Cobalt(III) carbene complex with an electronic excited state structure similar to cyclometalated iridium(III) compounds

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**General procedures.** All experiments were carried out under a nitrogen or an argon atmosphere using standard Schlenk or Glovebox techniques. Glassware was oven-dried at 130 °C. Solvents were distilled by standard procedures prior to use. $^1$H NMR spectra were recorded at 298 K on Bruker AVANCE III 500, Bruker AVANCE III 400, and Bruker AVANCE III 250 spectrometers. Chemical shifts ($\delta$) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are given in Hertz and are only reported for $^1$H-$^1$H couplings. Mass spectra were acquired on Bruker esquire 3000 plus and Bruker maxis 4G QTOF EDI spectrometers. Elemental analysis was carried out on a Vario Micro Cube instrument.

For cyclic voltammetry, a Versastat3-200 potentiostat from Princeton Applied Research was used. A glassy carbon disk electrode served as a working electrode, the counter electrode and quasi-reference electrode were two silver wires. Internal potential calibration occurred by addition of small amounts of ferrocene. The solvent was dry deaerated THF containing 0.1 M ($^n$Bu$_4$N)PF$_6$ (tetra-$n$-butylammonium hexafluorophosphate) as an electrolyte. Potential sweep rates were 0.1 V/s. The X-band electron paramagnetic resonance (EPR) spectrum was recorded on a Bruker ELEXSYS-II E500 CW-EPR spectrometer on a frozen solution at 77 K, using a EPR cold finger liquid nitrogen dewar.

All photophysical measurements were performed in dry and de-aerated solutions. Optical absorption spectroscopy was performed using a Cary 5000 instrument from Varian. Steady-state luminescence spectra were measured on a Fluorolog-322 from Horiba Jobin-Yvon, equipped with iHR320, a Xenon lamp 450 Watt Illuminator (FL-1039A/40A) and a water-cooled photomultiplier tube (PMT Hamamatsu R2658 or R928). The luminescence spectra were corrected for the spectral response of the system. An LP920-KS instrument from Edinburgh Instruments was employed for nanosecond transient absorption spectroscopy. The frequency-doubled output of a Quantel Brilliant b laser served as an excitation source. The laser pulse duration was $\sim$10 ns and the pulse frequency was 10 Hz. The typical pulse energy used for the nanosecond transient absorption studies was 10 mJ. Detection of transient UV-Vis absorption spectra occurred on an iCCD camera from Andor. Picosecond pump-probe (transient) absorption studies with sub-nanosecond time resolution were performed using a TRASS instrument from Hamamatsu and a mode-locked picosecond Nd:YVO$_4$/YAG laser (model PL2251B-20-SH/TH/FH with PRETRIG option) as an excitation source. The laser pulse duration was $\sim$30 ps and the pulse frequency was 10 Hz. The laser pulse energy of 8 mJ at 355 nm powered an Ekspla PG402-264 OPA with an energy output of 1 mJ at 430 nm. Femtosecond UV-Vis transient absorption spectra were recorded using a commercial pump-probe setup from LIGHT CONVERSION, which consists of a PHAROS fs-laser, an OPA called ORPHEUS, a HARPIA spectrometer, and a Kymera 193i-B2 iCCD camera from ANDOR. PHAROS is a compact Yb:KGW (ytterbium-doped potassium gadolinium tungstate) femtosecond pulsed laser with a maximal repetition rate of 50 kHz / 10 W (5 kHz / 1 W used in the current study), and a central wavelength of 1030 nm with a minimum pulse duration of 50 fs. When pumped with the PHAROS laser, ORPHEUS OPA can emit radiation between 185 and 2000 nm with pulse energies of up to 0.7 mJ. Probe pulses for the spectral range of 350 nm to 550 nm were generated using the fundamental PHAROS radiation (1030 nm) and a 5 mm thick sapphire white light supercontinuum (WLSc). The spectral range of 550 to 850 nm was generated by using the second optical harmonic of PHAROS (515 nm) with the same 5 mm sapphire WLSc. All the fs-data are analyzed by using the CarpetView software from LIGHT CONVERSION.
Scheme S1. Synthesis of the ligand precursor.

Synthesis of compound 2. Compound 2 was synthesized following a modified literature procedure.\(^1\) 3,6-Di-tert-butylcarbazole, 1 (2.000 g, 7.158 mmol, 1.0 equiv.) was dissolved in 100 mL glacial acetic acid in a 250 mL round bottom flask. To this mixture, \(\text{Br}_2\) (2.402 g, 15.032 mmol, 2.1 equiv.) in 10 mL acetic acid was added dropwise, and the resulting mixture was stirred at 25 °C for 3 h. Thereafter, the reaction mixture was added to 500 mL cold water in a beaker. The resulting off-white solid was filtered off and washed with water (3 × 100 mL). Then the off-white solid was dissolved in 100 mL dichloromethane and washed with saturated aqueous NaHCO\(_3\) solution (3 × 50 mL). The organic phase was dried over anhydrous Na\(_2\)SO\(_4\), and the solvent was evaporated to dryness to obtain compound 2 as an off-white solid (3.000 g, 6.862 mmol, 96%). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta\) 8.13 (br s, 1H), 7.98 (dd, \(J = 1.6, 0.5\) Hz, 2H), 7.64 (d, \(J = 1.6\) Hz, 2H), 1.44 (s, 18H) ppm. The spectral analytical data are consistent with those reported in the literature.\(^2\)

Synthesis of compound 3. Compound 3 was synthesized following a modified literature procedure.\(^3\) A 100 mL Schlenk flask containing a stir bar was charged with compound 2 (1.000 g, 2.287 mmol, 1.0 equiv.), imidazole (0.934 g, 13.722 mmol, 6.0 equiv.), K\(_2\)CO\(_3\) (1.90 g, 13.722 mmol, 6.0 equiv.), CuSO\(_4\)·5H\(_2\)O (114 mg, 0.457 mmol, 0.2 equiv.). The flask was evacuated and backfilled with N\(_2\) (3 times) and then 5 mL anhydrous dimethylsulfoxide was added. The resulting mixture was refluxed at 140 °C for 48 h. After cooling the reaction mixture to ambient temperature, 10 mL saturated aqueous NH\(_4\)Cl solution was added and stirred for 10 min, then the mixture was diluted with 100 mL water. The mixture was then extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with water (3 × 50 mL), dried over anhydrous Na\(_2\)SO\(_4\) and filtered. The solvent was removed \textit{in vacuo} to yield compound 3 (908 mg, 2.206 mmol, 96%) as an off-white solid. \(^1\)H NMR (250 MHz, DMSO-\(d_6\)): \(\delta\) 10.94 (br s, 1H), 8.35 (d, \(J = 1.7\) Hz, 2H), 8.21 (s, 2H), 7.72
The spectral analytical data are consistent with those reported in the literature.  

**Synthesis of ligand precursor (H$_3$L$_{CNC}$)(PF$_6$)$_2$.** A 50 mL Schlenk flask containing a stir bar was charged with compound 3 (0.300 g, 0.729 mmol, 1.0 equiv.). The flask was then evacuated and backfilled with N$_2$. 10 mL anhydrous acetonitrile was added, followed by the dropwise addition of iodomethane (0.310 g, 2.187 mmol, 3.0 equiv.) and the resulting suspension was stirred at ambient temperature for 48 h under exclusion of light. The solvent was evaporated under vacuum to obtain the crude diiodide salt, which was then dissolved in 10 mL methanol. Excess NH$_4$PF$_6$ (0.475 g, 2.916 mmol, 4.0 equiv.) was added and the mixture was stirred at ambient temperature for 16 h. The resulting precipitate was filtered off, washed with cold methanol and diethyl ether, and dried in vacuo to yield the ligand precursor (H$_3$L$_{CNC}$)(PF$_6$)$_2$ (0.308 mg, 0.421 mmol, 58%).  

**1H NMR (500 MHz, DMSO-d$_6$):** δ 11.45 (s, 1H), 9.72 (s, 2H), 8.65 (d, J = 1.4 Hz, 2H), 8.24 (t, J = 1.7 Hz, 2H), 8.04 (t, J = 1.7 Hz, 2H), 7.76 (d, J = 1.6 Hz, 2H), 4.01 (s, 6H), 1.47 (s, 18H) ppm.  

**13C{1H} NMR (125 MHz, DMSO-d$_6$):** δ 143.8, 137.9, 132.3, 125.4, 123.9, 123.5, 121.1, 119.4, 119.0, 36.0, 34.9, 31.6 ppm.  

**19F NMR (470 MHz, DMSO-d$_6$):** δ -70.1 (d, J = 711.5 Hz) ppm.  

**31P NMR (202 MHz, DMSO-d$_6$):** δ -144.2 (sept, J = 711.5 Hz) ppm. HRMS (ESI, positive ions): m/z 220.6443 (calcd for [H$_3$L$_{CNC}$]$^{2+}$ = 220.6441); m/z 440.2809 (calcd for [H$_2$L$_{CNC}$] = 440.2819); m/z 586.2536 (calcd for [(H$_3$L$_{CNC}$)PF$_6$]$^+$ = 586.2534). Anal. Calcd for (H$_3$L$_{CNC}$)(PF$_6$)$_2$ (C$_{28}$H$_{35}$N$_5$P$_2$F$_{12}$) (%): C, 45.97; H, 4.82; N, 9.57. Found: C, 45.81; H, 4.99; N, 9.52.

**Synthesis of [Co(L$_{CNC}$)$_2$(PF$_6$)$_2$.** To a 100 mL dry Schlenk flask was added (H$_3$L$_{CNC}$)(PF$_6$)$_2$ (100 mg, 0.136 mmol, 1.0 equiv.) and KOtBu (50 mg, 0.450 mmol, 3.3 equiv.), and the flask was evacuated and backfilled with N$_2$. To this mixture, dry THF (5 ml) was added under N$_2$ at 0°C, and the resulting suspension was stirred for 30 min at ambient temperature. In another dry flask CoCl$_2$ (9 mg, 0.068 mmol, 0.5 equiv.) was added in the glove box and 5 mL dry THF was added to it. Then the CoCl$_2$ solution was added to the first flask under N$_2$ and the resulting mixture was heated to 55°C for 18 h. After cooling the reaction mixture to ambient temperature, it was stirred in air for 1 h. The mixture was then dried and 20 mL water was added. Thereafter, the resulting suspension was extracted with 20 mL dichloromethane, dried, and washed with diethyl ether. The resulting product was re-dissolved in dichloromethane and filtered through a pad of Celite, and then the filtrate was dried to obtain [Co(L$_{CNC}$)$_2$]PF$_6$ as an orange solid (30 mg, 0.028 mmol, 41%).  

**1H NMR (500 MHz, DMSO-d$_6$):** δ 8.58 (s, 4H), 8.07 (s, 4H), 7.78 (s, 4H), 7.28 (s, 4H), 1.65 (12H), 1.47 (s, 36H) ppm.  

**13C{1H} NMR (125 MHz, DMSO-d$_6$):** δ 171.5, 139.4, 134.6, 127.0, 126.6, 123.8, 119.5, 114.7, 109.3, 35.7, 34.8, 31.9 ppm.  

**19F NMR (470 MHz, DMSO-d$_6$):** δ -69.8 (d, J = 711.2 Hz) ppm.  

**31P NMR (202 MHz, DMSO-d$_6$):** δ -144.2 (sept, J = 711.2 Hz) ppm. HRMS (ESI, positive ions): m/z 935.4646 (calcd for [CoL$_{CNC}$]$^{2+}$ = 935.4642). Anal. Calcd for [Co(L$_{CNC}$)$_2$(PF$_6$)$_2$ (C$_{56}$H$_{60}$N$_{10}$CoPF$_6$) (%): C, 62.22; H, 5.97; N, 12.96. Found: C, 61.93; H, 5.91; N, 12.93.
Synthesis of $[\text{Fe}(\text{L}^{\text{CNC}})_2](\text{PF}_6)$. To a 100 mL dry Schlenk flask was added $(\text{H}_3\text{L}^{\text{CNC}})(\text{PF}_6)_2$ (50 mg, 0.068 mmol, 1 equiv.) and $\text{KO}^{\text{tBu}}$ (25 mg, 0.225 mmol, 3.3 equiv.), and the flask was evacuated and backfilled with $\text{N}_2$. To this mixture, dry THF (5 ml) was added under $\text{N}_2$ at 0 °C, and the resulting suspension was stirred for 30 min at ambient temperature. $\text{FeBr}_2$ (7.3 mg, 0.034 mmol, 0.5 equiv.) was added to another dry flask in the glove box and 5 mL dry THF was added to it. Then the $\text{FeBr}_2$ solution was added to the first flask under $\text{N}_2$ and the resulting mixture was heated to 55 °C for 18 h. After cooling the reaction mixture to ambient temperature, it was stirred in air for 1 h. Then the mixture was dried and 20 mL water was added. Thereafter, the resulting suspension was extracted with 20 mL dichloromethane, dried and washed with diethyl ether. The resulting product was re-dissolved in dichloromethane and filtered through a pad of Celite, and then the filtrate was dried to obtain $[\text{Fe}(\text{L}^{\text{CNC}})_2](\text{PF}_6)$ as a green solid (14 mg, 0.013 mmol, 38%). HRMS (ESI, positive ions): $m/z$ 932.4651 (calcd for $[\text{Fe}(\text{L}^{\text{CNC}})_2]^+$ 932.4661). Anal. Calcd for $[\text{Fe}(\text{L}^{\text{CNC}})_2](\text{PF}_6)\cdot 1.5(\text{H}_2\text{O}) (\text{C}_{56}\text{H}_{64}\text{N}_{10}\text{FePF}_6\cdot 1.5(\text{H}_2\text{O}))$ (%): C, 60.86; H, 6.11; N, 12.68. Found: C, 60.83; H, 5.89; N, 12.58.

Figure S1. X-band EPR spectrum (black) and fit (red) of a frozen matrix of $[\text{Fe}(\text{L}^{\text{CNC}})_2](\text{PF}_6)$ in MeCN at 77 K (5 mM, microwave frequency, 9.516 GHz; modulation amplitude, 10 G; microwave power, 20 mW). Simulation of the experimental spectrum was carried out with the SL.esimX software package written by Dr. Eckhard Bill (Max Planck Institute for Chemical Energy Conversion).

X-ray crystallography. A suitable single crystal of $[\text{Co}(\text{L}^{\text{CNC}})_2](\text{PF}_6)\cdot 2\text{C}_2\text{H}_4\text{Cl}_2$ with dimensions 0.16×0.14×0.11 mm$^3$ was selected and mounted on a mylar loop in perfluoroether oil on a STOE STADIVARI diffractometer. The crystal was kept at a steady $T = 150$ K during data collection. The structure was solved with the ShelXT 2018 solution program and by using Olex2$^5$ as the graphical interface. The model was refined with ShelXL 2018$^6$ using full matrix least squares minimization on $F^2$. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. The asymmetric unit contains half formula unit of $[\text{Co}(\text{L}^{\text{CNC}})_2](\text{PF}_6)$ and one molecule of dichloroethane, which is disordered. The electron densities of disordered molecules are modelled over several positions. CCDC 2155721 ([Co(L^{CNC})$_2$](PF$_6$)$\cdot$2C$_2$H$_4$Cl$_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
Table S1. Crystallographic parameters for the structure of [Co(L\(^{CNC}\))\(_2\)](PF\(_6\))\(\cdot\)2C\(_2\)H\(_4\)Cl\(_2\).

| **Compound** | [Co(L\(^{CNC}\))\(_2\)](PF\(_6\))\(\cdot\)2C\(_2\)H\(_4\)Cl\(_2\) |
|--------------|--------------------------------------------------|
| **Formula**  | C\(_{60}\)H\(_{72}\)Cl\(_4\)CoF\(_6\)N\(_{10}\)P     |
| **\(D_{calc}\), g cm\(^{-3}\)** | 1.414 |
| **\(m/mm\)^1** | 4.686 |
| **Formula Weight** | 1278.97 |
| **Colour** | orange |
| **Shape** | block-shaped |
| **Size/mm\(^3\)** | 0.16×0.14×0.11 |
| **\(T/K\)** | 150 |
| **Crystal System** | monoclinic |
| **Space Group** | \(C2/c\) |
| **\(a/\AA\)** | 31.8165(8) |
| **\(b/\AA\)** | 13.3887(3) |
| **\(c/\AA\)** | 15.4260(3) |
| **\(\alpha^o\)** | 90 |
| **\(\beta^o\)** | 113.855(2) |
| **\(\gamma^o\)** | 90 |
| **\(V/\AA^3\)** | 6009.8(2) |
| **\(Z\)** | 4 |
| **\(Z'\)** | 0.5 |
| **Wavelength/\AA** | 1.54186 |
| **Radiation type** | Cu K\(_\alpha\) |
| **\(\Theta_{max}\)^\(\prime\)** | 3.634 |
| **\(\Theta_{max}\)^\(\prime\)** | 73.074 |
| **Measured Refl's.** | 28891 |
| **Indep't Refl's** | 5893 |
| **Refl's I \(\geq\) 2 \(\sigma(I)\)** | 5308 |
| **\(R_{int}\)** | 0.0250 |
| **Parameters** | 374 |
| **Restraints** | 85 |
| **Largest Peak** | 1.322 |
| **Deepest Hole** | -0.884 |
| **GoF** | 1.090 |
| **wR\(_2\) (all data)** | 0.2475 |
| **wR\(_2\)** | 0.2335 |
| **\(R_1\) (all data)** | 0.0924 |
| **\(R_1\)** | 0.0848 |

A suitable single crystal of [Fe(L\(^{CNC}\))\(_2\)](PF\(_6\))\(\cdot\)2C\(_2\)H\(_4\)Cl\(_2\) with dimensions 0.25×0.17×0.05 mm\(^3\) was selected and mounted on a mylar loop in perfluoroether oil on a STOE STADIVARI diffractometer. The crystal was kept at a steady \(T = 150\) K during data collection. The structure was solved with the ShelXT 2018\(^4\) solution program and by using Olex2\(^5\) as the graphical interface. The model was refined as described above. The asymmetric unit contains half a formula unit of [Fe(L\(^{CNC}\))\(_2\)](PF\(_6\)) and one molecule of dichloroethane. Both the PF\(_6\) anion and the dichloroethane solvent molecules are disordered. The electron densities of disordered molecules are modelled over several positions.
CCDC 2155722 ([Fe(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6})\textperiodcentered2C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2}) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table S2. Crystallographic parameters for the structure of [Fe(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6})\textperiodcentered2C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2}.

| Compound | [Fe(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6})\textperiodcentered2C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} |
|----------|-------------------------------------------------------------------|
| Formula  | C\textsubscript{60}H\textsubscript{72}Cl\textsubscript{4}F\textsubscript{6}FeN\textsubscript{10}P |
| \textit{D}_{calc}/ g cm\textsuperscript{-3} | 1.396 |
| \textit{m}/mm\textsuperscript{1} | 2.937 |
| Formula Weight | 1275.89 |
| Colour | green |
| Shape | plate |
| Size/mm\textsuperscript{3} | 0.25\times0.17\times0.05 |
| \textit{T}/K | 150 |
| Crystal System | monoclinic |
| Space Group | C2/c |
| \textit{a}/Å | 31.9599(9) |
| \textit{b}/Å | 13.3669(5) |
| \textit{c}/Å | 15.5316(5) |
| \textit{\alpha}/° | 90 |
| \textit{\beta}/° | 113.798(2) |
| \textit{\gamma}/° | 90 |
| \textit{V}/Å\textsuperscript{3} | 6071.0(4) |
| \textit{Z} | 4 |
| \textit{Z}' | 0.5 |
| Wavelength/Å | 1.34143 |
| Radiation type | GaK\textsubscript{a} |
| \textit{\Theta}_{\text{min}}/° | 2.629 |
| \textit{\Theta}_{\text{max}}/° | 57.943 |
| Measured Refl. | 39107 |
| Independent Refl. | 6311 |
| Reflections with I \geq 2 \sigma(I) | 6247 |
| \textit{R}_{int} | 0.0735 |
| Parameters | 183 |
| Restraints | 234 |
| Largest Peak | 1.467 |
| Deepest Hole | -1.418 |
| GooF | 1.083 |
| \textit{wR}_{2} (all data) | 0.2958 |
| \textit{wR}_{2} | 0.2953 |
| \textit{R}_{1} (all data) | 0.1103 |
| \textit{R}_{1} | 0.1097 |
NMR Spectra

Figure S2. $^1$H NMR spectrum of (H$_3$L$^{CNC}$)(PF$_6$)$_2$ (500 MHz, DMSO-$d_6$).

Figure S3. $^{13}$C{$^1$H} NMR spectrum of (H$_3$L$^{CNC}$)(PF$_6$)$_2$ (125 MHz, DMSO-$d_6$).
Figure S4. $^{19}$F NMR spectrum of (H$_3$L$^{CNC}$)(PF$_6$)$_2$ (470 MHz, DMSO-$d_6$).

Figure S5. $^{31}$P NMR spectrum of (H$_3$L$^{CNC}$)(PF$_6$)$_2$ (202 MHz, DMSO-$d_6$).
Figure S6. $^1$H NMR spectrum of [Co($L^{CNC}$)$_2$](PF$_6$) (500 MHz, DMSO-$d_6$).

Figure S7. $^{13}$C($^1$H) NMR spectrum of [Co($L^{CNC}$)$_2$](PF$_6$) (125 MHz, DMSO-$d_6$).
**Figure S8.** $^{19}$F NMR spectrum of $[\text{Co}(\text{L}^{\text{CNC}})_{2})(\text{PF}_6)]$ (470 MHz, DMSO-$d_6$).

**Figure S9.** $^{31}$P NMR spectrum of $[\text{Co}(\text{L}^{\text{CNC}})_{2})(\text{PF}_6)]$ (202 MHz, DMSO-$d_6$).
Mass spectra

Figure S10. Top: HRMS-ESI (positive ions) mass spectrum of [Co(L\text{CNC})_2]\text{PF}_6. Bottom: Simulated mass spectrum of [Co(L\text{CNC})_2]^+.

Figure S11. Top: HRMS-ESI (positive ions) mass spectrum of [Fe(L\text{CNC})_2]\text{PF}_6. Bottom: Simulated mass spectrum of [Fe(L\text{CNC})_2]^+.
Figure S12. Cyclic voltammogram of 1 mM ligand precursor, (H$_3$L$^{CNC}$)(PF$_6$) in acetonitrile with 0.1 M of (n-Bu$_4$N)(PF$_6$) as supporting electrolyte, recorded at a scan rate of 0.1 V/s.

Figure S13. Cyclic voltammograms of 1 mM (a) [Co(L$^{CNC}$)$_2$](PF$_6$) and (b) [Fe(L$^{CNC}$)$_2$](PF$_6$) in acetonitrile with 0.1 M of (n-Bu$_4$N)(PF$_6$) as supporting electrolyte, recorded at a scan rate of 0.1 V/s. Same data as in Figure 3 of the main paper.
Figure S14. UV-vis spectra of (H$_3$L$^{CNC}$)(PF$_6$)$_2$ (black line), [Co(L$^{CNC}$)$_2$(PF$_6$)] (red line) and [Fe(L$^{CNC}$)$_2$(PF$_6$)] (blue line), respectively, in acetonitrile. Same data as in Figure 4 of the main paper, but here displayed together in the same graphic for more direct comparison. The steep drop in absorbance below 230 nm in the black trace is an artefact caused by the onset of solvent absorption.

Figure S15. Emission spectrum of (H$_3$L$^{CNC}$)(PF$_6$)$_2$ in acetonitrile at 22 °C, $\lambda_{\text{exc}}$ = 410 nm. The asterisk mark peaks caused by Raman scattered excitation light.

Under identical conditions, the Co$^{III}$ complex did not show any reproducible emission, as noted in the main paper. The Fe$^{III}$ complex is non-emissive, which seems unsurprising given its excited-state lifetime of 1.3 – 1.4 ps.
Figure S16. Picosecond transient absorption (TA) spectrum of 100 µM de-aerated acetonitrile solution of [Co(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6}) at 22 °C, integrated over 2 ns following excitation at 430 nm with 30-ps laser pulses. Same data as in Figure 5a of the main paper.

Figure S17. Kinetic decays obtained from TA spectrum of [Co(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6}) at 380 (black line) and 440 nm (red line), respectively with lifetime (τ) of 1.3 ns. Same data in the inset of Figure 5a.
Figure S18a. UV-vis changes upon electrochemical (metal) oxidation of [Co(L\text{CNC})_2](PF_6) at a constant potential of 0.42 V vs Fe^{+/0} in acetonitrile. The electrolyte was 0.1 M (\text{nBu}_4\text{N})PF_6.

Figure 18b. UV-vis changes upon electrochemical oxidation of [Co(L\text{CNC})_2](PF_6) at a constant potential of 0.42 V vs Fe^{+/0} in acetonitrile. The electrolyte was 0.1 M (\text{nBu}_4\text{N})PF_6. The UV-vis absorption spectrum recorded prior to applying the potential served as a baseline. The four difference spectra (red, blue, green, ocher) were recorded after different durations
of applied potential, corresponding to increasing amounts of Co$^{IV}$ oxidation product. Signals marked by asterisks are artefacts caused by the instrument and the presence of air.

As discussed in the main paper, the first oxidation process of [Co(L$^{CNC}$)$_2$]$^+$ is attributable to a metal-centered redox event, in which cobalt(III) is oxidized to cobalt(IV), analogously to a recently reported hexacarbene cobalt(III) complex.$^7$ Due to the combination of two strongly $\pi$-donating amido donors and four strongly $\sigma$-donating (weakly $\pi$-accepting) NHC donors in our cobalt(III) complex, that metal-centered oxidation process occurs at even less positive potential than in the previously studied hexacarbene cobalt(III) complex. For the cobalt(III) analog of the iron(II) complex in Figure 1c,$^8$ the situation is very different. In this case, there are two amido donors and four only weakly $\sigma$-donating (as well as strongly $\pi$-accepting) phenanthrine-quinoline-amido donors, leading to a situation in which the first oxidation process is not metal-centered but rather ligand-based. The resulting aminyl radical formed upon one-electron oxidation of that cobalt(III) phenanthridine-quinoline-amido complex at 0.31 V vs Fe$^{+/0}$ manifested by an UV-vis absorption band extending from 1000 to 2300 nm.$^8$ For our [Co(L$^{CNC}$)$_2$]$^+$ complex, no such NIR absorption is observable upon electro-chemical oxidation at 0.46 V vs Fe$^{+/0}$ (Figure S18b), in line with the view that the first oxidation wave is metal-centered in our complex.

Another important difference between our [Co(L$^{CNC}$)$_2$]$^+$ complex and the previously studied cobalt(III) phenanthrine-quinoline-amido compound is that in our new complex the first reduction is ligand-based whereas in the previously studied compound this is a metal-centered reduction of cobalt(III) to cobalt(II). The fact that in [Co(L$^{CNC}$)$_2$]$^+$ the first oxidation is metal-centered and the first reduction is ligand-based leads to an energetically lowest excited state with substantial MLCT character.

![Figure S19. UV-vis changes upon electrochemical (ligand) oxidation of [Co(L$^{CNC}$)$_2$](PF$_6$) at a constant potential of 0.72 V vs Fe$^{+/0}$ in acetonitrile. The electrolyte was 0.1 M ($^t$Bu$_4$N)PF$_6$.](image)
Figure S20. UV-vis changes upon electrochemical (ligand) reduction of $[\text{Co(L}^{\text{CNC}}\text{)}_2](\text{PF}_6)$ at a constant potential of -2.3 V vs Fe$^{3+/0}$ in acetonitrile. The electrolyte was 0.1 M ($\text{Bu}_4\text{N})\text{PF}_6$.

Figure S21. Transient absorption spectra of $[\text{Co(L}^{\text{CNC}}\text{)}_2](\text{PF}_6)$ in deaerated acetonitrile at 22 °C at selected time points after excitation at 430 nm. ($c = 260 \mu\text{M}, 1 \text{ mm cuvette was used}$). Recorded on the fs-TA setup.
Figure S22. Decay-associated amplitude spectra (DAS) of 96 ± 25 ps (black line) and 1.24 ± 0.1 ns (red line) components, respectively, for the [Co(LCNC)₂](PF₆) in acetonitrile at 22 °C (λ_{exc} = 430 nm). Global analysis was carried out with a two-component fit in the time range from 0.5 ps to 6900 ps. Same data as in Figure 6 of the main paper.

Figure S23. Time trace at 380 nm, obtained after global two-component decay analysis for [Co(LCNC)₂](PF₆) in acetonitrile at 22 °C (λ_{exc} = 430 nm).
Figure S24. Time trace at 430 nm, obtained after global two-component analysis for [Co(L\textsubscript{CN}C)\textsubscript{2}](PF\textsubscript{6}) in acetonitrile at 22 °C (\(\lambda\text{exc} = 430\) nm).

Figure S25. (a) UV-vis spectrum of [Fe(L\textsubscript{CN}C)\textsubscript{2}](PF\textsubscript{6}) in acetonitrile. (b) Transient absorption spectra of [Fe(L\textsubscript{CN}C)\textsubscript{2}](PF\textsubscript{6}) in deaerated acetonitrile at 22 °C at selected time points after excitation at 700 nm. The asterisk (*) denotes an artefact caused by the excitation laser at 700 nm. (\(c = 420\) μM, 1 mm cuvette was used). Data recorded on the fs-TA setup.
**Figure S26.** Time trace at 840 nm with single-exponential fit to the experimental TA data of [Fe(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6}) in acetonitrile at 22 °C (λ\textsubscript{exc} = 700 nm, τ = 1.3 ps).

**Figure S27.** Transient absorption spectra of [Fe(L\textsuperscript{CNC})\textsubscript{2}](PF\textsubscript{6}) complex in deaerated acetonitrile at 22 °C at selected time points after excitation at 430 nm. The asterisk (*) denotes an artefact caused by the excitation laser at 860 nm. (c = 420 μM, 1 mm cuvette was used).
Figure S28. Time trace at 830 nm with a single-exponential fit to the experimental TA data of [Fe(LCNC)₂](PF₆) in acetonitrile at 22 °C (λ_{exc} = 430 nm, \tau = 1.4 ps).
Figure S29. Photostability studies of $[\text{Ru(bpy)}_3]^{2+}$ (a, b, c), $[\text{Ir(ppy)}_3]^{2+}$ (d, e, f) and $[\text{Co(LCNC)}_2]^{2+}$ (g, h) in deaerated acetonitrile at 20 °C upon continuous irradiation with a 447 nm (1.1 W) laser. The concentrations of all three complexes were chosen such as to reach an optical density of about 0.1 at 447 nm prior to photo-irradiation. (a) Loss of emission intensity of $[\text{Ru(bpy)}_3]^{2+}$ at 620 nm as a function of irradiation time. (b) UV-vis spectra of $[\text{Ru(bpy)}_3]^{2+}$ before (black line) and after irradiation for 66 minutes (red line). (The drop in absorbance below 230 nm is an artefact caused by solvent absorption). (c) Emission spectra of $[\text{Ru(bpy)}_3]^{2+}$ before (black line) and after irradiation for 66 minutes (red line). (d) Loss of emission intensity of $[\text{Ir(ppy)}_3]^{2+}$ at 525 nm as a function of irradiation time. (e) UV-vis spectra of $[\text{Ir(ppy)}_3]^{2+}$ before (black line) and after irradiation for 210 minutes (red line). (f) Emission spectra of $[\text{Ir(ppy)}_3]^{2+}$ before (black line) and after irradiation for 210 minutes (red line). (g) Absorbance of $[\text{Co(LCNC)}_2]^{2+}$ at 430 nm as a function of irradiation time, with UV-Vis spectra recorded in regular intervals of 10 minutes. (h) UV-vis spectra of $[\text{Co(LCNC)}_2]^{2+}$ after different time intervals during the photostability study (all spectra virtually superimposable).
**Computational calculations:**
Quantum chemical calculations were performed to investigate the electronic transitions of the investigated cobalt(III) complex by using density functional theory (DFT). The singlet ground state geometries were optimized using the Gaussian 09 software with Kohn-Sham orbital DFT in combination with the B3LXP functional and the def2SVP basis set for all atoms in vacuum to obtain full geometrical freedom. Vibrational frequency analysis confirmed the local minima of the optimized geometries by obtaining only positive eigenvalues. The frontier orbitals of the electronic ground state were obtained by single point calculations with the same level of theory, using the optimized vacuum ground-state geometry. Time-dependent DFT calculations were used to compute the first sixty vertical transitions (1-60 in Table S3) by single point calculations on the vacuum ground-state geometry in acetonitrile, employing the polarizable continuum model (PCM) and the same level of theory. All 60 vertical transitions are shown in Figure S30 with an additional (arbitrary) shift of 2140 cm\(^{-1}\) to the red region of the spectrum to better match with the experimental UV-Vis spectrum. Such arbitrary shifts of computed relative to experimental spectra seem to be more or less common practice. Furthermore, it seems that discrepancies between computed and experimental spectra are not uncommon for charge transfer transitions. In addition, for all 60 vertical transitions differential electron densities maps are visualized for the largest contribution of the corresponding transitions. By visual inspection, all transitions were assigned as summarized in Table S3. Transition 3 showed a relatively high calculated oscillator strength (0.224) with an energy of 2.88 eV (430 nm) and contained a relatively high contribution of metal-to-ligand charge transfer (MLCT) character from cobalt (t\(_{2g}\)) to imidazolin-2-yldene (\(\pi^*\)) and carbazole (\(\pi^*\)) moieties.

**Figure S30.** Experimental (red trace) and simulated (blue dotted trace) UV-vis spectra of [Co(L\(_{CNC}\)\(_2\))(PF\(_6\))] complex in acetonitrile; The blue bars mark the energies of DFT-calculated vertical transitions, the heights of these bars reflect relative oscillator strengths. Same data as in Figure 4b of the main paper. The dotted blue line was simulated using a Lorentzian line shape function with a full width at half maximum of 0.15 eV.
**Table S3.** TD-DFT calculated transitions of \([\text{Co(L}^{\text{CNC}}\text{)}_2]^+\). The assignments of the individual electronic transitions were made by visual inspection of the individual difference electron densities from an initial orbital “HOMO-N” (from which the electronic transition originates) to a final orbital “LUMO+M” (where the excited electron lands); N and M are natural numbers. The HOMO is orbital number 248, the LUMO is orbital number 249. The assignment reflects the largest contribution to each transition (1-60).

| State | E/eV | nm   | f    | HOMO-N | LUMO +M | HOMO-N (isosurface = 0.04) | LUMO+M (isosurface = 0.04) | Transition (isosurface = 0.002) | Assignment |
|-------|------|------|------|--------|---------|-----------------------------|-----------------------------|-------------------------------|------------|
| 1     | 2.24 | 553.1| 0.0019| 248    | 253     | ![Image](image1)              | ![Image](image2)              | ![Image](image3)               | MLCT, MC, ILCT               |
| 2     | 2.56 | 484.4| 0.0024| 248    | 252     | ![Image](image4)              | ![Image](image5)              | ![Image](image6)               | MLCT, MC, ILCT               |
| 3     | 2.88 | 430.5| 0.224 | 248    | 249     | ![Image](image7)              | ![Image](image8)              | ![Image](image9)               | MLCT, ILCT, π→π*             |
| 4     | 2.89 | 428.1| 0.0066| 244    | 252     | ![Image](image10)             | ![Image](image11)             | ![Image](image12)              | MLCT, MC                     |
| 5     | 2.90 | 427.2| 0.0004| 248    | 250     | ![Image](image13)             | ![Image](image14)             | ![Image](image15)              | MLCT, ILCT                   |
| 6     | 2.92 | 424.9| 0.0042| 247    | 251     | ![Image](image16)             | ![Image](image17)             | ![Image](image18)              | LMCT, ILCT                   |
| 7     | 3.01 | 411.4| 0.0193| 248    | 251     | ![Image](image19)             | ![Image](image20)             | ![Image](image21)              | ILCT, MLCT, MC               |
| 8     | 3.04 | 408.3| 0     | 247    | 249     | ![Image](image22)             | ![Image](image23)             | ![Image](image24)              | ILCT                       |
| 9     | 3.04 | 407.7| 0.0349| 247    | 250     | ![Image](image25)             | ![Image](image26)             | ![Image](image27)              | ILCT                       |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 10 | 3.15 | 393.4 | 0.0039 | 247 | 251 | ILCT, MLCT |
| 11 | 3.20 | 386.7 | 0.0126 | 247 | 252 | ILCT, MC |
| 12 | 3.44 | 360.8 | 0.0005 | 244 | 253 | ILCT, MC |
| 13 | 3.48 | 356.6 | 0.021  | 247 | 253 | ILCT, MC |
| 14 | 3.63 | 341.4 | 0.0067 | 248 | 254 | ILCT, MC |
| 15 | 3.66 | 339.0 | 0.0071 | 247 | 254 | ILCT, MC, LMCT |
| 16 | 3.79 | 327.2 | 0.0155 | 247 | 254 | ILCT, MC, LMCT |
| 17 | 3.84 | 323.1 | 0.0728 | 245 | 249 | ILCT |
| 18 | 3.88 | 319.7 | 0.2581 | 247 | 254 | ILCT, LMCT |
| 19 | 3.97 | 312.3 | 0.063  | 246 | 251 | ILCT, LMCT |
| 20 | 3.97 | 311.9 | 0.0003 | 246 | 250 | ILCT |
| 21 | 3.98 | 311.6 | 0.0627 | 246 | 251 | ILCT, LMCT |
| #  | E (eV) | EF (eV) | Eg (eV) | LUMO | HOMO | State       |
|----|--------|---------|---------|------|------|-------------|
| 22 | 4.00   | 309.6   | 0.0001  | 245  | 251  | ILCT, LMCT  |
| 23 | 4.05   | 306.4   | 0.0015  | 236  | 252  | MC          |
| 24 | 4.19   | 296.1   | 0.002   | 243  | 250  | ILCT, π→π* |
| 25 | 4.20   | 295.4   | 0.001   | 248  | 255  | ILCT, MLCT  |
| 26 | 4.21   | 294.7   | 0.022   | 244  | 250  | ILCT, MLCT  |
| 27 | 4.23   | 293.2   | 0       | 246  | 252  | LMCT        |
| 28 | 4.23   | 293.1   | 0.0123  | 245  | 252  | LMCT, ILCT  |
| 29 | 4.26   | 290.7   | 0.004   | 248  | 257  | MLCT, ILCT  |
| 30 | 4.28   | 289.9   | 0.0087  | 247  | 255  | ILCT        |
| 31 | 4.30   | 288.5   | 0.0014  | 237  | 252  | MC          |
| 32 | 4.32   | 287.1   | 0.0013  | 243  | 249  | π→π*        |
| 33 | 4.33   | 286.4   | 0.0011  | 243  | 250  | π→π*        |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 34 | 4.33 | 286.1 | 0 | 245 | 253 | ILCT, LMCT |
| 35 | 4.37 | 283.9 | 0.0385 | 246 | 253 | ILCT, LMCT |
| 36 | 4.40 | 281.9 | 0 | 247 | 257 | ILCT |
| 37 | 4.40 | 281.7 | 0.057 | 243 | 251 | ILCT, LMCT |
| 38 | 4.43 | 280.0 | 0 | 244 | 251 | ILCT, MC |
| 39 | 4.46 | 278.0 | 0.0143 | 248 | 259 | \(\pi\rightarrow\pi^*\) |
| 40 | 4.47 | 277.7 | 0.0458 | 248 | 256 | ILCT, MLCT |
| 41 | 4.52 | 274.3 | 0.2598 | 247 | 256 | ILCT |
| 42 | 4.53 | 273.8 | 0.0002 | 247 | 258 | ILCT, \(\pi\rightarrow\pi^*\) |
| 43 | 4.58 | 270.5 | 0 | 243 | 252 | LMCT |
| 44 | 4.59 | 270.4 | 0.6616 | 248 | 259 | \(\pi\rightarrow\pi^*, MC\) |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 45| 4.64| 267.5| 0.0532| 247| 259| $\pi \rightarrow \pi^*$ |
| 46| 4.65| 266.6| 0.1084| 242| 249| ILCT, MLCT |
| 47| 4.66| 266.1| 0.0013| 246| 254| ILCT, LMCT |
| 48| 4.68| 264.7| 0.0029| 245| 254| $\pi \rightarrow \pi^*$, LMCT |
| 49| 4.69| 264.4| 0.0109| 240| 249| ILCT |
| 50| 4.69| 264.3| 0.0028| 241| 249| ILCT |
| 51| 4.69| 264.3| 0.0050| 241| 250| ILCT |
| 52| 4.70| 264.0| 0.0264| 240| 250| ILCT |
| 53| 4.71| 263.1| 0.0008| 242| 250| ILCT |
| 54| 4.74| 261.8| 0.0007| 240| 251| MC, $\pi \rightarrow \pi^*$ |
| 55| 4.75| 261.2| 0.0375| 243| 253| $\pi \rightarrow \pi^*$, LMCT |
Vertical transitions are arbitrarily red shifted by 2140 cm\(^{-1}\) to obtain a better match with the experimental UV-vis absorption spectrum in acetonitrile.\(^{13-16}\) \(\pi\rightarrow\pi^*\) transitions are located on the carbazole subunit or on the imidazolin-2-ylidene moieties. ILCT transitions are either from carbazole (\(\pi\)) to imidazolin-2-ylidene (\(\pi^*\)), or from imidazolin-2-ylidene (\(\pi\)) to carbazole (\(\pi^*\)). MLCT transitions are from cobalt (\(t_{2g}\)) to imidazolin-2-ylidene (\(\pi^*\)) or to carbazole (\(\pi^*\)). LMCT transitions are from carbazole (\(\pi\)) or imidazolin-2-ylidene (\(\pi\)) to cobalt (\(e_g^*\)). MC transitions are from cobalt (\(t_{2g}\)) to cobalt (\(e_g^*\)).

**Table S4.** Fragment contributions (%) for selected ground state molecular orbitals (MOs) of [Co(L\(^{\text{CNC}}\)\(_\text{CNC}\)]\(^+\) using the Hirshfeld atomic population method (only fragments >1% were considered).

| MO       | Co | N\(_{\text{carbazole}}\) | C\(_{\text{carbazole}}\) | C\(_{\text{carbene}}\) | N\(_{\text{imidazolidene}}\) | C\(_{\text{imidazolidene}}\) |
|----------|----|----------------|----------------|----------------|----------------|----------------|
| LUMO+1   | 0  | 0             | 67             | 12             | 0              | 4              |
| LUMO     | 0  | 0             | 68             | 10             | 0              | 8              |
| HOMO     | 7  | 22            | 58             | 0              | 0              | 0              |
| HOMO-1   | 0  | 24            | 58             | 4              | 0              | 0              |

Based on the data in Table S4, the HOMO has a metal contribution of 7%, whereas the two \(\text{N-amido}\) atoms contribute with 22% to the HOMO. In the LUMO, the four weakly \(\pi\)-accepting imidazolidene (NHC) units contribute with 18%. Based
on this data (illustrated by Figure 4d in the main paper) it seems that the MLCT character of the lowest energy transition is in fact limited. However, the experimental data clearly signals a metal-centered primary oxidation event and a ligand-based primary reduction process (Figure 3a, Figures S18a/b and associated discussion above). Aside from the cyclic voltammetry and spectro-electrochemistry data, femtosecond transient absorption spectroscopy supports the assignment of the lowest excited state as an electronic transition with substantial MLCT character (Figure 6).

**Figure S31.** Calculated Kohn-Sham energy level diagram and electron density distribution of the HOMO, HOMO-1 and LUMO of [Co(L\text{CNC})\textsubscript{2}]\textsuperscript{+} based on DFT calculations.

| State | E/eV  | nm    | f     | Transition                        |
|-------|-------|-------|-------|-----------------------------------|
| 3     | 2.88  | 430.5 | 0.224 | 247 $\rightarrow$ 250 (32.7)  
248 $\rightarrow$ 249 (60.4) |
| 7     | 2.92  | 424.9 | 0.0193| 236 $\rightarrow$ 252 (14.8)  
247 $\rightarrow$ 252 (37.4)  
248 $\rightarrow$ 251 (50.2)  
248 $\rightarrow$ 253 (22.4) |
| 9     | 3.04  | 407.7 | 0.039 | 247 $\rightarrow$ 250 (61.6)  
248 $\rightarrow$ 249 (33.7) |
Table S6. Highest occupied natural transition orbitals (HONTO) and lowest unoccupied natural transition orbitals (LUNTO) with oscillation strengths greater than 0.03 and energies lower than 3.5 eV. All contributions larger than 20 % were considered.

| Transition | HONTO (isosurface = 0.04) | LUNTO (isosurface = 0.04) | HOMTO-1 (isosurface = 0.04) | LUNTO+1 (isosurface = 0.04) |
|------------|---------------------------|---------------------------|-----------------------------|-----------------------------|
| 3          | ![Image](image1.png)      | ![Image](image2.png)      | ![Image](image3.png)        | ![Image](image4.png)        |
|            | 73.3 %                    | 21.6 %                    |                             |                             |
| 7          | ![Image](image5.png)      | ![Image](image6.png)      | ![Image](image7.png)        | ![Image](image8.png)        |
|            | 61.3 %                    | 35.1 %                    |                             |                             |
| 9          | ![Image](image9.png)      | ![Image](image10.png)     | ![Image](image11.png)       | ![Image](image12.png)       |
|            | 76.4 %                    | 23.3 %                    |                             |                             |
Table S7. Cartesian coordinates of the DKT-KS calculated ground state geometry of the cobalt(III) complex.

| Atom | X-coordinates | Y-coordinates | Z-coordinates |
|------|---------------|---------------|---------------|
| Co   | 0.000000000000 | 0.000000000000 | 0.003556000000 |
| N    | -1.937476000000 | 0.004543000000 | 0.003321000000 |
| N    | 0.886372000000 | -1.891810000000 | -2.283057000000 |
| N    | -1.068680000000 | 2.389835000000 | 1.541143000000 |
| N    | -1.079789000000 | -2.386144000000 | -1.533738000000 |
| N    | 0.895792000000 | 1.886891000000 | 2.289994000000 |
| C    | -0.061288000000 | -1.470767000000 | -1.397010000000 |
| C    | -4.140281000000 | -0.664688000000 | 0.261904000000 |
| C    | -2.757331000000 | 2.006422000000 | 0.443395000000 |
| C    | -2.408897000000 | 2.213358000000 | 1.066377000000 |
| C    | -2.419030000000 | -2.200402000000 | -1.058230000000 |
| C    | -4.786844000000 | 2.870570000000 | 1.104511000000 |
| C    | -4.803907000000 | -2.847802000000 | -1.090801000000 |
| C    | -3.434072000000 | -3.119728000000 | -1.337350000000 |
| H    | -3.176605000000 | -4.076678000000 | -1.788896000000 |
| C    | 2.125620000000 | 1.207492000000 | 2.693406000000 |
| H    | 1.984023000000 | 0.124251000000 | 2.672791000000 |
| H    | 2.355699000000 | 1.511428000000 | 3.723146000000 |
| H    | 2.968753000000 | 1.475459000000 | 2.044453000000 |
| C    | -0.716918000000 | 3.381067000000 | 2.051260000000 |
| H    | -1.370337000000 | 4.201860000000 | 2.719385000000 |
| C    | -0.054269000000 | 1.470285000000 | 1.404112000000 |
| C    | 0.498365000000 | -3.065960000000 | -2.909069000000 |
| H    | 1.125043000000 | -3.566028000000 | -3.641887000000 |
| C    | -0.732993000000 | -3.378715000000 | -2.444250000000 |
| H    | -1.390338000000 | -4.196194000000 | -2.712984000000 |
| C    | -3.420179000000 | 3.137489000000 | 1.349074000000 |
| H    | -3.152630000000 | 4.089608000000 | 1.799035000000 |
| C    | -5.852688000000 | -3.931014000000 | -1.419522000000 |
C    -5.133443000000      1.610236000000      0.596138000000
H    -6.182178000000      1.346351000000      0.444346000000
C    -5.145211000000     -1.589111000000     -0.585240000000
H    -6.188404000000     -1.315313000000     -0.429587000000
C     2.119691000000     -1.218554000000     -2.686184000000
H     1.983323000000     -0.134671000000     -2.665840000000
H     2.348642000000     -1.523856000000     -3.715767000000
H     2.961098000000     -1.490625000000     -2.036764000000
C     0.513245000000      3.062431000000      2.915799000000
H     1.142412000000      3.560320000000      3.648206000000
C    -5.890153000000      3.907034000000      1.409975000000
C    -5.321801000000      5.220803000000      1.976990000000
H    -4.797593000000      5.066262000000      2.933596000000
H    -6.142383000000      5.929159000000      2.167847000000
H    -4.626857000000      5.708127000000      1.274631000000
C    -5.567408000000     -5.196161000000     -0.577102000000
H    -4.570267000000     -5.615417000000     -0.783925000000
H    -6.307749000000     -5.981875000000     -0.798392000000
H    -5.620797000000     -4.974023000000      0.500602000000
C    -7.283994000000     -3.459316000000     -1.105667000000
H    -7.410830000000     -3.210095000000     -0.040623000000
H    -8.000705000000     -4.260206000000     -1.343822000000
H    -7.567407000000     -2.577822000000     -1.701627000000
C    -5.785125000000     -4.288917000000     -2.922656000000
C    -5.985169000000     -3.405337000000     -3.549271000000
H    -6.535715000000     -5.057013000000     -3.169442000000
H    -5.807890000000     -4.689456000000     -3.211403000000
C    -6.876367000000      3.323395000000      2.448221000000
H    -7.361983000000      2.404858000000      2.085349000000
H    -7.672861000000      4.050767000000      2.674015000000
H    -6.361173000000      3.080472000000      3.391242000000
C    -6.654022000000      4.238111000000      0.106567000000
H    -5.977775000000      4.665566000000     -0.651024000000
H    -7.451690000000      4.972923000000      0.302458000000
H    -7.125806000000      3.345046000000     -0.330872000000
N    1.937476000000     -0.004543000000      0.003321000000
N  -0.886372000000  1.891810000000  -2.283057000000
N   1.068680000000  -2.389835000000   1.541143000000
N  -0.895792000000  -1.886891000000   2.289994000000
C   0.061288000000  1.470767000000  -1.397010000000
C   4.140281000000  0.664688000000  -0.261904000000
C   2.757331000000 -1.006422000000   0.443395000000
C   4.138175000000  -0.682339000000   0.268873000000
C   2.763509000000   0.992685000000  -0.436041000000
C   2.408897000000  -2.213358000000   1.066377000000
C   2.419030000000  -2.043020000000  -1.058523000000
C   4.786844000000 -2.870570000000   1.104511000000
C   4.803907000000  2.847802000000  -1.090801000000
C   3.434072000000  3.119728000000  -1.337335000000
H   3.176605000000  4.076678000000  -1.788869000000
C  -2.125620000000 -1.207492000000   2.693406000000
H  -1.984023000000 -0.124251000000   2.672791000000
H  -2.355699000000  -1.511428000000   3.723146000000
H  -2.968753000000  -1.475459000000   2.044453000000
C   0.716918000000  -3.381067000000   2.451126000000
H   1.370337000000  -4.201860000000   2.719358000000
C   0.054269000000  -1.470285000000   1.404112000000
C  -0.498365000000  3.065596000000  -2.909069000000
H  -1.125043000000  3.566028000000  -3.641888000000
C   0.732993000000  3.378715000000  -2.444250000000
H   1.390338000000  4.196194000000  -2.712985000000
C   3.420179000000  -3.137489000000   1.349074000000
H   3.152063000000  -4.089608000000   1.799035000000
C   5.852688000000  3.931015000000  -1.419522000000
C   5.133443000000 -1.610236000000   0.596138000000
H   6.182178000000  -1.346351000000   0.444346000000
C   5.145211000000  1.589111000000  -0.585240000000
H   6.188404000000  1.315313000000  -0.429587000000
C  -2.119691000000  1.218554000000  -2.686184000000
H  -1.983323000000   0.134671000000  -2.665841000000
H  -2.348643000000   1.523856000000  -3.715767000000
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -2.961  | 1.4906  | -2.0367 |
| C    | -0.5132 | -3.0624 | 2.9158  |
| H    | -1.1424 | -5.2208 | 1.9769  |
| C    | 5.8901  | -3.9070 | 1.4099  |
| C    | 5.3218  | -5.2208 | 1.9769  |
| H    | 4.7975  | -5.0662 | 2.9335  |
| H    | 6.1424  | -5.9291 | 2.1678  |
| H    | 4.6269  | -5.7081 | 1.2746  |
| C    | 5.5674  | 5.1961  | -0.5771 |
| H    | 4.5703  | 5.6154  | -0.7839 |
| H    | 6.3077  | 5.9819  | -0.7982 |
| H    | 5.6208  | 4.9740  | 0.5006  |
| C    | 7.2839  | 3.4593  | -1.1056 |
| H    | 7.4108  | 3.2101  | -0.0406 |
| H    | 8.0007  | 4.2602  | -1.3438 |
| H    | 7.5674  | 2.5778  | -1.7016 |
| C    | 5.7851  | 4.2889  | -2.9227 |
| H    | 5.9852  | 3.4053  | -3.5492 |
| H    | 6.5357  | 5.0570  | -3.1694 |
| H    | 4.8008  | 4.6894  | -3.2114 |
| C    | 6.8764  | -3.3234 | 2.4482  |
| H    | 7.3619  | -2.4048 | 2.0854  |
| H    | 7.6728  | -4.0507 | 2.6740  |
| H    | 6.3611  | -3.0804 | 3.3912  |
| C    | 6.6540  | -4.2381 | 0.1066  |
| H    | 5.9778  | -4.6656 | -0.6510 |
| H    | 7.4516  | -4.9729 | 0.3025  |
| H    | 7.1258  | -3.3450 | -0.3308 |
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