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Reaction of $[CpRu(CH_3CN)_3]PF_6$ with bidentate ligands: structural characterization of $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-}\eta^{1:1}\text{-dppe})](PF_6)_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] ☆

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Abstract

The reaction of $[CpRu(CH_3CN)_3]PF_6$ with the bidentate ligands L–L = 1,2-bis(diphenylphosphino)ethane, dppe, and (1-diphenylarsino-2-diphenylphosphino)ethane, dpadppe, affords mononuclear or dinuclear complexes of formula $[CpRu(\eta^2\text{-L–L})(CH_3CN)]PF_6$, $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-}\eta^{1:1}\text{-L–L})](PF_6)_2$ and $[\{CpRu(CH_3CN)\}_2(\mu\text{-}\eta^{1:1}\text{-L–L})_2](PF_6)_2$ (L–L = dppe, dpadppe). All of the compounds are characterized by microanalysis and NMR [^1H and $^{31}P\{^1H\}$] spectroscopy. The crystal structure of $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-}\eta^{1:1}\text{-dppe})](PF_6)_2$ has been determined by X-ray diffraction analysis. The complex exhibits a dppe ligand bridging two $CpRu(CH_3CN)_2$ fragments.

Keywords: Ruthenium cyclopentadienyl complexes; Bidentate ligands; Crystal structure

1. Introduction

The well-known half sandwich ruthenium complexes of the type $[(C_5R_5)Ru(L)(L')(L'')]$ (R = H, CH_3) have a prominent role in the chemistry of the late transition metals [1]. The $[(C_5R_5)Ru(L)_2]$ fragment, having kinetically stable ruthenium–L bonds and high π-donor ability, has been exploited to stabilize a variety of unstable π-acceptor ligands such as carbenes [2], vinylidenes [3a,3b,3c], allenylidenes [3d], sulphur oxides [4] or white phosphorus [5], just to name a few. The chemistry of the pentamethylcyclopentadienyl ruthenium fragment is largely based on the tetramer $[Cp^*RuCl]_4$ [6] and/or on the Tris–acetonitrile $[Cp^*Ru(CH_3CN)_3]PF_6$ adduct [7] which, upon addition of monodentate ligands, yield pseudotetrahedral complexes $[Cp^*RuCl(L)_2]$ [2b,3b,8] and $[Cp^*Ru(L)_2(CH_3CN)]PF_6$ [7], respectively. Both the chloride and the acetonitrile ligand in these complexes may be exchanged with L′ species offering an easy route to a vast variety of cationic compounds of formula $[Cp^*Ru(L)_2(L')]PF_6$ [9,7]. Additional interest in such species arises from their ability to form isolable, coordinatively unsaturated 16-electron complexes [10]. In contrast to the Cp^* derivatives, the chemistry of the cyclopentadienyl ruthenium fragment is largely based on the precursors $[CpRu(CO)_2Cl]$ and $[CpRu(PPh_3)_2Cl]$ [11]. However, the difficulties in performing selective replacements of the ancillary ligands (PPh_3 or CO) have greatly limited the synthetic utility of such species [12]. The easily prepared $[CpRu(CH_3CN)_3]PF_6$ [13], which readily dissociates the acetonitrile molecules [14], is a good synthon to prepare $[CpRu(L)_2(CH_3CN)]^+$ cations by reaction with a variety of monodentate phosphines [15], and to synthesize catalytically active species [16]. In an effort to further investigate the chemistry of $[CpRu(L)_2]$ toward small molecules incorporating fifth

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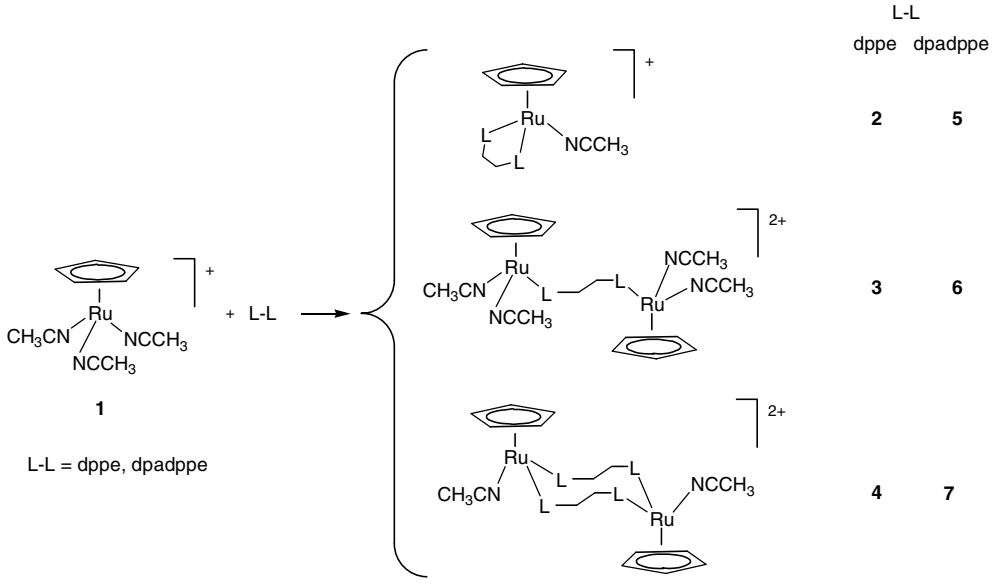
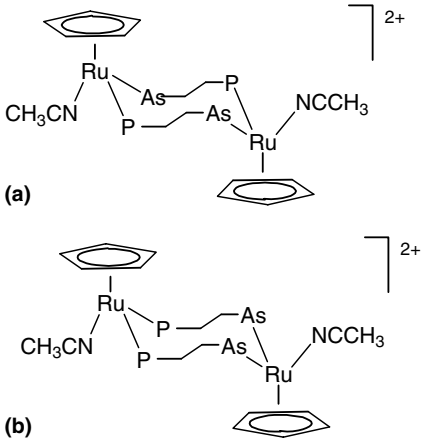
group atoms, [5,17] we have reacted [CpRu(CH_3CN)$_3$]PF_6 with bidentate chelating ligands, L–L, [L–L = 1,2-bis(diphenylphosphino)ethane, dppe, and (1-diphenylarsino-2-diphenylphosphino)ethane, dpadppe], with the aim to obtain [CpRu(L–L)(CH_3CN)]PF_6 complexes containing a replaceable solvent molecule. Apart from the originally targeted compounds, the reaction resulted also in the formation of unexpected diruthenium derivatives, whose synthesis and chemicophysical properties are herein reported.

2. Results and discussion

Three different products, as sketched in Scheme 1, have been obtained upon treatment of [CpRu(CH_3CN)$_3$]PF_6 (**1**) in CH_2Cl_2 with one equivalent of the ligands dppe or dpadppe, which present either two phophorus or one arsenic and a phosphorus atom as donors, respectively. The reaction produces a yellow crystalline precipitate of formula [{CpRu(CH_3CN)$_2$}$_2$(L–L)](PF_6)$_2$ [L–L = dppe (**3**), dpadppe (**6**)] and a yellow solution yielding a solid of the same colour upon removing the solvent. The extraction of the crude solid with cold THF leaves undissolved a yellow compound of formula [{CpRu(CH_3CN)}$_2$(L–L)$_2$](PF_6)$_2$ [L–L = dppe (**4**), dpadppe (**7**)], while the complexes [CpRu(CH_3CN)(L–L)]PF_6 [L–L = dppe (**2**), dpadppe (**5**)] are obtained from the THF extracts. The relative yields of the three compounds do not change significantly on changing the ligand (see Section 3). All of the compounds may be handled in the air in the solid state; **2** and **5** are soluble in common organic solvents; **3** and **6** dissolve in CH_3CN and CH_3NO_2; **4** and **7** are soluble in CH_2Cl_2, CH_3CN and CH_3NO_2; their solutions are stable under an inert atmosphere. The dimeric **4** and **7** complexes do not transform to **2** and **5** even if warmed in CH_2Cl_2 for 24 h. A similar inertness has been observed for the related neutral [{Cp*RuCl}$_2$(μ-η$^{1:1}$-dmpm)$_2$] species [dmpm = bis(dimethylphospino)methane] [8]. Similarly, the mononuclear species **2** and **5** do not transform, upon treatment with one equivalent of L–L, to **4** and **7**. Complexes **2**–**7** have been characterized by elemental analysis and NMR (^{1}H and ^{31}P) spectroscopy. Complexes **2** and **5** exhibit in their ^{31}P spectrum a low field singlet which is typical for a five-membered chelate ring [18]. The ^{1}H spectra present the uninformative resonances of the ligand protons (see Section 3), the cyclopentadiene singlet at ca. 4.9 ppm and the signals of the coordinated CH_3CN molecule which appear as a triplet (J = 1.2 Hz) in compound **2**, in accordance with their coupling to the two phosphorus donors of dppe and as a doublet in compound **5**, due to the presence of only one magnetically active phosphorus in the "mixed" dpadppe ligand. Compounds **3**, **4**, **6** and **7** exhibit in their ^{31}P NMR spectra resonances whose shifts are typical for η^1 bidentate ligands [18]. The intensities of the ligand, cyclopentadiene and CH_3CN proton signals agree with the proposed formulae. The spectra of compounds **6** and **7**, containing the "mixed" dpadppe ligand, show some interesting features: that of **6** exhibits two separate resonances for the cyclopentadiene and for the coordinated CH_3CN protons, due to the inequivalence of the two CpRu(CH_3CN)$_2$ moieties whose coordination is completed by either the P or the As donor of the dpadppe ligand. Compound **7** exhibits two singlets of slightly different intensities in the ^{31}P spectrum and two sets of proton resonances for both the



Scheme 1.



Scheme 2.

cyclopentadiene and the CH_3CN molecules (see Section 3): one set consists of a singlet for the cyclopentadiene and a doublet for the coordinated acetonitrile, whereas the other one consists of two singlets for the cyclopentadiene and two resonances (a triplet and a singlet) for the CH_3CN. Such data are consistent with the presence of two coordination isomers, Scheme 2, differing in the relative arrangement of the two dpadppe donors; isomer b forms in a higher yield (ca. 55%) compared with a; the metal atoms of isomer a are chiral. Notably, the two complexes **4** and **7**, containing two bridging $\eta^{1:1}$ bidentate ligands, represent a rare example of ten-membered dimetalla macrocyclic complexes [20].

Crystals of **3** suitable for an X-ray diffraction analysis were obtained directly from the reaction of **1** and dppe in CH_2Cl_2. The structure of **3** consists of $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-}\eta^{1:1}\text{-dppe})]^{2+}$ dimetal cations and PF_6^- anions in a 1:2 ratio. Each metal atom in the centrosymmetric cation is coordinated by the cyclopentadienyl ligand, by two acetonitrile nitrogens and by a dppe phosphorus atom. A view of the cation is shown in Fig. 1. Values of selected bond distances and angles are given in Table 2. The $RuC_{(Cp)}$ distances are in the range 2.153–2.217 Å and their 2.18(3) Å average value agrees with those, of 2.177(5) and 2.185 Å, respectively, found for the $[CpRu(PMe_3)(CH_3CN)_2]^+$ and $[CpRu(PCy_3)(CH_3CN)_2]^+$ monomeric complex cations [15]. On the other hand, the present $RuC_{(Cp)}$ distances are appreciably longer than those found for the less crowded $[CpRu(CH_3CN)_3]^+$ synthon (2.135 Å, average value) [14]. The RuN distances in **3**, with 2.072(10) Å mean value, are slightly longer than those [2.055(5) Å, mean] found for the two Kirchner's complexes formed with two CH_3CN ligands [15]. The present 2.318 Å RuP distance is intermediate between those, of 2.294(1) and 2.359 Å, respectively, found for the $[CpRu(PMe_3)(CH_3CN)_2]^+$ and $[CpRu(PCy_3)(CH_3CN)_2]^+$ cations [15].

The strong tendency of bidentate diphosphine ligands such as dmpm, dppm and dcpm [dppm = bis(diph-

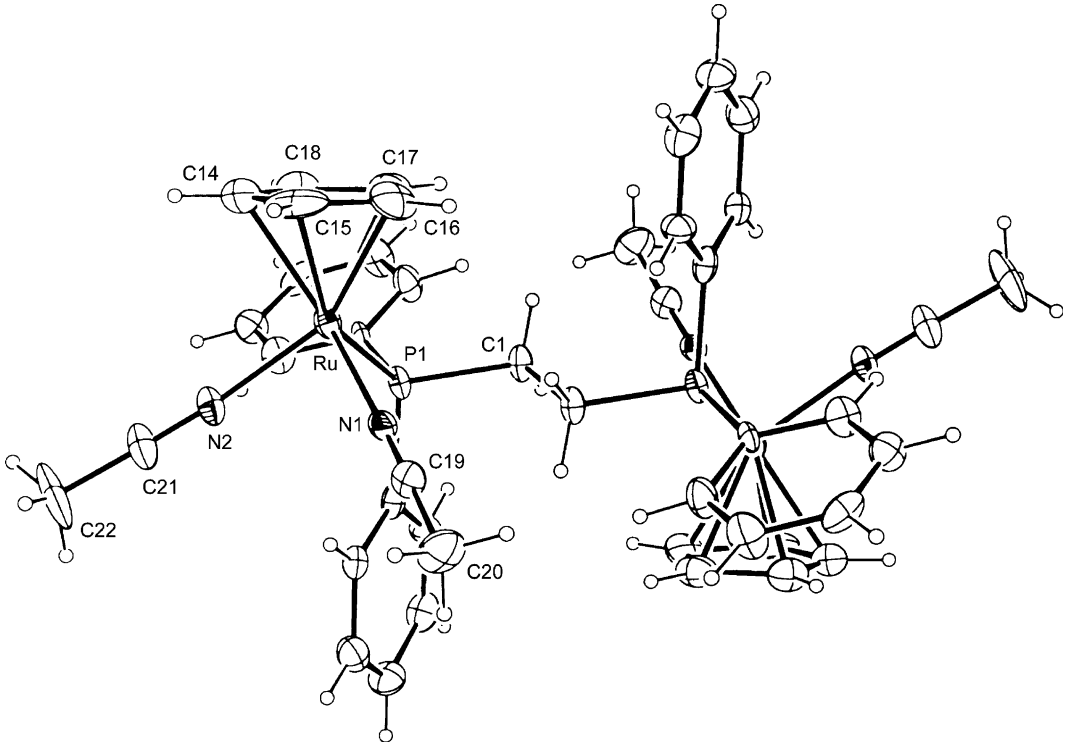


Fig. 1. A view of the $[\{CpRu(CH_3CN)_2\}_2(dppe)]^{2+}$ centrosymmetric cation. Displacement ellipsoids are traced at the 20% probability level and H atoms are shown as small circles with arbitrary radii. Only labels of symmetry-independent atoms are shown and those of phenyl carbon atoms are omitted for clarity.

enylphosphino)methane, dcpm = bis(dicyclohexylphosphino)methane] to adopt an η^1 or μ-$\eta^{1:1}$ (bridging) coordination mode in the presence of ruthenium cyclopentadienyl chloride fragments has been previously noticed [8,9,19] and has been ascribed to the small bite of the methylene backbone connecting the two donors. In order to obtain an insight on the factors controlling the formation of the mononuclear (**2** and **5**) and of the dimetallic complexes having either one (**3** and **6**) or two (**4** and **7**) bridging ligands, the reaction between **1** and dppe in 1:1 ratio has been investigated in CD_3CN and CD_3NO_2 solutions, all of the complexes being soluble in such solvents, by collecting ^{31}P NMR spectra at time intervals. Upon mixing the reagents in CD_3CN, **2** and **3** are detected in ca. 1:1 ratio, in addition to the free dppe ligand. Afterwards, an increase in the amount of the monoadduct **2** and a decrease in that of the free ligand are observed. After two days the presence of **4**, which forms from **3** and the free ligand, is detectable; the amount of **4** slowly increases for two days, after which no more transformation is observed and the relative molar ratios of the three compounds are: 60% for **2**, 19% for **3** and 21% for **4**. Compounds **2**, **3** and **4**, in addition to the uncoordinated dppe, are detected as soon as the reagents are mixed in CD_3NO_2: **2** forms in a small amount (8%), which does not change with time; **4** is the dominant complex (yield 65%) and **3** occurs in a 25% amount. In the following hours complex **3** and the free ligand slowly yield **4**. Constant ratios (8% for **2**, 7% for **3** and 85% for **4**) in the amounts of the three complexes are reached within 15 h.

The above results show that at least one route to the dimetal diligand complexes goes through the addition of dppe to the dimetal monoligand compounds. Such addition occurs easily in CD_3NO_2 and slowly in CD_3CN, where the dissociation of the coordinated solvent is disfavoured. Confirmatory evidence for the proposed formation of **4** from **3** is provided by a separate experiment in which pure **3** dissolved in CD_3NO_2 yields almost quantitatively **4** by treatment with the stoichiometric amount of dppe (**7** is recovered from **6**, by analogous treatment with dpadppe). It is admittedly difficult to rationalize the drastic change of the distribution of the different complexes on changing the solvent. Anyhow, as observed by Girolami and coworkers for the reaction of $[Cp^*RuCl]_4$ with dppm, CH_3CN favours the formation of the monometal complex [8]. On the other hand, CH_3NO_2, favours the formation of dimetallic compounds by easing the dissociation of the coordinated solvent. From a mechanistic viewpoint, it is likely that one acetonitrile molecule in **1** is easily replaced by a donor atom of the bidentate ligand to form a bis acetonitrile η^1-ligand metal intermediate. This may yield **2** (or **5**) by intramolecular replacement of a second acetonitrile ligand, or afford **3** (or **6**) via a dimolecular process, by substitution of one acetonitrile in a second tris–acetonitrile adduct. The first route is accessible in CH_3CN, the second one in CH_3NO_2.

3. Experimental

3.1. General

All reactions and manipulations were performed under an atmosphere of dry oxygen-free argon. The solvents were purified according to standard procedures [21]. The ^1H and ^{31}P–$\{^1H\}$ NMR spectra were measured on a Varian Gemini g300bb spectrometer, equipped with a variable-temperature unit, operating at 300 MHz (^1H) and 121.46 MHz (^{31}P). Chemical shifts are relative to tetramethylsilane (^1H) and to H_3PO_4 85% (^{31}P) as external standards at 0.00 ppm; coupling constants are given in Hertz. Micoranalyses were done by the Microanalytical Laboratory of the Department of Chemistry of the University of Firenze. $[CpRu(CH_3CN)_3]PF_6$ (**1**) was prepared according to the literature method [15]. The ligands 1,2-bis(diphenylphosphino)ethane (Aldrich), dppe, and (1-diphenylarsino-2-diphenylphosphino)ethane, (Pressure Chemical Company), dpadppe, were used as purchased.

3.2. Synthesis of the complexes

3.2.1. $[CpRu(dppe)(CH_3CN)]PF_6$ (2)

A solution of dppe (120 mg, 0.30 mmol) in CH_2Cl_2 (5 cm^3) was added at room temperature to $[CpRu(CH_3CN)_3]PF_6$ (**1**) (130 mg, 0.30 mmol) dissolved in CH_2Cl_2 (8 cm^3). The solution turned yellow immediately and a yellow crystalline solid formed after a few minutes. The mixture was left at room temperature overnight and filtered. The solvent of the filtrate was removed under vacuum leaving a yellowish residue, which was washed with diethyl ether (2×15 cm^3) and extracted with cold THF (2×10 cm^3). Yellow microcrystals of **2** were obtained by concentrating the THF extracts and by adding diethyl ether. The solid was washed with petroleum ether (b.p. 40–60 °C) and dried under vacuum. Yield: 95 mg (56%). Anal. Calc. (found) for $C_{33}H_{32}F_6NP_3Ru$: C, 52.81 (52.90); H, 4.30 (4.40); N, 1.87 (1.79). ^1H NMR [δ, $(CD_3)_2CO$, 20 °C]: 7.90–7.40 (20H, m, Ph), 4.89 (5H, s, Cp), 2.80 (2H, br, CH_2), 2.74 (2H, br, CH_2), 1.65 (3H, t, $^5J_{HP} = 1.2$, CH_3). ^{31}P NMR: 80.7 (2P, s, dppe), −142.7 (1P, sept, $^1J_{PF} = 709.5$, PF_6).

3.2.2. $[\{CpRu(CH_3CN)_2\}_2(\mu\text{-dppe})](PF_6)_2$ (3)

The complex was isolated as yellow crystals after washing with diethyl ether (2×15 cm^3) and drying the solid which separated out from the reaction of **1** with dppe in CH_2Cl_2 (see above). Yield: 73 mg (22%). Anal. Calc. (found) for $C_{44}H_{46}F_{12}N_4P_4Ru_2$: C, 44.60 (44.60); H, 3.91 (3.88); N, 4.73 (4.69). ^1H NMR (δ, CD_3NO_2, 20 °C): 7.60–7.41 (20H, m, Ph), 4.49 (10H, s, Cp), 2.59 (4H,

br, CH_2), 2.16 (12H, s, CH_3). ^{31}P NMR: 45.5 (1P, s, dppe), −142.9 (1P, sept, $^1J_{PF} = 707.5$, PF_6).

3.2.3. [{CpRu(CH$_3$CN)}$_2$(μ-dppe)$_2$](PF$_6$)$_2$ (4)

This product was obtained as yellow crystals collecting and drying the solid remaining after extraction with THF in the procedure described above. Yield: 11 mg (12%). Anal. Calc. (found) for $C_{66}H_{64}F_{12}N_2P_6Ru_2$: C, 52.81 (52.73); H, 4.30 (4.35); N, 1.87 (1.83).^{1}H NMR (δ, CD_2Cl_2, 20 °C) 7.61–7.04 (40H, m, Ph), 4.28 (10H, s, Cp), 2.45 (4H, m, CH_2), 2.26 (4H, m, CH_2), 1.96 (6H, s, CH_3). ^{31}P NMR: 38.7 (2P, s, dppe), −142.9 (1P, sept, $^1J_{PF} = 709.5$, PF_6).

The dpadppe compounds [CpRu(dpadppe)(CH_3CN)]PF_6 (**5**), [{CpRu(CH_3CN)$_2$}$_2$(μ-dpadppe)] (PF_6)$_2$ (**6**) and [{CpRu(CH_3CN)}$_2$(μ-dpadppe)$_2$](PF_6)$_2$ (**7**) were obtained by adding the stoichiometric amount of the ligand in CH_2Cl_2 (5 cm^3) to [CpRu(CH_3CN)$_3$]PF_6 (**1**) (0.3 mmol) in CH_2Cl_2 (7 cm^3) and working up the mixture as described above for the preparation of the dppe complexes **2**, **3** and **4**.

3.2.4. [CpRu(dpadppe)(CH$_3$CN)]PF$_6$ (5)

Yield: 122 mg (53%). Anal. Calc. (found) for $C_{33}H_{32}AsF_6NP_2Ru$: C, 49.89 (49.75); H, 4.06 (4.16); N, 1.76 (1.69). ^{1}H NMR [δ, $(CD_3)_2CO$, 20 °C]: 7.95–7.41 (20H, m, Ph), 4.92 (5H, s, Cp), 2.91 (2H, m, CH_2), 2.53 (2H, m, CH_2), 1.71 (3H, d, $^5J_{HP} = 1.3$, CH_3). ^{31}P NMR: 83.4 (1P, s, PPh_2), −142.7 (1P, sept, $^1J_{PF} = 708.0$, PF_6).

3.2.5. [{CpRu(CH$_3$CN)$_2$}$_2$(μ-dpadppe)](PF$_6$)$_2$ (6)

Yield: 54 mg (25%). Anal. Calc. (found) for $C_{44}H_{46}AsF_{12}N_4P_3Ru_2$: C, 43.01 (42.85); H, 3.77 (3.75); N, 4.56 (4.47). ^{1}H NMR (δ, CD_3NO_2, 20 °C): 7.58–7.41 (20H, m, Ph), 4.52 (5H, s, Cp), 4.49 (5H, s, Cp), 2.66 (2H, m, CH_2), 2.56 (2H, m, CH_2), 2.15 (6H, d, $^5J_{HP} = 1.4$, CH_3), 2.14 (6H, s, CH_3). ^{31}P NMR: 45.9 (1P, s, PPh_2), −142.9 (2P, sept, $^1J_{PF} = 707.5$, PF_6).

3.2.6. [{CpRu(CH$_3$CN)}$_2$(μ-dpadppe)$_2$](PF$_6$)$_2$ (7)

Yield: 28 mg (12%). Anal. Calc. (found) for $C_{66}As_2H_{64}F_{12}N_2P_4Ru_2$: C, 49.89 (49.66); H, 4.06 (3.97); N, 1.76 (1.72). ^{1}H NMR (δ, CD_2Cl_2, 20 °C) major isomer: 7.71–7.02 (40H, m, Ph), 4.37 (5H, s, Cp), 4.24 (5H, s, Cp), 2.44–2.23 (8H, m, CH_2), 2.03 (3H, t, $^5J_{HP} = 1.2$, CH_3), 1.80 (3H, s, CH_3). ^{31}P NMR: 40.9 (1P, s, PPh_2), −142.9 (1P, sept, $^1J_{PF} = 709.5$, PF_6). Minor isomer: 7.71–7.02 (40H, m, Ph), 4.32 (10H, s, Cp), 2.44–2.23 (8H, m, CH_2), 1.96 (6H, d, $^5J_{HP} = 1.4$, CH_3). ^{31}P NMR: 41.0 (1P, s, PPh_2), −142.9 (1P, sept, $^1J_{PF} = 709.5$, PF_6).

3.3. X-ray crystallography of [{CpRu(CH$_3$CN)$_2$}$_2$(μ-dppe)](PF$_6$)$_2$ (3)

Crystals of the compound were all of very small size, which posed limitations on the intensities of reflections. All operations were performed at room temperature using a Bruker CCD goniometer mounted on a rotating-anode generator, with Cu Kα radiation ($\lambda = 1.54184$ Å). Cell constants were obtained by least-squares refinement of the setting angles for 813 reflections in the range $7.6 < 2\theta < 100.9°$. A correction for absorption was applied with SADABS [22]. The structure was determined by direct methods [23] and refined on F^2 [24], anisotropically for the nonhydrogen atoms. Hydrogens were in calculated positions, riding, with isotropic temperature factors linked to the U_{eq} of the respective carrier atoms. Features in the final difference synthesis were low and devoid of chemical meaning. Computer programs used included PARST [25] for geometry calculations, and ORTEP [26,27] for graphics (Table 1).

Table 1
Crystal data and structure refinement parameters for **3**

Formula	$C_{44}H_{46}F_{12}N_4P_4Ru$
Formula weight	1184.87
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.909(1)
b (Å)	14.859(1)
c (Å)	18.924(1)
β (°)	99.94(1)
V (Å^3)	2467.5(3)
Z	4
D_{calc} (g cm^{-3})	1.595
μ (mm^{-1})	6.90
Transmission factors range	0.549–1.000
Crystal size (mm)	0.08 × 0.08 × 0.05
$F(000)$	1188
θ range (°)	3.80–50.80
Index ranges	$-8 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$
Reflections collected	8065
Independent reflections	2510 [$R_{int} = 0.089$]
Independent observed reflections	1900 [$I > 2\sigma(I)$]
Restraints/parameters	0/298
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.072$, $wR_2 = 0.165$
R indices (all data)	$R_1 = 0.101$, $wR_2 = 0.177$
Goodness of fit on F^2 (all data)	1.120
Residual electron densities (e Å^{-3})	0.80 to −0.63

Table 2
Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Ru–P	2.318(3)	Ru–C(15)	2.217(14)
Ru–N(1)	2.075(11)	Ru–C(16)	2.166(14)
Ru–N(2)	2.070(10)	Ru–C(17)	2.161(14)
Ru–C(14)	2.198(15)	Ru–C(18)	2.153(14)
Bond angles			
P–Ru–N(1)	93.2(3)	N(1)–Ru–N(2)	87.3(4)
P–Ru–N(2)	93.0(3)	C_n–Ru–C_m[a]	36.7(8)

[a] Mean value of angles to the metal formed by contiguous Cp carbons.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data No. 229312 for compound **3**.

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