probably subject to minor, unresolvable disorder [in particular: O(1), C(3), C(5), and C(7)] which results in some anomalous bond lengths and angles. Fourier peak heights indicated 1:1 disordering in **5**. Occupancy factors were fixed at 0.5 for the resolved atoms.

In the final stages of full matrix least-squares refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined (isotropic thermal parameters) for **4** and **6** and were fixed in positions idealized from observed positions [C(sp^3)–H = 0.98 Å, C(sp^2)–H = 0.97 Å, thermal parameters proportional to that of the bound atom] for the remaining compounds with the exception of the hydroxyl hydrogen atoms in **3** which were refined. Neutral atom scattering factors and anomalous scattering corrections (O and C for those structures solved with Cu radiation) were taken from ref 38. Parallel refinements of mirror-image structures were carried out for compounds **3** and **7**, which crystallize in noncentrosymmetric space groups. In each case, the model with the lower value of R_w was retained (R_w ratios are 1.0005 for **3** and 1.0023 for **7**). Isotropic type I extinction corrections[39-41] were applied for compounds **3**–**7**, the final values of g being 0.33 (6), 0.22 (9), 1.6 (2), 0.49 (9), and 0.32 (6) (all × 10^4), respectively.

Final positional and equivalent isotropic thermal parameters (U_{eq} = $^1/_3$ trace diagonalized U) for the non-hydrogen atoms are given in Table X.

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Registry No. 1, 116503-90-3; **2**, 116503-91-4; **3**, 116503-92-5; **4**, 116561-05-8; **5a**, 116531-32-9; **6a**, 116503-93-6; **7**, 116503-94-7; **8**, 116561-06-9; **9a**, 116561-07-0.

Supplementary Material Available: Tables (S1–S6) of hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and bond lengths and angles involving hydrogen atoms (30 pages); observed and calculated structure factors (Tables S7–S13) (109 pages). Ordering information is given on any current masthead page.

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(38) *International Tables for X-Ray Crystallography*. Kynoch: Birmingham, 1974; Vol. IV, pp 99–102, 149.

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(40) Coppens, P.; Hamilton, W. C. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1970**, *26*, 71.

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Communications to the Editor

Synthesis of $\mathrm{Os_2(CO)_8(\mu\text{-}CHCH_3)}$ from a Geminal Ditriflate and Its Reversible Carbonylation to a Ketene-Bridged Diosmacycle

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A number of reactions[1] may be explained by the insertion of CO into the M–C bonds of dimetallacyclopropanes,[2-5] but the formation of a dimetallacyclobutanone by such a process has never been directly observed.[6,7] In view of (1) the suggestion[8-12] that CO and C_2H_4 compete for the M–C bonds of surface alkylidenes in the Fischer–Tropsch reaction and (2) our previous success in observing the insertion of ethylene into the Os–C bonds of $\mathrm{Os_2(CO)_8(\mu\text{-}CH_2)}$ (**1**),[3b] we have investigated the reactivity of **1** and other diosmacyclopropanes toward CO. We now report the preparation of $\mathrm{Os_2(CO)_8(\mu\text{-}CHCH_3)}$ (**2**) from ethylidene ditriflate and the reversible carbonylation of **2** to a dimetallacyclobutanone.

Our earlier success in preparing $\mathrm{Os_2(CO)_8(\mu\text{-}CH_2CH_2)}$ from $\mathrm{TfOCH_2CH_2OTf}$[13] suggested alkylidene ditriflates as precursors to alkylidene-bridged $\mathrm{Os_2(CO)_8}$ derivatives. However, acylic geminal ditriflates containing α-hydrogens are thermally unstable and have not previously been isolated.[14,15] We have now found

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(1) (a) Keim, W.; Röper, W. R.; Strutz, H. *J. Organomet. Chem.* **1981**, *219*, C5. (b) Navarre, D.; Rose-Munch, F.; Rudler, H. *J. Organomet. Chem.* **1985**, *284*, C15. (c) Puddephatt, R. J.; Laws, W. J. *Inorg. Chim. Acta* **1986**, *113*, L23. (d) Nucciarone, D.; Taylor, N.J.; Carty, A. J.; Tiripicchio, A.; Camellini, M. T.; Sappa, E. *Organometallics* **1988**, *7*, 118. (e) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508. (f) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Solis, H. E.; Barcelo, I. D.; Butler, W. M. *J. Am. Chem. Soc.* **1987**, *109*, 3603.

(2) The formation of C–C bonds by the insertion of alkenes,[3] alkynes,[4] and CS_2[5] into the M–C bond of dimetallacyclopropanes has been either directly observed or implied by other experimental results.

(3) (a) Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293. (b) Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325. (c) Sumner, C. E.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (d) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. (e) Rudler, H.; Rudler, R. M.; Alvarez, C. *J. Mol. Catal.* **1982**, *15*, 81. (f) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489.

(4) (a) Rudler, H.; Daran, J. C.; Jeanin, Y. *J. Organomet. Chem.* **1985**, *279*, 413. (b) Adams, P. Q.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1983**, 222 and references therein. (c) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; MacPherson, K. A.; Mead, K. A.; Orpen, A. G.; Roué, J.; Woodward, P. *Philos. Trans. R. Soc. London A* **1982**, *308*, 67. (d) Jeffreys, J. A. D. *J. Chem. Soc., Dalton Trans.* **1980**, 435.

(5) Aumann, R.; Henkel, G.; Krebs, B. *Angew. Chem. Suppl.* **1982**, 506.

(6) The carbonylation of a methylene bridge to a ketene bridge has been observed in several cases in which there is no metal–metal bond between the centers bridged by the ketene: (a) Bassner, S. L.; Geoffroy, G. L.; Rheingold, A. L. *Polyhedron* **1988**, *7*, 791. (b) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1987**, *6*, 2207. (c) Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541. (d) Lin, Y.-C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1680.

(7) A dimetallacyclobutanone has been prepared by the rearrangement of $\mathrm{[CpRu(CO)_2]_2(\mu\text{-}CH_2)}$ without added CO: Lin, Y.-C. *J. Chin. Chem. Soc.* **1985**, *32*, 295.

(8) Such CO/C_2H_4 competition may determine the oxygenate/hydrocarbon product ratio in Fischer–Tropsch chemistry: (a) Lapidus, A. L.; Savel'ev, N. M. *Russ. Chem. Rev.* **1984**, *53*, 535. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (c) Biloen, P.; Sachtler, M. H. *Adv. Catal.* **1981**, *30*, 165. (d) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

(9) Recent studies by Ichikawa[10] show that molecularly adsorbed CO is incorporated into oxygenates formed from ^{13}C-labeled surface carbide. These results suggest that CO insertion processes[11] have a role in the formation of surface acyl species[12] under Fischer–Tropsch conditions.

(10) Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 148.

(11) (a) Van der Lee, G.; Ponec, V. *J. Catal.* **1986**, *99*, 511. (b) Sachtler, W. M. H.; Shriver, D. F.; Hollenberg, W. B.; Lang, A. F. *J. Catal.* **1985**, *92*, 429. (c) Henrici-Olivé, G.; Olivé, S. *J. Mol. Catal.* **1984**, *24*, 7.

(12) Fukushima, T.; Arakawa, H.; Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1985**, 729.

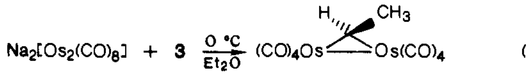
(13) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3468.

(14) A few geminal ditriflates without α-hydrogens have been reported: (a) Katsuhara, Y.; Desmarteau, D. D. *J. Fluorine Chem.* **1980**, *16*, 257. (b) Martínez, A. G.; Ríos, L. E.; Vilar, E. T. *Synthesis* **1979**, 382.

that geminal ditriflates can be prepared from geminal diiodides by metathesis with AgOTf[16-18] and that the **3** thus prepared (eq 1)[17,18] has a high vapor pressure (10 μmHg at 30–35 °C) and can be isolated by distillation. The reaction of **3** and $Na_2[Os_2(CO)_8]$[13,19] gives $Os_2(CO)_8(\mu\text{-}CHCH_3)$, **2**,[20] as expected.

$$CH_3CHI_2 + 2AgOTf \xrightarrow[CH_2Cl_2]{-23\ °C} CH_3CH(OTf)_2 \qquad (1)$$

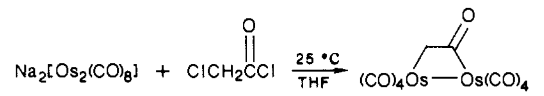
3



(2)

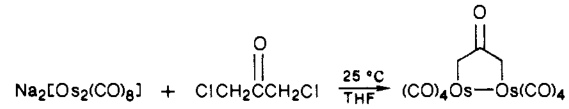
2

We have also found that diosmacycloalkanones (e.g., **4**[21] and **5**[22]) can be made from $[Os_2(CO)_8]^{2-}$ and the appropriate dichloride dielectrophile (eq 3 and 4). Although a variety of different ketene coordination modes have been reported,[23] dimetallacyclobutanones like **4** are rare.[7,24,25]



(3)

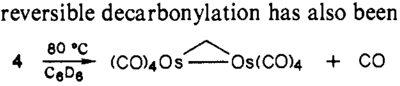
4



(4)

5

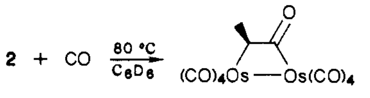
No **4** is formed when the unsubstituted diosmacyclopropane $Os_2(CO)_8(\mu\text{-}CH_2)$ (**1**) is treated with 1 atm of CO. When a solution of **4** is heated under vacuum in a sealed NMR tube, the equilibrium lies in the other direction: the ketene-bridged dinuclear complex **4** quantitatively decarbonylates at 80 °C to form **1** (eq 5). Such irreversible decarbonylation has also been reported by Knox and co-workers for their 1,2-diruthenacyclobutan-4-one.[25] The reaction models a probable step in the decarbonylation of ketene itself by metal surfaces[26-28] and may be related to the decarbonylation of substituted ketenes which a number of metal complexes can carry out.[23a]



(5)

1

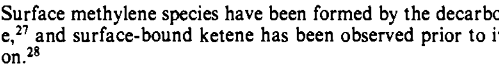
In contrast to the methylene-bridged **1**, the ethylidene-bridged **2** undergoes facile CO insertion. The contrast is illustrated when a mixture of **1** and **2** is treated with 1 atm of CO at 80 °C in benzene:[29] **2** is largely converted to the ketene-bridged diosmium complex **6**[30] (eq 6), while **1** does not react. When a solution of **6** is heated to 80 °C under vacuum in a sealed NMR tube, an equilibrium is attained in which only half of the **6** is converted back to **2**. The carbonylation equilibrium is thus much more favorable for the more substituted diosmacyclopropane. The origin of this substituent effect is arguably steric, as with the well-known accelerating effect of substituents on the rate of carbonylation of mononuclear alkyl complexes.[31]



(6)

6

While CO is known to react with several *mononuclear* methylene complexes,[32] the reaction in eq 6 is the first observed CO insertion into a dimetallacyclopropane. Of the reactions for which such a step has been postulated, the most important is the methanolysis of dimetallacyclopropanes to methyl esters, first reported by Keim for the Fe analogue of **1** (eq 7)[1a] and subsequently observed for several other dimetallacyclopropanes.[1b-d] We have thus treated **4** with CD_3OD and obtained $CH_2DCO_2CD_3$ in 87% yield (eq 8). However, significant accumulation of **1** occurs during this reaction, implying that the ketene-bridged **4** can only react with methanol after it forms **1**. We thus believe that reactions 7 and 8 occur by initial decarbonylation and subsequent alcohol attack at a terminal carbonyl[33]—a proposal offered



(7)

7

$$4 \xrightarrow{76\ °C} 1 \xrightarrow{CD_3OD} CH_2DCO_2CD_3 \qquad (8)$$

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(15) Other workers (Martinez, A. G.; Alvarez, R. M.; Fraile, A.; Subramanian, L. R.; Hanack, M. *Synthesis* **1987**, 49) have recently reported spectroscopic evidence for the low-temperature preparation of geminal ditriflates with α-hydrogens.

(16) This procedure is adapted from the preparation of methylene ditosylate: Emmons, W. D.; Ferris, A. F. *J. Am. Chem. Soc.* **1953**, *75*, 2257.

(17) Ethylidene ditriflate was prepared by adding ethylidene diiodide (0.62 g, 2.21 mmol) to AgOTf (1.19 g, 4.63 mmol) in 20 mL of CH_2Cl_2 under N_2 at 0 °C; light yellow AgI began to precipitate after 10 min. Stirring 12 h at −23 °C, filtration under N_2, and distillation of the filtrate on a Kugelrohr apparatus (30–35 °C, 10 μmHg) yielded 630 mg (87%) of ethylidene ditriflate: ^1H NMR ($CDCl_3$) δ 6.58 (q, J = 5.37, 1 H), 1.88 (d, J_{HH} = 5.37, 3 H); $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ 118.4 (q, J_{CF} = 319.2 Hz), 103.4 (J_{CH} = 180.8 Hz), 21.5 (J_{CH} = 131.4 Hz); ^{19}F NMR ($CDCl_3$) δ−41.28 (rel to $CFCl_3$); IR (film) 1427 (s), 1398 (s), 1241 (s), 1138 (s), 1079 (m), 1053 (m), 952 (m), 866 (s), 798 (s), 759 (s), 618 (s). Anal. Calcd for $C_4H_4F_6O_6S_2$: C, 14.73; H, 1.24; S, 19.66. Found: C, 14.59; H, 1.28; S, 19.73. Ethylidene ditriflate decomposes within a few hours at room temperature, but when pure it can be stored at −20 °C for months. It is 1.4 times less reactive toward Br^- than EtOTf at 23 °C (as judged from the reaction of $[Ph_3PMe]Br$ with an excess of both these reagents).

(18) Propylidene ditriflate can also be prepared by the method of note 17 but cannot be purified by distillation.

(19) Hsu, L.-Y.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1985**, *4*, 1483.

(20) For **2**, ^1H NMR (C_6D_6) δ 5.62 (q, J_{HH} = 7.6 Hz, 1 H), 2.87 (d, J_{HH} = 7.6 Hz, 3 H); (CD_3CN) δ 5.96, 3.01; IR (pentane) ν_{CO} = 2123 (w), 2079 (s), 2032 (s), 2017 (m), 2001 (s), 1991 (sh) cm^{-1}. Anal. Calcd for $C_{10}H_4O_8Os_2$: C, 18.99; H, 0.64. Found: C, 18.81; H, 0.73. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(21) For **4**, ^1H NMR (C_6D_6) δ 1.92; IR (hexane) ν_{CO} = 2130 (w), 2087 (m), 2069 (w), 2050 (m), 2039 (s), 2036 (sh), 2022 (s), 2008 (m) cm^{-1}; ν_{acyl} = 1648 (w) cm^{-1}. Anal. Calcd for $C_{10}H_2O_9Os_2$: C, 18.58; H, 0.31. Found: C, 18.73; H, 0.40. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(22) For **5**, ^1H NMR (C_6D_6) δ 1.67; IR (hexane) ν_{CO} = 2136 (w), 2095 (s), 2056 (s, sh), 2048 (vs), 2040 (m, sh), 2024 (m), 2004 (w) cm^{-1}; ν_{acyl} = 1617 (w) cm^{-1}. Anal. Calcd for $C_{11}H_4O_9Os_2$: C, 20.00; H, 0.61. Found: C, 20.00; H, 0.68. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

(23) (a) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1. Very recent cases in which a ketene ligand bridges centers not connected by a metal–metal bond: (b) Akita, M.; Kondoh, A.; Kawahara, T.; Takagi, T.; Moro-oka, Y. *Organometallics* **1988**, *7*, 366. (c) Weinstock, I.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 8298.

(24) Knox et al. have made a diruthenacyclobutanone via the hydration and rearrangement of a diruthenium acetylide complex.[25] Shapley et al. have treated a ruthenium carbonyl cluster with diazomethane and obtained a triruthenium cluster containing a diruthenacyclobutanone fragment which is further bound through the ketene oxygen to the third ruthenium.[1e]

(25) Doherty, N. M.; Fildes, M. J.; Forrow, N. J.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1355.

(26) Surface methylene species have been formed by the decarbonylation of ketene,[27] and surface-bound ketene has been observed prior to its decarbonylation.[28]

(27) (a) Brady, R. C., III.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (b) Blyholder, G.; Emmett, P. H. *J. Phys. Chem.* **1959**, *63*, 962; **1960**, *64*, 470.

(28) (a) McBreen, P. H.; Erley, W.; Ibach, H. *Surf. Sci.* **1984**, *148*, 292. (b) Erley, W.; McBreen, P. H.; Ibach, H. *J. Catal.* **1983**, *84*, 229.

(29) In acetonitrile the carbonylation of **2** to **6** proceeds smoothly at 45 °C—another example of the acceleration of CO insertion by polar solvents (Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345).

(30) For **6**, ^1H NMR (C_6D_6) δ 2.13 (q, J_{HH} = 6.3 Hz, 1 H), 1.38 (d, J_{HH} = 6.3 Hz, 3 H); (CD_3CN) δ 2.44, 1.27; IR (pentane) ν_{CO} = 2087 (m), 2049 (m), 2038 (s), 2021 (s), 2006 (w), 1999 (sh), cm^{-1}; ν_{acyl} = 1634 (w) cm^{-1}. A parent ion with the appropriate isotopic distribution was observed in the mass spectrum.

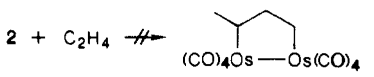
(31) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 356–376.

(32) (a) Roper, W. R.; Wright, A. H., unpublished observations in the following: Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (b) Miyashita, A.; Sitara, H.; Nohira, H. *Organometallics* **1985**, *4*, 1463. (c) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926.

(33) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919.

by Keim and co-workers[34] after they discovered that the carbonyl ligands of **7** were susceptible to attack by methoxide.

Finally, we have compared the reactivity of **2** toward C_2H_4 with its reactivity toward CO. Whereas **1** and C_2H_4 form a diosmacyclopentane,[3b] **8** is not formed when **2** is heated under 1 atm of ethylene.[35] Alkyl substitution on the carbon of a diosmacyclopropane thus affects its reactivity toward CO insertion and toward C_2H_4 in quite different ways.



(9)

8

Acknowledgment. We are grateful to the Department of Energy for support under Grant DE-FG02-84ER13299.A005 and to Bruce Bender for assistance in the preparation of this manuscript.

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[34] Keim, W.; Röper, M.; Strutz, H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 432.

[35] However, ^{1}H NMR (δ 1.75 in C_6D_6, d, $J = 2.3$ Hz, $CHCH_3$) and IR (2121, 2076, 2040, 2032, 2020, 2012, and 1994 cm^{-1}) spectra indicated that **8** had been formed by the reaction between $TfOCH_2CH_2CH(CH_3)OTf$ and $Na_2[Os_2(CO)_8]$. None of the butenes produced by the thermal decomposition (4 h at 81 °C and 3.5 h at 114 °C, in C_6D_6) of **8** thus prepared were seen when a solution of **2** was treated with an atm of C_2H_4 under the same conditions—an observation which eliminated the possibility that **8** was formed in reaction 9 but decomposed.

Clean TOCSY for ^{1}H Spin System Identification in Macromolecules

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Two-dimensional (2D) correlation spectroscopy (COSY)[1-3] and 2D nuclear Overhauser spectroscopy (NOESY)[4,5] provided the experimental basis that made nuclear magnetic resonance (NMR) an efficient method for the determination of three-dimensional protein structures in solution.[6,7] Recently, these two basic experiments were complemented by 2D experiments in the rotating frame which involve an extended mixing period in the presence of radio frequency irradiation. Total correlation spectroscopy (TOCSY,[8] sometimes called HOHAHA[9]) gives multistep COSY-type information. By virtue of the in-phase cross-peak multiplet structure, which contrasts with the antiphase structure in COSY spectra, TOCSY peaks are often stronger and hence easier to detect than the corresponding COSY peaks. Rotating frame cross-relaxation spectroscopy (CAMELSPIN,[10] here called ROESY[11]) is an alternative to NOESY where cross-peak intensity depends differently on molecular correlation times.[10]

Rotating frame experiments produce simultaneously coherence transfer through J coupling and through cross relaxation, which may lead to undesired interference and ambiguities between TOCSY and ROESY effects. In this communication we introduce a technique that provides, for the first time, clean TOCSY spectra and suppresses contributions from cross relaxation based on the opposite signs of longitudinal and transverse cross-relaxation rates in large molecules.[7,10]

A conventional TOCSY spectrum of the N-terminal domain 1-76 of the protein P22 c2 repressor is shown in Figure 1 (parts A and B). Apart from the positive peaks due to J transfer, it contains also negative peaks due to cross relaxation. Ambiguities arise whenever peaks of different sign coincide. A clean TOCSY spectrum of the same molecule, recorded with the modified technique to be described in the following, is given in Figure 1 (parts C and D). The absence of negative peaks is readily apparent, in particular in the regions containing cross peaks between different amide protons and between amide and α- or β-protons.

Cross relaxation between two nuclei i and k at specified chemical shifts is determined by the rate constant $\Gamma_{ik} = (1/t_c) \int_0^{t_c} \boldsymbol{n}_i(t)\boldsymbol{\Gamma}\boldsymbol{n}_k(t)\,dt$.[12] $\boldsymbol{\Gamma}$ is the diagonal relaxation matrix with the elements (Γ^{tcr}, Γ^{tcr}, Γ^{lcr}). Γ^{tcr} denotes the rate constant for cross relaxation of transverse components, while Γ^{lcr} applies to longitudinal components; t_c is the duration of one pulse cycle. The time-dependent vectors $\boldsymbol{n}_i(t)$ and $\boldsymbol{n}_k(t)$ are the so-called *invariant trajectories* of the two spins that depend on their chemical shifts and on the pulse sequence. Each is characterized by the unique property that a magnetization vector travelling on it during a multiple pulse sequence returns periodically to its origin.

In the case of an MLEV-17 pulse sequence[9,13] with the composite pulse $R = 90^\circ_x\, 180^\circ_y\, 90^\circ_x$ without intervals between the pulses, the invariant trajectory for on-resonance conditions starts along the y-axis, rotates during the first pulse to the z-axis, during the second pulse to the ($-z$)-axis, and during the third pulse back to the y-axis. The above expression for Γ_{ik} leads to the cross-relaxation rate constant $\Gamma_{ik} = {}^1/_2(\Gamma^{lcr} + \Gamma^{tcr})$, as the two trajectories $\boldsymbol{n}_i(t)$ and $\boldsymbol{n}_k(t)$ spend equal time in the longitudinal and transverse directions. In the case of nonideal pulses due to rf field inhomogeneity and off-resonance conditions, the two relaxation rate constants are differently weighted: $\Gamma_{ik} = (1 + \lambda)^{-1}\,(\Gamma^{lcr} + \lambda\Gamma^{tcr})$, where λ depends on the distribution of the effective pulse angles and on off-resonance frequencies. Trim pulses are applied before and after the MLEV-17 sequence to destroy all magnetization components that are not aligned along the initial and final orientation of the invariant trajectory. The simulated cross-relaxation rate constant under the standard MLEV-17 pulse sequence is plotted as a function of the two offset frequencies in Figure 2A. The calculation was based on the experimentally determined rf field distribution in our probe. Significant ROESY cross peaks are found in agreement with Figure 1 (parts A and B).

Cross relaxation can be suppressed when the effects of longitudinal and transverse relaxation are forced to compensate each other. This is possible by the introduction of two delays Δ before and after the 180°_y pulse in the MLEV-17 sequence, leading to the composite pulse $R' = 90_x{}^\circ - \Delta - 180_y{}^\circ - \Delta - 90_x{}^\circ$. The modified cross-relaxation rate constant on resonance is now $\Gamma_{ik} = (2 + r)^{-1}[\Gamma^{tcr} + (1 + r)\Gamma^{lct}]$ with $r = \Delta/\tau_{90}$ (τ_{90} is the duration of a 90° pulse). Thus, cross relaxation is suppressed when $r = -1 - \Gamma^{tcr}/\Gamma^{lcr}$. This equation has a physical solution when Γ^{lcr} is negative, i.e., for bulky molecules with $\omega_o\tau_c > \sqrt{5}/2$ (ω_o = res-

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