Electronic Supporting Information

Synthesis and Reactivity of Dinuclear Copper(I) Pyridine, Diimine Complexes

Michel Stephan, Wiebke Dammann, Peter Burger*

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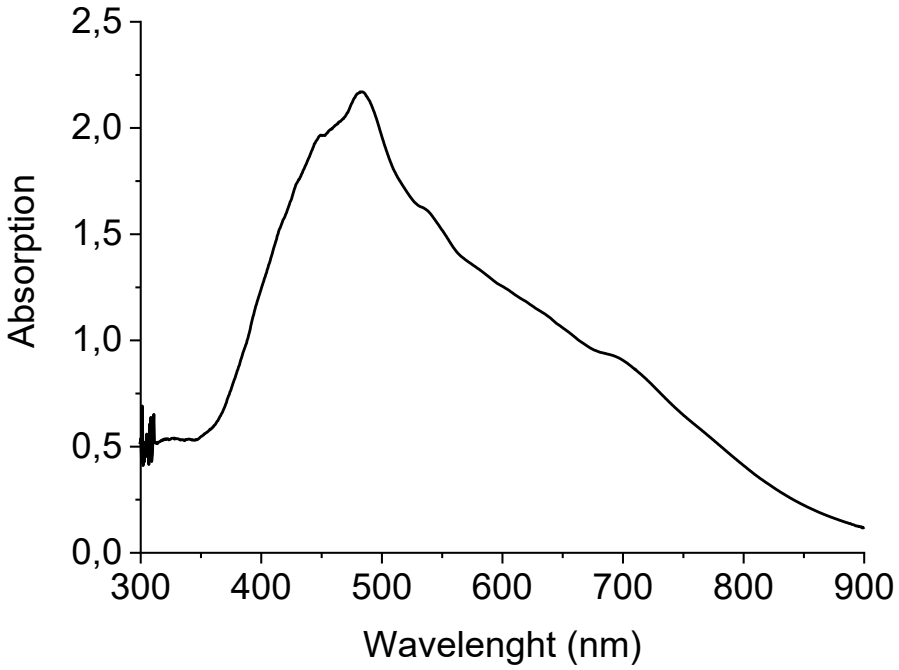

Fig. S1: UV/vis spectrum of complex **3** in DCM.

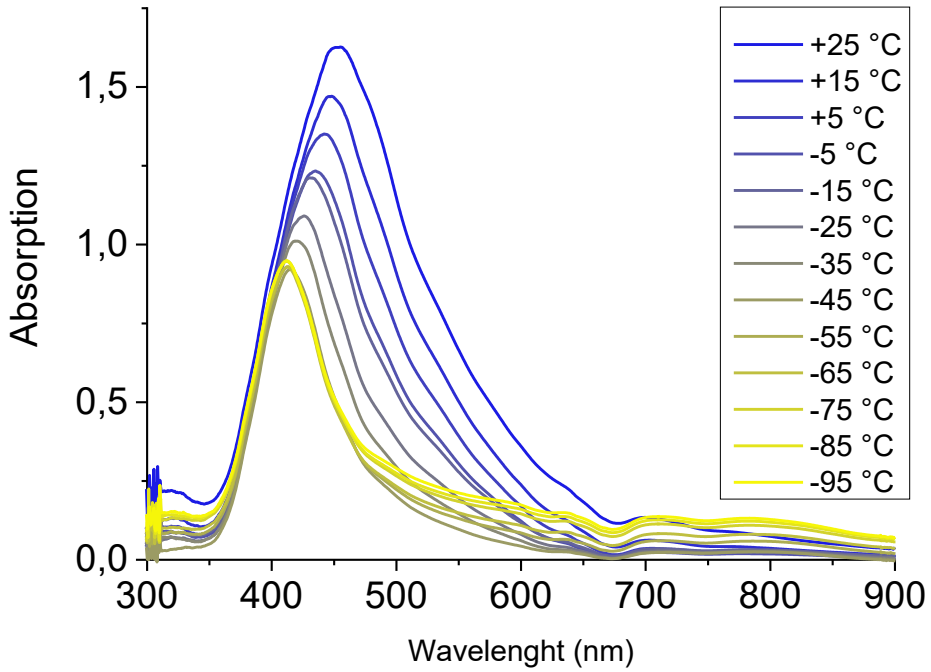

Fig. S2: UV/vis spectra of the adduct of complex **3** with CO in DCM at different temperatures.

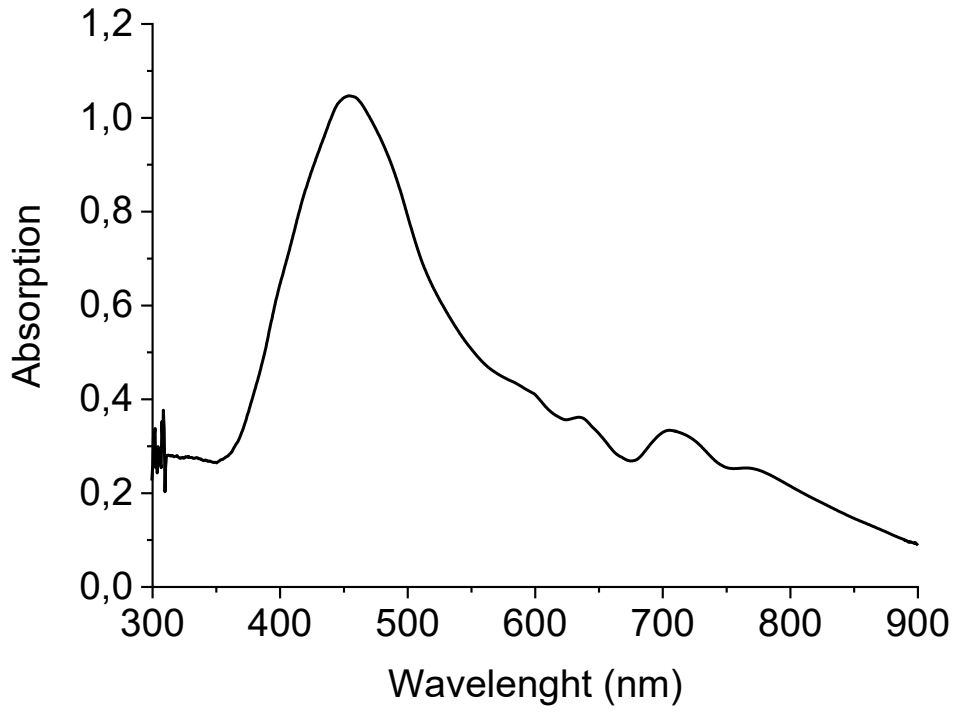

Fig. S3: UV/vis spectrum of complex **4** in DCM.

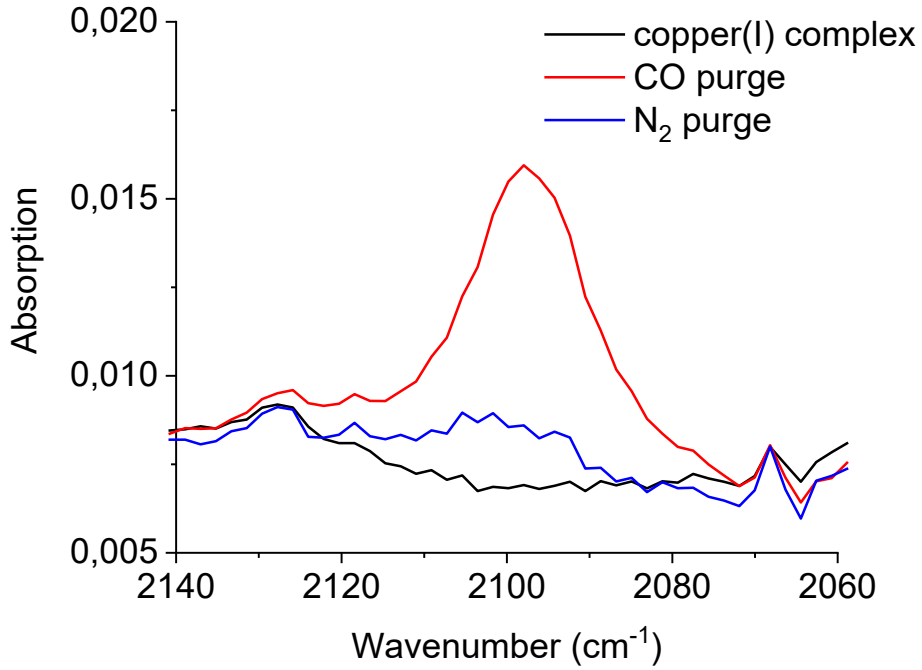

Fig. S4: In situ IR spectra for the reversible reaction of complex **4** with CO.

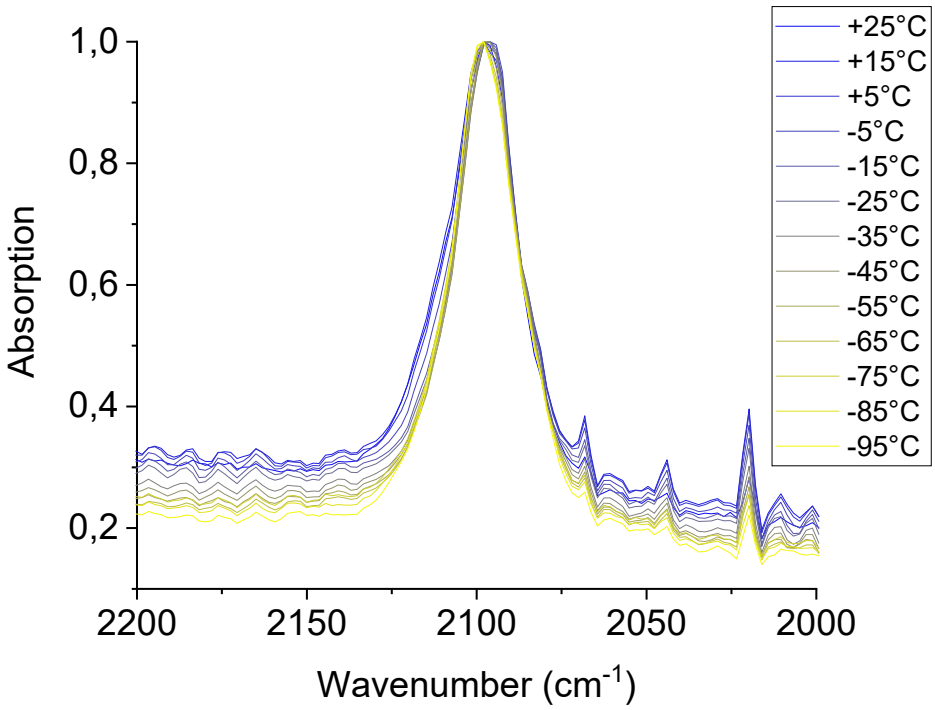

Fig. S5: In situ IR spectra of complex **3** carbonyl adduct at different temperatures.

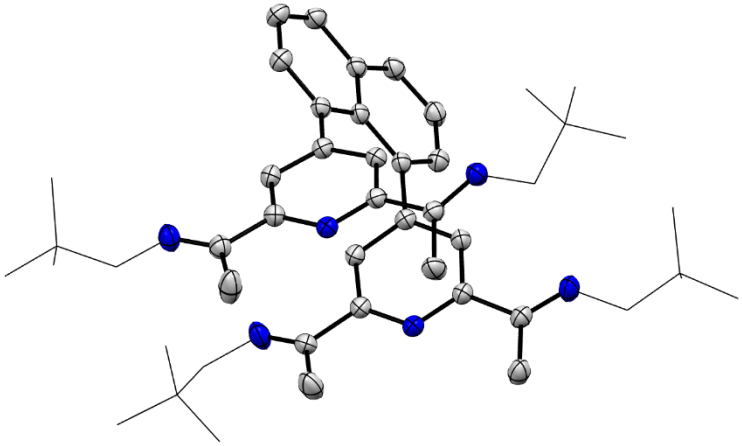

Fig. S6: Molecular structure of ligand **2** with anisotropic displacement parameters shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. *Neo*-pentyl moieties are displayed as sticks for a better overview.

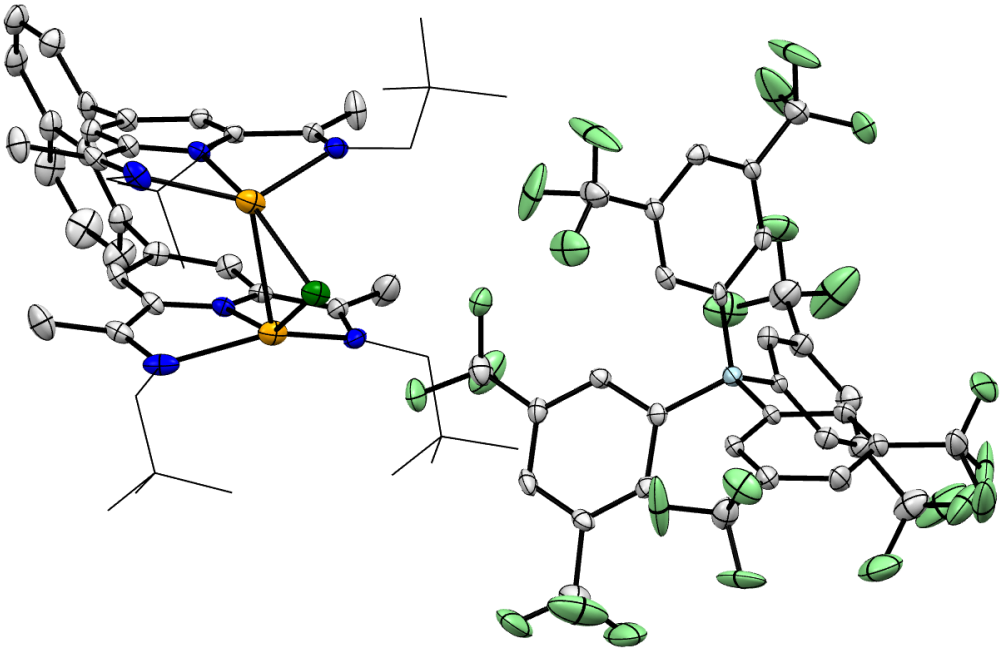

Fig. S7: Molecular structure of the complex **4** with anisotropic displacement parameters shown at 50 % probability level. Hydrogen atoms, displacement of the fluorine atoms and solvent molecules are omitted for clarity. *Neo*-pentyl moieties are displayed as sticks for a better overview.

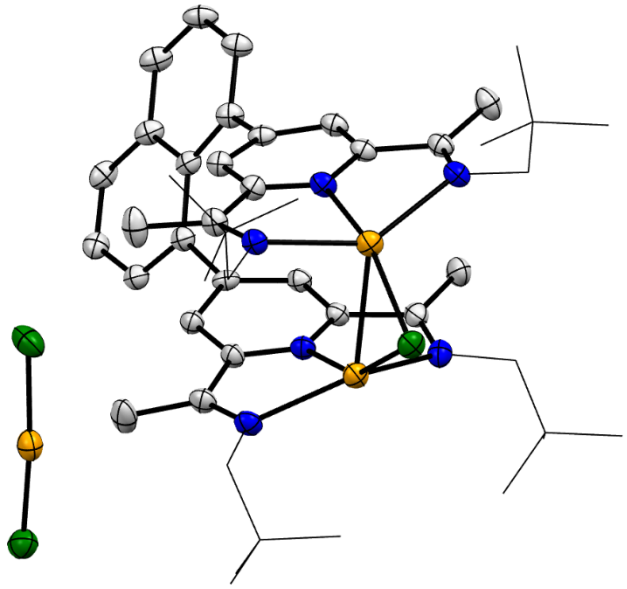

Fig. S8: Molecular structure of complex **3** with anisotropic displacement parameters shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. *Neo*-pentyl moieties are displayed as sticks for a better overview. Crystallized from THF/hexane.

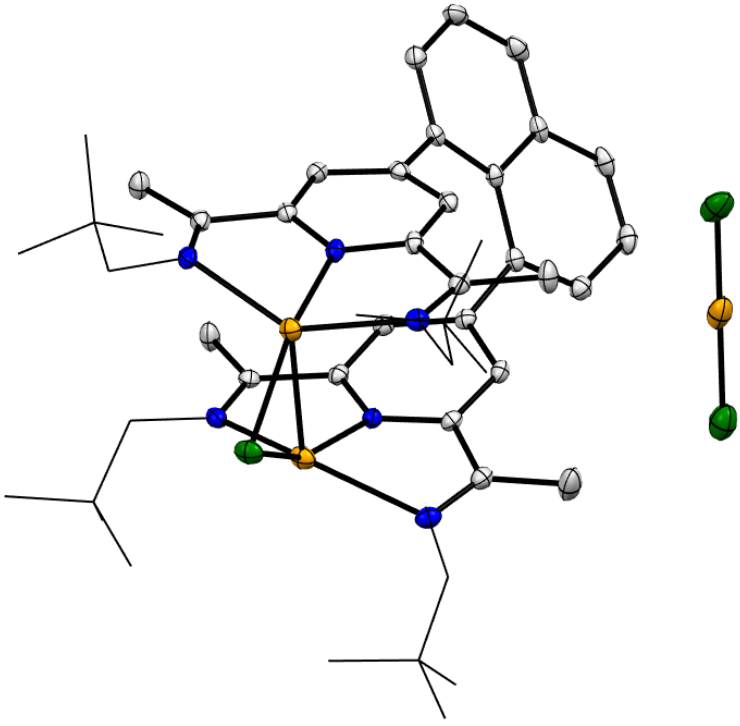

Fig. S9: Molecular structure of complex **3** with anisotropic displacement parameters shown at 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. *Neo*-pentyl moieties are displayed as sticks for a better overview. Crystallized from DCM/hexane.

Table S1: Summary of the crystal data and structure refinement for ligand **2**, complex **3** and **4**.

	Ligand **2**	Complex **3**	Complex **4**
Chemical formula	$C_{48}H_{66}N_6$	$C_{48}H_{66}Cl_3Cu_3N_6$	$C_{80}H_{78}BClCu_2F_{24}N_6$
Formula mass	726.53	1020.23	1750.43
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$ (No 2)	$P\bar{1}$ (No 2)	$P\bar{1}$ (No 2)
a [Å]	10.8210(3)	12.9709(3)	14.0607(19)
b [Å]	12.6112(4)	18.3585(3)	18.845(3)
c [Å]	19.3792(5)	24.0138(4)	19.069(3)
α [°]	82.496(2)	111.2060(10)	93.893(2)
β [°]	77.379(2)	92.281(2)	99.600(2)
γ [°]	85.977(2)	99.549(2)	94.627(2)
Unit cell volume [Å^3]	2556.23(13)	5226.16(18)	4948.9(11)
Temperature [K]	100	100	100
Z	2	4	2
Radiation type	CuK\α	CuK\α	MoK\α
Refections measured	54049	84178	75836
Independent reflections	8593	18545	11786
Data/restrains/parameters	10643/0/559	21635/99/1203	23784/560/1490
Θmax [°]/completeness	74.33/99.85	77.638/99.83	28.900/99.72
R_{int}	0.0405	0.0513	0.1118
Final R_1 valvues ($I>2\sigma(I)$)	0.0554	0.0476	0.0662
Final $wR(F^2)$ values ($I>2\sigma(I)$)	0.1503	0.1188	0.1051
Final R_1 valvues (all data)	0.0753	0.0564	0.1698
Final $wR(F^2)$ values (all data)	0.1656	0.1268	0.1313
Goodness of fit F^2	1.026	1.069	0.996
Max/min Δp [e·Å^3]	0.277/-0.311	1.025/-1.029	0.458/-0.666

Table S2: Summary of crystal data and structure refinement for complex **3** recrystallized in DCM/hexane.

Chemical formula	$C_{48}H_{66}Cl_3Cu_3N_6$
Formula mass	1020.23
Crystal system	triclinic
Space group	$P2_1/n$ (No 14)
a [Å]	25.448(2)
b [Å]	11.4613(9)
c [Å]	37.179(3)
α [°]	90
β [°]	104.453(1)
γ [°]	90
Unit cell volume [Å^3]	10500.7(14)
Temperature [K]	100
Z	8
Radiation type	MoK\α
Refections measured	164465
Independent reflections	18206
Data/restrains/parameters	25824/36/1195
Θmax [°]/completeness	28.860/100
R_{int}	0.0696
Final R_1 valvues ($I>2\sigma(I)$)	0.0410
Final $wR(F^2)$ values ($I>2\sigma(I)$)	0.0940
Final R_1 valvues (all data)	0.0750
Final $wR(F^2)$ values (all data)	0.0831
Goodness of fit F^2	1.033
Max/min Δp [e·Å^3]	0.666/-0.758

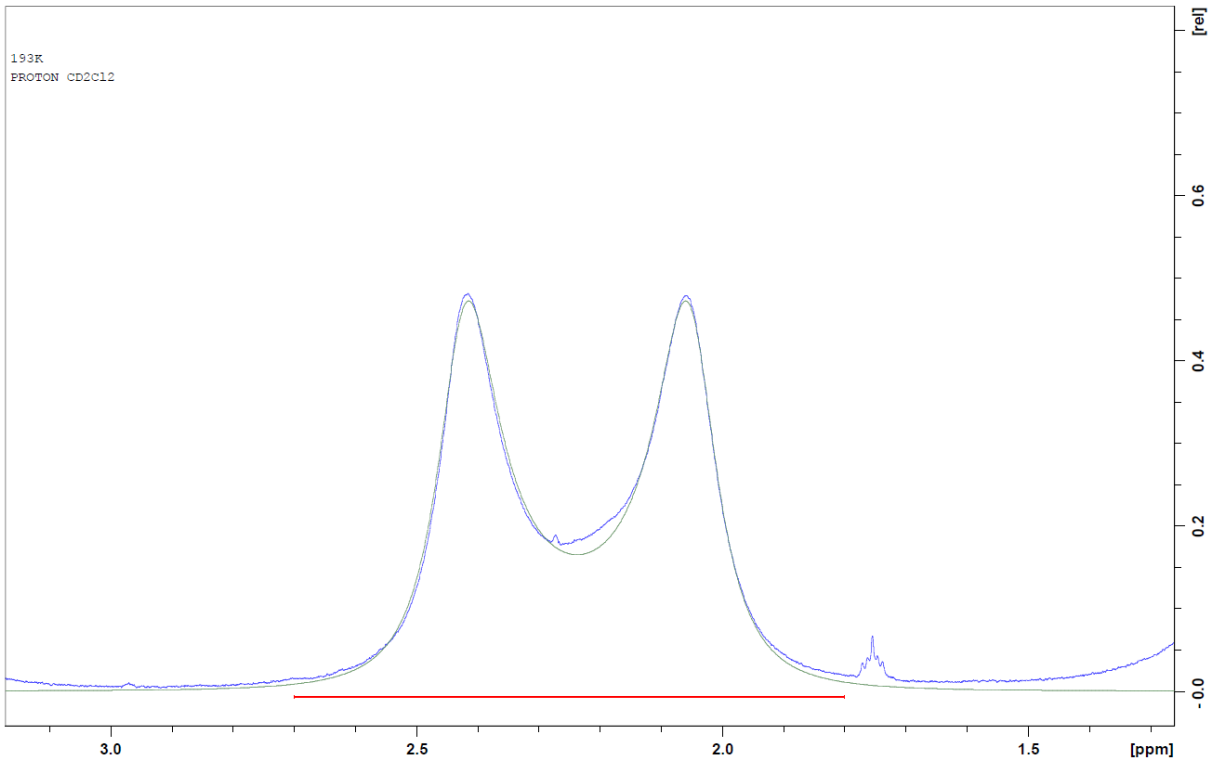

Fig. S10: ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at -80 °C between 3.0 ppm and 1.5 ppm (blue line = ^{1}H-NMR spectrum, red line = fit range, green line = fit curve). Fit was done by using the software suite TopSpin 4.0.9 from Bruker Corp..

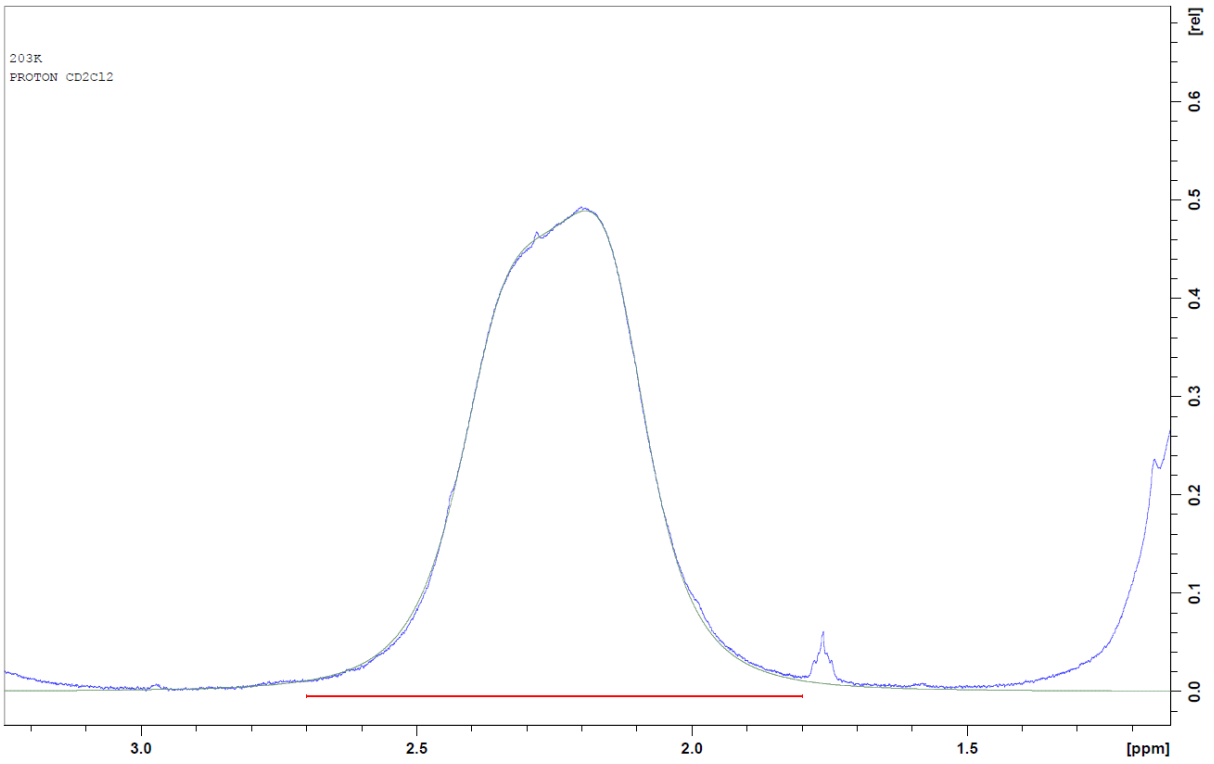

Fig. S11: ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at -70 °C between 3.0 ppm and 1.5 ppm (blue line = ^{1}H-NMR spectrum, red line = fit range, green line = fit curve). Fit was done by using the software suite TopSpin 4.0.9 from Bruker Corp..

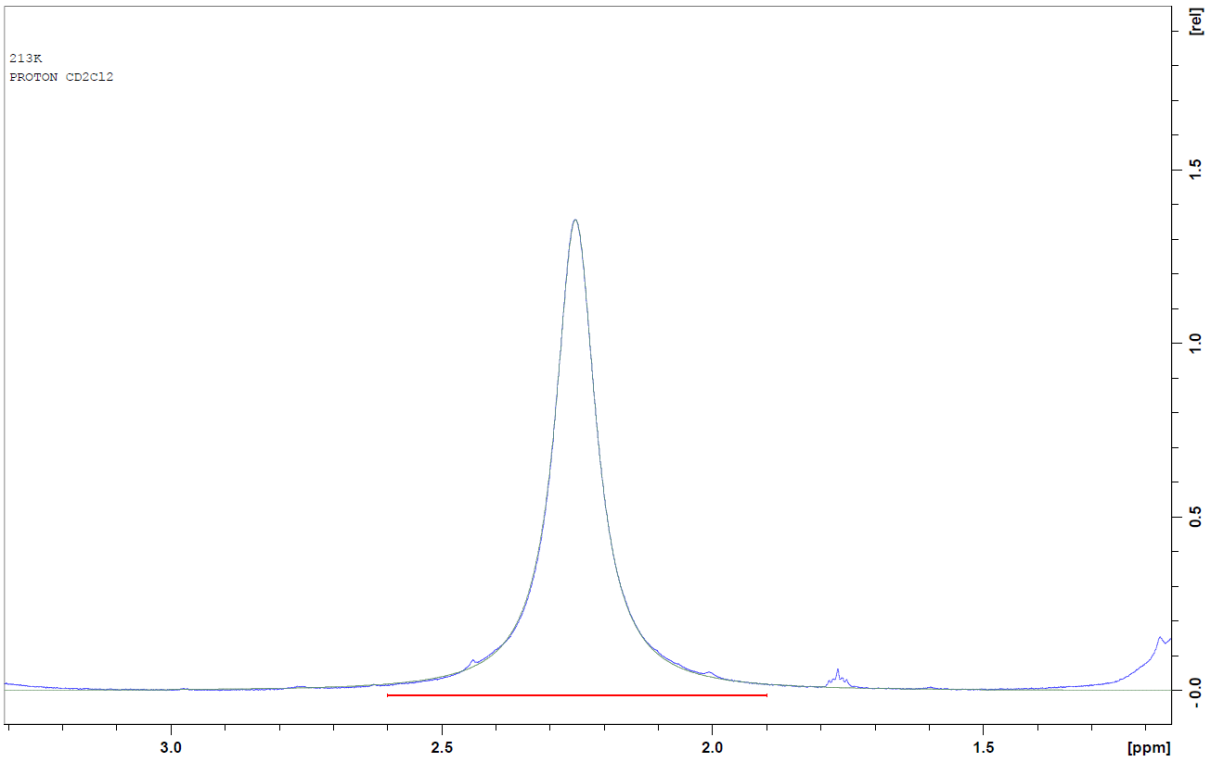

Fig. S12: ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at -60 °C between 3.0 ppm and 1.5 ppm (blue line = ^{1}H-NMR spectrum, red line = fit range, green line = fit curve). Fit was done by using the software suite TopSpin 4.0.9 from Bruker Corp..

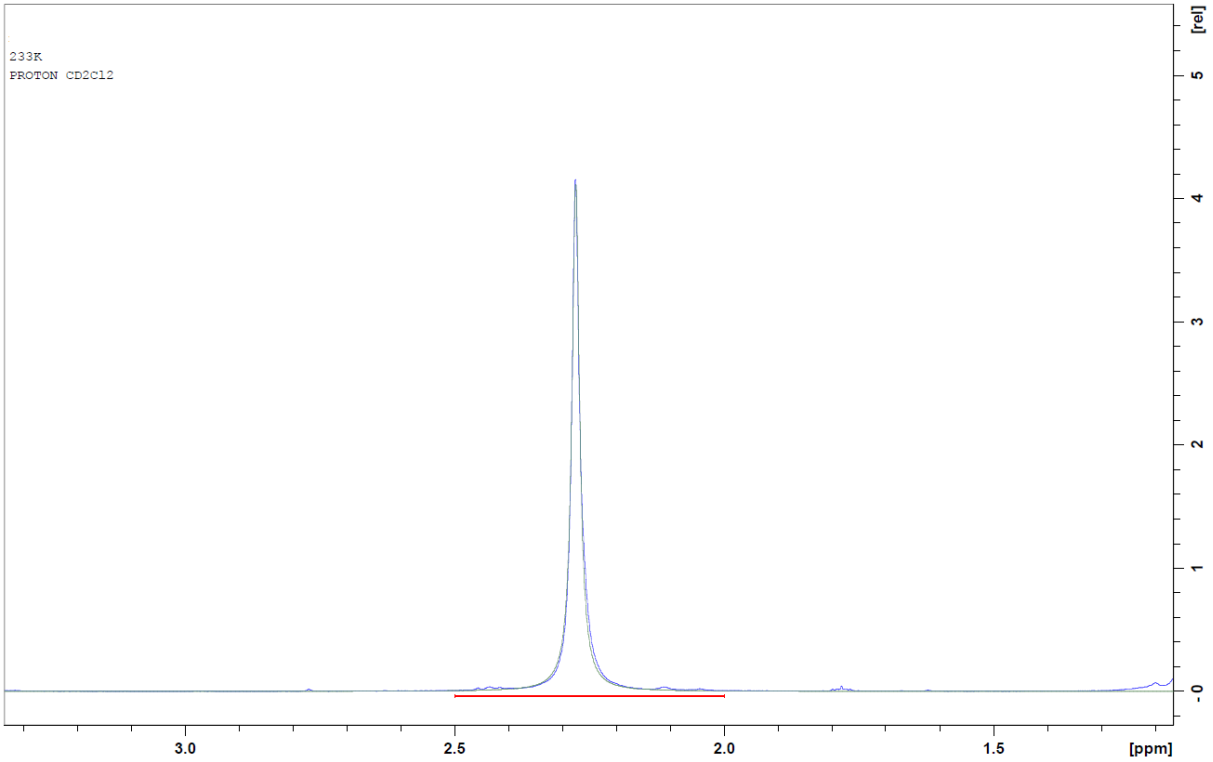

Fig. S13: ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at -50 °C between 3.0 ppm and 1.5 ppm (blue line = ^{1}H-NMR spectrum, red line = fit range, green line = fit curve). Fit was done by using the software suite TopSpin 4.0.9 from Bruker Corp..

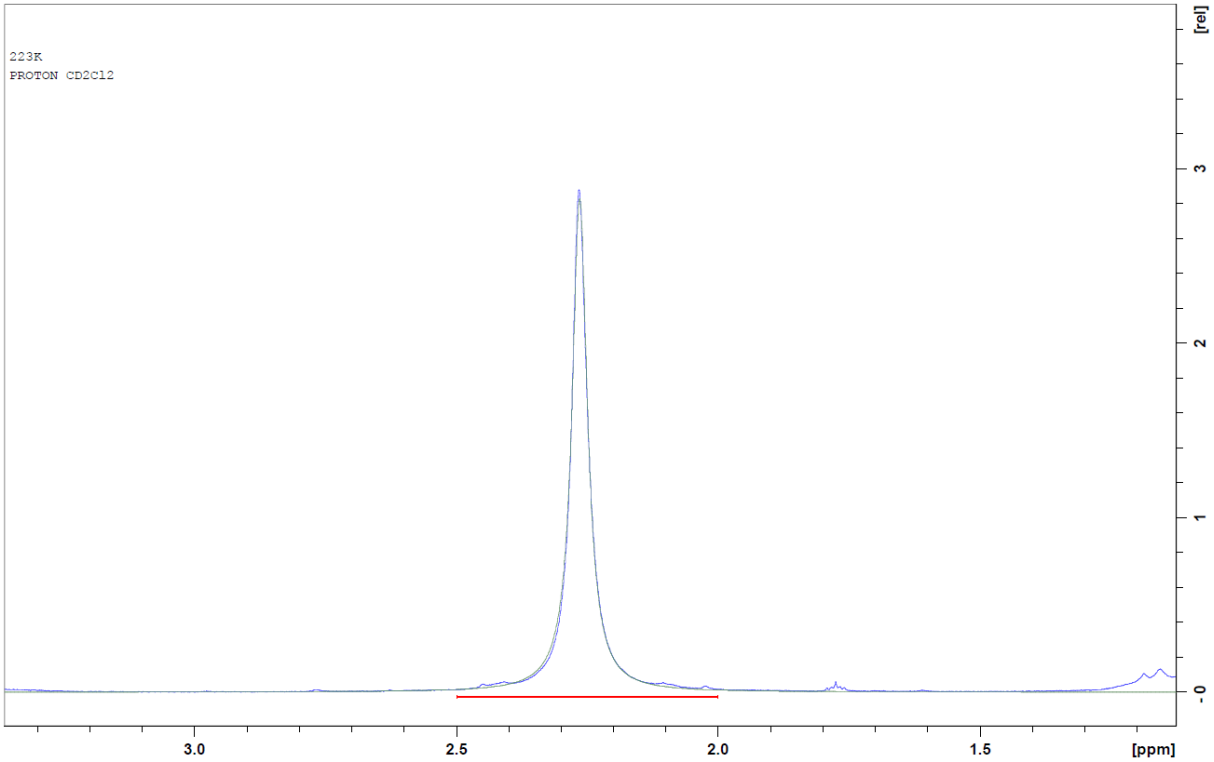

Fig. S14: ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at -40 °C between 3.0 ppm and 1.5 ppm (blue line = ^{1}H-NMR spectrum, red line = fit range, green line = fit curve). Fit was done by using the software suite TopSpin 4.0.9 from Bruker Corp..

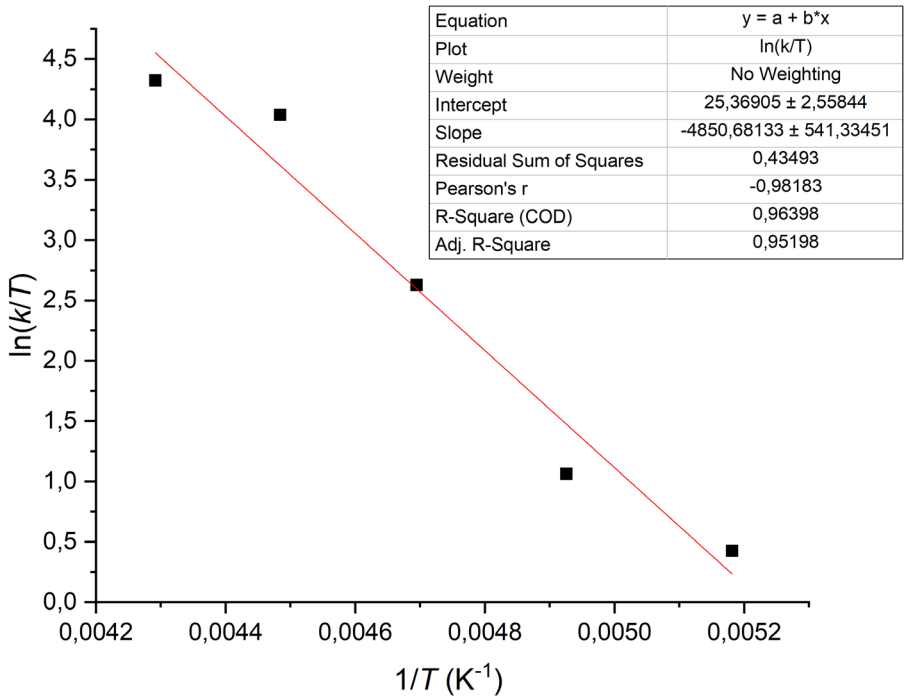

Fig. S15: Eyring plot based on the VT-^{1}H-NMR-Data of complex **3** in DCM-d_2 between -80 °C and -40 °C acquired by using rate constants derived with the software suite TopSpin 4.0.9 from Bruker Corp.. The kinetic parameters derived are $\Delta S^{\#}$ = 3.2 cal/mol·K and $\Delta H^{\#}$ = 9.6 kcal/mol.

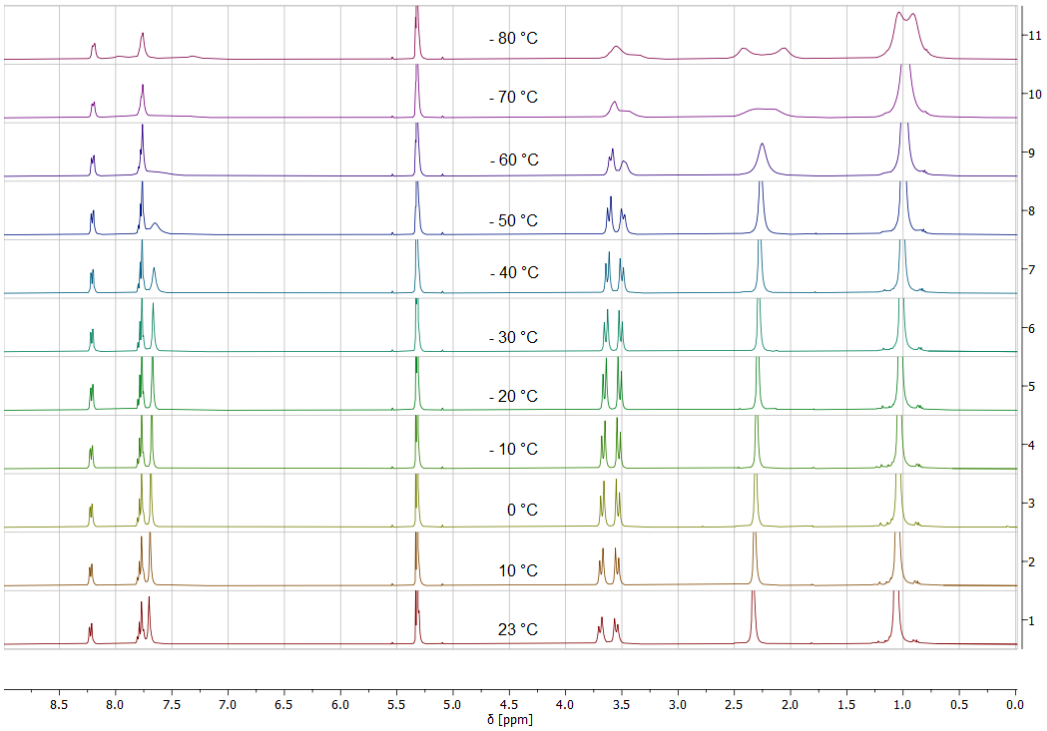

Fig. S16: ^{1}H-NMR spectra of complex **3** in DCM-d_2 between RT and -80 °C.

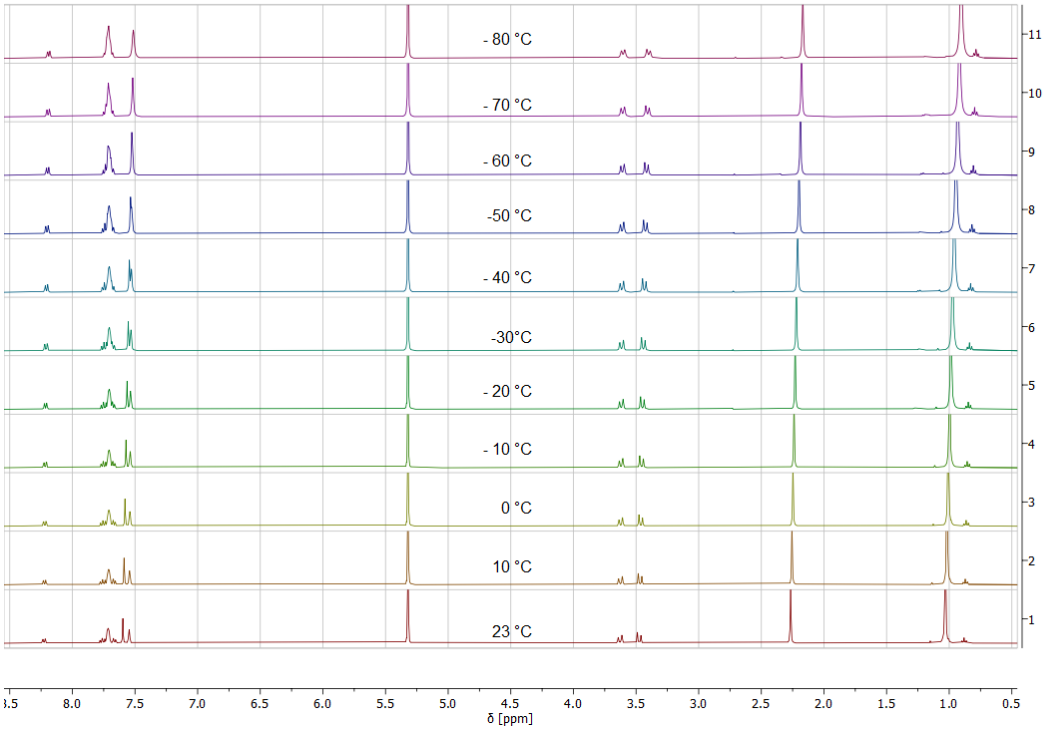

Fig. S17: ^{1}H-NMR spectra of complex **4** in DCM-d_2 between RT and -80 °C.

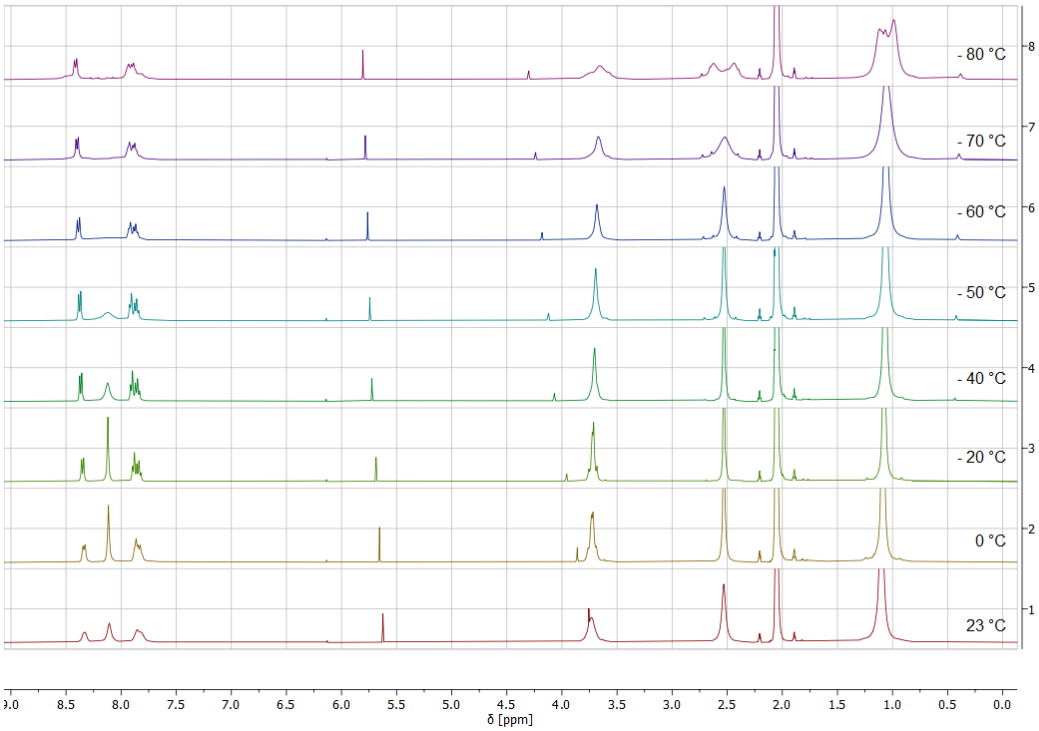

Fig. S18: ^{1}H-NMR spectra of complex **3** in acetone-d_6 between RT and -80 °C.

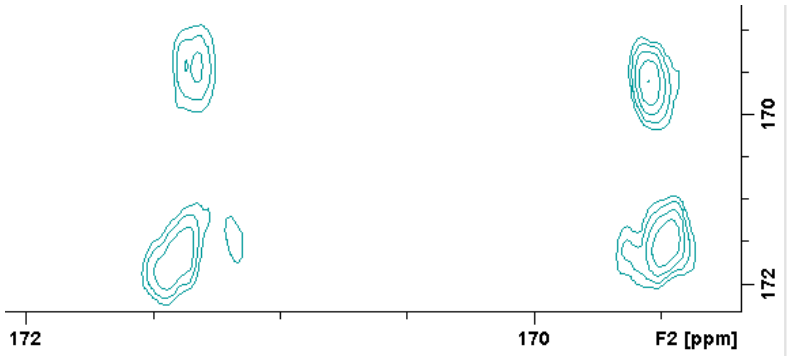

Fig. S19: ^{13}C-EXSY spectrum of complex **3** with 22 equivalents CO at -80 °C.

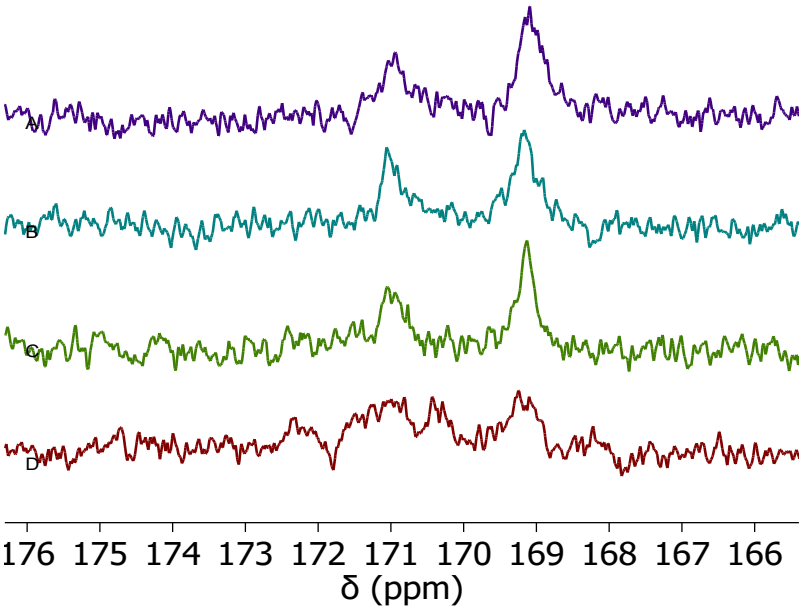

Fig. S20: SST-^{13}C-NMR spectra of complex **3** in DCM-d_2 at -80 °C with 22 equivalents. of ^{13}CO (A = 0.2 s, B = 0.5 s, C = 1 s, D = 3 s).

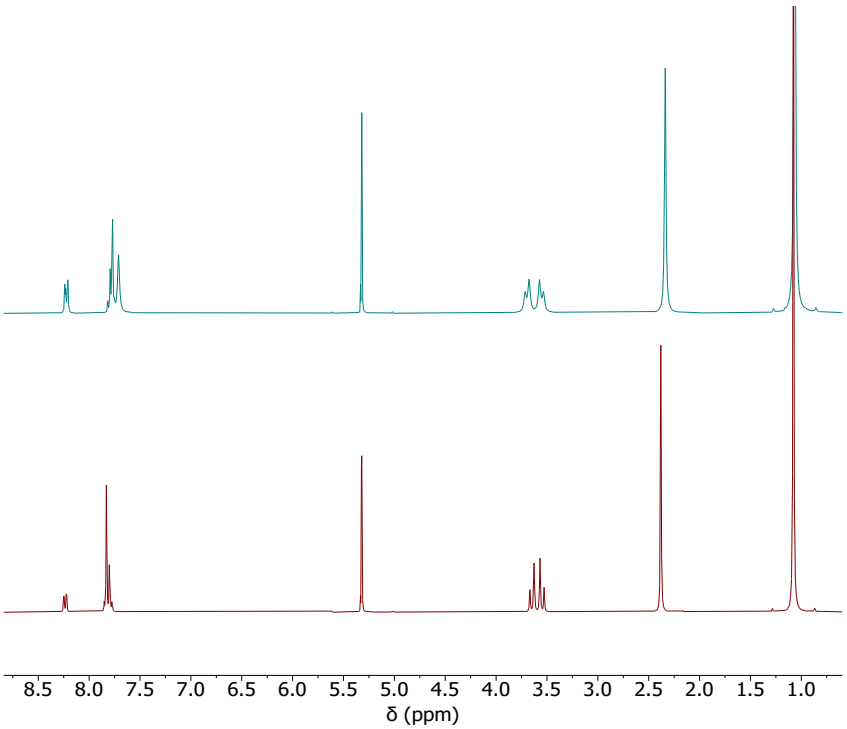

Fig. S21: ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at RT (top, blue line) and ^{1}H-NMR spectrum of complex **3** in DCM-d_2 at RT with 22 equivalents of ^{13}CO (bottom, red).

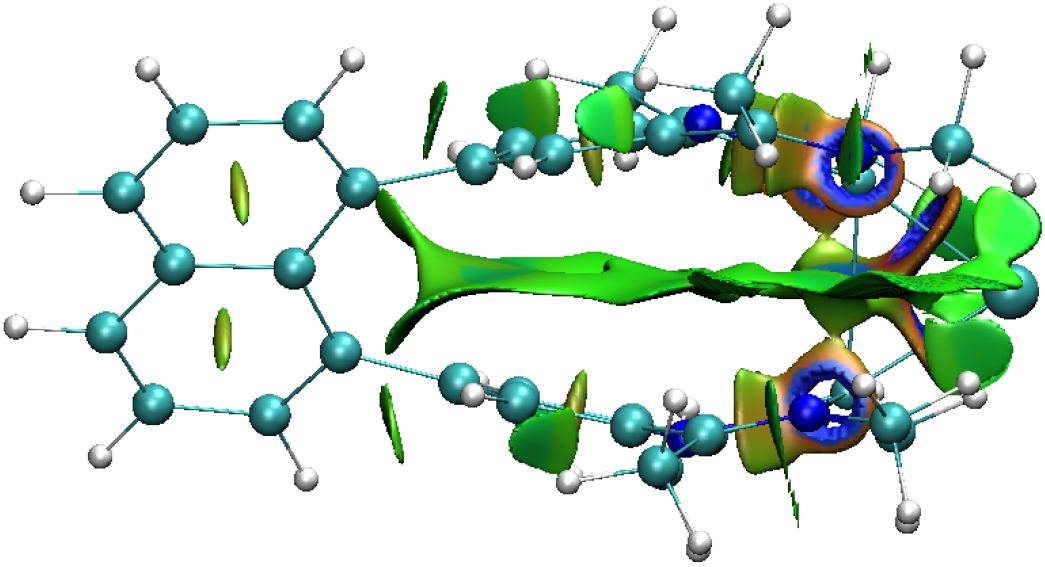

Fig. S22: NCI plot for the cationic methyl substituted model complex fragment viewed from the side.

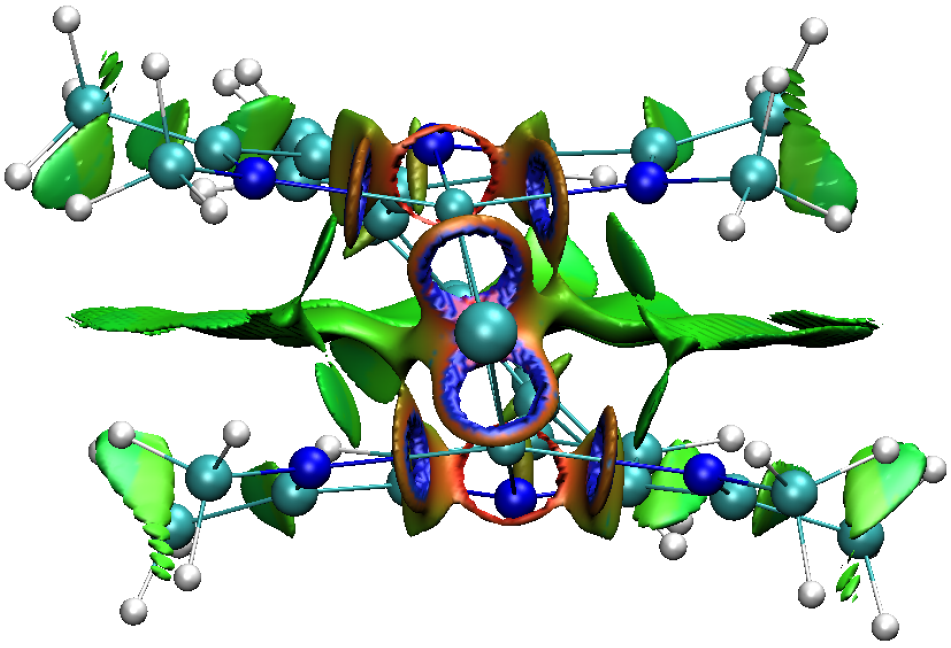

Fig. S23: NCI plot for the cationic methyl substituted model complex fragment viewed from the front.

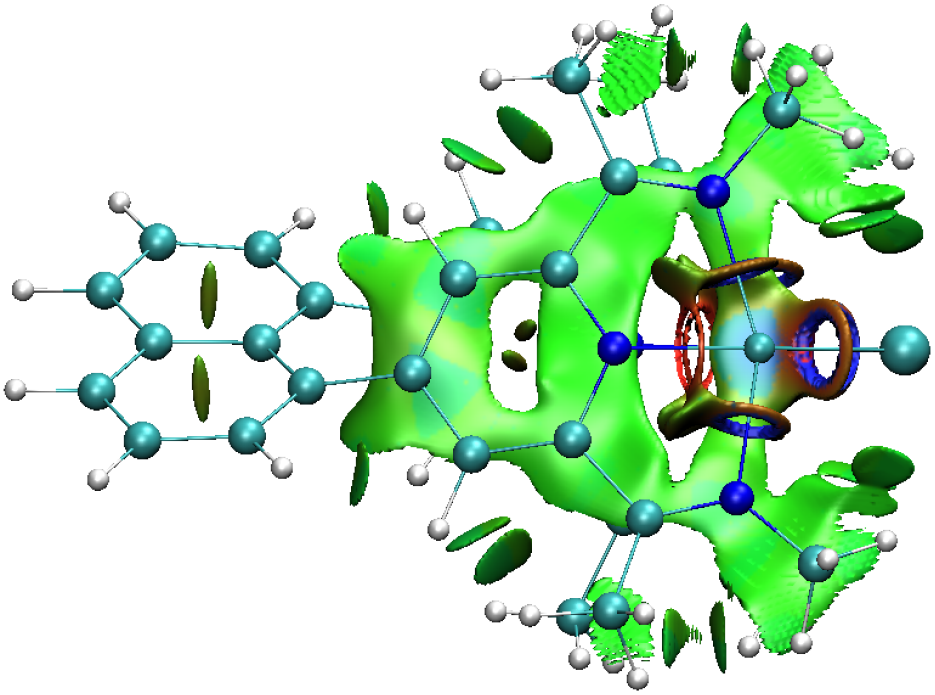

Fig. S24: NCI plot for the cationic methyl substituted model complex fragment viewed from the top.

CO / LNO-CCSD(T)

```
2
Total LNO-CCSD(T) energy with MP2 corrections [au]:     -113.159218660735
C          0.0000000000        0.0000000000       -0.6490082528
O          0.0000000000        0.0000000000        0.4869109472
```

$[Cu_2Cl]^+$ / LNO-CCSD(T)

```
75
C2-symmetry: Total LNO-CCSD(T) energy with MP2 corrections [au]:    -5304.117769595515
Cu        1.1508245413        0.7303276013        2.4167074629
Cu       -1.1508245413       -0.7303276013        2.4167074629
Cl       -0.0000000000        0.0000000000        4.2376469629
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C         0.9886866305        1.1063274495       -2.2829531371
C        -1.6673525589       -0.0294954128       -1.6820936371
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C         1.7757510393       -0.0094827172       -0.2921441371
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C        -1.1570393138       -2.1603177179       -4.4841715371
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C         1.0646794410        2.1870685722       -5.8884350371
H         1.4583530201        3.0395987315       -6.4415971371
C         2.4103775870       -1.0787738800        0.5179787629
C         0.5288821215        1.1052354132       -6.5491321371
H         0.5011106666        1.0765058308       -7.6394153371
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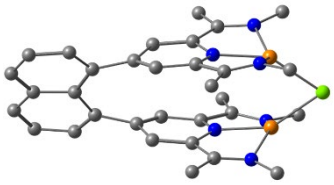

TS $[Cu_2Cl]^+$ / LNO-CCSD(T)

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75
C1-symnetry Total LNO-CCSD(T) energy with MP2 corrections [au]:    -5304.112410419160
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Cl        -0.0000000000         4.2490568048         0.0244149378
N         -0.0000000000         0.4354040706         1.5761763416
N         -0.0000000000         0.4685257427        -1.4974121025
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N          1.9906447000         2.0263430571        -1.8397246518
C         -1.2095488000        -1.5636604640        -1.5848169009
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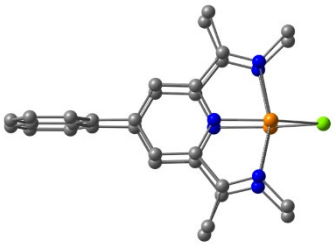
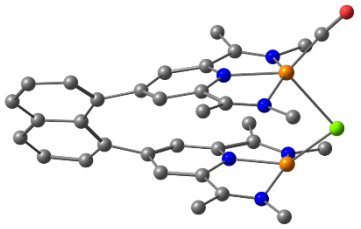


$[Cu_2Cl(CO)]^+$ / LNO-CCSD(T)

77
C_1-symmetry Total LNO-CCSD(T) energy with MP2 corrections [au]: -5417.301344748688



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$[Cu_2Cl(CO)_2]^+$ / LNO-CCSD(T)

79
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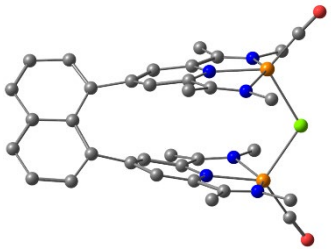

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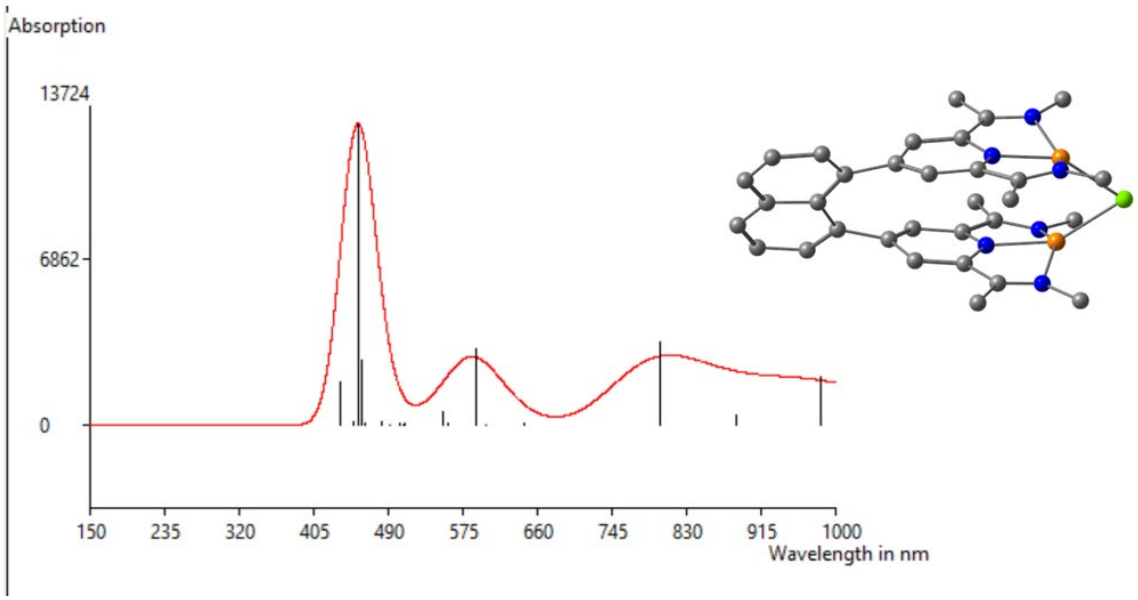

Fig. S25: NCI Simulated UV/vis spectrum of the model of complex **3** based on the MRCI-DFT calculation. The spectrum was produced with the SpecDis program ver. 1.71 using the default value of s=0.16 eV for Gauss broadening of the calculated transition energies. The vertical bars correspond to the calculated transitions.

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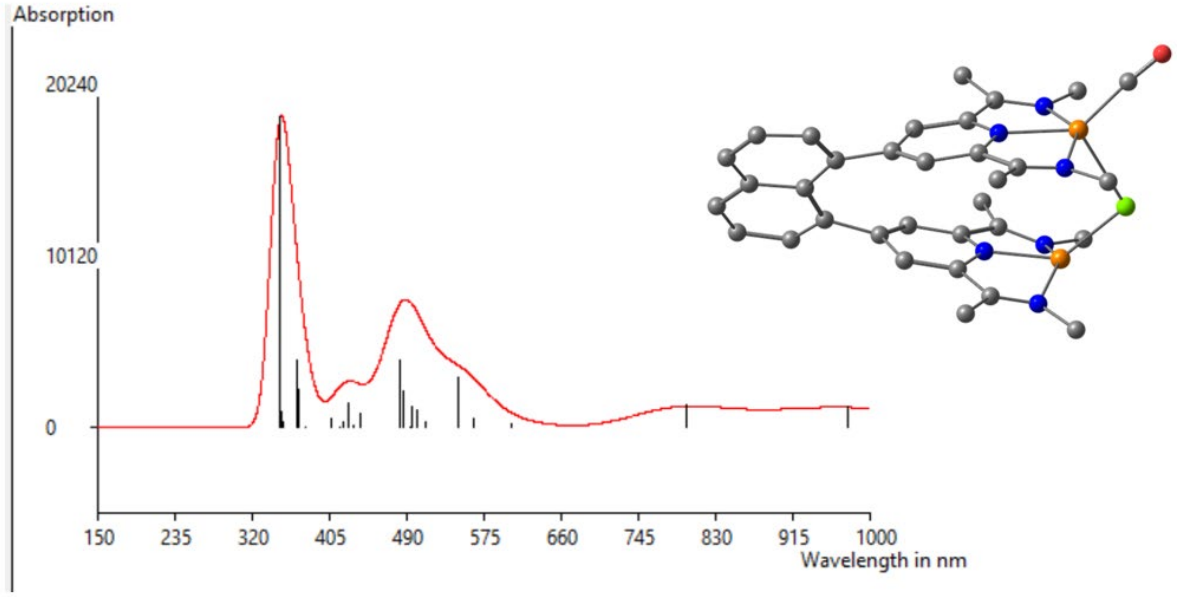

Fig. S26: NCI Simulated UV/vis spectrum of the model monocarbonyl complex based on the MRCI-DFT calculation. The spectrum was produced with the SpecDis program ver. 1.71 using the default value of s=0.16 eV for Gaussian broadening of the calculated transition energies. The vertical bars correspond to the calculated transitions.

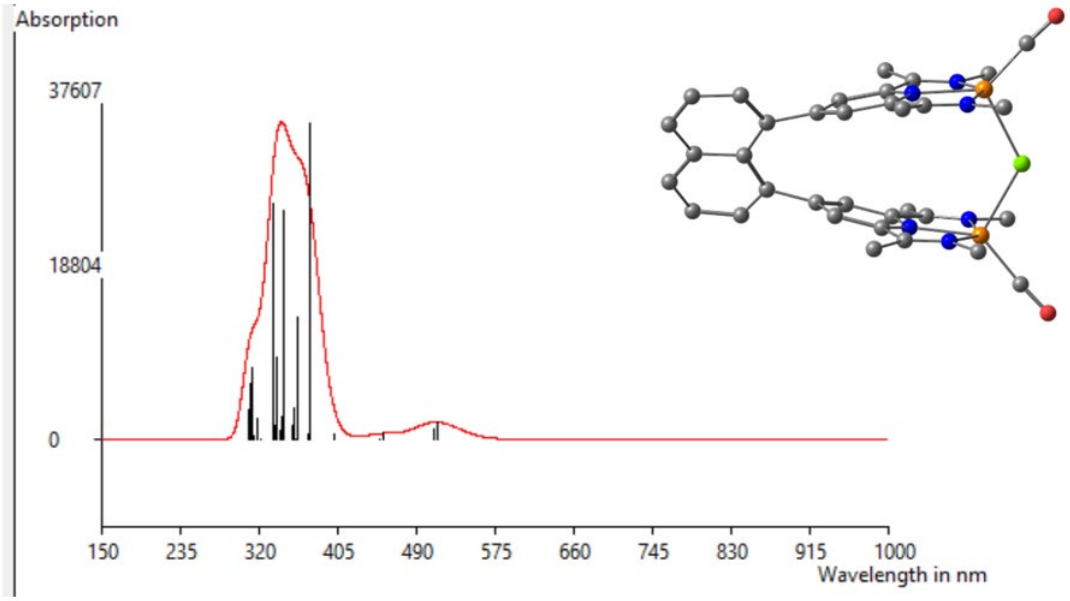

Fig. S27: NCI Simulated UV/vis spectrum of the model monocarbonyl complex based on the MRCI-DFT calculation. The spectrum was produced with the SpecDis program ver. 1.71 using the default value of s=0.16 eV for Gauss broadening of the calculated transition energies. The vertical bars correspond to the calculated transitions.