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Synthesis, structure and reactions of coordinatively unsaturated [RuCl(CO)(dppf)(PPh$_3$)]BF$_4$ where dppf is *trans*-spanning 1,1′-bis(diphenylphosphino)ferrocene

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A novel coordinatively unsaturated cationic 16-electron ruthenium(II) complex having dppf as a bidentate ligand, [RuCl(CO)(dppf)(PPh$_3$)]BF$_4$ (**1**·BF$_4$) is prepared from a hydride complex [RuClH(CO)(dppf)(PPh$_3$)] and an acetylide complex [RuCl(C≡CPh)(CO)(dppf)(PPh$_3$)] by treatment with HBF$_4$·Et$_2$O. X-Ray structure analysis of **1** reveals that the complex is the first example of the *trans*-spanning dppf coordinated to a d^6 ruthenium(II) centre and the vacant coordination site is sterically shielded effectively by the ferrocene moiety in the solid state. In solution complex **1** is fluxional, allowing the attack of two-electron monodentate ligands such as CO, ^{t}BuNC and CH$_3$CN to afford the corresponding six-coordinate octahedral 18-electron species with *cis*-chelating dppf.

Introduction

Bisphosphine ligands with a large bite angle have been an attractive subject in recent years, since their complexes show remarkably different chemical reactivities from the complexes with monodentate phosphines.[1] Especially, late transition-metal complexes containing bisphosphines spanning *trans* coordination sites on a single metal ion have been one of the most captivating targets in coordination chemistry.[2] However, when potentially *trans*-spanning bisphosphine ligands with flexible long chains are allowed to react with a transition metal, the bisphosphines prefer bridging two metal centres to chelating on a single metal centre.[3] Thus, only a limited number of bisphosphines with rigid skeletons, for example, xanthene,[4] 1,1″-biferrocene,[5] and benzo[*c*]phenanthrene,[6] which are structurally tailored to an exceptionally large bite angle, have exhibited the *trans*-spanning bidentate chelation mode. As for the metal centres, a restricted range of metal ions, such as rhodium(I), iridium(I), nickel(II), palladium(II) and platinum(II) have been complexed with those rigid *trans*-spanning bisphosphines, except for the complexes of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene reported by Venanzi and co-workers.[6] It is noteworthy that few ruthenium(II) complexes with *trans*-spanning bidentate bisphosphines have only occasionally been reported by three independent research groups.[7]

Although 1,1′-bis(diphenylphosphino)ferrocene (dppf) usually acts as a *cis*-chelating ligand, it is tolerant for bite angles from 90° to over 120°.[1] Two types of conformational flexibility of dppf, a tilting motion of two cyclopentadienyl ring planes to change their mutual dihedral angle and also torsionally rotative motion around the axis through the centres of the two rings, provide a wide range of bite angle allowance for dppf chelation. Therefore, dppf can serve as a *trans*-spanning ligand and thus several complexes of palladium[8,9] and rhenium[10] with the *trans*-spanning dppf have been characterized crystallographically.

We have now prepared a novel coordinatively unsaturated cationic d^6 ruthenium(II) complex having dppf as a *trans*-spanning bidentate ligand; [RuCl(CO)(dppf)(PPh$_3$)]BF$_4$ (**1**·BF$_4$). In the solid state, the dppf moiety spanning two *trans* coordination sites effectively protects the vacant site. Fluxional behaviour of **1** in solution has also been investigated. The *trans*–*cis* fluxionality of the dppf ligand allows the attack of some additional monodentate ligands to afford six-coordinate octahedral species with *cis*-chelating dppf.

Results and discussion

When a dppf-containing hydridoruthenium complex, [RuClH(CO)(dppf)(PPh$_3$)][11] in dichloromethane was treated with an equimolar amount of HBF$_4$·Et$_2$O, the novel five-coordinate cationic complex **1** was formed in an almost quantitative yield. The complex **1** was also prepared quantitatively from the reaction between an alkynyl complex, [RuCl(C≡CPh)(CO)(dppf)(PPh$_3$)][11] (**2**) and HBF$_4$·Et$_2$O at −78 °C with release of phenylacetylene (Scheme 1). The complex **1** was stable to air in the solid state and also in solution. The stability observed for **1** against dioxygen was in a sharp contrast to that of the coordinatively unsaturated ruthenium species [Cp*Ru(dppf)]$^+$.[12] Sato and co-workers have shown that [Cp*Ru(dppf)]$^+$ derived from [Cp*RuCl(dppf)] is unstable in acetone and readily reacts with dioxygen to give coordinatively saturated [Cp*Ru(η^2-O$_2$)(dppf)]$^+$. The intermediary [Cp*Ru(dppf)]$^+$ species has not been isolated.

Fluxional behavior of **1** in solution was observed on variable-temperature (VT) NMR spectra (Fig. 1), similar to the case of five-coordinate ruthenium(II) complexes with monodentate tertiary phosphines.[13] At 30 °C, the ^{31}P{^{1}H} NMR spectrum in CD$_2$Cl$_2$ showed two broad signals at δ 52.7 and −20.2 in an intensity ratio of 1 : 2. Upon cooling to −60 °C, these signals turned into a set of a triplet at δ 53.1 and a doublet at δ −22.1 (J(PP) = 19 Hz). The chemical shifts of the ^{31}P signals apparently drifted along with the decrease in temperature, probably showing that some structural isomers of **1** were in fast equilibrium. The AX$_2$ signal pattern of **1** observed at lower than −60 °C corresponds to two equivalent phosphorus atoms of dppf coupled with another phosphorus atom of triphenylphosphine.

The solid-state molecular structure of **1**·BF$_4$ was consistent with its VT-NMR spectra and revealed, notably, a *trans*-spanning coordination mode of dppf (Fig. 2). The two cyclopentadienyl rings in dppf are no longer parallel (dihedral angle = 20.2(3)°), and the P–Ru–P bite angle of dppf was enlarged unusually up to 151.15(5)° whereas typically bite angles for dppf are 90°–120°.[1,14] Although a similar coordination mode of some dppf-related bisphosphines has been found for Pd(II)

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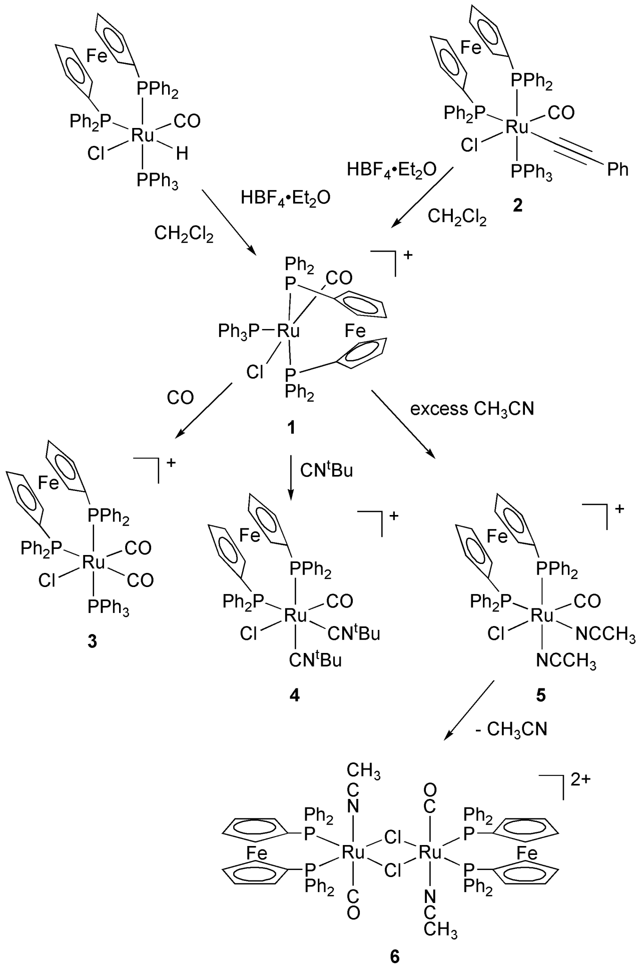


Scheme 1

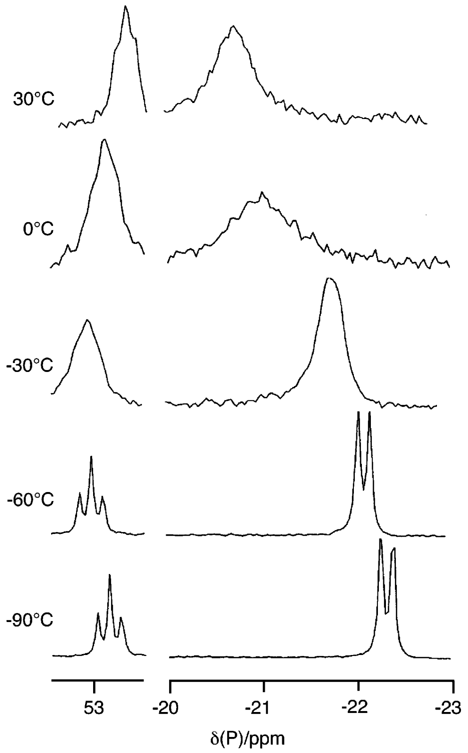


Fig. 1 Variable-temperature $^{31}P\{^1H\}$ NMR spectra of $\mathbf{1}\cdot BF_4$ in dichloromethane-d_2.

complexes,[8,9] complex **1** is the first example for a ruthenium complex having a bidentate *trans*-spanning dppf and its bite angle is the largest ever reported for dppf complexes in all geometries except for Sato's square planar $[Pd(dppf)(PPh_3)](BF_4)_2$ (bite angle = 155.9(1)°).[8] In Sato's Pd complex, the Pd–Fe distance is 2.877(2) Å, indicative of a Pd–Fe dative bond, *i.e.* a tridentate coordination mode of dppf through the two P and the Fe atoms. On the contrary, the Ru ··· Fe distance of **1** was 3.2828(8) Å, too long for the Ru and Fe atoms to be bound to each other, and thus it was concluded that the dppf ligand in **1** was an essentially bidentate bisphosphine ligand. Another example of *trans*-spanning dppf has recently been reported for a dirhenium–dppf complex, $[Cl_4ReReCl_2(dppf)]$,[10] in which the dppf spans the *trans* coordination sites of one of the two square-pyramidal rhenium centres. The dppf bite angles for two types of the crystals $[Cl_4ReReCl_2(dppf)]\cdot nC_6H_4Cl_2$ ($n = 4$ and 0) are 140.31(18) and 141.99(6)°, and the non-bonding Re ··· Fe distances are 3.585 and 3.539 Å, respectively.

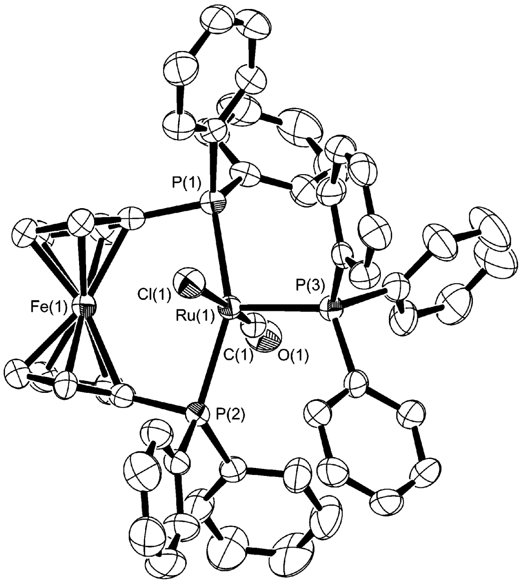


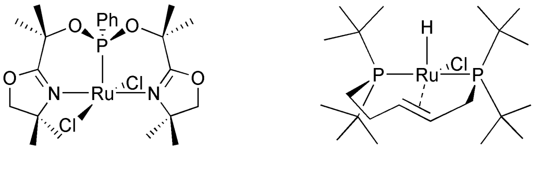
Fig. 2 Molecular structure of $\mathbf{1}\cdot BF_4$ with 50% thermal probability ellipsoids. Hydrogen atoms and a BF_4 anion are omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) 2.414(1), Ru(1)–P(1) 2.357(1), Ru(1)–P(2) 2.373(1), Ru(1)–P(3) 2.325(1), Ru(1)–C(1) 1.862(6), C(1)–O(1) 1.088(6); Cl(1)–Ru(1)–P(1) 89.32(5), Cl(1)–Ru(1)–P(2) 93.90(5), Cl(1)–Ru(1)–P(3) 89.76(5), Cl(1)–Ru(1)–C(1) 174.7(2), P(1)–Ru(1)–P(2) 151.15(5), P(1)–Ru(1)–P(3) 104.34(5), P(1)–Ru(1)–C(1) 88.8(2), P(2)–Ru(1)–P(3) 104.33(5), P(2)–Ru(1)–C(1) 85.4(2), P(3)–Ru(1)–C(1) 95.5(2), Ru(1)–C(1)–O(1) 175.9(5). Dihedral angle between two Cp rings (°): 20.2(3).

The UV-vis absorption spectrum of **1** shows a strong charge transfer band at $\lambda_{max} = 460$ nm ($\varepsilon = 9830$ M^{-1}cm^{-1}) in CH_2Cl_2. A similar band was observed also in the diffuse reflectance spectrum of powdered **1**. This band was characteristic for **1**; the related six-coordinate complexes with a *cis*-chelating dppf, a neutral $[RuClH(CO)(dppf)(PPh_3)]$ and a cationic $[RuH(CO)(NCCH_3)(dppf)(PPh_3)]^+$,[15] showed only a weak absorption band of an intraligand transition in dppf at around $\lambda = 400$–500 nm (ε = 230–300 M^{-1}cm^{-1}). Morokuma[16] pointed out that a weak attractive charge transfer interaction can emerge even when two atoms are situated at larger interatomic separations than a bonding distance. The observation of the charge transfer band for **1** implies that there is some weak attractive interaction between the Ru and Fe atoms both in solution and in the solid state. As indicated crystallographically, there was no bonding between the two metals in the solid state. Nevertheless there is a weak attractive interaction, somewhat stabilizing the unique coordination mode of dppf in **1**.

In spite of the unique coordination mode of dppf, the geometry of the five-coordinate $RuCl(CO)P_3$ core in **1** resembled closely those in the six-coordinate hydridoruthenium complexes $[RuClH(CO)(dppf)(PPh_3)]$ and $[RuH(CO)(NCCH_3)(dppf)(PPh_3)]^+$. The *trans* P–Ru–P angles were 151.15(5)° for **1**, 154.0(1)° for the neutral hydride complex, and 158.6 (1)° for the cationic complex. The *cis* P–Ru–P angles were 104.34(5) and 104.33(5)° for **1**, 102.2(1) and 103.1(1)° for the neutral complex, and 99.3(1) and 102.15(9)° for the cationic complex. The Cl–Ru–CO angles were 174.7(2)° for **1** and 177.6(5)° for the neutral complex, and the corresponding CH_3CN–Ru–CO angle was 171.4(4)° for the cationic complex. The five-coordinate **1**, therefore, seems to have almost the same geometry as the six-coordinate hydridoruthenium complexes. The conformational flexibility of dppf[1] allowed chelation with a large bite angle for **1**, minimizing the geometry change between the ruthenium centres for the five-coordinate **1** and of the six-coordinate hydridoruthenium complexes.

The structure of the five-coordinate **1** is therefore best described as an octahedral geometry with one vacant coordination site sterically covered with the ferrocene moiety of the *trans*-spanning dppf, on the basis of the following facts. First, the dppf bite angle of **1** was quite similar to that found in $[Pd(dppf)(PPh_3)](BF_4)_2$, and even significantly larger than that of $[Cl_4ReReCl_2(dppf)]$. Secondly, as described above, the coordination geometry of **1** agreed fairly closely with those of the six-coordinate hydridoruthenium complexes [RuClH(CO)(dppf)(PPh_3)] and $[RuH(CO)(NCCH_3)(dppf)(PPh_3)]^+$. Thirdly, the lack of a ligand *trans* to PPh_3 strengthens the Ru–PPh_3 coordination. The Ru–PPh_3 distance of **1** (2.325(1) Å) is fairly short compared with the average distance (2.372 Å) of five-coordinate Ru(II) complexes in the literature.[17] Finally, although a trigonal bipyramid with three phosphorus atoms on an equatorial plane might be an alternative description for the coordination geometry of **1**, the dppf bite angle observed for **1** was quite deviated from the ideal value of 120°. If the coordination geometry of **1** was a trigonal bipyramid, the dppf bite angle should be close to 120° since bite angles around 120° are not impossible for dppf because of its flexibility and since they have been described frequently for d^{10} trigonal-planar and tetrahedral complexes.[1,18]

Recent papers reported some five-coordinate Ru(II) complexes having sterically demanding tridentate *trans*-spanning ligands (so-called ‘pincer’ ligands) such as a bis(oxazolinyl)-phenylphosphonite ligand ($NOPON^{Me2}$)[19] and 1,5-bis(di-*tert*-butylphosphino)pentanes.[20] The bulky substituents of the reported Ru(II) complexes, $[RuCl_2(NOPON^{Me2})]$ and [RuHCl{$^tBu_2PCH_2CH_2$((*E*)-CH=CH)$CH_2P^tBu_2$}] (Scheme 2) prevented another ligand from getting access to the vacant coordination site. The five-coordinate geometries of these complexes resemble that of **1** with the *trans*-spanning dppf. Hence the octahedral coordination geometries in these complexes with the *trans*-spanning ligands were quite similar whether the ligands served as bidentate or tridentate.



$[RuCl_2(NOPON^{Me2})]$ [RuHCl{$^tBu_2PCH_2CH_2$((*E*)-CH=CH)$CH_2P^tBu_2$}]

Scheme 2

Complex **1** exhibited its chemical reactivity as an unsaturated five-coordinate 16-electron species when it reacted with monodentate ligands. Bubbling CO into the solution of **1** led readily to incorporation of one CO, yielding the coordinatively saturated dicarbonyl complex $[RuCl(CO)_2(dppf)(PPh_3)]BF_4$ (**3**·BF_4). The $^{31}P\{^1H\}$ NMR spectrum of **3** showed an ABX coupling pattern, which indicated three spectroscopically nonequivalent phosphorus atoms, *i.e.* a *cis* coordination mode of dppf. The ready conformational change of the dppf from the *trans*-form to the *cis*-chelation mode occurring in solution was assumed to be associated with the facile fluxional behavior of **1** as described above.

Similar reactions of **1** with ^tBuNC and CH_3CN gave $[RuCl(CO)(CN^tBu)_2(dppf)]BF_4$ (**4**·BF_4) and $[RuCl(CO)(NCCH_3)_2(dppf)]BF_4$ (**5**·BF_4), respectively. In the case of the nitrile complex **5**, one of the ligating nitriles was weakly bound and easily dissociated. When **5** was dissolved in chloroform, liberation of one nitrile molecule occurred, and an insoluble salt of dicationic bis(μ-chloro)diruthenium $[\{Ru(\mu\text{-}Cl)(CO)(NCCH_3)(dppf)\}_2](BF_4)_2$ (**6**·$(BF_4)_2$) was deposited from the solution. The X-ray structure analysis confirmed a chloride-bridged structure of the dicationic **6** (Fig. 3), which has a centre of symmetry at the node of the Ru ··· Ru and Cl ··· Cl axes, and indicated the coordination geometry around each Ru centre as a slightly distorted octahedron. The dppf ligand had a *cis* coordination mode and was situated *trans* to the bridging chloro ligands.

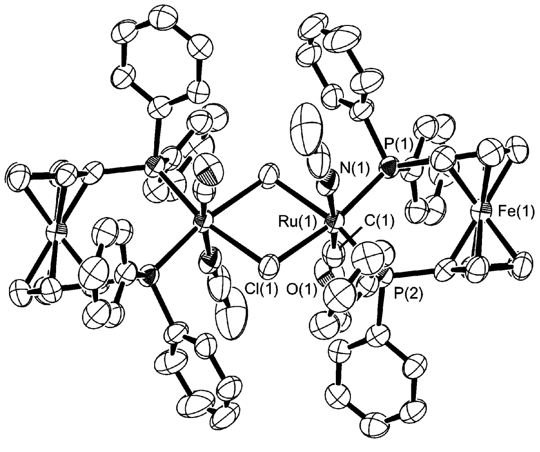


Fig. 3 Molecular structure of **6**·$(BF_4)_2$ with 50% thermal probability ellipsoids. Hydrogen atoms and BF_4 anions are omitted for clarity. The atoms with an asterisk (*) are generated by the symmetry operator, $-x, -y, -z$. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) 2.456(2), Ru(1)–Cl(1)* 2.481(2), Ru(1)–P(1) 2.353(2), Ru(1)–P(2) 2.337(2), Ru(1)–N(1) 2.115(7), Ru(1)–C(1) 1.837(9), N(1)–C(2) 1.14(1), C(2)–C(3) 1.45(2), C(1)–O(1) 1.15(1); Cl(1)–Ru(1)–Cl(1)* 79.74(7), Cl(1)–Ru(1)–P(1) 169.81(8), Cl(1)–Ru(1)–P(2) 87.43(6), Cl(1)–Ru(1)–N(1) 85.4(2), Cl(1)–Ru(1)–C(1) 91.8(3), Cl(1)*–Ru(1)–P(1) 92.61(7), Cl(1)*–Ru(1)–P(2) 167.08(7), Cl(1)*–Ru(1)–N(1) 86.6(2), Cl(1)*–Ru(1)–C(1) 87.1(2), P(1)–Ru(1)–P(2) 100.30(7), P(1)–Ru(1)–N(1) 87.4(2), P(1)–Ru(1)–C(1) 94.5(3), P(2)–Ru(1)–N(1) 93.9(2), P(2)–Ru(1)–C(1) 91.8(2), N(1)–Ru(1)–C(1) 173.5(3), Ru(1)–Cl(1)–Ru(1)* 100.26(7), Ru(1)–N(1)–C(2) 170.9(6), N(1)–C(2)–C(3) 177(1), Ru(1)–C(1)–O(1) 174.6(7). Dihedral angle between two Cp rings (°): 4.3(4).

Experimental

General

Reactions and manipulations were performed under a dry, oxygen-free nitrogen atmosphere with using Schlenk-type flasks or a glove box. The starting hydride complex [RuClH(CO)(dppf)(PPh_3)] was prepared according to the literature.[11] Solvents were dried and purified in the usual manner, and stored under nitrogen. All the other reagents were purchased and used without further purification. UV-vis and diffuse reflectance spectra were recorded on a Shimadzu UV-1600 and a Shimadzu UV-2550 spectrophotometer, respectively. Infrared spectra were recorded on a JASCO FT-IR 420 spectrometer using KBr disks. All NMR spectra were obtained on a JEOL GX-400 spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C) or 162 MHz (^{31}P). Chemical shifts were reported as δ values relative to $SiMe_4$ for ^1H and ^{13}C, and to 85% H_3PO_4 for ^{31}P. Elemental analyses were performed at the Center for Instrumental Analysis, Nagasaki University.

Preparations

[RuCl(CO)(dppf)(PPh$_3$)]BF$_4$ (1·BF$_4$). Using a hydridoruthenium complex [RuHCl(CO)(dppf)(PPh_3)] or [RuCl(C≡CPh)-

(CO)(dppf)(PPh_3)] (**2**), the complex **1** was obtained in a similar manner. The following preparation is typical.

Under nitrogen, HBF_4·Et_2O (40.8 μL, 0.30 mmol) was added to a solution of **2** (300 mg, 0.27 mmol) in dichloromethane (10 cm^3). The orange solution immediately turned red and was stirred for 1 h at room temperature. Addition of diethyl ether to the concentrated reaction mixture precipitated the product. The resulting reddish orange powder of **1**·BF_4 was collected, washed with diethyl ether and dried *in vacuo* (233 mg, 81%). **1**·BF_4: δ_H ($CDCl_3$, 30 °C): 7.50–6.80 (m, 35H, overlapped, Ph), 5.57 (br s, 2H, C_5H_4), 5.34 (br s, 2H, C_5H_4), 4.05 (br s, 2H, C_5H_4), 3.43 (br s, 2H, C_5H_4), δ_P (CD_2Cl_2, −60 °C): 53.1 (t, *J*(PP) = 19 Hz), −22.1 (d, *J*(PP) = 19 Hz), δ_C(CD_2Cl_2, 30 °C): 196.8 (q, C≡O, *J*(CP) = 12 Hz), 137–127 (m, overlapped, Ph), 82.8 (br s, C_5H_4), 81.3 (br s, C_5H_4), 73.8 (br s, C_5H_4), 72.0 (br s, C_5H_4), 47.9 (t, C_5H_4, *J*(CP) = 20 Hz), IR (CH_2Cl_2): 1968 cm^{-1} ν(C≡O), 1058 cm^{-1} ν(B–F). Calc. for $C_{53}H_{43}BClF_4FeOP_3Ru$·$CH_2Cl_2$: C, 56.26; H, 3.93%. Found: C, 55.96; H, 4.46%.

[RuCl(C≡CPh)(CO)(dppf)(PPh$_3$)] (2). In a Schlenk tube, a yellow suspension of [RuHCl(CO)(dppf)(PPh_3)] (2.33 g, 2.37 mmol) in a mixture of phenylacetylene (1.26 g, 12.39 mmol) and ethanol (80 cm^3) was refluxed under nitrogen. After 24 h, phenylacetylene (1.15 g, 11.27 mmol) was added to the suspension and the reaction mixture was allowed to reflux for further 24 h. After cooling, the resulting orange powder of **2** was collected, washed with ethanol and diethyl ether, successively, and dried *in vacuo* (1.86 g, 72%). **2**: δ_H ($CDCl_3$, 30 °C): 8.60–6.50 (m, 40H, Ph), 5.37 (br, 1H, C_5H_4), 4.88 (br, 1H, C_5H_4), 4.49 (br, 1H, C_5H_4), 4.30 (br, 1H, C_5H_4), 4.24 (br, 1H, C_5H_4), 4.19 (br, 1H, C_5H_4), 4.16 (br, 1H, C_5H_4), 3.91 (br, 1H, C_5H_4), δ_P ($CDCl_3$, 30 °C): 21.7 (dd, *J*(PP) = 344 and 17 Hz), 20.1 (dd, *J*(PP) = 344 and 22 Hz), −2.3 (dd, *J*(PP) = 22 and 17 Hz), δ_C (CD_2Cl_2, 30 °C): 200.3 (q, C≡O, *J*(CP) = 12 Hz), 139–124 (m, overlapped, Ph), 115.6 (d, RuC≡*C*, *J*(CP) = 24 Hz), 107.8 (dt, Ru*C*≡C, *J*(CP) = 90 and 26 Hz), 81–70 (m, overlapped, C_5H_4), IR (KBr): 2105 cm^{-1} ν(C≡C), 1952 and 1928 cm^{-1} ν(C≡O). Calc. for $C_{61}H_{48}ClFeOP_3Ru$: C, 67.69; H, 4.47%. Found: C, 68.09; H, 5.15%.

[RuCl(CO)$_2$(dppf)(PPh$_3$)]BF$_4$ (3·BF$_4$). Atmospheric CO was bubbled through a dichloromethane (10 cm^3) solution of **1**·BF_4 (50 mg, 0.05 mmol) for 1 h. The reddish orange solution turned pale yellow at once. After the reaction, the solvent was removed under reduced pressure. The residue was dissolved in a small amount of dichloromethane again. A yellow powder of **3**·BF_4 as a CH_2Cl_2 solvate was precipitated by addition of diethyl ether, collected on a filter, washed with diethyl ether and dried *in vacuo* (30 mg, 51%). **3**·BF_4: δ_H ($CDCl_3$, 30 °C): 7.80–7.10 (m, 35H, overlapped, Ph), 4.84 (br s, 1H, C_5H_4), 4.74 (br s, 1H, C_5H_4), 4.51 (br s, 2H, overlapped, C_5H_4), 4.49 (br s, 1H, C_5H_4), 4.46 (br s, 1H, C_5H_4), 4.45 (br s, 1H, C_5H_4), 4.35 (br s, 1H, C_5H_4), δ_P ($CDCl_3$): 18.5 (dd, *J*(PP) = 294 and 24 Hz), 16.8 (dd, *J*(PP) = 294 and 29 Hz), 5.6 (dd, *J*(PP) = 29 and 24 Hz), δ_C (CD_2Cl_2, 30 °C): 195.2 (m, C≡O), 191.0 (dt, C≡O, *J*(CP) = 102 and 16 Hz), 137–127 (m, overlapped, Ph), 78–71 (m, overlapped, C_5H_4), IR (CH_2Cl_2): 2064 and 2000 cm^{-1} ν(C≡O), 1084 cm^{-1} ν(B–F). Calc. for $C_{54}H_{43}BClF_4FeO_2P_3Ru$·$CH_2Cl_2$: C, 55.94; H, 3.84%. Found: C, 55.40; H, 4.18%.

[RuCl(CO)(CN^{t}Bu)$_2$(dppf)]BF$_4$ (4·BF$_4$). To a dichlromethane (10 cm^3) solution of **1**·BF_4 (50 mg, 0.05 mmol), ^{t}BuNC (12.5 mg, 0.15 mmol) was added and the mixture was stirred for 1 h. The resulting yellow solution was concentrated under reduced pressure. Addition of diethyl ether to the residue precipitated a yellow powder of **4**·BF_4, as a CH_2Cl_2 solvate, which was collected on a filter, washed with diethyl ether and dried *in vacuo* (39 mg, 74%). **4**·BF_4: δ_H ($CDCl_3$, 30 °C): 7.72–6.87 (m, 20H, Ph), 5.23 (br s, 2H, C_5H_4), 4.50 (br s, 2H, C_5H_4), 4.34 (br s, 2H, C_5H_4), 4.16 (br s, 2H, C_5H_4), 1.27 (s, 18H, ^{t}Bu), δ_P ($CDCl_3$, 30 °C): 22.0 (s), δ_C (CD_2Cl_2, 30 °C): 194.9 (t, C≡O, *J*(CP) = 14 Hz), 135–128 (m, overlapped, Ph), 77.5 (br s, C_5H_4), 77.4 (d, C_5H_4, *J*(CP) = 55 Hz), 75.9 (br s, C_5H_4), 73.9 (br s, C_5H_4), 72.7 (br s, C_5H_4), 60.1 (s, *C*(CH_3)$_3$), 30.0 (s, CH_3), IR (KBr): 2222 and 2197 cm^{-1} ν(C≡N), 2018 cm^{-1} ν(C≡O), 1058 cm^{-1} ν(B–F). Calc. for $C_{45}H_{46}BClF_4FeN_2OP_2Ru$·$CH_2Cl_2$: C, 52.27; H, 4.58; N, 2.65%. Found: C, 52.76; H, 4.92; N, 2.70%.

[RuCl(CO)(NCCH$_3$)$_2$(dppf)]BF$_4$ (5·BF$_4$). Addition of diethyl ether (10 cm^3) to a solution of **1**·BF_4 (50 mg, 0.05 mmol) in acetonitrile (5 cm^3) led to the solid product. One day later, a yellow powder of **5**·BF_4 was collected, washed with diethyl ether and dried *in vacuo* (36 mg, 81%). **5**·BF_4: IR (KBr): 2322 and 2296 cm^{-1} ν(C≡N), 1987 cm^{-1} ν(C≡O), 1083 cm^{-1} ν(B–F). Calc. for $C_{39}H_{34}BClF_4FeN_2OP_2Ru$: C, 52.76; H, 3.86; N, 3.16%. Found: C, 52.31; H, 4.45; N, 3.73%.

[{Ru(μ-Cl)(CO)(NCCH$_3$)(dppf)}$_2$](BF$_4$)$_2$ (6·(BF$_4$)$_2$). The compound **5**·BF_4 was dissolved in chloroform-*d*. Orange-coloured dimeric product **6**·(BF_4)$_2$ was crystallized quantitatively on standing for 1 h. The crystals were collected, washed with diethyl ether and dried *in vacuo*. **6**·(BF_4)$_2$: IR (KBr): 2320 and 2291 cm^{-1} ν(C≡N), 1990 cm^{-1} ν(C≡O), 1084 cm^{-1} ν(B–F). Calc. for $C_{74}H_{62}B_2Cl_2F_8Fe_2N_2O_2P_4Ru_2$: C, 52.48; H, 3.69; N, 1.65%. Found: C, 52.01; H, 4.14; N, 1.60%.

Since the sparingly soluble compound **6**·(BF_4)$_2$ was deposited immediately from the chloroform-*d* solution of the compound **5**·BF_4, NMR data for **5**·BF_4 and **6**·(BF_4)$_2$ were not available.

X-Ray crystallography

Single crystals suitable for structure analyses were obtained by recrystallization from dichloromethane–hexane for **1**·BF_4·CH_2Cl_2 and from chloroform-*d* solutions of **5**·BF_4 for **6**·(BF_4)$_2$·4.3$CDCl_3$. The intensity data were collected on a Rigaku AFC7S diffractometer equipped with an ADSC Quantum CCD area detector using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). The structures were solved by direct methods[21] for **1** and heavy-atom Patterson methods[22,23] for **6**. Calculations were performed using the teXsan crystallographic software package.[24] Details of the disorder and refinement are given in the CIF.

Crystal data: for **1**·BF_4: $C_{53}H_{43}ClFeOP_3Ru$·BF_4·CH_2Cl_2, M = 1152.95, monoclinic, space group $P2_1/c$ (no.14), a = 15.684(1), b = 14.740(2), c = 22.685(2) Å, β = 107.982(1)°, V = 4987.9(9) Å^3, Z = 4, D_c = 1.535 g cm^{-3}, T = 296 K, μ(Mo-Kα) = 9.05 cm^{-1}; no. of observations 44166, no. of unique reflections 11775 (R_{int} = 0.096); R = 0.116 and $wR2$ = 0.145 for all data, $R1$ = 0.061 for $I > 2\sigma(I)$ (6055 reflections), GOF = 1.08 for 623 variables.

For **6**·(BF_4)$_2$: $C_{74}H_{62}Cl_2Fe_2N_2O_2P_4Ru_2$·2$BF_4$·4.3$CDCl_3$, M = 2206.88, triclinic, space group $P\bar{1}$ (no. 2), a = 12.363(1), b = 13.627(2), c = 14.457(2) Å, α = 99.377(5), β = 110.241(1), γ = 93.587(2)°, V = 2236.0(5) Å^3, Z = 1, D_c = 1.639 g cm^{-3}, T = 296 K, μ(Mo-Kα) = 12.28 cm^{-1}; no. of observations 19548, no. of unique reflections 9652 (R_{int} = 0.053). The R values were not so good because of a significant loss of a $CDCl_3$ molecule in the crystal when measuring the intensities. The $CDCl_3$ molecules were treated as $CHCl_3$ in the final least-squares refinement; R = 0.115 and $wR2$ = 0.258 for all data, $R1$ = 0.082 for $I > 2\sigma(I)$ (6707 reflections), GOF = 1.07 for 551 variables.

CCDC reference numbers 175670 for **1**·BF_4·CH_2Cl_2 and 175671 for **6**·(BF_4)$_2$·4.3$CDCl_3$.

See http://www.rsc.org/suppdata/dt/b2/b212096h/ for crystallographic data in CIF or other electronic format.

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