Unprecedented dimethyl sulfoxide conformational equilibria and kinetics on $[Ir(Me_2SO)_3(\eta\text{-}C_5Me_5)][PF_6]_2$

Antonio Cusanelli, Urban Frey and André E. Merbach*

Institut de Chimie Minérale et Analytique, Université de Lausanne, CH-1015 Lausanne, Switzerland

Intermolecular dimethyl sulfoxide exchange on $[Ir(Me_2SO)_3(\eta\text{-}C_5Me_5)][PF_6]_2$ 1 proceeds *via* a dissociative mechanism, exclusively from a conformational isomer of 1 (1c) which is itself in equilibrium with a second more compact conformer (1a).

The coordination chemistry of dimethyl sulfoxide was initially extended to the half-sandwich complexes $[M(Me_2SO)_3(\eta\text{-}C_5Me_5)][PF_6]_2$ (M = Rh, Ir) by Maitlis and coworkers.[1] These workers showed that these complexes were valuable intermediates for the synthesis of related compounds and that, more interestingly, these complexes were capable of rapidly exchanging bound Me_2SO with free Me_2SO, although the kinetics of this exchange process were left unexplored. We now report the results of a dynamic ^1H NMR study on the iridium complex $[Ir(Me_2SO)_3(\eta\text{-}C_5Me_5)][PF_6]_2$ **1** which provides evidence in support of novel conformational equilibria and kinetics for the dimethyl sulfoxide exchange process.

In solution Me_2SO coordinates to the relatively soft metal centre in **1** exclusively through the sulfur atom. This bonding assignment was initially confirmed by Maitlis and coworkers from IR investigations conducted on both Me_2SO and $(CD_3)_2SO$ analogues of this complex[1] and this assignment is further corroborated by numerous X-ray crystal structures for similar iridium(iii) complexes, which in all cases show the Me_2SO ligand to be S bonded.[2] The spectroscopic results we have obtained for **1**† are in complete agreement with this assignment.

The low temperature ^1H NMR spectrum of **1**, acquired at 243.2 K in CD_3NO_2 containing excess free Me_2SO, did not show the expected two resonances corresponding to bound and free Me_2SO respectively, but instead exhibited five resonances at δ 3.16, 3.15, 3.11, 2.99 and 2.56 (Fig. 1); the latter was unequivocally assigned to free solvent and the remaining signals were attributed to **1**.

Also present in this spectrum were two unequally populated resonances at δ 1.79 and 1.64 assigned to two unique C_5Me_5 groups. The three resonances at δ 3.16–3.13 integrated to six protons each with respect to the more populated of the C_5Me_5 signals whereas the remaining bound Me_2SO resonance at δ 2.99 integrated to 18 protons with respect to the less populated C_5Me_5 moiety. Taken together, these results clearly suggest the presence of two stereoisomers of **1** (denoted as major and minor in Fig. 1), each composed of a C_5Me_5 group and three Me_2SO ligands.

Considering first the major isomer of **1**, two conformers can account for the three resonance pattern observed for this species and these are depicted as structures **1a** and **1b** in Fig. 2; the symmetry of both structures is defined by a plane bisecting the C_5Me_5 centroid, Ir, and an S–O bond such that two Me_2SO molecules and two Me groups are related by the mirror plane.

Upon closer inspection of the low-temperature limit NMR spectrum in Fig. 1, it is evident that the most deshielded resonance has a smaller linewidth at half-height ($\Delta\nu_{1/2}$ 1.7 Hz at 243.2 K) than the two adjacent resonances ($\Delta\nu_{1/2}$ 2.3, 2.2 Hz, respectively, at 243.2 K) which are broader but similar due, most likely, to a small unresolved $^4J_{HH}$ coupling ($^4J_{HH}$ couplings are *ca.* 0.1–0.4 Hz). Thus, one can assign the two broader resonances to the geminal methyl groups of the Me_2SO molecules, labelled as A and B in Fig. 2, which are expected to be coupled. The most deshielded signal is then assigned to the remaining methyl groups, labelled as C in Fig. 2. These experimental results are thus consistent with conformer **1a**, rather than conformer **1b**, since the methyl groups (*i.e.* Me_C) in the former structure are expected to be more deshielded because of their close proximity to the ring current induced by the π electrons of the C_5Me_5 moiety. In addition, conformer **1a** is also the sterically preferred structure since it minimises the contacts between the bulky C_5Me_5 group and the Me_2SO methyl groups.

With respect to the minor isomer of **1**, the single ^1H NMR resonance assigned to this conformer (Fig. 1) indicates that all three bound Me_2SO groups in this species have the same

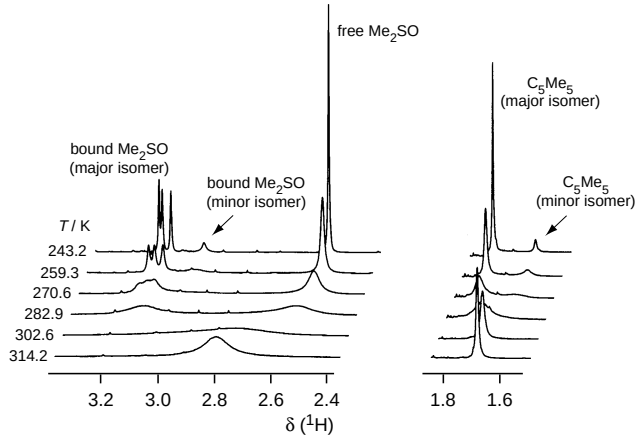

Fig. 1 Experimental ^1H NMR (400 MHz) spectra of **1** (0.010 m) in CD_3NO_2 diluent ([free Me_2SO] = 0.028 m) at various temperatures

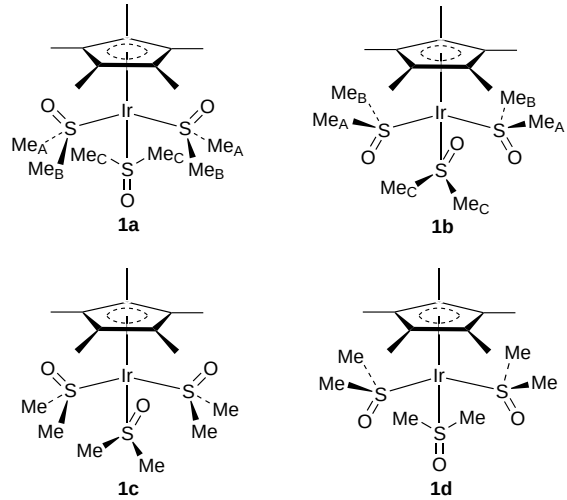

Fig. 2 Structural representations of the plausible conformers of **1**

chemical environment. This can be accounted for by structures **1c** or **1d**. However, structure **1c** is obviously the less sterically demanding structure and thus we suggest that it is the most likely candidate for the minor isomer of **1**. Finally, and of utmost importance, the major:minor isomer ratio observed for complex **1** is seen to reflect the differing steric demands imposed by the bulky C_5Me_5 and Me_2SO groups within the half-sandwich geometry and also supports assigning the major and minor isomers to **1a** and **1c** respectively.

As the temperature was raised to 314.2 K, all five resonances began to broaden, indicating that an intramolecular process and/or an intermolecular exchange(s) with free solvent was occurring over the same temperature interval (Fig. 1). Similar spectra were obtained when the variable-temperature study was repeated without excess Me_2SO, thus corroborating the interconversion between the two isomers of **1**. Notably, $^{13}C\{^1H\}$ NMR spectra of **1**, in the absence of free Me_2SO, acquired over a similar temperature interval also exhibited behaviour consistent with an interconversion process.

Having assigned the conformational identities of the two conformers of **1**, it is reasonable to conclude that their interconversion between structures **1a** and **1c** proceeds *via* a restricted rotation of the metal–sulfur bond. However, the question which remains unanswered is which of the conformers of **1** participates in the intermolecular exchange with free Me_2SO or are both involved? A two-dimensional ^1H NMR EXCSY (exchange correlation spectroscopy) spectrum of **1** in CD_3NO_2 at 243.5 K with excess Me_2SO provided the answer (Fig. 3).

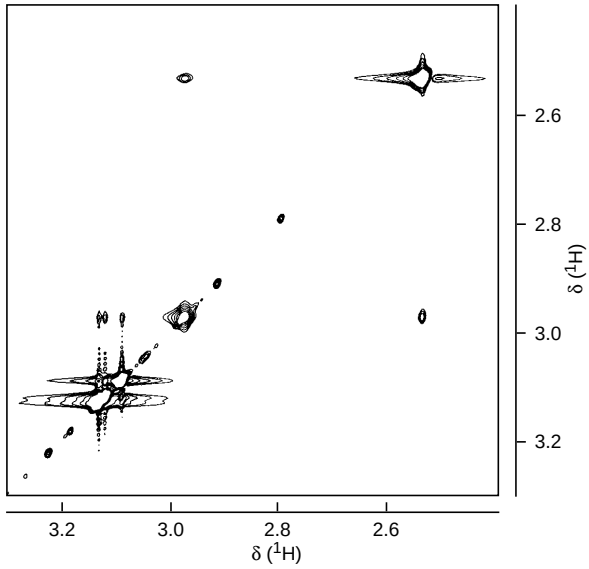

Fig. 3 Two-dimensional ^1H NMR (400 MHz) EXCSY spectrum of **1** (0.010 m) in CD_3NO_2 diluent ([free Me_2SO] = 0.026 m) at 243.5 K (see Fig. 1)

Under these conditions, the most intense cross-peak relates the resonance of the minor conformer **1c** with that of free Me_2SO, confirming that this intermolecular exchange is the fastest process. The cross-peaks between conformers **1a** and **1c** were smaller, and most importantly, the cross-peaks diagnostic of an intermolecular exchange between the major isomer **1a** and free Me_2SO were not observed, thus indicating that (*i*) the interconversion between **1a** and **1c** proceeds by an intramolecular pathway [eqn. (1)] and (*ii*) the exchange with free Me_2SO proceeds solely from conformer **1c** [eqn. (2)].

$$\text{major-}[Ir(Me_2SO)_3(\eta\text{-}C_5Me_5)]^{2+} \underset{}{\overset{k_{intra}}{\rightleftharpoons}} \text{minor-}[Ir(Me_2SO)_3(\eta\text{-}C_5Me_5)]^{2+} \quad (1)$$

$$\text{minor-}[Ir(Me_2SO)_3(\eta\text{-}C_5Me_5)]^{2+} + 3{*}Me_2SO \overset{k_{inter}}{\rightleftharpoons} \text{minor-}[Ir(*Me_2SO)_3(\eta\text{-}C_5Me_5)]^{2+} + 3Me_2SO \quad (2)$$

A detailed kinetic study of complex **1** and other related half-sandwich solvento complexes is presently under way in our laboratory to gain more insight into the mechanistic details of solvent exchange on these complexes.

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Footnote

† Complex **1** was prepared by modification to the literature method.[1] *Spectral data* for **1**: IR (acetone): 1126 cm^{-1} ν(SO). ^1H NMR (CD_3NO_2, 400 MHz, 243.2 K): δ 1.64 (s, 15 H, C_5Me_5; **1c**), 1.79 (s, 15 H, C_5Me_5; **1a**), 2.99 (s, 18 H, Me_2SO; **1c**), 3.11 (s, 6 H, Me_2SO; **1a**), 3.15 (s, 6 H, Me_2SO; **1a**), 3.16 (s, 6 H, Me_2SO; **1a**). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 100 MHz, 243.2 K): δ 8.92 (s, C_5Me_5; **1c**), 9.56 (s, C_5Me_5; **1a**), 39.33 (s, Me_2SO; **1c**), 39.55 (s, Me_2SO; **1a**), 40.36 (s, Me_2SO; **1a**), 41.59 (s, Me_2SO; **1a**), 85.40 (s, C_5Me_5; **1c**), 94.10 (s, C_5Me_5; **1a**). Elemental analysis: Calc.: C, 22.56; H, 3.91; F, 26.77; S, 11.29. Found: C, 22.70; H, 3.84; F, 26.51; S, 11.12%.

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