Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

2-(2´-pyridyl)-4,6-diphenylphosphinine *versus* 2-(2´-pyridyl)-4,6-diphenylpyridine: synthesis and characterization of novel Cr^0, Mo^0, and W^0 carbonyl complexes containing chelating P,N and N,N ligands

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General remarks: All reactions were performed under argon using Schlenk techniques or in a MBraun dry box unless stated otherwise. All glassware was dried prior to use. $[Cr(CO)_6]$, $[Mo(CO)_4$ (nbd)] and $[W(CO)_6]$ were purchased from STREM and used without further purification. 2-(2’-Pyridyl)-4,6-diphenylphosphinine (**1**) and 2-(2’-pyridyl)-4,6-diphenylpyridine (**2**) were prepared according to literature procedures.[1,2] All common solvents and chemicals were commercially available. The dry solvents were prepared by using custom-made solvent purification columns filled with Al_2O_3. The elemental analyses were performed on by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr (Germany). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 200 or 400 spectrometer and all chemical shifts are reported relative to residual proton resonance of the deuterated solvents. IR spectra were measured on a Shimadzu MIRacle10 FTIR-ATR spectrometer and UV-vis spectra on a Shimadzu UV-1650pc from $1.25 \cdot 10^{-4}$ M DCM solutions of the compounds. For reactions under UV radiation a Philips HPK 125W high-pressure mercury vapor lamp was used. Spectrometer Cyclic Voltammetry measurements were performed with VersaSTAT 4 Princeton Applied Research potentiostat and a three electron system with a Glassy-Carbon working electrode, platinum sheet counter electrode, and a saturated calomel electrode (SCE) reference electrode. Conducting salt tetrabutylammonium hexafluorophosphate (NBu_4PF_6, Fulka ≥99.0%) was used for electrochemical analysis and $5 \cdot 10^{-3}$ M THF solutions of the compounds were used. As reference ferrocene (98%, Aldrich) was used.

$[Cr(CO)_4(\mathbf{1})]$ (**3**): A mixture of $[Cr(CO)_6]$ (13 mg, 0.06 mmol, 1.0 equivalent) and **1** (20 mg, 0.06 mmol, 1.0 equivalent) was suspended in d-THF (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was irradiated with UV light for 8 hours at room temperature. Dark orange solid was obtained *via* slow diffusion of diethyl ether into a dichloromethane solution of the crude product. Yield after crystallization was 50%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.20 (1H, dd, $^{3}J_{(H,H)}$ = 7.2 Hz, $^{3}J_{(H,H)}$ = 6Hz; H$_{arom}$), 7.50 (6H, m; H$_{arom}$), 7.69 (2H, d, $^{3}J_{(H,H)}$ = 7.6 Hz; H$_{arom}$), 7.86 (3H, m; H$_{arom}$), 8.17 (1H, d, $^{3}J_{(H,H)}$ = 8.0 Hz; H$_{arom}$), 8.30 (1H, dd, $^{3}J_{(H,P)}$ = 16.4 Hz, $^{4}J_{(H,H)}$ = 1,2 Hz; H$_{arom}$), 8.52 (1H, dd, $^{3}J_{(H,P)}$ = 13.6 Hz, $^{4}J_{(H,H)}$ = 1,0 Hz; H$_{arom}$), 9.22 (1H, d, $^{3}J_{(H,H)}$ = 5.6 Hz; H$_{arom}$). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ (ppm) = 246.0. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) = 120.2 (d, $^{2}J_{(C,P)}$ = 11.7 Hz; CH), 123.8 (d, $^{4}J_{(C,P)}$ = 3.6 Hz; CH), 127.9 (d, $^{4}J_{(C,P)}$ = 2.2 Hz; CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 128.9 (d, $^{4}J_{(C,P)}$ = 1.6 Hz; CH), 129.5 (d, $^{3}J_{(C,P)}$ = 7.7 Hz; CH), 130.3 (d, $^{2}J_{(C,P)}$ = 12.7 Hz; CH), 137.9 (CH), 138.0 (d, $^{3}J_{(C,P)}$ = 11.3 Hz; CH), 140.3 (d, $^{4}J_{(C,P)}$ = 1.3 Hz; C$_q$), 140.5 (d, $^{4}J_{(C,P)}$ = 1.5 Hz; C$_q$), 142.1 (d, $^{4}J_{(C,P)}$ = 4.2 Hz; C$_q$), 156.9 (d, $^{3}J_{(C,P)}$ = 5,1 Hz; CH), 158.0 (d, $^{3}J_{(C,P)}$ = 6.4 Hz; C$_q$), 160.8 (d, $^{1}J_{(C,P)}$ = 19.7 Hz; C$_q$), 166.3 (d, $^{2}J_{(C,P)}$ = 9.3 Hz; C$_q$), 215.3 (d, $^{1}J_{(C,P)}$ = 19.5 Hz; C$_q$), 227.4 (d, $^{2}J_{(C,P)}$ = 11.7 Hz; CO equatorial), 228.2 (d, $^{2}J_{(C,P)}$ = 6.5 Hz; CO axial). Elemental analysis calculated (%) for $C_{26}H_{16}NPO_4Cr$ (489.38 g·mol^{-1}): C 63.81, H 3.30, N 2.86 %; found: C 63.28, H 3.71, N 2.78 %.

[Mo(CO)$_4$(**1**)] (**4**): A mixture of [Mo(CO)$_4$(nbd)] (14 mg, 0,05 mmol, 1.5 equivalents) and **1** (10 mg, 0.03 mmol, 1.0 equivalent) was suspended in d-THF (0.5 mL) and transferred to a young NMR-Tube in a dry box. After 1 hour at room temperature the reaction was complete. Dark orange crystals were obtained *via* slow diffusion of pentane into the reaction mixture. Yield after crystallization was 58%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.26 (1H, dd, $^{3}J_{(H,H)}$ = 6.0 Hz, $^{3}J_{(H,H)}$ = 6.8 Hz; H$_{arom}$), 7.59 – 7.45 (6H, m; H$_{arom}$), 7.71 (2H, d, $^{3}J_{(H,H)}$ = 8.1 Hz; H$_{arom}$), 7.94 (3H, m; H$_{arom}$), 8.26 (1H, d, $^{3}J_{(H,H)}$ = 8.3 Hz; H$_{arom}$), 8.36 (1H, d, $^{3}J_{(H,P)}$ = 16.1 Hz; H$_{arom}$), 8.59 (1H, d, $^{3}J_{(H,P)}$ = 13.3 Hz; H$_{arom}$), 9.23 (1H, d, $^{3}J_{(H,H)}$ = 5.6 Hz; H$_{arom}$). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ (ppm) = 216.0. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) = 120.49 (d, $^{3}J_{(C,P)}$ = 11.4 Hz; CH), 124.1 (d, $^{3}J_{(C,P)}$ = 3.5 Hz; CH), 127.9 (d, $^{4}J_{(C,P)}$ = 2.5 Hz; CH), 128.4 (CH), 128.5 (d, $^{3}J_{(C,P)}$ = 3.2 Hz; CH), 128.9 (d, $^{4}J_{(C,P)}$ = 2.1 Hz; CH), 129.6 (d, $^{4}J_{(C,P)}$ = 1.7 Hz; CH), 131.1 (d, $^{2}J_{(C,P)}$ = 12.8 Hz; CH), 137.3 (d, $^{2}J_{(C,P)}$ = 11.6 Hz; CH), 138.4 (CH), 140.28 (d, $^{2}J_{(C,P)}$ = 16.9 Hz; C$_q$), 140.78 (d, $^{1}J_{(C,P)}$ = 20.3 Hz; C$_q$), 142.10 (d, $^{4}J_{(C,P)}$ = 4,4 Hz; C$_q$), 156.8 (d, $^{3}J_{(C,P)}$ = 3.6 Hz; CH), 158.39 (d, $^{3}J_{(C,P)}$ = 7.1 Hz; C$_q$), 160.07 (d, $^{1}J_{(C,P)}$ = 18.5 Hz; C$_q$), 163.80 (d, $^{2}J_{(C,P)}$ = 8.4 Hz; CO axial), 204.70 (d, $^{2}J_{(C,P)}$ = 13.4 Hz; C$_q$), 217.69 (d, $^{2}J_{(C,P)}$ = 42.2 Hz; CO equatorial), 220.39 (d, $^{2}J_{(C,P)}$ = 7.9 Hz; CO axial). Elemental analysis calculated (%) for $C_{26}H_{16}NPO_4Mo$ (533.34 g·mol^{-1}): C 58.55, H 3.02, N 2.63 %; found: C 57.67, H 3.35, N 2.58 %.

$[\mathrm{W(CO)_4}(\mathbf{1})]$ (**5**): A mixture of $[\mathrm{W(CO)_6}]$ (21 mg, 0.06 mmol, 1.0 equivalent) and **1** (20 mg, 0.06 mmol, 1.0 equivalent) was suspended in d-THF (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was irradiated with UV light for 12 hours at room temperature. Dark orange crystals were obtained *via* slow diffusion of diethyl ether into a dichloromethane solution of the crude product. Yield after crystallization was 58%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.22 (1H, dddd, $^{3}J_{(H,H)}$ = 7.3 Hz, $^{3}J_{(H,H)}$ = 5.9 Hz, $^{4}J_{(H,H)}$ = 1.3 Hz, $^{4}J_{(H,P)}$ = 1.3 Hz; H_{arom}), 7.52 (6H, m; H_{arom}), 7.69 (2H, m; H_{arom}), 7.95 (3H, m; H_{arom}), 8.29 (1H, d, $^{3}J_{(H,H)}$ = 8.6 Hz; H_{arom}), 8.39 (1H, dd, $^{3}J_{(H,P)}$ = 17.8 Hz, $^{4}J_{(H,H)}$ = 1.4 Hz; H_{arom}), 8.59 (1H, dd, $^{3}J_{(H,P)}$ = 14.0 Hz, $^{4}J_{(H,H)}$ = 1.2 Hz; H_{arom}), 9.37 (1H, ddd, $^{3}J_{(H,H)}$ = 5.6 Hz, $^{4}J_{(H,H)}$ = 1.6 Hz, $^{5}J_{(H,P)}$ = 0.8 Hz; H_{arom}). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ (ppm) = 203.0 (t, $^{1}J_{(P,W)}$ = 139.0 Hz). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) = 120.5 (d, $^{2}J_{(C,P)}$ = 11.6 Hz; CH), 124.8 (d, $^{3}J_{(C,P)}$ = 3.7 Hz; CH) 127.9 (d, $^{4}J_{(C,P)}$ = 2.4 Hz; CH), 128.4 (CH), 128.6 (d, $^{3}J_{(C,P)}$ = 11.0 Hz; CH), 129.0 (d, $^{4}J_{(C,P)}$ = 1.9 Hz; CH), 129.6 (d, $^{4}J_{(C,P)}$ = 3.2 Hz; CH), 131.7 (d, $^{2}J_{(C,P)}$ = 12.4 Hz; CH), 138.0 (d, $^{3}J_{(C,P)}$ = 11.0 Hz; CH), 138.5 (CH), 139.9 (d, $^{2}J_{(C,P)}$ = 16 Hz; C_q), 140.2 (d, $^{1}J_{(C,P)}$ = 20.9 Hz; C_q), 142.1 (d, $^{4}J_{(C,P)}$ = 4.4 Hz; C_q), 157.9 (d, $^{4}J_{(C,P)}$ = 4.5 Hz; CH), 159.1 (d, $^{2}J_{(C,P)}$ = 14.3 Hz; C_q), 160.1 (d, $^{1}J_{(C,P)}$ = 17.7 Hz; C_q), 161.3 (d, $^{2}J_{(C,P)}$ = 17.3 Hz; C_q), 198.3 (d, $^{2}J_{(C,P)}$ = 10.9 Hz; C_q), 209.7 (d, $^{2}J_{(C,P)}$ = 5.2 Hz; CO axial), 211.3 (d, $^{2}J_{(C,P)}$ = 41.9 Hz; CO equatorial). Elemental analysis calculated (%) for $C_{26}H_{16}NPO_4W$ (621.22 g·mol^{-1}): C 50.27, H 2.60, N 2.25 %; found: C 50.10, H 2.82, N 2.37 %.

$[\mathrm{Cr(CO)_4}(\mathbf{2})]$ (**6**): A mixture of $[\mathrm{Cr(CO)_6}]$ (13 mg, 0.06 mmol, 1.0 equivalent) and **2** (19 mg, 0.06 mmol, 1.0 equivalent) was suspended in d-THF (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was irradiated with UV light for 24 hours at room temperature. THF was evaporated and dark red crystals were obtained *via* slow diffusion of diethyl ether into a dichloromethane solution of the crude product. Yield after crystallization was 60%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.39 (1H, dd, $^{3}J_{(H,H)}$ = 6.4 Hz, $^{3}J_{(H,H)}$ = 6.4 Hz; H_{arom}), 7.52-7.59 (6H, m; H_{arom}), 7.64 (2H, d, $^{3}J_{(H,H)}$ = 6.4 Hz; H_{arom}), 7.70 (1H, d, $^{4}J_{(H,H)}$ = 1.2 Hz; H_{arom}), 7.79 (2H, d, $^{3}J_{(H,H)}$ = 6.8 Hz; H_{arom}), 7.71 (1H, t, $^{3}J_{(H,H)}$ = 7.6 Hz; H_{arom}), 8.19 (1H, d, $^{3}J_{(H,H)}$ = 8.0 Hz; H_{arom}), 8.28 (1H, d, $^{4}J_{(H,H)}$ = 0.8 Hz; H_{arom}), 9.29 (1H, d, $^{3}J_{(H,H)}$ = 5.2 Hz; H_{arom}). ^{31}C NMR (CD_2Cl_2, 100MHz): δ (ppm) = 118.2 (CH), 122.5 (CH), 124.8 (CH), 125.1 (CH), 127.5 (CH), 128.8 (CH), 129.0 (CH), 129.7 (CH), 129.8 (CH), 130.5 (CH), 136.9 (C_q), 137.2 (CH), 143.2 (C_q), 149.5 (C_q), 153.5 (CH), 156.4 (C_q), 156.9 (C_q), 214.3 (C_q), 223.1 (C_q), 230.1 (C_q). Elemental analysis calculated (%) for $C_{26}H_{16}N_2O_4Cr$ (472.41 g·mol^{-1}): C 66.10, H 3.41, N 5.93 %; found: C 65.82, H 3.60, N 5.81 %.

[Mo(CO)$_4$(**2**)] (**7**): A mixture of [Mo(CO)$_4$(nbd)] (14 mg, 0.05 mmol, 1,5 equivalents) and **2** (10 mg, 0.03 mmol, 1,0 equivalent) was suspended in d-THF (0.5 mL) and transferred to a young NMR-Tube in a dry box. After 3 hour at room temperature the reaction was complete. Dark orange crystals were obtained *via* slow diffusion of pentane into the reaction mixture. Yield after crystallization was 75%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.43 (1H, ddd, $^3J_{(H,H)}$ = 5.2 Hz, $^3J_{(H,H)}$ = 5.6 Hz, $^4J_{(H,H)}$ = 1.2 Hz; H_{arom}), 7.55 – 7.64 (8H, m; H_{arom}), 7.77 (1H, d, $^4J_{(H,H)}$ = 1.8 Hz; H_{arom}), 7.81 (2H, m; H_{arom}), 8.00 (1H, m; H_{arom}), 8.27 (1H, d, $^2J_{(H,H)}$ = 8.0 Hz; H_{arom}), 8.35 (1H, d, $^4J_{(H,H)}$ = 1.6 Hz; H_{arom}), 9.20 (1H, m; H_{arom}). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) = 119.0 (CH), 123.2 (CH), 124.7 (CH), 125.4 (CH), 127.6 (CH), 128.8 (CH), 128.8 (CH), 129.9 (CH), 129.9 (CH), 130.6 (CH), 136.9 (C_q), 137.8 (CH), 143.0 (C_q), 150.2 (C_q), 153.4 (CH), 156.2 (C_q), 156.4 (C_q), 164.8 (C_q), 205.5 (C_q), 218.2 (C_q), 225.2 (C_q). Elemental analysis calculated (%) for $C_{26}H_{16}N_2O_4Mo$ (516.38 g·mol^{-1}): C 60.47, H 3.12, N 5.42 %; found: C 60.06, H 3.45, N 5.29 %.

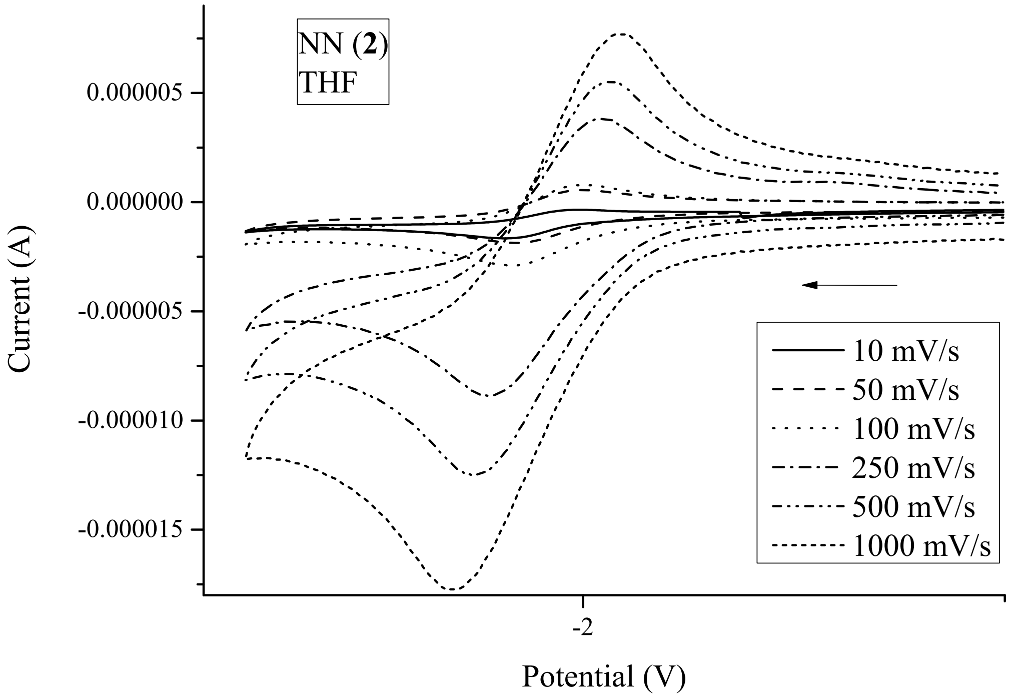
[W(CO)$_4$(**2**)] (**8**): A mixture of [W(CO)$_6$] (21 mg, 0.06 mmol, 1.0 equivalent) and **2** (19 mg, 0.06 mmol, 1.0 equivalent) was suspended in d-THF (0.5 mL) and transferred to a Young NMR-Tube in a dry box. The reaction was irradiated with UV light for 48 hours at room temperature. THF was evaporated and dark red crystals were obtained *via* slow diffusion of diethyl ether into a dichloromethane solution of the crude product. Yield after crystallization was 70%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ (ppm) = 7.43 (1H, ddd, $^3J_{(H,H)}$ = 5.6 Hz, $^4J_{(H,H)}$ = 1.2 Hz, $^4J_{(H,H)}$ = 2.0 Hz; H_{arom}), 7.58 (8H, m; H_{arom}), 7.80 (3H, m; H_{arom}), 8.02 (1H, ddd, $^3J_{(H,H)}$ = 7.6 Hz, $^4J_{(H,H)}$ = 1.6 Hz, $^4J_{(H,H)}$ = 1.6 Hz; H_{arom}), 8.29 (1H, d, $^3J_{(H,H)}$ = 8.4 Hz; H_{arom}), 8.37 (1H, d, $^4J_{(H,H)}$ = 2.0 Hz; H_{arom}), 9.30 (1H, ddd, $^3J_{(H,H)}$ = 5.6 Hz, $^4J_{(H,H)}$ = 1.6 Hz, $^4J_{(H,H)}$ = 0.8 Hz; H_{arom}). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ (ppm) = 119.4 (CH), 123.6 (CH), 125.2 (CH), 126.2 (CH), 127.5 (CH), 128.7 (CH), 128.8 (CH), 129.8 (CH), 129.9 (CH), 130.7 (CH), 136.7 (C_q), 137.6 (CH), 143.0 (C_q), 149.9 (C_q), 153.5 (CH), 157.3 (C_q) 157.4 (C_q), 164.7 (C_q), 202.3 (t, $^1J_{(C,W)}$ = 66 Hz; C_q), 210.8 (t, $^1J_{(C,W)}$ = 81 Hz; C_q), 217.2 (t, $^1J_{(C,W)}$ = 86 Hz; C_q). Elemental analysis calculated (%) for $C_{26}H_{16}N_2O_4W$ (604.26 g·mol^{-1}): C 51.68, H 2.67, N 4.64 %; found: C 51.45, H 2.81, N 4.70 %.

Cyclic voltammetry measurements:

Reversibility of ligand **2**:

Table S1 Electrochemical I_{pa} values of the first reduction wave from ligand **2** at different scan rates, determined by CV on a glassy carbon working electrode in 0.1 M $n\mathrm{Bu_4NPF_6}$ and $5\cdot10^{-3}$ M **2** THF solutions at $T = 298$ K.

Scan rate mV/s	Square root scan rate	I_{pa} ($\cdot10^{-6}$)
10	3.16	1.82
50	7.07	2.53
100	10	3.24
250	15.81	5.63
500	22.36	7.69
1000	31.62	10.33



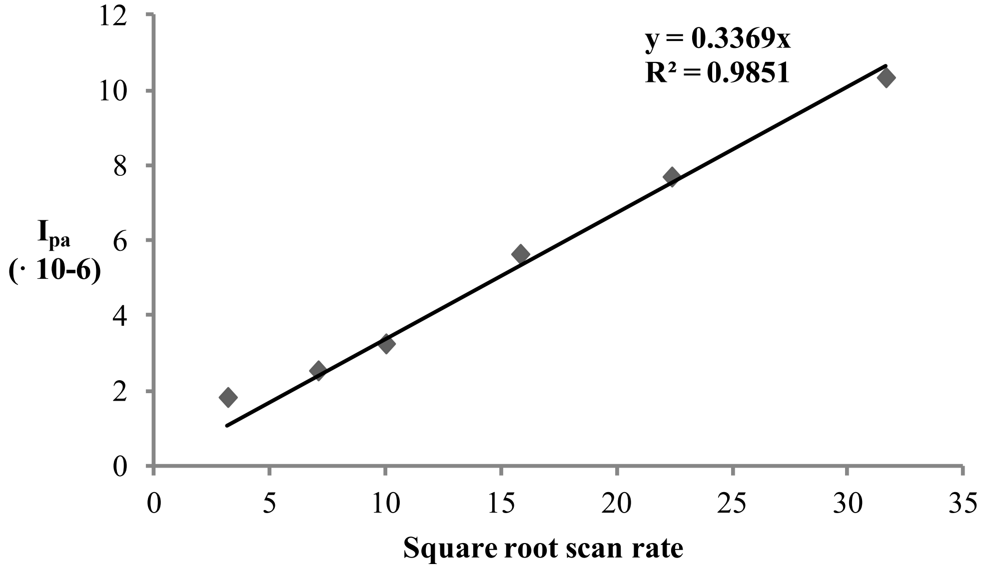


Figure S1: Electrochemical spectra of the first reaction wave from ligand **2** at different scan rates, determined by CV on glassy carbon working electrode in a 0.1 M $n\mathrm{Bu}_4\mathrm{NPF}_6$ and $5 \cdot 10^{-3}$ M **2** THF solution at T = 298 K. Bottom graph represents the linear regression between the square root of the different scan rates and the I_{pa} measured of ligand **2**, see Table S1for the values.

Table S2: Electrochemical DPV properties of ligand **2** and ferrocene determined by CV on a glassy carbon working electrode in 0.1 M *n*Bu_4NPF_6, $5 \cdot 10^{-3}$ M ferrocene and $5 \cdot 10^{-3}$ M **2** THF solutions at *T* = 298 K.

Compound	Peak position (V)	Peak area (A)
Ferrocene	0.50	$2.64 \cdot 10^{-7}$
2	-2.06	$2.83 \cdot 10^{-7}$

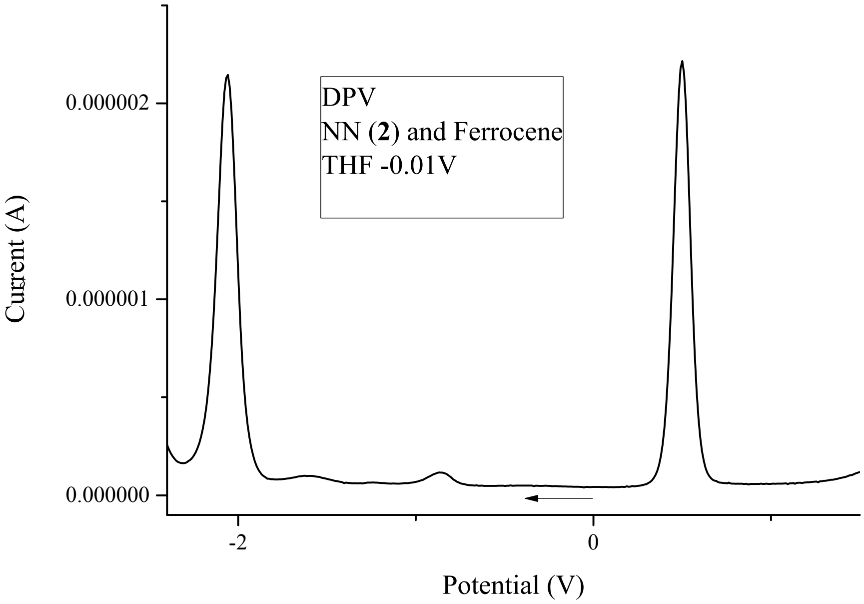
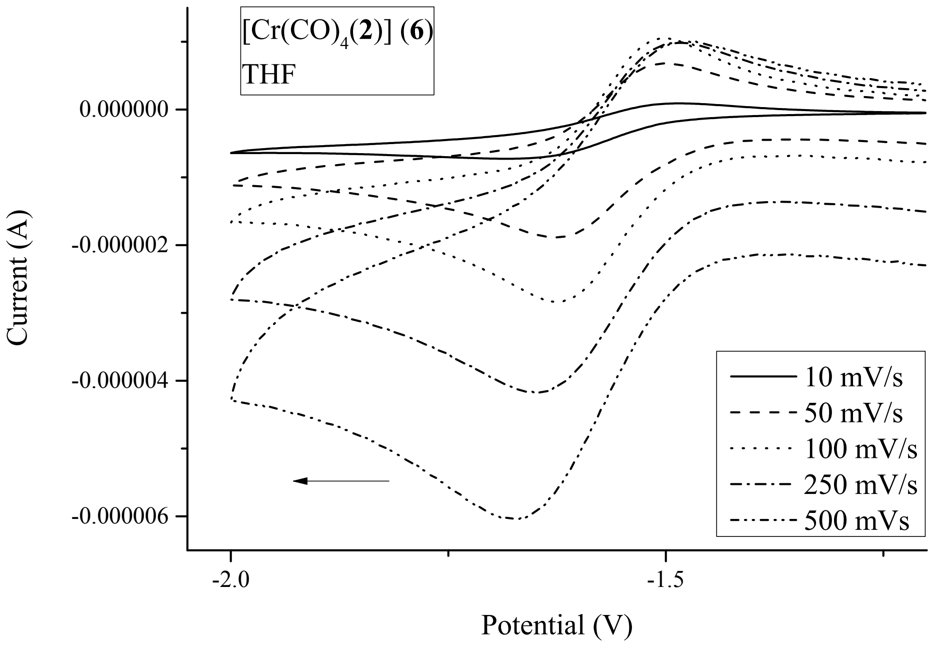


Figure S2: Electrochemical DPV spectrum of ligand **2** with ferrocene determined by CV on glassy carbon working electrode in a 0.1 M *n*Bu_4NPF_6, $5 \cdot 10^{-3}$ M ferrocene and $5 \cdot 10^{-3}$ M **2** THF solution at *T* = 298 K.

Reversibility of [Cr(CO)$_4$(**2**)] (**6**):

Table S3: Electrochemical I_{pa} values of the first reduction wave from **6** at different scan rates, determined by CV on a glassy carbon working electrode in 0.1 M *n*Bu$_4$NPF$_6$ and $5\cdot10^{-3}$ M **6** THF solutions at $T = 298$ K.

Scan rate mV/s	Square root scan rate	I_{pa} ($\cdot10^{-6}$)
10	3.16	0.38
50	7.07	1.18
100	10	1.51
250	15.81	2.14
500	22.36	2.81



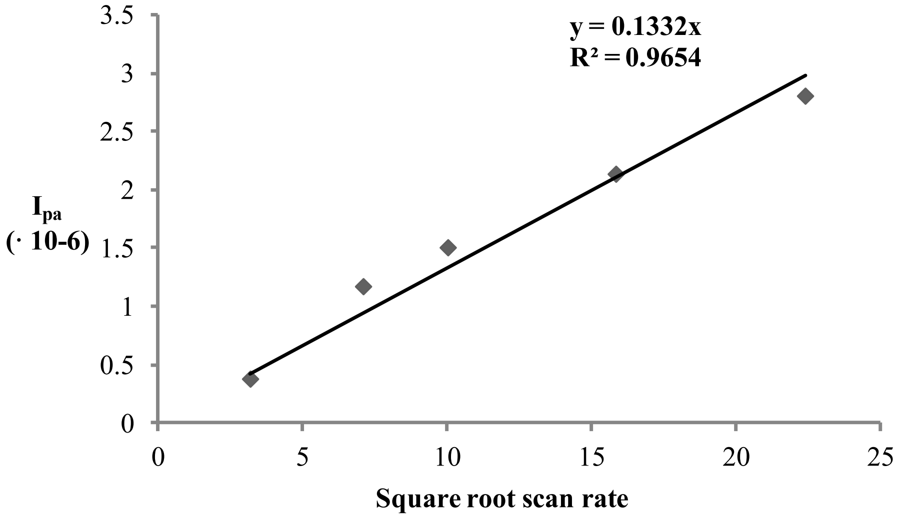


Figure S3: Electrochemical spectra of the first reaction wave from **6** at different scan rates, determined by CV on glassy carbon working electrode in a 0.1 M *n*Bu$_4$NPF$_6$ and $5 \cdot 10^{-3}$ M **6** THF solution at $T = 298$ K. Bottom graph represents the linear regression between the square root of the different scan rates and the I$_{pa}$ measured of **6**, see Table S3 for the values.

Reversibility of [Mo(CO)$_4$(**2**)] (**7**):

Table S4: Electrochemical I$_{pa}$ values of the first reduction wave from **7** at different scan rates, determined by CV on a glassy carbon working electrode in 0.1 M *n*Bu$_4$NPF$_6$ and $5 \cdot 10^{-3}$ M **7** THF solutions at $T = 298$ K.

Scan rate mV/s	Square root scan rate	I$_{pa}$ ($\cdot 10^{-6}$)
10	3.16	1.16
100	10	2.30
250	15.81	3.00
500	22.36	4.15
1000	31.62	5.74

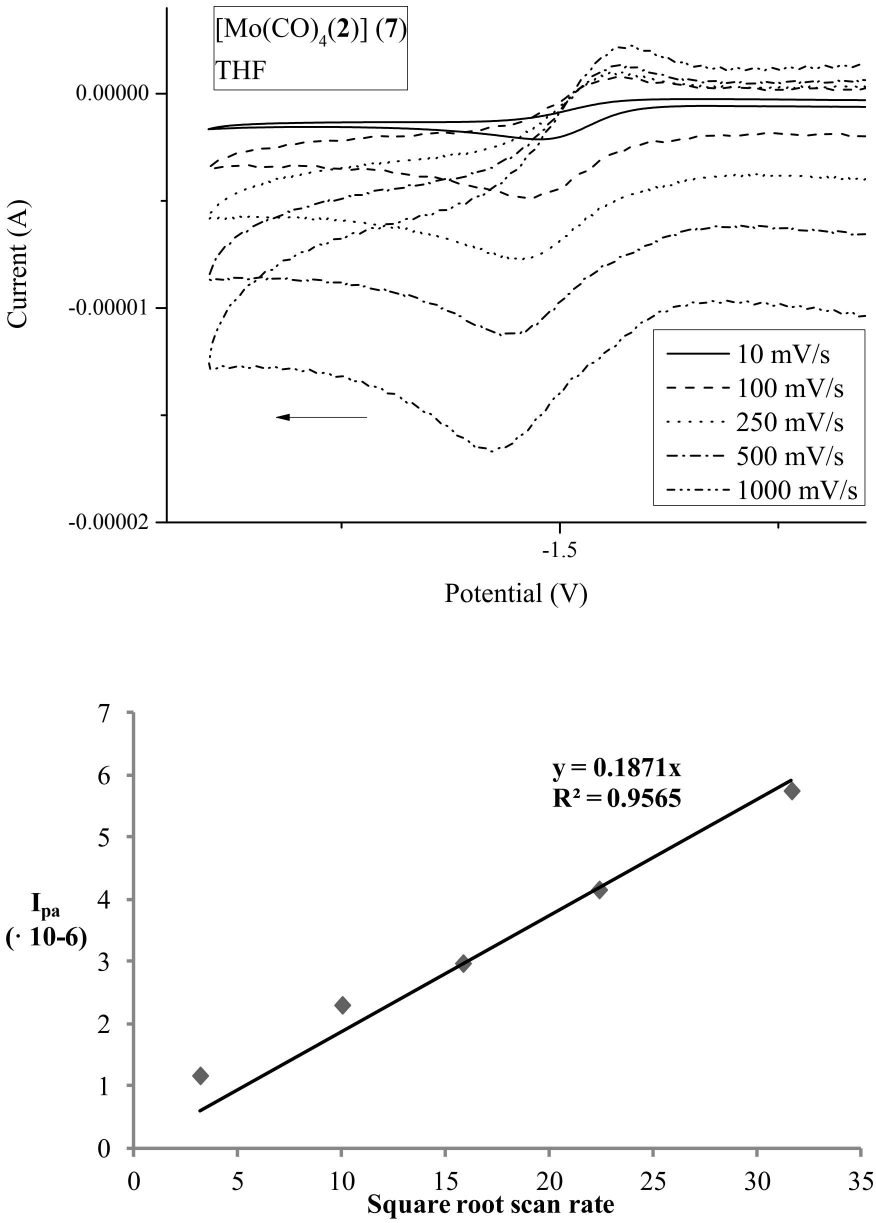
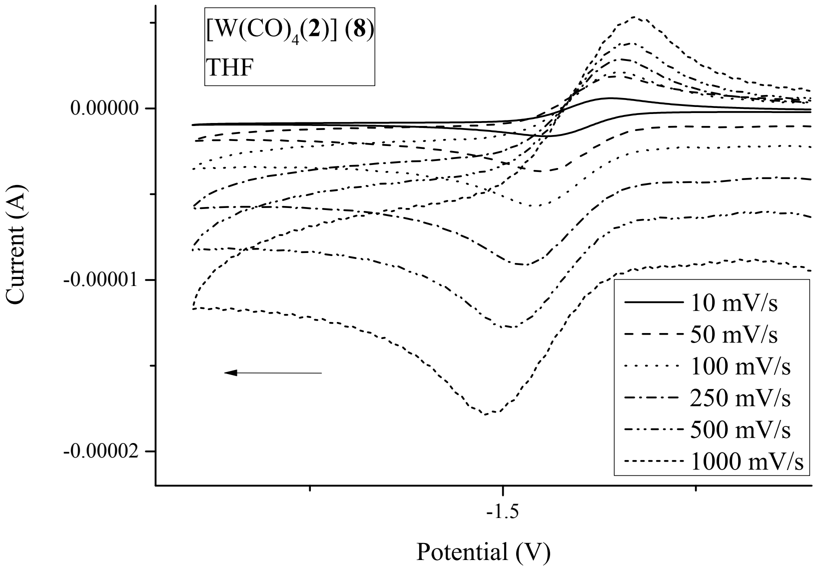


Figure S4: Electrochemical spectra of the first reaction wave from **7** at different scan rates, determined by CV on glassy carbon working electrode in a 0.1 M *n*Bu$_4$NPF$_6$ and $5 \cdot 10^{-3}$ M **7** THF solution at $T = 298$ K. Bottom graph represents the linear regression between the square root of the different scan rates and the I$_{pa}$ measured of **7**, see Table S4 for the values.

Reversibility of [W(CO)$_4$(**2**) (**8**):

Table S5: Electrochemical I_{pa} values of the first reduction wave from **8** at different scan rates, determined by CV on a glassy carbon working electrode in 0.1 M *n*Bu$_4$NPF$_6$ and $5 \cdot 10^{-3}$ M **8** THF solutions at $T = 298$ K.

Scan rate mV/s	Square root scan rate	I_{pa} ($\cdot 10^{-6}$)
10	3.16	1.20
50	7.07	2.02
100	10	2.94
250	15.81	4.47
500	22.36	5.66
1000	31.62	7.74



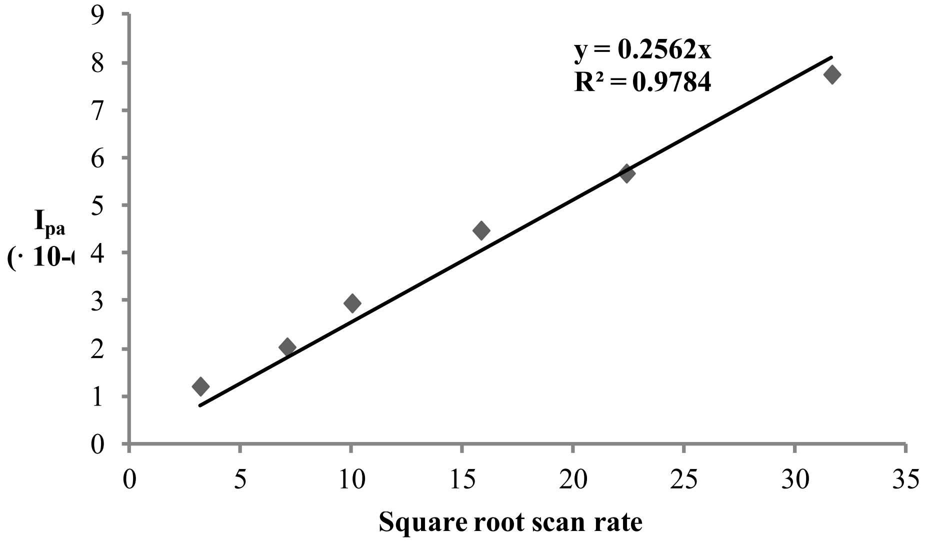


Figure S5: Electrochemical spectra of the first reaction wave from **8** at different scan rates, determined by CV on glassy carbon working electrode in a 0.1 M *n*Bu$_4$NPF$_6$ and $5{\cdot}10^{-3}$ M **8** THF solution at *T* = 298 K. Bottom graph represents the linear regression between the square root of the different scan rates and the I$_{pa}$ measured of **8**, see Table S5 for the values.

<u>X-ray crystal structure determinations:</u>

Compound 4. $C_{26}H_{16}MoNO_4P$, Fw = 533.31, orange block, 0.33 × 0.32 × 0.15 mm^3, orthorhombic, Pna2$_1$ (no. 33), a = 15.8048(5), b = 18.8955(5), c = 7.3079(2) Å, V = 2182.45(11) Å^3, Z = 4, D$_x$ = 1.623 g/cm^3, μ = 0.71 mm^{-1}. 25398 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. X-ray intensities were integrated with the Eval15 software.[3] Multiscan absorption correction and scaling was performed with SADABS[4] (correction range 0.68-0.75). 5011 Reflections were unique (R$_{int}$ = 0.021), of which 4776 were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.[5] Least-squares refinement was performed with SHELXL-2014[6] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 299 Parameters were refined with 1 restraint (floating origin). R1/wR2 [I > 2σ(I)]: 0.0169 / 0.0439. R1/wR2 [all refl.]: 0.0184 / 0.0444. S = 1.069. Refinement as inversion twin resulted in a Flack parameter[7] x = -0.01(2). Residual electron density between -0.25 and 0.37 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[8]

Compound 5. $C_{26}H_{16}NO_4PW$, Fw = 621.22, red block, 0.38 × 0.38 × 0.38 mm^3, orthorhombic, $Pna2_1$ (no. 33), a = 15.7856(4), b = 18.8326(5), c = 7.2886(2) Å, V = 2166.78(10) $Å^3$, Z = 4, D_x = 1.904 g/cm^3, μ = 5.44 mm^{-1}. 42028 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. X-ray intensities were integrated with the Saint software.[9] Analytical absorption correction and scaling was performed with SADABS[4] (correction range 0.17-0.35). 4970 Reflections were unique (R_{int} = 0.019), of which 4846 were observed [$I>2\sigma(I)$]. The structure was solved with direct methods using SHELXS-97.[10] Least-squares refinement was performed with SHELXL-2014[6] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 300 Parameters were refined with 1 restraint (floating origin). R1/wR2 [$I > 2\sigma(I)$]: 0.0108 / 0.0275. R1/wR2 [all refl.]: 0.0114 / 0.0278. S = 1.060. Refinement as inversion twin resulted in a Flack parameter[7] x = -0.006(5). Extinction parameter EXTI = 0.00074(8). Residual electron density between -0.35 and 0.41 $e/Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[8]

Compound 6. $C_{26}H_{16}CrN_2O_4$, Fw = 472.41, dark red block, 0.48 × 0.38 × 0.16 mm^3, triclinic, P**Error!** (no. 2), a = 9.5048(2), b = 10.4930(3), c = 12.1845(3) Å, α = 100.514(1), β = 107.177(1), γ = 104.629(1) °, V = 1079.05(5) $Å^3$, Z = 2, D_x = 1.454 g/cm^3, μ = 0.57 mm^{-1}. 19024 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. X-ray intensities were integrated with the Eval15 software.[3] Multiscan absorption correction and scaling was performed with SADABS[4] (correction range 0.70-0.75). 4942 Reflections were unique (R_{int} = 0.011), of which 4747 were observed [$I>2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.[5] Least-squares refinement was performed with SHELXL-2014[6] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Hydrogen atoms H2 and H4 of the phosphinine ring were refined freely with isotropic displacement parameters. All other hydrogen atoms were refined with a riding model. 306 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0247 / 0.0660. R1/wR2 [all refl.]: 0.0256 / 0.0664. S = 1.065. Residual electron density between -0.39 and 0.37 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[8]

Compound 7. $C_{26}H_{16}MoN_2O_4$, Fw = 516.35, black block, 0.81 × 0.60 × 0.36 mm^3, triclinic, P**Error!** (no. 2), a = 9.6294(4), b = 10.4368(4), c = 12.2967(4) Å, α = 100.380(2), β = 107.819(2), γ = 103.596(2) °, V = 1100.31(7) Å^3, Z = 2, D_x = 1.559 g/cm^3, μ = 0.63 mm^{-1}. 17388 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. X-ray intensities were integrated with the Eval15 software.[3] Multiscan absorption correction and scaling was performed with SADABS[4] (correction range 0.69-0.75). 5031 Reflections were unique (R_{int} = 0.010), of which 4941 were observed [$I>2\sigma(I)$]. Initial coordinates for the refinement were taken from the isostructural compound **6**. Least-squares refinement was performed with SHELXL-2014[6] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Hydrogen atoms H2 and H4 of the phosphinine ring were refined freely with isotropic displacement parameters. All other hydrogen atoms were refined with a riding model. 306 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0177 / 0.0462. R1/wR2 [all refl.]: 0.0182 / 0.0464. S = 1.102. Residual electron density between -0.39 and 0.38 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[8]

Compound 8. $C_{26}H_{16}N_2O_4W$, Fw = 604.26, dark red block, 0.12 × 0.12 × 0.08 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 8.0777(2), b = 15.6562(4), c = 18.1170(4) Å, β = 110.058(1) °, V = 2152.22(9) Å^3, Z = 4, D_x = 1.865 g/cm^3, μ = 5.40 mm^{-1}. 60945 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. X-ray intensities were integrated with the Eval15 software.[3] Multiscan absorption correction and scaling was performed with SADABS[4] (correction range 0.36-0.43). 4947 Reflections were unique (R_{int} = 0.019), of which 4638 were observed [$I>2\sigma(I)$]. The structure was solved with direct methods using SHELXS-97.[10] Least-squares refinement was performed with SHELXL-2014[6] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 298 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0114 / 0.0265. R1/wR2 [all refl.]: 0.0129 / 0.0268. S = 1.041. Residual electron density between -0.32 and 0.32 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[8]

CCDC 1056137 (compound **4**), 1056138 (**5**), 1056139 (**6**), 1056140 (**7**), and 1056141 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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