

Re–H⋯H–N interactions in the second-coordination sphere of crystalline [ReH₅(PPh₃)₂(imidazole)]

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The generality of intermolecular N–H⋯H–Re hydrogen bonding is demonstrated in the crystal structure of the title complex, in which an imidazole of crystallization is involved in a three-centre hydrogen bond with an ReH₂ group.

We know substantially more about the structure and reactivity of the first- or inner-coordination sphere of ligands that directly surrounds the metal in a transition-metal complex than we do about the outer- or second-coordination sphere of the solvent (in solution) or crystal lattice (in the solid). We have recently become interested in trying to characterize outer-sphere interactions. In this way we hope to achieve new ways of controlling structure and reactivity in transition-metal chemistry, including catalysis.

Our point of departure was the discovery^{1–5} of M–H⋯H–O and M–H⋯H–N interactions (M = transition metal), which we have called ‘dihydrogen bonds’. These are related to conventional hydrogen bonds except that M–H is the proton acceptor. To characterize such interactions, we first adopted a strategy in which the N–H or O–H group was grafted onto a first-sphere ligand, shown as strategy A (Fig. 1), and exemplified in compounds **1** and **2**. This allowed us and others^{4–5} to identify such interactions in a variety of species and even to measure the strength of the interaction. This approach has several problems. The interaction is not really outer sphere, but rather ‘intermediate sphere’ since the interaction is intramolecular instead of intermolecular. The data we obtain in this way is somewhat suspect in that the structural characteristics of the interaction may be modified in the intermediate-sphere case and not be truly representative of an intermolecular, outer-sphere interaction.

To avoid these problems we moved to the case in which the proton donor and acceptor are distinct molecules that we attempt to cocrystallize from solution (Fig. 1, strategy B). This proved successful in the case of compound **3**, where we were

able to obtain neutron crystallographic data that completely characterized the structural aspects of the interaction.⁶ Unfortunately, this approach is not general, because all other attempts to cocrystallize a transition-metal hydride with a proton donor have failed. Instead, the metal hydride complex and donor species crystallize separately. This is the principle of recrystallization and so is not unexpected.

We are now testing a third strategy (shown as C in Fig. 1), in which the donor and acceptor are covalently linked in such a way that intramolecular interactions are disfavoured. In such a case, we expect that crystallization of the complex should be no more difficult than crystallizing a conventional metal complex. By guaranteeing the presence of a 1:1 ratio of donor and acceptor in the crystal, we expect that the formation of intermolecular interactions would be favoured. This paper reports our first results.

[ReH₇(PPh₃)₂] (50 mg, 0.07 mmol) was treated with imidazole (Him) (10 mg, 0.15 mmol) in benzene at 20 °C for 20 h. After recrystallization from benzene–hexanes, a yellow product was obtained as a mixture of powder and single crystals. Spectral data of the powdered product suggested the structure [ReH₅(PPh₃)₂(Him)] **4** which proved to have an NMR spectrum similar to the related series of [ReH₅(PPh₃)₂(L)] (**5**, L = pyridine or 4-Me-, 4-MeO-, 4-Me₂N-pyridine).⁷

X-Ray diffraction of a single crystal obtained during the recrystallization step revealed that the crystals are 4·(0.5Him·1.5C₆H₆). The crystallographic results are shown in Fig. 2.† The computationally stable hydride positions were located in chemically reasonable positions completing a dodecahedron around the Re atom entirely in agreement with the positions determined by neutron diffraction for the very closely related species [ReH₅(PPh₃)₃] **3**.⁶ The CH and NH protons were placed in calculated positions. As is usual in studies of hydrogen bonding, we have normalized the H atom positions to those found in n-diffraction studies to avoid systematic errors in the derived H⋯H distances; all such distances reported in this paper are normalized in this way.

The packing diagram shows that the complexes do indeed align themselves in such a way that the N–H of one coordinated imidazole comes very close to two of the hydride ligands of the neighbouring molecule of **4** in the lattice. Superficially, we seem to have achieved our aim, but the H⋯H distances [3.55(7), 2.60(8) Å] are both longer than 2.4 Å, and we therefore regard them only as very weak H⋯H interactions.

In addition to the coordinated imidazole, however, we also find 0.5 molecules of free imidazole in the unit cell. One nitrogen atom of this free imidazole is very close to two of the Re hydrides, at a distance appropriate for an H⋯H interaction

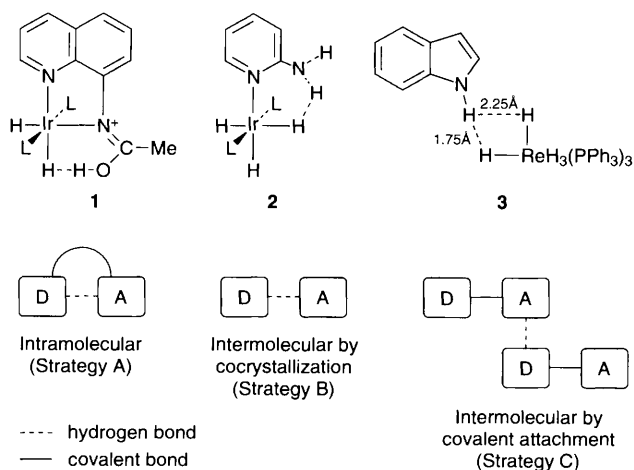
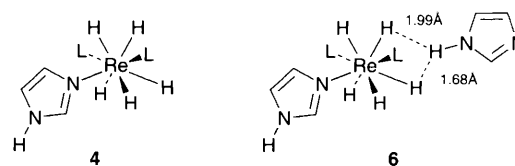


Fig. 1 Three strategies adopted for the study of outer-sphere interactions



shown in 6. In the IR spectrum of the crystal, a broad band appears at 3154 cm^{-1} , shifted by 302 cm^{-1} to lower wavenumber relative to the sharp band observed for the $\nu(\text{NH})$ of a dilute CH_2Cl_2 solution of pure imidazole, where hydrogen bonding does not occur; this shift is characteristic of dihydrogen bonding.^{8,9} An IR spectrum of an amorphous thin film of 4 (obtained by evaporating a CH_2Cl_2 solution of 4 on a NaCl plate) in the absence of any uncoordinated imidazole of solvation shows a $\nu(\text{NH})$ band at 3430 cm^{-1} , little shifted from free $\nu(\text{NH})$. However, an IR spectrum of an amorphous thin film of a 1 : 1 ratio of 4 : imidazole again shows a very broad band at 3150 cm^{-1} , different from that found for pure imidazole (Nujol mull) at 3110 cm^{-1} due to self association.¹⁰ These results indicate that the N–H of the non-coordinated imidazole in the crystal is strongly dihydrogen bonding, analogous to the situation in 3, but that the N–H of the coordinated imidazole is very weakly dihydrogen bonding, if at all. N(101) of the crystal structure therefore must correspond to the N–H rather than the N of imidazole. The imidazole N must therefore be disordered between the sites labelled C(103) and C(104).

We estimate the overall strength of the H...H interaction in 6 to be 22 kJ mol^{-1} based on the shift of the $\nu(\text{NH})$ of the uncoordinated imidazole in the IR spectrum of the crystal;^{9–12} a similar bond strength (18 kJ mol^{-1}) has been reported for 3.⁶ Two of the H...H distances between the N–H of the non-coordinated imidazole and the Re–H bonds of 4 are very short [$1.68(2)\text{ \AA}$ to H(2), $1.99(8)\text{ \AA}$ to H(1)], comparable with the values already found for 3 ($d_{\text{HH}} = 1.75, 2.25\text{ \AA}$). It is notable that the two Re–H bonds involved in the interaction are exactly the same as were involved in 3. We believe the interaction is therefore of the same type as seen in the previous structure.⁶

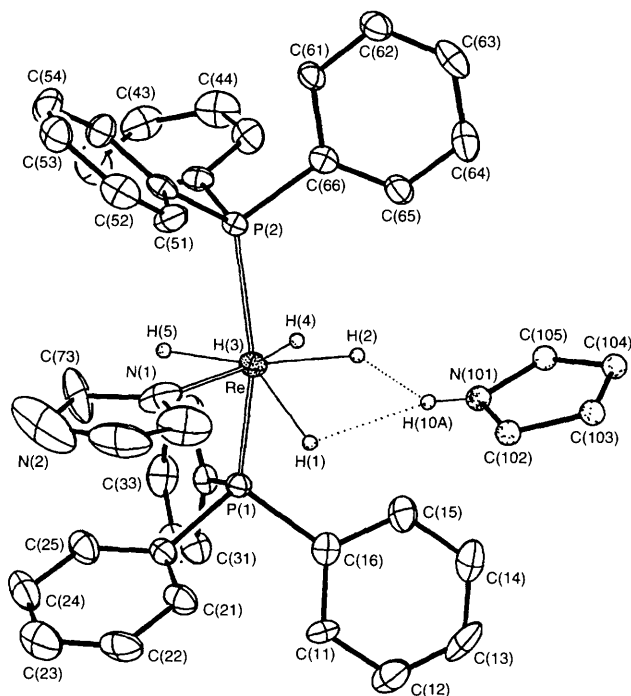


Fig. 2 An ORTEP diagram of 6 showing the intermolecular H...H interactions between the N–H of the non-coordinated imidazole and two of the hydride atoms of 4. Selected distances (Å): H(10A)...H(2) $1.68(2)$, H(10A)...H(1) $1.99(8)$.

We conclude that strategy C offers a possible route to study outer-sphere interactions, but that the imidazole link in 4 is too rigid for a close H...H interaction to be established. Further work will be required to see if flexible linker groups will be more successful. If so, we believe this may prove to be a general method for studying all types of outer-sphere interaction, including both dihydrogen bonding and charge-transfer types. Finally, in 6 we now have the second example of an intermolecular N–H...H–M dihydrogen bond, suggesting this type of interaction may be general.

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Footnotes

† Crystal data for 4·0.5Him·1.5 C₆H₆: $M = 935.57$, monoclinic, space group $P2_1/n$, $a = 20.704(4)$, $b = 8.848(1)$, $c = 25.443(5)\text{ \AA}$, $\beta = 113.00(2)^\circ$, $U = 4290(1)\text{ \AA}^3$, $Z = 4$, $T = 248\text{ K}$, $D_c = 1.449$, $F(000) = 1894$, $\mu = 29.44\text{ cm}^{-1}$, Siemens P4 diffractometer, Mo-K α radiation, $\lambda = 0.71073\text{ \AA}$, $\theta = 4\text{--}60^\circ$, crystal dimensions $0.2 \times 0.2 \times 0.3\text{ mm}$, 15086 total reflections of which 4863 with $I > 2\sigma(I)$, refinement converged at $R = 0.0625$, $wR = 0.1043$ after a semiempirical absorption correction. All non-hydrogen atoms were refined with anisotropic displacement coefficients except those of the uncoordinated disordered imidazole molecule which were refined isotropically; H atoms were treated as idealized contributions, except those located with the disordered imidazole molecule, which were ignored. The largest residual peak in the difference map (1.4 e \AA^{-3}) occurs at a chemically unreasonable position and was considered as noise. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors. Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/23.

‡ The details of the single-crystal X-ray structure of 4·0.5Him·1.5 C₆H₆ will be published elsewhere.

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