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IR Spectroscopic study of hydrogen bonding using a metal carbonyl probe

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The interaction of different hydrogen bond donors with [M(CO)$_5$L] [L = (*E*)-1,2-di-4-pyridylethene, M = Cr or W] was studied by means of IR spectroscopy. A clear shift to higher wavenumbers of the E and A$_1$ carbonyl vibration modes upon addition of the hydrogen bond donors is observed. The binding isotherms allowed calculation of both the equilibrium constants and free energies of formation of the adducts. These parameters depend on the nature of the carbonyl compound used, the pK_a of the hydrogen bond donor and the steric hindrance of its A–H bond.

During the last five decades a large number of investigations have been carried out on hydrogen bonding.[1] Much experimental data obtained from the application of different methods with a variety of hydrogen bonded systems have been published, and theoretical advances on the study of hydrogen bonding have approached a high level of development.

Typically, hydrogen bonds are weak interactions (2–12 kcal mol^{-1}) between proton donor groups and lone pairs of heteroatoms. Although this interaction has been mainly studied in organic and biological systems, many examples of inorganic and organometallic compounds have recently been published opening a great field of research and potential applications in molecular recognition and catalysis.

Most often the question in a potential hydrogen-bonding interaction is not 'does hydrogen bonding occur?', but 'to what extent, or with what energy, does hydrogen bonding occur?' It is usually easy to decide whether some interaction has occurred (A–H stretching frequency, proton magnetic resonance, *etc.*), but there are only a few examples in which simple methods to evaluate the energy have been reported.[2] In particular, one of the most widely used methods is based in the shift of the A–H frequency in the IR spectrum[2] although these methods have led to controversy regarding the validity and generality of such an approach.

The great structural diversity of organometallic compounds has led to a large number of hydrogen-bonded patterns being discovered in solution and in the solid state.[3] Recently, Crabtree and co-workers[4] found a new type of hydrogen bonding (or dihydrogen bond) of the type M–H···H–A, where M is a transition metal. The characterization of this intriguing type of interaction was carried out by means of IR and NMR spectroscopy, and the energies were found from both theoretical and experimental data. Shubina, Epstein and co-workers[5] have also found this kind of interaction in metal hydrides and have elegantly shown that the ν(CO) shift to higher wavenumbers of the carbonyl coligands is an indirect indication of the existence of hydrogen bonding to the hydride or the metal. In fact, an exhaustive study of the Cambridge Crystallographic data base by Braga *et al.*[6] has shown that H···H interactions have been known for more than thirty years, although the observations remained unexplained. Metal carbonyls such as [Cr(η^6-C$_6$H$_5$-CO$_2$H)(CO)$_3$] have also recently been used as 'IR-active organometallic pH probes', due to the shift of the CO band to lower wavenumbers upon increasing the pH of the solution, which favours deprotonation of the π bonded ligand.[7] In fact, detection of such (CO) modes offers substantial benefits when employed in spectroscopic sensing measurements, mainly because the bands are narrow relative to the overall spectral width (small shifts can be determined precisely) and because they occur in a region of the spectrum that is generally free from other absorptions.

With these ideas in mind, we decided to use metal carbonyl compounds as hydrogen bonding probes for various proton donors. Specifically, we have used tungsten and chromium pentacarbonyls with pyrazine- and bipyridine-like ligands, in order to allow hydrogen bonding by the proton donor to the lone pair of the unco-ordinated nitrogen atom of the ligand. In this paper we report the shift of the ν(CO) bands of pentacarbonyl(*E*)-1,2-di-4-pyridylethene)metal (metal = Cr or W) with several typical hydrogen-bonding donors such as indole, diphenylamine and 2,4,6-trimethylphenol, and its dependence on the hydrogen-bonding donor type and concentration.

Results and discussion

Syntheses of compounds

The compounds [M(CO)$_5$L] [L = pyrazine or (*E*)-1,2-di-4-pyridylethene; M = Cr or W] were obtained from photochemical reaction of the hexacarbonyl complex in THF to generate [M(CO)$_5$(THF)], and subsequent addition of the corresponding ligand in excess to avoid generation of the thermodynamically more favourable dinuclear compounds.[8] The IR spectra of the compounds so obtained are virtually identical, indicating the presence of a metal pentacarbonyl moiety, the bands being readily assigned to the two A$_1$, B$_2$ and E modes for the pseudo C_{4v} metal centre (see Fig. 1 for compounds **3** and **4**), by comparison with other monosubstituted metal carbonyl derivatives.[9] The ^{1}H NMR spectra confirm the η^1 co-ordination of the N-donor ligands, and ^{13}C NMR clearly shows the two carbonyl inequivalent sites of the pentacarbonyl fragments, so confirming the proposed geometry of the compounds.

Syntheses of the pyridyl compounds **3** (M = Cr) and **4** (M = W) also afford [{M(CO)$_5$}$_2$L] [L = (*E*)-1,2-di-4-pyridylethene, M = Cr or W] as minor products; in these compounds the N-donor behaves as an ambidentate bridging ligand as confirmed by ^{1}H and ^{13}C NMR spectroscopy. The IR spectra are

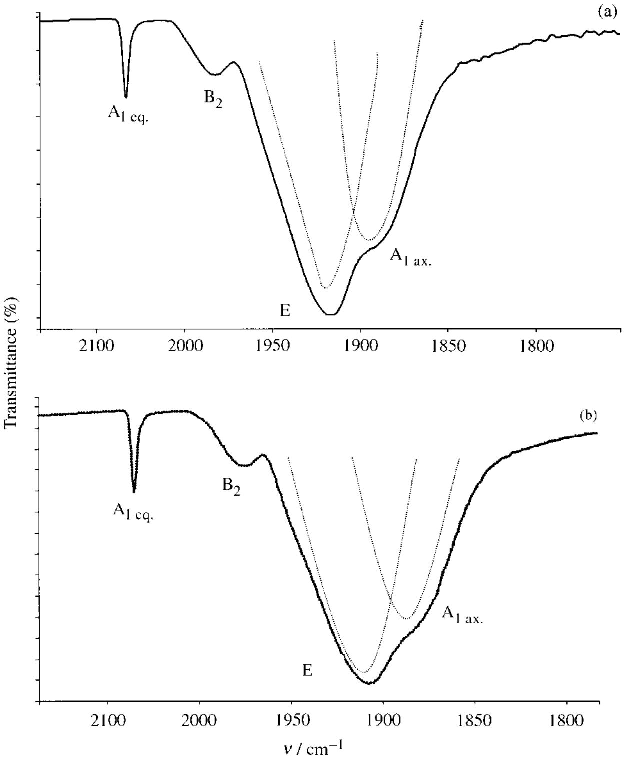
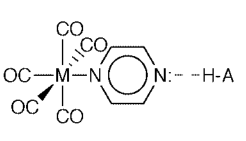


Fig. 1 The IR spectra of compounds **3** (a) and **4** (b) with the assignment of the bands.

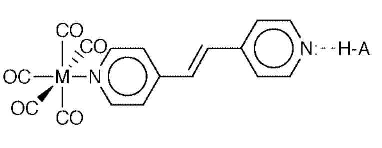
similar to those of the monometallic compounds, indicating a local C_{4v} symmetry about the metal atoms.

Addition of hydrogen-bonding donors

The initial objective was to investigate whether the addition of hydrogen-bonding donors to compounds **1**, **2**, **3** and **4** could be detected spectroscopically from changes in the wavenumber of the ν(CO) vibration modes. A hydrogen-bonding interaction with the electron pair of the unco-ordinated nitrogen atom would be expected to decrease the electron density of the metal carbonyl fragment *via* an inductive effect and so decrease the extent of electron back donation from the metal to the CO π^* antibonding orbitals. In this way, hydrogen bonding should lead to an increase of the wavenumber of the ν(CO) vibration modes.



M = Cr, **1**; M = W, **2**



M = Cr, **3**; M = W, **4**

H-A: *N*-diphenylamine, 4-nitrophenyl(phenyl)amine, pyrazole, imidazole, 2,4,6-trimethylphenol, indole, carbazole and 3,6-dibromocarbazole

To favour association between the donor and the metal complex we sought to prevent self association of the hydrogen bond donor. We therefore selected aromatic amines where the nitrogen lone pair is deactivated by resonance, and phenols where self association is sterically inhibited. These hydrogen-bond donors were: diphenylamine, 4-nitrophenyl(phenyl)amine, pyrazole, imidazole, 2,4,6-trimethylphenol, indole, carbazole and 3,6-dibromocarbazole. Only in the case of 4-nitrophenyl(phenyl)amine some self association is to be expected owing to the accepting character of the nitro group. The hydrogen bond donors also need to be sufficiently acidic to participate in bonding, but not so acidic as to induce complete proton transfer. With respect to our compounds, we have found that this requires a pK_a (DMSO) value in the range 17–25.

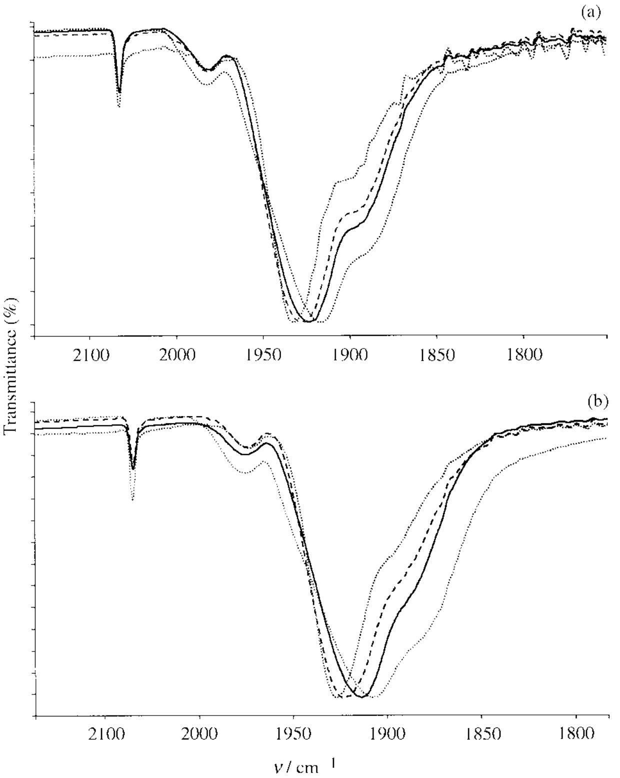


Fig. 2 The FTIR spectra in the carbonyl region for the reaction of compounds **3** (a) and **4** (b) with different amounts of diphenylamine (A–H).

Since typical thermodynamic values for bimolecular associative intermolecular interactions are in the range $-\Delta S°$ 5–20 J K^{-1} mol^{-1},[10] we carried out our experiments at high concentration where the process becomes most readily detectable. The best results were achieved when the mixtures of the solutions of the hydrogen-bond donor and acceptor in CH_2Cl_2 were evaporated on a NaCl plate, to obtain an amorphous thin film of the adducts. The experiments were performed by adding small aliquots of a solution of the complex (**1**, **2**, **3** or **4**) to a range of solutions of the eight hydrogen-bonding donors employed, to give a final composition in the range of M:A–H 1:0.25 to 1:20.

Addition of the hydrogen-bond donors to pyrazine compounds **1** and **2** failed to show any significant changes in the wavenumber of the ν(CO) vibration modes, indicating that, apparently, no hydrogen bonding is occurring in these complexes. We interpret this result as a consequence of the inductive deactivation of the unco-ordinated lone pair of the pyrazine upon co-ordination to the highly electron withdrawing metal fragment, $M(CO)_5$.

With the more basic complexes $[M(CO)_5L]$ [L = (*E*)-1,2-di-4-pyridylethene; M = Cr **3** or W **4**] addition of the hydrogen-bond donors produced an increase of the wavenumber of the ν(CO) vibration modes. The shift is large for the E and A_{1ax} (vibration of the CO *trans* to the pyridyl ligand) band, but insignificant for the B_2 and A_{1eq} (symmetric vibration mode of the equatorial carbonyl groups) carbonyl bands, as shown in Fig. 2. As stated before, this shift is attributed to hydrogen bonding to the lone pair of the co-ordinated pyridyl ligand. The experiments were completely reproducible and the ν(CO) shifts were highly

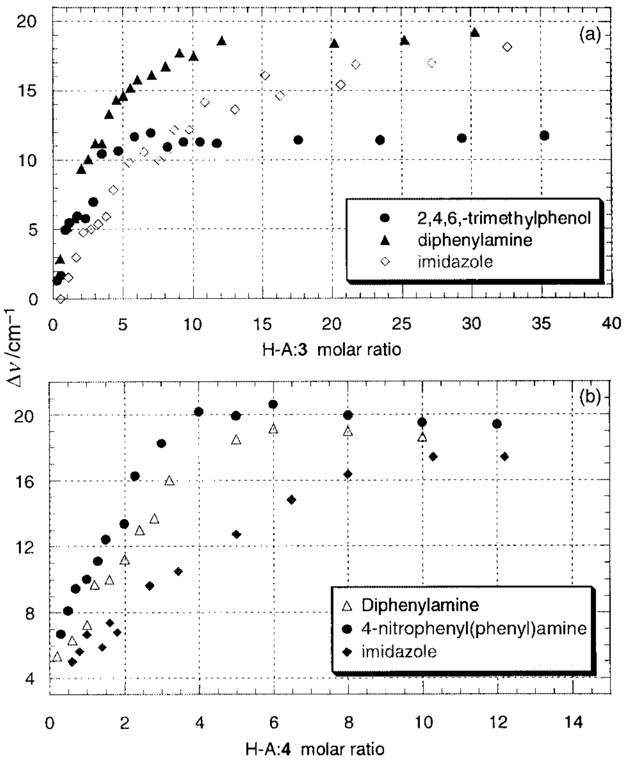


Fig. 3 Plots of $\Delta\nu$ *vs.* A–H : M ratio for the reaction of compounds **3** (a) and **4** (b) for different hydrogen-bonding donors.

dependent on the nature of the H-bond donor and its concentration relative to compounds **3** or **4**. The band shows an isosbestic point at 1949 cm^{-1} for **3** and 1944 cm^{-1} for **4**, indicating that two species are present in the solutions, the relative concentrations of which change with A–H concentration. A stepwise increase in the donor concentration resulted in a gradual increase of the ν(CO) wavenumber of the E and A_{1ax} vibration modes, until a frequency asymptote is achieved, as shown in Fig. 3. The maximum $\Delta\nu$(CO) value was 20 cm^{-1} for the two diphenylamine cases. Addition of an excess of a more powerful hydrogen-bond acceptor such as $OPPh_3$ to a mixture of **3** or **4** and the different donors resulted in a shift of ν(CO) to their original frequency, indicating that the A–H···$OPPh_3$ interaction is now preferred over formation of the M–N–N···H–A bond. Hydrogen bonding to the carbonyl ligands can also be ruled out in this case, since no decrease of the ν(CO) is observed at any concentration of the donors used. These results could also be interpreted in terms of hydrogen bonding to the metal[5] since this interaction should produce an increase of the ν(CO) shift as seen. However, the fact that compounds **1**, **2** and $[\{M(CO)_5\}_2L]$ [L = (*E*)-1,2-di-4-pyridylethene, M = Cr or W] failed to show this effect rules out this possibility.

We were a little concerned by the fact that only the E and A_{1ax} carbonyl vibration modes shifted upon hydrogen bond formation, while the B_2 and A_{1eq} bands remained practically unchanged. In order to confirm this unexpected spectroscopic behaviour we tried to protonate **3** and **4** and then get the IR spectra. Unfortunately these two compounds decompose upon protonation with loss of the bipyridyl ligand. The reaction of **3** and **4** with trimethylaluminium leads to the formation of the adducts $[(OC)_5MNC_5H_4C_2H_2C_5H_4NAlMe_3]$ which were characterized by IR spectroscopy. The spectra show that the E and A_{1ax} bands appear at a higher frequency than for **3** or **4** while the A_{1eq} and B_2 carbonyl bands appear at the same frequency (**3**·$AlMe_3$: E, 1934; B_2, 1984; A_{1eq}, 2068. **4**·$AlMe_3$: E, 1930; B_2, 1975; A_{1eq}, 2070 cm^{-1}; the A_{1ax} band appears as a hump of the E band, as for **3** and **4**).

The fact that a gradual shift of the E and A_{1ax} bands is observed, instead of the appearence of a new band due to the newly formed hydrogen-bonded species, is not surprising since similar studies have been reported leading to the same results.[6] Besides, it is known that IR spectra are usually, but not invariably, in slow exchange,[11] and adduct formation, with its low activation barrier, is one of the most rapid reaction processes. Only the reactions of **3** and **4** with carbazole and 3,6-dibromocarbazole showed separated bands for the free and hydrogen-bonded carbonyl species as shown in Fig. 4.

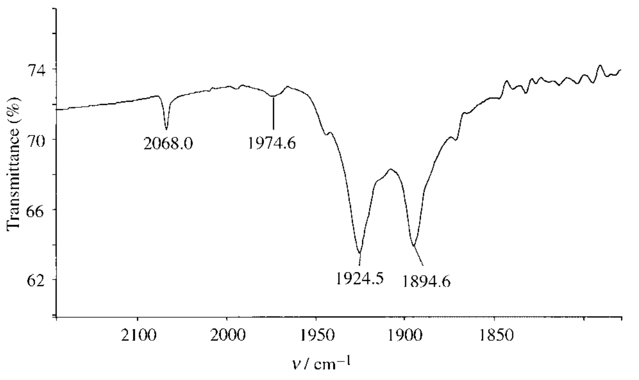


Fig. 4 The IR spectrum of compound **4** with 3,6-dibromocarbazole at a A–H : M 1 : 10 molar ratio.

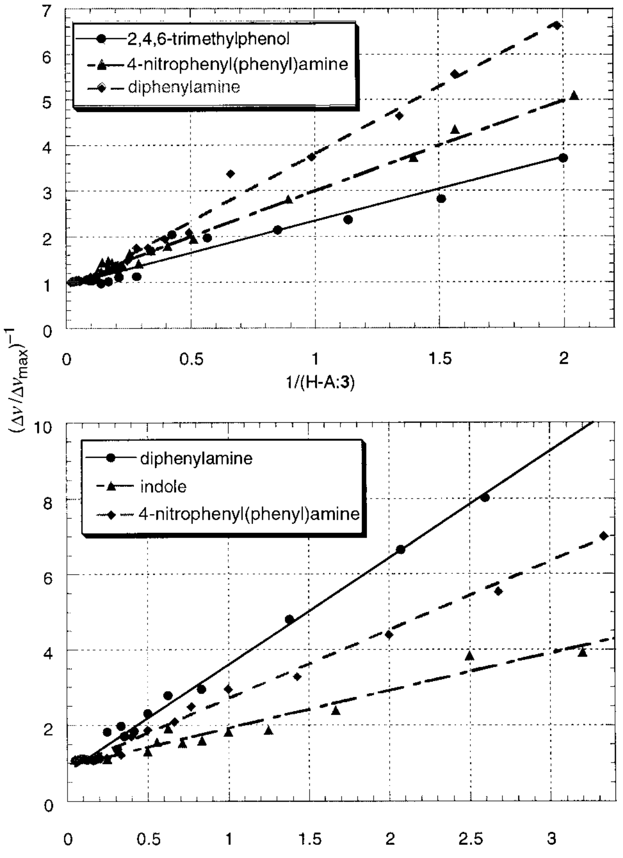


Fig. 5 Lineweaver–Burk plots of compounds **3** (a) and **4** (b) for different hydrogen-bonding donors.

A careful analysis of the binding isotherms shown in Fig. 3 allowed us to estimate the binding equilibrium constants assuming that 1 : 1 adducts are formed.[12] The Lineweaver–Burk[13] plots for the binding data of compounds **3** and **4** with the different hydrogen-bonding donors, from which the equilibrium constants are obtained, are shown in Fig. 5. Only for the carbazole and 3,6-dibromocarbazole cases, and for the reaction of **3** and indole, the separated bands for the free and hydrogen-bonded metal carbonyls made difficult the determination of the binding constants, since no binding isotherms

Table 1 Binding constants and free energies (kcal mol^{-1}, relative to the reaction of **3** + diphenylamine) determined from the binding isotherms of reactions of compounds **3** and **4** with A–H

A–H	pK_a [a]	$K_{(3+\text{A–H})}$ [b]	$K_{(4+\text{A–H})}$ [b]	$\Delta G_{(3+\text{A–H})}$ [c]	$\Delta G_{(4+\text{A–H})}$ [c]
Diphenylamine	24.95	0.338	0.353	0.00	−0.03
4-Nitrophenyl(phenyl)amine	16.85	0.503	0.549	−0.23	−0.28
Imidazole	18.6	0.120	0.152	0.60	0.47
2,4,6-Trimethylphenol	18.4	0.694	1.064	−0.42	−0.67
Pyrazole	19.8	0.079	0.120	0.849	0.60
Indole	20.95	—	1.101	—	−0.64

[a] In DMSO, from ref. 14. [b] In mol^{-1}. [c] In kcal mol^{-1}, relative to the reaction of **3** + diphenylamine.

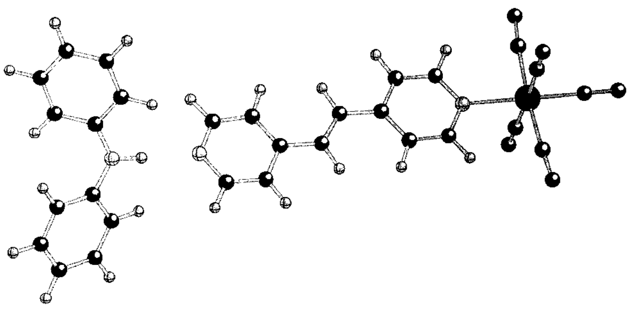


Fig. 6 Optimized structure of the adduct of compound **3** with diphenylamine obtained by means of HF/3-21G.

could be obtained. Table 1 shows the binding constants for the adducts studied, and the free energies (relative to the reaction of **3** and diphenylamine) obtained. The free energies for the formation of the adducts **4**···H–A are slightly lower (more negative) than those for **3**···H–A. This result may indicate the higher basicity of the tungsten carbonyl compound, probably because of the higher back donation capability of the metal. Since we have estimated the relative free energy values for the hydrogen-bond formation at room temperature, we cannot evaluate the entropy of the process, which we believe must show important differences for the different hydrogen-bond donors. For this reason, the binding constants do not show a clear trend when we compare them with the pK_a of the hydrogen-bond donors used. However, when we compare the binding constants and relative free energies of donors with similar steric size (which we believe must show a similar value of the formation entropy), we observe that those with lower pK_a show higher formation constants and hence lower formation free energies (this is the case for diphenylamine and 4-nitrophenyl(phenyl)amine, and imidazole and pyrazole).

Theoretical data on the structure and energy of the 3···H–A and 4···H–A hydrogen bonds

The theoretical studies of adducts of complexes **3** and **4** with diphenylamine revealed the existence of local minima on the potential energy surfaces corresponding to the structure presented in Fig. 6. The hydrogen-bond distances for the two adducts are 2.01 and 2.07 Å for **3** and **4** respectively, smaller than the sum of the van der Waals radii of H and N and close to those for other A–H···N hydrogen bonds. The N–H···N angles obtained for the two characterized compounds are in the range between 171 to 177° close to 180° for similar to classical hydrogen bonds and previous theoretical examples. The M–C and C–O distances of the hydrogen-bonded adducts did not show any significant differences compared to those of the free compounds **3** and **4**.

The calculated energies by which the adducts of compounds **3** and **4** with diphenylamine are stabilized relative to the separated molecules are 8.61 and 7.76 kcal mol^{-1} respectively, both being in the range of classical hydrogen bond energies.[1] It is important to point out that we expected a higher energy for the tungsten complex **4**, while we theoretically determined that **3** is the one that shows the higher energy. We believe that this difference between theoretical and experimental data is mainly due to the different theoretical methods used to optimize the structures of the adducts of **3** (HF/3-21G) and **4** with diphenylamine (B3LYP/LanL2DZ).

Conclusion

By using a metal carbonyl 'sensor' we have detected the hydrogen-bonding capability of several weak acids, based on FTIR spectroscopy of the carbonyl region. The hydrogen bond occurs to the non-bonding lone pair of the dipyridylethene ligand of compounds **3** and **4**, promoting an increase of the ν(CO) shift due to an inductive effect. Plots of the binding isotherms allowed us to determine the binding constants of the hydrogen-bonded adducts formed. The binding constants depend on the pK_a of the hydrogen bond donor used, the nature of the carbonyl compound and on the steric hindrance of its A–H bond. The geometry, energy and electron redistribution were theoretically analysed for two model complexes including the Cr and W atoms.

Experimental

General

All synthetic reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents for synthesis were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel 60 Å or alumina columns.

Proton and carbon NMR spectra were recorded on a Varian 300 MHz spectrometer, using $CDCl_3$ or CD_2Cl_2 as solvent, IR spectra on a Perkin-Elmer System 2000 FT-IR using NaCl plates.

Syntheses of compounds 1–4

The compound [$Cr(CO)_6$] or [$W(CO)_6$] (176 mg, 0.8 mmol) was dissolved in THF (20 ml) and the resulting suspension irradiated for 30 min to yield the yellow solvate [$M(CO)_5$(THF)]. Pyrazine (for **1** and **2**) or (*E*)-1,2-di-4-pyridylethene (for **3** and **4**) was then added (1 mmol) and the reaction mixture stirred for 20 min. The solution was filtered and the solvent removed under reduced pressure. Purification by column chromatography on alumina with CH_2Cl_2–hexane (1:1) afforded pure compounds **1** (yield: 51%) or **3** (yield 41%) (M = Cr) and **2** (yield 62%) and **4** (yield 57%) (M = W). The syntheses of **3** and **4** yielded the dimetallic compound [$\{M(CO)_5\}_2L$] [L = (*E*)-1,2-di-4-pyridylethene] as a minor product (*ca.* 20%).

Pentacarbonyl(pyrazine)chromium 1. ^{1}H NMR: δ 8.63 (s, 2 H, $C_5H_4N_2$) and 8.32 (s, 2 H, $C_5H_4N_2$). ^{13}C NMR: δ 217.1 (4 C, *cis* CO), 210.9 (1 C, *trans* CO), 152.9 (2 C, pyrazine) and 146.7 (2 C, pyrazine). IR (cm^{-1}): 2062.2w, 1992.6w and 1920.1s. Calc. for $C_9H_4CrN_2O_5$: C, 37.92; H, 1.48; N, 10.69. Found: C, 38.26; H, 1.85; N, 10.71%.

Pentacarbonyl(pyrazine)tungsten 2. ^{1}H NMR: δ 8.54 (s, 2 H, $C_5H_4N_2$) and 8.43 (s, 2 H, $C_5H_4N_2$). ^{13}C NMR: δ 211.1 (4 C, *cis* CO), 208.9 (1 C, *trans* CO), 149.9 (2 C, pyrazine) and 145.7 (2 C, pyrazine). IR (cm^{-1}): 2062.3w, 1997.2w and 1926.8s. Calc. for $C_9H_4N_2O_5W$: C, 26.76; H, 1.00; N, 6.93. Found: C, 27.05; H, 1.05; N, 6.71%.

Pentacarbonyl[(*E*)-1,2-di-4-pyridylethene] chromium 3. ^{1}H NMR: δ 8.66 (d, 2 H, $^3J_{H-H} = 5.4$, C_5H_4N), 8.57 (d, 2 H, $^3J_{H-H} = 6.2$, C_5H_4N), 7.40 (d, 2 H, $^3J_{H-H} = 5.4$, C_5H_4N), 7.30 (d, 2 H, $^3J_{H-H} = 6.0$, C_5H_4N), 7.25 (d, 1 H, $^3J_{H-H} = 16.2$, CH=CH) and 7.16 (d, 1 H, $^3J_{H-H} = 16.2$ Hz, CH=CH). ^{13}C NMR: δ 221.4 (1 C, *trans* CO), 215.0 (4 C, *cis* CO), 156.3 (2 C, C_5H_4N), 151.2 (2 C, C_5H_4N), 145.4 (1 C, C_5H_4N), 143.2 (1 C, C_5H_4N), 133.4 (2 C, C_5H_4N), 129.1 (1 C, C_5H_4N), 122.6 (1 C, CH=CH) and 121.9 (1 C, CH=CH). IR (cm^{-1}): 2067.0w, 1982.8w and 1914.4s. Calc. for $C_{17}H_{10}CrN_2O_5$: C, 54.56; H, 2.69; N, 7.48. Found: C, 55.05; H, 2.90; N, 7.45%.

Pentacarbonyl[(*E*)-1,2-di-4-pyridylethene]tungsten 4. ^{1}H NMR: δ 8.80 (d, 2 H, $^3J_{H-H} = 6.3$, C_5H_4N), 8.68 (d, 2 H, $^3J_{H-H} = 5.1$, C_5H_4N), 7.42 (d, 2 H, $^3J_{H-H} = 5.7$, C_5H_4N), 7.35 (d, 2 H, $^3J_{H-H} = 6.3$, C_5H_4N), 7.30 (d, 1 H, $^3J_{H-H} = 16.2$, CH=CH) and 7.18 (d, 1 H, $^3J_{H-H} = 16.2$ Hz, CH=CH). ^{13}C NMR: δ 202.8 (1 C, *trans* CO), 199.2 (4 C, *cis* CO), 156.8 (2 C, C_5H_4N), 151.2 (2 C, C_5H_4N), 145.4 (1 C, C_5H_4N), 143.0 (1 C, C_5H_4N), 133.8 (2 C, C_5H_4N), 129.0 (1 C, C_5H_4N), 123.3 (1 C, CH=CH) and 121.9 (1 C, CH=CH). IR (cm^{-1}): 2070.6w, 1978.6w and 1900.4s. Calc. for $C_{17}H_{10}N_2O_5W$: C, 40.34; H, 1.99; N, 5.54. Found: C, 40.58; H, 2.02; N, 5.78%.

μ-(*E*)-1,2-Di-4-pyridylethene-bis(pentacarbonylchromium). ^{1}H NMR: δ 8.69 (s, 4 H, C_5H_4N), 7.38 (s, 4 H, C_5H_4N) and 7.25 (s, 2 H, CH=CH). ^{13}C NMR: δ 221.4 (2 C, *trans* CO), 215.0 (8 C, *cis* CO), 156.5 (4 C, C_5H_4N), 144.6 (2 C, C_5H_4N) and 131.3 (4 C, C_5H_4N) and 122.7 (2 C, CH=CH). IR (cm^{-1}): 2068.2w, 1980.6w and 1915.4s. Calc. for $C_{11}H_5CrNO_5$: C, 46.66; H, 1.78; N, 4.95. Found: C, 47.06; H, 1.92; N, 4.95%.

μ-(*E*)-1,2-Di-4-pyridylethene-bis(pentacarbonyltungsten). ^{1}H NMR: δ 8.56 (d, 4 H, $^3J_{H-H} = 6.6$, C_5H_4N), 7.37 (d, 4 H, $^3J_{H-H} = 6.6$ Hz, C_5H_4N) and 7.25 (s, 2 H, CH=CH). ^{13}C NMR: δ 202.7 (2 C, *trans* CO), 199.2 (8 C, *cis* CO), 157.0 (4 C, C_5H_4N), 144.4 (2 C, C_5H_4N), 131.5 (4 C, C_5H_4N) and 123.4 (2 C, CH=CH). IR (cm^{-1}): 2070.6w, 1974.7w and 1903.1s. Calc. for $C_{11}H_5NO_5W$: C, 31.84; H, 1.21; N, 3.38. Found: C, 31.97; H, 1.34; N, 3.45%.

FTIR Measurements

Aliquots of a stock CH_2Cl_2 solution of the hydrogen-bond donors (A–H) were added to solutions of the complexes **1**, **2**, **3** and **4** in CH_2Cl_2 (typically 100 μL, 0.01 M). The donors were diphenylamine, 4-nitrodiphenylamine, pyrazole, imidazole, 2,4,6-trimethylphenol, indole, carbazole and 3,6-dibromocarbazole. The solutions so obtained had a M : A–H ratio in the range 1 : 0.25 to 1 : 10. The FTIR samples were prepared by evaporating the resulting CH_2Cl_2 solutions on a NaCl plate, to obtain an amorphous thin film of the adducts.

Computational details

Calculations have been performed with the GAUSSIAN 94 package of programs.[15] *Ab initio* molecular orbital calculations were made at the Hartree-Fock (HF) level with a 3-21G basis set and with methods based on density functional theory (DFT) using the LanL2DZ basis set.[15] We used Becke's 3 parameter functional (B3)[16] which includes Slater exchange along with corrections involving the gradient of the electron density, and the correlation functional of Lee, Yang and Parr, which includes both local and non-local terms (LYP).[17,18] The parameters are those determined by Becke by fitting to the G1 molecule set.[16b,19]

The geometries of adducts of compounds **3** and **4** with diphenylamine have been completely optimized using HF and DFT methods, respectively, and characterized as minima in the potential energy surface by computing the matrix of second energy derivatives (Hessian matrix). The requested convergence on the density matrix was 10^{-9} atomic units and the threshold value of maximum displacement was 0.0018 Å and that of maximum force was 0.00045 hartree bohr^{-1} using the Berny analytical gradient optimization routine.[20,21]

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