Electronic Supplementary Information

Spectroscopic characterization of carbon monoxide activation by neutral chromium carbides

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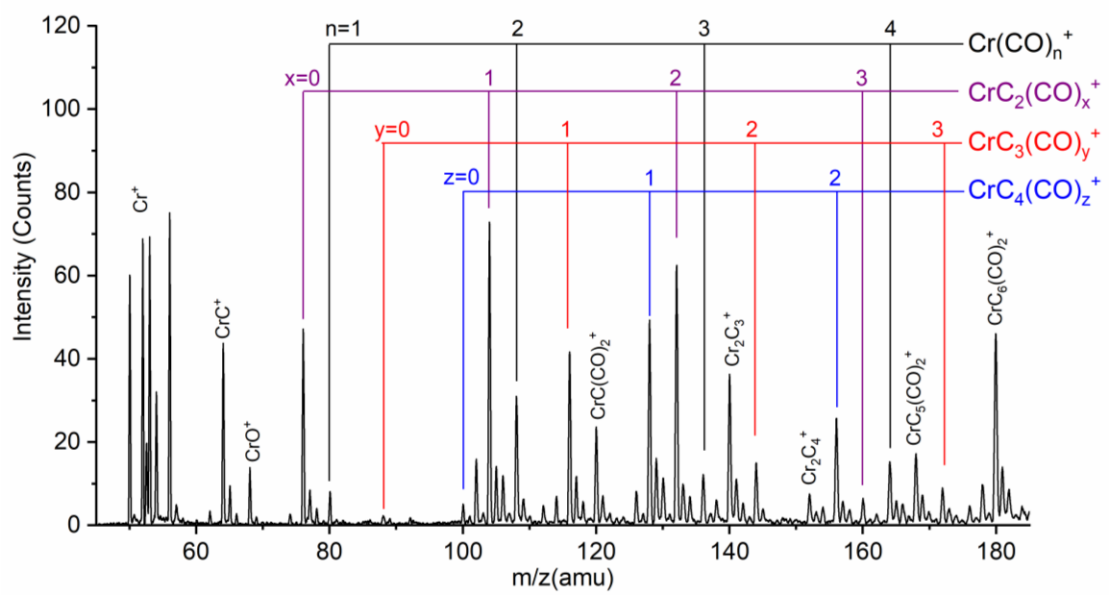


Figure S1. Time-of-flight mass spectrum of the species formed by the reaction between CO and chromium metal.

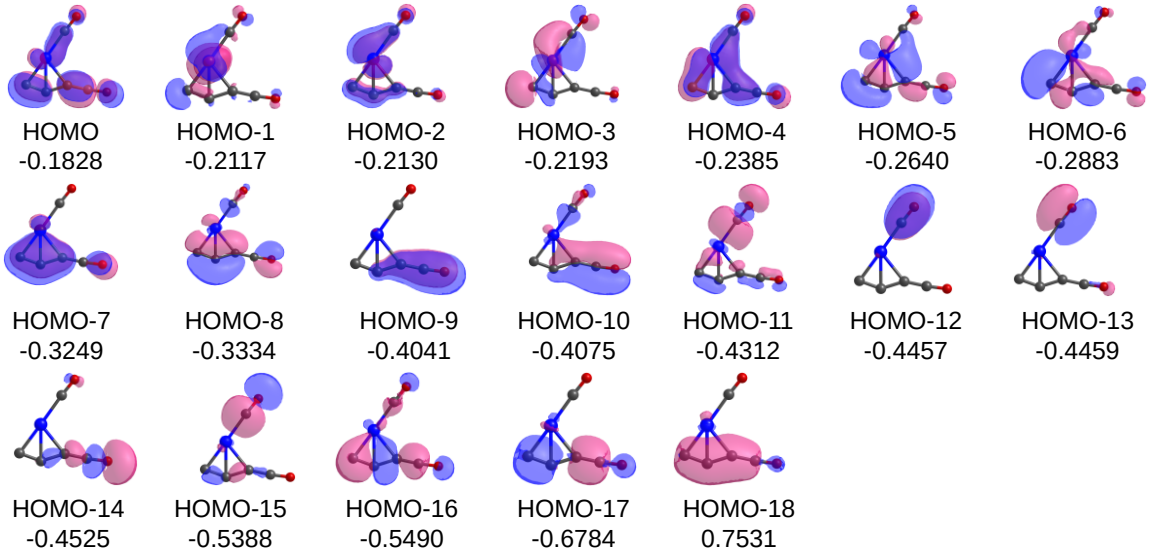


Figure S2. Kohn−Sham α-orbitals of $CrC_3(CO)_2$-I (3A). The isovalue of the orbital is set to 0.03. Relative energies are listed in Hartree.

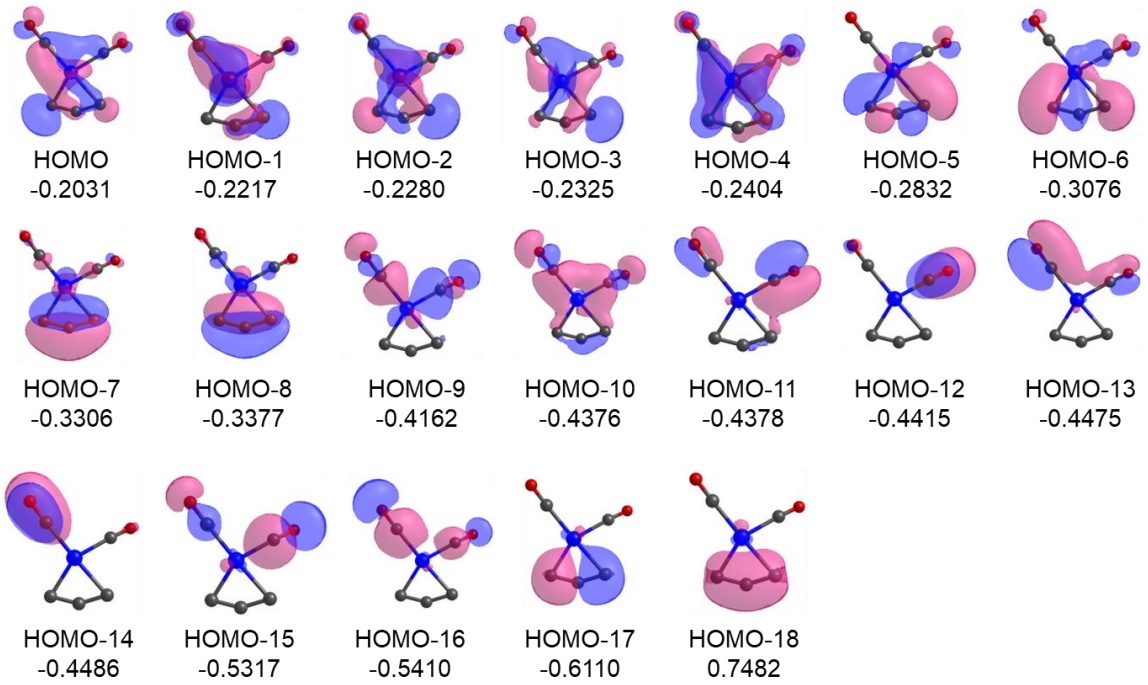


Figure S3. Kohn−Sham α-orbitals of $CrC_3(CO)_2$-II (3B). The isovalue of the orbital is set to 0.03. Relative energies are listed in Hartree.

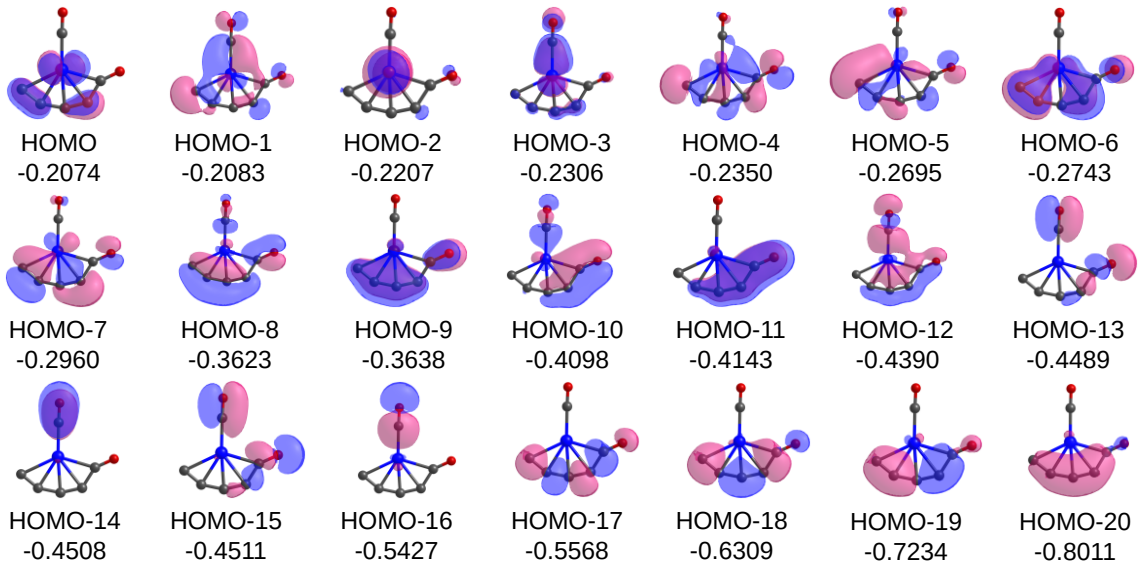


Figure S4. Kohn−Sham α-orbitals of $CrC_4(CO)_2$-I (4A). The isovalue of the orbital is set to 0.03. Relative energies are listed in Hartree.

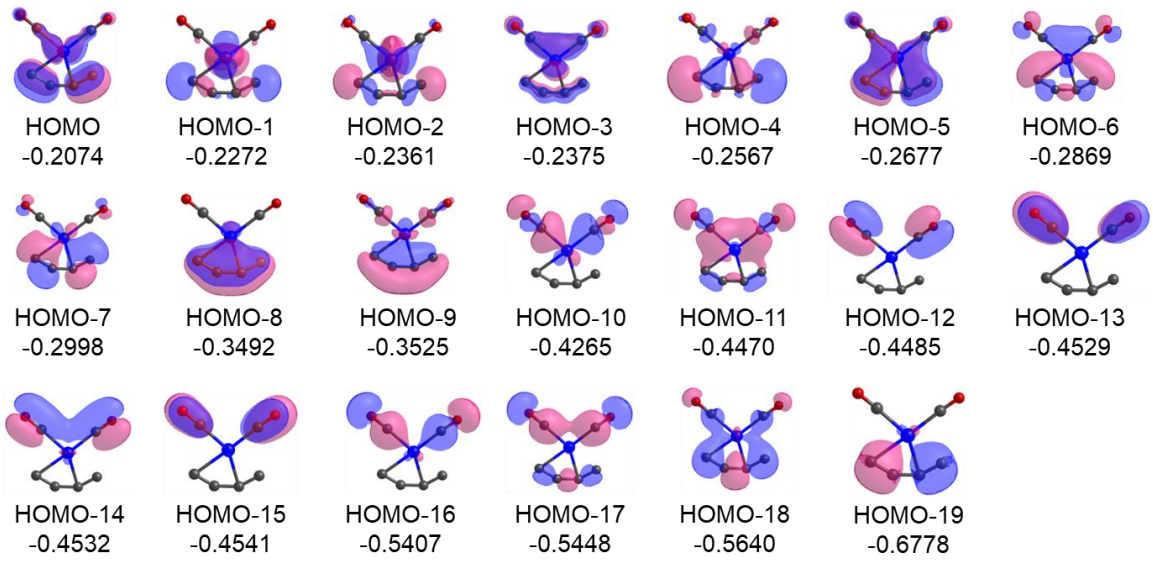


Figure S5. Kohn−Sham α-orbitals of $CrC_4(CO)_2$-II (4B). The isovalue of the orbital is set to 0.03. Relative energies are listed in Hartree.

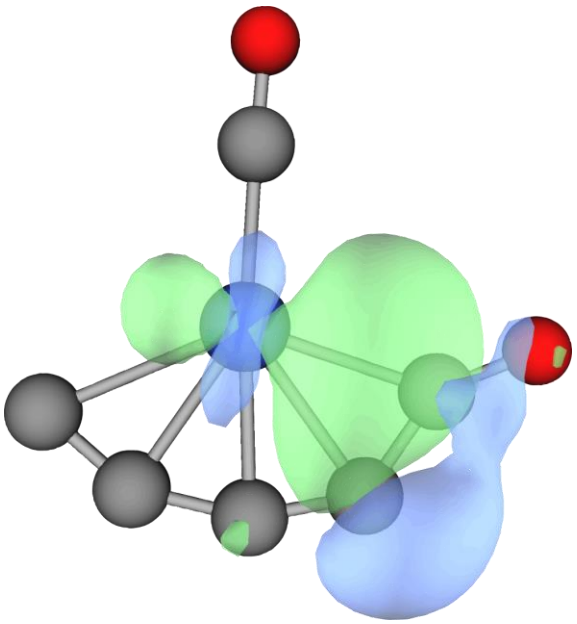
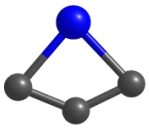
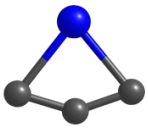


Figure S6. The AdNDP bonding analysis of isomer 4A for the 3c-2e bond of interest at the BLYP-D3(BJ) /def2-TZVPP level of theory (O, red; C, gray; Cr, blue). Occupation number (ON) is 1.71 |e| and the isovalue of orbital is set to 0.03.

Table S1. Relative energies (kcal/mol) of different isomers of CrC_3 calculated at different methods. The zero-point vibrational corrections are included, except for the CCSD(T)//BLYP-D3(BJ)/def2-TZVPP level of theory.



$^3B_1$



$^5B_2$

$^5\Pi$

Method	**$^3B_1$**	**$^5B_2$**	**$^5\Pi$**
BLYP-D3(BJ)/def2-TZVPP	0.0	3.6	4.7
BPW91/6-311+G(d)	0.0	3.5	6.9
MN15-L/def2-TZVPP	13.3	0.0	5.8
B2PLYPD3/def2-TZVPP	8.6	0.0	0.7
CCSD(T)//BLYP-D3(BJ) /def2-TZVPP	10.4	0.0	8.0

Cartesian coordinates of the low-lying isomers, intermediates, and transition states for $CrC_3(CO)_2$ and $CrC_4(CO)_2$ shown in Figures 3-6 and Figures S2-S6 calculated at the BLYP-D3(BJ)/def2-TZVPP level of theory.

CO

C	0.00000000	0.00000000	-0.64953300
O	0.00000000	0.00000000	0.48715000

CrC_3

Cr	0.00000000	0.00000000	0.74599900
C	0.00000000	0.00000000	-1.27606600
C	0.00000000	1.26191400	-0.85396500
C	0.00000000	-1.26191400	-0.85396500

$CrC_3(CO)$-I

Cr	-1.19915800	-0.64871200	0.00000100
C	-0.35830100	1.20719700	0.00003000
C	-1.63965500	1.29614900	-0.00005700
C	1.96380200	0.08275200	-0.00000700
C	0.68848900	0.30747200	0.00006800
O	3.10672100	-0.22404300	-0.00002800

$CrC_3(CO)$-II

Cr	-0.11113900	-0.16099100	-0.00015200
C	-1.95297000	-1.07941000	0.00026000
C	-1.46980500	1.38433600	0.00005000
C	-2.13763500	0.22787200	0.00025200
C	1.91929700	-0.00134600	-0.00022800
O	3.06425400	0.08438500	0.00020500

isomer 3A

Cr	0.78972000	-0.72306000	0.00011600
C	-1.10234300	-1.54186100	-0.00009800
C	-0.20513300	-2.45776500	-0.00005000
C	-2.02935000	0.86626400	-0.00007900
C	-1.26475700	-0.18082900	-0.00004800
C	1.82679000	1.00707600	-0.00007300
O	-2.64619800	1.87203100	-0.00000900
O	2.35813400	2.02748800	-0.00007900

isomer 3B

Cr	0.01842400	-0.26399300	0.01670600
C	2.19632700	-0.37095600	0.38341900
C	0.58303700	-2.21044200	-0.30024400

C	1.68045200	-1.50891000	-0.05407100
C	0.51141100	1.68931100	-0.06316600
C	-2.00023100	-0.15235400	0.02164900
O	0.85987200	2.77938000	-0.12605900
O	-3.14339100	-0.07238800	0.08524900

CrC_4

Cr	0.00000000	0.00000000	0.80912100
C	0.00000000	0.69116200	-1.19873700
C	0.00000000	1.70214800	-0.41950400
C	0.00000000	-0.69116200	-1.19873700
C	0.00000000	-1.70214800	-0.41950400

CrC_4(CO)-I

Cr	0.06317100	-0.42142800	0.00011100
C	1.42371900	1.21742100	-0.00009800
C	1.97751500	-1.22365400	-0.00006200
C	-1.96068900	-0.18542100	0.00001700
C	2.13727800	0.04237700	-0.00008300
C	0.27951800	1.78322700	-0.00008400
O	-3.08251800	0.03882100	-0.00010000

CrC_4(CO)-II

Cr	-0.30708700	-0.77016600	-0.00012000
C	-0.54503900	1.26743000	0.00015100
C	-1.80705000	0.80044100	0.00006200
C	-2.62963000	-0.18806400	-0.00006800
C	1.67627500	0.15207700	0.00008100
C	0.74531700	1.21096100	0.00017900
O	2.84135600	-0.12163500	0.00005500

isomer 4A

Cr	-0.05624600	-0.38784700	0.00007200
C	2.00045100	0.02674700	-0.00001200
C	1.92058800	-1.30909700	-0.00001400
C	1.25287600	-2.41115500	-0.00007500
C	0.28198800	1.81296300	-0.00019500
C	1.54904200	1.23343300	-0.00005300
C	-2.05105600	-0.61398500	0.00010500
O	-0.35252200	2.82319800	-0.00016100
O	-3.19415800	-0.71383700	0.00012600

isomer 4B

Cr	-0.00175700	0.08224800	-0.00009200
C	-0.65305700	2.10190400	0.00026600
C	1.81295500	1.43401200	-0.00070000

C	1.54837600	-1.22176100	0.00015200
C	-1.58071100	-1.18689000	-0.00022400
C	0.71388100	2.08067200	-0.00035000
C	-1.76956500	1.48594000	0.00104900
O	2.45951800	-1.91210700	0.00045200
O	-2.50815700	-1.85504300	-0.00032000

TS 1

Cr	0.48043700	-0.75305500	-0.07622000
C	2.06547900	0.46316100	0.38721900
C	-0.25802000	1.21045100	-0.36426000
C	1.02567800	1.19467600	-0.00921500
C	-1.38484300	-0.05137500	-0.00174400
O	-2.52753200	0.14648000	0.21966100

TS2

Cr	0.18644600	0.30446800	-0.01461700
C	-0.49223200	2.29927000	0.02425000
C	-2.06872900	0.24486700	-0.00671500
C	-1.51349800	1.44513100	0.01853900
C	2.12686800	-0.17237200	0.00191700
C	-1.07571300	-1.25725100	-0.04380900
O	3.23071900	-0.49527500	0.01320400
O	-1.52257800	-2.33786400	0.03501000

TS3

Cr	-0.26266400	-0.69435700	0.00002700
C	-2.45137400	-0.45948300	0.00000700
C	-1.88158000	0.68382100	-0.00003700
C	-0.68077900	1.33841200	-0.00005800
C	0.59608800	1.44315700	-0.00005600
C	1.67748500	-0.11262300	0.00001200
O	2.84311300	-0.08689200	0.00001700

TS4

Cr	-0.13312300	-0.14463900	0.00002300
C	-0.73343500	-2.30218600	0.00002200
C	0.53628200	-2.16102200	-0.00002100
C	1.61425300	-1.32661700	-0.00003600
C	2.22277000	-0.20124600	-0.00001900
C	1.06225900	1.47876400	0.00000700
C	-2.03916400	0.53160900	-0.00000600
O	1.52921400	2.53730100	-0.00000100
O	-3.12706800	0.88214000	-0.00003000