^{207}Pb, ^{13}C and ^{1}H Nuclear Magnetic Resonance Studies of Lead(IV) Carboxylates in Solution

T. D. W. Claridge,* E. J. Nettleton and M. G. Moloney,
The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, UK

Lead(IV) reagents are widely used for the mediation of oxidation and carbon–carbon bond-forming reactions, which are postulated to proceed by mechanisms involving ligand exchange processes at the metal centre. This paper reports multinuclear (^{207}Pb, ^{13}C and ^{1}H) magnetic resonance studies on lead(IV) carboxylates containing acetate, benzoate and cinnamate ligands, either as single-ligand (PbX_4) or as mixed-ligand (PbX_mY_n) species. At ambient probe temperatures (*ca.* 300 K), averaged spectra were observed for all solution species, arising from rapid intermolecular ligand exchange. At 225 K, exchange was sufficiently slow for mixed-ligand complexes, of general formula PbX_2Y_2, to exhibit spectra of five distinct complexes, which were shown to correspond to PbX_mY_{4-m} ($m = 0$–4). Analysis of the low-temperature spectra presented an overall picture of chemical shift changes throughout the complexes when ligand exchange takes place. These data provide some insight into the behaviour of these complexes in solution which help explain the observed chemistry of more elaborate lead(IV) carboxylates. © 1997 by John Wiley & Sons, Ltd.

Magn. Reson. Chem. 35, 159–167 (1997) No. of Figures: 9 No. of Tables: 4 No. of References: 21

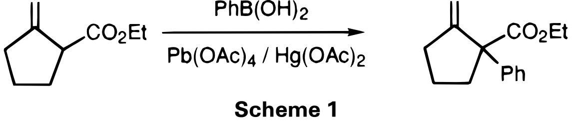
Keywords: NMR; ^{207}Pb NMR; ^{13}C NMR; ^{1}H NMR; lead(IV) carboxylates; ligand exchange

Received 30 May 1996; revised 23 September 1996; accepted 23 September 1996

INTRODUCTION

Lead (IV) reagents are widely used both as oxidants[1–3] and for the mediation of carbon–carbon bond-forming reactions.[4–6] For example, the α-phenylation of β-dicarbonyl nucleophiles (Scheme 1) has been extensively studied.[5] These transformations are postulated to proceed by mechanisms involving one or more ligand-exchange processes at lead(IV), thereby creating a species which collapses by a ligand coupling process[7] to the observed products.[8,9] In the context of a wider research programme to study the influence of ligands on the reactivity of lead(IV), we have used NMR spectroscopy to investigate further the nature of lead(IV) carboxylate species in solution. Our ultimate aim is to gain detailed information on the structure of lead(IV) complex in solution, and to use these data to design and construct ligand systems which facilitate and control the reactivity of the complex. One key goal is to develop reactions which proceed with asymmetry transfer from a complex possessing chiral ligands to products.

In previous work we have used 1D and 2D ^{207}Pb NMR to observe directly the metal environments of lead(IV) acetate and lead(IV) benzoate mixtures.[10] We have shown that the complexes formed in solution undergo intermolecular ligand exchange which is rapid at ambient probe temperatures (*ca* 300 K) but which becomes slow on the NMR time-scale at 225 K. Under these conditions discrete resonances were observed for five different ligand complexes. To this end, the ^{207}Pb nucleus has favourable properties for NMR observation in that it has a nuclear spin of $\frac{1}{2}$, has 22.6% natural abundance and has a receptivity that is 11.7 times that of ^{13}C.[11–14] Although observing lead alone provided us with an extremely useful probe of the reactive metal centre, it provided no direct information on the organic ligands in these complexes. In this work, we extended our studies on the lead(IV) carboxylate systems by taking an 'overall' view of the complexes by ^{207}Pb, ^{13}C and ^{1}H NMR observations. We describe the NMR properties of single- and mixed-ligand species derived from acetate, benzoate and cinnamate ligands. When describing the various ligand complexes we shall use the abbreviations PbA_mB_n or PbB_mC_n for convenience, where A, B, and C refer to acetate, benzoate and cinnamate, respectively. Except where stated otherwise, all discussions will relate to observations made at 225 K, where the intermolecular ligand exchange is slow on the NMR time-scale.



Scheme 1

EXPERIMENTAL

Synthesis of the lead(IV) complexes used in these studies has been published previously.[15] Samples for NMR analysis were prepared as approximately 100 mg ml^{-1} solutions of PbX_4 or stoichiometrically pure PbX_2Y_2 in deuteriochloroform and placed in 5 mm diameter NMR tubes. Spectra were acquired on a Bruker AMX500

* *Correspondence to*: T. D. W. Claridge.

CCC 0749–1581/97/030159–09 $17.50

instrument equipped with a broadband probe, which allowed the observation of all nuclei of interest in this work without the need for probe changes. Sample temperatures were regulated to ±0.1 K with a Bruker VT2000 temperature controller and each sample was allowed to equilibrate for at least 30 min before data acquisition. Acquisition and processing of the data sets were as given in Table 1.

Data sets were collected with around 500 (^{207}Pb) and 300 (^{13}C) scans for the single-ligand (PbX_4) complexes and 2000 (^{207}Pb) or 5000 (^{13}C) scans for the mixed-ligand complexes (PbX_2Y_2). Proton data were collected with 16 scans. Spectra were referenced to $CDCl_3$ or residual $CHCl_3$ of the solvent for ^{13}C (77.0 ppm) and ^{1}H (7.27 ppm), respectively. ^{207}Pb spectra were referenced externally to 80% Me_4Pb in toluene, whereby the reference frequency of this standard was calculated[14] from $\Xi(^{207}Pb) = 20.920597$ MHz[13,14] (when the ^{1}H frequency of Me_4Si is 100.000 MHz). Lead and carbon shifts are quoted to one and two decimal places, respectively, purely to show the *relative* shift differences between resonances within each spectrum, although such *absolute* accuracy is probably not significant in view of possible temperature- and concentration-dependent shifts in these dynamic systems.

Assignments of the multiple resonances observed in the mixed-ligand complexes were obtained by adding one equivalent at a time of a free carboxylic acid (acetate or cinnamate) to a starting solution of lead(IV) tetrabenzoate. At each stage the proton, carbon and lead spectra were recorded and the process was repeated until four equivalents of the acid had been added. By following the appearance and increasing intensity of the new resonances as more acid was added, it was possible to assign these resonances as belonging to complexes with a progressively greater proportion of the added ligand.

RESULTS AND DISCUSSION

In the following sections the chemical shift changes that are observed are described. In the case of lead shifts it is known that the paramagnetic term in the shielding constant dominates providing a deshielding influence on the nucleus. This is dependent upon a combination of the mean energy of excitation of electrons associated with the nucleus, the degree of electron imbalance in the chemical bonds to the metal and the mean inverse cube distance of the valence electrons from the nucleus (i.e. the radial-expansion term).[12,16] The electronic environment of the lead nucleus is known to be very sensitive to changes in chemical bonding to the metal[16] owing to its ready polarizability, and electron-withdrawing groups will tend to increase the electron imbalance within the bonds so increasing the paramagnetic term and causing deshielding of the nucleus. Likewise, π–π bonding with the lead will influence the electron excitation energies, again altering the paramagnetic term,[16] and some care is needed in the interpretation of heavy-metal shifts. In a series of tin(IV) alkylcarboxylates containing only a single acid ligand (the other three being invariant alkyl or aryl ligands), tin shifts have been shown to be influenced predominantly by the inductive effects of the acid ligands[17] and the behaviour of lead shifts is known to parallel closely those of tin,[11,16] although lead tends to be more sensitive. Differences between the complexes studied in our work lie solely in the acid 'side-chain' whereas the ligating functionality is a carboxylate in all cases. Thus, the observed lead chemical shift changes are considered to originate from electron redistribution made possible by the differing sidechains (particularly in the unsaturated species), although it is not possible to state precisely the influences on each of the paramagnetic terms. Although carbon chemical shifts are also influenced by the paramagnetic term, they are more readily correlated with inductive electron shifts and resonance effects, as seen in the case of protons (where, in fact, the diamagnetic term dominates).

Single-ligand complexes

Prior to the studies of the mixed ligand complexes, we first wished to define the properties of the carboxylate ligands alone and how these changed on binding to the lead(IV) nucleus. The ^{13}C and ^{207}Pb results for the three ligands and their corresponding complexes are summarized in Table 2. The carbon-13 shifts show that on ligating to the lead(IV) cation, there is a deshielding of the carbonyl carbon. This effect is transmitted throughout the organic ligand in all three cases, most notably for the unsaturated species. In the case of the benzoate and cinnamate ligands, high-frequency shifts of 0.81 and 0.44 ppm were observed for C-5 and C-7 respectively, suggesting changes in electron distribution as much as eight bonds away from the lead nucleus. The alternating shielding–deshielding patterns of the carbon nuclei are consistent with the canonical forms that may be drawn for these ligands that provide stabilization of the positive charge on the metal (Fig. 1), although the reason for shielding of C-2 in all ligands is not entirely clear.

Although the lead shifts of the PbA_4 and PbC_4 were similar (Table 2; the acetate ligand would appear to shield the metal centre slightly more effectively than the

Table 1. Acquisition parameters

Nucleus	Observation frequency (MHz)	Spectral width (kHz)	Real time-domain data points acquired	Spectrum size (including one zero-fill)	Line broadening (Hz)
^{207}Pb	104.40	4.2	4K	4K	1
^{13}C	125.73	26.0	64K	64K	1
^{1}H	499.98	6.0	32K	32K	0

Table 2. ^{13}C and ^{207}Pb chemical shifts and ^{13}C–^{207}Pb coupling constants recorded at 225 K for the free carboxylic acids, and the carboxylates when ligated to lead(IV) as PbX_4 (see also Fig. 1).[a]

Parameter	C-1	C-2	Acetate Pb δ (ppm)
Free ligand A δ (ppm)	179.16	21.37	–
Pb bound ligand A δ (ppm)	181.60	17.92	−1885.2
$^{n}J_{CPb}$/(Hz)	$^{2}J=131$	$^{3}J=141$	

	C-1	C-2	Benzoate C-3	C-4	C-5	Pb δ (ppm)
Free ligand B δ (ppm)	172.68	128.58	129.91	128.33	133.85	–
Pb bound ligand B δ (ppm)	175.79	125.49	131.92	128.54	134.66	−1896.8
$^{n}J_{CPb}$/(Hz)	$^{2}J=129$	$^{3}J=156$				

	C-1	C-2	Cinnamate C-3	C-4	C-5	C-6	C-7	Pb δ (ppm)
Free ligand C δ (ppm)	173.22	116.57	147.09	133.13	128.27	128.80	130.80	–
Pb bound ligand C δ (ppm)	175.94	112.26	150.76	133.19	128.50	128.86	131.24	−1881.2
$^{n}J_{CPb}$/(Hz)	$^{2}J=124$	$^{3}J=177$						

[a] Coupling constants were extracted from the ^{13}C spectra owing to the greater natural abundance of ^{207}Pb *vs* ^{13}C producing higher intensity satellites.

cinnamate ligand), that of PbB_4 suggests greater shielding of the lead nucleus when ligated by benzoate. For the simple tin carboxylates mentioned above, increased tin shifts have been shown to correlate inversely with the pK_as of the corresponding acid.[17] However, the pK_as of the three acids in our studies are similar ($A = 4.75$, $B = 4.19$ and $C = 4.44$[18]), as are the lead chemical shifts of the complexes, so making comparison less reliable, although the slightly lower pK_a of benzoate seems to correspond to a slightly lower lead chemical shift. This is in contrast to the tin results in which increased inductive electron withdrawal from the metal was used to explain the high-frequency tin chemical shifts. In our systems, which contain four rather than just one carboxylic acid in addition to unsaturation in the ligand, similar arguments appear not to be sufficient to account for the observed lead shift differences.

The application of proton decoupling during the acquisition of lead spectra significantly reduced the linewidth of the resonances, and indicated the presence of long-range ^{1}H–^{207}Pb coupling in all three species (Fig. 2). Considerable sharpening of the Pb resonance was observed for PbA_4 and PbB_4 whereas only a moderate effect was seen for PbC_4. Only in the proton-coupled lead spectrum of the benzoate species could proton couplings be resolved (Fig. 2); we believed this multiplicity to be that of a nonet, by virtue of coupling with the eight (equivalent) aromatic *ortho* protons ($^{5}J_{PbH} = 7$ Hz). This was shown to be the case on analysis of the mixed ligand species (see below). Other couplings were not resolved because of overlap of many lines for the acetate species (13 lines would be predicted for the PbA_4 species) or because the couplings were in fact small relative to the resonance linewidth (2 Hz in the decoupled spectra), which appears to be the case for the cinnamate ligands (Fig. 2).

In the presence of proton decoupling it was also possible to see evidence of scalar coupling between the

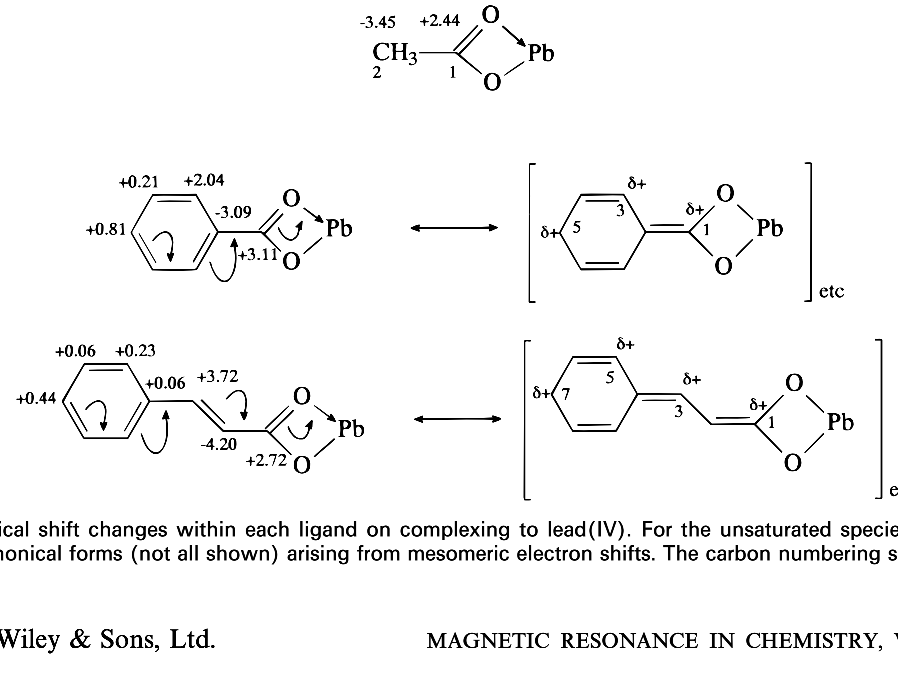


Figure 1. ^{13}C chemical shift changes within each ligand on complexing to lead(IV). For the unsaturated species, these changes largely correlate with the canonical forms (not all shown) arising from mesomeric electron shifts. The carbon numbering scheme used here is used throughout the text.

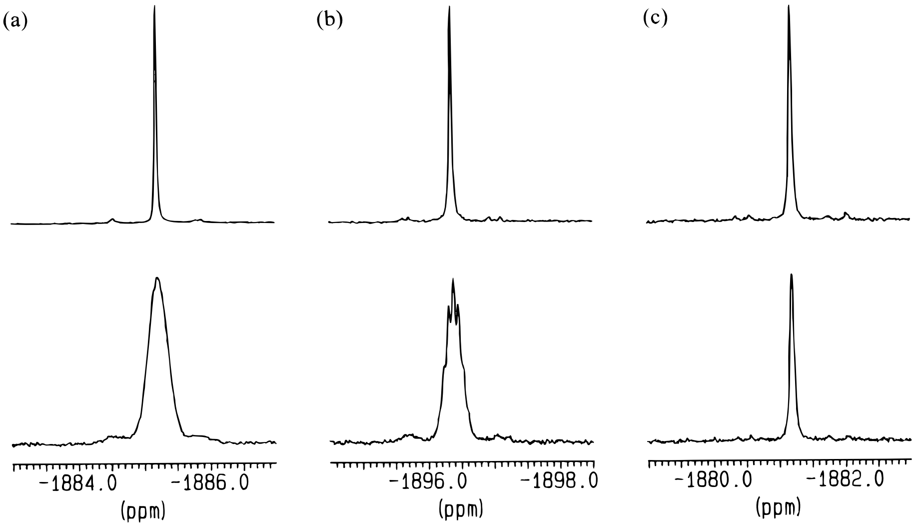


Figure 2. ^{207}Pb NMR spectra recorded at 225 K of (a) PbA_4, (b) PbB_4 and (c) PbC_4 without (lower traces) and with (upper traces) broadband proton decoupling. It is just possible to see the two- and three-bond ^{13}C satellites at the base of the resonances.

^{207}Pb and ^{13}C nuclei in both the lead spectra (Fig. 2) and carbon spectra (Fig. 3). Note that such coupling with carbon-13 or protons could not be observed in the lead spectra for any species at ambient temperature (*ca* 300 K) owing to the 'exchange decoupling'[19] brought about by rapid intermolecular ligand exchange.[10] The magnitudes of $^{2}J_{\mathrm{PbC}}$ couplings at low temperature (Table 2) were similar for all three ligands, whereas $^{3}J_{\mathrm{PbC}}$ showed significant variation which, presumably, reflects the differing hybridization of C-2 in the three ligands (sp^3, aromatic sp^2 and olefinic sp^2). Despite the presence of unsaturation in the benzoate and cinnamate systems, coupling between lead and carbon was not observed over four or more bonds. The inability to observe such coupling cannot be attributed to excessively large linewidths as these were only 4 and 2 Hz (at half-height) in the carbon and lead spectra, respectively, suggesting long-range coupling (if any) must be comparable to or smaller than these figures. The magnitudes of ^{2}J and ^{3}J are significantly larger than those reported for a number of organoplumbane compounds[14] (^{2}J typically 15–70 Hz, ^{3}J typically 50–80 Hz), for which two possible causes can be considered. First, our systems have oxygen on the coupling pathway and second it seems plausible that, if the ligands are bidentate, there exist two similar coupling pathways through the carboxylate functionality which may enhance the magnitude of J.

The presence of a single resonance for each carbon nucleus in the ligands suggested the carboxylates to be symmetrical in these simple complexes, with no differentiation between the four bound ligands. This was also

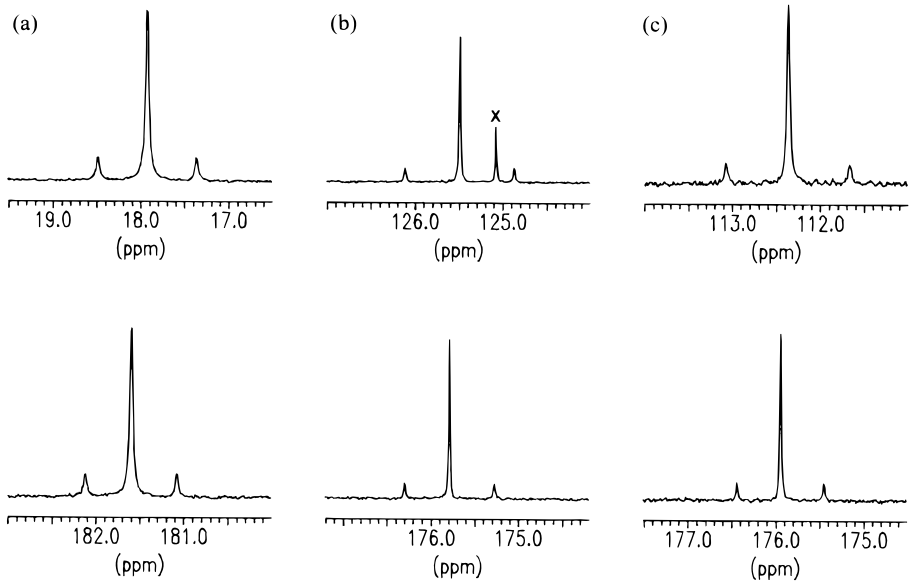


Figure 3. ^{13}C{^{1}H} NMR spectra recorded at 225 K showing the C-1 (lower traces) and C-2 (upper traces) regions of (a) PbA_4, (b) PbB_4 and (c) PbC_4. ^{207}Pb satellites (^{2}J and ^{3}J) are clearly visible for all these resonances, although no others exhibited such satellites. At 295 K no ^{13}C resonances displayed ^{207}Pb satellites owing to the rapid ligand exchange at the higher temperature (see text). The cross marks residual toluene from synthesis of the complexes.

borne out by the lead coupling to the eight *ortho* protons in the PbB_4 species with equal coupling constants, suggesting all these protons to be chemically equivalent, which was confirmed by the low temperature ^{1}H spectrum.

Mixed ligand complexes

Lead(IV) diacetate dibenzoate, PbA_2B_2. *^{207}Pb NMR.* We have shown previously[10] that at 295 K the ^{207}Pb spectrum of a mixture of PbA_4 and PbB_4 had a single broad resonance which, on reducing the temperature of the mixture to 225 K, produced a spectrum that contained five distinct lead(IV) resonances of complexes that were in slow exchange on the NMR chemical shift time-scale, and that these corresponded to the five possible mixed ligand species PbA_4, PbA_3B, PbA_2B_2, $PbAB_3$ and PbB_4 in a statistical ratio. We have also observed similar behaviour for the synthesized PbA_2B_2 preparation (that is, a sample prepared with no, or only trace quantities of, excess unbound ligand present in solution) [Table 3 and Fig. 4(a)]. This demonstrates that lead(IV) carboxylates that would be considered to be 'stoichiometrically pure' do in fact exist as mixtures of reactive species, a point we address further below. Clearly, the exchange of an acetate for a benzoate ligand had an additive shielding effect on the lead(IV) nucleus.

As was observed for the single-ligand species, both ^{1}H and ^{13}C coupling in the lead spectra could be seen (at least for the most intense resonances). Interpretation of the ^{1}H coupling was made possible by applying selective continuous decoupling to the acetate methyl ^{1}H resonances to leave only coupling to benzoate protons. The resulting lead multiplicities followed the pattern 1:3:5:7:9 for the A_4 to A_0 species respectively (although the nonet pattern could not be fully resolved which proved the existence of long-range five-bond Pb–H coupling.

^{13}C NMR. At 295 K the ^{13}C spectrum of PbA_2B_2 showed a single resonance for each chemically distinct environment of the acetate and benzoate ligand, in a similar manner to the free ligands. These resonances

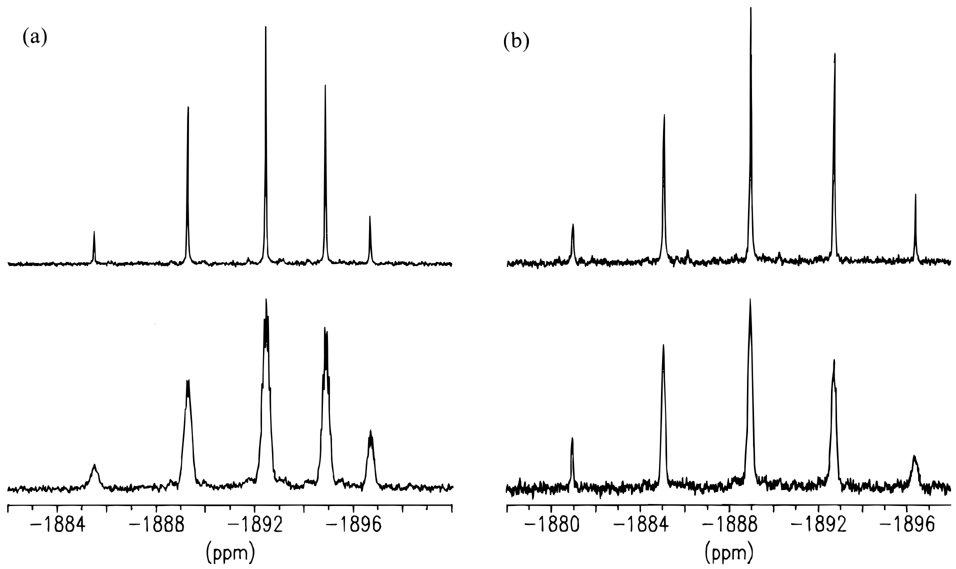


Figure 4. ^{207}Pb NMR spectra recorded at 225 K of (a) PbA_2B_2 and (b) PbB_2C_2 without (lower traces) and with (upper traces) broadband proton decoupling. The five lines in each spectrum may be attributed to the five possible species of PbX_mY_{4-m} ($m = 0$–4) which, at this temperature, are undergoing slow ligand exchange. At 295 K only a single, broad Pb resonance is observed.[10]

Table 3. ^{207}Pb, ^{13}C and ^{1}H chemical shifts (ppm) for the mixed ligand complexes of lead(IV) diacetate dibenzoate recorded at 225 K

				Complex		
		PbA_4	PbA_3B	PbA_2B_2	$PbAB_3$	PbB_4
δ ^{207}Pb		−1885.2	−1888.9	−1892.0	−1894.7	−1896.8
δ ^{13}C acetate	C^1	181.64	181.72	181.82	181.96	–
	C^2	18.01[a]				–
δ ^{1}H acetate	Me	2.254	2.266	2.279	2.292	–
δ ^{13}C Benzoate	C-1	–	175.48	175.55	175.64	175.76
	C-2	–	125.47[a]			
	C-3	–	131.79	131.83	131.87	131.90
	C-4	–	128.52			
	C-5	–	134.72			
δ ^{1}H benzoate	*ortho*	–	8.093	8.113	8.130	8.147
	meta	–	7.511			
	para	–	7.680			

[a] Separate resonances could not be resolved, although distortions of the resonance could be observed.

broadened on addition of free acid ligands in accordance with a dynamic equilibrium. Cooling a solution of a PbA_2B_2 preparation to 225 K caused many of these resonances to exhibit fine structure, in particular those that are in closest proximity to the lead nucleus, that is, within the smallest number of intervening bonds. The results are summarized in Table 3. It is the carbonyl resonances of each ligand that showed the greatest sensitivity [Fig. 5(a)] whilst smaller changes were also observed for the C-3 of the benzoate ligand. The shifts of all the newly observed lines were significantly removed from those of the free ligands at the same temperature. In addition, the resonances of nuclei within two or three bonds of the lead nucleus exhibited distinctive lead satellites [Fig. 5(a)]; thus the new resonances could all be associated with lead bound ligands. The ratios of the peak intensities within each cluster could also be related to those observed for the individual lead species in the ^{207}Pb spectra, and it was apparent that it should be possible to assign each resonance (and their associated lead satellites) to one of the five possible species known to exist in solution. Thus, detailed titration analysis was undertaken as described under Experimental to allow such an assignment. Furthermore, we were able to compare data for the single-ligand species, as describe above, which confirmed the assignment of the PbA_4 and PbB_4 resonances, and the consistency of our titration data. It was clear that, although the chemical shift differences between the different species was small (typically only 0.1 ppm), it was possible to resolve individual resonances for each lead(IV) complex in solution. For these five complexes it was clear that the greater the number of benzoate ligands around the lead(IV) center the more deshielded were the C-1 of acetate and the C-1 and C-3 of benzoate ligands (Table 3), paralleling the shielding effect on the lead itself.

^{1}H NMR. At 295 K the proton spectrum of PbA_2B_2 displayed sharp resonances with the only fine structure arising from proton coupling within the benzoate ring, the only noticable difference from the free ligands being the small differences in chemical shifts. At 225 K, however, the benzoate *ortho* protons appeared as a five line multiplet, corresponding to four overlapping doublets, and the acetate methyl displayed four resolved resonances. The *meta* and *para* benzoate protons showed some distortion, although separate resonances could not be resolved. As more benzoate groups ligate the lead, the methyl and *ortho* protons of all ligands are further deshielded (Table 3).

Lead(IV) dibenzoate dicinnamate, PbB_2C_2. *^{207}Pb NMR.* The behaviour of a solution of lead(IV) dibenzoate dicinnamate on cooling the solution was similar to that of the acetate–benzoate system described above, and again resulted in five distinct resonances in the ^{207}Pb spectrum at 225 K, which were assigned as PbB_4, PbB_3C, PbB_2C_2, $PbBC_3$, PbC_4 (Table 4) by the titration method. Clearly, the system was again one of rapid intermolecular ligand exchange. The low temperature spectrum showed a reduction of linewidth on application of proton decoupling [Fig. 4(b)], which is attributed largely to a loss of $^5J_{PbH}$ to the benzoate protons. The shift of the PbC_4 species was to slightly high frequency of the PbA_4 species, and a trend of greater (more positive) chemical shifts for the cinnamate-containing complexes relative to the equivalent acetate complexes was observed. Once more, addition of more benzoate ligands produced an increase in shielding of the lead nucleus in stepwise manner.

^{13}C NMR. At low temperature the fine structure observed in the acetate–benzoate mixture was also apparent in the cinnamate–benzoate mixture (Table 4). The carbonyl region was slightly more confusing in this complex owing to the small shift difference between the carbonyl resonances of the B and C ligands, leading to some overlap with the ^{207}Pb satellites [Figure 5(b)].

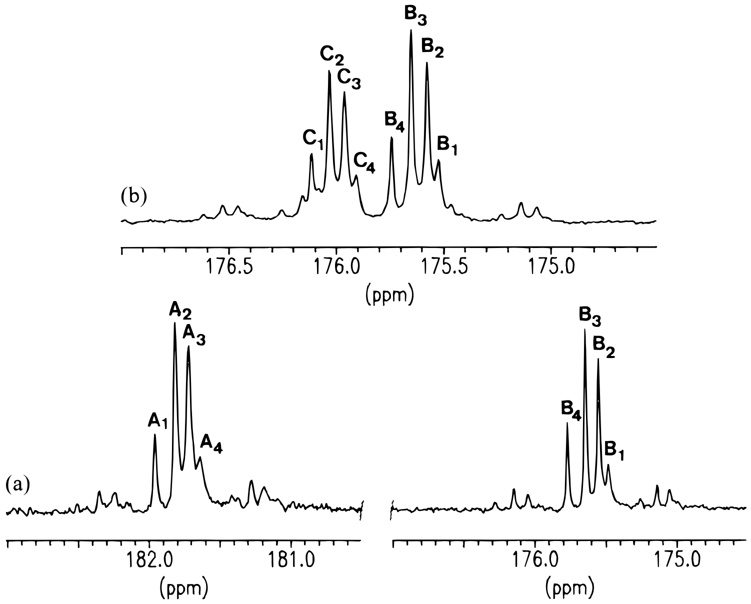


Figure 5. $^{13}C\{^1H\}$ NMR spectra recorded at 225 K showing the C-1 (carbonyl) resonances of (a) PbA_2B_2 and (b) PbB_2C_2. Each ligand (A, B and C) displays four resonances corresponding to the complex of formula PbX_mY_{4-m} ($m = 0$–4) and the associated ^{207}Pb satellites (which overlap with the major Pb resonances in the case of PbB_2C_2). These should be compared with the the simple spectra in Fig. 3.

Table 4. ^{207}Pb, ^{13}C and ^{1}H chemical shifts (ppm) for the mixed ligand complexes of lead(IV) dibenzoate dicinnamate recorded at 225 K

		Complex				
		PbC_4	$PbBC_3$	PbB_2C_2	PbB_3C	PbB_4
δ ^{207}Pb		−1881.2	−1885.1	−1889.0	−1892.7	−1896.8
δ ^{13}C benzoate	C-1	–	175.52	175.58	175.65	175.74
	C-2	–	125.73	125.67	125.57	125.45
	C-3	–	131.83			
	C-4	–	128.46			
	C-5	–	134.53	134.56	134.59	134.66
δ ^{1}H benzoate	*ortho*	–	8.220[a]			
	meta	–	7.541			
	para	–	7.704			
δ ^{13}C cinnamate	C-1	175.91	175.96	176.03	176.11	–
	C-2	112.26	112.22	112.15	112.05	–
	C-3	150.76	150.80	150.89	151.02	–
	C-4	133.05				–
	C-5	128.46				–
	C-6	128.80				–
	C-7	131.21				–
δ ^{1}H cinnamate	C-2H	~6.556[b]				–
	C-3H	8.008	7.996	7.990	7.987	–
	ortho	7.58 and 7.47				–
	meta					–
	para					–

[a] A number of resonances were evident although unresolved, leading to a broadened and unsymmetrical resonance.

[b] Four pairs of adjacent doublets were observed for the PbB_2C_2 preparation, although they could not be unambigously attributed to the four solution species from the titration data owing to interference from coincident free cinnamic acid.

Nevertheless, discrete resonances can be observed for the five solution complexes, and the shifts indicated that the addition of more benzoate ligands produced a deshielding of the carbonyl carbon in all ligands. Furthermore, four discrete resonances could be observed for the C-2 and C-3 carbons of the cinnamate ligands, in which the C-2 was shielded and the C-3 deshielded as more benzoate ligands complexed the lead, and of the C-2 resonances of the benzoate ligands, which were also shielded with more benzoate.

^{1}H NMR. The 225 K spectrum of PbB_2C_2 showed multiple resonances for benzoate *ortho* protons and the cinnamate C-2H and C-3H protons. The C-2H protons displayed four overlapping doublets, whereas the *ortho* and C-3H protons displayed multiple resonances that could not be resolved. It was apparent that C-3H became slightly shielded as more benzoate ligands complexed the lead, although the effect on C-2H could not be determined from the titration data as this resonance was coincident with that of the free cinnamic acid.

With the ^{13}C data it is possible to picture the chemical shift changes throughout these molecules that occur on ligand exchange. In the following considerations we discuss the effect of replacing an acetate or cinnamate ligand with a benzoate ligand, and note here that the qualitative effect of such an exchange is the same regardless of the original composition of the species. For any complex PbA_kB_l and PbB_mC_n, this exchange produced greater shielding of the lead nucleus and the corresponding ^{13}C data show that this is associated with deshielding of the carbonyl carbon *for all ligands bound to the metal* (Fig. 6). In addition, the C-3 of benzoate ligands in the acetate–benzoate mixture was deshielded on ligand exchange, although only minor ^{13}C shifts were observed for the acetate or benzoate C-2, and the exact nature of these shifts could not be determined. Furthermore, shielding could be reliably established for the benzoate and cinnamate C-2 positions, whereas deshielding was observed for the cinnamate C-3 in the benzoate–cinnamate mixture. It is also surprising to note that separate resonances could just be resolved for the benzoate C-5 in the benzoate–cinnamate mixture (Table 4), demonstrating the far-ranging effects of a single ligand exchange presumably transmitted through the π-electron system, and the exquisite sensitivity of the carbon chemical shift to these

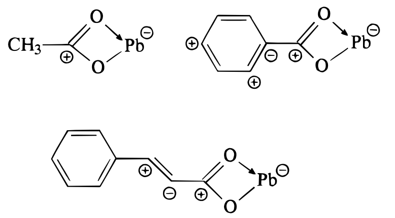
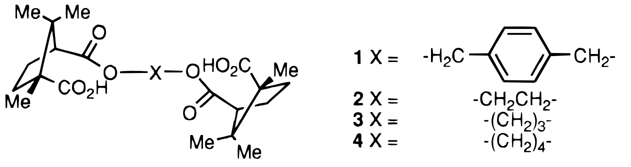


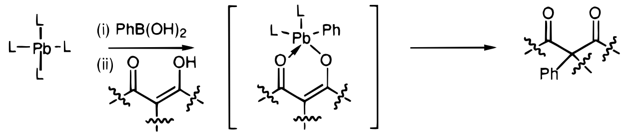
Figure 6. Relative ^{207}Pb and ^{13}C chemical shift changes of each ligand observed on exchange of an acetate or cinnamate ligand for a benzoate ligand in the PbA_kB_l or PbB_mC_n complexes, for example the exchange from PbA_3B to PbA_2B_2. A minus sign indicates a shift to lower frequency (greater shielding) and a plus sign indicates a shift to higher frequency (reduced shielding); no sign indicates that no shift changes could be resolved.



Scheme 2

changes. The overall pattern of ^{13}C shift changes parallels that observed when the free acids become complexed to the metal (compare Figs 1 and 6). Thus, the picture is one of an overall electron redistribution within the acids upon ligation to the lead, particularly for those containing unsaturated π-systems, and, interestingly, this effect is enhanced *for all ligands* as more benzoate ligands surround the metal. Exactly why the presence of more benzoate ligands should cause this enhancement is not clear. For the benzoate and cinnamate ligands, the alternating shielding–deshielding effects observed in the carbon spectra as one moved out from the lead centre can be viewed, in part at least, as a mesomeric shift of electrons toward the metal which may be anticipated since the positive metal centre would be expected to draw electron density toward it.

It is notable that only a single discrete resonance could be observed for each carbonyl carbon of acetate, benzoate or cinnamate in each PbA_kB_l or PbB_mC_n species. For example, in $PbAB_3$, all three benzoate carbonyl carbons exhibited the same chemical shift, so any electron redistribution throughout the molecule on ligand exchange effected all like ligands to a similar extent and the three remained indistinguishable. Furthermore, the carbon and proton data indicated that in all complexes there is no restriction of rotation of the aromatic rings. Although we have not undertaken such an extensive study on the PbA_2C_2 system, all evidence we have suggests that the behaviour of these complexes parallels those described in this work. For example, the variable-temperature lead spectra suggested dynamic exchange of ligands which again became slow at 225 K and produced five distinct lead resonances, although the dispersion between these was very much smaller owing to the similar PbA_4 and PbC_4 chemical shifts (−1885 and −1881, respectively).



5

Scheme 3

It is also noteworthy that, even at the relatively high fields and low temperatures used for these studies, relaxation of the lead(IV) nucleus by, in particular, chemical shift anisotropy did not become so rapid that coupling with the lead nucleus was lost in the ^{13}C spectra or that the lead linewidth was significantly broadened ($\Delta\nu_{1/2}$ = 2 Hz). Measurements of the exchange-averaged lead T_1s on an acetate–benzoate preparation at 225 K *via* the inversion–recovery experiment have shown these to be around 220 ms.

CONCLUSIONS

These results may have important implications for the understanding of the chemistry of these systems. The apparent enhancement of electron shifts with increasing numbers of benzoate ligands would be expected to provide stabilization of the positive charge on the metal and this can be related to the relative hydrolytic stability of PbB_4. Thus, PbA_4 and PbC_4 are more readily hydrolysed than PbB_4, and mixed ligand complexes containing benzoate ligands are more stable than similar complexes derived from acetate.[20] In other work, we have also found that the chiral complexes **1**–**4** (Scheme 2) do not induce efficient asymmetry transfer in phenylation reactions of β-dicarbonyl substrates (Scheme 3; *e.e.* values in the range 4–12% are observed).[20,21] This is surprising given the well documented[8,9] mechanism of these phenylations which involves reductive elimination from the lead(IV) intermediate **5**, produced by B–Pb transmetallation, followed by ligand exchange with the dicarbonyl nucleophile, a reaction which would be expected to be acutely sensitive to its surrounding ligand environment. This contrasts with high stereocontrol in other reactions mediated by transition metals, which has recently been widely exploited. However, the poor asymmetry transfer would be readily explained if the efficient ligand equilibration reported here was similarly in operation for these chiral complexes, and if the most reactive species produced in such an equilibrium was also achiral. Since in this reaction the B–Pb transmetallation also requires mercury(II) acetate as a catalyst, it is feasible that either PbA_4 or PbB_4 (or indeed both) is the most reactive species, and these would of course generate achiral products.

REFERENCES

1. R. N. Butler, in *Synthetic Reagents*, (edited by J. S. Pizey) p. 277, Ellis Horwood, Chichester (1977).
2. R. Criegee, in *Oxidation in Organic Chemistry*, edited by K. B. Wiberg, Chapt. 5. Academic Press, London (1965).
3. G. M. Rubottom, in *Oxidation in Organic Chemistry*, edited by W. H. Trahanovsky, Chapt. 1. Academic Press, London (1982).
4. D. H. R. Barton, in *Heteroatom Chemistry*, edited by E. Block, Chapt. 5. VCH, New York (1990).
5. J. T. Pinhey, *Aust. J. Chem.* **44**, 1353 (1991).
6. R. A. Abramovitch, D. H. R. Barton and J.-P. Finet, *Tetrahedron* **44**, 3039 (1988).
7. S. Oae and Y. Uchida, *Acc. Chem. Res.* **24**, 202 (1991).
8. J. Morgan, I. Buys, T. W. Hambley and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1* 1677 (1993).
9. J. Morgan and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1* 1673 (1993)
10. J. E. H. Buston, T. D. W. Claridge and M. G. Moloney, *J. Chem. Soc., Perkin Trans. 2* 639 (1995).
11. R. K. Harris J. D. Kennedy and W. McFarlane, in *NMR and the Periodic Table*, edited by R. K. Harris and B. E. Mann, Chapt 10. Academic Press, London (1978).
12. R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*. Longman, Harlow (1986).

13. W. McFarlane, *Proc. R. Soc. London, Ser. A* **306**, 185 (1968).
14. B. Wrackmeyer and K. Horchler, *Annu. Rep. NMR Spectrosc.* **22**, 249 (1989), and references cited therein.
15. J. E. H. Buston, A. Coop, R. Heady, M. G. Moloney and R. M. Thompson, *J. Chem. Res. (S)* 205 (1994).
16. J. D. Kennedy, W. McFarlane and G. S. Pyne, *J. Chem. Soc., Dalton Trans.* 2332 (1977).
17. W. McFarlane and R. J. Wood, *J. Organomet. Chem*, **40**, C17 (1972).
18. R. C. Weast (Ed.), *CRC Handbook of Chemistry and Physics*, 60th ed. CRC Press, Boca Raton, FL, (1979).
19. See e.g., R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Chapt. 5. Longman, Harlow (1986).
20. M. G. Moloney, R. M. Thompson and E. Wright, *Main Group Met. Chem.* **19**, 133 (1996).
21. M. G. Moloney, D. R. Paul and R. M. Thompson, *Main Group Met. Chem.* **18**, 295 (1995).