Fluxional processes in organotransition-metal C_{60} complexes

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Variable-temperature and EXSY ^{13}C NMR studies on $[M(NO)(PPh_3)_2(\eta^2\text{-}C_{60})]$ (M = Co, Rh), $[Ru(NO)(PPh_3)_2(\eta^2\text{-}C_{60})H]$ and $[Rh(CO)(PPh_3)_2(\eta^2\text{-}C_{60})H]$ show the presence of C_{60}–metal moiety rotation and migration processes and the data allow extensive assignment of $\delta(C_{60})$ ^{13}C NMR resonances.

The dynamical behaviour of organotransition-metal fullerene complexes has been little investigated. The only reported examples are fullerene–metal bond axis rotation for $[M(CO)_4(\eta^2\text{-}C_{60})]$ (M = Fe, Ru) and $[Fe(CO)_4(\eta^2\text{-}C_{70})]$[1,2] and metal moiety migration for $[Pd(PR_3)_2(\eta^2\text{-}C_{60})]$ [R_3 = Me_2Ph, $MePh_2$, $(OMe)_3$] from preliminary variable-temperature ^{13}C NMR studies.[3,4] Similar behaviour has been implicated for $[C_{60}\{Ir(CO)(PEt_3)_2Cl\}_2]$,[5] $[C_{60}\{Pt(PEt_3)_2\}_6]$,[6] $[\{Ru(\eta\text{-}C_5Me_5)(MeCN)_2\}_3(C_{60})]^{3+}[O_3SCF_3^-]_3$[7] and $[C_{70}\{Ir(CO)(PPh_3)_2Cl\}_2]$.[8]

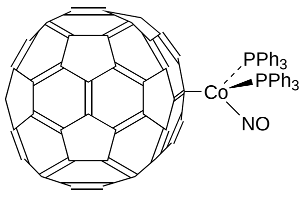
Here we report variable-temperature and two-dimensional EXSY ^{13}C NMR spectroscopic studies of $[M(NO)(PPh_3)_2(\eta^2\text{-}C_{60})]$ (M = Co **1**, Rh **2**), $[Ru(NO)(PPh_3)_2(\eta^2\text{-}C_{60})H]$ **3** and $[Rh(CO)(PPh_3)_2(\eta^2\text{-}C_{60})H]$ **4** which have allowed us to identify for the first time several fluxional processes. The ^1H and $^{31}P\{^1H\}$ NMR spectra remained unchanged between −90 and 50 °C, as expected. The new complexes were prepared by substitution of PPh_3 by C_{60} from the relevant precursor.

At low temperatures the ^{13}C NMR spectra of **1**–**4**, allowing for the commonly occurring accidental degeneracy of resonances, were consistent with a complex possessing C_s symmetry (Table 1). Thus the structures are very similar to those previously determined for **4**[9] and the related complex of **3**, $[Ru(NO)(PPh_3)_2(\eta^2\text{-}C_{60})Cl]$.[2]

On warming **2**, as illustrated in Fig. 1, the number and intensity of $\delta(C_{60})$ ^{13}C NMR signals changed to a 17 line C_{2v} symmetry pattern (allowance again being made for isochronous resonances). Such changes are indicative of the onset of free rotation about the metal–fullerene bond. Observation of coupling for the C(1) (δ 83) carbon atoms and partially resolved coupling for C(2) (δ 160; see Fig. 2 for numbering scheme) carbon atoms to the ^{103}Rh and ^{31}P nuclei shows that the rotation is non-dissociative. The $^{13}C\{^1H\}$ NMR spectra of **1** and **3** showed broadly similar features although signal coalescence occurred at different temperatures consistent with changes in the extent of π-back donation [$\Delta G^\ddagger$ *ca.* 9, 10 and 14 kcal mol^{-1} for **1** at −60 °C, **2** at −50 °C and **3** at 0 °C, respectively (1 cal = 4.184 J)].

Further warming of samples of **1**, **2** and **4** resulted in all $\delta(C_{60})$ resonances collapsing to a single broad peak at δ *ca.* 145 indicating that the metal moiety is migrating over the whole fullerene surface as all the carbon atoms have become chemically equivalent (I_h symmetry). This migration was investigated using two-dimensional ^{13}C EXSY NMR and, for the first time for a fullerene compound, it was possible to unambiguously assign it as a [1,3]-shift mechanism.

The two-dimensional ^{13}C EXSY NMR (τ_{mix} = 0.5) spectrum of **1** (Fig. 2) reveals the expected number and nature of correlations for a [1,3] shift. For example, most signals, including C(2) and C(3), have four correlations (corresponding



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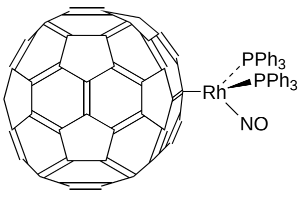

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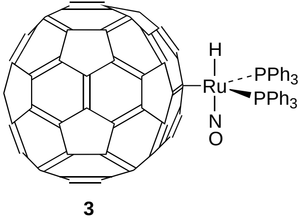

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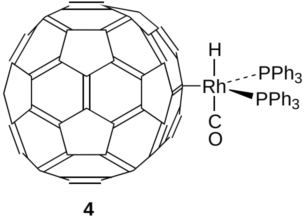

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Table 1 Summary of the $\delta(C_{60})$ ^{13}C NMR (125 MHz) intensity information for **1, 2, 3** and **4** and for model monoadducts with C_s, C_{2v} and I_h symmetry[a]

Complex	T/°C	No. of peaks (intensity)	T/°C	No. of peaks (intensity)	T/°C	No. of peaks
1	−90	11(br)[b]	−10	4(2) + 11(4) 1(8)	50	1(v br)[b,c]
2	−90	4(1) + 15(2) 1(4) + 1(6) 2(8)	−40	3(2) + 10(4) 1(6) + 1(8)	25	1(v br)[b]
3	−90	2(1) + 13(2) 2(4) + 2(5) 1(6) + 1(8)	50	4(2) + 11(4) 1(8)		
4	−90	2(1) + 19(2) 2(3) + 2(4) 1(6)			25	1(v br)[b,c]
C_s		4(1) + 28(2)				
C_{2v}				4(2) + 13(4)		
I_h						1(60)

[a] It is assumed that fullerene T_1 relaxation times do not vary significantly within a molecule. [b] Signals too weak and broad to be accurately integrated. [c] Recorded at 75 MHz.

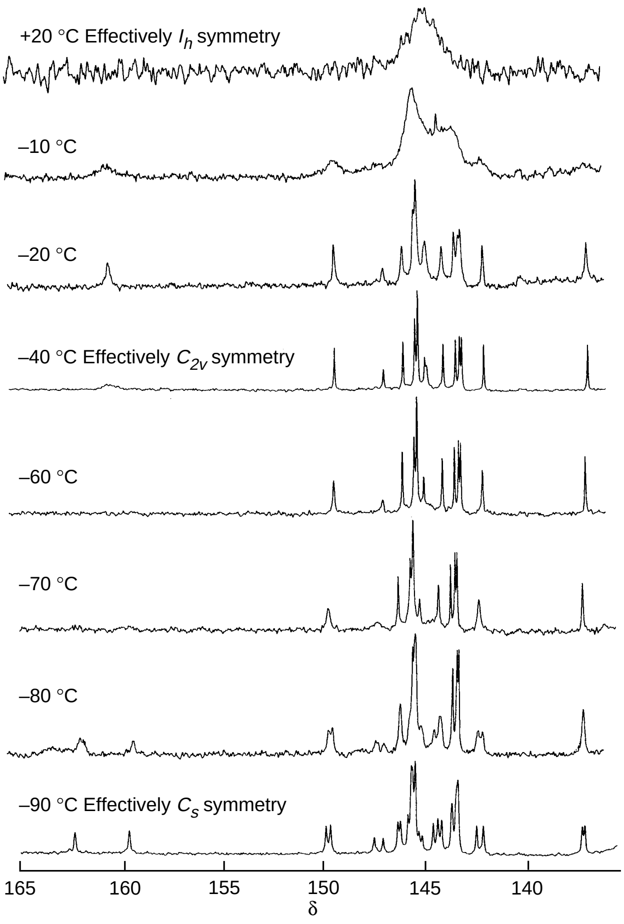

Fig. 1 The $^{13}C\{^1H\}$ NMR (125 MHz, −90 to 25 °C, C_4D_8O) spectrum of **2** in the fullerene sp^2 region

to metal migration to the four adjacent C=C bonds). Also, C(1) showed only two correlations [to C(2) and C(3)] again indicating that only one type of migration, namely a [1,3] shift, is occurring. Owing to resonance overlap only 16 lines are clearly observable, although the total intensity is consistent with the presence of 60 fullerene carbon atoms. Tracing the unique set of correlations additionally allows assignment of most of the $\delta(C_{60})$ resonances† and out of approximately 400 fullerene compounds characterised by ^{13}C NMR spectroscopy this is only the second example. Interestingly, the assignment order has many similarities with that previously determined for $[(C_{60})OsO_4(4\text{-}Bu^tC_5H_4N)_2]$ using two-dimensional NMR INADEQUATE spectroscopy on an expensive isotopically enriched sample.[10] In consonance with both these studies and by observation of scalar couplings, a useful generality for fullerene assignments becomes apparent: For all 6,6-closed fullerene organic or organometallic adducts the lowest field signal(s) (δ > *ca.* 150) are due to the C(2) atoms and one, two or four resonances are present for a C_{2v}, C_s or C_1 symmetry complex.

So far, we have not been able to unambiguously assign the mechanism to a dissociative (more likely) or an intramolecular η^4-C_{60} process.

In summary, we have described the dynamical ^{13}C NMR properties of the compounds **1**–**4**. These studies have shown that the compounds collectively undergo rotation about the metal–fullerene bond axis and migration of the metal fragment over the surface of C_{60}. In each case the symmetry of the complexes is different and results in a significantly different ^{13}C NMR spectrum.

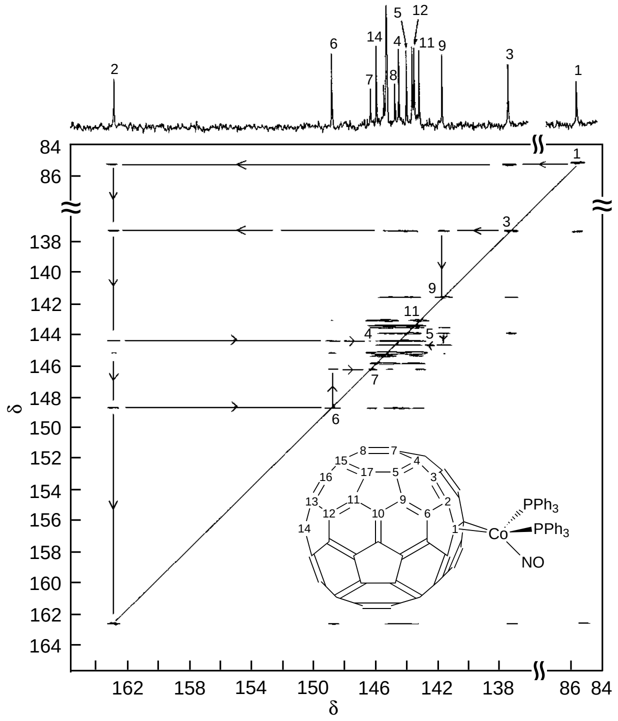

Fig. 2 ^{13}C–^{13}C NMR (125 MHz, 5 °C, C_4D_8O) EXSY spectrum of **1** (τ_{mix} = 0.5 s)

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Footnotes

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† *Selected ^{13}C NMR spectroscopic data for* **1**: (125 MHz, C_4D_8O, 5 °C) δ 162.6 [s, 4C, C(2)], 148.6 [s, 4C, C(6)], 146.1 [s, 2C, C(7)], 145.8 (s, 4C, C_{60}), 145.3 [s, 2C, C(14)], 145.1 (s, 4C, C_{60}), 145.0 (s, 8C, C_{60}), 144.6 [s, 2C, C(8)], 144.3 [s, 4C, C(4)], 143.8 [s, 4C, C(5)], 143.5 (s, 4C, C_{60}), 143.3 (s, 4C, C_{60}), 143.0 [s, 4C, C(11)], 141.5 [s, 4C, C(9)], 137.2 [s, 4C, C(3)], 135.2 (d, $^1J_{PC}$ 35 Hz, PPh_3, C_{ipso}), 135.1 (d, $^2J_{PC}$ 12 Hz, PPh_3 C_{ortho}), 130.8 (s, PPh_3, C_{para}), 129.3 (d, $^3J_{PC}$ 10 Hz, PPh_3, C_{meta}), 85.3 [s, 2C, C(1)]. See Fig. 2 for fullerene numbering scheme. C_{60} refers to fullerene carbon resonances that could not be unambiguously assigned.

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