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Preliminary communication

SYNTHESIS AND STRUCTURE OF A KETENE DINUCLEAR COMPLEX OF ZIRCONOCENE CHLORIDE OBTAINED BY CARBONYLATION OF A DIPHENYLPHOSPHINOMETHYLZIRCONIUM DERIVATIVE

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Summary

Treatment of $Cp_2ZrCl(CH_2PPh_2)$ ($Cp = \eta^5\text{-}C_5H_5$) with CO gave the dinuclear complex $(Cp_2ZrCl)_2[O{=}C{=}CH(PPh_2)]$; a single crystal X-ray diffraction study revealed a coplanar doubly-chelated arrangement Zr—O—C—C—P—Zr with electron delocalization throughout the six-atom nucleus.

In studies of carbon monoxide activation by organometallics, zirconium (and titanium) derivatives have shown unique reactivity patterns arising from the oxophilic character of the metals [1—8].

As part of our work on activation of carbon oxides by heterobimetallic d^0—d^8 complexes, we found that the phosphinozirconium derivatives prepared by Schore [9] are not only a convenient source of Zr—Rh complexes [10] but also react directly with CO_2 and CO. We report here the formation of a novel dinuclear zirconium species obtained by treatment of $Cp_2Zr(Cl)(CH_2PPh_2)$ (1) with CO, via a new type of reaction involving the formation of an oxyalkylidene group bridging two zirconium atoms accompanied by intermolecular elimination of one of the phosphine ligands:

$$\underset{(1)}{2\,Cp_2Zr(Cl)(CH_2PPh_2)} + CO \rightarrow \underset{(2)}{(Cp_2ZrCl)_2(OCC(H)PPh_2)} + PPh_2CH_3 \qquad (1)$$

The nature of the reaction was established by identification of the evolved phosphine PPh_2CH_3 and from analytical data (C, H, Cl, P, Zr), on a sample of 2, obtained as light yellow microcrystals by slow deposition from a THF solution (yield: 60% of crystallized 2; addition of pentane to the filtrate results in 100% recovery of 2, gave the same analysis). Under different experimental conditions

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the acyl species was obtained as white microcrystals, and characterized analytically (C, H, Zr, P) as previously reported) [10].

The structure of this new species, formally represented as a ketene adduct involving one molecule of the phosphinoketene O=C=C(H)PPh$_2$ bonded to two Cp$_2$ZrCl moieties, could not be studied by NMR spectroscopy because of its insolubility in all common solvents.

Crystals of 2 suitable for an X-ray structure determination* were obtained from THF solution. Figure 1 shows the molecular structure and a skeletal view of the ideal crystallographic planar arrangement for the immediate environment of the two zirconium atoms is given in Fig. 2. The OCCH(PPh$_2$) group is η^2-C,O bonded to Zr(1) (Zr(1)—C(1), 2.265(6); Zr(1)—O, 2.311(4); C(1)—O, 1.319(10) Å). The C(1)—C(2) distance of 1.327(8) is very similar to those in other ketene adducts: viz., 1.333(5) in [Cp$_2$Zr(O=C=CPh$_2$)]$_2$ [6] and 1.333(3) in (C$_5$Me$_5$)$_2$Zr(Py)(O=C=CH$_2$) [8], respectively. This value together with the coplanarity of C(1), C(2), H(C2) and P and with the C(1)—C(2)—H(C2) angle of 119.5° is characteristic for a double bonded C=CH(PPh$_2$) arrangement. The Zr(1)—O—Zr(2) angle is 162.0(2), with significantly different Zr—O distances

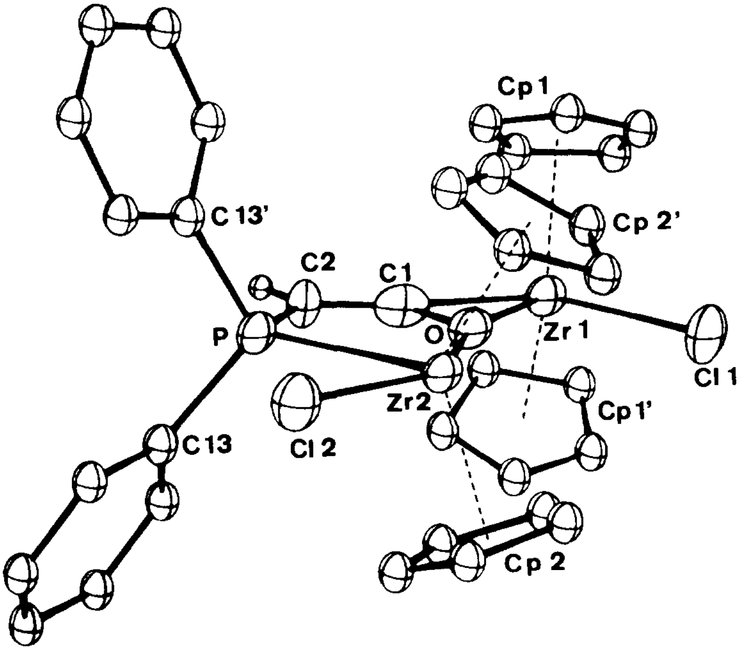

Fig. 1. ORTEP diagram (35% ellipsoids) of 2.

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*Crystal data: space group $C2/m$. Lattice constants were obtained from a least-squares fitting of the setting angles of 25 reflections: a 17.002(3), b 16.474(2), c 11.706(2) Å, β 112.72(2)°, V 3024.3 Å^3, Z = 4. The structure was solved by heavy atom methods using 2712 reflections measured on a CAD 4 diffractometer with Mo-K_α radiation. Refinement converged to R = 0.037.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

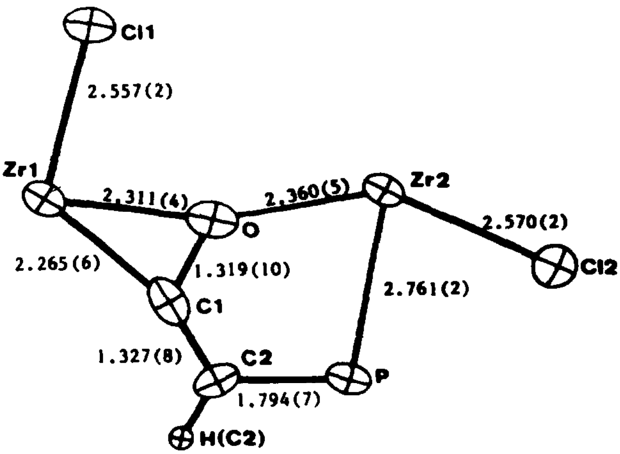
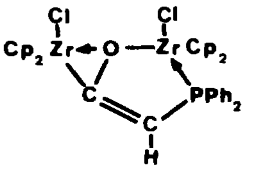


Fig. 2. Skeletal view of 2 showing important bond lengths of the coplanar arrangement.

(Zr(1)—O, 2.311(4); Zr(2)—O, 2.360(5) Å). The OCC(H)PPh$_2$ group is also O,P chelated to Zr(2). The Zr(2)—P distance of 2.761(2) Å can be compared with the values (2.803(1) and 2.794(1) Å) in ZrCl$_2$[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$, a compound with two five-membered rings chelated via P→Zr [11]. Thus both zirconium atoms are 18-electron and five-coordinated. The two chloride ligands.in *trans*-disposition are bonded at very similar distances, 2.557(2) and 2.570(2) Å, respectively, as are the cyclopentadienyl groups (Cp(1)—Zr(1) = Cp(1')—Zr(1), 2.227(8) Å; Cp(2)—Zr(2) = Cp(2')—Zr(2), 2.217(6) Å);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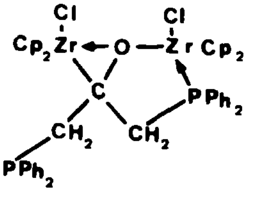
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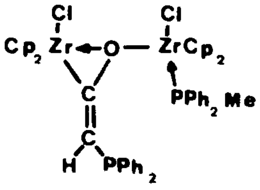
(5)

This novel doubly chelated arrangement bridging two zirconium atoms may be generated following initial formation of the expected acyl Cp$_2$ZrCl(COCH$_2$PPh$_2$) (3), which then reacts with a further molecule of 1 by an intermolecular insertion of the carbonyl of the acyl group of 3 into the Zr—CH$_2$PPh$_2$ bond of 1, giving the oxyalkylidene bridged species Cp$_2$(Cl)Zr—O—C(CH$_2$PPh$_2$)$_2$—Zr(Cl)Cp$_2$ (4), as in ref. 5. An alternative hypothesis is that there is a proton transfer from 3 to 1 to give Cp$_2$(Cl)Zr—O—C=CHPPh$_2$Zr(Cl)Cp$_2$, PPh$_2$Me (5). In both cases, elimination of the phosphine PPh$_2$Me results in formation of 2.

The intermediate 4 or 5 is observed in the reaction mixture by ^{1}H and ^{31}P NMR (^{1}H NMR (relative to Me$_4$Si at 26°C in C$_6$D$_6$): δ 6.05, 5.95 (s, C$_5$H$_5$); 1.09 ppm (d, J(P—H) 2.93 Hz; CH$_2$). ^{31}P{^{1}H} (relative to H$_3$PO$_4$ in D$_2$O): δ −2.6, −5.3 ppm. During the CO absorption, peaks of the unconsumed Cp$_2$ZrCl(CH$_2$PPh$_2$) [9] and free PPh$_2$Me are observed in ^{1}H and ^{31}P NMR spectra); the intensities of the peaks from the starting complex progressively decrease as microcrystals of **2** slowly separate from the solution, and at the same time the intensities of the peaks from PPh_2Me increase, in agreement with the proposed mechanism.

Hydrolysis of **2** does not give the phosphinoenol $HOCH{=}CH(PPh_2)$; unexpectedly, CO is released and the phosphine PPh_2CH_3 is produced, together with $(Cp_2ZrCl)_2O$ (the latter was characterized by IR, ^1H NMR spectroscopy and elemental analysis, and PPh_2Me by ^1H and ^{31}P NMR spectra). The mechanism of this reaction is not completely understood. Electron delocalization throughout the six-atom coplanar arrangement $\underline{\mathrm{Zr}-\overline{\mathrm{O}-\mathrm{C}}}\overline{-\mathrm{C}-\mathrm{P}-\mathrm{Zr}}$ may correspond with various mesomeric forms (only one of which is represented in **2**), which allows the possibility of various (and potentially novel) types of reactions.

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