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Arylations mediated by lead(IV) in the presence of formazan and imine ligands

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ABSTRACT

The use of formazan and imine ligands in arylations of β-dicarbonyl systems by phenyl boronic acid/lead(IV) carboxylates is examined.

The use of lead tetraacetate (LTA) for a wide variety of oxidative processes,[1–4] and more recently for cross-coupling reactions,[5–7] is well known; pyridine or other amine bases are important in these reactions, where they probably act as σ-donor ligands.[5,8] We have for some time been interested in the development of novel reaction processes mediated by lead(IV),[9–14] particularly for carbon–carbon bond formation, and have demonstrated their value for the synthesis of particularly hindered quaternary centres.[15,16] These processes may be considered to be analogous to ligand coupling processes mediated by a diverse range of metals and metalloids.[17] Lead tetracarboxylates derived from either monocarboxylic acids or dicarboxylic acids by metathesis of lead tetraacetate are readily accessible, and have generally been found to be stable amorphous powders, which can be successfully applied to the Pinhey arylation procedure,[5–7,18–20] and for the transmetallation of allylstannanes leading to the formation of allylic esters.[21] In an earlier work, we examined ligands, principally substituted benzoates, which are chemically inert to lead(IV), but of interest was the examination of other oxidatively stable ligand systems. Recent reports of the successful application of formazan ligand sets **1**, chosen as diketinimine mimics, for complexation to main group metals,[22,23] suggested that these ligands may be applied to lead(IV) systems. We report here an investigation of the formation and reactivity of lead(IV) formazan and imine systems.

The formazan ligands **2a–f** were readily obtained in good yield using literature precedent[24] by sequential reaction of phenylhydrazine with an aryl aldehyde followed by an aryl diazonium salt (47–70%, Scheme 1). In the case of the nitro-substituted systems **2d** and **2e**, single-crystal X-ray analysis was possible (Fig. 1), confirming the structure;[25] noteworthy was that both these systems adopted the 'closed' conformation, which has been previously reported,[26] in which the molecule is fully planar, and that the N–H proton bridges both N1 and N4, consistent with the tautomeric nature of these compounds. The ligands **3a,b** and **4** were readily prepared by condensation of pyridine-2-carboxaldehyde with the relevant amine.

Treatment of 1 equiv of lead tetracarboxylate (acetate, toluate, *m*-methoxybenzoate or thiophenecarboxylate, prepared as reported earlier[21]) with 1 equiv of the formazan ligands **2a–f** or imine ligands **3a,b** and **4** provided the corresponding 1:1 adducts as amorphous solids. These carboxylates were chosen for their spread of electronic properties, and in the case of thiophenecarboxylic acid, for its unusual activating effect.[27,28] Although change of some of the chemical shifts in the NMR spectra of these adducts suggested successful ligation, the spectra were generally complex, consistent with dynamic behaviour, and without the formation of a complex of single stoichiometry in solution; we have observed rapid ligand exchange of lead(IV) carboxylates in solution earlier,[8,29–31] and assume that similar exchange operates in this system. Signals in the IR spectrum in the region 1520–1540 cm^{-1} were consistent with the presence of carboxylate and amidine units,[32,33] but not with that of formazanyl anions, since Hicks reports that uncomplexed formazans have IR bands in the range 1595 (s), 1515 (s) and 1495 (s), but that the corresponding formazanyl boracycles exhibit signals at 1305 (s), 1250 (s) and 1055 (s) cm^{-1}.[26]

Reaction of the 1:1 lead(IV)–formazan mixtures with ethyl 2-oxocyclopentane carboxylate (Scheme 2) or methyl Meldrum's

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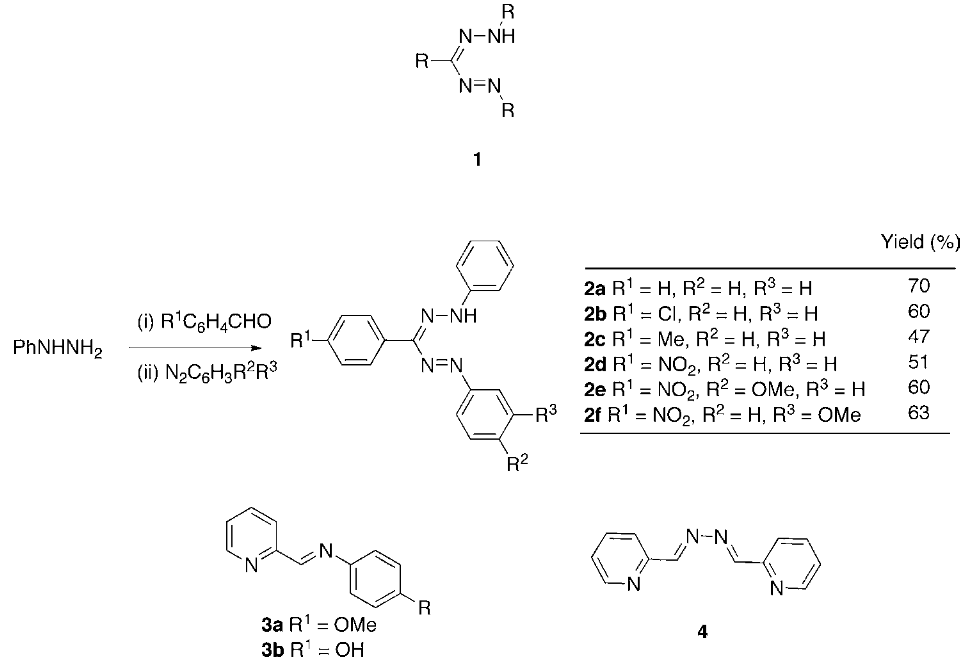


	Yield (%)
2a R^1 = H, R^2 = H, R^3 = H	70
2b R^1 = Cl, R^2 = H, R^3 = H	60
2c R^1 = Me, R^2 = H, R^3 = H	47
2d R^1 = NO_2, R^2 = H, R^3 = H	51
2e R^1 = NO_2, R^2 = OMe, R^3 = H	60
2f R^1 = NO_2, R^2 = H, R^3 = OMe	63

Scheme 1.

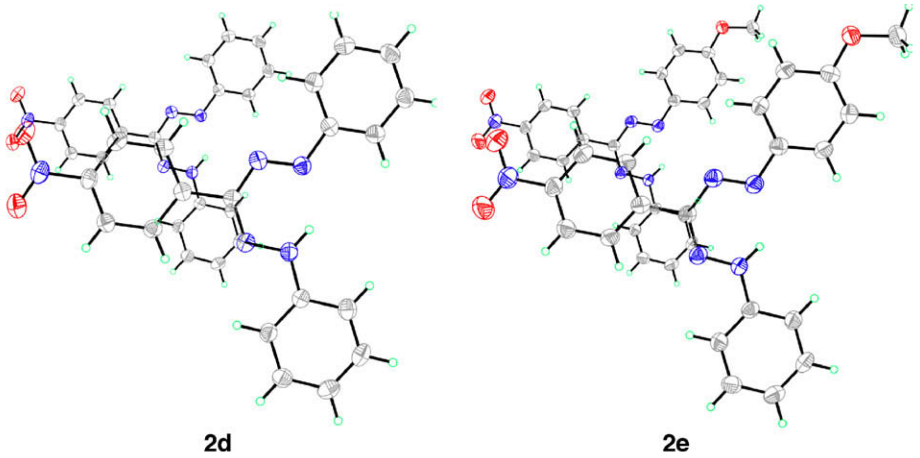
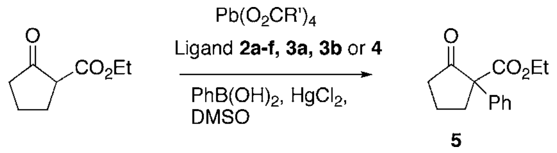
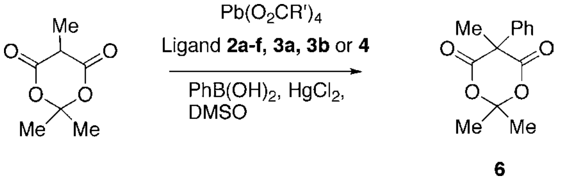


Figure 1. Thermal ellipsoid plots for compounds **2d** and **2e** drawn at the 50% probability level (disorder omitted for clarity).

acid (Scheme 3), and phenylboronic acid using mercury(II) catalysis to assist metal–metal exchange,[34] gave the corresponding arylated products **5** and **6**. Under these conditions, an aryllead(IV) intermediate is generated as the reactive arylating species.[5] The reactions were broadly independent of the carboxylate substituent, with acetate, toluate, *m*-methoxybenzoate and thiophenecarboxylate giving comparable yields (Table 1)[35,36] and this outcome is reminiscent of earlier work where no clear trend of structure or reactivity emerged for complexes derived from electronically diverse carboxylate ligands.[12–14] In both these reactions, the chloro-substituted **2b** and methyl-substituted formazan ligand **2c** gave amongst the highest yields, again independently of the carboxylate substituent. Nitro-substituted ligand systems performed poorly with lead(IV) acetates, but their reactivity improved in combination with toluate, *m*-methoxybenzoate and thiophenecarboxylate systems. The reactions of lead tetracarboxylate (toluate, *m*-methoxybenzoate or thiophenecarboxylate) in the presence of 1 equiv of imine ligands **3a,b** and **4** (Schemes 1 and 2, Table 2) were also examined. Noteworthy were the enhanced arylation yields obtained in the presence of diimine **4**, suggesting that a neutral bidentate imine ligand offers beneficial improvement to arylation yields relative to the formazan system. Significant, though, was that the observed yields were not superior to those achieved



Scheme 2.



Scheme 3.

Table 1

Yields of arylation products **5** and **6** formed according to Schemes 2 and 3 using a lead tetracarboxylate and ligands **2a**–**f**

Ligand	$Pb(O_2CR')_4$ R′ =	Yield **5** (%)	Yield **6** (%)
2a	CH_3	18	25
2b	CH_3	22	27
2c	CH_3	27	34
2d	CH_3	8	12
2e	CH_3	21	26
2f	CH_3	15	17
2a	p-MeC_6H_4	22	28
2b	p-MeC_6H_4	35	37
2c	p-MeC_6H_4	30	38
2d	p-MeC_6H_4	24	22
2e	p-MeC_6H_4	24	30
2f	p-MeC_6H_4	23	27
2a	m-$MeOC_6H_4$	23	27
2b	m-$MeOC_6H_4$	29	33
2c	m-$MeOC_6H_4$	27	34
2d	m-$MeOC_6H_4$	25	21
2e	m-$MeOC_6H_4$	24	28
2f	m-$MeOC_6H_4$	17	22
2a	2-Thienyl	27	31
2b	2-Thienyl	30	35
2c	2-Thienyl	26	32
2d	2-Thienyl	22	25
2e	2-Thienyl	27	32
2f	2-Thienyl	21	24

Table 2

Yields of arylation products **5** and **6** formed according to Schemes 2 and 3 using a lead tetracarboxylate and ligands **3a**, **3b** and **4**

Ligand	$Pb(O_2CR')_4$ R′=	Yield **5** (%)	Yield **6** (%)
3a	p-MeC_6H_4	21	27
3b	p-MeC_6H_4	20	25
4	p-MeC_6H_4	30	40
3a	m-$MeOC_6H_4$	17	21
3b	m-$MeOC_6H_4$	27	24
4	m-$MeOC_6H_4$	35	43
3a	2-Thienyl	27	30
3b	2-Thienyl	22	20
4	2-Thienyl	33	37

under previously reported conditions,[5,6] and unlike other amine ligands,[37] the formazan and imine systems did not appear to give a ligand acceleration effect.

We conclude from this work that although arylation reactions do proceed with lead(IV) salts in the presence of formazan and imine ligands, there is no observable rate acceleration effect and yields are not improved when compared to reactions conducted in the absence of nitrogen-containing ligands; however, it is clear that electronic factors may be important in the processes, and optimisation of the reaction may be possible.

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35. The lead(IV) complex (1.0 equiv), phenylboronic acid (1.1 equiv) and $HgCl_2$ (1.0 equiv) were dissolved in DMSO (10–25 mL) and stirred at 40 °C for 2 h. Ethyl 2-oxocyclopentane carboxylate (1.0 equiv) in pyridine (3.0 equiv) was added to the above reaction mixture dropwise, which was then stirred at 40 °C for 2 h and then at 80 °C for 10 h. The product was extracted from DMSO by washing with water and CH_2Cl_2. The combined organic fractions were then concentrated in vacuo. Purification by column chromatography (eluting with 95:5 pentane/ether) gave ethyl 2-oxo-1-phenylcyclopentanecarboxylate[5] as a colourless oil.
36. The lead(IV) complex (1.0 equiv), phenylboronic acid (1.1 equiv) and $HgCl_2$ (1.0 equiv) were dissolved in DMSO (10–25 mL) and stirred at 40 °C for 2 h. Methyl Meldrum's acid (1.0 equiv) in pyridine (3.0 equiv) was added to the above reaction mixture dropwise, which was then stirred at 40 °C for 2 h and then at room temperature for 10 h. The product was extracted from DMSO by washing with water and CH_2Cl_2. The combined organic fractions were concentrated in vacuo. Purification by column chromatography [eluting with CH_2Cl_2–petroleum ether (80:20)] gave 2,2,5-trimethyl-5-phenyl-1,3-dioxane-4,6-dione.[5]
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