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Double Aryl Migration to Carbon Monoxide in the Carbonylation of Bis(mesityl)(η^8-cyclo-octatetraene)zirconium(IV)

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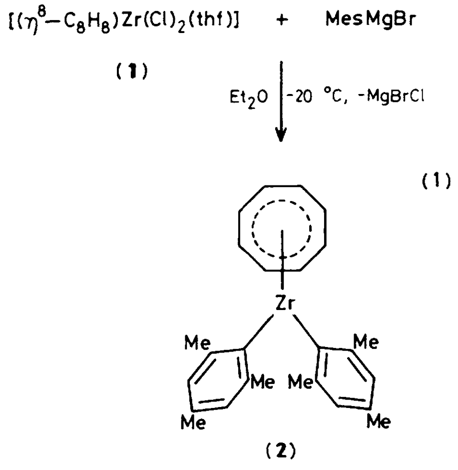
Bis(mesityl)(η^8-cyclo-octatetraene)zirconium(IV) undergoes rapid carbonylation at 0 °C to form, *via* migration of both mesityl (Mes) groups to carbon monoxide, $[(\eta^8\text{-}C_8H_8)Zr(\eta^2\text{-}OCMes_2)]_2$, which contains a side-on bonded diaryl ketone sharing the oxygen between two zirconium atoms.

Some of the most significant aspects of migratory insertion of carbon monoxide into a metal–carbon bond have been elucidated using as model compounds dialkyl- and diarylbis(cyclopentadienyl)zirconium(IV) derivatives, cp_2ZrR_2 (cp = η^5-C_5H_5).[1,2] This reaction leads to η^2-acyl complexes which may decarbonylate, but they are normally stable, $[cp_2Zr(\eta^2\text{-}COR)(R)]$.[2] Depending on the nature of the alkyl residue, the exclusive product of the carbonylation can be a ketene, as was observed for $[cp_2Zr(CHPh_2)_2]$ forming $[cp_2Zr(OCCPh_2)]_2$.[3] The deprotonation of an η^2-acyl to a ketene by a residual alkyl group on the metal or by an external strong base has been subsequently confirmed.[4] The second residual alkyl group on the metal can, however, be thermally forced to migrate to the acyl functionality to form a ketone, as observed in the transformation of $[cp_2Zr(COPh)(Ph)]$ into $[cp_2Zr(\eta^2\text{-}COPh_2)]_2$.[5] Such a double migration of an alkyl group was previously observed to occur spontaneously in the carbonylation of $[cp_2Ti(CH_2Ph)_2]$ to form $cp_2Ti(CO)_2$ and $(PhCH_2)_2CO$.[6]

It should be noted that the acyl rearrangements cited above occur on a metal having a closed shell configuration. We recently focused our attention on the synthesis and chemistry of electronically highly-deficient organometallic derivatives of early transition metals.[7] In this context we report the carbonylation of a fourteen electron zirconium(IV) complex, the bis(mesityl)(η^8-cyclo-octatetraene)zirconium(IV).



(1)

(1)

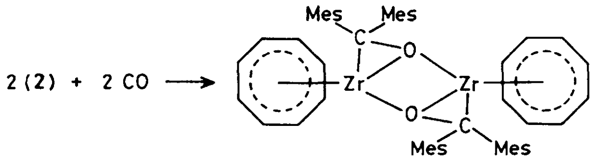
(2)

Mes = 2,4,6-$Me_3C_6H_2$, thf = tetrahydrofuran

Although alkyl derivatives of the $(\eta^8\text{-}C_8H_8)Zr$ moiety have been reported as being thermally unstable,[8] we have succeeded in the isolation and characterization of $[(\eta^8\text{-}C_8H_8)Zr(Mes)_2]$, (Mes = mesityl) which was synthesized by a conventional alkylation of (**1**)[9] at −20 °C in diethyl ether (yield *ca.* 40%), equation (1).

Complex (**2**) is a red-orange crystalline solid, thermally labile both in solution and in the solid state. A diethyl ether solution of (**2**) undergoes a very fast carbonylation at 0 °C changing from red-orange to deep-red in a few minutes. The solution, when left to stand at −5 °C, gave red crystals of (**3**) (yield *ca.* 78%), which crystallizes with a molecule of Et_2O, equation (2).

Complex (**3**) is stable at room temperature both in solution and in the solid state. Analytical and spectroscopic data (i.r., ^1H n.m.r.) are in agreement with the proposed structure, which was determined by an *X*-ray analysis.† An ORTEP view



(2)

(**3**)

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† *Crystal data:* $C_{54}H_{60}O_2Zr_2 \cdot Et_2O$, M = 997.64, monoclinic, space group $C2/c$, a = 25.856(9), b = 12.444(3), c = 15.571(8) Å, β = 92.59(3)°, U = 5005(3) Å^3, Z = 4, D_c = 1.32 g cm^{-3}, $F(000)$ = 2088, $\mu(\text{Cu-}K_\alpha)$ = 75.09 cm^{-1} (λ = 1.54178 Å), crystal dimensions 0.30 × 0.25 × 0.06 mm. Intensities of 3416 reflections were measured at 298 K on a Nicolet R3m diffractometer by using Cu-K_α radiation resulting in 2848 independent reflections. The structure was solved by the heavy atom method and refined by full-matrix least-squares. All calculations were carried out using the SHELX-TL program. For 1659 observed reflections $[I > 1.5\sigma(I)]$ the final R value was 0.112 (R_w = 0.111). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

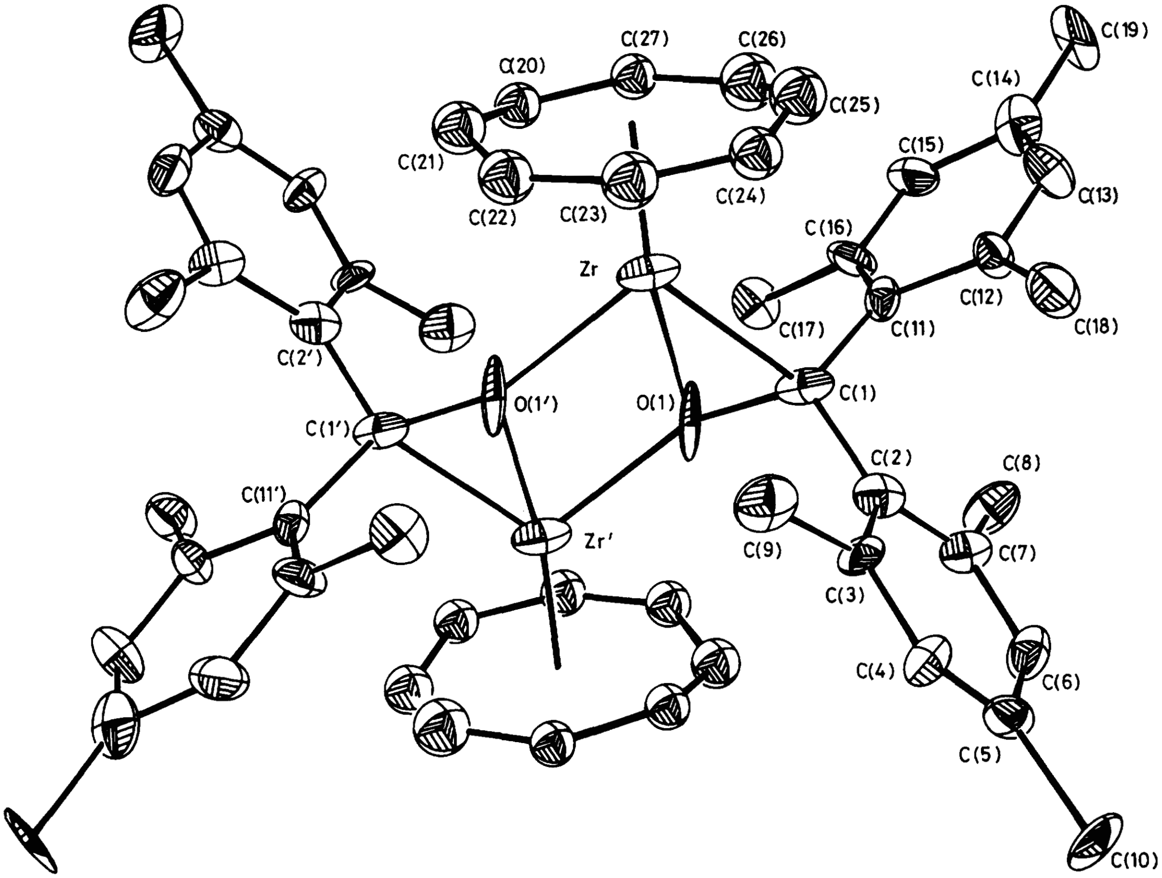

Figure 1. *X*-Ray structure of (**3**).

of the centrosymmetric dimer (**3**) is shown in Figure 1. The complex consists of two zirconium atoms, each η^8-bonded to cyclo-octatetraene and η^2-C,O bonded to dimesityl ketone. The oxygen atom of the ketone is almost symmetrically shared by the two zirconium atoms [Zr–O(1), 2.18(1); Zr–O(1′), 2.19(1) Å]. The carbon–oxygen bond distance approximates to a single bond [C(1)–O(1), 1.45(2) Å], Zr–O bond distances are significantly shorter than the corresponding Zr–C for the η^2-ketone [Zr–C(1), 2.33(2) Å]. A very close trend in Zr–C and Zr–O bond distances has been found in $[(cp_2ZrCl)_2(\mu\text{-}CH_2O)]$,[10] $[(cp_2Zr)(\mu\text{-}CH_2O)]_3$,[11] and $[(cp_2Zr)_2(\mu\text{-}H)(\mu\text{-}MeCHO)(H)]$.[12] The planar Zr,O(1),O(1′),Zr′ fragment forms a dihedral angle of 157.1° with the plane through Zr,O(1),C(1). The distances between zirconium and the C_8H_8 carbons are close to those found for the other zirconium derivatives in the literature.[9,13]

Formation of (**3**) may plausibly involve the intermediate formation of an undetected η^2-aroyl, to which the remaining σ-bonded mesityl migrates forming the side-on co-ordinated dimesityl ketone.

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References

1 D. J. Cardin, M. F. Lappert, C. L. Raston, and P. I. Riley in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch 23.2; G. Erker, *Acc. Chem. Res.*, 1984, **17**, 103; P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, 1980, **13**, 121.
2 G. Fachinetti, G. Fochi, and C. Floriani, *J. Chem. Soc., Dalton Trans.*, 1977, 1946; J. Jeffery, M. F. Lappert, N. T. Luong-Thi, M. Webb, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, 1981, 1593.
3 G. S. Bristow, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1982, 462.
4 L. M. Engelhardt, G. E. Jacobsen, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1984, 220; D. A. Straus and R. H. Grubbs, *J. Am. Chem. Soc.*, 1982, **104**, 5499; E. J. Moore, D. A. Straus, J. Armantrout, B. D. Santarsiero, R. H. Grubbs, and J. E. Bercaw, *ibid.*, 1983, **105**, 2068.
5 F. Rosenfeldt and G. Erker, *Tetrahedron Lett.*, 1980, **21**, 1637; *J. Organomet. Chem.*, 1982, **224**, 29; *Tetrahedron*, 1982, **38**, 1285.
6 G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, 1972, 654.
7 S. Stella and C. Floriani, unpublished results.
8 H. J. Kablitz and G. Wilke, *J. Organomet. Chem.*, 1973, **51**, 241.
9 D. J. Brauer and C. Krüger, *Inorg. Chem.*, 1975, **14**, 3053.
10 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1983, **105**, 1690.
11 K. Kropp, V. Skibbe, G. Erker, and C. Krüger, *J. Am. Chem. Soc.*, 1983, **105**, 3353.
12 G. Erker, K. Kropp, C. Krüger, and A. P. Chiang, *Chem. Ber.*, 1982, **115**, 2447.
13 D. J. Brauer and C. Krüger, *J. Organomet. Chem.*, 1972, **42**, 129.