

Electronic Supplementary Information

Electronic Communication in Phosphine Substituted Bridged Dirhenium Complexes – Clarifying Ambiguities Raised by the Redox Non-Innocence of the C₄H₂- and C₄-Bridges

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General Procedures

All the manipulations were carried out under a nitrogen atmosphere using Schlenk techniques or a glove box (M. Braun150B-G-II). Reagent grade benzene, toluene, hexane, pentane, diethyl ether and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl prior to use. Dichloromethane and acetonitrile were distilled from CaH₂. Complex [ReCl₂(N₂COPh)(PPh₃)₂] was prepared by the literature procedure.¹ Complex [ReCl(N₂)(PMe₃)₄] was prepared by using similar procedure described in literature.¹ All other chemicals were directly used as obtained from commercial suppliers. IR spectra were obtained on a Bio-Rad FTS-45 instrument. NMR spectra were measured on a Varian Mercury spectrometer at 200 MHz for ¹H, 81 MHz for ³¹P{¹H}, 188 MHz for ¹⁹F{¹H}, Varian Gemini-2000 spectrometer at 300 MHz for ¹H and 75 MHz for ¹³C{¹H}, and on a Bruker-DRX-500 spectrometer at 500 MHz for ¹H, 125.8 MHz for ¹³C{¹H}, 202.5 MHz for ³¹P{¹H}, and 99.4 MHz for ²⁹Si{¹H}. Chemical shifts for ¹H, ³¹P, ¹³C, and ²⁹Si are given in ppm relative to TMS and those for ³¹P relative to phosphoric acid. Cyclic voltammograms were obtained with BAS 100W voltammetric analyzer equipped with an Au working and a Pt counter electrode and a non-aqueous reference electrode. All sample solutions were approximately 5 × 10⁻³ M in substrate and in 0.1 M THF or CH₃CN solution of [nBu₄N][PF₆] and prepared under nitrogen. Ferrocene was subsequently added and the calibration of voltammograms performed. The BAS 100W program was employed for data analysis. IR and UV/Vis/NIR spectro-electrochemistry were performed in an OTTLE cell following the design of Hartl et al.² IR spectra were recorded on a Thermo is10 spectrometer. UV/vis/NIR spectra on a TIDAS fiberoptic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from j&m. X-band EPR spectra were obtained using Bruker EMX Electron Spin Resonance system. Magnetization measurements were carried out on a Quantum Design SQUID magnetometer, molar magnetic susceptibility was calculated according to the equation $\chi = (M \cdot M_w) / (m \cdot H)$, where M – experimental magnetization, M_w – molecular weight, m – sample weight, H – magnetic field.

Computational methodology: Molecular structures were optimized by means of the program package Turbomole,³ version 6.4, using Kohn–Sham density functional theory. The BLYP hybrid exchange–correlation density functional with 50% Hartree–Fock exchange^{4,6} in combination with def2-TZVP basis sets^{7,8} was employed as well as the resolution-of-the-identity density-fitting technique^{9,10}. Grimme’s D3 dispersion correction¹¹ was exploited in all calculations. Strict convergence criteria were applied where the orbitals were converged until the electronic energy was constant up to the seventh decimal place, and the length of the geometry gradient was lower than 10⁻⁴ a.u. Vibrational analysis of selected structures was performed with the help of the MOVIPAC package¹² and Turbomole. Antiferromagnetically coupled states were obtained via the broken-symmetry approach with starting structures generated from ferromagnetically coupled states using the “flip” feature as implemented in Turbomole. Several optimizations were also carried out with the B3LYP^{4,6,13} and PBE0¹⁴⁻¹⁶ hybrid density functionals containing an exact exchange amount of 20% and 25%, respectively, as well as the non-hybrid density functional BP86^{4,17}. We employed the solvent continuum model COSMO¹⁸ with the standard settings as implemented in Turbomole (i.e., a relative permittivity of $\epsilon = \infty$). Test calculations with $\epsilon = 1$ or $\epsilon = 8$ did not significantly influence the results.

Syntheses

***trans*-[ReCl(N₂)(PMe₃)₄] (1).** [N-Benzoylhydrazido (3-) N', O]dichlorobis (triphenylphosphine)rhenium (V) [ReCl₂(N₂COPh)(PPh₃)₂] (1.007 g, 1 mmol) and PMe₃ (0.7 mL, 6.6 mmol) in 1:1 benzene-methanol (6 mL) were heated at 70 °C for 2 h. The clear yellow solution was dried *in vacuo* and extracted with CH₂Cl₂. To the CH₂Cl₂ solution, a large amount of ether was added to precipitate off the impurities. After filtration, the pale orange solution was evaporated to dryness, washed with -30 °C cold ether (3 × 2 mL), and dried *in vacuo*. Yield: 0.364 g (0.066 mmol, 66% based on [ReCl₂(N₂COPh)(PPh₃)₂]). Anal. Calcd. for C₁₂H₃₆ClN₂P₄Re (553.98 g/mol): C, 26.02; H, 6.55; N, 5.06. Found: C, 26.19; H, 6.34; N, 4.99. IR (ATR, cm⁻¹): ν = 1914 (N≡N), 921 (C-P). MS (ESI): *m/z* (100%): 554.1 [M]. ¹H NMR (THF-d₈, 200 MHz, 22 °C): δ = 1.54 (s, 12H, PMe₃). ³¹P NMR (THF-d₈, 81 MHz, 22 °C): δ = -33.7 (s, PMe₃). ¹³C NMR (C₆D₆, 75 MHz, 22 °C): δ = 15.6 (s, PMe₃).

***trans*-[Re(CCH₃)(C≡CSiMe₃)(PMe₃)₄][PF₆] (2).** A mixture of *trans*-[ReClN₂(PMe₃)₄] (1) (61.5 mg, 0.111 mmol), TlPF₆ (77.6 mg, 0.222 mmol), HC≡CSiMe₃ (56 μL, 0.389 mmol), DIPEA (5 mL), and 5 mL of THF in a Young schlenk was heated at 95 °C for 24 h. After cooling to room temperature and keeping at this temperature for 12 h, the solvent was removed *in vacuo* and the residue was extracted with CH₂Cl₂ and filtered through celite. After evaporation of the solvent to dryness *in vacuo*, the pure product was obtained after recrystallization from THF/ether and washing with ether (3 × 2 mL). Yield: 81.1 mg (0.107 mmol, 90% based on 1). Anal. Calcd for C₁₉H₄₈F₆P₅ReSi (759.72 g/mol): C, 30.04; H, 6.37. Found: C, 29.99; H, 6.30. IR (ATR, cm⁻¹): ν = 2029 (C≡C), 939 (C-P), 827 (P-F). MS (ESI): *m/z* (100%): 615.1 [M]. ¹H NMR (CD₂Cl₂, 200 MHz, 22 °C): δ = 1.78 (m, 48H, PMe₃), 1.27 (quint, ⁴J_{PH} = 4.0 Hz, 3H, CH₃), 0.02 (m, 12H, SiMe₃); ¹³C NMR (CD₂Cl₂, 125.8 MHz, 10 °C): δ = 284.5 (quint, ²J_{PC} = 13.6 Hz, C_α), 134.7 (quint, ²J_{PC} = 18.9 Hz, C_α'), 125.7 (s, C_β'), 38.4 (s, C_β), 21.8 (m, P(CH₃)₃), 0.4 (s, Si(CH₃)); ³¹P NMR (CD₂Cl₂, 81 MHz, 22 °C): δ = -41.6 (s, PMe₃), -144.0 (sept, J = 710 Hz, PF₆); ¹⁹F NMR (CD₂Cl₂, 188 MHz, 22 °C): δ = -74.8 (d, J = 711 Hz, PF₆); ²⁹Si NMR (CD₂Cl₂, 99.4 MHz, 10 °C): δ = 24.8 (quint, ⁴J_{PSi} = 2.3 Hz, SiMe₃).

***trans*-[Re(=C=CH₂)(C≡CSiMe₃)(PMe₃)₄] (3).** To a THF solution of *trans*-[Re(≡C-CH₃)(C≡CSiMe₃)(PMe₃)₄][PF₆] (2) (7.6 mg, 0.010 mmol), KOtBu (1.8 mg, 0.016 mmol) was added. After 10 min the solvent was removed *in vacuo*, the residue was extracted with pentane and filtered through celite. Removal of the solvent *in vacuo*, gave the pure product. Yield: 6 mg, (0.0098 mmol, 98% based on 2). Anal. Calcd. for C₁₉H₄₈F₆P₅ReSi (613.76 g/mol): C, 37.78; H, 7.72. Found: C, 37.30; H, 7.59. IR (ATR, cm⁻¹): ν = 1982 (C≡C), 1558 (C=C), 930 (C-P). MS (ESI): *m/z* (100%): 615.2 [M+H]. ¹H NMR (C₆D₆, 200 MHz, 22 °C): δ = 1.53 (s, 48H, PMe₃); 1.35 (quint, ⁴J_{PH} = 3.5 Hz, 2H, CH₂), 0.31 (s, 12H, SiMe₃); ¹³C NMR (C₆D₆, 125.8 MHz, 10 °C): δ = 301.6 (quint, ²J_{PC} = 11.9 Hz, C_α), 150.1 (s, C_α'), 87.8 (m, C_β), 67.8 (s, C_β'), 21.3 (m, P(CH₃)₃), 1.9 (s, Si(CH₃)); ³¹P NMR (C₆D₆, 81 MHz, 22 °C): δ = -41.4 (s, PMe₃); ²⁹Si NMR (C₆D₆, 99.4 MHz, 10 °C): δ = -30.6 (quint, ⁴J_{PSi} = 1.9 Hz, SiMe₃).

***trans*-[Re(CCH₃)(C≡CSiMe₃)(PMe₃)₄]Cl (4).** To *trans*-[Re(=C=CH₂)(C≡CSiMe₃)(PMe₃)₄] (3) (26.4 mg, 0.043 mmol) in 1:3 THF/ether (3 mL), 1 M HCl ether solution (0.065 mL, 0.065 mmol) was added resulting in the immediate formation of a pale orange precipitate. The resulting suspension was stirred at room temperature for 30 min. The solvent was removed *in vacuo* and the pure product was obtained by recrystallization from THF/ether (1:2) and washed with ether (3 × 2 mL). Yield: 23.5 mg, (0.036 mmol, 84% based on 3). Anal. Calcd. for C₁₉H₄₈ClP₄ReSi (650.23 g/mol): C, 35.10; H, 7.44. Found: C, 35.01; H, 7.26. IR (ATR, cm⁻¹): ν = 2025 (C≡C), 941 (C-

P). MS (ESI): m/z (100%): 615.2 [M]. ^1H NMR (CD_2Cl_2 , 200 MHz, 22 °C): δ = 1.78 (m, 48H, PMe_3), 1.31 (quint, $^4J_{\text{PH}} = 4.0$ Hz, 3H, CH_3), 0.01 (m, 12H, SiMe_3); ^{13}C NMR (CD_2Cl_2 , 125.8 MHz, 10 °C): δ = 284.9 (m, C_α), 135.0 (s, C_α'), 125.8 (s, C_β'), 38.7 (s, C_β), 21.9 (m, $\text{P}(\text{CH}_3)_3$), 0.4 (s, $\text{Si}(\text{CH}_3)_3$); ^{31}P NMR (CD_2Cl_2 , 81 MHz, 22 °C): δ = -41.5 (s, PMe_3); ^{29}Si NMR (CD_2Cl_2 , 99.4 MHz, 10 °C): δ = -24.8 (quint, $^4J_{\text{PSi}} = 2.3$ Hz, SiMe_3).

***trans*-[($\text{Me}_3\text{SiC}\equiv\text{C}$)(PMe_3) $_4\text{Re}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{Re}(\text{PMe}_3)_4(\text{C}\equiv\text{CSiMe}_3)]$][PF_6] $_2$ (**5**). To a 1:3 $\text{CH}_3\text{CN}/\text{THF}$ (2 mL) solution of [Cp_2Fe][PF_6] (18.6 mg, 0.056 mmol) at -78 °C, *trans*-[$\text{Re}(\text{C}\equiv\text{CSiMe}_3)(=\text{C}=\text{CH}_2)(\text{PMe}_3)_4$] (**3**) (28.8 mg, 0.047 mmol) in THF (2 mL) was added. The reaction mixture was stirred at this temperature for 1.5 h. It was gradually warmed up to room temperature and stirred overnight. The residue was extracted with CH_3CN followed by filtration through celite. The solution was concentrated and diethyl ether was added to precipitate crude **5**. The pale yellow solid was collected and recrystallized from $\text{CH}_3\text{CN}/\text{ether}$. It was further washed with diethyl ether (3 \times 2 mL), and dried to give the pure product **5**. Yield: 32.8 mg, (0.022 mmol, 92% based on **3**). Single crystals suitable for X-Ray diffraction studies were grown by layering diethyl ether over an acetonitrile solution of the title compound. Anal. Calcd. for $\text{C}_{38}\text{H}_{94}\text{F}_{12}\text{P}_{10}\text{Re}_2\text{Si}_2$ (1517.46 g/mol): C, 30.08; H, 6.24. Found: C, 29.93; H, 6.16. IR (ATR, cm^{-1}): ν = 2027 ($\text{C}\equiv\text{C}$), 940 (C-P). MS (ESI): m/z (%): 1373 [M^+]. ^1H NMR (CD_2Cl_2 , 200 MHz, 22 °C) δ = 1.75 (s, $\text{P}(\text{CH}_3)_3$), 1.56 (s, CH_2), 0.05 (s, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (CD_2Cl_2 , 125.8 MHz, 10 °C) δ = 279.9 (t, $^2J_{\text{PC}} = 13.8$ Hz, C_α), 134.0 (t, $^2J_{\text{PC}} = 19.4$ Hz, C_α'), 126.6 (s, C_β'), 46.4 (s, C_β), 22.4 (m, $\text{P}(\text{CH}_3)_3$), 0.3 (s, $\text{Si}(\text{CH}_3)_3$); ^{31}P NMR (CD_2Cl_2 , 81 MHz, 22 °C) δ = -42.2 (s, $\text{P}(\text{CH}_3)_3$), -146.6 (sept, $J = 711$ Hz, PF_6); ^{19}F NMR (CD_2Cl_2 , 188 MHz, 22 °C) δ = -76.2 (d, $J = 711$ Hz, PF_6). ^{29}Si NMR (CD_2Cl_2 , 99 MHz, 10 °C): δ = -23.2 (s, SiMe_3).**

[($\text{Me}_3\text{SiC}\equiv\text{C}$)(PMe_3) $_4\text{Re}=\text{C}=\text{CH}-\text{CH}=\text{C}=\text{Re}(\text{PMe}_3)_4(\text{C}\equiv\text{CSiMe}_3)]$ (E-6**). Method a: To a THF (1 mL) solution of *trans*-[$\text{Re}(\text{C}\equiv\text{CSiMe}_3)(\equiv\text{C}-\text{CH}_2)(\text{PMe}_3)_4$][PF_6] $_2$ (**5**) (22.8 mg, 0.015 mmol), KOtBu (6.2 mg, 0.055 mmol) was added in two equal portions. The interval of the addition of KOtBu was 30 min. The resulting brownish green solution was dried *in vacuo*. The residue was extracted with pentane followed by filtration. Evaporation of the solution to dryness gave the crude neutral complex **E-6**, which was washed with pentane (3 \times 1 mL, -30 °C), and dried *in vacuo*. Yield: 16.0 mg (0.013 mmol, 87% based on **5**).**

Method b: To a THF (1 mL) solution of *trans*-[$\text{Re}(\text{C}\equiv\text{CSiMe}_3)(\equiv\text{C}-\text{CH}_2)(\text{PMe}_3)_4$][PF_6] $_2$ (**5**) (15.0 mg, 0.010 mmol), LDA (3.8 mg, 0.035 mmol) was added in two equal portions. The addition of LDA was done during 30 min. The resulting brownish green solution was dried *in vacuo*. The residue was extracted with pentane followed by filtration. Evaporation of the solution to dryness gave the crude neutral complex **E-6**, which was washed with -30 °C pentane (3 \times 1 mL) and dried *in vacuo*. Yield: 10.5 mg (0.008 mmol, 83% based on **5**).

Method c: To a THF solution of *trans*-[$\text{Re}(\text{C}\equiv\text{CSiMe}_3)(\equiv\text{C}-\text{CH})(\text{PMe}_3)_4$][PF_6] $_2$ (**E-6**[PF_6] $_2$) (13.6 mg, 0.009 mmol), LDA (2.0 mg, 0.019 mmol) was added. The resulting yellowish green solution was stirred at room temperature for 30 min and further the same amount of LDA was added. The color of the solution changed to dark blue, finally resulting in a brownish green solution. After removal of the solvent *in vacuo*, the residue was extracted with pentane followed by filtration. Evaporation of the pentane solution to dryness gave the crude neutral complex, which was washed with pentane (3 \times 1 mL, -30 °C), and dried *in vacuo*. Yield: 10.5 mg (0.008 mmol, 83% based on **E-6**[PF_6] $_2$).

Single crystals suitable for X-ray diffraction studies were grown by evaporation of a pentane solution of the title compound in a glove box. Anal. Calcd. for $\text{C}_{38}\text{H}_{92}\text{P}_8\text{Re}_2\text{Si}_2$ (1225.51 g/mol): C 37.24; H 7.57. Found: C 37.11; H 7.46. IR (ATR, cm^{-1}): ν = 1975 ($\text{C}\equiv\text{C}$), 1543 (C_4H_2), 933 (C-P). Raman (cm^{-1}): 1973 ($\text{C}\equiv\text{C}$), 1581 $\nu(\text{C}_4\text{H}_2)$. ^1H NMR ($\text{THF}-d_8$, 200 MHz, 22 °C): δ = 1.59 (s,

$P(CH_3)_3$), 2.50 (d, $^4J_{PH} = 4$ Hz, CH), -0.03 (s, $Si(CH_3)_3$); ^{13}C NMR (THF- d_8 , 125.8 MHz, 10 °C): $\delta = 309.4$ (quint, $^2J_{PC} = 12.8$ Hz, $Re\equiv C_\alpha$), 152.8 (quint, $^3J_{PC} = 16.0$ Hz, $Re-C_\alpha$), 127.8 (s, $\equiv C_{\beta-Si}$), 96.7 (s, C_β), 24.0 (s, $P(CH_3)_3$); 2.2 (s, $Si(CH_3)_3$). ^{31}P NMR (THF- d_8 , 81 MHz, 22 °C): $\delta = -40.5$ (s, $P(CH_3)_3$). ^{29}Si NMR (THF- d_8 , 99.4 MHz, 10 °C): $\delta = -31.8$ (s, $SiMe_3$).

***trans*-[($Me_3SiC\equiv C$)(PMe_3) $_4Re\equiv C-CH=CH-C\equiv Re(PMe_3)_4(C\equiv CSiMe_3)$][PF_6] (E-6[PF_6]).** Method a: To the THF solution of the dicationic complex *trans*-[($Me_3SiC\equiv C$)(PMe_3) $_4Re\equiv C-CH=CH-C\equiv Re(PMe_3)_4(C\equiv CSiMe_3)$][PF_6] $_2$ (E-6[PF_6] $_2$) (12.5 mg, 0.008 mmol), neutral complex *trans*-[($Me_3SiC\equiv C$)(PMe_3) $_4Re\equiv C-CH=CH-C\equiv Re(PMe_3)_4(C\equiv CSiMe_3)$] (E-6) (11.0 mg, 0.008 mmol) in THF was added. The resulting yellowish green solution was stirred at room temperature for 30 min. After removal of solvent, the solid was washed with ether (3 × 1 mL) and dried *in vacuo*. Yield: 19.6 mg (0.014 mmol, 87%, based on E-6).

Method b: To the mixture of neutral complex *trans*-[($Me_3SiC\equiv C$)(PMe_3) $_4Re\equiv C-CH=CH-C\equiv Re(PMe_3)_4(C\equiv CSiMe_3)$] (E-6) (21.0 mg, 0.017 mmol) and [Cp_2Fe][PF_6] (5.7 mg, 0.017 mmol), CH_3CN was added. The resulting yellowish green suspension was stirred at room temperature for 30 min. After filtration through celite, the solvent was removed *in vacuo*. The pure product was obtained by washing with THF and recrystallization from CH_3CN /ether. Yield: 19.0 mg (0.014 mmol, 82%, based on E-6). Single crystals suitable for X-ray diffraction studies were grown by layering ether on the top of a THF solution of the title compound. Anal. Calcd For $C_{38}H_{92}F_6P_9Re_2Si_2$ (1370.48 g/mol): C 33.30; H 6.77. Found: C 33.08; H 6.69. IR (ATR, cm^{-1}): $\nu = 1987$ ($C\equiv C$), 937 (C-P). 1H NMR (THF- d_8 , 200 MHz, 22 °C): $\delta = 0.89$ (s, $C_\beta H$), 0.10 (s, $Si(CH_3)_3$), -0.05 (br, $P(CH_3)_3$).

***trans*-[($Me_3SiC\equiv C$)(PMe_3) $_4Re\equiv C-CH=CH-C\equiv Re(PMe_3)_4(C\equiv CSiMe_3)$][PF_6] $_2$ (E-6[PF_6] $_2$).** To a THF solution of *trans*-[$Re(C\equiv CSiMe_3)(\equiv C-CH_2)(PMe_3)_4$][PF_6] (5) (32.8 mg, 0.022 mmol), LDA (6.7 mg, 0.062 mmol) was added. The resulting dark brownish green solution was kept stirring at room temperature for 30 min. Then [Cp_2Fe][PF_6] (14.3 mg, 0.043 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 1.5 h. After removal of solvent *in vacuo*, the residue was extracted with CH_3CN followed by filtration through celite. After concentration diethyl ether was added to precipitate the product as a brown-red solid. This was collected, washed with ether (3 × 2 mL), and dried *in vacuo*. Yield: 28 mg (0.018 mmol, 86% based on 5). Single crystals suitable for X-ray diffraction studies were grown by layering pentane over a dichloromethane solution of the title compound. Anal. Calcd For $C_{38}H_{92}F_{12}P_{10}Re_2Si_2$ (1515.45 g/mol): C 30.12; H 6.12. Found: C, 29.91; H, 6.04. IR (ATR, cm^{-1}): $\nu = 2022$ ($C\equiv C$), 942 (C-P). MS(ESI): m/z (100%): 1368 [M^+-2H]. 1H NMR (CD_2Cl_2 , 200 MHz, 22 °C): $\delta = 5.82$ (s, $C_\beta H$), 1.78 (s, $P(CH_3)_3$), 0.03 (s, $Si(CH_3)_3$); ^{13}C NMR (CD_2Cl_2 , 125.8 MHz, 10 °C): $\delta = 265.3$ (t, $Re\equiv C_\alpha$), 145.8 (s, $C_\beta H$), 135.5 (s, $Re-C_\alpha\equiv$), 130.9 (s, $\equiv C_{\beta-Si}$), 22.3 (s, $P(CH_3)_3$), 0.2 (s, $Si(CH_3)_3$); ^{31}P NMR (CD_2Cl_2 , 81 MHz, 22 °C): $\delta = -43.8$ (s, $P(CH_3)_3$), -143.9 (sept, $J = 710$ Hz, 1P, PF_6); ^{19}F NMR (CD_2Cl_2 , 188 MHz, 22 °C): $\delta = -73.9$ (d, $J = 711$ Hz, PF_6). ^{29}Si NMR (CD_2Cl_2 , 99.4 MHz, 10 °C): $\delta = -23.9$ (s, $SiMe_3$).

***trans*-[($Me_3SiC\equiv C$)(PMe_3) $_4Re\equiv C-C\equiv C-C\equiv Re(PMe_3)_4(C\equiv CSiMe_3)$][PF_6] $_2$ (7[PF_6] $_2$).** Method a: A mixture of *trans*-[$Re(C\equiv CSiMe_3)(\equiv C-CH_3)(PMe_3)_4$][PF_6] $_2$ (E-6[PF_6] $_2$) (21.4 mg, 0.014 mmol) and $KOtBu$ (8.0 mg, 0.070 mmol) in THF was stirred at room temperature for 12 h until a dark blue solution was obtained. With vigorous stirring, [Cp_2Fe][PF_6] (24.0 mg, 0.071 mmol) was added to this reaction mixture in two portions with an interval of 1 h. The solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2 and filtered through celite. The product was obtained by precipitation with ether, further washing with ether (3 × 2 mL) and drying *in vacuo*. Yield: 20 mg (0.013 mmol, 95% based on E-6[PF_6] $_2$).

Method b: To a mixture of *trans*-[Re(C≡CSiMe₃)(≡C-CH₃)(PMe₃)₄][PF₆] (**2**) (7.6 mg, 0.010 mmol) and KOtBu (2.2 mg, 0.020 mmol) in THF, [Cp₂Fe][PF₆] (6.6 mg, 0.020 mmol) was added in one portion at -30 °C. The reaction mixture was stirred at room temperature for 1h. The solvent was removed *in vacuo* and the residue was washed with hexane or pentane (3 × 2 mL). The resulting solid was dissolved in THF followed by the addition of KOtBu (1.4 mg, 0.012 mmol). The reaction mixture was stirred at room temperature for 20 min until a dark blue solution was obtained. Then [Cp₂Fe][PF₆] (4.0 mg, 0.012 mmol) was added resulting in a brown suspension and the reaction mixture was allowed to stir at room temperature for further 1h. After the solvent was removed *in vacuo*, the resulting brown solid was extracted with CH₂Cl₂ and the precipitation was effected with ether. The collected solid was washed with ether (3 × 2 mL), dried *in vacuo* and pure product of **7**[PF₆]₂ was obtained. Yield: 5 mg (0.003 mmol, 66% based on **2**). Single crystals suitable for X-Ray diffraction studies were grown by layering pentane over a dichloromethane solution of **7**[PF₆]₂. Anal. Calcd. for C₃₈H₉₀F₁₂P₁₀Re₂Si₂: C, 30.16; H, 5.99. Found: C, 30.27; H, 5.91. IR (ATR, cm⁻¹): ν = 2013 (C≡C), 940 (C-P). MS(ESI): *m/z* (100%): 1367 [M⁺]. ¹H NMR (CD₂Cl₂, 200 MHz, 22 °C): δ = 5.82 (s, C_βH), 1.82 (s, P(CH₃)₃), 0.26 (s, Si(CH₃)₃); ¹³C NMR (CD₂Cl₂, 125.8 MHz, 10 °C): δ = 235.0 (t, C_α), 135.5 (t, ²J_{PC} = 20.2 Hz, C_α'), 128.4 (s, C_β'), 95.8 (s, C_β), 22.2 (m, P(CH₃)₃), 0.4 (s, Si(CH₃)₃); ³¹P NMR (CD₂Cl₂, 81 MHz, 22 °C): δ = -43.6 (s, P(CH₃)₃), -143.9 (sept, *J* = 711 Hz, 1P, PF₆); ¹⁹F NMR (CD₂Cl₂, 188 MHz, 22 °C): δ = -74.1 (d, *J* = 711 Hz, PF₆); ²⁹Si NMR (CD₂Cl₂, 99.4 MHz, 10 °C): δ = -22.1 (s, SiMe₃).

***trans*-[(Me₃SiC≡C)(PMe₃)₄Re≡C-C≡C-C≡Re(PMe₃)₄(C≡CSiMe₃)] (**7**).**

To a solution of *trans*-[(Me₃SiC≡C)(PMe₃)₄Re≡C-C≡C-C≡Re(PMe₃)₄(C≡CSiMe₃)] [PF₆]₂ (**7**[PF₆]₂) (5 mg, 0.003 mmol) in THF was added at room temperature a suspension of KH and 18-crown-6 in THF in one portion. The reaction mixture was stirred at 22° C for 1h and then studied by ¹H NMR.

¹H NMR (THF, 200 MHz, 22 °C): δ = 1.10 (s, P(CH₃)₃), δ = 0.53 (s, Si(CH₃)₃). IR (THF, cm⁻¹) ν = 1958 (C≡C), 1738 (C₄). UV-vis (THF): 498, 533, 588 and 696 nm.

Single crystal X-ray diffraction studies

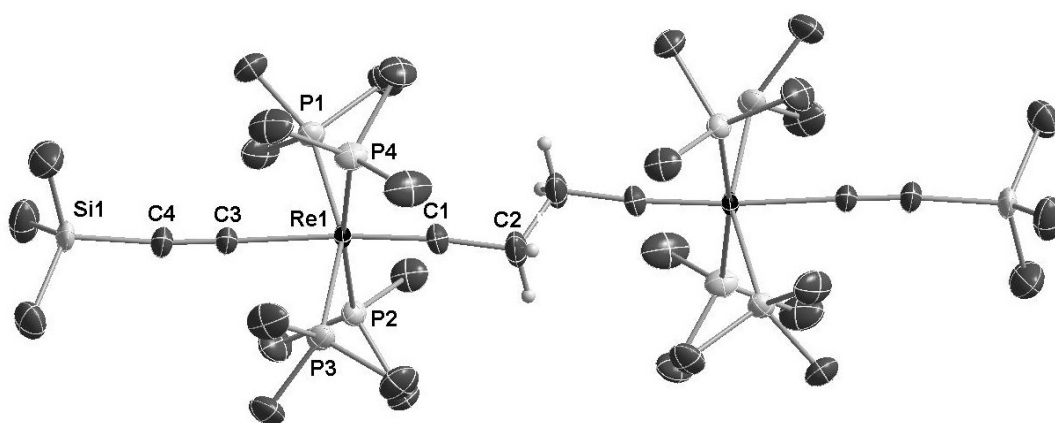


Figure 1. ORTEP like drawing of **6**[PF₆]₂. The thermal ellipsoids are drawn at 50% probability level. Solvent molecules, counterions and selected hydrogen atoms are omitted for clarity.

Data collection for all crystals were carried out on Stoe IPDS diffractometer (Imaging Plate Detector System with graphite-monochromated MoK α radiation, 0.71073 Å)¹⁹ and for others on Oxford Diffraction Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoK α radiation, 0.71073 Å²⁰ at 183(2) K using a cold N₂-gas stream from an Oxford Cryogenic System. Pre-experiment, data collection and data reduction (unit cell determination, intensity data integration and empirical absorption correction) were carried out with the Oxford *CrysAlisPro* software.²¹ The structures were solved with the unique data sets using the Patterson method of the program *SHELXS-97*.²² The structure refinements were performed with the program *SHELXL-97*.²² Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 . The hydrogen atoms of the organic groups were placed in calculated positions and refined with a riding model with a fixed temperature factor. The program *PLATON*²³ was used to check the result of the X-ray analyses. All structures were deposited at the Cambridge Crystallographic Data Centre and have been assigned the following numbers: CCDC 859304-859309. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for the structures of **2**, **5** and **6**.

Complexes	2	5	6
CCDC number	859304	859305	859306
Empirical formula	C ₁₉ H ₄₈ F ₆ P ₅ ReSi	C ₃₈ H ₉₄ F ₁₂ P ₁₀ Re ₂ Si ₂	C ₃₈ H ₉₂ P ₈ Re ₂ Si ₂
Formula weight (g·mol ⁻¹)	759.72	1517.43	1225.48
Temperature (K)	183(2)	183(2)	183(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	19.4556(3)	10.1955(2)	15.5085(11)
<i>b</i> (Å)	19.8765(2)	10.4458(1)	9.9898(4)
<i>c</i> (Å)	33.6182(5)	15.8038(3)	18.9014(8)
α (°)	90	90.942(1)	90
β (°)	90	108.673(1)	93.969(5)
γ (°)	90	91.938(1)	90
<i>V</i> (Å ³)	13000.5(3)	1592.94(5)	2921.3(3)
<i>Z</i> , density (calculated) (mg/m ³)	16, 1.553	1, 1.582	2, 1.393
Absorption coefficient (mm ⁻¹)	4.064	4.145	4.422
<i>F</i> (000)	6080	758	1236
Crystal size (mm)	0.34 × 0.19 × 0.13	0.35 × 0.31 × 0.11	0.27 × 0.17 × 0.08
ϑ range for data collection (°)	2.30 to 25.68	2.41 to 32.58	2.45 to 32.58
	-20 ≤ <i>h</i> ≤ 23	-15 ≤ <i>h</i> ≤ 15	-23 ≤ <i>h</i> ≤ 23
Limiting indices	-21 ≤ <i>k</i> ≤ 24	-15 ≤ <i>k</i> ≤ 15	-15 ≤ <i>k</i> ≤ 15
	-30 ≤ <i>l</i> ≤ 40	-23 ≤ <i>l</i> ≤ 23	-28 ≤ <i>l</i> ≤ 28
Reflections collected/unique	67596/24381 [<i>R</i> (int) = 0.0525]	45347/11599 [<i>R</i> (int) = 0.0396]	60610/10640 [<i>R</i> (int) = 0.0534]
Completeness to ϑ	99.8% (ϑ = 25.68)	100.0% (ϑ = 32.58)	100.0% (ϑ = 32.58)
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.668 and 0.496	0.717 and 0.308	0.719 and 0.412
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	24381/40/1176	11599/0/304	8371/0/241
Goodness-of-fit on <i>F</i> ²	0.942	0.973	1.018
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0413 <i>wR</i> ₂ = 0.0834	<i>R</i> ₁ = 0.0215 <i>wR</i> ₂ = 0.0497	<i>R</i> ₁ = 0.0280 <i>wR</i> ₂ = 0.0600
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0614 <i>wR</i> ₂ = 0.0866	<i>R</i> ₁ = 0.0257 <i>wR</i> ₂ = 0.0503	<i>R</i> ₁ = 0.0375 <i>wR</i> ₂ = 0.0623
Largest diff. peak and hole (e·Å ⁻³)	3.753 and -1.142	1.510 and -1.090	1.517 and -0.899

Table S2. Crystallographic data for the structures of **6[PF₆]**, **6[PF₆]₂** and **7[PF₆]₂**.

Complexes	6[PF ₆]	6[PF ₆] ₂	7[PF ₆] ₂
CCDC number	859307	859308	859309
Empirical formula	C ₈₀ H ₁₉₂ F ₁₂ OP ₁₈ Re ₄ Si ₄	C ₄₀ H ₉₆ Cl ₄ F ₁₂ P ₁₀ Re ₂ Si ₂	C ₄₀ H ₉₄ Cl ₄ F ₁₂ P ₁₀ Re ₂ Si ₂
Formula weight (g·mol ⁻¹)	2813.01	1685.27	1683.25
Temperature (K)	183(2)	183(2)	183(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, <i>P2₁/c</i>	Orthorhombic, <i>Pnmm</i>	Orthorhombic, <i>Pnmm</i>
<i>a</i> (Å)	10.0523(1)	16.0272(4)	16.2406(2)
<i>b</i> (Å)	21.4240(2)	15.8081(3)	15.7552(2)
<i>c</i> (Å)	30.5215(3)	14.4694(3)	14.4581(2)
α (°)	90	90	90
β (°)	92.588(1)	90	90
γ (°)	90	90	90
<i>V</i> (Å ³)	6566.42(11)	3665.96(14)	3699.45(8)
<i>Z</i> , density (calculated) (mg/m ³)	2, 1.423	2, 1.527	2, 1.511
Absorption coefficient (mm ⁻¹)	3.981	3.752	3.718
<i>F</i> (000)	2828	1680	1676
Crystal size (mm)	0.35 × 0.19 × 0.07	0.37 × 0.28 × 0.25	0.45 × 0.21 × 0.19
ϑ range for data collection (°)	2.67 to 25.00	2.54 to 30.50	2.59 to 30.50
	-11 ≤ <i>h</i> ≤ 11	-22 ≤ <i>h</i> ≤ 20	-20 ≤ <i>h</i> ≤ 23
Limiting indices	-25 ≤ <i>k</i> ≤ 25	-21 ≤ <i>k</i> ≤ 22	-22 ≤ <i>h</i> ≤ 22
	-36 ≤ <i>l</i> ≤ 28	-20 ≤ <i>l</i> ≤ 12	-20 ≤ <i>h</i> ≤ 16
Reflections collected/unique	48173/11516	18981/5804	31036/5859
	[<i>R</i> (int) = 0.0365]	[<i>R</i> (int) = 0.0322]	[<i>R</i> (int) = 0.0409]
Completeness to ϑ	99.7% (ϑ = 25.00)	99.9% (ϑ = 30.50)	99.9% (ϑ = 30.50)
Absorption correction	Analytical	Analytical	Analytical
Max. and min. transmission	0.758 and 0.429	0.487 and 0.379	0.570 and 0.358
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5860/7/564	5804/3/196	5859/3/189
Goodness-of-fit on <i>F</i> ²	0.879	0.969	0.981
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0379 <i>wR</i> ₂ = 0.1145	<i>R</i> ₁ = 0.0308 <i>wR</i> ₂ = 0.0674	<i>R</i> ₁ = 0.0257 <i>wR</i> ₂ = 0.0657
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0649 <i>wR</i> ₂ = 0.1241	<i>R</i> ₁ = 0.0501 <i>wR</i> ₂ = 0.0704	<i>R</i> ₁ = 0.0383 <i>wR</i> ₂ = 0.0676
Largest diff. peak and hole (e·Å ⁻³)	3.634 and -0.520	0.827 and -0.679	1.678 and -0.562

UV-Vis-NIR studies

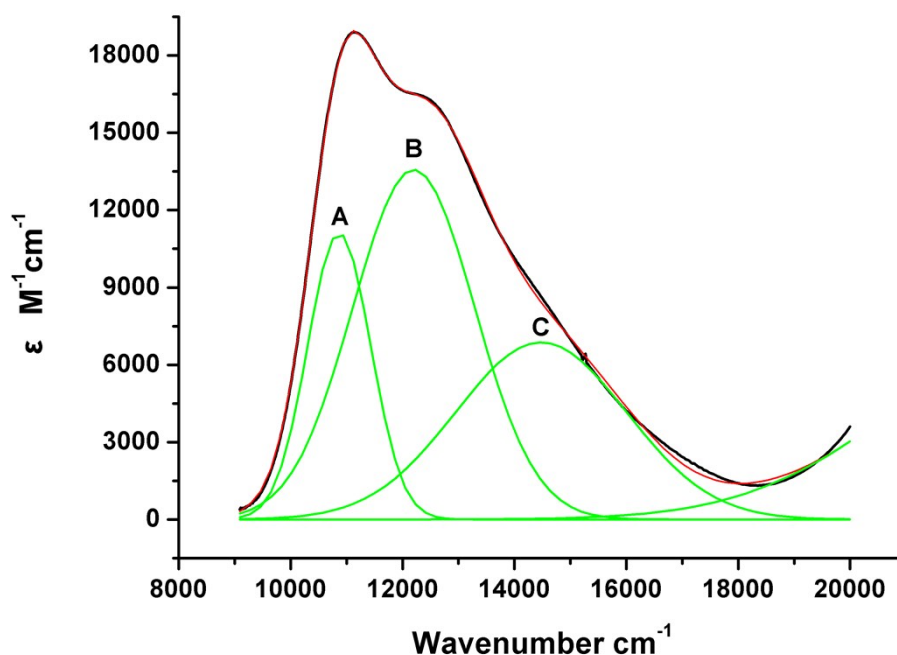


Figure S2. Comparison of the observed (black line) and the simulated (red line) IVCT band of **E-6[PF₆]** as obtained by spectral deconvolution into the four individual Gaussian bands shown in green

Table S3. Summary of the spectral data of the Gaussian analyses of the IVCT band absorptions of the MV complexes **E-6[PF₆]**

Complexes	λ_{\max} (nm)	ν_{\max} (cm ⁻¹)	ϵ_{\max} (M ⁻¹ cm ⁻¹)	$\Delta\nu_{1/2}$ (obsd, cm ⁻¹)	$\Delta\nu_{1/2}$ (calcd, cm ⁻¹)
E-6[PF₆]	A	920	1.09×10^4	1.11×10^4	1.13×10^3
	B	820	1.22×10^4	1.36×10^4	2.18×10^3
	C	691	1.45×10^4	6.87×10^3	3.05×10^3
Complexes	$d_{\text{Re-Re}}$ (Å)	$H_{\text{ab}}^{\text{II}}$ (cm ⁻¹)	$H_{\text{ab}}^{\text{III}} = \nu_{\max}/2$ (cm ⁻¹)	Γ	

	A		1.03×10^3	5.43×10^3	0.78
E-6[PF ₆]	B	7.371	1.68×10^3	6.10×10^3	0.59
	C		1.54×10^3	7.24×10^3	0.47

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