Supplementary Material (ESI) for Chemical Communications

Electronic Communication in "Chain-Like" Trimetallic Ruthenium Complexes with Two C_7 Carbon-Rich Conjugated Bridges

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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 (CH_2Cl_2, 0.1M Bu_4NPF_6), the working electrode was a Pt disk and ferrocene the internal reference**.** $[(dppe)_2RuCl][OTf]$,[1] $[(dppe)_2(Ru\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}SiMe_3)_2]$[2] , and $[(dppm)_2(Ru\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}SiMe_3)_2]$[3] were prepared as previously reported.

Spectroelectrochemistry. UV-vis-NIR spectroelectrochemistry (SEC) experiments were performed at 20 °C, under argon, with a home-made Optically Transparent Thin-Layer Electrosynthetic (OTTLE) cell, path length = 1 mm, using a Varian CARY 5000 spectrometer and an EG&G PAR model 362 potentiostat. A Pt mesh was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire as a pseudo-reference electrode. The electrodes were arranged in the cell such that the Pt mesh was in the optical path of the quartz cuvette. The anhydrous freeze-pump-thaw degassed sample-electrolyte solution (0.1 M *n*-$Bu_4N^+PF_6^-$) was cannula-transferred under argon into the cell previously thoroughly deoxygenated. The oxidation potentials were calibrated upon performing cyclic voltammetry before electrolysis. Stable isobestic points were observed during oxidation or reduction. At the end of the experiment, the original spectra were regenerated to (*ca*. 80 % optical yield). In every case re-reduced or re-oxidized samples displayed in the spectral region of interest no features other than those of the parent material. IR experiments were performed in similar conditions using a modified cell with KBr windows, and a Bruker IFS28 spectrometer.

EPR Spectroscopy. EPR spectra were recorded with an ESP300E spectrometer (BRUKER) operating at X-band and equipped with a standard rectangular cavity (TE 102). An ESR900 cryostat (Oxford Instruments) was used for the low temperature measurements. Computer simulations of the EPR spectra were performed with the help of Simfonia (BRUKER). Prior to recording their EPR spectra, the singly oxidized complexes were generated in situ in a

homemade cell. The electrolysis under Argon atmosphere was performed at controlled potential with a three electrode configuration (platinum wire working electrode, platinum wire auxiliary electrode and Ag wire as pseudo reference electrode). A dilute solution (ca. 10^{-3}M) of the precursor complexes was prepared with TBAHP (0.1M) as supporting electrolyte. The oxidation potentials were calibrated upon performing cyclic voltammetry before electrolysis.

trans-[Cl(dppe)$_2$Ru=C=C=C(CH$_3$)Ph][OTf] ([2][OTf]): In a Schlenk tube containing [(dppe)$_2$RuCl][OTf] (400 mg, 0.37 mmol.), and Ph(CH$_3$)C(OH)-C≡CH (118 mg, 0.80 mmol.), CH_2Cl_2 (40 mL) was added. The solution was stirred during 18 h at room temperature. After filtration, the solution was evaporated and the residue washed with diethyl ether (3 × 25 mL). Further crystallization in a dichloromethane/pentane mixture led to dark crystals (417 mg, 86%). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, TMS): δ= 41.04 (s, PPh_2). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ= 7.80- 6.90 (m, 45H, Ph), 2.80 – 3.3 (m, 8 H, CH_2), 1.63 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, TMS): δ= 310.10 (quint., C_α, ^2J(P,C) = 14 Hz), 209.62 (s, C_β), 162.90 (s, C_γ), 142.48-127.83 (Ph), 125.36 (quad., CF_3, ^1J(F,C) = 321 Hz), 31.54 (CH_3), 28.67 (CH_2, $|^1J(P,C)_+{}^3(P,C)|$ = 23 Hz). IR (KBr): υ_{max}/cm^{-1} 1933 (=C=C=C). HR-MS FAB$^+$ (*m/z*): 1061.2065 ([*M*]$^+$, calcd: 1061.2079). Analysis for $C_{63}H_{56}F_3ClO_3P_4SRu$: C 62.13, H 4.70, S 2.46 (Calcd: C 62.50, H 4.66, S 2.65).

***trans*-[Cl(dppe$_2$)Ru=C=C=C(Ph)-CH=C(CH$_3$)-C≡C-Ru(dppe$_2$)-C≡C-C(CH$_3$)=CH (Ph)=C=C=Ru(dppe$_2$)Cl][2TfO]$_2$ ([3a][OTf]$_2$):** In a Schlenk tube, a solution of **[2][OTf]** (242 mg, 0.2 mmol.) in CH_2Cl_2 (30 mL) was added to a solution of **1a** (114 mg, 0.1 mmol) in CH_2Cl_2 (30 mL). The addition was carried out slowly (51 hours) using a dropping funnel. The mixture was further stirred 4 days at room temperature. After filtration, the solution was evaporated, the residue was washed with diethylether (2 × 20 mL) and then dried under vacuum. Further crystallizations in a methylene chloride/pentane mixture led to blue crystals (177 mg, 52%). The following labeling is used for NMR peak attributions: [Ru$^{\mathbf{a}}$]=C$_1$=C$_2$=C$_3$(Ph)-C$_4$H=C$_5$(CH$_3$)-C$_6$≡C$_7$-[Ru^b]-C≡C-C(CH$_3$)=CH-C(Ph)=C=C=[Ru^a].
$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ= 51.63 (s, PPh_2 dppe), 44.90 (s, PPh_2 dppe). ^1H NMR (300 MHz, CD_2Cl_2): δ= 7.64- 6.82 (m, 130H, Ph), 5.76 (s, 2H, C=CH-C), 2.90 (m, 8 H, CH_2), 2.67 (m, 16 H, CH_2), 0.89 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ= 260.60 (quint., Ru^a=*C*$_1$, $^2J_{(P,C)}$ = 14 Hz), 193.02 (quint., Ru^b-*C*$_7$, $^2J_{(P,C)}$ = 14 Hz), 182.80 (s, Ru^a=C=*C*$_2$),

156.36 (s, Ru^b-C≡C_6), 149.01 (s, Ru^b-C≡C-C_5), 146.63 (s, Ru^a=C=C=C_3), 136.97 (s, Ru^a=C=C=C-C_4H), 145.58-127.77 (Ph), 31.31 (quint., CH_2 dppe Ru^b, $|^1J_{(P,C)} + {}^3J_{(P,C)}|$ = 23 Hz), 28.82 (quint., CH_2 dppe Ru^a, $|^1J_{(P,C)} + {}^3J_{(P,C)}|$ = 23 Hz), 24.07 (s, CH_3). IR (KBr): υ_{max}/cm^{-1} 1987 (C≡C, weak), 1884 cm^{-1} (=C=C=C, strong). HR-MS FAB$^+$ (*m/z*): 1559.3056 ($[M]^{++}$, calcd: 1559.3018). Analysis for $C_{186}H_{162}Cl_2P_{12}Ru_3F_6O_6S_2$: C 64.97, H 4.69 (Calcd: C 65.38, H 4.78).

***trans*-[Cl(dppe$_2$)Ru=C=C=C(Ph)-CH=C(CH$_3$)-C≡C-Ru(dppm$_2$)-C≡C-C(CH$_3$)=CH (Ph)=C=C=Ru(dppe2)Cl][2TfO]$_2$ ([3b][OTf]$_2$):** In a Schlenk tube, a solution of **[2][OTf]** (242 mg, 0.2 mmol.) in CH_2Cl_2 (30 mL) was added to a solution of **1b** (111 mg, 0.1 mmol) in CH_2Cl_2 (30 mL). The addition was carried out slowly (51 hours) using a dropping funnel. The mixture was further stirred 12 days at room temperature. After filtration, the solution was evaporated, the residue was washed with diethylether (2 × 20 mL) and then dried under vacuum. Further crystallizations in a methylene chloride/pentane mixture led to blue crystals (193 mg, 57%). The following labeling is used for NMR peak attributions:
[Ru^a]=C_1=C_2=C_3(Ph)-C_4H=C_5(CH_3)-C_6≡C_7-[Ru^c]-C≡C-C(CH_3)=CH-C(Ph)=C=C=[Ru^a].
$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ= – 6.27 (s, PPh_2 dppm), 43.30 (s, PPh_2 dppe). ^1H NMR (300 MHz, CD_2Cl_2): δ= 7.60- 6.49 (m, 130H, Ph), 5.51 (s, 2H, C=CH-C), 5.04 (m, 4 H, CH_2 *dppm*), 2.92 (m, 8 H, CH_2 dppe), 2.64 (m, 8 H, CH_2 dppe), 0.52 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ= 255.09 (quint., Ru^a=C_1, $^2J_{(P,C)}$ = 13 Hz), 195.26 (quint., Ru^c-C_7, $^2J_{(P,C)}$ = 14 Hz), 176.47 (s, Ru^a=C=C_2), 155.18 (s, Ru^c-C≡C_6), 151.57 (s, Ru^c-C≡C-C_5), 147.27 (s, Ru^a=C=C=C_3), 136.37 (s, Ru^a=C=C=C-C_4H), 146.07-127.44 (Ph), 50.51 (quint., CH_2 dppm, $|^1J_{(P,C)} + {}^3J_{(P,C)}|$ = 25 Hz), 28.11 (quint., CH_2 dppe, $|^1J_{(P,C)} + {}^3J_{(P,C)}|$ = 22 Hz), 23.07 (s, CH_3). IR (KBr): υ_{max}/cm^{-1} 1993 (C≡C, weak), 1889 cm^{-1} (=C=C=C, strong). HR-MS FAB$^+$ (*m/z*): 1545.7922 ($[M]^{++}$, calcd: 1545.7898). Analysis for $C_{184}H_{158}Cl_2P_{12}Ru_3F_6O_6S_2$: C 64.99, H 4.81, S 1.93 (Calcd: C 65.21, H 4.70, S 1.89).

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