Supporting Information

Photochemical or Electrochemical Bond Breaking – Exploring the Chemistry of (μ_2-alkyne)$Co_2(CO)_6$ complexes using Time-Resolved Infrared Spectroscopy, Spectro-electrochemical and Density Functional Methods

Jennifer C. Manton, Florian J.R. Cerpentier, Emma C. Harvey, Ian P. Clark, Gregory M. Greetham, Conor Long, and Mary T. Pryce

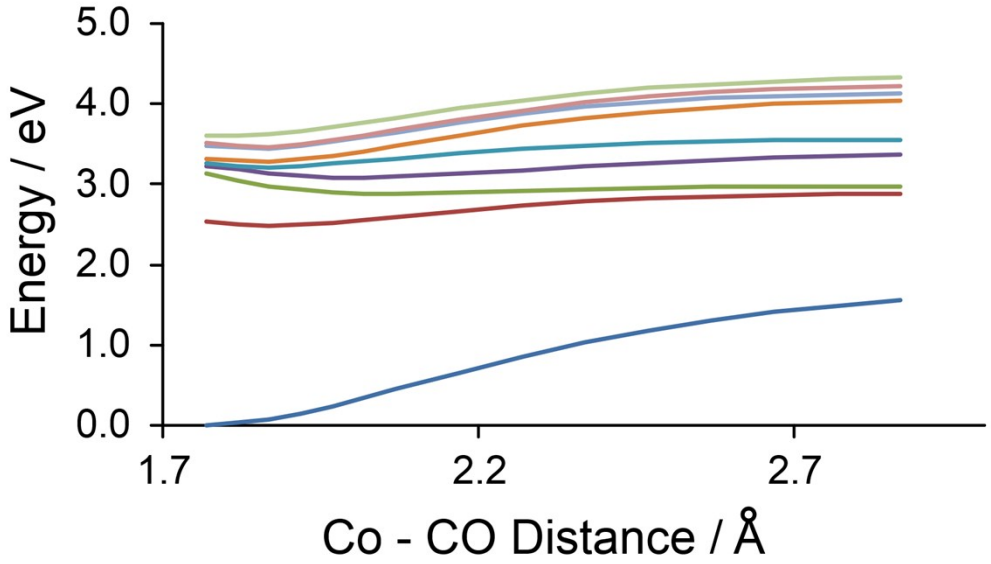

Figure SI1. The behavior of the ground-state and eight lowest energy singlet excited states of $(\mu_2\text{-}C_2H_2)Co_2(CO)_6$ along the axial CO-loss reaction coordinate

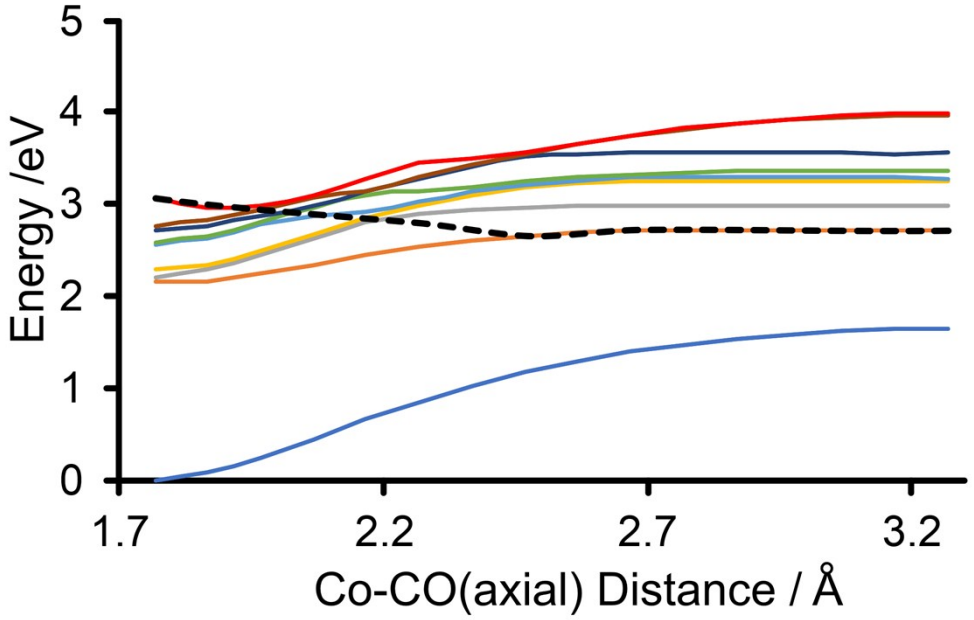

Figure SI2. The behaviour of the 10 lowest energy singlet excited states along the Co-CO (axial) reaction coordinate for **3**, the dashed curve represents the non-adiabatic path to CO-loss.

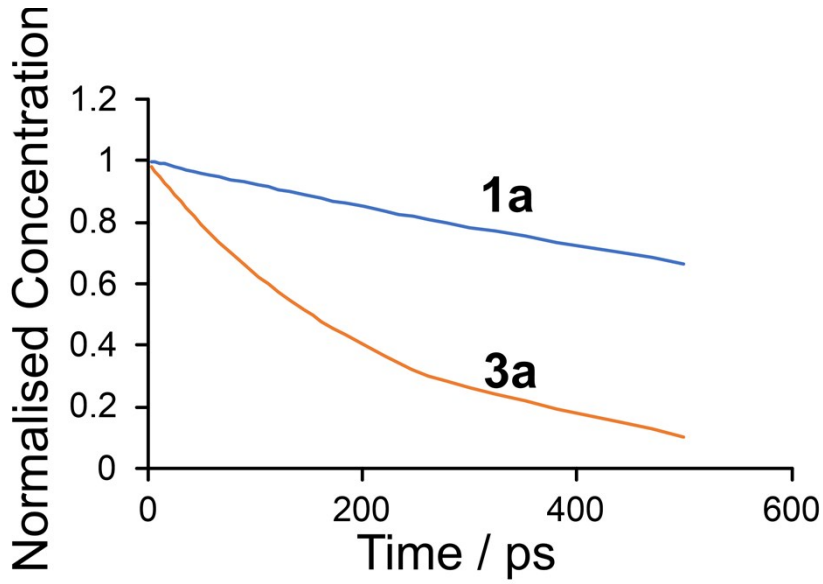

Figure SI3. The time-dependent behavior of the normalized concentration of the initially produced CO-loss species obtained by global analysis of the ps-TRIR data following excitation of **1** and **3** at 400 nm.

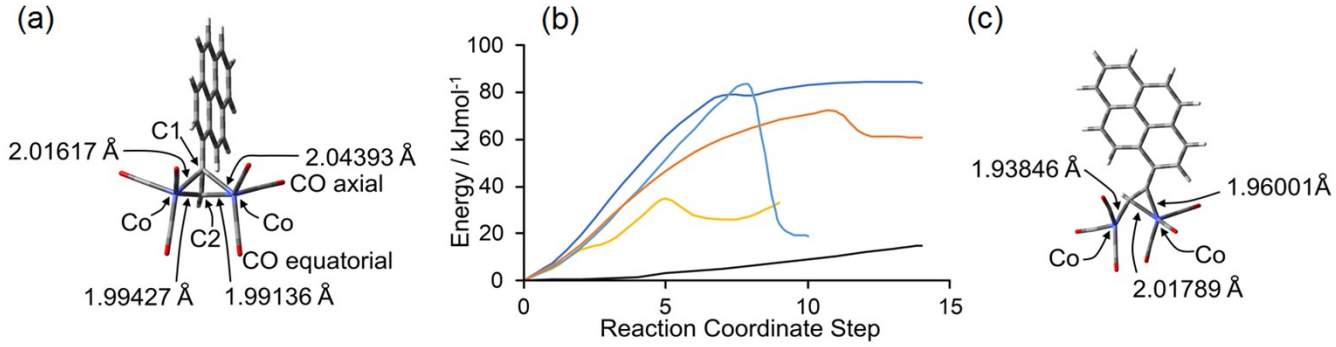

Figure SI4 . (a) The optimized structure of **1•-** with the atoms involved in the reaction coordinates indicated (atomic coordinates are provided in the supporting information; (b) the energy changes calculated along the Co-Co stretch reaction coordinate (grey), the Co-C1(alkyne) (yellow), the Co-C2(alkyne) (light blue), Co-CO(axial) (red) and Co-CO(equatorial) (dark blue); (c) the optimized structure at the local minimum, step 7 on the Co-C1 stretch reaction coordinate (yellow plot)

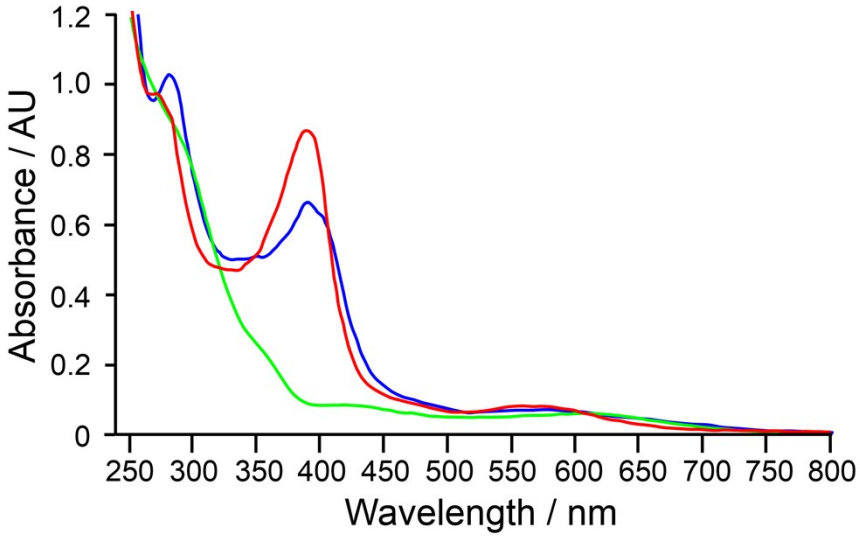

Figure SI5. Overlay of electronic absorbance spectra of (μ_2-R,R'-alkyne)-$Co_2(CO)_6$ complexes in DCM. **1** (red line, 1.2×10^{-2} M), **2** (blue line, 1.5×10^{-2} M) and **3** (green line, 1.6×10^{-2} M).

Complex	λ max (nm), ε ($\times 10^{-3}$ M^{-1} cm^{-1})
1	274 (20.5), 392 (19.1), 577 (1.1)
2	279 (18.7), 389 (11.7), 574 (1.3)
3	290 (17.1), 361 (4.4), 430 (1.8), 614 (1.14)

Table SI1. UV-vis absorption data for complexes in this study. All spectra were recorded in spectroscopic grade DCM.

Complex	Parent Spectrum (cm^{-1})	Vibrationally "hot" species (cm^{-1})	Diradical species (cm^{-1})	CO loss photoproduct (cm^{-1})
1	2092, 2056, 2030	2078, 2046, 2012	2081, 2048, 2016	2074,2034, 2007, 1977
2	2085, 2048, 2023	2067, 2034, 2003	2076, 2041, 2012	2064, 2004, 1970
3	2090, 2051, 2023	2069, 2039, 1999	2081, 2041, 2007	N/A

Table SI2. ps-TRIR spectral data for all complexes in this study, ps-TRIR for (μ_2-alkyne)$Co_2(CO)_6$ complexes were carried out in spectroscopic grade *n*-heptane

Quantum yield measurements for the CO-loss process.

The UV-vis absorbance spectra of both hexacarbonyl complexes show intense absorbances in the UV region up to 400 nm with broad but weak absorbances in the visible region extending to 700 nm. The triphenylphosphine pentacarbonyl derivatives of **1** and **2**; exhibit strong absorbances around 430 nm. Monitoring the absorbance change at 430 nm provides a convenient method for measuring the yield of photoinduced CO-loss species.

The conversion to photoproduct was limited to 10%, to minimize the effect of photoproduct absorbance at the excitation wavelengths (546 to 313 nm). See Table SI3 for quantum yields obtained. These results demonstrate that the quantum yield of CO-loss (Φ_{CO}) is strongly dependent on both the excitation wavelength and the nature of the alkyne substituent. Table SI3 shows that the quantum yield for CO loss (Φ_{CO}) from **1** increases from 4% to 25% when the excitation wavelength is reduced from 546 nm to 313 nm. In the case of **2**, however, the largest Φ_{CO} was obtained for 365 nm irradiation. All Φ_{CO} values are low compared to organometallic compounds such as $Cr(CO)_6$ or (η^6-benzene)$Cr(CO)_3$, where $\Phi_{CO} > 60\%$ have been reported. It should be noted that the Φ_{CO} values obtained at 405 nm are similar to those estimated using the ps-TRIR technique (400 nm excitation), based on the recovery of the parent ν_{CO} bands following excitation.

λ_{exc} (nm)	From ferrioxalate actinometry		Estimated from TRIR	
	1	2	1	2
313	25 %	8 %	-	-
365	10 %	19 %	-	-
405	9 %	13 %	10 %	15 %
546	4 %	10 %	-	-

Table SI3. Quantum yields of CO loss for 1 and 2 using potassium ferrioxalate actinometry and that estimated from recovery of parent bands during ps-TRIR experiments. Results recorded in spectroscopic grade *n*-heptane.

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4 Co4    -2.2085     1.0232    -0.7734 Co
5 C5    -2.4461     0.0778    -2.2882 C
6 C6    -3.7654     1.8933    -0.5081 C
7 C7    -1.2012     2.3473    -1.3783 C
8 C8    -2.9824    -2.0718    -0.2157 C
9 C9    -4.0415    -0.2112     1.6651 C
10 C10    -1.7753    -1.6752     2.2186 C
11 O11    -3.3070    -2.9121    -0.9314 O
12 O12    -5.0038     0.1544     2.1758 O
13 O13    -1.2929    -2.2730     3.0733 O
14 O14    -4.7533     2.4493    -0.3168 O
15 O15    -2.5894    -0.5288    -3.2542 O
16 O16    -0.5518     3.2134    -1.7649 O
17 H17    -1.2887     1.5897     1.8112 H
18 C18     0.4837    -0.5255    -0.1497 C
19 C19     1.7039     0.1196     0.2068 C
20 C20     0.5421    -1.7238    -0.8852 C
21 C21     2.9483    -0.4769    -0.1812 C
22 C22     1.7522     1.3573     0.9349 C
23 C23     1.7438    -2.3021    -1.2601 C
24 H24    -0.3890    -2.2083    -1.1613 H
25 C25     4.1863     0.1481     0.1669 C
26 C26     2.9668    -1.7009    -0.9178 C
27 C27     2.9332     1.9539     1.2623 C
28 H28     0.8229     1.8283     1.2269 H
29 H29     1.7461    -3.2318    -1.8226 H
30 C30     4.1930     1.3749     0.8967 C
31 C31     5.4278    -0.4501    -0.2149 C
32 C32     4.2271    -2.2793    -1.2879 C
33 H33     2.9345     2.8910     1.8133 H
34 C34     5.4203     1.9734     1.2288 C
35 C35     6.6308     0.1834     0.1397 C
36 C36     5.4048    -1.6827    -0.9517 C
37 H37     4.2211    -3.2113    -1.8472 H
38 C38     6.6249     1.3813     0.8534 C
39 H39     5.4201     2.9079     1.7840 H
40 H40     7.5734    -0.2733    -0.1511 H
41 H41     6.3521    -2.1321    -1.2384 H
42 H42     7.5655     1.8562     1.1180 H
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4 Co4     0.8481    -1.5443     1.5245 Co
5 C5     0.3830    -3.2603     1.8076 C
6 C6     2.4960    -1.3743     2.2369 C
7 C7    -0.1143    -0.7784     2.8001 C
8 C8     1.0282    -3.5108    -1.1350 C
9 C9     3.2127    -1.8830    -0.6417 C
10 C10     1.2955    -1.1172    -2.4727 C
11 O11     0.8045    -4.6215    -1.3319 O
12 O12     4.3486    -2.0100    -0.5110 O
13 O13     1.2049    -0.6877    -3.5358 O
14 O14     3.5480    -1.2465     2.6843 O
15 O15     0.0897    -4.3600     1.9706 O
16 O16    -0.7116    -0.3068     3.6618 O
17 C17    -1.6114    -1.0298    -0.4199 C
18 C18    -2.5261    -0.0002    -0.0440 C
19 C19    -2.1081    -2.1321    -1.1400 C
20 C20    -3.9032    -0.1088    -0.4286 C
21 C21    -2.1383     1.1488     0.7266 C
22 C22    -3.4381    -2.2372    -1.5161 C
23 H23    -1.4247    -2.9280    -1.4112 H
24 C24    -4.8377     0.9113    -0.0651 C
25 C25    -4.3608    -1.2356    -1.1785 C
26 C26    -3.0317     2.1170     1.0779 C
27 H27    -1.1076     1.2525     1.0347 H
28 H28    -3.7735    -3.1036    -2.0801 H
29 C29    -4.4102     2.0416     0.6942 C
30 C30    -6.2095     0.8059    -0.4561 C
31 C31    -5.7427    -1.3158    -1.5589 C
32 H32    -2.7021     2.9723     1.6625 H
33 C33    -5.3436     3.0332     1.0425 C
34 C34    -7.1072     1.8215    -0.0867 C
35 C35    -6.6279    -0.3396    -1.2152 C
36 H36    -6.0691    -2.1806    -2.1309 H
37 C37    -6.6771     2.9221     0.6540 C
38 H38    -5.0119     3.8914     1.6214 H
39 H39    -8.1490     1.7394    -0.3860 H
40 H40    -7.6718    -0.4127    -1.5095 H
41 H41    -7.3868     3.6969     0.9304 H
42 C42     1.1639     1.2582     0.0967 C
43 C43     0.9438     2.1296    -1.0253 C
44 C44     1.5488     2.0897     1.2047 C
45 C45     1.1555     3.4733    -0.6004 C
46 H46     0.6561     1.8119    -2.0186 H
47 C47     1.5254     3.4499     0.7776 C
48 H48     1.7945     1.7354     2.1969 H
49 H49     1.0780     4.3539    -1.2250 H
50 H50     1.7770     4.3088     1.3861 H
51 Fe51     2.8652     2.3759    -0.3372 Fe
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53 C53     4.1804     2.7397    -1.8774 C
54 C54     4.7720     2.7137     0.3551 C
55 H55     4.4787     4.6478    -0.7399 H
56 C56     4.2742     1.3779    -1.4618 C
57 H57     3.9016     3.0857    -2.8645 H
58 C58     4.6396     1.3615    -0.0808 C
59 H59     5.0199     3.0367     1.3581 H
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4 Co4     2.1602     0.9650    -0.2027 Co
5 C5      2.5788     1.1894     1.5263 C
6 C6      3.7288     0.7196    -1.0690 C
7 C7      1.7870     2.6341    -0.6528 C
8 C8      1.0579    -1.4742     1.8397 C
9 C9      2.8898    -2.0691    -0.2506 C
10 C10     0.2455    -2.5777    -0.5738 C
11 O11     0.8742    -1.5915     2.9687 O
12 O12     3.9216    -2.5422    -0.4374 O
13 O13    -0.4098    -3.4217    -1.0009 O
14 O14     4.7010     0.5897    -1.6687 O
15 O15     2.8520     1.3100     2.6377 O
16 O16     1.5356     3.7165    -0.9485 O
17 H17     0.8587    -0.1108    -2.4445 H
18 C18    -0.9672     0.9472     0.1200 C
19 C19    -1.7428     1.8480    -0.6964 C
20 C20    -1.5824     0.9218     1.4174 C
21 C21    -2.7997     2.3749     0.0988 C
22 H22    -1.5396     2.0831    -1.7331 H
23 C23    -2.7044     1.7976     1.4018 C
24 H24    -1.2455     0.3296     2.2578 H
25 H25    -3.5616     3.0669    -0.2361 H
26 H26    -3.3827     1.9737     2.2266 H
27 Fe27    -2.9313     0.3298    -0.0176 Fe
28 C28    -4.9031    -0.1311    -0.3704 C
29 C29    -4.1306    -0.3226    -1.5560 C
30 C30    -4.3710    -0.9812     0.6454 C
31 H31    -5.7317     0.5559    -0.2555 H
32 C32    -3.1202    -1.2892    -1.2724 C
33 H33    -4.2714     0.1923    -2.4976 H
34 C34    -3.2683    -1.6968     0.0895 C
35 H35    -4.7266    -1.0525     1.6652 H
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12 O12     -5.0394    -0.1109     2.1268 O
13 O13     -1.3476    -2.8404     2.7895 O
14 O14     -4.6559     2.5693     0.0078 O
15 O15     -2.5125     0.0081    -3.3300 O
16 O16     -0.3612     3.5561    -1.3116 O
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20 C20      0.5119    -1.6759    -1.0387 C
21 C21      2.9110    -0.4887    -0.2189 C
22 C22      1.7003     1.2196     1.0655 C
23 C23      1.7184    -2.2044    -1.4689 C
24 H24     -0.4178    -2.1349    -1.3589 H
25 C25      4.1450     0.1057     0.1948 C
26 C26      2.9399    -1.6348    -1.0710 C
27 C27      2.8755     1.7892     1.4568 C
28 H28      0.7621     1.6498     1.3918 H
29 H29      1.7265    -3.0758    -2.1195 H
30 C30      4.1412     1.2552     1.0434 C
31 C31      5.3928    -0.4455    -0.2386 C
32 C32      4.2047    -2.1657    -1.4908 C
33 H33      2.8695     2.6691     2.0960 H
34 C34      5.3643     1.8237     1.4392 C
35 C35      6.5908     0.1569     0.1834 C
36 C36      5.3793    -1.5996    -1.0941 C
37 H37      4.2057    -3.0389    -2.1391 H
38 C38      6.5739     1.2778     1.0126 C
39 H39      5.3562     2.6987     2.0847 H
40 H40      7.5376    -0.2636    -0.1467 H
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Mol File for High-Spin Diradical of **1**

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7 C7      1.0969     2.9577     0.7271 C
8 C8      3.6392    -1.5258     0.4921 C
9 C9      3.4722    -1.1246    -2.3173 C
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14 O14     4.7501     2.5495    -0.2047 O
15 O15     2.2536     0.5813     3.4296 O
16 O16     0.3724     3.8459     0.6973 O
17 H17     1.4806     1.1107    -2.0776 H
18 C18    -0.3882    -0.4341     0.3396 C
19 C19    -1.6035     0.0417    -0.2286 C
20 C20    -0.4510    -1.3127     1.4357 C
21 C21    -2.8513    -0.3962     0.3252 C
22 C22    -1.6454     0.9462    -1.3445 C
23 C23    -1.6560    -1.7345     1.9736 C
24 H24     0.4803    -1.6643     1.8699 H
25 C25    -4.0857     0.0618    -0.2316 C
26 C26    -2.8761    -1.2932     1.4361 C
27 C27    -2.8232     1.3830    -1.8722 C
28 H28    -0.7124     1.2886    -1.7734 H
29 H29    -1.6622    -2.4157     2.8206 H
30 C30    -4.0860     0.9598    -1.3413 C
31 C31    -5.3307    -0.3754     0.3196 C
32 C32    -4.1397    -1.7154     1.9692 C
33 H33    -2.8204     2.0691    -2.7157 H
34 C34    -5.3099     1.3982    -1.8733 C
35 C35    -6.5299     0.0896    -0.2453 C
36 C36    -5.3140    -1.2779     1.4364 C
37 H37    -4.1386    -2.3985     2.8150 H
38 C38    -6.5176     0.9660    -1.3290 C
39 H39    -5.3047     2.0822    -2.7183 H
40 H40    -7.4752    -0.2437     0.1756 H
41 H41    -6.2641    -1.6064     1.8505 H
42 H42    -7.4559     1.3145    -1.7517 H
@<TRIPOS>BOND
1 1 2 2
2 1 3 1
3 1 4 1
4 1 18 1
5 2 3 1
6 2 4 1
7 2 17 1
8 3 8 1
```

```
9 3 9 1
10 3 10 1
11 4 5 1
12 4 6 1
13 4 7 1
14 5 15 3
15 6 14 3
16 7 16 3
17 8 11 3
18 9 12 3
19 10 13 3
20 18 19 Ar
21 18 20 Ar
22 19 21 Ar
23 19 22 Ar
24 20 23 2
25 20 24 1
26 21 25 Ar
27 21 26 Ar
28 22 27 2
29 22 28 1
30 23 26 Ar
31 23 29 1
32 25 30 Ar
33 25 31 Ar
34 26 32 Ar
35 27 30 Ar
36 27 33 1
37 30 34 Ar
38 31 35 Ar
39 31 36 Ar
40 32 36 2
41 32 37 1
42 34 38 Ar
43 34 39 1
44 35 38 Ar
45 35 40 1
46 36 41 1
47 38 42 1
```

```
# B3LYP/6-31G(d) Tight Optimisation of Singlet pyrene acetyl dicobalt
hexacarbon
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Complex 1 with prop-1-ene and CO low-spin
53 57
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     0.4000    -0.0696    -0.4961 C
2 C2     1.1517     0.9472    -0.0251 C
3 Co3     1.9380     0.2870    -1.6664 Co
4 Co4     1.9298    -0.7277     0.5623 Co
5 C5     2.0085    -2.4787     0.1465 C
6 C6     3.6054    -0.2806     1.0486 C
7 C7     1.1544    -0.8087     2.1502 C
8 C8     2.2684    -1.2083    -2.6029 C
9 C9     3.5116     1.1666    -1.6215 C
10 C10     1.0576     1.2415    -2.8694 C
11 O11     2.4985    -2.1682    -3.1945 O
12 O12     4.4947     1.7615    -1.5735 O
13 O13     0.4748     1.8603    -3.6433 O
14 O14     4.6726     0.0196     1.3540 O
15 O15     2.0452    -3.5977    -0.1145 O
16 O16     0.6531    -0.8477     3.1839 O
17 H17     1.0840     1.9349     0.4106 H
18 C18    -0.9650    -0.5402    -0.7035 C
19 C19    -2.0888     0.0520    -0.0571 C
20 C20    -1.1780    -1.6309    -1.5669 C
21 C21    -3.3980    -0.4727    -0.3136 C
22 C22    -1.9752     1.1545     0.8573 C
23 C23    -2.4426    -2.1379    -1.8172 C
24 H24    -0.3186    -2.0829    -2.0519 H
25 C25    -4.5421     0.1041     0.3209 C
26 C26    -3.5751    -1.5752    -1.2048 C
27 C27    -3.0669     1.7005     1.4641 C
28 H28    -0.9940     1.5583     1.0694 H
29 H29    -2.5658    -2.9784    -2.4950 H
30 C30    -4.3891     1.2024     1.2198 C
31 C31    -5.8487    -0.4159     0.0613 C
32 C32    -4.8978    -2.0767    -1.4476 C
33 H33    -2.9466     2.5338     2.1518 H
34 C34    -5.5261     1.7550     1.8335 C
35 C35    -6.9571     0.1687     0.6970 C
36 C36    -5.9859    -1.5231    -0.8432 C
37 H37    -5.0128    -2.9153    -2.1296 H
38 C38    -6.7955     1.2419     1.5725 C
39 H39    -5.4044     2.5911     2.5175 H
40 H40    -7.9495    -0.2277     0.4978 H
41 H41    -6.9820    -1.9134    -1.0362 H
```

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42 H42    -7.6647     1.6802     2.0547 H
43 C43     0.9989     4.4263     1.7237 C
44 H44     0.3095     4.8663     1.0050 H
45 H45     0.5611     4.0121     2.6285 H
46 C46     2.3183     4.4138     1.5119 C
47 H47     2.9682     3.9709     2.2684 H
48 C48     3.0088     4.9782     0.3031 C
49 H49     3.7198     5.7648     0.5891 H
50 H50     3.5912     4.2058    -0.2159 H
51 H51     2.2930     5.4053    -0.4073 H
52 C52     3.6452    -3.1136     3.7488 C
53 O53     4.1485    -3.7565     4.5397 O
@<TRIPOS>BOND
1 1 2 2
2 1 3 1
3 1 4 1
4 1 18 1
5 2 3 1
6 2 4 1
7 2 17 1
8 3 4 1
9 3 8 1
10 3 9 1
11 3 10 1
12 4 5 1
13 4 6 1
14 4 7 1
15 5 15 3
16 6 14 3
17 7 16 3
18 8 11 3
19 9 12 3
20 10 13 3
21 18 19 Ar
22 18 20 Ar
23 19 21 Ar
24 19 22 Ar
25 20 23 2
26 20 24 1
27 21 25 Ar
28 21 26 Ar
29 22 27 2
30 22 28 1
31 23 26 Ar
32 23 29 1
33 25 30 Ar
34 25 31 Ar
35 26 32 Ar
36 27 30 Ar
37 27 33 1
38 30 34 Ar
39 31 35 Ar
40 31 36 Ar
41 32 36 2
42 32 37 1
43 34 38 Ar
44 34 39 1
```

```
45 35 38 Ar
46 35 40 1
47 36 41 1
48 38 42 1
49 43 44 1
50 43 45 1
51 43 46 2
52 46 47 1
53 46 48 1
54 48 49 1
55 48 50 1
56 48 51 1
57 52 53 3
```

```
# B3LYP/6-31G(d) Tight Optimisation of Triplet pyrene acetyl dicobalt he
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Complex 1 with prop-1-ene and CO high-spin
53 56
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -1.2194    -0.6381     0.2359 C
2 C2    -1.7431    -0.1690     1.3740 C
3 Co3    -2.8180    -1.7154     0.7507 Co
4 Co4    -2.2295     1.0958    -0.0606 Co
5 C5    -2.4973     1.0472    -1.8478 C
6 C6    -3.6463     1.9205     0.7111 C
7 C7    -0.9699     2.4639     0.0460 C
8 C8    -3.7021    -2.0277    -0.8246 C
9 C9    -4.0765    -1.6806     2.0368 C
10 C10    -2.0505    -3.3954     0.9314 C
11 O11    -4.2466    -2.1719    -1.8266 O
12 O12    -4.8779    -1.6434     2.8605 O
13 O13    -1.4696    -4.3717     1.0905 O
14 O14    -4.5695     2.3902     1.2104 O
15 O15    -2.6815     1.0039    -2.9822 O
16 O16    -0.1186     3.2186     0.1924 O
17 H17    -1.5231     0.0648     2.4061 H
18 C18    -0.0009    -1.0776    -0.4485 C
19 C19     1.2973    -0.8940     0.1070 C
20 C20    -0.1180    -1.6996    -1.7045 C
21 C21     2.4416    -1.3537    -0.6247 C
22 C22     1.5220    -0.2688     1.3815 C
23 C23     0.9875    -2.1385    -2.4157 C
24 H24    -1.1095    -1.8325    -2.1264 H
25 C25     3.7552    -1.1900    -0.0838 C
26 C26     2.2839    -1.9812    -1.8980 C
27 C27     2.7751    -0.1133     1.8955 C
28 H28     0.6696     0.0864     1.9461 H
29 H29     0.8547    -2.6139    -3.3840 H
30 C30     3.9378    -0.5667     1.1877 C
31 C31     4.8968    -1.6501    -0.8125 C
32 C32     3.4469    -2.4322    -2.6081 C
33 H33     2.9110     0.3617     2.8640 H
34 C34     5.2370    -0.4176     1.7029 C
35 C35     6.1770    -1.4785    -0.2591 C
36 C36     4.6971    -2.2748    -2.0905 C
37 H37     3.3066    -2.9066    -3.5761 H
38 C38     6.3431    -0.8695     0.9841 C
39 H39     5.3706     0.0528     2.6738 H
40 H40     7.0433    -1.8286    -0.8146 H
41 H41     5.5691    -2.6215    -2.6391 H
42 H42     7.3409    -0.7478     1.3961 H
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43 C43     3.4227     3.9323     0.7792 C
44 H44     3.3114     2.8513     0.8437 H
45 H45     2.5078     4.5063     0.6581 H
46 C46     4.6195     4.5190     0.8446 C
47 H47     4.6783     5.6066     0.7750 H
48 C48     5.9295     3.8016     1.0082 C
49 H49     6.6044     4.0151     0.1683 H
50 H50     6.4507     4.1318     1.9171 H
51 H51     5.7908     2.7167     1.0674 H
52 C52    -2.9120     5.2048    -1.5485 C
53 O53    -3.0987     6.2553    -1.9408 O
@<TRIPOS>BOND
1 1 2 2
2 1 3 1
3 1 4 1
4 1 18 1
5 2 3 1
6 2 4 1
7 2 17 1
8 3 8 1
9 3 9 1
10 3 10 1
11 4 5 1
12 4 6 1
13 4 7 1
14 5 15 3
15 6 14 3
16 7 16 3
17 8 11 3
18 9 12 3
19 10 13 3
20 18 19 Ar
21 18 20 Ar
22 19 21 Ar
23 19 22 Ar
24 20 23 2
25 20 24 1
26 21 25 Ar
27 21 26 Ar
28 22 27 2
29 22 28 1
30 23 26 Ar
31 23 29 1
32 25 30 Ar
33 25 31 Ar
34 26 32 Ar
35 27 30 Ar
36 27 33 1
37 30 34 Ar
38 31 35 Ar
39 31 36 Ar
40 32 36 2
41 32 37 1
42 34 38 Ar
43 34 39 1
44 35 38 Ar
45 35 40 1
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46 36 41 1
47 38 42 1
48 43 44 1
49 43 45 1
50 43 46 2
51 46 47 1
52 46 48 1
53 48 49 1
54 48 50 1
55 48 51 1
56 52 53 3
```

```
# B3LYP/6-31G(d) Tight Optimisation of Singlet alkene insertion pyrene
acetyl di
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Molecule Name Alkane insertion intermediate plus CO low-spin
53 55
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -1.0521    -1.2852    -0.2730 C
2 C2     -1.6110    -1.1210    -1.5563 C
3 Co3     -0.7605     1.6172     0.1967 Co
4 Co4     -2.7371    -1.9216    -0.0691 Co
5 C5     -2.9824    -1.9577     1.6918 C
6 C6     -4.3131    -1.2987    -0.6460 C
7 C7     -2.7951    -3.6356    -0.5693 C
8 C8     -2.0913     1.9330     1.3037 C
9 C9      0.1835     2.3132    -1.1200 C
10 C10      0.4984     1.9273     1.4139 C
11 O11     -2.9726     2.2777     1.9629 O
12 O12      0.7474     2.9115    -1.9290 O
13 O13      1.2824     2.2449     2.1934 O
14 O14     -5.2921    -0.8951    -1.1049 O
15 O15     -3.1947    -1.9855     2.8276 O
16 O16     -2.7777    -4.7443    -0.8893 O
17 C17      0.2064    -1.1318     0.3860 C
18 C18      1.4558    -0.9530    -0.3235 C
19 C19      0.2612    -1.2819     1.8020 C
20 C20      2.6779    -0.8962     0.4225 C
21 C21      1.5435    -0.8627    -1.7495 C
22 C22      1.4390    -1.2263     2.5096 C
23 H23     -0.6696    -1.4380     2.3318 H
24 C24      3.9268    -0.7169    -0.2491 C
25 C25      2.6694    -1.0269     1.8467 C
26 C26      2.7383    -0.6933    -2.3902 C
27 H27      0.6389    -0.9356    -2.3359 H
28 H28      1.4315    -1.3352     3.5903 H
29 C29      3.9699    -0.6063    -1.6692 C
30 C30      5.1444    -0.6520     0.4956 C
31 C31      3.9021    -0.9615     2.5687 C
32 H32      2.7649    -0.6267    -3.4746 H
33 C33      5.2076    -0.4279    -2.3132 C
34 C34      6.3592    -0.4704    -0.1880 C
35 C35      5.0901    -0.7782     1.9219 C
36 H36      3.8721    -1.0606     3.6500 H
37 C37      6.3888    -0.3587    -1.5776 C
38 H38      5.2324    -0.3454    -3.3964 H
39 H39      7.2826    -0.4188     0.3826 H
40 H40      6.0193    -0.7285     2.4833 H
41 H41      7.3368    -0.2194    -2.0884 H
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42 H42    -1.4070    -1.8830    -2.3105 H
43 C43    -2.2625     1.3683    -1.1818 C
44 H44    -3.1375     1.0162    -0.6260 H
45 C45    -1.8853     0.2522    -2.1637 C
46 H46    -2.7035     0.1434    -2.8952 H
47 H47    -1.0061     0.5486    -2.7581 H
48 C48    -2.6942     2.6393    -1.9198 C
49 H49    -3.5605     2.4300    -2.5655 H
50 H50    -2.9901     3.4309    -1.2226 H
51 H51    -1.9034     3.0456    -2.5609 H
52 C52    -0.7159     5.3947     0.8079 C
53 O53    -1.5828     5.9008     0.2732 O
@<TRIPOS>BOND
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2 1 4 1
3 1 17 Ar
4 2 4 1
5 2 42 1
6 2 45 1
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8 3 9 1
9 3 10 1
10 4 5 1
11 4 6 1
12 4 7 1
13 5 15 3
14 6 14 3
15 7 16 3
16 8 11 3
17 9 12 3
18 10 13 3
19 17 18 1
20 17 19 Ar
21 18 20 Ar
22 18 21 Ar
23 19 22 2
24 19 23 1
25 20 24 Ar
26 20 25 Ar
27 21 26 2
28 21 27 1
29 22 25 Ar
30 22 28 1
31 24 29 Ar
32 24 30 Ar
33 25 31 Ar
34 26 29 Ar
35 26 32 1
36 29 33 Ar
37 30 34 Ar
38 30 35 Ar
39 31 35 2
40 31 36 1
41 33 37 Ar
42 33 38 1
43 34 37 Ar
44 34 39 1
```

```
45 35 40 1
46 37 41 1
47 43 44 1
48 43 45 1
49 43 48 1
50 45 46 1
51 45 47 1
52 48 49 1
53 48 50 1
54 48 51 1
55 52 53 3
```

```
# B3LYP/6-31G(d) Initial Optimisation of Triplet alkene insertion
pyreneacetyl d
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Molecule Name Alkane insertion intermediate plus CO high-spin
53 54
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     0.8169    -0.1128    -0.1280 C
2 C2     1.0702     0.6796    -1.2580 C
3 Co3     2.0459    -1.6644     0.0756 Co
4 Co4     2.1642     1.4858     0.3630 Co
5 C5     3.1233     1.0279     1.8272 C
6 C6     3.2286     2.5340    -0.6526 C
7 C7     1.0951     2.8420     1.0222 C
8 C8     3.6477    -2.4474     0.4315 C
9 C9     1.1963    -2.8961    -1.0095 C
10 C10     1.3043    -2.1666     1.6703 C
11 O11     4.6777    -2.8961     0.6629 O
12 O12     0.6248    -3.4934    -1.8051 O
13 O13     0.8817    -2.5469     2.6640 O
14 O14     3.9247     3.1904    -1.2928 O
15 O15     3.8258     0.8549     2.7255 O
16 O16     0.3849     3.6679     1.3855 O
17 C17    -0.4949    -0.0064     0.5792 C
18 C18    -1.7197    -0.2575    -0.1102 C
19 C19    -0.5661     0.2823     1.9548 C
20 C20    -2.9672    -0.1541     0.5912 C
21 C21    -1.7700    -0.6417    -1.4974 C
22 C22    -1.7692     0.3808     2.6394 C
23 H23     0.3578     0.4476     2.4997 H
24 C24    -4.2040    -0.3852    -0.0900 C
25 C25    -2.9905     0.1792     1.9799 C
26 C26    -2.9479    -0.8714    -2.1431 C
27 H27    -0.8410    -0.7584    -2.0406 H
28 H28    -1.7692     0.6247     3.6988 H
29 C29    -4.2090    -0.7410    -1.4730 C
30 C30    -5.4467    -0.2658     0.6093 C
31 C31    -4.2513     0.2905     2.6579 C
32 H32    -2.9461    -1.1646    -3.1901 H
33 C33    -5.4342    -0.9614    -2.1250 C
34 C34    -6.6474    -0.4933    -0.0841 C
35 C35    -5.4270     0.0811     2.0035 C
36 H36    -4.2461     0.5480     3.7141 H
37 C37    -6.6390    -0.8363    -1.4357 C
38 H38    -5.4318    -1.2330    -3.1777 H
39 H39    -7.5902    -0.3998     0.4489 H
40 H40    -6.3749     0.1699     2.5282 H
41 H41    -7.5781    -1.0091    -1.9541 H
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42 C42    -0.5030     4.2267    -2.0187 C
43 O43    -1.1965     5.0979    -2.2481 O
44 H44     0.3336     1.4037    -1.6086 H
45 C45     3.0264    -0.8144    -1.5388 C
46 H46     3.7755    -0.1741    -1.0495 H
47 C47     2.0197     0.0873    -2.2642 C
48 H48     2.5376     0.8439    -2.8742 H
49 H49     1.4314    -0.5178    -2.9745 H
50 C50     3.7614    -1.7361    -2.5126 C
51 H51     4.2105    -1.1427    -3.3232 H
52 H52     4.5720    -2.2996    -2.0395 H
53 H53     3.0841    -2.4583    -2.9845 H
@<TRIPOS>BOND
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2 1 3 1
3 1 17 1
4 2 44 1
5 2 47 1
6 3 8 1
7 3 9 1
8 3 10 1
9 4 5 1
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13 6 14 3
14 7 16 3
15 8 11 3
16 9 12 3
17 10 13 3
18 17 18 Ar
19 17 19 Ar
20 18 20 Ar
21 18 21 Ar
22 19 22 Ar
23 19 23 1
24 20 24 Ar
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26 21 26 2
27 21 27 1
28 22 25 Ar
29 22 28 1
30 24 29 Ar
31 24 30 Ar
32 25 31 Ar
33 26 29 Ar
34 26 32 1
35 29 33 Ar
36 30 34 Ar
37 30 35 Ar
38 31 35 2
39 31 36 1
40 33 37 Ar
41 33 38 1
42 34 37 Ar
43 34 39 1
44 35 40 1
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45 37 41 1
46 42 43 3
47 45 46 1
48 45 47 1
49 45 50 1
50 47 48 1
51 47 49 1
52 50 51 1
53 50 52 1
54 50 53 1
```

```
# B3LYP/6-31G(d) Tight Optimisation of Singlet CO insertion pyreneacetyl
dicobal
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Molecule Name CO Insertion intermediate low spin
53 57
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -0.5605    -0.3595     0.3582 C
2 C2    -0.8405    -1.4823     1.1769 C
3 Co3    -1.9124     0.0141    -0.9382 Co
4 Co4    -2.1494     0.1044     1.4646 Co
5 C5    -2.8277     1.6578     0.9836 C
6 C6    -3.5992    -0.8173     1.9267 C
7 C7    -1.4552     0.5740     3.0377 C
8 C8    -3.5248     0.4858    -1.6192 C
9 C9    -2.0132    -1.7760    -1.5362 C
10 C10    -0.8225     0.4166    -2.3026 C
11 O11    -4.5490     0.7236    -2.0794 O
12 O12    -1.7437    -2.1344    -2.6516 O
13 O13    -0.0921     0.7206    -3.1305 O
14 O14    -4.5368    -1.3909     2.2798 O
15 O15    -3.3283     2.6866     0.8019 O
16 O16    -0.9941     0.8396     4.0587 O
17 C17     0.7354     0.3684     0.3822 C
18 C18     1.9773    -0.3030     0.1784 C
19 C19     0.7593     1.7655     0.5537 C
20 C20     3.2013     0.4432     0.2148 C
21 C21     2.0665    -1.7120    -0.0997 C
22 C22     1.9405     2.4927     0.5852 C
23 H23    -0.1807     2.2881     0.6947 H
24 C24     4.4571    -0.2166     0.0331 C
25 C25     3.1811     1.8550     0.4314 C
26 C26     3.2628    -2.3386    -0.2828 C
27 H27     1.1531    -2.2864    -0.1800 H
28 H28     1.9100     3.5679     0.7420 H
29 C29     4.5030    -1.6226    -0.2102 C
30 C30     5.6775     0.5274     0.0889 C
31 C31     4.4206     2.5781     0.4800 C
32 H32     3.2918    -3.4046    -0.4946 H
33 C33     5.7471    -2.2530    -0.3826 C
34 C34     6.8984    -0.1452    -0.0864 C
35 C35     5.6152     1.9441     0.3201 C
36 H36     4.3838     3.6514     0.6489 H
37 C37     6.9307    -1.5200    -0.3182 C
38 H38     5.7764    -3.3236    -0.5689 H
39 H39     7.8247     0.4219    -0.0407 H
40 H40     6.5466     2.5032     0.3606 H
41 H41     7.8848    -2.0220    -0.4522 H
```

```
42 H42    -0.1622    -1.6447     2.0184 H
43 C43    -2.4841    -2.7426    -0.4294 C
44 H44    -3.4163    -2.3293    -0.0361 H
45 C45    -1.4474    -2.7960     0.7082 C
46 H46    -1.9061    -3.3134     1.5585 H
47 H47    -0.6200    -3.4445     0.3787 H
48 C48    -2.7625    -4.1344    -1.0129 C
49 H49    -3.1126    -4.7997    -0.2164 H
50 H50    -3.5337    -4.0888    -1.7871 H
51 H51    -1.8598    -4.5660    -1.4551 H
52 C52    -1.8438     3.8313    -2.0261 C
53 O53    -1.9392     4.9630    -2.0666 O
@<TRIPOS>BOND
1 1 2 Ar
2 1 3 1
3 1 4 1
4 1 17 1
5 2 42 1
6 2 45 1
7 3 4 1
8 3 8 1
9 3 9 1
10 3 10 1
11 4 5 1
12 4 6 1
13 4 7 1
14 5 15 2
15 6 14 3
16 7 16 3
17 8 11 3
18 9 12 2
19 9 43 1
20 10 13 3
21 17 18 Ar
22 17 19 Ar
23 18 20 Ar
24 18 21 Ar
25 19 22 Ar
26 19 23 1
27 20 24 Ar
28 20 25 Ar
29 21 26 2
30 21 27 1
31 22 25 Ar
32 22 28 1
33 24 29 Ar
34 24 30 Ar
35 25 31 Ar
36 26 29 Ar
37 26 32 1
38 29 33 Ar
39 30 34 Ar
40 30 35 Ar
41 31 35 2
42 31 36 1
43 33 37 Ar
44 33 38 1
```

```
45 34 37 Ar
46 34 39 1
47 35 40 1
48 37 41 1
49 43 44 1
50 43 45 1
51 43 48 1
52 45 46 1
53 45 47 1
54 48 49 1
55 48 50 1
56 48 51 1
57 52 53 3
```

```
# Tight Optimisation of Triplet CO insertion pyreneacetyl dicobalt
hexacarbonyl
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Molecule Name CO insertion intermediate high=spin
53 56
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     0.8782    -0.6252    -0.3487 C
2 C2     1.3447    -1.9015    -0.6835 C
3 Co3     0.7717     0.2825     1.3680 Co
4 Co4     2.5221    -0.4041    -1.4979 Co
5 C5     2.9757     1.3430    -1.4762 C
6 C6     4.0594    -1.3458    -1.6366 C
7 C7     1.9049    -0.5239    -3.2288 C
8 C8     2.1706     1.4035     1.7063 C
9 C9     1.5454    -1.2381     2.2620 C
10 C10    -0.3782     0.7842     2.7218 C
11 O11     3.1577     1.9399     1.9623 O
12 O12     1.1352    -1.5708     3.3591 O
13 O13    -1.1298     1.0881     3.5326 O
14 O14     5.0235    -1.9698    -1.7120 O
15 O15     3.3352     2.4372    -1.5116 O
16 O16     1.3926    -0.6414    -4.2503 O
17 C17    -0.3821     0.0911    -0.5113 C
18 C18    -1.6882    -0.5265    -0.4219 C
19 C19    -0.3295     1.5153    -0.5455 C
20 C20    -2.8567     0.2941    -0.4326 C
21 C21    -1.8620    -1.9444    -0.3220 C
22 C22    -1.4796     2.3043    -0.5338 C
23 H23     0.6233     2.0029    -0.7079 H
24 C24    -4.1551    -0.3032    -0.3803 C
25 C25    -2.7497     1.7253    -0.4880 C
26 C26    -3.1019    -2.5153    -0.2664 C
27 H27    -0.9859    -2.5779    -0.2817 H
28 H28    -1.3834     3.3852    -0.5865 H
29 C29    -4.2907    -1.7217    -0.3033 C
30 C30    -5.3284     0.5154    -0.3991 C
31 C31    -3.9461     2.5206    -0.5051 C
32 H32    -3.1997    -3.5951    -0.1886 H
33 C33    -5.5778    -2.2917    -0.2537 C
34 C34    -6.5895    -0.0957    -0.3493 C
35 C35    -5.1779     1.9444    -0.4656 C
36 H36    -3.8426     3.6015    -0.5509 H
37 C37    -6.7109    -1.4859    -0.2780 C
38 H38    -5.6748    -3.3726    -0.1944 H
39 H39    -7.4798     0.5277    -0.3650 H
40 H40    -6.0747     2.5584    -0.4791 H
41 H41    -7.6975    -1.9387    -0.2393 H
```

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42 H42     0.8719    -2.4554    -1.4974 H
43 C43     2.6347    -2.0709     1.5570 C
44 H44     3.3779    -1.3564     1.1759 H
45 C45     2.0075    -2.8006     0.3516 C
46 H46     2.7748    -3.4263    -0.1195 H
47 H47     1.2438    -3.4972     0.7336 H
48 C48     3.3167    -3.0539     2.5146 C
49 H49     4.1228    -3.5881     1.9999 H
50 H50     3.7462    -2.5300     3.3744 H
51 H51     2.6030    -3.7908     2.8962 H
52 C52     1.5925     4.6803     0.2412 C
53 O53     2.2213     5.6261     0.2934 O
@<TRIPOS>BOND
1 1 2 Ar
2 1 3 1
3 1 4 1
4 1 17 1
5 2 42 1
6 2 45 1
7 3 8 1
8 3 9 1
9 3 10 1
10 4 5 1
11 4 6 1
12 4 7 1
13 5 15 3
14 6 14 3
15 7 16 3
16 8 11 3
17 9 12 2
18 9 43 1
19 10 13 3
20 17 18 Ar
21 17 19 Ar
22 18 20 Ar
23 18 21 Ar
24 19 22 Ar
25 19 23 1
26 20 24 Ar
27 20 25 Ar
28 21 26 2
29 21 27 1
30 22 25 Ar
31 22 28 1
32 24 29 Ar
33 24 30 Ar
34 25 31 Ar
35 26 29 Ar
36 26 32 1
37 29 33 Ar
38 30 34 Ar
39 30 35 Ar
40 31 35 2
41 31 36 1
42 33 37 Ar
43 33 38 1
44 34 37 Ar
```

```
45 34 39 1
46 35 40 1
47 37 41 1
48 43 44 1
49 43 45 1
50 43 48 1
51 45 46 1
52 45 47 1
53 48 49 1
54 48 50 1
55 48 51 1
56 52 53 3
```

```
# B3LYP/6-31G(d) Tight Optimisation of singlet Co2CO6 loss in dichloromethane
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Molecule Name Cyclopenteneone adduct low-spin
53 56
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -0.0669     2.4886    -0.4255 C
2 C2    -0.2926     3.8283    -0.4537 C
3 Co3    -1.1200    -1.1754    -0.5815 Co
4 Co4    -3.2982    -0.5727     0.3780 Co
5 C5    -2.8601    -1.5813     1.7648 C
6 C6    -4.7240     0.1152     1.0990 C
7 C7    -3.9708    -0.6905    -1.2515 C
8 C8     0.2609    -1.7590     0.3954 C
9 C9    -1.2884     1.8597     0.0684 C
10 C10    -1.9331    -2.6838    -0.7545 C
11 O11     1.1696    -2.2948     0.8682 O
12 O12    -1.5482     0.6342     0.1088 O
13 O13    -2.3685    -3.7474    -0.9286 O
14 O14    -5.7098     0.4988     1.5669 O
15 O15    -2.6772    -2.2620     2.6830 O
16 O16    -4.4996    -0.8002    -2.2759 O
17 C17     1.1732     1.8043    -0.8694 C
18 C18     2.0593     1.2128     0.0645 C
19 C19     1.4943     1.7976    -2.2333 C
20 C20     3.2556     0.5906    -0.4135 C
21 C21     1.8225     1.2303     1.4836 C
22 C22     2.6574     1.1944    -2.7003 C
23 H23     0.8118     2.2641    -2.9377 H
24 C24     4.1652    -0.0150     0.5062 C
25 C25     3.5513     0.5775    -1.8119 C
26 C26     2.6928     0.6540     2.3592 C
27 H27     0.9354     1.7277     1.8623 H
28 H28     2.8781     1.1956    -3.7643 H
29 C29     3.8905     0.0051     1.9072 C
30 C30     5.3576    -0.6419     0.0287 C
31 C31     4.7584    -0.0599    -2.2631 C
32 H32     2.4910     0.6820     3.4270 H
33 C33     4.7986    -0.5972     2.7941 C
34 C34     6.2352    -1.2333     0.9521 C
35 C35     5.6195    -0.6439    -1.3849 C
36 H36     4.9694    -0.0657    -3.3293 H
37 C37     5.9564    -1.2104     2.3186 C
38 H38     4.5874    -0.5807     3.8603 H
39 H39     7.1408    -1.7122     0.5887 H
40 H40     6.5277    -1.1234    -1.7410 H
41 H41     6.6474    -1.6735     3.0172 H
42 H42     0.4391     4.5509    -0.8038 H
43 C43    -2.2773     2.9120     0.5294 C
44 H44    -3.2352     2.7120     0.0348 H
45 C45    -1.6441     4.2335     0.0424 C
46 H46    -2.2273     4.6985    -0.7636 H
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47 H47    -1.5628     4.9871     0.8354 H
48 C48    -2.4854     2.8596     2.0567 C
49 H49    -3.2520     3.5830     2.3491 H
50 H50    -2.8106     1.8653     2.3754 H
51 H51    -1.5588     3.1078     2.5853 H
52 C52    -0.7305    -0.9023    -2.3030 C
53 O53    -0.4092    -0.9149    -3.4141 O
@<TRIPOS>BOND
1 1 2 2
2 1 9 1
3 1 17 1
4 2 42 1
5 2 45 1
6 3 4 1
7 3 8 1
8 3 10 1
9 3 52 1
10 4 5 1
11 4 6 1
12 4 7 1
13 5 15 3
14 6 14 3
15 7 16 3
16 8 11 3
17 9 12 2
18 9 43 1
19 10 13 2
20 17 18 Ar
21 17 19 Ar
22 18 20 Ar
23 18 21 Ar
24 19 22 Ar
25 19 23 1
26 20 24 Ar
27 20 25 Ar
28 21 26 2
29 21 27 1
30 22 25 Ar
31 22 28 1
32 24 29 Ar
33 24 30 Ar
34 25 31 Ar
35 26 29 Ar
36 26 32 1
37 29 33 Ar
38 30 34 Ar
39 30 35 Ar
40 31 35 2
41 31 36 1
42 33 37 Ar
43 33 38 1
44 34 37 Ar
45 34 39 1
46 35 40 1
47 37 41 1
48 43 44 1
49 43 45 1
50 43 48 1
51 45 46 1
52 45 47 1
53 48 49 1
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54 48 50 1
55 48 51 1
56 52 53 3
```

```
# B3LYP/6-31G(d) Initial Optimisation of Triplet cyclopentanone dicobalt
hexaca
# Created by GaussView 6.0.16
#

#
#

@<TRIPOS>MOLECULE
Molecule Name
53 56
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1      0.9960    -1.0048     0.2801 C
2 C2      1.4147    -2.3436     0.6453 C
3 Co3     0.8653     2.8215     0.5034 Co
4 Co4     2.7069    -1.6048    -0.7126 Co
5 C5      3.2650    -0.1392    -1.5129 C
6 C6      4.1772    -2.1505     0.0781 C
7 C7      2.2077    -2.6584    -2.0402 C
8 C8      2.5668     3.7473     0.7164 C
9 C9      1.6407    -0.1043     1.2087 C
10 C10      0.6148     3.0896    -1.3314 C
11 O11      3.5700     4.2735     0.7974 O
12 O12      1.6144     1.1643     1.2384 O
13 O13      0.5011     3.2525    -2.4564 O
14 O14      5.1540    -2.5453     0.5710 O
15 O15      3.6327     0.8490    -2.0002 O
16 O16      1.9936    -3.3844    -2.9216 O
17 C17     -0.2475    -0.6439    -0.4780 C
18 C18     -1.5238    -0.8026     0.1376 C
19 C19     -0.2011    -0.1434    -1.7867 C
20 C20     -2.7114    -0.4642    -0.5906 C
21 C21     -1.6855    -1.2968     1.4808 C
22 C22     -1.3501     0.1920    -2.4971 C
23 H23      0.7642    -0.0303    -2.2649 H
24 C24     -3.9996    -0.6202     0.0106 C
25 C25     -2.6196     0.0368    -1.9260 C
26 C26     -2.9127    -1.4401     2.0552 C
27 H27     -0.8022    -1.5650     2.0460 H
28 H28     -1.2647     0.5703    -3.5126 H
29 C29     -4.1157    -1.1103     1.3465 C
30 C30     -5.1818    -0.2843    -0.7212 C
31 C31     -3.8243     0.3635    -2.6390 C
32 H32     -2.9977    -1.8152     3.0722 H
33 C33     -5.3904    -1.2541     1.9201 C
34 C34     -6.4350    -0.4451    -0.1078 C
35 C35     -5.0485     0.2100    -2.0646 C
36 H36     -3.7343     0.7385    -3.6554 H
37 C37     -6.5358    -0.9237     1.1984 C
38 H38     -5.4738    -1.6277     2.9375 H
39 H39     -7.3325    -0.1904    -0.6658 H
40 H40     -5.9517     0.4606    -2.6152 H
41 H41     -7.5145    -1.0413     1.6553 H
42 H42      0.8214    -3.1961     0.3265 H
43 C43      2.3049    -0.8673     2.3640 C
44 H44      3.3882    -0.7100     2.3274 H
45 C45      1.9417    -2.3429     2.0772 C
```

```
46 H46     2.7838    -3.0236     2.2357 H
47 H47     1.1431    -2.6669     2.7626 H
48 C48     1.8051    -0.3519     3.7215 C
49 H49     2.2658    -0.9265     4.5326 H
50 H50     2.0642     0.7028     3.8586 H
51 H51     0.7171    -0.4511     3.8148 H
52 C52    -0.9453     2.5929     1.0856 C
53 O53    -2.0367     2.5002     1.3976 O
@<TRIPOS>BOND
1 1 2 1
2 1 9 Ar
3 1 17 1
4 2 4 1
5 2 42 1
6 2 45 1
7 3 8 1
8 3 10 1
9 3 52 1
10 4 5 1
11 4 6 1
12 4 7 1
13 5 15 2
14 6 14 2
15 7 16 2
16 8 11 3
17 9 12 2
18 9 43 1
19 10 13 3
20 17 18 Ar
21 17 19 Ar
22 18 20 Ar
23 18 21 Ar
24 19 22 Ar
25 19 23 1
26 20 24 Ar
27 20 25 Ar
28 21 26 2
29 21 27 1
30 22 25 Ar
31 22 28 1
32 24 29 Ar
33 24 30 Ar
34 25 31 Ar
35 26 29 Ar
36 26 32 1
37 29 33 Ar
38 30 34 Ar
39 30 35 Ar
40 31 35 2
41 31 36 1
42 33 37 Ar
43 33 38 1
44 34 37 Ar
45 34 39 1
46 35 40 1
47 37 41 1
48 43 44 1
49 43 45 1
50 43 48 1
51 45 46 1
52 45 47 1
```

```
53 48 49 1
54 48 50 1
55 48 51 1
56 52 53 3
```

Table SI 4. The calculated energies of the intermediate species in the catalytic cycle presented in the Scheme relative to the energy of 1, prop-1-ene and CO

	Complex 1		alkene insertion		CO insertion		cyclopentenone adduct	
	low-spin	high-spin	low-spin	high-spin	low-spin	high-spin	low-spin	high-spin
Energy kJ/mol	0	52	96	32	-29	20	-118	-111

Summary of Calculated Electronic Transitions for **1**

#	nm	1000 cm-1	eV	f	Assignment (excitations with contrib. greater than 10.0%)
1	589.2	16.97	2.104	0.0866	128->129(60.9%) 127->129(15.9%) 125->129(10.2%)
2	433.4	23.07	2.861	0.1116	127->129(31.4%) 128->129(29.4%) 125->129(16.6%)
3	401.9	24.88	3.085	0.0267	123->129(52.9%)
4	391.4	25.55	3.168	0.0041	121->129(38.2%) 119->129(20.4%) 122->129(15.0%)
5	387.0	25.84	3.204	0.4234	128->130(56.2%) 119->129(10.3%)
6	385.2	25.96	3.219	0.1094	119->129(25.7%) 128->130(18.8%) 121->129(13.1%) 118->129(12.7%)
7	378.5	26.42	3.276	0.0017	122->129(39.6%) 127->129(16.4%) 121->129(10.0%)
8	364.6	27.43	3.400	0.0338	117->129(28.7%) 127->129(12.3%) 118->129(10.7%) 126->129(10.6%)
9	359.4	27.82	3.450	0.0934	126->129(38.3%) 120->129(16.6%)
10	356.1	28.08	3.482	0.0171	120->129(48.4%) 118->129(10.4%)
11	348.1	28.73	3.562	0.0012	125->129(26.0%) 128->133(14.9%) 117->129(14.8%) 128->131(13.6%)
12	342.6	29.19	3.619	0.0111	128->131(55.2%)
13	338.8	29.51	3.659	0.0300	128->132(64.3%)
14	325.8	30.69	3.805	0.0070	127->130(31.2%) 125->129(26.7%) 128->133(25.5%)
15	317.0	31.55	3.912	0.0016	128->134(69.4%)
16	310.3	32.23	3.996	0.0091	126->130(39.9%) 128->135(15.6%)
17	307.5	32.52	4.032	0.0087	128->135(39.9%) 126->130(18.3%) 128->136(17.8%)
18	305.3	32.76	4.061	0.0630	127->130(27.9%) 128->133(17.2%)
19	302.6	33.04	4.097	0.0105	124->129(46.5%) 125->130(12.6%)
20	301.6	33.15	4.110	0.0055	128->137(51.5%) 128->136(13.2%)
21	300.5	33.28	4.126	0.0088	128->136(42.7%) 128->135(20.5%) 128->137(20.4%)
22	297.5	33.61	4.168	0.0091	128->139(32.4%) 128->138(13.3%) 125->130(10.3%)
23	294.6	33.95	4.209	0.0016	128->138(45.9%) 128->139(23.9%)
24	287.4	34.80	4.315	0.0186	126->131(23.0%) 126->132(19.1%) 128->140(12.8%)

25	287.0	34.84	4.320	0.0047	126->132(48.3%)
26	286.4	34.91	4.329	0.0496	128->140(38.2%) 128->141(25.0%)
27	284.5	35.14	4.357	0.0386	128->141(46.8%) 126->131(13.9%)
28	283.1	35.32	4.379	0.0408	127->131(16.4%) 127->132(10.1%)
29	280.8	35.61	4.415	0.0202	127->132(20.6%)
30	279.4	35.79	4.437	0.0718	127->131(18.1%) 125->130(10.5%) 126->131(10.4%)
31	277.5	36.03	4.467	0.1032	125->130(21.7%) 122->130(16.4%)
32	274.5	36.43	4.516	0.0076	123->130(34.6%)
33	273.2	36.60	4.538	0.0223	123->130(12.7%)
34	271.1	36.89	4.574	0.0029	126->134(59.0%)
35	269.1	37.16	4.608	0.0011	121->130(23.3%)
36	268.7	37.22	4.614	0.0094	128->144(10.5%)
37	267.6	37.37	4.633	0.0244	128->142(22.7%) 128->143(14.9%) 124->130(10.6%)
38	267.0	37.46	4.644	0.0075	128->143(32.0%)
39	266.6	37.51	4.651	0.0031	128->142(45.6%) 124->130(24.6%)
40	265.4	37.68	4.672	0.0063	128->144(24.1%) 128->145(11.8%)
41	264.8	37.76	4.682	0.0087	124->130(22.8%) 123->130(10.3%)
42	263.7	37.92	4.702	0.0038	128->143(12.4%) 128->144(12.3%) 122->131(11.6%)
43	263.5	37.96	4.706	0.0014	128->145(10.7%)
44	261.7	38.21	4.738	0.0037	
45	260.3	38.41	4.762	0.0167	
46	259.8	38.50	4.773	0.0439	121->130(10.9%) 122->132(10.4%)
47	258.5	38.68	4.796	0.0210	127->136(17.3%) 126->135(12.7%)
48	258.3	38.71	4.800	0.0421	122->132(13.2%) 121->132(10.1%)
49	256.8	38.94	4.828	0.1205	127->133(24.3%) 126->135(10.9%)
50	255.5	39.13	4.852	0.0039	128->145(20.7%) 127->133(11.6%)
51	255.2	39.19	4.859	0.0055	126->136(31.3%) 126->135(14.0%)
52	254.2	39.34	4.878	0.0100	
53	253.7	39.42	4.887	0.0071	126->137(18.7%) 120->132(13.8%)
54	253.0	39.52	4.900	0.0153	127->136(11.0%)
55	251.9	39.69	4.921	0.0282	127->137(11.9%)
56	251.4	39.78	4.932	0.0004	126->137(25.9%)
57	250.9	39.86	4.942	0.0137	

58	250.3	39.95	4.953	0.0004	120->130(15.2%)	125->131(13.4%)
59	248.7	40.21	4.986	0.0021	125->131(10.8%)	
60	248.5	40.24	4.989	0.0612	123->134(13.3%)	
61	247.8	40.36	5.004	0.0053	125->131(16.0%)	
62	246.9	40.49	5.021	0.0042	128->146(15.9%)	121->132(10.9%)
63	246.8	40.52	5.024	0.1242	127->138(14.1%)	
64	245.8	40.68	5.044	0.0194	121->134(10.5%)	128->146(10.1%)
65	245.3	40.76	5.054	0.0202	128->146(27.3%)	
66	244.9	40.83	5.062	0.0357		
67	244.1	40.96	5.079	0.0065	125->132(24.4%)	127->139(12.7%)
68	242.7	41.21	5.109	0.0243	126->133(15.5%)	126->138(11.2%)
69	242.0	41.32	5.122	0.0066		
70	241.4	41.43	5.136	0.0110	126->133(13.6%)	
71	240.5	41.58	5.155	0.0019	121->131(11.5%)	
72	240.1	41.65	5.164	0.0196	121->137(11.6%)	
73	239.7	41.72	5.173	0.0061		
74	239.5	41.75	5.176	0.0061		
75	238.6	41.92	5.197	0.0132	127->141(28.9%)	124->133(12.5%)
76	237.8	42.05	5.213	0.0093	127->140(11.3%)	
77	236.3	42.31	5.246	0.0263		
78	235.7	42.42	5.259	0.0670		
79	234.5	42.64	5.287	0.0829	116->129(24.2%)	
80	234.1	42.71	5.296	0.0492	118->130(12.6%)	

Summary of Calculated Electronic Transitions for **2**

#	nm	1000 cm-1	eV	f	Assignment (excitations with contrib. greater than 10.0%)
1	615.1	16.26	2.016	0.0478	175->176(54.5%) 172->176(14.1%)
2	556.0	17.99	2.230	0.0002	173->176(20.2%) 174->193(12.2%)
3	550.7	18.16	2.251	0.0067	174->176(18.9%)
4	509.4	19.63	2.434	0.0026	173->176(37.5%) 175->176(17.8%) 174->193(15.0%)
5	505.8	19.77	2.451	0.0112	174->176(64.4%)
6	472.8	21.15	2.623	0.0006	174->193(13.5%) 171->194(10.1%)
7	462.6	21.61	2.680	0.0100	171->193(17.8%)
8	454.0	22.03	2.731	0.0750	172->176(24.1%) 173->176(17.8%) 169->176(16.0%) 175->176(13.0%)
9	420.0	23.81	2.952	0.0134	170->176(23.4%) 172->176(17.2%) 169->176(17.1%) 168->176(10.2%)
10	406.8	24.58	3.048	0.1198	175->177(83.7%)
11	395.1	25.31	3.138	0.0219	174->177(87.9%)
12	390.9	25.58	3.172	0.1260	163->176(23.2%) 173->177(16.1%)
13	387.1	25.83	3.203	0.0170	171->176(24.4%) 159->176(24.2%)
14	385.6	25.93	3.215	0.0978	159->176(29.5%) 173->177(24.9%)
15	384.2	26.03	3.227	0.0776	173->177(20.7%) 166->176(13.8%) 160->176(11.3%) 171->176(10.6%)
16	376.0	26.60	3.298	0.0075	163->176(40.8%) 170->176(11.4%)
17	369.4	27.07	3.356	0.0304	158->176(25.6%) 168->176(13.4%)
18	360.0	27.78	3.445	0.0174	175->178(29.2%) 161->176(23.6%)
19	357.7	27.96	3.467	0.0075	175->179(19.3%) 158->176(13.0%) 161->176(10.7%)
20	355.6	28.12	3.486	0.0555	168->176(21.9%) 158->176(18.4%)
21	354.0	28.25	3.502	0.0064	171->193(16.8%) 175->179(11.6%)
22	351.7	28.43	3.525	0.0023	175->178(28.9%) 161->176(12.0%)
23	350.6	28.52	3.537	0.0167	175->179(22.5%) 173->179(13.6%)
24	349.1	28.64	3.551	0.0099	170->176(16.3%) 169->176(10.6%)
25	337.1	29.66	3.678	0.0011	174->178(78.6%)
26	335.3	29.82	3.698	0.0014	173->178(70.5%)
27	332.8	30.05	3.726	0.0039	175->180(47.9%) 175->181(23.9%)

28	331.5	30.17	3.740	0.0153	172->177(49.6%)
29	327.3	30.55	3.788	0.0069	173->179(37.7%) 174->179(22.7%)
30	325.9	30.69	3.804	0.0042	174->179(45.8%) 173->179(13.2%)
31	324.6	30.81	3.820	0.0308	170->177(22.7%) 175->181(13.3%)
32	316.4	31.60	3.918	0.0001	174->180(15.6%)
33	315.6	31.68	3.928	0.0004	174->180(32.1%) 174->181(17.7%) 173->180(17.1%)
34	314.5	31.80	3.942	0.0105	175->183(19.4%)
35	313.9	31.86	3.950	0.0006	167->176(84.9%)
36	313.6	31.89	3.954	0.0058	175->184(26.8%) 175->182(19.3%) 175->183(10.5%)
37	311.6	32.10	3.979	0.0053	175->183(27.0%) 173->180(15.0%) 173->181(11.4%)
38	310.0	32.26	3.999	0.0061	171->177(37.2%)
39	309.7	32.29	4.003	0.0056	175->182(21.6%) 169->177(16.6%)
40	308.4	32.42	4.020	0.0011	171->177(25.9%) 175->185(17.2%)
41	306.0	32.68	4.052	0.0204	169->177(19.9%) 175->182(12.4%) 175->185(10.8%)
42	305.3	32.76	4.062	0.0033	173->181(14.3%) 175->185(13.2%) 175->181(10.9%)
43	302.7	33.04	4.096	0.0002	174->181(33.8%) 174->180(14.3%) 165->176(14.0%) 166->176(10.6%)
44	302.0	33.11	4.106	0.0010	165->176(24.0%) 166->176(17.5%) 173->181(15.4%)
45	300.4	33.29	4.127	0.0003	175->186(22.5%)
46	299.5	33.39	4.140	0.0025	174->184(23.6%) 173->183(18.0%) 173->182(10.6%) 172->178(10.5%)
47	299.3	33.41	4.143	0.0022	174->184(32.7%) 174->183(24.7%)
48	299.1	33.43	4.145	0.0015	174->183(24.1%) 174->184(22.9%) 174->182(19.9%)
49	298.0	33.55	4.160	0.0017	173->184(43.9%) 174->182(14.4%)
50	296.7	33.70	4.179	0.0012	173->182(27.7%) 175->185(11.9%)
51	296.5	33.72	4.181	0.0058	174->183(24.5%) 174->182(15.0%)
52	296.0	33.79	4.189	0.0063	173->183(18.6%)
53	295.0	33.90	4.203	0.0137	168->177(19.8%) 173->183(16.7%)
54	294.0	34.01	4.217	0.0070	168->177(14.3%) 173->182(13.1%) 173->184(10.2%)
55	292.9	34.14	4.233	0.0194	174->185(35.0%)
56	292.0	34.25	4.247	0.0023	173->185(43.6%) 174->185(22.8%)
57	290.8	34.39	4.264	0.0268	173->185(15.2%) 174->185(10.2%)
58	289.0	34.60	4.290	0.0129	169->178(14.8%) 164->176(10.0%)

59	288.6	34.65	4.296	0.0028	175->188(15.3%)	164->176(11.7%)	
60	287.6	34.77	4.310	0.0074	174->187(20.9%)		
61	286.9	34.85	4.322	0.0097	164->176(27.8%)		
62	286.0	34.97	4.336	0.0019	174->187(36.1%)	174->186(13.4%)	
63	284.8	35.11	4.353	0.0419	174->186(36.7%)		
64	283.8	35.24	4.369	0.0804	173->186(24.3%)	174->186(21.0%)	
65	283.4	35.28	4.374	0.0145	173->187(41.8%)		
66	282.7	35.37	4.385	0.0207	172->180(24.1%)	172->181(13.4%)	
67	282.0	35.46	4.396	0.1308	173->186(17.1%)		
68	279.2	35.81	4.440	0.0314	162->176(41.9%)		
69	278.8	35.87	4.447	0.0123	175->189(54.4%)	175->188(10.7%)	
70	277.9	35.99	4.462	0.0147	162->176(37.4%)		
71	275.7	36.28	4.498	0.0013	171->178(28.1%)	168->178(14.7%)	
72	275.1	36.35	4.507	0.0009	169->180(17.6%)	170->180(14.3%)	169->181(10.5%)
73	273.4	36.57	4.535	0.0105	171->178(18.6%)		
74	272.1	36.74	4.556	0.0134			
75	271.5	36.83	4.567	0.0013	175->190(28.7%)		
76	271.0	36.90	4.575	0.0037			
77	270.1	37.02	4.590	0.0079	174->189(36.1%)		
78	269.9	37.04	4.593	0.0162	166->177(17.4%)	167->177(11.6%)	
79	269.7	37.08	4.598	0.0038	175->190(12.5%)	175->192(10.1%)	
80	268.6	37.22	4.615	0.0069	173->189(35.9%)	173->188(15.8%)	

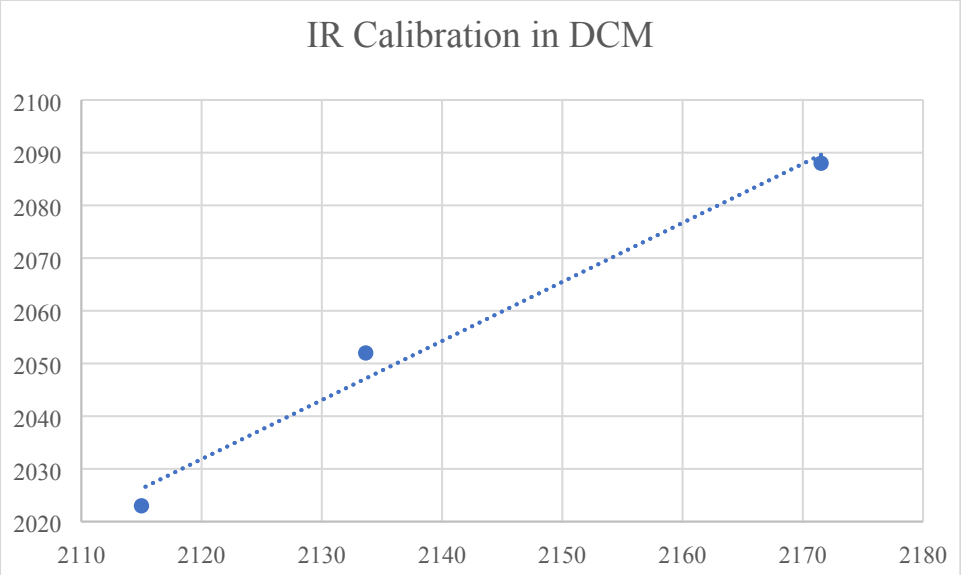
Summary of Calculated Electronic Transitions for **3**

#	nm	1000 cm-1	eV	f	Assignment (excitations with contrib. greater than 10.0%)
1	579.1	17.27	2.141	0.0285	123->124(46.7%) 121->124(27.6%)
2	558.7	17.90	2.219	0.0002	122->124(34.2%) 122->134(16.4%) 122->128(10.8%)
3	538.7	18.56	2.302	0.0008	121->124(31.4%) 123->134(13.5%)
4	481.6	20.76	2.574	0.0013	122->124(12.0%) 122->138(11.3%)
5	476.4	20.99	2.603	0.0014	122->124(23.4%) 123->138(11.1%) 123->136(10.9%)
6	454.9	21.98	2.726	0.0009	123->124(34.2%) 121->124(13.1%)
7	446.4	22.40	2.777	0.0009	122->124(24.4%) 120->138(13.2%)
8	404.2	24.74	3.067	0.0036	118->124(45.2%) 116->124(15.3%)
9	397.6	25.15	3.118	0.0029	116->124(41.9%) 111->124(14.5%) 114->124(11.8%)
10	384.2	26.03	3.227	0.0195	111->124(50.9%) 119->124(20.3%)
11	374.2	26.72	3.313	0.0068	114->124(46.4%)
12	369.8	27.04	3.352	0.0061	120->124(25.1%) 111->124(11.3%)
13	367.3	27.23	3.376	0.0268	119->124(21.0%) 116->124(19.5%) 114->124(12.5%)
14	356.9	28.02	3.474	0.0035	113->124(28.8%) 112->124(23.9%) 110->124(11.0%)
15	348.2	28.72	3.560	0.0004	120->138(18.9%) 120->136(14.1%) 123->136(11.0%) 122->128(10.3%)
16	342.9	29.17	3.616	0.0121	110->124(33.9%) 123->126(18.8%) 109->124(10.6%)
17	341.0	29.32	3.636	0.0037	120->124(30.4%) 120->134(11.4%)
18	335.6	29.79	3.694	0.0243	123->126(45.6%) 121->126(13.2%)
19	333.9	29.95	3.713	0.0098	123->125(56.2%) 121->125(23.1%)
20	321.6	31.09	3.855	0.0017	122->126(84.5%)
21	316.9	31.56	3.913	0.0000	122->125(78.2%) 122->126(10.5%)
22	313.9	31.85	3.950	0.0027	123->127(63.6%) 121->127(16.0%)
23	311.2	32.14	3.985	0.0049	121->126(42.9%) 123->126(21.1%)
24	308.3	32.44	4.022	0.0333	121->125(30.8%) 123->125(15.3%) 123->130(10.4%)
25	304.5	32.84	4.071	0.0452	123->128(31.4%) 123->129(17.7%)
26	304.4	32.86	4.074	0.0025	117->124(85.4%)
27	303.1	32.99	4.090	0.0017	123->129(15.6%) 123->130(14.3%)
28	301.4	33.18	4.114	0.0144	122->128(44.0%)

29	300.0	33.34	4.133	0.0064	122->127(49.4%)
30	299.5	33.38	4.139	0.0013	123->130(29.3%) 122->127(17.6%)
31	298.6	33.49	4.153	0.0395	115->124(16.1%) 122->127(14.7%) 109->124(11.1%) 118->124(11.0%)
32	295.7	33.81	4.192	0.0132	123->131(38.8%) 123->130(17.3%)
33	290.8	34.39	4.264	0.0007	122->130(83.7%)
34	289.2	34.58	4.287	0.0025	123->132(32.5%) 121->127(14.5%)
35	288.3	34.68	4.300	0.0026	122->129(28.8%) 121->127(15.6%) 123->132(12.8%)
36	288.0	34.72	4.305	0.0007	122->129(33.0%) 123->132(11.1%)
37	287.9	34.73	4.306	0.0032	123->133(27.1%) 119->126(13.3%) 121->127(13.3%)
38	286.8	34.86	4.323	0.0029	119->126(57.7%)
39	283.4	35.29	4.375	0.0363	121->128(17.7%) 123->129(12.4%) 121->129(10.1%)
40	282.6	35.38	4.387	0.0007	122->131(72.1%) 122->129(13.1%)
41	281.2	35.57	4.410	0.0471	123->133(20.9%) 119->125(20.0%)
42	279.7	35.75	4.433	0.0141	119->125(40.3%) 121->130(15.2%)
43	279.0	35.85	4.445	0.0009	122->132(66.7%) 122->133(16.8%)
44	277.8	35.99	4.463	0.0009	119->128(17.3%) 121->131(13.3%) 123->131(11.1%)
45	275.3	36.32	4.503	0.0016	122->133(61.8%) 122->132(17.1%)
46	274.3	36.46	4.521	0.0024	121->129(14.1%) 113->124(13.3%)
47	273.7	36.53	4.529	0.0077	115->124(22.1%) 119->127(15.3%)
48	273.3	36.60	4.537	0.0047	121->129(21.8%) 112->124(15.2%) 113->124(12.0%)
49	271.9	36.77	4.559	0.0106	121->131(14.1%) 119->128(11.0%)
50	270.6	36.95	4.581	0.0031	112->124(20.1%) 121->132(11.6%) 113->124(10.7%)

IR Calibration in the Metal Carbonyl Region

The following plot of calculated vs experimental metal carbonyl stretching bands was used to correct all calculated bands in DCM



The following plot of calculated vs experimental metal carbonyl stretching bands was used to correct all calculated bands in heptane