

Electronic Supplementary Information (ESI) for Chemical Communication

The long-sought seventeen-electron radical $[(C_6Me_6)Cr(CO)_3]^+$: isolation, crystal structure and substitution reaction

Wenqing Wang,^a Xingyong Wang,^a Zaichao Zhang,^b Ningning Yuan,^a
and Xinping Wang^{a,*}

^aState Key Laboratory of Coordination Chemistry, School of Chemistry and
Chemical Engineering, Collaborative Innovation Center of Advanced
Microstructures, Nanjing University, Nanjing 210093, China. ^bSchool of
Chemistry and Chemical Engineering, Huaiyin Normal University, Huai'an 223300,
China.

*Corresponding authors: xpwang@nju.edu.cn

Experimental Section

General Procedures

All experiments were carried out under a nitrogen atmosphere by using standard Schlenk techniques and a glovebox. Solvents were dried prior to use. $(C_6Me_6)Cr(CO)_3$,¹ $(C_6Me_6)Cr(CO)_2PPh_3$,¹ $Ag[Al(OR_{Me})_4]_2$ ($OR_{Me} = OC(CF_3)_2Me$) and $Ag[Al(OR_F)_4]_2$ ($OR_F = OC(CF_3)_3$) were synthesized according to the literature methods. PPh_3 (Alfa Aesar) was purchased and used upon arrival. EPR spectra were obtained using Bruker EMX plus-6/1 variable-temperature apparatus. Infrared spectra were collected on on VECTOR22 FT-IR spectrometer. Element analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences. X-ray crystal structures were obtained by using a Bruker APEX DUO CCD detector.

Synthesis of $1^+[Al(OR_{Me})_4]$. A solution of $Ag[Al(OR_{Me})_4]$ (0.26 g, 0.30 mmol) in CH_2Cl_2 was added dropwise to **1** (0.090 g, 0.30 mmol) at 25 °C while stirring. The resultant bright yellow solution was kept stirring at 25 °C for 1d and then filtered to remove the gray precipitate (Ag metal). The filtrate was then concentrated and stored around 5 °C for 24 h to afford X-ray-quality crystals of $1^+[Al(OR_{Me})_4]$. Isolated yield: 0.12 g, 39% (crystals); FT-IR ($\nu_{C=O}$): 2062, 1989 cm^{-1} ; Mp: 124.3 °C (decomp.); elemental analysis calcd (%): C 35.48, H 2.88; found: C 35.17, H 2.83.

Synthesis of $2^+[Al(OR_F)_4]$. A solution of $Ag[Al(OR_F)_4]$ (0.32 g, 0.30 mmol) in CH_2Cl_2 was added dropwise to **2** (0.16 g, 0.30 mmol) at 25 °C while stirring. The resultant orange solution was kept stirring at 25 °C for 1d and then filtered to remove the gray precipitate (Ag metal). The filtrate was then concentrated and stored around -25 °C for 24 h to afford X-ray-quality crystals of $2^+[Al(OR_F)_4]$. Isolated yield: 0.15 g, 34% (crystals); FT-IR (ν_{CO}): 1976, 1859 cm^{-1} ; Mp: 105.6 °C (decomp.); elemental analysis calcd (%): C 38.44, H 2.22; found: C 37.72, H 2.26.

Substitution reaction. A solution of PPh_3 (0.026 g, 0.098 mmol) in CH_2Cl_2 (8 ml) was added dropwise to $1^+[Al(OR_{Me})_4]$ (0.084 g, 0.080 mmol) at 25 °C while stirring. The resultant solution was kept stirring for 1d and then concentrated to 2 ml. Addition of 20 ml hexane into the concentration afforded orange powder, which was proved to be the salt of 2^+ by FT-IR (ν_{CO} : 1975, 1859 cm^{-1}).

Computational details

All the geometry optimizations were performed with the PBE0 functional. LanL2DZ ECP was applied for Cr atom and basis set 6-31G(d) for the rest of the atoms. Frequency calculations were carried out to confirm that all optimized geometries correspond to energy minima. All calculations were performed with the Gaussian 09 program suite.

References:

- 1 J. A. Chudek, G. Hunter, R. L. Mackay, P. Kremminger, K. Schlögl, W. Weissensteiner, *J. Chem. Soc., Dalton Trans.* **1990**, 2001.
- 2 I. Krossing, *Chem. –Eur. J.* **2001**, *7*, 490.

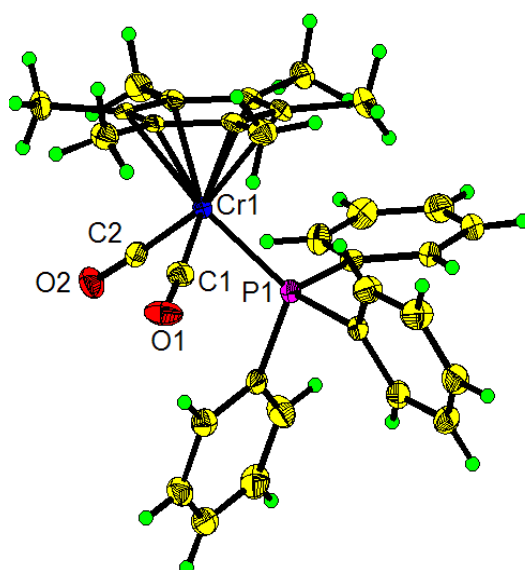


Fig. S1 Thermal ellipsoid (50%) drawing of 2. Yellow C, green H, red O, blue Cr and purple P. Selected bond distances (Å) and angles (deg): Cr1–C1 1.804(5), Cr1–C2 1.812(4), Cr1–P1 2.2988(17), C1–O1 1.174(6), C2–O2 1.170(5), Cr1–centroid 1.743(5), Cr1–C1–O1 174.9(4), Cr1–C2–O2 177.7(4), C1–Cr1–C2 89.42(19), C1–Cr1–P1 88.11(16), C2–Cr1–P1 87.30(15).

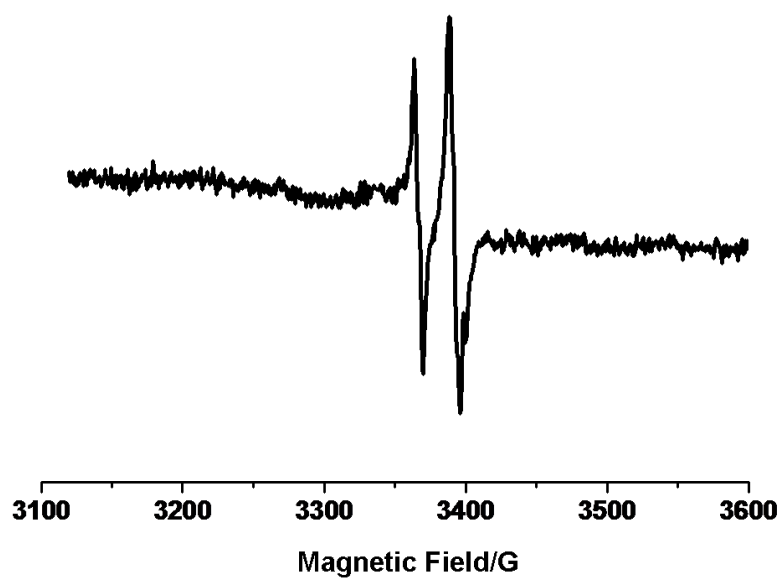


Fig. S2 Experimental EPR spectrum of 1×10^{-2} M solution of $2^+[\text{Al}(\text{OR}_F)_4]^-$ in CH_2Cl_2 at 298 K.

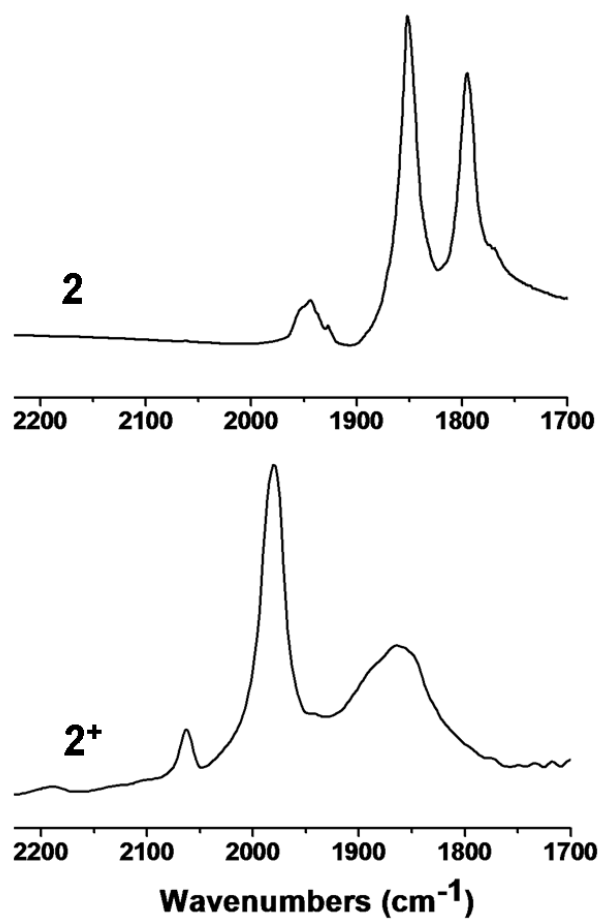


Fig. S3 Solid IR spectra of **2** (top) and **2⁺** (bottom) at 298K.

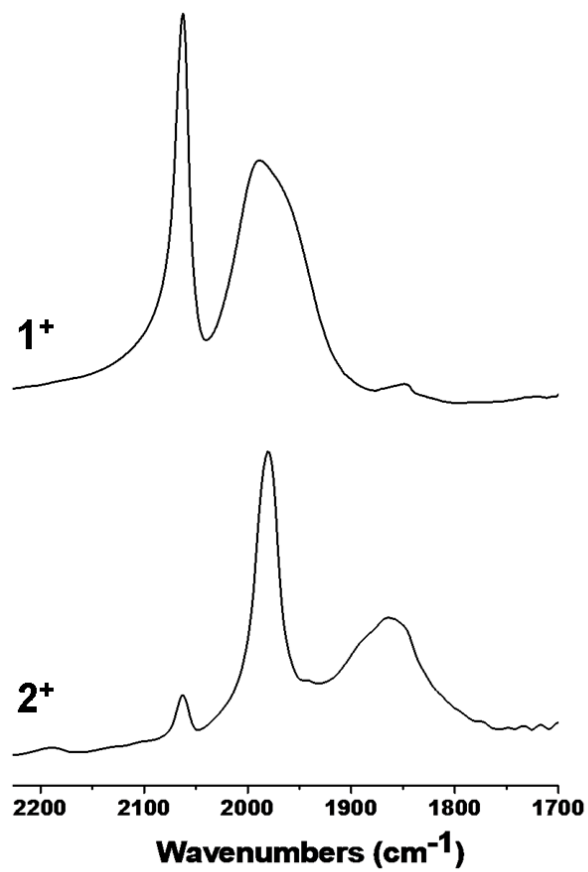


Fig.S4 Solid IR spectra of **1⁺** (top) and **2⁺** (bottom) at 298K.

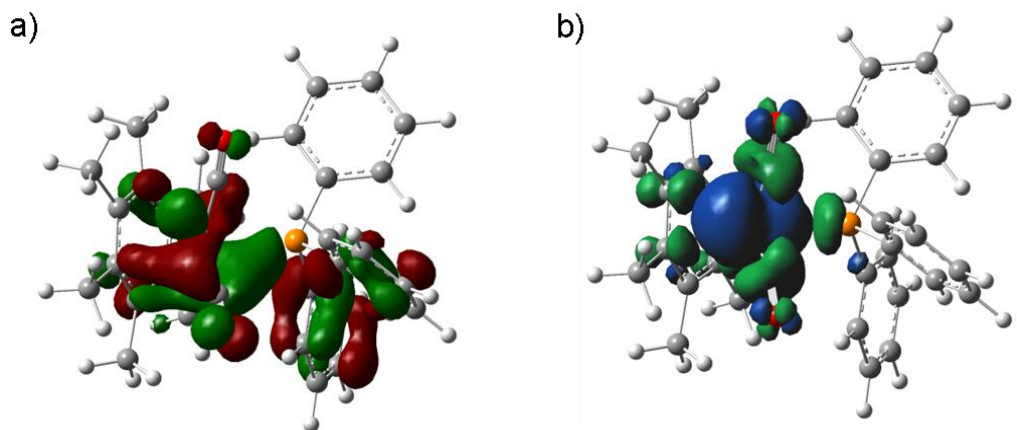


Fig. S5 SOMO (a) and spin density map (b) of 2^+ calculated at the level of UPBE0/6-31G(d)/LanL2DZ.

Coordinates for calculated geometries

1:

| | | | |
|----|--------------|--------------|--------------|
| Cr | -0.000425000 | -0.000134000 | 0.618824000 |
| O | 2.396937000 | -0.586545000 | 2.278031000 |
| O | -0.693120000 | 2.369544000 | 2.277175000 |
| O | -1.708961000 | -1.781807000 | 2.277851000 |
| C | -0.995116000 | 1.018444000 | -1.101770000 |
| C | -1.381517000 | -0.341622000 | -1.079491000 |
| C | -0.383141000 | -1.371774000 | -1.101253000 |
| C | 0.987974000 | -1.026474000 | -1.077783000 |
| C | 1.380877000 | 0.353198000 | -1.100874000 |
| C | 0.396240000 | 1.367886000 | -1.078048000 |
| C | 1.438162000 | -0.358901000 | 1.663840000 |
| C | -0.410166000 | 1.425394000 | 1.663334000 |
| C | -1.031612000 | -1.066268000 | 1.663469000 |
| C | -2.020741000 | 2.121861000 | -1.179658000 |
| C | -2.836856000 | -0.730380000 | -1.048518000 |
| C | -0.826065000 | -2.811726000 | -1.178969000 |
| C | 2.051490000 | -2.093165000 | -1.042098000 |
| C | 2.849250000 | 0.690374000 | -1.178734000 |
| C | 0.787660000 | 2.822444000 | -1.043761000 |
| H | -1.735115000 | 2.848136000 | -1.947803000 |
| H | -2.118835000 | 2.664088000 | -0.232479000 |
| H | -3.006309000 | 1.741840000 | -1.449714000 |
| H | -3.251960000 | -0.794966000 | -2.063518000 |
| H | -2.979329000 | -1.700600000 | -0.569588000 |
| H | -3.432656000 | -0.011490000 | -0.483568000 |
| H | -0.001989000 | -3.476763000 | -1.438290000 |
| H | -1.256677000 | -3.164753000 | -0.235199000 |
| H | -1.589998000 | -2.929052000 | -1.954727000 |
| H | 2.312601000 | -2.428096000 | -2.055191000 |
| H | 2.964261000 | -1.729324000 | -0.567361000 |

| | | | |
|---|-------------|--------------|--------------|
| H | 1.726227000 | -2.963809000 | -0.470145000 |
| H | 3.011995000 | 1.734398000 | -1.447484000 |
| H | 3.335402000 | 0.081374000 | -1.948054000 |
| H | 3.368409000 | 0.503405000 | -0.232027000 |
| H | 0.939485000 | 3.216904000 | -2.057722000 |
| H | 0.018971000 | 3.429955000 | -0.563172000 |
| H | 1.708242000 | 2.976685000 | -0.478307000 |

1⁺:

| | | | |
|----|--------------|--------------|--------------|
| C | 0.715765000 | -0.834527000 | -1.378583000 |
| C | 1.433421000 | 0.355102000 | -1.115300000 |
| C | -0.721619000 | -0.817961000 | -1.401006000 |
| C | 1.448445000 | -2.104517000 | -1.718931000 |
| Cr | -0.006489000 | -0.105528000 | 0.651741000 |
| C | -1.419455000 | 0.376464000 | -1.100184000 |
| C | -1.454119000 | -2.058709000 | -1.840134000 |
| C | -0.694129000 | 1.547814000 | -0.720223000 |
| C | -2.922431000 | 0.407362000 | -1.155414000 |
| C | 0.730784000 | 1.523709000 | -0.689410000 |
| C | -1.448325000 | 2.818616000 | -0.424053000 |
| C | 1.507592000 | 2.745308000 | -0.273384000 |
| C | 2.931048000 | 0.396445000 | -1.255378000 |
| H | 1.700740000 | -2.125548000 | -2.787086000 |
| H | 0.846990000 | -2.989837000 | -1.509508000 |
| H | 2.377146000 | -2.199587000 | -1.153375000 |
| H | -1.059582000 | -2.398011000 | -2.803939000 |
| H | -2.520586000 | -1.883065000 | -1.971445000 |
| H | -1.339254000 | -2.886611000 | -1.133035000 |
| H | -3.259550000 | 0.435162000 | -2.199216000 |
| H | -3.337162000 | 1.281342000 | -0.654761000 |
| H | -3.363634000 | -0.477077000 | -0.689804000 |

| | | | |
|---|--------------|--------------|--------------|
| H | -2.087981000 | 3.074963000 | -1.275396000 |
| H | -0.782525000 | 3.664094000 | -0.259309000 |
| H | -2.093965000 | 2.728233000 | 0.455697000 |
| H | 1.572437000 | 3.463173000 | -1.100919000 |
| H | 2.525474000 | 2.494899000 | 0.027297000 |
| H | 1.039469000 | 3.255321000 | 0.5711178000 |
| H | 3.236738000 | 1.330136000 | -1.735771000 |
| H | 3.299064000 | -0.421722000 | -1.874389000 |
| H | 3.445438000 | 0.341780000 | -0.288764000 |
| C | 1.413181000 | 0.093832000 | 1.870405000 |
| O | 2.303222000 | 0.218668000 | 2.576953000 |
| C | -0.015047000 | -1.883792000 | 1.225119000 |
| O | -0.024614000 | -2.980240000 | 1.555613000 |
| C | -1.439619000 | 0.103496000 | 1.853095000 |
| O | -2.333166000 | 0.240721000 | 2.552566000 |

2:

| | | | |
|----|--------------|--------------|--------------|
| Cr | 1.333625000 | -0.173844000 | 0.417213000 |
| P | -0.938686000 | -0.050080000 | 0.062494000 |
| C | -1.796226000 | -1.396425000 | -0.878270000 |
| C | 2.040667000 | 1.205832000 | -1.295386000 |
| C | -1.243138000 | 2.704286000 | -0.161796000 |
| H | -0.781226000 | 2.704848000 | 0.823223000 |
| C | 3.380993000 | -0.876681000 | 0.101013000 |
| C | 3.441136000 | 0.453602000 | 0.586956000 |
| C | -2.037862000 | -0.008004000 | 1.559390000 |
| C | 1.063095000 | 0.688290000 | 1.979654000 |
| C | 2.744405000 | 1.493266000 | -0.107664000 |
| C | -1.503072000 | 1.481584000 | -0.799668000 |
| C | 4.287921000 | 0.813296000 | 1.782376000 |
| H | 4.936201000 | -0.009646000 | 2.083944000 |

| | | | |
|---|--------------|--------------|--------------|
| H | 3.680782000 | 1.093408000 | 2.650535000 |
| H | 4.936961000 | 1.663479000 | 1.544094000 |
| C | -2.084320000 | 1.501755000 | -2.070463000 |
| H | -2.295862000 | 0.568684000 | -2.585007000 |
| C | 1.109490000 | -1.760164000 | 1.231230000 |
| C | -2.401289000 | 2.713311000 | -2.688334000 |
| H | -2.849835000 | 2.709024000 | -3.678551000 |
| C | 2.803401000 | 2.898409000 | 0.434668000 |
| H | 3.644259000 | 3.456450000 | 0.000499000 |
| H | 2.928484000 | 2.900425000 | 1.518950000 |
| H | 1.885726000 | 3.449743000 | 0.220641000 |
| C | 2.711444000 | -2.581385000 | -1.643386000 |
| H | 2.186468000 | -2.679296000 | -2.593557000 |
| H | 2.283703000 | -3.311498000 | -0.947206000 |
| H | 3.753131000 | -2.875163000 | -1.820636000 |
| C | 2.657543000 | -1.174914000 | -1.101386000 |
| C | -1.757329000 | -0.860208000 | 2.634197000 |
| H | -0.886672000 | -1.505530000 | 2.606092000 |
| C | -2.587485000 | -0.895913000 | 3.750475000 |
| H | -2.347775000 | -1.564397000 | 4.573098000 |
| C | 1.946332000 | -0.147324000 | -1.761989000 |
| C | 4.136633000 | -1.971140000 | 0.810717000 |
| H | 5.199587000 | -1.953548000 | 0.534395000 |
| H | 3.747456000 | -2.960006000 | 0.567487000 |
| H | 4.065774000 | -1.866792000 | 1.895395000 |
| C | 1.514179000 | 2.309001000 | -2.176152000 |
| H | 1.757565000 | 3.296917000 | -1.786109000 |
| H | 0.432270000 | 2.270079000 | -2.321714000 |
| H | 1.979734000 | 2.229182000 | -3.166848000 |
| C | -3.030432000 | -3.523393000 | -2.228981000 |
| H | -3.510214000 | -4.347389000 | -2.750686000 |
| C | -3.791168000 | -2.446876000 | -1.773817000 |

| | | | |
|---|--------------|--------------|--------------|
| H | -4.865712000 | -2.431575000 | -1.936988000 |
| C | -1.658903000 | -3.544572000 | -1.998866000 |
| H | -1.061351000 | -4.388257000 | -2.334811000 |
| C | -1.049007000 | -2.487073000 | -1.325943000 |
| H | 0.017782000 | -2.505138000 | -1.123886000 |
| C | -2.151026000 | 3.918175000 | -2.040668000 |
| H | -2.403374000 | 4.860092000 | -2.520260000 |
| C | -3.180576000 | -1.396108000 | -1.097664000 |
| H | -3.786869000 | -0.573687000 | -0.727227000 |
| C | -1.573036000 | 3.909420000 | -0.770733000 |
| H | -1.375545000 | 4.845740000 | -0.254954000 |
| C | 1.199668000 | -0.399131000 | -3.046499000 |
| H | 1.859334000 | -0.255256000 | -3.913834000 |
| H | 0.360513000 | 0.290839000 | -3.155539000 |
| H | 0.785890000 | -1.405900000 | -3.103752000 |
| C | -3.174943000 | 0.805552000 | 1.635799000 |
| H | -3.417648000 | 1.480474000 | 0.820654000 |
| C | -4.002331000 | 0.773091000 | 2.755866000 |
| H | -4.876346000 | 1.418341000 | 2.795806000 |
| C | -3.711475000 | -0.077503000 | 3.817648000 |
| H | -4.355361000 | -0.101298000 | 4.692908000 |
| O | 1.007222000 | 1.276994000 | 2.986354000 |
| O | 1.070992000 | -2.816020000 | 1.734820000 |

2⁺:

| | | | |
|---|-------------|--------------|-------------|
| C | 2.123504000 | -0.463744000 | 1.491619000 |
| C | 3.214878000 | -1.323372000 | 1.315118000 |
| C | 1.883862000 | 0.077816000 | 2.761138000 |
| P | 1.063562000 | 0.038841000 | 0.078856000 |
| C | 4.040864000 | -1.640421000 | 2.390499000 |
| H | 3.423947000 | -1.752665000 | 0.340270000 |

| | | | |
|----|--------------|--------------|--------------|
| C | 3.791744000 | -1.102253000 | 3.649265000 |
| H | 4.882067000 | -2.310882000 | 2.239696000 |
| C | 2.713544000 | -0.239913000 | 3.831049000 |
| H | 4.436371000 | -1.352718000 | 4.486712000 |
| H | 2.514280000 | 0.187624000 | 4.809347000 |
| H | 1.053676000 | 0.756200000 | 2.926067000 |
| C | 1.485077000 | -1.167022000 | -1.232680000 |
| C | 1.990408000 | -0.768477000 | -2.474557000 |
| C | 1.276179000 | -2.531401000 | -0.983414000 |
| C | 2.276423000 | -1.720666000 | -3.453027000 |
| H | 2.179266000 | 0.282329000 | -2.675445000 |
| C | 2.076910000 | -3.073505000 | -3.194849000 |
| H | 2.670705000 | -1.400938000 | -4.413437000 |
| C | 1.582797000 | -3.477908000 | -1.954623000 |
| H | 2.312775000 | -3.813496000 | -3.954104000 |
| H | 1.437501000 | -4.533689000 | -1.743287000 |
| H | 0.892900000 | -2.856690000 | -0.019048000 |
| C | 1.823644000 | 1.610123000 | -0.475658000 |
| C | 1.018760000 | 2.677773000 | -0.879945000 |
| C | 3.217589000 | 1.754961000 | -0.503014000 |
| C | 3.787328000 | 2.945847000 | -0.938874000 |
| H | 3.857294000 | 0.941026000 | -0.173452000 |
| C | 2.975964000 | 4.004269000 | -1.345891000 |
| H | 4.868214000 | 3.051402000 | -0.953340000 |
| C | 1.591277000 | 3.870309000 | -1.315375000 |
| H | 3.424990000 | 4.935468000 | -1.679088000 |
| H | 0.956341000 | 4.696900000 | -1.621735000 |
| H | -0.061535000 | 2.574280000 | -0.842990000 |
| C | -0.888929000 | -1.306897000 | 1.687908000 |
| O | -0.731290000 | -2.224920000 | 2.366990000 |
| Cr | -1.328486000 | 0.062980000 | 0.525868000 |
| C | -0.906303000 | 1.552349000 | 1.539144000 |

| | | | |
|---|--------------|--------------|--------------|
| O | -0.749064000 | 2.531016000 | 2.127784000 |
| C | -2.188803000 | -0.895685000 | -1.414272000 |
| C | -2.917555000 | -1.429708000 | -0.332110000 |
| C | -2.115078000 | 0.533595000 | -1.602079000 |
| C | -1.631966000 | -1.811476000 | -2.469551000 |
| C | -3.444657000 | -0.554601000 | 0.671076000 |
| C | -3.167067000 | -2.909370000 | -0.211215000 |
| C | -3.385778000 | 0.852034000 | 0.478756000 |
| C | -4.128920000 | -1.143316000 | 1.877418000 |
| C | -2.780569000 | 1.396955000 | -0.706395000 |
| C | -4.064906000 | 1.790198000 | 1.441247000 |
| C | -2.911828000 | 2.877917000 | -0.944302000 |
| C | -1.423967000 | 1.044309000 | -2.838836000 |
| H | -2.408688000 | -2.025144000 | -3.216703000 |
| H | -1.291752000 | -2.759827000 | -2.054748000 |
| H | -0.782263000 | -1.377545000 | -2.994779000 |
| H | -4.199239000 | -3.090680000 | 0.101622000 |
| H | -2.513569000 | -3.380687000 | 0.532285000 |
| H | -3.021626000 | -3.424669000 | -1.160069000 |
| H | -5.211648000 | -1.209908000 | 1.710686000 |
| H | -3.972339000 | -0.541327000 | 2.773788000 |
| H | -3.763756000 | -2.146618000 | 2.100916000 |
| H | -5.089130000 | 1.990220000 | 1.100574000 |
| H | -3.550440000 | 2.749635000 | 1.517569000 |
| H | -4.135160000 | 1.377530000 | 2.447345000 |
| H | -3.957703000 | 3.178438000 | -0.823036000 |
| H | -2.611237000 | 3.170480000 | -1.948907000 |
| H | -2.325519000 | 3.467576000 | -0.230208000 |
| H | -1.990674000 | 0.750482000 | -3.731044000 |
| H | -0.419575000 | 0.625465000 | -2.941088000 |
| H | -1.317966000 | 2.127189000 | -2.853636000 |