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# Observation of triple-quantum effects in the HMQC spectra of substituted derivatives of $Rh_6(CO)_{16}$ †

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**Triple-rhodium quantum effects in the HMQC spectra of $[Rh_6(CO)_{15}L]$ [L = MeCN, I, $PBu^n_3$, $P(OPh)_3$, $P(4\text{-}XC_6H_4)_3$; X = H, OMe, F] modulate the intensity and position of the correlations in the rhodium dimension; cross peaks are displaced from the true chemical shift, additional cross peaks are seen, and the intensity of the coherences varies as a function of the mixing time and coupling constant, going to zero at the conventional value of $1/(2J)$.**

Inverse detected multiple quantum coherence (HMQC) experiments[1] are now routinely used for the detection of insensitive nuclei such as $^{15}N$ and $^{13}C$ using $^{1}H$ as the detector nucleus. More recently there has been a small number of reports using *e.g.* $^{31}P$ as the detector nucleus to study metal nuclides such as $^{57}Fe$ and $^{183}W$ in inorganic systems.[2–4] In all these experiments the low natural abundance of the insensitive nucleus $I$ ensures that only single-quantum transitions of the $I$ spin are important. Extension of the HMQC experiment to metal cluster compounds in which the insensitive (*i.e.* metal) nucleus has high natural abundance is not straightforward since the detector nucleus may now couple to several $I$ spins. Multiple-quantum transitions, in which the assembly of metal spins acts as a unit, must now be considered. Although the effect of multiple-quantum transitions of the $I$ spins is well understood,[5] until now, it has been of little practical significance since, as mentioned above, studies using HMQC have concentrated on nuclei where multiple metal-quantum effects cannot be observed because of the low natural abundance of the $I$ spin.

Ruegger and Moskau have recently presented a set of rules for the interpretation of $^{31}P$ detected $^{195}Pt$–$^{31}P$ HMQC spectra (acquired without phase cycling to allow observation of resonances from multiple-quantum coherences normally suppressed by the phase cycling) of some platinum-phosphine systems in which the detector phosphorus nucleus can couple to two $^{195}Pt$.[6] We now report that where the detector nucleus can couple to three metal spins, *e.g.* when a face-bridging carbonyl is used to detect $^{103}Rh$ in rhodium carbonyl cluster compounds, not only are the correlations displaced from the "true" chemical shift in the rhodium dimension but also may be missing altogether as a result of modulation of the spectral intensity by the multiple metal-quantum transitions. Simple experimental modifications are described to overcome these effects.

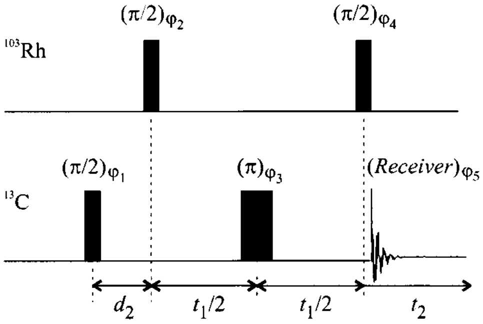

**Fig. 1** Pulse sequence used for obtaining inverse detected HMQC 2D spectra.

The effect of the HMQC pulse sequence, Fig. 1, on a face-bridging carbonyl coupled to three rhodium atoms can be described using the product operator formalism.[7,8] At the beginning of the evolution period $t_1$, just after the first $(\pi/2)$–$^{103}Rh$ pulse, the state of the four-spin face-bridging $^{13}C^{103}Rh_3$ system is given by eqn. (1)

$$\sigma = (0Rh) + (1Rh) + (2Rh) + (3Rh) \tag{1}$$

where

$$(0Rh) = C(\pi/2 - \Omega_C d_2)\cos^3\pi J d_2 \tag{2}$$

$$(1Rh) = 2C(\pi - \Omega_C d_2) \times \{Rh_1(\pi/2) + Rh_2(\pi/2) + Rh_3(\pi/2)\}\cos^2\pi J d_2 \sin\pi J d_2 \tag{3}$$

$$(2Rh) = 4C(3\pi/2 - \Omega_C d_2) \times \{Rh_1(\pi/2)Rh_2(\pi/2) + Rh_1(\pi/2)Rh_3(\pi/2) + Rh_2(\pi/2)Rh_3(\pi/2)\} \times \cos\pi J d_2 \sin^2\pi J d_2 \tag{4}$$

$$(3Rh) = 8C(2\pi - \Omega_C d_2) \times Rh_1(\pi/2)Rh_2(\pi/2)Rh_3(\pi/2)\sin^3\pi J d_2 \tag{5}$$

and $C(\varphi)$ and $Rh_i(\varphi)$ denote the carbon and rhodium spin operators respectively where, for arbitrary phase $\varphi$, and $S$ is

$$S(\varphi) = S_x\cos\varphi + S_y\sin\varphi \tag{6}$$

either $C$ or $Rh_i$. The chemical shift of carbon is $\Omega_C$, $J$ is the coupling constant and $d_2$ is the delay used in the pulse sequence for polarization transfer, Fig. 1. Spin operators belonging to the three different rhodium atoms are numbered by the subscripts 1, 2, and 3.

It is convenient to refer to the operators $(0Rh)$, $(1Rh)$, $(2Rh)$ and $(3Rh)$ as zero-, one-, two-, and three-rhodium spin coherences, respectively since we are interested principally in the order of the coherence with respect to rhodium.

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† *Supplementary data available*: the HMQC pulse program and phase cycling used in the experiments. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/1917/, otherwise available from BLDSC (No. SUP 57547, 2 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

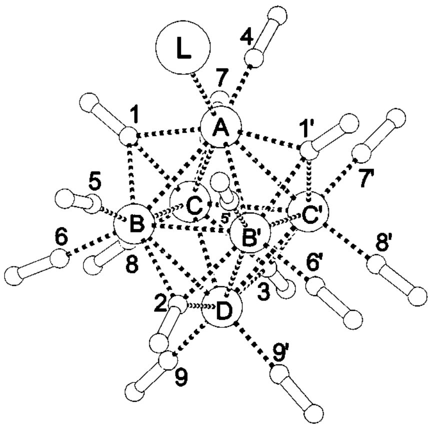

**Fig. 2** Structure of and labelling scheme for $[Rh_6(CO)_{15}\{P(4\text{-}FC_6H_4)_3\}]$.

The zero-rhodium spin coherence ($0Rh$) contains no rhodium spin operators so cannot be used to correlate the carbon and rhodium chemical shifts. Magnetization arising from this term is eliminated by the phase cycling used in the standard HMQC experiment.

The terms ($1Rh$), ($2Rh$) and ($3Rh$) evolve under the action of the rhodium chemical shifts, $\Omega_{Rh1}$, $\Omega_{Rh2}$ and $\Omega_{Rh3}$ and can be used to correlate carbon and rhodium shifts. Cross peaks resulting from ($2Rh$), through zero- and double-rhodium quantum coherences, are suppressed by the standard phase cycling whilst ($1Rh$) gives cross peaks at the expected rhodium chemical shifts through single-rhodium quantum transitions. These cross peaks appear as 1 : 1 : 1 : 1 quartets in the carbon dimension, F2. The magnitude of each component of the quartets is given by eqn. (7)

$$|(1/16)\cos^2\pi Jd_2\sin\pi Jd_2| \qquad (7)$$

and reaches a maximum of $\sqrt{3}/72$ when

$$d_2 = (1/\pi J)\mathrm{arctg}(\sqrt{2}/2) \approx 1/(5J) \qquad (8)$$

Thus the maximal magnitude of these one-rhodium spin cross peaks is a factor of *ca.* 10 weaker than the maximal amplitude of those arising from a terminal Rh(CO) moiety (which, as can be shown, is equal to 1/4). Importantly, the maximum does not occur at the conventional mixing delay of $1/(2J)$, *when the intensity of these cross peaks equals zero*, but at a delay $d_2$ that is *ca.* 2.5 times shorter.

The evolution of the three-rhodium spin coherence ($3Rh$) under the action of the rhodium chemical shifts produces four cross peaks in the 2D spectrum, three single-quantum peaks and one triple-quantum. All the cross peaks appear as 1 : 3 : 3 : 1 quartets centred at $\Omega_C$ in the carbon dimension, however in the rhodium dimension the three single-quantum peaks occur at $-\Omega_{Rh1} + \Omega_{Rh2} + \Omega_{Rh3}$, $\Omega_{Rh1} - \Omega_{Rh2} + \Omega_{Rh3}$ and $\Omega_{Rh1} + \Omega_{Rh2} - \Omega_{Rh3}$ whilst the triple quantum peak occurs at $-\Omega_{Rh1} - \Omega_{Rh2} - \Omega_{Rh3}$. The magnitude of the single- and triple-quantum peaks (the height of the inner quartet lines) is

$$|(3/64)\sin^3\pi Jd_2| \qquad (9)$$

and reaches a maximum of 3/64 at the conventional value of $d_2 = 1/(2J)$.

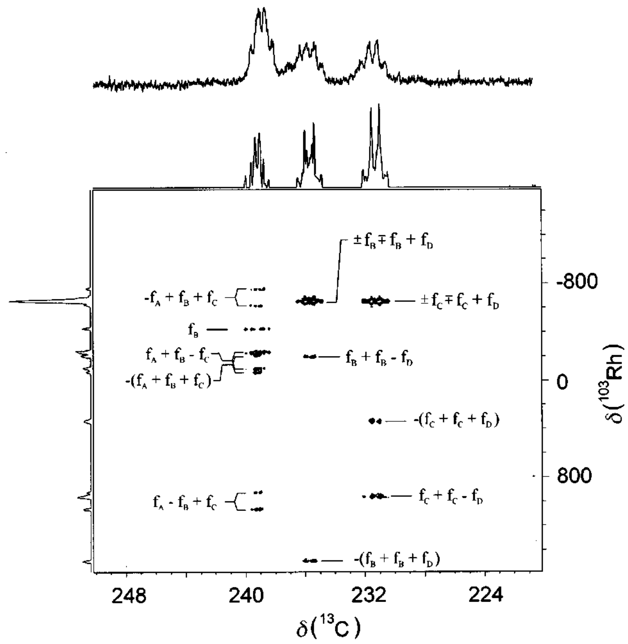

**Fig. 3** Experimental inverse detected HMQC $^{13}C$-$\{^{103}Rh\}$ NMR spectrum of $[Rh_6(CO)_{15}\{P(4\text{-}FC_6H_4)_3\}]$ (bridging region) obtained with a conventional delay $d_2 = 1/(2J) = 17.9$ ms, $J = 28$ Hz. The "expected" correlations to the face-bridging carbonyls are weak or entirely absent and correlations due to three-rhodium spin coherences are seen. The projections in the rhodium and carbon dimensions and a 1D $^{13}C$ spectrum are also shown.

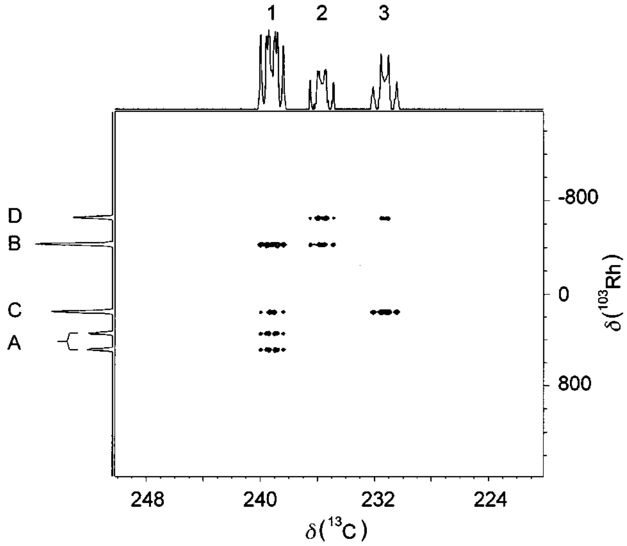

**Fig. 4** Experimental inverse detected HMQC $^{13}C$-$\{^{103}Rh\}$ NMR spectrum of $[Rh_6(CO)_{15}\{P(4\text{-}FC_6H_4)_3\}]$ (face-bridging region) obtained with a non-conventional delay $d_2 = 1/(5J) = 7.14$ ms, $J = 28$ Hz. Strong correlations to the bridging carbonyls are seen at the "correct" rhodium chemical shifts although the delay $d_2$ used is "unconventional".

The structure of, and labelling scheme for, $[Rh_6(CO)_{15}\{P(4\text{-}FC_6H_4)_3\}]$ are shown in Fig. 2.[9] Figs. 3 and 4 show respectively the inverse detected HMQC $^{13}C$-$\{^{103}Rh\}$ spectra of this cluster recorded under standard conditions using mixing times of $1/(2J)$, $J = 28$ Hz, a typical value for $^{103}Rh$ coupling to a face-bridging $^{13}CO$, and $1/(5J)$.[10] The only "correct" correlation (*i.e.* single-spin–single-quantum rhodium) seen in Fig. 3 is the correlation C(1)–Rh(B). All other "correct" correlations are too weak to be observed. All the remaining cross peaks seen are due to three-rhodium spin operators (triple-quantum and single-quantum with respect to rhodium). Two of the three-spin–single-quantum correlations are accidentally located at the expected coordinates of the 'correct' correlations C(2)–Rh(D) and C(3)–Rh(D) because the cluster contains two equivalent atoms Rh(B) and Rh(C). These "unexpected" correlations are reproduced in the simulated spectrum, Fig. 5. By contrast in Fig. 4, using the unconventional $1/(5J)$ mixing delay, cross peaks are observed at the 'correct' places even though the delay is sufficiently far removed from the conventional value that no correlations might have been expected to be observed. These single-quantum (with respect to rhodium) transitions are produced by one-rhodium spin operators and are observed due to their intensities reaching a maximum at $1/(5J)$ whilst the intensity of correlations due to multiple-rhodium spin transitions is close to zero for this delay. Fortuitously, for rhodium

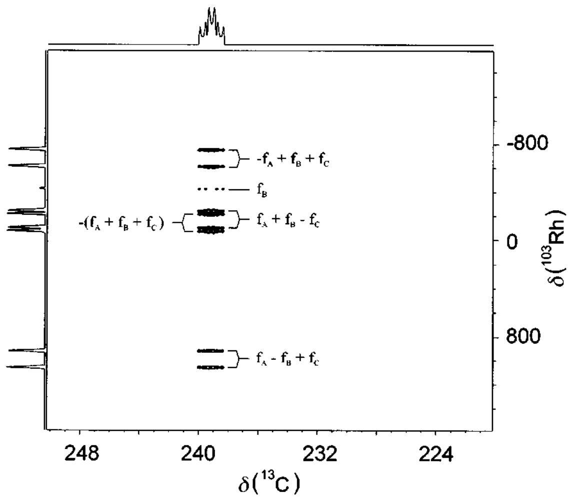

**Fig. 5** Simulated HMQC spectrum for C(1)O for the case of a conventional delay $d_2 = 1/(2J) = 17.9$ ms. $J$[Rh(A)–P] = 140 Hz, $J$[C(1)–Rh(A)] = 20 Hz, $J$[C(1)–Rh(B)] = 29 Hz, $J$[C(1)–Rh(C)] = 31 Hz.

carbonyl clusters, couplings to the terminal carbonyls (70 Hz) are approximately 2.5 times greater than those to face-bridging carbonyls (28 Hz) allowing the one-rhodium spin correlations to both face-bridging and terminal carbonyls to be observed in a single experiment.

These effects are not limited to [$Rh_3(\mu\text{-}CO)$] fragments but are expected whenever the detector nucleus is coupled to several metal spins that can act as a unit. Clearly care must be taken in the application and interpretation of HMQC experiments to the detection of insensitive nuclei in which the coupling of the detector nucleus to several insensitive spins can occur. In particular the spin system must be carefully analysed to determine the optimal value of the mixing delay to ensure that single metal spin transitions are observed.

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