

TITANIUM, ZIRCONIUM AND HAFNIUM
ANNUAL SURVEY COVERING THE YEAR 1980**

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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 abbreviations Cp (for $\eta^5\text{-C}_5\text{H}_5$) and Cp' (for any ring-substituted cyclopentadienyl group) are used throughout. Dates in parentheses refer to the survey for that year.

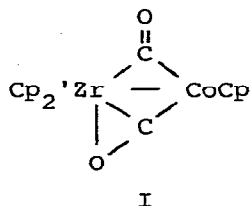
Russian language reviews on "Biorganometallic derivatives of titanium and zirconium" (1) and "Spectrometric determination of zirconium in organozirconium compounds" (2) have been cited in Chemical Abstracts.

CARBONYL AND DINITROGEN COMPLEXES

The crystal structure of $\text{Cp}_2\text{Zr}(\text{CO})_2$ has been determined; it is isomorphous to the Hf analog (1979), with $\text{Zr-C}(\text{O}) = 2.187 \text{ \AA}$ and a CZrC angle of 89.2° (3). The CO stretching frequency of $(\text{C}_5\text{Me}_5)_2\text{ZrH}_2(\text{CO})$, stable only at low temperature (1976) was observed at 2044 cm^{-1} (the Hf analog is at 2036 cm^{-1}). While these are relatively high values, considering that these are formally d^0 complexes one might have expected even less back donation to CO; interaction between M-H bonding orbitals and CO π^* was proposed (4). $(\text{C}_5\text{Me}_5)_2\text{ZrH}_2$ reacts with $\text{CpCo}(\text{CO})_2$ to give a bimetallic compound with two kinds of bridging CO (I); $\text{Co-Zr} = 2.926 \text{ \AA}$ (5).

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** Previous survey see J. Organometal. Chem., 196 (1980) 37-59.



Addition of CO to $\text{Ti}(\text{CH}_2\text{Ph})_4$ at -50° gives an apparent adduct, $\text{Ti}(\text{CH}_2\text{Ph})_2(\text{CO})_2$, which on standing affords yellow crystals characterized (analysis, IR hydrolysis to benzene and benzaldehyde) as $\text{Ti}(\text{CH}_2\text{Ph})_2(\text{COCH}_2\text{Ph})_2$. At -20° this loses CO to revert to the starting tetrabenzyl compound (6). Further studies on CO insertion reactions will be reported in the following section.

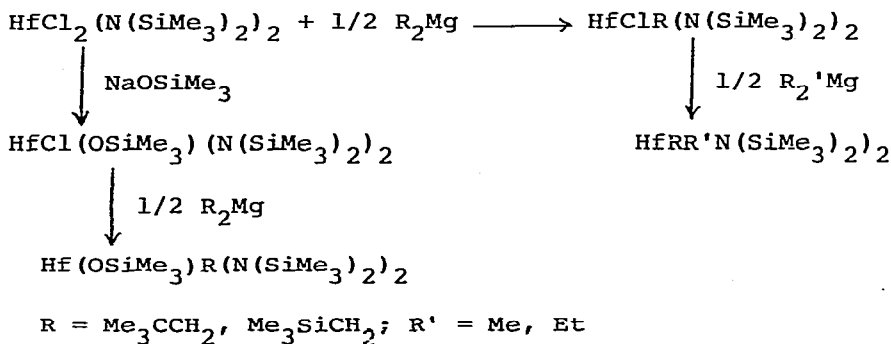
A patent covering $\text{Cp}_2'\text{ZrR}$, $\text{Cp}_2'\text{ZrR}(\text{N}_2)$ and $(\text{Cp}_2'\text{ZrR})_2\text{N}_2$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) (1978, 1979) has appeared; protonolysis of the dinitrogen complexes gives some hydrazine and ammonia (7). Cp_2ZrHCl reacts with the group VI metal dinitrogen complexes $\text{M}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$ at 50° to give ammonia (19% for Mo, 44% for W) (8).

ALKYL AND RELATED COMPLEXES

A review on methyl complexes includes a brief discussion of the group IV MMe_4 species (9). The complexes $\text{M}(\text{l-adamantylmethyl})_4$ were prepared for Ti and Zr; the former decomposes above 10° while the latter is much more stable (10). The tetrakis(1-camphenyl) complexes of all three metals were made and function as polymerization catalysts (11). Thermal decomposition of $\text{Ti}(\text{C}_6\text{F}_5)_4$ has been studied (12).

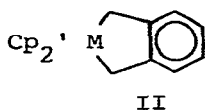
From TiX_4 and $\text{Zn}(\text{mesityl})_2$, the monomesityls $\text{TiX}_3(\text{Mes})$ ($\text{X} = \text{Cl}, \text{Br}$) were obtained; they are fairly thermally stable, but decompose in THF to give Mesh and Mes_2 (13). Electrolysis of a metal anode in the presence of an alkyl halide and a ligand has proven to be a useful route to complexes of type $\text{MX}_2\text{R}_2\text{L}$, where $\text{R} = \text{C}_2\text{H}_5, \text{PhCH}_2$ or Ph ; $\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{bipy}$ or 2 MeCN . Ligand-free compounds MBr_2Ph_2 and MIPh_3 were also obtained for Ti and Zr. All yields were about 50%, based on dissolved metal (14). The reaction of TiCl_4 with AlClBu_2^i gives NMR changes which were proposed to signal formation of TiCl_3Bu^i , although no definite characterization was available (15). Either Cp_2ZrPh_2 plus LiMe , or Cp_2ZrMe_2 plus LiPh , gives a crystalline product characterized (Zr analysis and reactions) as $\text{ZrMePh}(\text{Et}_2\text{O})_3$ (16).

Mixed alkyl (disilylamido)hafnium complexes can be prepared if one alkyl group is large:



The bis(trimethylsilylmethyl) complex was previously reported (1979); the bis(neopentyl) complex could not be made (17). Addition of Grignard reagents to TiF(tetraphenylporphyrin) gives new EPR signals assigned to TiR(TPP) (R = Ph, o-tolyl, PhCH₂) (18).

The o-xyllylidene-di-Grignard reagent, o-C₆H₄(CH₂MgCl)₂, was used to prepare the benzometallacyclopentenes II.

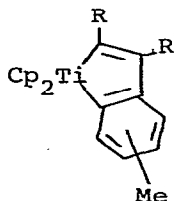


The crystal structure (Cp' = Cp, M = Zr) shows a normal Cp₂MX₂ structure (19). The 2,5-bis(trimethylsilyl) derivatives were also prepared; the appearance of two Cp signals in the NMR suggests a meso configuration (20). Reduction of complexes II with sodium naphthalene gives EPR signals which suggest structure III rather than IV (21).



A series of metal aryl complexes Cp₂'MAr₂, where Cp' = C₅H₅ or C₅H₄Me, and Ar = Ph, m-tolyl, p-tolyl, p-anisyl, p-chlorophenyl and 3,4-dimethylphenyl were prepared, as well as (Cp₂HfAr)₂O (22). As part of a study on methyl group exchange, it was determined that exchange takes place between Cp₂ZrMe₂ and CpCo(CD₃)₂(PPh₃) (23).

Thermolysis of Cp₂Ti(m- or p-tolyl)₂ in the presence of RC≡CR (R = Me, Ph, CF₃) gives V; the distribution of the methyl positions is consistent with an aryne intermediate (1977) (24).



V

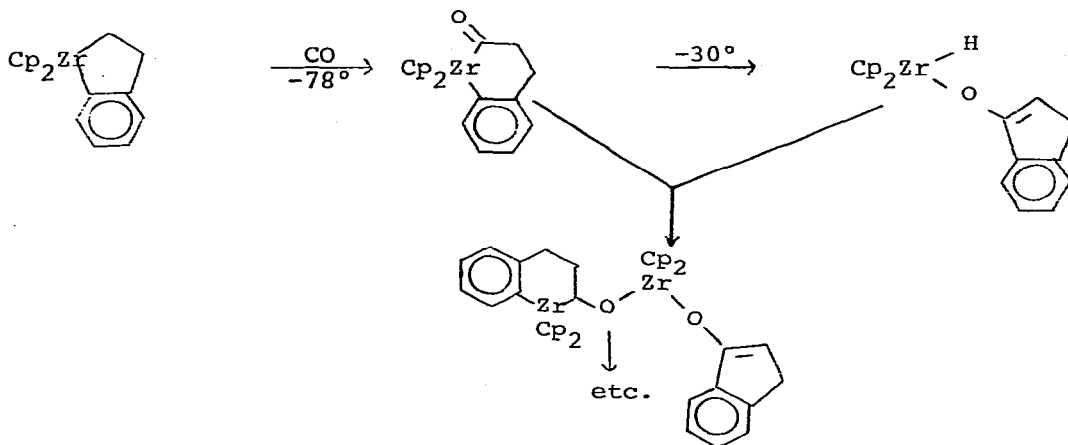
Reaction of $\text{CF}_3\text{C}\equiv\text{CCF}_3$ with $\text{Cp}_2\text{Ti}(\text{CO})_2$ gives an unexpected product, $\{\text{Cp}_2\text{Ti}(\text{C}(\text{CF}_3)=\text{CH}(\text{CF}_3))\}_2\text{O}$, characterized crystallographically. Presumably the H and O come from adventitious water (25).

The methyl compound Cp_2TiMe has not been previously made, although analogs with other alkyl groups are known. Addition of LiMe to Cp_2TiCl at -78° gives a green solution and an EPR suggesting $\text{Cp}_2\text{TiMe}(\text{Et}_2\text{O})$; it decomposes to methane and a purple solution even at -50° . The green solution reacts with isonitriles to give $\text{Cp}_2\text{Ti}(\text{MeC}=\text{NR})$ and with N_2 to give a dark blue color typical of related dinitrogen complexes (26). The divalent zirconium compound Cp_2ZrL_2 ($\text{L}=\text{PMe}_2\text{Ph}$, PMePh_2) oxidatively adds alkyl halides to form Cp_2ZrXR and/or Cp_2ZrX_2 ; primary alkyl groups favor the former product, tertiary the latter. Several lines of evidence indicate these proceed via a free-radical mechanism (as has been observed for many later transition metal systems), including rearrangement of alkyl groups and observation of CIDNP (27).

Zirconium acyls can be reduced by metal hydrides; the compound $\text{Cp}_2\text{ClZr-O-CHR-ZrClCp}_2$, obtained from Cp_2ZrHCl and $\text{Cp}_2\text{ZrCl}(\text{COR})$ (1978), shows temperature dependent NMR behavior: at low temperature four Cp signals are observed, while on warming these coalesce to two — but it appears that the non-equivalence of the two diastereotopic Cp's on each Zr is maintained, while the non-equivalence of the two Zr centers is averaged. A stereospecific exchange (inversion at C, retention at Zr) via a sort of $\mu-(\eta^2)_2$ -aldehyde-bridged intermediate was proposed (28). Reaction of $\text{Cp}_2\text{ZrMe}(\text{COMe})$ with Cp_2MOH_2 affords reduction of the acetyl group to an ethoxide: the product is $\text{Cp}_2\text{ZrMe}(\text{OEt})$. The tungsten analog gives a metastable product which is a likely intermediate: $\text{Cp}_2\text{MeZr-O-CHMe-WHCp}_2$; while with Cp_2ReH , the related $\text{Cp}_2\text{MeZr-O-CHMe-ReCp}_2$ can be isolated (29).

Several studies on insertion reactions have been described. The observation of a kinetically favored acyl isomer on carbonylation of Cp_2ZrPh_2 at -78° , and its isomerization to the thermodynamically preferred product (1978), has been extended to a variety of aryl complexes Cp_2ZrXAr . For Cp_2ZrMe_2 , the kinetic product can only be observed below -125° (30)! Carbonylation of zirconaindane

VI (1979) at room temperature and above gives a complex mixture of organometallic products and no organic product (in contrast to related Ti reactions); on hydrolysis 1-indanone and several other products are obtained. By following the reaction at low temperatures, evidence was obtained for a sequence of transformations, part of which is shown below (31).



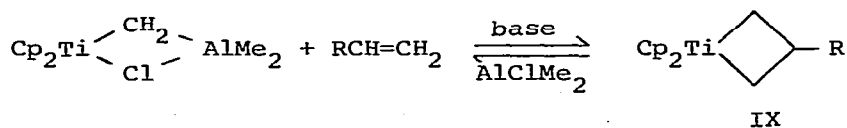
In the reaction $\text{Cp}_2\text{ZrCl}(\text{COMe}) + \text{Cp}_2\text{ZrMe}_2 \rightleftharpoons \text{Cp}_2\text{ZrClMe} + \text{Cp}_2\text{ZrMe}(\text{COMe})$, the equilibrium constant is 20, suggesting that the alkyl is favored relative to the acyl by the presence of a π -donor ligand such as Cl. In agreement, $\text{Cp}_2\text{ZrMe}(\text{OEt})$ will not even undergo CO insertion (32). The mixed aryl-alkyl $\text{Cp}_2\text{TiMe}(\text{C}_6\text{F}_5)$ reacts with CO to give $\text{Cp}_2\text{Ti}(\text{C}_6\text{F}_5)(\text{COMe})$, but with RNC to give $\text{Cp}_2\text{TiMe}(\text{RN}=\text{C}(\text{C}_6\text{F}_5))$, as does the phenyl analog (33). NO insertions of alkyls MCl_2R_2 and MR_4 ($\text{R}=\text{CH}_2\text{SiMe}_3$) give the usual type of cyclic products, $\text{MCl}_2(\text{ON}(\text{R})\text{NO})_2$ and $\text{M}(\text{ON}(\text{R})\text{NO})_4$, whereas with $\text{Cp}_2\text{TiR}'$ ($\text{R}' = \text{Ph}$ or PhCH_2), a product formulated as $\text{Cp}_3\text{Ti}_3\text{O}_4(\text{NO})$ is obtained (34).

Two types of bimetallic compound were reported: reaction of Cp_2TiCl_2 with cyantryl lithium gives $\text{Cp}_2\text{Ti}((\mu\text{-}\eta^1; \eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3)_2$; its crystal structure resembles that of Cp_4Ti (35). $\text{LiCH}_2\text{PPh}_2$ was used to prepare $\text{Cp}_2\text{ZrCl}(\text{CH}_2\text{PPh}_2)$ (VII) which acts as a ligand (through P) towards $\text{Cr}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$ fragments. The crystal structure of VII is normal; it is reduced by Na/Hg to a product with a large P coupling in the EPR, suggesting ($\eta^2\text{-CH}_2\text{PPh}_2$) bonding (36).

Reduction of TiCl_4 by Mg in THF gives substantial amounts of hydrocarbons (up to C_5 , and up to 63% yield following hydrolysis); formation of a metallacyclopentane was proposed (37).

ALKYLIDENE AND YLIDE COMPLEXES

Further work has been reported on $\text{Cp}_2\text{Ti}(\overline{\text{CH}_2\text{AlClMe}_2})$ (VIII) (1978, 1979); the crystal structure of the metallocyclobutene formed with $\text{PhC}\equiv\text{CPh}$ (1979) has been determined, and shows a planar ring with $\text{C}-\text{C} = 1.475$, $\text{C}=\text{C} = 1.344\text{\AA}$; hydrolysis gives methylstilbene (38). In the presence of a base to remove the AlClMe_2 group (preferably a vinylpyridine-styrene copolymer to facilitate separation) olefins give analogous reactions to form metallacyclobutanes:

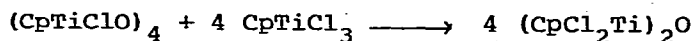
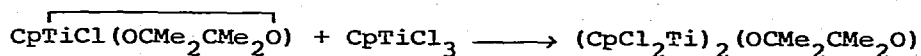


Thermolysis of IX at 85° ($\text{R}=\text{Pr}^i$, Bu^t) gives mostly $\text{RHC}=\text{CH}_2$ and methane; some ethane, RCH_2Me and RCHMe_2 are also formed (39). VIII is a useful methylenation reagent; e.g. esters (including conjugated unsaturated esters) can be converted to vinyl ethers in 80-97% yields (40).

Addition of Ph_3PCH_2 to $\text{Cp}_2\text{Zr}(\text{PMePh}_2)_2$ gives $\text{Cp}_2\text{Zr}(\text{CH}_2)(\text{PMePh}_2)_2$, which was not isolated but convincingly identified by NMR; it decomposes in solution over ca. 1 hr (41). In contrast, $\text{Cp}_2\text{Zr}(\text{dmpe})$ plus Me_3PCH_2 gives $\text{Cp}_2\text{ZrH}((\text{CH}_2)_2\text{PMe}_2)$ (also obtained from $\text{Cp}_2\text{ZrHR} + \text{Me}_3\text{PCH}_2$) which shows non-equivalent CH_2 groups - the only asymmetric $\text{R}_2\text{P}(\text{CH}_2)_2$ complex known. Reaction with methyl chloride gives $\text{Cp}_2\text{ZrCl}((\text{CH}_2)_2\text{PMe}_2)$ which at 50° rearranges to $\text{Cp}_2\text{ZrCl}(\text{CHPMe}_3)$ (42). Reaction of Cp_2MCl_2 ($\text{M}=\text{Zr}, \text{Hf}$) with Ph_3PCH_2 affords $\text{Cp}_2\text{MCl}(\text{CHPPH}_3)$; the crystal structure of the Zr compound shows a short Zr-C distance, 2.152 Å (43).

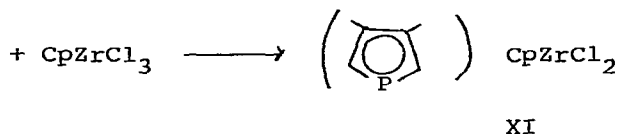
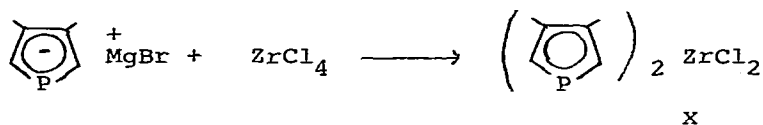
CYCLOPENTADIENYL COMPLEXES

ZDO-type MO calculations on first-row metallocenes include hypothetical Cp_2Ti (44). In attempting to generate the $[\text{Cp}_2\text{Ti}]^{2+}$ ion in the absence of a good coordinating anion, Cp_2TiCl_2 was treated with AgClO_4 and with $\text{AgOSO}_2\text{CF}_3$; but the first gave $[\text{Cp}_2\text{Ti}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (from trace water present) (45) and the second gave covalent $\text{Cp}_2\text{Ti}(\text{OSO}_2\text{CF}_3)_2$ (46); both have normal Cp_2MX_2 geometries. The role of π -donation in cyclopentadienyl complexes was examined: the following reactions both go to completion:

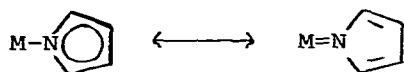


suggesting a tendency to distribute good π -donor ligands over as many metal centers as possible (32). The crystal structure of $(\text{CpCl}_2\text{Ti})_2(\text{OCMe}_2\text{CMe}_2\text{O})$ shows an exceptionally short Ti-O distance (1.750 Å) and obtuse Ti-O-C angle (166.2°), indicating particularly strong Ti-O π bonding in this substantially unsaturated compound, compared to $\text{Cp}_2\text{TiCl}(\text{OEt})$ whose structure shows more typical parameters (47).

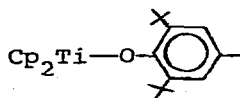
Two reports on heterocycle complexes appeared: formation of the phosphacyclopentadienyl complexes X and XI (48).



and the pyrrolyl complexes $\text{Cp}_2\text{M}(\eta^1\text{-NC}_4\text{H}_4)_2$ (M=Ti,Zr). The crystal structures of the latter show that M lies nearly in the plane of the pyrrolyl ring (in contrast to $\eta^1\text{-Cp}$ complexes), suggesting the following bonding picture (M-N distances are short) (49):

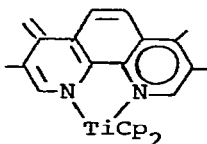


Condensation of sodium vapor into a slurry of Cp_2MCl_2 , $\text{P}(\text{OMe})_3$ and THF at -100° affords $\text{Cp}_2\text{M}(\text{P}(\text{OMe}_3))_2$; this compound was not attainable by standard "wet chemical" reduction methods (50). Cp_2TiCl_2 reacts with $\text{Ni}(\text{COD})_2$ and pyridine to give $\text{Cp}_2\text{TiCl}(\text{py})$ (51); although the zerovalent Ni complex is presumably acting as reducing agent, even Me_3N can reduce Cp_2TiCl_2 to Cp_2TiCl (52)! The latter reacts with a substituted phenoxide to give XII, whose crystal structure is normal; the large Ti-O-C angle (142°) is probably due to steric factors (53).



XII

EPR signals for Cp_2Ti -(substituted phenanthroline) complexes indicate the presence of low-lying triplet states, as previously found for bipy complexes (1979); from 3,4,7,8-tetramethylphenanthroline the product obtained instead is (54):



Electrochemistry on Cp_2TiX_2 species show a reversible one-electron reduction (in most cases followed by irreversible reduction waves); bulk electrolysis gives $[\text{Cp}_2\text{TiX}_2]^-$ for $\text{X} = \text{Cl}$ or Br , but CpTiX_2 for $\text{X} =$ alkoxide or alkyl (55, 56). Cp_2ZrCl_2 also undergoes reversible one-electron reduction to $[\text{Cp}_2\text{ZrCl}_2]^-$ (56).

Several studies deal with complexes with group IVa-group IVb metal bonds. Cp_2TiCl_2 plus $\text{Al}(\text{SiMe}_3)_3$ gives $\text{Cp}_2\text{TiCl}(\text{SiMe}_3)$, whose crystal structure is disordered but basically normal, with $\text{Ti-Si} = 2.67 \text{ \AA}$ (57). Similarly, Cp_2ZrCl_2 plus $\text{Hg}(\text{SiMe}_3)_2$ gives a mixture of $\text{Cp}_2\text{ZrCl}(\text{SiMe}_3)$ and $\text{Cp}_2\text{Zr}(\text{SiMe}_3)_2$ (58). Reaction of $\text{Cp}_2\text{Ti}(\text{CO})_2$ with SiHCl_3 gives a mixture of products, suggested to include (by analysis only) $\text{Cp}_2\text{TiH}(\text{SiCl}_3)$ and $\text{Cp}_2\text{TiH}(\text{SiCl}_3)(\text{CO})$ (59). $\text{Cp}_2\text{TiCl}(\text{GeEt}_3)$ decomposes at 400° to a Ti/Ge film and organo-germanium compounds (60). The polysilane anion $[\text{Si}_4\text{Ph}_8]^{2-}$ reacts with Cp_2TiCl_2 to give a pentametalacycle, $\text{Cp}_2\text{Ti}(\text{SiPh}_2)_4$; it shows a quasi-reversible reduction at -1.54 V by cyclic voltammetry (61).

In further work on bis(cyclopentadienyl) systems with chirality elements, the reaction of a single diastereomer of $\text{CpCp}'\text{TiCl}(\text{OAr})$ with NCS^- gave two diastereomers of product $\text{CpCp}'\text{Ti}(\text{NCS})(\text{OAr})$. Although this substitution is not stereospecific, when the latter compound was separated and one isomer treated with HBr , only one isomer of $\text{CpCp}'\text{TiBr}(\text{NCS})$ was produced, apparently with retention of configuration (62). Other compounds prepared include $\text{CpCp}'\text{TiI}_2$, $\text{CpCp}'\text{Ti}(\text{NCO})_2$, $\text{CpCp}'\text{Ti}(\text{NCO})(\text{OAr})$ and $\text{CpCp}'\text{TiBr}(\text{NCO})$ (63).

Compounds $[\text{Cp}_2\text{Ti}(\text{acac})]^+$ and $[(\text{MeCp})_2\text{Ti}(\text{acac})]^+$ were isolated with a variety of counterions (64, 65). Carboxylate complexes $(\text{MeCp})_2\text{Ti}(\text{O}_2\text{CR})_2$ (66) and monothiocarboxylates $\text{Cp}_2\text{Ti}(\text{O}(\text{S})\text{CR})_2$ (67) were also reported. Additional work on reactions of Cp_2Ti complexes with nitrogen oxides (1978) includes the formation of $(\text{Cp}_2\text{Ti})_2\text{O}$ from " Cp_2Ti " and N_2O ; the reaction of $\text{Cp}_2\text{Ti}(\text{CO})_2$ with N_2O to give $(\text{Cp}_2\text{Ti})_4(\text{CO}_3)_2$ (1979); and the formation of $(\text{Cp}_2\text{TiCl})_2\text{O}$ from

$(\text{Cp}_2\text{TiCl})_2$ and N_2O (68). The last product can also be obtained by hydrolysis of Cp_2TiClMe with trace water; its crystal structure closely resembles analogous compounds, with $\text{Ti-O-Ti} = 173.8^\circ$ (69). Cp_2TiCl_2 reacts with $\text{Ti}(\text{OPr}^i)_2\text{L}_2$ to give $\text{Cp}_2\text{ClTi-O-Ti}(\text{OPr}^i)\text{L}_2$, where L is a dioxygen-bonded ligand such as acac (70).

Cp_2TiCl_2 (and the indenyl analog) reacts with dioximes and related compounds to give $\text{Cp}_2\text{Ti}(\text{dioximate})$ products (71). A variety of Cp_2Ti -(Schiff base) complexes were also prepared (72). Complexes $\text{Cp}_2\text{ZrCl}(\text{S}_2\text{CNHAr})$ are 5-coordinate by IR (73). Various approaches to making Cp_2MS_n species, where n can vary, gave only Cp_2MS_5 (already known for Ti); conformational fluxionality was examined by NMR (74).

The compounds $(\text{MeCp})_2\text{TiX}_2$ (75) and $\text{Cp}(\text{MeCp})\text{TiX}_2$ (76), where $\text{X} = \text{N}_3$, NCS, NCO or NCSe, all have exclusively N-bonded pseudohalide ligands according to IR. Trimethylsilyl azide was used to prepare $\text{Cp}_2\text{TiCl}(\text{N}_3)$ and $\text{CpTiCl}_2(\text{N}_3)$; the latter reacts with PPh_3 to give $\text{CpTiCl}_2(\text{NPPH}_3)$ (77), and with alcohols to give $\text{CpTiCl}_2(\text{OR})$ (78). Cp_2ZrCl_2 reacts with NaNO_2 to give $\text{Cp}_2\text{Zr}(\text{NO}_2)_2$, but with AgNO_2 to give $\text{Cp}_2\text{Zr}(\text{ONO})_2$ (79). Potentially chelating imidazole derivatives such as 2-(2-pyridyl)imidazole react with Cp_2TiCl to give $[\text{Cp}_2\text{TiL}]^+$ complexes; these could not be oxidized to Ti(IV), but Ti(II) complexes such as $\text{Cp}_2\text{Ti}(\text{bipy})$ react with NO^+ salts to give $[\text{Cp}_2\text{Ti}(\text{bipy})]^{2+}$ (80).

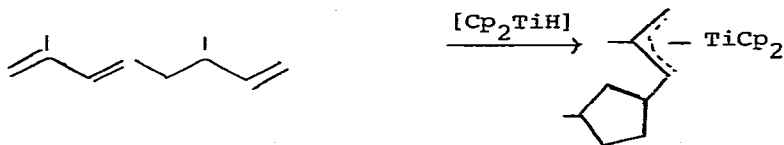
CpTiX_3 can be prepared from TiX_4 and CpSiMe_3 ; the chloride was obtained in 92% yield. It forms adducts with phen or diars but not with glyme, dppe or $\text{MeS}(\text{CH}_2)_4\text{SMe}$ (81). CpTiCl_3 (and $(\text{MeCp})\text{TiCl}_3$) were also obtained on refluxing Cp_2TiCl_2 with SO_2Cl_2 in SOCl_2 , in over 90% yield (82). Exposure of $(\text{MeCp})\text{TiCl}_3$ to moist air gives $\{(\text{MeCp})\text{TiClO}\}_4$ (the simple Cp analog was made in 1970); the crystal structure shows a nearly planar Ti_4O_4 ring, with tetrahedral geometry about each Ti, an average Ti-O-Ti angle of 161.5° , and short Ti-O distances ascribed to π bonding (83). Systems $\text{CpTiCl}_3/\text{ethylaluminum chlorides}$ were investigated by EPR; a variety of product structures were deduced, including $\text{CpTiAl}_2\text{Cl}_{8-n}\text{Et}_n$, $n = 1-4$ (84).

The cyano-acac complex $\text{CpZr}(\text{CH}_3\text{C}(\text{O})\text{C}(\text{CN})\text{C}(\text{O})\text{CH}_3)_3$ was prepared; IR indicates all three diketonates are bidentate but there is no M-CN interaction (85). CpZr acac complexes can be brominated on the acac group by N-bromosuccinimide (86). The 7-coordinate complexes $(\text{MeCp})\text{Ti}(\text{S}_2\text{CNMe}_2)_3$ (87) and $\text{CpHf}(\text{S}_2\text{CNR}_2)_3$ (88) were reported.

OTHER π -BONDED COMPLEXES

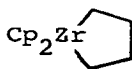
The gas phase reaction of Ti^+ with halocarbons, as studied by ion cyclotron resonance, provides evidence for ions which appear to have η^2 -ligands, such as $\text{Ti}(\text{C}_2\text{H}_2)^+$, $\text{Ti}(\text{CH}_2\text{CHCl})^+$, and $\text{TiCl}(\text{C}_6\text{H}_4)^+$ (89).

Reaction of CpMCl_3 with $\text{CH}_3\text{CH}=\text{CHCH}_2\text{MgX}$ gives $\text{CpM}(\text{C}_4\text{H}_7)(\text{C}_4\text{H}_6)$; the Ti compound is known (1975). An intermediate, $\text{CpM}(\text{C}_4\text{H}_7)_3$, could be isolated for Hf only (90). Treatment of Cp_2TiCl_2 with Pr^iMgBr gives a hydride species which reacts with a variety of di- and trienes to give allylic complexes, sometimes with cyclization as in (91):



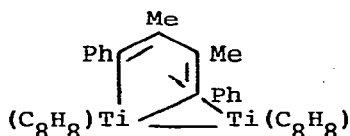
Fluxionality was studied in $\text{Hf}(\eta^3\text{-allyl})_4$ and $(\text{C}_8\text{H}_8)\text{Zr}(\text{allyl})_2$ by high-field NMR: for the first, coalescence did not occur until -110° even at 400 MHz (92).

Photolysis of Cp_2ZrPh_2 in the presence of dienes gives $\text{Cp}_2\text{Zr}(\eta^4\text{-diene})$ for a variety of acyclic and cyclic 1,3-dienes. For the former two isomers, *s-cis* and *s-trans*, can be distinguished by NMR in most cases; they interconvert photochemically or thermally. The temperature-dependent NMR suggests that the Zr travels from one face of the diene to the other, presumably via an intermediate like XIII. In fact, the crystal structure of



XIII

$\text{Cp}_2\text{Zr}(\text{s-cis-CH}_2=\text{CMe-CMe=CH}_2)$ shows substantial contribution of form XIII in the ground state: $\text{Zr-C}_1 = 2.300$, $\text{Zr-C}_2 = 2.597$; $\text{C}_1\text{-C}_2 = 1.451$, $\text{C}_2\text{-C}_3 = 1.398$ Å. A crystal structure was also obtained for $\text{Cp}_2\text{Zr}(\text{s-trans-C}_4\text{H}_6)$; here $\text{Zr-C}_1 = 2.48$ and $\text{Zr-C}_2 = 2.33$ Å (93). Reaction of $\{(\text{C}_8\text{H}_8)\text{TiCl}(\text{THF})\}_2$ with isopropyl Grignard in the presence of acetylenes gives products of formula $\{(\text{C}_8\text{H}_8)\text{Ti}(\text{RCCR}')\}_2$; the crystal structure for R=Me , $\text{R}'=\text{Ph}$ shows structure XIV. The NMR shows only one peak for C_8H_8 indicating fluxionality (94).



XIV

Reduction of $\text{TiCl}_4(\text{dmpe})_2$ by sodium amalgam in the presence of butadiene gives $\text{Ti}(\text{dmpe})(\text{C}_4\text{H}_6)_2$. In contrast to the Zr analog which gives 7-coordinate adducts preferentially (1979), there is no tendency to add any ligand. Both the Ti and Zr complexes catalyze olefin oligomerization, probably via metallocyclic intermediates (95). Similar treatment of $\text{ZrCl}_4(\text{dmpe})_2$ with cyclic 1,3-dienes (C_6 or C_8) gives $\text{ZrH}(\eta^5\text{-dienyl})(\text{dmpe})_2$; although the H was not detected by NMR there is chemical evidence for it, and a crystal structure on the cyclooctadienyl complex locates it tentatively ($\text{Zr-H} = 1.67 \text{ \AA}$). With cyclooctatetraene, $\{(\text{C}_8\text{H}_8)_2\text{Zr}\}_2(\text{dmpe})$ is obtained (96).

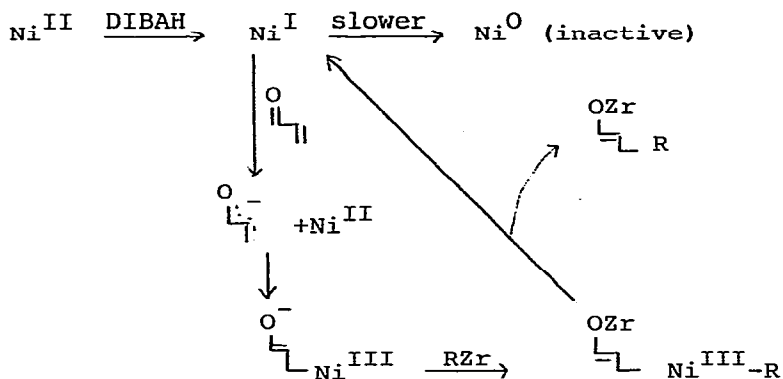
Evaporation of metal vapors into a (methyl)(phenyl) silicone polymer gives apparent arene-like complexes of Ti (97, 98) as well as of mixed Ti-Mo clusters (97). The metal vapor reaction of Zr or Hf with cycloheptatriene gives an uncharacterized red solid, which on vacuum sublimation yields $\text{M}(\text{C}_7\text{H}_7)(\text{C}_7\text{H}_9)$ (99), as previously found for Ti (1976). EPR and ENDOR spectroscopy on $\text{CpTi}(\text{C}_8\text{H}_8)$ has been carried out; the latter shows larger hyperfine coupling to the protons of C_8H_8 ring than the Cp ring (100).

APPLICATIONS IN SYNTHESIS AND CATALYSIS

A review of cleavage reactions of hydrozirconation-derived alkyls Cp_2ZrClR has appeared (101). Hydrozirconation of bicyclic olefins (102), and the preparation of Cp_2ZrHfCl and its use for "hydrohafniation" in similar fashion (103) have been examined. Alkenyl zirconium complexes derived from alkynes add to allylic palladium complexes to form C-C bonds; stereochemistry differs from that found in reactions of corresponding carbanions with allyl-Pd, in a way that suggests the $\text{Cp}_2\text{ZrCl}(\text{alkenyl})$ alkylates first at Pd, rather than by direct attack on the allyl group (104).

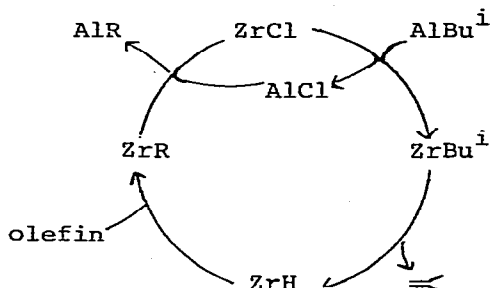
Nickel-catalyzed conjugate addition reactions of alkyl zirconium species (1977) have received further attention. Alkenyl complexes $\text{Cp}_2\text{ZrCl}(\text{CH=CHR})$ undergo 1, 4-addition to enones in the presence of Ni(II); the reaction proceeds much more efficiently if the Ni catalyst is prerduced with DIBAL (105). Electrochemical studies

appear consistent with an electron-transfer mechanism (106):



TiCl_4 catalyzes conjugate addition of alkynylborates to enones (107).

A Japanese-language review on Ti- and Zr- catalyzed hydroalumination of olefins has appeared (108). Cp_2TiCl_2 catalyzes hydroalumination of terminal olefins and internal acetylenes by a variety of hydridoaluminum species (109). The combination $\text{Bu}_3^i\text{Al} + \text{Cp}_2\text{ZrCl}_2$ effects hydroalumination, presumably via the following sequence (110):



Cp_2ZrCl_2 plus LiAlH_4 hydroaluminates allylic alcohols (111), while the titanium analog gives mostly deoxygenation (for allylic ethers, benzyl alcohols, ketones and acids as well) (112).

A number of studies relate to Ziegler-Natta polymerization. A review has appeared on stereospecific propylene polymerization (113). The reaction of Cp_4Zr with AlEt_3 gives new compounds, including $\text{Cp}_3\text{Zr}(\text{CH}_2\text{CH}(\text{AlEt}_2)_2)$ and $\text{Cp}_3\text{Zr}(\text{HA}(\text{Et}_3))$; these can polymerize ethylene, especially if some water is present (114). The system $\text{Zr}(\text{OBU})_4/\text{Et}_2\text{AlCl}/\text{PPh}_3$ catalyzes dimerization of 1,3-dienes (115). EPR studies on the system $\text{Cp}_2\text{TiCl}_2/\text{Et}_n\text{AlCl}_{3-n}/\text{SiO}_2$ were compared to the unsupported analog; the systems have similar polymerization

activity (116). The interactions of C_2H_2 , C_2H_4 and C_3H_6 with $Zr(BH_4)_4/Al_2O_3$ were examined by inelastic electron tunneling spectroscopy (117).

Modified extended Hückel type calculations, using $[TiCl_3Me]^{n-}$ as a model, suggest titanacyclopentane formation is particularly favorable; a possible polymerization mechanism would thus be:



For propylene polymerization, favorability of diequatorial substitution in the metallacycle might account for stereoregularity (118). Calculations were also reported for the systems $TiCl_3$ plus Me_2AlCl (119) and Cp_2TiClR plus $AlCl_3$ (120).

The dihydrides $Cp_2'MH_2$ ($M=Zr, Hf$) can be made more easily than for ordinary Cp (here $Cp' = C_5H_4Pr^i$ or $C_5H_4Bu^t$) since the intermediates $Cp_2'MHCl$ are soluble. The dihydrides are dimeric by NMR - both bridging and terminal hydrides are observed. The chiral compounds $(C_5H_4CH_2CH(Et)(R))_2MH_2$ are hydrogenation catalysts, but with prochiral alkenes only 1-2% induction is obtained (121). Photolysis of Cp_2TiR_2 generates hydrogenation catalysts; for $R=Ph$ continued irradiation is needed for activity and good selectivity for diene to monoene conversion is observed (122). Addition of ZrR_4 ($R=allyl$ or neopentyl) to silica gives a good catalyst for olefin isomerization; slower hydrogenation is also found (123). $Cp_2TiCl_2/LiAlH_4$ or dimeric titanocene catalyzes isomerization in cyclic polyenes (124).

Alkyltitanium compounds can be used to alkylate tertiary alkyl chlorides (125-127) or to convert carbonyl compounds to alcohols (128). $TiCl_3/LiAlH_4$ couples 1,3-diols to cyclopropanes stereospecifically, so diradicals are not intermediates (129). In the presence of $TiCl_4/NaBH_4/glyme$, olefins are converted to alcohols; the mechanism is unclear but probably involves air oxidation (130). Cp_2TiS_5 reacts with oxalyl chloride to give cyclo- $S_{10}(CO)_4$ (131). Several $Ti(IV)$ compounds catalyze the formation of Cp_2Mg from cyclopentadiene and Mg metal at room temperature (132).

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