Bis(cyclopentadienyl)zirconium(III) Complexes containing a Metal–Metal Bond: Synthesis and Properties of Zirconium(II) and Zirconium(III) Complexes †

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The synthesis of dicarbonylbis(cyclopentadienyl)zirconium(II), $[Zr(cp)_2(CO)_2]$ (cp = η^5-C_5H_5), from reductive carbonylation of $[Zr(cp)_2(BH_4)_2]$ in NEt_3 is described in detail. From the reaction of $[Zr(cp)_2(CO)_2]$ with zirconium(IV) derivatives, $[Zr(cp)_2X_2]$ (X = Cl or SPh), the first bis(cyclopentadienyl)zirconium(III) derivatives, $[\{Zr(cp)_2X\}_2]$, have been obtained as dimers containing a zirconium–zirconium bond, accounting for the diamagnetism of the compounds.

The chemistry of low-valent zirconium is surprisingly poor.[1-3] Reduction of zirconium(IV) to a lower oxidation state is very difficult even when carried out in the presence of appropriate ligands like CO, phosphines, and cyclopentadienyl (cp). A significant contribution to this area was the recent discovery of a few zirconium(II) model compounds, namely $[\{Zr(\eta^5\text{-}C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$,[4] $[Zr(cp)_2(CO)_2]$,[5,6] and $[Zr(cp)_2(PPh_2Me)_2]$.[7] Their chemistry showed that they can be considered as highly reactive functional equivalents of monomeric 'zirconocene'. Isolation of bis(η^5-cyclopentadienyl)zirconium(II) non-stabilized by any ancillary ligand like N_2, PR_3, or CO was unsuccessful because of its high reactivity involving the cp ligands.[3,8] In this paper we report an unusual synthesis of $[Zr(cp)_2(CO)_2]$, through the reductive carbonylation of a hydridozirconium(IV) species and we relate such a result to the very well known chemistry of Zr–H bonds with carbon monoxide.[9,10] Moreover, $[Zr(cp)_2(CO)_2]$ has been used as a starting material for the facile synthesis of dimeric zirconium(III) complexes, $[\{Zr(cp)_2X\}_2]$ (X = Cl or SPh), which unlike the corresponding titanium compounds are diamagnetic, a consequence of a strong zirconium–zirconium bond.

Whereas the final oxidation state +3 is common for titanium and mild reducing agents can affect the $Ti^{IV} \longrightarrow Ti^{III}$ conversion, organometallic complexes of zirconium(III) are rather rare species.[2] The synthesis of $[Zr(cp)_2(CO)_2]$ has been briefly communicated.[5]

Results and Discussion

Until 1976 zirconium and hafnium were devoid of any type of carbonyl derivatives, and the carbonyl chemistry of the Group 4 metals was restricted to two titanium complexes, $[Ti(cp)_2(CO)_2]$[11] and $[Ti(cp)_2(CO)(PhC{\equiv}CPh)]$.[12] In 1976 three different syntheses were discovered for $[Zr(cp)_2(CO)_2]$, although in rather low yields.[5,6]

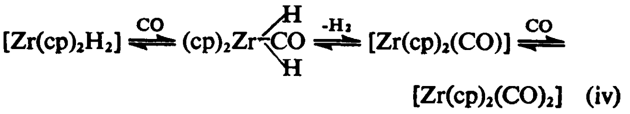
Unconventional syntheses were carried out by the carbonylation of tetrahydroborate derivatives in the presence of NEt_3 [equation (i); M = Ti, n = 1; M = Zr, n = 2]. For M = Ti, an 80% yield is achieved even under 1 atm of CO. In the case of zirconium the reaction must be carried out under pressure (100 atm CO); nevertheless, the yield of $[Zr(cp)_2(CO)_2]$ is less than 20%. The CO consumption is far greater than could be imagined from the low yield.

$$\underset{(1)}{[M(cp)_2(BH_4)_n]} \xrightarrow[NEt_3]{CO} \underset{(2)}{[M(cp)_2(CO)_2]} + n\,NEt_3{\cdot}BH_3 + \text{unidentified products} \quad \text{(i)}$$

Let us discuss briefly a plausible route leading to the synthesis of $[Zr(cp)_2(CO)_2]$. It is known that zirconium tetrahydroborates are decomposed to hydrides by tertiary amines, NR_3[13] [equations (ii) and (iii)]. It is rather difficult to relate the mode of formation of $[Zr(cp)_2(CO)_2]$ to complexes (3) and (4), since we found that they reacted with carbon monoxide either in the presence or absence of $NEt_3{\cdot}BH_3$ without forming any zirconium carbonyl compound.[14] Moreover, reduction of carbon monoxide is supposed to occur in reactions related to those reported for other mono- and di-hydrido-zirconium complexes.[9,10] We would like, however, to draw attention to the difference in molecular complexity, a crucial point in this chemistry, between (4) and $[Zr(\eta^5\text{-}C_5Me_5)_2H_2]$ (5), (4) being polymeric[13] and (5) monomeric.[9] Substituents at the cyclopentadienyl ring have been found to affect the molecular complexity, and in consequence the bonding mode of the hydrido-ligand, for example in $[\{Zr(\eta^5\text{-}C_5H_4Me)H)_2(\mu\text{-}H)\}_2]$.[15] This is directly reflected in the reactivity of the hydrido-ligand. As to a monomeric transient $[Zr(cp)_2H_2]$ complex, it should have a reactivity pattern close to that of $[Zr(\eta^5\text{-}C_5Me_5)_2H_2]$.[9] Reduction of carbon monoxide by the Zr–H bond can be concurrent to some extent with the decomposition of the dihydrido-complex as suggested for the pentamethylcyclopentadienylzirconium dihydrido-complex [equation (iv)].

$$[Zr(cp)_2(BH_4)_2] + NR_3 \longrightarrow NR_3{\cdot}BH_3 + \underset{(3)}{[Zr(cp)_2H(BH_4)]} \quad \text{(ii)}$$

$$[Zr(cp)_2(BH_4)_2] + 2\,NR_3 \longrightarrow 2\,NR_3{\cdot}BH_3 + \underset{(4)}{\tfrac{1}{n}[\{Zr(cp)_2H_2\}_n]} \quad \text{(iii)}$$



$$[Zr(cp)_2H_2] \overset{CO}{\rightleftharpoons} (cp)_2Zr(H)_2(CO) \overset{-H_2}{\rightleftharpoons} [Zr(cp)_2(CO)] \overset{CO}{\rightleftharpoons} [Zr(cp)_2(CO)_2] \quad \text{(iv)}$$

Recently a related phosphine ligand-induced reductive elimination from $[Zr(cp)_2(H)R]$, to form a zirconium(II) complex, $[Zr(cp)_2(PPh_2Me)_2]$ (R = cyclohexylmethyl) was

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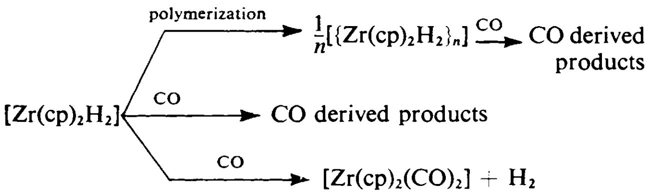
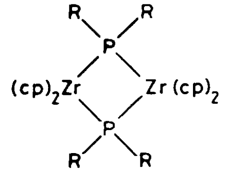
† *Non-S.I. units employed:* atm = 101 325 N m^{-2}; Torr ≈ 133 Nm^{-2}; B.M. = 0.927 × 10^{-23} A m^2; $\chi_{c.g.s.} = \chi_{S.I.} \times 10^6/4\pi$.

observed.[7] Therefore the possible transformations of the monomeric [Zr(cp)$_2$H$_2$] in the presence of carbon monoxide can be summarized above. In effect, the reported yield of [Zr(cp)$_2$(CO)$_2$] is obtained only if the reaction bomb is pressurized with carbon monoxide immediately after contacting [Zr(cp)$_2$(BH$_4$)$_2$] and triethylamine.

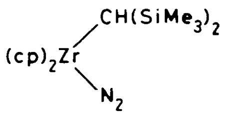


The work-up procedure to isolate the dicarbonyl product is rather cumbersome (see Experimental section) because the amine–borane adduct has similar volatility and crystallizing attitude. Therefore, after preliminary vacuum distillation of the bomb contents, the residue is chromatographed over alumina and then sublimed. The violet-brown product has been characterized by elemental analysis, gas-volumetric measurement of the CO evolved on iodine oxidation, cryoscopy, n.m.r., i.r., and mass spectroscopy (see Experimental section). Finally, an *X*-ray structural analysis has been carried out.[16] All other syntheses of [Zr(cp)$_2$(CO)$_2$] so far reported employed the reduction of [Zr(cp)$_2$Cl$_2$] in the presence of CO,[6] and the most recent method is an improvement for small scale production.[17]

From the present results we suggest that [Zr(cp)$_2$(CO)$_2$] can be an excellent starting material for the synthesis of bis(cyclopentadienyl)zirconium(III) derivatives, [{Zr(cp)$_2$X}$_n$], for which no general synthetic procedure has so far been described and whose structures are rather obscure.[2] Attempts to synthesize such complexes by conventional reduction of the corresponding zirconium(IV) complexes, [Zr(cp)$_2$X$_2$], were unsuccessful.[8] At the present time there is no unambiguous characterization of a neutral zirconium(III) complex of formula [{Zr(cp)$_2$X}$_n$], except for two compounds: the phosphido-bridged dimer (6) [18] and a dinitrogen complex (7),[19] containing the bulky substituent CH(SiMe$_3$)$_2$.



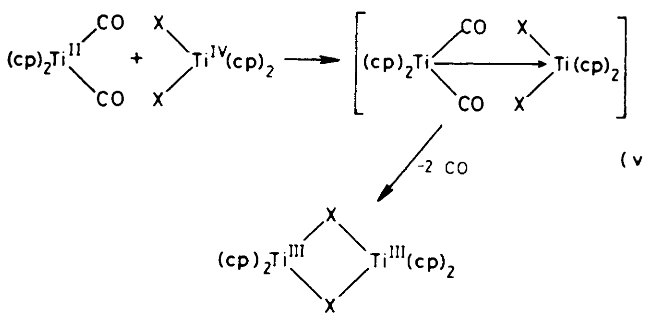
(6)
R = Et or Bu^n



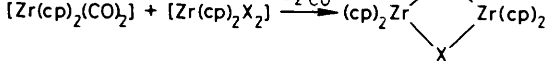
(7)

A general synthesis leading to bis(cyclopentadienyl)titanium(III) complexes [20] can be extended to zirconium analogues. Such a reaction occurs between [Ti(cp)$_2$(CO)$_2$] and a titanium(IV) complex, [Ti(cp)$_2$X$_2$] [equation (v); X = Cl, SPh, or SC$_6$H$_4$Me-*p*]. The general reaction (v), in which the Lewis-base titanium(II) attacks the Lewis-acid titanium(IV), applies quite well to zirconium. By refluxing a benzene solution of [Zr(cp)$_2$(CO)$_2$] in the presence of [Zr(cp)$_2$X$_2$] (X = Cl or SPh), carbon monoxide is lost and the corresponding zirconium(III) complexes, (10) and (11), have been obtained [equation (vi)]. The dimeric nature of (10) was proven by cryoscopy in benzene.

Whereas (8) is readily available, complex (9) can be synthesized by the oxidative addition of the corresponding disulphide to [Zr(cp)$_2$(CO)$_2$] in good yield [equation (vii)]. Complexes (9) and (12) have been fully characterized (see Experimental section).[21]

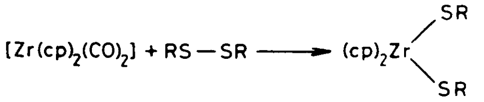


(v)



(vi)

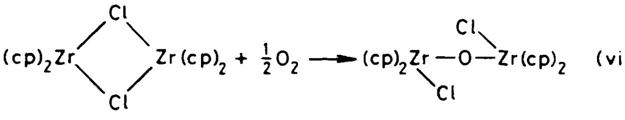
(8) X = Cl (10) X = Cl
(9) X = SPh (11) X = SPh



(vii)

(9) R = Ph
(12) R = Et

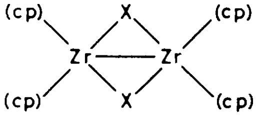
Concerning the nature of complexes (10) and (11), it was observed that in reactions leading to low-valent complexes the involvement of the cp ligand can make the reaction and the structure of the final compounds rather intriguing. In order to prove the presence of the intact cp ligand we tried to monomerize (10) by reaction with pyridine. Complex (10) was, however, recovered unchanged. However, we think that reaction (viii) proves that the Zr(cp)$_2$ fragment remains intact in complex (10). Absorption of 0.475 mol of O$_2$ per dimer (10) was observed and the well known complex (13) formed [22] in good yield.



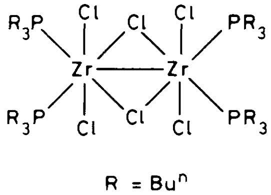
(viii)

(10) (13)

The most striking result is that both (10) and (11) are diamagnetic. In the titanium analogues, magnetic moments are a little lower than the expected value for one unpaired electron per metal atom, 1.4—1.5 B.M. instead of 1.73 B.M.; this was explained by suggesting a partial spin coupling through the bridging chlorine ligands.[23] The diamagnetism of the Zr^{III} dimers is better explained by taking into account the greater diffuseness of the [Zr(cp)$_2$] fragment orbitals; this allows an efficient overlap between the two non-bonding orbitals with consequent Zr–Zr bond formation.[24] Evidence has so far been produced on the tendency of zirconium to form metal–metal bonds. Schrock and co-workers [25] synthesized and structurally characterized the diamagnetic dimeric zirconium(III) complex shown below having a zirconium–zirconium bond distance of 3.182(11) Å.[25] Very similar zircon-



ium-zirconium bond distances have been found in some cluster compounds, for example Zr_6I_{12} and Zr_6Cl_{15}.[26] More recently it was found that zirconium(IV) compounds, [Zr(cp)$_2$XY] (X = Cl, Y = Cl, Me, or OBu^t), can establish a metal-metal bond with a Ru^0 complex, [Ru(cp)(CO)$_2$]$^-$,[27] in a reaction which is reminiscent of reaction (vi) occurring between a basic and an acidic zirconium.



Experimental

Unless stated otherwise, all experiments were performed under purified nitrogen, using solvents which had been dried by standard techniques. Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer, n.m.r. spectra on a Varian 60 AP instrument, and magnetic measurements carried out using the Gouy method. [Zr(cp)$_2$Cl$_2$] [28] and [Zr(cp)$_2$(BH$_4$)$_2$] [29] were prepared as already described.

Preparation of [Zr(cp)$_2$(CO)$_2$].—[Zr(cp)$_2$(BH$_4$)$_2$] (21.0 g, 83 mmol) was introduced into a 700-cm^3 reaction bomb together with triethylamine (30 cm^3). The bomb was immediately loaded with carbon monoxide at 100 atm and stirred overnight at room temperature. The resulting mixture was filtered and evaporated to dryness *in vacuo*. The oily residue (containing a few crystals) was dissolved in toluene–heptane (1 : 4; 30 cm^3) and chromatographed over a neutral alumina column (diameter = 2 cm; height = 40 cm) by elution with toluene–heptane (1 : 4). The chromatographed liquid, dried *in vacuo*, and sublimed (75 °C, 10^{-2} Torr) gave violet-brown crystals (4.2 g, 18%) (Found: C, 51.60; H, 3.80. $C_{12}H_{10}O_2Zr$ requires C, 51.95; H, 3.60%). Gas-volumetric analysis (iodine oxidation in pyridine): 1.98 mol of CO per gram atom of Zr. I.r. spectrum: ν_{CO} (heptane solution) at 1 887 and 1 976 cm^{-1}. Cryoscopy (benzene solution): *M* calc., 277; found, 281. ^{1}H N.m.r. spectrum (C_6D_6): δ = 4.49 p.p.m. (s, cyclopentadienyl protons). Mass spectrum (peaks in agreement with the percentages of the naturally occurring zirconium isotopes) *m/e* = 276, 277, 280 [M^+]; 248, 249, 250, 252 [Zr(cp)$_2$(CO)]; 220, 221, 222, 224 [Zr(cp)$_2$].

Reaction between [Zr(cp)$_2$(CO)$_2$] and [Zr(cp)$_2$Cl$_2$].—Benzene (50 cm^3) was added to [Zr(cp)$_2$Cl$_2$] (8) (2.04 g, 7.0 mmol) and [Zr(cp)$_2$(CO)$_2$] (1.93 g, 7.0 mmol) and the mixture was refluxed for 90 min. The green solution was cooled to room temperature; n-hexane (50 cm^3) was added, and the resulting green precipitate dried *in vacuo*, yield 2.68 g (75%) (Found: C, 46.2; H, 4.30; Cl, 13.0%; *M* (cryoscopy in benzene), 531. [{Zr(cp)$_2$Cl}$_2$], $C_{20}H_{20}Cl_2Zr_2$, requires C, 46.5; H, 3.9; Cl, 13.6%; *M*, 513). ^{1}H N.m.r. spectrum (C_6D_6): δ = 6.25 p.p.m. (s, cyclopentadienyl protons). $\chi_M^{corr} = 50 \times 10^{-6}$ c.g.s.units at 292 K.

Reaction between [{Zr(cp)$_2$Cl}$_2$] *and Oxygen*.—Compound (10) (0.315 g, 0.614 mmol) dissolved in toluene (10 cm^3) was treated with dry oxygen at atmospheric pressure. From the solution separated a light brown solid, whose yield was improved by addition of n-hexane (50 cm^3). After recrystallization from toluene–n-hexane, the product was dried *in vacuo* (yield 70%); its i.r. spectrum in Nujol was superimposable on that of [{Zr(cp)$_2$Cl}$_2$O].[22] Complex (10) absorbed 0.475 mol of O_2 per mol of complex in toluene at 16 °C.

Reaction between [Zr(cp)$_2$(CO)$_2$] *and* Ph_2S_2.—[Zr(cp)$_2$(CO)$_2$] (0.66 g, 2.4 mmol) and diphenyl disulphide (2.0 g, 9.16 mmol) were kept in toluene (50 cm^3) under reduced pressure for 20 h, to give a clear yellow solution. This was concentrated *in vacuo* and n-heptane (100 cm^3) added: a yellow product was thus obtained, which was filtered off and dried *in vacuo* (yield 0.6 g, 57%) {Found: C, 59.60; H, 4.35. [Zr(cp)$_2$(SPh)$_2$], $C_{22}H_{20}S_2Zr$, requires C, 60.05; H, 4.55%}. The i.r. spectrum in Nujol was superimposable on that of [Zr(cp)$_2$(SPh)$_2$].[21]

Reaction between [Zr(cp)$_2$(CO)$_2$] *and* Et_2S_2.—By warming (70 °C) a solution of [Zr(cp)$_2$(CO)$_2$] (1.0 g, 3.6 mmol) and diethyl disulphide (0.8 cm^3, 6.5 mmol) in toluene (20 cm^3), gas evolution was observed and in 10 min the solution turned light yellow. After concentrating *in vacuo*, adding n-hexane (50 cm^3), and cooling to −78 °C, yellow leaflets were filtered off and dried *in vacuo* (yield 1.05 g, 84%) (Found: C, 48.70; H, 5.65%; *M* (cryoscopy in benzene), 395. [Zr(cp)$_2$(SEt)$_2$], $C_{14}H_{20}S_2Zr$, requires C, 48.95; H, 5.85%; *M*, 343). ^{1}H N.m.r. spectrum (C_6D_6): δ = 1.6 (t, 6 H, Me), 3.2 (q, 4 H, CH$_2$), and 6.0 p.p.m. (s, 10 H, cp).

Reaction between [Zr(cp)$_2$(CO)$_2$] *and* [Zr(cp)$_2$(SPh)$_2$].—To a solution of (11) (0.530 g, 1.2 mmol) in benzene (30 cm^3), [Zr(cp)$_2$(CO)$_2$] (0.347 g, 1.25 mmol) was added. After refluxing for 50 min a red precipitate was filtered off, washed with benzene (20 cm^3), and dried *in vacuo* (yield 0.510 g, 64%) (Found: C, 57.55; H, 4.75; S, 9.80. [Zr(cp)$_2$(SPh)$_2$], $C_{32}H_{30}S_2Zr_2$, requires C, 58.20; H, 4.5; S, 9.70%). The product is practically insoluble in benzene and diamagnetic ($\chi_M^{corr} = 35 \times 10^{-6}$ c.g.s. units at 292 K).

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