupling between the two phosphorus atoms (Table 2), thus indicating that the phosphine ligand is attached to the Ru atom unbound to the phosphido ligand. This structural proposal is also supported by the stronger *cis*-labilizing effect of the azavinylidene ligand as compared to that of the phosphido ligand, which has a softer character than the azavinylidene ligand.

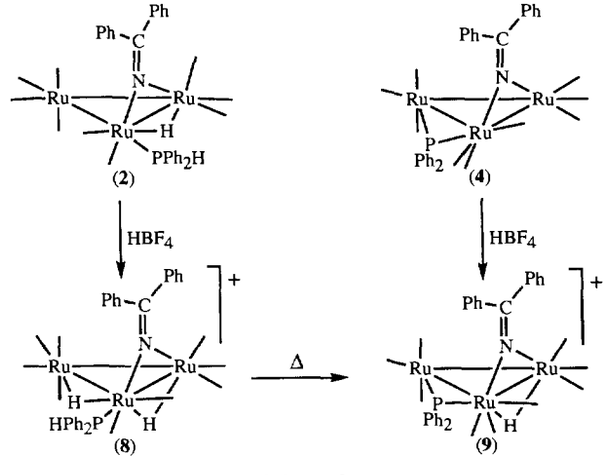
Thermolysis of compound **5** in 1,2-dichloroethane at reflux temperature led to a 3:1 mixture of the asymmetric (**6**) and symmetric (**7**) bis(phosphido) isomers of $[Ru_3(\mu\text{-H})(\mu\text{-N=CPh}_2)(\mu\text{-PPh}_2)_2(CO)_7]$. The composition of the mixture was established by integration of the $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction solution. Both compounds were separated by chromatographic methods. The structures proposed for these complexes in Scheme 2 are based on their spectroscopic data. Complex **6** shows two doublets in its $^{31}P\{^{1}H\}$ NMR spectrum, whereas that of compound **7** contains only one singlet. Accordingly, the ^{1}H NMR spectra of these compounds show the hydride resonance as a double doublet and as a triplet, respectively (Table 2). An alternative structural proposal for compound **6**, analogous to that of compound **7** but with the hydride ligand spanning one of the phosphido-bridged Ru–Ru edges, cannot be ruled out. However, we think that this structure is less probable than that depicted in Scheme 2 because hydride ligands in cluster complexes can, in general, move readily between metal edges to give the thermodynamically most stable derivative [41,42]. Unfortunately, no single crystals of compound **6** could be obtained and therefore its structure could not be unambiguously determined. The structure of the symmetric compound $[Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7]$, related to complex **7**, has been established by X-ray diffraction methods [37].

2.2. Cationic derivatives of compound *1*

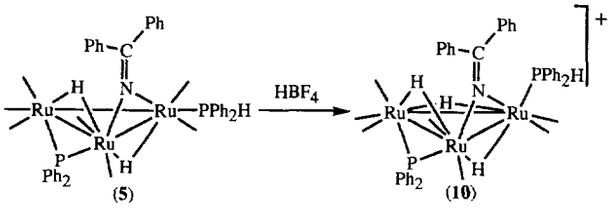
Protonation of compound **2** with an excess of $HBF_4 \cdot OEt_2$ in dichloromethane led to the cationic dihydride $[Ru_3(\mu\text{-H})_2(\mu\text{-N=CPh}_2)(PPh_2H)(CO)_9][BF_4]$ (**8**) in quantitative spectroscopic yield (Scheme 3). This reaction is related to those reported for the complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-ampy})(L)(CO)_8]$ (L = PPh_2H [34], PC_3 [42], PPh_3 [43]) and $[Ru_3(\mu\text{-H})(\mu_3$-



Scheme 2.



Scheme 3.



Scheme 4.

ampy)$(PPh_3)_2(CO)_7$] (Hampy=2-amino-6-methylpyridine) [44], which undergo protonation to give cationic dihydrido derivatives in which the phosphine ligand has moved from its original position in the corresponding neutral precursor to an adjacent equatorial position *cis* to the new bridging hydride ligand.

Thermolysis of compound **8** in 1,2-dichloroethane at reflux temperature led to the cationic phosphido-bridged derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_9][BF_4]$ (**9**) as the major component of a mixture of products which could not be separated due to their cationic character. Alternatively, compound **9** could be cleanly prepared by protonation of compound **4** with $HBF_4 \cdot OEt_2$ in dichloromethane.

The reactions that lead to compound **9** are exceptional in the sense that previous attempts to protonate neutral phosphido-bridged carbonyl cluster complexes have failed [34]. Analogously, previous attempts to obtain phosphido-bridged cationic carbonyl cluster compounds by thermolysis of $[BF_4]^-$ salts of cationic precursors having hydride and diphenylphosphine ligands have also been unsuccessful [34], since these reactions lead to HBF_4 and to neutral phosphido-bridged derivatives which do not undergo protonation. Therefore, compound **9** is a rare example of a cationic phosphido-bridged carbonyl cluster complex. However, the protonation of non-carbonyl phosphido-bridged binuclear complexes has been achieved in some instances [30,31].

In an attempt to make a cationic carbonyl cluster complex containing two bridging phosphido ligands, compound **8** was treated with diphenylphosphine in 1,2-dichloroethane at reflux temperature, but this reaction led to a mixture of compounds **7** and **9**.

Compound **3** reacted with $HBF_4 \cdot OEt_2$ in dichloromethane solution to give products which could not be identified. However, its substituted derivative **5** underwent protonation under similar conditions to give the cationic phosphido-bridged cluster $[Ru_3(\mu\text{-}H)_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(PPh_2H)(CO)_7][BF_4]$ (**10**). The structure proposed for this complex in Scheme 4 is based on analytical and spectroscopic data (Tables 1 and 2). Its cationic character was clearly evidenced by its IR spectrum, which shows the carbonyl absorptions at much higher wavenumbers than those of its neutral precursor (Table 1), reflecting a decrease of electron density in the metal atoms on protonation (the same occurs with the cationic compounds **8** and **9**). Three hydride resonances are observed in the proton NMR spectrum, all coupled to phosphorus atoms, as corresponds to a trihydride compound. This structural proposal would not be supported by X-ray diffraction studies, since we could not obtain appropriate single crystals of the compound.

In a further attempt to prepare a cationic carbonyl cluster complex containing two bridging phosphido ligands, we carried out the thermolysis of compound **10** in 1,2-dichloroethane at reflux temperature, but we obtained a mixture of many compounds that we could not separate.

3. Concluding remarks

This article describes new compounds in which diphenylphosphine and/or diphenylphosphido ligands coexist with 1-azavinylidene ligands in the coordination shell of trinuclear ruthenium carbonyl clusters. It also reports the first preparation of cationic phosphido-bridged carbonyl cluster compounds by protonation of neutral precursors. This class of compounds is uncommon and the few previously known examples have been made by sophisticated methods [32,33]. Moreover, previous attempts to make compounds of this type by protonation of neutral precursors have been unsuccessful [34].

Unlike some triphenylphosphine and bis(diphenylphosphino)metane derivatives of complex **1**, in which the 1-azavinylidene ligand behaves as a 5-electron donor ligand or shows orthometallation of one of the phenyl rings [24], the diphenylphosphine and diphenylphosphido derivatives of compound **1** described in this paper contain the 1-azavinylidene ligand in its normal edge-bridging, 3-electron N-donor, coordination mode. [3]

4. Experimental section

4.1. General data

Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitro-

[3] The ^{13}C NMR chemical shifts of the azavinylidene carbon $N{=}CPh_2$ in compounds containing this ligand as an edge-bridging 3-electron N-donor are within the range 190–180 ppm, whereas those of compounds containing this ligand as a face-bridging 5-electron donor are within the range 130–150 ppm [24].

gen prior to use. Unless otherwise stated, the reactions were carried out under nitrogen at room temperature, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot thin layer chromatography (TLC). Compound **1** was prepared as described previously [24]. All other reagents and TLC plates were used as received from Aldrich. Infrared spectra were recorded on a Perkin–Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were run at 20°C with Bruker AC-200 and AC-300 instruments, using $SiMe_4$ (internal, for ^1H and ^{13}C) or 85% H_3PO_4 (external, for ^{31}P) as standards ($\delta = 0$ ppm). Fast atom bombardment mass spectra were obtained on a Finningan Mat-95 spectrometer, using nitrobenzyl alcohol as matrix and cesium as bombarding gas. Microanalyses were obtained from the University of Oviedo Analytical Service. Carbonyl IR absorptions and relevant ^1H and ^{31}P NMR data are given in Tables 1 and 2, respectively.

4.2. $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(PPh_2H)(CO)_9]$ (2)

Diphenylphosphine (100 μl, 0.576 mmol) was injected into a solution of compound **1** (200 mg, 0.260 mmol) in THF (20 ml). After stirring for 12 h, the solvent was removed under reduced pressure and the residue was washed with hexane (5 ml) to give complex **2** as an orange solid (180 mg, 74%). Anal. Found: C, 44.13; H, 2.65; N, 1.40. Calcd for $C_{34}H_{22}NO_9PRu_3$: C, 44.26; H, 2.40; N, 1.52. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 215 K): 209.3 (s, 1 C), 207.7 (d, $J = 6.6$, 1 C), 206.9 (s, 1 C), 202.5 (s, 1 C), 197.3 (d, $J = 6.5$, 1 C), 196.6 (s, 1 C), 195.2 (d, $J = 9.2$, 1 C), 194.5 (s, 1 C), 186.7 (s, 1 C) (9 CO ligands); 179.3 (s, 1 C, N=CPh_2), 148.7 (s, 1 C, C'_{ipso} of N=CPh_2), 143.9 (s, 1 C, C'_{ipso} of N=CPh_2) ppm.

4.3. $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_8]$ (3)

A solution of compound **2** (80 mg, 0.087 mmol) in THF (10 ml) was stirred at reflux temperature for 2 h. The solvent was removed under reduced pressure and the residue was separated by column chromatography (neutral alumina, activity I, 15 × 2 cm). Hexane–toluene (1:1) eluted two bands. The first band (pale yellow) was not investigated. The second band (yellow) afforded compound **3** as a yellow-orange solid (70 mg, 90%). Anal. Found: C, 44.95; H, 2.52; N, 1.49. Calcd for $C_{33}H_{22}NO_8PRu_3$: C, 44.30; H, 2.49; N, 1.57. MS (m/z): 895 (M^+). Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 295 K): 203.2 (s, 1 C), 202.3 (s, 1 C), 199.9 (d, $J = 3.8$, 1 C), 198.5 (d, $J = 6.1$, 1 C), 194.2 (s, 1 C), 193.4 (d, $J = 5.9$, 1 C), 191.4 (d, $J = 8.4$, 1 C), 184.8 (s, 1 C) (8 CO ligands); 180.4 (s, 1 C, N=CPh_2), 146.3 (s, 1 C, C_{ipso} of N=CPh_2), 145.1 (s, 1 C, C'_{ipso} of N=CPh_2) ppm.

4.4. $[Ru_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_9]$ (4)

Carbon monoxide was bubbled through a solution of compound **3** (50 mg, 0.056 mmol) in THF (10 ml) for 1 h. The solvent was removed under reduced pressure and the residue was washed with pentane (2 ml) to give compound **4** as an orange solid (45 mg, 87%). Anal. Found: C, 44.62; H, 2.33; N, 1.39. Calcd for $C_{34}H_{20}NO_9PRu_3$: C, 44.35; H, 2.19; N, 1.52. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 200 K): 204.8 (s, 1 C), 203.3 (m, 3 C), 200.4 (s, 1 C), 199.2 (s, 1 C), 193.4 (s, 2 C), 193.0 (s, 1 C) (9 CO ligands); 182.3 (s, 1 C, N=CPh_2), 146.3 (s, 1 C, C_{ipso} of N=CPh_2), 136.4 (s, 1 C, C'_{ipso} of N=CPh_2) ppm.

4.5. $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(PPh_2H)(CO)_7]$ (5)

Diphenylphosphine (7.8 μl, 0.045 mmol) was injected into a solution of compound 3 (40 mg, 0.045 mmol) in THF (10 ml). The colour changed from orange to red. After stirring for 15 min, the solvent was removed under reduced pressure. The residue was dissolved in hexane (2 ml) and was separated by column chromatography (neutral alumina, activity IV, 15 × 2 cm). Hexane–toluene (5:1) eluted an orange band which gave complex **5** as an orange-red solid (30 mg, 63%). Anal. Found: C, 50.45; H, 3.34; N, 1.18. Calcd for $C_{44}H_{33}NO_7P_2Ru_3$: C, 50.19; H, 3.16; N, 1.33. Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 200 K): 206.9 (m, 1 C), 206.6 (m, 1 C), 202.0 (m, 1 C), 200.1 (m, 1 C), 198.0 (s, 1 C), 194.3 (d, $J = 8.5$, 1 C), 193.9 (s, 1 C) (7 CO ligands); 180.3 (s, 1 C, N=CPh_2), 149.7 (s, 1 C, C_{ipso} of N=CPh_2), 146.2 (s, 1 C, C'_{ipso} of N=CPh_2) ppm.

4.6. $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)_2(CO)_7]$ (Isomer 6)

A solution of compound **5** (30 mg, 0.029 mmol) in 1,2-dichloroethane (20 ml) was stirred at reflux temperature for 12 h. The solvent was removed under reduced pressure and the residue was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed a 3:1 mixture of the isomers **6** and **7**. The dry residue was dissolved in toluene (1 ml) and the solution was applied onto preparative TLC plates (silica gel). Hexane–toluene (10:3) eluted two bands. The first band, pale yellow, contained a small amount of compound **7** (IR identification). The second band, orange, afforded compound **6** as an orange solid (15 mg, 49%). Anal. Found: C, 50.63; H, 3.15; N, 1.19. Calcd for $C_{44}H_{31}NO_7P_2Ru_3$: C, 50.29; H, 2.97; N, 1.33.

4.7. [$Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)_2(CO)_7$] (Isomer 7)

A solution of compound **8** (50 mg, 0.050 mmol) and diphenylphosphine (10 μl, 0.058 mmol) in 1,2-dichloroethane (20 ml) was stirred at reflux temperature for 45 min. The solvent was removed under reduced pressure and the residue was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy, which showed a 2:3 mixture of compounds **7** and **9**. The dry residue was dissolved in dichloromethane (1 ml) and the solution was applied onto preparative TLC plates (silica gel). Hexane–dichloromethane (1:1) eluted a yellow band which afforded compound **7** as a yellow solid (10 mg, 19%). Anal. Found: C, 50.51; H, 3.12; N, 1.25. Calcd for $C_{44}H_{31}NO_7P_2Ru_3$: C, 50.29; H, 2.97; N, 1.33.

4.8. [$Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(PPh_2H)(CO)_9$][$BF_4$] (8)

A solution of compound **2** (150 mg, 0.163 mmol) in dichloromethane (10 ml) was treated with an excess of $HBF_4 \cdot OEt_2$ (0.5 ml). The solvent was removed under reduced pressure and the residue was washed with diethyl ether (3 × 5 ml) to give compound **8** as an orange solid (140 mg, 85%). Anal. Found: C, 40.63; H, 2.34; N, 1.24. Calcd for $C_{34}H_{23}BF_4NO_9PRu_3$: C, 40.41; H, 2.29; N, 1.39. MS (*m/z*): 924 (M^+). Selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 200 K): 197.5 (s, 1 C), 196.7 (s, 1 C), 195.7 (d, J = 10.1, 1 C), 193.5 (s, 1 C), 190.8 (d, J = 13.6, 1 C), 190.2 (s, 1 C), 187.6 (d, J = 12.6, 1 C), 185.0 (s, 1 C), 183.9 (s, 1 C) (9 CO ligands); 183.1 (N=CPh_2), 146.8 (s, 1 C, C_{ipso} of N=CPh_2), 144.6 (s, 1 C, C'_{ipso} of N=CPh_2) ppm.

4.9. [$Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(CO)_9$][$BF_4$] (9)

4.9.1. Method (a)

A solution of compound **4** (30 mg, 0.033 mmol) in dichloromethane (10 ml) was treated with an excess of $HBF_4 \cdot OEt_2$ (0.1 ml). The solvent was removed under reduced pressure and the residue was washed with diethyl ether (3 × 5 ml) to give compound 9 as an orange solid (25 mg, 75%). Anal. Found: C, 40.80; H, 2.33; N, 1.46. Calcd for $C_{34}H_{21}BF_4NO_9PRu_3$: C, 40.49; H, 2.10; N, 1.39.

4.9.2. Method (b)

A solution of compound **8** in 1,2-dichloroethane (20 ml) was stirred at reflux temperature for 1 h. The solution was concentrated under reduced pressure to ca. 2 ml and diethyl ether (20 ml) was added. An orange solid precipitated. The ^1H and $^{31}P\{^1H\}$ NMR spectra of this solid showed the presence of compound **9** accompanied by minor impurities of other compounds which could not be separated due to their cationic nature.

4.10. [$Ru_3(\mu\text{-}H)_3(\mu\text{-}N{=}CPh_2)(\mu\text{-}PPh_2)(PPh_2H)(CO)_7$][$BF_4$] (10)

A solution of compound **5** (30 mg, 0.029 mmol) in dichloromethane (10 ml) was treated with an excess of $HBF_4 \cdot OEt_2$ (0.1 ml). The colour changed from orange to yellow. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (3 × 5 ml) to give compound **10** as a yellow solid (25 mg, 76%). Anal. Found: C, 46.60; H, 3.14; N, 1.04. Calcd for $C_{44}H_{34}BF_4NO_7P_2Ru_3$: C, 46.33; H, 3.00; N, 1.23.

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