Reversible Carbonylation of Dialkylbiscyclopentadienylzirconium(IV): Synthesis and Structure of π-Acyl Derivatives of Zirconium and *X*-Ray Structure of Biscyclopentadienyl(π-acetyl)methylzirconium

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Summary Dimethyl- and dibenzyl-biscyclopentadienylzirconium(IV) react reversibly with carbon monoxide at atmospheric pressure giving the corresponding stable alkyl–acyl derivatives; the *X*-ray structure of the methyl derivatives shows the acyl group acting as a three-electron donor ligand.

Considerable interest centres around insertions into metal-carbon σ bonds of the early transition metals,[1] in view of their relevance to polymerisation systems[1] and organic syntheses.[2] Complexes like (cp)$_2$MXY (cp = η^5-C_5H_5) are useful models for gaining insight into general aspects of insertion reactions.[3] Reaction of carbon monoxide with complexes containing only one M–C σ bond generally gave normal insertion products,[4] but in the presence of more than one alkyl group either a variety of non-stoicheiometric products[1,5] are obtained or intramolecular reductive eliminations occur.[6]

Dimethyl- and dibenzyl-biscyclopentadienylzirconium(IV), [(cp)$_2$ZrMe$_2$] (I) and [(cp)$_2$Zr(CH$_2$Ph)$_2$] (II) in toluene solution at 20 °C and atmospheric pressure absorb CO, which is released *in vacuo*. The i.r. spectra of the carbonylated solutions do not show metal–acyl or metal–carbonyl bands (1600–2000 cm^{-1}). The n.m.r. spectra (C_6D_6) show non-equivalence of the two methylene or methyl groups of the carbonylated products, and also show that the CO absorption was reversible. From the carbonylated solutions, under an atmosphere of CO and upon addition of heptane, [(cp)$_2$Zr(COMe)Me] (III), and [(cp)$_2$Zr(COCH$_2$Ph)CH$_2$Ph] (IV), were isolated as yellow crystals (*ca.* 80%). Compounds (III) and (IV) are stable towards release of CO in the solid state, but in solution can be reconverted *in vacuo* into the starting compounds (I) and (II). In the light of the present results, our previous report, based on the quantitative recovery of starting material, that (II) does not undergo carbonylation, should be regarded as incorrect.[6]

The formulation proposed for (III) and (IV) is based on CO absorption measurements (1 mol of CO per mol of Zr), analytical data, and n.m.r. and i.r. spectra [τ (C_6D_6) 9·55 (3H, s, Me), 7·59 (3H, s, Me), and 4·65 (10H, s, cp) for (III); 7·42 (2H, s, CH$_2$), 6·26 (2H, s, CH$_2$), 4·86 (10H, s, cp), and 2·88 br (10H, m, Ph) for (IV); ν_{CO} (Nujol) 1545 (III) and 1540 (IV) cm^{-1}]. Compounds (III) and (IV) are monomeric in benzene [*M* for (III) 264, for (IV) 448]. A *X*-ray structural determination of (III) was undertaken in order to rationalise the unusually low CO stretching of the acyl group.

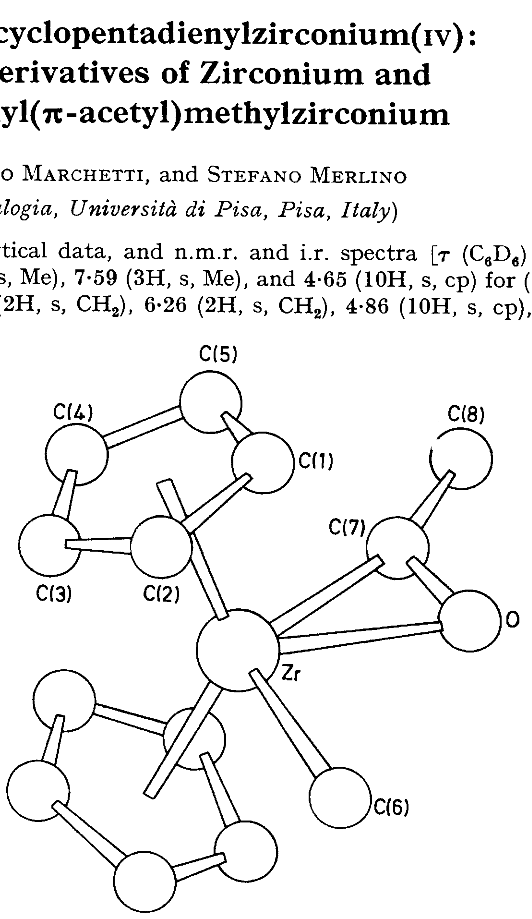
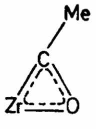


Figure. Molecular structure of [(cp)$_2$Zr(COMe)Me]. Bond distances (in Å): Zr–C(6), 2·336(7); Zr–C(7), 2·197(6); Zr–O, 2·290(4); C(7)–C(8), 1·492(10); C–C(cp), 1·384 av.; bond angles (°): Zr–C(7)–C(8), 159·8(5); Zr–C(7)–O, 78·6(4); C(6)–Zr–C(7), 110·8(2); C(7)–Zr–O, 31·2(2).

Crystal data: $C_{13}H_{16}OZr$; *M* = 279, orthorhombic; *a* = 12·397(1); *b* = 7·086(1); *c* = 14·051(1) Å; *U* = 1234·3

Å^3, $Z = 4$, $D_c = 1{\cdot}54$ g/cm^3; space group *Pnma*. A total of 1395 independent reflections were measured by an on-line Siemens AED diffractometer, using Mo-K_α radiation, θ–2θ scan, and 'four-points' technique. 1039 reflections with $I > 3\sigma(I)$ were used for the structure determination. The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares procedures. A Fourier difference synthesis revealed all the hydrogen atoms. The final R factor was 0·03.



(A)

The crystals are built up of discrete monomeric molecules with C_s (m) symmetry. The Figure shows a view of the complex, with the more relevant bond distances and angles. Each Zr atom is η^5 bonded to two cp rings that are bent away from the horizontal mirror plane containing the σ bonded methyl group and *C,O* bonded acyl ligand. The C_s symmetry requires eclipsing of the cp rings. The average Zr–C (cp) distance, 2·511 Å, compares favourably with the average for other η^5-cyclopentadienyl compounds.[8] The metal atom resides 2·217 Å out of the plane of the five-membered rings. The main interest in the structure is in the nature of the metal–acyl bonding. The C(8), C(7), C(6), O, and Zr atoms are coplanar.

The bond angles associated with the acetyl ligand differ markedly (Figure) from the expected sp^2 angles. The Zr–O, 2·290(4) Å,[9] as well as the Zr–C(7), 2·197(6) Å,[10] and C(7)–O, 1·211(8) Å,[11] bond distances can be interpreted in terms of the acyl group acting as a three-electron ligand (structure A). This type of interaction explains the absence of the C–O stretching vibration in the usual range.[12] In all similar cases a shortening of the metal–C (acyl) bond was observed which is generally accounted for by a metal–carbene-like interaction.[11] This olefin-like model of the acyl group is supported by comparison with the similar structure found for $[(cp)_2Nb(Et)(C_2H_4)]$.[13] The existence of π-acyl derivatives of Ru has been proposed but not further proved by structure determination.[14]

The Zr–C(6) bond distance, 2·336(7) Å, is significantly longer than the Zr–C(σ) distance of 2·25 Å[10] in the corresponding bis-(η^5-indenyl)dimethylzirconium(IV), suggesting the presence of a labilised Zr–C(σ) bond, as a consequence of the interaction of oxygen with zirconium.

Migration of C(6) to C(7) may be the path through which $(PhCH_2)_2CO$ is formed during the carbonylation of $[(cp)_2Ti(CH_2Ph)_2]$.[6]

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