Synthesis and Reactivity of Novel π-Allylcyclopentadienyl Cobaltolactone Complexes

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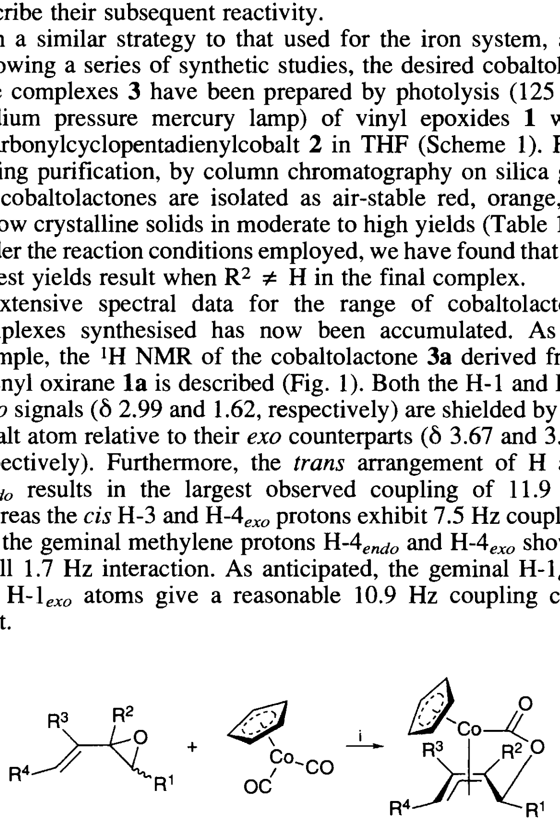
A range of novel cobaltolactone complexes are prepared under photolytic conditions from dicarbonylcyclopentadienylcobalt and vinyl epoxides; their subsequent reactivity under a selected series of reaction conditions is described.

For several years the preparation and use in organic synthesis of tricarbonyliron lactone complexes[1] has been an area of considerable interest with the results achieved being regarded as significant contributions to the field of organometallic chemistry as applied to organic synthesis.[2] Consequently, it was considered important that new areas of metallolactone chemistry be explored. In this communication, we report the synthesis of the first range of cobaltolactone complexes[3,4] and describe their subsequent reactivity.

In a similar strategy to that used for the iron system, and following a series of synthetic studies, the desired cobaltolactone complexes **3** have been prepared by photolysis (125 W, medium pressure mercury lamp) of vinyl epoxides **1** with dicarbonylcyclopentadienylcobalt **2** in THF (Scheme 1). Following purification, by column chromatography on silica gel, the cobaltolactones are isolated as air-stable red, orange, or yellow crystalline solids in moderate to high yields (Table 1).† Under the reaction conditions employed, we have found that the lowest yields result when $R^2 \neq H$ in the final complex.

Extensive spectral data for the range of cobaltolactone complexes synthesised has now been accumulated. As an example, the ^1H NMR of the cobaltolactone **3a** derived from ethenyl oxirane **1a** is described (Fig. 1). Both the H-1 and H-4 *endo* signals (δ 2.99 and 1.62, respectively) are shielded by the cobalt atom relative to their *exo* counterparts (δ 3.67 and 3.79, respectively). Furthermore, the *trans* arrangement of H and H_{endo} results in the largest observed coupling of 11.9 Hz whereas the *cis* H-3 and H-4_{exo} protons exhibit 7.5 Hz coupling and the geminal methylene protons H-4_{endo} and H-4_{exo} show a small 1.7 Hz interaction. As anticipated, the geminal H-1_{endo} and H-1_{exo} atoms give a reasonable 10.9 Hz coupling constant.



Scheme 1 *Reagents and conditions*: i, *hv*, THF, room temp.

Table 1 Synthesis of cobaltolactones **3** from vinyl epoxides **1** and Co(η-C_5H_5)$(CO)_2$ **2**

1	R^1	R^2	R^3	R^4	3 Yield (%)
a	H	H	H	H	65
b	H	H	H	Ph	83
c	H	Me	H	H	43
d	H	H	H	C_6H_4OMe-*o*	48
e	H	Me	H	Ph	22
f	H	Ph	H	Ph	43
g	H	Me	Me	H	26
h/i[a]	H/Me	H	H	Me/H	70

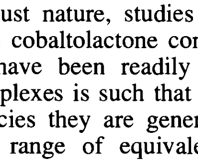
[a] A mixture of four epoxides, each of the C-4 and C-1 epimers of **1h** and **1i** respectively, were utilised to give a mixture of the four cobaltolactones, each of the C-4 and C-1 epimers of **3h** and **3i** respectively.

Overall, the novel cobaltolactone complexes have all shown remarkable stability when compared to the equivalent iron species. These compounds can be handled routinely for prolonged periods outwith an inert atmosphere and are stable indefinitely when stored under nitrogen at low temperature.

Due to their robust nature, studies on the reactivity and potential use of the cobaltolactone complexes as reagents in organic synthesis have been readily initiated. Indeed, the stability of the complexes is such that when compared to the analogous iron species they are generally more resistant to oxidation under a range of equivalent conditions. Under optimised oxidative conditions with cerium(IV) ammonium nitrate (CAN) either vinyl carbonates or vinyl ketals are formed depending on the reaction solvent employed. As shown in Scheme 2, reaction of the 4-phenyl substituted complex **3b** with CAN in acetonitrile, under sonication conditions, gives the vinyl carbonate **4**,‡ whereas reaction between the same complex and oxidising agent in acetone yields the vinylic ketal **5**. Furthermore, CAN oxidation in methanol gives methoxy butenol **6**. Under these oxidative conditions it is proposed that the observed products are formed due to the attack of nucleophilic solvent species (or, in the formation of vinyl carbonates, oxidant nucleophiles) at the 2-position of the organocobalt complex.

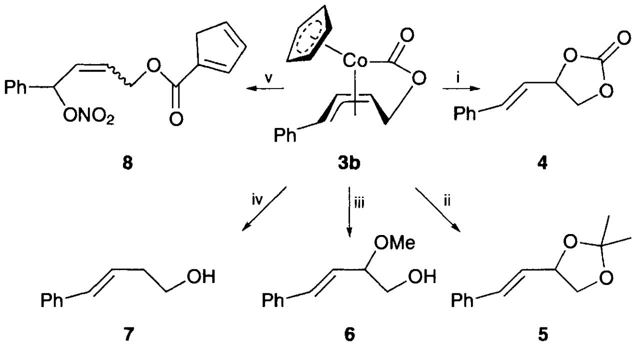
To support this mode of nucleophilic reaction we have demonstrated hydride attack at the same 2-position by reduction of the cobaltolactone **3b** with $LiAlH_4$ to yield the homoallylic alcohol **7**.

^1H NMR ($CDCl_3$) δ	
H^1_{endo}	2.99
H^1_{exo}	3.67
H^2	5.26
H^3	5.01–5.17
H^4_{endo}	1.62
H^4_{exo}	3.79
C_5H_5	5.09



^1H coupling constants / Hz	
$J_{1exo,1endo}$	10.9
$J_{1exo,2}$	6.5
$J_{1endo,2}$	2.6
$J_{2,3}$	—
$J_{3,4exo}$	7.5
$J_{3,4endo}$	11.9
$J_{4exo,4endo}$	1.7

Fig. 1 ^1H NMR data for complex **1a** (250 MHz)



Scheme 2 *Reagents and conditions*: i, CAN, MeCN,))), 1.25 h (45%); ii, CAN, Me_2CO,))), 1.25 h (57%); iii, CAN, MeOH,))), 1.25 h (33%); iv, $LiAlH_4$, THF, room temp., 0.5 h (52%); v, CAN, CH_2Cl_2, room temp., 2 h (20%)

In related oxidation reactions to those already described, the analogous oxidant, cerium(IV) triethylammonium nitrate (CTAN), in dichloromethane solution, yields products assigned as cyclopentadiene esters (*e.g.* **8**) possessing allylic nitrate functionality.

In conclusion, a number of novel cobaltolactone complexes, which have a variety of potential synthetic utility, have been routinely synthesised from readily available starting materials. Their synthesis under a range of alternative techniques and studies on their further reactivity are ongoing within our laboratory.

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Footnotes

† All compounds exhibited satisfactory analytical and spectral data.

‡ The vinyl carbonate **4** can also be formed in an improved yield of 65% when the reaction of **3b** with CAN is carried out at room temperature in the presence of *p*-methoxybenzonitrile in acetonitrile solution (1.5 h). The equivalent reaction without *p*-methoxybenzonitrile gives only a 31% yield of **4** over 17 h.

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2 *Organometallic Chemistry and Organic Synthesis: The Influence of Organometallic Chemistry on Organic Synthesis: Present and Future*, Proceedings of a Royal Society Discussion Meeting, 24th and 25th Feb. 1988, ed. M. L. H. Green and S. G. Davies.

3 A single cobaltolatone complex is mentioned briefly in ref. 1(*f*) as unpublished results. Despite a ^{1}H NMR spectrum having been reported, no experimental conditions for its preparation are disclosed.

4 More recently a related aminocarbene complex has been synthesised which is presumed to have formed *via* a cobaltolactone species: R. Schobert, F. Hampel, K.-D. Roth and M. Stöss, *J. Organomet. Chem.*, 1995, **493**, 113.