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Synthesis and properties of the ruthenium vinylidene and acetylide complexes containing 1,1′-bis(diphenylphosphino)ferrocene

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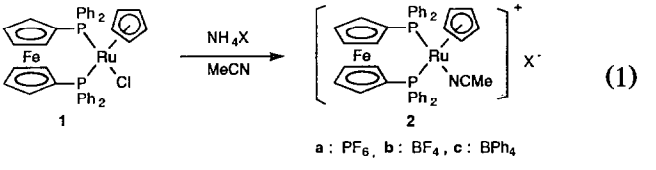
Abstract

RuCl(dppf)(η-C_5H_5) was treated with NH_4PF_6 in acetonitrile to give the cationic complex [Ru(CH_3CN)(dppf)(η-C_5H_5)]PF_6 in good yield, in which no bonding interaction between iron and ruthenium atoms was found. The reaction of RuCl (dppf) (η-C_5H_5) with terminal acetylene in the presence of NH_4PF_6 gave the corresponding vinylidene complexes, which were converted on treatment with base or alumina to the corresponding acetylide complexes. A similar reaction with methyl propiolate at room temperature gave the corresponding vinyl ether complex rather than the acetylide complex as a main product, and a novel degradation reaction to the cationic carbonyl complex was also observed.

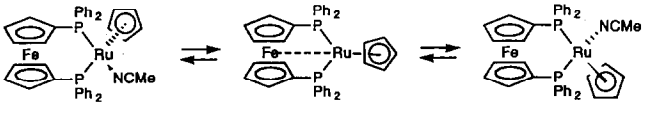
The ferrocene derivatives having an electron-donating heteroatom at the 1,1′-positions are superior starting materials for preparing hetero-bimetallic complexes [1]. Since the Group VI metal carbonyl complexes of 1,1′-(dimethylarsino)ferrocene were first synthesized by Bishop and Davison [2], numerous such complexes have been reported [3–16]. We have also prepared transition-metal complexes of polythia[*n*](1,1′)ferrocenophanes [17–20] and 1,1′-bis(diphenylphosphino)-ferrocene (dppf) [21], with a view to studying the metal–metal interaction, and confirmed the presence of the weak dative bond between the iron atom of a ferrocene moiety and the Pd^{II} and Pt^{II} atoms. However, there have been few reports concerning the reaction of the ferrocene-containing bimetallic complexes. We report here on reactions of chloro (η-cyclopentadienyl) [1,1′-bis(diphenylphophino)ferrocene-*P*,*P*′]ruthenium(II), RuCl(dppf)(η-C_5H_5) (**1**).

Recently, Bruce et al. reported the preparation of RuCl(dppf)(η-C_5H_5) (**1**) [22]. Compound **1** was treated with NH_4PF_6 in acetonitrile to give [Ru(CH_3CN)-(dppf)(η-C_5H_5)]PF_6 (**2a**) as yellow needles in a yield of 66%. The use of NH_4BF_4 and $NaB(C_6H_5)_4$ instead of NF_4PF_6 gave the corresponding complexes **2b** and **2c**



(1)

respectively. Treatment of **1** with $AgBF_4$ and $AgB(C_6H_5)_4$ in acetonitrile gave a similar result, but the same reaction in acetone gave a complicated mixture. In the ^1H NMR spectrum of **2a**, the protons of the ferrocenyl ring appeared at δ 4.31, 4.36, 4.39, and 4.40. On warming at 100°C, the ^1H NMR spectrum showed no substantial change. This asymmetrical and fixed character around the ferrocenyl ring suggested that the ruthenium atom in the complex maintains a piano-stool configuration. This is consistent with the fact that the coordination geometry of both [Ru(CH_3CN)(PPh_3)$_2$-(η-C_5H_5)]$^+$ [23] and [Ru(CH_3CN)($Ph_2PCH_2CH_2$-PPh_2)(η-C_5H_5)]$^+$ [24] is of piano-stool type. These results seem to indicate that there is no interconver-



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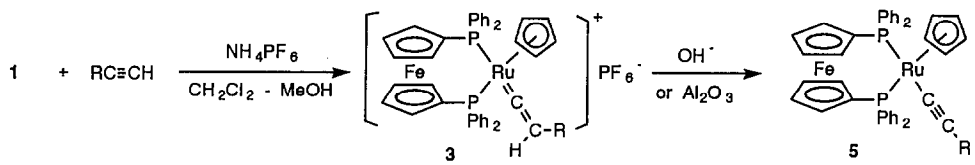


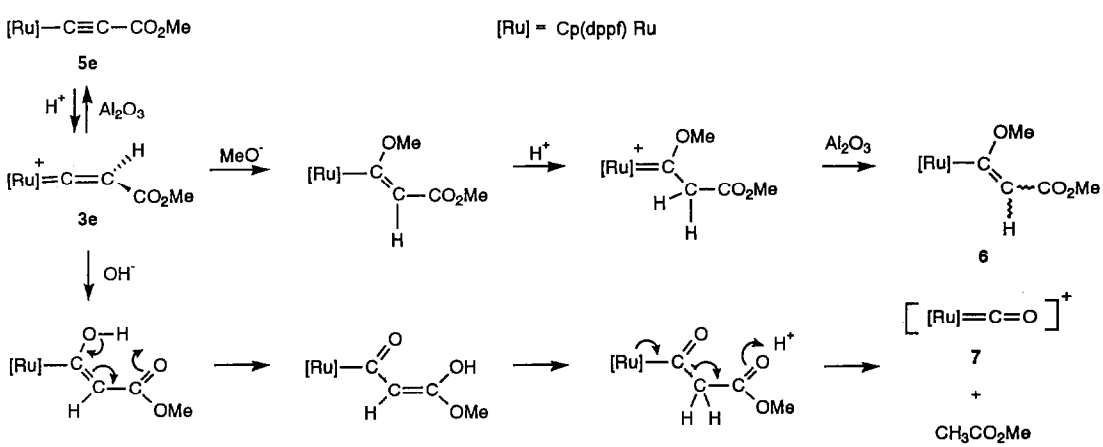
(3)

a : R=Ph, b : R=t-Bu, c : R=C_6H_{13}, d : R=Fc (Ferrocenyl), e : R=COOMe

sion as shown below and no interaction between the ruthenium and iron atoms in the complex **2a**, although coordinatively unsaturated ruthenium complexes, such as (η-C_5H_5)Ru(P^iPr_3)Cl, are known, the geometry of which is a two-legged piano-stool [25].

When complex **1** was reacted with phenylacetylene in the presence of NH_4PF_6 in dichloromethane–methanol at room temperature for 3 h, the vinylidene complex **3a** was obtained in 98% yield. tert-Butyl (**3b**) and ferrocenyl derivatives (**3d**) were also isolated in 98% and 89% yields respectively, but the definite product could not be isolated from the reaction mixture of **1** with 1-octyne or methyl propiolate under similar conditions. The ^1H NMR spectrum of **3a** showed the four protons of a ferrocenyl ring at δ 4.40, 4.47, 4.65, and 4.75 and the vinyl proton at δ 5.61. The signal of the cyclopentadienyl (Cp) ring coordinated to the ruthenium atom shifted from δ 4.10 in **1** to δ 5.32 in **3a**. In the ^{13}C NMR spectrum of **3a**, the signal of the carbenic carbon appeared at 356.5 ppm as a low-intensity triplet [$J(^{13}C-^{31}P) = 17.0$ Hz]. These spectral data indicate that the complex **3a** involves a vinylidene structure as shown in [Ru(C=CHPh)(PPh_3)$_2$(η-C_5H_5)]PF_6 (**4**) [26]. The appearance of four proton and carbon signals for the ferrocenyl ring in the ^1H and ^{13}C NMR spectra respectively, suggests that an asymmetrical and rigid structure of the complexes is maintained at least at room temperature. The assignment of the ferrocenyl ring protons in the ferrocenyl vinylidene derivatives **3d** was accomplished using the 2D H,H-COSY experiment. The signals of δ 4.49 and 4.40 are correlated with each other and concurrently to the signals at δ 4.79 and 4.64 respectively. No correlation between the latter signals was observed. This indicates that the former and the latter signals are assigned to the β- and α-protons of the ferrocenyl ring of dppf respectively. The remaining two signals at δ 3.71 and 4.10 are correlated only to each other and are therefore assigned to the ring protons of the ferrocenyl group connected to the vinylidene carbon.

The vinylidene complex **3a** was treated with methanolic KOH under stirring to give the corresponding acetylide complex **5a** in 76% yield. Similarly, the ferrocenyl acelylide complex **5d** was acquired from the vinylidene derivative **3d** in good yield. In this conversion, alumina can be used as a weak base [24]. For example, **3b** was converted to **5b** by column chromatography on alumina in quantitative yield. When the reaction mixture of **1** with phenylacetylene in the presence of NH_4PF_6 was directly chromatographed on alumina, **5a** was obtained in quantitative yield. The octyne derivative **5c** was prepared in 49% yield using this procedure, although the stable vinylidene complex **3c** could not be isolated. These compounds showed the stretching vibration of the C≡C bond near 2100 cm^{-1}. In the ^{13}C NMR spectra of these complexes the signal

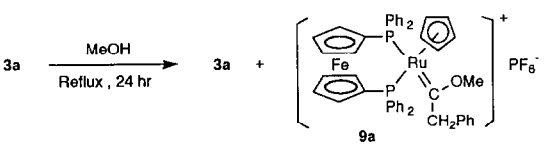


Scheme 1.

of the acetylene carbon connected to the ruthenium atom was detected as a triplet in the range 85–120 ppm, but the other carbon atom of the acetylene ligand appeared near 115 ppm. These spectral data confirm these compounds to be an acetylide complex.

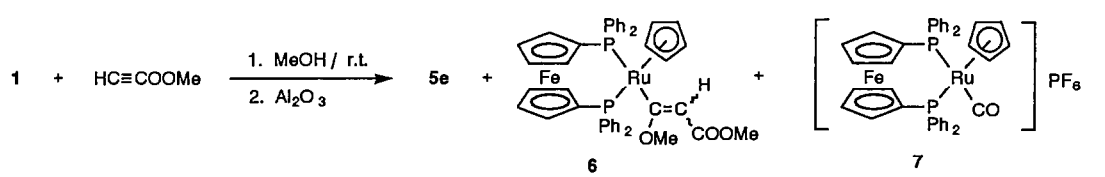
The reaction of **1** and methyl propiolate in the presence of NH_4PF_6 in refluxing methanol, followed by column chromatography of the condensed reaction mixture on alumina, gave only an intractable mixture. However, when the reaction was carried out at room temperature, three products were isolated. One of them was a trace amount of the acetylide complex **5e**, which was prepared alternatively in good yield in a similar reaction using acetone in place of methanol as a solvent. The main product was the vinyl complex **6**. Complex **6** was obtained as a mixture of two isomers in 54% yield, the ratio of which was calculated to be 7:1 from the intensity of the methyl signals of the methoxycarbonyl group. The structure of **6** was assigned by the ^1H NMR spectrum, which gave the vinyl proton at δ 4.98 and the two methoxyl protons at δ 4.43 and 4.58 in the major isomer. The ^{13}C NMR spectrum of **6** supported the above assignment: the signals of the carbonyl and olefinic carbons in the major isomer of **6** appeared at δ 154.85 and 105.77 respectively, and the olefinic carbon connected to the ruthenium atom was observed at δ 90.04. The last product was assigned as the cationic carbonyl complex **7**, in which ν(CO) was observed at 1974 cm^{-1} and the carbon signal for the metal carbonyl appeared at δ 203.34 ppm which is in the range of resonance of typical carbonyl carbons connected to the metal atom (190–220 ppm) [27]. This is an unprecedented product in such reactions, although the reaction of the vinylidene complex **4** and water was reported to give the benzylcarbonyl complex (η-C_5H_5)(Ph_3P)Ru(CO)CH_2Ph [28]. Complex **7** seems to be formed from the addition of OH^- to the intermediate vinylidene complex and subsequently the proton transfer shown in Scheme 1, because (i) the formation of **7** was hardly observed in CH_2Cl_2–acetone, and (ii) the acetylide complex **5e** was almost quantitatively converted to **7** in wet THF/CH_2Cl_2 in the presence of acid after 1 h. The reaction of **5e** and a drop of 48% HBF_4 aqueous solution in CD_2Cl_2–$C_4D_8O_2$ was pursued by ^1H NMR spectroscopy. Immediately after the addition of 48% HBF_4 aqueous solution, the signals due to the vinylidene complex **3e** appeared (δ 5.37 (s, 5H), 5.24 (s, 1H), 4.97, 4.74, 4.60, 4.54 (s, 2H × 4), 3.43 (s.3H), but after 10 h these signals had nearly disappeared and new signals due to complex **7** (δ 5.00 (s, 5H), 4.83, 4.67, 4.56, 4.43 (s, 2H × 4)) and methyl acetate (δ 2.00 (s) and 3.61 (s)) were observed.

It has been reported that the vinylidene complex **4** is converted to the carbene complex [(η-C_5H_5)(Ph_3P)$_2$-Ru{C(OMe)CH_2Ph}]PF_6 (**8**) in refluxing methanol for 24 h in a high yield [28]. Under similar conditions, however, the vinylidene complex **3a** gave an inseparable mixture (1:1) of **3a** and the corresponding carbene complex (**9a**). Thus, the reactivity of **3a** for methanol is lower than that of **4**. However, we found that the vinyl complex **6** was obtained in 54% yield from the reaction of **1** with methyl propiolate and NH_4PF_6 in methanol



9a (5)

at room temperature for 4 h followed by subsequent chromatography on alumina. Alternatively, it has been reported that the reaction of (η-C_5H_5)(Ph_3P)$_2$RuCl with methyl propiolate in the presence of NH_4PF_6 in refluxing methanol for 45 min gave the vinylidene complex [(η-C_5H_5)(Ph_3P)$_2$Ru(C=CHCO_2Me)]PF_6 (**10**) in 47% yield [26], and the vinylidene complex (**10**) (prepared from the acetylide complex (η-C_5H_5)(Ph_3-P)$_2$Ru(C≡CCO_2Me) (**11**)) furnished the carbene complex [(η-C_5H_5)(Ph_3P)$_2$Ru{C(OMe)CH_2Ph}]PF_6 at room temperature only for 2 h in 72% yield [28]. Therefore, the carbomethoxy vinylydene complex **3e** is also considered to be less reactive with methanol than the bis(triphenylphosphine) analogue (**10**). Bruce and Swinger [28] confirmed that the reactivity of the vinylidene complex towards methanol was predominantly controlled by steric effects and was inversely proportional to the cone angle of the ligands. The cone angle of the dppf ligand seems to be similar to that of triphenylphosphine, but the bite angle in the dppf complex is fairly different from that in bis(triphenylphosphine). Therefore, the retardation in the reaction of **3a** and **3e** compared with **4** and **10** respectively, is ascribed to the steric effects which are dependent on the different bite



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angle of the two bis-phosphine ligands around the ruthenium atom.

1. Experimental details

The melting points were measured using a differential scanning calorimeter, Seiko DSC-20. The IR spectra were taken using a Hitachi 270-50 IR spectrometer. The ^1H and ^{13}C NMR spectra were obtained on a Brucker AM-400 spectrometer, TMS being chosen as the standard material.

1.1. Materials

$RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [29], ferrocenylacetylene [27] and 1,1'-bis(diphenylphosphino)ferrocene [30] were prepared by the methods described in the literature. $RuCl(dppf)(\eta\text{-}C_5H_5)$ (**1**) was prepared by a modification of the procedure reported by Bruce et al. [22]: slight excess of dppf (1.11 g, 2.0 mmol) and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (1.38 g, 1.9 mmol) were refluxed for 8 h in benzene (30 ml). After evaporation, the residue was chromatographed on alumina to give **1**, which was recrystallized from CH_2Cl_2–EtOH (98% yield).

1.2. [Ru(CH$_3$CN)(dppf)(η-C$_5$H$_5$)](PF$_6$) (2a)

1.2.1. Method A

To a suspension of **1** (76 mg, 0.1 mmol), NH_4PF_6 (20 mg, 0.13 mmol) in dry acetonitrile (25 ml) was added, and the mixture was refluxed for 3 h. After evaporation under vacuum, the residue was extracted with CH_2Cl_2 (5 ml). The extract was filtered through Celite and evaporated. The residue was recrystallized from CH_3CN–ether to give **2a** as a yellow solid (58 mg, 66% yield).

1.2.2. Method B

To a suspension of **1** (76 mg, 0.1 mmol) in acetonitrile (20 ml) was added $AgPF_6$ (25 mg, 0.1 mmol), and the mixture was stirred for 1 h. The yellow solution was filtered and evaporated under vacuum. The residue was recrystallized from CH_3CN–ether to give **2a** as yellow needles (86 mg, 59.2%), m.p. 240°C. Found: C, 54.24; H, 4.26; N, 2.96. $C_{41}H_{36}NF_6P_3FeRu \cdot CH_3CN$ calcd.: C, 54.50; H, 4.14; N, 2.95%. ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 4.29, 4.42 (s × 2, 8H, $(C_5H_4)_2Fe$), 4.38 (s, 5H, CpRu) and 7.2–7.6 (m, 20H, Ph). ^{13}C NMR ($CDCL_3$): δ 4.53 (CH_3CN), 71.49 (s), 72.39 (s), 74.45 (J = 5.4 Hz), 75.39 (t, J = 5.4 Hz), 82.50 (t, J = 27.4 Hz) (Fc), 83.24 (s, CpRu), 130.06 (s, CH_3CN), 128.15, 128.38 (t × 2, J = 4.9 Hz, C_m), 130.06, 130.61 (s, C_p), 132.15, 134.92 (t × 2, J = 5.4 Hz, C_o), 134.92, and 139.12 (t × 2, J = 23.9 Hz, P–C). IR (KBr): 2024 (CN) and 836 cm^{-1} (PF6).

1.3. [Ru(CH$_3$CN)(dppf)(η-C$_5$H$_5$)](BF$_4$) (2b)

This complex was prepared using $AgBF_4$ instead of $AgPF_6$ according to Method B, giving yellow needles (53 mg, 59.2%), m.p. 211°C. Found: C, 58.17; H, 4.48; N, 3.06. $C_{43}H_{39}B_2F_8N_2P_2FeRu$ calcd.: C, 58.28; H, 4.62; N, 3.10%. ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 4.30, 4.39 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.28 (s, 5H, CpRu) and 7.4–7.6 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 4.64 (s, CH_3CN), 71.35, 72.32 (t × 2, J = 3.0 Hz), 74.45 (t, J = 3 Hz), 75.39 (t × 2, J = 4.7 Hz), 82.31 (t, J = 26.3 Hz) (Fc), 83.23 (s, CpRu) and 130.31 (s, CH_3CN). IR (KBr): 2040 (CN) and 1056 cm^{-1} (BF_4).

1.4. [Ru(CH$_3$CN)(dppf)(η-C$_5$H$_5$)](BPh$_4$) (2c)

This compound was prepared according to Method B using $AgBPh_4$, giving orange crystals (61 mg, 56.0%), m.p. 250°C (dec.). **2c** (159.5 mg, 73.0%) was also obtained from the reaction of **1** (142 mg, 0.2 mmol) with $NaBPh_4$ (68 mg, 0.2 mmol) according to Method A. Found: C, 71.72; H, 5.30; N, 2.49. $C_{67}H_{59}BN_2P_2FeRu$ calcd.: C, 71.74; H, 5.42; N, 2.21%. ^1H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3CN), 4.19, 4.25, 4.27, 4.34 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.19 (s, 5H, CpRu) and 6.8–7.5 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$): δ 3.9 (s, CH_3CN), 71.54 (s), 72.54 (S), 74.29 (t, J = 4.2 Hz), 75.39 (t, J = 4.2 Hz), 82.41 (t, J = 25.5 Hz) [$(C_5H_4)_2Fe$], 83.23 (s, CpRu) and 139.93 (s, CH_3CN).

1.5. [Ru(C=CHPh)(dppf)(η-C$_5$H$_5$)](PF$_6$) (3a)

Complex **1** (76 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (5 ml) and a solution of NH_4PF_6 (20 mg, 0.13 mmol) in MeOH (20 ml) was added. To the resulting solution phenylacetylene (three drops, an excess) was added. The mixture was stirred for 3 h to give a deep red solution, which was then filtered through Celite and evaporated. The residue was extracted with CH_2Cl_2 (5 ml) and the extract was filtered into an excess of hexane to give pink precipitates of **3a**, m.p. 151°C (95 mg, 98%). Found: C, 58.41%; H, 4.06. $C_{47}H_{39}F_6P_3FeRu$ calcd.: C, 58.33; H, 4.38%. ^1H NMR ($CDCl_3$): δ 4.40, 4.47, 4.65, 4.75 (s × 4, 8H, $(C_5H_4)_2Fe$), 5.32 (s, 5H, CpRu), 5.61 (s, 1H, =CH) and 6.6–7.7 (m, 25H, Ph). ^{13}C NMR ($CDCl_3$): δ 71.17 (s), 73.20 (t, J = 3.5 Hz), 74.99 (t, J = 5.5 Hz), 75.19 (t, J = 2.4 Hz), 83.91 (m) [$(C_5H_4)_2Fe$], 94.17 (s, CpRu) 119.47 (s, =CH) and 356.48 (t, J = 17.0 Hz, Ru=C). IR (KBr): 1646 (C=C) and 836 cm^{-1} (PF_6).

1.6. [Ru(C=CH^{t}Bu)(dppf)(η-C$_5$H$_5$)](PF$_6$) (3b)

t-Butyl acetylene (three drops, an excess) was added to a solution of **1** (0.1 mmol) and NH_4PF_6 (0.1 mmol) in MeOH (20 ml)–CH_2Cl_2 (5 ml). The solution was stirred for 8 h at room temperature to give orange precipitates of **3b** (94 mg, 98% yield), m.p. 150°C

(dec.). ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 9H, CMe_3), 4.44 (s, 1H, =CH), 4.48, 4.52, 4.61, 4.78 (s × 4, 8H, $(C_5H_4)_2Fe$), 5.17 (s, 5H, CpRu) and 7.2–7.6 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 31.92 (s, CMe), 31.50 (s, CH_3), 71.41 (t, J = 2.4 Hz), 73.10 (t, J = 2.4 Hz), 73.74 (t, J = 3.5 Hz), 75.00 (t, J = 5.4 Hz), 84.01 (m) [$(C_5H_4)_2Fe$], 93.20 (s, CpRu), 119.47 (s, =CH), and 347.67 (t, J = 17.0 Hz, Ru=C). IR (KBr): 1668, 1642 (C=C), 836 cm^{-1} (PF_6).

1.7. [Ru(C=CHFc)(dppf)(η-C_5H_5)](PF$_6$) (3d)

Ferrocenylacetylene (24 mg, 0.1 mmol) was added to a 0.1 mmol solution of **1** and NH_4PF_6 in MeOH (20 ml)–CH_2Cl_2 (5 ml). The solution was stirred for 3 h at room temperature under bubbling of nitrogen. The dark brown precipitates formed were collected and washed with benzene; they were almost pure **3d** (90 mg, 89% yield), m.p. 158–159°C. Found: C, 57.28; H, 4.24. $C_{51}H_{43}F_6P_3Fe_2Ru$ calcd.: C, 56.95; H, 4.02%. ^{1}H NMR ($CDCl_3$): δ 3.71, 4.10 (s × 2, 4H, C_5H_4Fe), 4.17 (s, 5H, CpFe), 4.40, 4.49, 4.64, 4.79 (s × 4, 8H, $(C_5H_4)_2Fe$), 5.23 (s, 5H, CpRu), 5.33 (s, 1H, =CH) and 7.3–7.9 (m, 20H, Ph). IR (KBr): 1642 (C=C) and 836 cm^{-1} (PF_6). This compound decomposed on the accumulation for ^{13}C measurement because of its instability in solution.

1.8. [Ru(C≡CPh)(dppf)(η-C_5H_5) (5a)

To a solution of complex **1** (76 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) was added a solution of NH_4PF_6 (20 mg, 0.13 mmol) in MeOH (20 ml). Phenylacetylene (three drops, an excess) was added to the solution. After the mixture had been stirred for 3 h, a solution of KOH (6 mg, 0.1 mmol) in MeOH (2 ml) was added to the reaction mixture. The colour of the solution turned immediately from deep red to yellow. The yellow solution was filtered and evaporated under vacuum. The residue was chromatographed on alumina by elution of CH_2Cl_2 to afford **5a** (62 mg, 76%) as yellow crystals, m.p. 271°C. When alumina was used as base instead of KOH, **5a** was obtained in 98% yield. Found: C, 68.46; H, 4.56. $C_{47}H_{38}P_2FeRu$ calcd.: C, 68.70; H, 4.66%. ^{1}H NMR ($CDCl_3$): δ 4.00, 4.15, 4.30, 5.33 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.30 (s, 5H, CpRu) and 7.0–7.9 (m, 25H, Ph). ^{13}C NMR ($CDCl_3$): δ 67.78 (s), 71.28 (s), 73.00 (s), 76.52 (t, J = 5.1 Hz), 88.67 (t, J = 24 Hz) [$(C_5H_4)_2Fe$], 84.58 (s, CpRu) 112.25 (s, ≡CPh), 116.73 (t, J = 26.1 Hz, Ru–C≡), 123.08, 128.48, 128.98 and 130.60 (s × 4, Ph). IR (KBr): 2112 cm^{-1}.

1.9. [Ru(C≡C'Bu)(dppf)(η-C_5H_5)] (5b)

t-Butyl acetylene three drops, excess) was added to a solution of **1** (0.1 mmol) and NH_4PF_6 (1 mmol) in MeOH (20 ml)–CH_2Cl_2 (5 ml). Then the mixture was stirred for 8 h. The resulting solution was filtered and evaporated under vacuum. The residue was chromatographed on alumina by elution of CH_2Cl_2 to afford **5b** (79 mg, 87%) as yellow crystals, m.p. 255°C. Found: C, 67.44; H, 5.47. $C_{45}H_{42}P_2FeRu$ calcd.: C, 67.41; H, 5.28%. ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 9H, CH_3), 3.95, 4.20, 4.28, 5.55 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.14 (s, 5H, CpRu) and 7.2–7.9 (m, 25H, Ph). ^{13}C NMR ($CDCl_3$): δ 29.99 (s, CMe), 33.10 (s, CH_3), 67.56 (s), 70.65 (s), 72.72 (s), 77.24 (t, J = 7.0 Hz), 89.18 (t, J = 23.1 Hz) [$(C_5H_4)_2Fe$], 84.49 (s, CpRu), 86.93 (t, J = 26.2 Hz, Ru–C≡), 117.99 (s, ≡CBu). IR (KBr): 2084 (C≡C) cm^{-1}.

1.10. [Ru(C≡C^{n}hex)(dppf)(η-C_5H_5)] (5c)

This complex was prepared using the same procedure described above, giving yellow crystals (42 mg, 49%), m.p. 192.5–193°C. Found: 67.34; H, 5.80. $C_{47}H_{46}P_2FeRu \cdot \frac{1}{2}(C_2H_5)_2O$ calcd.: C, 67.60; H, 5.79%. ^{1}H NMR (CD_2Cl_2): δ 0.89 (t, J = 7.0 Hz, CH_3), 1.2–1.5 (m, 8H, CH_2), 2.44 (t, J = 7.0 Hz, CH_2C–), 4.01, 4.24, 4.27, 5.35 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.20 (s, 5H, CpRu) and 7.2–7.9 (m, 25H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.42 (CH_3), 23.20, 23.56, 29.52, 31.69, 32.29 (CH_2 × 5), 68.39 (s), 71.42 (t, J = 2.5 Hz), 73.46 (s), 77.29 (t, J = 4.9 Hz), 89.85 (t, J = 23 Hz) [$(C_5H_4)_2Fe$], 84.46 (s, CpRu), 90.64 (t, J = 26.4 Hz, Ru–C≡), 109.29, (s, ≡CHex). IR(KBr): 2100 cm^{-1} (C≡C).

1.11. [Ru(C≡CFc)(dppf)(η-C_5H_5)](PF$_6$) (5d)

Ferrocenylacetylene (24 mg, 0.1 mmol) was added to a solution of **1** (0.1 mmol) and NH_4PF_6 (0.1 mmol) in MeOH (20 ml)–CH_2Cl_2 (10 ml). The solution was stirred for 3 h at room temperature under bubbling of nitrogen. To the reaction mixture a solution of NaOMe (sodium (2.3 mg, 0.1 mmol) in MeOH (2 ml)) was added. The orange precipitates formed were collected and recrystallized from CH_2Cl_2–hexane to give **5d** as orange fine needles (85 mg, 92%), m.p. 300°C. Found: C, 65.74; H, 4.84. $C_{51}H_{42}P_2Fe_2Ru$ calcd.: C, 65.89; H, 4.55%. ^{1}H NMR ($CDCl_3$): δ 4.01 (s, 5H), 4.02, 4.21 (t × 2, J = 1.6 Hz, 4H) (Fc), 4.07, 4.34, 4.36, 5.53 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.28 (s, 5H, CpRu), and 7.3–7.9 (m, 20H, Ph). IR (KBr) 2080 cm^{-1} (C≡C). The ^{13}C NMR spectrum could not be obtained because of its instability in solution.

1.12. Reaction of complex 1 with methyl propiolate

To a solution of **1** (76 mg, 0.1 mmol) in CH_2Cl_2 (20 ml)–MeOH (10 ml) was added NH_4PF_6 (20 mg, 0.1 mmol). After methyl propiolate (three drops, an excess) had been added, the mixture was stirred for 8 h at room temperature under nitrogen. The solvent was evaporated under vacuum and the residue was chromatographed on alumina by elution of CH_2Cl_2. The following three compounds were isolated.

1.12.1. (η-C_5H_5)(dppf)Ru(C≡CCOOMe) (5e)

Yellow crystals (recrystallized from CH_2Cl_2–hexane), m.p. 277°C. Found: C, 65.17; H, 5.24%. $C_{43}H_{36}O_2P_2FeRu \cdot \frac{1}{2}C_6H_{14}$ calcd.: C, 65.33; H, 5.00%. ^{1}H NMR (CD_2Cl_2): δ 3.65 (s, 3H, OMe), 4.06, 4.31, 4.34, 5.44 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.36 (s, 5H, CpRu), 7.3–7.7 (m, 20H, −Ph). ^{13}C NMR (CD_2Cl_2): δ 51.37 (s, OMe), 68.34 (t, J = 2.7 Hz), 71.97 (t, J = 3.2 Hz), 73.51 (s), 76.47 (t, J = 5.4 Hz), 88.23 (t, J = 25.6 Hz) [$(C_5H_4)_2Fe$], 85.52 (t, J = 2.2 Hz, CpRu), 105.76 (s, ≡CCO_2Me), 137.12 (t, J = 24.2 Hz, Ru–C≡), 153.10 (s, CO). IR (KBr): 2048 (C≡C) and 1662 (CO) cm^{-1}.

1.12.2. (η-C_5H_5)(dppf)Ru[C(OMe)=CHCOOMe] (6)

Yellow needles (recrystallized from CH_2Cl_2–hexane), m.p. 204–205°C. Found: C, 61.06; H, 5.09. $C_{44}H_{40}O_3P_2FeRu \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 60.87; H, 4.82%. ^{1}H NMR ($CDCl_3$): (major isomer) δ 3.44, 3.58 (s × 2, 6H, OMe), 4.01 (s, 2H), 4.29 (s, 4H), 4.75 (s, 2H)[$(C_5H_4)_2Fe$], 4.31 (s, 5H, CpRu), 4.51 (s, 1H), and 7.2–7.6 (m, 20H, Ph); (minor isomer) δ 3.09, 3.30 (s × 2, 6H, OMe), 4.09, 4.25, 4.31, 4.35 (s × 4, 8H) [$(C_5H_4)_2Fe$)], 4.42 (s, 5H, CpRu), and 5.56 (s, 1H). ^{13}C NMR (CD_2Cl_2): (major isomer) δ 51.36, 62.51 (s × 2, OMe), 68.34 (s), 71.98 (s), 73.52 (s), 76.47 (t, J = 5.7 Hz), 88.22 (t, J = 24.1 Hz) [$(C_5H_4)_2Fe$], 85.51 (s, CpRu), 90.04 (RuC=), 105.77 (s, =CH), and 154.85 (CO); (minor isomer) δ 49.04, 54.01 (s × 2, OMe), 68.15 (s), 71.20 (s), 73.36 (s), 76.59 (t, J = 5.7 Hz) [$(C_5H_4)_2Fe$], 85.76 (s, CpRu), 91.35 (RuC=), 106.77 (s, =CH), and 162.25 (CO). IR (KBr): 1744 cm^{-1}.

1.12.3. [(η-C_5H_5)(dppf)RuCO]PF_6 (7)

Yellow oil. ^{1}H NMR ($CDCl_3$): δ 4.43, 4.48, 4.68, 4.74 (s × 4, 8H, $(C_5H_4)_2Fe$), 4.91 (s, 5H, CpRu), 7.4–7.6 (m, 20H, Ph). IR (KBr): 1974 cm^{-1}.

When the reaction was carried out in anhydrous CH_2Cl_2 (20 ml)–acetone (10 ml), only the acetylide complex **5e** was obtained in 79% yield.

1.13. [(η-C_5H_5)(dppf)RuCO]BF_4

To a solution of **5e** (25 mg, 0.03 mmol) in CH_2Cl_2 (2 ml)–THF (4 ml) was added aqueous tetrafluoroboric acid (0.5 ml). The solution was stirred for 1 h. After evaporation of the solvent under vacuum, the residue was dissolved in CH_2Cl_2. The solution was washed with water and dried. After evaporation, the residue was chromatographed on alumina by elution with CH_2Cl_2 to give the title compound (23 mg, 88%) as yellow oil, which was crystallized from CH_2Cl_2–hexane to yield yellow–orange crystals, m.p. 142°C (dec.). Found: C, 57.90; H, 4.42%. $C_{40}H_{33}BF_4OP_2FeRu$ calcd.: C, 57.80; H, 4.40%. IR (KBr): 1974 (M–CO) and 1020–1100 cm^{-1} (BF_4). ^{1}H NMR ($CDCl_3$): δ 4.43 (s, 2H), 4.47 (s, 2H), 4.70 (s, 2H), 4.72 (s, 2H), 4.95 (s, 5H), and 7.4–7.6 (m, 20H). ^{13}C NMR ($CDCl_3$): d 71.29 (s), 73.21 (s), 75.20 (s), 73.92 (t, J = 5.2 Hz), 83.75 (t, J = 30.5 Hz) [$(C_5H_4)_2Fe$], 90.01 (s, CpRu), 203.34 (s, RuCO).

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