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Synthesis of Ru^{II} hydride and alkenyl amidine complexes. The crystal structure of $[Ru(CO)(CH{=}CHCMe_3)\{NH{=}C(Me)(Me_2pz)\}(PPh_3)_2]PF_6$

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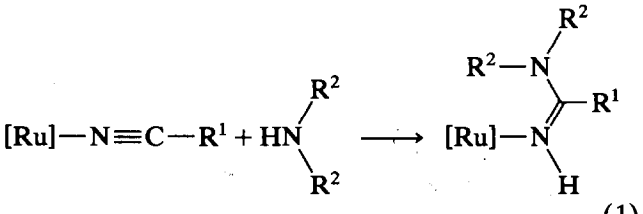
Abstract

The reaction of the ruthenium hydrides $[Ru(CO)H(R^1CN)_2(PPh_3)_2]A$ ($A = ClO_4$ or PF_6) (R^1 = Me or CH_2Ph) or the alkenyl derivatives $[Ru(CO)(CH{=}CHR^1)(R^2CN)_2(PPh_3)_2]PF_6$ ($R^1 = CMe_3$, Ph; R_2 = Me or CH_2Ph) with pyrazole or 3,5-dimethylpyrazole gives the ruthenium(II) pyrazolylamidine complexes $[Ru(CO)H\{NH{=}C(R^1)(het)\}(PPh_3)_2]A$ or $[Ru(CO)(CH{=}CHR^1)\{NH{=}C(R^2)(het)\}(PPh_3)_2]A$, respectively (het = pz or Me_2pz). The stereochemistry of the resulting complexes has been determined by NOEDIFF experiments and by the X-ray structure determination of $[Ru(CO)(CH{=}CHCMe_3)\{NH{=}C(Me)(Me_2pz)\}(PPh_3)_2]PF_6$.

1. Introduction

We have reported in a preliminary communication the formation of the amidine complex $[Ru(CO)H\{NH{=}C(Me)(Me_2pz)\}(PPh_3)_2]ClO_4$ in the reaction of $[Ru(CO)H(MeCN)_2(PPh_3)_2]ClO_4$ with 1-hydroxymethyl-3,5-dimethylpyrazole [1]. A related complex was obtained in the reaction between $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ and $K[HB(Me_2pz)_3]$ in acetonitrile [2]. Only three other examples of formation of this type of amidine derivative in transition metal complexes with coordinated nitriles have been reported [3–5]. These reactions are related to the well known nucleophilic attack of amines on coordinated nitrile ligands to give amidine complexes [6–8] (eqn. (1)). Similar processes are probably involved in the synthetically useful ruthenium-catalyzed amidation of nitriles, which proceeds under neutral conditions [9]. In this paper we report a more extensive study of the synthesis of amidine hydride and alkenylruthenium(II) complexes by reaction of pyrazole and 3,5-dimethylpyrazole with the corresponding ruthenium(II) nitrile complexes.



(1)

2. Results and discussion

Cationic hydride complexes **1** [10], **2** [11] and **3** react with pyrazole or 3,5-dimethylpyrazole in methanol or ethanol under reflux to yield white amidine complexes **4–9** with structures **I** or **II** (Scheme 1). The reaction is most probably initiated by substitution of one of the nitrile ligands by the pyrazole, followed by an intramolecular nucleophilic attack of the pyrazole on the *cis* nitrile ligand.

The amidine hydride complexes are characterized by sharp absorptions in the IR at 3340–3270 cm^{-1}

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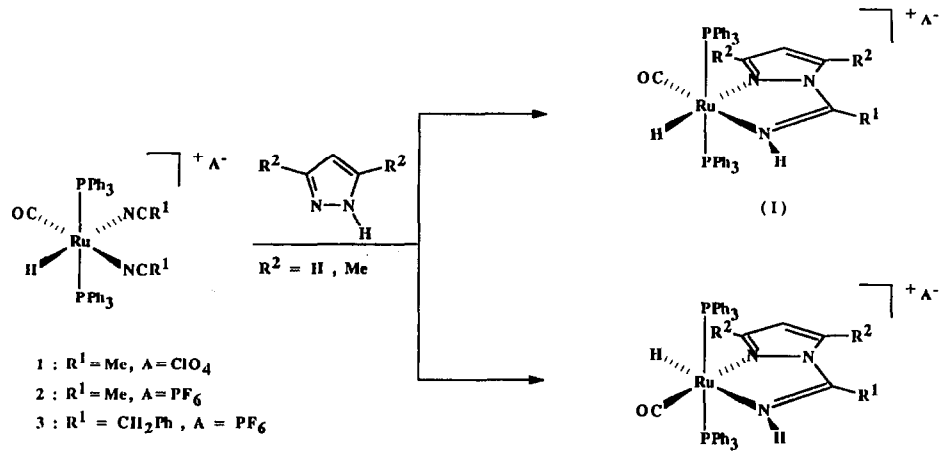
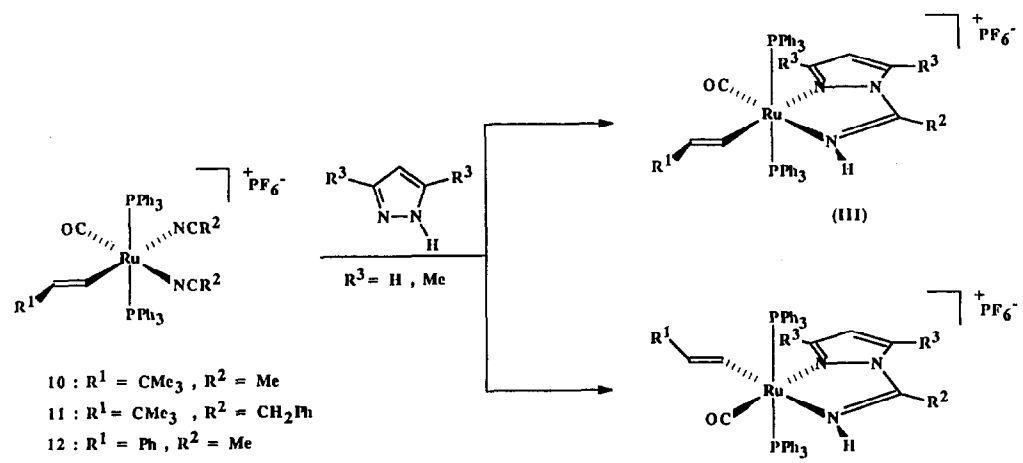


[4: R^1 = Me, R^2 = H, A = ClO_4
5: R^1 = Me, R^2 = H, A = PF_6
6: R^1 = CH_2Ph, R^2 = H, A = PF_6] (I) + (II)

[7: R^1 = R^2 = Me, A = ClO_4
8: R^1 = R^2 = Me, A = PF_6
9: R^1 = CH_2Ph, R^2 = Me, A = PF_6] (II)

Scheme 1.



[13 : R^1 = CMe_3, R^2 = Me, R^3 = H] (III) + (IV)

[14 : R^1 = CMe_3, R^2 = R^3 = Me
15 : R^1 = CMe_3, R^2 = CH_2Ph, R^3 = H
16 : R^1 = CMe_3, R^2 = CH_2Ph, R^3 = Me
17 : R^1 = Ph, R^2 = R^3 = Me] (III)

Scheme 2.

corresponding to ν(N–H) and low-field solvent-dependent NH signals between 12 and 8 ppm in the ^{1}H nuclear magnetic resonance (NMR) spectra. The stereochemistry around the ruthenium centre is probably dictated by steric effects since the bulkier 3,5-dimethylpyrazole gives derivatives **II** exclusively whereas the reactions of hydrides **1–3** with pyrazole afford mixtures of amidine complexes **I** and **II**. Their stereochemistries were assigned by comparison of their spectroscopic data with those of **7**, whose structure has been determined by X-ray diffraction [1]. Furthermore, a NOEDIFF experiment on **8** fully supports the assigned structure.

Similarly, cationic alkenyl complexes **10–12** yielded amidine complexes **13–17** with structures **III** and **IV** as yellow crystalline products (Scheme 2). The structure of amidine complex **14** was assigned by spectroscopic methods, including NOEDIFF experiments, and by X-ray diffraction. The stereochemistries of the remaining derivatives were assigned by analogy with that of **14**.

Amidine complex **17** was also prepared by treatment of the acetonitrile pyridine ruthenium complex **18** [12] with 3,5-dimethylpyrazole. This reaction proceeds by selective displacement of the pyridine ligand *trans* to the alkenyl ligand (eqn. (2)).

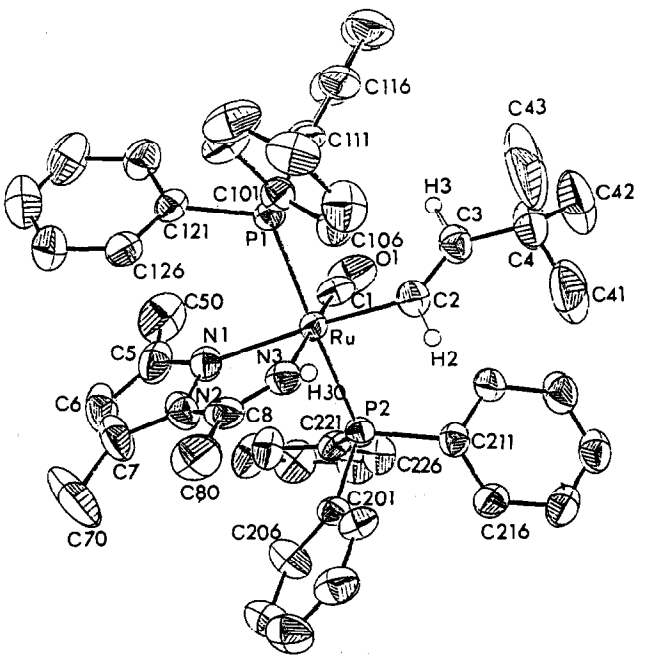
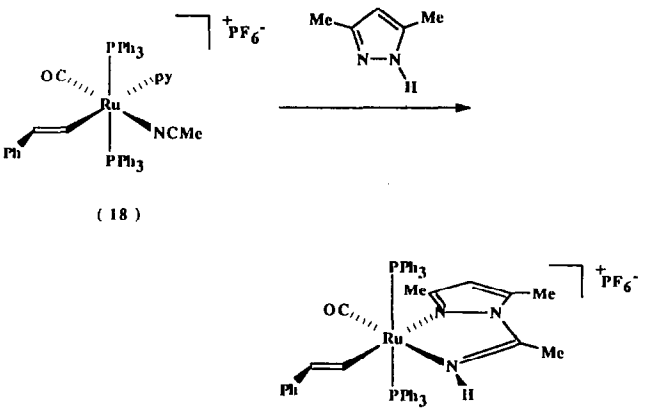
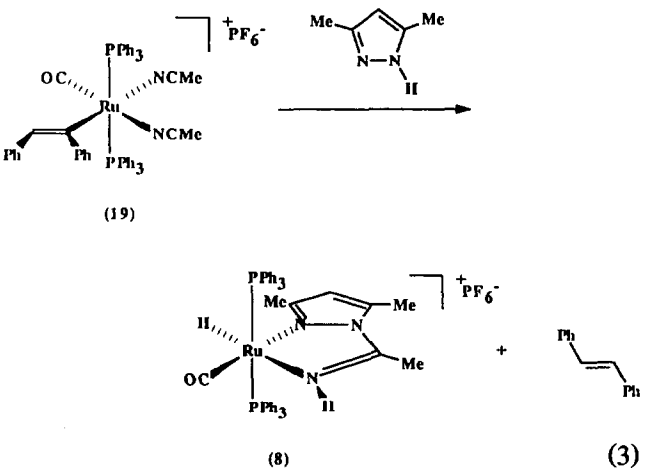


Fig. 1. ORTEP drawing of the structure of the cationic species [Ru(CO)(CH=CHCMe$_3$){NH=C(Me)(Me$_2$pz)}(PPh$_3$)$_2$]$^+$ (atom numbering as in Tables 1 and 3). Numbering of the carbon atoms of the phenyl rings and the hydrogen atoms of the phenyl, methyl and pyrazolyl groups omitted for clarity.



(2)

On the other hand, [Ru(CO)(PhC=CHPh)(MeCN)$_2$(PPh$_3$)$_2$]PF$_6$ (**19**) [13] reacts with 3,5-dimethylpyrazole in ethanol under reflux to give amidine hydride **8** and *trans*-stilbene (eqn. (3)). This result can be explained by the known lability of alkenyl complex **19** under the reaction conditions, yielding hydride **2** and stilbene by reaction with ethanol [13]. Further reaction of hydride **2** with the heterocycle gives the hydride amidine complex **8**.



(3)

Amidine hydride ruthenium complexes **4–9** were unreactive towards 1-alkynes under a variety of reaction conditions. This lack of reactivity shows that the pyrazolylamidine ligand is strongly coordinated, similarly to bipy or phen, whose hydride complexes [Ru(CO)H(L$_2$)(PPh$_3$)$_2$]A (L$_2$ = bipy or phen) are unreactive in the hydroruthenation reaction with alkynes.

2.1. Structure for [Ru(CO)(CH=CHCMe$_3$){NH=C(Me)(Me$_2$pz)}(PPh$_3$)$_2$]PF$_6$ · CH$_2$Cl$_2$ (14)

The X-ray structure of amidine complex **14** revealed the [Ru(CO)(CH=CHCMe$_3$){NH=C(Me)(Me$_2$pz)}(PPh$_3$)$_2$]$^+$ cations (Fig. 1) and the PF$_6^-$ anions, held together only by electrostatic interactions. The crystal

TABLE 1. Selected bond lengths (Å) and angles (°) for compound **14**[a]

Bond lengths			
Ru–P1	2.408(2)	N1–C5	1.32(1)
Ru–P2	2.398(2)	C5–C50	1.49(2)
Ru–C1	1.850(8)	C5–C6	1.41(2)
Ru–C2	2.067(8)	C6–C7	1.33(2)
Ru–N1	2.180(7)	C7–C70	1.49(2)
Ru–N3	2.113(6)	N2–C7	1.36(1)
C1–O1	1.12(1)	C2–C3	1.32(1)
N3–C8	1.24(1)	C3–C4	1.51(1)
C8–C80	1.51(1)	C4–C41	1.57(2)
N2–C8	1.39(1)	C4–C42	1.50(2)
N1–N2	1.40(1)	C4–C43	1.46(2)
Bond angles			
P1–Ru–N1	91.7(2)	N3–C8–C80	124(1)
P1–Ru–N3	90.4(2)	N2–C8–C80	120(1)
P1–Ru–P2	177.62(8)	N2–N1–C5	105.2(7)
P1–Ru–C2	89.8(2)	N1–N2–C7	110.4(8)
P1–Ru–C1	85.0(2)	N1–C5–C6	110(1)
N1–Ru–N3	72.8(3)	N1–C5–C50	120.2(9)
N1–Ru–P2	90.6(2)	C5–C6–C7	108(1)
N1–Ru–C1	104.19(3)	C6–C5–C50	130(1)
N3–Ru–P2	89.6(2)	C6–C7–C70	127(1)
N3–Ru–C2	92.5(3)	N2–C7–C70	126(1)
N3–Ru–C1	174.8(3)	C7–N2–C8	133.7(9)
P2–Ru–C2	87.9(3)	Ru–C2–C3	132.9(7)
P2–Ru–C1	95.1(2)	C2–C3–C4	129.2(9)
C2–Ru–C1	90.0(4)	C3–C4–C41	110.6(9)
Ru–C1–O1	175.9(7)	C3–C4–C42	111(1)
Ru–N1–C5	141.8(7)	C3–C4–C43	111(1)
Ru–N1–N2	112.8(5)	C41–C4–C42	107(1)
N1–N2–C8	115.1(7)	C42–C4–C43	111(1)
N2–C7–C6	197(1)	C43–C4–C41	108(1)
N2–C8–N3	116.4(8)		

[a] Mean bond distances: P–C in PPh_3 ligands = 1.832(8) Å; C–C in Ph rings = 1.39(2) Å; P3–F in PF_6^- = 1.55(2)Å. Mean bond angles: C–P–C in PPh_3 ligands = 103.1(4)°; C–C–C in Ph rings = 120.0(9)°; Ru–P–C = 115.3(3)°, F–P3–F in PF_6^- = 90(1)°.

also contains a CH_2Cl_2 molecule. Selected bond distances and angles are given in Table 1. The Ru atom displays distorted octahedral coordination with C1, C2, N1, and N3 in the equatorial plane and the two triphenylphosphines in approximately axial positions. The complex has structure **I** (Scheme 1) with the carbonyl ligand *trans* to the iminic N3 atom of the pyrazolylamidine chelating ligand. The C2–C3 bond distance of 1.30(4) Å is within the range observed for σ-alkenyl ruthenium(II) complexes [14]. The C=N bond distance (N3–C8) of 1.24(1) Å is similar to that found for **7** [1].

3. Experimental details

IR spectra were recorded with a Pye Unicam SP-3-300S spectrophotometer using KBr disks. Only the most significant frequencies are given. NMR spectra were recorded on Varian XL 300 (^{1}H NMR, 300 MHz), Bruker AM 200 (^{13}C{^{1}H} NMR, 50 MHz), and Bruker WP-80 (^{13}P{^{1}H} NMR, 32 MHz) at 30°C in the reported solvents. Elemental analyses were performed at the Instituto de Química Orgánica (CSIC).

[Ru(CO)H(MeCN)$_2$(PPh$_3$)$_2$]ClO$_4$ (**1**) [10], [Ru(CO)H(MeCN)$_2$(PPh$_3$)$_2$]PF$_6$ (**2**), [Ru(CO)(CH=CHCMe$_3$)(MeCN)$_2$(PPh$_3$)$_2$]PF$_6$ (**10**), [Ru(CO)(CH=CHPh)(MeCN)$_2$(PPh$_3$)$_2$]PF$_6$ (**12**) [11], and [Ru(CO)(CH=CHPh)(MeCN)(py)(PPh$_3$)$_2$]PF (**18**) [12] were prepared as described previously.

3.1. [Ru(CO)H(PhCH$_2$CN)$_2$(PPh$_3$)$_2$]PF$_6$ (3)

A mixture of benzyl cyanide (4.0 ml, 34.6 mmol) and Ru(CO)ClH(PPh$_3$)$_3$ [15] (243 mg, 0.26 mmol) in EtOH (20 ml, was heated under reflux for 30 min. The mixture was partially evaporated and then treated with NH_4PF_6 (65 mg, 0.40 mmol). The white solid was filtered off and washed with EtOH, Et_2O and hexane to yield **3** (230 mg, 87%). IR (cm^{-1}): ν(C ≡ N) 2290vw, 2250vw, ν(Ru–H) 2010w, ν(C ≡ O) 1940vs. ^{1}H NMR ($CDCl_3$): δ 7.60–7.08 (m, 36H, Ph), 6.76 (d, J = 7.3 Hz, 2H, Ph), 6.42 (d, J = 7.3 Hz, 2H, Ph), 3.59 (s, 2H, CH_2), 3.30 (s, 2H, CH_2), −12.82 (t, J = 17.6 Hz, 1H). Anal. Found: C, 61.34; H, 4.43; N, 2.60. $C_{53}H_{45}F_6N_2OP_3Ru$ calc.: C, 61.57; H, 4.39; N, 2.71%.

3.2. [Ru(CO)H{NH=C(Me)(pz)}(PPh$_3$)$_2$]ClO$_4$ (4)

A mixture of hydride **1** (84 mg, 0.1 mmol) and pyrazole (7 mg, 0.1 mmol) in EtOH (5 ml) was heated under reflux for 30 min. After cooling to room temperature, the white solid was filtered off and washed with EtOH and Et_2O to give **4** (62 mg, 73%) as a 35:65 mixture of isomers I and II. Recrystallization (CH_2Cl_2–hexane) gave partially purified isomers.

4-I. IR (cm^{-1}): ν(NH) 3290m, ν(CO) 1950vs, ν(amidine C=N) 1640m, ν(pyrazole CN) 1520w. ^{1}H NMR ($CDCl_3$): δ 9.06 (s, 1H, NH), 7.56 (m, 1H, pz), 7.50–7.20 (m, 30H, Ph), 6.92 (m, 1H, pz), 6.26 (m, 1H, pz), 1.58 (s, 3H, Me), −11.47 (t, J = 19.0 Hz, 1H).

4-II. IR (cm^{-1}): ν(NH) 3275m, ν(CO) 1935s, ν(amidine C=N) 1648m, ν(pyrazole CN) 1520w. ^{1}H NMR ($CDCl_3$): δ 10.81 (s, 1H, NH), 7.53 (m, 1H, pz), 7.50–7.20 (m, 30H, Ph), 6.47 (m, 1H, pz), 6.02 (m, 1H, pz), 1.26 (s, 3H, Me), −10.95 (t, J = 19.0 Hz, 1H).

Anal. Found (mixture of **4-I** and **4-II**): C, 58.86; H, 4.57; N, 4.80. $C_{42}H_{38}ClN_3O_5P_2Ru$ calc.: C, 58.43; H, 4.44; N, 4.87%.

3.3. [Ru(CO)H{NH=C(Me)(pz)}(PPh$_3$)$_2$]PF$_6$ (5)

A mixture of hydride **2** (100 mg, 0.1 mmol) and pyrazole (7 mg, 0.1 mmol) in EtOH (5 ml) was heated under reflux for 30 min. After cooling to room temperature, the white solid was filtered off and washed with EtOH and Et_2O to give **5** (87 mg, 84%) as a 20:80

mixture of isomers **I** and **II**. Recrystallization (CH_2Cl_2–Et_2O) gave partially purified isomers.

5-I. IR (cm^{-1}): ν(NH) 3332m, ν(CO) 1938vs, ν(amidine C=N) 1634m, ν(pyrazole CN) 1523w. ^1H NMR (DMSO-d_6): δ 10.67 (s, 1H, NH), 8.43 (m, 1H, pz), 7.96 (m, 1H, pz), 7.45–7.26 (m, 30H, Ph), 6.48 (m, 1H, pz), 1.77 (s, 3H, Me), −12.14 (t, J = 19.2 Hz, 1H).

5-II. IR (cm^{-1}): ν(NH) 3330m, ν(CO) 1928vs, ν(amidine C=N) 1635, ν(pyrazole CN) 1522w. ^1H NMR (DMSO-d_6): δ 11.63 (s, 1H, NH), 7.89 (m, 1H, pz), 7.45–7.26 (m, 30H, Ph), 7.25 (d, J = 1.7 Hz, 1H, pz), 6.14 (m, 1H, pz), 1.98 (s, 3H, Me), −10.61 (t, J = 19.2 Hz, 1H).

Anal. Found (mixture of **5-I** and **5-II**): C, 55.32; H, 4.33; N, 4.57. $C_{42}H_{38}F_6N_3OP_3Ru$ calc.: C, 55.51; H, 4.21; N, 4.62%.

3.4. $[Ru(CO)H\{NH{=}C(CH_2Ph)(pz)\}(PPh_3)_2]PF_6$ (6)

A mixture of hydride **3** (210 mg, 0.2 mmol) and pyrazole (13.8 mg, 0.2 mmol) in CH_2Cl_2–EtOH (1:1, 20 ml) was heated at 40 °C for 30 min. After cooling to room temperature, the mixture was partially evaporated. Addition of hexane gave a white precipitate, which was filtered off and washed with hexane and Et_2O to give **6** (157 mg, 79%) as a 56:44 mixture of isomers I and II. Recrystallization (CH_2Cl_2–Et_2O) gave partially purified isomers.

6-I. IR (cm^{-1}): ν(NH) 3330m, ν(CO) 1939vs, ν(amidine C=N) 1625m, ν(pyrazole CN) 1525w. ^1H NMR (DMSO-d_6): δ 10.88 (s, 1H, NH), 8.14 (m, 1H, pz), 8.11 (d, J = 2.9 Hz, 1H, pz), 7.61 (s, 1H, pz), 7.45–7.20 (m, 30H, Ph), 7.19–6.86 (m, 3H, Ph), 6.74 (d, J = 7.0 Hz, 2H, Ph), 6.18 (t, J = 2.5 Hz, 1H, pz). 3.68 (s, 2H, CH_2), −11.40 (t, J = 18.3 Hz, 1H).

6-II. IR (cm^{-1}): ν(NH) 3330m, ν(CO) 1932vs, ν(amidine C=N) 1625m, ν(pyrazole CN) 1522 w. ^1H NMR (DMSO-d_6): δ 11.89 (s, 1H, NH), 7.45–7.20 (m, 30H, Ph), 7.19–6.86 (m, 3H, Ph), 6.74 (d, J = 7.0 Hz, 2H, Ph), 5.95 (t, J = 2.6 Hz, 1H, pz), 3.83 (s, 2H, CH_2), −10.73 (t, J = 19.6 Hz, 1H).

Anal. Found (mixture of **6-I** and **6-II**): C, 58.25; H, 4.53; N, 4.39. $C_{48}H_{42}F_6N_3OP_3Ru$ calc.: 58.54; H, 4.30; N, 4.27%.

3.5. $[Ru(CO)H\{NH{=}C(Me)(Me_2pz)\}(PPh_3)_2]ClO_4$ (7)

A mixture of hydride **1** (84 mg, 0.1 mmol) and 3,5-dimethylpyrazole (10 mg, 0.1 mmol) in EtOH (5 ml) was heated under reflux for 30 min. After cooling to room temperature, the white solid was filtered off and washed with EtOH and Et_2O to give **7** (67 mg, 75%) (structure II). This compound is identical with the complex prepared previously from **1** and 1-hydroxymethyl-3,5-dimethylpyrazole [1]. IR (cm^{-1}): ν(NH) 3270m, ν(CO) 1930vs, ν(amidine C=N) 1640m, ν(pyrazole CN) 1570w. ^1H NMR (DMSO-d_6): δ 11.32 (s, 1H, NH), 7.54–7.32 (m, 30H, Ph), 5.75 (s, 1H, pz), 2.21 (s, 3H, Me), 2.17 (s, 3H, Me), 1.36 (s, 3H, Me), −10.57 (t, J = 19.2 Hz, 1H). Anal. Found: C, 58.92; H, 4.64; N, 4.80. $C_{44}H_{42}ClN_3O_5P_2Ru$ calc.: 59.29; H, 4.75; N, 4.71%.

3.6. $[Ru(CO)H\{NH{=}C(Me)(Me_2pz)\}(PPh_3)_2]PF_6$ (8)

This amidine complex was prepared by the same procedure starting from hydride **2** (90 mg, 0.1 mmol) to give **8** (75 mg, 78%) (structure II). IR (cm^{-1}): ν(NH) 3340m, ν(CO) 1930vs, ν(amidine C=N) 1635m, ν(pyrazole CN) 1570m. ^1H NMR (acetone-d_6): δ 10.92 (s, 1H, NH), 7.59–7.34 (m, 30H, Ph), 5.88 (s, 1H, pz), 2.39 (s, 3H, Me), 2.35 (s, 3H, Me), 1.47 (s, 3H, Me), −10.55 (t, J = 19.2 Hz, 1H). ^1H NMR (DMSO-d_6): δ 11.33 (s, 1H, NH), 7.61–7.51 (m, 12H, Ph), 7.50–7.27 (m, 18H, Ph), 5.75 (s, 1H, pz), 2.22 (s, 3H, Me), 2.17 (s, 3H, Me), 1.34 (s, 3H, Me), −10.56 (t, J = 19.4 Hz, 1H). ^1H NOEDIFF (DMSO-d_6) showed the following nOe enhancements on irradiation of the corresponding signals: −10.56 [δ 1.34 (2%), δ 11.33 (0%)], 11.33 [δ 2.22 (3%)], 5.75 [δ 2.17 (1%) and δ 1.34 (1%)]. Anal. Found: C, 56.54; H, 4.73; N, 5.05. $C_{44}H_{42}F_6N_3OP_3Ru$ calc.: C, 56.41; H, 4.52; N, 4.49%.

3.7. $[Ru(CO)H\{NH{=}C(CH_2Ph)(Me_2pz)\}(PPh_3)_2]PF_6$ (9)

A mixture of hydride **3** (118 mg, 0.11 mmol) and 3,5-dimethylpyrazole (23 mg, 0.24 mmol) in EtOH (15 ml) was heated under reflux for 45 min. After cooling to room temperature, the solvent was evaporated and the residue was triturated with Et_2O and washed with Et_2O and hexane to give crude amidine complex. Recrystallization (CH_2Cl_2–Et_2O) gave **9** (95 mg, 82%) (structure **II**). IR (cm^{-1}): ν(NH) 3320m, ν(CO) 1925vs, ν(amidine C=N) 1625m, ν(pyrazole CN) 1570 m. ^1H NMR ($CDCl_3$): δ 8.20 (s, 1H, NH), 7.45–7.22 (m, 33H, Ph), 6.56 (d, J = 7.0 Hz, 2H, Ph), 5.64 (s, 1H, pz), 3.88 (s, 2H, CH_2), 2.48 (s, 3H, Me), 1.13 (s, 3H, Me), −10.80 (t, J = 19.2 Hz, 1H). ^1H NMR (DMSO-d_6): δ 10.95 (s, 1H, NH), 7.52–7.35 (m, 18H, Ph), 7.34–7.20 (m, 12H, Ph), 7.16–7.11 (m, 3H, Ph), 6.51 (d, J = 7.4 Hz, 2H, Ph), 5.74 (s, 1H, pz), 4.08 (s, 2H, CH_2), 2.22 (s, 3H, Me), 1.00 (s, 3H, Me), −10.55 (t, J = 20.0 Hz, 1H). Anal. Found: C, 58.94; H, 4.60; N, 4.32. $C_{50}H_{46}F_6N_3OP_3Ru$ calc.: C, 59.29; H, 4.58; N, 4.15%.

3.8. $[Ru(CO)(CH{=}CHCMe_3)(NCCH_2Ph)_2(PPh_3)_2]PF_6$ (11)

A mixture of hydride **3** (189 mg, 0.18 mmol) and 3,3-dimethyl-1-butyne (0.10 ml, 0.8 mmol) in CH_2Cl_2 (15 ml) was stirred at 23 °C for 24 h. The mixture was filtered and the filtrate was evaporated. The residue

was triturated with Et_2O to yield **11** (120 mg, 59%). IR (cm^{-1}): $\nu(C\equiv N)$ 2280w, $\nu(CO)$ 1940vs. ^1H NMR ($CDCl_3$): δ 7.55–7.48 (m, 18H, Ph), 7.34–7.25 (m, 18H, Ph), 7.20–7.14 (m, 8H, Ph), 6.68 (d, $J = 7.2$ Hz, 2H, Ph), 6.17 (dt, $J = 16.5$, 3.4 Hz, 1H, =CH), 4.72 (br d, $J = 16.5$ Hz, 1H, = CH), 3.49 (s, 2H, CH_2), 3.42 (s, 2H, CH_2), 0.61 (s, 9H, CMe_3). ^{13}C NMR ($CDCl_3$): δ 203.85 (t, $J = 14.7$ Hz), 147.26, 134.01, 131.22 (t, $J = 22$ Hz), 130.16, 128.85, 128.77, 128.21 (t, $J = 4.9$ Hz), 127.82, 127.74 (br), 125.01, 36.12, 29.31, 24.06, 23.63. Anal. Found: C, 63.30; H, 4.74; N, 2.62. $C_{59}H_{55}F_6N_2OP_3Ru$ calc.: C, 63.49; H, 4.97; N, 2.51%.

3.9. $[Ru(CO)(CH{=}CHCMe_3)\{NH{=}C(Me)(pz)\}(PPh_3)_2]PF_6$ (13)

A mixture of alkenyl complex **10** (142 mg, 0.15 mmol) and pyrazole (30 mg, 0.45 mmol) in EtOH (15 ml) was heated under reflux for 45 min. After cooling to room temperature, the solvent was evaporated and the residue was triturated with Et_2O to give **13** (110 mg, 75%) as a 60 : 40 mixture of isomers **III** and **IV** (see Scheme 2). Recrystallization (CH_2Cl_2-hexane) gave almost pure isomers.

13-III. IR (cm^{-1}): ν(NH) 3320m, ν(CO) 1928vs, ν(amidine C=N) 1640m, ν(pyrazole CN) 1520w. ^1H NMR ($CDCl_3$): δ 7.93 (d, $J = 2.0$ Hz, 1H, pz), 7.72 (s, 1H, NH), 7.59 (d, $J = 1.0$ Hz, 1H, pz), 7.40–7.33 (m, 18H, Ph), 7.32–7.25 (m, 12H, Ph), 6.48 (dt, $J = 16.5$, 3.2 Hz, 1H, =CH), 6.37 (m, 1H, pz), 4.92 (dt, $J = 16.5$, 1.6 Hz, 1H, =CH), 1.83 (s, 3H, Me), 0.49 (s, 9H, CMe_3). ^1H NMR (DMSO-d_6): δ 10.30 (s, 1H, NH), 8.44 (br s, 1H, pz), 7.98 (d, $J = 2.9$ Hz, 1H, pz), 7.43–7.31 (m, 18H, Ph), 7.30–7.19 (m, 12H, Ph), 6.49 (dt, $J = 16.4$, 3.2 Hz, 1H, =CH), 6.42 (m, 1H, pz), 5.60 (br d, $J = 16.4$, 1H, =CH), 1.78 (s, 3H, Me), 0.46 (s, 9H, CMe_3).

13-IV. IR (cm^{-1}): ν(NH) 3322m, ν(CO) 1942vs, ν(amidine C=N) 1630m, ν(pyrazole CN) 1520w. ^1H NMR ($CDCl_3$): δ 8.95 (s, 1H, NH), 7.64 (d, $J = 2.0$ Hz,

TABLE 2. Crystal structure analysis parameters for compound **14**

Formula	$C_{50}H_{52}F_6N_3OP_3Ru.CH_2Cl_2$
Crystal size (mm)	0.18 × 0.30 × 0.15
Unit cell dimensions (Å)	14.321(1), 20.654(1), 17.675(1) $\beta = 91.80(1)°$
Symmetry	Monoclinic, $P2_1/n$
Packing: V (Å^3), Z	5225.4(5), 4
$D_{(calc)}$ (g cm^{-3}), M, $F(0, 0, 0)$	1.4032, 1103.89, 2264
μ (cm^{-1})	48.43
Experimental data	
Technique	Four circle diffractometer Philips PW 1100, monochromated Cu Kα, θ_{max} 58°
No. of reflections	
Measured	7753
Observed	5106 ($I \geq 4\sigma(I)$ criterion)
Standard reflections	−153 and 1-5-3 reflections every 90 min, no variation
Solution and refinement	
Solution	Patterson and Fourier synthesis
Refinement	Least squares on F_o with 3 blocks
Absorption correction	Yes; max and min, 1.380 and 0.187
H atoms	Difference Fourier synthesis. H2, H3 and H50 were located. The phenyl hydrogen atoms were fixed at calculated positions. For methyl hydrogen atoms, alternative positions with site occupancies 0.5 were considered.
Parameters	
No. of variables	580
Computer and programs	VAX 6410, XRAY80, SYSTEM, DIRDIF, PESOS [a]
Scattering factors and anomalous dispersion	*Int. Tables for X-Ray Crystallography* [b]
Final R and R_w	0.069, 0.068

[a] J.M. Stewart, F.A. Kundell and J.C. Baldwin, *The XRAY 80 System of Crystallographic Programs*, Computer Science Center, University of Maryland, College Park, MD. P.T. Beurskens, W.P. Bosman, H.M. Doesburg, R.O. Gould, T.E.M. Van Der Hark, P.A. Prick, J.H. Noordik, G. Beurskens, V. Parthasarathi, H.J. Bruins Slot and R.C. Haltiwanger, *DIRDIF System of Computer Programs*, Technical Report 1983/1, Crystallography Laboratory: Toernooiveld, 6525 ED Nijmegen, The Netherlands, 1983. M. Martínez-Ripoll and F.H. Cano, *PESOS program* Instituto de Química Física "Rocasolano", Serrano 119 E, 28006 Madrid, Spain, 1975. [b] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, 1974.

TABLE 3. Atomic coordinates and thermal parameters for compound **14** ($U_{eq} = (1/3)\cdot\Sigma[U_{ij}a_i^*\cdot a_j^*\cdot a_i\cdot a_j\cdot\cos(a_i, a_j)]\times 10^4$)

Atom	x	y	z	U_{eq}
Ru	0.24215(9)	0.00255(7)	0.24779(8)	310(1)
C1	0.3380(5)	0.0036(5)	0.3204(5)	484(25)
O1	0.3924(4)	0.0061(5)	0.3671(4)	746(26)
C2	0.2427(6)	0.1026(4)	0.2451(5)	415(25)
C3	0.3105(7)	0.1461(4)	0.2490(5)	486(29)
C4	0.3047(9)	0.2186(5)	0.2410(6)	678(38)
C41	0.2025(13)	0.2426(6)	0.2530(12)	1097(74)
C42	0.3648(14)	0.2500(7)	0.3015(13)	1142(83)
C43	0.3325(27)	0.2386(7)	0.1659(12)	2051(178)
N1	0.2131(5)	−0.0998(3)	0.2284(4)	441(23)
N2	0.1273(6)	−0.1103(4)	0.1907(4)	533(26)
C5	0.2460(9)	−0.1581(4)	0.2443(6)	647(36)
C6	0.1808(12)	−0.2054(5)	0.2197(7)	838(53)
C7	0.1085(10)	−0.1750(6)	0.1863(6)	755(44)
C50	0.3396(11)	−0.1658(7)	0.2822(8)	874(52)
C70	0.0201(15)	−0.2053(8)	0.1563(10)	1291(79)
N3	0.1252(4)	−0.0030(4)	0.1721(3)	417(19)
C8	0.0872(6)	−0.0557(5)	0.1570(5)	506(31)
C80	0.0019(7)	−0.0630(8)	0.1051(7)	818(49)
P1	0.1406(1)	0.0054(1)	0.3537(1)	353(5)
C101	0.1274(6)	0.0827(4)	0.4022(5)	411(25)
C102	0.0418(6)	0.1046(4)	0.4273(5)	479(28)
C103	0.0360(8)	0.1609(5)	0.4708(6)	628(35)
C104	0.1168(9)	0.1942(5)	0.4914(6)	643(36)
C105	0.2011(8)	0.1728(5)	0.4681(6)	649(37)
C106	0.2082(7)	0.1172(4)	0.4219(6)	516(30)
C111	0.1779(5)	−0.0482(4)	0.4329(4)	402(24)
C112	0.1890(8)	−0.1142(4)	0.4184(5)	565(33)
C113	0.2196(9)	−0.1551(5)	0.4752(6)	693(39)
C114	0.2384(8)	−0.1324(6)	0.5470(6)	708(40)
C115	0.2242(8)	−0.683(6)	0.5625(6)	703(39)
C116	0.1925(7)	−0.0252(4)	0.5051(5)	506(28)
C121	0.0207(5)	−0.0193(4)	0.3306(4)	399(24)
C122	−0.0197(7)	−0.0753(5)	0.3559(5)	582(32)
C123	−0.1105(8)	−0.0932(6)	0.3338(6)	704(38)
C124	−0.1599(7)	−0.0545(6)	0.2843(6)	669(38)
C125	−0.1230(6)	0.0027(6)	0.2585(5)	588(30)
C126	−0.0323(6)	0.0206(4)	0.2803(5)	475(27)
P2	0.3430(1)	0.0045(1)	0.1421(1)	350(5)
C201	0.2998(5)	0.0452(4)	0.0558(5)	391(24)
C202	0.2341(6)	0.0944(4)	0.0589(5)	461(27)
C203	0.2047(8)	0.1259(5)	−0.0081(6)	622(34)
C204	0.2383(7)	0.1083(5)	−0.0758(5)	588(33)
C205	0.3013(7)	0.0584(6)	−0.0802(5)	677(37)
C206	0.3325(6)	0.0268(5)	−0.0150(5)	567(31)
C211	0.4577(5)	0.0409(4)	0.1594(5)	437(26)
C212	0.5138(6)	0.0169(5)	0.2210(6)	571(32)
C213	0.6003(7)	0.0462(7)	0.2385(7)	768(44)
C214	0.6323(8)	0.0969(8)	0.1947(9)	876(51)
C215	0.5786(8)	0.1188(6)	0.1351(8)	807(45)
C216	0.4911(6)	0.0909(5)	0.1173(6)	614(36)
C221	0.3676(6)	−0.0764(4)	0.1047(4)	399(24)
C222	0.2925(6)	−0.1098(5)	0.0693(5)	541(30)
C223	0.3040(8)	−0.1722(5)	0.0433(6)	667(37)
C224	0.3894(11)	−0.2013(5)	0.0487(7)	795(47)
C225	0.4648(9)	−0.1691(6)	0.0805(7)	797(43)
C226	0.4549(7)	−0.1057(5)	0.1089(6)	572(33)
P3	−0.0685(2)	0.1688(1)	0.1163(2)	700(10)
F1	−0.0680(9)	0.1790(6)	0.0294(5)	1393(50)
F2	−0.0712(11)	0.1601(5)	0.2046(5)	1533(59)
F3	−0.1672(7)	0.2026(7)	0.1186(7)	1564(59)
F4	−0.0305(12)	0.2373(6)	0.1319(8)	1852(75)
F5	−0.1180(16)	0.1043(6)	0.1012(9)	2111(99)
F6	0.0219(10)	0.1331(10)	0.1172(9)	2418(94)
C11	0.3984(0)	0.0816(0)	0.5992(0)	2546(50)
C12	0.4793(0)	0.1398(0)	0.4660(0)	3352(79)
C12	0.4839(0)	0.1392(0)	0.5577(0)	2777(173)

1H, pz), 7.49–7.30 (m, 18H, Ph), 7.29–7.22 (m, 12H, Ph), 7.09 (d, $J = 1.5$ Hz, 1H, pz), 6.47 (dt, $J = 16.4$, 3.2 Hz, 1H, =CH), 6.16 (m, 1H, pz), 5.08 (br d, $J = 16.3$, 1H, =CH), 2.04 (s, 3H, Me), 0.63 (s, 9H, CMe_3). ^{1}H NMR (DMSO-d_6): δ 11.23 (s, 1H, NH), 8.03 (d, $J = 2.9$ Hz, 1H, pz), 7.43–7.31 (m, 18H, Ph), 7.30–7.19 (m, 13H, Ph + 1H pz), 6.41 (dt, $J = 16.5$, 3.2 Hz, 1H, =CH), 6.29 (m, 1H, pz), 5.03 (br d, $J = 16.5$ Hz, 1H, =CH), 2.00 (s, 3H, Me), 0.57 (s, 9H, CMe_3).

Anal. Found (mixture of **13-I** and **13-IV**): C, 57,89; H, 5.01; N, 4.43. $C_{48}H_{48}F_6N_3OP_3Ru$ calc.: C, 58.18; H, 4.88; N, 4.24%.

3.10. [Ru(CO)(CH=CHCMe$_3$){NH=C(Me)(Me$_2$pz)}(PPh$_3$)$_2$]PF$_6$ (14)

A mixture of alkenyl complex **10** (164 mg, 0.17 mmol) and 3,5-dimethylpyrazole (27 mg, 0.28 mmol) in EtOH (8 ml) was heated under reflux for 2 h. After cooling to room temperature, the solvent was evaporated and the residue was triturated with hexane to give crude **14**. Recrystallization (1:1 CH_2Cl_2–hexane) gave yellow crystals of **14**·CH_2Cl_2 (130 mg, 69%) (structure III) suitable for X-ray structure determination. IR (cm^{-1}): ν(NH) 3326m, ν(CO) 1930vs, ν(amidine C=N) 1630m, ν(pyrazole CN) 1570m. ^{1}H NMR ($CDCl_3$): δ 8.41 (s, 1H, NH), 7.45–7.27 (m, 18H, Ph), 7.26–7.16 (m, 12H, Ph), 6.62 (dt, $J = 16.3$, 3.2 Hz, 1H, =CH), 5.96 (s, 1H, pz), 5.09 (dt, $J = 16.3$, 1.8 Hz, 1H, =CH), 2.25 (s, 3H, Me), 2.17 (s, 3H, Me), 1.67 (s, 3H, Me), 0.49 (s, 9H, CMe_3). ^{1}H NOEDIFF ($CDCl_3$) showed the following nOe enhancements on irradiation of the corresponding signals: 2.25 [δ 5.96 (9%)], 8.41 [δ 5.09 (10%), δ 6.62 (4%), and δ 2.17 (4%)], 2.17 [δ 8.41 (3%)]. ^{13}C NMR ($CDCl_3$) δ 207.26 (t, $J = 14.3$ Hz), 162.01, 156.25, 149.14, 144.95, 133.24 (t, $J = 5.1$ Hz), 131.49, 130.85 (t, $J = 21.2$ Hz), 130.10, 128.42 (t, $J = 4.5$ Hz), 114.73, 36.20, 29.25, 21.15, 15.01, 14.58. Anal. Found: C, 55.72; H, 4.49; N, 3.89. $C_{50}H_{52}F_6N_3OP_3Ru$-CH_2Cl_2 calc.: C, 55.49; H, 4.93; N, 3.81%.

3.11. [Ru(CO)(CH=CHCMe$_3$){NH=C(CH$_2$Ph)(pz)}(PPh$_3$)$_2$]PF$_6$ (15)

A mixture of alkenyl complex **11** (56 mg, 0.05 mmol) an pyrazole (10 mg, 0.15 mmol) in EtOH (8 ml) was

heated under reflux for 30 min. After cooling to room temperature, the yellow crystals were filtered off and washed with Et_2O and hexane to give **15** (48 mg, 89%) (structure III). IR (cm^{-1}): ν(NH)3318m, ν(CO) 1925vs, ν(amidine C=N) 1630m, ν(pyrazole CN) 1525w. ^1H NMR ($CDCl_3$): δ 8.11 (s, 1H, NH), 8.04 (d, J = 3.2 Hz, 1H, pz), 7.34–7.30 (m, 12H, Ph), 7.29–7.24 (m, 21H, Ph), 6.64 (br s, 1H, pz), 6.43 (d, J = 2H, Ph), 6.43 (dt, J = 16.3, 3.2 Hz, 1H, =CH), 6.01 (m, 1H, pz), 5.10 (br d, J = 16.3 Hz, 1H, =CH), 3.82 (s, 2H, CH_2), 0.63 (s, 9H, CMe_3). Anal. Found: C, 60.67; H, 4.83; N, 4.05. $C_{54}H_{52}F_6N_3OP_3Ru$ calc.: C, 60.79; H, 4.91; N, 3.94%.

3.12. $[Ru(CO)(CH=CHCMe_3)\{NH=C(CH_2Ph)(Me_2pz)\}(PPh_3)_2]PF_6$ (16)

A mixture of alkenyl complex **11** (167 mg, 0.15 mmol) and 3,5-dimethylpyrazole (10 mg, 0.15 mmol) in EtOH (15 ml) was heated under reflux for 1 h. After cooling to −15°C, the yellow crystals were filtered off, washed with Et_2O and hexane, and recrystallized (1:1 CH_2Cl_2–Et_2O) to give **16** (125 mg, 76%) (structure III). IR (cm^{-1}): ν(NH) 3320m, ν(CO) 1930vs, ν(amidine C=N) 1630m, ν(pyrazole CN) 1570 m. ^1H NMR ($CDCl_3$): δ 7.49 (s, 1H, NH), 7.48–7.35 (m, 6H, Ph), 7.34–7.25 (m, 14H, Ph), 7.13–7.06 (m, 13H, Ph), 6.62 (d, J = 7.7 Hz, 2H, Ph), 6.27 (dt, J = 16.2, 3.2 Hz, 1H, =CH), 5.95 (s, 1H, pz), 5.01 (dt, J = 16.2, 1.9 Hz, 1H, =CH), 3.88 (s, 2H, CH_2), 2.48 (s, 3H, Me), 1.48 (s, 3H, Me), 0.38 (s, 9H, CMe_3). ^1H NMR (DMSO-d_6): δ 9.70 (s, 1H, NH), 7.50–7.24 (m, 20H, Ph), 7.23–7.11 (m, 13H, Ph), 6.77 (dt, J = 16.2, 2.4 Hz, 1H, =CH), 6.58 (d, J = 7.4 Hz, 2H, Ph), 5.98 (s, 1H, pz), 4.92 (dt, J = 16.2, 1.2 Hz, 1H, =CH), 4.18 (s, 2H, CH_2), 2.22 (s, 3H, Me), 1.49 (s, 3H, Me), 0.50 (s, 9H, CMe_3). Anal. Found: C, 61.15; H, 5.07; N, 3.83. $C_{56}H_{56}F_6N_3OP_3Ru$ calc.: C, 61.42; H, 5.15; N, 3.84%.

3.13. $[Ru(CO)(CH=CHPh)\{NH=C(Me)(Me_2pz)\}(PPh_3)_2]PF_6$ (17)

A mixture of alkenyl complex **12** (59 mg, 0.6 mmol) and 3,5-dimethylpyrazole (15 mg, 0.15 mmol) in EtOH (10 ml) was heated under reflux for 1 h. After cooling to room temperature, the solvent was evaporated. The residue was triturated with Et_2O and washed with Et_2O and hexane to give **17** (46 mg, 77%) (structure III). IR (cm^{-1}): ν(NH) 3320m, ν(CO) 1932vs, ν(amidine C=N) 1628m, ν(pyrazole CN) 1570w. ^1H NMR($CDCl_3$): δ 8.71 (s, 1H, NH), 8.11 (dt, J = 16.6, 3.4 Hz, 1H, =CH), 7.34–7.15 (m, 30H, Ph), 7.06 (t, J = 7.5 Hz, 2H, Ph), 6.92–6.85 (m, 1H, Ph), 6.71 (d, J = 7.1 Hz, 2H, Ph), 6.00 (s, 1H, pz), 5.89 (br d, J = 16.6 Hz, 1H, =CH), 2.27 (s, 3H, Me), 2.21 (s, 3H, Me), 1.74 (s, 3H, Me). ^{31}P NMR ($CDCl_3$): δ 25.8 (s), −148.8 (hept., J = 713 Hz). ^{13}C NMR ($CDCl_3$): δ 206.89 (t, J = 14.5 Hz), 162.47 (t, J = 2.8 Hz), 156.54, 147.35 (t, J = 13.4), 145.38, 140.70, 139.53 (t, J = 4.2 Hz), 133.34 (t, J = 5.2 Hz), 130.78 (t, J = 21.5 Hz), 130.26, 128.56 (t, J = 4.6 Hz), 127.82, 124.39, 124.31, 114.66, 21.32, 15.16, 14.61. Anal. Found: C, 60.33; H, 4.60; N, 4.05. $C_{52}H_{48}F_6N_3OP_3Ru$ calc.: C, 60.12; H, 4.66; N, 4.04%.

3.14. X-ray diffraction data for compound 14

Table 2 gives the crystal structure analysis parameters of compound **14**. Table 3 gives the final atomic coordinates and thermal parameters for all non-hydrogen atoms of this compound. Lists of structure factors and thermal parameters are available from the authors.

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