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[9] Compounds **1**–**4** were synthesized as 1:1 mixtures of isomers having different orientations of the sulfur atom of the thienylene analogue(s) of *p*-terphenoquinone, since four different *t*Bu signals and four different signals for the quinoid ring protons $\alpha$ to $CH_2$ for **1** and four different thienyl ring proton signals for **2** were observed in the $^1H$ NMR spectra (600 MHz, $CDCl_3$, 25 °C, TMS). All spectral data were recorded on the mixtures. **1**: m.p. 128–129 °C; $^1H$ NMR: $\delta =$ 1.340, 1.342, 1.36, 1.37 (four singlets, 9H each, *t*Bu), four pairs of doublets at 3.58, 3.59, 3.61, 3.63 ($H_A$, $H_{A'}$) and at 3.81, 3.84, 3.84, 3.87 ($H_B$, $H_{B'}$, $^2J(H,H) = 14$ Hz); IR (KBr): $\tilde{\nu} = 1590$ cm$^{-1}$ (C=O); UV/Vis (MeCN): $\lambda_{max}$ (lg $\varepsilon$) = 579 (5.02), 540 (5.08), 496 sh (4.59), 349 (4.24), 332 (4.09), 284 (4.18), 273 (4.20), 262 (4.18); FAB-MS: *m*/*z* (%): 1129 (100) [$M^+$+$Na^+$], 1108 (61) [$M^+$+2], 1106 (23) [$M^+$]. **2**: m.p. 223–225 °C; $^1H$ NMR: $\delta = 1.37$, 1.38, (two singlets, 18H each, *t*Bu), 3.36 and 3.40 ($H_A$, $H_{A'}$, $^2J(H,H) = 14$ Hz), 3.85–4.00 ($H_B$, $H_{B'}$); IR (KBr): $\tilde{\nu} =$ 1593 cm$^{-1}$ (C=O); UV/Vis (MeCN): $\lambda_{max}$ (lg $\varepsilon$) = 577 (5.06), 542 (5.05), 499 sh (4.63), 350 (4.26), 336 sh (4.19), 298 (4.06), 283 (4.09), 274 (4.11); FAB-MS: *m*/*z* (%): 1154 (100) [$M^+$+4], 1153 (54) [$M^+$+3], 1150 (5) [$M^+$]. **3**: m.p. 240–241 °C; $^1H$ NMR: $\delta = 1.32$, (s, 9H, *t*Bu), 1.37, (s, 9H, *t*Bu), two pairs of doublets at 2.93 or 2.96 ($H_A$) and 4.44 or 4.47 ($H_B$) ($^2J(H,H) = 16$ Hz), two pairs of doublets at 3.24 and 3.24 ($H_{A'}$) and 4.45 or 4.46 ($H_{B'}$) ($^2J(H,H) = 14$ Hz); IR (KBr): $\tilde{\nu} =$ 1589 cm$^{-1}$ (C=O); UV/Vis (MeCN): $\lambda_{max}$ (lg $\varepsilon$) = 568 (4.91), 488 sh (4.07), 347 (3.97), 334 sh (3.89), 281 sh (3.83), 273 (3.86), 263 (3.84); FAB-MS: *m*/*z* (%): 873 (39) [$M^+$+$Na^+$], 852 (100) [$M^+$+2], 850 (8) [$M^+$]. **4**: m.p. 252–253 °C; $^1H$ NMR: $\delta = 1.37$ (s, 9H, *t*Bu), 1.39 (s, 9H, *t*Bu), four pairs of doublets of the methylene protons at 3.48 ($H_{A1}$), 3.43 ($H_{A2}$) ($^2J(H,H) = 12$ Hz), 3.74–3.81 ($H_{B1}$, $H_{B2}$, $CH_3CH_2\mathit{CH_2}$), 3.09 and 3.10 ($H_{A1'}$, $H_{A2'}$), 4.08 or 4.09 ($H_{B1'}$, $H_{B2'}$) ($^2J(H,H) = 13$ Hz); IR (KBr): $\tilde{\nu} = 1591$ cm$^{-1}$ (C=O); UV/Vis (MeCN): $\lambda_{max}$ (lg $\varepsilon$) = 566 (4.74), 509 sh (4.28), 350 (3.73), 334 (3.65), 294 (3.66), 277 (3.77), 272 (3.78); FAB-MS: *m*/*z* (%): 836 (100) [$M^+$+2], 834 (7) [$M^+$].

[10] Single crystals of **4**: monoclinic, space group $P2_1/n$, $Z = 4$, $a =$ 15.684(4), $b = 10.589(4)$, $c = 29.278(4)$ Å, $\beta = 96.52(2)°$, $V =$ 4830(2) Å$^3$ ($R = 0.114$ and $Rw = 0.140$ for 2393 observed reflections with $I > 3.00\sigma(I)$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137583. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] Compounds **1**–**4** do not exist as mixtures of different conformers. This was proved by NMR spectroscopic analyses with DEPT, HMQC, HMBC, $^1H$-$^1H$ COSY, and $^{13}C$-$^1H$ COSY methods.

[12] Gaussian 94, Revision C.3: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanav, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1995**.

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[15] In addition to the calculated absorption bands listed in Table 1, a new, forbidden transition, assignable to the weak absorption band at around 630 nm (Figure 2), resulted for **1**-$Na^+$ and **3**-$Na^+$ only when the $Na^+$ ion was taken into account in the INDO/s calculation. Therefore, this weak band may originate from the ion–dipole interaction between the encapsulated alkali metal cation and the carbonyl groups of the heteroquinones.

[16] Stable cone conformations were optimized for both **3** and **3**-$Na^+$ with the same calculation method as for **1** and **1**-$Na^+$.

# In Situ $^1H$ MAS NMR Spectroscopic Observation of Proton Species on a Mo-Modified HZSM-5 Zeolite Catalyst for the Dehydroaromatization of Methane**

Ding Ma, Yuying Shu, Weiping Zhang, Xiuwen Han, Yide Xu, and Xinhe Bao*

Zeolites and oxide-modified zeolites have been widely used in light-paraffin aromatization reactions.[1, 2] It has been generally accepted that the acidic sites, together with the dehydrogenation centers of the metal oxide components, play key roles in paraffin activation and the subsequent aromatization. In 1993, we were the first to report that methane, an ultra stable molecular, could undergo aromatization on molybdenum modified HZSM-5 catalysts under nonoxidative conditions.[3] Subsequent investigations[4] demonstrated that the Brønsted acidity and the channel structure of the zeolites, as well as the oxidation states of the Mo species, are crucial factors that affect the performance of the catalysts. However, most of the discussions concerning the nature of the active species, for instance the location of the Mo species on or in the zeolite and the variation of the zeolitic acidity, are based on data obtained from off-line characterizations using "ideal" catalysts under conditions far from those in the real catalytic processes.[4a–e]

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[*] Prof. Dr. X. Bao, D. Ma, Y. Shu, W. Zhang,
Prof. X. Han, Y. Xu
State Key Laboratory of Catalysis
Dalian Institute of Chemical Physics
Dalian 116023 (P. R. China)
Fax: (+86) 411-4694447
E-mail: xhbao@ms.dicp.ac.cn

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Recently, the development of in-situ NMR spectroscopic methods has opened up a realistic way to investigate in situ heterogeneous catalytic reactions. Although several novel techniques, such as high temperature MAS-rotor,[5] flowing MAS experiments,[6] and different experimental methods[7, 8] have been reported to be powerful tools for the characterization of steady state processes in catalytic reactions, none of these methods has been shown to be effective for high temperature reactions, especially at temperatures greater than 800 K. Following the idea of the CAVERN device[8] from Haw's group, we have developed a method applicable to the NMR analysis of high-temperature catalytic reactions. Using a specially designed apparatus (Figure 1) a real fixed-bed catalytic reaction can be conducted in the temperature range of 300–1123 K. After the reaction the catalyst can be transfered to a conventional MAS-rotor and sealed in situ. Herein, we present the in situ $^1$H MAS NMR spectroscopic results of the dynamic variation of the proton signals in a Mo modified ZSM-5 catalyst for the catalytic methane aromatization reaction. This reaction was carried out under conditions identical to those in the real catalytic processes.

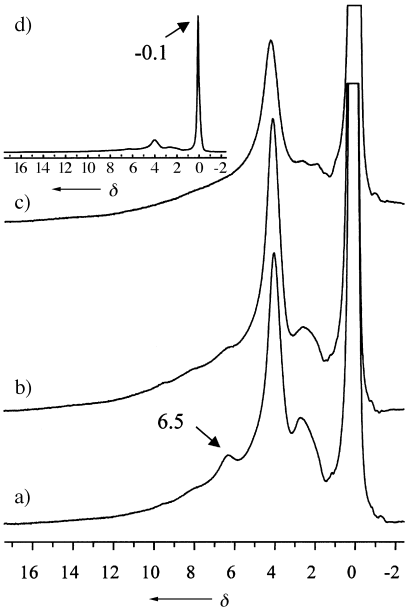

Figure 2. $^1$H MAS NMR spectra of a Mo/HZSM-5 catalyst (6% Mo) treated with a methane flow (1500 mL g$^{-1}$h$^{-1}$, 1 atm) for 1 h at a) 573 K, b) 673 K, and c) 873 K. Spectrum d) is the whole spectrum of (c), the resonance at about $\delta = -0.1$ is from the remaining methane inside the zeolite channels.

Figure 2 shows the $^1$H MAS NMR spectra of a Mo/HZSM-5 catalyst (6% Mo) treated with a methane flow (1500 mL g$^{-1}$ h$^{-1}$) for 1 h at 573, 673, and 873 K. In addition to a very sharp resonance ($\delta \approx -0.1$) due to residual methane remaining in the crystal channels of the zeolite, the signals of zeolitic hydroxyl species are clearly resolved. This result demonstrated that treatment with a flow of methane for only 1 h at 573 K can efficiently remove the water molecules adsorbed onto the zeolite surface, whereas a complete dehydration of such samples by conventional methods can only be achieved by degassing at 673 K and $10^{-2}$ Pa for more than 18 h.[9] The signal at $\delta = 4.1$ is assigned to the Brønsted acid sites, while the signals at $\delta = 1.7$ and 2.4 are due to the silanol groups at framework defects or at the external surface of the zeolite, and to OH groups at nonframework aluminum species, respectively.[9] Moreover, the partially obscured small and broad signals at about $\delta = 6.5$ can be, depending on the shape of the spectral line,[10] attributed to water molecules

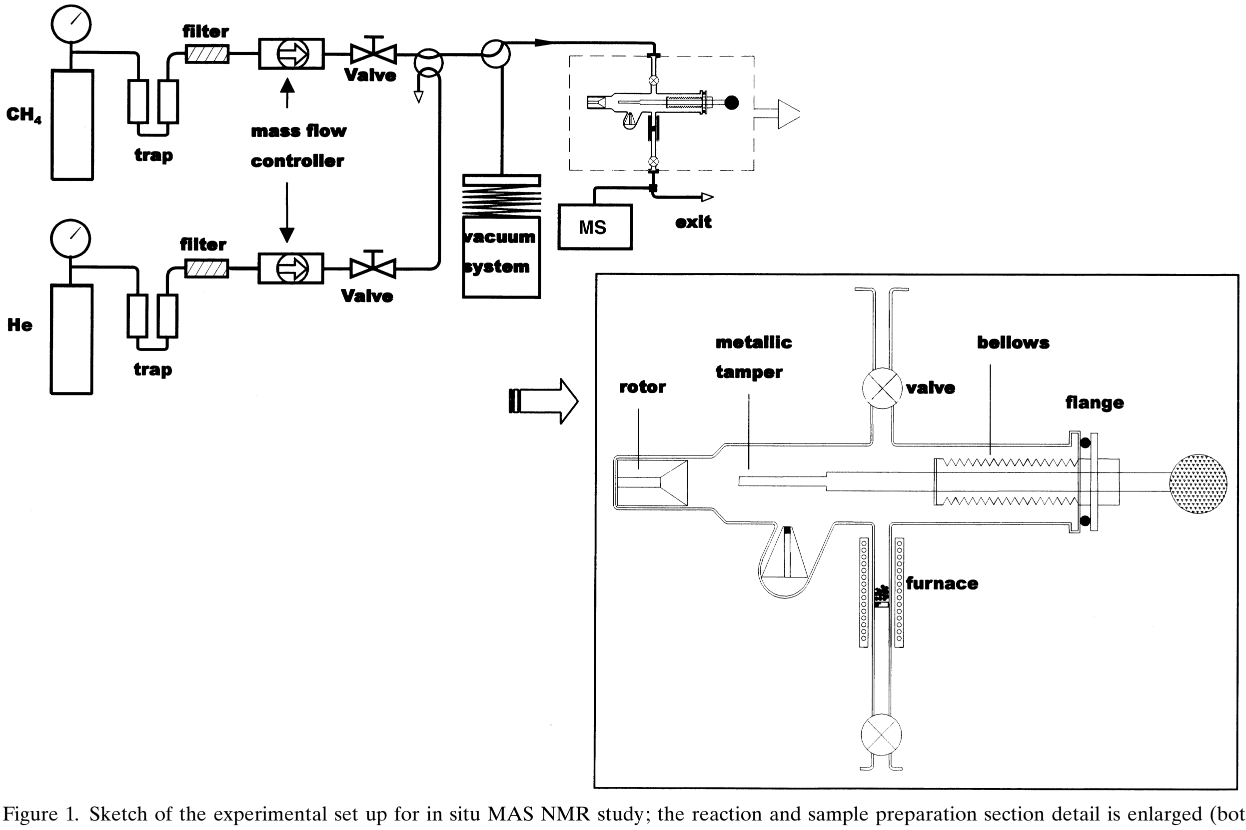

Figure 1. Sketch of the experimental set up for in situ MAS NMR study; the reaction and sample preparation section detail is enlarged (bottom right).

adsorbed onto Lewis acid sites or another kind of Brønsted acid sites.

During treatment at higher temperatures the narrow resonance for the adsorbed water gradually disappeared (Figure 2). The amount of zeolitic hydroxyl species appeared to diminish, particularly in the temperature range of 673–873 K. However, no other significant variations were observed in the proton MAS spectra. This observation indicates that the water molecules, including those strongly adsorbed onto Lewis sites of the zeolite, desorb during the temperature-raising process before the reaction starts. At the same time, apart from a small decrease of the Brønsted acid sites as a result of temperature effects, no reaction products or byproducts were observed at or below 873 K.

On increasing the temperature to 973 K for 10 min the color of the catalyst changed from blue-white to black which is the typical color of molybdenum carbide. In conjunction with this observation a distinct change in the proton NMR signals occurred (Figure 3a and b). The Brønsted acid signal at $\delta = 4.1$ decreased dramatically, and two new resonances at $\delta = 6.8$ and 7.9 emerged clearly when the reaction time was prolonged (Figure 3c). The first of these two new signals can be assigned to the water molecules formed and adsorbed during the reaction [Eq. (1); the formula is nonstoichiometric].

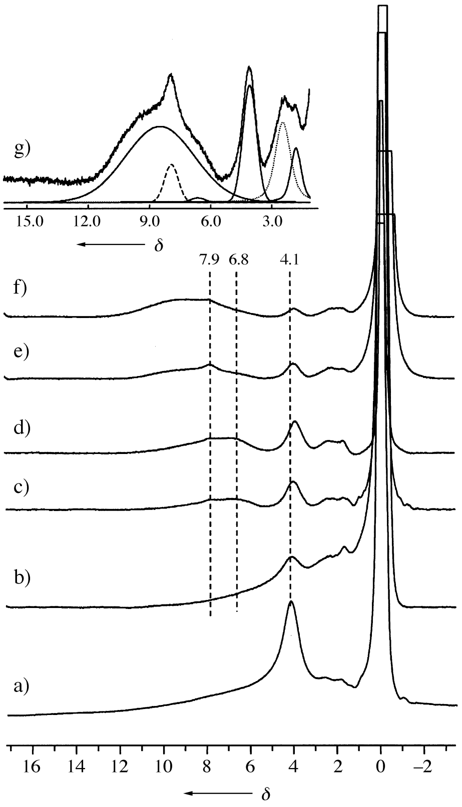

Figure 3. $^1$H MAS NMR spectra of Mo/HZSM-5 (6%) treated with a) methane flow at 873 K for 1 h. b)–f) after the methane dehydroaromatization reaction (973 K, 1500 mL g$^{-1}$ h$^{-1}$, 1 atm) reaction times: b) 10 min, c) 30 min, d) 1 h, e) 3 h, f) 6 h. Spectrum (g) is an expansion of spectrum (e), with six lines simulating the original spectrum.

$$MoO_3 + CH_4 \longrightarrow Mo_2C + CO_2 + CO + H_2O \qquad (1)$$

During their diffusion over the surface or through the gas phase the water molecules can reabsorb on the nearby Lewis acid sites. The signal at $\delta = 7.9$ is assigned to the hydrogen atoms of the aromatic species that are produced on the aromatization centers—the Brønsted acid sites[4a]—and are then adsorbed on the catalyst. At the same time the intensity of the Brønsted acid signal decreases further, an indication that Brønsted acid sites take part in the aromatization or hydrogen transfer process of the reaction. Choudary et al.[11] and Buckles et al.[2] suggested that in the aromatization of propane or of a mixture of propane/propene and methane, Brønsted protons participated in the paraffin activation and the subsequent hydrogen transfer reaction. Direct observation of the variations in the proton signal during the methane dehydroaromatization provides strong support for an acid-induced aromatization mechanism. As we previously reported no benzene formation is observed when the Na form of the ZSM-5 zeolite is used instead of a proton form.[4a] Thus, we could conclude that Brønsted protons are essential to the methane dehydroaromatization reaction.

From TPSR experiments it has been observed that the water formation began at 973 K and that at the same temperature benzene started to appear 15 min later.[12] This is in good agreement with our present proton MAS NMR results. Moreover, a signal corresponding to a methylene species at about $\delta = 1.2$,[13] which in ref. [4g] is suggested as the intermediate species and as being responsible for the formation of the possible primary product of ethane,[4b] could not be observed. Even if this species exists, it may overlap with the rather broad line of the nonframework Al-OH species.

The reaction process was stable up to 1 h (Figure 3d). After a further 2 h reaction time a new signal with similar chemical shift to the signal at $\delta = 7.9$ but with a much broader form appeared, while the amount of adsorbed water ($\delta = 6.7$) is greatly reduced (Figure 3e). A clearer $^1$H MAS NMR profile of Figure 3e can be found in Figure 3g in which an enlarged spectrum and the simulated lines are presented. The broad signal can be attributed to the more condensed aromatic materials, that is aromatic carbonaceous deposits on the catalyst surface. The broad line width reveals its mixed composition and complicated nature. In fact, this signal can be observed even at the beginning of the reaction (Figure 3c), though it is very weak at this time. It is difficult to determine the exact ratio of the two overlapping signals at about 8 ppm, but in Figure 3c–f we can find that the amount of the aromatic carbonaceous deposits greatly increased with the reaction time. This is in an agreement with the thermogravimetric measurements and with carbon number balance calculation based on GC results of the residue.[4e]

For the first time the variation of the amount of Brønsted acid sites during a real high-temperature reaction (973 K), as well as the formation of water, benzene, and aromatic carbonaceous deposits in the reaction process have been directly observed. This gives a more detailed description of what has happened on the catalyst surface during the reaction than data from the gas phase analysis (mass spectrometer).

## *Experimental Section*

A series of Mo/HZSM-5 catalysts were prepared as described in ref. [4b]. HZSM-5 powders were impregnated with aqueous solutions containing a given amount of ammonia heptamolybdate (AHM), then dried at RT and 373 K for 12 and 8 h, respectively. After calcined at 773 K for 5 h, the catalysts were crushed and sieved to yield granules of 20–60 mesh.

A specially designed device was built for the MAS NMR study. It contains a gas flow section, a reaction and sample preparation section, and an on-line mass spectrometer (Figure 1). After the reaction (the temperature can be as high as 1123 K), the reaction and sample preparation section can be taken off and turned through 90°. Then, in the reaction atmosphere the sample can be transferred into a NMR-rotor with the aid of a tamper (to pack the sample into the tube) that is mounted in a bellows attatched to the upper side of the flange. The rotor is then sealed with a cap in a rack with the aid of tamper. A spin rate as high as 12 kHz can be reached following this sample filling method. In the present case, the samples were treated with a methane flow ($SV = 1500\,mL\,g^{-1}\,h^{-1}$, 1 atm) for 1 h at 573, 673, and 873 K. Subsequently, the catalysts were subjected to reactions of 10 min, 0.5 h, 1 h, 3 h, and 6 h. In all the cases, the temperature was raised at a rate of $15\,^{\circ}C\,min^{-1}$.

Proton MAS NMR spectra were recorded in 4 mm $ZrO_2$ rotors at 400.13 MHz on a Bruker DRX-400 spectrometer fitted with a MAS probe. For each spectrum, a $\pi/10$ pulse and a 4 s relaxation delay were used, and 400 scans were accumulated. Samples were spun at 8 kHz, and the DSS (DSS = sodium 4,4-dimethyl-4-silapentane sulfonate) signal was taken as the reference for the $^1H$ chemical shifts. The deconvolution of the spectra was conducted using WINNMR, supplied by the spectrometer manufacturer.

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[12] In the TPSR (temperature program surface reaction) profile of this reaction (detected by the on-line mass spectrometer) water was shown to be produced when the temperature reached 973 K, with a maximum at about 13 min after the reaction began. Two minutes later (15 min after the start of the reaction) the start of benzene formation is observed. The formation of water stopped about 1 h later at the same temperature, but that of benzene increases slowly in the first hour, and then appears to be constant. This indicates that the water formation is a stoichiometric (not catalytic) reaction [see Eq. (1)], where as benzene formation is a catalytic reaction.

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# First Crystal Structure of a Medicinally Relevant Gold Protein Complex: Unexpected Binding of $[Au(PEt_3)]^+$ to Histidine**

Juan Zou, Paul Taylor, Jacqueline Dornan, Stephen P. Robinson, Malcolm D. Walkinshaw,* and Peter J. Sadler*

Antiarthritic gold(I) compounds such as the injectable drugs aurothiomalate[1] (Myochrysine) and aurothioglucose (Solganol),[2] and the oral drug[3] $[Au^I(PEt_3)$ (2,3,4,6-tetra-*O*-acetyl-$\beta$-D-thioglucose-*S*)] (auranofin) are “prodrugs”, which undergo facile ligand displacement reactions.[4, 5] The critical target sites are thought to be thiolate sulfurs (cysteine residues) in proteins and enzymes,[5] $Au^I$ being a very “soft” (class ‘b’) metal ion.[6, 7] However, there is a lack of structural data on adducts of antiarthritic $Au^I$ complexes with proteins.[8] We report here investigations of reactions between the enzyme cyclophilin and the antiarthritic complex[9, 10] $[Au(PEt_3)Cl]$ (**1**), and the first X-ray crystal structure of a protein adduct with a $Au^I$ phosphane complex. Unexpectedly, in cyclophilin crystals, $Au^I$ binds to the nitrogen atom of an active site His residue, despite the presence of four Cys thiol groups. The results have implications for understanding the biological chemistry of gold antiarthritic complexes. Additional interest in this work arises from the need for site-specific heavy-atom reagents for X-ray crystallography.[8]

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[*] Prof. Dr. M. D. Walkinshaw, Dr. P. Taylor, J. Dornan, S. P. Robinson
Institute of Cell and Molecular Biology
Michael Swann Building
The University of Edinburgh, King’s Buildings
West Mains Road, Edinburgh EH9 3JR (UK)
Fax: (+44) 131-650-7055
E-mail: M.Walkinshaw@ed.ac.uk

Prof. Dr. P. J. Sadler, Dr. J. Zou
Department of Chemistry
The University of Edinburgh, King’s Buildings
West Mains Road, Edinburgh EH9 3JJ (UK)
Fax: (+44) 131-650-6452
E-mail: P.J.Sadler@ed.ac.uk

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