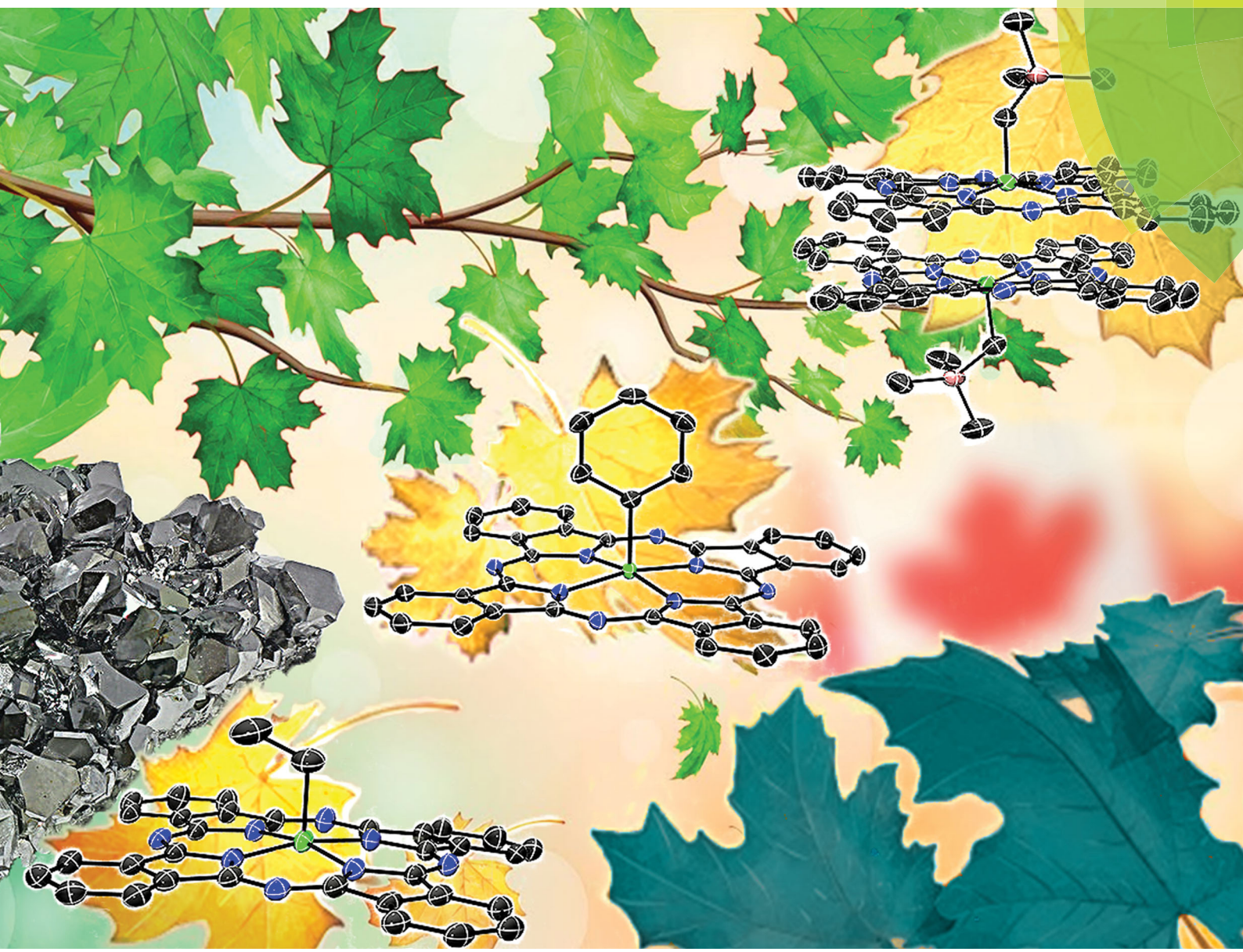
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Phthalocyanine as a redox-active platform for organometallic chemistry†

Wen Zhou and Daniel B. Leznoff *

A systematic approach to the synthesis of σ-organometallophthalocyanines is described. Structurally characterized σ-organoPcM complexes are presented, including the first PcCr–aryl, PcCr–alkynyl, and PcCr–Wittig complexes – representing the first examples of these classes of complexes for any metallophthalocyanine – and the first PcCr–alkyl complexes, which span three chromium and two Pc-ring oxidation states. This represents a rational marriage of the broad organometallic and phthalocyanine fields, opening the door for the exploration of this classical, stable, redox-active macrocycle as an ancillary ligand in metal–carbon chemistry.

Metallophthalocyanines (PcM) are ubiquitous macrocyclic materials that are commonly used as blue-green dyes and pigments.[1] Everyday applications include industrial use as pigments, high-speed CD-RW media, electro-optical computer components and photodynamic cancer therapy.[2] Despite their widespread use, organometallic applications are uncommon. PcM-based σ-alkyl complexes are especially rare[3,4] and aryl and alkynyl-containing structures are unreported. Early reports on harnessing PcM complexes for organometallic reactivity show enticing results (especially with PcFe and Co systems),[5,6] but none of the complexes were structurally characterized, leaving key information of the (often paramagnetic) compounds ambiguous. To address this surprising absence in the literature, we synthesized and characterized of a series of PcCr–CR systems, motivated by the widespread use of Cr in organometallic chemistry and catalysis.[7] This proved to be a fruitful testing ground due to the broad range of Cr and Pc oxidation states that can be accessed.[8]

Pc materials are thermally stable and chemically inert, but the ring is redox-active, with accessible oxidation states varying from −6 to 0.[9] Pcs are typically thought of as insoluble, which is perhaps an underlying reason that their application in organometallic chemistry is sparse. We surveyed thousands of PcM crystal structures for molecules containing M–C bonds, and there are only a few examples, which include a small number of PcM–CN,[10,11] PcM–isocyanide,[12] PcM–carbonyl[13] and PcM–carbide[14] containing molecules. CpFe- and Ru-fragments have been appended to the Pc-ring[15] but metallophthalocyanin-ocene PcM-Cp type sandwiches were only recently reported.[16]

A typical starting material for organometallic PcCr chemistry could be PcCrBr(THF), a moderately soluble Cr(III) system.[8] However, attempts to metathesize the Cr–Br bond with a wide range of alkylating agents, including alkyl/aryl lithium and Grignards all resulted in reduction to PcCr(II). We thus turned to **1** directly as an alternative starting point.

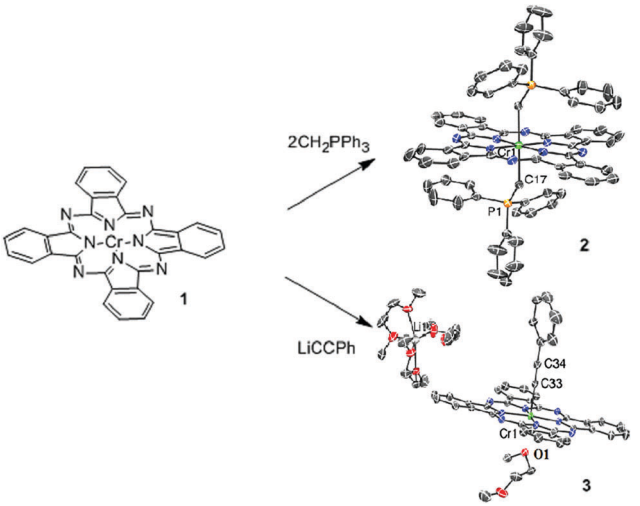
Although **1** has a low solubility in most organic solvents due to extensive aggregation, upon refluxing in THF, the soluble $PcCr(THF)_2$ can be prepared[6,8] since the addition of axial ligands can disrupt the PcCr stack. Addition of PPh_3 and ^{Mes}NHC to **1** can act in a similar fashion, with dissolution of **1** to a green colour (λ_{max} = 669 nm), although the products were not structurally characterized.

The neutral carbon-based Wittig reagent CH_2PPh_3 can also act in this fashion. Upon addition of two equiv. of CH_2PPh_3 in THF to **1**, the solubility of the material increased dramatically, yielding a bright green homogeneous solution of $PcCr(CH_2PPh_3)_2$ (**2**), which exhibits UV-vis absorptions with λ_{max} at 337 (B-band), 627 and 664 (Q-bands) nm and has a low-spin Cr(II) centre (μ_{eff} = 2.83 μ_B). X-ray quality crystals were obtained from a DME/hexanes solution (51% yield). The solid-state structure (Scheme 1) shows the PcCr ring with a pseudo-octahedral Cr(II) centre, where the metal lies in the plane of the Pc ring. The Cr–C bond distances are long, at 2.231(5) and 2.261(5) Å and the Cr–C–P bond angles of 131.8(3)° and 127.7(3)° are also large, indicating that the Wittig reagent is weakly bound to the Cr(II) centre. This contrasts with the reported addition of CH_2PPh_3 to $U(NR_2)_3$, whereby oxidation to a U(IV)–carbene system was observed.[17] Complex **2** represents the first structurally characterized example of a Wittig reagent interacting with a PcM fragment.

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† Electronic supplementary information (ESI) available: Experimental details; crystallographic data in cif format. CCDC 1573726–1573733; crystal structure figures for **5** and **10**; HSQC spectrum of the decomposition of **7** showing ethylene production; UV-visible spectra of the synthesis and decomposition of PcCrEt. For ESI and crystallographic data in CIF or other electronic format. see DOI: 10.1039/c7cc08781k

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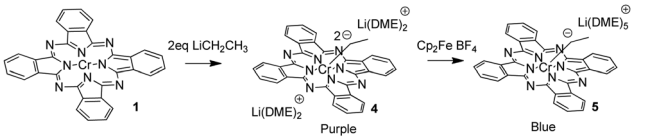


Scheme 1 Synthesis and molecular structure (50% ellipsoids) of **2** and **3**. All H atoms and Li(DME)$_3$ cation in **3** are omitted for clarity. Selected bond lengths [Å] in **2**: Cr–C 2.231(5), 2.261(5), Cr–N 1.974(4)–1.982(4), P1–C17 1.730(4), 1.732(5); in **3**: Cr–C 2.003(2), Cr–N 1.9685(19), 1.9871(19), C33–C34 1.214 (3) and Cr–O 2.2642(16). Colour scheme: Cr: green, P: yellow, N: blue, O: red and C: gray.

In order to avoid the redox-chemistry associated with the attempted alkylation of PcCrBr, carbanions were added directly to **1**, targeting Cr(II)–C containing alkyl ate-complexes. Thus, addition of LiCCPh resulted in an immediate colour change from green to blue and complete solubilization of all material. X-ray quality crystals of [Li(DME)$_3$]PcCrCCPh(DME) (**3**) were obtained from DME (52% yield) (Scheme 1). In the structure, the Cr(II) centre has a typical octahedral geometry, with an axial alkynyl ligand (Cr–C bond length = 2.003(2) Å) and an axially-bound DME. As expected for a Pc^{2-} macrocycle, it is quite flat as indicated by the dihedral angles between Pc quadrants (7.3 and 2.46°). This ate-complex can be contrasted with KPcCr(CN)$_2$, a cyano-Cr(III) ate-complex anion.[11]

Although **3** represents the first structurally characterized PcM–alkynyl complex, LiR-addition to PcCr is not a general route to such ate-complexes; addition of numerous other alkylating agents, including LiR, KR and RMgX resulted in reduction of the phthalocyanine ring to generate [cation][Pc^{3-}Cr], and not a [PcCr–R]–anion.[8] Similarly, ring reduction induced by NaCp and LiCp* was also observed in PcZrCl$_2$.[18] We thus considered harnessing this ring-reduction rationally to access other Cr(II) and Cr(III)–alkyl complexes. As an example, addition of LiEt to LiPcCr does not induce a second reduction[16] to Pc^{4-} but rather forms the purple ate-complex of the reduced Pc^{3-}Cr system (λ_{max} = 350 and 580 nm) [Li$_2$(DME)$_4$]Pc^{3-}Cr(CH$_2$CH$_3$), (62% yield) (**4**, Scheme 2); attempts to crystallize this compound were not successful. However, this intermediate can be readily oxidized, *e.g.* with [Cp$_2$Fe][BF$_4$]; one equivalent regenerates the Pc^{2-} ring (λ_{max} = 350 and 668 nm), cleanly forming Li(DME)$_5$PcCr(CH$_2$CH$_3$) (**5**), a Cr(II) alkyl-ate complex (40% yield) (Scheme 2).

An X-ray crystal structure of the analogous K(DME)PcCr(CH$_2$CH$_3$) (**6**) (35% yield) (Fig. S1, ESI†) shows a five-coordinate Cr(II) centre with an axial ethyl unit, similar to **3** but lacking the axial DME.



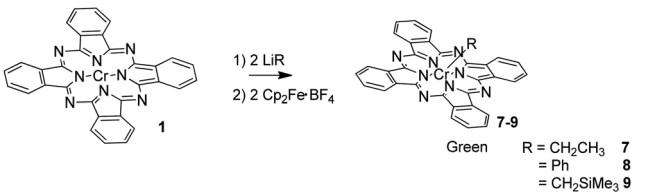
Scheme 2 Synthetic route to Li$_2$PcCr(CH$_2$CH$_3$) (**4**) and LiPcCr(CH$_2$CH$_3$) (**5**).

This Cr(II)–ethyl complex does not readily undergo β-hydride elimination, consistent with observations of other Cr(II)–alkyl complexes with β-hydrogen atoms.[19]

A further one-electron oxidation of the Cr(II)–alkyl ate complexes **5** or **6** provides access in a roundabout fashion to the PcCr(III)–R complexes. Thus, while addition of one equivalent of [Cp$_2$Fe][BF$_4$] to **3** gives the Cr(II)–ate system **5**, two equivalents generates PcCrEt (**7**), the Cr(III)–alkyl product directly. Indeed, the procedure can be carried out in a one pot fashion (Scheme 3). For example, addition of two equivalents of LiCH$_2$SiMe$_3$ to **1** followed by two equivalents of [Cp$_2$Fe][BF$_4$] generated first the Pc ring-reduced Pc^{3-} system, followed by further colour changes from purple to blue and finally green (λ_{max} = 337, 668 nm) PcCrCH$_2$SiMe$_3$ (**9**). PcCrPh (**8**) can also be prepared using the same synthetic methodology but with LiPh as the reducing and arylating agent (Scheme 3).

These PcCr(III) complexes **7–9** (54%, 40% and 55% yield) have all been structurally characterized; the metal adopts a square pyramidal geometry in all three cases (Fig. 1). Non-octahedral Cr(III) complexes are very rare;[20] these systems are five-coordinate due to the propensity of the Pc-ring to π-stack (Fig. 1), effectively blocking the last axial site in the solid-state. The Cr(III)–C bond lengths (2.073(4), 2.030(2) and 2.060(4) Å in **7–9** respectively) are similar to that in **6** (2.072(6) Å); all are slightly shorter compared with typical Cr(III)–C bond lengths (2.10–2.13 Å) in other non-PcM complexes.[21] These crystal structures of Pc-transition metal–alkyl complexes are extremely rare; only PcCoCH$_2$CH$_3$ and PcMCH$_3$ (M = Fe, Co, Rh) were previously reported to our knowledge.[3,4]

While the Cr(II)–ethyl complexes **5** and **6** are stable, the analogous PcCr(III)–CH$_2$CH$_3$ (**7**) system converts to PcCr(DME)$_2$ in dilute DME solution over days, as monitored by UV-visible spectral changes (Fig. S2–S5, ESI†). However, in THF PcCrCH$_2$CH$_3$ could not be isolated; decomposition to PcCr(THF)$_2$ – which was complete within 10 minutes and was isolated – is substantially faster than in DME (Fig. S6, ESI†), with no PcCrCH$_2$CH$_3$ observed while following the reaction by UV-visible spectroscopy. No putative PcCrH was detected or isolated either; such species are known to be unstable to Cr–H bond homolysis.[22] The production of



Scheme 3 Synthetic route to PcCrEt (**7**), PcCrPh (**8**), and PcCrCH$_2$SiMe$_3$ (**9**).

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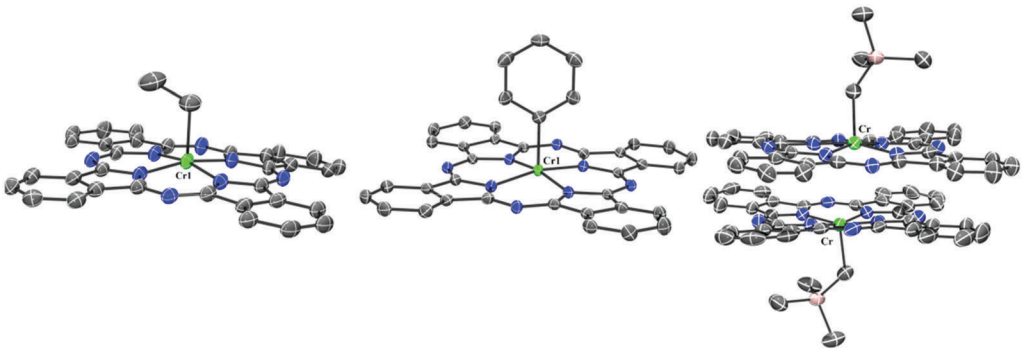
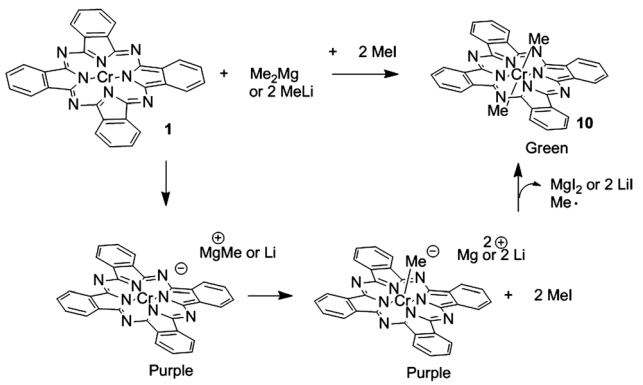


Fig. 1 Molecular structures (50% ellipsoids) of **7**, **8**, and π–π stacked dimer of **9**. All H atoms are omitted for clarity. Selected bond lengths [Å]: Cr–C 2.073(4) (in **7**), 2.030(2) (in **8**) and 2.060(4) (in **9**); Cr–N 1.9737(17)–1.9836(17) overall. Colour scheme: Cr: green, Si: pink, N: blue and C: gray.

ethylene was detected by HSQC NMR, (Fig. S7, ESI†), consistent with an active β-hydride elimination pathway. The stability difference of PcCrEt in DME (and other more non-coordinating solvents) *vs.* THF is noteworthy.

The oxidative addition of alkyl halides can also be harnessed to access PcCr–alkyl complexes. For example, addition of one equiv. of MeI to **1** gives the expected mixture of PcCrI(THF) and presumably PcCrMe, however these cannot be readily separated; the reduction–reoxidation route (Scheme 2) gives a higher yielding clean product of the alkyl complex while PcCrI can be accessed *via* I_2 oxidation of PcCr.[8] However, utilizing RI reagents in place of $[Cp_2Fe][BF_4]$ in Scheme 2 opens the door to very rare Cr(IV) complexes.[23] Thus, addition of one equivalent of Me_2Mg to **1** generates $[Pc^{3-}CrMe]^{2-}Mg$ (two equivalents of MeLi yields the analogous Li_2-salt) (Scheme 4). Subsequent addition of two equivalents of MeI formed the Cr(IV)–dialkyl complex $PcCrMe_2$ (**10**) in 40% yield; the oxidation state of the Pc ring remains at −2 (λ_{max} of 340, 664 nm) and a μ_{eff} of 3.0 B.M. is consistent with a Cr(IV) centre. The UV-vis spectrum of **10** is different than that of $PcCrCl_2$, where distinctive peaks consistent with an oxidized Pc^{1-} ring are observed; in **10** it is the Cr-centre that becomes oxidized.[24] Using MeI and $MgMe_2$ as a combination of alkylating reagents was previously reported in the synthesis of CpCr(NacNac)Me.[25] More traditional oxidative addition of alkyl halide to a reduced KPcCo(I) complex formed the aforementioned five-coordinate $PcCoCH_3$ and $PcCoCH_2CH_3$ complexes.[4]



Scheme 4 Synthesis of $PcCrMe_2$ (**10**) and postulated intermediates.

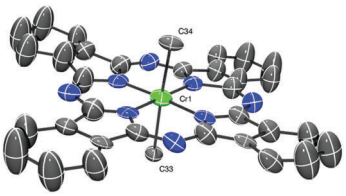


Fig. 2 Molecular structure (50% ellipsoids) of **10**. All H atoms are omitted for clarity. Selected bond lengths [Å]: Cr–C 2.222(18), Cr–N 2.008(15). Colour scheme: Cr: green, Si: pink, N: blue and C: gray.

The crystal structure of **10** (Fig. 2) reveals a pseudo-octahedral geometry for the Cr(IV) centre, which lies in the plane of the Pc ring with Cr–N bond distances of 2.008(15) Å. The Cr bond distances of 2.222(18) Å are long but still consistent with the range found for mono-methyl complexes of chromium in the III to V oxidation states,[26] and may reflect the fact that the methyl groups have a distal DME associated therewith (Fig. S8, ESI†). Well-characterized alkylchromium(IV) compounds are rare, and include the CrR_4 system (R = C_6H_{12}, Ph or CH_2CMe_2Ph).[27]

In order to provide evidence to support the proposed reaction scheme accessing **10**, the reducing/alkylating agent was altered to LiPh; subsequent treatment with MeI (Scheme S1, ESI†) should generate the mixed PcCrPhMe (**11**), which was indeed isolated *via* this route (32% yield). Although the crystal quality is poor (precluding a detailed analysis), the identity and connectivity is nevertheless unambiguous (Fig. 3). Spectroscopically, **11** is similar to **10** and other $Pc^{2-}Cr$ systems (λ_{max} = 340, 664 nm).[8]

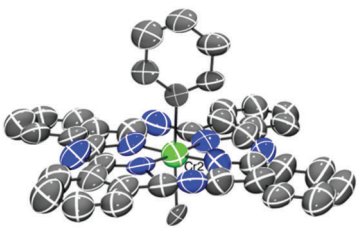


Fig. 3 Molecular structure (50% ellipsoids) of **11**. All H atoms and co-crystallized, DME-solvated LiI are omitted for clarity. Colour scheme: Cr: green, N: blue, C: gray, O: red, Li: silver and I: light green.

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In summary, it is clear that the redox-active Pc-ring can indeed be harnessed as an ancillary ligand in organometallic chemistry, particularly *via* the reduction–reoxidation route described herein. Collectively, this study illustrates the first structurally characterized PcM–alkynyl, PcM–aryl and doubled the reported PcM–alkyl structures, in the process spanning three oxidation states of Cr (+2 to +4) and two of the Pc-ring; a wider range of ring-redox activity is still accessible.[8] The door is now open to new explorations of the Pc ring as a redox active ancillary ligand in organometallic chemistry, effectively and systematically marrying these two diverse, broad areas.

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Conflicts of interest

There are no conflicts to declare.

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