Experimental Section

6′: A solution of **5′** (0.105 g, 0.107 mmol) in CH_3CN (20 mL) was added to a solution of $AgPF_6$ (0.054 g, 0.214 mmol) in CH_3CN (2 mL). After 12 h the slurry was centrifuged for 15 min at 5000 rpm. The supernatant was allowed to stand for a further 24 h, and the solvent was evaporated to give a yellow oil (further AgCl was removed by filtration through Celite). The oil was extracted into ≈ 3 mL of CH_3CN. The addition of 50 mL of Et_2O gave 0.078 g of product (60 % based on **5′**). ^1H NMR (500 MHz, $[D_3]CH_3CN$, 22 °C, TMS): $\delta = 5.71$ (s, 20 H, C_5H_5), 2.34 (q, 8 H, CH_3CH_2), 1.77 (d, 48 H, $(CH_3)_4C_5$), 1.17 (t, 12 H, CH_3CH_2); ^{13}C NMR (125 MHz, $[D_3]CH_3CN$, 22 °C, TMS, sample enriched to 30 % ^{13}C): $\delta = 132.4$ ppm (s, CN); IR (KBr pellet): $\tilde{\nu} = 2180$ cm^{-1} ($C\equiv N$); elemental analysis calcd for $C_{76}H_{88}N_{12}Co_4F_{24}P_4Rh_4$: C 38.09, H 3.70, N 7.01; found (two independently synthesized batches): batch A: C 37.61, H 3.74, N 6.51; batch B: C 37.75, H 3.75, N 6.40.

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[12] X-ray structure analysis of **6′**-4 $PF_6 \cdot 6$ MeCN ($C_{88}H_{106}N_{18}Co_4F_{24}P_4Rh_4$): crystal dimensions $0.28 \times 0.20 \times 0.06$ mm; $T = 175$ K; $\lambda = 0.71073$ Å; monoclinic, space group $P2_1/c$: $a = 15.177700(10)$, $b = 49.7980(6)$, $c = 16.1562(2)$ Å, $\beta = 116.1830(10)°$; $Z = 4$; $V = 10957.7(2)$ Å^3; $\rho_{calcd} = 1.602$ g cm^{-3}; 32454 reflections ($R_{int} = 0.1116$), 5656 observed reflections ($I > 2\sigma(I)$); GOF on $F^2 = 1.048$; R_1(observed data) = 0.122, $wR_2 = 0.2835$. Data were collected on a Siemens CCD diffractometer. The structure was solved by direct methods (SHELX suite). The PF_6^- counterions are disordered. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101173. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acylzirconocene Chloride as an "Unmasked" Acyl Anion[**]

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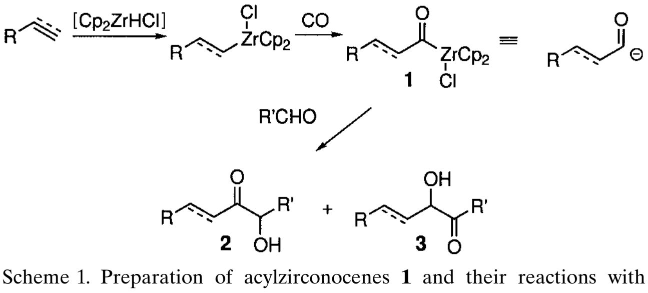
Easy access to stable acylzirconocene chloride derivatives **1** through a sequential treatment of alkenes or alkynes with zirconocene hydrochloride ($[Cp_2ZrHCl]$, Schwartz reagent) and carbon monoxide has brought about the synthetic utility of **1** for the preparation of carboxylic acids and their derivatives.[1] Extensive structural studies and work on the reactivity of acylzirconocene compounds have been carried out by many research groups[2] to elucidate the characteristic features of the acylzirconocene derivatives. While the generation of very reactive acylmetals in which the metal species is a main group metal is a very attractive field,[3] their use as an "unmasked" acyl anion for organic synthesis is limited due to their instability. The transition metal acyl complexes have also long attracted much attention because of their intrinsic usefulness as an acyl anion equivalent in organic synthesis.[4] To the best of our knowledge, there is no report regarding the carbon–carbon bond forming reactions of **1** with carbonyls in which an acyl group of **1** reacts as an acyl anion to give α-ketol derivatives **2**. We describe here the first reactions of acylzirconocene chloride complexes **1** with aldehydes to give α-ketol derivatives **2** in fair to good yields under mild Lewis acid mediated conditions (Scheme 1).



Scheme 1. Preparation of acylzirconocenes **1** and their reactions with aldehydes.

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Table 1. α-Hydroxyketone derivatives **2** and **3** from acylzirconocene chlorides **1** and aldehydes.

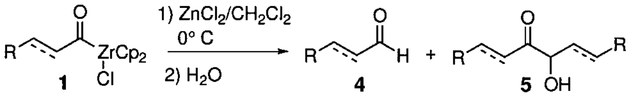
Entry	Alkene or alkyne	Conditions[a] starting material	R′	Additive	Yield [%][b]	
					2	**3**
1	n-$C_6H_{13}CH{=}CH_2$	A	Ph	$AgBF_4$	22[c]	–
2	n-$C_6H_{13}CH{=}CH_2$	A	Ph	$AgAsF_6$	34[c]	–
3	n-$C_6H_{13}CH{=}CH_2$	B	Ph	$BF_3 \cdot OEt_2$	79[c]	–
4	n-$C_6H_{13}CH{=}CH_2$	B	Ph	$ZnCl_2$	58[c]	–
5	n-$C_6H_{13}CH{=}CH_2$	B	Ph	$TiCl_4$	60[c]	–
6	n-$C_6H_{13}CH{=}CH_2$	B	Ph	$TiCl_2(O$*i*$Pr)_2$	25[c]	–
7	n-$C_6H_{13}CH{=}CH_2$	B	Ph	$AlCl_3$	9[c]	–
8	n-$C_6H_{13}CH{=}CH_2$	B	$Ph(CH_2)_2$	$BF_3 \cdot OEt_2$	49[c]	29[c]
9	n-$C_6H_{13}CH{=}CH_2$	B	p-$MeOC_6H_4$	$BF_3 \cdot OEt_2$	62[c]	18[c]
10	n-$C_6H_{13}CH{=}CH_2$	B	(E)-PhCH=CH	$BF_3 \cdot OEt_2$	–	59[c]
11	n-$C_6H_{13}CH{=}CH_2$	B	(S)-$H_3CCH(OBn)$	$BF_3 \cdot OEt_2$	53[c,d]	–
12	n-$C_6H_{13}CH{=}CH_2$	B	(S)-$H_3CCH(OTBDMS)$	$BF_3 \cdot OEt_2$	77[c,e]	–
13	$BnO(CH_2)_2CH{=}CH_2$	C	Ph	$BF_3 \cdot OEt_2$	74[f]	–
14	$BnO(CH_2)_2CH{=}CH_2$	C	(E)-$H_3CCH{=}CH$	$BF_3 \cdot OEt_2$	22[f]	53[f]
15	n-$C_4H_9C{\equiv}CH$	C	Ph	$BF_3 \cdot OEt_2$	69[f]	–
16	$Ph(CH_2)_2C{\equiv}CH$	C	Ph	$BF_3 \cdot OEt_2$	43[f]	–
17	$Ph(CH_2)_2C{\equiv}CH$	C	Et	$BF_3 \cdot OEt_2$	48[f]	–
18	$PhC{\equiv}CH$	C	Ph	$BF_3 \cdot OEt_2$	65[f]	–
19	$PhC{\equiv}CH$	C	$Ph(CH_2)_2$	$BF_3 \cdot OEt_2$	60[f]	–

[a] A: See the experimental procedure except the molar ratio of alkene:$[Cp_2ZrHCl]$:R′CHO:additive = 2:1:1:1.2. B: Same as A except the ratio of alkene:$[Cp_2ZrHCl]$:R′CHO:additive = 4:2:1:2. C: Same as A except the ratio of alkene or alkyne:$[Cp_2ZrHCl]$:R′CHO:additive = 1:1.5:2:2. [b] Yield of isolated product. [c] Based of aldehyde. [d] *syn/anti* = 5.4. [e] *syn/anti* = 3.5. [f] Based on alkene or alkyne. Bn = benzyl. TBDMS = *tert*-butyldimethylsilyl.

Synthetic routes to **2** through the reactions of an "unmasked" acyl anion with carbonyl compounds are not common. Previous reports concerning "unmasked" acyl anions give acyllithium[3] and/or acylsamarium[4a] as the reagents of choice for the preparation of **2**. However, the generation and reactions of the acyllithium species with carbonyls require extreme conditions ($\approx -110\,^\circ$C). Similarly, the reactions of acylsamarium—generated by treating alkyl halide or acyl halide with a low-valent samarium complex—with carbonyls depend on the nature of the substrate.

The results of the reactions of **1** with aldehydes in the presence of an additive are listed in Table 1.[5] The Lewis acidic silver ion is known to activate the carbonyl group and to accelerate the nucleophilic reactivity of the organozirconocene chloride complex by abstracting a chlorine atom to form a cationic organozirconocene species.[6] Treatment of a mixture of **1** and aldehyde in dichloromethane with a silver salt at $-20\,^\circ$C gives **2** in modest yields (18–34 %) (entries 1–2). In the absence of the silver salt, no **2** could be observed in the reaction mixture. Although the yield of **2** is modest, the preferred silver salt is silver hexafluoroarsenate $[AgAsF_6]$ (entry 2) as judged by the reaction rate and the clearness of the reaction medium.

Replacing the silver salt with a variety of other Lewis acids revealed that the yields of **2** depend largely on the specific Lewis acid employed. Thus, the yield of **2** was significantly improved to 79 % when a stoichiometric amount (1 equivalent with respect to **1**) of boron trifluoride etherate ($BF_3 \cdot OEt_2$) was employed at 0 °C (entry 3). α,β-Unsaturated acylzirconocene complexes **1** also reacted with aldehydes under the same reaction conditions to give **2** (entries 15–19). Steric bulk in the alkyl group of the aldehyde severely impeded the reaction. Thus, pivalaldehyde failed to react with **1** to give **2**. Furthermore, neither ketones nor acid chlorides react with **1**. In the $BF_3 \cdot OEt_2$-mediated reaction of **1**, isomeric α-ketol **3** was isolated as a side product (entries 8, 9) or a major product (entries 10, 14), while the reaction of **1** derived from alkyne did not give the isomeric α-ketol product **3** (entries 15–19). The formation of **3** as a side product has also been reported in the reaction of acylsamarium with aldehydes.[4a] It should be noted that the reactions of α-alkoxy aldehydes with **1** gave a 1,2-*syn* isomer as the major product (a *syn/anti* ratio from 3.5 to 5.4) (entries 11, 12).[7] The exact role of the added Lewis acid in the present reaction is unclear. However, it is worth mentioning that the reaction of **1** with $ZnCl_2$ at 0 °C without adding aldehyde gave the aldehyde **4** and α-ketol **5** in a 1:1 ratio [Eq. (1)]. This observation suggests that the transmetalation of **1** with $ZnCl_2$ giving an acylzinc derivative might be partially involved in the present reaction since the easy isomerization of acylzinc to an oxycarbene intermediate and the formation of α-ketol product **5** have been suggested.[8]



(1)

The addition of $AlCl_3$, which is also reported to give acylaluminum[9] by the transmetalation of **1**, yielded **2** in 9 % yield (entry 7). We must await further study to be able to differentiate between the following mechanisms: a) the nucleophilic addition of the acyl group of **1** to the Lewis acid activated aldehyde, or b) the nucleophilic addition of the acyl group of the cationic species of **1** to aldehyde, or c) the transmetalation of **1** with Lewis acid.

In any event **1** is an excellent candidate as an "unmasked" acyl anion precursor, since the reported procedure in the literature for the generation and the reaction of the "unmasked" acyl anion is usually carried out at extremely low temperature and is hampered by the difficulty of the experimental procedure.

Experimental Section

A typical procedure for the reaction of **1** with benzaldehyde: To a suspension of $[\mathrm{Cp_2ZrHCl}]$ (507 mg, 2.0 mmol) in CH_2Cl_2 (8 mL) was added 1-octene (0.62 mL, 4.0 mmol), and the resulting mixture was stirred for 30 min at ambient temperature. After the mixture had been stirred under an atmosphere of CO for 2 h, benzaldehyde (0.10 mL, 1.0 mmol) and $BF_3 \cdot OEt_2$ (0.24 mL, 2.0 mmol) were added at $-20\,^{\circ}C$, and the mixture was stirred at $0\,^{\circ}C$ for 1 h. The reaction mixture was treated with aqueous $NaHCO_3$ and extracted with ether (3×15 mL). The combined ethereal extracts were washed with saturated sodium chloride solution, dried over $MgSO_4$, and concentrated under reduced pressure to give a crude oil, which was purified by flash column chromatography (silica gel, hexane:EtOAc = 20:1 → 15:1 → 10:1) to give 1-hydroxy-1-phenyl-2-decanone (193 mg, 79 %). Spectroscopic data for 1-hydroxy-1-phenyl-2-decanone: mp 33.3–35.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.84-0.88$ (3H, m), 1.15–1.28 (10H, m), 1.43–1.55 (2H, m), 2.29 (1H, ddd, $J = 6.9, 7.9, 16.8$ Hz), 2.37 (1H, ddd, $J = 6.5, 8.2, 16.8$ Hz), 4.35 (1H, d, $J = 4.2$ Hz), 5.08 (1H, d, $J = 4.2$ Hz), 7.30–7.40 (5H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$); $\delta = 14.0$, 22.5, 23.6, 28.87, 28.94, 29.1, 31.7, 37.7, 79.6, 127.4, 128.6, 128.9, 138.1; IR (KBr) $\tilde{\nu} = 3431$ (broad), 2917, 1716 cm^{-1}; EIMS m/z 248 $[M^+]$. Analysis calcd for $C_{16}H_{24}O_2$: C 77.38, H 9.74; found: C 77.14, H 9.57.

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Keywords: acylations · aldehydes · Lewis acids · nucleophilic additions · zirconium

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Highly Enantioselective One-Pot Synthesis of Chiral Tri- and Tetrasubstituted Ferrocenes from 1,1′-Ferrocenedicarbaldehyde[**]

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Owing to the increasing involvement of ferrocene derivatives in various fields[1] such as asymmetric synthesis and catalysis[2] and materials chemistry (especially for nonlinear optics),[3] new methods for obtaining pure enantiomers of substituted ferrocenes with planar chirality are of current interest. Several efficient syntheses of chiral disubstituted ferrocenes are based on diastereoselective lithiation of ferrocenyl derivatives in the position *ortho* to substitutuents that exhibit asymmetric induction, such as tertiary amines,[4] acetals,[5] sulfoxides,[6] and oxazolines.[7] Recently, enantioselective *ortho* lithiation of nonchiral monosubstituted ferrocenes (direct synthesis)[8] with chiral tertiary amines as auxiliaries was reporeted. This led to disubstituted ferrocenes with enantioselectivities of up to 99 % *ee*.[8b] The enantioselective synthesis of C_2-symmetric tetrasubstituted ferrocene derivatives with planar chirality has so far received little attention, and all the reported methods followed the diastereoselective *ortho* lithiation strategy.[9] However, C_2-symmetric tetrasubstituted ferrocenes are important starting materials for the design of chiral ligands that have given enantiomeric excesses of up to 99 % in asymmetric syntheses.[10]

In 1981 Comins and Brown described a straightforward method in which the addition of a lithium amide to an aromatic aldehyde produced an aminal anion as a temporary protecting/directing group for *ortho* metalation.[11] Recently, Alexakis et al.[12] reported the enantioselective *ortho* lithiation of a benzaldehyde complex of tricarbonylchromium by applying the same strategy with chiral amides. We described a new method for the synthesis of 1,1′-disubstituted ferrocenes by a one-pot procedure based on the addition of the lithium salt of *N*-methylpiperazine to ferrocenecarbaldehyde. This produced an aminoaminal anion that protects the formyl group of one ring while its amino group directs the deprotonation in the other ring.[13]

Here we report an extension of this procedure to the enantioselective synthesis of C_2-symmetric tetrasubstituted ferrocenes **5** from 1,1′-ferrocenedicarbaldehyde (**1**) by means of the lithium salt of (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine (**2**; Scheme 1). Treatment of the diaminal dianion **3** with *t*BuLi (1.5 equiv) at $-78\,^{\circ}C$ followed by reaction with the electrophile trimethylsilyl chloride afforded (*R*)-**4**, which after hydrolysis and purification by flash chromatography was obtained in 29 % yield with an enantiomeric excess[14] of 96 %

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