

# **Unsaturation in Binuclear Cyclobutadiene Cobalt Carbonyls: Comparison with Isoelectronic Binuclear Cyclopentadienyliron Carbonyls**

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## **Supporting Information**

**Tables S1 to S17.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_n$  derivatives ( $n = 4, 3, 2, 1$ ).

**Table S1.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **Ia-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_4$  with  $C_2$  symmetry

	B3LYP	BP86	B3LYP	BP86
a	14(0)	18i(0)	b	30(0)
	46(0)	42(1)		58(0)
	72(0)	69(0)		67(0)
	73(0)	69(0)		100(0)
	97(0)	93(0)		97(0)
	110(0)	107(0)		126(0)
	123(1)	118(1)		134(8)
	173(0)	174(0)		131(7)
	384(0)	381(0)		372(0)
	387(7)	384(5)		374(23)
	429(1)	421(2)		376(19)
	438(0)	435(0)		409(0)
	473(20)	469(21)		437(5)
	502(0)	504(0)		465(0)
	528(52)	541(0)		500(106)
	542(0)	549(36)		526(0)
	565(0)	568(0)		544(128)
	637(0)	612(0)		562(91)
	727(0)	698(0)		567(75)
	800(4)	761(0)		633(1)
	802(0)	776(6)		718(30)
	850(0)	811(0)		607(2)
	938(15)	912(0)		800(0)
	939(0)	915(12)		781(83)
	953(0)	922(0)		849(42)
	960(1)	934(0)		936(9)
	1175(0)	1128(0)		938(0)
	1198(1)	1175(0)		952(26)
	1263(0)	1230(0)		922(24)
	1353(2)	1306(6)		962(0)
	1362(0)	1318(0)		936(0)
	2049(1604)	1962(1367)		1175(0)
	2082(0)	1998(0)		1203(0)
	3246(0)	3167(0)		1263(24)
	3258(0)	3180(0)		1230(17)
	3270(0)	3192(0)		1354(0)
	3284(0)	3205(0)		1360(13)
				1316(12)
				1306(0)
				1948(0)
				1966(971)
				3270(0)
				3284(7)
				3205(5)

**Table S2.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **1b-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_4$  with  $C_{2h}$  symmetry

	B3LYP	BP86	B3LYP	BP86	
a <sub>g</sub>	79(0) 147(0) 231(0) 391(0) 412(0) 464(0) 503(0) 528(0) 780(0) 814(0) 916(0) 963(0) 1199(0) 1283(0) 1337(0) 1936(0) 2081(0) 3261(0) 3280(0)	77(0) 145(0) 233(0) 387(0) 415(0) 460(0) 518(0) 535(0) 750(0) 776(0) 891(0) 939(0) 1174(0) 1256(0) 1289(0) 1856(0) 1992(0) 3183(0) 3202(0)	b <sub>g</sub>	50(0) 84(0) 116(0) 230(0) 297(0) 395(0) 478(0) 556(0) 631(0) 744(0) 839(0) 944(0) 967(0) 1176(0) 1384(0) 3245(0) 3265(0) 43(1) 94(0)	50(0) 87(0) 130(0) 258(0) 315(0) 389(0) 477(0) 553(0) 604(0) 715(0) 797(0) 911(0) 940(0) 1129(0) 1342(0) 3167(0) 3187(0) 44(1) 91(1)
a <sub>u</sub>	48(1) 59(0) 119(1) 347(25) 435(4) 507(48) 628(1) 743(6) 838(1) 939(5) 967(16) 1176(0) 1384(0) 1896(1181) 3245(0) 3265(0) 3261(1) 3280(4)	50(0) 58(1) 117(1) 346(17) 439(1) 509(39) 602(1) 714(8) 796(2) 905(2) 940(15) 1129(0) 1341(2) 1830(917) 3166(0) 3187(0) 3183(1) 3202(3)	b <sub>u</sub>	139(1) 220(1) 386(3) 438(0) 471(6) 501(73) 533(57) 638(588) 777(22) 814(126) 915(17) 957(0) 1189(9) 1281(10) 1336(13) 2068(1596) 1979(1377)	136(1) 217(2) 380(4) 433(2) 467(15) 508(47) 541(50) 646(499) 749(29) 777(115) 891(16) 933(0) 1162(13) 1253(5) 1288(13) 1979(1377)

**Table S3.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **Ic-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_4$  with  $C_{2v}$  symmetry

	B3LYP	BP86		B3LYP	BP86
a <sub>1</sub>	50(0) 91(0) 126(0) 228(0) 386(4) 414(0) 454(0) 485(0) 507(18) 551(63) 778(1) 813(81) 914(9) 964(1) 1196(1) 1288(10) 1334(1) 1937(0)	52(0) 89(0) 123(0) 230(1) 382(5) 416(2) 458(2) 481(3) 516(5) 554(56) 747(1) 774(75) 889(6) 941(0) 1171(3) 1261(6) 1286(2) 1858(2)	b <sub>1</sub>	59(0) 88(0) 125(1) 349(24) 412(0) 474(38) 547(14) 630(1) 739(7) 834(1) 942(5) 971(20) 1178(0) 1388(0) 1898(1182) 3245(0) 3265(0) 89(0)	60(0) 87(0) 122(1) 349(17) 411(2) 479(24) 544(14) 605(0) 708(10) 790(2) 908(2) 944(18) 1131(0) 1345(2) 1833(919) 3166(0) 3187(1) 87(0)
	2099(1467)	2011(1195)	b <sub>2</sub>	153(0)	149(1)
	3261(0) 3281(0)	3183(0) 3202(0)		216(1) 389(1)	213(1) 385(0)
a <sub>2</sub>	43(0) 58(0) 98(0) 230(0) 298(0) 405(0) 540(0) 625(0) 731(0) 825(0) 942(0) 968(0) 1175(0) 1386(0) 3244(0) 3264(0)	45(0) 57(0) 112(0) 259(0) 318(0) 399(0) 538(0) 598(0) 700(0) 781(0) 907(0) 941(0) 1128(0) 1343(0) 3165(0) 3186(0)		441(3) 496(59) 508(0) 642(577) 772(9) 795(59) 912(8) 954(0) 1187(7) 1286(3) 1331(12) 2071(323) 3260(1) 3280(4)	432(1) 498(47) 526(5) 646(494) 742(9) 756(61) 887(8) 931(1) 1160(11) 1258(0) 1284(12) 1984(314) 3182(1) 3202(3)

**Table S4.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **Id-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_4$  with  $C_2$  symmetry

	B3LYP	BP86	B3LYP	BP86
a	32(0)	27(0)	b	44(0)
	58(0)	38(0)		62(0)
	61(0)	60(0)		82(0)
	70(0)	66(0)		93(0)
	94(0)	90(0)		126(0)
	108(0)	106(0)		121(1)
	127(0)	120(0)		136(7)
	170(0)	174(0)		373(16)
	374(0)	367(0)		387(10)
	387(4)	387(6)		422(0)
	412(0)	403(0)		431(5)
	436(1)	433(0)		475(26)
	470(3)	466(5)		470(32)
	507(5)	510(0)		489(98)
	525(12)	535(5)		522(42)
	541(2)	545(6)		542(105)
	567(67)	569(57)		549(31)
	632(0)	606(2)		562(27)
	721(1)	697(2)		609(2)
	786(21)	751(33)		683(24)
	796(34)	766(12)		779(27)
	842(21)	802(24)		791(7)
	935(8)	908(7)		740(30)
	946(0)	915(0)		762(9)
	953(0)	929(0)		842(30)
	968(0)	945(0)		907(4)
	1179(0)	1132(0)		945(14)
	1203(1)	1180(2)		952(13)
	1266(9)	1237(7)		913(13)
	1352(1)	1302(2)		930(13)
	1365(0)	1324(0)		960(9)
	2042(154)	1955(145)		936(7)
	2103(1229)	2017(986)		1177(0)
	3244(0)	3164(0)		1130(0)
	3258(0)	3180(0)		1200(10)
	3271(0)	3191(0)		1265(15)
	3287(0)	3205(0)		1236(6)
			2040(1136)	1236(6)
			2052(589)	1350(9)
				1301(11)
				1264(3)
				1364(9)
				1175(17)
				1323(8)
				1959(1111)
				1972(267)
				3244(3)
				3258(0)
				3164(3)
				3180(1)
				3271(0)
				3191(1)
				3286(8)
				3205(5)

**Table S5.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **Ie-t** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_4$  with  $C_{2h}$  symmetry

	B3LYP	BP86	B3LYP	BP86	
a <sub>g</sub>	77(0) 121(0) 183(0) 362(0) 365(0) 414(0) 482(0) 510(0) 724(0) 802(0) 941(0) 957(0) 1187(0) 1269(0) 1369(0) 1884(0) 2077(0) 3263(0) 3280(0)	75(0) 126(0) 190(0) 352(0) 372(0) 420(0) 478(0) 513(0) 685(0) 760(0) 926(0) 934(0) 1173(0) 1240(0) 1324(0) 1816(0) 1983(0) 3185(0) 3202(0)	b <sub>g</sub>	29(0) 80(0) 127(0) 249(0) 320(0) 371(0) 430(0) 490(0) 582(0) 737(0) 825(0) 925(0) 932(0) 1178(0) 1338(0) 3243(0) 3262(0) 41(1) 88(0)	37(0) 80(0) 130(0) 253(0) 303(0) 358(0) 412(0) 460(0) 550(0) 703(0) 782(0) 895(0) 900(0) 1131(0) 1291(0) 3165(0) 3183(0) 46(2) 85(0)
a <sub>u</sub>	29(0) 58(1) 104(1) 338(4) 412(3) 461(15) 592(3) 739(0) 825(2) 929(22) 944(3) 1178(0) 1339(9) 1877(802) 3245(0) 3262(0) 3263(0) 3280(11)	37(0) 57(1) 103(0) 336(4) 411(0) 457(7) 564(4) 706(1) 781(1) 900(24) 910(0) 1131(0) 1292(10) 1804(692) 3167(0) 3183(0) 3185(0) 3202(5)	b <sub>u</sub>	128(1) 191(7) 308(32) 385(9) 416(6) 445(17) 486(36) 540(84) 718(30) 802(127) 892(4) 954(17) 1131(14) 1267(39) 1369(10) 2064(1884) 1970(1621)	126(0) 199(3) 296(12) 379(10) 409(10) 469(44) 497(2) 545(70) 681(42) 762(126) 892(4) 927(18) 1111(13) 1237(19) 1324(5) 1970(1621)

**Table S6.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IVf-t** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_4$  with  $C_{2v}$  symmetry

	B3LYP	BP86	B3LYP	BP86	
a <sub>1</sub>	38(1) 82(0) 118(0) 175(1) 359(3) 365(1) 415(0) 436(1) 487(13) 548(84) 721(2) 798(84) 941(3) 956(2) 1188(0) 1268(7) 1368(0) 1886(5) 2094(1575)	38(1) 79(0) 117(0) 185(1) 353(3) 371(1) 422(0) 434(4) 484(4) 553(71) 681(3) 752(79) 924(5) 932(0) 1175(0) 1239(6) 1321(1) 1817(0) 2001(1295)	b <sub>1</sub>	8(0) 80(0) 113(0) 338(5) 394(0) 426(12) 491(5) 591(2) 736(1) 820(2) 929(25) 945(2) 1177(0) 1340(8) 1879(806) 3244(1) 3261(0) 84(0) 130(2)	15i(0) 76(0) 110(0) 336(4) 385(1) 435(5) 477(2) 563(3) 700(2) 771(1) 899(25) 911(0) 1129(0) 1292(9) 1805(693) 3165(1) 3182(0) 82(0) 128(1) 196(2) 301(7)
a <sub>2</sub>	15i 55(0) 105(0) 252(0) 331(0) 372(0) 481(0) 579(0) 730(0) 808(0) 922(0) 931(0) 1176(0) 1338(0) 3241(0) 3261(0)	21i 55(0) 107(0) 256(0) 307(0) 356(0) 452(0) 548(0) 693(0) 756(0) 892(0) 898(0) 1127(0) 1289(0) 3163(0) 3182(0)	b <sub>2</sub>	374(11) 432(19) 479(30) 506(1) 712(19) 783(57) 886(2) 949(10) 1127(18) 1266(33) 1366(9) 2066(533) 3261(0) 3280(10) 1975(436) 3182(0) 3201(5)	366(9) 449(42) 493(1) 511(2) 673(21) 734(68) 887(2) 921(11) 1107(12) 1235(16) 1320(4) 1975(436) 3182(0) 3201(5)

**Table S7.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IIa-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_3$  with  $C_s$  symmetry

	B3LYP	BP86	B3LYP	BP86
a'	32(1)	30(2)	a"	38(0)
	61(1)	67(1)		47(0)
	92(0)	90(1)		73(0)
	139(0)	140(0)		71(0)
	208(2)	207(3)		102(1)
	218(0)	220(0)		122(1)
	397(1)	395(2)		251(1)
	414(4)	407(1)		336(10)
	416(8)	415(7)		343(26)
	430(0)	427(5)		386(2)
	463(3)	450(7)		445(4)
	498(2)	498(5)		496(11)
	510(21)	504(11)		525(14)
	534(43)	542(30)		601(0)
	654(525)	649(397)		597(0)
	773(16)	744(3)		720(1)
	785(51)	745(69)		693(4)
	790(15)	758(4)		726(3)
	804(39)	769(31)		701(3)
	899(14)	875(11)		815(0)
	902(9)	877(10)		767(0)
	947(8)	929(2)		831(0)
	959(0)	937(0)		788(1)
	1173(1)	1146(1)		926(0)
	1184(0)	1157(1)		889(0)
	1296(14)	1266(8)		939(2)
	1311(21)	1268(8)		907(1)
	1313(8)	1274(7)		946(7)
	1320(7)	1281(13)		980(10)
	1918(19)	1840(19)		951(9)
	2077(913)	1990(748)		1175(0)
	3251(0)	3172(0)		1129(0)
	3262(0)	3184(0)		1127(0)
	3272(2)	3192(1)		1396(0)
	3282(1)	3204(1)		1352(1)
			1884(1242)	1361(0)
				1816(987)
			3235(0)	3155
			3246(0)	3168
			3256(0)	3177
			3267(0)	3189

**Table S8.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IIb-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_3$  with  $C_{2v}$  symmetry

	B3LYP	BP86	B3LYP	BP86
$a_1$	80(1)	81(1)	$b_1$	124(1)
	112(0)	110(0)		196(3)
	242(0)	246(0)		213i(0)
	373(0)	382(1)		303(0)
	420(0)	421(0)		407(8)
	457(18)	467(10)		448(1)
	520(7)	525(11)		567(162)
	564(17)	553(9)		572(139)
	770(0)	736(1)		768(33)
	801(0)	764(0)		798(82)
	897(26)	873(24)		873(0)
	958(1)	937(0)		944(13)
	1182(1)	1156(0)		922(4)
	1307(0)	1269(14)		1163(0)
	1315(12)	1279(0)		1299(57)
	1935(319)	1855(355)		1266(22)
	2014(424)	1908(255)	$b_2$	1315(0)
	3256(0)	3179(0)		1271(12)
	3277(0)	3200(0)		3256(0)
$a_2$	42(0)	54(0)		3277(6)
	70(0)	103(0)		3199(3)
	218(0)	246(0)		42i
	320(0)	339(0)		97i
	466(0)	467(0)		64(1)
	606(0)	582(0)		105(2)
	710(0)	683(0)		408(12)
	823(0)	779(0)		489(29)
	936(0)	903(0)		283(1)
	978(0)	949(0)		344(41)
	1176(0)	1129(0)		412(14)
	1404(0)	1358(0)		478(40)
	3241(0)	3163(0)		607(0)
	3261(0)	3185(0)		709(9)
				818(0)
				775(1)
				903(4)
				978(15)
				875(1)
				949(15)
				1176(0)
				1403(0)
				1129(0)
				1357(0)
				1887(1296)
				1826( 964)
				3237(2)
				3161(0)
				3261(0)
				3185(0)

**Table S9.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IIIc** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_3$  with  $C_{2v}$  symmetry

	B3LYP	BP86	B3LYP	BP86
$a_1$	67(2)	68(2)	$b_1$	42(0)
	106(0)	104(0)		150(0)
	243(0)	246(0)		182(1)
	355(11)	358(9)		337(0)
	391(1)	407(0)		417(26)
	441(11)	456(6)		437(27)
	512(24)	515(19)		492(90)
	531(2)	535(0)		731(1)
	734(1)	703(2)		798(128)
	798(0)	758(1)		896(0)
	937(17)	916(23)		944(0)
	953(9)	936(1)		1141(0)
	1193(1)	1189(0)		1260(70)
	1263(0)	1231(0)		1355(1)
	1355(2)	1309(4)		3259(0)
	1939(954)	1854(758)		3277(11)
	1973(4)	1889(7)	$b_2$	20 <i>i</i>
	3259(0)	3181(0)		74(2)
	3278(0)	3199(0)		105(0)
$a_2$	6(0)	18 <i>i</i> (0)		345(11)
	24 <i>i</i>	107(0)		391(1)
	153(0)	186(0)		445(18)
	327(0)	336(0)		520(20)
	434(0)	428(0)		618(0)
	607(0)	579(0)		734(0)
	731(0)	701(0)		816(3)
	815(0)	771(0)		939(21)
	925(0)	900(0)		950(5)
	940(0)	913(0)		1176(0)
	1176(0)	1129(0)		1350(2)
	1351(0)	1306(0)		1936(1017)
	3240(0)	3162(0)		3242(0)
	3259(0)	3181(0)		3259(0)
				1850(803)
				3164(0)
				3181(0)

**Table S10.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IIIa-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_2$  with  $C_{2v}$  symmetry

	B3LYP	BP86	B3LYP	BP86
$a_1$	36(1)	50(2)	$b_1$	151(2)
	79(0)	87(0)		180(3)
	216(0)	229(1)		248(3)
	379(21)	367(17)		393(0)
	394(1)	411(0)		464(10)
	469(10)	474(3)		733(1)
	546(1)	556(3)		790(114)
	725(0)	700(0)		933(4)
	792(0)	751(0)		970(0)
	948(0)	933(0)		1167(23)
	970(29)	942(26)		1287(32)
	1186(0)	1169(0)		1391(0)
	1289(0)	1261(0)		3257(0)
	1391(0)	1345(2)		3274(6)
	1957(31)	1863(74)	$b_2$	46(0)
	3257(0)	3177(1)		100(0)
	3274(0)	3194(0)		406(1)
$a_2$	32(0)	$37i$		440(0)
	129(0)	125(0)		514(28)
	216(0)	226(0)		606(0)
	316(0)	333(0)		766(2)
	462(0)	451(0)		816(0)
	609(0)	578(0)		915(17)
	772(0)	733(0)		945(0)
	808(0)	766(0)		1177(0)
	915(0)	884(0)		1326(12)
	927(0)	897(0)		1939(1297)
	1177(0)	1130(0)		3238(0)
	1324(0)	1279(0)		3254(0)
	3236(0)	3155(0)		1844(987)
	3254(0)	3175(0)		3175(0)

**Table S11.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IIIb-t** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_2$  with  $C_s$  symmetry.

	B3LYP	BP86	B3LYP	BP86
a'	38(1)	36(2)	a''	14(0)
	61(0)	63(1)		38(0)
	145(0)	163(0)		97(0)
	184(2)	188(2)		119(0)
	208(0)	217(0)		254(0)
	329(3)	375(3)		275(0)
	380(2)	399(8)		318(1)
	398(9)	409(0)		324(0)
	412(1)	421(0)		382(10)
	462(7)	449(2)		407(0)
	472(16)	510(39)		448(0)
	517(0)	522(0)		497(25)
	726(2)	716(3)		513(13)
	755(1)	722(0)		601(0)
	787(69)	748(102)		568(0)
	793(41)	749(0)		616(0)
	895(38)	900(13)		574(0)
	933(5)	907(0)		711(0)
	936(32)	910(29)		699(0)
	943(1)	932(0)		740(2)
	1142(32)	1138(16)		708(2)
	1188(0)	1182(0)		764(0)
	1250(37)	1225(47)		809(0)
	1265(37)	1228(0)		764(1)
	1345(3)	1298(8)		898(0)
	1346(1)	1298(0)		923(17)
	1902(3)	1814(0)		938(7)
	3255(0)	3176(1)		952(10)
	3257(0)	3176(0)		911(1)
	3274(6)	3194(3)		922(0)
	3275(3)	3194(0)	1890(1269)	1130(0)
				1801(949)
			3237(0)	3157(0)
			3239(0)	3158(0)
			3256(0)	3177(0)
			3257(0)	3177(0)

**Table S12.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IIc** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_2$  with  $C_{2h}$  symmetry

	B3LYP	BP86	B3LYP	BP86	
a <sub>g</sub>	96(0) 173(0) 228(0) 357(0) 467(0) 552(0) 573(0) 726(0) 785(0) 920(0) 956(0) 1190(0) 1214(0) 1327(0) 2052(0) 3241(0) 3259(0)	96(0) 166(0) 217(0) 348(0) 467(0) 559(0) 580(0) 702(0) 756(0) 881(0) 935(0) 1165(0) 1179(0) 1271(0) 1960(0) 3157(0) 3175(0)	b <sub>g</sub>	97(0) 186(0) 318(0) 471(0) 632(0) 678(0) 813(0) 923(0) 929(0) 1168(0) 1316(0) 3226(0) 3243(0) 47(1) 113(1) 329(2) 449(0)	98(0) 164(0) 319(0) 468(0) 602(0) 643(0) 776(0) 884(0) 911(0) 1120(0) 1275(0) 3142(0) 3160(0) <i>42i</i> 98(2) 291(2) 451(4)
a <sub>u</sub>	24 <i>i</i> 96(0) 128(4) 236(6) 451(6) 584(31) 657(4) 804(0) 913(8) 933(19) 1169(0) 1311(11) 3223(2) 3242(0)	46 <i>i</i> 86(1) 119(3) 224(2) 453(4) 559(23) 617(1) 769(0) 876(2) 912(22) 1121(0) 1273(15) 3140(2) 3160(0)	b <sub>u</sub>	541(21) 543(47) 645(9) 770(78) 910(1) 937(58) 1175(95) 1205(25) 1327(6) 2033(2539) 3239(7) 3259(2) 1945(1956) 3155(6) 3175(3)	539(16) 563(21) 639(20) 745(59) 873(0) 919(43) 1146(82) 1178(22) 1272(5) 1945(1956) 3155(6) 3175(3)

**Table S13.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **III $d$ -t** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})_2$  with  $C_i$  symmetry

	B3LYP	BP86	B3LYP	BP86
$a_g$	64(0)	58(0)	$a_u$	30(1)
	83(0)	90(0)		57(0)
	121(0)	118(0)		66(0)
	157(0)	164(0)		73 <i>i</i>
	184(0)	198(0)		95(0)
	230(0)	272(0)		189(4)
	359(0)	361(0)		215(2)
	404(0)	410(0)		354(0)
	414(0)	421(0)		423(6)
	496(0)	508(0)		364(6)
	518(0)	530(0)		442(12)
	598(0)	570(0)		484(48)
	722(0)	686(0)		528(38)
	766(0)	702(0)		597(47)
	801(0)	751(0)		692(32)
	849(0)	780(0)		777(78)
	894(0)	882(0)		710(71)
	906(0)	890(0)		786(55)
	955(0)	917(0)		745(44)
	985(0)	945(0)		840(25)
	1094(0)	1071(0)		777(18)
	1175(0)	1144(0)		915(14)
	1193(0)	1178(0)		887(1)
	1309(0)	1275(0)		953(11)
	1442(0)	1332(0)		986(16)
	2068(0)	1961(0)		915(18)
	3165(0)	3060(0)		1098(25)
	3205(0)	3148(0)		1075(11)
	3220(0)	3157(0)		1173(5)
	3235(0)	3178(0)		1147(9)
				1199(12)
				1278(5)
				1314(1)
				1445(5)
				2052(2542)
				1333(6)
				1937(2445)
				3165(6)
				3061(4)
				3205(5)
				3148(2)
				3219(7)
				3157(5)
				3236(3)
				3178(0)

**Table S14.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IVa-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})$  with  $C_1$  symmetry

	B3LYP	BP86		B3LYP	BP86
a	33(0)	36(0)	a	900(23)	874(17)
	41(0)	41(0)		905(10)	877(14)
	53(0)	67(0)		924(16)	896(7)
	74(1)	81(0)		935(5)	900(8)
	92(0)	88(0)		938(4)	912(2)
	122(1)	124(1)		944(2)	924(1)
	183(1)	198(1)		968(11)	938(14)
	286(9)	281(4)		972(8)	942(9)
	352(4)	359(5)		1165(18)	1122(1)
	363(2)	369(5)		1170(0)	1124(0)
	368(5)	385(3)		1172(0)	1135(12)
	421(3)	415(4)		1178(2)	1148(1)
	433(10)	423(11)		1264(20)	1239(17)
	490(5)	474(6)		1285(17)	1251(17)
	500(3)	494(6)		1313(6)	1262(8)
	535(27)	534(30)		1319(6)	1269(6)
	600(23)	571(8)		1393(3)	1341(2)
	611(2)	575(3)		1399(2)	1348(2)
	615(16)	633(18)		1704(440)	1608(313)
	673(4)	645(24)		3218(1)	3139(1)
	707(15)	667(4)		3223(1)	3143(1)
	757(22)	710(11)		3239(1)	3149(4)
	760(26)	726(20)		3240(1)	3159(2)
	779(27)	736(26)		3245(1)	3170(2)
	781(36)	746(6)		3254(1)	3177(1)
	802(6)	751(13)		3263(1)	3185(0)
	808(11)	764(11)		3268(0)	3187(1)

**Table S15.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IVb-t** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})$  with  $C_s$  symmetry

	B3LYP	BP86		B3LYP	BP86
a'	56(0)	143(0)	a''	$63i$	$49i$
	84(0)	160(3)		28i(0)	37(1)
	181(1)	236(1)		34(0)	101(0)
	249(1)	256(0)		78(0)	162(2)
	348(11)	358(1)		268(0)	305(2)
	367(4)	379(4)		363(5)	388(7)
	394(14)	397(4)		387(3)	404(4)
	409(2)	432(3)		583(1)	577(7)
	524(6)	482(3)		600(0)	586(4)
	585(42)	511(5)		660(1)	644(10)
	671(7)	630(37)		733(3)	711(2)
	707(3)	702(32)		764(0)	721(2)
	754(62)	735(12)		799(0)	768(0)
	772(61)	757(45)		908(13)	856(9)
	862(79)	876(1)		914(0)	885(4)
	935(6)	900(5)		927(23)	906(0)
	938(9)	915(19)		938(5)	931(14)
	967(11)	931(10)		1171(0)	1107(1)
	1124(23)	1082(13)		1174(0)	1127(0)
	1176(6)	1161(17)		1319(5)	1210(8)
	1255(43)	1178(8)		1330(2)	1330(2)
	1264(16)	1241(25)		3227(0)	3120(1)
	1344(1)	1328(15)		3235(0)	3175(1)
	1392(6)	1291(4)		3249(1)	3139(2)
	1694(583)	1828(604)		3252(0)	3148(1)
	3254(0)	3166(2)		3254(0)	3160(0)
	3271(1)	3136(1)			
	3275(2)	3192(1)			

**Table S16.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IVc-s** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})$  with  $C_1$  symmetry

	B3LYP	BP86		B3LYP	BP86
a	54(0)	43i(0)	a	848(9)	830(3)
	74(1)	45(1)		888(7)	860(3)
	84(0)	77(0)		895(14)	878(7)
	91(0)	84(0)		913(6)	878(1)
	140(1)	151(1)		925(1)	898(0)
	169(1)	154(4)		954(11)	919(11)
	198(0)	192(3)		954(41)	927(14)
	233(2)	241(2)		968(4)	968(33)
	302(7)	325(3)		1120(1)	1066(2)
	346(8)	345(14)		1142(70)	1105(0)
	395(4)	387(7)		1157(0)	1109(57)
	402(2)	405(1)		1159(0)	1110(0)
	436(7)	449(9)		1160(45)	1125(24)
	465(2)	473(0)		1225(21)	1185(30)
	532(25)	515(16)		1285(5)	1231(6)
	535(12)	520(18)		1336(4)	1277(6)
	538(35)	523(21)		1346(1)	1283(0)
	579(14)	575(13)		1348(2)	1300(0)
	607(3)	577(6)		2039(1360)	1948(1075)
	617(25)	583(20)		2918(5)	2685(6)
	690(20)	647(17)		3143(1)	3078(1)
	711(26)	669(17)		3158(5)	3093(5)
	732(31)	697(12)		3209(2)	3123(3)
	764(32)	739(21)		3213(3)	3126(4)
	819(0)	772(2)		3228(4)	3141(4)
	837(13)	800(6)		3274(0)	3197(0)
	844(2)	809(14)		3280(1)	3200(0)

**Table S17.** Harmonic vibrational frequencies (in  $\text{cm}^{-1}$ ) and infrared intensities (in parentheses, in  $\text{km/mol}$ ) for the structure **IVd-t** of  $(\text{C}_4\text{H}_4)_2\text{Co}_2(\text{CO})$  with  $C_1$  symmetry

	B3LYP	BP86		B3LYP	BP86
a	37(1)	63(0)	a	860(6)	846(7)
	58(1)	69(0)		892(4)	851(12)
	88(0)	78(0)		906(12)	866(9)
	113(2)	87(1)		916(0)	871(2)
	147(0)	128(0)		920(6)	885(1)
	174(4)	140(1)		933(52)	908(8)
	176(1)	194(0)		948(6)	922(13)
	255(0)	240(1)		953(2)	929(5)
	271(6)	321(3)		1104(11)	1056(1)
	329(1)	343(6)		1152(1)	1097(8)
	336(0)	355(1)		1160(0)	1117(10)
	368(1)	385(5)		1167(19)	1134(1)
	422(1)	420(3)		1206(23)	1141(13)
	440(2)	436(1)		1246(10)	1166(11)
	479(9)	457(3)		1252(42)	1231(7)
	550(14)	537(12)		1302(2)	1273(1)
	557(23)	549(8)		1328(1)	1285(4)
	603(32)	557(8)		1382(30)	1309(5)
	606(40)	580(11)		2045(1125)	1937(1145)
	623(8)	647(16)		3179(0)	3052(2)
	650(3)	667(3)		3197(2)	3057(2)
	653(2)	672(3)		3202(0)	3099(1)
	684(22)	679(7)		3215(1)	3135(2)
	729(88)	713(50)		3221(0)	3143(2)
	764(1)	727(37)		3236(0)	3157(2)
	772(4)	753(11)		3242(0)	3160(2)
	786(0)	760(1)		3259(0)	3168(0)