Dicarbonylbiscyclopentadienylzirconium(II): the Carbonylation of Metal Tetrahydroborate Derivatives as a Route to Metal Carbonyls

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Summary The carbonylation of the tetrahydroborato-biscyclopentadienyl derivatives of titanium(III) and zirconium(IV), $[(cp)_2Ti(BH_4)]$ and $[(cp)_2Zr(BH_4)]_2$, in the presence of triethylamine, gave the corresponding dicarbonyls $[(cp)_2Ti(CO)_2]$ and $[(cp)_2Zr(CO)_2]$, the latter being the first reported carbonyl of zirconium and an authentic stable complex of zirconium(II).

THE metal carbonyl chemistry of the group IVA elements is restricted to that of $[(cp)_2Ti(CO)_2]$,[1,2] (cp = η^5-C_5H_5), and $[(cp)_2Ti(CO)(PhC{\equiv}CPh)]$.[3] There have been many recent reports on the synthesis of $[(cp)_2Ti(CO)_2]$, all starting from titanium(IV) derivatives, *e.g.* $[(cp)_2TiR_2]$ (R = CH_2Ph or Me),[4-6] but the methods which were successful for titanium failed to generate a carbonyl derivative of zirconium,[1,4,6,7] carbonyl complexes of which are not yet known.[8] We report a general synthetic route to carbonyls, including $[(cp)_2Zr(CO)_2]$ from the widely available and well characterised metal tetrahydroborates.[9]

Treatment of $[(cp)_2Ti(BH_4)]$,[10] (I), in Et_3N with CO at atmospheric pressure for 4 days, gave a brown solution, which was evaporated to dryness. Treatment of the residue with warm heptane gave $[(cp)_2Ti(CO)_2]$ (II),[1] in *ca.* 80% yield. It has been reported that Et_3N does not induce the usual decomposition of (I) to the corresponding metal-hydride species.[11] A similar reaction in Et_3N with $[(cp)_2Zr(BH_4)_2]$,[11] (III), gave, as shown by the i.r. spectrum, a carbonyl species (ν_{CO} 1885s and 1980s cm^{-1}). The carbonyl derivative may best be isolated by treatment of a freshly prepared suspension of (III) in Et_3N with CO at 100 atm and 50 °C for 2 days, followed by evaporation to dryness of the resulting suspension of a white solid in a brown solution and chromatography of the residue on alumina with heptane–benzene as eluent. $[(cp)_2Zr(CO)_2]$ (IV) was obtained as violet air-sensitive crystals in *ca.* 15% yield. Treatment of (III) with Et_3N is known to give both $[(cp)_2ZrH(BH_4)]$ and $[(cp)_2ZrH_2]_n$,[11] but we know nothing yet about the active species being carbonylated. Analytical data for (IV) were in agreement with the proposed formulation and it evolved 2 mol of CO per Zr atom when oxidised by iodine in pyridine solution. The physical properties of (IV) are quite similar to those of titanium analogue (II). Complex (IV) sublimes easily at 70 °C and 10^{-2} mm Hg; it is soluble in hydrocarbons and monomeric in benzene (*M* 281). Its i.r. spectrum shows two C–O stretching bands of similar intensity at 1887 and 1976 cm^{-1} (heptane solution). That (IV) is diamagnetic is suggested by the single sharp n.m.r. peak at τ 5·10 (C_6D_6). For comparison, $[(cp)_2Ti(CO)_2]$ shows C–O i.r. peaks (heptane) at 1897 and 1975 cm^{-1}, and an n.m.r. peak (C_6D_6) at τ 5·42 (s). Complex (IV) showed mass spectral peaks at *m/e* 276, 277, 278, 280 $(M)^+$; 248, 249, 250, 252 $[(cp)_2Zr(CO)]$; and 220, 221, 222, 224 $[(cp)_2Zr]$ whose positions and relative intensities are in agreement with the natural isotopic mixture of zirconium.

Complex (IV) is a rare example of a monomeric complex of zirconium(II). The co-ordination or organometallic chemistry of the low oxidation states of zirconium is practically non-existent.[8] Only recently some aspects of the reactivity of the rather elusive species $[(cp)_2Zr]$[12] and $[(\eta^5\text{-}Me_5C_5)_2Zr]$[13] have been reported. The isolation of (IV) may be especially important for the synthesis of organometallic derivatives of Zr^{IV}, Zr^{III}, and Zr^{II}. $[(cp)_2Ti(CO)_2]$ was shown to be both an interesting d^2 carbene-like reactivity model and an important source of highly reactive biscyclopentadienyltitanium(II) for the synthesis of many organometallic derivatives in different oxidation states of titanium.[3,14]

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