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## COMMUNICATION

# Hydrogen-bonded adducts between neutral molecules and $[\text{Mo}(\eta^3\text{-methallyl})(\text{CO})_2(\text{HOC}(\text{py})_3)]^+$ : snapshots of a deprotonation†

Dolores Morales,<sup>‡,\*</sup> Julio Pérez,<sup>\*</sup> Héctor Martínez-García, Marcos Puerto and Ignacio del Río

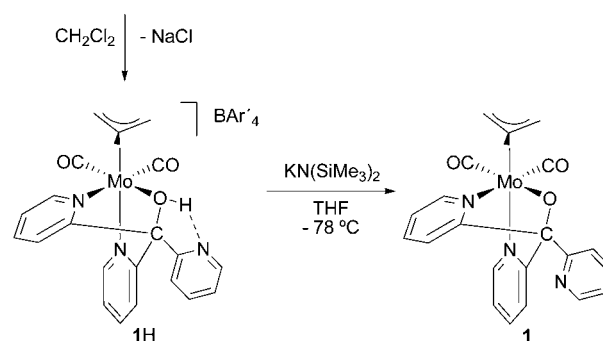
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**Hydrogen-bonded adducts between the title metal alcohol complex and several neutral bases, showing different degrees of  $\text{H}^+$  transfer, display distinctive  $\nu\text{CO}$  bands.**

$\text{AH}\cdots\text{B}$  and  $\text{A}\cdots\text{HB}$  adducts of the AH hydrogen-bond donor (the acid) and the B hydrogen-bond acceptor (the base) are intermediate situations along the reaction coordinate in  $\text{H}^+$  transfer, the simplest chemical reaction.<sup>1</sup> For a set of adducts showing different degrees of  $\text{H}^+$  transfer between a given hydrogen-bond donor and different acceptors, could conventional characterization methods reveal their intermediate properties? The development of supramolecular systems able to modulate a response upon guest binding is a challenging area.<sup>2</sup> Hydrogen-bond donor groups in the periphery of metal complexes have been used for second-sphere binding of molecular or ionic guests.<sup>3</sup> Metal complexes can be interrogated by a variety of techniques, so the choice of a metal fragment as the hydrogen bond donor could make the sought characterization a more complete one. In particular, the position of the  $\nu\text{CO}$  IR bands of metal carbonyl complexes is highly sensitive to the electron density at the metal center. Our previous attempts to employ *fac*- $[\text{Re}(\text{CO})_3(\text{Hpz})_3]\text{BAR}'_4$  (Hpz = generic pyrazole,  $\text{Ar}' = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$ ) for IR sensing of anions resulted in very small variations in the position of the IR  $\nu\text{CO}$  bands.<sup>4</sup> We hypothesized that, for an XH hydrogen bond donor group with X directly bound to the metal, those  $\nu\text{CO}$  IR bands could also report on the strength of the hydrogen bond formed between XH and an external acceptor.

When high binding strength and selectivity are the goal in the design of an artificial host using hydrogen bonding for guest binding, multipoint interactions involving several geometrically convergent

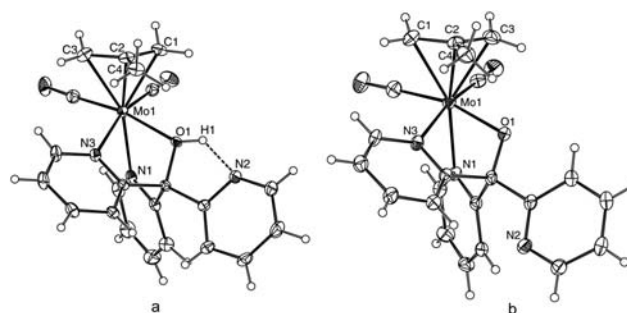
Scheme 1 Synthesis of compounds **1H** and **1**.

donor groups are employed.<sup>3</sup> Here, to reduce complexity, a single-point interaction will be used. To avoid that this would result in too weak an interaction, an OH group, a stronger acid, was chosen instead of N–H groups, the one most often employed in supramolecular hosts. Since alcohols coordinated to low-valent transition metal fragments are very labile ligands, we have employed a tridentate ligand featuring, besides the hydroxyl group, three 2-pyridyl (py) groups,<sup>5</sup> which are good donors for a variety of metal centers.<sup>5,6</sup> Compound  $[\text{Mo}(\eta^3\text{-methallyl})(\text{CO})_2(\text{HOC}(\text{py})_3)]\text{BAR}'_4$  (**1H**) was prepared by reaction of tris(2-pyridyl)carbinol<sup>7</sup> with  $[\text{MoCl}(\eta^3\text{-methallyl})(\text{CO})_2(\text{NCMe})_2]$ <sup>8</sup> and  $\text{NaBAR}'_4$ <sup>9</sup> (Scheme 1). The  $\text{BAR}'_4$  tetraarylborate was chosen due to its low coordinating character.<sup>3d</sup> The reaction of **1H** with  $\text{KN}(\text{SiMe}_3)_2$  in THF afforded the

Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, Cl Julián Clavería, no. 8, 33006 Oviedo, Spain. E-mail: moralesdolores.uo@uniovi.es; japm@uniovi.es; Fax: +34 985103446

† Electronic supplementary information (ESI) available: Experimental section, crystal structure determination and molecular structure representation of **1H**; **1H**-DMPU, **1H**-py and **1H**-TEA; <sup>1</sup>H NMR of **1H** at different concentrations, VT <sup>1</sup>H NMR of **1H**-DMPU and <sup>1</sup>H NMR titration showing the displacement of THF by DMPU in **1H**-THF. CCDC reference numbers 786107 (**1H**), 786108 (**1**), 786109 (**1H**-THF), 786110 (**1H**-DBU), 786111 (**1H**-DMPU), 786112 (**1H**-py), 786113 (**1H**-TEA) and 786114 (**1H**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00688b

‡ Present address: Fundación ITMA, Parque Tecnológico de Asturias, 33248 Llanera, Spain. E-mail: m.morales@itma.es

Fig. 1 Thermal ellipsoid (30%) plot of the cation in **1H** (a) and compound **1** (b).

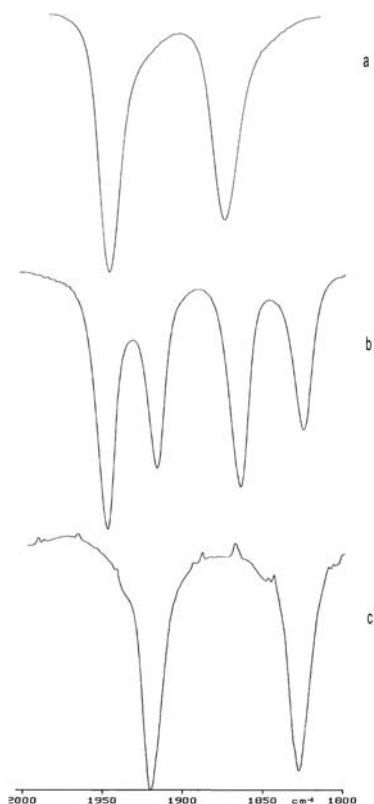


Fig. 2 IR  $\nu\text{CO}$  ( $\text{cm}^{-1}$ ) in THF solution of: (a) **1H**; (b) after 15 min, mixture of **1H** and **1**; (c) **1**.

deprotonated alkoxo form, complex **1**, and both compounds were characterized by IR ( $\nu\text{CO}$  bands at: **1H**: 1956 and 1869  $\text{cm}^{-1}$ , **1**: 1918 and 1820  $\text{cm}^{-1}$ ), NMR and X-ray diffraction (Fig. 1). In both solid

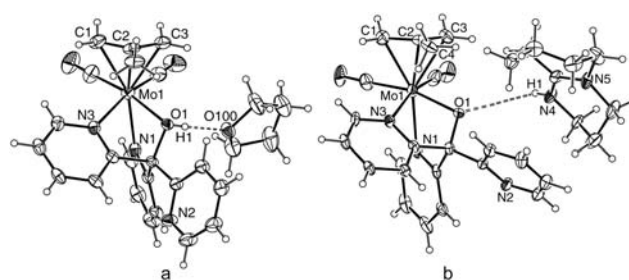


Fig. 3 Thermal ellipsoid (30%) plot of the cation in **1H**-THF (a) and **1H**-DBU (b).

state structures, the tridentate ligand is coordinated through the nitrogens of two of the py groups—one *trans* to one of the CO groups and the other *trans* to the methallyl group, and the oxygen, and the third pyridine remains un-coordinated. At low temperature, the  $^1\text{H}$  NMR spectra indicate that the same geometry exists in solution, with three chemically non-equivalent py groups and an asymmetric  $\eta^3$ -methallyl ligand, whereas at room temperature a dynamic process renders apparently equivalent the two coordinated py groups. In the structure of **1H** there is an intramolecular hydrogen bond between the coordinated OH and the nitrogen of the un-coordinated pyridine, characterized by  $\text{O}\cdots\text{N} = 2.415(3)$  Å and  $\text{OHN} = 132.87(7)^\circ$ .

The change in the  $^1\text{H}$  chemical shift of the OH signal upon dilution reveals the presence of additional, intermolecular hydrogen bonds in solution. To shed some light on the hydrogen bonding in **1H**, compound **1'H**, differing from **1H** only in that the dangling group is a phenyl ring rather than a pyridine, was synthesized and characterized in solution and solid state. Dilution of **1'H** did not shift the OH  $^1\text{H}$  NMR signal, demonstrating that intermolecular hydrogen bonds in **1H** are of the  $\text{OH}\cdots\text{N}$  type. Additionally, **1'H** was found to be isostructural with **1H**, showing that the adoption of the N,N',O

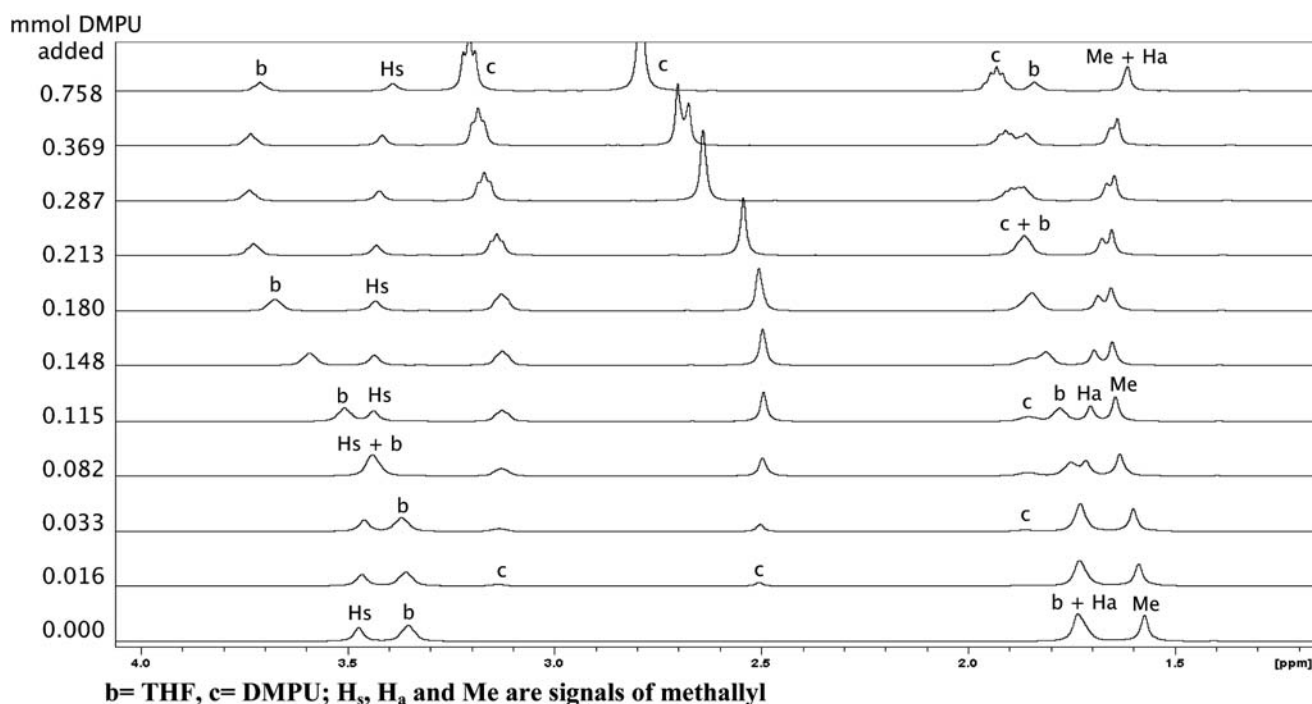


Fig. 4  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) in the 4.0–1.2 ppm region, showing the displacement of the THF molecule by DMPU in **1H**-THF.

coordination mode in **1H** is not dictated by the intramolecular hydrogen bond.

IR ( $\nu$ CO) monitoring of a THF (a solvent of very low basicity) solution of **1H** showed a gradual (and reversible) transformation into **1**, highlighting the acidity of the OH ligand (Fig. 2).

A **1H**-THF adduct could be isolated by slow crystallization of a  $\text{CH}_2\text{Cl}_2$  solution of **1H** containing a large excess of THF. Its  $^1\text{H}$  NMR featured the signals of a THF molecule slightly upfield from those of free THF, and the results of an X-ray diffraction study revealed the hydrogen bond showed in Fig. 3 as a dashed line. The formation of this  $\text{OH}\cdots\text{O}$  hydrogen bond takes place at the expense of the  $\text{OH}\cdots\text{N}$  hydrogen bond with the dangling pyridine ring; actually, the pyridine ring is rotated so that its N atom is away from the Mo-coordinated OH group. The same feature has been found in the majority of adducts discussed below. The  $^1\text{H}$  NMR titration of a  $\text{CD}_2\text{Cl}_2$  solution of **1H**-THF with the cyclic urea 1,3-dimethyl-3,4,5,6-tetrahydro-2(**1H**)-pyrimidinone (DMPU), an excellent hydrogen bond-acceptor, showed the gradual shift of the THF signals towards the position of free THF (Fig. 4). On addition of DMPU, the broad OH signals shift downfield, reflecting the formation of stronger hydrogen bonds, and soon broadens and disappears, becoming visible at low temperature. The crystalline adduct **1H**-DMPU was isolated by slow diffusion of hexane from an equimolar mixture of **1H** and DMPU in  $\text{CH}_2\text{Cl}_2$  and characterized by IR, NMR and X-ray diffraction (ESI $^\dagger$ ). Whereas the IR  $\nu$ CO bands of **1H**-THF were indistinguishable from those of **1H**, indicating the very weak interaction between THF and the OH group in this 1 : 1 adduct, those of **1H**-DMPU (1952 and 1864  $\text{cm}^{-1}$ ) occur at wavenumber values significantly lower. This stronger hydrogen bond interaction is largely due to the significant contribution of an urea resonance form with a single C–O bond and a negative charge on oxygen, as shown by the shift to lower frequency of the urea  $\nu$ CO band (1558  $\text{cm}^{-1}$  in **1H**-DMPU, 1630  $\text{cm}^{-1}$  in free DMPU). The O $\cdots$ O hydrogen bond distance in **1H**-DMPU, 2.491(5) Å, shorter than in **1H**-THF (2.588(4) Å), is attributed to the stronger hydrogen bond interaction in the former.

From equimolar solutions of **1H** and pyridine (py), triethylamine (TEA) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the 1 : 1 adducts **1H**-py, **1H**-TEA and **1H**-DBU respectively were isolated by crystallization and characterized by IR (see Table 1), NMR and X-ray diffraction. In the solid state, 1 : 1 adducts were encountered, now with the nitrogen atom of the neutral base involved in the hydrogen bonding. The hydrogen atom was found to be closer to O in **1H**-THF and **1H**-DMPU, and closer to N in **1H**-py, **1H**-TEA and **1H**-DBU, consistent with the higher basicity of the N-bases. Nonetheless, it must be noted that the addition of equimolar amounts

**Table 1** IR  $\nu$ CO ( $\text{cm}^{-1}$ ) data in  $\text{CH}_2\text{Cl}_2$  solution

<b>1H</b>	<b>1H</b> -THF	<b>1H</b> -DMPU	<b>1H</b> -py	<b>1H</b> -TEA	<b>1H</b> -DBU	<b>1</b>
1956	1956	1852	1945	1930	1927	1918
1869	1869	1864	1856	1837	1832	1820

of the bases to **1H** does not result in deprotonation to yield **1**; rather, distinct, isolable 1 : 1 adducts are formed.

In summary, 1 : 1 adducts were formed between the alcohol complex **1H** and THF, DMPU, py, TEA and DBU. Despite the fact that these are neutral molecules (therefore, there is no ion–ion attraction) and there is a single hydrogen bond, the adducts could be isolated and characterized in solid state and in  $\text{CH}_2\text{Cl}_2$  solution, where their IR  $\nu$ CO bands are intermediate between those of **1H** and **1**, with  $\nu$ CO decreasing in the order **1H**  $\approx$  **1H**-THF > **1H**-DMPU > **1H**-py > **1H**-TEA > **1H**-DBU > **1**, indicating a variation in the degree of  $\text{H}^+$  transfer from **1H** to the neutral molecule in the same order. Since the timescale of IR spectroscopy makes it a fast technique, these pairs of bands correspond each to a single species, not to averages of **1H** and **1**, which, when present, give rise to distinct, well separate pairs of bands, like those seen when **1H** was dissolved in THF. Thus, simple IR monitoring in solution using the  $\nu$ CO region reports the relative extent of  $\text{H}^+$  transfer from an acidic metal carbonyl complex to different bases.

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