

Unsaturation in Binuclear Cyclopentadienyliron Carbonyls

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Supporting Information

Table S1. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_s dibridged *trans*- $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**Ia**)

Table S2. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} dibridged *cis*- $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**Ib**)

Table S3. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2h} unbridged *trans*- $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (**Ic**)

Table S4. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_{2v} tribridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ (**IIa**)

Table S5. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_s tribridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ (**IIb**)

Table S6. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_{2v} singly bridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$ (**IIc**)

Table S7. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} singly bridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$ (**IId**)

Table S8. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} dibridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2$ (**IIIa**)

Table S9. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_s dibridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2$ (**IIIb**)

Table S10. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2h} *trans*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**IIIc**)

Table S11. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_i *trans*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**III d**)

Table S12. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} *cis*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**III e**)

Table S13. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_{2v} *cis*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**III f**)

Table S14. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_s monobridged $\text{Cp}_2\text{Fe}_2(\text{CO})(\mu\text{-CO})$ (**III g**)

Table S15. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_1 bridged $\text{Cp}_2\text{Fe}_2(\text{CO})$ (**IV a**)

Table S16. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_s bridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})$ (**IV b**)

Table S17. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_1 unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})$ (**IV c**)

Figure 1. The 17 $\text{Cp}_2\text{Fe}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) structures discussed in this paper.

Table S1. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_s dibridged *trans*- $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**1a**)

	B3LYP	BP86		B3LYP	BP86
a	58(1)	59(2)	a''	16(0)	20(0)
	97(0)	95(0)		30(0)	36(0)
	106(0)	104(0)		63(1)	62(2)
	142(1)	151(0)		95(0)	93(0)
	154(0)	139(1)		124(0)	124(1)
	225(0)	226(0)		142(0)	153(0)
	236(2)	233(2)		248(0)	259(0)
	320(7)	315(9)		309(1)	320(1)
	334(0)	331(0)		324(11)	340(1)
	367(6)	368(1)		381(1)	383(0)
	407(1)	402(1)		449(3)	452(1)
	439(0)	445(0)		512(0)	511(0)
	491(2)	499(6)		568(35)	566(0)
	540(3)	556(46)		587(1)	558(12)
	548(75)	568(2)		599(11)	581(27)
	577(1)	566(2)		617(1)	606(0)
	593(15)	570(3)		831(5)	799(5)
	597(4)	583(2)		842(2)	811(2)
	604(41)	607(51)		846(0)	815(0)
	677(660)	675(547)		851(5)	819(5)
	835(76)	804(65)		927(3)	884(3)
	839(48)	809(42)		928(0)	885(0)
	845(0)	814(1)		1025(10)	995(10)
	850(42)	820(42)		1031(6)	1001(6)
	860(5)	830(6)		1073(1)	1042(1)
	872(6)	841(6)		1076(1)	1045(0)
	933(5)	892(0)		1275(0)	1225(0)
	934(0)	896(4)		1277(0)	1226(0)
	1015(9)	985(7)		1402(0)	1362(0)
	1024(6)	992(5)		1402(1)	1364(0)
	1074(1)	1042(1)		1462(2)	1413(2)
	1074(1)	1044(0)		1470(3)	1420(3)
	1140(1)	1109(1)		1858(1125)	1796(859)
	1140(1)	1110(1)		3244(0)	3170(0)
	1456(3)	1404(4)		3245(0)	3172(0)
	1456(3)	1406(3)		3261(0)	3186(0)
	1901(0)	1820(0)		3261(0)	3187(0)
	2037(1475)	1946(1209)			
	2051(34)	1961(37)			
	3241(1)	3167(1)			
	3248(0)	3174(0)			
	3255(0)	3182(0)			
	3257(0)	3183(0)			
	3269(0)	3194(0)			
	3270(0)	3195(0)			
	1402(3)	1361(2)			
	1402(1)	1364(2)			

Table S2. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} dibridged *cis*- $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})_2$ (**Ib**)

	B3LYP	BP86		B3LYP	BP86
a_1	70(1)	70(1)	b_1	30i(0)	36i(0)
	106(0)	104(0)		98(0)	96(0)
	144(0)	144(0)		131(0)	128(1)
	219(0)	223(0)		315(10)	314(11)
	332(1)	329(3)		440(0)	441(0)
	416(0)	411(0)		512(29)	511(21)
	443(3)	449(2)		589(1)	565(0)
	491(2)	503(1)		615(21)	607(20)
	563(24)	569(8)		841(4)	808(9)
	599(1)	574(3)		844(10)	810(4)
	617(48)	618(44)	923(3)	880(1)	
	838(31)	808(22)	1032(11)	1001(12)	
	852(27)	820(27)	1075(3)	1044(2)	
	876(14)	847(10)	1276(0)	1226(0)	
	939(3)	906(7)	1404(2)	1364(0)	
	1013(13)	982(11)	1470(5)	1420(5)	
	1074(0)	1043(0)	1857(1132)	1795(863)	
	1141(2)	1111(4)	3243(0)	3169(0)	
	1402(0)	1362(0)	3258(0)	3183(0)	
	a_2	1454(1)	1403(2)	b_2	97(0)
1898(4)		1819(3)	155(0)		0148(0)
2079(1431)		1991(1153)	227(1)		0223(1)
3248(0)		3173(0)	325(3)		0321(1)
3261(0)		3186(0)	372(2)		0373(0)
3279(2)		3201(4)	529(42)		0548(45)
46i(0)		53i(0)	565(14)		0558(0)
63(0)		62(0)	591(2)		0577(2)
126(0)		133(0)	684(674)		0680(577)
248(0)		254(0)	811(48)		0770(30)
313(0)		338(0)	845(0)	0815(4)	
389(0)		400(0)	853(48)	0821(50)	
579(0)		564(0)	915(1)	0870(2)	
596(0)		582(0)	1012(5)	0981(4)	
840(0)		807(0)	1073(1)	1042(0)	
842(0)		809(0)	1140(1)	1109(1)	
921(0)		879(0)	1401(3)	1360(3)	
1026(0)		993(0)	1452(3)	1401(4)	
1068(0)		1035(0)	2042(185)	1956(199)	
1274(0)		1223(0)	3247(0)	3173(0)	
1402(0)	1363(0)	3259(2)	3185(2)		
1469(0)	1418(0)	3272(0)	3199(0)		
3243(0)	3169(0)				
3258(0)	3183(0)				

Table S3. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2h} unbridged *trans*- $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (**1c**)

	B3LYP	BP86		B3LYP	BP86
a_g	82(0)	77(0)	b_g	53(0)	49(0)
	111(0)	107(0)		62(0)	55(0)
	119(0)	119(0)		132(0)	129(0)
	178(0)	175(0)		362(0)	364(0)
	327(0)	327(0)		417(0)	411(0)
	370(0)	378(0)		498(0)	494(0)
	511(0)	525(0)		576(0)	569(0)
	580(0)	570(0)		595(0)	596(0)
	601(0)	581(0)		844(0)	813(0)
	644(0)	645(0)		856(0)	826(0)
	842(0)	811(0)		921(0)	877(0)
	847(0)	817(0)		1013(0)	981(0)
	857(0)	824(0)		1073(0)	1041(0)
	936(0)	893(0)		1273(0)	1222(0)
	1029(0)	997(0)		1399(0)	1360(0)
	1072(0)	1041(0)		1452(0)	1400(0)
	1138(0)	1106(0)		1999(0)	1918(0)
	1404(0)	1363(0)		3242(0)	3168(0)
	1466(0)	1413(0)		3257(0)	3183(0)
	a_u	2057(0)		1973(0)	b_u
3248(0)		3174(0)	117(0)	115(0)	
3259(0)		3184(0)	142(5)	141(5)	
3271(0)		3196(0)	326(1)	327(6)	
36(1)		37(1)	360(3)	369(2)	
50(0)		49(0)	501(83)	522(54)	
91(0)		88(0)	571(247)	565(200)	
122(0)		119(1)	599(21)	576(42)	
361(5)		362(6)	47(79)	647(70)	
460(1)		456(1)	842(52)	811(30)	
506(9)		497(12)	846(101)	816(97)	
576(70)		566(4)	854(18)	822(16)	
594(4)		597(45)	934(4)	891(2)	
844(0)		812(0)	1028(8)	997(10)	
855(11)		825(13)	1072(2)	1040(2)	
921(0)		877(0)	1138(3)	1106(4)	
1012(17)		980(15)	1404(2)	1363(0)	
1072(1)		1039(2)	1465(8)	1413(9)	
1273(0)		1222(0)	2013(1275)	1947(927)	
1396(4)		1356(4)	3248(0)	3174(0)	
1452(3)	1400(4)	3259(3)	3184(4)		
2016(1499)	1931(1240)	3271(0)	3196(0)		
3242(1)	3168(1)				
3257(0)	3183(0)				

Table S4. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_{2v} tribridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_3$ (**IIa**)

	B3LYP	BP86		B3LYP	BP86
a ₁	81(2)	78(2)	b ₁	23i(0)	24i(0)
	110(0)	108(0)		78(2)	75(2)
	212(0)	215(0)		115(0)	113(0)
	318(9)	323(9)		306(7)	306(10)
	424(0)	428(0)		415(0)	406(0)
	493(11)	497(6)		491(10)	493(5)
	507(0)	519(0)		569(24)	556(15)
	575(23)	562(12)		600(1)	576(3)
	601(3)	580(7)		844(5)	813(5)
	827(0)	796(0)		847(2)	817(3)
	832(4)	800(4)		915(2)	873(3)
	846(0)	816(0)		1023(19)	993(17)
	917(1)	876(1)		1073(1)	1043(1)
	1020(22)	991(21)		1274(0)	1224(0)
	1073(1)	1043(1)		1397(0)	1360(0)
	1138(0)	1110(0)		1461(5)	1410(7)
	1398(0)	1362(0)		1904(982)	1819(779)
	1455(3)	1406(4)		3241(0)	3167(0)
	1905(1009)	1820(800)		3254(0)	3179(0)
	a ₂	1951(0)	1862(0)	b ₂	96(0)
3241(0)		3167(0)	181(0)		203(0)
3253(0)		3179(0)	201(1)		225(0)
3265(0)		3190(0)	304(3)		323(1)
25i(0)		25i(0)	323(88)		341(20)
105(0)		137(0)	441(0)		447(0)
182(0)		218(0)	555(239)		558(22)
309(0)		325(0)	581(15)		592(232)
429(0)		435(0)	825(153)		795(111)
579(0)		559(0)	830(8)		798(9)
837(0)		809(0)	837(11)		810(9)
843(0)		814(0)	915(2)		875(4)
913(0)		872(0)	1020(0)		991(0)
1023(0)		993(0)	1069(0)		1040(0)
1070(0)		1041(0)	1137(9)		1109(7)
1274(0)		1224(0)	1391(0)		1356(1)
1390(0)		1355(0)	1455(0)		1406(0)
1461(0)		1410(0)	3241(0)		3166(0)
3241(0)		3166(0)	3253(0)	3179(0)	
3254(0)	3179(0)	3265(0)	3190(1)		

Table S5. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_s dibridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})$ (**IIb**)

	B3LYP	BP86		B3LYP	BP86
A	27(1)	24(2)	A''	20i(0)	31i(0)
	88(2)	90(1)		21(0)	4(0)
	105(0)	118(0)		74(0)	66(1)
	150(0)	158(0)		117(1)	116(1)
	200(0)	203(0)		151(0)	153(0)
	234(3)	232(3)		256(0)	256(0)
	342(3)	344(3)		316(17)	315(17)
	364(3)	363(0)		334(0)	348(4)
	384(2)	397(1)		412(3)	410(1)
	418(3)	418(15)		449(0)	468(4)
	453(4)	457(1)		517(10)	512(1)
	508(2)	527(12)		564(21)	540(10)
	545(37)	530(12)		586(0)	562(4)
	590(0)	562(2)		594(2)	566(9)
	595(1)	571(1)		831(2)	790(1)
	605(35)	583(34)		841(0)	806(7)
	696(550)	674(352)		843(9)	810(1)
	829(29)	798(6)		843(2)	814(4)
	834(36)	803(30)		912(3)	866(3)
	840(0)	808(6)		924(3)	882(2)
	848(46)	819(44)		1025(7)	993(8)
	852(6)	823(12)		1032(6)	1004(7)
	860(9)	835(10)		1072(1)	1041(0)
	916(1)	872(5)		1076(1)	1045(0)
	927(0)	885(1)		1273(0)	1223(0)
	1011(7)	981(8)		1277(0)	1228(0)
	1013(16)	982(11)		1396(3)	1352(0)
	1070(1)	1041(1)		1399(0)	1359(0)
	1074(1)	1045(0)		1464(1)	1414(1)
	1137(6)	1105(8)		1474(3)	1426(3)
	1139(1)	1108(1)		1842(1158)	1781(918)
	1400(3)	1359(2)		3235(0)	3161(0)
	1402(2)	1361(1)		3244(0)	3169(0)
	1449(1)	1396(2)		3255(0)	3179(0)
	1452(3)	1401(5)		3263(0)	3187(0)
	1880(29)	1807(77)			
	2047(832)	1949(550)			
	3239(0)	3162(0)			
	3246(0)	3169(0)			
	3247(0)	3171(1)			
	3255(0)	3179(0)			
	3263(0)	3186(0)			
	3270(0)	3194(0)			

Table S6. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_{2v} singly bridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$ (**IIc**)

	B3LYP	BP86		B3LYP	BP86	
a_1	116(1)	135(2)	b_1	602i	49i	
	125(0)	145(0)		35i	36(2)	
	178(0)	220(0)		55(0)	122(0)	
	313(5)	314(15)		168(2)	290(4)	
	356(0)	378(0)		320(5)	404(1)	
	378(0)	410(0)		378(7)	485(20)	
	505(59)	506(22)		572(7)	560(1)	
	569(13)	568(0)		788(10)	763(1)	
	596(0)	589(8)		833(5)	806(0)	
	815(25)	785(22)		917(3)	874(1)	
	841(1)	813(1)		1032(65)	1003(35)	
	878(13)	844(15)		1068(0)	1040(0)	
	941(0)	904(0)		1272(0)	1222(0)	
	1003(12)	973(9)		1390(15)	1353(1)	
	1069(0)	1037(2)		1481(2)	1431(2)	
	1137(1)	1106(0)		3244(8)	3175(0)	
	1404(0)	1356(2)		3258(8)	3187(0)	
	1438(3)	1394(4)		b_2	86(2)	61(2)
	1862(565)	1735(433)			168(5)	169(16)
	2055(1349)	1954(946)	282(50)		251(76)	
3237(1)	3168(0)	303(36)	300(7)			
3253(0)	3182(0)	354(3)	316(0)			
3268(0)	3197(0)	400(429)	466(69)			
a_2	786i	838i	498(13)		503(8)	
	56i	68i	585(228)		567(0)	
	45(0)	42(0)	597(88)		610(10)	
	199(0)	219(0)	814(122)		780(13)	
	346(0)	337(0)	840(4)	811(32)		
	572(0)	550(0)	877(2)	841(25)		
	774(0)	741(0)	941(6)	902(43)		
	834(0)	804 (0)	1003(5)	972(13)		
	917(0)	874(0)	1068(1)	1036(1)		
	1029(0)	999(0)	1137(2)	1103(6)		
	1068(0)	1039(0)	1404(14)	1350(60)		
	1272(0)	1222(0)	1438(6)	1394(13)		
	1388(0)	1351(0)	1989(85)	1892(324)		
	1481(0)	1431(0)	3237(0)	3168(5)		
	3244(0)	3173(0)	3253(0)	3182(1)		
	3257(0)	3186(0)	3268(0)	3197(1)		

Table S7. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} singly bridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})$ (**II**d)

	B3LYP	BP86		B3LYP	BP86
a ₁	141(0)	146(1)	b ₁	32i	29i
	149(1)	151(1)		48(0)	48(0)
	226(0)	234(0)		135(0)	132(0)
	337(16)	345(21)		357(8)	361(9)
	394(0)	404(0)		418(3)	409(3)
	416(0)	423(1)		549(34)	528(22)
	518(44)	518(27)		590(1)	560(0)
	591(4)	569(1)		828(0)	787(0)
	597(1)	585(9)		843(0)	811(0)
	835(10)	797(6)		930(2)	881(3)
	848(11)	817(9)	1031(29)	1000(28)	
	885(18)	851(16)	1073(0)	1041(0)	
	951(0)	913(0)	1274(0)	1222(0)	
	1015(9)	979(9)	1404(1)	1363(0)	
	1074(1)	1040(1)	1471(3)	1420(4)	
	1141(0)	1108(1)	3252(0)	3174(0)	
	1407(0)	1370(0)	3264(0)	3186(0)	
	1446(4)	1389(4)	b ₂	94(4)	89(3)
	1796(540)	1730(438)		195(0)	199(0)
	2042(1176)	1949(954)		316(7)	314(5)
3246(0)	3169(0)	335(2)		342(2)	
3260(0)	3182(0)	377(0)		388(1)	
3275(1)	3195(0)	463(43)		480(91)	
a ₂	67i	67i		502(23)	521(0)
	46(0)	49(0)		587(3)	571(4)
	159(0)	159(0)		613(45)	632(99)
	362(0)	370(0)		834(23)	796(3)
	438(0)	442(0)	847(63)	815(59)	
	590(0)	562(0)	886(0)	852(0)	
	829(0)	789(0)	951(18)	913(22)	
	844(0)	813(0)	1015(1)	979(2)	
	930(0)	881(0)	1074(2)	1039(5)	
	1031(0)	1000(0)	1141(9)	1107(11)	
	1073(0)	1041(0)	1407(0)	1369(2)	
	1274(0)	1222(0)	1446(2)	1389(0)	
	1404(0)	1362(0)	1975(363)	1890(232)	
	1471(0)	1420(0)	3246(0)	3169(1)	
	3252(0)	3174(0)	3260(0)	3182(0)	
3264(0)	3186(0)	3275(0)	3195(0)		

Table S8. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} dibridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2$ (**IIIa**)

	B3LYP	BP86		B3LYP	BP86	
a ₁	64(2)	64(2)	b ₁	41(0)	40(1)	
	106(0)	98(0)		111(0)	105(0)	
	214(0)	217(0)		356(10)	354(11)	
	368(10)	366(11)		448(0)	429(0)	
	432(1)	433(0)		540(30)	537(13)	
	502(0)	495(0)		588(1)	558(4)	
	581(16)	565(0)		842(0)	809(0)	
	597(2)	584(13)		863(8)	828(7)	
	825(0)	786(0)		917(0)	870(0)	
	832(1)	796(0)		1016(17)	980(17)	
	845(0)	813(0)		1071(0)	1039(0)	
	917(0)	865(1)		1274(0)	1223(0)	
	1027(27)	997(25)		1396(0)	1353(0)	
	1072(0)	1041(0)		1446(5)	1390(6)	
	1137(0)	1105(0)		1918(1207)	1828(899)	
	1403(1)	1365(0)		3240(0)	3164(0)	
	1465(3)	1418(3)		3251(0)	3175(0)	
	1939(202)	1851(195)		b ₂	160(0)	151(0)
	3240(0)	3163(0)			195(0)	211(1)
3258(0)	3180(1)	356(3)	358(4)			
3266(0)	3189(0)	388(10)	403(7)			
a ₂	30(0)	29(0)	453(36)		499(52)	
	142(0)	132(0)	595(10)		567(17)	
	202(0)	219(0)	827(3)		787(0)	
	338(0)	351(0)	828(88)		792(74)	
	466(0)	464(0)	842(15)		807(8)	
	585(0)	553(0)	916(3)		863(3)	
	841(0)	806(0)	1028(0)		997(0)	
	863(0)	827(0)	1072(1)		1040(1)	
	916(0)	868(0)	1137(17)		1104(19)	
	1015(0)	980(0)	1403(0)		1366(0)	
	1069(0)	1035(0)	1465(0)		1417(1)	
	1274(0)	1222(0)	3240(0)		3163(0)	
	1392(0)	1347(0)	3258(0)		3181(0)	
	1446(0)	1390(0)	3266(0)		3189(0)	
	3240(0)	3164(0)				
	3251(0)	3175(0)				

Table S9. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_s dibridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2$ (**IIIb**)

	B3LYP	BP86		B3LYP	BP86
a	40(1)	43(1)	a	91i	22i
	86(2)	86(0)		35i	25(0)
	134(0)	102(1)		28(0)	101(1)
	161(7)	197(2)		97(1)	130(0)
	196(0)	204(1)		158(2)	247(0)
	270(2)	282(2)		234(4)	304(5)
	320(18)	339(0)		326(0)	324(12)
	346(20)	347(7)		399(2)	413(0)
	380(1)	411(0)		420(0)	448(0)
	427(65)	493(1)		520(26)	533(13)
	488(70)	513(29)		587(0)	552(2)
	536(34)	559(3)		595(0)	562(0)
	593(1)	563(8)		799(2)	796(5)
	596(4)	569(16)		839(0)	799(2)
	798(85)	785(51)		840(0)	800(0)
	804(45)	790(29)		854(3)	811(0)
	826(5)	789(1)		890(0)	859(0)
	831(52)	798(4)		919(0)	863(0)
	843(1)	810(24)		1011(9)	990(5)
	846(1)	816(0)		1019(13)	990(15)
	891(0)	858(5)		1066(0)	1036(0)
	911(2)	863(0)		1068(0)	1039(0)
	1018(19)	987(22)		1271(0)	1221(0)
	1027(14)	986(4)		1273(0)	1222(0)
	1065(0)	1037(4)		1388(0)	1344(0)
	1070(0)	1039(0)		1393(0)	1354(0)
	1134(1)	1102(9)		1446(2)	1402(3)
	1135(3)	1104(1)		1455(1)	1403(0)
	1381(2)	1350(2)		1901(1244)	1798(963)
	1396(3)	1356(0)		3233(0)	3165(0)
	1456(1)	1400(1)		3243(0)	3168(0)
	1468(1)	1401(4)		3248(0)	3180(0)
	1918(100)	1820(89)		3254(0)	3181(0)
	3229(0)	3163(1)			
	3238(0)	3167(0)			
	3245(1)	3178(0)			
	3254(0)	3178(0)			
	3259(1)	3190(0)			
	3266(0)	3190(0)			

Table S10. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2h} *trans*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**IIIc**)

	B3LYP	BP86		B3LYP	BP86	
a_g	57(0)	56(0)	b_g	66i	73i	
	131(0)	119(0)		136(0)	134(0)	
	198(0)	191(0)		332(0)	350(0)	
	357(0)	355(0)		510(0)	515(0)	
	404(0)	415(0)		585(0)	550(0)	
	531(0)	549(0)		813(0)	769(0)	
	572(0)	566(0)		836(0)	799(0)	
	595(0)	582(0)		907(0)	863(0)	
	824(0)	752(0)		1007(0)	958(0)	
	835(0)	796(0)		1062(0)	1023(0)	
	856(0)	820(0)		1264(0)	1205(0)	
	916(0)	868(0)		1372(0)	1308(0)	
	1004(0)	969(0)		1460(0)	1403(0)	
	1069(0)	1037(0)		3240(0)	3162(0)	
	1124(0)	1084(0)		3256(0)	3177(0)	
	1400(0)	1358(0)		b_u	99(0)	88(0)
	1433(0)	1372(0)			166(4)	173(7)
	2013(0)	1920(0)			351(3)	347(6)
	3246(0)	3167(0)			388(5)	397(2)
3261(0)	3177(0)	526(113)	517(86)			
3289(0)	3186(0)	535(37)	557(32)			
a_u	84i	78i	592(16)		576(27)	
	40i	39i	823(80)		767(10)	
	94(0)	91(0)	826(16)		783(40)	
	287(9)	302(7)	855(32)		821(42)	
	440(11)	478(17)	918(11)		866(13)	
	592(0)	559(1)	1004(13)		970(10)	
	822(0)	781(0)	1068(0)		1035(2)	
	838(2)	802(3)	1122(11)		1082(12)	
	907(2)	863(3)	1399(19)		1357(6)	
	1006(21)	959(23)	1434(1)		1372(2)	
	1063(4)	1024(7)	1988(2620)		1904(2035)	
	1264(0)	1206(0)	3246(3)		3166(7)	
	1374(0)	1312(0)	3261(2)		3175(7)	
	1460(3)	1402(2)	3287(3)	3185(2)		
	3240(1)	3162(0)				
	3255(0)	3177(1)				

Table S11. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_i *trans*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**III**d)

	B3LYP	BP86		B3LY	BP86
a_g	59(0)	74(0)	a_u	33i	65i
	88(0)	98(0)		55(0)	3(2)
	113(0)	123(0)		69(1)	78(1)
	113(0)	133(0)		90(1)	100(0)
	147(0)	180(0)		141(0)	172(2)
	264(0)	296(0)		264(1)	228(29)
	286(0)	324(0)		286(7)	329(14)
	317(0)	387(0)		316(4)	349(3)
	431(0)	462(0)		395(1)	408(4)
	516(0)	530(0)		514(75)	507(9)
	540(0)	544(0)		525(36)	539(80)
	578(0)	547(0)		571(1)	545(37)
	588(0)	563(0)		587(3)	563(3)
	744(0)	665(0)		760(61)	679(26)
	791(0)	759(0)		787(126)	751(51)
	813(0)	785(0)		813(23)	786(14)
	832(0)	793(0)		835(9)	797(3)
	837(0)	809(0)		839(1)	811(19)
	880(0)	839(0)		877(5)	833(3)
	914(0)	873(0)		914(12)	873(13)
	999(0)	959(0)		999(31)	957(11)
	1023(0)	985(0)		1022(44)	985(33)
	1062(0)	1022(0)		1060(9)	1021(5)
	1069(0)	1036(0)		1069(1)	1036(2)
	1122(0)	1083(0)		1121(6)	1082(12)
	1264(0)	1206(0)		1264(1)	1206(1)
	1380(0)	1328(0)		1377(3)	1329(1)
	1386(0)	1342(0)		1386(4)	1343(1)
	1436(0)	1377(0)		1435(4)	1377(12)
	1451(0)	1390(0)		1451(7)	1390(5)
	2015(0)	1919(0)		1998(2536)	1897(2330)
	3162(0)	3033(0)		3160(4)	3029(3)
	3237(0)	3161(0)		3237(1)	3161(2)
	3246(0)	3170(0)		3247(1)	3170(2)
	3254(0)	3175(0)		3254(2)	3175(4)
	3262(0)	3185(0)		3262(1)	3185(0)

Table S12. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_{2v} *cis*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**IIIe**)

	B3LYP		BP86
a ₁	111(0)	b ₁	138i
	130(0)		36i
	164(0)		311(16)
	324(1)		365(9)
	384(3)		584(5)
	521(28)		800(13)
	557(1)		834(8)
	590(2)		894(1)
	820(47)		1023(37)
	837(1)		1066(6)
	850(8)	1269(0)	
	916(6)	1391(1)	
	1001(18)	1457(0)	
	1064(1)	3233(5)	
	1129(8)	3248(0)	
	1383(0)	b ₂	50(1)
	1447(0)		198(4)
	2047(1508)		370(1)
	3235(0)		461(16)
	3257(0)		516(45)
3285(1)	556(46)		
a ₂	55i		723(79)
	7(0)		815(42)
	146(0)		838(9)
	334(0)		880(32)
	495(0)	995(7)	
	590(0)	1054(105)	
	811(0)	1067(30)	
	834(0)	1352(715)	
	893(0)	1391(102)	
	1018(0)	1566(2051)	
	1059(0)	2443(4137)	
	1267(0)	3234(2)	
	1392(0)	3259(54)	
	1456(0)	3283(270)	
3233(0)			
3248(0)			

Table S13. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_{2v} *cis*-unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ (**III**f)

	B3LYP	BP86		B3LYP	BP86
a ₁	100(0)	90(0)	b ₁	24i	247i
	115(0)	117(0)		72(0)	44(8)
	142(0)	157(1)		301(4)	79(0)
	326(0)	343(8)		428(5)	426(1)
	356(2)	372(0)		580(0)	528(36)
	518(30)	542(15)		819(1)	730(122)
	539(1)	552(5)		838(1)	796(1)
	593(1)	564(4)		901(0)	841(27)
	816(49)	793(23)		1023(21)	932(122)
	833(9)	798(5)		1069(2)	1015(0)
	845(18)	812(17)		1272(0)	1219(3)
	911(3)	872(6)		1390(1)	1230(109)
	1014(17)	983(15)		1458(3)	1398(6)
	1069(0)	1037(0)		3233(1)	3154(0)
	1133(4)	1100(8)		3248(2)	3172(0)
	a ₂	1394(1)		1355(1)	b ₂
1450(0)		1397(0)	89(2)	117(0)	
2049(1589)		1951(1289)	316(6)	334(4)	
3234(0)		3154(0)	324(43)	438(3)	
3258(0)		3183(0)	507(86)	520(43)	
3279(2)		3201(4)	532(20)	544(27)	
49i		92i	586(10)	593(4)	
41i		48i	783(47)	745(1)	
110(0)		130(0)	814(76)	791(36)	
290(0)		295(0)	834(4)	798(28)	
428(0)		496(0)	890(15)	853(1)	
569(0)		544(0)	1011(8)	980(6)	
817(0)		787(0)	1068(1)	1035(5)	
832(0)		804(0)	1135(5)	1105(31)	
902(0)		856(0)	1395(8)	1359(5)	
1017(0)		981(0)	1447(0)	1397(14)	
1058(0)	1025(0)	1976(404)	1905(367)		
1269(0)	1217(0)	3233(3)	3154(3)		
1384(0)	1349(0)	3257(1)	3183(1)		
1456(0)	1396(0)	3272(0)	3200(0)		
3233(0)	3154(0)				
3248(0)	3172(0)				

Table S14. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_s monobridged $\text{Cp}_2\text{Fe}_2(\text{CO})(\mu\text{-CO})$ (**IIIg**)

	B3LYP	BP86		B3LYP	BP86
a	80(0)	89(0)	a''	334i	92i
	100(1)	107(0)		26i	13(0)
	117(1)	121(2)		16i	27(0)
	163(0)	176(0)		40(0)	42(0)
	203(4)	223(0)		70(1)	92(0)
	248(1)	272(2)		220(0)	258(3)
	325(30)	369(3)		257(5)	335(4)
	345(0)	345(4)		311(5)	378(0)
	368(2)	395(2)		413(0)	456(2)
	421(38)	459(21)		580(0)	549(0)
	494(50)	514(8)		601(0)	562(1)
	534(88)	545(42)		785(10)	772(0)
	591(21)	558(1)		795(0)	770(2)
	593(1)	567(7)		834(2)	801(0)
	603(0)	597(19)		842(0)	804(1)
	784(22)	738(3)		887(1)	844(1)
	796(130)	772(55)		904(4)	862(2)
	815(51)	765(25)		1009(18)	971(5)
	830(12)	791(24)		1016(29)	979(27)
	843(3)	808(23)		1063(2)	1027(5)
	848(0)	812(3)		1065(3)	1031(1)
	887(0)	849(5)		1266(0)	1213(0)
	899(6)	855(1)		1270(0)	1219(0)
	997(8)	969(5)		1369(13)	1324(0)
	1019(16)	990(12)		1386(1)	1340(2)
	1066(0)	1033(2)		1453(1)	1397(1)
	1067(0)	1037(1)		1470(0)	1408(1)
	1125(3)	1089(9)		3228(1)	3157(1)
	1133(0)	1100(6)		3239(4)	3165(0)
	1381(1)	1337(5)		3244(1)	3174(0)
	1398(2)	1362(1)		3253(1)	3178(0)
	1435(2)	1379(5)			
	1455(1)	1405(1)			
	1906(366)	1795(344)			
	2040(1440)	1959(1164)			
	3201(1)	3131(0)			
	3221(0)	3149(0)			
	3240(1)	3168(1)			
	3245(0)	3171(1)			
	3257(1)	3186(1)			
	3262(0)	3186(1)			

Table S15. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for triplet C_1 bridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})$ (**IVa**)

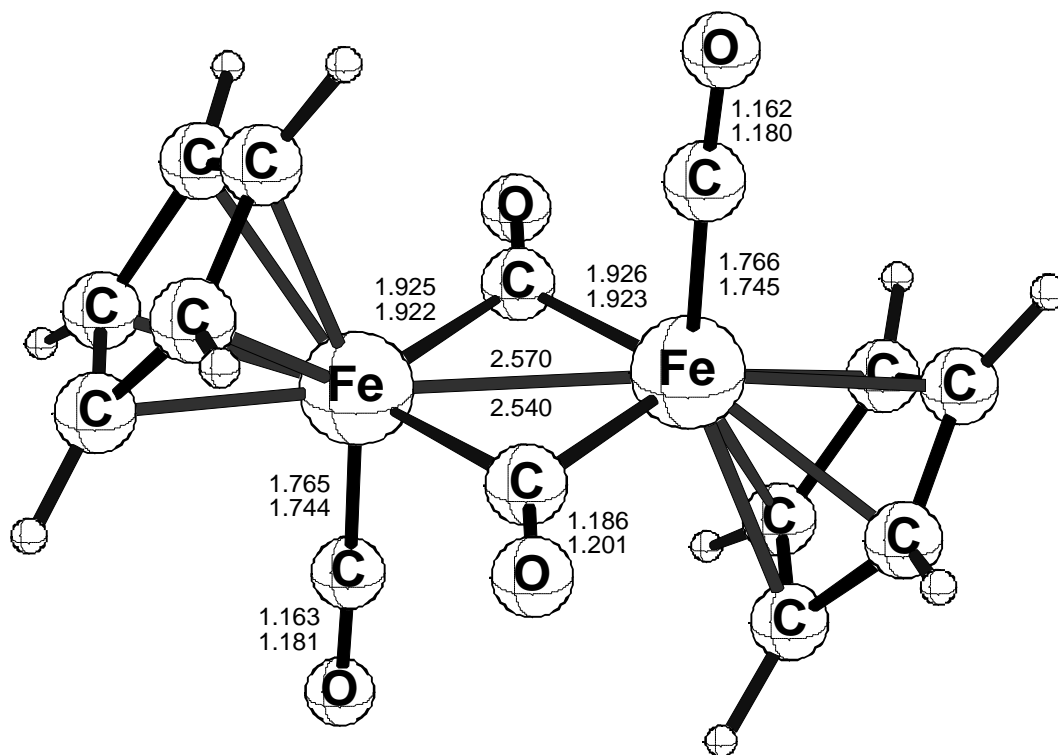
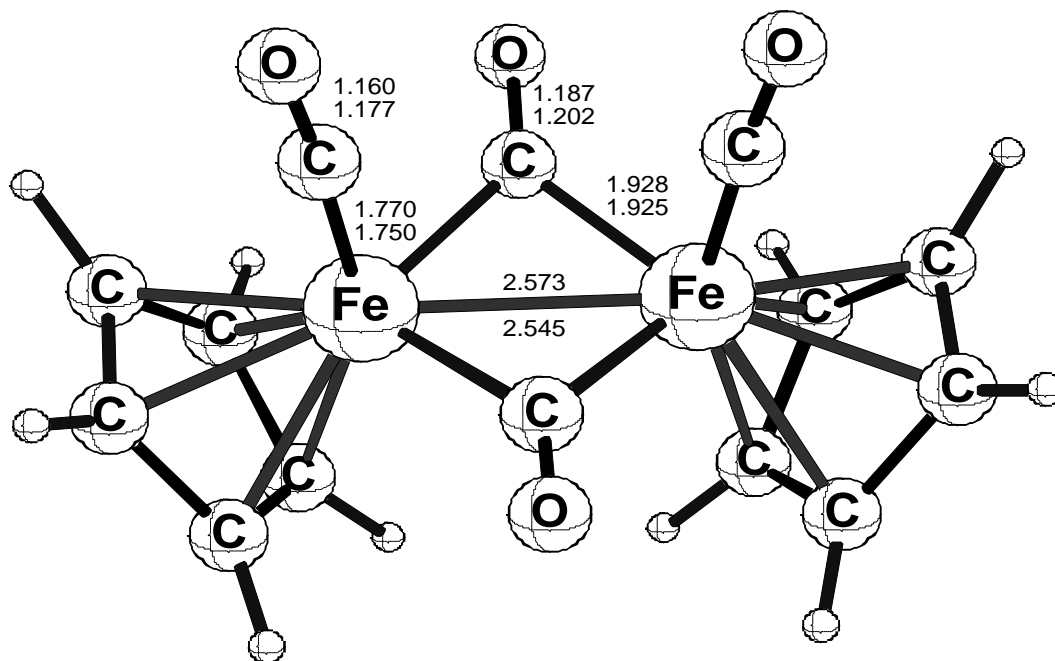
	B3LYP	BP86		B3LYP	BP86
a	35i(1)	8(0)	a	895(1)	851(3)
	13(0)	35(0)		900(2)	853(1)
	28(0)	57(0)		1013(20)	979(19)
	39(0)	60(0)		1016(14)	983(11)
	50(1)	91(0)		1017(14)	986(13)
	93(1)	107(1)		1019(14)	987(13)
	168(2)	180(3)		1063(0)	1031(0)
	173(0)	191(2)		1065(0)	1033(0)
	264(4)	269(1)		1070(0)	1040(0)
	282(5)	290(2)		1071(1)	1040(1)
	296(1)	319(2)		1131(2)	1098(8)
	305(3)	336(3)		1133(6)	1101(5)
	361(17)	360(1)		1270(0)	1220(0)
	406(9)	377(6)		1273(0)	1220(0)
	431(3)	429(2)		1378(0)	1333(0)
	444(12)	465(9)		1379(1)	1341(0)
	536(5)	541(6)		1385(1)	1347(1)
	578(1)	550(1)		1387(0)	1356(1)
	592(2)	551(1)		1449(1)	1398(3)
	595(1)	567(1)		1456(2)	1399(2)
	610(1)	574(2)		1459(2)	1404(1)
	792(91)	757(54)		1461(1)	1413(2)
	796(49)	764(29)		1949(830)	1864(638)
	798(11)	765(0)		3229(0)	3157(0)
	800(12)	770(15)		3229(0)	3160(0)
	803(19)	772(21)		3232(0)	3161(0)
	811(6)	777(7)		3234(0)	3164(0)
	834(3)	800(2)		3244(1)	3172(1)
	837(1)	801(1)		3245(0)	3174(1)
	842(0)	809(0)		3246(1)	3174(1)
	845(1)	810(0)		3249(1)	3177(1)
	879(1)	832(1)		3258(1)	3185(1)
	879(1)	838(0)		3259(0)	3187(0)

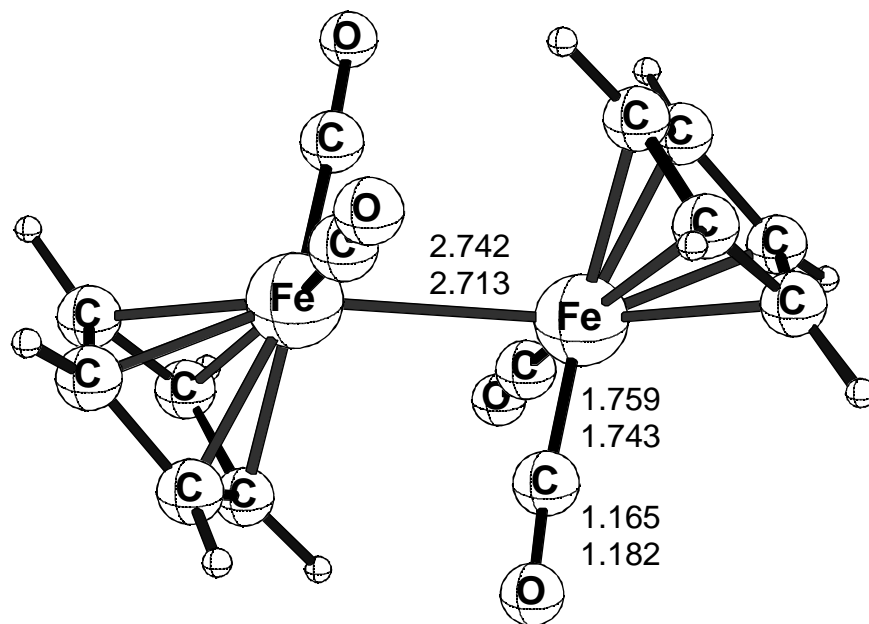
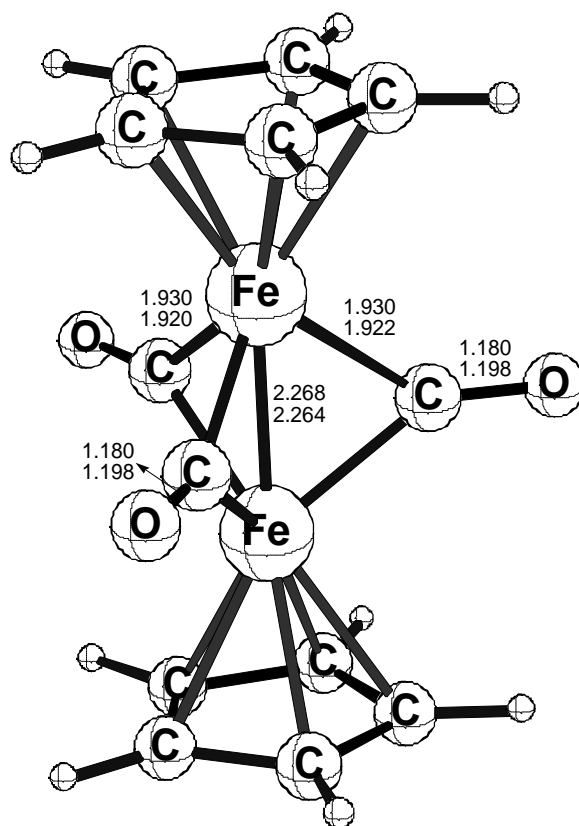
Table S16. Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_s bridged $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})$ (**IVb**)

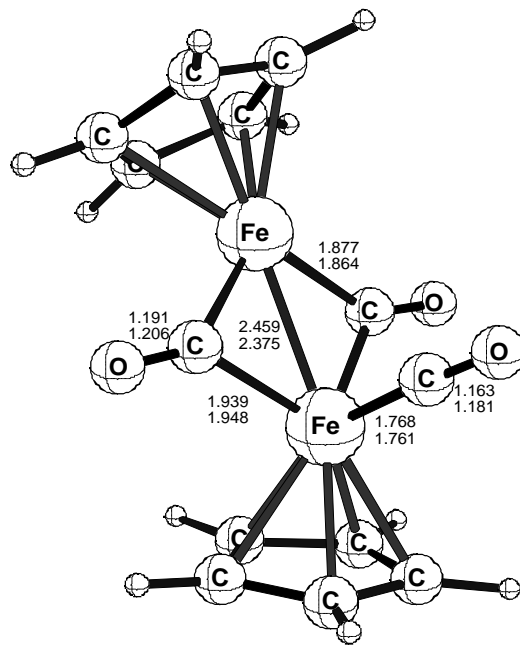
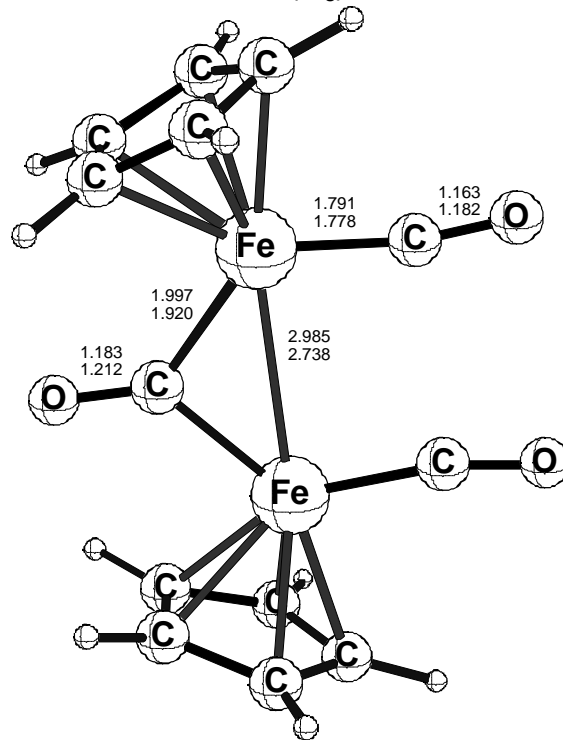
	B3LYP	BP86		B3LYP	BP86
a ₋	5i (0)	32i (0)	a''	28(0)	44i (19)
	50(2)	84(0)		98(1)	46(0)
	74(1)	69(1)		122(0)	128(0)
	186(1)	193(0)		214(0)	213(5)
	361(4)	363(10)		353(8)	364(14)
	370(21)	367(23)		385(0)	407(1)
	452(11)	445(9)		404(0)	421(2)
	478(1)	465(4)		473(34)	477(1)
	527(8)	535(2)		574(1)	536(10)
	584(2)	551(3)		583(0)	550(0)
	586(2)	557(2)		792(0)	756(0)
	789(4)	749(6)		808(49)	773(45)
	815(5)	778(3)		831(11)	788(3)
	834(4)	797(1)		832(48)	793(62)
	836(2)	801(4)		835(0)	800(18)
	847(3)	811(4)		880(9)	834(18)
	890(3)	845(2)		891(0)	846(0)
	894(0)	847(0)		994(8)	955(16)
	998(23)	960(18)		1019(0)	987(0)
	1019(39)	987(38)		1054(0)	1024(0)
	1059(2)	1025(2)		1057(0)	1026(0)
	1060(1)	1030(0)		1115(16)	1076(5)
	1122(5)	1085(3)		1265(0)	1214(0)
	1265(0)	1214(0)		1357(30)	1309(74)
	1373(3)	1323(2)		1379(0)	1345(0)
	1388(0)	1351(0)		1428(5)	1377(1)
	1429(1)	1377(2)		1449(0)	1395(0)
	1450(0)	1395(0)		3217(0)	3141(0)
	1894(635)	1789(474)		3239(0)	3155(0)
	3217(0)	3141(0)		3244(2)	3161(1)
	3238(0)	3154(0)		3251(0)	3167(0)
	3244(1)	3161(2)		3260(1)	3176(7)
	3251(0)	3167(2)			
	3261(0)	3176(0)			

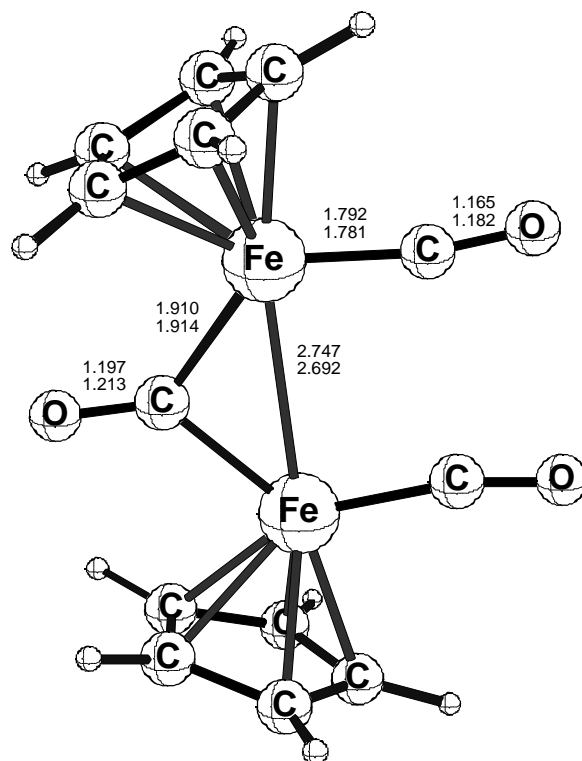
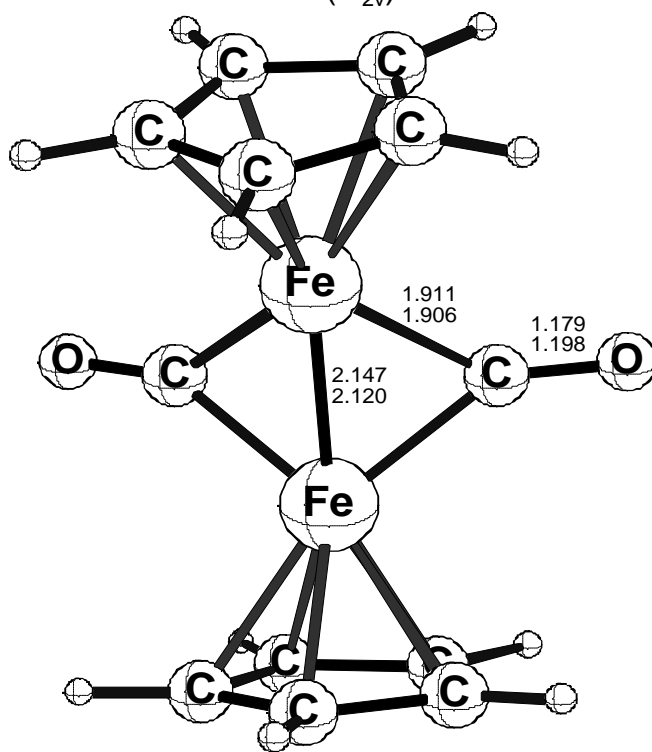
Table S17 Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for singlet C_1 unbridged $\text{Cp}_2\text{Fe}_2(\text{CO})$ (**IVc**)

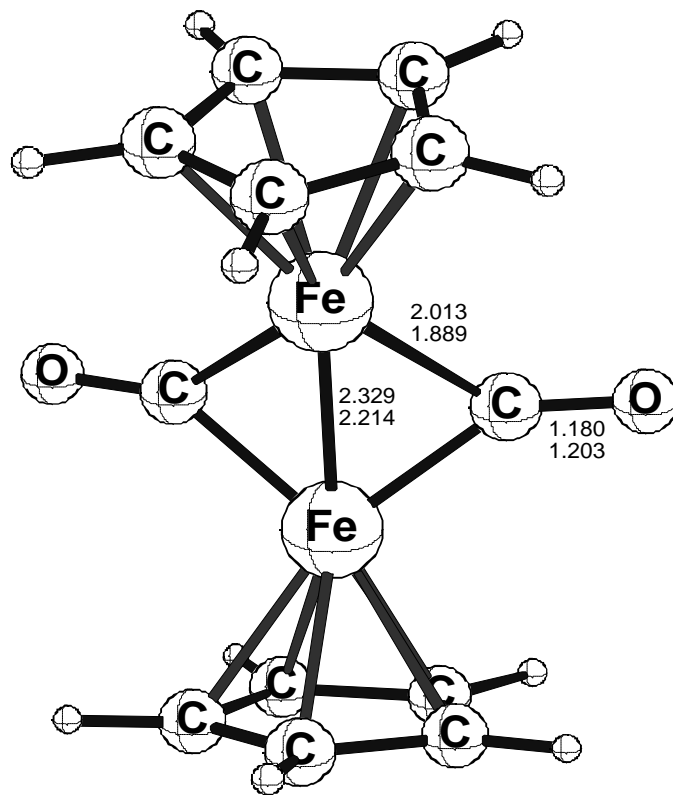
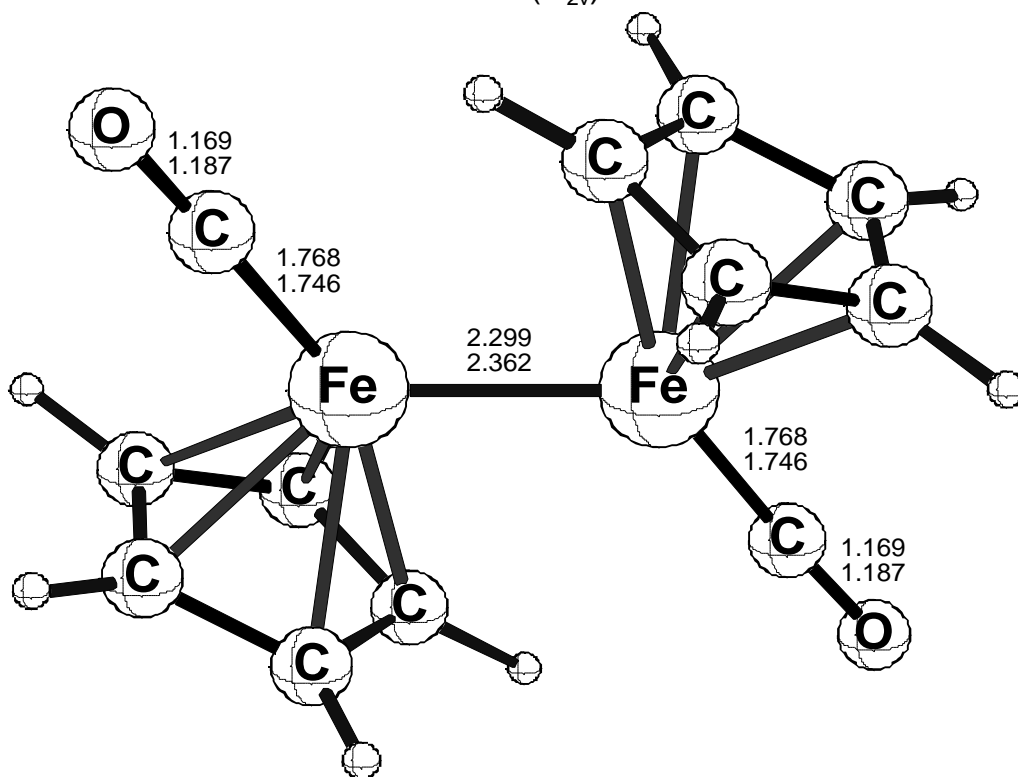
	B3LYP	BP86		B3LYP	BP86
a	20(0)	57(0)	a	887(1)	865(5)
	61(1)	75(0)		908(5)	877(8)
	66(0)	92(2)		951(13)	923(7)
	86(0)	101(0)		969(18)	930(18)
	95(0)	147(0)		991(16)	951(8)
	142(1)	184(5)		996(11)	993(8)
	178(2)	202(3)		1036(15)	1007(10)
	226(1)	242(1)		1059(4)	1022(2)
	316(4)	318(1)		1059(0)	1025(2)
	326(2)	327(9)		1062(2)	1043(13)
	336(9)	379(20)		1080(12)	1064(13)
	380(4)	398(12)		1115(14)	1080(17)
	395(5)	428(4)		1251(0)	1188(1)
	415(2)	456(8)		1258(0)	1194(0)
	439(5)	488(22)		1316(21)	1269(5)
	537(18)	516(14)		1355(1)	1288(1)
	545(19)	544(16)		1365(1)	1316(0)
	579(6)	547(3)		1389(7)	1327(1)
	581(3)	567(3)		1410(0)	1349(3)
	585(4)	574(1)		1414(1)	1350(1)
	597(24)	607(9)		1423(2)	1364(0)
	667(18)	668(20)		1455(0)	1389(1)
	718(10)	705(1)		1987(1429)	1908(1084)
	786(25)	741(4)		3130(1)	2627(2)
	798(3)	757(3)		3166(0)	2989(9)
	801(8)	760(13)		3202(4)	3079(3)
	807(19)	765(1)		3226(0)	3139(2)
	816(15)	777(24)		3229(0)	3145(1)
	823(2)	785(0)		3234(2)	3149(4)
	828(8)	809(6)		3237(1)	3157(1)
	843(20)	818(6)		3249(1)	3160(5)
	850(1)	821(1)		3249(3)	3168(1)
	884(4)	825(1)		3255(0)	3174(2)

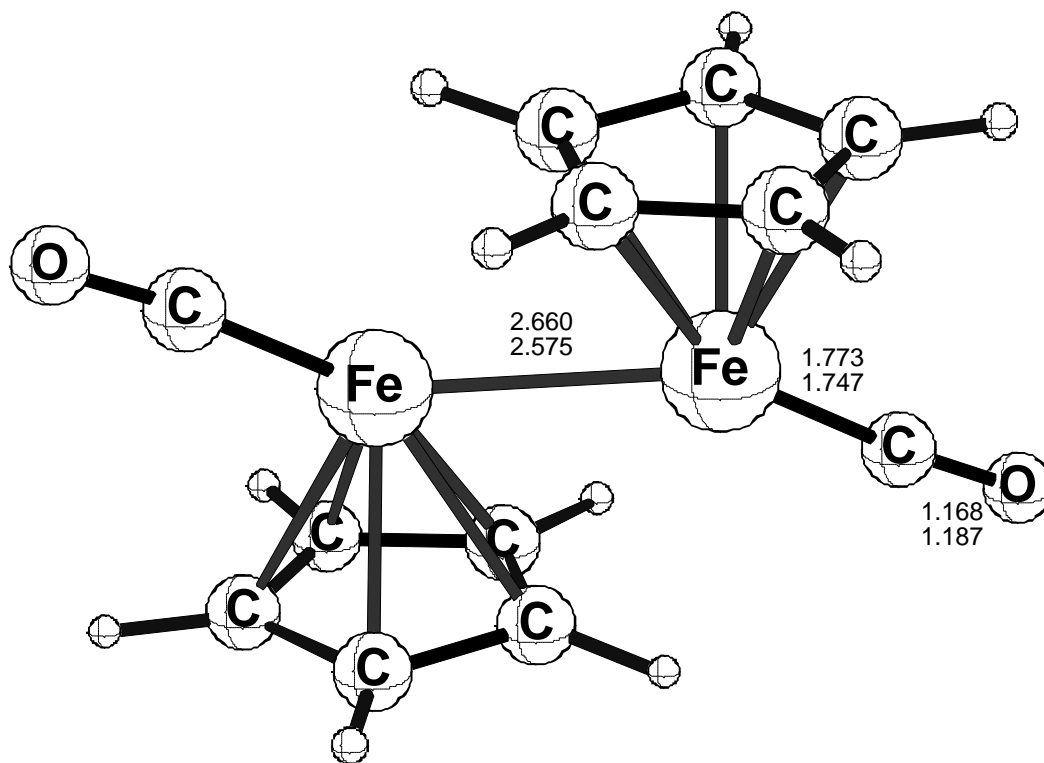
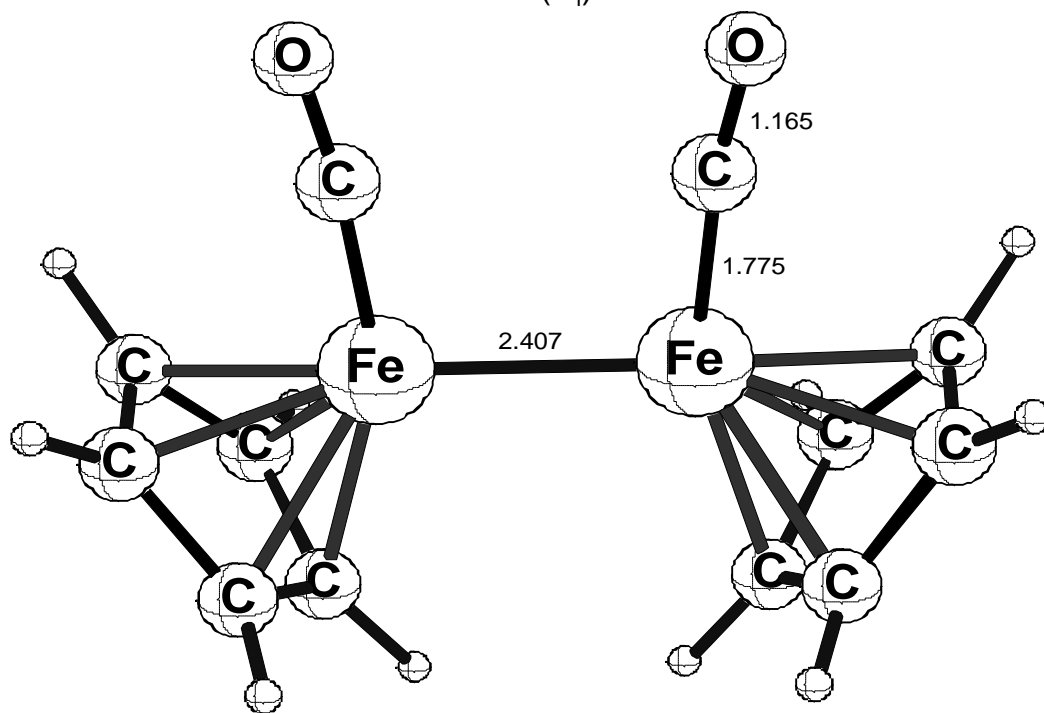
1a (C_s)1b (C_{2v})

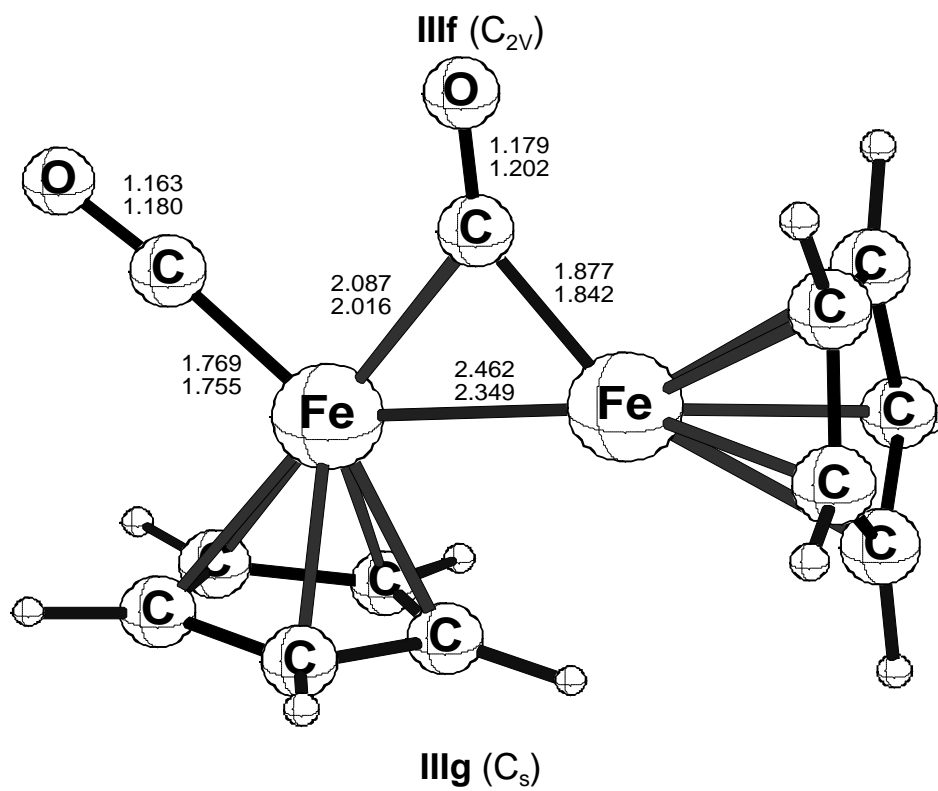
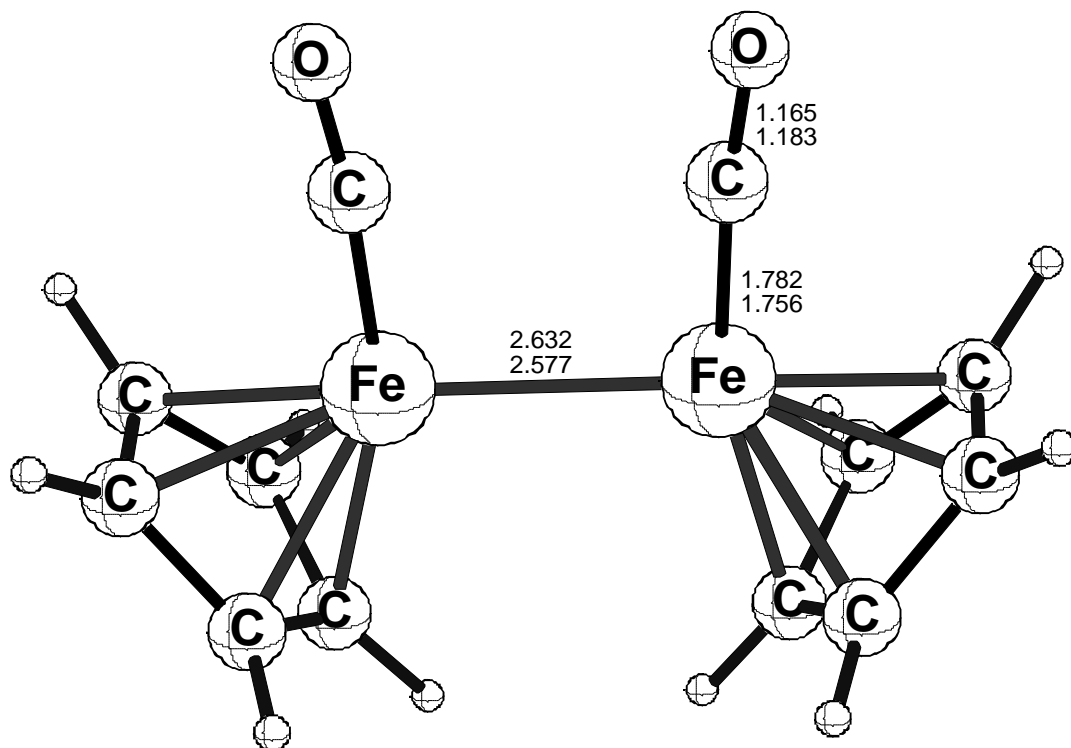
**Ic** (C_{2h})**IIa** (C_{2v})

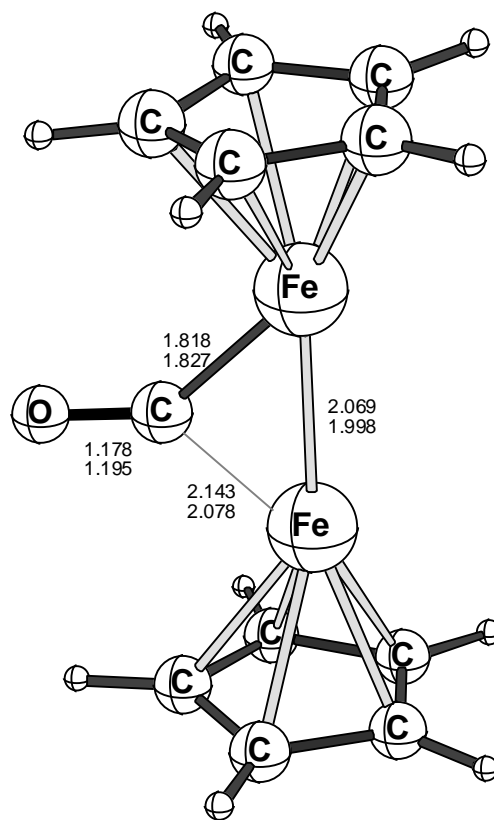
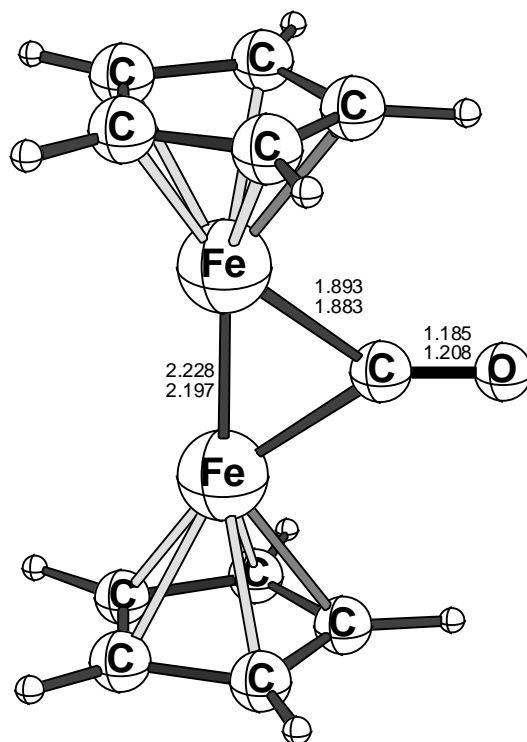
**IIb (C_s)****IIc (C_{2v})**

IIId (C_{2v})IIIa (C_{2v})

IIIb (C_{2v})IIIc (C_{2h})

III d (C_1)III e (C_{2v})



IVa (C_1)IVb (C_s)

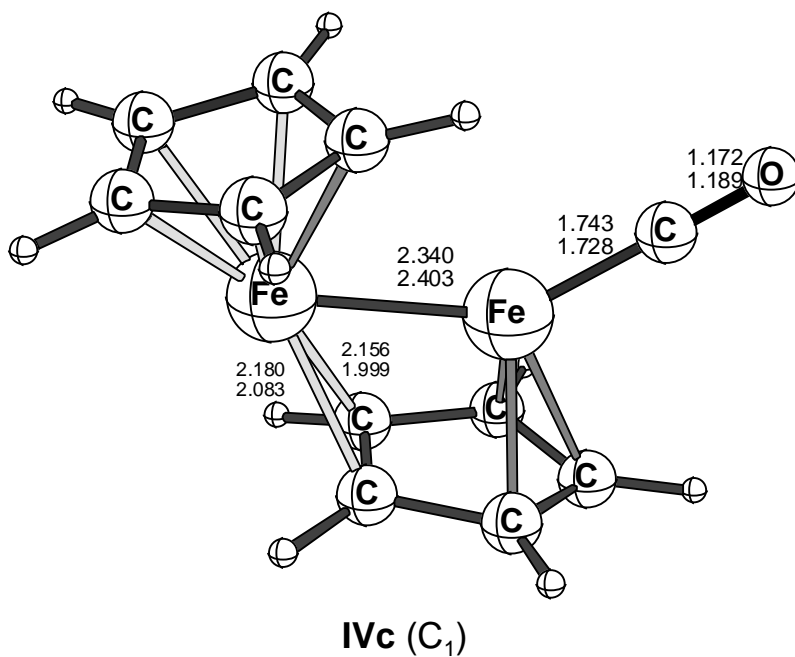


Figure 1. The 17 $\text{Cp}_2\text{Fe}_2(\text{CO})_n$ ($n = 4, 3, 2, 1$) structures discussed in this paper.