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Synthesis and reactivity of bis(3,5-dimethylpyrazol-1-yl)methanes functionalized by *2*-halophenyl groups on the methine carbon

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ABSTRACT

Three new bis(3,5-dimethylpyrazol-1-yl)methanes [(2-XC_6H_4)$CH(3,5\text{-}Me_2Pz)_2$, *X* = F, Cl and Br] functionalized by 2-halophenyl groups on the methine carbon atom have been synthesized. Upon heating (2-XC_6H_4)$CH(3,5\text{-}Me_2Pz)_2$ with $Mo(CO)_6$ or $W(CO)_5THF$ in THF at reflux, complexes (2-XC_6H_4)$CH(3,5\text{-}Me_2Pz)_2M(CO)_4$ (*X* = F or Cl, M = Mo or W) were obtained. While the similar reaction of (2-BrC_6H_4)$CH(3,5\text{-}Me_2Pz)_2$ led to the oxidative addition of the C–Br bond to the Mo or W center to give complexes $(C_6H_4)CH(3,5\text{-}Me_2Pz)_2M(CO)_3Br$ (M = Mo or W). In addition, 2-$ImC_6H_4CH(3,5\text{-}Me_2Pz)_2$ (Im = imidazol-1-yl) has been obtained by the reaction of (2-BrC_6H_4)$CH(3,5\text{-}Me_2Pz)_2$ with imidazole, which subsequently reacted with $PhCH_2Cl$ to form 1-{2-[bis(3,5-dimethylpyrazol-1-yl)methyl]phenyl}-3-benzylimidazium chloride. Treatment of this imidazole salt with Ag_2O and succeedingly with $W(CO)_5THF$ or $Ru_3(CO)_{12}$ yielded *N*-heterocylic carbene complexes $LW(CO)_5$ and $LRu_3(CO)_8(\mu\text{-}H)(\mu\text{-}Cl)$ (*L* = 1-{2-[bis(3,5-dimethylpyrazol-1-yl)methyl]phenyl}-3-benzylimidazol-2-ylidene), respectively. In the former, L acts as a monodentate ligand by the carbene carbon to the tungsten atom, and two pyrazolyl nitrogen atoms do not take part in the coordination to the metal center. While in the latter, L serves as a bridging bidentate ligand by one pyrazolyl nitrogen and the carbene carbon atoms to a Ru–Ru bond, and a hydride along with a chloride ligand bridges this metal–metal bond.

1. Introduction

Bis(pyrazol-1-yl)methanes modified by organic functional groups on the bridging carbon atom have drawn extensive attention in recent years, owing to their versatile coordination chemistry toward main group and transition metals [1–3]. Our existing investigations on bis(pyrazol-1-yl)methanes indicate that modification of these ligands with organic groups on the methine carbon can provide unusual reactivity [4–7]. For instance, the reaction of bis(pyrazol-1-yl)methanes functionalized by 2-hydroxyphenyl or 2-methoxyphenyl on the bridgehead carbon atom with $W(CO)_5THF$ resulted in the cleavage of a C_{sp3}–N bond to form novel pyrazole derivatives [4], which inspires us to expand this investigation to gain deeper understanding, such as the effect of other substituents of the phenyl group on this reaction. On the other hand, although the oxidative addition of the C–X bond to the tungsten(0) atom appeared in 1987 [8], the cases of the oxidative addition of the C–X bond to group 6 metal(0) are still rare in literature [8–16]. In addition, the coupling reactions of aryl halides with heteroatom-containing nucleophiles have also been one of the most useful and practical methods for the formation of the carbon-heteroatom bonds [17]. Thus, it should be interesting to synthesize and exploit the relative reactivity of bis(3,5-dimethylpyrazol-1-yl)methanes functionalized by 2-halophenyl groups.

2. Results and discussion

2.1. Synthesis and reaction of 2-halophenylbis(3,5-dimethylpyrazol-1-yl)methanes

2-Halophenylbis(3,5-dimethylpyrazol-1-yl)methanes were easily obtained by the catalyzed Peterson rearrangement [18–20] starting from bis(3,5-dimethylpyrazol-1-yl)methanone and 2-halobenzenealdehydes (Scheme 1). These ligands have demonstrated different reactivities, upon treatment with group 6 metal carbonyl complexes. For example, reactions of ligands **1** and **2** with $Mo(CO)_6$ or $W(CO)_5THF$ in refluxing THF yielded the decarbonylation complexes **4**–**7**, while the similar reaction of ligand **3** resulted in the oxidative addition of the C–Br bond to the molybdenum(0) or tungsten(0) atom to give novel heterometallacyclic complexes **9** and **10**. These results are well correlated with the C–X bond strengths [11]. In addition, irradiation of ligand **3** with $W(CO)_6$

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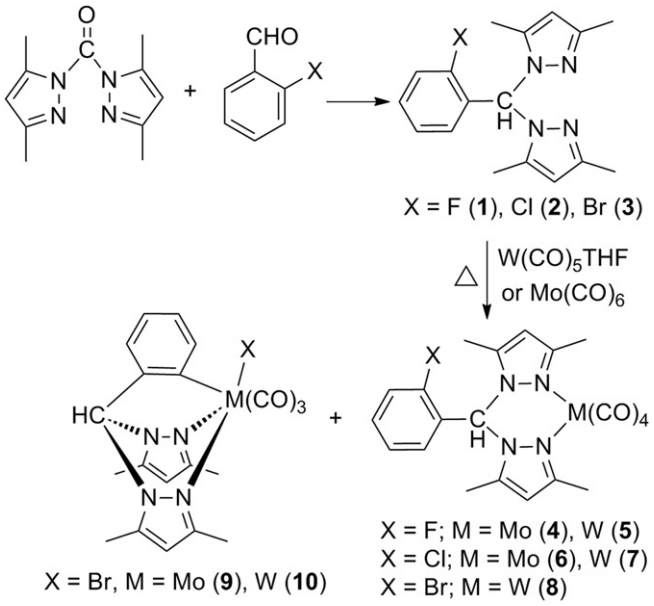


Scheme 1. Synthesis and reaction of 2-halophenylbis(pyrazol-1-yl)methanes.

at room temperature afforded the decarbonylation complex **8**, and subsequently heating this complex in refluxing THF also led to the oxidative addition of the C–Br bond to form complex **10**.

Although complexes **4**–**10** were slightly air-sensitive, their solutions could be manipulated in the air without notable decomposition. These complexes have been characterized by elemental analyses, IR and NMR spectroscopy. The IR spectra of complexes **4**–**8** are markedly different from those of complexes **9** and **10**. Four strong ν_{CO} bands in the range of 1814–2014 cm^{-1} are observed in complexes **4**–**8**, indicating a typical *cis*-tetracarbonyl arrangement. While three such absorption peaks in the range of 1896–2014 cm^{-1} are found in complexes **9** and **10**, consistent with the structure of the seven-coordinated tricarbonyl species [8,13]. It is noteworthy that a proton signal of the phenyl group markedly shifts upfield by *ca.* 1 ppm in complexes **4**–**8**, compared with those of free ligands **1**–**3**. The most reasonable interpretation of these remarkable changes in NMR would be the effect of the pyrazole ring when the proton is located in the shielding region of the magnestically anisotropic ring. The explanation was then confirmed by the X-ray crystal structure of complex **7** (Fig. 1) which shows that the proton on the C(5) atom is situated over the N(4)–N(3)–C(13)–C(14)–C(15) pyrazolyl plane. The free rotation of the phenyl ring around the C–C bond may be prevented by the steric repulsion among substituents. Similar results are observed in other arylbis(pyrazol-1-yl)methane derivatives [4,21].

The structures of complexes **7** and **10** have been further confirmed by X-ray structural analyses, and presented in Figs. 1 and 2, respectively. Fig. 1 shows that ligand **2** acts as an *N*,*N*-bidentate chelating ligand in complex **7**, and the tungsten atom adopts a distorted octahedral coordination geometry. The phenyl ring locates on the axial position of the boat conformation of the metallacyle, and is perpendicular to the N(4)–N(3)–C(13)–C(14)–C(15) pyrazolyl plane with a dihedral angle of 90.0°. The average W–N bond distance is 2.278 Å, similar to that in (2-$MeOC_6H_4$)$CH(3,5\text{-}Me_2Pz)_2W(CO)_4$ (2.271 Å) [4]. The angles of W(1)–C(21)–O(4) (167.8(4)°) and W(1)–C(19)–O(2) (171.9(5)°) remarkably deviate from linearity, reflecting the presence of large steric repulsion between these two carbonyls with ligands, especially with the phenyl and the 3-position methyl groups of pyrazolyl rings.

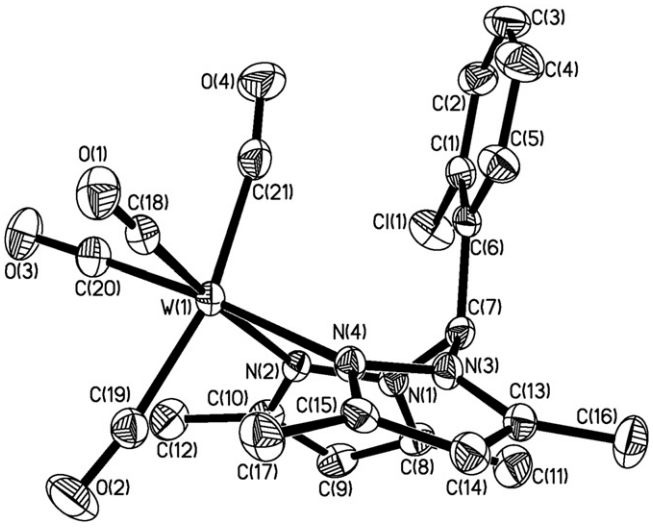


Fig. 1. The molecular structure of **7**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–N(2) 2.268(3), W(1)–N(4) 2.288(4), C(7)–N(1) 1.444(5), C(7)–N(3) 1.450(6) Å; W(1)–C(18)–O(1) 179.9(4), W(1)–C(19)–O(2) 171.9(5), W(1)–C(20)–O(3) 176.5(4), W(1)–C(21)–O(4) 167.8(4), C(19)–W(1)–C(21) 164.9(2), N(2)–W(1)–N(4) 79.4(1), N(1)–C(7)–N(3) 109.3(3), N(3)–C(7)–C(6) 112.6(4)°.

Fig. 2 clearly displays that the bromine atom has been transferred to the tungsten center, and new tungsten–carbon bond and tungsten–bromine bond have been formed by the oxidative addition reaction of the C–Br bond to the tungsten(0) atom. The ligand acts as a tridentate and monoanionic κ^3-[N,C,N] chelating ligand through one phenyl carbon and two pyrazolyl nitrogen atoms. The dihedral angles of the phenyl ring with two pyrazolyl rings are 62.3° (the N(2)–C(7) plane) and 70.9° (the N(4)–C(12) plane), respectively. The W(1)–C(16) distance is 2.235(4) Å, comparable to those in $BrC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4W(CO)_3Br$ (**A**) (2.20(2) Å) [8] and $C_6H_4CH{=}NC_6H_4NH_2W(CO)_3F$ (2.232(6) Å) [9]. The W(1)–Br(1) bond

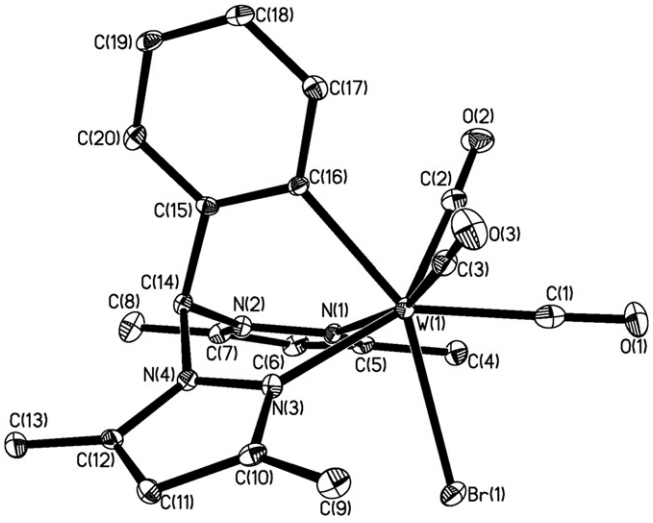


Fig. 2. The molecular structure of **10**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–N(1) 2.226(6), W(1)–N(3) 2.227(6), W(1)–Br(1) 2.699(2), W(1)–C(16) 2.235(4), C(14)–N(2) 1.451(7), C(14)–N(4) 1.461(7) Å; W(1)–C(1)–O(1) 175.9(5), W(1)–C(2)–O(2) 177.2(5), W(1)–C(3)–O(3) 177.8(5), N(1)–W(1)–N(3) 82.9(2), N(2)–C(14)–N(4) 110.1(4), N(2)–C(14)–C(15) 112.2(3), C(16)–W(1)–Br(1) 153.5(1), N(1)–W(1)–C(3) 164.9(2), N(1)–W(1)–Br(1) 80.2(1)°.

distance is 2.699(2) Å, slightly longer than the corresponding bond in complex **A** (2.651(2) Å) [8] and (η^5-C_9H_7)$W(CO)_3Br$ (2.6453(3) Å) [16]. The average W–N bond distance is 2.2265 Å, slightly shorter than that in complex **7**, possibly since the relative strong Lewis acidity of the tungsten(II) atom in complex **10** strengthens the W–N bond.

2.2. Synthesis of NHC complexes bearing bis(3,5-dimethylpyrazol-1-yl)methyl group

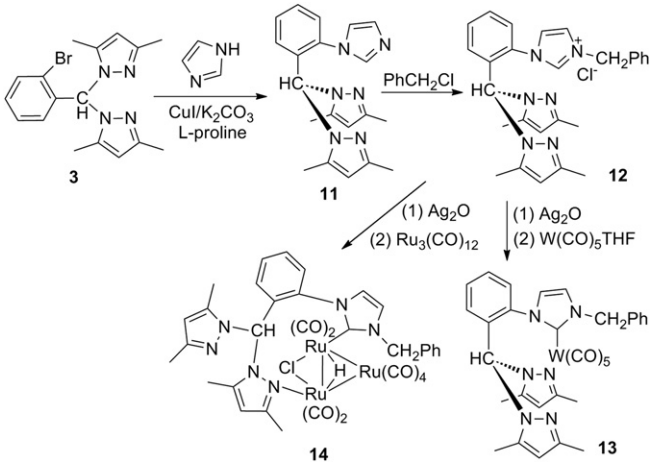
Since the first stable free *N*-heterocyclic carbene (NHC) was isolated and characterized [22], the NHC chemistry has been flourishing over two decades [23–25]. In recent years, lots of nitrogen-, oxygen- and sulfur-functionalized NHC ligands have been obtained [26–28]. Owing to the introduction of the additional donor atoms on the side-arm of NHCs, these functionalized NHCs often exhibit novel reactivity patterns in the reactions with transition metals, and provide relatively stable and efficient catalysts or catalyst precursors. On the other hand, as one of the most popular nitrogen-containing donor ligands, bis(pyrazol-1-yl)methanes have been extensively exploited to form various transition metal complexes [1–3]. Thus we reason that NHCs bearing bis(pyrazol-1-yl)methyl fragment can act as very useful ligands for transition metals.

Ligand **11** was obtained by the coupling reaction of ligand **3** with imidazole (Scheme 2), which subsequently reacted with $PhCH_2Cl$ to form the imidazole salt **12**. Treatment of **12** with Ag_2O and succeedingly with $W(CO)_5THF$ yielded *N*-heterocylic carbene complex **13**, which was characterized by elemental analyses, IR and NMR spectroscopy. The IR spectrum of **13** shows a ν_{CO} absorption at 2060 cm^{-1}, corresponding to the A_{1eq} mode for the pseudo C_{4v} metal center in a metal pentacarbonyl moiety [29], consistent with the existing of $W(CO)_5$ fragment in this complex. Its ^{13}C NMR spectrum also supports the proposed structure, which unambiguously shows two signals of the carbonyl carbon atoms with *ca.* a 1:4 intensity ratio. In addition, ^1H NMR spectrum of **13** indicates the methylene protons of the benzyl group are not equivalent, and an AB system is observed at room temperature. Furthermore, two sets of ^1H and ^{13}C signals of the pyrazolyl moiety are observed in these spectra. These results suggest that large steric repulsion should exist in **13**, which prevents the free rotation of the pyrazolyl and benzyl groups.

The structure determination of complex **13** reveals that the NHC acts as a monodentate ligand by the carbene carbon to the tungsten atom, and two pyrazolyl nitrogen atoms do not take part in the coordination to the metal center (Fig. 3), consistent with the spectroscopic analyses of IR and NMR. The W-C_{NHC} bond distance is 2.268(3) Å, falling within the range of values observed in NHC-supported $W(CO)_5$ complexes (2.242–2.299 Å) [30–34]. The angles of N(1)–C(6)–C(7) (113.8(2)°) and N(5)–C(22)–C(21) (114.6(2)°) deviate from the tetrahedral geometry of the sp^3-hybridized carbon atoms. Five carbonyls, especially two *cis*-carbonyls (C(1)O(1) and C(4)O(4)), are distorted. These geometric features suggest a large steric repulsion in this complex, as mentioned by its NMR spectra. To decrease the steric repulsion, the phenyl ring of benzyl group and pyrazolyl rings are driven away from the metal center. At the same time, the steric repulsion hinders the polydentate NHC's ability to act as a [N,C] bidentate or [N,N,C] tridentate ligand in mononuclear tungsten derivatives. Complex **13** decomposed upon heated at high temperature.

Recently, the coordination chemistry of polydentate NHCs toward transition metal carbonyl clusters has received increasing attention [35]. Remarkable C–H bond activation processes were often observed in the reactions of polydentate NHCs with transition metal carbonyl clusters, especially triruthenium and triosmium clusters [36,37]. Herein, we found that the direct thermolysis of the imidazole salt **12** with $Ru_3(CO)_{12}$ in THF at reflux resulted in the decomposition of the ligand. While the reaction of **12** with Ag_2O and succeeding treatment with $Ru_3(CO)_{12}$ yielded NHC derivative **14** (Scheme 2). Although no C–H bond activation was detected in this reaction, the eliminated HCl molecule did not depart from the reaction system, but coordinated to a Ru–Ru bond to form a hydride and a chloride bridges. In the ^1H NMR spectrum of complex **14**, the signal of the hydride ligand appeared at −11.3 ppm. The NMR resonance of the carbene carbon was observed at 179.0 ppm. Although it seems that **14** can be regarded as a product of the direct reaction of **12** with $Ru_3(CO)_{12}$, the corresponding reaction of these two compounds does not occur at room temperature and leads to the decomposition of the ligand at reflux in THF. The possible pathway of the formation of **14** is not entirely clear at present, which should involve NHC transferring reaction of Ag–NHC complex in the first step.

The molecular structure of **14** was determined by X-ray diffraction analysis, which consisted of two crystallographically



Scheme 2. Synthesis of NHC complexes bearing bis(pyrazol-1-yl)methanes.

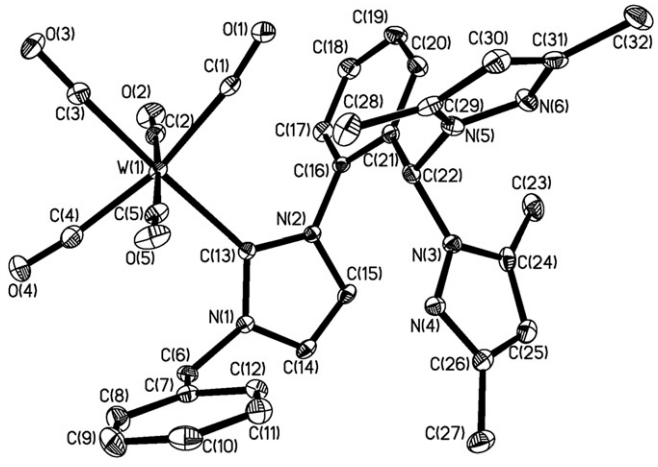


Fig. 3. The molecular structure of **13**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–C(1) 2.047(3), W(1)–C(3) 1.999(3), W(1)–C(13) 2.268(3), C(22)–N(3) 1.458(3), C(22)–N(5) 1.449(3) Å; W(1)–C(1)–O(1) 171.4(2), W(1)–C(2)–O(2) 176.7(3), W(1)–C(3)–O(3) 177.6(3), W(1)–C(4)–O(4) 173.5(3), W(1)–C(5)–O(5) 176.3(3), N(1)–C(6)–C(7) 113.8(2), N(1)–C(13)–N(2) 102.8(2), N(3)–C(22)–N(5) 110.6(2), N(3)–C(22)–C(21) 113.5(2), N(5)–C(22)–C(21) 114.6(2), N(1)–C(13)–W(1) 129.9(2), C(1)–W(1)–C(4) 168.0(1), C(3)–W(1)–C(13) 178.0(1), C(2)–W(1)–C(13) 90.7(1)°.

independent molecules with similar structural parameters. One of them is shown in Fig. 4. The NHC acts as a bridging bidentate ligand by one pyrazolyl nitrogen and the carbene carbon to a Ru–Ru bond, and a hydride along with a chloride ligand bridges this metal–metal bond. The hydride-bridged Ru–Ru bond distance (Ru(1)–Ru(3) 2.8504(5) Å) is slightly longer than the corresponding unbridged Ru–Ru bond distances (Ru(1)–Ru(2) 2.8038(7) Å and Ru(2)–Ru(3) 2.8161(5) Å). These three Ru–Ru bond distances fall in the range of Ru–Ru distances found in other triruthenium NHC complexes [36,37]. The Ru–C_{NHC} bond distance (Ru(3)–C(28)) is 2.100(2) Å, comparable to the Ru–C_{NHC} bond distances found in [Ru_3(μ-H)(μ3-pyCH$_2$ImMe)(CO)$_9$] (2.059(3 Å) and [Ru_3(μ-H)$_2$(μ3-HCpyCH$_2$ImMe)(CO)$_8$] (2.092(7) Å) [36].

In summary, three new bis(3,5-dimethylpyrazol-1-yl)methanes functionalized by 2-halophenyl groups on the methine carbon atom can be easily obtained. Oxidative addition reaction only takes place on the C–Br bond to the Mo or W center when these three ligands react with Mo(CO)$_6$ and W(CO)$_5$THF. The NHC complexes bearing bis(pyrazol-1-yl)methyl group have been successfully synthesized, in which the polydentate NHC ligands show variable coordination modes, depending on different metal atoms.

3. Experimental

Solvents were dried and distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of argon. NMR (^{1}H and ^{13}C) were recorded on a Bruker 400 spectrometer using CDCl$_3$ as solvent unless otherwise noted, and the chemical shifts were reported in ppm with respect to the reference (internal SiMe$_4$ for ^{1}H and ^{13}C NMR spectra). IR spectra were recorded as KBr pellets on a Nicolet 380 spectrometer. Element analyses were carried out on an Elementar Vairo EL analyzer. HR mass spectra were carried out on a Varian QFT-ESI spectrometer. Melting points were measured with an X-4 digital micro melting-point apparatus and were uncorrected. Bis(3,5-dimethylpyrazol-1-yl)methanone [21] was prepared according to the literature method.

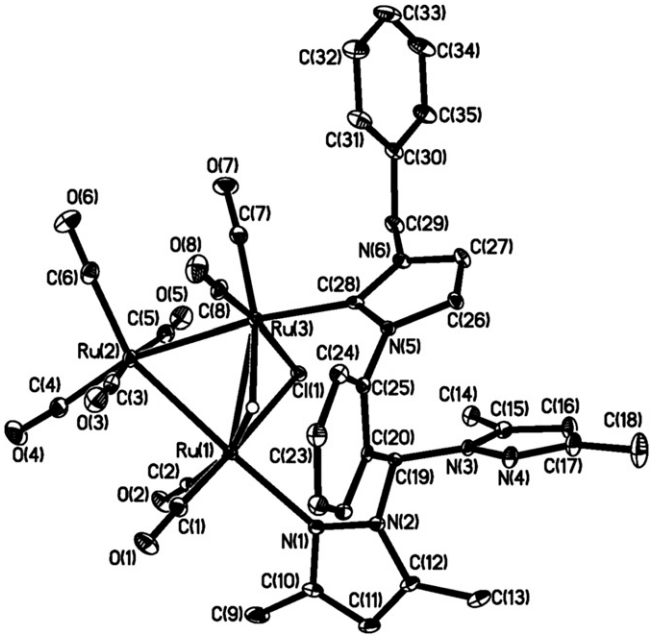


Fig. 4. The molecular structure of **14**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.8038(7), Ru(1)–Ru(3) 2.8504(5), Ru(2)–Ru(3) 2.8161(5), Ru(1)–Cl(1) 2.4669(8), Ru(1)–N(1) 2.301(2), Ru(1)–H(1) 1.89(3), Ru(3)–Cl(1) 2.4900(8), Ru(3)–H(1) 1.90(3), Ru(3)–C(28) 2.100(2), C(19)–N(2) 1.471(3), C(19)–N(3) 1.454(3) Å; Ru(1)–Ru(2)–Ru(3) 60.954(9), Ru(1)–Cl(1)–Ru(3) 70.20(2), Ru(1)–H(1)–Ru(3) 97.7(1), Ru(2)–Ru(1)–Ru(3) 59.74(1), N(1)–Ru(1)–Ru(2) 176.58(5), N(1)–Ru(1)–Ru(3) 117.19(5), C(28)–Ru(3)–Ru(2) 172.67(7), N(2)–N(1)–Ru(1) 129.6(2), N(5)–C(28)–Ru(3) 127.1(2), N(2)–C(19)–N(3) 111.3(2), N(6)–C(29)–C(20) 113.5(2)°.

3.1. Synthesis of (2-FC$_6$H$_4$)CH(3,5-Me$_2$Pz)$_2$ (**1**)

The mixture of bis(3,5-dimethylpyrazol-1-yl)methanone (3.06 g, 14 mmol), CoCl$_2$·6H$_2$O (22 mg, 0.092 mmol) and 2-FC$_6$H$_4$CHO (1.74 g, 14 mmol) was stirred and heated at 80 °C for 1 h. Then the reaction temperature was elevated to 115 °C, and the reaction mixture was continuously stirred for 1 h. After cooling to room temperature, CH$_2$Cl$_2$ (80 ml) was added to the reaction mixture to dissolve the solid. The CH$_2$Cl$_2$ solution was washed with water three times (3 × 40 ml), and dried over anhydrous MgSO$_4$. After removing of the solvent, the residue was recrystallized from benzene/hexane to give white crystals of **1**. Yield: 2.52 g (60%), mp 118–120 °C. ^{1}H NMR: δ 2.14, 2.22 (s, s, 6H, 6H, CH_3), 5.86 (s, 2H, H^4 of pyrazole), 6.88 (t, J = 7.4 Hz, 1H), 7.04–7.15 (m, 2H), 7.32–7.39 (m, 1H) (C$_6H_4$), 7.71 (s, 1H, CH) ppm. ^{13}C NMR: δ 11.2, 13.7 (CH_3), 69.4 (CH), 106.9 (C^4 of pyrazole), 115.3 (d, J_{FC} = 20.9 Hz), 124.1, 124.2, 128.9, 130.5 (d, J_{FC} = 8.1 Hz), 158.4 (C$_6$H$_4$), 140.3, 148.3 (C^3 and C^5 of pyrazole) ppm. Anal. Calc. for C$_{17}$H$_{19}$FN$_4$: C, 68.44; H, 6.42; N, 18.78. Found: C, 68.20; H, 6.76; N, 18.41%.

3.2. Synthesis of (2-ClC$_6$H$_4$)CH(3,5-Me$_2$Pz)$_2$ (**2**)

This compound was obtained similarly using 2-ClC$_6$H$_4$CHO instead of 2-FC$_6$H$_4$CHO as described above for **1** as white crystals, but the reaction temperature was 80 °C, and the reaction time was 1 h. Yield: 70%, mp 144–146 °C. ^{1}H NMR: δ 2.09, 2.18 (s, s, 6H, 6H, CH_3), 5.86 (s, 2H, H^4 of pyrazole), 6.83 (d, J = 7.9 Hz, 1H), 7.19–7.29 (m, 2H), 7.34–7.37 (m, 1H) (C$_6H_4$), 7.62 (s, 1H, CH) ppm. ^{13}C NMR: δ 11.1, 13.8 (CH_3), 71.8 (CH), 106.8 (C^4 of pyrazole), 127.1, 129.1, 129.6, 129.9, 133.2, 134.5 (C$_6$H$_4$), 140.3, 148.4 (C^3 and C^5 of pyrazole) ppm. Anal. Calc. for C$_{17}$H$_{19}$ClN$_4$: C, 64.86; H, 6.08; N, 17.80. Found: C, 64.41; H, 6.54; N, 17.82%.

3.3. Synthesis of (2-BrC$_6$H$_4$)CH(3,5-Me$_2$Pz)$_2$ (**3**)

This compound was obtained similarly using 2-BrC$_6$H$_4$CHO instead of 2-FC$_6$H$_4$CHO as described above for **1** as white crystals. Yield: 61%, mp 153–154 °C. ^{1}H NMR: δ 2.11, 2.21 (s, s, 6H, 6H, CH_3), 5.89 (s, 2H, H^4 of pyrazole), 6.83 (d, J = 7.7 Hz, 1H), 7.23–7.29 (m, 2H) (C$_6H_4$), 7.57–7.59 (m, 2H, C$_6H_4$ and CH) ppm. ^{13}C NMR: δ 11.1, 13.8 (CH_3), 73.7 (CH), 106.8 (C^4 of pyrazole), 123.1, 127.7, 129.4, 130.1, 132.9, 136.1 (C$_6$H$_4$), 140.4, 148.4 (C^3 and C^5 of pyrazole) ppm. Anal. Calc. for C$_{17}$H$_{19}$BrN$_4$: C, 56.83; H, 5.33; N, 15.59. Found: C, 56.41; H, 5.78; N, 15.09%.

3.4. Synthesis of (2-FC$_6$H$_4$)CH(3,5-Me$_2$Pz)$_2$Mo(CO)$_4$ (**4**)

The solution of **1** (0.30 g, 1.0 mmol) and Mo(CO)$_6$ (0.26 g, 1.0 mmol) in THF (50 ml) was stirred and heated at reflux for 4 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica using CH$_2$Cl$_2$/hexane (2/1 v/v) as eluent. The eluate was concentrated to dryness and the residual solid was recrystallized from CH$_2$Cl$_2$/hexane to give yellow–green solids of **4**. Yield: 0.32 g (63%). ^{1}H NMR: δ 2.48, 2.59 (s, s, 6H, 6H, CH_3), 6.11 (s, 2H, H^4 of pyrazole), 6.15–6.18 (m, 1H), 7.04–7.18 (m, 2H), 7.37–7.43 (m, 1H) (C$_6H_4$), 7.48 (s, 1H, CH) ppm. ^{13}C NMR: δ 11.7, 16.5 (CH_3), 65.2 (CH), 108.0 (C^4 of pyrazole), 117.3 (d, J_{FC} = 21.7 Hz), 121.3 (d, J_{FC} = 10.1 Hz), 125.5, 128.1, 132.1 (d, J_{FC} = 8.5 Hz), 142.1 (C$_6$H$_4$), 155.5, 158.4 (C^3 and C^5 of pyrazole), 202.6

(1C), 205.8 (1C), 220.9 (2C) (*C*O) ppm. IR: ν_{CO} = 2014.6 (s), 1892.9 (vs), 1868.2 (vs), 1814.0 (vs) cm^{-1}. Anal. Calc. for $C_{21}H_{19}FMoN_4O_4.0.25CH_2Cl_2$: C, 48.38; H, 3.73; N, 10.62. Found: C, 48.80; H, 3.48; N, 11.00%.

3.5. Synthesis of (2-FC_6H_4)CH(3,5-$Me_2Pz)_2W(CO)_4$ (**5**)

Compound **1** (0.27 g, 0.91 mmol) was added to a solution of $W(CO)_5THF$ in THF, prepared *in situ* by the irradiation of a solution of $W(CO)_6$ (0.32, 0.91 mmol) in THF (40 ml) with a 300 W high-pressure mercury lamp for 8 h, and the reaction mixture was stirred and heated at reflux for 10 h. Then the solvent was removed under reduced pressure, and the residual solid was purified by column chromatography on silica using CH_2Cl_2/hexane (2/1 v/v) as eluent. The eluate was concentrated to dryness and the residual solid was recrystallized from CH_2Cl_2/hexane to give yellow–green solids of **5**. Yield: 0.25 g (47%). ^{1}H NMR (acetone-d_6): δ 2.40, 2.51 (s, s, 6H, 6H, CH_3), 6.35 (s, 2H, H^4 of pyrazole), 6.21 (t, J = 8.1 Hz), 7.11–7.19 (m, 2H), 7.40–7.45 (m, 1H) (C_6H_4), 8.07 (s, 1H, C*H*) ppm. ^{13}C NMR: δ 11.8, 17.3 (*C*H_3), 65.8 (*C*H), 108.2 (C^4 of pyrazole), 117.5 (d, J_{FC} = 21.8 Hz), 120.8 (d, J_{FC} = 10.9 Hz), 125.7, 127.9, 132.3 (d, J_{FC} = 8.6 Hz), 158.4 (C_6H_4), 142.2, 156.1 (C^3 and C^5 of pyrazole), 200.5 (1C), 203.5 (1C), 212.0 (2C) (*C*O) ppm. IR: ν_{CO} = 2003.0 (s), 1891.0 (vs), 1850.7 (vs), 1821.0 (vs) cm^{-1}. Anal. Calc. for $C_{21}H_{19}FN_4O_4W.0.25CH_2Cl_2$: C, 41.47; H, 3.19; N, 9.10. Found: C, 41.24; H, 3.62; N, 9.60%.

3.6. Synthesis of (2-ClC_6H_4)CH(3,5-$Me_2Pz)_2Mo(CO)_4$ (**6**)

This complex was obtained similarly using compound **2** instead of compound **1** as described above for **4**. Yield: 56%. ^{1}H NMR: δ 2.47, 2.53 (s, s, 6H, 6H, CH_3), 6.09 (s, 2H, H^4 of pyrazole), 6.04–6.07 (m, 1H), 7.20–7.21 (m, 1H) (C_6H_4), 7.30–7.33 (m, 2H, C_6H_4 and C*H*), 7.37–7.41 (m, 1H, C_6H_4) ppm. ^{13}C NMR: δ 12.1, 16.5 (*C*H_3), 67.0 (*C*H), 108.2 (C^4 of pyrazole), 128.2, 128.9, 131.2, 131.3, 131.8, 132.4 (C_6H_4), 142.5, 155.8 (C^3 and C^5 of pyrazole), 202.5 (1C), 205.7 (1C), 221.0 (2C) (*C*O) ppm. IR: ν_{CO} = 2009.8 (vs), 1888.3 (vs), 1855.5 (vs), 1818.9 (vs) cm^{-1}. Anal. Calc. for $C_{21}H_{19}ClMoN_4O_4$: C, 48.25; H, 3.66; N, 10.72. Found: C, 48.24; H, 3.39; N, 10.82%.

3.7. Synthesis of (2-ClC_6H_4)CH(3,5-$Me_2Pz)_2W(CO)_4$ (**7**)

This complex was obtained similarly using compound **2** instead of compound **1** as described above for **5**. The eluent was CH_2Cl_2/hexane (1/1 v/v). Yield: 35%. ^{1}H NMR (acetone-d_6): δ 2.41, 2.53 (s, s, 6H, 6H, CH_3), 6.20 (s, 2H, H^4 of pyrazole), 6.01 (d, 1H, J = 7.8 Hz), 7.14–7.27 (m, 3H) (C_6H_4), 7.84 (s, 1H, C*H*) ppm. ^{13}C NMR (acetone-d_6): δ 12.1, 17.4 (*C*H_3), 69.1 (*C*H), 109.1 (C^4 of pyrazole), 129.2, 129.8, 132.2, 132.5, 132.6, 133.3 (C_6H_4), 145.9, 156.8 (C^3 and C^5 of pyrazole), 201.5 (1C), 205.0 (1C), 212.8 (2C) (*C*O) ppm. IR: ν_{CO} = 2002.4 (s), 1879.3 (vs), 1846.8 (vs), 1817.3 (vs) cm^{-1}. Anal. Calc. for $C_{21}H_{19}ClN_4O_4W.0.25CH_2Cl_2$: C, 40.39; H, 3.11; N, 8.87. Found: C, 40.57; H, 3.23; N, 9.13%.

3.8. Synthesis of (2-BrC_6H_4)CH(3,5-$Me_2Pz)_2W(CO)_4$ (**8**)

The solution of compound **3** (0.11 g, 0.31 mmol) and $W(CO)_6$ (0.11 g, 0.31 mmol) in THF (30 ml) was irradiated with a 300 W high-pressure mercury lamp for 8 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica using CH_2Cl_2/hexane (2/1 v/v) as eluent. The green–yellow eluate was concentrated to dryness, the residue was recrystallized from CH_2Cl_2/hexane to give green–yellow solids of **8**. Yield: 0.10 g (49%). ^{1}H NMR (acetone-d_6): δ 2.42, 2.54 (s, s, 6H, 6H, CH_3), 6.20 (s, 2H, H^4 of pyrazole), 5.98 (d, 1H, J = 7.0 Hz), 7.11–7.23 (m, 2H), 7.49–7.52 (m, 1H) (C_6H_4), 7.78 (s, 1H, C*H*) ppm. ^{13}C NMR (acetone-d_6): δ 12.3, 17.4 (*C*H_3), 69.7 (*C*H), 109.2 (C^4 of pyrazole), 120.6, 129.6, 129.8, 132.1, 134.0, 136.9 (C_6H_4), 146.0, 156.8 (C^3 and C^5 of pyrazole), 201.3 (1C), 204.9 (1C), 212.6 (2C) (*C*O) ppm. IR: ν_{CO} = 2002.1 (s), 1880.2 (vs), 1847.5 (vs), 1818.3 (vs) cm^{-1}. Anal. Calc. for $C_{21}H_{19}BrN_4O_4W$: C, 38.50; H, 2.92; N, 8.55. Found: C, 38.57; H, 2.62; N, 8.67%.

3.9. Synthesis of (2-C_6H_4)CH(3,5-$Me_2Pz)_2Mo(CO)_3Br$ (**9**)

This complex was obtained similarly using compound **3** instead of compound **1** as described above for **4**. Yield: 44%. ^{1}H NMR (DMSO-d_6): δ 2.33, 2.65 (s, s, 6H, 6H, CH_3), 6.22 (s, 2H, H^4 of pyrazole), 7.07–7.21 (m, 2H), 7.33 (dd, J = 7.1 Hz, J = 1.3 Hz, 1H), 7.97 (dd, J = 7.1 Hz, J = 1.5 Hz, 1H) (C_6H_4), 7.58 (s, 1H, C*H*) ppm. ^{13}C NMR (DMSO-d_6): δ 10.7, 15.4 (*C*H_3), 70.4 (*C*H), 107.7 (C^4 of pyrazole), 124.7, 128.7, 128.9, 136.7, 142.1, 161.4 (C_6H_4), 142.2, 152.5 (C^3 and C^5 of pyrazole), 236.9 (*C*O) ppm. IR: ν_{CO} = 2013.7 (vs), 1942.3 (vs), 1903.7 (vs) cm^{-1}. Anal. Calc. for $C_{20}H_{19}BrMoN_4O_3$: C, 44.55; H, 3.55; N, 10.39. Found: C, 44.65; H, 3.76; N, 10.28%.

3.10. Synthesis of (2-C_6H_4)CH(3,5-$Me_2Pz)_2W(CO)_3Br$ (**10**)

Compound **3** (0.32 g, 0.91 mmol) was added to a solution of $W(CO)_5THF$ in THF, prepared *in situ* by the irradiation of a solution of $W(CO)_6$ (0.32, 0.91 mmol) in THF (40 ml) with a 300 W high-pressure mercury lamp for 8 h, and the reaction mixture was stirred and heated at reflux for 24 h. Then the solvent was removed under reduced pressure, and the residual solid was purified by column chromatography on silica using ethyl acetate/hexane (1/1 v/v) as eluent. The first yellow–green band was characterized as complex **8**. Yield: 35 mg (5.9%). The second yellow band was confirmed as complex **10**. Yield: 0.15 g (27%). ^{1}H NMR (DMSO-d_6): δ 2.35, 2.67 (s, s, 6H, 6H, CH_3), 6.30 (s, 2H, H^4 of pyrazole), 7.02 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.1 Hz, 1H), 7.33 (d, J = 7.1 Hz, 1H), 7.95 (d, J = 7.2 Hz, 1H) (C_6H_4), 7.62 (s, 1H, C*H*) ppm. ^{13}C NMR (DMSO-d_6): δ 10.7, 16.0 (*C*H_3), 71.0 (*C*H), 108.0 (C^4 of pyrazole), 124.0, 128.1, 129.4, 135.5, 141.6, 157.0 (C_6H_4), 142.1, 152.4 (C^3 and C^5 of pyrazole), 233.1 (*C*O) ppm. IR: ν_{CO} = 2008.2 (vs), 1926.5 (vs), 1896.3 (vs) cm^{-1}. Anal. Calc. for $C_{20}H_{19}BrN_4O_3W$: C, 38.30; H, 3.05; N, 8.93. Found: C, 38.45; H, 3.35; N, 8.83%.

3.11. Heating complex **8** in THF

The solution of complex **8** (0.10 g, 0.15 mmol) in THF (30 ml) was stirred and heated at reflux for 24 h. The solvent was removed under reduced pressure, the residual solid was purified by column chromatography on silica using ethyl acetate/hexane (1/1 v/v) as eluent to give complex **10** as a yellow–green solid. Yield: 80 mg (85%).

3.12. Synthesis of (2-ImC_6H_4)CH(3,5-$Me_2Pz)_2$ (**11**) (Im = imidazol-1-yl)

The solution of compound **3** (0.72 g, 2.0 mmol) imidazole (0.16 g, 2.4 mmol), CuI (0.1 g, 0.52 mmol), anhydrous Cs_2CO_3 (1.64 g, 5.0 mmol) and L-proline (0.12 g, 1.0 mmol) in DMF (5 ml) was stirred and heated at 120 °C for 24 h. After cooling to room temperature, water (100 ml) was added to the above-mentioned solution. The aqueous solution was extracted with ethyl acetate (3 × 100 ml). The organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, the residual oil was purified by column chromatography on silica. First, an ethyl acetate/hexane (1/1 v/v) mixture was used as eluent to remove the starting materials, then an ethyl acetate/methanol (5/1 v/v)

mixture was used as eluent to give a yellow eluate. After removing the solvents, compound **11** was obtained as a slightly yellow solid. Yield: 0.24 g (35%), mp 136–137 °C. ^{1}H NMR: δ 1.86, 2.14 (s, s, 6H, 6H, CH_3), 5.82 (s, 2H, H^4 of pyrazole), 6.63 (s, 1H, C_6H_4), 7.04–7.11 (m, 4H), 7.24 (s, 1H), 7.44 (s, br, 2H) (C_6H_4, C*H* and protons of imidazole) ppm. ^{13}C NMR: δ 9.6, 12.6 (*C*H$_3$), 68.9 (*C*H), 106.2 (C^4 of pyrazole), 119.2, 126.5, 127.8, 128.3, 128.6, 132.4, 134.5, 136.5 (C_6H_4 as well as carbons of imidazole), 139.2, 147.5 (C^3 and C^5 of pyrazole) ppm. HRMS (ESI, *m*/*z*): 369.1793 (Calcd for $C_{20}H_{22}N_6Na$: 369.1798, $[M + Na]^+$, 100%).

3.13. Synthesis of [PhCH$_2$(2-Im)C$_6$H$_4$]CH(3,5-Me$_2$Pz)$_2$(Cl) (**12**)

The solution of compound **11** (0.41 g, 1.18 mmol) and $PhCH_2Cl$ (0.15 g, 1.18 mmol) in CH_3CN (40 ml) was stirred and heated at reflux for 24 h. After cooling to room temperature, the solution was concentrated to approximately 5 ml under reduced pressure and 20 ml of dry ethyl ether was slowly added. After standing at 4 °C overnight, a brown precipitate was formed, which was filtered off and washed with ethyl ether to give compound **12**. Yield: 0.50 g (90%), mp 112–114 °C. ^{1}H NMR: δ 1.99, 2.03 (s, s, 6H, 6H, CH_3), 5.48 (s, 2H, CH_2), 5.76 (s, 2H, H^4 of pyrazole), 6.65 (d, J = 4.8 Hz, 1H, C_6H_4), 7.44–7.54 (m, 5H, C_6H_4 and protons of imidazole), 7.63–7.71 (m, 3H), 7.94–8.05 (m, 2H) (C_6H_5), 7.80 (s, 1H, C*H*), 10.08 (s, 1H, proton of imidazole) ppm. ^{13}C NMR: δ 10.7, 13.2 (*C*H$_3$), 51.8 (*C*H$_2$), 69.5 (*C*H), 106.6 (C^4 of pyrazole), 122.2, 123.8, 128.2, 128.3, 128.6, 128.7, 128.8, 130.2, 131.0, 132.5, 133.0, 134.3, 137.1, 140.3, 147.6 (C_6H_4, C_6H_5, C^3 and C^5 of pyrazole as well as carbons of imidazole) ppm. HRMS (ESI, *m*/*z*): 437.2443 (Calcd for $C_{27}H_{29}N_6$: 437.2448, $[M–Cl]^+$, 100%).

3.14. Synthesis of complex **13**

The mixture of compound **12** (0.24 g, 0.50 mmol) and Ag_2O (0.12 g, 0.50 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 24 h. The solution was filtered off and concentrated to dryness. Then, the residue was added to the solution of $W(CO)_5$THF in THF, prepared *in situ* by the irradiation of a solution of $W(CO)_6$ (0.18, 0.50 mmol) in THF (40 ml) with a 300 W high-pressure mercury lamp for 8 h, and the reaction mixture was stirred and heated at reflux for 5 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica using CH_2Cl_2 as eluent. The green-yellow eluate was concentrated to dryness, and the residue was recrystallized from CH_2Cl_2/hexane to give green-yellow crystals of **13**. Yield: 0.12 g (32%). ^{1}H NMR: δ 1.87 (s, 3H), 2.04 (s, 3H), 2.21 (s, 3H), 2.31 (s, 3H) (CH_3), 5.37 (d, J = 15.1 Hz, 1H), 5.67 (d, J = 15.1 Hz, 1H) (CH_2), 5.67, 5.84 (s, s, 1H, 1H, H^4 of pyrazole), 6.12 (d, J = 1.9 Hz, 1H), 6.64 (d, J = 1.9 Hz, 1H) (protons of imidazole), 7.29–7.45 (m, 6H), 7.55–7.60 (m, 3H) (C_6H_4 and C_6H_5), 7.03 (s, 1H, C*H*) ppm. ^{13}C NMR: δ 11.2, 11.3, 13.6, 14.0 (*C*H$_3$), 57.1 (*C*H$_2$), 68.3 (*C*H), 106.6, 107.1 (C^4 of pyrazole), 120.9, 123.5 (carbons of imidazole), 127.9, 128.5, 129.1, 129.7 (C_6H_5), 130.1, 130.4, 130.5, 134.7, 135.7, 139.6 (C_6H_4), 139.2, 139.9, 147.8, 149.5 (C^3 and C^5 of pyrazole), 182.0 (C_{NHC}), 198.1 (4C), 200.3 (1C) (*C*O) ppm. These assignments were confirmed by standard Bruker gradient enhanced HMBC and HMQC pulse sequences. IR: ν_{CO} = 2060.0 (m), 1965.5 (vs), 1926.9 (vs), 1901.8 (vs), 1882.5 9 (vs) cm^{-1}. Anal. Calc. for $C_{32}H_{28}N_6O_5W$: C, 50.54; H, 3.71; N, 11.05. Found: C, 50.41; H, 3.22; N, 11.06%.

3.15. Synthesis of complex **14**

3.15.1. Method A

The mixture of compound **12** (0.22 g, 0.47 mmol) and Ag_2O (0.11 g, 0.47 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 24 h. The resulted solution was filtered and concentrated to dryness. Then the residue was added to the solution of $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) in THF (40 ml), and the reaction mixture was stirred and heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica. First, hexane was used as eluent to give $Ru_3(CO)_{12}$, then CH_2Cl_2 as eluent to yield red-orange solids of complex **14**. Yield: 70 mg (15%). ^{1}H NMR: δ −11.3 (s, 1H, Ru*H*), 1.61 (s, 3H), 1.66 (s, 3H), 2.02 (s, 3H), 2.65 (s, 3H) (CH_3), 5.65 (m, 2H) (CH_2), 5.62, 6.06 (s, s, 1H, 1H, H^4 of pyrazole), 6.51 (d, J = 1.3 Hz, 1H), 6.61 (d, J = 1.3 Hz, 1H) (protons of imidazole), 6.79 (d, J = 7.5 Hz, 1H),

Table 1
Crystal data and refinement parameters for complexes **7**, **10**, **13** and **14**.

Complex	**7**	**10**	**13**	**14**
Formula	$C_{21}H_{19}ClN_4O_4W$	$C_{20}H_{19}BrN_4O_3W$	$C_{32}H_{28}N_6O_5W$	$C_{35}H_{29}ClN_6O_8Ru_3$
Formula weight	610.70	627.15	760.45	1000.30
Crystal size (mm)	0.20 × 0.20 × 0.15	0.24 × 0.22 × 0.10	0.20 × 0.18 × 0.10	0.24 × 0.20 × 0.18
T (K)	293(2)	113(2)	113(2)	113(2)
λ (MoKα) (Å)	0.71073	0.71075	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$/n	$C2$/c	$P2_1$/n	$P\bar{1}$
a (Å)	10.312(2)	26.79(2)	12.513(3)	11.566(3)
b (Å)	13.937(3)	10.007(7)	13.334(3)	16.626(4)
c (Å)	15.208(3)	16.773(12)	18.517(4)	21.954(5)
α(°)	90	90	90	107.931(3)
β(°)	90.04(3)	113.405(8)	94.020(5)	98.908(2)
γ(°)	90	90	90	104.869(2)
V (Å)^3	2185.6(8)	4127(5)	3082.2(12)	3754.5(14)
Z	4	8	4	4
D_c (g cm^{-3})	1.856	2.019	1.639	1.770
F(000)	1184	2400	1504	1976
μ (mm^{-1})	5.443	7.576	3.798	1.321
θ Range (°)	3.05–27.48	1.66–27.86	1.88–27.87	1.36–27.90
No. of measured reflections	22,842	20,237	28,927	42,190
No. of unique reflections (R_{int})	5008 (0.0532)	4897 (0.055)	7329 (0.0492)	17,614 (0.0454)
No. of observed reflections with ($I > 2\sigma(I)$)	4084	3869	5709	12,960
No. of parameters	284	266	401	971
GOF	1.055	1.001	1.006	0.876
Residuals R, R_w	0.0368, 0.0656	0.0337, 0.0765	0.0256, 0.0531	0.0381, 0.0563

7.31 (m, 1H), 7.40–7.45 (m, 3H) 7.59–7.69 (m, 4H) (C_6H_4 and C_6H_5), 7.08 (s, 1H, C*H*) ppm. ^{13}C NMR: δ 10.5, 11.1, 13.4, 14.1 (CH_3), 55.6 (CH_2), 68.0 (*C*H), 106.9, 110.6 (C^4 of pyrazole), 119.6, 122.2 (carbons of imidazole), 127.0, 128.1, 128.5, 129.0 (C_6H_5), 129.9, 130.4, 130.5, 134.8, 135.3, 139.0 (C_6H_4), 141.5, 142.6, 146.9, 153.8 (C^3 and C^5 of pyrazole), 179.0 (C_{NHC}), 193.2, 193.8, 204.1, 204.7, 205.6, 206.3 (*C*O) ppm. IR: ν_{CO} = 2072.3 (m), 1999.1 (vs), 1990.3 (vs), 1932.5 (m), 1922.8 (w) cm^{-1}. Anal. Calc. for $C_{35}H_{29}ClN_6O_8Ru_3$: C, 42.02; H, 2.92; N, 8.40. Found: C, 41.65; H, 3.12; N, 8.24%.

3.15.2. Method B

The mixture of compound **12** (69 mg, 0.16 mmol) and Ag_2O (38 mg, 0.16 mmol) in THF (30 ml) was stirred at room temperature for 24 h. $Ru_3(CO)_{12}$ (0.10 g, 0.16 mmol) was added to the resulted solution, and the reaction mixture was stirred and heated at reflux for 3 h. After the solvent was removed under reduced pressure, the residue was purified by the same procedure as shown in method A to yield red-orange solids of complex **14**. Yield: 40 mg (25%).

No reaction took place in the treatment of compound **12** with $Ru_3(CO)_{12}$ in THF at room temperature. The ligand decomposed upon heating these two compounds at reflux in THF while no identifiable product was obtained.

3.16. Crystal structure determinations

Crystals of **7**, **13** and **14** suitable for X-ray analyses were obtained by slow diffusion of hexane into their CH_2Cl_2 solutions at −18 °C. While crystals of **10** suitable for X-ray analyses were obtained by slow diffusion of ethyl ether into its DMF solution at 4 °C. Intensity data were collected on an SCX-MINI CCD diffractometer for **7** and Rigaku Saturn CCD detector for **10**, **13** and **14**, respectively. Semi-empirical absorption corrections were applied using the Crystalclear program [38]. The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL [39] by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for **7**, **10**, **13** and **14** is listed in Table 1.

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Appendix A. Supplementary material

CCDC 873103, 873104, 873105 and 873106 contain the supplementary crystallographic data for **7**, **10**, **13** and **14**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary material associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012.08.004. These data include MOL files and InChiKeys of the most important compounds described in this article.

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