Organometallics **1996,** *15,* 1451−1456

IR-Active Organometallic pH Probes

Christopher E. Anson,[†,‡] Tina J. Baldwin,[‡] Colin S. Creaser,*[,†] Mark A. Fey,[‡] and
G. Richard Stephenson*[,‡]

*Department of Chemistry and Physics, Nottingham Trent University,
Nottingham, NG11 8NS, U.K., and the School of Chemical Sciences,
University of East Anglia, Norwich, NR4 7TJ, U.K.*

Received July 31, 1995[⊗]

Tricarbonylmetal π-complexes of unsaturated organic ligands containing CO_2H, OH, and NH_2 substituents are used as FTIR-readable molecular probes of solution pH. Wavenumber shifts in the ν^{sym}(CO) and ν^{asym}(CO) bands in the FTIR spectra of the complexes $[(\eta^4\text{-}CH_3CH{=}CHCH{=}CHCO_2H)Fe(CO)_3]$, $[(\eta^4\text{-}CH_3CH{=}CHCH{=}CHCO_2H)Fe(CO)_2(PPh_3)]$, $[(\eta^6\text{-}C_6H_5CO_2H)Cr(CO)_3]$, $[(\eta^6\text{-}o\text{-}C_6H_4(CO_2H)_2)Cr(CO)_3]$, $[(\eta^6\text{-}C_6H_5NH_2)Cr(CO)_3]$, $[(\eta^6\text{-}p\text{-}CH_3C_6H_4OH)Cr(CO)_3]$, and $[(\eta^6\text{-}p\text{-}CH_3O_2CC_6H_4OH)Cr(CO)_3]$, resulting from deprotonation or protonation of the complexes, can be correlated with the pH of the solution, enabling straightforward spectroscopic readout of pH. It is shown that, by appropriate choice of pH-sensitive functional group, a complex can be selected to respond over a particular pH range and that the pH response can be fine-tuned by the presence of other substituents on the organic unit. The narrow bandwidths of the ν(CO) vibrational modes allow the simultaneous use of more than one such complex in a solution. This approach, which we term the use of "dual-sensor" systems, has several advantages over single sensors, and its potential in the analysis of multianalyte systems is described.

Introduction

Spectroscopically based pH sensors have been widely investigated[1] because of their importance in biological studies. While pH-sensing molecules with readout based on UV−visible absorption spectroscopy have been in use for many years, there have been more recent developments of sensors based either on luminescence[2] or on fluorescent photoinduced electron transfer spectroscopies.[3] In general, these optical sensors combine a group or substituent that can be either protonated or deprotonated (the sensing group) with a spectroscopically active chromophore (the reporting group); these two units may be directly bonded or connected, physically and electronically, through a conductive linking group. Scherson[4] has used Fourier transform infrared reflection absorption spectroscopy (FTIRRAS) to monitor the pH of solutions in thin-layer electrochemical cells, measuring bands arising from carbonate, bicarbonate, acetate, and acetic acid species. However, the development of molecular sensors involving IR-active reporting groups otherwise has received little attention to date, mainly as a result of the perceived lack of sensitivity of infrared spectroscopy and the low intrinsic intensity of many IR-active vibrational transitions.

In contrast to the often broad and weak absorption bands of organic molecules, the ν(CO) vibrational modes of organometal−carbonyl complexes give rise to very strong absorptions in the 2100−1800 cm^{-1} region of the infrared spectrum.[5] The high intrinsic intensities of such modes, coupled with recent advances in the technology of FTIR spectroscopy, have resulted in an increase in sensitivity[6] that is sufficient for infrared-based sensing molecules to be used in situations where luminescence and UV−visible absorbance-based sensors currently are employed. The absorptions from such ν(CO) modes offer substantial benefits when employed in spectroscopic sensing measurements. First, they occur in a region of the spectrum that is generally free from other interfering absorptions, even in aqueous solutions and biological systems.[7] Secondly, the IR bands are very narrow relative to the overall spectral width, so that not only can their wavenumbers and small shifts be determined precisely[8a] but more than one organometal carbonyl complex can be examined spectroscopically in a single sample.[8b]

The effects of a coordinated tricarbonylchromium unit on the pK_a of benzoic acid[9,10] and phenols[10,11] and on the pK_b of aniline[10] have been investigated, but only one previous study[12] has considered the converse effect of deprotonation on the spectroscopic response of the tricarbonylchromium unit. Unstable (η^6-1,4-dihy-

---

[†] Nottingham Trent University.

[‡] University of East Anglia.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1996.

(1) Nuccitelli, R., Deamer, D. W., Eds. *Intracellular pH: Its Measurement, Regulation and Utilisation in Cellular Functions*; Liss: New York, 1982.

(2) Leiner, M. J. P. *Anal. Chim. Acta* **1990**, *255*, 209−222.

(3) (a) Bryan, A. J.; de Silva, A. P.; de Silva, S. A.; Rupasinghe, R. A. D. D.; Sandanayake, K. R. A. S. *Biosensors* **1989**, *4*, 169. (b) de Silva, A. P.; de Silva, S. A.; Dissanayake, A. S.; Sandanayake, K. R. A. S. *J. Chem. Soc., Chem. Commun.* **1989**, 1148−1150. (c) Bissell, R. A.; de Silva, A. P. *J. Chem. Soc., Chem. Commun.* **1991**, 1054−1056.

(4) Bae, I. T.; Scherson, D. A.; Yeager, E. B. *Anal. Chem.* **1990**, *62*, 45−49.

(5) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(6) Salmain, M.; Vessieres, A.; Jaouen, G.; Butler, I. S. *Anal. Chem.* **1991**, *63*, 2323−2329.

(7) Anson, C. E.; Creaser, C. S.; Egyed, O.; Fey, M. A.; Stephenson, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 39−40.

(8) (a) Creaser, C. S.; Fey, M. A.; Stephenson, G. R. *Spectrochim. Acta* **1994**, *50A*, 1295−1299. (b) Varenne, A.; Vessières, A.; Salmain, M.; Brossier, P.; Jaouen, G. *Immunoanal. Biol. Spec.* **1994**, *9*, 205−214.

(9) Nicholls, B.; Whiting, M. C. *J. Chem. Soc.* **1959**, 551−556.

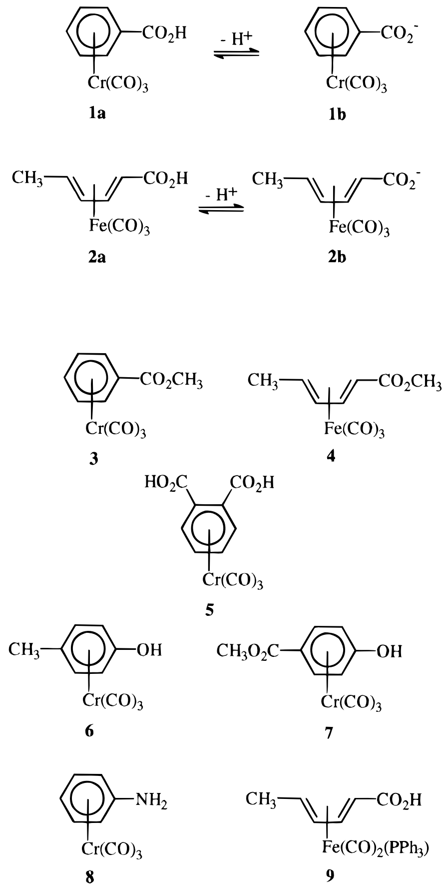
(10) Fischer, O. F.; Ofele, K.; Essler, H.; Frohlich, W.; Mortensen, J. P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763−2772.

(11) Wu, A.; Biehl, E. R.; Reeves, P. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 449−451.

(12) Schumann, H.; Arif, A. M.; Richmond, T. G. *Polyhedron* **1990**, *9*, 1677−1681.

0276-7333/96/2315-1451$12.00/0

Scheme 1



droxyarene)Cr(CO)$_3$ complexes have been prepared in solution,[12,13] and substantial variations in the wavenumbers of the ν(CO) modes in the resulting solutions were attributed by Richmond[12] to differing degrees of deprotonation of the product, depending on the reaction conditions used. However, at least some of this observed variation may have arisen from solvent effects, which are likely to be considerable for complexes such as these.[8] In addition, no attempt was made to correlate the variations of ν(CO) with solution pH.

In this paper, we describe pH-sensing molecules that are based on the combination of a Cr(CO)$_3$, Fe(CO)$_3$, or Fe(CO)$_2$(PPh$_3$) IR-active reporting group and a pH-sensitive group (CO$_2$H, OH, or NH$_2$), placed in electronic communication within an organometallic π-complex (Scheme 1). We show that variations in ν(CO) with pH reported here specifically result from protonation or deprotonation of the sensing groups and not from simple solvent effects. This work represents a significant development from our previously reported[8] studies in which organometal–carbonyl complexes were used as probes of the more general solvent environment and shows that such complexes can be used as sensors for the detection of a *specific* analyte.[14] We have also recently shown[15] that tricarbonylchromium complexes of benzocrown ethers can be used as molecular sensors for alkali metal cations. Organometal carbonyl complexes have been used previously as molecular sensors for small molecules such as CO, but changes in electrochemistry rather than in the IR spectrum were used for readout purposes.[16]

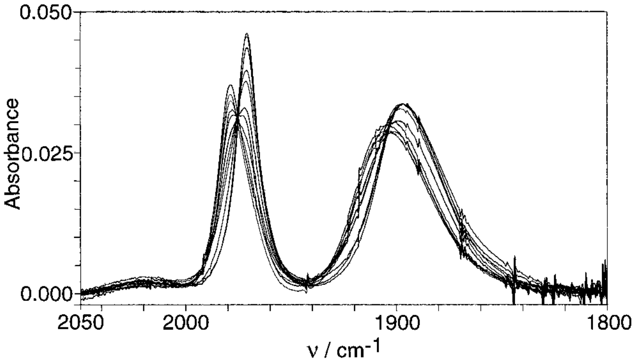


Figure 1. FTIR spectra in the 2050–1800 cm^{-1} region of (η^6-1-carboxybenzene)Cr(CO)$_3$ (**1a**) in buffer solutions over the pH range 2.1–6.0.

Results and Discussion

Single Sensors. The initial objective was to investigate whether changes in ionization of the sensing group could be read out spectroscopically from changes in the wavenumber of ν(CO) modes of the organometal–carbonyl reporting group. Small aliquots of a methanol solution of the complex **1a** were added to each of a range of aqueous buffer solutions to give a final solvent composition of 91% water/9% methanol, and the FTIR spectrum of each solution was measured. The solubilities of the complexes used in this study were such that it was necessary to add them to the buffer solutions predissolved in methanol. This was not a problem here as the purpose of this study was to demonstrate the principle and the practicality of the method. Provided that the same small proportion of methanol is added to a solution of unknown pH as to the known buffer solutions, the unknown pH can be read directly from a plot of ν(CO) against buffer pH. In any case, it was found that the addition of methanol to the buffer solutions did not significantly perturb the pH of the buffers. It would, of course, be a straightforward matter to prepare similar organometal–carbonyl complexes bearing substituents rendering them water-soluble, if it was desired to use the method to investigate the pH of purely aqueous systems.

The spectra are shown in Figure 1. At pH 2.1, two bands are observed in the 2100–1800 cm^{-1} region of the spectrum; the sharp band at 1979.0 cm^{-1} is assigned to the symmetric ν(CO) mode, and the rather broader band system at 1904.9 cm^{-1} is assigned to the two overlapped quasi-degenerate components of the antisymmetric ν(CO) mode, of the undissociated complex **1a**. As the pH increases, the wavenumbers of these bands decrease and reach limiting values of 1971.0 and 1896.9 cm^{-1}, respectively, at pH 6.0. We assign these two new bands to the symmetric and antisymmetric ν(CO) modes

---

(13) Wright, M. E. *J. Organomet. Chem.* **1989**, *376*, 353–358.

(14) It is possible that readily coordinated cations such as Li$^+$ might interact with the terminal oxygen atoms of the carbonyl ligands, shifting the wavenumbers of the ν(CO) modes and thus interfering with the spectroscopic sensing of pH. The ν(CO) modes of the complex (η^6-benzo-12-crown-4)Cr(CO)$_3$ in methanol solution have been found[15b] not to be shifted significantly by concentrations of Li$^+$ up to 1 mol dm^{-3}, so that such cations are unlikely to be a source of interference here.

(15) (a) Anson, C. E.; Creaser, C. S.; Stephenson, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2175–2176. (b) Anson, C. E.; Creaser, C. S.; Stephenson, G. R. Manuscript in preparation.

(16) Mirkin, C. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 8596–8597. See also references listed in Lorkovic, I. M.; Wrighton, M. S.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6220–6228.

Table 1. Spectroscopic Data for Complexes 1, 2, and 5 at Different pH Values[a]

	complex **1**		complex **2**		complex **5**	
pH	ν^{sym}(CO)	ν^{asym}(CO)	$A_{2059.4}/A_{2050.7}$	ν^{asym}(CO)	$A_{1986.1}/A_{1970.7}$	ν^{asym}(CO)
2.1	1979.0	1904.6	4.32	1994.1	5.58	1919.0
2.2	1979.0	1904.0				
2.5	1978.9	1903.2				
2.7	1978.2	1902.3				
2.9	1975.5	1901.2	3.92	1994.1	4.23	1917.2
3.1	1972.4	1899.8	3.73	1993.9		
3.5	1971.6	1898.4	3.56	1993.6		
3.7	1971.3	1897.6	3.27	1993.1		
4.0	1971.2	1897.4	2.37	1991.6		
4.3			1.67	1988.5	1.65	1913.2
4.5			1.13	1986.4	1.49	1911.4
4.8			0.65	1985.6	0.85	1904.8
5.0	1971.0	1897.0	0.47	1985.3	0.78	1902.9
5.3			0.32	1985.0	0.55	1901.2
5.6			0.21	1984.7	0.42	1899.9
6.0	1971.0	1896.9			0.24	1898.5
6.3			0.10	1984.4		
6.8			0.06	1984.2		
7.0					0.11	1897.5

[a] All ν(CO) are in cm^{-1}. A_x is the absorbance value at x cm^{-1}.

of the dissociated η^6-benzoate anion **1b**. In a complex such as (η^6-carboxybenzene)tricarbonylchromium(0)[9] (**1a**), deprotonation of the carboxylic acid substituent would be expected to increase the electron density on the organochromium moiety and so increase the extent of electron back-donation from the metal to the CO π^*-antibonding orbitals. In this way, deprotonation of the complex should lead to a lowering in wavenumber of the ν(CO) modes, an effect that allows the use of these vibrational modes to give a spectroscopic readout defining the pH of a solution. The higher wavenumber band shows a well-defined isosbestic point at 1975.7 cm^{-1}; the lower wavenumber band also shows an isosbestic point at *ca.* 1905 cm^{-1}, which is rather less well defined as the baseline tends to drift slightly in this region of the spectrum near the cutoff of the InSb detector. These observations indicate that two species are present in the solutions, the relative concentrations of which change with pH. This was confirmed by curve-fitting analysis of the spectra at intermediate pH values; these could be decomposed into superpositions of the spectra of **1a** and **1b**. It may be noted that the slight baseline drift noted earlier will not significantly affect the accuracy of the data, since we are primarily concerned with the wavenumber of the band maximum (Table 1).

The wavenumbers of the band maxima of the composite ν^{sym}(CO) and ν^{asym}(CO) features are plotted against pH in Figure 2. These plots enable the readout of the solution pH from the spectroscopic data. The apparently sharper response of the ν^{sym}(CO) band to pH is a consequence of the narrower bandwidth relative to the shift in wavenumber between the bands from **1a** and **1b**. By allowing for the difference in the absorbtivities for the bands of **1a** and of **1b** (those of **1b** are the stronger), the pK_a of **1a** in this solvent mixture can be estimated from Figure 2 as *ca.* 2.9. This can be compared with 4.21, the pK_a of uncomplexed benzoic acid in water;[17] the decrease in pK_a by 1.3 pH units upon complexation by tricarbonylchromium is in line with previous studies.[9,10]

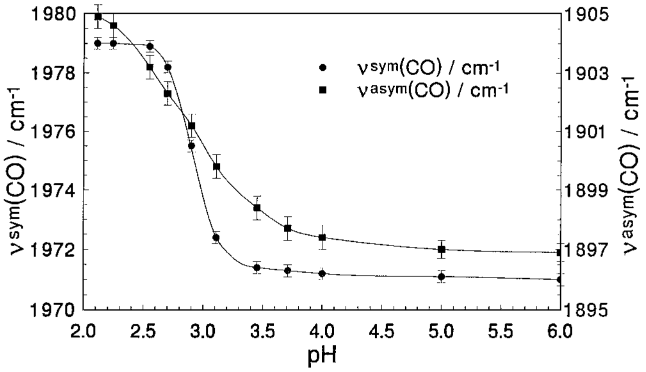


Figure 2. ν^{sym}(CO) and ν^{asym}(CO) for (η^6-1-carboxybenzene)Cr(CO)$_3$ (**1a**) plotted against pH.

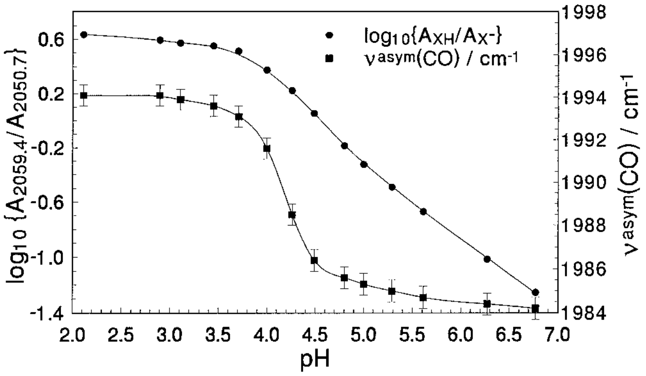


Figure 3. log$_{10}$($A_{2059.4}/A_{2050.7}$) and ν^{asym}(CO) for (η^4-1-carboxy-1,3-pentadiene)Fe(CO)$_3$ (**2a**) plotted against pH, where $A_{2059.4}$ and $A_{2050.7}$ are the absorbances at 2059.4 and 2050.7 cm^{-1} (ν^{sym}(CO) of **2a** and **2b**), respectively.

FTIR spectra of the complex tricarbonyl(η^4-1-carboxy-1,3-pentadiene)iron(0) (**2a**) were also measured over a range of pH values. Results were obtained that were similar to those from the chromium complex, with comparable wavenumber shifts being observed upon deprotonation and isosbestic points again indicating differing relative concentrations of two species in solution. Thus, bands at 2059.4 and 1994.1 cm^{-1} at pH 2.1, assigned to **2a**, were replaced at pH 6.8 by bands at 2050.7 and 1984.2 cm^{-1}, assigned to **2b**. The wavenumber of the composite ν^{asym}(CO) band can again be plotted against pH, as in Figure 3. However, the separate ν^{sym}(CO) bands from **2a** and **2b** could be resolved at intermediate pH values, and so a plot of the wavenumber of the overlapped band maximum would not be useful for the determination of the solution pH, since it would have an apparent discontinuity at the pH at which the bands from **2a** and **2b** have equal intensity. An alternative approach was necessary to obtain pH information from the ν^{sym}(CO) band in this case. If the ν^{sym}(CO) bands of **2a** and **2b** were totally non-overlapping, then the ratio of the absorbances of the bands would be directly proportional to their relative concentrations, and a plot of log$_{10}$[A(**2a**)/A(**2b**)] against pH would give a straight line. In practice, the bands do overlap, but a plot of log$_{10}$($A_{2059.4}/A_{2050.7}$) against pH, also shown in Figure 3, does give a convenient readout of solution pH, from which the pK_a for **2a** can be estimated as 4.2.

To establish that these effects result from the specific sensing of pH by the CO_2H moieties in complexes **1** and **2**, and not from simple solvent effects, the FTIR spectra of the corresponding ester complexes **3** and **4** were also measured. Over the same pH range, the wavenumber

---

[17] Nims, L. F. *J. Am. Chem. Soc.* **1936**, *58*, 987.

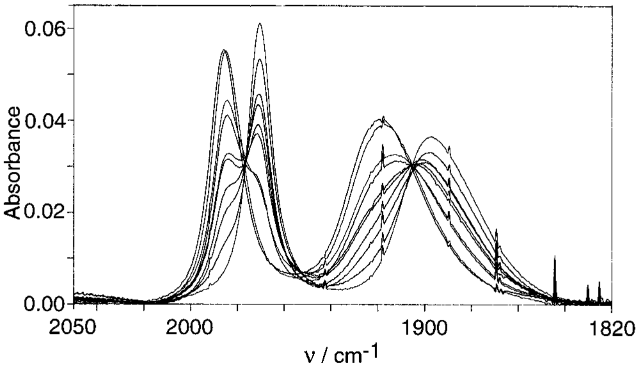


Figure 4. FTIR spectra in the 2050−1820 cm^{-1} region of (η^6-1,2-dicarboxybenzene)Cr(CO)$_3$ (**5**) in buffer solutions over the pH range 2.1−7.0.

shifts of the ν(CO) modes were very much smaller than those for the acid complexes (e.g., ≤0.2 cm^{-1} for **4**) and did not show the sigmoidal responses seen in Figure 2. There was also no evidence for the presence of more than one species in solution, as would be expected for a system where the complex cannot respond directly to pH within the range examined and only nonspecific solvent effects can be operative. This confirms that the spectroscopic effects found for **1** and **2** were responses to the specific sensing of pH by changes in ionization of the CO$_2$H substituents of the complexes.

FTIR spectra of the complex (η^6-1,2-dicarboxybenzene)tricarbonylchromium(0) (**5**) over the pH range 2−7 are shown in Figure 4. It was anticipated that the sequential deprotonation of the two carboxylic acid groups would increase the useful pH range for the complex, as the pK_a values for the uncomplexed acid in aqueous solution have been reported[18] as 2.95 and 5.41. However, it is clear from the spectra that only two species are observed over this pH range, and no further change in the spectra was observed up to pH 11. Given the values of pK_a for the uncomplexed acid and the expected decrease in pK_a upon complexation (*vide supra*), it is probable that it is the second deprotonation that is being observed, with the first occurring with a pK_a below 2. The spectral data were treated in the same way as for complex **2**. The bands corresponding to ν^{sym}(CO) for the singly and doubly deprotonated forms of **5** are well resolved, at 1986.1 and 1970.7 cm^{-1}; the wavenumber shift between them is rather greater than that for **1** and **2**. A plot of $\log_{10}(A_{1986.1}/A_{1970.7})$ against pH provides readout over the pH range 2−7, while ν^{asym}(CO) plotted against pH also yields a spectroscopic readout of solution pH over the pH range 2.0−6.5. Over the pH range 2−3, complex **5** is present mainly as the monoanion and thus can be considered as a complex of benzoic acid with a deprotonated carboxylate substituent in the *ortho* position. The pK_a for the observed deprotonation to the dianion, 4.6, can be compared with the pK_a of **1a**, 2.9. Clearly the substituent on the ring has shifted the useful pH range of **5** upward by *ca.* 1.5 pH units, demonstrating the possibility of tuning the pH response of a complex by introducing appropriate substituents onto the organic unit.

To access different pH ranges, complexes with other ionizable functional groups were studied. The FTIR spectra of two tricarbonylchromium complexes of 4-substituted phenols, **6** and **7**, were measured over a range of pH values. The pK_a values of the two complexes in 50% aqueous ethanol have been reported[11] as 7.32 and 6.40, respectively. The FTIR spectra of complex **7**, over the pH range 2−9, are shown in Figure 5. The wavenumber shifts upon deprotonation are larger than those seen for the previous complexes, presumably a result of the site of deprotonation being fewer bonds away from the tricarbonylmetal unit. The spectroscopic data were processed in the same way as for **2a** and **5**, and pK_a values for **6** and **7** were estimated at 6.7 and 5.2, respectively, giving an additional example of tuning the response of a pH probe molecule by varying the organic substituents. The pK_a values are lower than those previously reported[11] as a result of the higher water: alcohol ratio of the solutions used here (Table 2).

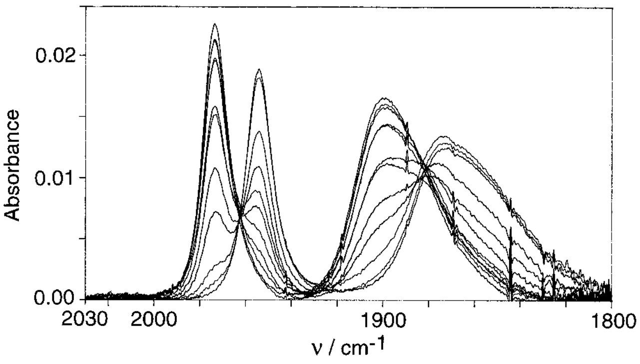


Figure 5. FTIR spectra in the 2030−1800 cm^{-1} region of (η^6-1-(methylcarboxy)-4-hydroxybenzene)Cr(CO)$_3$ (**7**) in buffer solutions over the pH range 2.1−9.3.

Table 2. Spectroscopic Data for Complexes 6 and 7 at Different pH Values[a]

	complex **6**		complex **7**	
pH	$A_{2059.4}/A_{2050.7}$	ν^{asym}(CO)	$A_{1986.1}/A_{1970.7}$	ν^{asym}(CO)
2.1			9.83	1900.0
2.9			10.10	1899.6
3.7			6.69	1899.2
4.0	7.26	1876.1		
4.3			4.95	1899.0
4.5			3.44	1898.7
4.8	6.29	1875.5	2.09	1898.0
5.0			1.71	1896.0
5.3	4.74	1874.7	0.99	1880.8
5.6			0.52	1876.3
6.3	1.79	1864.9	0.15	1874.5
6.5	1.13	1861.3		
6.8	0.89	1859.4		
7.0	0.58	1858.0		
7.3	0.45	1857.0		
7.7	0.27	1855.8		
9.3	0.16	1855.2	0.04	1873.4
10.0	0.16	1855.1		

[a] All ν(CO) are in cm^{-1}. A_x is the absorbance value at x cm^{-1}.

The aminobenzene complex **8** was also investigated as a potential pH probe for use in more acidic media, and FTIR spectra of the complex over the pH range 2.1−5.6 are shown in Figure 6. At pH 5.6, two bands are observed at 1954.9 and 1870.7 cm^{-1}. These remain unchanged up to pH 11. As the pH decreases, a high-wavenumber shoulder at *ca.* 1971 cm^{-1} becomes apparent on the ν^{sym}(CO) band, and this is assigned to the protonated η^6-phenylammonium complex. However, even at pH 2.1, the protonated complex clearly is still the minority species in solution, reflecting the greatly

---

[18] Brown, H. C.; McDaniel, D. H.; Hafliger, O. In *Determination of Organic Structures by Physical Methods;* Braude, E. A., Nachod, F. C., Eds.; Academic Press: New York, 1955; Vol. 1, pp 567−662.

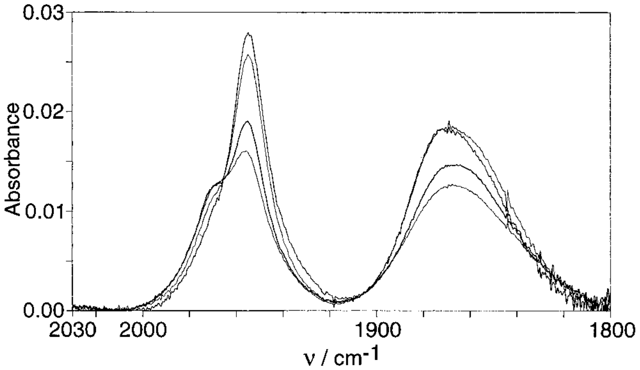


Figure 6. FTIR spectra in the 2030−1800 cm^{-1} region of (η^6-aminobenzene)Cr(CO)$_3$ (**8**) in buffer solutions over the pH range 2.1−5.6.

reduced basicity of the complex (pK_b = 13.3 in 82% ethanol/18% water)[10] relative to the free ligand, and the complex is not particularly useful as a pH probe over the range studied here, although it might well be suitable as a probe for the pH range 0−2.

Dual Sensors. The narrow bandwidths of the ν(CO) modes relative to the overall wavenumber range allow for the simultaneous use of two different sensing molecules in the same system, such that the FTIR spectra of both complexes can be measured simultaneously without the bands from the different reporting groups overlapping. This approach, which we term the use of "dual sensors", is of particular value where the sensors have differing responses to the analyte under investigation or separate responses to more than one analyte. A single spectroscopic measurement can report on the responses of each of the individual sensors and, thus, yield more information than can be obtained from a comparable system containing just one type of sensing molecule. For a single-analyte system, such as pH, this has two important consequences. First, the interrogation of two different spectroscopic probes allows two simultaneous but independent measurements of the analyte concentration, and hence a more reliable estimate of the concentration can be made. Second, the use of two complexes responding to different concentration ranges of the analyte extends the overall useful concentration range of the sensor system.

To investigate the potential of a dual-sensor system, a methanol solution containing both **1a** and **2a** was added to a range of buffer solutions. The spectra of the pH 2.2 and 3.7 solutions are shown in Figure 7. It can be seen that the ν^{sym}(CO) band of **1a** and the ν^{asym}(CO) band of **2a** do, in fact, overlap to some extent. However, we have shown that, for a given complex, either of the two ν(CO) bands can be used independently to give a readout of the solution pH, so that the observed overlap of one of the bands from each complex does not prevent the use of these two complexes as a dual sensor. The spectroscopic data for the ν^{asym}(CO) band of **1a** and the ν^{sym}(CO) band of **2a** were processed in the same way as for the individual complexes and were found to give pH responses consistent with those of the single-sensor systems, indicating that the response of each complex is not perturbed by the presence of the other.

As an alternative approach to dual sensing, complex **2a** was used in combination with the related complex dicarbonyl(η^4-1-carboxy-1,3-pentadiene)(triphenylphosphine)iron(0) (**9**). The replacement of a carbonyl ligand by the phosphine modifies the reporting group, shifting the ν(CO) modes to lower wavenumbers relative to those of **2a**. It also decreases the pK_a of the sensing group, since the phosphine ligand increases the electron density on the metal center compared with the tricarbonyl complex **2a**, thus reducing the extent to which the negative charge on the anion is stabilized. IR spectra of **2a** and **9** in 40% methanol/60% water were measured at different pH values, and plots of ν(CO) against pH showed the expected behavior, with pK_a values in this solvent mixture for the two complexes estimated at 5.4 and 3.1, respectively. The higher methanol content of the solvent mixture in this experiment was necessary as a consequence of the poor solubility of the triphenylphosphine complex **9** in 91% water/9% methanol. Spectra of solutions containing both **2a** and **9** were then measured. They showed that the ν^{asym}(CO) band of **2a** and the ν^{sym}(CO) band of **9** overlapped, but that the ν^{sym}(CO) band of **2a** and the ν^{asym}(CO) band of **9** could still be used to give independent readouts of pH. Again, the readout from one complex was unperturbed by the presence of the other.

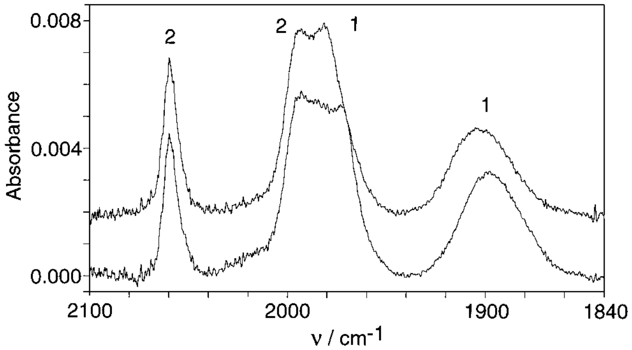


Figure 7. FTIR spectra in the 2100−1840 cm^{-1} region of (η^6-1-carboxybenzene)Cr(CO)$_3$ (**1a**) and (η^4-1-carboxy-1,3-pentadiene)Fe(CO)$_3$ (**2a**) in pH 2.2 and 3.7 buffer solutions. (The spectrum measured at pH 2.2 is offset upward by 0.02*A* for clarity.) Bands assigned to the chromium or iron complexes are labeled 1 or 2, respectively.

The use of dual sensors, while useful for a single-analyte system such as pH, becomes far more important when multianalyte systems are considered. When more than one related analyte is present, the responses of a single sensor to each of them would, to a certain extent, mutually interfere. The use of two or more complexes with differing selectivities for, and spectral responses to, the analytes in question could allow simultaneous spectroscopic determination of the analytes. The extension of our results with dual sensors to the measurement of other analytes (for example, alkali metal cations)[15] is currently under investigation. The work with pH sensors reported here, however, demonstrates the practicality of the approach.

Experimental Section

The complexes (η^4-1-carboxy-1,3-pentadiene)Fe(CO)$_3$ (**1a)** and (η^4-1-(methylcarboxy)-2,4-hexadiene)Fe(CO)$_3$ (**3**) were prepared by the literature method,[19] and (η^4-1-(methylcarboxy)-2,4-hexadiene)Fe(CO)$_2$(PPh$_3$)[20] was provided by Dr. J. A. S. Howell, University of Keele, U.K. The tricarbonylchromium

---

[19] Cais, M.; Moaz, N. *J. Organomet. Chem.* **1966**, *5*, 370−383.

[20] Adams, C. M.; Hafner, A.; Koller, M.; Marcuzzi, A.; Prewo, R.; Solana, I.; Vincent, B.; von Philipsborn, W. *Helv. Chim. Acta* **1989**, *72*, 1658−1675.

complexes (η^6-4-hydroxytoluene)$\mathrm{Cr(CO)_3}$ (**6**),[21] (η^6-(methylcarboxy)-4-hydroxybenzene)$\mathrm{Cr(CO)_3}$ (**7**),[10] (η^6-aminobenzene)$\mathrm{Cr(CO)_3}$ (**8**),[8,9] and (η^6-1,2-bis(methylcarboxy)benzene)$\mathrm{Cr(CO)_3}$[22] were prepared by the standard method,[23] and (η^6-1-(methylcarboxy)benzene)$\mathrm{Cr(CO)_3}$ (**4**) was purchased from Aldrich Chemical Company. Hydrolysis of the methyl ester **4** by the method of Nicholls and Whiting[8] afforded (η^6-carboxybenzene)$\mathrm{Cr(CO)_3}$ (**2a**).

Hydrion buffers[24] were purchased from Aldrich Chemical Co. and made up with water according to the instructions to give buffer solutions with integer pH values over the range pH 2−11; it was found that the pH 2 and 3 buffer solutions prepared actually had pH values of 2.1 and 2.9, respectively. Solutions with intermediate pH values were obtained by mixing appropriate Hydrion solutions; the pH values of these new solutions were measured using a Radiometer PHM82 pH meter.

Synthesis of (η^6-1,2-Dicarboxybenzene)$\mathrm{Cr(CO)_3}$ (5). The complex (η^6-1,2-bis(methylcarboxy)benzene)$\mathrm{Cr(CO)_3}$ (100 mg, 0.303 mmol) and KOH (192 mg, 3.53 mmol) were dissolved in a degassed mixture of methanol (10 mL) and water (0.25 mL) and stirred under a nitrogen atmosphere in the dark for 48 h at ambient temperature. The resulting yellow precipitate was collected by filtration and dissolved in water. This solution was acidified with concentrated aqueous HCl and extracted with diethyl ether (3 × 30 mL). The organic phase was separated and dried over $\mathrm{MgSO_4}$, and the solvent was removed *in vacuo* to yield reddish-orange microcrystals (89 mg, 81%): mp 164−168 °C (dec); IR ($\mathrm{CH_2Cl_2}$) 1997, 1934 $\mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, acetone-d_6) δ 6.07 (2H, dd, J = 5.0, 2.7 Hz, H^3, H^6), 5.80 (2H, dd, J = 4.8, 2.7 Hz, H^4, H^5); EI-MS m/z 302 (5, $\mathrm{M^{+\bullet}}$), 284 (23, $[\mathrm{M} - \mathrm{H_2O}]^{+\bullet}$), 258 (4, $[\mathrm{M} - \mathrm{CO_2}]^{+\bullet}$), 246 (3, $[\mathrm{M} - 2\mathrm{CO}]^{+\bullet}$), 218 (13, $[\mathrm{M} - 3\mathrm{CO}]^{+\bullet}$), 200 (53, $[\mathrm{M} - 3\mathrm{CO} - \mathrm{H_2O}]^{+\bullet}$), 105 (100). Anal. Found: C, 43.60; H, 2.02. $\mathrm{C_{11}H_6CrO_7}$ requires: C, 43.72; H, 2.00.

Synthesis of (η^4-1-Carboxy-1,3-pentadiene)$\mathrm{Fe(CO)_2(PPh_3)}$ (9). A solution of (η^4-1-(methylcarboxy)-2,4-hexadiene)$\mathrm{Fe(CO)_2(PPh_3)}$[18] (32 mg, 0.062 mmol) in THF (20 mL) was added to 0.2 M aqueous NaOH (50 mL), giving a cream suspension. This mixture was heated at 68 °C (at which temperature the suspension redissolved) under an argon atmosphere for 5 days, when the reaction was shown to be complete by TLC ($\mathrm{SiO_2}$/diethyl ether). The reaction mixture was diluted with water (100 mL), acidified with concentrated aqueous HCl, and extracted with diethyl ether (3 × 30 mL). The organic phase was separated and dried over $\mathrm{MgSO_4}$, and the solvent was removed *in vacuo* to yield a yellow powder. This was recrystallized from $\mathrm{CH_2Cl_2}$/hexane, giving the product as yellow microcrystals (23 mg, 72%): IR ($\mathrm{CH_2Cl_2}$) 1991, 1931, 1702 $\mathrm{cm^{-1}}$; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ 12.6 (1H, br, $\mathrm{CO_2H}$), 7.56 (5H, m, $\mathrm{PPh_3}$), 7.39 (10H, m, $\mathrm{PPh_3}$), 5.76 (1H, m, H^3), 5.02 (1H, dd, J = 8.2, 4.6 Hz, H^4), 1.27 (1H, d, J = 3.0 Hz, H^2), 1.16 (3H, d, J = 6.2 Hz, $\mathrm{CH_3}$), 0.88 (1H, dd, J = 6.6, 6.2 Hz, H^5); FAB-MS m/z 487 (11, $[\mathrm{MH}]^+$), 430 (62, $[\mathrm{M} - 2\mathrm{CO}]^{+\bullet}$), 318 (69, $[\mathrm{FePPh_3}]^{+\bullet}$), 262 (73, $[\mathrm{PPh_3}]^{+\bullet}$), 183 (100). Anal. Found: C, 63.92; H, 4.85. $\mathrm{C_{26}H_{23}FeO_4P}$ requires: C, 64.22; H, 4.77.

FTIR Measurements. Aliquots (0.2 mL) of a stock methanol solution of one of the complexes (typically 10 mg/mL for the chromium complexes and 4 mg/mL for **2a**, which was appreciably less soluble in the aqueous buffer/methanol mixture) were added to 2.0 mL of each of a range of the buffer solutions. The FTIR spectrum (Perkin-Elmer 1720X spectrometer equipped with InSb detector, resolution 0.5 $\mathrm{cm^{-1}}$, 0.1 mm $\mathrm{CaF_2}$ solution cell) over the range 2100−1800 $\mathrm{cm^{-1}}$ of each solution was then measured, using a 91:9 buffer/methanol mixture as reference. The poor solubility of the complexes in water precluded direct addition to the buffer solution, and predissolution in methanol was found to be necessary. Decomposition of overlapped features in the FTIR spectra into the component bands was achieved by using the IR band-fitting program PCCAP.[25]

Acknowledgment. We thank the EPSRC (C.E.A.) and the BBSRC and British Technology Group Ltd. (M.A.F.) for financial support. We are grateful to Dr. J. Varga and Dr. J. Lejtovicz (Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest) for the use of their IR curve analysis program PCCAP prior to publication. We thank Dr. J. A. S. Howell for a sample of (η^4-1-(methylcarboxy)-1,3-pentadiene)$\mathrm{Fe(CO)_2(PPh_3)}$.

OM950589O

---

(21) Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1967**, *7*, 427−440.

(22) van Meurs, F.; Baas, J. M. A.; van Bekkum, H. *J. Organomet. Chem.* **1977**, *129*, 347−360.

(23) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154−158.

(24) Hydrion buffers are a range of buffers giving solutions with integral pH values between 2.00 and 11.00; they contain mixtures of sulfamic acid and sodium or potassium salts of phthalates, phosphates, or carbonates, as appropriate.

(25) Varga, J.; Lejtovicz, J. Unpublished software.