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Supporting Material to the Manuscript:

Diffusional and Internal Rotation in Single and Linked Trinuclear Bis-Carbyne Cluster Complexes Determined by ^{13}C NMR Relaxation Time Measurements

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Table S-1: ^{13}C T_1 relaxation times (sec^{-1}) for the phenyl and Cp ring carbons of **1a**

T / K	$T_{1,meta}$	$T_{1,ortho}$	$T_{1,para}$	$T_{1,Cp}$	$T_1^{DD}{}_{,Cp}$
321	6.4	6.7	2.4	7.5	8.3
311	6.1	6.1	2.3	7.0	7.8
300	5.3	5.2	2.1	6.6	7.3
278.4	3.9	4.0	1.7	4.6	5.1
267.8	3.4	3.5	1.2	4.4	4.9

Table S-2: ^{13}C T_1 relaxation times (sec^{-1}) for the phenyl and Cp ring carbons in **2**

T / s	$T_{1,ortho}$	$T_{1,meta}$	$T_{1,middle}$	$T_{1,para}$	$T_{1,Cp}$	$T_{1,Cp}^{DD}$
300	-	2.5	1.6	0.37	1.7	2.5
318	3.5	3.4	2.3	0.59	3.1	4.3
308	3.3	3.0	2.0	0.46	2.7	3.8
302	3.0	3.0	2.0	0.48	2.6	3.6
290.2	2.3	2.3	1.6	0.36	2.0	2.9
274.6	1.7	1.8	1.1	0.33	1.6	2.3
268.5	1.7	1.6	1.0	0.30	1.4	2.0
249.7	1.2	1.2	0.81	0.23	1.2	1.7

Table S-3: ^{13}C T_1 relaxation times (sec^{-1}) for the phenyl and Cp ring carbons in **3**

T / K	1-CCo_3 phenyl		1,4-(CCo_3,alkyne) phenyl	1-alkyne phenyl			Cp
	$T_{1,para}$	$T_{1,meta}$	T_1	$T_{1,para}$	$T_{1,ortho}$	$T_{1,meta}$	$T_{1,Cp}$
311	0.65	3.2	3.0	0.84	4.6	4.4	3.3
306	0.57	2.7	2.7	0.68	3.7	3.5	2.9
300	0.54	2.8	2.4	0.67	3.8	3.6	2.8
278	0.41	2.0	1.8	0.48	2.6	2.5	2.0
257	0.32	1.4	1.3	0.33	1.9	1.8	1.5

Table S-4: ^{13}C T_1 relaxation times (sec^{-1}) in **4**

T / K	$T_{1,para}$	$T_{1,ortho}$	$T_{1,meta}$	$T_{1,inner}$
300.0	0.83	4.8	4.6	3.9
289.2	0.75	4.1	4.0	3.6
278.4	0.59	3.6	3.5	3.0
267.7	0.57	3.2	3.1	2.7
256.9	0.47	2.6	2.7	2.4

Equations used to calculate diffusion coefficients in 2:

In the case of **2** the extreme narrowing limit is no longer valid and the more general frequency dependent equations have to be used:

$$\frac{1}{T_1} = \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r^6} \frac{1}{10}[\ J(\omega_C-\omega_H) + 3\cdot J(\omega_C) + 6\cdot J(\omega_C+\omega_H)\ ] \qquad \textbf{(S-1)}$$

$J(\omega)$ is the spectral density with $\omega_C = 2\pi\nu_C$ and $\omega_H = 2\pi\nu_H$ where ν_H and ν_C are the proton and carbon Lamor frequencies.

The spectral density can be related to the correlation time and the diffusion coefficients following the same procedures as above. For the tumbling motion described by $D_\perp$ one obtains

$$J_\perp(\omega) = \frac{1}{1 + \frac{\omega^2}{6}D_\perp} \quad ;\ \omega = (\omega_C+\omega_H),\ \omega_C,\ (\omega_H-\omega_C) \qquad \textbf{(S-2)}$$

where ω takes the values $(\omega_C+ \omega_H)$, ω_C and $(\omega_H- \omega_C)$ to give the three terms in (S-1). Similarly one obtains for the spinning motion D_s

$$J_s(\omega) = \frac{1}{384D_\perp\ (1+(\frac{\omega}{6D_\perp})^2)} + \frac{9}{16(5D_\perp+D_s)\ (1+(\frac{\omega}{5D_\perp+D_s})^2)} + \frac{27}{64\ (2D_\perp+4D_s)\ (1 + (\frac{\omega}{2D_\perp+4D_s})^2)} \qquad \textbf{(S-3)}$$

In the fast narrowing limit where $D_\perp \gg \omega$, equations (S-2) and (S-3) simplify to (2) and (3).