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Reductive decomplexation of π-allyltricarbonyliron lactone complexes; a new route to stereo-defined 1,7-diols and 2,3-diene-1,7-diols†

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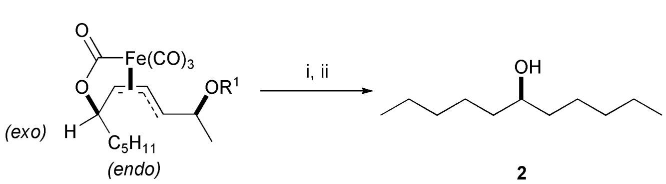
Treatment of π-allyltricarbonyliron lactone complexes bearing an adjacent leaving group, with lithium naphthalenide causes decomplexation to acyclic dienols in excellent yield and without any scrambling of the allylic centre.

The availability of a range of methods for removal of the ligating iron moiety in a predictable manner[1] is crucial to the use of π-allyltricarbonyliron lactone complexes in synthesis. To date four methods have been reported for decomplexation: barium hydroxide mediated decarboxylation[2] followed by oxidative release of the organic ligand to afford dienes; exhaustive carbonylation to furnish δ-lactones;[2] single electron oxidation to give β-lactones[3] and borohydride reagents to yield enediols.[4] By understanding the behaviour of these complexes in differing chemical and physical environments, a more detailed picture of the bonding within the complexes emerges which allows for better planning of new synthetic transformations. The advent of highly selective hydride, alkyl and alkynyl additions to ketones adjacent to the η^3 unit[5] and Mukaiyama aldol reactions of appended silyl enol ethers[6] gives access to functionalised polyol fragments at the periphery of the organic ligand. Here we report a new decomplexation method that leads to a new range of products.

Initial studies focused on the iron lactone complex **1a**.[4] After screening a number of reagents it was found that treatment with lithium dimethylcuprate caused the stereo-controlled removal of the iron. Reaction of complex **1a** with the dimethyl copper lithium at −78 °C in THF for 12 h followed by warming to room temperature afforded a mixture of dienes which had formed *via* elimination of the appended alcohol. Hydrogenation of the mixture afforded a single symmetrical molecule undecan-6-ol **2** and thereby also confirmed the regiochemistry of the reaction (Scheme 1).

Consideration of a possible mechanism for this cuprate decomplexation reaction led to the idea that the cuprate was acting as a single electron reductant and that the iron by-product was most likely to be dilithium tetracarbonylferrate [$Li_2Fe(CO)_4$], the analogous sodium salt being well known in the literature.[7] Four electron equivalents would be required if this process was operating which is also what was observed. Optimisation of this route focused on two main considerations. First, a better leaving group than an appended hydroxyl group would be sensible. Secondly the copper species may be bonding to the hydroxyl aiding its ability to leave and/or affecting its oxidative lability and therefore the other modification was to employ a strong single electron reductant such as lithium naphthalenide. As iron complexes bearing acetates could be prepared in high yield they were examined first. Treatment of lactone complex **1b** with lithium naphthalenide in THF at −78 °C for 12 h followed by warming to room temperature and subsequent hydrogenation of the product(s) once again gave the undecan-6-ol **3** but in a much improved yield (92%) (Scheme 1).



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1a R^1 = H, **1b** R^1 = Ac

Scheme 1 *Reagents and conditions*: for **1a**: (i) $LiCuMe_2$, THF −78 °C to rt; (ii) H_2, Pd/C, EtOAc, 78%. For **1b**: (i) lithium naphthalenide, THF −78 °C to rt; (ii) H_2, Pd/C, EtOAc, 92%.

A range of substrates were then prepared and treated with lithium naphthalenide, using methods previously developed by our group.[5] The chosen substitution patterns would produce a diverse range of diols (Table 1).

Once all these substrates were in hand, they were subjected to the newly developed decomplexation conditions and the diene mixtures that were produced were reduced to afford alkanediols (Table 1). Where the leaving group was an acetate **5a**–**6b** the reaction proceeded smoothly and in excellent yield **13a**–**16b**. It was also possible to use an alternative procedure for the diacetate precursors **5a,b**. Use of excess lithium naphthalenide followed by methanol work-up cleaved the remaining acetate and furnished unprotected diols in good yield **13a,b**. When a mesylate was used in place of an acetate group **7** the reaction yielded no isolable product on a 0.15 mmol scale. The cyclic carbonate **9a** underwent the same elimination with the loss of CO_2 to give an unprotected 1,7-alkanediol **13b**.

From analysis of the ^{1}H 600 MHz NMR spectra of the isolated mixtures of dienes from decomplexations carried out with lithium naphthalenide, three components were identified. Examination of the coupling constants indicated that these three components were (2*E*,4*E*), (2*Z*,4*E*), (2*E*,4*Z*) in all cases where the allylic alcohol is 1-C (Fig. 1). These mixtures represented almost total mass recovery (92–98% yield) and therefore their NMR spectra could be viewed as reasonably accurate representations of the selectivity of the reactions. In total six examples were studied. In the case of *endo* complexes with acetate leaving groups **5b**–**6a,8a** the main component was found to be (2*E*,4*E*)-**10a**–**d** with approximately equal amounts of (2*Z*,4*E*)-**11a**–**d** and (2*E*,4*Z*)-**12a**–**d**. For cyclic carbonates, no (2*E*,4*Z*)-**12e** isomer was observed and the yield of the other two components **10e,11e** increased. When an *exo* iron lactone complex **6b** was employed the major product switched from (2*E*,4*E*)-**10c** to (2*Z*,4*E*)-**11c**. Three components were still present with the minor two being the same geometry as previously observed.

In summary an extremely high yielding single electron decomplexation technique for π-allyltricarbonyliron lactone

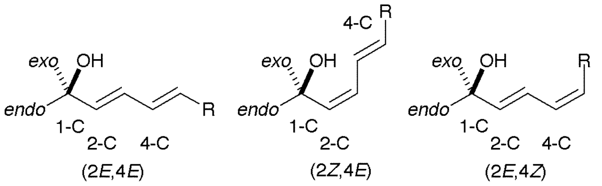

Fig. 1 Diene geometries recorded after demetallation.

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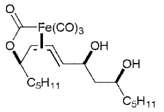
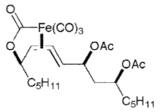
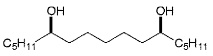
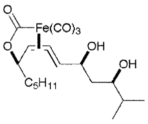
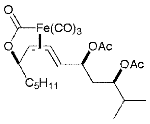
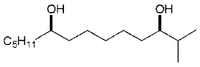
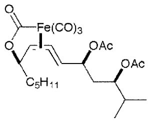
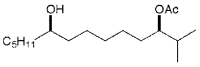
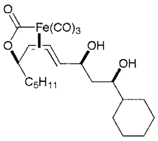
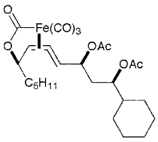
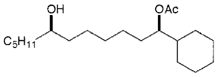
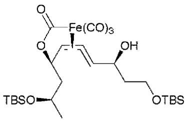
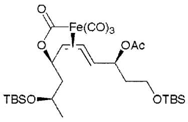
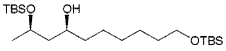
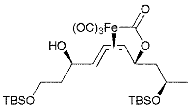
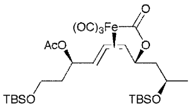
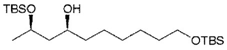
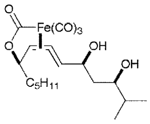
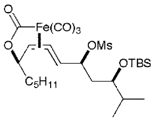
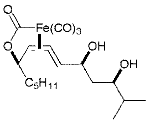
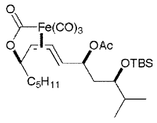
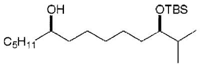
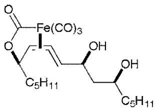
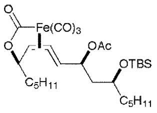
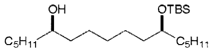
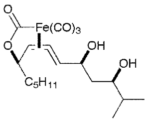
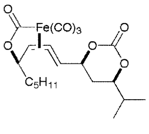
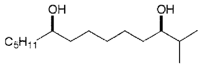
† Electronic supplementary information (ESI) available: experimental procedures. See http://www.rsc.org/suppdata/cc/b2/b206406p/

Table 1 *Reagents and conditions:* (a) Ac_2O, DMAP, NEt_3, CH_2Cl_2, 0 °C; (b) (i) TBSOTf, NEt_3, CH_2Cl_2, 0 °C; (ii) MsCl, NEt_3, CH_2Cl_2, 0 °C; (c) (i) TBSOTf, NEt_3, CH_2Cl_2, 0 °C; (ii) Ac_2O, DMAP, NEt_3, CH_2Cl_2, 0 °C; (d) TBSOTf, NEt_3, CH_2Cl_2, 0 °C then Ac_2O, DMAP; (e) CDI, DMAP, CH_2Cl_2; (f) (i) Li naphthalenide (10 equiv.), THF, −78 °C to rt, MeOH; (ii) H_2, Pd/C, EtOAc; (g) (i) Li naphthalenide (5 equiv.), THF, −78 °C to rt; (ii) H_2, Pd/C, EtOAc

Initial alcohol[a]	Procedure	Derivatised alcohol	Yield (%)	Decomplexation procedure	Diene geometry[bc] (*E*,*E*):(*Z*:*E*):(*E*,*Z*)	Decomplexed product	Yield[d] (%)
3a 	a	**5a** 	96	f		**13a** 	81
3b 	a	**5b** 	93	f		**13b** 	83
		5b 		g	0.70:0.17:0.13 **10a 11a 12a**	**14a** 	93
3c 	a	**5c** 	91	g	0.53:0.19:0.28 **10b 11b 12b**	**14b** 	91
4a 	a	**6a** 	97	g	0.62:0.15:0.23 **10c 11c 12c**	**15** 	96
4b 	a	**6b** 	95	g	0.26:0.67:0.07 **10c 11c 12c**	**15** 	96
3b 	b	**7** 	66[a]	g		No isolable product	
3b 	c	**8a** 	75[a]	g	0.62:0.20:0.18 **10d 11d 12d**	**16a** 	95
3a 	d	**8b** 	76	g		**16b** 	89
3b 	e	**9a** 	72	g	0.74:0.26:0.00 **10e 11e 12e**	**13b** 	96

[a] Isolated yield for two steps. [b] Where recorded. [c] As determined by the ^1H 600 MHz NMR spectra. [d] Isolated yield for two steps.

complexes has been developed to afford stereodefined 1,7-alkanediols after hydrogenation. It generates predictable diene geometry with good selectivity, in that *endo* complexes give (*E*,*E*)-dienes while *exo* complexes produce (*Z*,*E*)-dienes.

Notes and references

1 For a review of these complexes see S. V. Ley, L. R. Cox and G. Meek, *Chem. Rev.*, 1996, **96**, 423.

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