Organometallic Chemistry of Ambident Dianions. Reactions of Acetone Dianions as C,O Dinucleophiles with Group 4 Metallocene Dichlorides[†]

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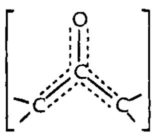
Summary: Acetone dianions, $[CH_2C(O)CR_2]^{2-}$ (R = Ph, H), react with group 4 metallocene dihalides (M = Zr, Hf) as C,O dinucleophiles. The products in solution are (by VPO) monomeric 2-metallaoxacyclobutanes, but in the solid state they are "dimers", 1,5-dimetalla-2,6-dioxacyclooctanes. The structure of 1,1,5,5-tetrakis(η^5-cyclopentadienyl)-3,7-bis(diphenylmethylene)-1,5-dizircona-2,6-dioxacyclooctane was determined by X-ray crystallography.

Double deprotonation of acetone and appropriately substituted acetones results in formation of delocalized dianions, **1**.[1] In reactions of such dianions with organic substrates C–C bond formation usually is observed. Studies by Kemmitt and co-workers[2] have shown that with *cis*-$[L_2PtCl_2]$ and *trans*-$[L_2PdCl_2]$ complexes the dianion derived from dibenzyl ketone reacts as a C,C dinucleophile, giving oxotrimethylenemethane complexes, **2** (R = Ph), as products (eq 1). (The alternate description as 3-metallacyclobutanones, **3**, also is used.)



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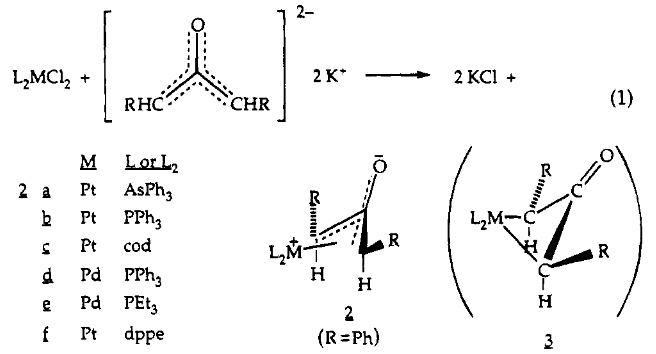
Since dianions of type **1** should be ambident, in principle, they could react with dihalides of oxophilic metals as C,O dinucleophiles, giving 2-metallaoxacyclobutanes (or, in an alternate description, η^3-oxatrimethylenemethane complexes). The possibility of such reactivity is the subject of our ongoing studies, and we report here some initial results.



(1)

The possibility that dianions of type **1** could react as C,O dinucleophiles was examined using group 4 metallocene dichlorides as substrates, since titanium, zirconium, and hafnium are strongly oxophilic. In our initial experiment the dianion of 1,1-diphenyl-2-propanone was allowed to react with zirconocene dichloride in THF solution.[3] The product, a yellow, slightly air-sensitive solid, was obtained in 55–60% yield.

The expected structure of the product of the $[CH_2C(O)CPh_2]^{2-}/Cp_2ZrCl_2$ reaction was the 2-zirconaoxacyclobutane **4** (Scheme 1). The EI mass spectrum of the yellow solid obtained in this reaction, however, showed as the highest mass peak one whose *m/z* was exactly twice the molecular weight of **4**. The dimer of **4** could have two different structures: it could be the coordination dimer **5** or the "open" dimer, the 1,5-dizircona-2,6-dioxacyclooctane, **6**. Zirconaoxacycloalkanes of ring size ≤5 which are dimeric in the solid state as a result of double O→Zr coordination (as in **5**) are well-known.[4–8]

[†] Dedicated, with all best wishes, to Professor Eugene G. Rochow on the occasion of his 85th birthday.

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(3) A red THF solution of the dianion derived from 2.62 g (12.5 mmol) of 1,1-diphenyl-2-propanone[1c] was added dropwise to a solution of 3.64 g (12.5 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in 100 mL of THF at −78 °C (under nitrogen). The resulting mixture was allowed slowly to warm to room temperature and was stirred overnight. The resulting orange suspension was evaporated at reduced pressure. The residue was extracted with 3 × 100 mL of toluene. Filtration through Celite was followed by concentration of the orange filtrate to ~30 mL and addition of 150 mL of hexane. The resulting yellow precipitate was washed with hexane and dried *in vacuo.* This material was pure by ^1H NMR. The analytical and crystallography samples were obtained by slow diffusion of hexane into a concentrated solution of the yellow solid in CH_2Cl_2. A CH_2Cl_2 solvate was obtained. The yields in several experiments were in the 55–60% range. Mp: 185–187 °C dec. Anal. Calcd for $C_{25}H_{22}OZr\cdot 0.5CH_2Cl_2$: C, 64.85; H, 4.92; Cl, 7.51. Found: C, 64.56; H, 4.91; Cl, 7.60. Mol wt (CH_2Cl_2-free sample) (VPO, $CHCl_3$): 410 (calcd 429). ^1H NMR (300 MHz, C_6D_6): δ 1.81 (br, s, 2H), 4.25 (s, CH_2Cl_2), 5.51 (br, s, 5H), 6.00 (br, s, 5H), 7.10–7.70 (m, 10H). VT ^1H NMR (300 MHz, toluene-d_8, at −17 °C): δ 1.86 (d, J = 11 Hz, 1H), 2.00 (d, J = 11Hz, 1H), 5.56 (s, 5H), 6.07 (s, 5H), 7.10–7.67 (m, 10H). VT ^1H NMR (300 MHz, toluene-d_8, at 90 °C): δ 1.91 (s, 2H), 5.88 (s, 10H), 7.10–7.70 (m, 10H).

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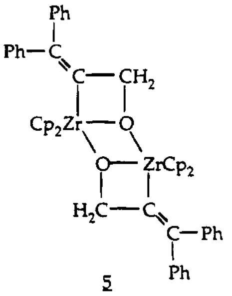

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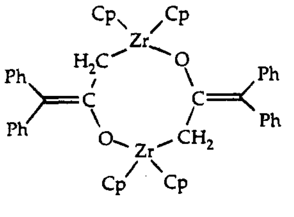

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Generally, the tendency to form such coordination dimers increases as the metallaoxacyclic ring size decreases.[9] Noteworthy is the case of Erker's (dialkyl tartarato)zirconocene dimers for which both the coordination dimer and the "open" dimer could be isolated.[10]

To determine if the solid state dimer of **4** was **5** or **6**, an X-ray structure analysis was undertaken.[11] An ORTEP representation of the observed structure is shown in Figure 1. The product is **6**, not **5**; i.e., it exists as an "open" eight-membered ring species rather than as a tricyclic coordination dimer. Selected bond distances and angles are given in the figure caption. The Zr(1)–O(1) and Zr(2)–O(2) bond distances of 1.954(3) Å are shorter than the value estimated from the sum of the covalent radii of Zr and O (2.11–2.14 Å)[12] and are comparable with the Zr–O bond distances of (1.941(2) and 1.946(4) Å in known zirconaoxacycles.[13,14] The Zr–O bond distances in **6** also are shorter than those of many other 2-zirconaoxacycloalkanes (2.103–2.227 Å).[4-8] One may conclude that there is multiple bond character in the Zr–O bond in **6** involving π-donation from the oxygen atom to a vacant Zr orbital. The Zr(1)–O(2) and Zr(2)–O(1) distances of 3.438(3) and 3.409(3) Å, respectively, indicate that there are no transannular bonding interactions, thus eliminating a coordination dimer structure from consideration. The Zr(1)–O(1)–C(5) and Zr(2)–O(2)–C(2) bond angles in **6**, 148.2(3) and 151.7(3)°, respectively, are similar to known Zr–O–C bond angles.[13,14] The C(2)–C(3) and C(5)–C(6) bond distances, 1.349(5) and 1.337(6) Å, respectively, are typical of C–C double bonds.[15]

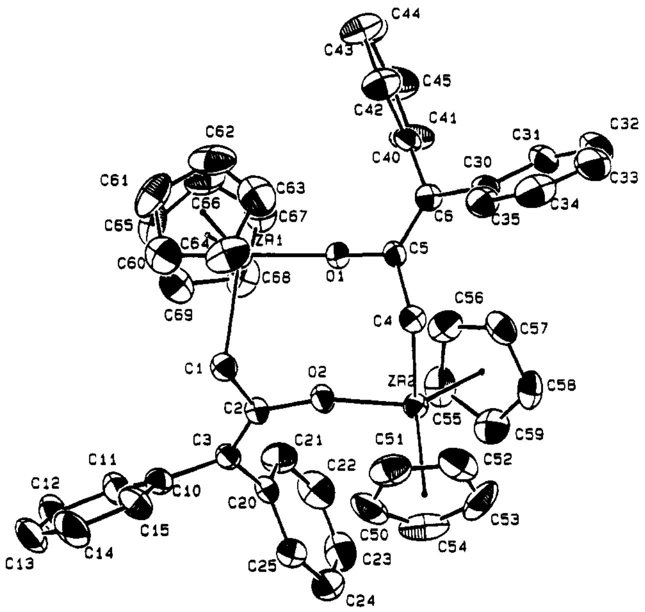

Figure 1. ORTEP plot of **6** showing 35% probability ellipsoids. Important bond distances (Å) and angles (deg): Zr(1)–O(1) = 1.954(3); Zr(2)–O(2) = 1.953(3); Zr(1)–C(1) = 2.307(4); Zr(2)–C(4) = 2.335(4); C(1)–C(2) = 1.483(6); C(4)–C(5) = 1.450(6); O(1)–C(5) = 1.354(5); O(2)–C(2) = 1.350(5); C(2)–C(3) = 1.349(5); C(5)–C(6) = 1.337(6); O(1)–Zr(1)–C(1) = 97.5(1); Zr(1)–O(1)–C(5) = 148.2(3); Zr(2)–O(2)–C(2) = 151.7(3); Zr(1)–C(1)–C(2) = 115.6(3); O(2)–C(2)–C(1) = 113.1(4); Zr(2)–C(4)–C(5) = 116.6(3); O(1)–C(5)–C(4) = 111.8(4); C(10)–C(3)–C(20) = 115.3(4); C(30)–C(6)–C(40) = 115.2(4).

A direct comparison of these results vis-á-vis those that would be obtained using $(Ph_3P)_2MCl_2$ (M = Pd, Pt) rather than Cp_2ZrCl_2 proved not to be possible since the products of the $[CH_2C(O)CPh_2]^{2-}/(Ph_3P)_2MCl_2$ (M = Pd, Pt) reactions did not appear to be stable. However, such a comparison was possible with the $[CH_2C(O)CH_2]^{2-}$ anion. Its reaction with $(Ph_3P)_2PtCl_2$ gave **2** (R = H),[17] whose spectroscopic properties (IR and ^1H, ^{13}C, and ^{31}P NMR) were identical with those reported by Kemmitt and his co-workers[2b] for this compound (prepared by reaction of $Me_3SiCH_2C(O)CH_2Cl$ with Pt(*trans*-stilbene)$(PPh_3)_2$). On the other hand, the zirconocene dichloride-derived product was the dimer **7**, according to its EI mass spectrum, presumably analogous to **6** (except that it has exo $=CH_2$ rather than $=CPh_2$ groups).[17]

The solution properties of **6** are of some interest. A determination of its molecular weight by vapor pressure osmometry (VPO) in chloroform solution gave a value of 410. This is, within experimental error, the molecular weight of the four-membered ring compound, **4**, 429. It thus would appear that the eight-membered ring compound, **6**, dissociates when dissolved in chloroform. We

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(11) Crystal data for *6*·CH_2Cl_2: yellow, prismatic, monoclinic, a = 15.318(2) Å, b = 18.155(2) Å, c = 16.384(2) Å, β = 109.89(3)°, V = 4285(2) Å^3, space group $P2_1/c$ (No. 14), Z = 4, fw = 944.27, calcd density = 1.464 g/cm^3. Data in the range $3.00 < 2\theta < 55.0°$ were collected at -80 ± 1 °C using Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by full matrix least squares techniques. The non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using the method of N. Walker and D. Stuart (*Acta Crystallogr.* **1983**, *A39*, 1581). Final R = 0.051 and R_w = 0.042 for 6171 observed reflections $(h,\pm k,\pm l)$ $[F_o^2 \geq 3\sigma F_o^2]$ and 524 variables. The largest peak on the final difference Fourier map was 0.65 e/Å^3. During the solution of the structure a solvent molecule was located on a difference Fourier map. The solvent molecule was identified as a methylene chloride moiety on the basis of chemical information. As refinement proceeded, the moiety was noticeably disordered in one chlorine atom. The top two peaks (Cl(2) and Cl(3)) in the region were assigned one-half occupancy chlorine and eventually refined anisotropically to their current values. Average distances and angles within the solvent molecule are consistent with methylene chloride, and no other chemically significant peaks were found near the moiety.

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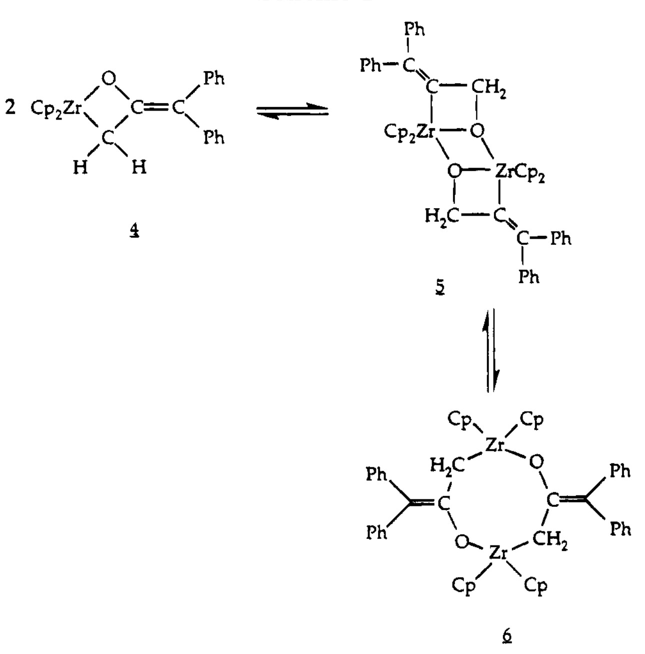
(17) See supplementary material for characterization data.

Scheme 1

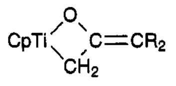


suggest that in solution the eight-membered ring is sufficiently flexible to allow transannular interactions to give the coordination dimer **5**. The latter then dissociates to give **4**. The suggested dimerization/dissociation process is shown in Scheme 1.

Some (oxotrimethylenemethane)palladium and -platinum complexes undergo ring inversion in solution, as evidenced by their temperature-dependent ^{1}H NMR spectra. The experimental activation energies for this process lie between 8.4 and 12.2 kcal/mol.[2b,c] Interestingly, the species obtained on dissolution of **6**, presumably the four-membered ring complex, **4**, shows similar behavior. ^{1}H NMR spectra taken at selected temperatures are shown in Figure 1 of the supplementary material. At room temperature two broad resonances were observed for cyclopentadienyl rings. The Zr−CH_2 protons appeared as a broad resonance. At −17 °C, the CH_2 proton signal was resolved into two doublets which showed a typical AB pattern, and the Cp signals became two sharp singlets. At 50 °C, the Cp signals coalesced into a single peak, reaching the fast exchange value at 90 °C. The same coalescence temperature of 50 °C was observed in variable-temperature ^{1}H NMR experiments in which three different concentrations of **4** were used. This indicates that the inversion rate is independent of concentration, i.e., that the ring inversion is an intramolecular process.[16] The free energy of activation of the ring inversion, indicated by these results, is estimated to be 15.3 kcal/mol.

The reaction of the $[CH_2C(O)CPh_2]^{2-}$ anion with Cp_2HfCl_2 gave **8**, the hafnium analog of **6**.[17] The same behavior was observed when it was dissolved in chloroform: although the EI mass spectrum of the solid product showed a molecular ion indicative of the eight-membered ring compound, its molecular weight, determined by VPO in $CHCl_3$, was equivalent to that of the four-membered ring.

Our attempts to prepare the titanium analogs of **4** and **7** by the dianion route have to date been unsuccessful in that pure products have not been isolated. ^{1}H NMR spectra of the crude products indicated the presence of the expected 2-titanaoxacyclobutanes, but the presence of impurities in large amounts prevented their isolation. However, the titanium analogs of **4** and **7** had been reported earlier by Grubbs and co-workers,[18] who used very different preparative routes not involving acetone dianion reactions. Monomeric structures in solution were indicated for **9a** and **b** on the basis of cryoscopic molecular weight measurements and their ^{1}H NMR spectra. In particular, a VT ^{1}H NMR study of **9a** and **b** gave results similar to those obtained with our zirconium analog **4**. A puckered ring structure that undergoes facile ring flip at room temperaure was suggested. The free energy of activation of this ring-inversion was found to be 13 kcal/mol for **9a** and 19 kcal/mol for **9b**. Crystals of **9a** or **b** suitable for an X-ray structure determination could not be obtained, so their solid state structures remain unknown. An "open" dimer structure is a possibility.



9a, R = H
b, R = Ph

This study has shown that $[CH_2C(O)CR_2]^{2-}$ (R = H, Ph) are indeed ambident in their reactions with metal dihalides, demonstrating C,O dinucleophilic reactivity toward oxophilic metal centers. A feature of special interest is that the products of these reactions in solution are monomeric species, but "open" dimers, 1,5-dimetalla-2,6-dioxacyclooctanes, in the solid state.

These are only the first examples of the C,O dinucleophile reactivity of acetone dianions. Our studies of the reactions of acetone dianions with inorganic dihalides are continuing and will not be limited to transition metal dihalides. Indeed, we have found in the case of silicon chlorides, as might be expected, acetone dianions react as C,O dinucleophiles.[19]

Acknowledgment. The authors are grateful to the National Science Foundation for support of this work and to Dr. John M. Birmingham (Boulder Scientific Co.) for gifts of metallocene dichlorides.

Supplementary Material Available: ^{1}H NMR spectra of **4**, a textual presentation of experimental procedures, and an X-ray structural report including PLUTO and ORTEP diagrams (30% probability ellipsoids), a textual description of experimental details, and tables of experimental results, positional and thermal parameters, bond distances and angles, torsion angles, and intermolecular contacts (38 pages). Ordering information is given on any current masthead page.

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