

Stereospecific Synthesis of a Metallo-enolate: E -[Zr{OC(SiMe₃)=CHAr}Cl(η-C₅H₅)₂] (Structurally Characterised) via Carbonylation of [Zr{CH(SiMe₃)Ar}Cl(η-C₅H₅)₂] (Ar = 9-Anthryl)†

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Treatment of Li{CH(SiMe₃)Ar}(tmeda) (Ar = 9-anthryl, tmeda = Me₂N[CH₂]₂NMe₂) with zirconocene(IV) chloride in tetrahydrofuran at 20 °C affords [Zr{CH(SiMe₃)Ar}Cl(η-C₅H₅)₂], which rapidly reacts with carbon monoxide (P_{CO} 1 atm, 20 °C) in toluene to afford exclusively the E -metallo-enolate [Zr{OC(SiMe₃)=CHAr}Cl(η-C₅H₅)₂], having Zr–O 1.950(4) Å and < Zr–O–C 157.7(3)°.

There has been recent interest in unusual ambident benzylic carbanions R⁻ derived from the hydrocarbons RH = 2,3-dimethylnaphthalene¹ or a 9-substituted 9-methylantracene.² The proton attacks LiR(tmeda) [tmeda = (Me₂NCH₂)₂] at a benzylic carbon atom. In contrast a bulky Lewis acid reacted at an aromatic centre, as illustrated by the formation of (1) from SiClMe₃ and Li{CH(SiMe₃)Ar}(tmeda) (Ar = 9-anthryl), (2), (reaction iii in Scheme 1).²

We now report the first transition metal complex derived from one of these novel ambident R⁻ ligands: [Zr{CH(SiMe₃)Ar}Cl(η-C₅H₅)₂], (3). The formation of this alkyl (3) is regiospecific and metallation of the ligand occurs in the benzylic position. Thus, surprisingly, the sterically demanding group 4a metal d⁰ electrophile [ZrCl(η-C₅H₅)₂]⁺ behaves like the proton but unlike ⁺SiMe₃, Me⁺, or ⁺C(O)Ph.²

The highly hindered ligand [CH(SiMe₃)Ar]⁻, R⁻, is of interest not only for the dichotomy of its ligation, but also for its chirality in either bonding mode. However, compound (3) with excess of LiR'(tmeda), (2), failed to yield [ZrR'₂(η-C₅H₅)₂]; thus it was not possible to test the diastereoselectivity (*meso*- or *rac*-) of the dialkylation of Zr^{IV}, *cf.*,³ [ZrR'₂(η-C₅H₅)₂] [R' = CH(SiMe₃)C₆H₄Me-*o*].

Complex (3) undergoes a remarkable carbonylation reaction (v in Scheme 1) under mild (ambient) conditions,

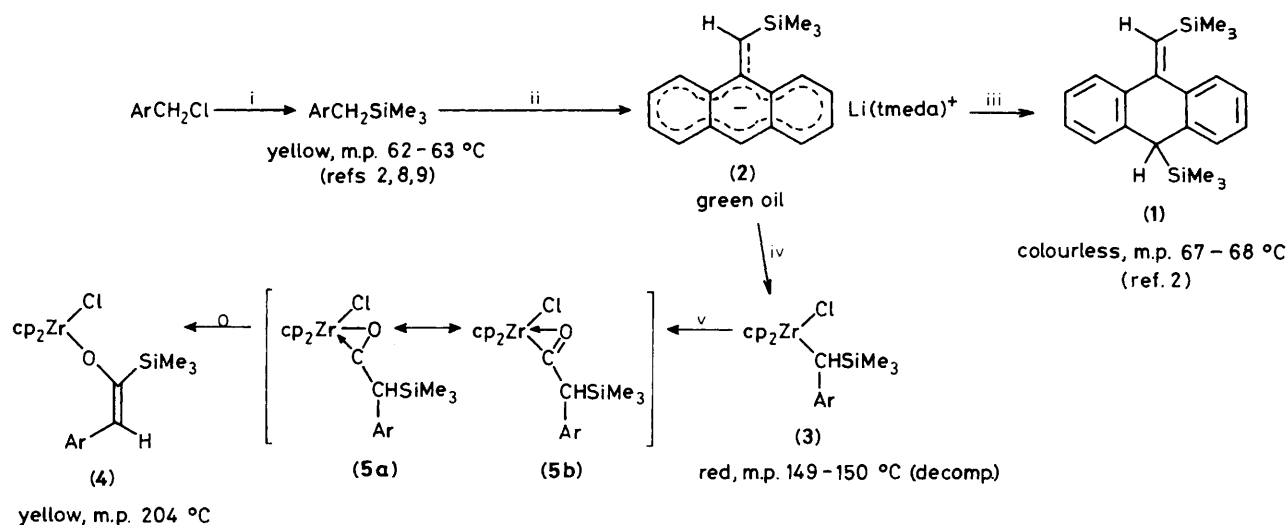
whereby the enolato-zirconocene(IV) chloride (4) is obtained. Significant features are (i) the 1,2-trimethylsilyl migration from the presumed η²-acyl(chloro)zirconocene(IV) complex (5) intermediate; and (ii) the stereoselectivity of the reaction, complex (4) having the E -configuration. Evidence for (5) as an intermediate rests on (a) the prior art regarding carbonylation of zirconocene(IV) alkyls,⁴ and (b) the isolation⁵ of [Zr{η²-C(O)R'''}Cl(η-C₅H₅)₂] {a compound closely related to (5), from [ZrClR'''(η-C₅H₅)₂] + CO} which, however, does not undergo 1,2-SiMe₃ migration [R''' = CH(SiMe₃)C₆H₄Me-*p*].

There is a recent precedent for a related 1,2-trimethylsilyl migration under somewhat more vigorous conditions: [Th(CH₂SiMe₃)(η-C₅H₅)₃] + CO yielded [Th{OC(SiMe₃)=CH₂}(η-C₅H₅)₃];⁶ and a related C–Si cleavage reaction was believed to occur in the carbonylation of [Zr{CH₂SiMe₂N-SiMe₃}₂(dmpe)] to furnish a product formulated as [Zr{OC(=CH₂)SiMe₂N-SiMe₃}₂(dmpe)] [dmpe = (Me₂-PCH₂)₂].⁷

The immediate organic precursor (*cf.*, ii in Scheme 1) for LiR'(tmeda), (2), is ArCH₂SiMe₃. We now report its preparation by a new and simple Grignard *in situ* trapping reaction (i in Scheme 1, 90%). Alternatively ArCH₂SiMe₃ is available from the pre-prepared Grignard reagent Mg(CH₂Ar)Cl⁸ or LiCH₂Ar.² A different route involves a nickel-catalysed cross-coupling of Mg(CH₂SiMe₃)Cl and ArBr.⁹

Selected bond distances and angles of the zirconium and enolato environments of (4) are shown in Figure 1. Noteworthy aspects are (i) the Zr–O distance 1.950(4) Å, *cf.*,

† No reprints available.



Scheme 1. Abbreviations: Ar = 9-anthryl; cp = ($\eta\text{-C}_5\text{H}_5$). Reagents and conditions: i, Mg, tetrahydrofuran, thf, SiClMe_3 then ArCH_2Cl , 20 °C; ii, $\text{LiBu}^n(\text{tmeda})$ in $n\text{-C}_6\text{H}_{14}$, 0 °C; iii, SiClMe_3 in $n\text{-C}_6\text{H}_{14}$, 0 °C; iv, $[\text{ZrCl}_2\text{cp}_2]$, thf, 20 °C; v, CO (1 atm), PhMe, 20 °C. Characterisation: (a) ^1H n.m.r. (3) (C_6D_6): δ 0.20 (9H, s, SiMe_3), 2.65 (1H, s, CHSi), 5.77 (10H, s, C_5H_5), 7.37 (4H, m, ArH), 7.92 (3H, m, ArH), and 8.35 (2H, m, ArH); (4) (C_6D_6): δ 0.50 (9H, s, SiMe_3), 5.33 (10H, s, C_5H_5), 6.25 (1H, s, $\text{SiC}=\text{CH}$), 7.52 (4H, m, ArH), 7.89 (2H, m, ArH), 8.11 (1H, s, ArH), and 8.42 (2H, m, ArH); also (1); (b) ^{13}C n.m.r., i.r., and mass spectra for (1), (3), and (4); (c) X-ray structure determinations of (3) (unpublished results) and (4) (see Figure 1).

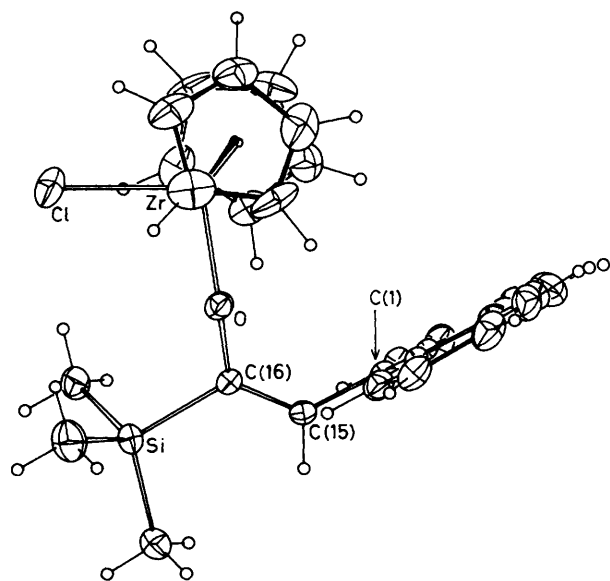


Figure 1. Molecular structure of $E\text{-}[\text{Zr}\{\text{OC}(\text{SiMe}_3)=\text{CHAr}\}\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$ (Ar = 9-anthryl), (4), showing 20% thermal ellipsoids for the non-hydrogen atoms; the projection is onto the enolato plane. Important distances (Å) and angles (°) are: Zr–O 1.950(4), Zr–Cl 2.469(2), Zr–cyclopentadienyl centroids (cen) 2.202 and 2.207, Zr– $\eta\text{-C}$ 2.472(7)–2.518(8), O–C(16) 1.360(6), C(16)–Si 1.895(6), C(15)–C(16) 1.334(7), C(1)–C(15) 1.463(8); O–Zr–Cl 98.8(1), cen–Zr–cen 128.3, Zr–O–C(16) 157.7(3), O–C(16)–Si 114.8(4), Si–C(16)–C(15) 122.8(4), O–C(16)–C(15) 122.4(5), C(16)–C(15)–C(1) 127.2(5).

1.948(1) (X = Me) and 1.945(3) (X = Cl) Å in $[\{\text{ZrX}(\eta\text{-C}_5\text{H}_5)_2\}_2(\mu\text{-O})]$,¹⁰ and 1.946(4) Å in $\text{Zr}[\text{Zr}\{\text{CH}_2\text{CHCHCH}_2\text{CPh}_2\text{O}\}(\eta\text{-C}_5\text{H}_5)_2]$ ¹¹ which has a smaller Zr–O–C angle [150.5(4)°] than (4) [157.7(3)°]; (ii) a large angle at one olefinic carbon atom C(16)–C(15)–C(1), 127.2(5)°, most likely a consequence of steric compression; and (iii) the orthogonal relationship of the enolato and anthryl planes.

X-Ray quality crystals of (4) were grown from toluene–hexane at –30 °C. Crystal data for (4)†: $\text{C}_{29}\text{H}_{29}\text{ClOSiZr}$, monoclinic, $P2_1/c$, $a = 9.315(5)$, $b = 16.47(1)$, $c = 17.49(1)$ Å, $\beta = 93.76(5)^\circ$, $U = 2678$ Å³, $Z = 4$, $D_c = 1.354$ g cm^{–3}. The structure was determined at room temperature [295(1) K] (heavy atom method) from 2314 independent ‘observed’ reflections [$I > 2\sigma(I)$] (Mo- K_α radiation): $R = 0.047$, $R' = 0.034$.

We thank the Royal Society (fellowship to C. L. R.) and the Australian Research Grants Scheme for support.

Received, 6th December 1984; Com. 1721

References

- R. H. Mitchell, T. W. Dingle, and R. V. Williams, *J. Org. Chem.*, 1983, **48**, 903.
- T. A. Engler and H. Shechter, *Tetrahedron Lett.*, 1984, **24**, 4645.
- M. F. Lappert and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1981, 173.
- Cf.*, G. Erker, *Acc. Chem. Res.*, 1984, **17**, 103.
- W.-P. Leung and C. L. Raston, unpublished results.
- D. C. Sonnenberger, E. A. Mintz, and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 3484.
- R. P. Planalp and R. A. Andersen, *Organometallics*, 1983, **2**, 1675.
- C. L. Raston and G. Salem, *J. Chem. Soc., Chem. Commun.*, 1984, 1702.
- K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1958.
- W. E. Hunter, D. C. Hrcncir, R. V. Bynum, R. A. Pentilla, and J. L. Atwood, *Organometallics*, 1983, **2**, 750; J. F. Clarke and M. G. B. Drew, *Acta Crystallogr., Sect. B*, 1974, **30**, 2267.
- G. Erker, K. Engel, J. L. Atwood, and W. E. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 494.

† Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.