TITANIUM, ZIRCONIUM AND HAFNIUM *
ANNUAL SURVEY COVERING THE YEAR 1979

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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 η^5-cyclopentadienyl) and Cp' (for any ring-substituted cyclopentadienyl group) are used throughout. Dates cited in parentheses indicate a reference to material discussed in the survey for that year.

A Japanese-language review on organozirconium compounds has been cited in Chemical Abstracts (1).

CARBONYL AND DINITROGEN COMPLEXES

In a paper presenting the design for a high-pressure reactor and infrared/electronic spectroscopy cell, the reaction of $TiCl_3(PEt_3)_2$ with CO (800 psi) gave a new peak at 1875 cm^{-1} assigned as $TiCl_3(CO)(PEt_3)_2$; the isolated (not pure) product loses CO to revert to starting material (2).

The crystal structure of $Cp_2Hf(CO)_2$ has been determined; it is quite similar to that of the Ti analog (1977) with expected differences in bond lengths; also the Cp rings are staggered for Hf and eclipsed for Ti. One of the CO's can be replaced by phosphine ligands PPh_3, PMe_3, $Ph_2PCH_2CH_2PPh_2$ (only one end coordinates) and PF_3 (photochemically); with diphenylacetylene the hafniacyclopentadiene complex $Cp_2Hf(C_4Ph_4)$ forms (3). The ultraviolet photoelectron spectrum of $Cp_2Ti(CO)_2$ shows a lowest ionization at 6.35 eV, assigned to Ti 3d electrons (4).

The CO-reducing ability of group IV metal hydrides is clearly illustrated by the reaction of $(C_5Me_5)_2ZrH_2$ with carbonyl complexes of other metals, even at -80°, to give zirconoxyalkylidene complexes:

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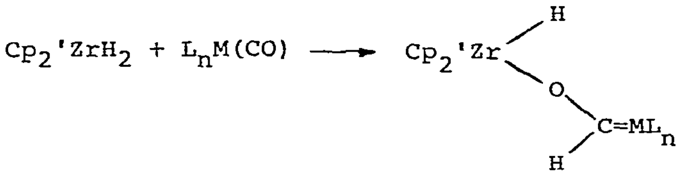
* Titanium, zirconium and hafnium, Annual Survey covering the year 1978 see J. Organometal. Chem., Vol. 180(1979)187-203.

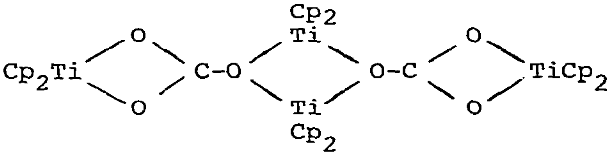


where L_nM = Cp_2W or Cp_2NbH. The crystal structure of the W complex was determined. Both products react with H_2 to give $Cp_2'ZrH(OCH_3)$ and L_nMH_2, thus achieving overall reduction of CO to methoxide; these reactions thus complement the reaction of $Cp_2'ZrH_2$ with CO (1976) and may be mechanistically relevant. The W complex also adds ethylene at 70° to give $Cp_2'Zr(Et)(OCHWCp_2)$ (5). A related reaction is the observation that Cp_2ZrHCl slowly reduces $CpRe(NO)(PPh_3)(CHO)$ to $CpRe(NO)(PPh_3)(CH_3)$ (6).

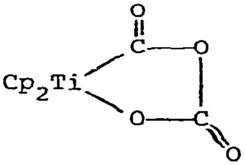
$Cp_2Ti(CO)_2$ reacts with CO_2 at 50° according to the stoichiometry:

$$4\ Cp_2Ti(CO)_2 + 4\ CO_2 \longrightarrow [(Cp_2Ti)_2CO_3]_2 + 10\ CO$$

Labelling shows that the carbonato ligands, as well as two of the ten CO's, come from CO_2. A crystallographic determination gave the following structure:



The magnetic moment (1.70 per Ti) indicates no interaction between the four (formally) Ti(III) centers. An intermediate such as



was proposed; this is related to a product previously observed (1978) from the reaction of diphenylketene with $Cp_2Ti(CO)_2$ and could extrude CO to leave the carbonate moiety. In contrast, $Cp_2Zr(CO)_2$ reacts with CO_2 at 74° to give $(Cp_2ZrO)_3$, whose structure (also determined crystallographically) contains a virtually planar 6-membered Zr_3O_3 ring, a trimer of the hypothetical "zirconyl" unit $Cp_2Zr{=}O$. Similarly, $(Cp_2TiCl)_2$ reacts with CO_2 at 90° to give $(Cp_2TiCl)_2O$ (7).

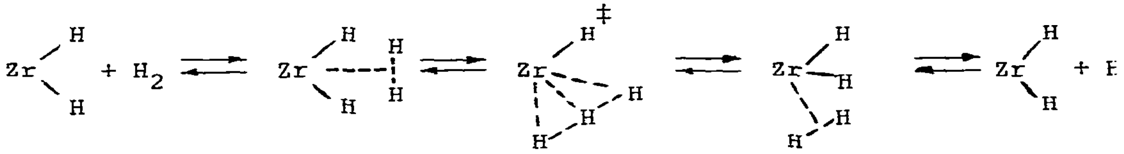
The crystal structure of $[Cp_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$ has been determined; the molecule contains a linear M-N-N-M bridge, as in $(Cp_2'Ti)_2N_2$ and $[Cp_2'Zr(N_2)]_2N_2$ (1976). The N-N distance (1.162 Å) is virtually the same as in the above Ti(II) species (1.160 Å) but the Ti-N distance is considerably shorter (1.962 vs 2.017 Å). Coordination around Ti is fairly normal for a Cp_2MX_2 system; notably the Ti_2N_2 unit and <u>both</u> p-tolyl groups are all coplanar. It is suggested that the resulting interaction of the two Ti a_1 orbitals (both singly occupied) with the <u>same</u> π^* orbital of N_2 accounts for the observed diamagnetism of this Ti(III) complex (8).

A full paper on the reduction of $Cp_2ZrCl(CH(SiMe_3)_2)$ with Na/Hg under N_2 has appeared. As communicated last year, the product is a paramagnetic monomer, $Cp_2ZrR(N_2)$ (in contrast to the behavior of the analogous Ti system, see above); the appearance of equal hyperfine coupling to two N's in the ESR suggest a side-bonded η^2-N_2 ligand. N_2 is not displaced by PEt_3, but recrystallization leads to the analog of the above Ti complex, diamagnetic $(Cp_2ZrR)_2N_2$. Changing R or putting substituents on Cp generally results in no N_2 complex being formed at all (9).

The formation of naphthylamines from the system $TiCl_4$/Li/naphthalene/N_2 has been examined. With Ti:Li:NpH = 1:50:6, about 1% $NpNH_2$ (α and β) and 73% NH_3 were obtained after hydrolysis. Addition of ligands such as PPh_3 or bipyridyl inhibited formation of $NpNH_2$ (but not NH_3) while causing some N_2 evolution, suggesting intact N_2 rather than a nitride species is an intermediate. Addition of some air during hydrolysis gives an increased yield of $NpNH_2$ (10). Reduction of N_2 by Cp_2TiCl_2/Li/NpH (as well as other metal salts) has been re-examined (11).

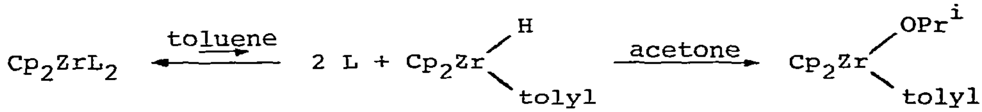
ALKYL AND RELATED COMPLEXES

An attempt to explain the reactivity of the Zr(IV) complexes, Cp_2ZrHR, towards H_2 (see last year's survey) has been made using (extended Hückel) MO analysis. The addition of $H_2(D_2)$ to Cp_2ZrH_2, leading to H-D exchange, has a low calculated activation barrier even though the initial complex is d^0; the suggested mechanism is not a true oxidative addition but involves a sort of allylic transition state:

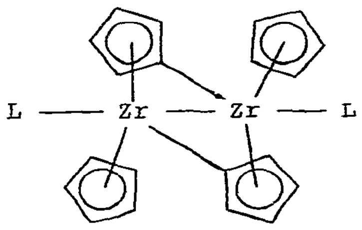


The energy difference between the two intermediates ("inside" vs. "outside" coordination of the H_2 molecule) is also calculated to be small. For $Cp_2ZrH(CH_3)$ attack outside CH_3 is preferred, which does not agree with the observation that H-D exchange is faster than H_2-induced reductive elimination (1978) (12).

If reductive elimination from $Cp_2ZrH(CH_2C_6H_{11})$ is induced by phosphine ligands, Zr(II) products Cp_2ZrL_2 (L = $PMePh_2$, PMe_2Ph, or L_2 = $Me_2PCH_2CH_2PMe_2$) are obtained, although only the last was isolated. These react (at room temperature) with CO to give ($Cp_2Zr(CO)L$; with RCCR or with octa-1,7-diene to give metallacycles (the latter giving an equal mixture of *cis*- and *trans*-1,2-dimethylcyclohexane on hydrolysis), and with alkyl halides to give Cp_2ZrRX. Arenes can be metallated (the reverse of reductive elimination) as indicated by the trapping of metallated toluene by acetone:



while slow decomposition is observed in hydrocarbon solution, giving a product resulting from Cp metallation:



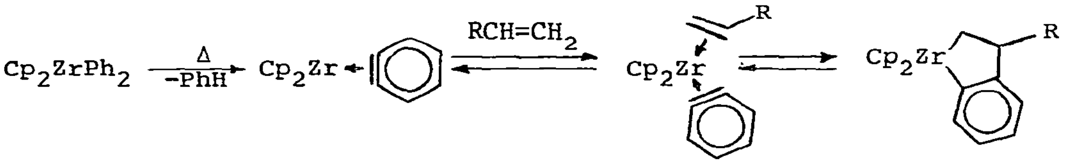
The same product (characterized by ^{13}C NMR) was also obtained from "Cp_2Zr" (the product of reductive elimination from Cp_2ZrHR) plus Cp_2ZrL_2 (13).

Two further studies on thermal decomposition of deuterium-labelled Cp_2TiMe_2 (1976) have appeared. In one, two stages of decomposition were identified; during the first (~ 2 hours at 340 K) about 10% of the starting material is consumed; darkening but no precipitate was observed; and all of the hydrogens in the evolved methane comes from methyl groups. Subsequently the solution becomes opaque, all the starting material is consumed, and substantial scrambling of label is found in the methane. It was suggested that in the first stage loss of methane is strictly intramolecular and involves (formally, at least) α-hydrogen abstraction; a very large isotope effect was found (for $Ti(CH_3)_2$ vs. $Ti(CD_3)_2$). In the second stage, ring hydrogens must exchange with methyl hydrogens, possibly <u>via</u> methylene intermediates, e.g.

$$(C_5H_5)_2TiCH_2 \rightleftharpoons (C_5H_5)(C_5H_4)TiCH_3$$

Of note is the importance of the large isotope effect since this strongly affects product isotopic purity; for example, $(C_5D_5)_2Ti(CD_3)_2$ gives (in the early stage) equal amounts of CD_3H and CD_4; the former comes from the H in the CD_3 groups (about 1%) which is preferentially eliminated (14). In the other study (involving $(C_5D_5)_2MR_2$, M = Ti, Zr; R = Me, Ph) two stages were not distinguished, but the same conclusions regarding ring-alkyl hydrogen exchange for the overall process were reached. Furthermore, this exchange was shown to be intermolecular as well; decomposition of Cp_2MR_2 in the presence of $(C_5D_5)_2V$ led to vanadocene-d_x where x = 0-10 (15).

Decomposition of $Cp_2TiEtCl$, thermally (80-140°) or photochemically, gives C_2H_4, C_2H_6 and traces of C_4H_{10}; the first two are roughly equal for the neat compound but much more C_2H_6 is obtained in hydrocarbon solution; in toluene-d_8 some C_2H_5D is obtained. The proposed mechanism involves homolysis to give Et•, which abstracts H from the ethyl group of the starting compound to give C_2H_6 + C_2H_4, or from solvent to give only C_2H_6 (16). The proposed benzyne intermediate from decomposition of Cp_2ZrPh_2 can be trapped with olefins to give zirconaindanes:



The reversibility of the last two steps is shown by the fact that the products exchange with $R'CH=CH_2$; a similar equilibrium between (simple) metallacycles and bis(olefin) complexes has been inferred for Ti (1978). The zirconaindanes decompose above 100° to $PhCH(CH_3)R$, with the additional hydrogens needed apparently coming from the Cp rings (17). Decomposition of titanium neophyls, prepared from $PhMe_2CCH_2MgCl$ and $TiCl_4$ at -70°, give mostly $(PhMe_2CCH_2)_2$ and $PhCMe_3$; the absence of rearranged species shows radicals are not involved (18). Symmetry arguments for such reactions indicate a d^0 alkyl should not give R_2 formation; a cluster intermediate was suggested to account for the observation of R_2 in the above Ti system (19).

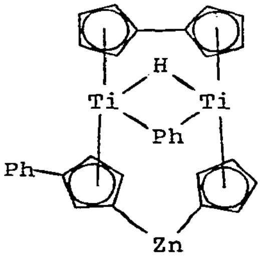
Two groups have examined one-electron reduction of Cp_2MR_2. Reaction of Cp_2MR_2 (M = Ti, Zr; R = Me, $PhCH_2$, Me_3CCH_2, Me_3SiCH_2, Ph_2CH) with sodium naphthalenide gives $Cp_2MR_2^{\dot{-}}$, characterized by ESR; the Hf analogs are much less stable and ESR studies are plagued by small amounts of Zr impurities (20). Cp_2TiR_2 (R = Me_3SiCH_2; or $R_2 = CH_2(SiMe_2)X(SiMe_2)CH_2$, where X = CH_2 or O) plus potassium in DME/THF gives $Cp_2TiR_2^{\dot{-}}$ which have half-lives of 20 min or more at room temperature. BuLi at -90° can also be used as reductant, but at room temperature an ESR signal assigned to $Cp_2TiBu_2^{\dot{-}}$ grows in, indicating alkyl group exchange (21). The reaction of Cp_2ZrR_2 with R'Li (R,R' = Me, Ph) gives alkane, CpLi and $CpZrR_2$ or ZrR_2 (depending upon how much RLi is used); the mechanism which was proposed is:

$$Cp_2ZrR_2 + R'Li \rightarrow (Cp_2ZrR_2R')Li \rightarrow (R,R')H + CpZr(R,R')_2 + CpLi \rightarrow \text{etc.}$$

but the source of the hydrogen atoms was not accounted for (22). Cp_2TiPh_2 reacts with $ZnPh_2$ at 60° by the following stoichiometry:

$$2\ Cp_2TiPh_2 + ZnPh_2 \longrightarrow 4\ PhH + \text{"}(C_5H_4)_4Ti_2Ph_2Zn\text{"}$$

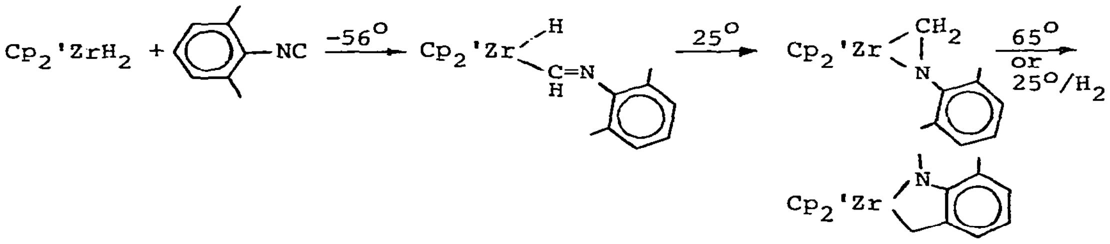
The organometallic product gives 1 mole each of H_2 and PhH on protonolysis, and 1 mole of phenylcyclopentadiene on cleavage with HOAc; the IR suggests a fulvalenide ligand, implying the structure



An apparently analogous species (without the ring-phenyl) was obtained from $(C_{10}H_8)(CpTiH)_2$ plus $ZnPh_2$ (23). Protonolysis of $Ti(CH_2Ph)_4$ with R_fCOOH ($R_f = C_2F_5$, C_3F_7) gives $(PhCH_2)_3Ti(O_2CR_f)$; only one benzyl group is cleaved even with excess acid (24).

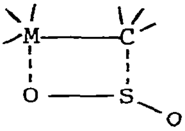
A number of studies on insertion reactions have appeared. Cp_2TiR reacts with isonitriles R'NC (R = o-tolyl, 2,6-dimethylphenyl) to give adducts $Cp_2TiR(CNR')$ which are stable for R = Cl, C_6F_5; for R = C_6H_5, o-tolyl these rearrange to give $Cp_2Ti(CR{=}NR')$ whose molecular weight and magnetic properties are in accord with monomeric Ti(III) complexes. These are oxidized by I_2 or PhSSPh to $Cp_2TiX(CR{=}NR')$ for which IR and ^{13}C NMR suggest η^2-coordination of the iminoacyl ligand (25). In the Ti(III) species, IR alone cannot give unequivocal indication of coordination mode; a crystal structure on $Cp_2Ti(CPh{=}N(2,6\text{-}C_6H_5Me_2))$ shows η^2-bonding, with bond lengths C-N = 1.28, Ti-C = 2.096, Ti-N = 2.149 Å (26). The same Cp_2TiR species react with CO, giving adducts $(C_5Me_5)_2TiCl(CO)$ (dimerization in simple Cp_2TiCl prevents reaction) and $Cp_2Ti(C_6F_5)(CO)$, and acyl $Cp_2Ti(COR)$ (R = o-tolyl); the latter is oxidized to Ti(IV) acyls by HCl or PhSSPh. IR CO stretching frequencies in both oxidation states (1575 cm^{-1} for Ti(IV), 1470 cm^{-1} for Ti(III) indicate η^2-coordination. For R = Ph the reaction is more complex; treatment of the product with HCl gives some benzil (27).

Zirconium alkyls Cp_2ZrClR (R = CH_2CMe_3, CH_2SiMe_3, $CH(SiMe_3)_2$) give insertion products, acyls or iminoacyls, with CO or (p-tolyl)NC respectively; all appear to have η^2-ligands. With mixed alkyls such as $Cp_2Zr(CH(SiMe_3)_2)Me$ only the bulkier alkyl group undergoes insertion (28). With C_5Me_5 systems, $Cp_2'ZrMe_2$ gives analogous isonitrile insertion products $Cp_2'ZrMe(CMe{=}NR)$. Insertion into Zr-H is also found: $Cp_2'ZrH_2$ reacts with MeNC at -65° to give $Cp_2'ZrH(CH{=}NMe)$ which is hydrogenated at 25° to $Cp_2'ZrH(NMe_2)$. With $(2,6\text{-}C_6H_3Me_2)NC$ the analog is obtained at low temperature, but at room temperature a second insertion gives an η^2-imine complex which at higher temperatures metallates a ring methyl group:



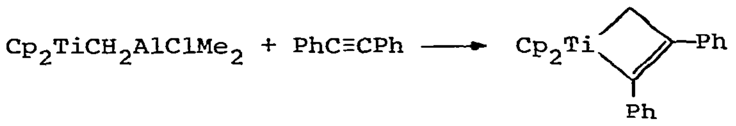
Reaction of $(Cp_2'ZrN_2)_2N_2$ with RNC gives $Cp_2'Zr(CNR)_2$. These reactions are all reminiscent of CO chemistry in this system (1978) (29). Insertion into metal-halide bonds is also possible; MCl_4 (M = Ti, Hf) plus (t-butyl)NC gives $[MCl_3(CNR)(CCl{=}NR)]_2$. One or both of the RNC groups can be replaced by chelators, suggesting insertion is reversible (30).

In examining the stereochemistry at metal during SO_2 insertions, it was first found that $Cp_2TiMe(C_6F_5)$ reacts with SO_2 to give two isomers of $Cp_2Ti(C_6F_5)(SO_2Me)$. The major species shows a doubling of Cp signals in the NMR, which coalesce at 78°; this was assigned at the O-sulfinate, with NMR splitting due to the chiral center at S, where inversion becomes rapid at elevated temperature. The minor isomer (~ 10%) is assigned as the O,O'-sulfinate; its NMR signals remain distinct even at 78°. $CpCp'Ti(C_6F_5)(SO_2Me)$ ($Cp' = C_5H_4CMe_3$) exists as two diastereomers, as expected since there are two chiral centers, but these could not be separated, and rapidly interconvert at 78° (31). With an additional element of chirality, $CpCp''Ti(C_6F_5)Me$ ($Cp'' = C_5H_4CHMePh$) can be separated into its two diastereomers (1976); either pure diastereomer reacts with SO_2 to give a single isomer of $CpCp''Ti(C_6F_5)(SO_2Me)$ which is cleaved by HCl to give a single isomer of $CpCp''Ti(C_6F_5)Cl$; NMR data indicate that stereochemistry at Ti is retained in both steps. Along with the previous finding of retention at C in a related Zr system (1975), this result implies a 4-center transition state for insertion.



(Both a preliminary (32) and full (33) report of this work appeared.)

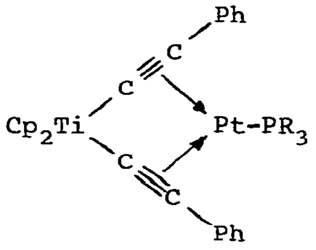
The titanium methylene compound $Cp_2TiCH_2AlClMe_2$ (1978) undergoes metathesis-type reactions; e.g. with $^{13}CH_2{=}CMe_2$ label is incorporated into the Ti species (about 30 hr. at 52° are required to reach equilibrium), and $^{13}CH_2{=}CMe_2$ exchanges label with methylenecyclohexane in the presence of the compound. These results, as well as olefin homologation and cyclopropanation (1978) are interpreted in terms of a titanacyclobutane intermediate; with PhC≡CPh, a stable metallacycle is formed (34).



Reaction of Cp_2TiCl with $LiAlMe_4$ gives a methyl-bridged compound, $Cp_2Ti(Me_2AlMe_2)$. Related reactions include Cp_2TiCl with Al_2Me_6, giving $Cp_2Ti(AlMe_3Cl)$ of uncertain structure; with $NaAlH_2Me_2$, giving $Cp_2Ti(H_2AlMe_2)$ (by ESR); and Cp_2TiCl_2 with $LiAlMe_4$, giving Cp_2TiMe_2 (35).

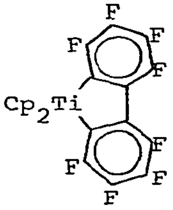
Treatment of MCl_4 (M = Zr, Hf) with 3 moles of $LiN(SiMe_3)_2$ followed by LiMe gives $MeM(N(SiMe_3)_2)_3$, surprisingly stable to air, water, acid and CO_2, probably for steric reasons (36). With only 2 equivalents of the amide, followed by R_2Mg (R = Me, Et, CH_2SiMe_3), $R_2M(N(SiMe_3)_2)_2$ can be obtained; these undergo CO_2 insertion to give carbamates, $R_2Hf(O_2CN(SiMe_3)_2)_2$, and react with (t-butyl)NC to give $((Me_3Si)_2N)_2Hf(CR{=}NBu^t)_2$ (37). Monoalkenyl complexes $MCl_3(CPh{=}CMe_2)$ were prepared from MCl_4 (M = Ti, Zr, Hf) and $Me_3Sn(CPh{=}CMe_2)$; only the Ti compound was isolated (38). Lithiation of 1,1'-dichloroferrocene followed by reaction with Cp_2TiCl_2 gives Cp_2Ti(1,1'-dichloroferrocen-2-yl)$_2$ as a roughly equal mixture of dl and meso isomers; these were separated by extraction (the dl is more soluble) (38). Tolylhafnium complexes Cp_2Hf(o, m or p-tolyl)$_2$ were obtained from Cp_2HfCl_2 and the corresponding lithium reagent (40). Benzylmagnesium chloride plus $(Cp_2ZrCl)_2O$ gives $(Cp_2Zr(CH_2Ph))_2O$ (41). A patent covering preparation of titanacycles $Cp_2Ti(CH_2XCH_2)$ (X=$(SiMe_2)CH_2(SiMe_2)$, $(SiMe_2)O(SiMe_2)$, $(SiMe_2)_3$, $(SiMe_2)_2$, $SiMe_2$) has been issued (42).

Alkynyl complexes $Cp_2M(CCR)_2$ (Cp = C_5H_5, C_5H_4Me; R = Ph, cyclo-C_6H_{11}, n-C_6H_{13}, Ph_2CHCH_2, $Ph_2C(CN)CH_2$) have been prepared for M = Ti (43) and Zr (44). $Cp_2Ti(CCPh)_2$ reacts with $Pt(C_2H_4)_2(PR_3)$ to give $Cp_2Ti(CCPh)_2Pt(PR_3)$; spectral properties suggest the two acetylenic groups are η^2-coordinated to Pt:



The acetylenic carbons show very different ^{13}C signals -- one (assigned as Ti-bonded) is at much lower field and is only weakly coupled to ^{31}P and ^{195}Pt (45).

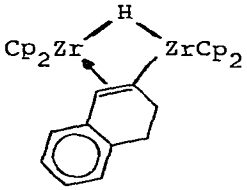
Ab initio calculations were performed for TiH_4 and $TiMe_4$; the calculated Ti-C distance in the latter (2.10 Å) is close to that previously found for $Ti(CH_2Ph)_4$ (2.13 Å) (46). An extended Hückel study on metallacyclopentadienes, including $Cp_2Ti(CH)_4$, suggests little difference between this d^0 species and complexes which are not d^0 (47). Mass spectral studies on the perfluorotitanofluorene:



show loss of Cp and HF as important processes; the largest peak corresponds to $CpTiF^+$ (48). A full paper on ^{13}C relaxation mechanisms in methyl complexes (1978) includes Cp_2ZrMe_2 (49).

CYCLOPENTADIENYL COMPLEXES

In contrast to the Ti analog (1976), low-temperature reduction of Cp_2ZrCl_2 with potassium naphthalenide gives a naphthyl product, $(Cp_2Zr)_2(C_{10}H_7)H$, whose crystal structure shows a bridging $\eta^1:\eta^2$ - naphthyl group:

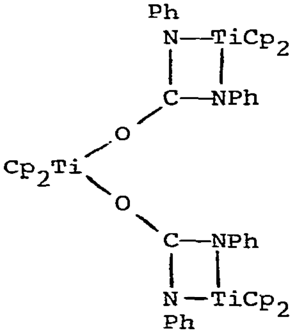


The bridging H was not located but its presence is shown by NMR and the reaction with CH_3I to give 1 mole of CH_4. The complex is inert to N_2; with H_2 it gives naphthalene and Cp_2ZrH_2 (50).

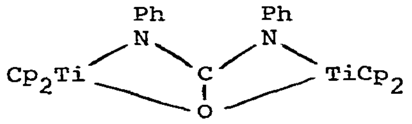
The crystal structures of ring-linked Cp_2TiCl_2 species, $(CH_2)_n(C_5H_4)_2TiCl_2$ (n=1 and 2; the latter is a new compound) were determined and compared to those of previously determined $(CH_2)_3(C_5H_4)_2TiCl_2$ and Cp_2TiCl_2. The methylene bridged species (n=1) shows substantial strain; the C-C-C angle at the methylene is only 97° and the exo-C-C bond on each ring is bent well out of the ring plane (16°). The dihedral angle between the two ring planes, 65°, is a compromise between preferred values imposed by the methylene bridge (109°) and the metal geometry (49.5° in unbridged Cp_2TiCl_2); in contrast, the ethylene-bridged compound is relatively strain-free with a ring dihedral angle of 51.8°. ^1H and ^{13}C NMR spectra of the three bridged species as well as the corresponding $(Cp-Cp)TiMe_2$ and $-(CO)_2$ compounds are reported; an interpretation of chemical shift differences between the ring 2- and 3-positions based on electronic distributions resulting from geometry is offered (51).

A summary of preparations and reactions of Cp_2ZrClY, where Y = alkoxide, carboxylate, N=CHR (derived from RCN) and Cp ligands, includes the new complex $(MeCp)_4Zr$ (52). Preparative details for Cp_2ZrH_2 and Cp_2ZrHCl are given in Inorganic Syntheses (53). Improved syntheses of $(MeCp)_2TiY_2$ (X = F, Cl, Br, I) involve making the chloride from $TiCl_4$ and CpTl, followed by halide exchange with NH_4F, BBr_3 or BI_3 (54). Reaction of Cp_2Pb with $TiCl_4$ gives a mixture of Cp_2TiCl_2, $CpTiCl_3$ and CpPbCl (55).

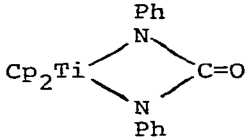
The crystal structures of $Cp_2M(NCO)_2$ (M = Ti, Zr) show M-NCO linkages as earlier deduced from dipole moment measurements; they have typical Cp_2MX_2 geometry. IR suggests the Hf analog has the same structure (56). Reaction of $CpTi(OR)_3$ with phenyl isocyanate gives $CpTi(OR)_{3-n}(NPhCO_2R)_n$; n=1-3 (57). PhNCO with $Cp_2Ti(CO)_2$ gives several interesting structures containing the diphenylureylene moiety. With excess PhNCO at room temperature a trimeric complex is obtained, whose crystal structure is:



From an equimolar reaction at 60° a dimer is obtained, whose crystal structure was also determined (as the toluene solvate):

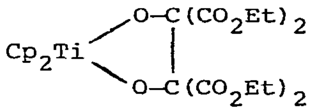


Heating the trimer to 90° gives the dimer plus a monomeric species, suggested to have structure

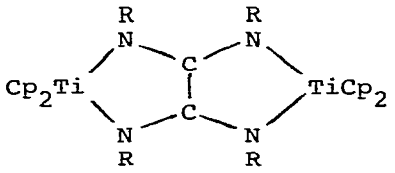


The latter is also obtained from the trimer by reaction with phenanthrenequinone (along with $Cp_2Ti(phen)$), and reacts with $Cp_2Ti(CO)_2$ to give the dimer. The monomer is diamagnetic as expected for Ti(IV); the dimer shows a magnetic moment of 1.73 B.M. per Ti (2 Ti(III)'s); oxidation state formulation in the trimer is unclear (58).

In related reactions, $Cp_2Ti(CO)_2$ plus $O{=}C(CO_2Et)_2$ gives



The pinacol-like C-C bond formation may be contrasted with the products obtained from $Cp_2Ti(CO)_2$ and CO_2 (vide supra) or diphenylketene (1978). Similarly, $Cp_2Ti(CO)_2$ reacts with p-tolylcarbodiimide to give:



Both structures were determined crystallographically (59).

Dibenzoylmethane reacts with $(Cp_2ZrCl)_2O$ to give the β-diketonate complexes $Cp_2ZrCl(PhCOCHCOPh)$ and $CpZrCl(PhCOCHCOPh)_2$. Reaction of the former with water gives $(Cp_2Zr(PhCOCHCOPh))_2O$, which when treated with more diketone leads to $CpZr(PhCOCHCOPh)_3$ (60). Similarly, Cp_2MCl_2 (M = Ti, Zr, Hf) plus ferrocenoylacetone yields $CpMCl(FcCOCHCOCH_3)_2$ (61). Fluoroalkoxy compounds $CpTiCl(OR)_2$, $CpTi(OR)_3$ and $CpTi(OR)_2Me$ ($R = CH_2CF_3$) have been prepared; the last two initiate polymerization of methyl methacrylate (62). The aqueous chemistry of the Cp_2Ti^{2+} fragment has been investigated; depending on pH and halide X species $Cp_2Ti(OH_2)_2{}^{2+}$, $Cp_2Ti(OH)(OH_2)^+$, $(Cp_2Ti(OH))_2O$ and $(Cp_2TiX)_2O$ were detected (63). The polyanion $CpTiMo_5O_{18}{}^{3-}$ was obtained from Cp_2TiCl_2 and $Mo_2O_7{}^{2-}$; its structure was established by ^{17}O NMR (64). In the presence of moisture $Cp_2Zr(SPh)_2$ led to crystallization of $(Cp_2Zr(SPh))_2O$, whose X-ray structure was determined. The Zr-O-Zr angle is 165.8°; the S-Zr-O angles (98.7 and 103.3°) are in the range expected for a d^0 Cp_2MX_2 species (65).

Complexes $Cp_2'Ti(NCS)_2$ were prepared, where Cp' is un-, mono- or disubstituted Cp; IR suggests N-coordination (66). $Cp_2TiCl(NCS)$ reacts with NaOAr (Ar = aryl group) to give $Cp_2Ti(NCS)(OAr)$, although symmetrization is a problem (67). $Cp_2Ti(CO)_2$ adds $(SeCN)_2$ to give $Cp_2Ti(NCSe)_2$ and $X(CN)_2$ to give $Cp_2Ti(CN)(NCX)$ (X = S, Se) (68). Group IVb derivatives $Cp_2MCl(GeEt_3)$ (M = Ti, Zr) were prepared from Cp_2MCl_2 and $LiGeEt_3$; attempts to make the Sn analogs or to make $Cp_2M(GeEt_3)_2$ led only to reduction to lower-valent species (69).

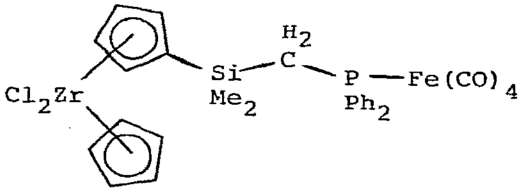
Aryldithiocarbamate complexes $Cp_2Ti(S_2CNHAr)_2$ (70) and $(MeCp)_2TiCl(S_2CNHAr)$ (71) contain bidentate dtc ligands, as do all previous analogs examined. Several zirconium complexes of sulfur-containing Schiff bases were prepared, including Cp_2ZrClL and Cp_2ZrL_2 (LH = $R_2C=N-N=C(SH)(SMe)$), which appear to be S,N-coordinated; and Cp_2ZrL' ($L'H_2$ = o-$HOC_6H_4CH=N-N=C(SH)(SMe)$) which is O,S,N-coordinated (by IR) (72).

In further studies on chirality, possible configurational stability in CpCp'TiX was examined by reducing diastereoisomerically pure CpCp'TiXCl (Cp' = $C_5H_4CHMePh$; X = C_6F_5 or OAr) with Al or Zr metal and reoxidizing with CCl_4. In both cases an equal mixture of diastereomers was obtained, showing that the intermediate Ti(III) has no configurational identity and, furthermore, that no induction occurs in reoxidation. With the chiral bridged species, $(C_5H_4CHMeCH_2CH_2C_5H_4)TiCl(OAr)$, induction was observed, in that either starting diastereomer led to the same unequal mixture of isomers after reoxidation (73). Attempts to make chiral complexes with only one Cp involved treating $CpTiCl_2$ with diols; for example, $Cp'TiCl_2$ (Cp = $C_5H_4CHMePh$) plus 4-methylbenzene-1,2-dithiol, followed by CCl_4, gave a mixture of diastereomers of Cp'TiCl(S-S), which however could not be separated (74). Reaction of 1,3-dibromopropane with $C_5H_4CMe_3^-$, $TiCl_3$, and HCl in succession gave $(CH_2)_3(C_5H_3CMe_3)_2TiCl_2$; NMR indicates only one product was formed, the dl isomer with both rings 1,3-disubstituted. Attempted resolution with (S)-(-)-1,1'-bi-2-naphthol gave only one diastereomer; models suggest only the S,S-isomer of the dichloride can form an adduct with the S-diol. Cleavage of the latter with HCl gives back a highly optically active dichloride, indicating configurational stability during these interconversions (75).

A phosphine ligand-substituted Cp ligand was prepared for the purpose of designing mixed bimetallic compounds by the following route:

$$Ph_2PCH_2Li + Me_2SiCl_2 \longrightarrow Ph_2PCH_2SiMe_2Cl \xrightarrow{LiCp} Ph_2PCH_2SiMe_2C_5H_5$$

After deprotonation with BuLi, the anion was used to make $Cp_2'ZrCl_2$ and $CpCp'ZrCl_2$. The latter reacts with $Fe_2(CO)_9$ to give (76).



Group IVb substituted cyclopentadienes were used to make a variety of substituted Cp titanum compounds, e.g.

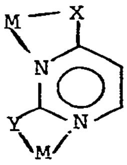
$$C_5H_4(EMe_2)(MMe_3) + TiCl_4 \longrightarrow (C_5H_4EMe_2)TiCl_3 + Me_3MCl$$

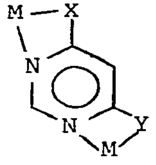
E = As, Sb; M = Si, Sn

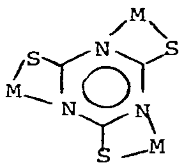
Also prepared were $(C_5H_4MMe_3)TiCl_3$ (M = Si, Ge, Sn); $(C_5H_3(SiMe_3)_2)$-$TiCl_3$ (77); $(C_5H_4BX_2)TiCl_3$ (X = Cl, Br, OEt, Me) and $(C_5H_3(BX_2)(SiMe_3))TiCl_3$ (78).

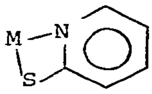
Cp_2Ti(bipyridyl), previously known to be weakly paramagnetic, has been studied by ESR, magnetic susceptibility and theoretical methods. The first two indicate that paramagnetism is due to a thermally accessible (~600 cm^{-1} above the ground state) triplet excited state; preliminary X-ray data indicate there are no M-M interactions. Calculations (Fenske-Hall type) show that the bipyridyl ligand has no π-acceptor orbital of the right symmetry to stabilize the ground state, but has a π^* orbital lying not far above the metal orbitals in energy, suggesting the excited state should be an MLCT state, Ti(III)-bipy$^{\cdot-}$. In agreement, the zero-field splitting in the ESR can be used to calculate a separation of 3.5 Å between electrons in the triplet. The oxidized compound, $Cp_2Ti(bipy)^+PF_6^-$, behaves as a normal d^1 complex (79).

Cp_2Ti adducts of pyrimidine ligands and analogs:









where M = $(MeCp)_2Ti$ and X,Y = (variously) O,S,Se have been prepared; the crystal structure of the 2,4-dithiopyrimidine adduct was determined (80). All show weak exchange properties, either antiferromagnetic or ferromagnetic (81).

Photolysis of Cp_2TiCl_2 gives Ti(III) ESR signals; in the presence of the spin trap nitrosodurene, Cp(Ar)NO• is formed; in ROH $CpTi(OR)Cl_2$ is obtained (all quantum yields are about 0.35). The common first step, $Cp_2TiCl_2 \longrightarrow Cp\cdot + CpTiCl_2$ was proposed (82). Treatment of Cp_2ZrCl_2 with D_2 and $Mn_2(CO)_{10}$ gave no ring deuteration, in contrast to Cp_2WH_2 (83). Cp_2TiCl_2 was found to have antitumor activity (84).

OTHER π-BONDED COMPLEXES

The mechanism of photoinduced decomposition of η^3-allyl complexes has been investigated using CIDNP; both $Hf(allyl)_4$ and $(C_8H_8)M(allyl)_2$ (M = Zr, Hf), on irradiation, show polarization for the signals due to the product 1,5-hexadiene. $Zr(allyl)_4$ shows a different pattern as well as polarization in starting complex signals. A possible mechanism is

$$M(allyl)_2 \overset{h\nu}{\rightleftharpoons} M(allyl)\cdot + allyl\cdot \longrightarrow \text{hexadiene}$$

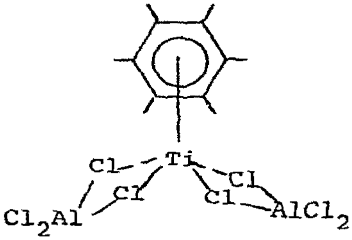
with the reversal of the first step significant only for $Zr(allyl)_4$. No CIDNP was observed under thermal conditions (85).

Reduction of $ZrCl_4(dmpe)_2$ with Na/Hg in the presence of butadiene gives a Zr(0) complex, $(Zr(C_4H_6)_2(dmpe))_2(\mu\text{-dmpe})$ which (by NMR) is in equilibrium, in solution, with $Zr(C_4H_6)_2(dmpe)$ and free dmpe. Reaction with CO at -45° precipitates $Zr(C_4H_6)_2(dmpe)(CO)$ which loses CO at room temperature in solution; the resulting $Zr(C_4H_6)_2(dmpe)$ picks up other ligands to give $Zr(C_4H_6)_2(dmpe)L$.

NMR was used to propose structures; the bonding of butadiene appears essentially the same as in complexes of later transition metals. Reaction with H_2 gives metallic Zr and butane, while slow catalytic hydrogenation is observed with added olefin (86). Cleavage with HCl gives butenes, and exposure to O_2 liberates C_4H_6. Reduction of $ZrCl_4(dmpe)_2$ in the presence of 1,3-cyclohexadiene (a diene with allylic hydrogens, in contrast to C_4H_6) gives $ZrH(\eta^5-C_6H_7)(dmpe)_2$, identified spectroscopically and by formation of HD with DCl (the Zr-H was not observed by NMR or IR). Thermal decomposition gives benzene and H_2; the compound catalyzes disproportionation of C_6H_8 (87). The electronic structure of Ti^{3+} complexes of butadiene and propylene have been studied (88).

Another Zr(0) complex was prepared by cocondensing Zr (also Hf) vapor with an arene (benzene or toluene) and PMe_3 giving $(arene)_2M(PMe_3)$, highly sensitive to air and water as well as apparently reacting with N_2 (89). Vaporization of Ti into a poly(methylphenylsiloxane) gave rise to visible absorption peaks assigned to polymer-supported bis(arene)Ti species; additional metal leads to small Ti clusters or to mixed Cr-Ti clusters stabilized by interaction with the polymer (90).

The crystal structure of $(C_6Me_6)TiAl_2Cl_8$ (benzene solvate) shows a pyramidal structure



The ring C-C distances are irregular, but the ring is reasonably planar and the Ti lies over the center; the Ti-ring center distance (2.06 Å) is long compared to Cp-Ti structures (91). $(C_6H_6)Ti(AlX_4)_2$ (X = Cl, Br) reacts with cyclopentadiene to give a Ti(III) ESR signal, assigned to $CpTi(AlX_4)_2$. With excess C_5H_6, the known signal of $Cp_2Ti(AlX_4)$ is obtained. The first reaction corresponds to $(arene)Ti(II) + CpH \longrightarrow CpTi(III) + arene + \frac{1}{2} H_2$, although less than the expected amount of H_2 was measured (92). $(C_6H_5Me)Ti(AlCl_4)_2$ is a poor catalyst for hydrogenation of benzene at 125°; $(C_6H_5Me)_2Ti$ is completely inactive at 20° (93). Colored complexes between arenes $C_6H_{6-n}Me_n$ (n=0-3) or phenols and Ti(IV) can be observed in H_2SO_4 (94).

An improved ESR study on $(C_8H_8)TiCp$ (and the indenyl analog) shows hyperfine coupling to both sets of ring protons as well as to Ti; earlier studies had problems of impurities and no hyperfine was observed. The absorption spectrum was also determined and compared with theoretical studies (95).

Titanium-intercalated graphite, $C_{32}Ti$, was prepared from C_8K and $Ti(OPr^i)_4$; X-ray analysis shows a mixture of two stages with a Ti layer between every two C layers or after every fourth C layer, respectively; the Ti-containing layers are 5.6 Å thick (96).

APPLICATIONS IN SYNTHESIS AND CATALYSIS

A full paper has appeared on the use of hydrozirconation followed by transfer of the alkyl (or alkenyl) group to $AlCl_3$ for C-C bond formation (1977); reaction of the resulting $RAlCl_2$ with R'COCl gives RCOR'. Alkenyls transmetallate faster than alkyls; retention at C is found. Reaction of $Cp_2ZrCl(COR)$ with $AlCl_3$ gives $(RCO)AlCl_2$ which reacts with R'COCl to give some RCOCOR' but mostly $RCHClO_2CR'$ (97). Preparation of Cp_2ZrHCl by hydrogenation of Cp_2ZrCl_2 was disclosed in a patent (98).

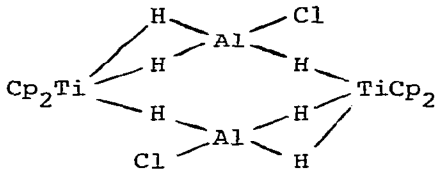
Carboalumination of alkynes can be mediated by group IV metals; RC≡CH plus excess $AlMe_3$, in the presence of Cp_2ZrCl_2 (1 equivalent per acetylene), followed by iodination, gives E-R(Me)C=CHI, in good yield (70-85%) and excellent regio- and stereospecificity ($\geq$ 97% isomerically pure). Olefinic double bonds in R (conjugated or remote) do not interfere (99). A reinvestigation of the reaction of $RC{\equiv}CSiMe_3$ with $R'AlCl_2/Cp_2TiCl_2$ followed by D_2O shows that $RR'C{=}CDSiMe_3$ is formed with 95% net cis addition and complete deuteration; however, if amines or THF are added before deuterolysis a mixture of isomers and little or no deuteration are found, indicating C-M bond breaking and H-abstraction from solvent occur (100). Cp_2TiCl_2 (or $(MeCp)_2TiCl_2$) catalyzes the reaction of $HO(CH_2)_nC{\equiv}CH$ with Et_2AlCl, giving $HO(CH_2)_nC(Et){=}CH_2$ and E-$HO(CH_2)_nCH{=}CHEt$; regioselectivity is relatively low. With internal alkynes nearly stoichiometric amounts of Ti complex are required for good yields (101).

The reaction of olefins $CH_2{=}CHR$ with Cp_2TiCl_2 and AlR_3' (relative amounts 1:2:2) gives $CH_2{=}CRR'$. The mechanism is unclear but is suggested to be related to Ziegler-Natta polymerization; alkylation of Ti; insertion of olefin to give $Ti{-}CH_2{-}CHRR'$; β-hydride elimination to give disubstituted olefin. R can include a Br, OH or ester functionality without interference (102).

Catalyzed hydrometallation continues to attract interest.

Cp_2TiCl_2 is the best catalyst (as determined by yield and amount of deuteration after D_2O quenching) for the addition of $(i\text{-}Pr_2N)_2AlH$ to olefins; $TiCl_3$ and $TiCl_4$ give good yields but lower D content. With internal olefins isomerization occurs: iodination gives 1-iodoalkanes. 1,5-hexadiene gives hex-1-ene and hexane in THF but methylcyclopentane in benzene, suggesting a vacant site on Al (blocked by THF) is required for cyclization (103). Alkynes undergo similar reactions; internal alkynes behave cleanly but terminal alkynes give substantial amounts of alkane, ascribed both to double addition and to catalyst decomposition producing H_2 which hydrogenates double bonds (104). The combination of Cp_2TiCl_2 (as well as $Ti(O\text{-}i\text{-}Pr)_4$) with $AlH_3{\cdot}NMe_3$, $(Me_2N)AlH_2$ or $(HAlNR)_n$ gives olefin hydrogenation catalysts (105). Cp_2TiCl_2 catalyzes hydroboration of olefins by $LiBH_4$ (106).

The systems Cp_2TiCl_2 and $CpTiCl_3$ plus $LiAlH_4$ (in varying ratios) have been studied by ESR and calorimetric titration; a variety of species were identified. Most interesting is the 1:1 product of Cp_2TiCl_2 plus $LiAlH_4$, which shows a 17-line ESR spectrum tentatively ascribed to



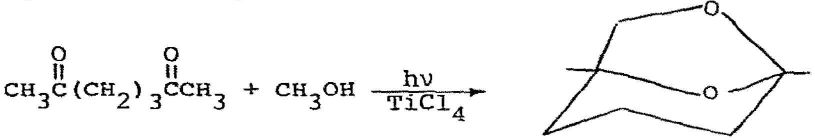
An olefin hydrogenation catalyst was obtained with 2:1 $LiAlH_4$/Cp_2TiCl_2 (107,108). Reaction of chiral $Cp_2'TiCl_2$ (Cp' = menthyl- or neomenthyl C_5H_4) with Red-al gives catalysts which hydrogenate CH_2=CEtPh with 7-15% optical yield (109).

Polymer-supported catalysts have been prepared: $TiCl_4$ on silica gel, or polymer-attached Cp_2TiCl_2, catalyze olefin hydroalumination by $LiAlH_4$ (110). $CpTiCl_3$ attaches to alumina (1 Ti per surface OH); reduction with BuLi gives a Ti(III) species (by ESR) which catalyzes olefin hydrogenation (111).

CNDO calculations have been performed on $MeTiCl_3$-C_2H_4 as a model for Ziegler-Natta polymerization (112). The products from Cp_2TiCl_2 and AlR_3 or AlR_2Cl have been studied by ESR and as C_2H_4 polymerization catalysts (113). $CpTi(OSiMe_3)_3$ plus MeMgI catalyzes codimerization of ethylene with butadiene giving mostly vinylcyclobutane (114), and with isoprene, giving acyclic C_7 dienes (115). $Ti(OBu)_4$ plus $AlEt_3$ catalyzes oligomerization of vinyltrimethylsilane (116), as well as codimerization of $CH_2{=}CHSi(OMe)_3$ with olefins (117).

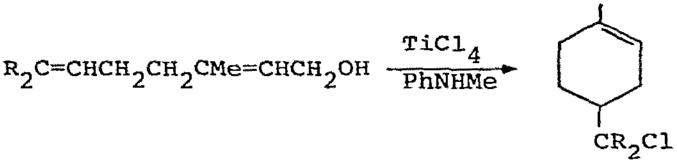
Deposition of Zr atoms in alkane matrices followed by warming affords black solids which on hydrolysis give H_2 and alkanes; for example, neopentane leads to formation of .25 moles neopentane-d_1 after treatment with D_2O, plus smaller amounts of butanes, propane, ethane, and methane, all polydeuterated, and .8 moles HD. These results indicate Zr atoms cleave C-H and C-C bonds in the alkane matrix. Ti shows some reactivity; all other metals are essentially inert (118). Condensation of Ti vapor with quadricyclane gave little isomerization, in contrast to some other metals (119).

$(C_6H_6)_2Ti$ deoxygenates ketones, allylic and benzylic alcohols, and epoxides at 80°; products are generally olefins ($PhCH_2OH$ gives toluene and some biphenyl) (120). Irradiation of heptane-2,6-dione in CH_3OH with $TiCl_4$ gives frontalin (121);



$$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3OH \xrightarrow[TiCl_4]{h\nu}$$

Dienes are cyclized in the presence of $TiCl_4$; e.g. (122);



$$R_2C{=}CHCH_2CH_2CMe{=}CHCH_2OH \xrightarrow[PhNHMe]{TiCl_4}$$

$PdCl_2$-catalyzed carbonylation of nitrobenzene is affected by additives such as Cp_2TiCl_2 (123). It is not clear whether any of the foregoing involve actual organometallic intermediates.

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