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Rate enhancing ligands for lead(IV)-mediated arylations

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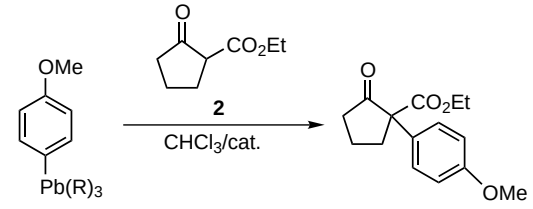
Abstract—The level of acceleration of the reactions of aryllead(IV) tricarboxylates with β-dicarbonyl reagents in the presence of several catalysts has been determined; in the case of 1,10-phenanthroline, almost a thousandfold increase in rate over the uncatalysed reaction was observed.

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] Pyridine also catalyses ligand redistribution in some aryllead(IV) compounds.[8] We have been interested in expanding the repertoire of lead(IV)-based processes, and particularly in the development of asymmetric carbon–carbon coupling reactions. However, our initial work in this area has been disappointing, as although the preparation of chiral carboxylate ligands suitable for lead(IV) was relatively straightforward, their derived complexes proved to be remarkably unreactive and the observed e.e. values for arylation reactions were low, typically in the range 6–16%.[9,10] Detailed NMR investigations suggested that the cause of the problem lay with fast ligand exchange, which favoured the replacement of the chiral but bulky ligands, with smaller achiral ones inevitably present in the reaction medium to give more reactive but achiral complexes; substantial attrition of asymmetric induction therefore ensues. This outcome is the exact reverse of ligand accelerated catalysis, a phenomenon crucial to the success of many modern asymmetric transition metal processes.[11] However, there have been some recent developments in this area, since Konopelski has shown that aryllead(IV) reagents can exhibit high levels of diastereoselectivity[12] and Yamamoto has shown that asymmetric coupling of phenols using aryllead reagents with amine catalysts is possible.[13] In related chemistry, there has been a recent report of the asymmetric α-phenylation of β-keto ester enolates using (phenyl)iodonium tetrafluoroborates giving moderate e.e.s.[14]



1a R = O_2CMe
1b R = O_2CCMe_3
1c R = $O_2CC_6H_3Cl_2$
1d R = $O_2CC_4H_3S$
1e R = $O_2CC_3H_5$
1f R = $O_2CC_4H_7$
1g R = $O_2C_7H_5$

Scheme 1.

In view of literature reports which suggested that pyridine was either essential for, or at least improved, the reactivity of aryllead(IV) compounds,[5] we examined a number of ligands which contained a tethered pyridine sub-unit, but found these systems to be unreactive in arylation reactions.[9,10,15] We therefore undertook a more detailed examination of the effect of ligands on the reactions of aryllead(IV) compounds. Our goal was to identify ligands which may induce rate acceleration and therefore ultimately offer the potential for chiral induction. That such a goal is realistic is supported by some of our recent observations which indicated that thiophenecarboxylate ligands could have significant effects on the reactivity of lead(IV), having been crucial in the development of a simple but effective method for the oxidation of benzyl and other reactive alcohols[16] and for novel alkylation, lactonisation and carbon–carbon bond forming processes.[17] Furthermore, recent independent work clearly indicates that ligand modification can produce useful

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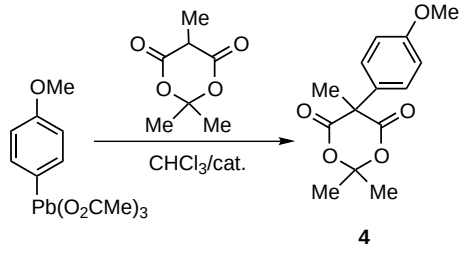
enhancements of reactivity in arylations with aryllead(IV) derivatives.[7]

Results and discussion

An initial survey of the effect of carboxylate ligands of aryllead(IV) tricarboxylates in arylation reactions was made (Scheme 1). The required *p*-methoxyphenyllead(IV) species **1b–g** were readily obtained by ligand metathesis of *p*-methoxyphenyllead(IV) triacetate **1a**[18] with pivalic, 2,6-dichlorobenzoic, thiophene-2-carboxylic, 3-butenoic, or 4-pentenoic acids, or with tropolone;[19] in addition, it was found to be possible to obtain a 1:1 adduct of *p*-methoxyphenyllead(IV) triacetate with DABCO, simply by stirring an equimolar mixture of each in toluene and removing the solvent. Each of the compounds **1b–g** was treated with dicarbonyl **2** in chloroform and pyridine as catalyst (3 equiv.) overnight at room temperature, giving the product **3** in yields of 52, 74, 40, 18, 37 and 0% respectively, with the **1a**·DABCO adduct also giving a yield of 75% of adduct **3**. This compares to a yield of **3** of 65% for **1a** alone. The good yields using lead(IV) compounds **1b**,**c** indicated that systems more sterically congested than the normally used acetate could possess good levels of reactivity, but that this could not be maintained indefinitely, as indicated by the unreactivity of the tropolonate **1g**. The moderate yield for thiophenecarboxylate derivative **1d** is surprising, since recent work has demonstrated the exceptional efficacy of this ligand in novel lactonisation and coupling processes.[17] The ω-unsaturated compounds **1e**,**f** are the first reported examples of this type of ligand for aryllead(IV) compounds.



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Scheme 2.

The success of the **1a**·DABCO reaction suggested that other nucleophilic and/or basic species might prove to be useful catalysts in these reactions. Therefore, 1-hydroxybenzotriazole, sodium methoxide, propylamine, and triphenylphosphine were examined in place of pyridine (3 equiv.) in the reaction of Scheme 1 with *p*-methoxyphenyllead(IV) triacetate; the yields of adduct **3** were 53, 62, 10 and 0%, respectively, clearly indicating that the reaction was highly sensitive to the nature of the added catalyst. The enhancements achieved with 1-HOBt and methoxide are the first reported arylation reactions which use a catalyst *other* than an amine.

In view of these results, a wider study of the rate enhancements achieved by catalysts suitable for lead(IV)-mediated arylation reactions was made; for this purpose, the arylation reaction of Scheme 2 was chosen, since this was particularly convenient to follow by ^{1}H NMR spectroscopy, in which the disappearance of the H-5 quartet and the methyl doublet of the starting material are easily quantified. Under the standard conditions for this reaction ($CDCl_3$, 40°C, 5 h), several potential catalysts were examined, and initial rate and final yield data for **4** are indicated in Table 1. These results are the first quantitative data for reactions of this type, and although it has been widely reported in earlier literature that pyridine and less commonly 1,10-phenanthroline are effective catalysts,[5,6] the level of this catalysis has hitherto remained unappreciated (entries 9, 12 and 13); interestingly, benzoquinoline was particularly ineffective. Once again, the suitability of an sp^3 hybridised system was illustrated by the good conversion and rate acceleration with DABCO (entry 8), but a triamine (entry 4) was not successful. Other notable catalysts include imidazole and DMAP (entries 10 and 11). We have recently shown that pyridine appears to act as a ligand donor, rather than a base, in a related aryllead(IV)-diaryllead(IV) disproportionation reaction,[8] and it would seem likely that the catalysts shown in Table 1 function in the same way for the reaction in Scheme 2.

Table 1. Initial rate and final yield data for the reaction given in Scheme 2

Entry	Additive[a]	Initial (relative) rate	Final yield (%)[b]
1	None	1	2
2	CD_3CN	1	5
3	Benzo[*h*]quinoline	2	5
4	1,1,4,7,7-Pentamethyldiethylenetriamine	4	10
5	NaOMe	18	60
6	1,3-Diphenylguanidine	22	35
7	1-HOBt	40	35
8	DABCO	88	50
9	Pyridine	133	70
10	Imidazole	180	90
11	DMAP	284	95
12	1,10-Phenanthroline (1 equiv.)	300	90
13	1,10-Phenanthroline	980	100

[a] 3 equiv. unless otherwise indicated.
[b] After 5 h reaction.

This is the first detailed investigation of catalysts suitable for lead(IV)-mediated arylations. The results indicate that significant levels of rate acceleration are possible using diverse ligand donors, and suggest that further rate enhancement may be possible using suitably designed systems. This is likely to be of considerable importance in the design of systems capable of asymmetric arylations, as well as other novel processes. Further efforts in this endeavour will be reported in due course.

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