TITANIUM, ZIRCONIUM AND HAFNIUM

ANNUAL SURVEY COVERING THE YEAR 1982

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This survey is organized by ligand type, with complexes containing more than one class of ligand listed according to the feature of primary interest. The abbreviation Cp (for η^5-cyclopentadienyl), RCp (for η^5-substituted cyclopentadienyl), Cp^* (for η^5-pentamethylcyclopentadienyl), and Ind (for η^5-indenyl) are used throughout.

Several reviews on organotitanium, zirconium and hafnium complexes have appeared in 1982: titanium hydrides [1], 1,3-diene complexes of zirconium and hafnium [2], bis(cyclopentadienyl)aryloxy and aryl compounds [3], and organic synthesis using organotitanium reagents [4]. Two Russian-language [5, 6], one Chinese-language [7], and one Japanese-language [8] reviews have been cited in Chemical Abstracts.

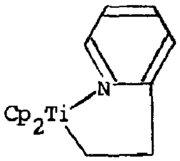
CARBONYL AND DINITROGEN COMPLEXES

The structure of $Ti(CO)_3(dmpe)_2$, 1, (dempe = 1,2-bis(dimethylphosphino)-ethane) has been determined by x-ray diffraction and found to be a distorted monocapped octahedron. Compound 1 was found to be labile, rapidly exchanging carbonyl with PF_3 or ^{13}CO at room temperature. Based on variable temperature ^{13}C and ^{31}P NMR studies 1 was found to undergo two separate dynamic processes, with free energies of activation of 7.77 and 11.57 kcal/mole [9].

Cyclic voltammetry of Cp_2TiX_2 (X = Cl, Br) under CO (3 atm) in THF with Bu_4NPF_6 as the supporting electrolyte gave, after two one electron reductions, $Cp_2Ti(CO)_2$. Electrolysis of Cp_2TiX_2 under these conditons in THF at -1.8 V vs.

SCE gave $Cp_2Ti(CO)_2$ in high yield [10].

Treatment of $Cp_2Ti(CO)_2$ with $[CpMo(CO)_2]_2$ in THF gave $Cp_2Ti(THF)(\mu\text{-}\eta^2\text{-}OC)Mo(CO)_2Cp$, which was determined by X-ray diffraction to contain a $\mu\text{-}\eta^2$ bridging carbonyl with a Mo–C distance of 1.873 Å, a Ti-O (carbonyl) distance of 2.143 Å and a C–O (μ–CO) distance of 1.201 Å [11]. $Cp_2Ti(CO)_2$ reacts with 2-vinylpyridine to give a mixture of complexes **2** and 3 [12]. Reaction of $Cp_2Ti(CO)_2$ with phthalazine results in an electron transfer upon complexation to give **4** [13].



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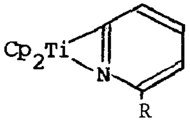
R = $CH{=}CH_2$, CH_2CH_3



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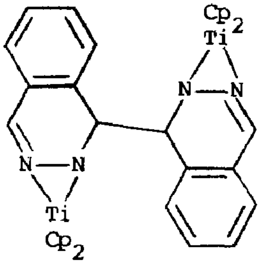

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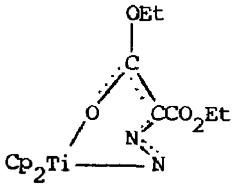
Reaction of $Cp_2Ti(CO)_2$ with diethyl diazomalonate leads to loss of CO to give 5 in moderate yield. The analogous reaction of $Cp_2Ti(CO)_2$ with diphenyldiazomethane gave the trinuclear species **6**. Complexes 5 and **6** were



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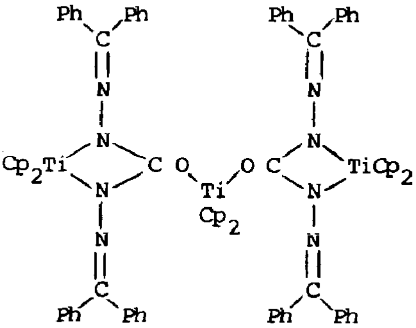

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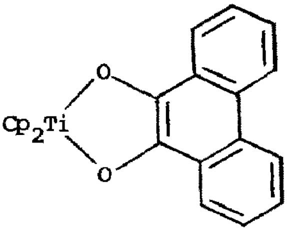
characterized by X-ray diffraction analysis. Reaction of **6** with 9,10-phenathrenquinone gave **7** and **8** [14].



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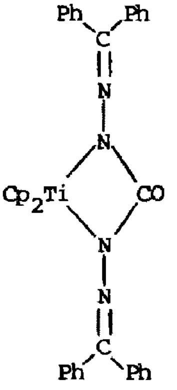

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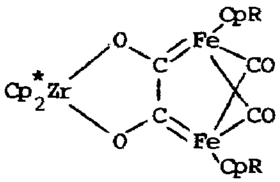
N_2 reacts reversibly with $[\mu-(\eta^1:\eta^5-C_5H_4)]Cp_3Ti_2]$, **9**, in hydrocarbon solvents to give a deep blue complex, $[\eta^1:\eta^5-(C_5H_4)Cp_3Ti_2]_2N_2$. Reaction of **9** with N_2 (10 atm) in 1,2-dimethoxyethane gave an N_2 complex which, upon successive treatment with THF/glyme and bis(2-methoxyethyl)ether ($C_6H_{14}O_3$) gave $(\mu_3-N_2)[(\eta^5:\eta^5-C_{10}H_8)Cp_2Ti_2][\eta^1:\eta^5-C_5H_4)Cp_3Ti_2]\cdot[Cp_2(C_6H_{14}O_3)Ti]\cdot C_6H_{14}O_3$, **10**, which was shown by x-ray diffraction to contain an N_2 coordinated to three Ti atoms. Treatment of solutions of **10** with H_2 gas, or dry HCl, resulted in the loss of the coordinated N_2. However, aqueous hydrolysis of **10** yields mostly NH_3 [15].

Quantum-chemical molecular calculations were carried out for dinitrogen complexes $[Cp_2TiR]_2N_2$ (R = H, p-tolyl) [16].

The reaction of $Cp^*_2ZrN_2$ with $[(RCp)Fe(CO)]_2$ (R = H, Me) in toluene above -20°, gave $Cp^*_2Zr(CO)_4Fe_2(RCp)_2$, **11**, which upon treatment with CO (2 atm, 25) gave $Cp^*_2Zr(CO)_2$ and $[(RCp)Fe(CO)_2]_2$ [17].



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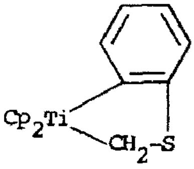
The reaction of $Cp_2Zr(PPh_2Me)_2$ with RX (R = n-Bu, s-Bu, t-Bu, X = Br, Cl) was monitored by ESR. Signals assigned to $Cp_2ZrX(PPh_2Me)$ and $Cp_2ZrR(PPh_2Me)$ were reported. It was proposed that the oxidative addition of alkyl halides to $Cp_2Zr(PPh_2Me)_2$ proceeds via paramagnetic intermediates [18].

ALKYL AND RELATED COMPLEXES

Treatment of $[CpZrCl_3]_X$ with ArLi (Ar = C_6H_5, m-MeC_6H_4) gave $CpZrAr_3$ [19]. Treatment of $[Cp^*ZrCl_3]_X$ with 3 equivalents of RMgBr (R = Me, $PhCH_2$, C_6H_5) in diethyl ether gave Cp^*ZrR_3 in good yield. Mono- and dialkyl complexes were also prepared. Hydrogenolysis of Cp^*ZrMe_3 with H_2 (95 atm) gave $(Cp^*ZrH_3)_X$ [20].

Treatment of Cp_2TiCl_2 with α-thienyllithium gave Cp_2Ti(α-thienyl)$_2$, which upon treatment with CCl_4, Br_2 or I_2 gave Cp_2TiX_2 (X = Cl, Br, I). The reaction of Cp_2Ti(α-thienyl)$_2$ with carboxylic acids, RCOOH (R = $(O_2N)_2C_6H_3$, C_6F_5, CF_3, CCl_3, CBr_3), gave the corresponding carboxylate complexes $Cp_2Ti(O_2CR)_2$ in high yield [21].

Reaction of Cp_2TiCl_2 with two equivalents of sulfinyl carbanions Li[RCHS(O)R'] (R = H, Ph; R' = Me, Ph) leads to the formation of TiO_2, $Cp_2Ti(SR')_2$, $(R'SCHR)_2$, $(R'S)_2CHR$ and R'SSR'. In contrast to this, treatment of $[Cp_2TiCl]_2$ with 1 equivalent of $Li[CH_2S(O)Ph]$ and 1 equivalent of n-BuLi at -78°, followed by warming to room temperature, gave 12 in 31% yield [22].



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Treatment of $(RCp)_2MCl_2$ (R = H, Me; M = Ti, Zr, Hf) with aryllithium reagents gave $(RCp)_2MAr_2$, 13. The titanium derivatives were reported to be stable to hydrolysis, while the zirconium and hafnium derivatives could be hydrolyzed to give $[(RCp)_2M(Ar)]_2O$. Treatment of 13 with hydrogen halides (HF, HCl, HBr), acetylchloride, or acetylbromide gave the corresponding metallocene dihalides [23]. Treatment of Cp_2HfCl_2 with RCCNa (R = Phenyl, Cyclohexyl, n-hexyl, 2,2-diphenylethyl, 2-cyano-2,2-diphenylethyl) in dioxane at 50° for

8 hr gave $Cp_2Hf(CCR)_2$ in 60-65% yield [24].

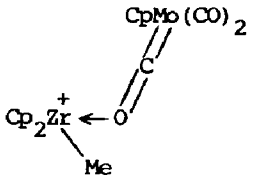
The reaction of diphenylacetylene with titanocene and benzyne, generated in situ by the reaction of Cp_2TiCl_2 and o-$F_2C_6H_4$ with Mg, gave $Cp_2\overline{Ti[o\text{-}C_6H_4C(Ph)=C}(Ph)]$ in 15% yield. The reduction of Cp_2TiCl_2 in the presence of diphenylacetylene gave $Cp_2\overline{TiC(Ph)=C(Ph)C(Ph)=C}(Ph)$ in 82% yield [25]. Bis(η^5-cyclopentadienyl)zirconacyclopentadienes were prepared by the reduction of Cp_2ZrCl_2 with magnesium, activated with $HgCl_2$, in THF in the presence of various alkynes [26]. Cis and trans-2,3-diphenylzirconaindans were formed stereospecifically from cis and trans stilbene and $Cp_2Zr(\eta^2\text{-}C_6H_4)$, which was generated by thermolysis of Cp_2ZrPh_2 [27].

Treatment of $Li_2[(2\text{-}CH_2C_6H_4)_2]$ with Cp_2MCl_2 (M = Ti, Zr, Hf) gave the corresponding metallacycles, $Cp_2M[(2\text{-}CH_2C_6H_4)_2]$, which were found to be much more thermally robust then the corresponding dibenzyl complexes $Cp_2M(CH_2C_6H_5)_2$ [28]. Treatment of Cp_2MCl_2 (M = Zr and Hf) with $Li_2[1,8\text{-}(CHSiMe_3)_2C_{10}H_6]$ gave $Cp_2M[1,8\text{-}(CHSiMe_3)_2C_{10}H_6]$ [29].

The thermal decomposition of Cp_2HfR_2 (R = Me, Ph) produces RH, with both the ring hydrogens and the methyl or phenyl groups serving as hydrogen sources. Differential thermal analysis indicated that the thermal stability of Cp_2HfR_2 exceeds that of the analogous titanium and zirconium complexes [30].

Treatment of a C_6D_6 solution of $Cp_2TiCl(CH_2Ph)$ with CCl_4 at ambient temperature gave Cp_2TiCl_2, $PhCH_2CCl_3$ and $(PhCH_2)_2$. The benzyl protons of $Cp_2TiCL(CH_2Ph)$ and $PhCH_2CCl_3$ exhibited enhanced CIDNP absorption [31].

The reaction of Cp_2ZrMe_2 with $CpMo(CO)_3$ gave $Cp_2(Me)Zr\text{-}\mu\text{-}CO\text{-}Mo(CO)_2Cp$, 14. Reaction of $CpMo(CO)_3H$ with $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$ in THF gave 15 as the principal



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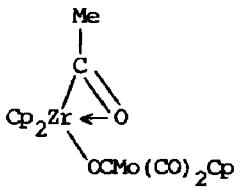

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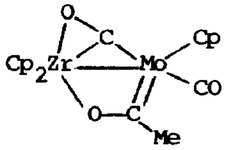

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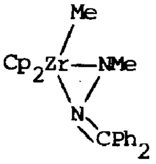
product. Carbonylation of 14 (1 atm CO) gave 15, which underwent decarbonylation under vacuum at room temperature to give **16**. Treatment of **14** with H_2O or CF_3COOH gave 1/3 $[Cp_2ZrO]_3$ or $Cp_2Zr(O_2CCF_3)$, respectively, and $CpMo(CO)_3H$ and acetaldehyde [32].

Extended Hückel molecular orbital calculations were carried out on $Cp_2ZrCl(CH_2PH_2)$ in order to explain the experimentally determined structure of $Cp_2ZrCl(CH_2PPh_2)$, **17**. The structural and chemical consequences of a one-electron reduction of **17** were also interpreted on the basis of the molecular orbital calculations [33]. Trans-$\{[Cp_2ZrCl(CH_2PPh_2)]_2Rh(CO)Cl]\}$, **18**, was prepared by the reaction of **17** with $[Rh(CO)_2Cl]_2$. Treatment of **18** with CO gave an unexpected terminal carbonyl complex $Cp_2Zr(CO)Cl(CH_2PPh_2)]_2Rh(CO)Cl]$, which was characterized by NMR, whereas the additon of CO to **17** gave $Cp_2ZrCl[C(O)CH_2PPh_2]$ [34].

Treatment of Cp_2ZrMe_2 or $Cp_2Zr(H)Cl$ with diphenyldiazomethane leads to the insertion of the diazo unit into a Zr-Me or Zr-H bond to give complexes 19 and 20 respectively. Both of these reactions can be viewed as occuring through the initial formation of an adduct such as 21 followed by methyl or hydride migration [35].



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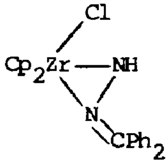

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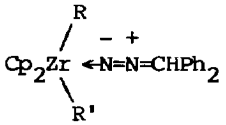
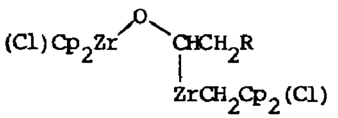


R = R' = Me
R = H, R' = Cl

21

$Cp_2Zr(R)H$ (R = Me, Et, $CH_2\overline{CH(CH_2)_4CH}_2$) were prepared by the reduction of $Cp_2Zr(R)Cl$ with $LiAlH(O\text{-}t\text{-}Bu)_3$ in DME. The cyclohexylmethyl complex exhibits bridging hydrogens by ^1H NMR and IR spectra and was found to be dimeric in benzene. The methyl and ethyl hydride complexes were found to be reasonably stable at room temperature. In contrast to this the cyclohexyl-methyl hydride complex slowly metathesizes to $Cp_2Zr[CH_2\overline{CH(CH_2)_4CH}_2]_2$ and Cp_2ZrH_2. The (cyclohexyl)methyl hydride complex was also found to undergo hydrogenolysis at room temperature with H_2 (1 atm) over several hours to give Cp_2ZrH_2 and methylcyclohexane. The chloro complex, $Cp_2Zr(CH_2\overline{CH(CH_2)_4CH_2})Cl$, was found to very slowly undergo hydrogenolysis under similar conditions. The reaction of $Cp_2Zr[C(O)CH_2\overline{CH(CH_2)_4CH_2}]Cl$ with $Cp_2Zr(H)Cl$ gave **22** which reacts with H_2 (95 atm) at room temperature to give alkoxide **23** [36].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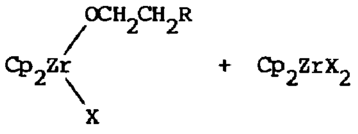
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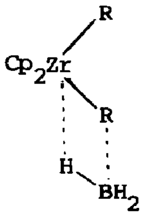
$R = \overline{CH(CH_2)_4CH_2}$; X = H, Cl

$CpCp^*ZrH_2$ was prepared by treatment of $CpCp^*ZrCl_2$ with n-BuLi in toluene [20]. $Cp^*_2HfH_2$ was found to react with RN_3 (R = Ph, p-tolyl) to give $Cp^*_2Hf(NHNNR)H$, **24**, which upon thermolysis at 80° loses N_2 to form the corresponding arylamido complexes $Cp^*_2Hf(NHR)H$, **25**. Complex **25** was also prepared by treating $Cp^*_2ZrH_2$ with RNH_2. Treating $Cp^*_2ZrH_2$, **24**, or **25** with excess RN_3 lead to the formation of $Cp^*_2Hf(NHR)_2$ [37].

The reaction of $Cp_2Zr[C(O)Me]Me$ with excess $BH_3{\bullet}THF$ in THF at 0° lead to the rapid formation of $Cp_2Zr(BH_4)_2$. It was proposed that this reaction proceeds via Cp_2ZrMe_2 which is in equilibrium with $Cp_2Zr[C(O)Me]Me$. Further study of the reaction of Cp_2ZrMe_2 with $BH_3{\bullet}THF$ indicates that this reaction involves an initial Lewis acid-base adduct such as **26** [38].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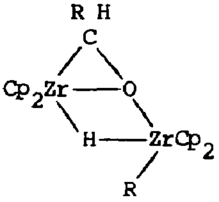
Treatment of $Cp_2Zr[C(O)R]R$ and $Cp_2Zr[C(O)R]Cl$ (R = Me, Ph) with $(Cp_2ZrH_2)_X$ or $[Cp_2Zr(Cl)H]_X$ gave binuclear μ-aldehyde-dizirconocene hydride complexes **27** and **28**. Complex **28** undergoes a degenerate dyotropic rearrangement as detected by ^1H NMR spectroscopy. Complex **28** was found to react with CO to give **29** [39].

Treatment of diphenylacetylene with $Cp_2Zr(Cl)H$, $(t\text{-}BuCp)_2ZrH_2$, or



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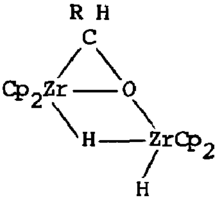

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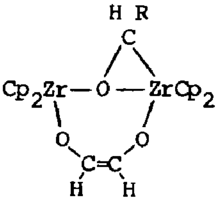

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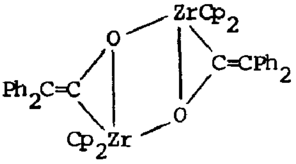
(t-BuCp)$_2$HfH$_2$ lead to the formation of cis and trans stilbene with the trans isomer predominating [40].

The treatment of Cp$_2$Zr(CHPh$_2$)R, 30, (R = Me, CH$_2$SiMe$_3$) with CO produces [Cp$_2$Zr(O=C=CPh$_2$)]$_2$, 31, and Cp$_2$Zr[η^2-C(O)R]CHPh$_2$. In contrast to this, treatment of Cp$_2$Zr(CHPh$_2$)$_2$ with CO under the same conditions gave only the acyl complex, Cp$_2$Zr[η^2-C(O)CHPh$_2$]CHPh$_2$. In an analogous fashion, treatment of complex 30 with methylisonitrile gave Cp$_2$Zr[η^2-C(NMe)CHPh$_2$]R [41]. Treatment of Cp$_2$Ti[C(O)Me]Cl, 32, with CH$_2$=PPh$_3$ or NaN(SiMe$_3$)$_2$ produces ketene complex 33, which exhibits two isomers. Treatment of 33 with 1 equivalent of HCl gas in toluene at -50° gave 32. Complex 33 reacts with ethylene and acetylene to give 34 and 35 respectively. Treatment of 32 with PMe$_2$Ph produces an adduct which reacts with acetylene to give 35. In an analogous fashion, treatment of Cp$_2$Ti[C(O)CH$_2$CH$_2$CMe$_3$]Cl with NaN(SiMe$_3$)$_2$ in toluene at room temperature gave the dimeric ketene complex 36, which was found to be inert towards ethylene and acetylene [42].



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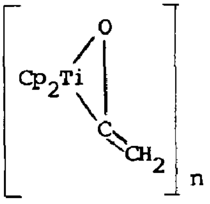

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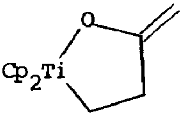

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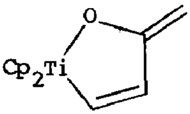

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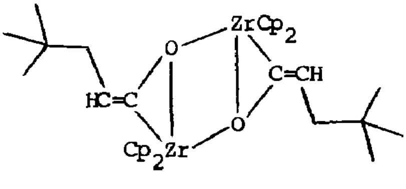

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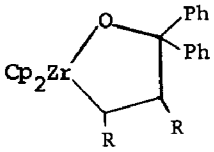
Thermolysis of $Cp_2Zr[C(O)Ph]Ph$ produces $Cp_2Zr(\eta^2\text{-}C(O)Ph_2)$, **37**, which was isolated as a dimer. Treatment of 37 with olefins or acetylenes gave metalacycles 38 and 39 respectively [43]. Treatment of 37 with alkyl halides,



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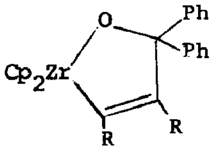

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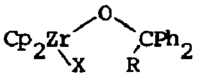
RX, (R = Me, Et, tetrahydrofuryl, 2-propyl, 2-octyl, t-Bu) gave **40**, **41**, and **42**. Treatment of 37 with 6-bromohexene or 6-bromo-6-methylheptene gives 43 as the



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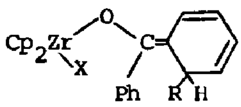

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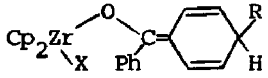

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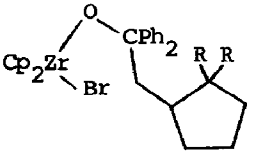
major product suggesting that this reaction proceeds via a geminate radical recombination of a radical pair such as **44** [44].



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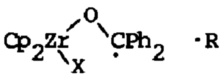

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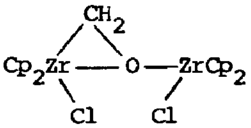
Dinuclear formaldehyde complexes **45**, were prepared by treating the known μ-aldehydezirconocene complex **46** with aryllithium reagents. Complexes 45 and



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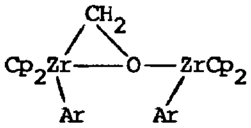


45

46 were found to exhibit dynamic behavior, readly undergoing a dyotropic rearrangement as determined by NMR [45].

The reaction of $Cp^*ZrCl(COT)$ with lithium and Grignard reagents, MR, (M = MgCl, Li; R = n-alkyl, aryl, vinyl, acetylide, substituted allyl) gave

$Cp^*Zr(R)(\eta^8\text{-}COT)$ in greater than 60% yield. In contrast to this, treatment of $Cp^*ZrCl(COT)$ with $ClMgCH_2CH{=}CH_2$ gave $Cp^*Zr(\eta^3\text{-}C_3H_5)(\eta^{1-4}\text{-}COT)$ which was structurally characterized by x-ray crystallography [46].

The reaction of $TiMe_4$ with $(CH_2{=}CHCH_2)_3B$ in Et_2O at -50° gave $TiMe_3(\eta^1\text{-}CH_2CH{=}CH_2)$, which could be stabilized by 2,2'-bipyridine as a 1:1 complex. $TiCl_4$ was found to react with $CH_2{=}CMeCH_2MgCl$ at -50° in Et_2O to give $Ti(CH_2{=}CMeCH_2)_4$ which was found to be fluxional by ^1H NMR, and at -70° exhibits an η^1-allyl structure. Thermal decomposition of $Ti(CH_2{=}CMeCH_2)_4$ lead to the formation of $Ti(CH_2{=}CMeCH_2)_2$ [47].

Treatment of $TiEtCl_3$ with $Me_2PCH_2CH_2PMe_2$ gave $Ti(Me_2PCH_2CH_2PMe_2)EtCl_3$, **47**, which was characterized by X-ray crystallography. The Ti-C-C bond angle in **47** was found to be 85.9° and the methyl group exhibited a direct hydrogen to titanium interaction with a Ti-H bond distance of 2.29 Å [48]. $Ti(Me_2PCH_2CH_2PMe_2)MeCl_3$, **48**, was prepared in a similar fashion by the additon of 1 equivalent of $Me_2PCH_2CH_2PMe_2$ to $TiMeCl_3$ at -15° in light petroleum. An X-ray crystallography analysis of **48** showed a Ti-C-H bond angle of 70° and a Ti-H bond distance of 2.03 Å. The Ti-H bonding in 47 and 48 was described in terms of 3-center, 2-electron bond [48,49].

Near UV irradiation of $Ti(NOR)_4$ (NOR = 1-norbornyl) in hexane produced norbornane and 1,1'-binorbornyl, and in CCl_4 leads to the formation of C_2Cl_6 and 1-chloronorborane as the major organic products. The dominant electronic absorption of $Ti(NOR)_4$ was assigned to a ligand to metal charge transfer (LMCT) transition [50]. A patent describing the disproportionation of TiR_4 with TiX_4 (X = Cl, Br) to give mixed alkyltitanium halides has appeared [51].

The reactions of $MR_2(Et_2O)_3$ (R = Ph, $PhCH_2$; M = Ti, Zr) with Me_2CO, Ph_2CO, CO, CO_2, AcOH and $(PhCOO)_2$ have been reported [52].

Treatment of TiL_2Cl_2 (LH = salicylaldehyde, acetylacetone, benzoylacetone, dibenzoylmethane, Me salicylate, benzoylphenylhydroxylamine) with PhLi gave TiL_2Ph_2, which upon treatment with SO_2, produced the insertion product $TiL(PhSO_2)_2$ [53].

ALKYLIDENE AND YLIDE COMPLEXES

The relative stabilities of six alkyl-substituted biscyclopentadienyltitanacyclobutanes were examined. It was found that for monosubstituted metallacycles β substitution is preferred, and that a second β substituent results in significant destabilization [54]. The kinetics for the reaction of $Cp_2\overline{TiCH_2CH_2CH_2}$ with diphenylacetylene was found to be first order in titanacyclobutane and zero order in diphenylacetylene. It was proposed that this reaction proceeds via a rate limiting opening of the titanacyclobutane ring to give $Cp_2Ti{=}CH_2$ [55].

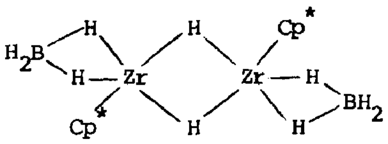
The reaction of titanacyclobutanes, deuterium labeled in the α and β positions, with Me_2AlCl lead to rapid reversible scrambling at the α carbon via a trans-metallation, and in a slower step metallacycle cleavage to produce the original olefin with scrambled stereochemistry and $Cp_2\overline{Ti(CH_2AlClMe_2})$. This cleavage reaction was found to be second order; first order in both titanacyclobutane and $AlMe_2Cl$ [56].

Ab initio molecular orbital calculations carried out on $(Cl)_2\overline{TiCH_2CH_2CH_2}$ suggest a planar structure, however, the energy to pucker the ring was found to be small [57].

The reaction of TiX_4 (X = BuO, Cl), and $Zr(OBu)_4$ with $Li_2[C(Me)HCH_2CH_2C(Me)H]$ in decane at 60-80° gave propylene. The formation of a metallacyclopentane intermediate was proposed [58].

CYCLOPENTADIENYL COMPLEXES

$CpZrCl_3$ was prepared by the photochemically initiated chlorination of Cp_2ZrCl_2 with Cl_2 in CCl_4 [59]. Cp^*ZrCl_3 was prepared by treatment of Cp^*Li or $Cp^*MgCl{\cdot}THF$ with $ZrCl_4$. When ethereal solvents of small amounts of Lewis bases were present the Cp^*ZrCl_3 moiety was initially isolated as a Lewis acid-Lewis base adduct. Solvent free $(Cp^*ZrCl_3)_X$ was prepared by refluxing Cp^*Li and $ZrCl_4$ in toluene at 110° for 48 hr. Treatment of Cp^*ZrCl_3 with excess $LiBH_4$ in toluene gave $Cp^*Zr(BH_4)_3$ in high yield. Treatment of $Cp^*Zr(BH_4)_3$ with 8-10 equivalents of Me_3N in toluene produces **49** in 40% yield [20].



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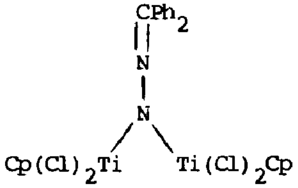
Treatment of $[CpTiCl_2]_X$ with diphenyldiazomethane gave **50**. Heating complex **50** in THF led to loss of $CpTiCl_3$ and formation of **51**. Treatment of $[CpTiCl_2]_X$ with azobenzene in THF gave complex **52** and $CpTiCl_3$ [60].



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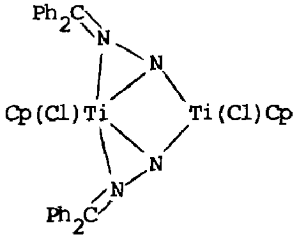

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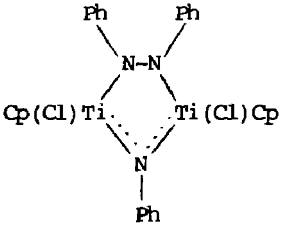


52

Treatment of $CpTiCl_3$ with PhOH and Et_3N gave $CpTi(OPh)_3$, which upon treatment with $CpTiCl_3$ gave $CpTiCl(OPh)_2$ [61].

$CpTiCl_3$ reacted with 1 or 2 equivalents of HL (HL = R1R2C=NNHCOPh, R1 = furyl, Ph, 4-$MeOC_6H_4$; R = H, Me, Ph; R_1R_2 = $(CH_2)_4$, $(CH_2)_5$) in refluxing CH_2Cl_2 to give $CpTiCl_2L$ or $CpTiClL_2$. Treatment of $CpTiCl_3$ with dibasic Schiff base derivatives HL' (HL' = RR'C=NNHCOPh, R = 2-HOC_6H_4, 4,3-$HO(MeO)C_6H_4$; R' = H, Me) in refluxing CH_2Cl_2 gave RTiClL' [62]. Treatment of $CpTiCl_3$, $CpTiCl_2(OMe)$, and $CpTiCl(OMe)_2$ with silylated Schiff bases, $(o\text{-}Me_3SiC_6H_4CH{=}NCH_2)_2$ (btsalne) and $o\text{-}C_6H_4(o\text{-}Me_3SiC_6H_4CH{=}NC)_2$ (btsalphen) gave CpTiCl(salen), CpTi(OMe)(salen), $Ti(OMe)_2$(salen), CpTiCl(salphen), CpTi(OMe)(salphen), and $Ti(OMe)_2$(salphen) respectively. Treatment of CpTiCl(salen) with MeSH, Me_3SiNMe_2, Me_3SiN_3 and Tl(acac) gave CpTi(salen)X (X = SMe, NMe_2, N_3, acac). The reaction of CpTi(salen)$[NMe_2]$ with $Sn(Ph)_3H$ gave CpTi(salen)$[(Sn(Ph)_3]$ [63].

The crystal structure of the seven-coordinate $CpTi(NO_3)_3$ indicates an approximately pentagonal-bipyramidal geometry with bidentate NO_3 groups, and the Cp group occupying one axial position [64].

Extended Hückel molecular orbital calculations were performed on $Cp_6Ti_6(\mu_3\text{-}O)_8$ in order to explain its structure and magnetic properties [65].

The standard enthalpies of formation $Cp_2Ti(Ph)_2$ and $Cp_2Ti[(C_5H_4)FeCp]_2$ were determined to be 294. and 542. kJ/mol respectively by reaction-solution calorimetry at 298.15 K [66]. Negative chemical ionization (NCI) mass spectra with methane of titanocene and zirconocene complexes showed the complementarity and specificity of this technique to electron impact mass spectra. The NCI mass spectra show very little fragmentation. Some chlorinated titanocene complexes showed an ion-molecule attachment peaks corresponding to $[M + Cl]^-$ [67]. The electronic structures of Cp_2ZrX_2 (X = F, Cl, I), were studied by the extended Hückel molecular orbital method. The orbital energy levels of all 3 complexes were found to be similar. None of the molecular orbitals were composed chiefly of Zr d orbitals. The charge on the Zr atom was found to decrease in the order: F > Cl > I, consistent with the electronegativities [68]. The low energy photoelectron spectra of $Cp_2Ti(CO)_2$ and Cp_2TiX_2 (X = F, Cl, Br) have been studied using by CNDO/INDO semiempirical molecular orbital calculations. The electronic structure of Cp_2TiX_2 could be rationalized, and fit well the with experimentally determined photoelectron spectral data in the literature [69].

The detailed preparation of Cp_2TiCl by the reaction of two equivalents of CpTl with $TiCl_3$ has been reported [70].

The structures of $(EtCp)_2MCl_2$ (M = Ti, Zr, Hf) were determined by x-ray diffraction [71]. $[Me_3ECp]_2MX_2$ (E = C, Si, Ge; M = Ti, Zr, Hf; X = F, Cl, Br, I, SCN) were prepared by known methods and their properties and spectral data reported [72]. $CpCp^*ZrCl_2$ was prepared in high yield by refluxing CpNa with $(Cp^*ZrCl_3)_x$ in toluene for 2 days. $(1\text{-}MeInd)Cp^*ZrCl_2$ and $(1,2,3\text{-}Me_3Cp)Cp^*ZrCl_2$ were prepared in good yield in an analagous manner. The treatment of $(1,2,3\text{-}Me_3Cp)Cp^*ZrCl_2$ and $(1\text{-}MeInd)Cp^*ZrCl_2$ with 2 equivalents of MeMgBr in ether gave the corresponding dimethyl complexes in high yield [20].

The reactions of $Li[Ph_2P(CH_2)_n(C_5H_4)]$ (n = 0, 2) with MCl_4 (M = Ti, Zr) and $CpTiCl_3$ gave $[Cp(CH_2)_nPPh_2]_2MCl_2$, **53**, and $Cp[Cp(CH_2)_nPPh_2]TiCl_2$, **54**, respectively, in good yields. Reduction of these complexes under CO is described. New heterobimetallic complexes were prepared by the reactions of 53 and 54 with with $Mo(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$, and $(COD)Mo(CO)_4$. Reduction of $[Cp(Cp(CH_2)_nPPh_2)TiCl_2]Mo(CO)_5$ with Al under CO gave a new heterobimetallic coxplex containing a low-valent Ti. Treatment of $[Rh(\mu\text{-}Cl)(CO)(C_2H_4)]_2$ with 53 gave $\{RhCl(CO)[Cp(CH_2)_nPPh_2]_2MCl_2]\}x$, which the authors assumed to be a dimer with 53 serving as a bridging diphosphine ligand between the Rh atoms [73].

Ansa-metallocene $[Ind(CH_2)_2Ind]TiCl_2$, 55, was prepared by the treatment of $TiCl_4$ with $Li_2[Ind(CH_2)_2Ind]$. Reduction of 55 with Adam's catalyst in CH_2Cl_2 gave ethylenebis(4,5,6,7-tetrahydro-1-indenyl)$TiCl_2$, 56, in good yield. Treatment of 56 with (S)-(-)-1,1'-bi-2-naphthol lead to the isolation of ethylenebis(4,5,6,7-tetrahydro-(S)-1-indenyl)Ti((S)-1',1"-bi-2-naphtholate) 57 which could be cleaved to give pure (S,S)-55. The molecular structures of meso-56 and 57 were determined [74].

Polymer bound titanocene was prepared by treating poly(2,6-dimethyl-1,4-phenylene oxide) containing cyclopentadienyl ligands attached to the benzyl carbons, sequentially with methyllithium, $CpTiCl_3$, and n-BuLi. The resulting polymer bound titanocene catalyzed the hydrogenation of cyclohexene at a rate 10-70 times faster than homogeneous titanocene [75]. The reduction of Cp_2TiCl_2 and $(MeCp)_2TiCl_2$ with K naphthalide in THF at -80° produced highly reactive pyrophoric products [76].

$Cp_2Ti(PhN{=}C(Ph)C(Ph){=}NPh)$ was prepared by three different methods: by the treatment of Cp_2TiCl_2 with $Na_2[PhNC(Ph){=}C(Ph)NPh]$, photolysis of Cp_2TiPh_2 with $PhN{=}C(Ph)C(Ph){=}NPh$, or by treatment of $Cp_2Ti(CO)_2$ with $PhN{=}C(Ph)C(Ph){=}NPh$ [77].

$Cp_2M(OAr)_2$ (M = Ti, Zr, Hf) have been prepared by treating Cp_2MCl_2 with phenols in the presence of $NaNH_2$ or NaH [78-81]. Treatment of these aryloxy complexes with HX (X= Cl, Br, I) regenerated the corresponding metallocene-dihalides in high yield [78, 80, 81]. NMR and IR studies of these aryloxy complexes were carried out [80, 82]. The oxo bridged complexes $[Cp_2Zr(OR)]_2O$ were prepared by the treatment of $[Cp_2ZrCl]_2O$ with phenols in the presence of Et_3N [80]. The X-ray structure of $Cp_2Ti(O\text{-}2,4,6\text{-}Cl_3C_6H_2)_2$ was reported [83].

$Cp_2Ti(OXPh)Cl$ ($X = CH_2$, CH_2CH_2) were prepared by the treatment of Cp_2TiCl_2 with HOXPh in the presence of Et_3N [84]. Treatment of Cp_2MCl_2 ($M = Ti, Zr$) with and β naphthol or the corresponding Na salts in a 1:1 or 1:2 ratio produced $Cp_2MCl(ONap)$ and $Cp_2M(ONap)_2$ respectively [85]. Perfluoroalkyl and aryl titanocene derivatives $Cp_2Ti[OCH_2(CF_2CF_2)_nH]_2$ ($n = 1-4$) and $Cp_2Ti(XC_6F_5)_2$ ($X = O, S$) were prepared by the reaction of Cp_2TiCl_2 with the corresponding polyfluoroalkanols, C_6F_5OH, or C_6F_5SH. $Cp_2Ti(OCH_2CF_2CF_2H)_2$ exhibited high catalytic activity for the polymerization of acrylonitrile, methylmethacrylate, and styrene under photochemical conditions at room temperature and at 80-100° [86].

Sulfanilate, metanilate and o-toludinesulfonate derivatives of $Cp_2Ti(IV)$ and $(Ind)_2Ti(IV)$ were prepared by treating the corresponding metallocenedichlorides with the appropriate acids [87]. The reaction of Cp_2TiCl_2 with oxalic or maleic acid in water gave $Cp_2Ti(C_2O_4)$ and $Cp_2Ti(OOCCH{=}CHCOOH)_2$ [88].

The structures of $[(RCp)_2Zr(o\text{-}MeC_6H_4)]_2O$ ($R = H$, Me) were determined by x-ray diffraction [89].

An x-ray structure of $Cp_2TiCl\text{-}O\text{-}(Cp)TiCl\text{-}O\text{-}(Cp_2)TiCl$, prepared by the hydrolysis of Cp_2TiCl_2 at a pH greater than 3.5 or by treating Cp_2TiCl_2 with Ag_2O and H_2O in $CHCl_3$, has been reported [90].

The trinuclear hafnium complex $[Cp_2HfO]_3$, prepared from $HfOCl_2$ and NaC_5H_5, was found by x-ray crystallography not to be isostructural with its Zr analogue [91].

Treatment of $Cp^*_2TiCl_2$ with Li_2S_2 and S_8 gave $Cp^*_2Ti(S_3)$, which was characterized by X-ray diffraction, in moderate yield [92]. Treatment of RCCR ($R = CO_2Me$, CF_3) with $(RCp)_2TiX_5$ ($R = H$, Me, $X = S$, Se) gave $(RCp)_2TiX_2C_2R_2$, which was characterized by x-ray diffracation [93]. Reaction of $(RCp)_2Ti(X_5)$, ($R = H$, Me; $X = S$, Se) with $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ gave $[Ir(Ph_2PCH_2CH_2PPh_2)_2X_2]Cl$ and $(RCp)_4Ti_2(S_4)$ when $R = Me$; $X = S$ [94].

The reaction of Ph_2X_2 ($X = S$, Se) with $(RCp)_2ZrMe_2$ ($R = H$, Me_3C) gave $(RCp)_2Zr(XPh)Me$ and PhXMe, which upon UV irradiation produced $(RCp)_2Zr(XPh)_2$.

This complex was also prepared by the irradiation of a mixture of $(RCp)_2ZrPh_2$ and Ph_2X_2 [95].

Proton spin lattice relaxation time measurements were used to determine the barriers to rotation of the cyclopentadienyl rings in $CpTiCl_3$ and Cp_2TiS_5 [96].

$Cp_2M(S_2CNRR')Cl$ and $CpM(S_2CNRR')_3$ (M = Ti, Zr; R = H, R' = cyclopentyl, cycloheptyl; R = Et, R' = m-tolyl) were prepared by the reaction of Cp_2MCl_2 with NaS_2CNRR' in refluxing CH_2Cl_2 [97]. Treatment of $Cp(MeCp)TiCl_2$ and $Cp(Ind)TiCl_2$ with three equivalents of sodium dithiocarbamates, $Na(S_2CNRR')$, (R = R' = Me, Et, Me_2CH; R = Me, R' = Ph) gave $(MeCp)Ti(S_2CNRR')_3$ and $CpTi(S_2CNRR')_3$ respectively [98]. $Cp_2M\{S_2CNHP(S)(OEt)_2\}Cl$, $(MeCp)_2M\{S_2CNHP(S)(OEt)_2\}Cl$, and $Ind_2M\{S_2CNHP(S)(OEt)_2\}Cl$ (M = Ti, Zr) have been prepared by the treatment of the corresponding metallocenedihalide with $K(EtO)_2P(S)NHCS_2$ in refluxing CH_2Cl_2 [99]. Treatment of $Cp(\eta^5\text{-pyrrolyl})MCl_2$, $Ind(\eta^5\text{-pyrrolyl})MCl_2$ (M = Ti, Zr), and $Cp(Ind)TiCl_2$ with 8-hydroxyquinoline (oxine) gave [(R)(R')ML]+ Cl- (R = Cp, Ind, R' = $\eta^5\text{-}C_4H_4N$; R = Cp, R' = Ind; L = conjugate base of oxine). $[(R)(R')TiL]^+ Cl^-$, upon treatment with dithiocarbamate anions in water, gave $[(R)(R')TiL]^+ X^-$ (X = Me_2NCS_2-, Et_2NCS_2-, $(Me_2CH)_2NCS_2$-) [100-102]. Refluxing Cp_2MCl_2 (M = Ti, Zr) in THF with 2-mercaptoquinazol-4-ones (HL) gave Cp_2MLCl and Cp_2ML_2 (M = Ti, Zr; R = Me, Ph, o-MeC_6H_4), where L act as an N, S, bidentate chelating agent [103].

The reaction of HNO_3 with Cp_2ZrR_2, $CpZrR_3$, Cp_2ZrRX and $CpZrR_2X$ (R = $(MeC(O))_2CH$, $(C_6H_5CH_2)_2CH$; X = Cl, Br) at low temperature was examined [104].

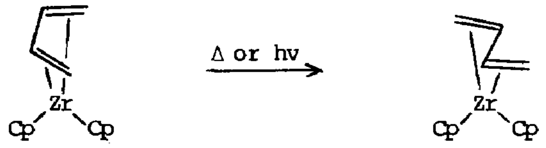
Cp_3HfX (X = H, D) was prepared by the treatment of Cp_4Hf with $LiAlH_4$ and $LiAlD_4$ respectively. The IR and Raman spectra of Cp_3MX (M = Zr, Hf; X = H, D) was also studied [105].

OTHER π-BONDED COMPLEXES

The reaction of $Cp_2Ti(\eta^3\text{-}CH_2CH{=}CHR)$, 58, (R = H, Me) with CO_2, PhNCO, MeCN Me_2CO, or PhCH=NPh, gave insertion products via σ-allyl migration. Treatment of **58** with RNC (R = 2,6-xylyl) led to the normal insertion product.

Carbonylation of **58** gave $Cp_2Ti(CO)_2$ and $(CH_2{=}CHCH_2)_3COH$. Reaction of **58** with CS_2 or C_2Ph_2 gave $CP_2Ti(\eta^2{-}CS_2)$ and $Cp_2TiC(Ph){=}C(Ph)C(Ph){=}C(Ph)$ respectively [106].

Reduction of Cp_2ZrCl_2 with Li, or photochemically induced reductive elimination of biphenyl from Cp_2ZrPh_2 in the presence of acyclic conjugated dienes, was found to produce (s-trans-η^4-diene)zirconocenes, **59**, in good yield. Complex **59a** equilibrates thermally or photochemically with the corresponding (s-cis-η^4-diene)zirconocene **59b**. Both the s-cis and s-trans complexes were characterized by NMR spectroscopy, s-trans-η^4-butadienezirconocene was chacacterized by X-ray diffraction[107]. Treatment of Cp_2ZrCl_2 with $[MgCH_2CR{=}CRCH_2]_n$ (R = H, Me), gave the corresponding 1,3-diene zirconocene complexes which were reported to be fluxional based on ^1H NMR. These complexes exhibited the $Cp_2Zr[s\text{-}cis\text{-}\eta^4{-}CH_2{=}CR{-}CR{=}CH_2]$ structure below -40°. In contrast to this, treatment of Cp_2HfCl_2 with enediylmagnesium, $[MgCH_2CR{=}CRCH_2]_n$ (R = H, Me), produces the metallacyclopentene complexes, $Cp_2Hf[CH_2CR{=}CRCH_2]$. Treatment of Cp_2ZrCl_2 and Cp_2HfCl_2 with $[MgCH(Ph)CH{=}CHCH(Ph)]_n$ produces $Cp_2Zr[s\text{-}trans\text{-}\eta^4{-}CH(Ph){=}CH{-}CH{=}CH(Ph)]$ and $Cp_2Hf[s\text{-}cis\text{-}\eta^4{-}CH(Ph){=}CH{-}CH{=}CH(Ph)]$ respectively [108]. An X-ray crystallographic study on $Cp_2Zr[CH(Ph){=}CH{-}CH{=}CH(Ph)]$ confirmed the s-trans-η^4 structure determined by NMR [109]. An ^1H NMR study of the fluxional behavior of $Cp_2M(\eta^4{-}C_4H_6)$ (M= Zr, Hf) has also been reported [110].



59a 59b

Treatment of Cp_2Zr(s-cis-1,3 diene) with CO followed by hydrolysis produced cyclopentenones [111]. The reaction of $Cp_2M(\eta^4{-}C_4H_6)$ (M = Zr, Hf) with C_2H_4 gives either $Cp_2\overline{MCH_2CH_2CH_2CH_2}$ (M = Zr, Hf) or Cp_2M(1-3:6-η-hexenylene) depending on the reaction conditions [112]. The ^1H NMR spectra of [(butadiene)(cyclooctatetraene)]M (M = Ti, Zr, Hf) complexes were recorded at various temperatures and an analysis of the spectra suggested an s-cis-η^4-butadiene conformation in these complexes [110].

Treatment of $TiBr_4$ with 1-t-butyl-2-methyl-1,2-azaborolinyllithium gives bis(1-t-Butyl-2-methyl-1,2-azaborolinyl)$TiBr_2$ in 14 % yield, which was shown by x-ray crystallography to have a bent sandwich structure [113].

Photochemically induced reductive elimination of biphenyl from Cp_2ZrPh_2 in the presence of 2,3,5,6,-tetrakis(methylene)bicyclo[2.2.2]octane gave the bis olefin complex Cp_2Zr[2,9:6,12-η-2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]-octane], which undergoes isomerization to the corresponding conjugated diene complex upon heating [114].

The reaction of $TiCl_2$, prepared in situ, with 2,4-dimethylpentadienylpotassium leads to the bis(pentadienyl)titanium sandwich complex, Ti(2,4-$C_7H_{11})_2$, which upon treatment with CO gave a 16 electron monocarbonyl complex [115].

An x-ray structure analysis of η^6-$C_6H_6Ti(Cl_2AlCl_2)_2$ confirmed that the ring is η^6 analogous to the known hexamethylbenzene analogue. The distance between Ti and the ring center is 2.07 Å and the mean Ti-C-(ring) distance is 2.49 Å [116]. $(C_3H_5Ph)_2Ti$ and $[C_3H_5(CH_2)_3Ph]_2Ti$ were were prepared in 25-40% yield by metal atom condensation with the corresponding ligand [117].

$Cp(\eta^7$-$C_7H_6PPh_2)Ti$, **60**, was prepared by treatment of $Cp(\eta^7$-$C_7H_7)Ti$ with n-BuLi in ether followed by reaction with $ClPPh_2$. Complex **60** displaces one carbonyl from $Ni(CO)_4$, $Fe(CO)_5$, and $Mo(CO)_6$ to give the corresponding heterobimetallic complexes $Cp(\eta^7$-$C_7H_6PPh_2)Ti[M(CO)_n]$. An x-ray structure determination of $Cp(\eta^7$-$C_7H_6PPh_2)Ti[Mo(CO)_5]$ was carried out [118].

Single crystal x-ray diffraction studies have been carried out on (η^8-cyclooctatetraenyl)(η^{3-}allyl)(t-butoxy)zirconium and (η^8-cyclooctatetraenyl)-(η^3,$\eta^{3'}$-deca-2,7-diene-4,9-diyl)zirconium [119,120].

APPLICATIONS IN SYNTHESIS AND CATALYSIS

Allyltitanium ate complexes were found to react selectively with aldehydes and ketones [121]. Trans-$RCH{=}CHCH_2Ti(OPh)_3$ (R = Me, $CHMe_2$, Bu) adds to ketones to give high yields of tertiary homoallylic alcohols which are diastereoisomerically enriched up to 98% [122]. The stereospecific addition of

$MeCH=CHCH_2Ti(OPh)_3$ to RCHO (R = $CHMe_2$, $CHEt_2$, CMe_3, $PhCH_2CH_2$, Ph_2CH, Ph, p-tolyl, p-FC_6H_4, p-$MeOC_6H_4$, p-$O_2NC_6H_4$, p-NCC_6H_4) followed by hydrolysis gave β-methylhomoallylic alcohols in 56-94 % yield with 77-99% diastereoselectivity [123]. The condensation of (E)-$MeCH=CHCH[Ti(NEt_2)_3]O_2CN(CHMe_2)_2$ with RCHO gave 97-99 % (Z)-threo-$RCH(OH)CHMeCH=CHO_2CN(CHMe_2)_2$ (R = Me_3C, Me, Me_2CH, $Me_2C=CH$) [124]. The reaction of $Cp_2Ti(\eta^3\text{-}CH_2=CHCH_2SiMe_3)$ with aldehydes gave excellent yields of (+-)-(R,S)-3-(trimethylsilyl)-4-hydroxy-1-alkenes, which were deoxysilylated to give either (E)- or (Z)-1,3-dienes [125].

The reaction of benzil with $MeTi(OR)_3$ (R = Et, $CHMe_2$), $Me_2Ti(OCHMe_2)_2$, or Me_4Ti gave threo- and erythro-meso-PhCMe(OH)CMe(OH)Ph with the former predominant, whereas reaction of benzil with $MeZr(OCHMe_2)_3$, MeLi, or MeMgBr gave mostly the latter isomer. PhC(O)CH(OH)Ph reacted with $MeTi(OCHMe_2)_3$ or Me_4Ti to give only erythro-PhCMe(OH)CH(OH)Ph [126].

Schwartz's reagent, $Cp_2Ti(H)Cl$, was reported to be a good reducing agent for cyclic ketones. However, it is a poor reducing agent for aromatic ketones [127].

$Cp_2TiSiMe_2Ph$, **61**, was prepared by the reaction of Cp_2TiCl_2 with two equivalents of $PhMe_2SiLi$ or by the reaction of Cp_2TiCl with one equivalent of $PhMe_2SiLi$. Treatment of **61** with acetylenes and 1,3-dienes lead to highly regio- and stereoselective silyltitanation [128]. Cp_2ZrX_2 (X = Cl,I) in the presence of R_3Al has been shown to be effective for the carboalumination of alkynes to produce stereospecifically vinylalanes which were then used for selective carbon-carbon bond formation [129-131].

The rate of catalytic isomerization of alpha-olefins by Cp_2TiH_2AlXX' (X = H, Cl, Br) and $[(CH_2)_nC_5H_4]_2TiAlH_4$ (n = 1-3) were studied [132]. $Cp_2Ti(III)$ complexes catalytically isomerized C8-C12 cycloalkadienes to an equilibrium mixture of isomers [133].

The stereochemistry of the reduction of cis- and trans-4-methylcyclohexyl-1-d bromide with 95:5 $Me_2CHMgBr\text{-}Cp_2TiCl_2$ and of the unlabeled bromides with $(CD_3)_2CHMgBr\text{-}Cp_2TiCl_2$ was determined by ^2H NMR of the resulting cis- and trans-4-methylcyclohexane-1-d. Complete stereoequilibration was found to occur. Radical involvement was confirmed by cyclization of 6-bromo-1-hexene and 6-bromo-1-heptene during reduction [134].

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