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Metal Fragment Rotation in Triangular Metal Clusters: ^{1}H, ^{2}H, and ^{13}C NMR Studies of the Fluxional Behavior of the Anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$

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Variable-temperature ^{13}C NMR spectroscopy, 1D SPT, and 2D EXSY experiments have been used to investigate the fluxionality of the triangular cluster anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$. The ^{13}CO resonances have been assigned through ^{1}H−^{13}C 2D HMQC and ^{13}C 2D DQF-COSY experiments and through the measurement of the ^{13}CO longitudinal relaxation times. The exchange pattern observed in the ^{13}C 2D EXSY experiments proved the occurrence of a synchronous axial−axial and equatorial−equatorial carbonyl exchange on the apical metal. The rate constants at 303 and 313 K compare well with those previously measured, through ^{1}H NMR spectroscopy, for the exchange of the two hydrides bridging the lateral edges of the cluster. The rigid rotation of the whole apical $[H_2Re(CO)_4]$ moiety around an axis passing through the midpoint of the basal bimetallic fragment is in agreement with these results. A deuterium kinetic isotope effect $k_H/k_D = 1.45(24)$ has been measured through ^{1}H and ^{2}H 2D EXSY experiments, supporting the involvement of the hydrides in the rate-determining step of the exchange process.

Introduction

Stereochemical nonrigidity is a feature commonly displayed by metal cluster compounds and has been extensively studied in the last two decades.[1] A number of different kind of processes involving either the ligands[1] or the metal cage itself[1f,2] have been observed, providing both information relevant in understanding the mobility and the reactivity of small molecules onto surfaces[1,3] and an experimental ground for the theoretical studies of the bonding between metals and metals or metals and ligands.[4] We report here a NMR study of the dynamic behavior observed in the hydridocarbonyl anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ (**1**)**,** which allowed us to prove the occurrence of intramolecular metal fragment mobility in a triangular cluster.

The anion **1**, formed by the reaction of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with pyridine,[5] has the structure shown in Chart 1 and its ^{1}H NMR spectrum shows three hydridic resonances at $\delta = -11.98$, -13.09, and -14.70 ppm, respectively. These signals have been assigned to H_b, H_c, and H_a, respectively, on the basis of the low-field shift of the hydridic resonances observed in rhenium clusters when one of the axial carbonyls is substituted by ligands with greater σ-donor capability.[6] Experiments performed with deuterated pyridine in order to investigate the mechanism of the ortho metalation showed[5] that H_2 elimination occurred from the cluster before the pyridine oxidative addition, resulting in the incorporation of one deuterium atom into the cluster. The deuterium atom appeared equally distributed on both the singly bridged cluster edges, suggesting the occurrence of some dynamic process. Variable-temperature ^{1}H 1D NMR spectra, performed on the protiated derivative, have indeed shown that above room temperature the two high-field signals broaden and eventually collapse. Computer line shape simulation allowed[5] the estimate of the rate constants ($k = 0.4$, 1.0, 2.2, 4.5, 9.0, 18, and 35 s^{-1} at 300, 309, 318, 327, 335, 345, and 354 K, respectively) and of the activation energy of the process ($E_a = 72(1)$ kJ/mol). Migration of the bridging hydrides among the cluster edges is commonly observed in hydridic clusters[1a,b,7] but usually it requires the presence of at least one unbridged metal−metal interaction. In **1**, all the cluster edges are bridged and therefore the equalization of the hydrides can hardly be ascribed to a simple interchange of their positions.

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(1) (a) Band, E.; Mutterties, E. L. *Chem. Rev.* **1978**, *6*, 639. (b) Johnson, B. F. G.; Benfield, R. E. In *Transition Metal Clusters;* Johnson, B. F. G., Ed.; Wiley: Chichester, U.K., 1980; Chapter 7. (c) Aime, S.; Milone, L. *Progr. NMR Spectrosc.* **1977**, *11*, 183. (d) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3, Chapter 20. (e) Farrugia, L. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science Ltd.: Exeter, U.K., 1995; Vol. 10, Chapter 4. (f) Salter, I. D. *Adv. Dyn. Stereochem.* **1988**, *2*, 57.

(2) For some examples, see: (a) Chi, Y.; Su, C.; Farrugia, L. J.; Peng, S.; Lee, G. *Organometallics* **1994**, *13*, 4167 and references therein. (b) Adams, R. D.; Wang, S.; *Inorg. Chem.* **1985**, *24*, 4449. (c) Garlaschelli, L.; Fumagalli, A.; Martinengo S.; Heaton, B. T.; Smith, D. O.; Strona, L. *J. Chem. Soc., Dalton Trans.* **1982**, 2265. (d) Gladfelter, W. L.; Fox, J. R.; Smegal, J. A.; Wood, T. G.; Geoffroy, G. L. *Inorg. Chem.* **1981**, *20*, 3223. (e) Brown, C.; Heaton, B. T.; Towl, A. D. C.; Chini, P.; Fumagalli, A.; Longoni, G. *J. Organomet. Chem.* **1979**, *181*, 233.

(3) See, for instance: (a) *The Synergy Between Dynamics and Reactivity at Clusters and Surfaces*; Farrugia, L. J. Ed.; NATO ASI Series C; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. 465. (b) Johnson, B. F. G.; Rodgers, A. In *The Chemistry of Metal Cluster Complexes*; Schriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 6.

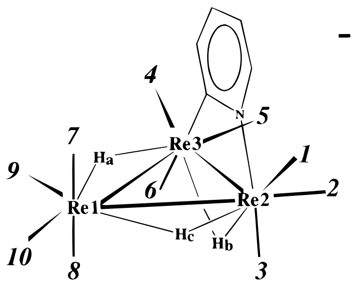
(4) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (c) Johnson, B. F. G., *J. Chem. Soc., Chem. Commun.* **1986**, 27. (d) Mingos, D. M.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall Inc.: Englewood Cliffs, NJ. 1990.

(5) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Organometallics* **1993,** *12*, 4863.

(6) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1986**, 2691 and references therein.

S0276-7333(96)00875-8 CCC: $14.00

Chart 1



The presence of an unsaturated ligand bound to the cluster could suggest that the exchange of the hydrides is due to a dynamic behavior of the organic ligand itself, e.g., a σ, n interchange of carbon and nitrogen on the two basal metals, resulting in cluster enantiomerization. This process reminds the σ, π flip of unsaturated molecules,[8] as the one observed in 1975 by Shapley et al. for the vinyl group in $[Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}]$.[8a]

A ^{13}C NMR study was therefore undertaken in order to clarify the nature of the dynamic process. In fact, due to the C_1 symmetry of **1**, 10 separate carbonyl resonances are expected. The σ, n interchange of the unsaturated ligand would create a pseudomirror plane equalizing all the carbonyls in couples, apart from the two mutually *trans* on the apical rhenium (***7*** and ***8*** in Chart 1), while the direct exchange of the hydrides would not affect the ^{13}C spectra.

Results and Discussion

$^{13}C\{^1H\}$, $^1H-^{13}C$ HMQC, and ^{13}C DQF-COSY NMR Spectra. The $^{13}C\{^1H\}$ NMR solution spectra of a ^{13}CO-enriched sample of **1** recorded at 208 and 295 K are shown in Figure 1. Almost all the resonances display a temperature dependence of the chemical shifts and, in the low-field region, this results in the overlap of two signals at room temperature. Also, the line width is temperature dependent and at room temperature three of the low-field resonances remain sharp while all the others broaden.

$^1H-^{13}C$ 2D HMQC experiments, optimized for J_{CH} = 3, 5, and 7 Hz have been performed in different conditions of temperature and field and the results of one of them (J_{CH} = 7 Hz, 208 K, 11.7 T) are reported in Figure 2. At this temperature the 1D ^{13}C spectrum shows 10 resolved signals. The hydride H_b, which belongs to the basal doubly bridged edge, shows strong correlations with all the low-field resonances (even if the resolution does not allow to establish whether the lowest field correlation is with resonance a, b, or both), and smaller cross peaks appear with resonances h and l. The other hydrides show strong correlations with both high- and low-field resonances: H_c correlates with carbonyls c, e, f, h, i, and l and H_a with the resonances g, h, l and with one or both of the couple a−b. Performing the experiment at the same temperature and field,

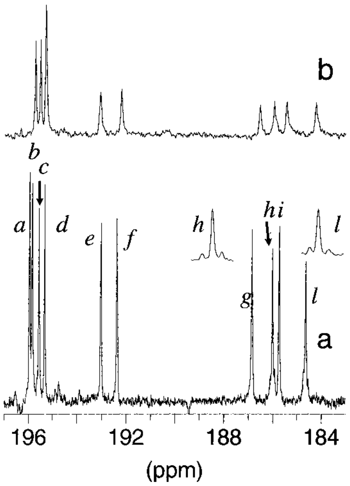


Figure 1. Carbonyl region of the $^{13}C\{^1H\}$ NMR spectra of **1** (125.78 MHz, acetone-d_6 250 μL/toluene-d_8 250 μL): (a) 208 K; (b) 295 K.

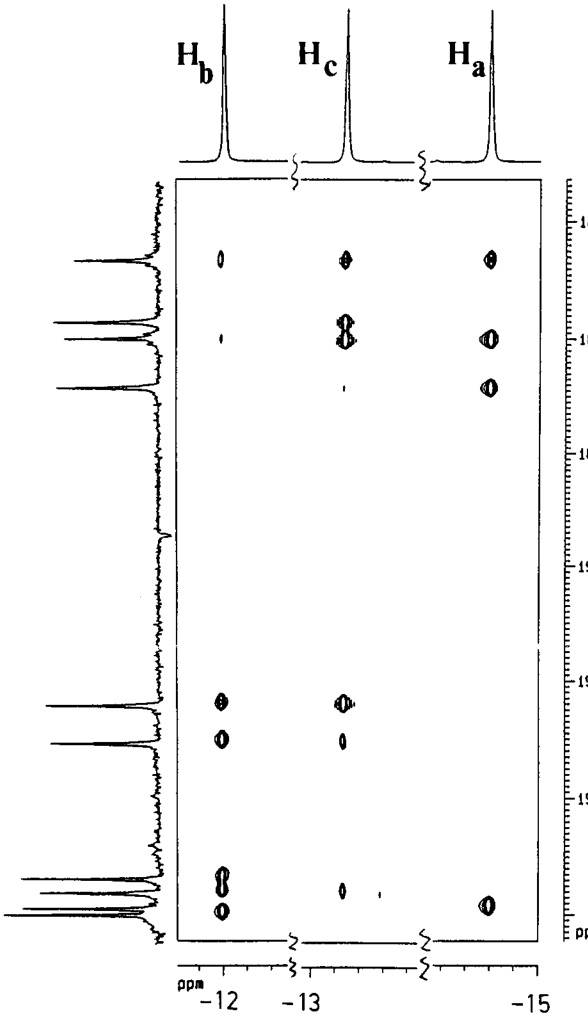


Figure 2. $^1H-^{13}C$ 2D HMQC spectrum (208 K, 11.7 T, acetone-d_6 250 μL/toluene-d_8 250 μL). 1K data points were acquired on a spectral width of 2500 Hz in F2 for each of the 180 increments in t_1. The data were zero filled to 1K in F1 and weighted with a shifted sine-bell function.

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(7) See, for instance: (a) Aime, S; Botta, M.; Gobetto, R.; Milone, L; Osella, D.; Gellert, R.; Rosenberg, E. *Organometallics* **1995**, *14*, 3693. (b) Farrugia, L. J.; Rae, S. E. *Organometallics* **1992**, *11*, 196.(c) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P. *Organometallics* **1991**, *10*, 394. (d) Ewing, P.; Farrugia, L. J.; Rycroft, D. S. *Organometallics* **1988**, *7*, 859. (e) Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 963. (f) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1988**, 1281. (g) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Mann, B. E.; Pickup, B. T.; Spencer, C. M. *J. Chem. Soc., Chem. Commun.* **1986**, 796.

(8) See, for instance: (a) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. B. *J. Organomet. Chem.* **1975,** *94*, C43. (b) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528. (c) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644. (d) Farrugia, L. J.; Chi, Y.; Tu, W. *Organometallics* **1993**, *12*, 1616. (e) Cherkas, A. A.; Randall, L. H.; MacLaughlin, S. A.; Mott, G. N. Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 969.

but optimized for J_{CH} = 3 Hz, a correlation of carbonyl g with H_c can be observed (Supporting Information). On raising the temperature, the signals a, b, and c undergo a sizable high-field shift, at variance from d, so that at room temperature, in the solvent mixture used (see Experimental Section), the low-field resonances c and d overlap at 195.26 ppm (Figure 1b). This different pattern of the signals allows us to solve the ambiguities concerning the correlations of the signals a and b. A $^{1}H-^{13}C$ 2D HMQC experiment optimized for J_{CH} = 5 Hz (294 K, 4.7 T; Supporting Information) clearly shows the correlations of H_b with the resonance a and of H_a with both resonances a and b.[9]

The common correlations allow the assignments of the resonances c, e, and f to the carbonyls bound to Re(2) (the metal bearing the nitrogen of the pyridyl ligand), while resonances d and a are attributable to carbonyls bound to Re(3). The resonances h and l clearly belong to carbonyls in the apical Re(1) moiety, as the resonance i does, for exclusion. Resonance g can also be assigned to Re(1), both for the results of the HMQC optimized for J_{CH} = 3 Hz and for its chemical shift. Indeed it is at high field, together with the resonances unambiguously attributed to Re(1), and it is known that the substitution of a carbonyl by a ligand with weaker π acceptor capability has a deshielding effect on the ^{13}CO resonances,[10] as is observed for the resonances of the carbonyls bound to Re(2) and Re(3). The low-field signal b results therefore assigned to Re(3). It is interesting to note that in Figure 2 correlations due to $^{3}J_{CH}$ coupling are observable between H_b and resonances h and l (attributable to the axial carbonyls of Re(1); see below). Similar ^{3}J couplings have previously been observed in the triangular cluster anion $[Re_3(\mu\text{-}H)_4(CO)_9(PPh_3)]^-$, between one of the hydrides bridging the basal edge and the axial phosphine ligand on the apical metal.[11]

The signals h and l show mutual coupling, appearing, at high fields, as the superposition of a singlet and of a doublet due to the presence of isotopomers with one or two NMR-active carbon atoms (Figure 1a, inset). No other coupling is observed even in the high-field 1D spectra, either at high or low temperature. A ^{13}C double-quantum filtered correlation experiment (DQF-COSY) was attempted in order to detect further couplings. The experiment, performed at 295 K due to the long accumulation time required, has shown significant cross peaks (Figure 3) between resonances h and l, as expected, and among a, b, and one of the overlapped resonances at low field, which should be signal d for the HMQC results. These results confirm that a, b, and d are bound to Re(3) and therefore the assignment of resonance g to Re(1) for exclusion. No cross peaks are shown by resonances g and i, while among resonances c, e, and f only some small coupling features are observable (Supporting Information).

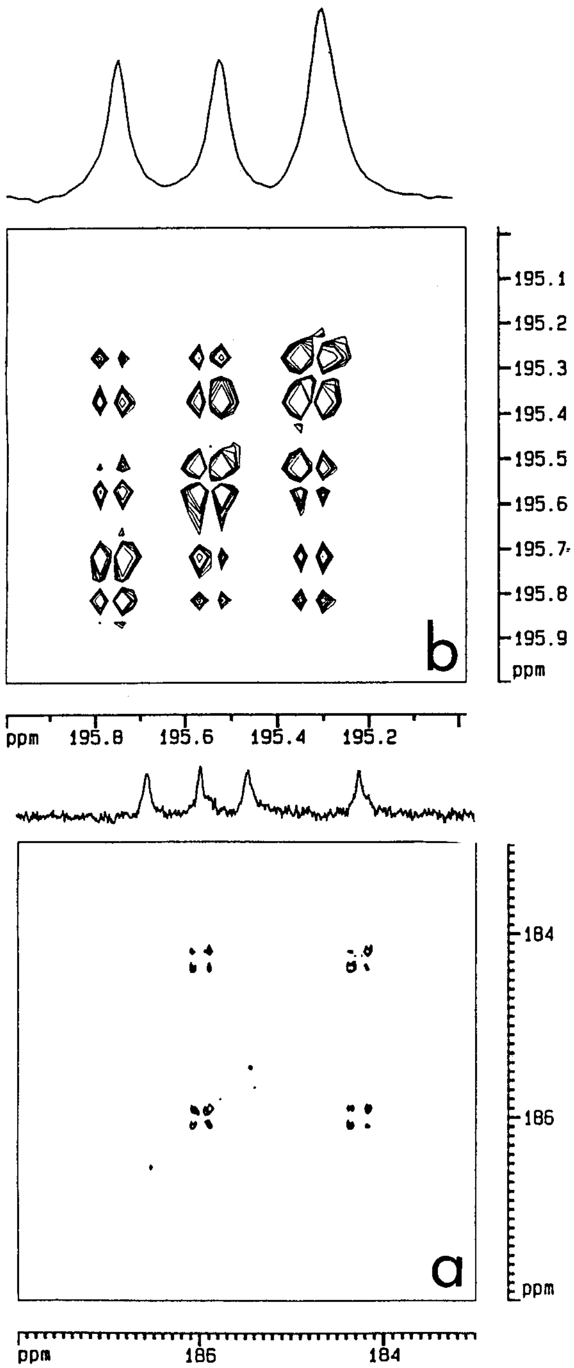

Figure 3. Selected regions of the ^{13}C 2D DQF-COSY (125.78 MHz, 295 K, acetone-d_6 250 μL/toluene-d_8 250 μL): (a) high-field region; (b) low-field region.

The coupling constant between carbonyls a, b, and d (~6 Hz) can be measured from the cross peaks of the 2D DQF-COSY, since the level of enrichment makes negligible the amount of the isotopomer with all the three carbonyls labeled. The coupling constant between resonances h and l is 23 Hz. This last value is comparable, albeit slightly smaller, with those measured in osmium clusters for two nonequivalent *trans* diaxial carbonyls,[12] and it suggests the assignment of these signals to the two nonequivalent mutually *trans* carbonyls ***7*** and ***8*** in the $Re(CO)_4$ fragment (Chart 1). However, the specific identification of each resonance, *syn* or *anti* with respect to the pyridyl moiety, is not possible.

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(9) The four low-field signals are also sensitive to changes in the composition of the solvent mixture. Indeed, at 313 K in the solvent mixture used for the 2D EXSY and DANTE experiments (See Experimental Section), they show a pattern 1:2:1. In principle, in these conditions, the specific assignment of these four resonances is not warranted but it can be inferred from the line width of the signals, and in any case, this does not invalidate the discussion of the fluxional behavior (vide infra).

(10) Mann, B. E. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 10.

(11) Beringhelli, T.; D'Alfonso, G.; M. Freni; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1986**, 2691.

Table 1. Chemical Shifts, Metals to Which Each ^{13}CO Is Bound, and ^{13}C Longitudinal Relaxation Times

reson	chem shift[a]/ ppm (208 K)	assgnt[b]	chem shift[c]/ ppm (313 K)	T_1[c,d]/s
a	195.95(1)	Re(3)	196.3(1)	0.59(4)
b	195.84(1)	Re(3)	195.5(2)	0.46(1)
c	195.57(1)	Re(2)		
d	195.32(1)	Re(3)	195.3(1)	0.39(2)
e	193.01(1)	Re(2)	193.5(1)	0.60(6)
f	192.39(1)	Re(2)	192.2(1)	0.53(2)
g	186.85(1)	Re(1)	186.6(1)	1.01(10)
h	186.00(1)	Re(1)	185.8(1)	1.35(7)
i	185.72(1)	Re(1)	185.5(1)	0.97(10)
l	184.64(1)	Re(1)	184.9(1)	1.33(16)

[a] Measured at 11.7 T. [b] Metal to which the carbonyls are bound according the spectrum at 208 K and 11.7 T. [c] Sample for the 2D EXSY experiment and T_1 measurements. (4.7 T, 313 K, acetone-d_6/toluene-d_8 150 μL/350 μL, relative intensities in parentheses). [d] Measured at 4.7 T and 313 K. In parentheses, the uncertainties of the last digits.

^{13}C Relaxation Times Measurements. We have previously proved[13] that the longitudinal relaxation times of ^{13}CO and ^{31}P bound to rhenium are dominated by the mechanism of the scalar coupling of the "second kind",[14] due to the rapid fluctuations of the spin state of the quadrupolar isotopes of rhenium (^{185}Re natural abundance 37.07%, $I = {}^5/_2$; ^{187}Re natural abundance 62.93%, $I = {}^5/_2$). This mechanism is modulated by the T_2 of the quadrupolar metal and by the coupling constant ^1J(Re−C). The analytical dependence is such that the greater the coupling constant the shorter is T_1. The coupling constant, in turn, is dependent on the nature of the ligand *trans* to the ligand itself. The comparison of the relaxation times of the carbonyls bound to the same metal can therefore be helpful for the relative assignment.

The relaxation times measured at 4.7 T and 313 K for the nine resonances observed under these conditions (see ref 9 and Experimental Section) are reported in Table 1. The resonances h and l at 185.8 and 184.9 ppm, assigned to the mutually *trans* carbonyls **7** and **8** of the apical moiety, have indeed the longest relaxation times, as expected for their high *trans* influence. Also the relaxation time of resonance g is rather long and similar to that of resonance i. For what was discussed above, the relaxation times depend on the nature of the *trans* ligand. In spite of the difference of the actual values of T_1, the ratio of the relaxation times of carbonyls *trans* to carbonyls and carbonyls *trans* to a bridging hydride bound to the same rhenium (typically axial vs equatorial) would be similar even in different compounds, provided that the rhenium atoms have the same coordination sphere. Indeed we have obtained almost identical ratios between the ^{13}C relaxation times of axial and equatorial carbonyls belonging to $H_2Re(CO)_4$ moieties: 1.38 in the triangular cluster anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$,[13d] and 1.36 in the neutral $[Re_3(\mu\text{-}H)_3(CO)_{12}]$.[15] These ratios compare with those calculated in the present case (range 1.36−1.32), assuming that the resonance g is due to an equatorial carbonyl, and compare also with those calculated for the resonance i (1.39−1.37), further supporting their assignment.

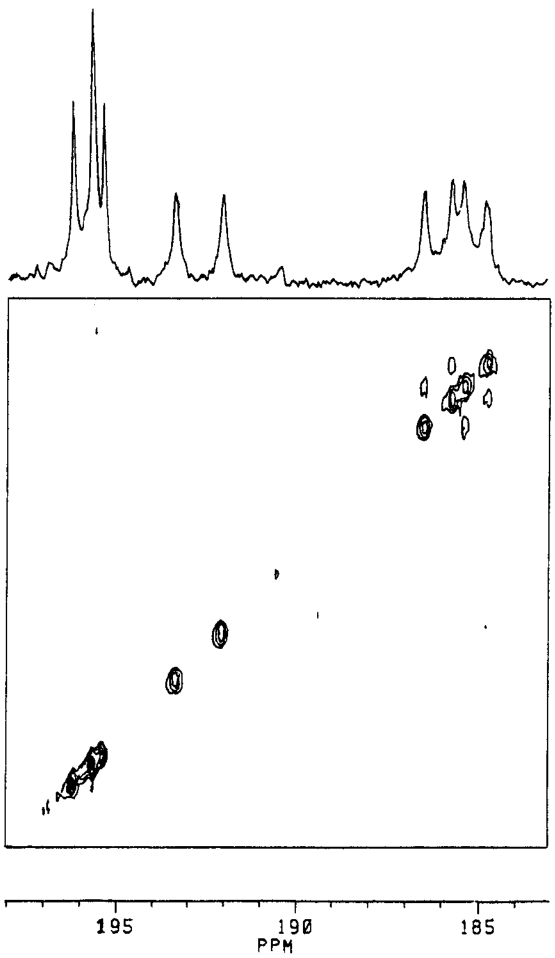

Figure 4. 2D map of the ^{13}C EXSY experiment at 313 K with $\tau_m = 0.25$ s (50.33 MHz, acetone-d_6 150 μL/toluene-d_8 350 μL). A repetition delay of 2.5 s was used for the 200 scans accumulated over a spectral width of 1600 Hz (1K data points) for each of the 128 t_1 increments. Shifted sine-bell weighting function was applied in F1 after zero filling to 1K.

^{13}C 2D EXSY and Magnetization Transfer Experiments. ^{13}C 2D EXSY experiments (4.7 T) have been performed at 303 (mixing time $\tau_m = 0.5$ s) and 313 K ($\tau_m = 0.25$ and 0.4 s). In all the experiments, only two cross peaks have been observed: one between the signals g and i, and the other one between signals h and l (Figure 4). The rate constants for the two exchanges, evaluated according the procedures described previously,[16] were found to be the same, indicating a synchronous exchange ($k = 0.28(5)$ s^{-1} at 303 K, $\tau_m = 0.5$ s; $k = 1.03(10)$ and $1.00(23)$ s^{-1} at 313 K, for $\tau_m = 0.4$ and 0.25 s, respectively). Moreover these rate

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(12) For example: (a) $^2J_{CC} = 35.2$ Hz in $(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}C{=}N(CH_2)_3)Os_3(CO)_{10}$ (Kabir, S. E.; Rosemberg, E.; Day, M.; Hardcastle, K.; Wolf, E.; McPhillips, T. *Organometallics* **1995**, *14*, 721); (b) $^2J_{CC} = 30$ Hz in $CpWOs_3(CO)_{12}(\mu_3\text{-}CTol)(\mu\text{-}H)_2$ (Chi, Y.; Shapley, J. R.; Churchill, M. R.; Li, Y. *Inorg. Chem.* **1986**, *25*, 4165). (b) $^2J_{CC} = 35$ Hz in $Os_3(CO)_{10}(C_7H_8)$ (Tachikawa, M.; Ricther, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *128*, C9).

(13) (a) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Minoja, A. P. *Inorg. Chem.* **1996**, *35*, 2393. (b) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Minoja, A. P. *Inorg. Chem.* **1992**, *31*, 848. (c) Beringhelli, T.; D'Alfonso, G.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1987**, 2083. (d) Beringhelli, T.; Molinari, H.; Pastore, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1899.

(14) (a) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961. (b) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy;* Pitman Ed.: London, 1983.

(15) Beringhelli, T.; D'Alfonso, G., unpublished results.

(16) (a) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935. (b) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P. *Organometallics* **1994**, *13*, 663 and references therein.

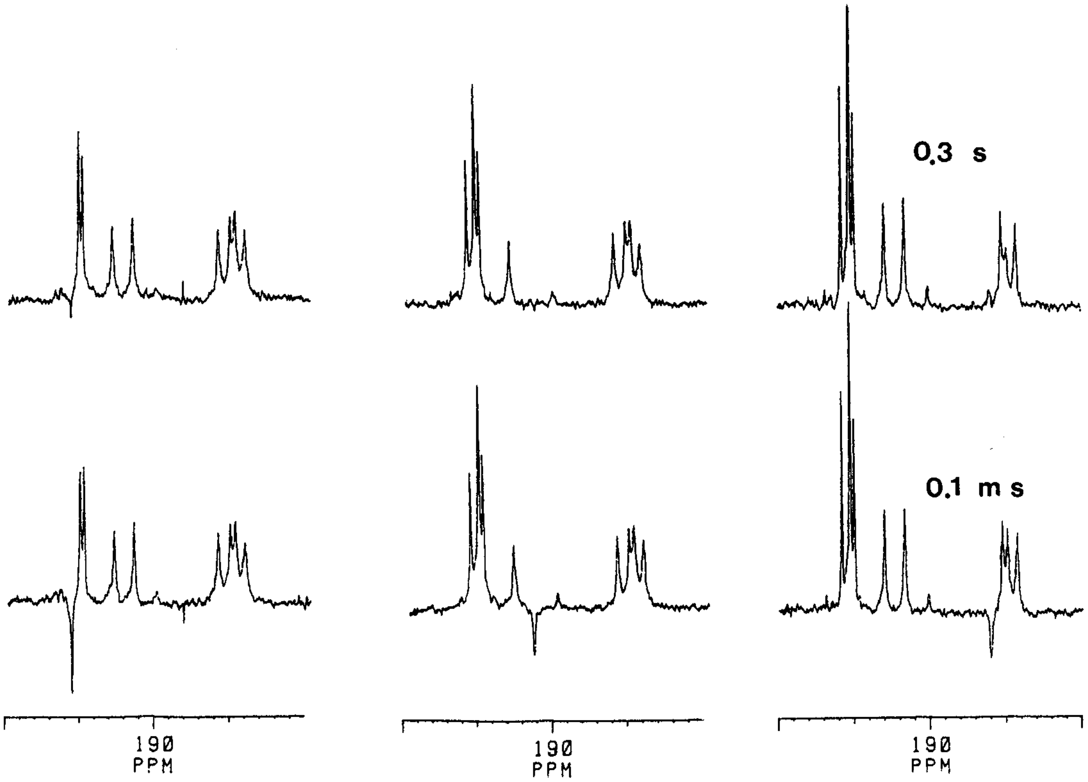

Figure 5. Selected results of the ^{13}C SPT experiments (50.33 MHz, 313 K, acetone-d_6 150 μL/toluene-d_8 350 μL). Lower: spectra recorded 0.1 ms after the selective inversion of the resonances at δ 196.3, 192.2, and 186.6 ppm, respectively. In the first spectrum, for the small separation between the low-field signals, there is some spillover on the near resonance. Upper: spectra recorded 0.3 s after each selective inversion.

constants are comparable, within the experimental uncertainties, with those previously obtained[5] through the 1D ^{1}H spectra at similar temperatures (0.4 and 1.0 s^{-1} at 300 and 309 K, respectively).

The broadening shown above room temperature by some of the low-field resonances (see Figures 1b and 4) could suggest the occurrence of some other exchange process of comparable rate not observed through 2D EXSY for the different relaxation times of the two groups of carbonyls. To rule out this possibility, we have simulated the intensities of the cross and diagonal peaks expected in a 2D EXSY map for the exchange of two equally populated sites having short T_1 (0.53 s) and the intensities expected for signals with long T_1 (1.35 s). At $\tau_m = 0.25$ s, the cross peaks expected in the two cases would have an intensity ratio of 0.77:1 and therefore the one-to-one exchange of the fast relaxing signals should have been definitively distinguishable from the noise (Supporting Information).

A further proof that this broadening was not due to exchange is provided by 1D ^{13}C magnetization and saturation transfer experiments performed at 313 K. No transfer was observed after any waiting time from the inversion of the resonances at δ 196.3 and 192.2 ppm of the basal moiety, while, after 0.3 s from the inversion of the apical resonance g, magnetization transfer to signal i is clearly detectable (Figure 5). No modifications appeared in the spectrum after the saturation of signal f for 4 T_1, while sizable effects appeared on resonance h after applying the same perturbation to resonance l (Supporting Information).

Deuterium Kinetic Isotope Effects. In order to check the involvement of the hydrides into the fluxional process observed in **1**, a fully deuterated sample of **1** (**1**-d_7) was prepared and the rate constants for the exchange of the hydrides and of the deuterides were independently measured through 2D ^{1}H and ^{2}H EXSY experiments, respectively. In acetone at 313 K, the rate constants resulted 1.19(5) s^{-1} for the fully protiated sample and 0.82(13) s^{-1} for the fully deuterated sample, an average of four experiments in both cases. This lead to a kinetic isotope effect $k_H/k_D = 1.45(24)$.

Exchange Process. The assignment of the ^{13}C resonances is a key point for understanding the exchange process observed in **1**. Even if a specific assignment of each signal could not be achieved, the overall evidence obtained through the experiments described above allowed the unambiguous identification of the rhenium atom to which each carbonyl is bound and a more detailed assignment of the carbonyls bound to Re(1).[17]

The exchange pattern shown by the ^{13}C EXSY spectra therefore involves only the carbonyls bound to the apical rhenium atom and this rules out any σ, π interchange of the unsaturated ligand. Localized exchange in M(CO)$_3$ or M(CO)$_4$ moieties, occurring through a trigonal twist or a pairwise exchange, has been ubiquitously observed

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[17] Figure 2 shows that the hydrides H$_a$ and H$_c$, bridging the lateral edges, have strong correlations with three of the four carbonyls bound to Re(1). Two of these correlations are with the *trans* diaxial carbonyls h and l, *cis* to the hydrides. Likely also the third correlation is the result of a similar coupling constant and geometry. Therefore g and i can be assigned to the carbonyls ***9*** and ***10***, *cis* to H$_a$ and H$_c$, respectively. Other previous observations have shown[17a–c] that in rhenium hydrido carbonyl clusters *trans* $^{2}J_{CH}$ coupling constants can be very small or not observable at all. (a) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666. (b) Beringhelli, T.; D'Alfonso, G.; Molinari, H. *J. Organomet. Chem.* **1985**, *295*, C35. (c) Top, S.; Gunn, M.; Jaouen, G.; Vaissermann, J.; Daran, J.-C.; McGlinchey, M. J. *Organometallics* **1992**, *11*, 1201.

in cluster compounds.[1a−c,18] Similar localized processes do not occur at 313 K in **1** since they imply the mixing of axial *and* equatorial carbonyls, while in the present case axial and equatorial carbonyls *do not mix with each other*. Moreover similar processes would not scramble the hydrides.[19]

The above results indicate therefore that in $[Re_3(\mu\text{-}H)_3(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_{10}]^-$ the whole apical fragment $H_2Re(CO)_4$ undergoes a rigid rotation with respect to the basal bimetallic moiety. Such a process requires significant modifications of the $Re(2){-}H_c$ and $Re(3){-}H_a$ bonds. The isotope effect that we have measured is consistent with the proposed mechanism and our value, 1.45(24), compares well with literature data concerning reactions or fluxionality of bridging hydrides. Rosenberg et al. measured $k_H/k_D = 1.8$ for the hydride scrambling in $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}HC{=}C\text{-}t\text{-}Bu)]^{2+}$,[20a] and $k_H/k_D = 1.6$ in $[M_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}S)]$, both for M = Ru and M = Os.[20b] Slightly smaller effects, $k_H/k_D = 1.24(10)$, were observed by Keister et al. for the isomerization of $[Ru_3(\mu\text{-}H)(\mu\text{-}NCMe_2)(CO)_9(AsPh_3)]$,[21] occurring with the opening of the hydride bridge, while Shore et al. reported $k_H/k_D = 1.40(1){-}1.7(4)$ for the associative pathway of CO exchange in $[HRu_3(CO)_{11}]^-$, which requires the change of the hydride from a bridging to a terminal location.[22]

1 can be thought as a trimetallacyclopropane, according to the isolobal analogy[4a] used by Stone[4b] to put on rational bases the synthesis of cluster compounds, and the hindered rotation of a vertex in a trimetallacyclopropane is not unprecedented. Indeed, in 1984, Stone and co-workers[23] reported the "alkene"-like behavior of the unsaturated fragment $[MRh(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2]$ (M = Co, Rh) when bonded to $Mo(CO)_5$ in $[MoMRh(\mu\text{-}CO)_2(CO)_5(\eta^5\text{-}C_5H_5)_2]$ (M = Co, Rh) (**2**). Other examples comprise 46-valence-electrons triangular clusters, e.g. $[Re_3(\mu\text{-}H)_3(CO)_{10}]^{-2}$ (**3**),[7g] $[Rh_2Pt(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta^5\text{-}C_5Me_5)_2]^+$ (**4**),[24] and $[Re_2Pt(\mu\text{-}H)_2(PPh_3)_2(CO)_8]$ (**5**).[25] In all these cases, the complexes can be formally described as "alkene"- (**2**, **4**, **5**) or "alkyne"- (**3**) like bimetallic fragments bound to electron short mononuclear fragments (16 or 14 valence electrons). In **1**, the rotating fragments can be described as $[Re_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}NC_5H_4)(CO)_6]$ vs $[H_2Re(CO)_4]^-$, that is an alkyne-like dimer and an 18-electron mononuclear complex. Indeed, $[H_2Re(CO)_4]^-$ is a known species[26] and its dynamic coordination to the coordinatively unsaturated fragment $Re_2(CO)_9$ has been recently demonstrated.[27] In that case, a "windshield wiper" motion of the $[H_2Re(CO)_4]^-$ fragment interchanged the Re−H σ donor interactions on a single metal, while in **1** the fluxionality interchanges the two Re−H interactions with two metals. Hindered rotations of similar 18-electron metal fragments over a trimetallic moiety have also been proposed to explain the dynamic behavior of some tetranuclear rhenium compounds, namely, for $[Re_4(\mu\text{-}H)_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)]^-$ [28] and $[Re_4(\mu\text{-}H)_4(CO)_{13}]^{-2}$.[29]

Conclusions

In **1**, the unequivalence of the hydrides in **1** has been the accidental probe of the rigid rotation of the apical $[H_2Re(CO)_4]$ moiety with respect to the doubly bridged basal dimetallic fragment. However, this behavior could be much more widespread and we are planning a systematic investigation of a series of $[Re_3(\mu\text{-}H)_3(\mu\text{-}X)(CO)_{10}]^-$ derivatives in order to clarify, on changing the nature of the X ligand, the requirements for the existence of this dynamic process.

Experimental Section

The NEt_4^+ salts of the anion **1** and of its isotopomer **1**-d_7 were prepared following the procedure described in the literature.[6,30] The sample enriched in ^{13}CO was synthesized using as precursor $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$, the enrichment of which was described elsewhere.[17a] The solutions were prepared by dissolving 15.0 mg of $[NEt_4]$-**1** in 500 μL of acetone-d_6 and 18.3 mg of $[NEt_4]$-**1**-d_7 in 500 μL of acetone-h_6, for ^1H and ^2H measurements, respectively. A 24.7 mg sample of the ^{13}CO-enriched salt, dissolved in a mixture of acetone-d_6 and toluene-d_8 (150 μL/350 μL or 250 μL/250 μL), was used for the ^{13}C NMR experiments. All the samples have been prepared using the Schlenk technique and kept under N_2. ^1H NMR hydridic region (200.13 MHz, 294 K, acetone-d_6/toluene-d_8 250 μL/250 μL) δ −11.98(1), −13.09(1), −14.70(1) ppm; ^{13}C NMR carbonyl region (50.33 MHz, 294 K, acetone-d_6/toluene-d_8 250 μL/250 μL) δ 195.7(1), 195.4(1), 195.3(2), 193.0(1), 192.2(1), 186.5(1), 185.9(1), 185.4(1), 184.2(1) ppm. Two of the $^1H{-}^{13}C$ HMQC experiments at 208 K and the ^{13}C DQF-COSY at 295 K were obtained on a Bruker AMX 500 spectrometer operating at 125.78 MHz for ^{13}C. All the other measurements (two $^1H{-}^{13}C$ HMQC at 294 K, the relaxation times at 313 K, ^{13}C, ^1H, and ^2H 2D EXSY experiments, and magnetization/saturation transfer experiments) were performed on a Bruker AC 200 spectrometer, equipped with an external BSV3 unit and a 5-mm "inverse" probe. Before and after each experiment, the temperatures were measured using the standard glycol/DMSO-d_6 or CH_3OH/CD_3OD solution. The T_1 values were obtained by the three-parameter fit of the intensities of the signals in the spectra recorded with the standard inversion

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(18) For instance, two distinct trigonal twist processes involving the two equatorial and, in turn, one of the axial carbonyls have been observed in the case of a $M(CO)_4$ fragment with inequivalent axial carbonyls, as in $[Os_3(\mu\text{-}H)(CO)_{10}(\mu_3\text{-}CPh)]$[18a] or $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}COEt)]$.[18b] (a) Yeh, W.-Y.; Shapley, J. R.; Li, Y.; Churchill, M. R. *Organometallics* **1985**, *4*, 767. (b) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* **1978**, *162*, 389.

(19) We cannot rule out the onset of similar dynamic processes on Re(1) or on Re(2) at $T > 313$ K. However, at 335 K, the resonances of the carbonyls bound to Re(3) remain sharp (Supporting Information), so the occurrence of localized rotations of the carbonyls on Re(3) as well as of dynamic processes that equalize the carbonyls bound to Re(2) and Re(3) can be ruled out. The broadening observed at 313 K for the three resonances bound to Re(2) is likely due to scalar coupling with the quadrupolar nitrogen-14: on raising the temperature, ^{14}N T_2 becomes longer and the spin $^1/_2$ ^{13}C nuclei are no more "relaxation decoupled".

(20) (a) Rosenberg, E. *Polyhedron* **1989**, *8*, 383 and references therein. (b) Bracker-Novak, J.; Hajela, S.; Lord, M.; Zhang, M.; Rosenberg, E.; Gobetto, R.; Milone, L.; Osella, D. *Organometallics* **1990**, *9*, 1379.

(21) Shaffer, M. R.; Keister, J. B. *Organometallics* **1986**, *5*, 561.

(22) Payne, M. W.; Leussing, D. L.; Shore, S. G. *Organometallics* **1991**, *10*, 574.

(23) (a) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1983**, 759. (b) Barr, R. D.; Green, M.; Howard, J. A. K.; Marder, T. B.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2757.

(24) Green, M.; Mills, R. M.; Pain, G. N.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1982**, 1321.

(25) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P.; Mynott, R. in ref 3a.

(26) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1978**, *152*, 85.

(27) Bergamo, M.; Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Moret, M.; Sironi, A., *Organometallics* **1996**, *15*, 3876.

(28) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P.; Ciani, G.; Proserpio, D. M. *Inorg. Chem.* **1993**, *32*, 803.

(29) Beringhelli, T.; D'Alfonso, G.; Minoja, A. P.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1992**, *440*, 175.

(30) Beringhelli, T.; Carlucci, L.; D'Alfonso, G.; Ciani, G.; Proserpio, D. M. *J. Organomet. Chem.*, **1995**, *504*, 15.

recovery pulse sequence using 10 variable delays. 2D $^1H-^{13}C$ HMQC were performed using the BIRD[31] pulse sequence optimized for J_{CH} = 3, 5, 7, and 10 Hz. This latter experiment (294 K, 4.7 T) showed few correlations, none of which increased the information obtained from the other HMQC experiments. DQF-COSY was acquired in the phase-sensitive mode using 1K data points in F2 for 512 t_1 increments, zero filled to 1K. All the 2D EXSY experiments were acquired in the phase-sensitive mode.[32] The spectrometer routine was used for measurement of the volume of the relevant peaks. The volume of the noise measured with a comparable box was assumed as the uncertainty of each volume. The calculation of the rate constants (and of their uncertainties) and the simulation of the intensities on varying the mixing time were performed through a program written by the authors, under the MATLAB framework. The ^1H and ^2H 2D EXSY experiments were repeated four times, changing the repetition delay, the spectral width, or the number of transients. The rate constants obtained accordingly are 1.23, 1.20, 1.14, and 1.19 s^{-1} and 1.01, 0.73 0.70, and 0.83 s^{-1} for ^1H and ^2H, respectively. The DANTE pulse sequence,[33] implemented as suggested by Mann,[7g] was used for the ^{13}C SPT experiments. A DANTE pulse train was also used for the saturation transfer experiments and applied for 4 T_1 at the selected frequencies.

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Supporting Information Available: Figures of two 2D $^1H-^{13}C$ HMQC experiments (208 K, 11.7 T, J_{CH} = 3 Hz and 294 K, 4.7 T, J_{CH} = 5 Hz); the overall map of the ^{13}C 2D DQF-COSY experiment (295 K, 11.7 T); ^{13}C saturation transfer spectra at 313 K; $^{13}C\{^1H\}$ variable-temperature spectra at 9.4 T; computer simulation of the time course of the intensities of the cross and diagonal peaks in a 2D EXSY experiments (7 pages). Ordering information is given on any current masthead page.

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[31] (a) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301. (b) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.

[32] (a) Bodenhausen, G., Kogler, H.; Ernst, R. R. *J. Magn. Reson.* **1984**, *58*, 370. (b) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1985; Chapter 9.

[33] Morris, G. A.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 433.