Neutral and anionic pyrazolyl-bridged triruthenium carbonyl cluster complexes. Reactions with bis(diphenylphosphino)methane, triphenylphosphine and diphenylphosphine

Javier A. Cabeza*, Ignacio del Río, Víctor Riera

Instituto de Química Organometálica Enrique Moles, Facultad de Química, Universidad de Oviedo-CSIC, 33071 Oviedo, Spain

Abstract

The reactions of the neutral and anionic pyrazolyl-bridged triruthenium clusters $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(CO)_{10}]$ (1) and $[Et_4N][Ru_3(\mu\text{-}dmpz)(\mu\text{-}CO)_3(CO)_7]$ (2) (Hdmpz = 3,5-dimethylpyrazole) with three different phosphine ligands have been studied. Complexes 1 and 2 react with bis(diphenylphosphino)methane (dppm) to give the asymmetric substituted products $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(\mu\text{-}dppm)(CO)_8]$ (3a) and $[Et_4N][Ru_3(\mu\text{-}dmpz)(\mu\text{-}dppm)(\mu\text{-}CO)_2(CO)_6]$ (4) respectively, in which the dppm and pyrazolyl ligands span different Ru–Ru edges. Protonation of the anionic complex 4 with CF_3CO_2H affords the asymmetric neutral hydride 3a. Complex 3a slowly undergoes an isomerization reaction in solution at room temperature to give a symmetric derivative (3b) in which the diphosphine, hydride and pyrazolyl ligands span the same Ru–Ru edge. The reactions of compound 1 with PPh_3 and $PHPh_2$ at room temperature give $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(PPh_3)(CO)_9]$ (5) and $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(PHPh_2)(CO)_9]$ (6) respectively. In compounds 5 and 6, the phosphine ligand occupies an equatorial site cis to the pyrazolyl and hydride ligands. The anionic complex 2 does not react with PPh_3 or $PHPh_2$ at room temperature, but gives mixtures of many products at higher temperatures. Compounds 3–6 are thermally unstable, decomposing in THF at reflux temperature into mixtures of many compounds. The diphenylphosphido derivatives $[Ru_2(\mu\text{-}dmpz)(\mu\text{-}PPh_2)(CO)_6]$ (7) and $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(\mu\text{-}PPh_2)_2(CO)_7]$ (8) have been isolated from the thermolysis of complex 6.

Keywords: Ruthenium; Clusters; Carbonyls; Reactions with phosphines; Pyrazolato complexes

1. Introduction

Recently, we have reported a high-yield synthesis of the neutral triruthenium pyrazolyl cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(CO)_{10}]$ (1) (Hdmpz = 3,5-dimethylpyrazole) by protonation of the anionic precursor $[Et_4N][Ru_3(\mu\text{-}dmpz)(\mu\text{-}CO)_3(CO)_7]$ (2) with trifluoroacetic acid [1]. Complex 2 can also be made in high yield by treatment


(1)   (2)

of $[Et_4N][Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]$ with 3,5-dimethylpyrazole [1]. The previously reported thermal reaction of $[Ru_3(CO)_{12}]$ with 3,5-dimethylpyrazole only gives low yields of complex 1 [2,3] and binuclear ruthenium(I) derivatives [3,4].

The efficient preparations of clusters 1 and 2 have allowed a study of their reactivity. We now report a comparative study of the reactions of these two cluster complexes with three different types of phosphine ligands, namely bis(diphenylphosphino)methane, triphenylphosphine and diphenylphosphine. Very few anionic ruthenium cluster complexes containing N-donor heterocycles have been reported to date [1,5,6], and their derivative chemistry is yet to be investigated.
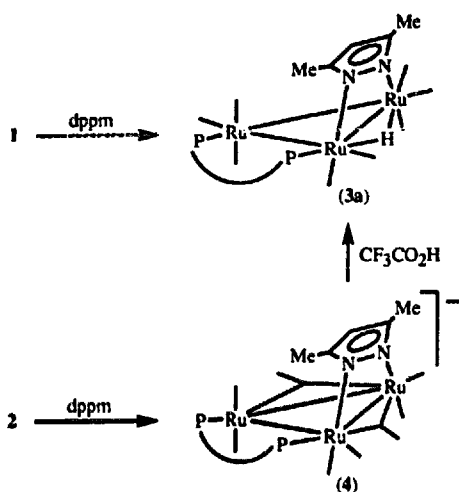
2. Results and discussion

2.1. Bis(diphenylphosphino)methane derivatives

Complex 1 reacts with bis(diphenylphosphino)methane (THF, 15 min, room temperature) to give the disub-
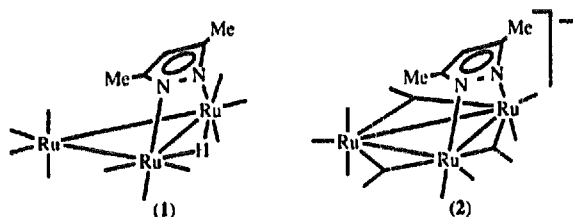
* Corresponding author. Fax: (+34) 8 5103446; e-mail: jac@sauron.quimica.uniovi.es.

Scheme 1.

stituted asymmetric derivative [Ru$_3$(μ-H)(μ-dmpz)(μ-dppm)(CO)$_8$] (3a, Scheme 1) (dppm = bis(diphenyl-phosphino)methane), as the kinetically controlled product (vide infra). The asymmetry of this complex was clearly revealed by its NMR spectra. Its ^{31}P{^{1}H} NMR spectrum consists of two doublets at positive chemical shifts, indicating two symmetry-unrelated coordinated phosphorus atoms [7]. Its ^{13}C{^{1}H} NMR spectrum shows the resonances of eight carbonyl and five dmpz carbon atoms. Accordingly, its ^{1}H NMR spectrum shows two singlets for the methyl groups; also, in this spectrum, the two J(P–H) coupling constants of the hydride resonance (doublet of doublets) are considerably different (40.9 and 4.0 Hz), as expected for a hydride ligand which spans a Ru–Ru edge different from that bridged by the dppm ligand. All these data support the structure proposed for compound 3 in Scheme 1. It should be noted that other neutral dppm-bridged trinuclear ruthenium carbonyl clusters containing bridging N-donor ligands are symmetric and have both bridging ligands spanning the same Ru–Ru edge [8].

Complex 3a undergoes an isomerization reaction in solution (Scheme 2) to give an equilibrium mixture of 3a and 3b. The equilibrium constant, [3b]/[3a] = 0.77 at 20°C in THF solution, was established by ^{31}P{^{1}H} NMR spectroscopy. In this case, the NMR data of 3b (singlet in the ^{31}P{^{1}H} NMR spectrum, triplet for the hydride in the ^{1}H NMR spectrum) indicate that the
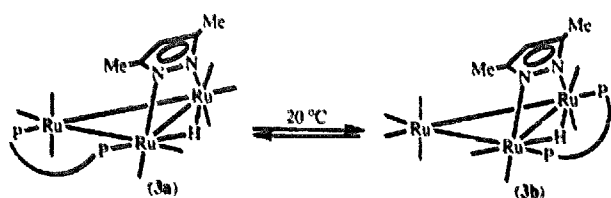
cluster is symmetric (C_s). Although, as far as we know, there are no precedents for isomerization reactions involving changes of coordination sites for dppm ligands in neutral clusters, there is one precedent in a cationic cluster, namely one isomer of the cluster [Ru$_3$(μ-H)$_2$(μ_3-ampy)(μ-dppm)(CO)$_7$][BF$_4$] (Hampy = 2-amino-6-methylpyridine), which has the dppm ligand spanning a Ru–Ru edge different from those bridged by the hydride ligands; this isomerizes into a derivative in which the dppm ligand spans a hydride-bridged Ru–Ru edge [8].

The anionic character of [Et$_4$N][Ru$_3$(μ-dmpz)(μ-CO)$_3$(CO)$_7$] (2) makes it less prone to react with nucleophiles than complex 1. In fact, compound 2 does not react with dppm at room temperature, but gives the disubstituted derivative [Et$_4$N][Ru$_3$(μ-dmpz)(μ-dppm)(μ-CO)$_2$(CO)$_6$] (4, Scheme 1) in THF at reflux temperature. Its NMR data are comparable with those of cluster 3a, suggesting an asymmetric structure. Its IR spectrum indicates the presence of bridging CO ligands (1784, 1752 cm^{-1}). The asymmetric structure proposed for this complex in Scheme 1 is also supported by the fact that it reacts instantaneously with protic acids, at room temperature, to give the neutral compound 3a. As occurs in other protonation reactions of anionic clusters, the bridging CO ligands of the starting material move to terminal positions in the final neutral product [1,5].

2.2. Triphenylphosphine derivatives

Complex 1 reacts readily with triphenylphosphine at room temperature to give the monosubstituted product [Ru$_3$(μ-H)(μ-dmpz)(PPh$_3$)(CO)$_9$] (5). The structure proposed for this compound in Scheme 3 based on its ^{1}H NMR spectrum, which shows the hydride as a doublet with a J(P–H) coupling constant of 13.0 Hz, typical of a cis arrangement of the hydride and phosphine ligands [9]. Compound 5 is the only product formed at room temperature, regardless of the amount of phosphine used. In an attempt to prepare disubstituted derivatives, complex 1 was treated with two equivalents of triphenylphosphine in THF at reflux temperature, but a mixture of many products was obtained (^{31}P NMR).

Scheme 2.

R = Ph (5)
R = H (6)
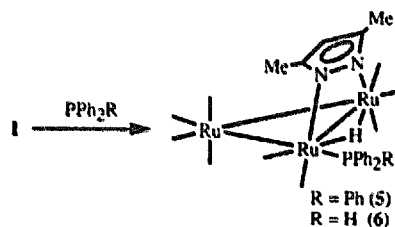
Scheme 3.

The anionic complex 2 does not react with triphenylphosphine at room temperature but gives mixtures of many compounds at higher temperatures, even using a 1:1 cluster to ligand ratio.

It seems apparent that, just above room temperature, in both the neutral and the anionic compounds, the coordinated PPh_3 ligands undergo degradation via P–C and C–H bond activation reactions with no regioselectivity, leading to mixtures of compounds containing orthometallated fragments and/or bridging diphenyl-phosphido ligands (^{31}P NMR) [10,11].

2.3. Diphenylphosphine derivatives

The reaction of complex 1 with diphenylphosphine at room temperature gives the monosubstituted derivative $[Ru_3(\mu-H)(\mu-dmpz)(PHPh_2)(CO)_9]$ (6, Scheme 3). The hydride resonance of its ^1H NMR spectrum is a doublet with $J(P–H) = 11.4$ Hz, suggesting a cis coupling of the phosphine and hydride ligands [9], and its IR spectrum is comparable with that of compound 5. These data indicate that compounds 5 and 6 are isostructural.

It is known that carbonyl clusters containing diphenylphosphine lead to phosphido-bridged derivatives through P–H bond activation reactions under thermal conditions [12–14]. In fact, the thermolysis of complex 6 (THF, reflux temperature, 45 min) followed by a chromatographic separation led us to isolate and characterize the diphenylphosphido derivatives $[Ru_3(\mu-dmpz)(\mu-PPh_2)(CO)_8]$ (7) and $[Ru_3(\mu-H)(\mu-dmpz)(\mu-PPh_2)_2(CO)_7]$ (8). The clusters $[Ru_3(CO)_{12}]$, $[Ru_4(\mu-H)_4(CO)_{12}]$ and the known phosphido derivatives $[Ru_3(\mu-PPh_2)_2(CO)_6]$ [13], $[Ru_3(\mu-H)_3(\mu-PPh_2)_3(CO)_8]$ [13,14] and $[Ru_4(\mu-PPh_2)_2(CO)_{11}]$ [15] are also formed in this reaction.

The structures proposed for compounds 7 and 8 are supported by their analytical and spectroscopic data; in particular, their ^{31}P and ^1H NMR spectra indicate that both compounds contain a mirror plane that cuts the pyrazolyl ligand into two identical halves (singlet ^{31}P resonance and equivalent methyl groups of the dmpz ligand). Thus, the structure of compound 7 is related to those of $[Ru_2(\mu-dmpz)_2(CO)_6]$ [3] and $[Ru_2(\mu-PPh_2)_2(CO)_6]$ [13], but it is a rare example of a diruthenium(I) complex in the sense that it contains two different bridging ligands [16]. The structure of complex 8 can be related to that of $[Ru_3(\mu-H)(\mu-PPh_2)_3(CO)_7]$

(7)   (8)
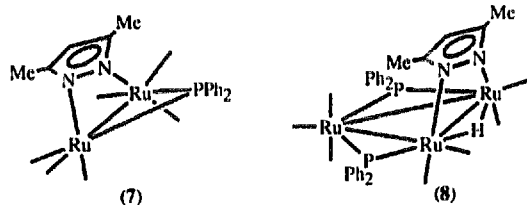
[13,14b], in which the phosphido ligand which spans the same Ru–Ru edge as the hydride ligand has been formally replaced by the isoelectronic (three-electron donor) dmpz ligand.

As occurred with triphenylphosphine (vide supra), no reaction was observed between the anionic cluster 2 and diphenylphosphine in THF at room temperature. However, a complicated mixture of products was detected by ^{31}P NMR spectroscopy when the reaction was carried out at reflux temperature. Unfortunately, the ionic nature of these products prevented a chromatographic separation.

3. Experimental details

3.1. General data

Solvents were dried over sodium diphenyl ketyl (THF, diethyl ether, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen (Schlenk-vacuum line techniques) and were monitored by solution IR spectroscopy (carbonyl stretching region) and by qualitative TLC on silica gel. The compounds 1 and 2 were prepared as described previously [1]; all other reagents (reagent grade) were used as received from commercial suppliers. Microanalyses were obtained from the University of Oviedo Analytical Service. Infrared spectra were recorded in solution on a Perkin–Elmer FT 1720-X spectrophotometer, using a 0.1 mm CaF_2 cell. NMR spectra were run at 20°C in Bruker AC-200 and AC-300 spectrometers, using internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P) as standards ($\delta = 0$ ppm).

3.2. $[Ru_3(\mu-H)(\mu-dmpz)(\mu-dppm)(CO)_8]$ (3a)

A solution of dppm (29 mg, 0.074 mmol) and complex 1 (50 mg, 0.074 mmol) in THF (10 ml) was stirred for 15 min. The solvent was removed under reduced pressure and the residue chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–dichloromethane 1:1 eluted a trace amount of compound 1 followed by a red compound which was identified as complex 3a (67 mg, 90%). Anal. Found: C, 45.38; H, 2.97; N, 2.77. $C_{38}H_{30}N_2O_8P_2Ru_3$. Calc.: C, 45.29; H, 3.00; N, 2.78%. IR (hexane): 2069 (s), 2022 (m), 2008 (vs), 1997 (s), 1989 (w), 1963 (m), 1941 (vw) cm^{-1}. ^1H NMR (CD_2Cl_2): 7.7–6.8 (m, 20 H, Ph), 5.73 (s, 1 H, pyrazolyl CH), 4.96 (dd, $J = 24.0$ and 11.1 Hz, 1 H, CH of dppm), 4.34 (dd, $J = 23.0$ and 11.0 Hz, 1 H, CH of dppm), 2.17 (s, 3 H, Me of dmpz), 1.74 (s, 3 H, Me of dmpz), −12.97 (dd, $J = 40.9$ and 4.0 Hz, 1 H, μ-H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 10.4 (d, $J = 38.4$ Hz, 1 P), 5.8 (d, $J = 38.4$ Hz, 1 P) ppm. $^{13}C\{^1H\}$ NMR

(CD$_2$Cl$_2$): δ(CO): 215.9 (d, $J = 10.6$ Hz), 215.1 (d, $J = 7.8$ Hz), 208.9 (d, $J = 14.5$ Hz), 203.6 (s), 199.2 (d, $J = 5.1$ Hz), 197.9 (d, $J = 19.6$ Hz), 190.1 (d, $J = 5.0$ Hz), 187.1 (d, $J = 8.7$ Hz); δ(dmpz): 150.8, 150.5, 107.6, 15.4, 13.3 (all singlets); δ(dppm): 134.9–128.1 (4 Ph), 54.6 (t, $J = 24.9$ Hz, CH$_2$) ppm.

3.3. Isomerization of complex 3a into 3b

Complex 3a (15 mg) was dissolved in 0.5 ml of THF in a 5 mm NMR tube. A capillary containing D$_2$O was also introduced into the tube in order to use D$_2$O as NMR lock). The evolution was monitored at 20°C by ^{31}P{^{1}H} NMR spectroscopy, which showed the progressive isomerization of complex 3a into 3b. After 36 h no more changes were observed; at this point the integration of the peaks resulted in a [3b]/[3a] ratio of 0.77. The solution was evaporated to dryness and the residue was dissolved in CDCl$_3$. Selected NMR data for 3b: ^{1}H NMR (CDCl$_3$): −13.57 (t, $J = 18.0$ hz, μ-H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 8.1 (s) ppm.

3.4. [Et$_4$N][Ru$_3$(μ-dmpz)(μ-dppm)(μ-CO)$_2$(CO)$_6$] (4)

A solution of complex 2 (50 mg, 0.062 mmol) and dppm (24 mg, 0.063 mmol) in THF (10 ml) was stirred at reflux temperature for 45 min. The solvent was removed under reduced pressure and the residue washed with diethyl ether (2 × 5 ml) and dried under vacuum to give complex 4 as a yellow-brown solid (52 mg, 74%). Anal. Found: C, 49.18; H, 4.26; N, 3.83. C$_{46}$H$_{49}$N$_3$O$_8$P$_2$Ru$_3$. Calc.: C, 48.59; H, 4.34; N, 3.70%. IR (THF): 2004 (m), 1963 (vs), 1936 (m), 1905 (sh), 1898 (vs), 1784 (m, br), 1752 (m, br) cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.7–6.7 (m, 20 H, Ph), 5.61 (dd, $J = 23.0$ and 11.0 Hz, 1 H, CH of dppm), 5.24 (s, 1 H, pyrazolyl CH), 3.65 (dd, $J = 23.0$ and 11.0 Hz, 1 H, CH of dppm), 2.09 (s, 3 H, Me of dmpz), 1.79 (s, 3 H, Me of dmpz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 50.5 (d, $J = 90.0$ Hz, 1 P), 30.1 (d, $J = 90.0$ Hz, 1 P) ppm.

3.5. Protonation of complex 4

Trifluoroacetic acid (4.8 μl, 0.045 mmol) was added to a solution of compound 4 (50 mg, 0.044 mmol) in dichloromethane (5 ml). The colour changed immediately from yellow to dark red. The solvent was removed under reduced pressure and the residue chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–dichloromethane 1:1 eluted a red band which contained complex 3a (40 mg, 90%).

3.6. [Ru$_3$(μ-H)(μ-dmpz)(PPh$_3$)(CO)$_9$] (5)

A solution of complex 1 (37.5 mg, 0.055 mmol) and PPh$_3$ (14.5 mg, 0.055 mmol) in THF (15 ml) was

stirred for 1 h. The colour changed from yellow to red. The solvent was removed under reduced pressure and the residue washed with hexane (2 × 5 ml) to give complex 5 as a red solid (49 mg, 97%). Anal. Found: C, 42.13; H, 2.67; N, 2.95. C$_{32}$H$_{23}$N$_2$O$_9$PRu$_3$. Calc.: C, 42.06; H, 2.54; N, 3.07%. IR (THF): 2087 (m), 2050 (s), 2015 (vs), 2007 (s), 1985 (w), 1972 (w), 1951 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.5–7.0 (m, 15 H, Ph), 5.60 (s, 1 H, pyrazolyl CH), 2.09 (s, 3 H, Me of dmpz), 1.38 (s, 3 H, Me of dmpz), −12.70 (d, $J = 13.0$ Hz, 1 H, μ-H) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 26.3 (s) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ(CO): 208.7 (s), 205.7 (d, $J = 6.5$ Hz), 202.2 (d, $J = 5.8$ Hz), 202.0 (d, $J = 5.8$ Hz), 199.6 (s), 197.0 (s), 194.3 (s), 193.0 (d, $J = 11.7$ Hz), 185.9 (s); δ(dmpz): 150.9, 149.9, 109.6, 12.8, 12.2 (all singlets); δ(PPh$_3$): 135.0–128.6 (3 Ph) ppm.

3.7. [Ru$_3$(μ-H)(μ-dmpz)(PHPh$_2$)(CO)$_9$] (6)

A solution of complex 1 (50 mg, 0.074 mmol) and PHPh$_2$ (25.5 μl, 0.147 mmol) in dichloromethane (10 ml) was stirred for 13 h. The colour changed from yellow to orange. The solvent was removed under reduced pressure and the residue chromatographed on a column (10 × 2 cm) of neutral alumina (activity III). Hexane eluted two bands: the first one (yellow) contained a small amount of starting material; the second band contained complex 6, which was obtained as an orange solid (40 mg, 65%). Anal. Found: C, 37.52; H, 2.36; N, 3.18. C$_{26}$H$_{19}$N$_2$O$_9$PRu$_3$. Calc.: C, 37.28; H, 2.29; N, 3.34%. IR (CH$_2$Cl$_2$): 2088 (m), 2050 (s), 2017 (vs), 2009 (s), 1984 (w), 1956 (vw) cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.6–7.2 (m, 10 H, Ph), 6.46 (d, $J = 345.2$ Hz, 1 H, PH), 5.60 (s, 1 H, pyrazolyl CH), 2.06 (s, 3 H, Me of dmpz), 1.78 (s, 3 H, Me of dmpz), −12.99 (d, $J = 11.4$ Hz, 1 H, μ-H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 11.0 (s) ppm.

3.8. Thermolysis of complex 6

A solution of complex 6 (100 mg, 0.119 mmol) in THF (20 ml) was stirred at reflux temperature for 45 min. The solution was concentrated under reduced pressure to ca. 2 ml and the residue supported on preparative TLC silica gel plates. The use of hexane–dichloromethane 5:1 as eluant afforded the following compounds in order of elution (IR and NMR characterization): [Ru$_3$(CO)$_{12}$], [Ru$_3$(μ-H)$_4$(CO)$_{12}$], 6, [Ru$_3$(μ-dmpz)(μ-PPh$_2$)(CO)$_6$] (7), [Ru$_3$(μ-PPh$_2$)$_2$(CO)$_6$], [Ru$_3$(μ-H)$_2$(μ-PPh$_2$)$_2$(CO)$_8$], [Ru$_3$(μ-H)(μ-dmpz)(μ-PPh$_2$)$_2$(CO)$_7$] (8) and [Ru$_3$(μ-PPh$_2$)$_2$(CO)$_{13}$]. All were obtained in very small amounts (less than 10 mg).

Analytical and spectroscopic data for compound 7. Anal. Found: C, 42.61; H, 2.85; N, 4.05. C$_{23}$H$_{17}$N$_2$O$_6$PRu$_3$. Calc.: C, 42.47; H, 2.63; N, 4.30%. IR (THF): 2078 (m), 2044 (vs), 2009 (m), 1991 (m),

1948 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.8–7.1 (m, 10 H, Ph), 5.13 (s, 1 H, pyrazolyl CH), 2.07 (s, 6 H, Me$_2$ of dmpz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 153.2 (s) ppm.

Analytical and spectroscopic data for compound **8**. Anal. Found: C, 44.91; H, 3.13; N, 2.75. C$_{36}$H$_{28}$N$_2$O$_7$P$_2$Ru$_3$. Calc.: C, 44.77; H, 2.92; N, 2.90%. IR (THF): 2034 (m), 2004 (vs), 1966 (m), 1951 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.8–7.0 (m, 20 H, Ph), 5.38 (s, 1 H, pyrazolyl CH), 2.01 (s, 6 H, Me$_2$ of dmpz), −7.18 (t, $J = 30.0$ Hz, 1 H, μ-H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 235.2 (s) ppm.

Acknowledgement

References and notes

[1] J.A. Cabeza, R.J. Franco, V. Riera, S. García-Granda and J.F. Van der Maelen, *Organometallics, 14* (1995) 3342.

[2] M.I. Bruce, M.G. Humphrey, M.R. Snow, E.R.T. Tiekink and R.C. Wallis, *J. Organomet. Chem., 314* (1986) 311.

[3] J.A. Cabeza, C. Landázuri, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem., 322* (1987) C16.

[4] (a) F. Neumann and G. Süss-Fink, *J. Organomet. Chem., 367* (1989) 175. (b) J.A. Cabeza, C. Landázuri, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc. Dalton Trans.*, (1989) 1093.

[5] N. Lugan, F. Laurent, G. Lavigne, T.P. Newcomb, E.W. Limata and J.J. Bonnet, *Organometallics, 11* (1992) 1351.

[6] For a review on ruthenium clusters containing N-donor ligands,

[7] The ^{31}P{^{1}H} NMR spectra of monocoordinated dppm ligands consist of two doublets, one at positive and the other at negative chemical shifts. See, for example: (a) S.J. Sherlock, M. Cowie, E. Singleton and M.M. de V. Steyn, *Organometallics, 7* (1988) 1663. (b) A.J. Deeming, D. Nuel, N.P. Randle and C. Whittaker, *Polyhedron, 8* (1989) 1537. (c) J.A. Cabeza, J.M. Fernández-Colinas, V. Riera, M.A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc. Dalton Trans.*, (1991) 371.

[8] P.L. Andreu, J.A. Cabeza, J.L. Cuyás and V. Riera, *J. Organomet. Chem., 427* (1992) 363.

[9] (a) P.L. Andreu, J.A. Cabeza, M.A. Pellinghelli, V. Riera and A. Tiripicchio, *Inorg. Chem., 30* (1991) 4611. (b) P.L. Andreu, J.A. Cabeza, V. Riera, C. Bois and Y. Jeannin, *J. Chem. Soc. Dalton Trans.*, (1990) 3347.

[10] (a) P. Briard, J.A. Cabeza, A. Llamazares, L. Ouahab and V. Riera, *Organometallics, 12* (1993) 1006. (b) J.A. Cabeza, R.J. Franco, A. Llamazares, V. Riera, E. Pérez-Carreño and J.F. Van der Maelen, *Organometallics, 13* (1994) 55.

[11] For reviews on metal-mediated P-C bond cleavage reactions, see: (a) P.E. Garrou, *Chem. Rev., 85* (1985) 171. (b) G. Lavigne, in D.F. Shriver, R.D. Adams and H.D. Kaesz (eds.), *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, Chapter 5, p. 201.

[12] P.L. Andreu, J.A. Cabeza and V. Riera, *Inorg. Chim. Acta, 186* (1991) 225.

[13] R.P. Rosen, G.L. Geoffroy, C. Bueno, M.R. Churchill and R.P Ortega, *J. Organomet. Chem., 254* (1983) 89.

[14] (a) V.D. Patel, A.A. Cherkas, D. Nucciarone, N.J. Taylor and A.J. Carty, *Organometallics, 4* (1985) 1792. (b) L.M. Bullock, J.S. Field, R.J. Haines, E. Minshall, F. Mulla, D.N. Smit and L.M. Steer, *J. Organomet. Chem., 381* (1990) 429.

[15] (a) G. Hogarth, J.A. Phillips, F. Van Gastel, N.J. Taylor, T.B. Marder and A.J. Carty, *J. Chem. Soc. Chem. Commun.*, (1988) 1570. (b) G. Hogarth, N. Hadj-Bagheri, N.J. Taylor and A.J. Carty, *J. Chem. Soc. Chem. Commun.*, (1990) 1352.

[16] For a review on diruthenium(I) complexes containing bridging N-donor ligands, see: J.A. Cabeza and J.M. Fernández-Colinas, *Coord. Chem. Rev., 126* (1993) 319.