

## Formation of Co-ordinated Diphenylketen from Carbon Monoxide and an Alkylzirconocene(IV) Benzhydryl Complex; X-Ray Structure of $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{OC}=\text{CPh}_2)\}_2]$

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The zirconocene(IV) dialkyls  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CHPh}_2)\text{R}]$  [ $\text{R} = \text{Me}$ , (1), or  $\text{CH}_2\text{SiMe}_3$ , (2)] react under ambient conditions with CO during 1—2 days in  $\text{OEt}_2$  or  $\text{C}_6\text{H}_6$  to give  $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{OCCPh}_2)\}_2]$  (3), [58% from (2)], as well as  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{O})\text{R}\}\text{CHPh}_2]$  [24% from (2)]; the X-ray structure of complex (3) shows

that the molecule contains the nucleus  $\text{Zr}-\text{C}-\text{O}-\text{Zr}-\text{C}-\text{O}$ , with each of the Zr—O distances equal, 2.165(3) Å, and Zr—C = 2.204(3) Å.

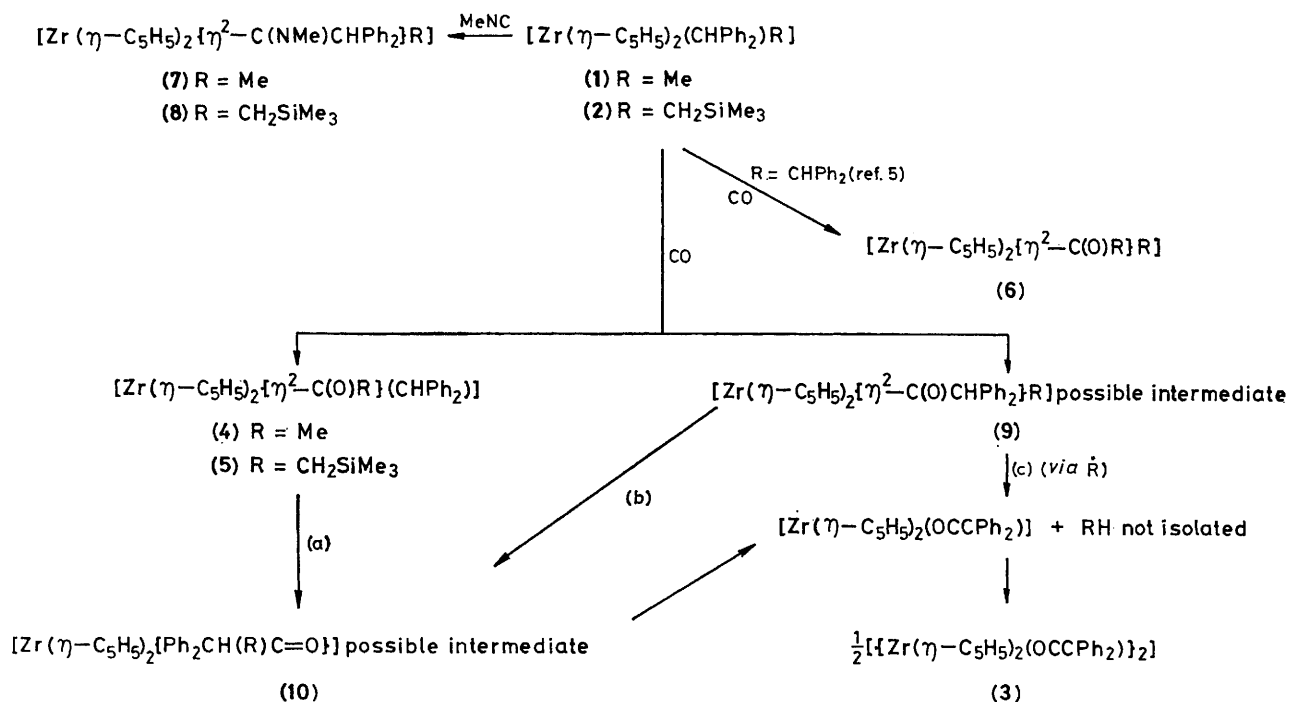
It is established that the carbonylation of a zirconocene(IV) dialkyl  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{R}^1\text{R}^2]$  yields an  $\eta^2$ -acylmethyl complex  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{X})\text{R}^1\}\text{R}^2]$  ( $\text{X} = \text{O}$ ), which may decarbonylate, but is generally otherwise stable.<sup>1–3</sup> Similarly an isonitrile  $\text{R}^3\text{NC}$  gives the  $\eta^2$ -iminoacylmethyl complex ( $\text{X} = \text{NR}^3$ ); and, if  $\text{R}^1 \neq \text{R}^2$ , earlier evidence<sup>2</sup> indicated that insertion of CO or  $\text{R}^3\text{NC}$  takes place into the more sterically demanding of the two groups  $\text{R}^1$  and  $\text{R}^2$ .

We now find that when the dialkyl is  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CHPh}_2)\text{R}]$  [ $\text{R} = \text{Me}$ , (1); or  $\text{R} = \text{CH}_2\text{SiMe}_3$ , (2)], then CO under ambient conditions affords the co-ordinated diphenylketen complex (3),  $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{O}=\text{C}=\text{CPh}_2)\}_2]$ . We further observe that the co-product is  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{O})\text{R}\}\text{CHPh}_2]$  if  $\text{R} = \text{Me}$ , (4), or  $\text{R} = \text{CH}_2\text{SiMe}_3$ , (5), but becomes the exclusive product, (6), when  $\text{R} = \text{CHPh}_2$ . With methyl isonitrile, on the other hand, even the mixed alkyl-benzhydryl (1) or (2) affords a single iminoacyl  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{NMe})\text{CHPh}_2\}\text{R}]$  [ $\text{R} = \text{Me}$ , (7); or  $\text{R} = \text{CH}_2\text{SiMe}_3$ , (8)]. These data are summarised in Scheme 1, which additionally indicates three alternative proposed pathways to complex (3): (a), (b), or (c), with complexes (9) and/or (10) as possible intermediates. Finally, we show

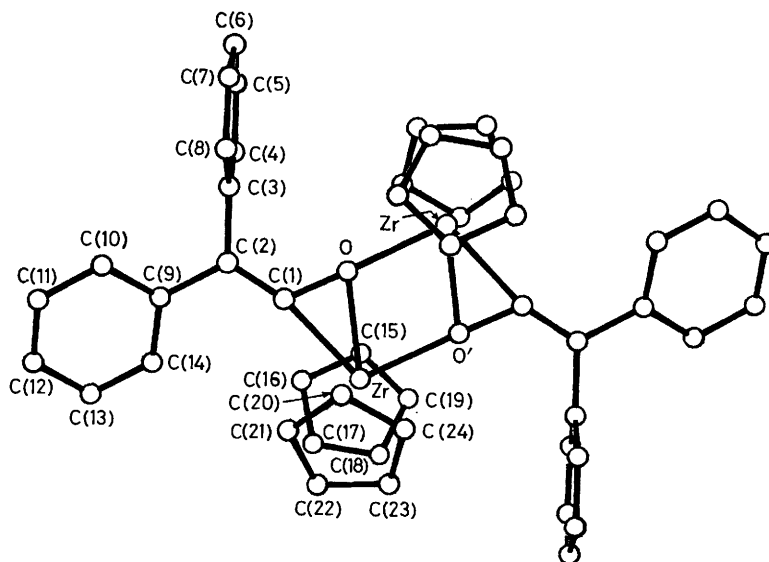
that the molecular structure of (3), the first keten-zirconium derivative, is closely similar (see Figure 1) to that of the isoleptic titanium complex,<sup>4</sup> which, however, was obtained from the metal(II) precursor  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2]$  and diphenylketen.

Pathway (a) appears to be the least likely, because the keten complex (3) does not form from (4) or (5) under the conditions of the experiment; thus a prolonged reaction time does not result in an increased yield of (3). This yield [58% from (2) or 24% from (1) in  $\text{OEt}_2$  at 20 °C under 1 atm of CO, after 1—2 days; the isolated yield of (5) or (4) is 24 or 50%, respectively] is gauged with accuracy, as analytically pure (3) is precipitated from the solution, and is totally insoluble in the solvent.

Circumstantial evidence favours pathway (b), in so far as this requires a co-ordinated ketone-metal complex such as (10) as an intermediate. Thus we note that (i)  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{Ph})_2]$  with carbon monoxide affords  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{O})\text{CH}_2\text{Ph}\}\text{CH}_2\text{Ph}]$ , which reacts with further CO to give  $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2]$  and the ketone  $(\text{PhCH}_2)_2\text{CO}$ ;<sup>6</sup> and (ii)  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{O})\text{Ph}\}\text{Ph}]$  upon heating furnishes the complex  $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-Ph}_2\text{CO})\}_2]$ .<sup>7</sup> Furthermore, this pro-



**Scheme 1.** Reactions of some alkylzirconocene benzhydriyls with CO or MeNC under ambient conditions, and alternative pathways [(a), (b), or (c)] for the formation of the diketene complex (3); there is no direct evidence for the possible intermediates (9) or (10); complexes (1)–(8) gave satisfactory analytical and spectroscopic data.



**Figure 1.** The molecular structure of  $[\{\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-O}=\text{C}=\text{CPh}_2)\}_2]$ , (3). Some important dimensions are C(1)–C(2) 1.333(5), C(1)–O 1.371(4) Å, C(2)–C(1)–O 123.6(3)°, Zr–C(1) 2.204(3), Zr–O 2.164(2), and Zr–O' 2.165(2) Å.

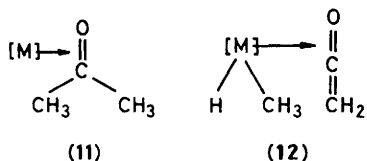
posol provides a neat model for the well known heterogeneously catalysed conversion of acetone into ketene, using a Cr–Ni alloy filament at 700–750 °C,<sup>8</sup> whereby we propose that intermediates (11) and (12) [the oxidative addition product of (11)] are implicated in the catalytic cycle, with reductive elimination of methane generating from (12) the coordinatively unsaturated precursor of (11). Alternatively complex (11) could be  $\eta^1\text{-O}$ -bonded, as in the isoelectronic d<sup>2</sup> cation  $[\text{V}(\eta\text{-C}_5\text{H}_5)_2(\text{OCMe}_2)]^+$ .<sup>9</sup>

In complex (9), the Zr–R bond is expected to be labile; this would facilitate the formation either of (10) [pathway (b)], or of the radical pair  $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-C}(\text{O})\text{CHPh}_2\}]\text{-R}\cdot$ , a

possible intermediate for (c). In support of this bond-weakening, we note that the Zr–Me bond of complex (7), a close analogue of (9), is the longest Zr–C(sp<sup>3</sup>) bond yet found, 2.431(5) Å.<sup>10</sup>

*Crystal data for complex (3):*  $\dagger$  C<sub>48</sub>H<sub>40</sub>O<sub>2</sub>Zr<sub>2</sub>, *M* = 831.29, triclinic, *P* $\bar{1}$ , *a* = 8.187(2), *b* = 10.642(4), *c* = 11.761(2) Å,

$\dagger$  The 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.



$\alpha = 110.02(2)$ ,  $\beta = 98.47(2)$ ,  $\gamma = 101.69(3)^\circ$ ,  $Z = 1$ . The structure was solved by heavy-atom methods and refined by least-squares methods to  $R = 0.040$  for 2450 reflections measured on a CAD 4 diffractometer using Mo- $K_\alpha$  radiation. The two halves of the dimer are related by a crystallographic inversion centre.

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