Supporting Information

for

Angew. Chem. Int. Ed. Z19650

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69451 Weinheim, Germany
Unprecedented Coupling of Allenylidene and Diynyl Metal Complexes: New Bimetallic Ruthenium System with a C7 Conjugated Bridge.

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Experimental Section

General comments. The reactions were carried out under an inert atmosphere using the Schlenk techniques. Solvents were freshly distilled under argon using standard procedures. Electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat (CH2Cl2, 0.1M Bu4NPF6), the working electrode was a Pt disk and ferrocene the internal reference. Cis-[(dppe)2RuCl2], [(dppe)2RuCl]BF4, [Cl(dppe)2Ru-C≡C≡C-SiMe3] and Ph(C2H5)C(OH)-C≡CH were prepared as previously reported.

1a: In a Schlenk tube containing 400 mg of [(dppe)2RuCl]BF4 (0.4 mmol.), and 81 mg (CH3)2C(OH)-C≡CH (1.00 mmol.), 40 mL of CH2Cl2 was added. The solution was stirred during 18 h at room temperature. After filtration, the solution was evaporated and then the residue washed with diethyl ether (3 × 25 mL). Further crystallisation in a dichloromethane/pentane mixture, led to 356 mg of dark crystals (82%). 31P{1H} NMR (121 MHz, CD2Cl2): δ = 42.2 (s, PPh2); 1H NMR (300 MHz, CD2Cl2): δ = 7.38-6.78 (m, 40H, Ph), 2.60-3.00 (m, 8 H, CH2), 1.26 (s, 6H, CH3); 13C{1H} NMR (75 MHz, CD2Cl2): δ = 319.67 (quint., 2J(P,C) = 14 Hz, Cα), 201.21 (s, Cβ), 175.80 (s, Cγ), 133.75-127.87 (Ph), 35.86 (CH3), 29.19 (m, 1J(P,C) + 3J(P,C) = 23 Hz, CH2); IR: ν = 1958 (=C=C=C), ν = 1059 (BF) cm⁻¹; HR-MS FAB+ (m/z): 999.1928 ([M]+, calcd: 999.1908); Analysis for C57H54P4F4ClBRu: C 62.99, H 5.22 (Calcd: C 63.02, H 5.01).

1b: The procedure was identical with 408 mg of [(dppe)2RuCl]BF4 (0.4 mmol.), and 27 mg of Ph(CH3)C(OH)-C≡CH (1.00 mmol.), and yielded to 417 mg of dark red crystals (91%). 31P{1H} NMR (121 MHz, CD2Cl2, TMS): δ = 40.4 (s, PPh2); 1H NMR (300 MHz, CD2Cl2): δ = 7.38-6.78 (m, 40H, Ph), 2.60-3.00 (m, 8 H, CH2), 1.26 (s, 6H, CH3); 13C{1H} NMR (75 MHz, CD2Cl2): δ = 319.67 (quint., 2J(P,C) = 14 Hz, Cα), 201.21 (s, Cβ), 175.80 (s, Cγ), 133.75-127.87 (Ph), 35.86 (CH3), 29.19 (m, 1J(P,C) + 3J(P,C) = 23 Hz, CH2); IR: ν = 1958 (=C=C=C), ν = 1059 (BF) cm⁻¹; HR-MS FAB+ (m/z): 999.1928 ([M]+, calcd: 999.1908); Analysis for C57H54P4F4ClBRu: C 62.99, H 5.22 (Calcd: C 63.02, H 5.01).
MHz, CD₂Cl₂, TMS): δ = 7.60-7.00 (m, 45H, Ph), 2.70-3.2 (m, 8H, CH₂), 1.55 (s, 3H, CH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, TMS): δ = 310.57 (quint., ²J(P,C) = 14 Hz, Cₐ), 210.19 (s, Cₐ), 162.18 (s, C₉), 142.88-128.26 (Ph), 31.94 (CH₃), 29.06 (m, ³J(P,C), ⁵J(P,C) = 23 Hz, CH₂); IR: ν = 1932 (≡C=≡C=), ν = 1056 (BF) cm⁻¹; HR-MS FAB⁺ (m/z): 1061.2076 ([M⁺], calcd: 1061.2079); Analysis for C₆₂H₅₆P₄F₄ClBRu: C 64.82, H 5.05 (Calcd: C 64.85, H 4.92).

1c: The procedure was identical with 306 mg [(dppe)₂RuCl]BF₄ (0.30 mmol.), 112 mg of Ph(C₂H₅)C(OH)-C≡CH (0.75 mmol.), and yielded to 280 mg of dark red crystals (80%). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, TMS): δ = 40.1 (s, PPh₂); ¹H NMR (300 MHz, CD₂Cl₂, TMS): δ = 7.55-6.82 (m, 45H, Ph), 2.70-3.20 (m, 8H, CH₂), 2.24 (quad., ³J(H,H) = 7 Hz, 2H, CH₂), 1.10 (t, ⁴J(H,H) = 7Hz, 3H, CH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂, TMS): δ = 311.76 (quint., ²J(P,C) = 14 Hz, Cₐ), 210.02 (s, Cₐ), 169.75 (s, C₉), 142.81-128.24 (Ph), 38.51 (CH₂-CH₃), 29.27 (m, ¹J(P,C) + ³J(P,C) = 23 Hz, CH₂), 12.75 (CH₃); IR: ν = 1933 (≡C=≡C=), ν = 1062 (BF) cm⁻¹; HR-MS FAB⁺ (m/z): 1075.2231 ([M⁺], calcd: 1075.2236); Analysis for C₆₃H₅₈P₄F₄ClBRu: C 65.14, H 5.11 (Calcd: C 65.10, H 5.03).

2: In a Schlenk tube containing 1.05 g (1 mmole) of [Cl(dppe)₂Ru-C≡C≡CSiMe₃] dissolved in 50 mL of THF, 1.10 mL (1.10 mmol) of a commercial solution of Bu₄NF (1 M in THF) was added. The reaction medium was stirred for 1 h. After evaporation, the residue was washed with water and dried and 880 mg of 2 were recovered (95%). ³¹P{¹H} NMR (121 MHz, CDCl₃, TMS): δ = 49.0 (s, PPh₂); ¹H NMR (300 MHz, CDCl₃, TMS): δ = 7.46-6.99 (m, 40H, Ph), 2.66 (m, 8H, CH₂), 1.28 (s, CH); ¹³C{¹H} NMR (75 MHz, CDCl₃, TMS): δ = 135.61-127.12 (Ph), 123.17 (quint., ²J(P,C) = 16 Hz, Cₐ), 94.46 (s, Cₐ), 74.51 (s, C₉), 50.89 (C₉), 30.57 (m, ¹J(P,C) + ³J(P,C) = 23 Hz, CH₂); IR: ν = 3264 (C≡CH), ν = 2102 (C≡C) cm⁻¹; Analysis for C₅₆H₄₉P₄ClRu: C 68.76, H 4.97 (Calcd: C 68.47, 5.03).

3a: In a Schlenk tube containing 163 mg of 1a (0.15 mmol.), 30 mL of CH₂Cl₂ was added. In another tube, 158 mg of 2 (0.15 mmol.) was dissolved in 100 mL of CH₂Cl₂.
This solution was slowly added to the first one over 6 hours, using a dropping funnel. This mixture was further stirred during 18 h at room temperature. After filtration, the solution was evaporated and then the residue washed with diethyl ether (3 × 25 mL). Crystallizations in a CH$_2$Cl$_2$/pentane mixture yielded 233 mg of dark green crystals of 3a (75%). $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 47.1 (s, PPh$_2$); $^1$H NMR (300 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 7.35-6.95 (m, 80H, Ph), 5.50 (s, 1H, CH), 2.40-2.90 (m, 16 H, CH$_2$), 1.35 (s, 6H, CH$_3$); $^{13}$C{$^1$H} NMR (75 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 224.20 (quint., $^2$J(P,C) = 14 Hz, C$_{\alpha}$), 157.10 (s, C$_{\beta}$), 152.50 (s, CH), 137.4 (s, C$_{\gamma}$), 135.65-127.76 (Ph), 30.20 (m, $^1$J(P,C) + $^3$J(P,C) = 23 Hz, CH$_2$), 29.74 (CH$_3$); IR: $\nu$ = 1903 (C=C=C), $\nu$ = 1054 (BF) cm$^{-1}$; HR-MS FAB$^+$ (m/z): 1981.3527 ([M]$^+$, calcd: 1981.3463); Analysis for C$_{113}$H$_{103}$P$_8$Cl$_2$Ru$_2$BF$_4$: C 65.85, H 5.18 (Calcd: C 65.61, H 5.02).

3b: The procedure was identical with 58 mg 1b (0.05 mmol.), 53 mg of 2 (0.05 mmol.), and yielded to 77 mg of dark green crystals (72%). $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 47.0 (s, PPh$_2$), 49.7 (s, PPh$_2$); $^1$H NMR (300 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 7.41-6.83 (m, 85H, Ph), 5.79 (s, 1H, CH), 2.40-2.90 (m, 16 H, CH$_2$), 0.92 (s, 3H, CH$_3$); $^{13}$C{$^1$H} NMR (75 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 230.21 and 223.95 (quint., $^2$J(P,C) = 14 Hz, C$_{\alpha}$ and C$_{\alpha}''$), 162.61 and 162.22 (s, C$_{\beta}$ and C$_{\beta}''$), 153.61 and 137.91 (s, C$_{\gamma}$ and C$_{\gamma}''$), 151.73 (s, CH), $\delta$ 145.76-127.71 (Ph), 30.83 and 29.78 (m, $^1$J(P,C) + $^3$J(P,C) = 23 Hz, CH$_2$), 25.97 (CH$_3$); IR: $\nu$ = 1897 (C=C=C), $\nu$ = 1054 (BF) cm$^{-1}$; HR-MS FAB$^+$ (m/z): 2043.3657 ([M]$^+$, calcd: 2043.3581); Analysis for C$_{118}$H$_{105}$P$_8$Cl$_2$Ru$_2$BF$_4$: C 66.26, H 5.31 (Calcd: C 66.52, H 4.97).

3c: The procedure was identical with 58 mg of 1b (0.05 mmol.), 53 mg of 2 (0.05 mmol.), and yielded to 73 mg of dark green crystals (69%). $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 49.6 (s, PPh$_2$), 43.8 (s, PPh$_2$); $^1$H NMR (300 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 7.68-6.40 (m, 85H, Ph), 2.40-3.00 (m, 16 H, CH$_2$), 1.27 and 1.06 (s, 3H, CH$_3$); $^{13}$C{$^1$H} NMR (75 MHz, CD$_2$Cl$_2$, TMS): $\delta$= 245.26 and 220.37 (quint., $^2$J(P,C) = 14 Hz, C$_{\alpha}$ and C$_{\alpha}''$), 170.47 and 158.22 (s, C$_{\beta}$ and C$_{\beta}''$), 157.99 and 146.64 (s, C$_{\gamma}$ and C$_{\gamma}''$), 152.11 (s, C$_{8}$$-\text{CH}_3$), 145.52-127.56 (Ph), 31.01 and 28.97 (m, $^1$J(P,C) + $^3$J(P,C) = 23 Hz, CH$_2$), 30.70 (s, C$_{\gamma}$$-\text{CH}_3$), 22.47 (C$_{8}$$-\text{CH}_3$); IR: $\nu$ = 1889 (C=C=C), $\nu$ = 1055 (BF) cm$^{-1}$.
HR-MS FAB\(^+\) (\(m/z\)): 2058.3908 ([M]\(^+\), calcd: 2058.3781); Analysis for C\(_{119}\)H\(_{107}\)P\(_8\)Cl\(_2\)Ru\(_2\)BF\(_4\): C 66.49, H 5.06 (Calcd: C 66.64, H 5.03).