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Phthalocyanine as a Redox-Active Platform for Organometallic Chemistry

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Experimental

General Procedures and Materials

All techniques and procedures were carried out under a nitrogen atmosphere either with an Mbraun Labmaster 130 glovebox or using standard Schlenk and vacuum-line techniques. All glassware was dried overnight at 160 °C prior to use. For reactions heated above 120 °C, a paraffin light oil bath was used (saybolt viscosity at 100 °F about 130 SUS). Toluene, tetrahydrofuran (THF), dimethoxyethane (DME) and diethyl ether (Et_2O) were distilled from sodium/benzophenone under nitrogen. Hexanes were distilled from sodium under nitrogen. PcCr (**1**), $K(DME)_4Pc^{3-}Cr(II)$ and $K_2(DME)_8Pc^{4-}Cr(II)$ were prepared as previously reported.[i] CH_2PPh_3[ii] and $MgMe_2$[iii] were prepared from literature procedures. All other reagents were purchased from commercial sources and used without further purification. Evans method[iv] spectra were recorded at 294 K on a 400 MHz Bruker Avance III spectrometer. All ^{1}H NMR shifts are reported relative to the impurity of internal solvent. Elemental analyses (C, H, N) were performed at Simon Fraser University by Mr. Paul Mulyk on a Carlo Erba EA 1110 CHN elemental analyzer.

UV-vis and NIR spectra were recorded on a Varian Cary 5000 spectrophotometer in a 0.1 cm quartz cell or a 0.1 cm quartz cell equipped with a Kontes PTFE plug, HI-VAC value for air-sensitive samples.

Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) experiments were determined with a Bruker Autoflex Speed spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a 1 kHz smartbeam-II laser. Positive ion mass spectra were acquired typically within the 300- to 7000-m/z range. The mass spectrometer was operated in the reflection mode and the mass spectrum obtained for each image position corresponds to the averaged mass spectra of a minimum of 5000 consecutive laser shots. Flex Control 3.4 and flexAnalysis 3.4 software packages (Bruker Daltonics, Bremen, Germany) were used to control the mass spectrometer, set spectrum parameters and visualize spectral data. For sample preparation, approximately 15-20 mg of the sample was added to a 1 mL solution of the respective solvent under an inert atmosphere in a glovebox. A 2 μL solution was then pipetted on a ground steel plate, dried by evaporation, and irradiated without a matrix.

Synthetic Procedures

$PcCr(CH_2PPh_3)_2$ (2)

To a solution of CH_2PPh_3 (58.2 mg, 0.211 mmol) in 15 mL THF, PcCr (56.5 mg, 0.100 mmol) was added slowly, causing the solution to become dark green. After being stirred for 20 h, the solvent was removed *in vacuo*, the residue was washed with ether (10 mL), and then extracted with 10 mL DME. The extracts were filtered through Celite and pumped *in vacuo* to leave a deep green powder of $PcCr(CH_2PPh_3)_2$ (**2**) (57.2 mg, 51.2%). Anal. Calcd for $PcCr(CH_2PPh_3)_2$•0.5PcCr: C, 73.81; H, 4.18; N, 12.01. Found C, 73.64; H, 4.32; N, 12.44. The green powder was extracted with 4 mL DME/2 mL hexanes sequentially and recrystallized to give green crystals of **2**. UV-vis: (THF) λ_{max} 337, 624, 664 nm. Evans Method: 2.83 μ_B.

$Li(DME)_3PcCrCCPh(DME)$ (3)

To a suspension of PcCr (56.5 mg, 0.100 mmol) in 15 mL DME, a solution of LiCCPh (11.0 mg, 0.100 mmol) in 10 mL DME was added slowly, causing the solution to become dark blue. After being stirred for 20 h, the solvent was removed *in vacuo*, the residue was washed with ether (10 mL), and then extracted with 10 mL DME. The extracts were filtered through Celite and pumped *in vacuo* to leave a deep blue powder of $Li(DME)_3PcCrCCPh(DME)$ (**3**) (34.9 mg, 51.7%). The powder was extracted with 6 mL DME/2 mL hexanes sequentially and recrystallized to give black/blue crystals of **3**. UV-vis: (THF) λ_{max} 335, 671 nm. Anal. Calcd. for $Li(DME)_4PcCrCCPh$: C, 66.23; H, 5.45; N, 11.88. Found C, 65.90; H, 5.73; N, 12.25.

$[Li(DME)_2]_2PcCH_2CH_3$ (4)

To a suspension of PcCr (56.6 mg, 0.100 mmol) in 10 mL THF, $LiCH_2CH_3$ (73.0 mg, 0.200 mmol) was added slowly as a solid, generating a dark blue solution. After being stirred for 20 h, the solvent was removed *in vacuo*, the residue was washed with ether (10 mL), then extracted with 6 mL DME/2 mL hexanes sequentially, and the extracts were filtered through Celite. A dark purple powder of $[Li(DME)_2]_2PcCH_2CH_3$ (**4**) was isolated (60.1 mg, 62.0%). UV-vis: (THF) λ_{max} 335, 580 nm. Anal. Calcd for

$[Li(DME)_2]_2PcCrCH_2CH_3$: C, 62.04; H, 6.35; N, 11.58. Found C, 61.99; H, 6.25; N, 11.75.

$Li(DME)_5PcCH_2CH_3$ (5)

To a suspension of PcCr (56.6 mg, 0.100 mmol) in 10 mL THF, $LiCH_2CH_3$ (7.3 mg, 0.200 mmol) was added slowly as a solid. After 20 h, Cp_2FeBF_4 (27.2 mg, 0.100 mmol) was added and left to stir at room temperature. After 20 h. the solvent was removed *in vacuo*, the residue was washed with hexanes (10 mL), and then extracted with 4 mL DME/2 mL hexanes sequentially, and the extracts were filtered through Celite. A dark blue powder of $Li(DME)_5PcCH_2CH_3$ (**5**) was isolated (42.1 mg, 40.1%). UV-vis: (THF) λ_{max} 335, 668 nm; Anal. Calcd for $Li(DME)_5PcCH_2CH_3$: C, 61.70; H, 6.58; N, 10.66. Found C, 61.56; H, 6.58; N, 10.10.

$K(DME)PcCH_2CH_3$ (6)

To a solution of $K_2(DME)_8PcCr$ (82.5 mg, 0.100 mmol) in 10 mL THF, $LiCH_2CH_3$ (7.3 mg, 0.200 mmol) was added slowly as a solid. After 20 h, Cp_2FeBF_4 (54.5 mg, 0.200 mmol) was added and left to stir at room temperature. After 20 h, the solvent was removed *in vacuo*, the residue was washed with hexanes (10 mL) and the extracts were filtered through Celite and pumped *in vacuo* to leave a deep blue powder of $K(DME)PcCH_2CH_3$ (**6**) (32.0 mg, 35.4%). Anal. Calcd for $K(DME)PcCH_2CH_3{\bullet}2DME$: C, 61.18; H, 5.69; N, 12.41. Found C, 59.58; H, 4.56; N, 11.90. This powder was extracted with 6 mL DME/2 mL hexanes sequentially and recrystallized to give black/blue crystals of **6**. UV-vis: (THF) λ_{max} 337, 668 nm.

$PcCrCH_2CH_3$ (7)

To a solution of **4** (96.8 mg, 0.100 mmol) in 20 mL DME, Cp_2FeBF_4 (56.2 mg, 0.206 mmol) was added and left to stir at room temperature. After 20 h, the solvent was removed *in vacuo*, the residue was washed with hexanes (10 mL) and then extracted with 10 mL DME. The extracts were filtered through Celite and removed *in vacuo* to leave a deep green powder of $PcCrCH_2CH_3$ (**7**) (31.9 mg, 54.1%). Anal. Calcd for $PcCH_2CH_3{\bullet}(LiBF_4)_2(DME)$ 52.39; H, 3.59; N, 12.86. Found C, 51.33; H, 3.13; N, 12.33.

($LiBF_4$ cannot readily be separated via the DME extraction). Extraction with 4 mL DME/2 mL hexanes sequentially and recrystallization gave black/green crystals of **7**. UV-vis: (THF) λ_{max} 335, 686 nm. MALDI-TOF: 593 and 564 (M^+ of 30% PcCrEt, and 70% PcCr).

PcCrPh (8)

To a suspension of PcCr (56.5 mg, 0.100 mmol) in 20 mL THF, a solution of LiPh (0.11 mL of 1.8 M solution in ether, 0.203 mmol) was added slowly and the resulting mixture was stirred for 20 h. Then Cp_2FeBF_4 (56.2 mg, 0.206 mmol) was added as a solid and the mixture was stirred at room temperature for 20 h. The solvent was then removed *in vacuo*, the residue was washed with hexanes (10 mL) and then extracted with 10 mL DME. The extracts were filtered through Celite and removed *in vacuo* to leave a deep green powder of PcCrPh (**8**) (25.9 mg, 40.3%). Anal. Calcd. for $PcCrPh{\bullet}(LiBF_4)(DME)_2$: C, 60.34; H, 4.51; N, 12.24. Found C, 60.81; H, 4.78; N, 11.85. ($LiBF_4$ cannot readily be separated via the DME extraction). This powder was extracted with 4 mL DME/2 mL hexanes sequentially and recrystallized to give black/green crystals of **8**. UV-vis: (THF) λ_{max} 337, 677 nm. MALDI-TOF: 640 (100% M^+, PcCrPh).

$PcCrCH_2SiMe_3$ (9)

To a suspension of PcCr (56.5 mg, 0.100 mmol) in 20 mL THF, $LiCH_2SiMe_3$ (19.1 mg, 0.203 mmol) was added slowly as a solid and the resulting solution was stirred for 20 h to yield a solution containing $LiPcCrCH_2SiMe_3$. Cp_2FeBF_4 (56.2 mg, 0.206 mmol) was added as a solid and the mixture was left to stir at room temperature. After 20 h, the solvent was removed *in vacuo*, the residue was washed with hexanes (10 mL) and then extracted with 10 mL toluene. The extracts were filtered through Celite and pumped *in vacuo* to leave a deep green powder of $PcCrCH_2SiMe_3$ (**9**) (35.9 mg, 55.1%). Anal. Calcd. for $PcCrCH_2SiMe_3$: C, 66.34; H, 4.18; N, 17.19. Found C, 66.35; H, 4.16; N, 16.26. This powder was extracted with 4 mL toluene/2 mL hexanes sequentially and recrystallized to give black/green crystals of **9**. UV-vis: (THF) λ_{max} 337, 668 nm. Evans Method: 3.72 μ_B. MALDI-TOF: 651 (100% M^+, $PcCrCH_2SiMe_3$).

$PcCrMe_2(DME)_2$ (10)

To a suspension of PcCr (77.7 mg, 0.138 mmol) in 15 mL DME, $MgMe_2$ (26.5 mg, 0.134 mmol) was added as a solid and the solution stirred for 1 h. MeI was subsequently added (10 μL, 0.160 mmol) and the resulting blue/green solution was stirred at room temperature for 20 h. The solvent was removed *in vacuo*, the residue was washed with ether (10 mL) and then extracted with 10 mL DME. The extracts were filtered through Celite and solvent removed *in vacuo* to leave a deep blue powder of $PcCrMe_2(DME)_2$ (**10**) (31.7 mg, 39.8%), This powder was extracted with 10 mL toluene and recrystallized to give black/green crystals of **10**. UV-vis: (THF) λ_{max} 340, 670 nm. Evans Method: 3.05 μ_B. Anal. Calcd for powder of $PcCrMe_2(DME)_2$: C, 65.10; H, 5.46; N, 14.46. Found C, 63.64; H, 4.59; N, 14.28. MALDI-TOF: 594 and 579 (M^+ of 40% $PcCrMe_2$, 60% PcCrMe).

$[(LiI)(DME)_3]PcCrPhMe$ (11)

To a suspension of PcCr (56.5 mg, 0.100 mmol) in 10 mL DME, LiPh (0.11 mL of 1.8 M solution in ether, 0.203 mmol) was added and the solution was stirred for 12 h. MeI was subsequently added (13 μL, 0.200 mmol) and the resulting blue/green solution was stirred at room temperature for 20 h. The solvent was removed *in vacuo*, the residue was washed with ether (10 mL) and then extracted with 10 mL DME. The extracts were filtered through Celite and the solvent removed *in vacuo* to leave a deep blue powder of PcCrPhMe (**11**) (20.8 mg, 31.7%). This powder was extracted with 4 mL DME/2 mL hexanes sequentially and recrystallized to give black/green crystals of **11**, which co-crystallize with solvated LiI. UV-vis: (THF) λ_{max} 340, 672 nm; Anal. Calcd for powder of $[(LiI)(DME)_3]PcCrPhMe$: C, 57.74; H, 5.13; N, 10.56. Found C, 58.56; H, 5.29; N, 10.89. MALDI-TOF: 656 and 640 (M^+ of 30% PcCrPhMe; and 70% PcCrPh).

Single crystal X-ray Diffraction

All crystals were mounted on a 150 mm MiTeGen Dual-Thickness MicroMount using Paratone oil and measurements were made on a Bruker X8 APEX II diffractometer with TRIUMPH-monochromated Mo Kα radiation or Cu Kα radiation from a Cu-microsource. The data were collected at a temperature of 150 K in a series of scans in

0.50° oscillations. Data were collected and integrated using the Bruker SAINT software package[v] and were corrected for absorption effects using the multi-scan technique (SADABS)[vi] or (TWINABS)[vii]. All structures were solved by direct methods.[viii] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but not refined. All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS.[ix] The molecular drawings were generated by the use of POV.[x]

Additional crystallographic information can be found in Table **S1**.

Complexes **2, 9** and **11** crystallize with two of one half independent molecules in the asymmetric unit. In **3, 6,** and **10** one of the DME molecules is disordered and was modeled in two orientations. Complex **10** crystallizes with a quarter of molecule residing on a four-fold axis of rotation; in addition, methyl and phenyl groups are disordered and were modeled in two orientations.

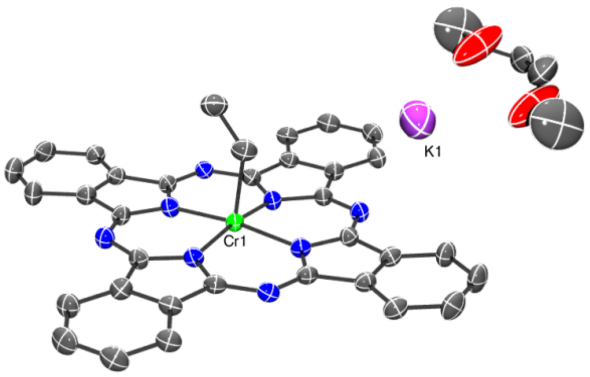


Figure S1. Crystal structure of **5** (50 % ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Cr-C 2.070(6), Cr-N 1.973(4) - 1.983(4). Colour scheme: Cr: green, N: blue, C: gray, K: purple and O: red.

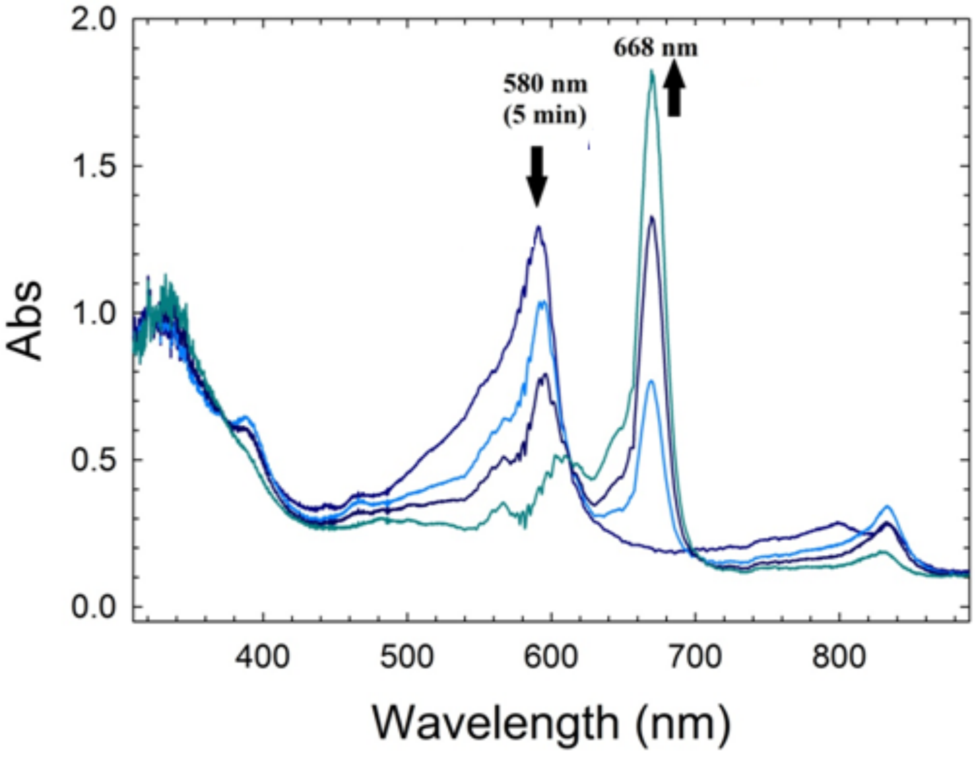


Figure S2. Monitoring the spectral change in DME (at 10^{-4} M), the addition of one equivalent of Cp_2FeBF_4 to $[Li(DME)_2]_2PcCH_2CH_3$ (**4**, λ_{max}: 580 nm) yielded $Li(DME)_2PcCH_2CH_3$ (**5**, λ_{max}: 668 nm). Spectra collected every 5 min for 20 minutes.

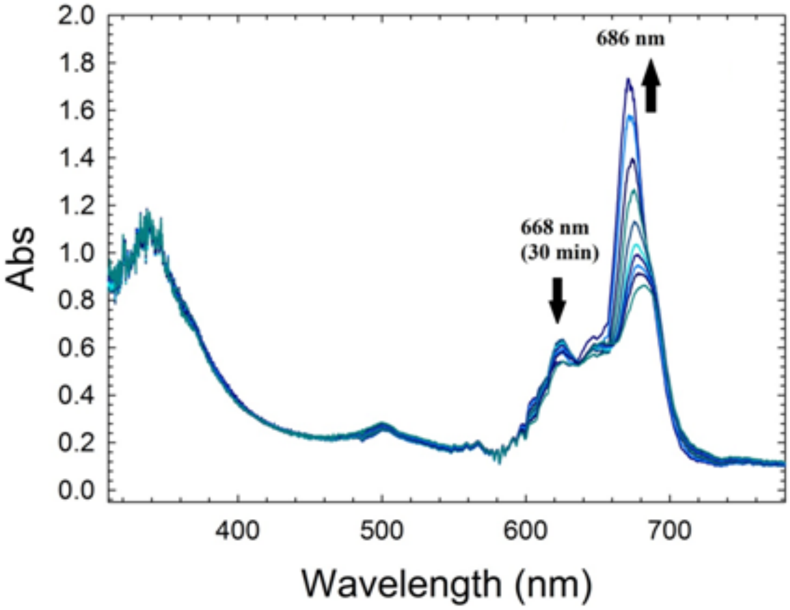


Figure S3. Conversion of Li(DME)$_2$PcCH$_2$CH$_3$ (**5**, λ_{max}: 668 nm) to PcCrCH$_2$CH$_3$ (**7**, λ_{max}: 686 nm). Spectra collected every 30 min for 4 h.

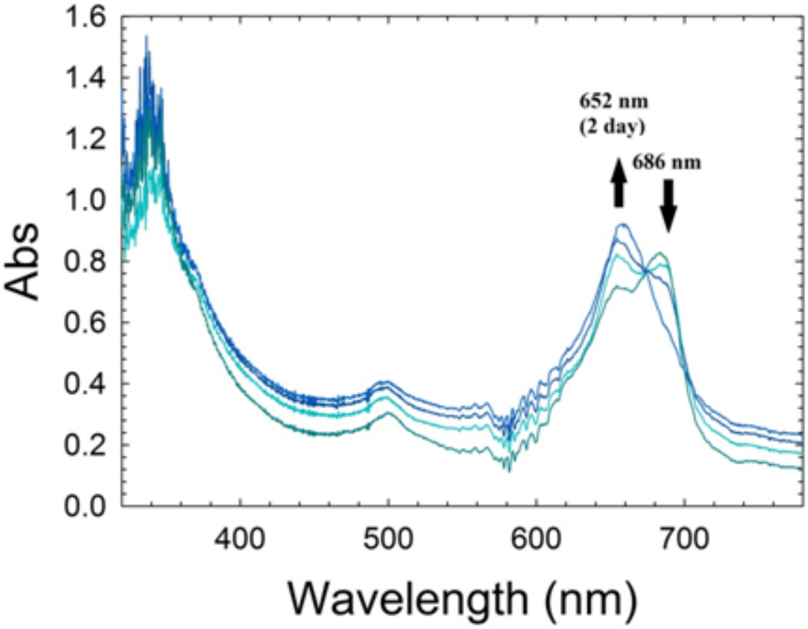


Figure S4. Decomposition of PcCrCH$_2$CH$_3$ (**7**, λ_{max}: 686 nm) to PcCr(DME)$_2$ (λ_{max}: 652 nm) over two days. (MALDI-TOF: 744, 654 and 564 (M+ of 35% PcCr(DME)$_2$, 30% PcCr(DME) and 35% PcCr))

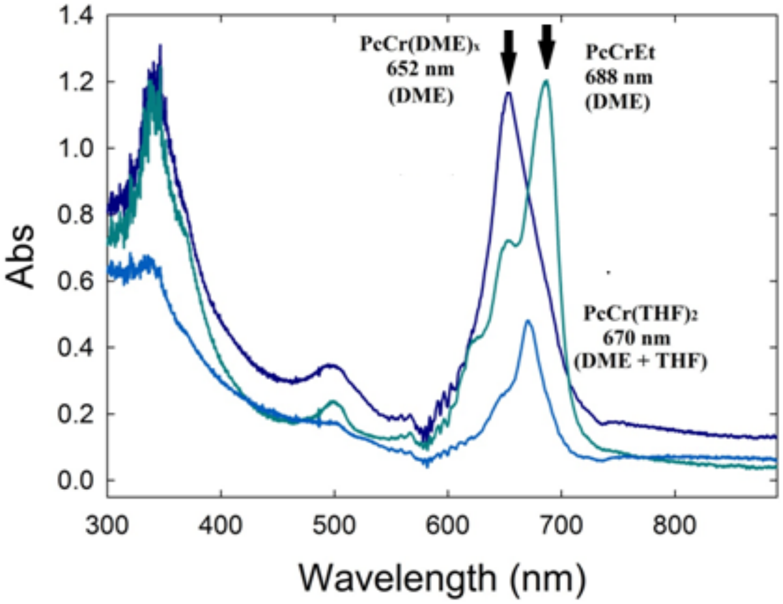


Figure S5. Both PcCrCH$_2$CH$_3$ (**7**, λ_{max}: 686 nm) and PcCr(DME)$_2$ (λ_{max}: 652 nm) convert rapidly to PcCr(THF)$_2$ (λ_{max}: 670 nm) by addition of 0.5 mL THF.

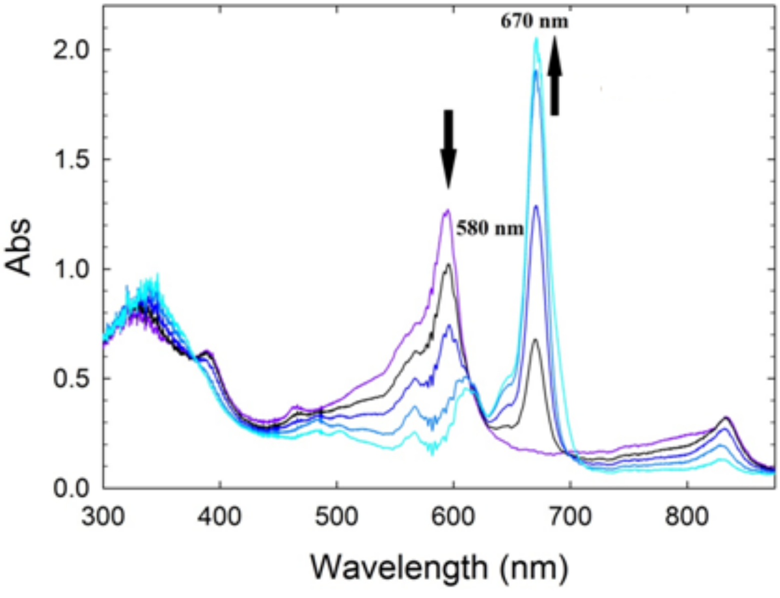


Figure S6. [Li(DME)$_2$]$_2$PcCH$_2$CH$_3$ (**4**, λ_{max}: 580 nm) in THF converts rapidly to PcCr(THF)$_2$ (λ_{max}: 670 nm) over 10 min.

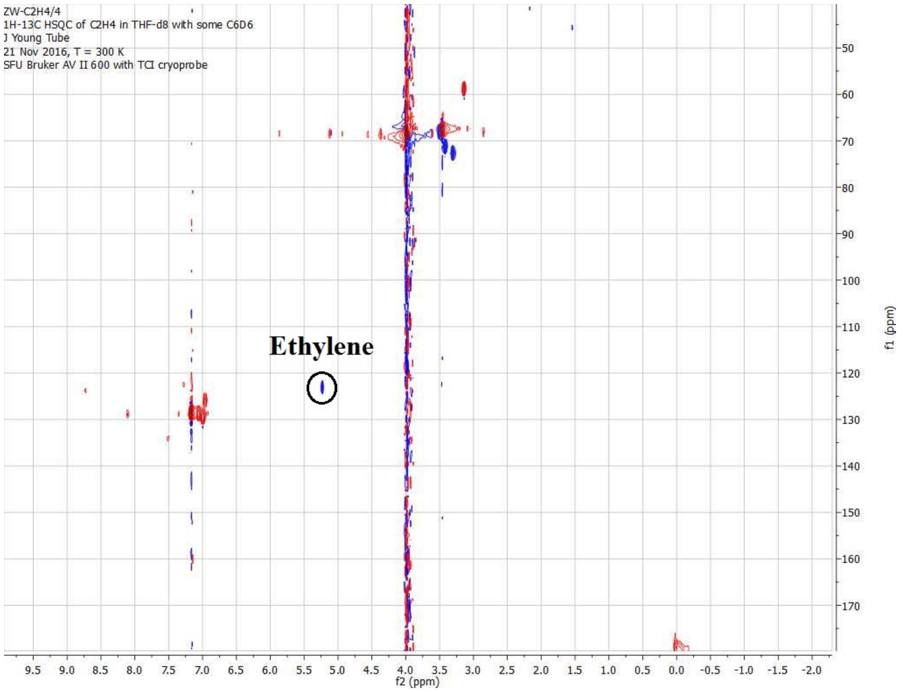


Figure S7. HSQC spectrum (d^8 THF) showing ethylene production upon decomposition of **7** in THF.

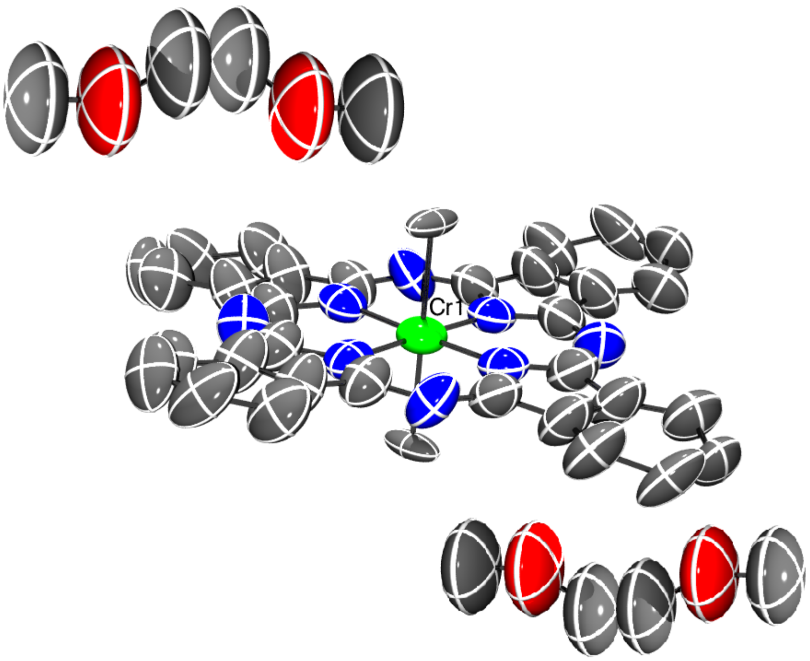
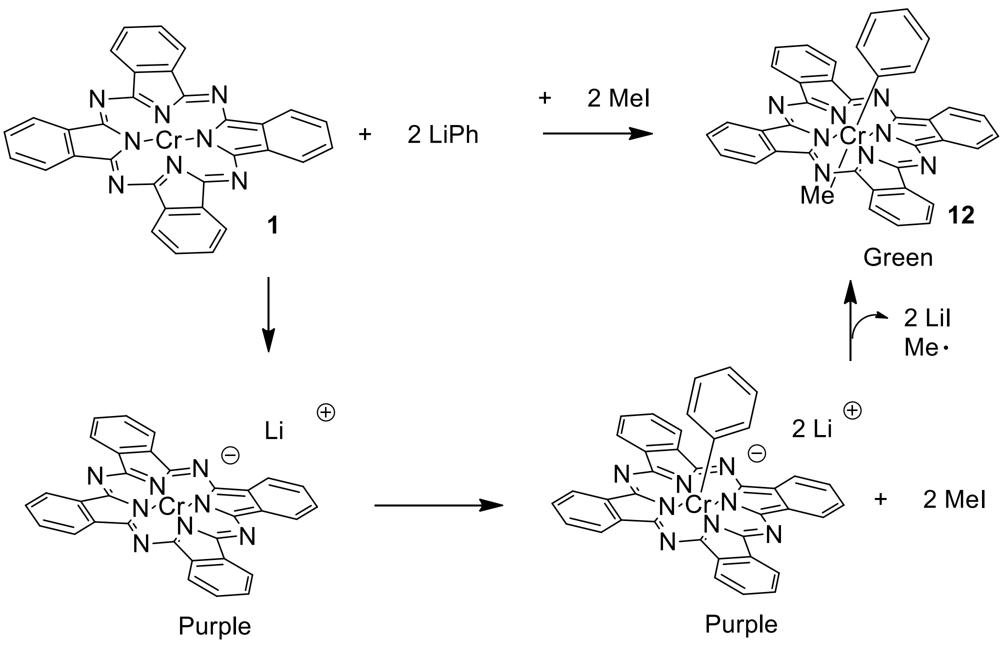


Figure S8. Molecular structure (50 % ellipsoids) of **10**; co-crystallized distal DME is also shown. All H atoms are omitted for clarity. Colour scheme: Cr: green, N: blue, C: gray and O: red.



Scheme S1. Synthesis of PcCr(IV)PhMe (**11**) and proposed intermediates from stepwise reaction of PcCr (**1**) with LiPh and MeI.

Table S1. X-ray crystallographic data for **2**, **3**, **6**, **7**, **8**, **9**, **10** and **11**

Compound reference	**PcCr(CH_2PPh_3)$_2$ (2)**	**Li(DME)$_3$PcCrCCPh(DME) (3)**	**K(DME)PcCH$_2$CH$_3$ (6)**	**PcCrCH$_2$CH$_3$ (7)**
Empirical formula	$C_{76}H_{65}CrN_8O_3P_2$	$C_{60}H_{71}CrLiN_8O_{10}$	$C_{36}H_{25.51}CrKN_8O$	$C_{34}H_{21}CrN_8$
Formula weight	1252.30	1123.18	677.25	593.59
Temperature/K	150(2)	150(2)	150(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	P2$_1$/c	P2$_1$/c	P2$_1$/n
a/Å	12.6533(11)	12.2590(5)	12.4386(2)	15.768(2)
b/Å	13.4790(11)	27.9724(12)	14.7836(3)	8.5743(13)
c/Å	19.7139(17)	17.8044(8)	16.9880(3)	19.542(3)
α/°	78.8950(16)	90	90	90
β/°	81.5270(16)	108.6500(10)	108.1990(10)	93.190(11)
γ/°	80.4130(16)	90	90	90
Volume/Å^3	3230.1(5)	5784.8(4)	2967.61(9)	2637.9(6)
Z	2	4	4	4
ρ_{calc} g/cm^3	1.288	1.290	1.516	1.495
μ/mm^{-1}	0.283	0.263	4.804	3.905
F(000)	1310.0	2376.0	1394.0	1220.0
Crystal size/mm^3	0.354 × 0.264 × 0.154	0.584 × 0.298 × 0.180	0.765 × 0.119 × 0.068	0.228 × 0.072 × 0.042
2Θ range for data collection/°	3.11 to 50.7	2.82 to 50.7	7.482 to 133.346	7.016 to 137.276
Reflections collected	45151	53146	20306	16527
Independent reflections	11814 [R_{int} = 0.0516, R_{sigma} = 0.0608]	10582 [R_{int} = 0.0333, R_{sigma} = 0.0262]	5238 [R_{int} = 0.0444, R_{sigma} = 0.0391]	4797 [R_{int} = 0.0557, R_{sigma} = 0.0548]
Goodness-of-fit on F^2	1.034	1.066	1.061	1.244
Final R indexes [I>2σ (I)]	R_1 = 0.0889, wR_2 = 0.2334	R_1 = 0.0516, wR_2 = 0.1147	R_1 = 0.0849, wR_2 = 0.2573	R_1 = 0.0630, wR_2 = 0.1681
Final R indexes [all data]	R_1 = 0.1294, wR_2 = 0.2673	R_1 = 0.0656, wR_2 = 0.1220	R_1 = 0.0962, wR_2 = 0.2682	R_1 = 0.0753, wR_2 = 0.1780
Largest diff. peak/hole / e Å^{-3}	1.50/-0.77	0.58/-0.48	0.71/-2.27	0.92/-0.62
CCDC	1573726	1573727	1573728	1573729

Compound reference	**PcCrPh (8)**	**$PcCrCH_2SiMe_3$ (9)**	**$PcCrMe_2(DME)_2$ (10)**	**$[(LiI)(DME)_3]PcCrPhMe$ (11)**
Empirical formula	$C_{38}H_{21}CrN_8$	$C_{36}H_{27}CrN_8Si$	$C_{79}H_{44}Cr_2N_{16}O_4$	$C_{182}H_{84}Cr_4I_2Li_2N_{32}O_{10}$
Formula weight	641.63	651.74	1385.30	3354.76
Temperature/K	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	cubic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	Pm-3n	Ibca
a/Å	10.0731(2)	11.3864(2)	17.1137(4)	24.4994(14)
b/Å	12.0863(2)	25.8865(5)	17.1137(4)	24.2314(16)
c/Å	22.7664(3)	41.3004(9)	17.1137(4)	35.7646(18)
α/°	90	90	90	90
β/°	96.3950(10)	91.6120(10)	90	90
γ/°	90	90	90	90
Volume/$Å^3$	2754.48(8)	12168.6(4)	5012.2(4)	21232(2)
Z	4	16	3	4
ρ_{calc} g/cm^3	1.547	1.423	1.377	1.050
μ/mm^{-1}	3.792	3.801	3.215	4.363
F(000)	1316.0	5392.0	2130.0	6752.0
Crystal size/mm^3	0.242 × 0.079 × 0.032	0.116 × 0.097 × 0.038	0.256 × 0.252 × 0.157	? × ? × ?
2Θ range for data collection/°	7.814 to 136.82	4.028 to 133.27	7.304 to 132.85	4.372 to 118.094
Reflections collected	25491	79663	17563	41403
Independent reflections	5055 [R_{int} = 0.0431, R_{sigma} = 0.0305]	21244 [R_{int} = 0.0981, R_{sigma} = 0.0944]	831 [R_{int} = 0.0969, R_{sigma} = 0.0339]	6929 [R_{int} = 0.2346, R_{sigma} = 0.1545]
Goodness-of-fit on F^2	1.027	1.009	2.691	1.600
Final R indexes [I>2σ (I)]	R_1 = 0.0360, wR_2 = 0.0917	R_1 = 0.0549, wR_2 = 0.1234	R_1 = 0.2046, wR_2 = 0.5975	R_1 = 0.2937, wR_2 = 0.5450
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.0968	R_1 = 0.0969, wR_2 = 0.1439	R_1 = 0.2388, wR_2 = 0.6213	R_1 = 0.4574, wR_2 = 0.6296
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.38	0.30/-0.62	0.81/-0.80	1.59/-0.75
CCDC	1573730	1573731	1573732	1573733

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