

## The Photochemical Synthesis of $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ in Solution: I.r. Evidence for Co-ordinated Molecular Dihydrogen

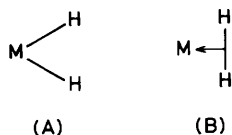
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$[\text{Cr}(\text{CO})_5(\text{H}_2)]$  (**1**) is synthesised by u.v. photolysis of  $[\text{Cr}(\text{CO})_6]$  dissolved in liquid Xe doped with  $\text{H}_2$  at 200 K and the co-ordinated molecular dihydrogen has a  $\nu_{\text{H-H}}$  i.r. band at  $3030\text{ cm}^{-1}$ ;  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  can also be generated photochemically in n-heptane at room temperature under high pressures (100 atm) of  $\text{H}_2$ .

There is considerable interest in the co-ordination of  $\text{H}_2$  by unsaturated transition metal centres, largely because of its relevance to homogeneous catalysis. Particularly intriguing is the question of whether  $\text{H}_2$  will co-ordinate as a dissociated dihydride (A), or as a sideways-bonded molecular dihydrogen group (B). Recently Kubas and co-workers have reported the first isolable complex  $[\text{W}(\text{CO})_3(\text{Pr}^i)_2(\text{H}_2)]$  containing co-ordinated molecular dihydrogen.<sup>1</sup>

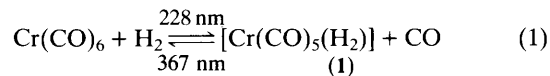


One of the simplest hydrogen complexes of a  $d^6$  metal is  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ , a postulated intermediate in the water-gas shift reaction<sup>2</sup> and the subject of several theoretical studies.<sup>3</sup> I.r. bands in the  $\nu_{\text{C-O}}$  region probably due to  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  were observed<sup>4,5</sup> when  $[\text{Cr}(\text{CO})_6]$  was photolysed in solid Ar matrices doped with  $\text{H}_2$ . However, despite intense effort, no i.r. bands associated with co-ordinated  $\text{H}_2$  in matrix-isolated  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  have been detected and it has proved impossible, so far, to characterize the compound.<sup>5</sup>

In this communication we report a definitive i.r. characterization of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  in liquid xenon solution (hereafter abbreviated to LXe). LXe is now becoming established as a low-temperature solvent for stabilizing reactive or unstable transition metal complexes.<sup>6</sup> In the case of hydrogen complexes, LXe has two important advantages over solid matrices: (i) much longer pathlengths<sup>†</sup> can be used to detect weak

i.r. absorptions; (ii) the solution can be contained in a high-pressure i.r. cell<sup>7</sup> and the hydrogen cannot escape.  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  is surprisingly stable and at the end of this communication we show that the compound has a half-life of  $\sim 25$  s in n-heptane solution at room temperature under 100 atm (10 MPa) pressure of  $\text{H}_2$ . In the following communication,<sup>8</sup> time-resolved i.r. spectroscopy is used to study quantitatively the formation and decomposition of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  in room-temperature solution.

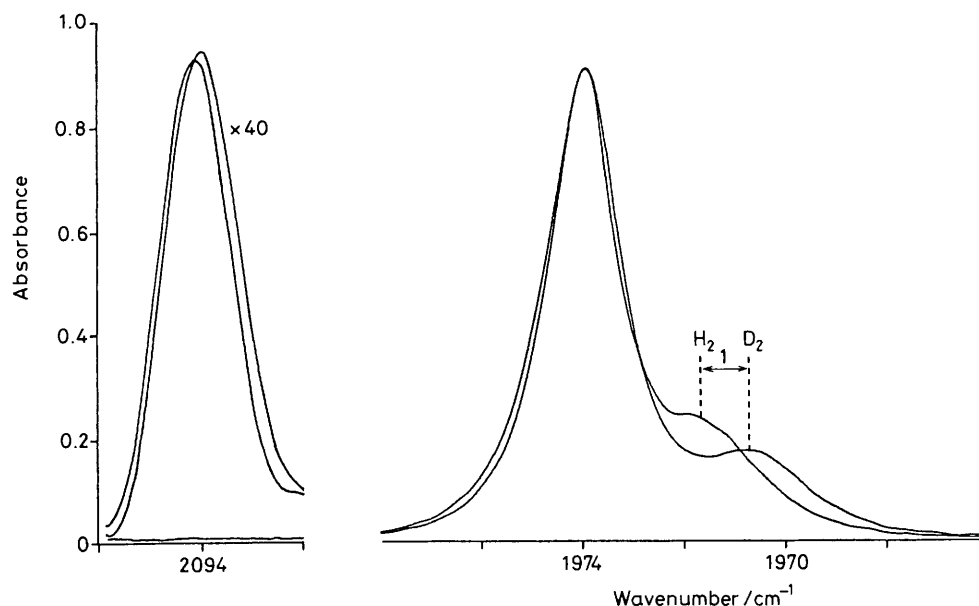
U.v. photolysis of  $[\text{Cr}(\text{CO})_6]$  dissolved in LXe doped with  $\text{H}_2$  leads to formation of a new carbonyl-containing species,<sup>‡</sup> which is not observed in the absence of  $\text{H}_2$ . This species (**1**) has a broad near-u.v. absorption at  $\sim 370$  nm and is destroyed by u.v. light of this wavelength.



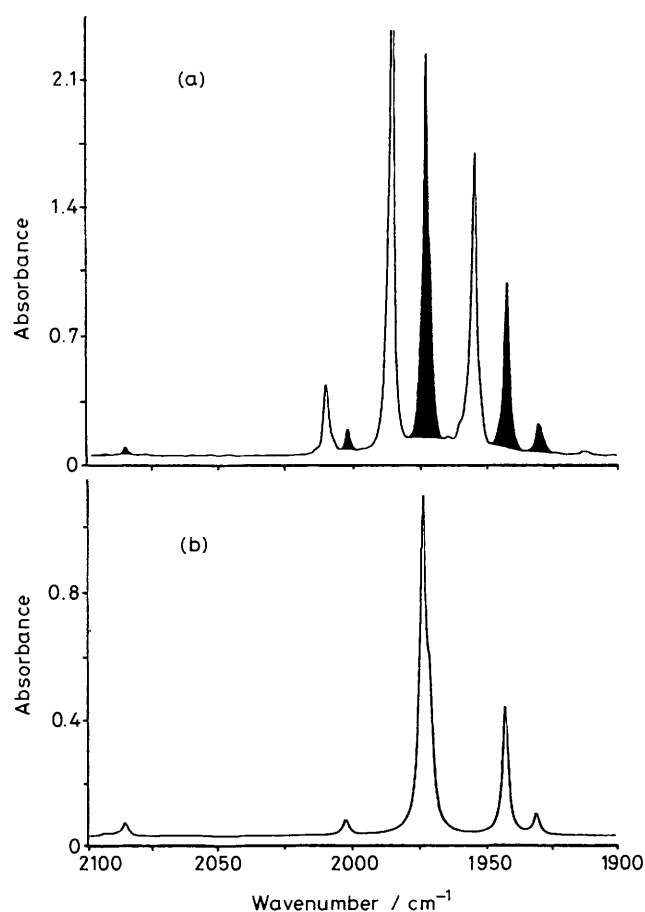
We now show that (**1**) is  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ , with co-ordinated molecular dihydrogen. Complex (**1**) has three i.r. absorptions in the  $\nu_{\text{C-O}}$  region: one weak high-frequency band and two stronger overlapping bands. Complex (**1**) can be prepared using either  $\text{H}_2$  or  $\text{D}_2$  and there is a small but reproducible

<sup>†</sup> Our liquid cell<sup>7</sup> has a path length of 2.7 cm compared to  $<1$  mm, the usual thickness of a matrix.

<sup>‡</sup> All spectra were recorded with a Nicolet MX-3600 FT-IR interferometer with 16K data points ( $2\text{ cm}^{-1}$  resolution) or 32K data points ( $0.7\text{ cm}^{-1}$  resolution). U.v. photolysis was with high pressure Hg arc or Cd lamp (228 nm). Xe and  $\text{H}_2$  (BOC Research Grade), and  $\text{D}_2$  (99%, BDH), were used.  $\text{H}_2$  or  $\text{D}_2$  up to a pressure of 15 atm were added above the LXe.



**Figure 1.** Superimposed i.r. absorption spectra of (1) ( $\sim 10^{-5}$  M) obtained by photolysis of  $[\text{Cr}(\text{CO})_6]$  in LXe doped with  $\text{H}_2$  or  $\text{D}_2$ , showing the shift in the lowest frequency band between  $\text{H}_2$  and  $\text{D}_2$ . Note the  $\times 40$  expansion of the absorbance of the highest frequency band. {The origin of  $\nu_{\text{H-H}}/\nu_{\text{C-O}}$  coupling in  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  will be discussed in detail in a later publication.}



**Figure 2.** (a) I.r. absorption spectra obtained after u.v. photolysis of  $[\text{Cr}^{12}\text{CO}_5(^{13}\text{CO})]$  in LXe, doped with  $\text{H}_2$ , at  $-74^\circ\text{C}$ . Bands coloured black are due to the hydrogen-containing photoproduct (1) and uncoloured bands are those of unphotolysed  $[\text{Cr}^{12}\text{CO}_5(^{13}\text{CO})]$ . (b) Spectrum predicted for a  $^{13}\text{CO}$  enriched  $\text{C}_{4v}$   $\text{Cr}(\text{CO})_5$  moiety (see Table 1).

**Table 1.** Wavenumbers (in  $\text{cm}^{-1}$ ) of observed and calculated C–O stretching bands of  $^{13}\text{CO}$  enriched  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ .

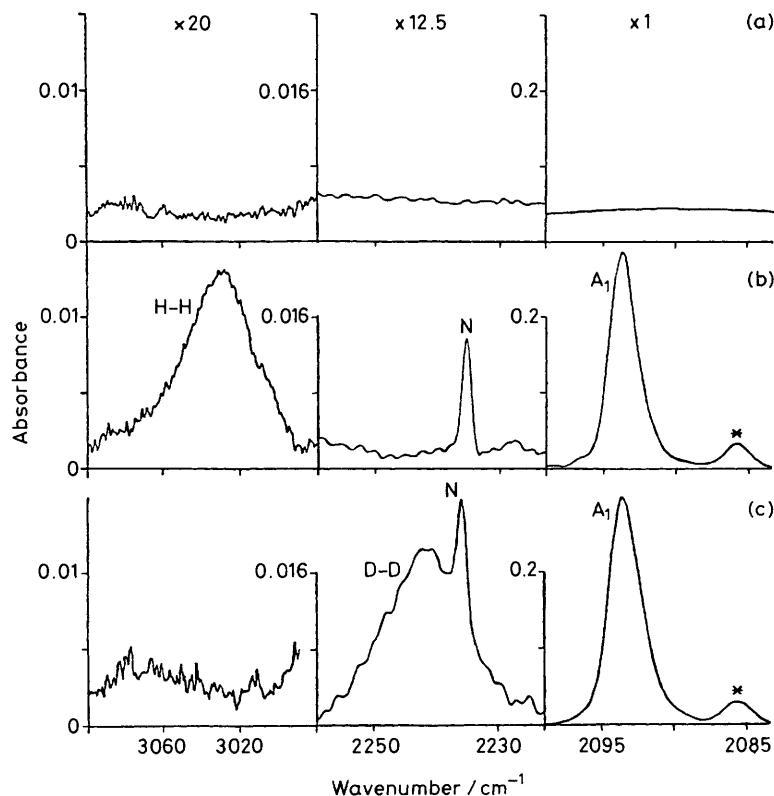
Observed	Calculated <sup>a</sup>	Assignment <sup>b</sup>
2094.0	2093.8	0
2086.1	2086.2	$1_{\text{eq}}$
2002.6	2002.6	$1_{\text{eq}}$
1974.3	1974.2	0, $1_{\text{ax}}$ , $1_{\text{eq}}$
1971.9	{ 1971.7	$1_{\text{eq}}$
	{ 1971.5	0
1943.4	1943.5	$1_{\text{eq}}$
1930.9	1931.4	$1_{\text{ax}}$

<sup>a</sup> Calculated for a  $\text{C}_{4v}$   $\text{Cr}(\text{CO})_5$  geometry. Force constants<sup>11</sup> ( $\text{N m}^{-1}$ )  $k_{\text{ax}}$  1593.63,  $k_{\text{eq}}$  1631.87,  $k_{\text{ax,eq}}$  32.28,  $k_{(\text{eq,eq-cis})}$  29.24,  $k_{(\text{eq,eq-trans})}$  57.30. Band intensities in Figure 2 were calculated assuming a Lorentzian line shape (full width at half-maximum  $2.8 \text{ cm}^{-1}$ ) an axial-equatorial bond angle of  $90^\circ$ , and a dipole derivative ratio of 1. <sup>b</sup> Molecules abbreviated as follows: 0,  $[\text{Cr}^{12}\text{CO}_5(^{13}\text{CO})]$ ;  $1_{\text{eq}}$ ,  $[\text{Cr}^{12}(\text{CO})_4(^{13}\text{CO}_{\text{equatorial}})]$ ;  $1_{\text{ax}}$ ,  $[\text{Cr}^{12}(\text{CO})_4(^{13}\text{CO}_{\text{axial}})]$ .

shift,  $\sim 1 \text{ cm}^{-1}$ , between the positions of the lowest frequency  $\nu_{\text{C-O}}$  band in the  $\text{H}_2$  and  $\text{D}_2$  experiments; see Figure 1. This shift is not a solvent effect, because no other  $\nu_{\text{C-O}}$  bands are appreciably affected, and is similar to shifts reported for other hydrogen-containing species.<sup>1,9</sup> Thus (1) contains hydrogen.

The three  $\nu_{\text{C-O}}$  bands are consistent with a  $\text{Cr}(\text{CO})_5$  moiety with local  $\text{C}_{4v}$  symmetry ( $2a_1 + e$ ). This assignment can be confirmed by generating (1) from  $[\text{Cr}^{12}\text{CO}_5(^{13}\text{CO})]$ ,<sup>10</sup> where  $^{13}\text{CO}$  substitution provides four extra  $\nu_{\text{C-O}}$  bands. Figure 2 shows that there is excellent agreement between the observed spectrum (bands coloured black) and the spectrum predicted<sup>11</sup> for a  $\text{C}_{4v}$   $\text{Cr}(\text{CO})_5$  moiety, Figure 2(b). The frequencies and C–O factored force constants are summarized in Table 1.

Thus (1) contains hydrogen and  $\text{Cr}(\text{CO})_5$  but how is the hydrogen bonded? Complex (1) has C–O factored force constants very similar to other  $[\text{Cr}(\text{CO})_5\text{L}]$  complexes, e.g.  $[\text{Cr}(\text{CO})_5(\text{N}_2)]$ ,<sup>12</sup> suggesting that the Cr is still in the zero oxidation state. Metal hydridocarbonyls usually have  $\nu_{\text{M-H}}$



**Figure 3.** I.r. spectra which provide the principal evidence for co-ordinated molecular dihydrogen in  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  (1). (a) and (b) Spectra taken before and after u.v. photolysis of  $[\text{Cr}(\text{CO})_6]$  in LXe +  $\text{H}_2$  at  $-74^\circ\text{C}$ . (c) Spectra obtained after u.v. photolysis of  $[\text{Cr}(\text{CO})_6]$  in LXe +  $\text{D}_2$ . The bands are labelled as follows: H-H,  $\nu_{\text{H-H}}$  of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ ; D-D,  $\nu_{\text{D-D}}$  of  $[\text{Cr}(\text{CO})_5(\text{D}_2)]$ ; N,  $\nu_{\text{N-N}}$  of  $[\text{Cr}(\text{CO})_5(\text{N}_2)]$  formed by reaction with traces of  $\text{N}_2$  impurity,  $\sim 1\text{ p.p.m.}$ , in LXe;  $\text{A}_1$ , high-frequency  $\nu_{\text{C-O}}$  of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  and  $[\text{Cr}(\text{CO})_5(\text{D}_2)]$ ,  $\sim 10^{-4}\text{ M}$  (cf. Figure 1); \*,  $\nu_{\text{C-O}}$  of natural abundance  $^{13}\text{C}$   $[\text{Cr}(^{12}\text{CO})_4(^{13}\text{CO})(\text{H}_2)]$  (cf. Figure 2 and Table 1) overlapped with the much weaker  $\nu_{\text{C-O}}$  band of  $[\text{Cr}(\text{CO})_5(\text{N}_2)]$ . Note that the bands of  $[\text{Cr}(\text{CO})_5(\text{N}_2)]$  have been partially removed by computer subtraction. Note also that although the wavenumber and absorbance scales in each of the spectral regions are different, the integrated absorption intensities of the three bands  $\nu_{\text{H-H}}$ ,  $\nu_{\text{D-D}}$ , and  $\nu_{\text{C-O}}$  are comparable.

bands<sup>13</sup> in the region  $2200\text{--}1800\text{ cm}^{-1}$ , while the tungsten dihydrogen complex has a reported<sup>1</sup>  $\nu_{\text{H-H}}$  band at  $2690\text{ cm}^{-1}$ . Thus, if (1) contains co-ordinated molecular dihydrogen, one would expect a  $\nu_{\text{H-H}}$  band at a frequency  $\gg 2000\text{ cm}^{-1}$ . Such a band would necessarily be weak and one is greatly aided in the search for the band by the absence of i.r. bands due to the LXe solvent. Further, the intensity of the band must show the same growth and decay pattern as the strong  $\nu_{\text{C-O}}$  bands of (1) during photolysis and the band must display a large wavenumber shift on deuteration.

Figure 3 illustrates a broad band, at  $3030\text{ cm}^{-1}$ , which fulfils these conditions. On deuteration, the band shifts to  $2241\text{ cm}^{-1}$ . This shift is slightly less than predicted for an isolated  $\text{H}_2$  diatomic oscillator but is not unreasonable in view of the coupling to  $\nu_{\text{C-O}}$  vibrations, cf. Figure 1. We assign these bands to the H-H and D-D stretches of co-ordinated molecular dihydrogen in  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ . We also observe a number of weaker absorptions due to low frequency deformations and combination bands. The detailed assignment of these bands will be discussed elsewhere.

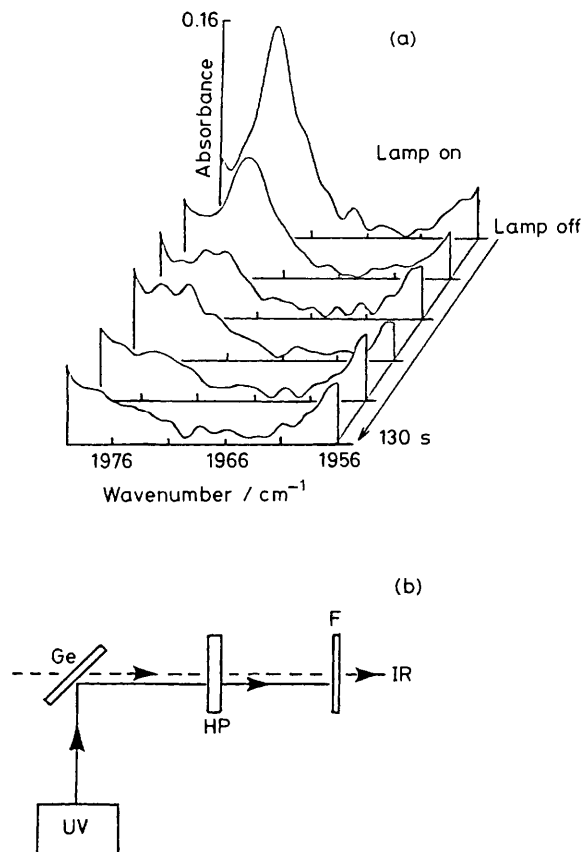
$[\text{Cr}(\text{CO})_5(\text{H}_2)]$  is quite stable up to the highest temperature,  $-35^\circ\text{C}$ , attainable in our present LXe cell,<sup>7</sup> even when most of the excess  $\text{H}_2$  has been pumped off. Attempts to record the  $^1\text{H}$  n.m.r. spectrum of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  in LXe are now under way. This high thermal stability of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  in LXe, and the flash photolysis results reported in a separate communication<sup>8</sup> prompted us to generate  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  in room-temperature solution under  $\text{H}_2$  pressure. With *continuous* u.v.

irradiation of  $[\text{Cr}(\text{CO})_6]$  in n-heptane with 100 atm  $\text{H}_2$  pressure we observed a band at  $1974\text{ cm}^{-1}$ , identical in frequency to that found during flash photolysis<sup>8</sup> of  $[\text{Cr}(\text{CO})_6]/\text{H}_2$ .§ This band decayed with  $t_{1/2} \sim 25\text{ s}$  when the u.v. lamp was switched off, Figure 4(a).¶ When the  $\text{H}_2$  was vented from the cell, the band was no longer produced by u.v. irradiation. Thus, the band can be reasonably assigned to  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ . Even with our rather unfavourable irradiation optics, Figure 4(b), it was possible to maintain a steady-state concentration of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ ,  $>5\%$  of that of  $[\text{Cr}(\text{CO})_6]$ , for periods of longer than 15 min.

Our results provide strong evidence that  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  contains co-ordinated molecular dihydrogen. Thus, as in the Kubas complex, co-ordination of  $\text{H}_2$  by an unsaturated  $\text{d}^6$  metal centre does not appear to require dissociation of the H-H bond, as predicted by simple bonding models.<sup>3,14</sup> The

§ A very weak i.r. band,  $1968\text{ cm}^{-1}$ , has previously been attributed to  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  in low temperature hydrocarbon solution (M. Remy-Wyart, Thesis, Université Libre de Bruxelles, 1976, p. 78). The difference between this work and ours may be a combination of solvent and temperature effects.

¶ The high pressure cell [W. Rigby, R. Whyman, and K. Wilding, *J. Phys. E. (Sci. Instrum.)*, 1970, 3, 572] could not be stirred very effectively and the  $\text{H}_2$  dissolved in the n-heptane (BDH AnalaR) may well have not been completely equilibrated with the high-pressure gas. Cell volume was  $\sim 50\text{ ml}$ ; optical path length was  $\sim 1\text{ mm}$ .



**Figure 4.** (a) I.r. spectra showing the band due to  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  (overlapping e and  $a_1$   $\nu_{\text{C-O}}$  modes) produced by continuous u.v. irradiation of  $[\text{Cr}(\text{CO})_6]$ ,  $10^{-3}$  M n-heptane solution at 25 °C under 100 atm pressure of  $\text{H}_2$ . When the lamp is switched off, the band decays because of the thermal decomposition of  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$ . Each spectrum was recorded in 26 s. (b) Schematic optical diagram for recording high pressure spectra. The labelled components are as follows: IR, FT-IR interferometer beam; UV, High-pressure Hg arc with quartz lens; Ge, Germanium plate acting as a u.v. mirror; HP, High-pressure cell; F, i.r. bandpass filter to block u.v. light.

synthesis of hydrogen complexes by photolysis of metal carbonyls in LXe doped with  $\text{H}_2$  appears to be quite general. We have recently observed the production of  $[(\eta^4\text{-C}_4\text{H}_6)\text{-Fe}(\text{CO})_2\text{H}_2]$ ,  $[\text{Co}(\text{CO})_2(\text{NO})\text{H}_2]$ , and  $[\text{Fe}(\text{CO})(\text{NO})_2\text{H}_2]$  and, when we have established how  $\text{H}_2$  is bonded in these compounds, we shall be able to test current bonding models<sup>3,14</sup> more rigorously.

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